

Detection and Characterization of Engineered Nanomaterials in the Environment: Current State-of-the-Art and Future Directions

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Final Report Prepared by:

Manuel D. Montañño and James Ranville
Colorado School of Mines, Department of Chemistry

Gregory V. Lowry
Carnegie Mellon University, Department of Civil and Environmental Engineering

Julie Blue, Nupur Hiremath, Sandie Koenig, and Mary Ellen Tuccillo
The Cadmus Group, Inc.

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Task Order Manager

Steven P. Gardner
*Characterization and Monitoring Branch
U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Las Vegas, NV 89119*

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U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

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Acronyms

AF4	Asymmetric Flow Field Flow Fractionation
ATR	Attenuated total reflectance
CCD	Charge-coupled device
CFUF	Cross-flow ultra-filtration
CNT	Carbon nanotube
CPE	Cloud point extraction
DCS	Differential centrifugal sedimentation
DLS	Dynamic light scattering
EDS	Energy dispersive spectroscopy
ENM	Engineered nanomaterial
ENP	Engineered nanoparticle
ESEM	Environmental SEM
FFF	Field flow fractionation
FI-FFF	Flow FFF
FTIR	Fourier-transform infrared spectroscopy
HDC	Hydrodynamic chromatography
HS	Humic substances
ICP-MS	Inductively coupled plasma mass spectrometry
IR	Infrared
LCA	Life cycle assessment
LIBD	Laser-induced breakdown detection
MALS or MALLS	Multi-angle light scattering
MAS	Magic angle spinning
MS	Mass spectrometry
NIR	Near infrared
NIRF	Near-infrared fluorescence spectroscopy
NM	Nanomaterial
NMR	Nuclear magnetic resonance spectroscopy
NOM	Natural organic matter
NP	Nanoparticle
NTA	Nanoparticle tracking analysis
PCS	Photon correlation spectroscopy
PECs	Predicted environmental concentrations
PEG	Polyethylene glycol
ppq	Parts per quadrillion
ppt	Parts per trillion
ROS	Reactive oxygen species
SdFFF	Sedimentation FFF
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SEIRA	Surface enhanced infrared absorbance
SLS	Static light scattering
SPE	Solid-phase extraction
SP-ICP-MS	Single particle ICP-MS

SPM	Suspended particulate matter
SWCNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
UV	Ultraviolet
UV-Vis	UV-visible spectroscopy
XAS	X-ray absorption spectroscopy

1. INTRODUCTION

Nanotechnology has become a prominent industrial and scientific field. Its global market value is estimated to exceed \$1.5 trillion by the year 2015[1-3]. With increasing production and wider applications, engineered nanoparticles (ENPs) are expected to become routinely present in natural ecosystems. Although ENPs will certainly enter the environment through unintentional releases, the possible development and application of nanomaterial-based agrochemicals could lead to widespread intentional environmental dispersion [3, 4, 5].

Risk assessment models are being used to address the implications of ENPs for human health and the environment. Development of accurate ENP risk assessment models will require robust and efficient detection, characterization, and quantification of these materials in the environment [2-4].

Nanomaterials (NMs) in the environment pose unique detection and quantification problems because of their small size and low concentration and because of the high background level of incidental and naturally occurring nanoparticulate matter, often with similar elemental composition. Distinguishing between engineered and naturally occurring nanoparticles requires improvement in the selectivity of nanometrology (the science of measurement at the nanoscale level) rather than improvements in method sensitivity. It also requires understanding how a nanoparticle may be altered in specific environmental conditions.

This paper provides an overview of the challenges to nanoparticle detection and focuses on analytical methods applicable to dispersed nanoparticles. It provides details on possible methods for detecting, quantifying, and characterizing engineered NMs in complex environmental matrices (e.g., water and soil/sediment), particularly against high background levels of ambient ENPs and naturally occurring nanoparticles. Nanoparticle characteristics that may facilitate discrimination between engineered and natural NMs are emphasized. Future directions in nanometrology development are identified. Estimates of ENP releases in life cycle assessments (LCAs) suggest that the aqueous and soil/sediment environments will be the ultimate reservoir of engineered NMs [5, 6]. Despite being significant sources of ambient NMs in the environment, incidental nanoparticles (those created unintentionally), particularly atmospheric incidental nanoparticles, have been excluded from this study. Methods for the detection and characterization of atmospheric NMs have been reviewed elsewhere [7].

In this paper we first introduce the characteristics of ENPs and the major synthesis routes, which through well-controlled conditions can lead to relatively monodispersed and chemically well-defined ENPs. The identity and characteristics of natural nanoparticulate matter is then discussed, particularly with respect to the difficulty their presence causes in the detection and quantification of ENPs. After that section we introduce the transformation processes to which ENPs are subject and discuss how these processes affect ENP detection. The existing nanometrology tool kit is then described, followed by a discussion of possible new measurement approaches that may overcome some of our current limitations for ENP analysis in complex matrices.

Definition and properties of nanoparticles

A commonly accepted definition of an NM is a material with at least one dimension between 1 and 100 nanometers (nm) long [3]. This definition allows for the inclusion of thin plate-like (one nano dimension) and long fibrous (two nano dimensions) microscopic materials. NMs occupy the smallest size range of colloidal materials, generally defined as sub-micron-size particulate matter. The choice of 100 nm as the upper limit for the definition of NMs is somewhat arbitrary, and it may be more accurate to define NMs by the size at which their chemical and physical properties start to differ significantly from their bulk counterparts [12]. For example, NMs have high specific surface area and a high fraction of surface atoms, leading to increased reactivity and in some cases a size dependent change in their optical, electrical, and magnetic properties (i.e., a “nano-effect”). Nano-effects for metal and metal oxide particles tend to be most pronounced below about 10–20 nm.

Any material having the appropriate dimensions can be classified as an NM, but only certain nanoscale materials exhibit the properties (e.g., solubility, reactivity, conductivity, optical properties) desired for engineering applications. Common engineered NMs and some typical applications are listed in Table 1. NM composition may be simple (e.g., nano-Ag) or quite complex (e.g., CdSe/ZnS/polymer core shell materials) and is generally well defined and free of major impurities. Natural NMs, on the other hand, tend to be chemically impure. Such differences in chemical purity might suggest new analytical approaches for ENP detection. However, chemical transformations in the environment may significantly alter ENPs’ chemical compositions (see Section 3), thereby reducing the potential for using composition as a distinguishing characteristic.

Table 1. Common engineered nanomaterials and typical applications

ENP Classification	Elemental Composition Examples	Typical Applications	Refs
Zerovalent metals	Au, Ag, Fe	Catalysts, bactericides, groundwater remediation	[8],[9],[10]
Metal oxides	SiO ₂ , TiO ₂ , ZnO, CeO ₂	Photocatalysts, pigments, sunscreens, cosmetics, polishing agents	[11],[12],[13]
Semiconductors	CdSe, CdTe	Electronics, drug delivery, bio-imaging	[14]
Carbonaceous materials	Carbon nanotubes, fullerenes	Super capacitors, hydrogen storage, ultra-high-strength materials	[15],[16]
Dendrimers	Multi-functional polymers	Chemical sensors, drug delivery	[17]

Size distribution is an important property routinely assessed when characterizing nanoparticles. Size distributions can be number-based or mass-based (see Section 4). Metrics may also be based on instrument measurements such as intensity or on physicochemical properties such as surface area. Minimum characterization of size distribution can include the mean size, the mode size, and the polydispersity index.

Nanotechnology relies on properties that scale with size, and thus ENPs are designed and synthesized to be physically uniform (in addition to chemically pure) because they best exhibit their nanoscale properties (e.g., photonic, catalytic) when the particles have a narrow size

distribution (i.e., are monodisperse). Several approaches to the synthesis of NMs and the resulting properties are provided in Table 2. Although synthesis often aims to produce monodisperse particles, it should be noted that production of nanomaterials intended for large scale use (e.g., nanoscale zerovalent iron for in situ remediation [13]) often results in heterogeneous polydisperse materials as well because it can be challenging to carefully control ENP properties when producing ENPs on a large scale.

Natural nanoparticles generally display a broader range of sizes (polydispersity), although there can be notable exceptions (e.g., biogenic nanoparticles). This difference in particle polydispersity between ENPs and naturally occurring nanoparticles may be useful for distinguishing between engineered and natural particles. In environmental samples, however, transformation processes (see Section 3) will tend to alter the size distribution of engineered nanoparticles, likely eliminating narrow size distributions as a possible distinguishing property.

Table 2. Common methods of synthesis

Process	Elemental Composition Examples	Characteristics	Refs
Chemical reduction	Zerovalent metals Au, Ag, Fe	Mono-elemental in composition, (Au, Ag) monodisperse and often as spheres or wires	[18],[19]
Sol-gel	Metal oxides SiO ₂ , TiO ₂ , ZnO, CeO ₂	Single metal, moderate polydispersity, 2-D and 3-D nanoscale dimension	[20],[21]
Solvosynthesis	Semiconductors CdSe/ZnS, CdTe	Multi-metal composition, low polydispersity	[22]
Vapor-phase	Carbonaceous materials, metal oxides Carbon nanotubes, fullerenes	Polydisperse, 2-D nanoscale dimension	[23],[24]
Organic synthesis	Multi-functional polymers	Carbon-based, monodisperse, 3-D nanoscale dimensions	[25]

Highly engineered surface coatings are a key component of engineered nanoparticles and help to control properties such as solubility and reactivity. Common coatings range from organic proteins (i.e. protein coronas) and polymers (e.g. polyvinyl pyrrolidone) to inorganic ligands and surfactants (e.g., cysteine, citrate, carbonate) [26-28]. These coatings generally serve to limit aggregation of the NMs and can act via electrostatic and/or steric stabilization. Electrostatic stabilizers use charge repulsion to prevent particle aggregation, while steric stabilizers, because of their large size, physically prevent aggregation [2, 3, 29, 30]. These highly specialized coatings can be unique macromolecules and may provide a means for detecting ENPs (through mass-spectrometry) and perhaps differentiating them from ambient nanoparticles with natural organic macromolecular coatings. Upon entry into the environment, however, surface coatings may be altered, over-coated, or replaced by natural organic matter such as organic acids and humic substances [28, 31, 32]. Changes in coatings and the associated surface properties of NMs are an ongoing area of study with implications for the effects, fate, and transport of NMs in the environment and, for this discussion, ENP identification.

Due to the ubiquity of natural nanoparticles and their role in several important geochemical and biological chemical processes [5, 6], it is thought that organisms have adapted to their potential toxic effects. However, the release of ENPs into the environment introduces a new class of potentially toxic contaminants with a vast range of physiochemical properties, the impacts of which are not yet fully understood [33]. Furthermore, differentiation and comparison between natural and engineered nanoparticles may help in understanding the environmental behavior of ENPs because the natural and engineered particles share some stability and transport properties. For example, in addition to their own potential toxicity, ENPs may have the potential to serve as vectors for the transport of other contaminants, much as natural colloids are known to do (see Section 3). These concerns provide motivation to develop nanometrology that can both differentiate ENPs from the natural nanoparticle background and quantify ENP concentrations.

Engineered nanomaterials (ENMs) can undergo changes throughout their manufacture, use, and subsequent entry into and passage through the environment, and the resulting changes may affect their chemical and physical forms, reactivity, potential mobility, detectability, and toxicity [34]. Physicochemical properties (e.g., size, charge, elemental composition, shape, coating) need to be examined. For these properties, robust characterization and quantification metrologies do exist, but their application outside the laboratory, and for other than simple ENMs, remains underdeveloped. The aspects of ENM use, and subsequent release, most relevant to nanometrology relate to analysis of ENPs in natural systems. ENPs are incorporated into nano-enabled products, and pristine ENPs may be modified for incorporation into these products. Furthermore, ENPs can be altered during normal product use. To enter the environment, ENMs and ENPs must be released from the product through weathering, after which further transformations can occur. Therefore, the ENM in an environmental sample may bear little resemblance to the pristine ENP that was incorporated into the product.

Advances in the life cycle assessment of NMs provide predictions of where these materials will flow during their production, use, disposal, and eventual introduction into the environment. For example, LCA has demonstrated that wastewater treatment, in particular the production of treatment residuals (i.e., biosolids), is a major pathway to the environment for ENMs released from consumer products[34]. Predicted environmental concentrations (PECs) are important as they relate to nanometrology sensitivity requirements. Most assessments suggest very low ENM mass concentrations ($< \mu\text{g/L}$) are likely. However, current data on the prevalence of ENP use and the release of ENPs into the environment is limited. This lack of data poses a significant hurdle to accurate risk assessment for NMs [35-38].

To illustrate some of the analytical challenges unique to ENPs, it is useful to compare the case of other trace contaminants in wastewater. Although ENMs and pharmaceuticals are both released into the environment via wastewater treatment residuals, pharmaceuticals are much more easily detected and characterized due to the use of established, highly sensitive, and selective analytical techniques. They also have a defined molecular structure, making them amenable to treatment as chemicals, not materials. Methods such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography- mass spectrometry (GC-MS) respond directly to the compound of concern, so pharmaceuticals analysis has much less interference from background constituents. Furthermore, these techniques are highly sensitive and such compounds can be

detected and quantified at environmentally relevant and extremely low (parts per quadrillion [ppq] or parts per trillion [ppt]) levels in environmental samples.

2. NATURAL COLLOIDS AND NANOPARTICLES

The detection and characterization of engineered nanoparticles in the environment is complicated by ubiquitous naturally occurring colloids and NMs that are present in much larger concentrations than the engineered particles. This section provides background information on naturally occurring NMs and discusses some common interferences they create for ENP detection.

The feasibility of differentiating ENPs from natural nanoparticles may depend in part on particle size. In natural waters, number-based particle size distributions for natural particles have been found to follow Pareto's power law, the differential form of which is:

$$\frac{dN}{dx} = Zx^{-\beta}$$

Where:

N = the number of particles with sizes smaller than x.

Z = an empirical constant that describes the total amount of suspended particles.

β is an empirical constant generally found to be approximately 3 for natural waters [39], although very little data exists for particles smaller than 100 nm. This relationship implies that there are 1,000 times more 10-nm particles than there are 100-nm particles. Such a size distribution means that interference from an abundance of naturally occurring nanoparticles will be more problematic as nanoparticle size decreases. However, although there are fewer particles at the upper end of the nanoscale size range, these larger particles will pose a problem for light scattering methods, which exhibit strong size dependence in their capabilities. Nonetheless, given that many ENPs are designed to be monodisperse, with clear upper and lower size limits, the addition of ENPs into waters of low particle concentrations might be detectable as a perturbation in the size distribution expected for naturally occurring particles.

These natural materials, which are included in what has classically been considered the dissolved fraction in aqueous systems (can pass through a 0.45 μ m filter), vary in size, shape, elemental composition, and properties. These materials also exist at relatively high mass concentrations in the environment, ranging from 1 ppb to 1 ppm in groundwater, 1–1,000 ppm in surface waters, and 0.01–80 ppm in marine environments [40]. The comparatively high concentrations of naturally occurring NMs interfere with the detection and characterization of ENPs and thus complicate accurate assessment of environmental exposure to ENPs.

Natural NMs will interfere with non-specific sizing techniques such as dynamic light scattering; such methods do not analyze the composition of particles, and natural and engineered particles cannot be differentiated.

Some natural materials are similar in elemental composition to their engineered analogs and can complicate X-ray-based methods or element-specific methods such as inductively coupled plasma-mass spectrometry (ICP-MS). Examples of chemically similar particle types include:

- Metal oxide minerals and engineered oxides.
- Natural metal sulfides and some quantum dots.
- Natural organic matter and carbon nanotubes (CNTs).

Despite similarities between natural and engineered nanoparticles, specific morphological or chemical differences (e.g., elemental ratios) may provide a means of differentiation.

Classification and origin of biogenic and geogenic materials

Nearly all minerals found in the environment undergo a nano-phase transformation at some point in their life cycle, either during their initial formation (crystallization) or during weathering. Nanoscale minerals have important implications for soil stability, contaminant transport in groundwater, and (bio)geochemical reactions that play a role in the overall ecosystem [5, 41-43]. It has been proposed that nanoscale minerals be divided into two classes: nanominerals and mineral nanoparticles [5, 6].

- Nanominerals are materials that do not possess a bulk-phase equivalent and only exist at the nanoscale (1 to 100 nm). An example of a nanomineral is ferrihydrite, a common iron hydroxide. Nanominerals are formed by precipitation from supersaturated solutions due to changes in redox conditions or solution composition, sometimes mediated by biological processes.
- Mineral nanoparticles can exist at nano and larger scales. They form either through weathering of larger minerals or through precipitation and crystal growth.

Chemical weathering of silicates, oxides, and phosphates under environmental conditions is an important mechanism for the formation of authigenic (formed where they are found) nanoscale minerals. Nanoscale minerals can also be formed via biological pathways in which bacteria sequester metal ions for use in metabolic redox reactions during which nanoparticles form within the cytoplasm and excrete them [6, 42, 43].

Composition and interferences of some common natural nanoscale minerals

Nanoscale minerals may be composed of inorganic materials such as aluminosilicates (e.g., clay minerals) and metal oxides (e.g., iron and manganese oxyhydroxides) and of organic materials such as complex organic acids (humic substances) and biopolymers. Common natural NMs and some of their key characteristics are presented in Table 3.

Table 3. Common naturally occurring nanomaterials[5, 6, 42, 44]

Material	Composition	Characteristics
Clay fraction	Variable Al, Si, O with other metallic cations	Provide ubiquitous surface for particles to bind to. Possible to have different charges on basal planes (positive) and edges (negative)
Iron and aluminum oxides	Fe ₂ O ₃ (Hematite) FeOOH(-OCl) (Akaganéite) Fe ₅ HO ₈ •4H ₂ O (Ferrihydrite) AlOH ₃ (Gibbsite)	High specific surface area, strong binding affinity for metallic contaminants
Metal sulfides	Ag ₂ S, ZnS, CdS, FeS	Size-dependent morphology, frequently present in anoxic environments associated with microbial processes
Humic substances	Variable C, H, O, N, abundance of carboxylic acid and phenolic groups	Can impart stability to particle suspensions due to abundance of carboxyl and phenolic groups; might be more appropriately described as dissolved species

Although all the materials listed in Table 3 may interfere with detecting engineered NMs, three examples are particularly relevant and are discussed in more detail below.

Example #1 Iron Oxides. There are an estimated 100,000 teragrams by mass of iron oxides in soils (one teragram equals 1 million metric tons)[45]. Given that amorphous iron oxides are largely nanoparticulates and a significant fraction of other iron oxides are nanoscale, iron oxide nanoparticles may account for at least 1 percent of all inorganic nanoparticles globally [6]. Iron oxides are highly effective at scavenging several potent contaminants such as arsenic and uranium, significantly affecting their fate and transport[46-48]. Iron oxide particles are readily formed in the environment, generally as part of the redox cycling of iron between the relatively soluble Fe²⁺ and insoluble Fe³⁺ forms. Several types of iron oxides are present in the environment, including ferrihydrite, hematite, magnetite, goethite, and akaganéite. The formation of these various iron oxides is a function of numerous environmental factors such as temperature, pH, and aqueous chemical composition. These materials can form through abiotic and biological pathways, which determine the morphology of the iron oxide formed. Several nanoscale iron oxides can be formed from pre-existing iron oxides that undergo phase transformations under certain environmental conditions. For example, ferrihydrite (approximately Fe₅HO₈•4H₂O) is an exclusively nanoscale iron oxide that commonly occurs as aggregates of primary particles having a narrow size distribution of 2–7 nm. The aggregation, rearrangement, and dehydration of ferrihydrate can lead to the formation of more thermodynamically stable colloidal phases of iron oxides such as goethite and hematite [42, 43, 45, 49].

Example #2 Clay Minerals. Clay minerals are the most prevalent natural nanomaterials, particularly in the soil environment. The clay-sized fraction of soils is defined as particles smaller than 2 µm, encompassing both the colloidal fraction (1–1,000 nm) and the nano fraction (<100 nm). Nanoscale clay minerals (phyllosilicates) and clay-sized particles are formed via one of three abiotic pathways: 1) erosion of a pre-existing bulk material, 2) transformation of the outer layer of a mineral to form two distinct mineral regions, and 3) neoformation, which is a

result of precipitation or crystallization from cation complexes in solution[5]. Some minerals, such as mica, can form via all three pathways, while others can only form through one process (e.g., neoformation in the case of kaolinite). Clay-sized nanoparticles can also be formed biologically as the negative surfaces of bacterial cells collect positively charged cations, which can then complex with numerous anions present in solution to precipitate out as a nano-sized material[5]. Clay minerals may be effective at destabilizing nanoparticle suspensions due to the electrostatic charge on their surface, which can make the detection and characterization of individual, dispersed ENPs problematic [42, 43].

Example #3 Metal Sulfides. Metal sulfides are abundant in anoxic environments that may have high metal content (i.e., acid mine drainage waste sites). Abiotic sulfide formation is generally not favored thermodynamically, but ubiquitous sulfate-reducing bacteria (often *Desulphobacteriaceae*) can catalyze processes that result in the formation of a variety of metal sulfides (i.e., HgS, As₂S₃, ZnS, etc.). Using a carbon source as an electron donor, these bacteria reduce sulfate to sulfide, which then complexes with the metals present, forming insoluble metal sulfides. These metal sulfides, such as zinc sulfide (ZnS), are in the nanoscale range, typically forming particles between 2 and 10 nm in size and forming aggregates between 500 nm and 1 μm. Because metal sulfides are frequently found in reduced waters and sediments, they can potentially interfere with the detection of metallic and semi-conductor ENPs. This is particularly true for ENPs made from class B and related soft metal cations, including silver nanoparticles because silver sulfide (Ag₂S) is easily formed under environmental conditions [43, 50-52].

Estimates of ENP behavior and fate

Although the examination of nanoscale processes on mineral surfaces is a relatively new field, there is considerable understanding of the colloidal behavior of mineral nanoparticles. The processes of surface charge development, flocculation behavior, solubility, and ion adsorption are well understood, at least for materials in the submicrometer size range. Although unique reactivity arises for some metal and metal oxide NMs less than 10–20 nm in size, their environmental stability has been successfully described by much of classical colloid theory. This includes filtration theory for transport in porous media and flocculation and sedimentation behavior in surface waters. Only when the ENPs are extremely small and under very low ionic strength conditions do the underlying assumptions of Derjaguin, Landau, Verwey and Overbeek (DLVO) theory break down [36]. Thus, the large body of work examining environmental colloids has direct application to predicting the fate and behavior of engineered nanoparticles.

NM-facilitated contaminant transport in the subsurface

The colloidal nature of nanominerals and mineral nanoparticles is of concern when considering contaminant transport in groundwater systems. It has long been understood that colloids are important components in the fate and transport of contaminants dissolved in groundwater. The ability of colloids and nanoparticles—and by inference ENPs—to serve as vectors for contaminant transport through the subsurface depends on several factors[53]:

- Contaminant association with the particle surface.
- The concentration of dissolved organic carbon.
- The hydrogeologic properties (e.g., hydraulic conductivity) of the aquifer.

Research at one of the most contaminated nuclear waste sites in the world, near Mayak, Russia, revealed that colloids are responsible for the long-distance transport of plutonium and other actinides. As much as 70–90 mole percent plutonium was associated with colloids. It was determined that amorphous iron (hydr)oxide colloids are responsible for the adsorption of Pu (IV) hydroxides and carbonates as well as uranium carbonates, which can then be transported through groundwater by way of this nano-vector [46, 47].

Similar behavior was seen at the Nevada Field Site, where actinides and rare earth elements were also found to bind to iron oxides, manganese oxides, and clay minerals, which can facilitate transport as far as 4 km from the source of the contamination [54, 55]. Up to 100 percent of the manganese, cobalt, cerium, and europium detected was associated with colloids [55]. These observations lead to concerns that ENPs, under favorable conditions, might be significantly transported in groundwater either as individual ENPs, as ENP aggregates, or as ENP-colloid heteroaggregates.

3. REACTIVITY AND PERSISTENCE

The very high reactivity of NMs suggests that these materials will readily transform in the environment. High reactivity has been observed for many NMs [41] and is a result of their large surface-to-volume ratio or novel nanoscale properties. Predicting environment-specific ENM transformations is not yet possible, making it difficult to forecast the fate, transport, reactivity, and toxicity of NMs in environmental systems. Furthermore, because transformations can greatly affect the particles' properties (e.g., chemical composition, size, charge, coating), they also affect the ability to detect and quantify ENMs in environmental and biological matrices.

Transformations of ENMs in biological and environmental matrices will affect the properties of the core and shell of the NMs and the ability to extract, detect, and quantify them in complex biological and environmental matrices. Methods developed for the detection of NMs in real matrices will have to consider the composition of the transformed NMs in that matrix in order to be applied successfully. Additionally, their physicochemical state may have also been altered as a result of environmental transformation, which may also affect the efficacy of the analytical technique applied.

ENMs can be made from a single material (e.g., silver or gold), but often have a core-shell configuration (Figure 1). Transformations of NMs in the environment can affect the core, shell, or polymeric organic coating. The “shell” can be an organic molecule or macromolecule, or it can be a coherent or incoherent metal oxide or metal sulfide.

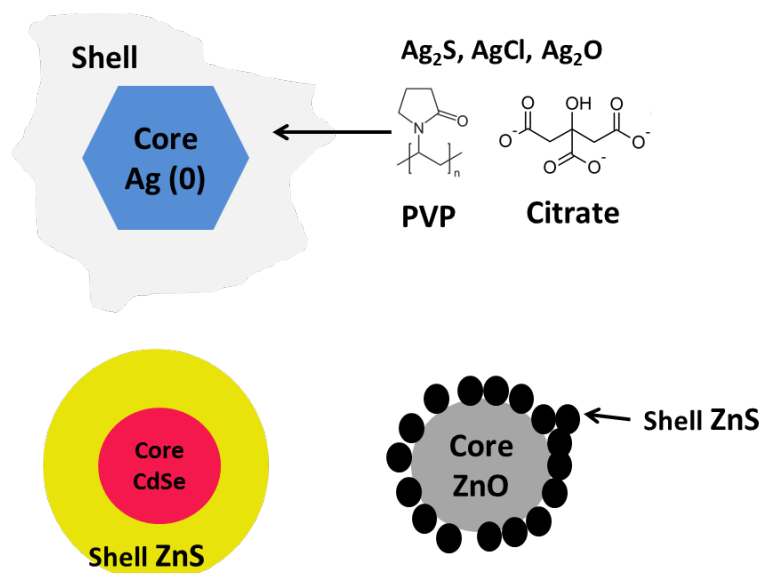


Figure 1. Typical core/shell structures of Ag, ZnO NPs and CdSe/ZnS quantum dot

Several important transformations can occur in biological and environmental media and may affect the chemical composition of nanomaterials as well as their properties (including reactivity and persistence). These changes can affect natural and engineered materials and include:

1. Alterations in the organic coating of the particle.
2. Dissolution and ligation.
3. Oxidation and reduction (redox) reactions.
4. Aggregation.

These transformations greatly affect the potential toxicity of the NM [56, 57] and can inhibit the ability to isolate, detect, or characterize the materials in environmental and biological media. These transformations are discussed in the subsections below.

Alterations in Organic Coatings

The surface coatings on nanoparticles (e.g., surfactants or polymers [Figure 1]) strongly affect how nanoparticles interact with other nanoparticles, via homoaggregation, and with mineral surfaces (e.g., iron oxides) and organisms (e.g., bacteria or plant roots), via heteroaggregation. This in turn can influence reactivity, transport, and fate in the environment. Surface coatings can also affect properties of the nanoparticles that are often used for characterization such as hydrodynamic radius, effective density, and charge. Changes in surface coatings therefore alter the ability to detect and quantify nanoparticles in environmental and biological matrices.

Alteration of surface coatings can result from:

- Loss of engineered surface coating.
- Overcoating by adsorption of natural organic macromolecules.
- Replacement of the engineered coating by natural organic macromolecules.

Loss of coatings

Nearly all ENPs are designed with an organic coating to control aggregation, enable mixing into polymeric matrices, or to provide specific functionality to the material. In all cases, there is the potential for the release of these organic coatings. However, the degree to which release is expected to occur depends on the nature of the interaction of the coating with the ENP. Coatings can be strongly or weakly adsorbed to nanoparticles, or they can be covalently bound with suitable chemistry (e.g., thiol linkages or silane linkages). Desorption is likely for ENP coatings that are surfactants (e.g., cetrimonium bromide or sodium dodecylbenzenesulfonate). These coatings typically are bound weakly to the ENPs through van der Waals interactions or electrostatic attraction. Desorption of higher molecular weight polymeric coatings or proteins is possible, but because they are strongly bound to the nanoparticle surfaces at multiple points, the loss of such coatings is much slower [43, 44]. Hence, these coatings are often considered irreversibly bound [58].

The loss of surfactant and polymeric coatings can change ENP charge and hydrodynamic radius and therefore can affect interactions with other particles and surfaces (e.g., electrostatic repulsion, steric repulsion, and electrosteric repulsion). This has significant consequences for the behavior of nanoparticles in the environment and can also affect detection and characterization techniques that leverage these properties for separation. These effects are discussed in detail at the end of this section.

Overcoating or Alteration of Coatings

Overcoating or the alteration of an existing coating is more likely than the loss of strongly bound coatings [41]. Biomacromolecules (e.g., proteins) are ubiquitous in living cells and in the environment (e.g., natural organic matter [NOM], albumin, polysaccharides), and their adsorption is expected to occur in all environments. Once discharged into the environment, uncoated or coated NMs interact with naturally occurring biomacromolecules or geomacromolecules including proteins, polysaccharides and humic substances (HS). The adsorption of biomacromolecules on NM surfaces or within the organic macromolecular coating of the particle can significantly alter surface chemistry and resulting behavior in biological and environmental systems [59, 60].

Most work on NM-NOM interactions has used extracted HS. This organic material is a mixture of macromolecules having different functional groups and range of molecular weight distributions [28, 31]. Adsorbed NOM can form relatively “flat” monolayers or more extended (thicker) monolayers or multilayers. The coherence and thickness of the layer depends on the particle properties and the conditions (e.g., pH and ionic strength) during interaction. The adsorbed NOM provides both charge and steric stabilization of NMs [31, 61], although it may also result in bridging flocculation [62] or disaggregation [32]. The effects of adsorbed NOM layers are complex and can be difficult to predict. Inability to predict the effects of NOM on nanoparticle behavior largely stems from poor characterization of the macromolecules in the NOM mixture. For example, while it is known that the higher molecular weight fraction (~700 kDa) of NOM provides significantly better steric stabilization of gold nanoparticles compared to the low molecular weight fraction (~13 kDa) [63], NOM derived from different sources and at different times of the year will have varying molecular weight distributions. This makes it difficult to predict how NOM will affect nanoparticle behavior. For larger molecular weight

polymeric coatings that are strongly bound, mixed polymer-NOM layers may form on NMs. However, in some cases, interactions with NOM may be minimal [64]. The conditions under which mixed layers form and the influence of those layers on NM behavior has yet to be explored.

Adsorption of lower molecular weight organic ligands, such as those containing thiol groups (e.g., cysteine), is another interaction that may change NM dissolution, charge, and stability against aggregation. Organics present in the atmosphere can also condense onto airborne NMs, altering their surface chemistry [65]. Adsorbed protein coatings form in biological fluids for several classes of NMs [66]. Adsorbed proteins are dynamic in nature, with the proteins continuously exchanging between free and bound forms. Similar transformations may occur in environmental media as well.

Adsorption of metal cations or oxo-anions can also occur, and this affects the NM's properties [28, 31]. Understanding the effects of organic ligands and adsorbed co-contaminants on NM properties and the ability to detect them in complex matrices are necessary to advance research on the environmental behavior and health and safety implications of nanomaterials.

Interactions of colloids with NOM (a common biomacromolecule in the environment) are well-studied phenomena, and much is known about how these interactions affect the behavior of natural colloids in the environment. The observed interactions of ENPs with NOM are analogous to those known for environmental colloids [34, 67]. They are also analogous to the interactions with proteins in biological systems, which have been the subject of more intensive research reaching similar conclusions; the behavior of ENPs depends highly on the types and amounts of biological and environmental constituents associated with particle surfaces.

Impact of coating loss or gain on the ability to detect NPs

Many proteins and other macromolecules are irreversibly adsorbed by nanoparticles over relevant time scales [58, 68]. Therefore, they partly determine the properties of the NMs (e.g., size, electrophoretic mobility, and surface composition) and subsequent environmental behavior and biological response. Methods used to characterize NMs in environmental and biological matrices often must consider these coatings as part of the nanomaterial. Otherwise, the coatings can be obstacles to NM detection and characterization, especially if the methods used were developed for pristine NMs.

For example, the use of field flow fractionation (FFF) for nanoparticle separation relies on differences in the diffusion coefficients of materials. Because the loss or gain of a macromolecular coating influences the diffusion coefficient of a particle, such alterations would change the effectiveness of this method for separating ENPs. In addition, FFF presumes no interaction between the nanoparticles and the membrane used in the device. The loss or gain of coating may increase or decrease such interactions. Similar influences of surface charge on hydrodynamic chromatography (HDC) separations have been observed [69]. Adsorption of NOM has also been known to alter surface chemistry, for example, changing the oxidation state of cerium oxide (ceria) NMs [62]. Changing the oxidation state of the NM affects properties such as charge, density, and chemical composition. These changes alter the sensitivity of methods used to quantify NMs and, in some cases, can make a method useless. For example, oxidation of

metallic iron (Fe^0) or magnetite particles to hematite can make them non-magnetic and decrease their reactivity with water. Magnetic measurements for the presence of Fe^0 or tri-iron tetroxide (Fe_3O_4) would thus be rendered useless.

Dissolution and Ligation

Many metal and metal oxide nanomaterials made from soft metal cations (e.g. silver, zinc, and copper) may undergo dissolution or complex with strong ligands, complicating detection and other analyses. For example, in the absence of sulfide and in oxic environments, silver nanoparticles will oxidize and readily react with chloride ions to form a silver chloride ($\text{AgCl}[\text{s}]$) shell around the silver (Ag^0) particle core [70].

Dissolution and strong ligation may greatly affect the properties of NMs (size, charge, chemical composition), making their detection in biological and environmental media difficult. This can increase or decrease the difficulty of separating these ENPs from the environmental matrix. Formation of a relatively insoluble metal-sulfide shell on the particle surface can also induce aggregation [71], which can affect the ability to detect the number and size of ENPs in a sample. Partial dissolution and strong ligation of the metal may form a shell on the particles. This change in chemical composition may alter particle properties used for detection, including ultraviolet absorbance, resonance, fluorescence, or reduction in ion release (e.g., dissolved cadmium, selenium, tellurium, etc. could be an indicator for the presence of quantum dots).

Oxidation and Reduction (Redox) Reactions

Oxidation and reduction (i.e., redox reactions) are coupled processes in natural systems and involve the transfer of electrons to and from chemical moieties (i.e., NM surfaces, functional groups). NMs made from elements that can achieve multiple oxidation states (e.g., cerium, silver, iron, and manganese) are potentially redox active. The occurrence of redox reactions involving NMs depends on the standard potential for the redox transformation and the availability of a suitable oxidant or reductant.

Dynamic redox environments (e.g., tidal zones, wetting/drying soils) create great potential for the cycling of NMs between oxidation states. Many NMs undergo reduction, oxidation, or both in aquatic and terrestrial environments. For example, NMs made from metals such as silver [72, 73] and iron [74] are readily oxidized in natural waters. Nanoscale zero-valent iron particles are specifically engineered to be readily oxidized by environmental contaminants such as chromium or chlorinated solvents [75]. Ceria nanoparticles are redox-labile under environmental conditions and in biological media [76]. Sorption of macromolecules has been shown to alter the ratio of Ce(III) to Ce(IV) on the nanoparticle surface [62]. Non-metallic elements in NMs may also be susceptible to oxidation. For example, the sulfur and selenium in some metal sulfide and selenide NMs (such as quantum dots) are susceptible to oxidation [77, 78]. The oxidation of reduced sulfur to elemental sulfur, sulfite, or sulfate in these materials results in the release of soluble, toxic metal ions such as cadmium (Cd^{2+}) [79].

Sunlight-catalyzed redox reactions (e.g., photooxidation, photoreduction) may affect NM coatings, oxidation states, generation of reactive oxygen species (ROS), and persistence in the environment. This may be particularly important for titanium dioxide nanoparticles and carbonaceous NMs such as fullerene and fullerene-like NMs [80, 81]. Exposure of aqueous fullerene suspensions to sunlight can result in the oxidation of the carbon structure,

functionalizing the surfaces with hydroxyl and carboxyl groups. Sunlight exposure can also degrade the polymeric coatings on the NM. In one study, exposure to natural light caused the degradation of gum arabic coatings on silver nanoparticles and induced aggregation and sedimentation of the silver nanoparticles from solution [82].

A variety of outcomes from redox transformations can affect the ability to isolate, separate, and detect NMs in environmental and biological matrices. Redox transformations can change the size and morphology of the particles. Oxidation of metal NMs can result in the formation of an oxide shell, enhance dissolution, alter the surface charge of the particle, or change the crystal phase of the material (e.g., oxidation of magnetite to maghemite) [83]. These alterations can also lead to the loss of the organic coating from the particle, which may significantly impact their fate, transport, behavior, and consequently their ability to be detected with current analytical techniques.

Aggregation

Aggregation of ENMs reduces surface-area-to-volume effects on ENM reactivity. Increases in aggregate size change ENMs' transport in porous media, sedimentation, reactivity, uptake by organisms, and toxicity. Aggregation includes homoaggregation of particles of the same NMs and heteroaggregation of an NM and another particle in the environment (e.g., clay, ferrihydrite or soft biogenic matter). Both aggregation processes can affect the ability to detect these materials in biological and environmental matrices. When aggregation occurs, the count of NMs in the suspension decreases with a concomitant increase in their effective (aggregate) size (i.e., hydrodynamic diameter). Aggregation can also decrease the available surface area of the materials, thereby decreasing reactivity. However, the decrease in surface area will depend on particle number and size distribution and on the fractal dimensions of the aggregate [84]. Aggregation can therefore affect detection methods that may rely on reactivity (e.g., fluorescence [85, 86] or ability to produce ROS) with the nanomaterial surface. Aggregation may also decrease the rate of dissolution or degradation, which may affect detection as described in the previous section on dissolution and ligation.

In most cases, a higher concentration of environmental solids than NMs will result in heteroaggregation. Heteroaggregation of NMs and comparatively larger particles (e.g., clay) will change the overall size of the nanoparticles, their charges, and their associated organic coatings. If the NM-clay heteroaggregates have properties similar to clay particles, separation becomes difficult, especially if the matrix has a large background of clay particles [87]. In addition, if the NM of interest is made from elements that are common in the environment (e.g., aluminum, Si, Fe), detection by chemical methods (e.g., single particle ICP-MS [SP-ICP-MS]) can be difficult once NM heteroaggregates form.

Biological Transformations

Biological transformations of NMs are inevitable in living tissues and environmental media (e.g., soils). These transformations are predominantly redox reactions that occur intracellularly in the cytoplasm, cell wall, and cell membrane and extracellularly via redox-labile enzymes and cytochromes[57]. Ancillary intracellular ROS production, such as hydroxyl radical or hydrogen peroxide (H_2O_2) production, can also cause biological transformations of nanoparticles. For example, *Geobacter* and *Shewanella* spp. bacteria can respire naturally occurring nanoscale iron

oxides, effectively reducing an Fe(III) oxide to a mixed Fe(II)/Fe(III) oxide [88]. The oxidation and carboxylation of carbon nanotubes (CNTs) by hydroxide (OH) radicals produced from the horseradish peroxidase enzyme has been demonstrated [89]. This oxidation increases the surface charge of the CNTs and their stability against aggregation while decreasing hydrophobicity. This can affect the ability to extract the CNTs from environmental matrices [90] and the ability to detect single-walled CNTs (SWCNTs) in environmental media, because the oxidation of the tubes changes their near-infrared (NIR) absorption [91].

Biotransformation of polymer coatings used on many NMs for biomedical applications is also feasible. For example, bound polyethylene glycol (PEG) coatings on ENMs were shown to be bioavailable to microorganisms isolated from an urban stream [92]. Moreover, the biotransformation of the PEG coating caused the NMs to aggregate. These transformations, if they occur in the natural environment at fast enough rates, will change the properties of the particles and affect detection methods that rely on detecting the particles' organic coating.

Another characteristic behavior of NMs is persistence in the given media. Even NMs that can dissolve or transform can persist continuously in a single location provided the appropriate environmental conditions. Some studies have shown that silver nanoparticle dissolution for instance will dissolve according to known particle dissolution kinetics [93]. However, when these materials are applied to wetland soils in low concentrations via biosolid application, they result in unique nanoparticle-specific effects on microbial populations and nitrogen cycling in the soil. This is believed to result from their distinctive spatial distribution and long-term slow release of silver ions in the vicinity of the nanoparticles compared to the Ag^+ ion (added as silver nitrate [AgNO_3]) [94].

4. NANOMETROLOGY

Assessing ENP fate, transport, and toxicity in the environment depends on the ability to analyze ENPs in complex matrices. Many options exist for analyzing pristine ENPs in simple matrices. Validation and application of these tools to environmental nanometrology, however, is relatively underdeveloped. Several authors have reviewed the status of nanometrology [56, 95]. Therefore, this paper focuses on the broader issues of environmental nanometrology and provides an update on recent literature.

Nanometrology methods can be classified as detection, quantification, or characterization methods.

- Detection determines ENP presence or absence. The detection of ENPs alone has limited use, but may be helpful for specific studies such as rapidly screening nano-containing products for NM weathering.
- Quantification of ENPs is required for some questions such as: What is the degree of ENP uptake by exposed organisms?
- Characterization methods provide additional details on the physical properties (e.g., size or shape) and chemical composition of the NMs and facilitate analyses of ENP fate and transformation. Although relatively straightforward in pristine samples, measurement of properties such as size, shape, and reactivity becomes increasingly complex in environmental samples.

Processes such as aggregation, dispersion, and dissolution may affect the environmental state of ENPs. In addition, the ubiquity of naturally occurring colloidal material may further complicate detection, quantification, and characterization. It is therefore important to determine the most appropriate metrics for detection, quantification, and characterization of NMs in environmental and biological media. Multiple metrics may be used to quantify ENPs.

The method for expressing concentration of ENPs is influenced by the research question at hand and by the anticipated analytical methods. Mass concentrations (mass/vol, molarity) are generally used for non-particulate contaminants and may also be appropriate metrics for some ENPs. For readily soluble ENPs such as zinc oxide (ZnO), mass concentration may be the most important metric, because organism exposure is often via the soluble metal, and organism uptake is expressed on a mass basis. Particle number concentration has also long been recognized as an important metric for particulate contaminants, including contaminants in surface waters [39, 96]. Some analytical methods, such as transmission electron microscopy (TEM) and nanotracking analysis (NTA), rely on detecting and quantifying individual particles. Other methods such as FFF-ICP-MS determine the mass-to-size-ratio using the integrated signal of the many thousands of particles present in any given elution volume. Information on ENP size, shape, and density allows conversion between mass- and number-based concentrations, at least for simple ENPs. Homo- and heteroaggregation, however, may increase the difficulty of accurately determining number concentration. Aggregates can be difficult to quantify and by their very nature have constantly changing number concentrations.

Given the importance of surface-mediated reactions, a measurement of total ENP surface area per volume could provide a highly relevant concentration metric. However, no available methodology provides this measurement in aqueous media at environmentally relevant nanoparticle concentrations. Traditional measurements of surface area (e.g., Brunauer–Emmett–Teller nitrogen and ethylene glycol monoethyl ether adsorption) cannot be performed because these measurements must be conducted in non-aqueous environments. Nuclear magnetic resonance spectroscopy (NMR) techniques can provide surface area information in aqueous media, but the required concentration range (on the order of a few weight percent) makes it impractical for application to natural samples. Rather, surface area must generally be inferred indirectly from both geometric characterization (size, shape, porosity) and mass or number concentration.

Characterization of ENPs provides data on properties such as bulk chemical composition, particle size and shape, and mineralogy. Particle size and distribution are often valuable measurements because of their importance in fate, transport, and possible ecotoxicity [96]. However, particle size, although simple in concept, is a somewhat ambiguous property. Defining size by a single metric, such as radius or diameter, ignores non-spherical particle geometry, which is clearly an important characteristic of CNTs. In addition, different nanoparticle sizes are obtained depending on the methodology employed. Examples of sizing methodology are:

- The particle diameter of electron-dense material as determined by electron microscopy.
- A hydrodynamic diameter obtained by dynamic light scattering.
- A radius of gyration given by static light scattering.

Furthermore, particle size distribution can be described in different ways, particularly for polydisperse materials. Methods for determining size distribution respond differently to various components of the size distribution depending on how the concentration of materials across the size range is expressed. Size distribution can be defined as:

- A number-weighted distribution, which is applied primarily when using particle-counting techniques.
- A volume- or mass-weighted distribution, obtained using methods that determine the amount of material in given size or mass ranges.

For metallic ENPs, dissolved metal content is a very important parameter to determine in environmental samples, although this property is often not considered a component of particle size distribution. Intensity-weighted distributions, although not ecologically relevant, are common for light-scattering-based methods. These distributions are skewed to larger sizes due to the strong dependence of light scattering on particle size.

Engineered surface coatings might allow for selective ENP detection and characterization in the presence of ambient natural nanoparticulate matter. Physical and chemical properties of the particle surface are key NM characteristics. Many engineered NMs are highly functionalized with surface coatings to enhance their stability and reactivity. Coating material composition can be highly varied, and many materials can be used to impart a desired chemical function (e.g., chemical reactivity, electrostatic or steric stabilization). Adsorbed mass and surface conformation of adsorbed molecules are also key NM characteristics, but the latter is difficult to measure directly on ENPs in suspension [82].

Because several parameters need to be determined for full characterization of ENMs, multiple analytical techniques should be used to accurately assess ENPs in environmental samples. The following sections discuss several analytical techniques and some available instrumentation in the nanometrology tool kit. Table 4 reviews current analytical approaches for characterizing ENMs in environmental samples as a framework for determining potential future directions, namely element-specific methods (i.e. spICPMS and FFF-ICPMS), for the detection, quantification, and characterization of ENMs in the environment. Established methods to facilitate ENP characterization in complex media are also re-evaluated [97].

Table 4. Analytical approaches: Limitations and needs for ENP analysis in environmental media

Measured Property	Current Analytical Approaches	Obstacles to Accurate Detection/Characterization	Potential Need
Particle size	TEM, SEM, sP-ICP-MS, UV-vis, DLS, FI-FFF, Sed-FFF, HDC, NTA	- Introduction of artifacts from sample drying (TEM/SEM) - No elemental specificity (DLS) - Inability to differentiate between ENMs and NNPs of similar elemental composition (sP-ICP-MS, TEM, SEM) - Obstructed by high background of natural particles (sP-ICP-MS, TEM, SEM, DLS, FFF)	- Analysis of samples in situ with minimal sample preparation - Elemental specificity to differentiate between dissimilar nanomaterials - Requires another measured property to differentiate between particles of similar elemental composition
Surface groups	NMR, FTIR, Zeta potential	- Original coating may have been replaced or overcoated in the environment (NMR, FTIR, Zeta potential) - Ensemble techniques unable to characterize individual particle populations without prior fractionation steps (FTIR, NMR, zeta potential)	- Ability to differentiate between different particle populations in situ - Knowledge of how surface groups are attached may help determine if original coating persists
Particle number concentration	spICP-MS, NTA	- Unable to determine aggregates from single particle without parallel imaging/sizing technique - NTA is nonspecific for particle type	- Require knowledge pertaining to aggregation state of ENMs
Elemental composition	SEM/EDX, sP-ICP-MS, ICP-MS, ICP-OES	- Unable to discern particles of natural or engineered origins - May require acidification, eliminating particle integrity (ICP-MS, ICP-OES) - Sample preparation may alter sample representativeness	- Determination of elemental composition in situ with additional sample preparation (i.e. acidification)
General Considerations			
Mass detection limit		- ENMs are expected to enter into the environment at very low concentrations (ppt)	
Size detection limit		- Most nanomaterials are between 1–100nm (many smaller than 20 nm)	
Aggregation state		- Some nanomaterials are not expected to preserve monodisperse state in the environment - Degree of dispersion/aggregation is not static and will likely vary in time - Need ability to discern aggregated from single particle material.	
Naturally occurring nanomaterials		- Concentration of NNPs in the environment are several orders of magnitude above that of ENMs (ppm vs. ppt) - Some NNPs have similar elemental composition and morphologies to ENMs. - Natural nanoparticles tend to be very polydisperse and can interact with ENMs in the environment.	

A. Review of available analytical methodologies

Methods based on separation by size

A very useful, and perhaps necessary, step in the analysis of nanoparticles in the environment is the separation of particles by size. Separation by size can provide important information on mass-based size distributions, determine compositional variations with size, and possibly distinguish ENMs from natural nanoparticles and naturally occurring colloids. The operationally simplest methods are filtration and centrifugation, but they have been shown to be susceptible to artifacts and to suffer from low size resolution, particularly for low-density ENMs. As a result, analytical techniques such as FFF and size exclusion chromatography (SEC)/hydrodynamic chromatography (HDC) have been developed into very powerful methods for high-resolution separation and sizing of particles over a wide size distribution. Their characterization power is enhanced when coupled with other techniques for characterization and chemical analysis of the size fractions. Disc centrifugation, while lacking the capability of fraction collection or online coupling to other instruments, provides extremely high-resolution information.

a. Filtration and centrifugation

One of the most common methods used for the pre-fractionation of nanoparticles prior to characterization is filtration, specifically membrane filtration and cross-flow ultra-filtration (CFUF). Filtration is limited, however, to only two size distributions: those larger and those smaller than the membrane pore size. Greater resolution in size fractionation can be achieved through multi-stage filtration, and its simplicity makes this technique highly attractive for determining size distributions obtained by chemical analysis of size fractions. However, the incomplete passage of small particles through membranes can create significant artifacts. But it is possible that filtration can be used to separate nanoparticles from dissolved constituents if the membrane size is on the order of a few nanometers [98].

Membrane filtration—particularly “dead-end” filtration, which uses pore sizes typically greater than 100 nm—is a common method of fractionation, but it is prone to several issues and artifacts. Concentration polarization, the collection of particles on the membrane surface due to collisions and electrostatic attraction, can lead to the aggregation of nanoparticles on the membrane surface, which biases the particle size distribution. This is particularly problematic for particles that have no surface-attached stabilizing groups, which enables aggregation to occur readily. Physical clogging of the pores and the buildup of a filter cake are other issues that affect the passage of nanoparticles smaller than the filter pore size. CFUF partially overcomes these artifacts by constantly recirculating the sample tangentially across the top of the membrane. The resulting shear forces limit the amount of sample that accumulates at the membrane surface. As a result, only small fractions of the filtered particles pass through the membrane at each cycle. Although promising for some applications (e.g., for the large-scale separation of nanoparticles), CFUF also has the potential to alter the aggregation state that arises from the increase in colloid concentration [99].

Centrifugation can also be used to separate particles while minimizing sample perturbation. The separation of particles is contingent upon the settling velocity overcoming the Brownian motion of the particles. The settling velocity is controlled by a number of factors such as particle size and shape, the g-force applied, and the density difference between the particle and the medium.

As such, centrifugation is more effective at removing dense inorganic particles as opposed to almost neutrally buoyant organic material. One of the most pertinent problems with this technique is that settling particles may scavenge smaller particles due to different settling velocities, thereby altering the particle size distribution [98].

A hybrid of these methods, centrifugal filtration, is becoming increasingly common for defining the dissolved fraction of a sample. Several configurations are commercially available. While centrifugal forces are employed in this method, centrifugation is used to force the sample through the membrane and is not used to determine particle size.

b. Field flow fractionation

FFF is a very powerful and versatile technique for continuous separation of particles over a broad size range according to their hydrodynamic diameter (Stokes diameter) [96]. The particles are separated by the combination of an applied field and a longitudinal channel flow; the separation all occurs in the mobile phase (as the fluid moves along the channel). The extent to which the particles act against the applied field (back diffusion) is responsible for the fractionation of the particle sizes.

The two most applicable types of FFF for the fractionation of nanoparticles are flow FFF (Fl-FFF) and sedimentation FFF (Sd-FFF) [98]. Both techniques have enhanced characterization power through online coupling of various detection methods, such as ICP-MS and light scattering. This allows the sequential analysis of sample fractions that have narrow size distributions. The linkage of the method to ICP-MS in particular may lead to the elemental specificity needed to chemically identify particles and perhaps distinguish nanoparticle types (e.g., ENPs and natural nanoparticles) in complex mixtures.

Generating particle size distributions relies on converting retention times into sizes and detector response into a concentration metric. While uncertainty in sizing can arise in FFF, determining the concentration metric depends greatly on the detector type. ICP-MS gives a direct measure of the mass concentration of nanoparticles eluting at any given size. The responses of absorbance and light scattering detectors are influenced by the optical properties of the nanoparticles, which are both material and size dependent. Depending on the extent of the size range under investigation, analysis times can be long—on the order of 20 minutes to more than one hour. Consequently, FFF does not readily lend itself to high throughput analyses, although advances in automated analysis can allow continuous operation of FFF.

In Asymmetric Flow Field Flow Fractionation (AF4), particles are injected into a ribbon like-channel (75–250 μm thick) where a fluid cross-flow acts on the particles, causing the nanoparticles to move towards an accumulation wall covered by an ultrafiltration membrane that retains particles in the channel [67, 100]. The concentration of particles forms an equilibrium cloud, where the thickness of the cloud depends on the velocity of the cross-flow field and on the diffusion coefficient of the particles. According to the Stokes-Einstein equation, the diffusion coefficient depends on both the viscosity of the medium and the hydrodynamic radius of the particle. As a result, smaller particles will migrate away from the accumulation wall and towards the middle of the channel. The geometry of the channel creates a parabolic flow profile, carrying particles in the middle along streamlines of higher velocity than those closer towards the accumulation wall [67, 98, 100, 101]. Sufficiently

high fields can be generated so that nanoparticles as small as about 2 nm can be analyzed. Some drawbacks of AF4 include possible membrane interactions, as well as laborious method optimization [67, 95].

Sedimentation FFF (SdFFF) uses centrifugal force, rather than fluid flow, as the applied field. This causes particles to separate according to their effective mass, which is the difference between the particle's true mass and the mass of the liquid displaced by the particle. Currently available instruments provide g-forces sufficient to analyze gold particles as small as 5–10 nm, with materials of lower density having consequently larger size detection limits. Resolution in SdFFF is considerably higher than in FI-FFF. Buoyant mass is determined and particle hydrodynamic diameter is a secondary property that can only be determined if particle density is known [32, 100, 102, 103]. For unknown samples, compositional data obtained by SdFFF-ICP-MS may allow for an estimate of particle density, and thus allow sizing. In addition, by combining the buoyant mass obtained by SdFFF and the hydrodynamic diameter from FI-FFF the density can be directly computed. Another advantage of SdFFF over FI-FFF may be the reduced degree of non-ideal interactions with the stainless steel channel, contrary to polymeric membranes of the FI-FFF, making method optimization simpler. The tradeoff is that SdFFF works best for larger, denser particles.

c. Size exclusion and hydrodynamic chromatography

Column chromatography, both SEC and HDC, also has application in the fractionation and sizing of nanoparticles for detection and characterization. Analysis times for SEC and HDC are generally faster than for FFF, and automation may lead to high throughput applications. For these techniques, size measurement relies on the analysis of known standards, which (presumably) behave in a manner similar to the analytes of interest during separation. As in FFF, direct coupling to ICP-MS may give the specificity necessary to differentiate nanoparticle types. Interpretation of the size distribution depends on the detector used.

In SEC, the particle mixture passes through a column that contains porous packing material whose pore sizes are in the range of the particles to be fractionated. Separation of the nanoparticles depends on the length of the flow paths of the analyte. Larger particles will have access to fewer of the pores than smaller particles. Therefore, the particles are separated by hydrodynamic volume (both shape and size). The effectiveness of SEC depends mainly on the pore size of the packing material being within the range of the particles being fractionated [26, 98]. Several problems are associated with SEC, including:

- Irreversible adsorption to the packing material is common among ENMs due to the high surface area of the stationary phase (pore volume) and the high surface activity of the nanoparticles [104].
- Electrostatic interactions may degrade the purely size-dependent transport of particles through the column. The high ionic strength carriers commonly employed to minimize this problem, however, may result in aggregation.
- SEC has been shown to have low resolution when distinguishing particles of similar hydrodynamic volume. One possible solution is to recycle the analyte through the column, thereby increasing the resolution ratio with the square root of the cycle number, according to both theory and experimental data. Performing this recycling step not only increases resolution, it also reduces the problems associated with a longer column, such

as an increase in back pressure [105]. However, this approach greatly increases analysis time.

HDC is another column chromatography method that can be used to separate nanoparticles according to hydrodynamic diameter. Unlike SEC, HDC uses a column packed with nonporous beads. Flow channels are built up near the surface of the packing material, where the flow velocity approaches zero near the surface of the bead and reaches its maximum velocity at a certain distance away from the surface of the stationary phase. Accordingly, larger particles will elute sooner than smaller particles, as the smaller particles will approach the packing material closer and interact with the lower velocity areas. Because the separation of the analyte is based solely on the hydrodynamic size of the particles, the dynamic range of the packed column runs from molecular sizes up to micron-sized particles [106-108].

Compared to SEC and FFF, HDC has poor peak resolution. But, unlike SEC, this technique largely avoids phase interactions and has a very large operating range [109]. Several factors can affect the rate of transport of nanoparticles through the HDC column. At lower ionic strength, particles are repelled from the stationary phase due to electrostatic repulsion. Conversely, higher ionic strength compresses the electrical double layer, allowing for van der Waals interactions between the stationary phase and the particles, which can reduce the transport rate. If the particles are sufficiently large, van der Waals interactions may also result from the greater area over which these attractive forces may interact with one another [108].

d. Differential Centripetal Sedimentation

Recent advances in instrumentation have made differential centripetal sedimentation (DCS) an attractive means of obtaining high-resolution size information, provided the density of the particles is known. In DCS, a sample is injected into a transparent spinning disc that contains a fluid in which a density gradient has been created. The sample particles are accelerated towards the outside of the disc and pass through a beam of visible light. The resulting data (absorbance versus time) are converted into a particle size distribution using Stokes law, assuming a spherical geometry. Depending on the particle density and degree of polydispersity, analysis times can be on the order of a few minutes [68]. This short analysis time would make DCS amenable to high throughput analysis. However, only a limited number of samples, on the order of a few dozen, can be injected before the analysis must be stopped, the disc drained, and the fluid replaced.

Ensemble particle detection and characterization methods

Several techniques collect data from a large number (i.e., an ensemble of particles) of nanoparticles simultaneously, in contrast to the single-particle techniques described below. These ensemble techniques (e.g., light-scattering, light adsorption) can be useful for characterizing samples with or without prior fractionation. Information such as particle size, surface characterization, and particle size distribution can be obtained. Some of these techniques exploit quantum confinement effects that are unique to NMs, while others rely solely on the particles' physical characteristics. Although the data obtained from these measurements are complicated by the inherent polydispersity of the sample, they can be helpful in providing general information about the sample as a whole.

a. Dynamic Light Scattering

Dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS) or

quasi-elastic light scattering, is the most commonly used method for sizing nanoparticles in aqueous media. The advantages to DLS include its simple operation, its non-destructive nature, and its short analysis time. (Results are often available in less than a minute.) DLS is a very powerful method for monodisperse particles with a narrow size distribution.

DLS measures the rate of fluctuations in light scattered from the nanoparticles. These fluctuations arise when neighboring particles in solution either constructively or destructively interfere with the scattered light. The rate of these intensity fluctuations in the scattered light is analyzed as an autocorrelation function. Due to Brownian motion, smaller particles diffuse light more rapidly than larger particles and the autocorrelation function decays more quickly. The diffusion coefficient of the particle can be calculated using this decay rate, the refractive index of the solvent, the scattering angle, and the wavelength of incident light. The diffusion coefficient can then be used to determine the hydrodynamic radius of the materials based on the Stokes-Einstein relationship [98].

DLS has several compounding factors when analyzing polydisperse samples:

- Light scattering depends greatly on particle size; smaller particles exhibit scattering intensity according to the Rayleigh approximation (for $D_h < \lambda/20$, scattering intensity: $I \sim D_h^6$) and large particles exhibit light scattering according to the Debye approximation ($\lambda/20 < D_h < \sim \lambda$, scattering intensity: $I \sim D_h^2$). Large particles can mask the scattering intensity of smaller particles in the autocorrelation function and bias the measurement to larger particle sizes.
- DLS measurements can be very sensitive to dust contamination and have a low size resolution.
- DLS provides no chemical specificity and cannot distinguish ENP types.
- DLS assumes spherical particles and cannot provide information about the particle morphology.

Despite these problems, DLS is still useful for quickly determining the size distribution of nanoparticles in simple media without pretreatment of the sample [96, 98, 110]. Used alone it is not suitable for analysis of environmental samples. However, DLS has been used as an online detector for FFF and SEC, because introducing fractionated nanoparticles into the scattering cell reduces the issue of polydispersity and dust contamination.

b. Static light scattering

Static light scattering (SLS)—also known as multi-angle light scattering (MALS or MALLS), classical light scattering, or Rayleigh scattering—is a technique that also uses the light scattering properties of nanoparticles to determine the size of the analyte of interest. Unlike DLS, which uses the relative motion of the particles to determine particle size, SLS relies on the angular dependency of the scattered light derived from particle size. This is based on the principle that particles of different sizes will generate constructive and destructive interference at certain angles. As a result, the scattered intensity of light is measured at different angles over time and averaged. This information can then be used to obtain particle properties such as size and the root mean squared of the radius of gyration. Unlike DLS, SLS can also be used to obtain information about particle structure and morphology, which can be used in conjunction with data from DLS to determine particle shape. Like DLS, SLS depends on the Rayleigh-Gans-Debye

approximation, which requires the refractive index difference between solvent and particle to be negligible and for light absorption to approach zero as particle concentration decreases [96, 98, 110]. One of the most successful applications of SLS is the use of MALLS as an online detector for FFF and SEC. By providing particle fraction prior to MALLS analysis, the problem of sample polydispersity is reduced. The disadvantage of online coupling is that dilution occurring during separation creates a need to work at high nanoparticle concentrations, on the order of milligrams per liter.

Spectroscopy techniques

Various spectroscopy techniques can also be used for nanoparticle detection and characterization. At the nanometer scale, some particles can experience quantum confinement effects that result in unique absorbance and fluorescence effects, which depend on particle composition, shape, and size. Measurement techniques such as infrared (IR) spectroscopy and NMR spectroscopy can be used to study the surface of these particles, giving information about surface functionality.

a. Absorption and photo-luminescent spectroscopy

A common method for characterizing nanoparticle size is UV-visible spectroscopy (UV-Vis), which uses UV radiation to excite the sample and measure its absorbance as a function of the intensity of light initially transmitted through the sample. Due to their size, several nanoparticles have the capacity to exhibit unique optical-electrical properties caused by quantum confinement effects. These effects are responsible for both size-dependent band gaps within ENMs (band gaps increase with decreasing particle size) and size-dependent absorption extinction coefficients (absorptivity increases as particle size increases) [111]. Some ENMs also exhibit a surface plasmon resonance band, which is caused by the oscillation of electrons at the metal-dielectric interface, leading to a characteristic absorption band that is dependent on size. These properties can be used to characterize the size, shape, and surface functionality [98, 112] of a given nanoparticle. UV-Vis has been used to study the aggregation state of functionalized and bare gold nanoparticles. When the gold nanoparticles aggregated, the surface plasmon degenerated into two bands: a transverse resonance band that absorbed shorter wavelengths of light and a longitudinal resonance band that absorbed longer wavelengths of light. Both bands were detectable by UV-Vis, demonstrating the ability to monitor stability and surface functionality of the gold particles [31, 113]. The surface plasmon resonance is also affected by the shape of the ENM because the interface between the surface of the ENM and the dielectric medium depends on the shape and size of the nanoparticle [114]. Application of UV-Vis to complex multi-component systems requires pre-fractionation by methods such as FFF or HDC.

b. Infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR), which can determine functional groups based on their vibrational stretching modes and molecular symmetry, has the capability to characterize not only the NM but also the surface groups attached to the surface of the nanoparticle. In particular, near-infrared fluorescence spectroscopy (NIRF) has been used to characterize carbonaceous NMs such as CNTs and both C₆₀ and C₇₀ fullerenes [115]. Although the number of IR active vibrational modes in the analysis of CNTs is diameter-independent, the location of the peaks is highly dependent on tube diameter. Smaller diameter tubes have been shown to exhibit greater absorption intensity at shorter wave-numbers, which may be useful in distinguishing

single-walled and multi-walled CNTs from one another [116]. The use of NIRF for the analysis of CNTs is very promising due to its high sensitivity, ease-of-use, and low background signal due to the fact that biological and naturally occurring molecules rarely fluoresce in the near-infrared region [56].

FTIR is also commonly used to characterize fullerenes because four strong vibrational modes are present in C₆₀ fullerenes due to their truncated icosahedral symmetry [117]. This can distinguish C₆₀ fullerenes from C₇₀ fullerenes, which exhibit six vibrational modes due to their relatively lower symmetry [118]. By using a rough metal surface, the FTIR signal can be enhanced in both reflected and attenuated total reflectance (ATR) modes. This is accomplished by exploiting surface plasmon effects of the substrate, increasing measurement sensitivity. This technique is known as surface enhanced infrared absorbance (SEIRA) and has been used to characterize C₆₀ NMs [119].

IR spectroscopy has also been useful in characterizing the functional groups attached to the surfaces of NMs because the technique is specifically attuned to the vibrational stretching of the bond between one element and another. It has been used to characterize the surface groups on a wide range of NMs, from mesoporous silica such as mobile crystalline material-41 to gold nanoparticles and iron oxide nanoparticles [120-122]. Application to natural samples, where nanoparticle concentrations are low and possible interferences are present, may limit this technique's applicability.

c. Nuclear magnetic resonance

NMR can be used to study the local arrangement of atoms in a nanomaterial. In particular, solid-state magic angle spinning (MAS) NMR has been used to characterize a wide array of ENMs, ranging from the structural arrangement of amorphous zinc phosphate nanoparticles to the characterization of zeolites used in the dehydrogenation of benzene [115, 123, 124]. In addition to studying the local arrangement of atoms in a material, NMR can be employed to study the binding of surface groups to nanoparticles [125]. NMR has been used to investigate water adsorption to CNTs, specifically by using hydrogen (¹H) MAS NMR to increase spatial resolution [126]. In addition, phosphorous (³¹P) NMR was used to investigate the binding of phosphoric acid to tin dioxide (SnO₂) nanoparticles [125]. Despite its high sensitivity and ability to characterize a material at the atomic level, this technique has a number of drawbacks. They include difficulty in selecting an appropriate isotope for analysis and interference from naturally occurring magnetic materials such as iron oxides.

Particle counting and characterization methods

In contrast to the previously discussed methods, the following methods determine the characteristics of NMs one particle at a time:

- Electron microscopy.
- Nanoparticle tracking analysis.
- Single particle ICP-MS.
- Laser-induced breakdown detection.

The particle-number-based methods give information on the physical characteristics of the NMs and in some cases can provide number concentration data.

a. Electron microscopy

Several electron microscopy techniques can give direct size and characterization information about a single particle in a sample:

- In TEM, the electron beam passes through the sample, interacting with the electron density of the sample to produce an image. This gives a physical image of the particle shape and size and can be used on particle sizes ranging from micron to sub-nanometer materials.
- SEM also uses an electron beam, but instead of passing through the sample, the beam is reflected back at an angle towards a detector that gives a surface image of the particle. In doing so, a better picture of the shape and morphology of the particle can be obtained.
- Cryogenic SEM has been used in some studies to obtain a snapshot of the sample that preserves the state of the ENM in an environmental sample [30, 96, 98, 127].

Most transmission and scanning electron microscopes come equipped with energy dispersive X-ray capability, which allows the user to determine the chemical composition of the material being imaged. Though the size information obtained from electron microscopy is very precise, it would require many images of the sample to obtain a statistically significant particle number concentration. In addition, these techniques require high vacuum, which alters the natural state of the ENM in an environmental sample.

b. Nanoparticle tracking analysis

Like previously discussed light scattering techniques, nanoparticle tracking analysis (NTA) uses Brownian motion and diffusion coefficients to determine the size of a nanoparticle. Unlike DLS and MALS, however, a single nanoparticle is tracked by a charge-coupled device (CCD) camera. The particle first is detected by light scattering, then tracked from its initial position as a function of the distance moved in a given time interval determined by the camera's frame speed. The distance traveled is then related back to the hydrodynamic radius using a modified Stokes-Einstein relationship. An obstacle to the use of NTA is the need to choose a travel distance long enough for a statistically relevant number of particles to be sized so that a particle size distribution can be determined while still maintaining accuracy in the measurement [128-130]. Some information on particle aggregation can be obtained by comparing the intensity of light scattered by particles of the same size.

c. Single particle ICP-MS

ICP-MS has been a mainstay in determining the elemental content of aqueous and environmental samples. Typically, this technique has only been used to determine total elemental concentration in a sample, but recent advances have made it possible to determine the elemental composition of single particles in the sample. This technique has been used for a wide range of applications including the detection of CNTs, the analysis of silver nanoparticles in wastewater, and the release of nanoparticles from consumer products [131-133]. In single particle ICP-MS (SP-ICP-MS) an undigested sample is first nebulized into an argon plasma, which decomposes the sample and ionizes the constituent atoms. The ions then pass through a mass selector (e.g., quadrupole, magnetic sector) and are detected. Determining the elemental composition of single particles is achieved by reducing the dwell time (the duration for which the instrument takes a reading) to a microsecond value. This allows a nanoparticle to be detected as a pulse of intensity above a

background of ambient ion signal. The assumption is that each pulse correlates to one nanoparticle event, which allows a particle number concentration to be calculated as the number of pulses obtained during a reading divided by the volume of sample analyzed. Size information can also be obtained by generating a calibration curve of intensity for a given mass of dissolved analyte and using a standard particle to determine the efficiency of the mass flux for a given intensity. The signal intensity produced by a given particle event can then be used to calculate the equivalent mass of the particle, which can be converted into a size if the density of the material is known. Samples often need to be diluted for this technique so that the concentration will be sufficiently low (low parts per trillion to parts per billion, depending on particle size) to ensure that only one particle enters the plasma at a time [128, 131, 133-135]. Because only particles containing the element of interest are detected by the ICP-MS, other background particles do not interfere with the method.

d. Laser-induced breakdown detection.

A highly sensitive single particle characterization technique is laser-induced breakdown detection (LIBD), which uses a pulsed laser to form a plasma when a particle passes within the focal volume of the optical cell. This technique is based on the principle that the energy required to breakdown the dielectric properties of water surrounding a nanoparticle will be less than that of pure water. As such, breakdown should only occur when the particle passes through the path of the laser. Either a piezo-electro crystal attached to the cuvette or a CCD camera captures the breakdown event. LIBD measures the breakdown probability, which depends on particle size and concentration. The main drawback of this technique is its extreme sensitivity to small particle sizes and low concentration (less than parts per trillion). However, this technique is not able to distinguish between particle types, and variation in particle composition may cause problems in relating the information obtained during the measurement back to the calibration curve [67, 98, 136].

Optical and biological sensors

A relatively new method for the direct detection and characterization of NMs is the application of sensors. Two types of sensors typically are employed. The first type is nano-enabled sensors that incorporate nanoscale materials. Chemical sensors, such as fluorophores, can be used to detect NMs at very low concentrations. For instance, a rhodamine-derivative fluorophore can be transformed into oxazoline in the presence of Ag^+ (resulting from the oxidation of a silver nanoparticle), which elicits a strong fluorescent response. This enables detection of the presence of silver nanoparticles down $\mu\text{g L}^{-1}$ concentration levels, although this particular technique's effectiveness can be reduced by ambient silver ions in the environment as well as other ions that may interfere with sensors that are less-ion specific [26, 96, 137]. Biological sensors are the second type of sensor used to detect ENPs. Antibody-antigen recognition can be a highly selective mechanism for the identification of nanoparticles. For example, oligonucleotides with repeating cytosine bases combined with a fluorophore can be used to detect silver nanoparticles. Coordination between surface-associated silver ions and cytosine leads to a conformational shift in the oligonucleotide from a random coil to a hairpin structure, which greatly enhances the fluorescence signal [26].

Biological sensors are used more commonly to detect the toxicological response to ENPs in biological systems. In particular, several techniques measure the generation of reactive oxygen

species as a result of ENM cytotoxicity. Dissolved oxygen sensors also can be used to monitor a cell's respiration, giving insight into ENP toxicity. Last, more complex biological systems, such as the Langerdorff heart, can be used to monitor the toxicity of ENPs [138]. Though these sensor techniques have the potential to be tailored to ENMs, several possible interferences, such as dissolved constituents, may bias the measurements [96].

B. ENP Characterization in Complex Laboratory Matrices

Although nanotechnology is a fast-growing commercial enterprise, and some of its materials incorporate ENMs, its widespread integration into commercial products is relatively recent (i.e., occurring over the past 15 years). While a goal of many government agencies is to determine the extent of the risks nanotechnology may pose to the environment, very little is known about how ENMs behave in environmental matrices. The appropriate application of nanometrology for the detection and characterization of NMs in complex systems is still in its early stages. As a result, a great deal of effort has been spent studying nanoparticles in a controlled laboratory setting, where researchers can precisely control variables that may mimic environmental matrices. Some key characteristics that need to be identified in the environment are:

- Size.
- Surface charge.
- Aggregation or dispersion state.
- The extent of dissolution.

This section reviews research that has been performed to characterize and identify these metrics under controlled conditions that mimic those that may be found in environmental systems.

Size, morphology, and aggregation state

Information about the size of NMs may be key in determining the extent of potential bioaccumulation and transport of these materials in the environment. Some ENP dispersions may have narrower size distributions than their naturally occurring counterparts as nanomaterials produced anthropogenically are tailored for specific, size-dependent properties; whereas, naturally occurring nanomaterials generally will not have such restrictions.

Most electron microscopy measurements can be performed in conjunction with elemental analysis via energy dispersive spectroscopy (EDS), which can give particle-specific information about composition. This technique has been used to characterize a wide variety of NMs in different matrices, including silver nanoparticles that had been synthesized in the presence of natural organic matter and metallic NMs found in various food and commercial products [110, 130, 139]. Despite its utility, there are some disadvantages to this technique. Many images are required to generate an appropriate size distribution, because the technique determines the size of individual particles one at a time, and, because NMs are found in very low concentrations in the environment, it may be necessary to evaporate the sample in order to concentrate it enough for a TEM measurement [134]. Due to the high background level of naturally occurring nanoparticles in the environment, it may also be difficult to find ENPs in a TEM sample image. Last, TEM requires the samples be dried for analysis, which may disturb the state in which the NMs are found in the environment.

In addition to microscopy, DLS is one of the most frequently used methods for determining the size of nanoparticles in aqueous media [98, 110]. Many studies have recorded DLS measurements in short time intervals, in what is known as time-resolved DLS. Using DLS to measure hydrodynamic size rapidly allows the growth of aggregates to be monitored over time. This capability has been used to understand the effect of humic and fulvic acid interactions with particles, particle homoaggregation, and particle heteroaggregation with clay minerals in an aqueous environment [28, 31, 32, 140]. Unlike some other measurements, there is no need to generate a calibration curve or pretreat a sample in order to record a DLS measurement. Despite its many uses, the information available through DLS measurements is limited, because the light scattering mechanics cannot account for the shape or chemical composition of the particle. In addition, larger particles may mask the signal from smaller particles, making the analysis of polydisperse samples (the norm for environmental samples) intractable.

The size of some NMs may be indirectly determined using UV-Vis spectroscopy and exploiting the surface plasmon resonance of the nanoparticle. This technique has been used frequently to monitor the size and aggregation kinetics of gold nanoparticles [141-143]. Studies have shown that the intensity of the surface plasmon resonance maxima may decrease with aggregation, or red-shift from the transverse plasmon band to the longitudinal band upon aggregation [31]. UV-Vis has also been used to study the shape-dependent properties of silver nanoparticles, which may be useful in characterizing the shape of NMs in aqueous samples [114].

FFF can also be used to size nanoparticles. With a standard calibration curve, one can separate and size a poly-dispersed sample of NMs. When coupled with the appropriate detector, other important properties such as surface charge and composition can be ascertained. Both flow and sedimentation FFF have been used in a variety of complex biological and environmental matrices. Although FFF cannot distinguish between natural and engineered nanoparticles on its own, element-specific information can be obtained when it is coupled with ICP-MS. This coupling can aid in differentiating ENPs from high background levels of naturally occurring NMs [101, 144]. This technique has also been applied to silica nanoparticles extracted via acid digestion from rat tissue homogenate and human endothelial cell lysate [102]. FFF can also be used to monitor aggregate growth, as was shown in solutions of silver nanoparticles in wastewater [144].

One other technique capable of sizing nanoparticles is SP-ICP-MS, which can provide element-specific information about individual particles that are ablated in the plasma. This technique has been used to size a variety of NMs such as silver, gold, and metal oxide particles in various complex media (e.g., wastewater, bovine serum albumin). Although this technique requires information regarding particle shape and is currently limited by the size of the nanoparticle, it can be a powerful technique for characterizing NMs at environmentally relevant concentrations and does not require any prior fractionation [128, 131, 135, 145].

Surface charge/surface groups

The surface groups attached to ENMs may help in distinguishing them from naturally occurring NMs. Surface groups serve many purposes, such as stabilizing the particles to prevent aggregation or imparting binding specificity to the nanoparticle for a specific use. As such, characterizing these surface groups is important to the characterization of ENPs. Different

methods can be employed to study nanoparticle-surface group interactions. These methods include NMR and IR spectroscopy. FTIR spectroscopy has been used to study humic acid sorption onto silica and magnetite ENPs, which may be an important mechanism upon release into the environment [146-148].

Similarly, zeta potential is an important property to measure and has implications for the transport and retention of NMs in the environment. Although most ENPs are coated with specific surface groups, these groups may be replaced or overcoated in aqueous environments by ubiquitous organic acids. Many studies have shown that ENPs in the presence of humic acid exhibit a strong negative charge, a result of the many carboxylic acid and phenolic groups present on the molecule [28, 31]. Surface charge is important because strong charges (both positive and negative) tend to lead to more stable particle dispersions. In contrast, as surface charge approaches zero, particles are less electrostatically stabilized, leading to a higher incidence of aggregation [140]. Measuring the surface charge of ENPs in environmental matrices (e.g., soil and sediment pore water) is not possible without isolating the specific ENPs of interest from other charged particles in the matrix.

Dissolved ions vs. nanoparticulates

In addition to high background levels of incidental and naturally occurring NMs, many environmental samples will contain a high concentration of dissolved ions that, when using chemical analysis-based methods, may overestimate the amount of material present in nanoparticle form. One way of distinguishing between nanoparticles and dissolved forms of the material is through filtration methods, whereby particles can be size-fractionated, with the remaining fraction composed of dissolved ions. Similarly, centrifugation can also be employed where particles may settle out under the centrifugal force, and the supernatant that is decanted should contain the dissolved forms of the material [147, 149].

SP-ICP-MS can also distinguish between dissolved and nanoparticulate forms of the material, as NMs will be represented as pulses above the background levels and dissolved forms are present as an elevated background signal. Although still under development, this technique has already shown promise in its ability to distinguish between nanoparticles and dissolved forms of the nanoparticle [128, 131, 135, 145].

C. ENP Detection and Characterization in Environmental Samples

Despite efforts to recreate the conditions ENPs are exposed to in the environment, the primary goal of most research is to develop sufficient techniques to detect and characterize these materials in environmental samples. Several challenges impede the ability to effectively characterize ENPs, including their expected low aqueous exposure concentrations (measured in ng/L), the high background levels of naturally occurring suspended colloidal material, and the inability of current techniques to isolate the ENPs from the matrix without introducing artifacts or perturbing the sample. These challenges are compounded for soil and sediment systems by the even higher concentrations of background particles ranging from nanometer to micron size. Although few reports on detecting ENPs in environmental samples exist, their number can only be expected to grow as a greater number of manufactured NMs are increasingly released into the environment. The following section is a brief summary of research into the detection and

characterization of ENPs in environmental media. The section also discusses general considerations for the analysis of these materials in complex environmental matrices.

Expected low ENP concentrations

Current risk assessment models and projections have determined that ENPs will enter the environment at parts-per-trillion (ng/L) concentrations [26, 150]. As such, the ability to detect and characterize these materials may be limited by the detection limits of the chosen instrumentation. Various sizing techniques for the characterization of ENPs in simulated lake water were reviewed[151]. They determined only electron microscopy techniques could operate at the appropriate concentration levels for the study (1–100 mg/L). Some techniques, such as NTA, could not generate a sufficient light-scattering signal to analyze the sample properly. Many of these sizing techniques require higher concentrations of analyte to operate than are found in the environment [151].

To characterize ENPs in environmental samples, it may be necessary to pre-concentrate the sample. Occasionally, concentrating ENPs in a sample can be simple, such as evaporation or centrifugation [26, 152]. Other techniques, such as cloud point extraction (CPE) and solid-phase extraction (SPE), have been used to separate nanoparticles from their environmental media in order to concentrate and characterize them [153, 154]. Many of these pre-concentration steps may introduce artifacts into the sample, which obscure the sample's environmental state. It is therefore important to either choose the appropriate technique to analyze the sample at the expected concentrations, or be aware of the many artifacts that can develop when concentrating the sample. A higher concentration of particles can also result in agglomeration of the smaller colloids, distorting the representativeness of the sample [151, 152].

Elevated natural NP / colloid background

The many analytical challenges resulting from the low concentrations of ENPs in environmental samples are further compounded by the relatively high concentration of naturally occurring nanoparticles and incidental nanoparticles that are ubiquitous in the environment. These natural nanoparticles arise from various biological and abiotic processes in the environment that produce particles of similar sizes, shapes, and in some cases composition, to the ENPs expected to enter the environment [5, 6]. ENPs are likely to constitute a very small fraction of the total colloidal population in environmental systems. Sample prefractionation methods that separate ENP from natural background materials may facilitate detection and characterization.

The most widely used fractionation techniques are centrifugation and filtration [152, 155]. These techniques have been applied to soil leachates and wastewaters to fractionate particle size distributions with mixed results. Although filtration is the preferred method due to its relative ease of use and cost, artifacts can be introduced as a result of particle adhesion and aggregation at the membrane surface [152, 156]. Similarly, centrifugation can induce aggregation as the differential settling velocities during the centrifugation process can result in a higher number of particle collisions [98, 152].

To limit the generation of fractionation artifacts, many researchers use FFF as a suitable alternative for the separation of nanoparticles. AF4 has been used in the analysis of organic macromolecules and inorganic colloids in different environmental media such as lakes, oceans,

and soils [98, 101]. SdFFF has also been applied to the fractionation of colloids from soil leachate and is both a complement and an alternative to centrifugation and filtration fractionation methods [152]. The ability to characterize the separated fractions, however, will be reliant on the detector coupled to the FFF. Whereas light-scattering detectors require relatively high concentrations (< 1 mg/L) to achieve sufficient scattering (DLS, MALLS or absorption [UV-Vis]), FFF may be coupled to ICP-MS to produce detection limits as low as ng/L for some elements, approximately the concentration expected for ENPs in the environment [131, 144, 151].

The surface properties imparted by engineered coatings may allow for selective extraction of these colloids from environmental samples. This is most often the case with carbonaceous materials such as fullerenes. Their hydrophobic nature is exploited via extraction with a non-polar solvent (i.e., toluene) and subsequently analyzed. For functionalized water-soluble nanoparticles, extraction by toluene may be insufficient and salt addition, evaporation, or solid-phase extraction may be necessary [154]. In addition to extraction, sensors may be developed to interact specifically with nanoparticle coatings and selectively detect the NMs in a complex matrix. The greatest obstacle in using this technique is either the degradation or over-coating of the surface coating in the environment as a result of natural processes [26, 96].

Selective detection and characterization of SWCNTs in the environment has been achieved using NIRF. SWCNTs can be classified as metallic or semi-conducting based on their chiral-wrapping index, with the semi-conducting type accounting for nearly two-thirds of the distribution of chiralities. These semi-conducting CNTs fluoresce in the NIR range when excited by visible/NIR light at wavelengths between 600 and 800 nm. Such emission allows for specific detection of SWCNTs even against the high background levels of other organic and carbonaceous materials that are abundant in environmental samples. The emission wavelength is also directly related to the diameter of the CNT, making this a useful characterization technique as well. This technique has been used to detect different diameters of SWCNTs in estuarine, sediment, and biological matrices [91]. The extraction and pre-treatment of these samples will be extremely important. Yet, the selective identification and characterization of SWCNTs shows that NIRF spectroscopy is a promising and powerful tool for the detection of semi-conducting CNTs in the environment [90, 91].

X-ray Absorption Spectroscopy

Many nanomaterials are crystalline metal or metal-oxide materials, or they are made from semi- or highly ordered arrays of atoms. One technique for determining the speciation of metal nanoparticles in environmental and biological samples is X-ray absorption spectroscopy (XAS). This technique has been used to speciate metals in environmental samples for several decades [157]. One advantage of XAS over other techniques is that absorption spectra can be collected directly from wet samples, including soil, sediment, and tissue. This non-destructive, in situ analysis eliminates the need to isolate the NMs from the sample prior to measurement provided that the NMs are present in sufficient concentrations. Another advantage of the technique is that it is element specific, i.e., information can be collected on only a specific element in the sample such as cerium, silver, or titanium. While detection limits are energy dependent and element specific, the speciation of metal and metal oxide nanoparticles can be determined in samples with concentrations of metal as low 10 to 100 mg/kg [56]. With fairly simple sample

concentration techniques (e.g., collection of fines from specific samples), the lower end of the detection limit may be extended.

Disadvantages of XAS include:

- The spectra provide an “average” speciation of the specific element in the samples and therefore cannot provide particle-specific information.
- XAS must be performed at a synchrotron facility, which is highly specialized and expensive to operate.
- ENMs made from very common environmental elements such as iron or aluminum could be difficult to characterize using XAS due to the presence of high background concentrations of that element.

Despite these limitations, XAS is perhaps the only technique that can provide in situ determinations of the speciation of metal ENPs directly in environmental samples and so is a critical tool to advancing research in the environmental health and safety of ENMs.

XAS can provide two principal types of information:

- The first type is the average oxidation state of the metal in the sample being investigated. This information comes from the X-ray Absorption Near Edge Region known as XANES (X-ray Absorption Near Edge Structure) or Near Edge X-ray Absorption Fine Structure (NEXAFS). Simply stated, the ability to eject a core electron from the metal atom with X-ray photons is easier for less oxidized materials, so the energy at which a sample begins to absorb X-ray photons indicates the oxidation state of the metal in that material. For example, the oxidation state (or ratio of oxidation state) of cerium in cerium dioxide nanoparticles was evaluated using XANES [158]. XANES can also be used to indicate the degree to which redox transformation of the ENM may have occurred.
- Second, XAS provides information about the local bonding environment surrounding the metal being probed. This information is garnered from the X-ray Absorption Fine Structure (XAFS) or Extended X-ray Absorption Fine Structure (EXAFS) region of the XAS spectra, or it can be determined from the XANES region if different species have distinct XANES features. Simply stated, this allows the determination of what elements the metal is bonded to. For example, silver will have all silver nearest neighbors in a Ag(0) ENP, but will have oxygen or sulfur nearest neighbors in silver oxide (Ag₂O) and silver sulfide (Ag₂S), respectively. This gives rise to unique spectra that can be used to determine the average speciation of the ENP in the samples. The shape of the spectra and bonding distances can also be used to obtain structural order information about the metal in the sample.

Both XANES and EXAFS have been used to monitor the transformation of ENPs in environmental samples such as biosolids, soils, sediments, plants, and other biological tissues. For example, the speciation of silver was monitored using EXAFS during an 18-month, simulated wetland mesocosm experiment [159] and using XANES in biosolids [160]. Speciation of ZnO and CuO NPs were determined using XANES in the shoots of wheat plants exposed to these nanomaterials [161]. The transformation of the speciation of titanium dioxide nanoparticles (anatase vs. rutile ratio) inside plant tissues was identified using XANES [162].

Preserving sample representativeness

Arguably the greatest challenge in characterizing of ENPs in the environment is the ability to analyze these materials *in situ* with minimal perturbation. Currently, no field instrumentation exists that can detect ENPs in environmental samples. Therefore, great care must be taken when sampling these materials to minimize any perturbation that would diminish the sample's representativeness.

The imaging of ENPs is a particular challenge, because the mainstay of nanoparticle imaging, TEM, requires a vacuum that can introduce artifacts such as aggregation from the concentration of particles, the formation of a meniscus that can obstruct particle imaging, the precipitation of salts and other dissolved species that obscure particle imaging, and the introduction of several interferences into the EDS spectrum. To this end, some researchers have used environmental SEM, which operates above vacuum pressure. However, the residual water layer obstructs some of the particle imaging and reduces the resolution due to interactions of the electrons with the water vapor [98]. A relatively new imaging technique, WetSEM, uses electron-transparent capsules, which allow for imaging of the ENPs under fully liquid conditions. Tiede et al. [146] used this technique to image metal oxide nanoparticles under fully liquid conditions and investigated various capsule membrane coatings to adhere the particles of interest to the membrane wall to improve imaging. Although more work is required to fully develop this technique, it has several advantages over conventional SEM, as the various drying artifacts are avoided and an accurate EDS spectrum can be obtained [163].

Another rapidly developing technique that could allow for the characterization of ENPs is SP-ICP-MS. By detecting individual particles and aggregates as pulses of intensity during a given dwell time, the signal intensity generated can be converted to mass and, assuming a particular morphology, determine particle size. This technique has been applied to various metal oxides, gold and silver nanoparticles, and CNTs, demonstrating the technique's utility for characterizing these materials under environmentally relevant conditions [128, 131, 133, 135, 144, 145, 164]. Although data on its application to environmental samples are limited, this technique has been used to detect silver nanoparticles in wastewater effluent, confirming that current wastewater treatment methods are insufficient at removing ENPs from waste streams [131].

5. NEW APPROACHES

The need for the development of sensitive and selective techniques for the detection and characterization of ENMs stems from their unknown ecological risk. The current paradigm is that risk is a combination of exposure and hazard. Hazard will be a result of the inherent ecotoxicity of the ENM. It can be assumed that most exposure will come from NMs used (and released) from consumer products or product manufacture. If either of these components is considered "high," then risk is possible. Exposure can be conceptually related to a number of life cycle components in the following equation:

$$E = \Sigma (S \times f) \times D$$

Where

E is the exposure potential that varies as a function of S .

S is the sum of the NM source mass in various commercial products.

f is the fraction of NMs released from the various products.

D is the distribution of NMs within environmental compartments.

Whereas current studies are ongoing in assessing the hazard of these nanomaterials, the instrumentation and methodology necessary to quantitatively assess the exposure is still underdeveloped. Though many of the previous analytical techniques discussed can be employed to nanomaterials in pristine conditions, and in some cases complex environmental matrices, there is still a need for instrumentation that is sufficiently selective, sensitive, and robust to overcome the significant challenges to ENM detection in the environment. This section details potential future directions for nanometrology and its ability to overcome: the challenges of environmental transformations of ENMs; low expected release concentrations; and the ubiquity of naturally occurring nanomaterials that obstruct the detection of ENMs in the environment.

Mass spectrometry-based methods

MS has become the workhorse for both inorganic and organic environmental analysis. Organic contaminant analysis by MS, generally coupled with some form of chromatography, allows evaluation of exposure concentrations and the study of contaminant transformations at exceedingly small concentrations (e.g., parts per quadrillion). Similarly, inorganic analysis, generally by ICP-MS, can give information on elemental concentrations at parts-per-trillion levels. The addition of chromatography allows the form of the metal and its speciation to be determined. This can be essential to risk assessments of metals, because not all metal species are equally bioavailable. Although powerful, MS is challenged by NMs. In general, NMs do not display molecular structures that MS can identify and distinguish from background components as readily as MS can for organic contaminants. Furthermore, physical characteristics and chemical composition must be determined to fully characterize NMs. Despite these limitations, a number of applications of MS may serve to detect and quantify NMs in environmental and biological media.

Element Ratios

A number of important ENMs contain relatively common elements such as silicon, iron, titanium, and cerium. These are manufactured as pure oxides and thus contain only oxygen in addition to the metallic element. In contrast, in natural background particles, these elements generally either exist largely in more complex, multi-element-containing minerals, or contain trace element impurities. Thus, in environmental samples containing only natural particles, water samples in particular, a specific ratio of these elements to other background elements will exist. The element ratios should be a fingerprint of the natural particle population and reflect the source materials (i.e., watershed soils or aquifer materials). The introduction of elementally pure materials should perturb the natural ratio. The ability to detect ENPs through perturbations in the natural ratio depends on the amount of ENPs introduced, the concentration of background elements, and the accuracy of the MS in quantifying the ratios.

In general, high-resolution ICP-MS instruments can measure element ratios to 0.1 percent (one part per thousand) accuracy. For example, a bulk sample analysis of element ratios, in order for

an engineered titanium dioxide particle to be detected, it must contribute at least 1/1,000 of the total titanium mass in the sample. If background particulate matter is in the mg/L range, with titanium present as a few percent of the particle mass, then titanium from ENPs must be present in the range of a few hundred micrograms per liter ($\mu\text{g/L}$). Although certainly possible, for most elements associated with ENPs, these levels are not expected in most environments. Methods to separate ENPs from the larger particles in the matrix and concentrate them will further improve the sensitivity of this method.

Both FFF-ICP-MS and SP-ICP-MS may provide a partial solution. With FFF-ICP-MS, the element ratio within a narrower size range can be determined. If the ENP is somewhat monodisperse, the isotopic ratio across this size range would be more highly perturbed than across the entire size spectrum, which is what is examined by bulk analysis. Thus, by using FFF-ICP-MS, the effective detection limit for ENPs could be substantially reduced. Recent developments in “fast scan” SP-ICP-MS may allow for the simultaneous detection of multiple elements in a nanoparticle-generated elemental pulse. Whereas bulk isotope ratio measurements rely on the ratio of masses of elements in background particles and ENPs, SP-ICP-MS relies on detecting a certain number of ENPs in the presence of a much larger number of natural particles. To make an analogy to the previous discussion, the question arises “Can one ENP be robustly detected in the presence of 999 natural particles?” If the background particles are considerably larger than the ENPs, then there are fewer of them and the mass-based detection limit is reduced when using SP-ICP-MS. The “fast scan” approach also allows for higher particle number concentrations to be examined, which provides better counting statistics for short data acquisition times.

Isotope methods

Somewhat analogous to the element ratio approach, stable isotopes of the elements making up ENPs and background particles might be used. Discrimination might be possible if the source of the materials used in making the ENP has a very different isotopic signature than the background particles present in the environment into which the ENPs are released. Furthermore, detection would be facilitated if isotopic fractionation occurred during ENP manufacture. These natural differences are likely small and would probably result in a detection limit higher than the element-ratio-based approach. A more likely scenario would be to purposely introduce a unique isotopic composition into the ENP. This has been done for a number of research studies, particularly those examining zinc oxide bioavailability [165-167]. However, it is rather unlikely that manufacturers will take on the financial burden of creating isotopically labeled ENPs for use in nano-enabled products.

MALDI-TOF-MS and LDI-TOF-MS

The accurate size determination of ultras-small ($>1\text{nm}$) ENMs by conventional electron microscopy is challenging as a result of drying artifacts introduced by the vacuum in TEM which may incorrectly represent the size of the nanocluster. To this end, matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF-MS) has been used to determine the mass of these ultras-small particles, which can then be converted to a volume assuming a spherical geometry. This technique has so far been applied to titanium dioxide nanoparticles in a dithranol matrix (as dithranol lacks an acidic proton allowing for accurate determination of peaks). The maximum of the broad, normal distribution obtained was then used

to calculate the diameter of the particles assuming a spherical geometry. Laser desorption ionization time-of-flight mass spectrometry (LDI-TOF-MS) was also used to characterize the particles showing a maxima at $m/z = 167$, which corresponds to titanium(III) oxide (Ti_2O_3) with a sodium ion, a frequent contaminant. With more development, this technique may be a valuable tool in the characterization of sub-nanometer particles [168].

6. SITE-SPECIFIC ENM RELEASE SCENARIOS

Due to the many challenges involved in detecting and characterizing ENMs in environmental samples, it may be beneficial to narrow the analysis to focus on only certain NMs. Knowing the source of the ENP release could aid in the analysis of the environmental sample and increase the efficacy of the techniques used. ENPs may be released from a variety of sources in forms different from their initial, pristine morphologies. In addition to unintentional environmental exposure through the use of nano-containing products, the intentional application of NMs to soils (i.e., remediation via zero-valent iron, nanopesticides) could be a source of ENPs in environmental samples. NMs could enter the environment from a variety of potential point and non-point sources, as discussed below.

ENP production site

The most likely exposure to pristine, unaltered NMs will occur at the site of manufacturing. Several studies have investigated the effects of workplace exposure to NMs, particularly airborne exposure. In particular, CNTs have been investigated due to their similarities to other known toxic high-aspect-ratio materials (e.g., asbestos). In addition to inhaling NMs, it is possible those working in the production and synthesis of these materials may come into dermal contact with these ENPs [169-171].

Site of ENP use

A common exposure route of nanomaterials will occur at the site where the nanomaterial product is employed. Studies have attempted to model the expected environmental exposure to silver nanoparticles. All of the current models used to predict nanomaterial environmental exposure rely on extrapolation from limited production-quantity data, which makes predicting environmental concentrations of these materials difficult. Understanding the potential use of nanomaterials may aid in determining which ENPs can be expected to be used at a particular area. For instance, as titanium dioxide and zinc oxide ENPs are common components of sunscreens and lotions, their concentrations might be higher near coastal areas and beaches. Some nanomaterials, such as zero-valent iron, are directly applied to the environment in order to remediate other contaminants such as trichloroethylene (TCE) [83]. Information on where the ENPs are most likely applied may help narrow the search for them in the environment [3, 34-36, 172, 173].

Transport accident

Nanomaterials may be accidentally released into the environment during transport. In these situations, detailed knowledge of the composition and quantity of the ENPs may assist in an accurate assessment of the risk posed by the environmental exposure to them. The detection and characterization of these materials would also be assisted by this knowledge, leading to a quicker response to and remediation of these potential contaminants [36].

Non-point sources

Lastly, there are several non-point sources that are likely to contain ENPs. Exposure to these sources will most likely occur through the treatment of the waste in which these materials may be contained. For instance, many of the waters containing ENPs will likely be treated at a wastewater treatment plant. The biosolids collected at these treatment facilities may then contain certain ENPs that can be applied to soils and enter the environment [94]. In some countries, waste incineration is a common practice. Although this process may destroy carbon-containing nanomaterials, inorganic and metallic nanoparticles may persist and be released into the atmosphere. Locational information on these waste processes and waste disposal areas may aid in the detection of ENPs that enter the environment [34, 36, 174, 175].

7. SUMMARY

Responsible development of nanotechnology requires an understanding of potential ENP releases throughout the life cycle. Some points of the life cycle (e.g., manufacturing) may not offer substantial challenges to existing nanometrology. Whereas other points, such as end-of-life may be more challenging. Detecting, quantifying, and characterizing ENMs in environmental and biological samples continues to be difficult. Current research is focused on developing new methods and procedures for applying existing methods that will likely become more accessible to a broader user base in the next few years. Quantitative measurements of inorganic ENMs are already being advanced by developments in spICP-MS and FFF-ICP-MS, as well as by improvements in sample preparation for automated electron microscopy. For carbon nanotubes, strides have been made through the use of near-infrared fluorescence spectroscopy. While many of these methods are already sufficiently developed for laboratory and microcosm experiments on ENP reactivity and behavior, they are not ready for application to environmental monitoring. For example, environmental transformations of nanomaterials may reduce the efficacy of these analytical techniques that insofar have been developed for laboratory measurements under pristine or minimally complex scenarios.

Although improvements in methodology are expected, low predicted environmental concentrations for ENMs and background particles will remain a challenge to any given set of techniques. Methods that can separate ENPs from the environmental matrix and concentrate them (e.g., cloud point extraction) without altering their chemistry would improve our ability to detect and quantify them. However, it will be necessary to preserve the representativeness of the ENMs' environmental state, as this will likely affect how they interact with the ecosystem [153]. In addition to the separation of ENMs from environmental constituents, such as DOC and mineral colloids, the high concentration of naturally occurring NMs will require new, sophisticated analytical techniques that can distinguish between these two particle types. The advent of microsecond spICP-MS and ICP-TOF-MS may allow for the differentiation of engineered and natural nanoparticles by virtue of their elemental ratios [176-178]. For nanomaterials with naturally occurring analogues, this detection of ENMs in the environment will require the exploitation of ENM properties that are rarely encountered in environmental samples. Other techniques may be developed to take advantage of ENP-specific properties such as their size distribution and highly engineered surface coatings, but will require further study into how the environment affects these properties.

A critical capability of future nanometrologies will be quick, highly automated methods to allow analysis of the large number of samples needed for quantitative ENP risk assessment. The dynamic nature of nanomaterials ensures that their physicochemical states can change within short time frames, and as such, it will be necessary to develop appropriate methodologies to rapidly characterize these nanomaterials in their altered, environmental state. As previously established, various potential artifacts that can be introduced in the sampling and measurement of ENMs will require multiple orthogonal techniques to confirm the presence and characteristics of these materials found in the environment.

As additional research is performed to assess the ecotoxicity of these materials, it is important to also consider the exposure and its contribution to environmental risk analysis. Although much work still needs to be done, the continued development of nanometrology, specific to the detection and characterization of ENMs in the environment, is a step towards assessing the environmental risk and impact these materials may pose.

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Annotated bibliography in support of:

**Detection and characterization of engineered nanomaterials in the
environment: current state-of-the-art and future directions**

Report, annotated bibliography, and image library

RESEARCH AND DEVELOPMENT

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Steven P. Gardner

U.S. Environmental Protection Agency
Office of Research and Development
National Environmental Research Laboratory
Environmental Sciences Division
Characterization and Monitoring Branch
944 E. Harmon Ave.
Las Vegas, NV 89119

Julie Blue, Ph.D.¹

Manuel Montañó²

James F. Ranville, Ph.D.²

Gregory V. Lowry, Ph.D.³

Nupur Hiremath¹

Clare Stankwitz¹

Sandie Koenig¹

¹The Cadmus Group, Inc.
100 5th Avenue, Suite 100
Waltham, MA 02451

²Colorado School of Mines
1500 Illinois Street
Golden, CO 80401

³Carnegie Mellon University
5000 Forbes Avenue
Pittsburgh, PA 15213

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U.S. Environmental Protection Agency
Office of Research and Development
Washington DC 20460

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1	Stability of nanoparticles in water	Brant, J. and Labille, J.	2010	Nanomedicine, 5(6), 985-989	Published journal	Labille and Brant (2010) present a review of manufactured nanoparticles and their interactions in aqueous media. Three categories of nanoparticles are covered in this review: metal oxides, pure metals, and fullerenes. The interactions of nanoparticles with surrounding media (e.g., water) are largely governed by the surface of the particle, which may be oxidized, reduced, or dissolved. Due to their small radius of curvature, nanoparticles have high surface tension, which serves as an attractive force causing agglomeration that can lead to greater thermodynamic stability in nanoparticles. High surface tension, which leads to thermodynamically unstable nanoparticles, may result in unique properties such as increased dissolution, phase transformation, or crystallization. Nanoparticles may release chemical solutes during dissolution, which may be more mobile and stable than the parent nanoparticles, and therefore may be a greater environmental concern than the nanoparticles themselves. Similarly, nanoparticle agglomerates may interact differently with the environment than their constituent nanoparticles. The formation of agglomerates depends on acid-base interactions (attractive for hydrophobic or non-polar surfaces and repulsive for hydrophilic or polar surfaces), electrostatic interactions (which occur when surfaces are charged), and van der Waals interactions (which change as the distance between particles increases). Manufactured nanoparticles are surface-modified, functionalized, or coated to modify their surface properties for specific commercial and industrial applications. Most occurrences of manufactured nanoparticles in the environment will be of degraded or transformed nanoparticles, whose surface properties, which dictate their fate and transport, may vary according to the environmental conditions and the mode of degradation or transformation. This article suggests that future research efforts should focus on understanding the types and properties of nanomaterial degradation or transformation/conversion products.	Brant, J. and Labille, J. 2010. Stability of nanoparticles in water. Nanomedicine, 5(6), 985-989.
2	Nanoparticles in aquatic systems	Delay, M. and Frimmel, F.H.	2012	Analytical and Bioanalytical Chemistry, 402(2), 583-582	Published journal	Delay and Frimmel summarize the interactions, fate, and transport of nanoparticles, both natural and engineered (ENPs), in natural aquatic systems. The most important properties of ENPs are: surface chemistry (functionalization and charge), agglomeration (size, shape, and fractal dimensions), chemical composition and crystal structure, and solubility. Natural nanoparticles may enter aquatic systems through formation by biotic or abiotic activity or by human activity, while ENPs may enter the aquatic environment through accidental or intentional anthropogenic release. Natural nanoparticles have a greater variety of physical and chemical properties than ENPs. Isotope-labeling may help distinguish between natural nanoparticles and ENPs in the environment. Of the nanoparticles present in the natural environment, only a small fraction are ENPs. The article lists the following 13 representative ENPs: gold, iron, silver, aluminum oxides, zinc oxides, cerium oxides, silicon dioxide, titanium dioxide, fullerenes, single- and multi-walled carbon nanotubes, dendrimers, and nanoclays. Surface modifications made to these ENPs for industrial or commercial applications may be lost or altered in the natural environment, resulting in significant changes in their behavior and making it more challenging to detect them using known analytical methods. Challenges with detection include: low concentrations of nanoparticles; difficulties in sample preparation; artifacts and sample stability; polydispersity; and lack of reference and standard materials for calibration and validation. Delay and Frimmel suggest that future research focus on identifying reference nanoparticles as a baseline for comparison with ENPs.	Delay, M. and Frimmel, F.H. 2012. Nanoparticles in aquatic systems. Analytical and Bioanalytical Chemistry, 402(2), 583-582.
4	Silver Nanoparticles: A Microbial Perspective	Sweet, M.J. and Singleton, I.	2011	Advances in Applied Microbiology, 77, 115-133	Published journal	Sweet and Singleton (2011) document the formation, microbial properties and application, and environmental implications of naturally-occurring nanosilver particles and engineered nanosilver particles (silver ENPs). The article summarizes key literature that documents the production of nanosilver in the natural environment by bacteria (e.g., <i>Pseudomonas stutzeri</i> , bacteria isolated from silver mines in Africa, which produce spherical-, triangular-, and hexagonal-shaped nanosilver particles) and by fungi (e.g., <i>Verticillium</i> sp. and <i>Fusarium oxysporum</i> , which can reduce silver nitrate solution to 25-nm-sized silver particles). Naturally-synthesized nanosilver particles demonstrate the same properties as commercially-synthesized nanosilver ENPs. ENPs are typically released into the natural environment as a part of a matrix rather than as individual particles. Release may largely be associated with use and disposal of consumer products. Transformation or degradation due to light, microbes, oxidants, or other environmental factors may result in the release of free ENPs from the matrix. Silver ENPs may have adverse effects on soil (e.g., they may reduce denitrification rates), but the authors note that additional research is needed to document adverse effects and toxic potential.	Sweet, M.J. and Singleton, I. 2011. Silver Nanoparticles: A Microbial Perspective. Advances in Applied Microbiology, 77, 115-133.
5	Engineered nanoparticles and their identification among natural nanoparticles	Zanker, H. and Schierz, A.	2012	Annual Review of Analytical Chemistry, 5(1), 107-132	Published journal	Zanker and Schierz (2012) present a summary of methodologies for identifying and characterizing engineered nanoparticles (ENPs). Identifying risks posed by ENPs is challenging due to interactions between ENPs and natural nanoparticles, the presence of organic matter coatings on ENPs, surface modifications introduced during manufacturing of ENPs, subsequent surface changes due to interactions with the natural environment, and the tendency of contaminants to adhere to ENPs. Parameters for nanoparticle characterization include size, size distribution, shape, concentration, dispersion or aggregation, structure and chemical composition, surface properties (area, charge, functional groups, speciation), desorption or dissolution rates, and the nature and stability of coatings. Analytical methods for identification and characterization of nanoparticles covered in this article include particle fractionation (e.g., microfiltration, field-flow fractionation, capillary electrophoresis), spectroscopy and related techniques (e.g., photon correlation spectroscopy, laser-induced breakdown detection), visualization (e.g., scanning, transmission, and/or atomic force electron microscopy), and deployment of sensors that can detect specific types of nanoparticles (e.g., optical sensors, biosensors). Of these, Zanker and Schierz identify flow field-flow fractionation (FFF), sedimentation FFF, capillary electrophoresis, and liquid phase extraction as the most reliable methods for nanoparticle identification and characterization. However, the authors note that knowledge of the type of nanoparticles present in a sample is key to selecting the best method for their detection, as there are many challenges associated with detecting unknown particles in environmental media.	Zanker, H. and Schierz, A. 2012. Engineered nanoparticles and their identification among natural nanoparticles. Annual Review of Analytical Chemistry, 5(1), 107-132.
6	Characterization of surface hydrophobicity of engineered nanoparticles	Xiao, Y. and Wiesner, M.R.	2012	Journal of Hazardous Materials, 215-216, 146-151	Published journal	Xiao and Wiesner present an evaluation of the surface hydrophobicity of coated and uncoated carbon- and metal-based engineered nanoparticles (ENPs). Hydrophobicity is important because it can affect the fate, transport, and bioavailability of ENPs. The seven ENPs characterized in this study are: aqueous nC60, tetrahydrofuran-nC60, fullerol, nanogold coated with citrate, nanosilver coated with polyvinylpyrrolidone (PVP), nanosilver coated with citrate, and nanosilver coated with gum arabic. Three methods were used to evaluate surface hydrophobicity: surface adsorption (using organic dye and naphthalene adsorption), affinity coefficient (using octanol and water phases), and contact angle measurement (using a thin film of ENPs). The results of this study show that aqueous nC60 and tetrahydrofuran-nC60 are the most hydrophobic, followed by nanosilver and nanogold with the citrate-functionalized surfaces, followed by nanosilver coated with PVP or gum arabic, and lastly, fullerol.	Xiao, Y. and Wiesner, M.R. 2012. Characterization of surface hydrophobicity of engineered nanoparticles. Journal of Hazardous Materials, 215-216, 146-151.
7	Clay particles destabilize engineered nanoparticles in aqueous environments	Zhou, D., Abdel-Fattah, A.I., and Keller, A.A.	2012	Environmental Science and Technology, 46(14), 7520-7526	Published journal	Zhou et al. examine the interactions that two of the most commonly produced engineered nanoparticles (ENPs), nanosilver and nano-titania, have with clay, in order to determine how these interactions affect particle stability. Montmorillonite, a clay mineral, has a sheet-like structure, with two layers of silicon tetrahedra that flank a layer of aluminum octahedra. At the typical pH of clay minerals, which ranges between 5 and 8, negative charges develop on the planes while positive charges develop at the edges. A stock suspension of montmorillonite was mixed with nano-titania solution and with citrate-coated nanosilver solution. The resultant mixtures were analyzed by dynamic light scattering to determine hydrodynamic data and by Laser Doppler Velocimetry to determine electrophoretic mobility. At a pH of 8, there was no change in the stability of the montmorillonite system with either nanosilver or nano-titania. However, at pH 4, the critical coagulation concentration of the system shifts to a lower ionic strength, causing montmorillonite/nanosilver or montmorillonite/nano-titania agglomerates, demonstrating the ability of the clay mineral to destabilize both positively charged (titania) and negatively charged (silver, which is negatively charged due to the citrate coating) ENPs. The authors note under real-world conditions, clay-nanoparticle interactions may be affected by varying clay/nanoparticle concentration ratios, the presence of naturally-occurring oxides and hydroxides and organic matter, and other factors.	Zhou, D., Abdel-Fattah, A.I., and Keller, A.A. 2012. Clay particles destabilize engineered nanoparticles in aqueous environments. Environmental Science and Technology, 46(14), 7520-7526.
8	Transport of engineered nanoparticles in saturated porous media	Tian, Y., Gao, B., Silveira-Batista, C., and Ziegler, K.	2009	Journal of Nanoparticle Research, 12(7), 2371-2380	Published journal	Tian et al. (2010) examine the fate and transport of two engineered nanoparticles (ENPs), nanosilver and single-walled carbon nanotubes, in saturated porous media to simulate fate and transport in soil. Two types of porous media were used: quartz sand washed sequentially with tap water and deionized water and baked at 550 deg C, and quartz sand washed sequentially with tap water and 10% nitric acid and baked at 550 deg C. The sand was packed into columns 2.5 cm in diameter and 15 cm in height. Solutions of carbon nanotubes and nanosilver in aqueous sodium dodecylbenzene sulfonate (or SDBS, an anionic surfactant) were added to the columns. Solutions of montmorillonite (a clay mineral) in deionized water or in SDBS were also added to the columns. Bromide was used as a tracer. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory for estimating interactive forces between the nanoparticles and the sand grains was applied, and the colloid filtration theory was used to simulate retention, transport, and re-mobilization of the ENPs. The results showed the transport of carbon nanotubes through the sand was similar to that of colloidal montmorillonite with 100% recovery at the bottom of the column. Similarly, nanosilver also mimicked the transport of colloidal clay with a 75% recovery at the bottom of the column, demonstrating that ENPs may move fairly quickly through saturated porous media. Some combinations (e.g., carbon nanotubes and SDBS-dispersed montmorillonite), however, deviated from the DLVO and colloid filtration theory. The authors assert that these deviations are due to the presence of the surfactant.	Tian, Y., Gao, B., Silveira-Batista, C., and Ziegler, K. 2009. Transport of engineered nanoparticles in saturated porous media. Journal of Nanoparticle Research, 12(7), 2371-2380.

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9	Environmental and Colloidal Behavior of Engineered Nanoparticles	Xing, B.	2010	In Molecular Environmental Soil Science at the Interface in the Earth's Critical Zone, 246-248	Book	Xing (2010) examines the colloidal behavior of three types of engineered nanoparticles (ENPs) in the natural environment: carbon nanotubes (single- and multi-walled), fullerenes, and oxides (aluminum oxide, zinc oxide, and titanium dioxide). Suspensions of ENPs with humic acid were created. Colloidal stability, particle stability, and zeta potentials were examined with a Zetasizer, and pH, presence of cations, and presence of organic matter were also assessed. Adsorption capacity of ENPs was examined with polyaromatic hydrocarbons (phenanthrene, naphthalene, pyrene) and endocrine disrupting compounds (17 α -ethinyl estradiol, bisphenol A) as adsorbates. Adsorption isotherms were obtained by batch equilibration. Toxicity of these ENPs to plants, bacteria, and nematodes was also assessed. Of the ENPs, single-walled carbon nanotubes had the highest sorption capacity and fullerenes had the lowest sorption capacity. The sorption capacity of carbon nanotubes was particularly high for endocrine disrupting compounds. Zinc oxide ENPs were taken up easily by roots and inhibited plant growth. All oxide ENPs showed higher toxicity to bacteria and nematodes than their bulk counterparts. Humic acid was found to increase the dispersibility, and therefore the stability, of carbon nanotubes and aluminum oxide in suspension.	Xing, B. 2010. Environmental and Colloidal Behavior of Engineered Nanoparticles. In Molecular Environmental Soil Science at the Interface in the Earth's Critical Zone, 246-248.
10	Occurrence, behavior and effects of nanoparticles in the environment	Nowack, B. and Bucheli, T.D.	2007	Environmental Pollution, 150(1), 5-22	Published journal	Nowack and Bucheli (2007) present a review of engineered nanoparticles (ENPs) and naturally-occurring nanoparticles, documenting: how they are produced; their characteristics and properties; methods for analyzing them; release, occurrence, fate, and transport in the natural environment; and uptake by and toxicity for organisms. Natural nanoparticles can be geogenic or pyrogenic (e.g., carbon nanotubes, fullerenes), biogenic (e.g., magnetite), or atmospheric (e.g., sea salt). Anthropogenic nanoparticles are those produced inadvertently through human activities, such as combustion (e.g., soot), or deliberately engineered (e.g., functionalized nanosilver or nanotitanium). Types of nanoparticles featured in this study are: soot (natural and unintentionally produced), fullerenes and carbon nanotubes (natural, unintentionally produced, engineered), and inorganic particles (natural, unintentionally produced, engineered). The article discusses specific processes for and sources of formation for each of these nanoparticles. It also presents specific methods for analyzing each of these types of nanoparticles, including microscopic methods (e.g., electron microscopy, atomic force microscopy), size fractionation techniques (e.g., ultrafiltration, flow-field fractionation, centrifugation), and chromatography (e.g., size-exclusion, gel permeation). Behavior of natural nanoparticles and ENPs in various media, including water and porous media, and in environments with different adsorbents (e.g., organic contaminants, metals), is documented. The uptake of these types of nanoparticles and their ecotoxicity in plant, animal, and microbial species is discussed. Functionalization for industrial or commercial applications or coating of nanoparticles by natural compounds in the environment affects their fate and transport; this is an area that requires additional research.	Nowack, B. and Bucheli, T.D. 2007. Occurrence, behavior and effects of nanoparticles in the environment. Environmental Pollution, 150(1), 5-22.
11	Nanoparticles: structure, properties, preparation, and behavior in environmental media	Christian, P., von der Kammer, F., Baalousha, M., and Hofmann, T.	2008	Ecotoxicology, 17(5), 326-343	Published journal	Christian et al. (2008) present a review of the surface chemistry of nanoparticles (both natural and engineered) and how it may influence fate and transport in the natural environment. Engineered nanoparticles (ENPs) have three layers: the core material; shell material that may be intentionally added (e.g., zinc sulfide on cadmium selenide nanoparticle cores) or may form from the particle itself (e.g., iron oxide, which forms on the surface of iron nanoparticle cores); and outer surface with added functional groups (e.g., metal ions, small molecules, surfactants, or polymers) designed for a specific application. The morphology of ENPs (e.g., rod, wire, tetrapod, tear drop, dumbbell, dendrite) may be dependent on the phases of the components in the system surrounding the nanoparticle as well as on the properties of the nanoparticles themselves. The authors provide a detailed discussion of additional properties of ENPs, including particle mobility, surface energy, and colloidal interactions (e.g., charge stabilization and steric stabilization), optical properties, and potential for catalysis. Detailed top-down (breaking off ENPs from larger pieces of material) and bottom-up (growing from simple molecules) approaches for the preparation of engineered nanoparticles (ENPs), including metal oxides, polymers, nanowires, nanotubes, and others, are outlined. The behavior of ENPs in the aquatic environment, their interaction with pollutants, the formation of nanoparticle coatings by natural organic matter, aggregation of nanoparticles (including the effect of humic acid and cations), and their behavior in porous media are further documented in this article.	Christian, P., von der Kammer, F., Baalousha, M., and Hofmann, T. 2008. Nanoparticles: structure, properties, preparation, and behavior in environmental media. Ecotoxicology, 17(5), 326-343.
12	An approach to the natural and engineered nanoparticles analysis in the environment by inductively coupled plasma mass spectrometry	Jimenez, M.S., Gomez, M.T., Bolea, E., Laborda, F., and Castillo, J.	2011	International Journal of Mass Spectrometry, 307(1-3), 99-104	Published journal	Jimenez et al. (2011) review analytical methods for detection of nanomaterials. They review a series of techniques using inductively coupled mass spectrometry (ICP-MS) to detect nanoparticles containing metals. They begin with a discussion of a technique used to detect natural nanoparticles, using polyacrylamide gel electrophoresis laser ablation (PAGE-LA) as a separation technique and ICP-MS for detection. PAGE has commonly been used for characterization of dissolved organic matter but has recently found more use in detecting nanoparticles with metals. The article cites a study that used PAGE-LA-ICP-MS to examine lead complexes. The paper reviewed several studies that examined metal complexes with humic and fulvic acids. The paper also discusses how PAGE-LA has been used to detect metals bound in proteins. One problem encountered in use of PAGE-LA-ICP-MS is metal loss in complexes that are not strongly bound. The problem may be reduced by using native PAGE instead of denaturing PAGE. The paper then discusses analytical methods for engineered nanoparticles (ENPs). These methods use either chromatography or field-flow fractionation (FFF) as a separation technique for ICP-MS. Size-exclusion chromatography (SEC), a common method for characterization of ENPs, involves passing the ENPs through a column with a stationary phase containing pores. The size range of ENPs that can be detected depends on the pore size of the stationary phase. Hydrodynamic chromatography (HC), on the other hand, passes the ENPs through a column filled with packed beads. This separation technique depends only on particle size and is independent of density and particle type. FFF uses an external field to separate particles and does not have a stationary phase. FFF is good for particles in the 300 Da to 100 nm range. A few studies have used FFF ICP-MS for ENP characterization. Single particle detection uses ICP-MS to detect single particles: on entering the plasma, a particle produces a flash of gaseous ions. To use this method, concentrations must be low enough so that two particles do not enter the ICP at the same time (usually less than 109 particles per liter). The concentration must also be high enough to allow a minimum number of counting events. The particle must also be large enough to produce enough gaseous ions. This method can provide information on: differentiation between dissolved metals and nanoparticles, size distribution of nanoparticles, mass of dissolved and nanoparticle metal, and number and concentration of nanoparticles. Faster electronics, allowing faster dwell times, can improve the time resolution. Increasing the transmission efficiency from the skimmer to the detector will improve size detection. Use of simultaneous double focusing sector field spectrometers will allow detection of more than one metal at a time.	Jimenez, M.S., Gomez, M.T., Bolea, E., Laborda, F., and Castillo, J. 2011. An approach to the natural and engineered nanoparticles analysis in the environment by inductively coupled plasma mass spectrometry. International Journal of Mass Spectrometry, 307(1-3), 99-104.
13	Characterization of nanoparticles released during construction of photocatalytic pavements using engineered nanoparticles	Dylla, H. and Hassan, M.M.	2012	Journal of Nanoparticle Research, 14(4), 825	Published journal	Dylla and Hassan (2012) studied release of titanium dioxide ENPs during construction of self-cleaning cements. They performed both lab and field experiments. A scanning mobility particle sizer (SMPS) was used to determine particle concentrations emitted from construction activities. In the lab, application of a mortar overlay was studied; 5 percent (by weight) of titanium particles with diameters between 15 to 28 nm was added to the mortar overlay either as a powder or as a liquid. Both methods produced higher concentrations than the control. The mortar overlay application with nanoparticles in powdered form released approximately 1×10^6 particles/cm ³ compared to 4×10^5 particles/cm ³ without the nanoparticles. The liquid application produced slightly more nanoparticles, but most of the release was during the measurement of the powder and the mixing of the powder with the liquid. The size distribution of the released particles varied from 30 to 52 nm, with a surface area of between 1.9 and 5.4×10^9 nm ² /cm ³ and a mass concentration of between 3.9 and 10.8 μ g/m ³ . In the field, investigators studied the application of a spray coating with 2 percent titanium dioxide nanoparticles. Particle concentrations released were higher than in the mortar overlay experiments, at 2×10^8 particles/cm ³ . Particles were smaller than in the mortar overlay, at between 23 and 37 nm with a surface area of between 1 and 9×10^{11} nm ² /cm ³ . Released particles were examined for shape. They appeared spherical, whereas the applied particles were rod-shaped. The resolution, however, was not clear and the shape appeared to change over time, possibly suggesting volatile particles. The authors suggest further study to better define particle morphology. Additional studies on release during wear and runoff events are also suggested.	Dylla, H. and Hassan, M.M. 2012. Characterization of nanoparticles released during construction of photocatalytic pavements using engineered nanoparticles. Journal of Nanoparticle Research, 14(4), 825.

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14	The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges and future needs	Handy, R.D., Owen, R., and Valsami-Jones, E.	2008	Ecotoxicology, 17(5), 315-325	Published journal	Handy et al. (2008) present a review of the ecotoxicology and environmental chemistry of natural nanoparticles and engineered nanoparticles (ENPs). Natural nanoparticles can be produced by geologic processes (e.g., weathering, authigenesis/neoformation, volcanic eruptions), which typically generate inorganic nanoparticles, and by biological processes (e.g., formation by microorganisms, degradation of biological matter). Natural nanoparticles may be less of a concern than ENPs as they may dissolve in aqueous media or become larger through aggregation. However, some natural nanoparticles (e.g., volcanic acid) have are known to be toxic or to bind to contaminants in the environment to become toxic. The article covers the physico-chemistry of nanoparticles (natural and engineered), summarizing properties (particle shape, size, surface area, and surface charge), aggregation chemistry, adsorption of particles onto surfaces, and the effect of abiotic factors (e.g., pH, water hardness, and presence of natural organic matter) on behavior. The authors also summarize literature on the ecotoxicity of nanoparticles in aquatic, marine, and terrestrial species, including microbes as well as more complex species. The authors note that there are major research needs associated with nanoparticle ecotoxicity, including chemical characterization of the ecotoxicology test materials, reference nanomaterials for regulatory ecotoxicology, modifications to methods to adapt them for testing regulatory ecotoxicity of nanoparticles, and additional testing methods.	Handy, R.D., Owen, R., and Valsami-Jones, E. 2008. The ecotoxicology of nanoparticles and nanomaterials: current status, knowledge gaps, challenges and future needs. Ecotoxicology, 17(5), 315-325.
15	Nanoparticle analysis and characterization methodologies in environmental risk assessment of engineered nanoparticles	Hasselov, M., Readman, J.W., Ranville, J.F., and Tiede, K.	2008	Ecotoxicology, 17(5), 344-361	Published journal	Hasselov et al. (2008) provide a review of characterization techniques for nanoparticles. Important parameters include not only concentration but also size distribution, surface area, surface charge, composition, and shape. Nanoparticle sampling needs to be conducted in such a way as to minimize disturbance of the particles, and traditional assumptions about adsorption to sampling apparatus need to be reexamined. Prefractionation of samples before analysis is often necessary. This can include centrifugation, filtration, or settling. Centrifugation minimizes particle disturbance but can cause aggregation. Filtration is the most common method but can cause aggregation as well. Cross-flow filtration can minimize particle aggregation. Dialysis can also be used as a separation technique but can result in particle dissolution and ionic strength effects. Field-flow fractionation (FFF) separates samples based on diffusion coefficients in a thin channel. It depends only on particle size. It requires appropriate ionic strength and use of surfactants to prevent aggregation. Size-exclusion chromatography passes the sample through a series of different sized pores. Hydrodynamic chromatography uses flow in narrow capillaries. It has poor separation efficiency but an excellent size range. Light scattering is a technology for measuring particle size. Dynamic light scattering (DLS) is rapid, simple, and has low sample perturbation but can be difficult to interpret. Larger particles can ruin the signal of nanoparticles, so small size ranges and lack of contamination are necessary. Static light scattering is used in conjunction with DLS to give information on particle shape. Measurement of turbidity can give information for well-defined particles with a small size distribution. Laser induced breakdown detection (LIBD) tunes a laser so water passing through will break down dielectrically when a particle is present. It is very sensitive and can detect concentrations down to parts per trillion, but is unable to distinguish types of particles and needs to be calibrated for each different particle type. Fluorescence can be used for particle detection in combination with chromatography or FFF. It is more sensitive than light scattering. Microscopy techniques are single particle methods that require sample preparation. Drying of particles may alter them. Scanning electron microscopes (SEM) can give 3-dimensional pictures. Environmental SEM allows variable pressure and humidity in the sample but decreases resolution. Transmission electron microscopy (TEM) requires staining of light elements but can give atom-by-atom resolution. Atomic force microscopy can be used in liquids but can overestimate lateral dimensions. X-ray diffraction can be used with microscopy to determine composition. The Brunauer, Emmett, and Teller (BET) method can be used to determine surface area. With all nanoparticle techniques, careful attention must be paid to standards and quality control.	Hasselov, M., Readman, J.W., Ranville, J.F., and Tiede, K. 2008. Nanoparticle analysis and characterization methodologies in environmental risk assessment of engineered nanoparticles. Ecotoxicology, 17(5), 344-361.
16	Quantitative analysis of fullerene nanomaterials in environmental systems: a critical review	Isaacson, C.W., Kleber, M., and Field, J.A.	2009	Environmental Science and Technology, 43(17), 6463-6474	Published journal	Isaacson et al. (2009) provide a critical review of analytical methods available to examine fullerene engineered nanoparticles (ENPs) both in their original form and their functionalized form. The authors note that the greatest challenge in analyzing these nanoparticles is their dual nature, in that they can change from hydrophobic to hydrophilic upon exposure to aqueous media or other charged surroundings. The authors review the various methods available for extraction (deriving fullerenes from solids), separation (separating fullerene forms), detection (differentiating fullerene forms), and quantitative analytical methods for detection in geological, biological, and aqueous matrices. The authors note that there are no known natural occurrences of fullerenes in the environment, and they document processes for fate and transport of these nanoparticles in the natural environment. Further, the authors note the lack of research conducted to date on quantitative assessments of biological exposure to fullerenes, and on defining the properties of dissolved fullerenes and fullerene aggregates, which can affect their resultant toxicity.	Isaacson, C.W., Kleber, M., and Field, J.A. 2009. Quantitative analysis of fullerene nanomaterials in environmental systems: a critical review. Environmental Science and Technology, 43(17), 6463-6474.
17	Monitoring nanoparticles in the environment	Simonet, B.M. and Valcarcel, M.	2009	Analytical and Bioanalytical Chemistry, 393(1), 17-21	Published journal	Simonet and Valcarcel (2009) present a review of methodologies for effectively monitoring engineered nanoparticles (ENPs) in the environment. The article presents an overview of appropriate sample preparation and handling techniques (noting the lack of in situ detection methods) and methods for separating nanoparticles in environmental samples (e.g., ultrafiltration, field-flow fractionation, inductively coupled plasma mass spectrometry or ICP-MS, size-exclusion chromatography). It summarizes detection methods at three scales: nanoscale (e.g., transmission electron microscopy or TEM, atomic force microscopy or AFM), microscale (e.g., scanning electron microscopy or SEM), and bulk-scale (e.g., atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy or ICP-AES, and ICP-MS). The authors note that the accurate analysis of ENPs depends on the development of effective preconcentration methods, detection techniques with variable resolution, and more sensitive and selective analytical methods.	Simonet, B.M. and Valcarcel, M. 2009. Monitoring nanoparticles in the environment. Analytical and Bioanalytical Chemistry, 393(1), 17-21.
18	Considerations for environmental fate and ecotoxicity testing to support environmental risk assessment for engineered nanoparticles	Tiede, K., Hasselov, M., Breitbarth, E., Chaudhry, Q., and Boxall, A.B.	2009	Journal of Chromatography A, 1216(3), 503-509	Published journal	Tiede et al. (2009) present a review of literature on the characteristics, methods of detection, fate, exposure, and effects of engineered nanoparticles (ENPs) in the environment. The authors present detailed information on the development of testing materials (noting that these should be well-characterized prior to any testing), selection of test concentrations that are environmentally relevant to allow determination of aggregation behavior, and selection of test conditions (e.g., pH, organic carbon concentrations, humic substance content) that accurately reflect environmental conditions. The authors state that the selection of the appropriate analytical method for ENP detection will depend on the question being asked and the environmental conditions being simulated. The authors provide an overview of existing analytical techniques (e.g., scanning electron microscopy or SEM, transmission electron microscopy or TEM, energy-dispersive spectrometry or EDS, electron energy loss spectrometry or EELS, field-flow fractionation, hydrodynamic chromatography and size-exclusion chromatography).	Tiede, K., Hasselov, M., Breitbarth, E., Chaudhry, Q., and Boxall, A.B. 2009. Considerations for environmental fate and ecotoxicity testing to support environmental risk assessment for engineered nanoparticles. Journal of Chromatography A, 1216(3), 503-509.

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19	Evaluating engineered nanoparticles in natural waters	Weinberg, H., Galyean, A., and Leopold, M.	2011	Trends in Analytical Chemistry, 30(1), 72-83	Published journal	Weinberg et al. (2011) review characterization techniques for nanoparticles (NP) in the environment. Treatment processes are not optimized to remove engineered nanoparticles (ENPs), so therefore ENPs are likely to find their way into water sources. Their fate will depend on particle properties such as size, composition, surface area and charge. During sampling aggregation, adsorption to sampling devices needs to be minimized. To measure ENPs, concentration techniques are required. Stepwise centrifuging is one method for separation. Stepwise filtration has also been used but may experience aggregation or precipitation of particles. Cross-flow filtration can minimize such problems. Fullerenes, a type of ENP, have been extracted using a destabilizing agent and solvent. Size-exclusion chromatography (SEC) is a common extraction technique which depends on the pore size of the stationary phase. Columns may need to be modified to deal with electrostatic repulsion or steric hindrance by ligands. Environmental samples will require pretreatment to prevent clogging of pores. Field-flow fractionation (FFF) does not require a stationary phase. FFF can reduce sample complexity while providing information on different size groupings. It can experience significant agglomeration and may require preconcentration if concentrations are low. Asymmetric flow FFF allows for a wide range of size distributions. It does require selecting an appropriate carrier fluid to prevent ENP alteration. Capillary electrophoresis (CE) can be used, although modification of the capillary surface to prevent retention may be required. The detector used after CE may be fluorescence or UV adsorption. Mass spectrometry (MS) could be used but has not been reported. After separation, ENPs must be characterized for a number of properties that will require a number of techniques. Quantitative techniques such as mass spectrometry are often coupled with qualitative techniques such as microscopy to obtain a full set of information. Electron and scanning probe microscopy can be used at the nanometer level. Near-field scanning optical microscopy may also be useful. Transmission electron microscopy, scanning electron microscopy (SEM), and atomic force microscopy are the preferred microscopy methods and can give information on shape, size, aggregation, and sorption. Analytical electron microscopy and Auger electron spectroscopy can determine composition. Environmental SEM can examine ENPs in their natural state. Dynamic light scattering can give in-situ particle size information. Laser-induced breakdown detection is a new method that can give concentration and number weighted mean diameter. Visible spectroscopy has been used for noble metal ENPs to determine size distribution. X-ray spectroscopy can determine surfaces and coating of ENPs. Separation techniques must be coupled with characterization techniques for appropriate analysis, for example FFF with MS or filtration with microscopy. The authors go on to state more work is needed on sensors specifically designed to characterize ENPs. They give an example of fluorescence based detectors being designed to detect silver and gold ENPs.	Weinberg, H., Galyean, A., and Leopold, M. 2011. Evaluating engineered nanoparticles in natural waters. Trends in Analytical Chemistry, 30(1), 72-83.
20	Fullerene nanoparticles exhibit greater retention in freshwater sediment than in model porous media	Zhang, W., Issacson, C.W., Rattanaudompol, U.S., Powell, T.B., and Bouchard, D.	2012	Water Research, 46(9), 2992-3004	Published journal	Zhang et. al (2012) investigated the retention of two fullerene types (aqu/C60 and water-soluble C60-TPA) in model porous media, taking into account various aquatic parameters such as pH and ionic strength. The researchers also investigated retention time in Iota quartz, Ottawa sand, and sediment. They found that surface heterogeneity plays a large role in the retention of fullerene particles. In addition, higher pH systems may facilitate greater transport of the nanomaterial as there is stronger electrostatic repulsion between the surface and the fullerene nanomaterial. The implications of this study show that various parameters play a role in the retention of nanomaterials, and that model porous media may not adequately reflect the conditions nanomaterials (NMs) may be exposed to. Due to these various parameters, the vadose zone may also play a role in preventing NM transport.	Zhang, W., Issacson, C.W., Rattanaudompol, U.S., Powell, T.B., and Bouchard, D. 2012. Fullerene nanoparticles exhibit greater retention in freshwater sediment than in model porous media. Water Research, 46(9), 2992-3004.
21	Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies	von der Kammer, F., Ferguson, P.L., Holden, P.A., Mason, A., Rogers, K.R., Klaine, S.J., Koelmans, A.A., Horne, N., and Unrine, J.M.	2012	Environmental Toxicology and Chemistry, 31(1), 32-49	Published journal	Von der Kammer et al (2012) provided a critical review of several aspects of the analysis and characterization of nanoparticles in the environment. Specific attention was given to various aspects of sample preparation, separation from environmental media, and distinguishing between engineered nanoparticles (ENPs) and naturally-occurring nanomaterials. Four case studies were presented. The use of near-infrared spectroscopy (NIR) to detect and characterize nanomaterials was discussed at length. The challenges of characterizing nanomaterials (specifically CdSe quantum dots and TiO2 ENPs) in biological media and cells was discussed. Difficulties encountered in detecting CeO2 and TiO2 in natural sediment samples were addressed, and possible solutions involving isotopic abundance, single-particle electron microscopy, and mass spectrometry techniques were discussed. For silver nanoparticles in wastewater, with different separation methods reviewed, including field-flow fractionation (FFF) coupled with an element-specific detector such as ICP-MS. In short, this paper provides a comprehensive review of the challenges that arise from the analysis of engineered nanoparticles in environmental media and proposes theoretical solutions to begin to address these issues.	von der Kammer, F., Ferguson, P.L., Holden, P.A., Mason, A., Rogers, K.R., Klaine, S.J., Koelmans, A.A., Horne, N., and Unrine, J.M. 2012. Analysis of engineered nanomaterials in complex matrices (environment and biota): general considerations and conceptual case studies. Environmental Toxicology and Chemistry, 31(1), 32-49.
22	State of the science literature review: nano titanium dioxide environmental matters	U.S. Environmental Protection Agency	2010	2010	Unreviewed EPA document	This EPA report summarizes available information pertaining to the manufacturing, processing, use, and end-of-life for nanoscale titanium dioxide (nano-TiO2). Primary data gaps identified in the report include: domestic production volumes for nano-TiO2; identities of domestic manufacturers, processors, and industrial users (and corresponding throughput of nano-TiO2 at these facilities); standardized sampling and analysis methods; a better understanding of the fate and transport of nano-TiO2 after release into the environment; and a thorough review of human health and toxicological data.	U.S. Environmental Protection Agency 2010. State of the science literature review: nano titanium dioxide environmental matters. 2010.
23	Nanomaterial case studies: nanoscale titanium dioxide in water treatment and in topical sunscreen	U.S. Environmental Protection Agency	2009	2009	Peer reviewed EPA document	In this report EPA presents two case studies of nanotechnology applications. The goal was to apply life cycle analysis methodology to evaluate the ecological and human health risks from nanotechnologies. The two case studies chosen were the known use of nano-TiO2 as a physical blocker in sunscreens, and the possible use of nano-TiO2 to remove arsenic from drinking water. The report summarizes available information about routes of entry of coated and uncoated nano-TiO2 into environmental media (during manufacture, use, and disposal), fate and transport in environmental media, and analytical methods, among other topics. The report summarizes data gaps and suggested research priorities, including an assessment of the appropriateness of standard health and ecological toxicity testing protocols for use with nano-TiO2, and development of improved methods for physicochemical characterization of nanomaterials under controlled conditions, in environmental matrices, and in biological systems.	U.S. Environmental Protection Agency 2009. Nanomaterial case studies: nanoscale titanium dioxide in water treatment and in topical sunscreen. 2009.
24	Electrochemical detection of chloride at the multilayer nano-silver modified indium-tin oxide thin electrodes	Chu, L. and Zhang, X.	2012	Journal of Electroanalytical Chemistry, 665, 26-32	Published journal	Zhang and Chu, 2012 used SEM to study the surface of an electrode containing silver nanoparticles. They were able to determine particle size, shape, and spacing.	Chu, L. and Zhang, X. 2012. Electrochemical detection of chloride at the multilayer nano-silver modified indium-tin oxide thin electrodes. Journal of Electroanalytical Chemistry, 665, 26-32.

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101	Coating Fe ₃ O ₄ magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water	Liu, J., Zhao, Z., and Jiang, G.	2008	Environmental Science and Technology, 42(18), 6949-6954	Published journal	Liu et. al (2008) investigated the coprecipitation of Fe ₃ O ₄ with humic acid to form magnetic nanoparticles with a humic acid coating. The nanoparticles synthesized were approximately 10nm in diameter. The uncoated nanoparticles had a p <i>H</i> _{PZC} ~ 6.0, whereas those coated with humic acid saw a sharp decrease in the point of zero charge (~3.7). These particles were then studied to determine their efficacy in the removal of heavy metals from groundwater via sorption onto the nanoparticles. In all conditions, the nanoparticles coated with humic acid showed a greater sorption and removal of heavy metals than the uncoated particles. The results indicate a method for the development of a relatively inexpensive nanoparticle that can be used for the remediation of heavy metals in a variety of natural systems.	Liu, J., Zhao, Z., and Jiang, G. 2008. Coating Fe ₃ O ₄ magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. Environmental Science and Technology, 42(18), 6949-6954.
102	Preparation and characterization of magnetite nanoparticles coated by amino silane	Ma, M., Zhang, Y., Yu, W., Shen, H., Zhang, H., and Gu, N.	2003	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 212(2-3), 219-226	Published journal	Ma et. al (2003) synthesized magnetic Fe ₃ O ₄ particles with an average diameter of 7.5nm and coated with an amino silane. Preparation occurred through the co-precipitation of FeCl ₃ and FeSO ₄ . The particles were characterized using TEM, EDS and powder x-ray diffraction. The binding of the amino silane to the surface of the nanoparticle was confirmed through the use of fourier transform infrared spectroscopy. An enzyme (horseradish peroxidase) assay was used to determine the absorbance efficacy of the coated nanoparticles; the coating was found to dramatically increase adsorption.	Ma, M., Zhang, Y., Yu, W., Shen, H., Zhang, H., and Gu, N. 2003. Preparation and characterization of magnetite nanoparticles coated by amino silane. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 212(2-3), 219-226.
103	Synthesis and magnetic properties of CoO nanoparticles	Ghosh, M., Sampathkumaran, E., and Rao, C.	2005	Chemistry of Materials, 17(9), 2348-2352	Published journal	Ghosh et al. (2005) synthesized stable CoO nanoparticles using a solvothermal method involving the decomposition of a Cobalt (II) cupferronate in the presence of an organic solvent (i.e. Decalin). Obtaining stable CoO nanoparticles presented a challenge due to the ready reducibility of CoO to Co metal as well as the presence of the more stable Co ₃ O ₄ . Nanoparticles were characterized using XRD, TEM, FT-IR, and TGA. The addition of the organic coating provides stability and prevents the oxidation of the nanoparticles. In the larger nanoparticle sizes synthesized (16 and 18nm), an antiferromagnetic transition was observed at temperatures around 300 deg K. This procedure demonstrates a method of synthesizing stable CoO nanoparticles that are resistant to oxidation.	Ghosh, M., Sampathkumaran, E., and Rao, C. 2005. Synthesis and magnetic properties of CoO nanoparticles. Chemistry of Materials, 17(9), 2348-2352.
104	Ion and pH sensing with colloidal nanoparticles: influence of surface charge on sensing and colloidal properties	Zhang, F., Ali, Z., Amin, F., Feltz, F., Oheim, M., and Parak, W.	2010	Chemphyschem: A European Journal of Chemical Physics and Physical Chemistry, 11(3), 730-735	Published journal	Zhang et al. (2010) looked at the effect of pH on the ion-sensing capability of simple and modified colloidal nanoparticles (NPs). Counter-ions are expected to concentrate near the nanoparticle surface due to electrostatic attraction, as explained by the Debye-Huckel model, and these may interfere with the ability of an ion-sensing fluorophore attached to the NP to determine ion concentrations in the medium. The results of the study confirm this. The pKa can be modified by varying the distance between the NP surface and the fluorophore through modification of the length of the PEG (poly-ethylene glycol) polymer that attaches the analyte-sensitive fluorophores to the particle.	Zhang, F., Ali, Z., Amin, F., Feltz, F., Oheim, M., and Parak, W. 2010. Ion and pH sensing with colloidal nanoparticles: influence of surface charge on sensing and colloidal properties. Chemphyschem: A European Journal of Chemical Physics and Physical Chemistry, 11(3), 730-735.
105	Surface and related bulk properties of titania nanoparticles recovered from aramid-titania hybrid films: A novel attempt	Al-Omani, S., Bumajdad, A., Sagheer, F., and Zaki, M.	2012	Materials Research Bulletin, 47(11), 3308-3316	Published journal	Al-Omani et al. (2012) synthesized anatase-TiO ₂ nanoparticles using an aramid-titania hybrid film as the parent precursor. The titani species were bonded to the polymer backbone using ICTOS (3-isocyanatopropyltriethoxysilane), which helped prevent agglomeration of the nanoparticles. The film was then thermally degraded, yielding anatase-TiO ₂ nanoparticles. The material produced was thermally stable up to high temperatures (800 deg C) and also exhibited a highly stable surface chemical composition. It was found that the higher the titanium loading on the precursor film, the more thermally stable the surface texture but the less thermally stable the surface chemical composition.	Al-Omani, S., Bumajdad, A., Sagheer, F., and Zaki, M. 2012. Surface and related bulk properties of titania nanoparticles recovered from aramid-titania hybrid films: A novel attempt. Materials Research Bulletin, 47(11), 3308-3316.
106	Effect of surface properties of silica nanoparticles on their cytotoxicity and cellular distribution in murine macrophages	Nabeshi, H., Yoshikawa, T., Arimori, A., Yoshida, T., Tochigi, S., Hirai, T., Akase, T., Nagano, K., Abe, Y., Kamada, H., Tsunoda, S., Itoh, N., Yoshioka, Y., and Tsutsumi, Y.	2011	Nanoscale Research Letters, 6(1), 93	Published journal	Nabeshi et al. (2011) investigated the role surface groups and surface charge play in the cytotoxicity of silica nanoparticles to a murine macrophage cell (RAW264.7). Uncoated silica nanoparticles were found to penetrate into the nucleus of the cell and deliver the greatest toxic effect (EC ₅₀ =121.5 µg/L). The coated nanoparticles (an amine-coated nanoparticle and a carboxylated nanoparticle) showed a significant reduction in toxicity, with very little toxicity occurring even at concentrations of up to 1000 µg/L. Confocal laser scanning microscopy also visualized the uptake of the uncoated silica particles into the nucleus, whereas no uptake was observed for the treated particles. The surface processing of nanoparticles should be tuned in order to synthesize safer materials that are limited in their ability to produce a cytotoxic effect.	Nabeshi, H., Yoshikawa, T., Arimori, A., Yoshida, T., Tochigi, S., Hirai, T., Akase, T., Nagano, K., Abe, Y., Kamada, H., Tsunoda, S., Itoh, N., Yoshioka, Y., and Tsutsumi, Y. 2011. Effect of surface properties of silica nanoparticles on their cytotoxicity and cellular distribution in murine macrophages. Nanoscale Research Letters, 6(1), 93.

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107	Surface structural characteristics and tunable electronic properties of wet-chemically prepared Pd nanoparticles	Cook, S., Padmos, J., and Zhang, P.	2008	The Journal of Chemical Physics, 128(15), 154705	Published journal	Cook et al. (2008) used X-ray techniques to study the surface of palladium nanoparticles. They used X-ray absorption fine structure (XAFS) and X-ray photoelectron spectroscopy (XPS) to characterize the surface. The XAFS examination used total electron yield primarily to analyze the surface, although fluorescence yield was measured as well. XAFS gave information on the chemical composition and bonding of molecules on the particle surface. TEM was also used to determine particle size and counts.	Cook, S., Padmos, J., and Zhang, P. 2008. Surface structural characteristics and tunable electronic properties of wet-chemically prepared Pd nanoparticles. The Journal of Chemical Physics, 128(15), 154705.
108	Surface properties and dye loading behavior of Zn ₂ SnO ₄ nanoparticles hydrothermally synthesized using different mineralizers	Annamalai, A., Eo, Y., Im, C., and Lee, M.	2011	Materials Characterization, 62(10), 1007-1015	Published journal	Annamalai et al. (2011) investigated the hydrothermal synthesis of ZnSnO ₄ nanoparticles for use in dye-sensitized solar cell (DSSC) applications. By manipulating the mineralizer component during synthesis, they were able to tune the isoelectric point (IEP) of the material in order to achieve a greater extent of N719 dye loading. The isoelectric points of the different ZnSnO ₄ nanoparticles were 5.1, 7.4, and 8.1 for Na ₂ CO ₃ , KOH and tert-butyl amine mineralizers, respectively. As the IEP of the ZnSnO ₄ nanoparticles synthesized with butyl amine was highest, it showed the greatest adsorption of dye due to the carboxylic groups of the dye preferentially binding to the numerous positive sites on the ZnSnO ₄ surface. Such work has applications for improving the properties of DSSCs.	Annamalai, A., Eo, Y., Im, C., and Lee, M. 2011. Surface properties and dye loading behavior of Zn ₂ SnO ₄ nanoparticles hydrothermally synthesized using different mineralizers. Materials Characterization, 62(10), 1007-1015.
109	Tuning the properties of ZnO, hematite, and Ag nanoparticles by adjusting the surface charge	Zhang, J., Dong, G., Thurber, A., Hou, Y., Gu, M., Tenne, D., Hanna, C., and Punnoose, A.	2012	Advanced Materials, 24(9), 1232-1237	Published journal	Zhang et al. (2012) investigated the effect of surface on zinc oxide, hematite (iron oxide), and silver nanoparticle by coating the materials with varying concentrations of poly (acryl) acid (PAA), thereby modifying the zeta potential and making it increasingly negative. By doing so, they found that properties such as saturation magnetization, surface plasmon resonance and cytotoxicity could be modified by changing the surface charge. The cytotoxicity of the nanomaterials was enhanced the more positively charged they were, as this would increase the electrostatic attraction between the particles and the negatively-charged cells. The silver nanoparticle surface plasmon resonance diminished with decreasing surface charge. The coercive force of the hematite NPs dropped from 70 to 9 Oe as surface charge was decreased. Overall, the case was made that several properties can be tuned with the introduction of variance into the surface charge of the material.	Zhang, J., Dong, G., Thurber, A., Hou, Y., Gu, M., Tenne, D., Hanna, C., and Punnoose, A. 2012. Tuning the properties of ZnO, hematite, and Ag nanoparticles by adjusting the surface charge. Advanced Materials, 24(9), 1232-1237.
110	Physicochemical properties and cellular toxicity of nanocrystal quantum dots depend on their surface modification	Hoshino, A., Fujioka, K., Oku, T., Suga, M., Sasaki, Y., Ohta, T., Yasuhara, M., Suzuki, K., and Yamamoto, K.	2004	Nano Letters, 4(11), 2163-2169	Published journal	Hoshino et al. (2004) investigated the effect of surface modification on the cytotoxicity of quantum dots. The group used CdSe quantum dots coated with various surface groups ranging from carboxylic groups stemming from an MUA coating, and aminated quantum dots with a positive charge. Only slight cytotoxicity was observed with quantum dots coated with carboxylic acid groups, whereas no toxicity was observed with the aminated QDs, though this may be a result of the amines interacting with the MTT reagents. Using a comet assay, it was determined that the QD-COOH samples caused very slight DNA damage that was repaired after a 12-hour exposure, whereas all other quantum dot types induced no DNA damage at the concentrations studied. The coatings themselves were found to induce some amount of cytotoxicity by themselves. The toxicity of quantum dots may not be wholly dependent on the chemical composition of the core material, and may vary with the chemistry of the functionalized surface.	Hoshino, A., Fujioka, K., Oku, T., Suga, M., Sasaki, Y., Ohta, T., Yasuhara, M., Suzuki, K., and Yamamoto, K. 2004. Physicochemical properties and cellular toxicity of nanocrystal quantum dots depend on their surface modification. Nano Letters, 4(11), 2163-2169.
111	Aggregation and surface properties of iron oxide nanoparticles: influence of pH and natural organic material	Baalousha, M., Manculea, A., Cumberland, S., Kendall, K., and Lead, J.R.	2008	Environmental Toxicology and Chemistry, 27(9), 1875-1882	Published journal	Baalousha et al. (2008) investigated the influence of humic acid and pH on the aggregation state of iron oxide nanoparticles. They found that the addition of humic acid shifted the point of zero charge of the iron nanoparticles to lower pH, resulting in extensive aggregation. It was also found that at higher pH (pH >4), aggregation of iron oxide nanoparticles occurred more readily. Aggregation was confirmed through flow field-flow fractionation (FI-FFF) and DLS and TEM measurements which showed increasing aggregation at higher pH and at greater concentrations of humic acid. Aggregation by humic acid results in more compact aggregates than those formed at higher pH in the absence of humic acid. The results have implications for nanomaterial fate and transport in the environment as suspended particles will likely travel further in aqueous media. Those nanoparticles that settle out in the water column will more likely impact benthic organisms.	Baalousha, M., Manculea, A., Cumberland, S., Kendall, K., and Lead, J.R. 2008. Aggregation and surface properties of iron oxide nanoparticles: influence of pH and natural organic material. Environmental Toxicology and Chemistry, 27(9), 1875-1882.

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112	Methods of detection and identification of manufactured nanoparticles	Gendrickson, O.D., Safenkova, I.V., Zherdev, A.V., Dzantiev, B.B., and Popov, V.O.	2011	Biophysics, 56(6), 965-994	Published journal	Hendrickson et al., 2011 reviewed methods for detection and identification of biologically active nanoparticles. Particles of interest included fullerenes, carbon nanotubes, and nanoparticles of various metals including: gold, silver, alumina, zinc, cerium, titanium, and silicon. In order to assess risks posed by engineered nanoparticles (ENPs), measurement of the following characteristics must be known: particle size, size distribution, shape, crystallinity, presence of agglomeration/aggregation, characteristics of surface properties—surface area, porosity, charge, reactive ability, presence of defects; solubility, and thermal and UV stability. After a discussion of effects of ENPs, the authors discuss methods of detection and identification. Items to consider in method selection include: detection limit, ability to quantitate particles, preservation of original state, correctness in measuring dimensional parameters, ability to distinguish ENPs from natural nanoparticles, availability of standard protocols, suitability for homogenous preparations, and ability to identify composition. Microscopy is good at detecting particle size but loses sensitivity and requires difficult sample preparation. Near scale optical microscopy can detect particles to 50 nm. X-ray microscopy can measure particle size and composition and can provide resolution to 30 nm. Confocal laser scanning microscopy determines the distribution of fluorescing nanoparticles. It has a larger depth of field than most microscopy and can be used to measure particles throughout a volume. Transmission electron microscopy (TEM) provides sub-nanometer resolution. TEM passes through samples that are very thin and can be enhanced by energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Scanning electron microscopy makes use of the scattering of electrons from the surface. Microscopy requires attention to sample preparation to minimize aggregation and large particle size differences arising from the support structure. TEM has the advantage of being well established and being able to measure the entire volume of the sample. Its drawbacks include difficult sample preparation, expensive equipment, and the fact that the structure of the particles depends of the orientation on the matrix. TEM with EELS can spatially determine composition of particles. Atomic force microscopy (AFM) scans the surface of particles at a few angstroms' depth. One AFM technology, scanning transmission electron microscopy, can measure biological components without contrasting metals, unlike TEM. Environmental scanning electron microscopy can measure components in natural environments. AFM techniques can measure samples in natural atmospheres, do not require a vacuum, and are cheaper than electron microscopy. But these methods cannot detect nanoparticles below the surface, have a small field of view, and can be distorted. Some new AFM techniques such as electron force microscopy (EFM) can distinguish between organic and metallic particles by using a second scan that measures electrical properties. Scanning tunneling microscopy (STM) can determine composition of metallic elements. Different methods exist to separate ENPs for analysis. Gel permeation chromatography uses movement of a liquid front through pores of a stationary phase. It has good separation of particles but suffers from artifacts from interaction with the stationary phase. Field flow fractionation (FFF) is used for samples of complicated composition. Capillary electrophoresis can also separate ENPs. Dynamic light scattering (DLS) is used to determine hydraulic radius and agglomeration of ENPs. Transmission gratings can enhance the signal-to-noise ratio of DLS. DLS does not work well with large particle size distributions. Small-angle x-ray scattering (SAXS) uses x-ray scattering to determine size, shape, orientation, structure, composition, and distribution of particles. Small angle neutron scattering (SANS) can detect nonuniformities in colloids. Spectrometry is not well suited for samples with multiple components but can be with proper extraction techniques. Infrared spectroscopy can be used to quantify some ENPs such as fullerenes. Fluorescent spectroscopy can be used for fluorescing nanoparticles. Laser-induced breakdown detection can detect ENPs regardless of the physical state of the sample but must be calibrated independently for quantification. Raman spectroscopy has been used to detect ENPs in-vivo. Nuclear magnetic resonance has been used to detect some types of ENPs such as silicon dioxide. X-ray spectroscopy enables quantification of composition of ENPs. Mass spectrometry can identify ENPs after separation. ICP-MS has been used with electrospray ionization matrix assisted laser desorption/ionization to measure ENPs. Other methods include single particle mass spectrometry, and aerosol time of flight spectroscopy. Particle counters measure ENPs by measuring the change in conductivity of an electrolyte containing nanoparticles.	Gendrickson, O.D., Safenkova, I.V., Zherdev, A.V., Dzantiev, B.B., and Popov, V.O. 2011. Methods of detection and identification of manufactured nanoparticles. Biophysics, 56(6), 965-994.
115	Characterization of the effluent from a nanosilver producing washing machine	Farkas, J., Peter, H., Christian, P., Gallego Urrea, J.A., Hasselov, M., Tuoriniemi, J., Gustafsson, S., Olsson, E., Hylland, K., and Thomas, K.V.	2011	Environmental International, 37(6), 1057-1062	Published journal	Farkas et al. (2011) examined the effluent from a "nanowashing" laundry machine that utilizes silver nanoparticles for its anti-bacterial properties. An average concentration of 11 ppb silver was found in the effluent of the washing machine. The presence of silver nanoparticles were confirmed using single particle ICP-MS, nanotracking analysis, transmission electron microscopy, and ultrafiltration techniques. The average size of the silver nanoparticles were found to be approximately 10 nm. The effluent from the washing machine was found to significantly reduce the viability of a bacterial community when compared to the control. The results of this study show that washing machines such as this can be a major source of release of engineered nanoparticles into the environment.	Farkas, J., Peter, H., Christian, P., Gallego Urrea, J.A., Hasselov, M., Tuoriniemi, J., Gustafsson, S., Olsson, E., Hylland, K., and Thomas, K.V. 2011. Characterization of the effluent from a nanosilver producing washing machine. Environmental International, 37(6), 1057-1062.
116	Nanoparticle silver released into water from commercially available stock fabrics	Benn, T.M. and Westerhoff, P.	2006	Environmental Science and Technology, 42(11), 4133-4139	Published journal	Benn and Westerhoff (2006) investigated the release of silver from sock fabrics. Five of the six sock samples were found to contain silver via an acid digestion analysis by ICP-OES. Three of the six sock samples were found to contain nanoparticulate silver. The nanoparticulate silver was confirmed via SEM imaging; particle sizes ranged from 100 to 500 nm. Physical separation by both filtration and ion selective electrode analysis suggest that both dissolved and nanoparticulate silver leach from the sock material. The sorption of silver to biomass suggests that wastewater treatment facilities have the potential to treat high quantities of silver that may be released into the environment.	Benn, T.M. and Westerhoff, P. 2006. Nanoparticle silver released into water from commercially available stock fabrics. Environmental Science and Technology, 42(11), 4133-4139.
117	The release of nanosilver from consumer products used in the home	Benn, T., Cavanagh, B., Hristovski, K., Posner, J.D., and Westerhoff, P.	2010	Journal of Environmental Quality, 39(6), 1875-1882	Published journal	Benn et al. (2010) investigated the release of silver nanomaterials from a wide range of products such as textiles, toothpastes, and detergents. Silver was found to be released in concentrations up to 45 µg Ag/g product. The presence of silver nanoparticles was confirmed by SEM and EDX analysis in addition to acid digestion analysis by ICP-OES. Toxicity characterization was carried out using the toxicity characterization leaching procedure (USEPA, 1992). The likelihood of silver binding to biosolids in waste treatment plants was also investigated. The possibility of silver leaching from commercial products and entering the environment is discussed as apparent and inevitable, with implications for environmental as well as human health.	Benn, T., Cavanagh, B., Hristovski, K., Posner, J.D., and Westerhoff, P. 2010. The release of nanosilver from consumer products used in the home. Journal of Environmental Quality, 39(6), 1875-1882.
119	Quantification of fullerene aggregate nC ₆₀ in wastewater by high-performance liquid chromatography with UV-vis spectroscopic and mass spectrometric detection	Wang, C., Shang, C., and Westerhoff, P.	2010	Chemosphere, 80(3), 334-339	Published journal	Wang et al. (2010) compare liquid-liquid extraction (LLE) and solid phase extraction (SPE) for determination of fullerenes. They also compare UV-visible spectrometry to mass spectrometry for quantification of the nanoparticles. LLE was applicable in several wastewater matrices, while SPE required filtration in more concentrated wastewaters. SPE also had poorer recoveries and smaller detection ranges. UV-visible spectrometry and mass spectrometry performed similarly. Mass spectrometry had a smaller detection range but provided specificity from the mass/charge ratio.	Wang, C., Shang, C., and Westerhoff, P. 2010. Quantification of fullerene aggregate nC ₆₀ in wastewater by high-performance liquid chromatography with UV-vis spectroscopic and mass spectrometric detection. Chemosphere, 80(3), 334-339.

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121	Beyond nC ₆₀ : strategies for identification of transformation products of fullerene oxidation in aquatic and biological samples	Pycke, B.F., Herckes, P., Westerhoff, P., and Halden, R.U.	2012	Analytical and Bioanalytical Chemistry, 404(9), 2583-2585	Published journal	Pycke et al. (2012) reviewed the occurrence of carbonaceous nano-materials in the environment and possible methods of detection and quantitation in environmental and biological samples. The most obvious impediment to fullerene and CNT detection in the environment is the regular occurrence of naturally-occurring carbon-containing nanomaterials in the environment. Possible strategies for detection and quantification involve either functionalization or defunctionalization of these materials in order to manipulate their solubility and subsequent separation for detection. However, the ready transformation of these materials once released into the environment may compromise accurate quantification in the environment.	Pycke, B.F., Herckes, P., Westerhoff, P., and Halden, R.U. 2012. Beyond nC ₆₀ : strategies for identification of transformation products of fullerene oxidation in aquatic and biological samples. Analytical and Bioanalytical Chemistry, 404(9), 2583-2585.
122	Synthesis and optical properties of naturally occurring fluorescent mineral, ferroan sphalerite, inspired (Fe,Zn)S nanoparticles.	Boyle, T.J., Pratt III, H.D., Hernandez-Sanchez, B.A., Lambert, T.N., Headley, T.J.	2007	Journal of Materials Science, 42(8), 2792-2795	Published journal	Boyle et al. (2007) investigated alternatives to lead and cadmium chalcogenide semiconducting nanomaterials by synthesizing a naturally-occurring fluorescent material in ferroan sulfide. As lead and cadmium are toxic materials, the goal was to find a relatively non-toxic material that still exhibited potential for narrow emission wavelengths based on quantum confinement principles. Using various solvothermal and solution synthesis processes, [(Fe,Zn)S] was synthesized in particles of size 3 nm or less with an emission wavelength of 400 nm when excited by UV. It may be possible to manipulate the bandgap of this material with non-toxic doping techniques. This nanomaterial could serve as a non-toxic alternative to the current lead- and cadmium-based semi-conducting nanoparticles.	Boyle, T.J., Pratt III, H.D., Hernandez-Sanchez, B.A., Lambert, T.N., Headley, T.J. 2007. Synthesis and optical properties of naturally occurring fluorescent mineral, ferroan sphalerite, inspired (Fe,Zn)S nanoparticles. Journal of Materials Science, 42(8), 2792-2795.
123	A sorption kinetics model for arsenic adsorption to magnetite nanoparticles	Shipley, H.J., Yean, S., Kan, A.T., and Tomson, M.B.	2010	Environmental Science Pollution and Research, 17(5), 1053-1062	Published journal	Shipley et al. (2010) developed a model to study arsenic sorption onto iron oxide nanoparticles in the presence of various counter-ions in order to accurately predict the amount of arsenic removal in variable water chemistry. Silicate, bicarbonate, fulvic acid, sulfate and ferrous/ferric ions were all introduced to study the competing sorption of arsenic onto the magnetite particles. As expected, the addition of negative counter-ions such as bicarbonate and phosphate impeded arsenic removal with increasing concentration. The addition of ferric ions, on the other hand, created nucleation sites that allowed for greater removal of arsenic from solution. The model created had very good agreement with experimental results, though it consistently over-predicted the amount of arsenic removal from the system.	Shipley, H.J., Yean, S., Kan, A.T., and Tomson, M.B. 2010. A sorption kinetics model for arsenic adsorption to magnetite nanoparticles. Environmental Science Pollution and Research, 17(5), 1053-1062.
124	Influence of nano-material on the expansive and shrinkage of soil behavior	Taha, M.R. and Taha, O.M.E	2012	Journal of Nanoparticle Research, 14, 1190	Published journal	Taha et al. (2012) performed expansion and shrinkage tests on residual soils with different ratios of bentonite (0, 5, 10, 20% bentonite) when different nano-materials (i.e. nano-clay, nano-alumina, nano-copper) were added. It was found that the addition of nano-clay does not necessarily improve these properties of the soil. However, it was found that the addition of nano-alumina and nano-copper can improve soil properties such as compaction, shrinkage strain, and expansive strain, and can reduce the crack intensity factor (CIF). There is an upper limit to the improvement, however, as the addition of nanomaterials may lead to significant aggregation which can increase pore size, leading to increased water content and greater shrinkage and swelling strain.	Taha, M.R. and Taha, O.M.E 2012. Influence of nano-material on the expansive and shrinkage of soil behavior. Journal of Nanoparticle Research, 14, 1190.
125	Soil organic matter in nano-scale structures of a cultivated Black Chernozem	Monreal, C.M., Sultan, Y., and Schnitzer, M.	2010	Geoderma, 159(1-2), 237-242	Published journal	Monreal et al. (2010) studied a soil organic matter (SOM) collected from a cultivated Black Chernozem of Canada, specifically using TEM, pyrolysis field ionization mass spectrometry, and radiocarbon dating to characterize both the nano-sized structure and the clay fraction of the SOM. Using TEM, they found that SOM in the nanosized fraction occurred both in organo-mineral complexes and within humic substances that formed nano-scale carbonaceous networks. It was found that the humic substances dictated the arrangement of minerals within the SOM and were responsible for the physical and physio-chemical stabilization of the SOM. Using Py-FIMS, it was found that the SOM found in the nano-structured fraction possessed greater thermal stabilization than those found in the clay fraction. Lastly, the nano-sized fraction was primarily comprised of carbohydrates, peptides, and N-heterocyclics whereas the clay fraction was rich in fatty acids, phenols, and lipids.	Monreal, C.M., Sultan, Y., and Schnitzer, M. 2010. Soil organic matter in nano-scale structures of a cultivated Black Chernozem. Geoderma, 159(1-2), 237-242.
126	Lead coprecipitation with iron oxyhydroxide nano-particles	Lu, P., Nuhfer, N.T., Kelly, S., Li, Q., Konishi, H., Elswick, E., and Zhu, C.	2011	Geochemica et Cosmochimica Acta, 75(16), 4547-4561	Published journal	Lu et al. (2011) investigated the removal of lead from solution by either coprecipitation with Fe ³⁺ or by adsorption onto ferrihydrite particles. High resolution transmission and analytical electron microscopy was utilized to analyze lead sorption to the iron materials. It was found that coprecipitation was a more efficient technique for removing lead from solution when compared to adsorption experiments. The subsequent removal of lead from these iron complexes with addition of EDTA also led to differences in sorption behavior as removal from adsorbed iron ferrihydrite followed a parabolic relationship, whereas the same behavior was linear in coprecipitation experiments. It is hypothesized that lead first adsorbs onto the initial nucleus of forming iron oxide particles in coprecipitation experiments and is subsequently incorporated into the particle with further growth, lending itself to greater sequestration of lead in the iron oxyhydroxide complex.	Lu, P., Nuhfer, N.T., Kelly, S., Li, Q., Konishi, H., Elswick, E., and Zhu, C. 2011. Lead coprecipitation with iron oxyhydroxide nano-particles. Geochemica et Cosmochimica Acta, 75(16), 4547-4561.
128	The nano-mechanical morphology of shale	Bobko, C. and Ulm, F.J.	2008	Mechanics of Materials, 40(4-5), 318-337	Published journal	Bobko et al. (2008) studied the nanomorphology of shale by validating a nanoindentation technique to investigate the properties of the clay particles that comprise shale materials. The results from this study led to an improved model for the nano-mechanical behavior of shale, with a spherical particle as the elementary building block. These spherical building blocks exhibit a non-granular behavior and are responsible for the packing density and subsequent composite behavior of porous clay. The results of this study will aid in the development of more precise models of elasticity and strength for micromechanical substances.	Bobko, C. and Ulm, F.J. 2008. The nano-mechanical morphology of shale. Mechanics of Materials, 40(4-5), 318-337.
129	Interactions of humic acid with nanosized inorganic oxides	Yang, K., Lin, D., and Xing, B.	2009	Langmuir, 25(6), 3571-3576	Published journal	Yang et al. (2009) investigated the adsorption behavior of humic acid on various metal oxide nanoparticles (TiO ₂ , SiO ₂ , Al ₂ O ₃ , and ZnO) using zeta potentiometry, Fourier transform infrared spectroscopy, and elemental analysis by a Perkin Elmer 2400 CHN Elemental Analyzer. As expected, the surface of these particles there was a strong affinity for humic acid on the surface of these particles through either electrostatic attraction or ligand exchange (except for SiO ₂ , which has a negative zeta potential across most pH, lending itself to electrostatic repulsion). Humic acid imparts a strong negative charge to the nanoparticles, which could possibly stabilize them in environmental systems and allow for greater transport through the environment. As humic acid has a high potential to bind hydrophobic organic compounds (HOCs), these nanoparticles could potentially serve as vectors to transport toxic materials through the environment.	Yang, K., Lin, D., and Xing, B. 2009. Interactions of humic acid with nanosized inorganic oxides. Langmuir, 25(6), 3571-3576.

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130	Adsorption of cadmium(II) on humic acid coated titanium dioxide	Chen, Q., Yin, D., Zhu, S., and Hu, X.	2012	Journal of Colloid and Interface Science, 367(1), 241-248.	Published journal	Chen et al. (2012) modeled the sorption of Cd(II) onto nano-TiO ₂ with and without a humic acid coating in order to demonstrate the ability of the engineered nanoparticle to strongly sorb a toxic metal. As expected, the nano-TiO ₂ coated with humic acid sorbed more cadmium in all cases when compared to bare TiO ₂ . The sorption of Cd(II) also increased with increasing pH. Sorption also increased slightly with increasing salinity to a point, but then decreased due to electrostatic repulsion. These results show that the introduction of nanoparticles into the environment may alter the bioavailability of toxic metals as a result of their association with humic substances.	Chen, Q., Yin, D., Zhu, S., and Hu, X. 2012. Adsorption of cadmium(II) on humic acid coated titanium dioxide. Journal of Colloid and Interface Science, 367(1), 241-248.
131	Transport behavior of humic acid-modified nano-hydroxyapatite in saturated packed column: Effects of Cu, ionic strength, and ionic composition.	Wang, D., Chu, L., Paradelo, M., Peijnenburg, W., Wang, Y., and Zhou, D.	2011	Journal of Colloid and Interface Science, 360(2), 308-407	Published journal	Wang et al. (2011) investigated the efficacy of nano-hydroxyapatite (n-HAP) to remediate contaminated soils when coated with humic acid. Using column experiments, the transport of n-HAP was investigated under various conditions where the ionic strength, ion composition and contaminant (Cu) concentration were variable. As predicted by DLVO theory, deposition of the nanoparticles increased at higher ionic strength. In addition, divalent cations (viz., Ca ²⁺) were more effective at the deposition of these nanoparticles due to cation bridging effects. Cupric ions (Cu ²⁺) were even more effective due to their ability to form complexes with the surface of n-HAP. The transport of these particles varied considerably depending on the ionic strength, ion composition, and contaminant concentration. Results such as these hold significance for the efficacy of nano-hydroxyapatite in remediation of contaminated soils.	Wang, D., Chu, L., Paradelo, M., Peijnenburg, W., Wang, Y., and Zhou, D. 2011. Transport behavior of humic acid-modified nano-hydroxyapatite in saturated packed column: Effects of Cu, ionic strength, and ionic composition. Journal of Colloid and Interface Science, 360(2), 308-407.
132	Adsorption and desorption of humic and fulvic acids on SiO ₂ particles at nano- and micro-scales.	Liang, L., Luo, L., and Zhang, S.	2011	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 384(1-3), 126-130	Published journal	Liang, Luo, and Zhang (2011) studied the adsorption/desorption behavior of fulvic and humic acid on silica nanoparticles of different sizes (20, 100, 500nm) at different pH and electrolyte concentrations. Due to the higher specific surface area, the 20nm SiO ₂ particles adsorbed humic and fulvic acid to a greater extent than the larger particles. The sorption of fulvic and humic acid decreased with increasing pH, most likely due to electrostatic repulsion between the silica surface and the negatively-charged humic molecules. A lesser extent of adsorption occurred at higher ionic strengths, though this effect was less pronounced with fulvic acid than it was with humic acid. These results will have obvious implications for transport of the particle through the environment.	Liang, L., Luo, L., and Zhang, S. 2011. Adsorption and desorption of humic and fulvic acids on SiO ₂ particles at nano- and micro-scales. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 384(1-3), 126-130.
135	Transformations of nanomaterials in the environment	Lowry, G.V., Gregory, K.B., Apte, S.C., and Lead, J.R.	2012	Environmental Science and Technology, 46(13), 6893-6899	Published journal	Lowry et al. (2012) summarize various transformations that may affect manufactured nano-materials upon release into the environment. These processes include chemical transformations, physical transformation, and nanomaterial/macromolecule interactions. Among chemical transformations, dissolution, oxidation, and sulfidation are all important processes that may affect the toxicity and persistence of nanomaterials in the environment. Physical processes such as aggregation (both homo- and heteroaggregation) may play a large role in the transport of these materials in the environment, as well as influencing their reactivity as aggregated particles have a reduced surface area that is thereby less reactive. Interactions with macromolecules such as proteins and humic substances may influence the aggregation state of nanomaterials as well as their reactivity. In short, once released into the environment, the nanomaterial will quickly transform from its "pristine" or manufactured state into a more complex particle with possibly different properties from its original state. The authors state that research is needed on the chemical and physical properties of nanomaterials in their transformed states in the environment.	Lowry, G.V., Gregory, K.B., Apte, S.C., and Lead, J.R. 2012. Transformations of nanomaterials in the environment. Environmental Science and Technology, 46(13), 6893-6899.
136	Natural nanoparticles structure, properties and reactivity from x-ray studies.	Waychunas, G.A., Gilbert, B., Banfield, J.F., Zhang, H., Jun, Y.S., and Kim, C.S.	2009	Powder Diffraction, 24(2), 89-93	Published journal	Waychunas et al. (2009) studied synthetic analogues of naturally-occurring nanomaterials using X-ray techniques to gain an understanding of some of their physical and chemical properties in the environment. Both ZnS and TiO ₂ nanoparticles exhibit a core-shell structure with a strained outer layer that is highly distorted. This strained layer can be manipulated and relaxed through the binding of ligands to the surface. The distortions in TiO ₂ are so extensive that the crystal structure is almost amorphous, similar to that of silicate glass. The chemistry of iron oxyhydroxide appears to be size-dependent. Iron oxyhydroxide's oriented aggregation may help contaminants caught up in the structure persist in the environment.	Waychunas, G.A., Gilbert, B., Banfield, J.F., Zhang, H., Jun, Y.S., and Kim, C.S. 2009. Natural nanoparticles structure, properties and reactivity from x-ray studies. Powder Diffraction, 24(2), 89-93.
137	The current state of engineered nanomaterials in consumer goods and waste streams: the need to develop nanoproperty-quantifiable sensors for monitoring engineered nanomaterials	Wise, K. and Brasuel, M.	2011	Nanotechnology, Science and Applications, 4, 73-86	Published journal	Wise and Brasuel (2011) review the current medical applications and subsequent potential toxicity of common nanomaterials such as silver nanoparticles, carbon nanotubes, quantum dots, and gold nanoparticles. They conclude that the same properties that make nanomaterials unique and beneficial could possibly be detrimental to human health. Current regulations for nanotechnology are minimal, and many of these products are regarded as safe for use. Yet detection and characterization methods needed to assess the toxicity of these materials are lacking. The authors propose that new techniques are necessary to fully understand the potential toxic effect of nanomaterials and properly regulate their use in the medical community.	Wise, K. and Brasuel, M. 2011. The current state of engineered nanomaterials in consumer goods and waste streams: the need to develop nanoproperty-quantifiable sensors for monitoring engineered nanomaterials. Nanotechnology, Science and Applications, 4, 73-86.

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201	Challenges and Opportunities of Nanomaterials in Drinking Water	Water Research Foundation	2011	2011	Unreviewed Water Research Foundation document	Tuccillo et al. (2011) discuss the state of knowledge regarding nanomaterials in the environment and identify data gaps, with a particular focus on issues relevant to drinking water. The report includes information on nanomaterials, human health effects, fate and transport in the environment, detection methods, the potential of drinking water treatment processes to remove nanomaterials, potential applications of nanomaterials in drinking water treatment and water quality monitoring, and regulatory developments. The authors conclude by identifying the following data gaps: environmental occurrence data for engineered nanomaterials; information on the effectiveness of drinking water treatment processes for removing both natural and engineered nanoparticles; research on analytical methods for characterization and quantification of nanomaterials; research on the effects of water chemistry on the aggregation or disaggregation of different types of nanomaterials; research on the fate and transport of nanomaterials; and research on human health effects.	Water Research Foundation 2011. Challenges and Opportunities of Nanomaterials in Drinking Water. 2011.
202	Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia	Novikov, A.P., Kalmykov, S.N., Utsunomiya, S., Ewing, R.C., Horreard, F., Merkulov, A., Clark, S.B., Tkachev, V.V., and Myasoedov, B.F.	2006	Science, 314(5799), 638-641	Published journal	Novikov et al. (2006) studied the migration of plutonium hydroxides and carbonates at the Far-Field of the Mayak Production Association, Russia. The study confirmed that the amorphous iron oxide colloids were responsible for adsorbing and transporting plutonium long distances (4 kilometers in approximately 55 years) and noted that this was comparable to the rate seen at the Nevada Test Site. In addition, it was observed that uranium under oxidizing conditions also adsorbed to the colloids. The authors conclude that site-specific investigations should be conducted for actinide colloids due to the differences in physico-chemical conditions at potential nuclear waste repository sites.	Novikov, A.P., Kalmykov, S.N., Utsunomiya, S., Ewing, R.C., Horreard, F., Merkulov, A., Clark, S.B., Tkachev, V.V., and Myasoedov, B.F. 2006. Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia. Science, 314(5799), 638-641.
203	Competitive actinide interactions in colloidal humic acid-mineral oxide systems	Righetto, L., Bidoglio, G., Azimonti, G., and Bellobono, I.R.	1991	Environmental Science and Technology, 25(11), 1913-1919	Published journal	Righetto et al. (1991) studied the adsorptive behavior of americium, thorium, neptunium, and plutonium in the presence of inorganic particles (γ-alumina or amorphous silica) and humic acid colloids from a clay formation rich in organics. The actinides' sorption selectivity was similar to that of other complex formations when reacting with hydrous mineral hydroxides. The actinides' adsorption when humic acid colloids were added to the solution depended on the coordinating strengths of humic acid on the surface and in the solution. The pH of the water also played a role in adsorption of the actinides, with adsorption improving in lower-pH waters. Righetto et al. conclude that the particle transport dynamics between actinides and humic acid be studied using packed beds and porous media.	Righetto, L., Bidoglio, G., Azimonti, G., and Bellobono, I.R. 1991. Competitive actinide interactions in colloidal humic acid-mineral oxide systems. Environmental Science and Technology, 25(11), 1913-1919.
204	Groundwater nanoparticles in the far-field at the Nevada test site: mechanism for radionuclide transport	Utsunomiya, S., Kersting, A.B., and Ewing, R.C.	2009	Environmental Science and Technology, 43(5), 1293-1298	Published journal	Utsunomiya et al. (2008) studied colloidal nanoparticles and their ability to transport contaminants, specifically radionuclides, in groundwater. In the study, nanoparticles were sampled in the groundwater at the far-field at the Nevada Test Site, using advanced electron microscopy techniques. The samples were found to contain colloidal nanoparticles associated with fission product elements, such as strontium and cesium, and an actinide, uranium. The authors conclude that at this test site, the colloidal nanoparticles' ability to adsorb and transport fission-product elements and actinides must be considered in order to accurately model the transport of these contaminants.	Utsunomiya, S., Kersting, A.B., and Ewing, R.C. 2009. Groundwater nanoparticles in the far-field at the Nevada test site: mechanism for radionuclide transport. Environmental Science and Technology, 43(5), 1293-1298.
205	Iron oxides as geochemical nanovectors for metal transport in soil river systems	Hasselöv, M. and von der Kammer, F.	2008	Elements, 4(6), 401-406	Published journal	Hasselöv and von der Kammer (2005) studied the effects natural nanoparticles have on soils contaminated with heavy metals. The authors measured natural nanoparticles and colloidal organic matter in soil and river samples using a nanoparticle separation technique combined with elemental detection. In this study, it was determined through sampling that iron oxide colloidal nanoparticles, ubiquitous in nature, efficiently transport heavy metals such as lead from soils through rivers to estuaries. In the estuary, the particles accumulate via flocculation and settle.	Hasselöv, M. and von der Kammer, F. 2008. Iron oxides as geochemical nanovectors for metal transport in soil river systems. Elements, 4(6), 401-406.
207	Nanogeoscience: from origins to cutting edge applications	Hochella, M.F.	2008	Elements, 4(6), 373-379	Published journal	Hochella (2008) discusses natural nanomaterials and their presence in the environment. The article discusses the properties of natural nanomaterials and how they can differ from their bulk material counterparts (or may not exist as a larger-sized material), as well as their global occurrence and distribution in the atmosphere, oceans, ground and surface water, soils, and most living organisms. The author also discusses the importance of nanomaterials: elemental distribution, biological-abiogenic Earth interaction, heterogeneous catalysis, reaction pathways, and mineral growth, transformation, and weathering all take place at the nano-scale. He also notes that what happens at this scale has no equivalent on smaller and larger scales. The author concludes that understanding natural nanoparticles will provide another perspective for understanding Earth's chemical and physical properties.	Hochella, M.F. 2008. Nanogeoscience: from origins to cutting edge applications. Elements, 4(6), 373-379.
208	Nanomaterials in the environment: behavior, fate, bioavailability and effects	Klaine, S.J., Alvarez, P.J., Batley, G.E., Fernandes, T.F., Handy, R.D., Lyon, D.Y., Mahendra, S., McLaughlin, M.J., and Lead, J.R.	2008	Environmental Toxicology and Chemistry, 27(9), 1825-1891	Published journal	Klaine et al. (2008) discuss the key aspects pertaining to nanomaterials in the environment, including where naturally-occurring nanoparticles exist (e.g., soil, water, air) and the classes of manufactured nanoparticles, their commercial applications, and their potential to be released into the environment. The article discusses what is known of the fate, behavior, disposition, and toxicity of nanoparticles in the environment through existing research, with a focus on manufactured nanoparticles. The authors state that immediate research is needed to develop quantitative measures of both exposure to and effects of nanoparticles in the environment, so that the risks they pose to the environment and human health can be better understood and so that regulators may have the tools to adequately manage nanoparticles in the environment. The authors note challenges in research regarding the variability of nanoparticles produced from different manufacturers, as well as the need for standard testing protocols, including standardization of methods for creating test media and particle and particle suspension characterization requirements so that researchers can adequately interpret the results of their research. Klaine et al. also discuss the need for research in freshwater, marine, and soil ecosystems. They state that the focus should be testing with organisms in sediment and soils since this will most likely be where nanoparticles are deposited. They also point out that further research is needed regarding the interaction between nanoparticles and natural organic matter (NOM) in aquatic environments since NOM has been shown to stabilize nanoparticles in the water column.	Klaine, S.J., Alvarez, P.J., Batley, G.E., Fernandes, T.F., Handy, R.D., Lyon, D.Y., Mahendra, S., McLaughlin, M.J., and Lead, J.R. 2008. Nanomaterials in the environment: behavior, fate, bioavailability and effects. Environmental Toxicology and Chemistry, 27(9), 1825-1891.

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209	Nanominerals, mineral nanoparticles, and earth systems	Hochella, M.F., Lower, S.K., Maurice, P.A., Penn, L.R., Sahai, N., Sparks, D.L., and Twining, B.S.	2008	Science, 319(5870), 1631-1635	Published journal	Hochella et al. (2008) discuss the origin and occurrence of nanominerals and mineral nanoparticles, and their distribution in the atmosphere, oceans, groundwater and surface waters, soils, and in and/or on most living organisms. The article also discusses the distinction between nanominerals and mineral nanoparticles (i.e., nanominerals only exist in the nano size range and mineral nanoparticles are minerals that can also exist in larger sizes), and their characteristics, including changes that occur with mineral size, their reactivity and stability, and their influence on Earth's chemistry. The authors note that nanophase minerals can influence the movement of heavy metals, and they cite an example of a newly discovered nanocrystalline vernadite-like mineral (a manganese oxyhydroxide), found at the Clark Fork River Superfund Complex in western Montana, that has transported lead, arsenic, copper, and zinc over hundreds of kilometers within the Clark Fork River drainage basin. The authors acknowledge that more research is necessary to understand nanominerals and mineral nanoparticles and their effects in the environment.	Hochella, M.F., Lower, S.K., Maurice, P.A., Penn, L.R., Sahai, N., Sparks, D.L., and Twining, B.S. 2008. Nanominerals, mineral nanoparticles, and earth systems. Science, 319(5870), 1631-1635.
210	Nanoparticles in the atmosphere	Buseck, P.R. and Adachi, K.	2008	Elements, 4(6), 389-394	Published journal	Buseck and Adachi (2008) discuss human exposure to nanoparticles in air, the nature of nanoparticles in the atmosphere (e.g., concentration and composition), and the mechanisms that introduce these particles into the atmosphere, including vehicles, industries, vegetative and sea spray, and volcanoes. The authors state that since nanoparticles react rapidly in the atmosphere, they grow into larger particles that can affect the earth's radiative balance and therefore affect climate. The authors note that due to recent improvements in analytical instrumentation, both natural and anthropogenic nanoparticles can be detected in the atmosphere. The authors suggest that it is necessary to conduct more research to evaluate the long-term effects of nanoparticles on the atmosphere and living organisms.	Buseck, P.R. and Adachi, K. 2008. Nanoparticles in the atmosphere. Elements, 4(6), 389-394.
211	Nanoparticles in the soil environment	Theng, B.K.G. and Yuan, G.	2008	Elements, 4(6), 395-399	Published journal	Theng and Yuan (2008) discuss naturally-occurring inorganic and organic nanoparticles that can be found in soils. The article focuses on clay minerals, metal oxides and hydroxides, humic substances, and substances (e.g., allophane and imogolite) that are abundant in volcanic soils. The authors note that very few nanoparticles exist discreetly in soils (e.g., organic colloids are associated with their inorganic counterparts), which makes it difficult to obtain adequate yields and conduct analyses. In addition, the sorptive properties of a discrete nanoparticle can be greatly altered if an interaction with another particle occurs. While sophisticated methods are used to characterize soil nanoparticles, nanoparticles are also very reactive towards external solute molecules. To avoid these issues, laboratory-synthesized materials have been used in research, but the authors note that even then the results are not easy to interpret. Theng and Yuan conclude that due to the intrinsic complexity of soil physicochemical processes, a multidisciplinary approach and advanced instrumental techniques are necessary to improve our understanding of sorption phenomena and nanoparticle interactions. The authors acknowledge that soil is also a repository for engineered nanoparticles and that there are concerns regarding their potential adverse effects on animal and human health, but state that detailed treatment of that topic was beyond the scope of the paper.	Theng, B.K.G. and Yuan, G. 2008. Nanoparticles in the soil environment. Elements, 4(6), 395-399.
212	Structure, chemistry, and properties of mineral nanoparticles	Waychunas, G.A. and Zhang, H.	2008	Elements, 4(6), 381-387	Published journal	Waychunas and Zhang (2008) provide a general discussion of the unique characteristics and properties of nanomaterials compared to their bulk counterparts. The authors emphasize that the size of the particle directly affects chemical reactivity, molecular and electronic structure, and mechanical behavior and that major differences in properties can result from these variations. Surface properties of nanoparticles can locally disrupt the organization of water molecules, which may create unusual aggregation, sorption, or other chemical effects. The article also specifically discusses some mineral-based naturally-occurring nanoparticles (e.g., silica and silicates), but acknowledges that little research has been conducted on mineral-based nanoparticles. They conclude that more insight into naturally-occurring nanoparticles can serve to help predict how manufactured nanomaterials will behave in the environment.	Waychunas, G.A. and Zhang, H. 2008. Structure, chemistry, and properties of mineral nanoparticles. Elements, 4(6), 381-387.
300	Marine sedimentation of nano-quartz forming flint in North Sea Danian chalk	Lindgreen, H. and Jakobsen, F.	2012	Marine and Petroleum Geology, 38(1), 73-82	Published journal	Lindgreen and Jakobsen (2012) proposed a new theory for the formation of flint in the North Sea Danian Ekofisk chalk formation. The proposed theory involves the sedimentation of nano-sized α -quartz particles that were crystallized from the dissolution of radiolarians. This theory was investigated by applying XRD, AFM, SEM and thermal analysis (DTA-EGA) to sedimentary features in the silicon-containing chalk. The flint in the chalk was composed of 100-300 nm silica spheres, which had perfect 3-dimensional order but slightly larger cell dimension than standard α -quartz.	Lindgreen, H. and Jakobsen, F. 2012. Marine sedimentation of nano-quartz forming flint in North Sea Danian chalk. Marine and Petroleum Geology, 38(1), 73-82.
302	Biocompatibility assessment of Si-based nano- and micro-particles	Jaganathan, H. and Godin, B.	2012	Advanced Drug Delivery Reviews, 64(15), 1800-1819	Published journal	Jaganathan and Godin (2012) reviewed the toxicity of SiO_2 nanoparticles and the methods used to test the toxicity of these materials. Though silica is generally not considered toxic, it has been shown that crystalline SiO_2 is more toxic than amorphous silica and elemental Si. It is apparent, however, that there is a lack of standardization among toxicity tests, making comparison between laboratories a difficult challenge.	Jaganathan, H. and Godin, B. 2012. Biocompatibility assessment of Si-based nano- and micro-particles. Advanced Drug Delivery Reviews, 64(15), 1800-1819.
303	Bioavailable iron in the Southern Ocean: the significance of the iceberg conveyor belt	Raiswell, R., Benning, L.G., Tranter, M., and Tulaczyk, S.	2008	Geomedical Transactions, 9(7)	Published journal	Raiswell et al. (2008) present the results of a study of iceberg samples. They demonstrate that bioavailable Fe is tied into ferrihydrite and goethite nanoclusters found in the glacial landmass. Due to their small size and high reactivity, these iron nanoparticles are more soluble than crystalline iron oxyhydroxides. These nanoparticles are also transported from coastal regions to the ocean. Upon dissolution the iron becomes bioavailable, leading to an increase in phytoplankton production. It is hypothesized that identifying icebergs as a significant source of bioavailable Fe may help explain and predict how oceans respond to climate change.	Raiswell, R., Benning, L.G., Tranter, M., and Tulaczyk, S. 2008. Bioavailable iron in the Southern Ocean: the significance of the iceberg conveyor belt. Geomedical Transactions, 9(7).
304	Naturally occurring nanoparticles from English ivy: an alternative to metal-based nanoparticles for UV protection	Xia, L., Lenaghan, S., Zhang, M., Zhang, Z., and Li, Q.	2010	Journal of Nanobiotechnology, 8(12)	Published journal	Xia et al. (2010) synthesized organic nanoparticles from English Ivy and investigated them as an alternative to TiO_2 and ZnO , which have previously shown to be cytotoxic. The UV absorption of the naturally synthesized particles was better than TiO_2 nanoparticles at the same concentration. Examination of toxicity to HeLa cell lines via flow cytometry demonstrated that the ivy nanoparticles were much less toxic than TiO_2 nanoparticles at the same concentration. The biodegradability of the ivy nanoparticles also help assuage concerns of environmental contamination. A mathematical model was applied to estimate the penetration of the ivy nanoparticles into the stratum corneum (SC) layer of the skin. It was determined that ivy particles with a diameter of 65.3 nm will not reach the bottom of SC layer in normal conditions for short periods of time after application. This investigation shows the possibility of utilizing naturally-derived nanoparticles as a safer alternative to the photoreactive engineered nanomaterials that are currently used in cosmetics. The naturally-derived particles warrant further investigation.	Xia, L., Lenaghan, S., Zhang, M., Zhang, Z., and Li, Q. 2010. Naturally occurring nanoparticles from English ivy: an alternative to metal-based nanoparticles for UV protection. Journal of Nanobiotechnology, 8(12).

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305	Naturally occurring iron oxide nanoparticles: morphology, surface chemistry and environmental stability	Guo, H. and Barnard, A.	2013	Journal of Material Chemistry A, 1(1), 27-42	Published journal	Guo and Barnard (2013) reviewed various physical and chemical properties of nanostructured iron oxides and iron oxyhydroxides. Several phases of iron found in water, soil, and sediment were studied. It was determined that increases in crystallinity of ferrihydrite or the formation of more crystalline phases (such as hematite and goethite) can cause a significant decrease in adsorbed arsenic and uranium. The phases of iron oxide found in the environment can also supply detailed information about the conditions under which they were formed (i.e., acidity, water content, etc.). The nanostructures may also give insight into the precursors that formed them.	Guo, H. and Barnard, A. 2013. Naturally occurring iron oxide nanoparticles: morphology, surface chemistry and environmental stability. Journal of Material Chemistry A, 1(1), 27-42.
306	Interaction between manufactured gold nanoparticles and naturally occurring organic macromolecules	Diegoli, S., Maniculea, A., Begum, S., Jones, I., Lead, J., and Preece, J.	2008	Science of the Total Environment, 402(1), 51-61	Published journal	Diegoli et al. (2008) investigated the influence of humic acid on the stability of gold nanoparticles. As expected, the addition of humic acid caused a significant decrease in the zeta potential of these particles, enhancing their stability. At high ionic strength, particles tended to agglomerate even with the addition of humic acid. Agglomeration without humic acid was detected by TEM and also indicated by a shift in the surface plasmon resonance from the transverse to the longitudinal plasmon band. Though agglomeration was still evident with the addition of humic acid at high ionic strength, there was no shift in the plasmon band as the humic acid coating was thick enough to keep the particles far enough apart to preserve the surface plasmon resonance. It is still unknown whether humic acid overcoats the particle coating or instead undergoes a ligand exchange with the existing surface groups; this remains an active area of research.	Diegoli, S., Maniculea, A., Begum, S., Jones, I., Lead, J., and Preece, J. 2008. Interaction between manufactured gold nanoparticles and naturally occurring organic macromolecules. Science of the Total Environment, 402(1), 51-61.
307	Extraction and characterization of natural soil nanoparticles from Chinese soils	Li, W., He, Y., Wu, J., and Xu, J.	2012	European Journal of Soil Science, 63(5), 754-761	Published journal	Li et al. (2012) collected several Chinese soil samples (one mollisol, three alfisols, six ultisols, and two entisols) and used ultrasonic centrifugation to disperse and extract nanoparticles. These nanoparticles were then analyzed by XRD, TEM, FTIR, XRD and zeta potentiometry. The mollisols and alfisols released a significant quantity of nanoparticles (80-130 mg NP/g soil) with relatively small sizes (less than 25 nm) and were mainly comprised of muscovite and montmorillonite. These particles were generally round and could be dispersed in solution. The other soils, conversely, released much fewer nanoparticles that were larger in size (~70nm) and were generally not as stable in aqueous suspension.	Li, W., He, Y., Wu, J., and Xu, J. 2012. Extraction and characterization of natural soil nanoparticles from Chinese soils. European Journal of Soil Science, 63(5), 754-761.
308	Humic acid-induced silver nanoparticle formation under environmentally relevant conditions	Akaike, N., MacCuspie, R., Navarro, D., Aga, D., Banerjee, S., Sohn, M., and Sharma, V.	2011	Environmental Science and Technology, 45(9), 3895-3901	Published journal	Akaike et al. (2011) investigated the formation of silver nanoparticles via reduction of dissolved silver (Ag ⁺) by humic acid under environmentally relevant conditions. Aliphatically-rich humic substances such as those found in aquatic and sedimentary humic acids were able to reduce silver ions to colloidal silver at temperatures ranging from room temperature (22 deg C) up to 90 deg C (a temperature relevant for hot springs and other thermally active environments). Other humic acids derived from soils were found to only reduce silver ions at elevated temperatures. UV-vis, DLS, and a suite of microscopy techniques were used to investigate the size distributions of the colloidal silver formed. Many samples were polydisperse, but could be made more mono-disperse with greater addition of humic acid. Results show that colloidal and nano-particulate silver found in the environment may not originate from exclusively anthropogenic sources and that the fate and transformation of silver nanoparticles in the aqueous environment may be subject to changing redox conditions.	Akaike, N., MacCuspie, R., Navarro, D., Aga, D., Banerjee, S., Sohn, M., and Sharma, V. 2011. Humic acid-induced silver nanoparticle formation under environmentally relevant conditions. Environmental Science and Technology, 45(9), 3895-3901.
309	Natural and anthropogenic environmental nanoparticles: Their microstructural characterization and respiratory health implications	Murr, L. and Garza, K.	2009	Atmospheric Environment, 43(7), 2683-2692	Published journal	Murr and Garza (2009) studied various naturally-occurring nanomaterials found in both indoor and outdoor environments by collecting them through filtration, electrostatic precipitation, and thermophoretic precipitation and analyzing them by TEM, SEM and EDS. Toxicity assays were also performed, investigating ROS production and cytokine release in human epithelial (lung model) cells. Approximately 42% of all outdoor particulate matter is carbonaceous nanoparticulates. It was discovered that more than 80% of all nanoparticulate matter is agglomerated. Cytokine (IL-8) release was detected for Fe ₂ O ₃ , chrysotile asbestos, black carbon, and multi-walled carbon nanotube aggregate material. Reactive oxygen species were demonstrated with all these species as well as with various collections of soot material. Natural soot material also produced extensive cell death. These results demonstrate that engineered nanomaterials may be capable of causing a variety of respiratory health problems.	Murr, L. and Garza, K. 2009. Natural and anthropogenic environmental nanoparticles: Their microstructural characterization and respiratory health implications. Atmospheric Environment, 43(7), 2683-2692.
310	Biodegradability of organic nanoparticles in the aqueous environment	Kümmerer, K., Menz, J., Schubert, T., and Thielemans, W.	2011	Chemosphere, 82(10), 1387-1392	Published journal	The biodegradability of various organic nanoparticles was investigated by Kümmerer et al. (2011) in response to concerns about environmental exposure to engineered nanoparticles. Fullerenes, single and multi-walled CNTs (both functionalized and unfunctionalized), cellulose, and starch nanoparticles were all looked at for their biodegradability. Fullerenes and carbon nanotubes showed no degradation over the experimental time frames. The starch and cellulose nanoparticles did show degradation, even at higher rates than their bulk counterparts, but none of the nanomaterials investigated qualified as "readily biodegradation" per OECD standards (60% degraded by 28 days).	Kümmerer, K., Menz, J., Schubert, T., and Thielemans, W. 2011. Biodegradability of organic nanoparticles in the aqueous environment. Chemosphere, 82(10), 1387-1392.

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311	Nanoparticles in the environment	Banfield, J. and Zhang, H.	2001	Reviews in Mineralogy and Geochemistry, 44(1), 1-58	Published journal	This article introduces examples of the types of solids that are commonly encountered as nanoparticles in natural systems, describes some of the inorganic and biological processes that generate nanoparticles in the environment, reviews the special properties (including stability and reactivity) of naturally occurring nanoparticles that make them significant in natural processes and geological systems, and identifies research needs in this area. Natural nanoparticles may have geologic origins (e.g., clays) or biological origins (e.g., ferritins). Low-temperature environments, such as the earth's surface, are the most favorable environments for formation of nanoparticles. All crystal formation passes through a nano size phase. Geochemical or biological processes that generate high degrees of supersaturation lead to production of very many crystal nuclei, and therefore many nanoparticles. Geochemical examples include undersea hydrothermal vents, regions where streams of highly acidic solutions mix with neutral pH water, zones of mixing between groundwater fluids, and sites of evaporation of soil water solutions. Biological examples include microorganisms that generate metabolic energy by pathways that involve inorganic ions that participate in redox reactions. Challenges for future research include: synthesis of materials suitable for quantification of size-related phenomena; characterization of nanoparticles of varying sizes and the ways they contrast with their bulk counterparts; study of the role of nanoparticles in complex organic-inorganic systems; understanding the self-organization of nanoparticles; characterization of early-growth crystals that are smaller than nanoscale; and study of transport in aqueous media.	Banfield, J. and Zhang, H. 2001. Nanoparticles in the environment. Reviews in Mineralogy and Geochemistry, 44(1), 1-58.
312	Inorganic nanotubes and fullerene-like nanoparticles	Tenne, R.	2006	Nature Nanotechnology, 1(2), 103-111	Published journal	Tenne (2006) reviewed inorganic nanomaterials that were similar in structure to carbon nanotubes and fullerenes. Such material include inorganic nanotubes of WS ₂ , MoS ₂ , BN, and V ₂ O ₅ that have unique physical, mechanical, and tribological properties. The fullerene-like structures also have shown excellent lubrication behavior that could make them appropriate for many applications in kitchen appliances, medical technology, and the aerospace industry. Though these materials have several interesting properties, the manipulation of their size, shape, and composition is still in its beginning stages and may warrant further research.	Tenne, R. 2006. Inorganic nanotubes and fullerene-like nanoparticles. Nature Nanotechnology, 1(2), 103-111.
411	Research Priorities to Advance Eco-Responsible Nanotechnology	Alvarez, P.J.J., Colvin, V., Lead, J., and Stone, V.	2009	ACS Nano, 3(7), 1616-1619	Published Journal	Alvarez et al. (2009) introduced several topics for consideration in advancing the eco-responsible design and regulation of engineered nanomaterials. Research needs include: structure-activity relationships to predict functional stability of engineered nanoparticles (ENPs); protocols that assess ENP bioavailability, trophic transfer, and sublethal effects, and validated transport models. One of the areas that requires the greatest amount of work is proper analytical techniques to detect and characterize engineered nanoparticles in environmental and biological samples. Proactive risk assessment is also necessary to guide further research and determine the future of nanomaterial production.	Alvarez, P.J.J., Colvin, V., Lead, J., and Stone, V. 2009. Research Priorities to Advance Eco-Responsible Nanotechnology. ACS Nano, 3(7), 1616-1619.
502	Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry	Mitrano, D.M., Leshner, E.K., Bednar, A., Monsrud, J., Higgins, C.P., and Ranville, J.F.	2012	Environmental Toxicology and Chemistry, 31(1), 115-121	Published journal	Mitrano et al. (2012) utilized single-particle ICP-MS to detect and characterize silver nanoparticles in both wastewater and a commercially-available colloidal silver product. Using this technique, one is able to distinguish between nanoparticulate silver and dissolved silver in the sample, and to quantify particle number and size. Samples of wastewater showed that the wastewater treatment facility was able to remove dissolved silver through the treatment process but was unable to remove the silver nanoparticles. The applicability of filters to the quantification of dissolved silver in a sample was also examined, but the binding of silver to the filter membranes may reduce the accuracy in the quantification of silver in solution. With these results, the applicability of single particle ICP-MS to the detection of nanoparticles in environmental samples was demonstrated, and further work is needed to validate this method.	Mitrano, D.M., Leshner, E.K., Bednar, A., Monsrud, J., Higgins, C.P., and Ranville, J.F. 2012. Detecting nanoparticulate silver using single-particle inductively coupled plasma-mass spectrometry. Environmental Toxicology and Chemistry, 31(1), 115-121.
503	Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry	Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Higgins, C.P., and Ranville, J.F.	2011	Analytical Chemistry, 83(24), 9361-9369	Published journal	Pace et al. (2011) presented a framework to count and size nanoparticles using ICP-MS run using single particle mode (i.e., short dwell times, dilute samples). Different strategies for evaluating the transport efficiency (i.e., the nebulization efficiency) were discussed. Single particle ICP-MS (SP-ICP-MS) was shown to be an effective analytical technique for determining particle number concentration and particle size for metal-containing nanoparticles.	Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Higgins, C.P., and Ranville, J.F. 2011. Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry. Analytical Chemistry, 83(24), 9361-9369.
504	Single Particle Inductively Coupled Plasma Mass Spectrometry: A Performance Evaluation and Method Comparison in the Determination of Nanoparticle Size	Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Gray, E.P., Higgins, C.P., and Ranville, J.F.	2012	Environmental Science and Technology, 46(22), 12272-12280	Published journal	Pace et al. (2012) compare various methods used in sizing metallic nanoparticles and demonstrate the performance of single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) in comparison to other sizing techniques such as dynamic light scattering (DLS), nanotracking analysis (NTA), transmission electron microscopy (TEM), and differential centrifugal sedimentation (DCS). The results show the ability of SP-ICP-MS to size and count nanoparticles with elemental specificity. One major drawback, however, is the inability of the techniques to distinguish between particles of the same elemental composition (i.e., silver NP vs. silver chloride NP). Overall, with the continued development of this technique, it may one day be applied to the detection and characterization of nanoparticles in the environment.	Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Gray, E.P., Higgins, C.P., and Ranville, J.F. 2012. Single Particle Inductively Coupled Plasma Mass Spectrometry: A Performance Evaluation and Method Comparison in the Determination of Nanoparticle Size. Environmental Science and Technology, 46(22), 12272-12280.
505	Toxic potential of materials at the nanolevel	Nel, A., Xia, T., Mädler, L., and Li, N.	2006	Science, 311(5761), 622-627	Published journal	Nel et al. (2006) outline the potential mechanisms of toxicity resulting from nanomaterial exposure. In particular, special attention is paid to how nanomaterials may elicit a biological response either through dissolution and/or generation of reactive oxygen species. Different pathophysiological effects that arise from different nanomaterials effects are outlined. Lastly, the challenges that are present in the <i>in vivo</i> and <i>in vitro</i> characterization of nanomaterials are discussed.	Nel, A., Xia, T., Mädler, L., and Li, N. 2006. Toxic potential of materials at the nanolevel. Science, 311(5761), 622-627.

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506	Economics and governance of nanomaterials: potential and risks	Delgado, G.C.	2010	Technology in Society, 32(2), 137-144	Published journal	Delgado (2010) discusses the economic potential of nanomaterials, and the need for standardization in assessing the toxicological and environmental impact of nanomaterials. Figures of note include plots detailing the number of patents in the U.S. and Europe dedicated to nanomaterials, the distribution of nanomaterials in different industries, and estimated global production of nanomaterials for various applications. The paper concludes that there is a pressing need to develop nanotechnology in a safe and responsible manner.	Delgado, G.C. 2010. Economics and governance of nanomaterials: potential and risks. Technology in Society, 32(2), 137-144.
507	Do nanoparticles present ecotoxicological risks for the health of the aquatic environment?	Moore, M.N.	2006	Environment International, 32(8), 967-976	Published journal	Moore (2006) reviews the potential toxicological impact, environmental entry, and biological uptake of nanomaterials. Some attention is paid to how nanomaterials enter into biological cells and result in <i>in vivo</i> toxicity. How the environment may change nanomaterial fate, behavior, and toxicity are also discussed. It is postulated that the regulation and governance of nanomaterials may need to be performed on a material-by-material basis, rather than treating all nanomaterials similarly.	Moore, M.N. 2006. Do nanoparticles present ecotoxicological risks for the health of the aquatic environment?. Environment International, 32(8), 967-976.
508	A review of selected engineered nanoparticles in the atmosphere: sources, transformations, and techniques for sampling and analysis	Majestic, B.J., Erdakos, G.B., Lewandowski, M., Oliver K.D., Willis, R.D., Kleindienst, T.E., and Bhawe, P.V.	2010	International Journal of Occupational and Environmental Health, 16(4), 488-507	Published journal	Majestic et al. (2010) review the various processes by which atmospheric nanoparticles are generated, the processes they are subject to in the environment, and the appropriate instrumentation and methodology by which to study and characterize them in the environment.	Majestic, B.J., Erdakos, G.B., Lewandowski, M., Oliver K.D., Willis, R.D., Kleindienst, T.E., and Bhawe, P.V. 2010. A review of selected engineered nanoparticles in the atmosphere: sources, transformations, and techniques for sampling and analysis. International Journal of Occupational and Environmental Health, 16(4), 488-507.
509	Heteroaggregation with nanoparticles: effect of particle size ratio on optimum particle dose	Yates, P.D., Franks, G.V., Biggs, S., and Jameson, G.J.	2005	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 255(1-3), 85-90	Published journal	Yates et al. (2005) investigated heteroaggregation between negatively charged silica nanoparticles and positively charged alumina colloids (310 nm). The addition of increasing sizes of silica and increasing concentration of silica were investigated with respect to the optimum dose that produces the greatest extent of heteroaggregation. It was found that the size ratios and concentrations that produce a 50% surface coverage of the alumina particles produce the greatest amount of heteroaggregation, as these conditions result in a zeta-potential close to zero (where electrostatic repulsive forces are neutralized).	Yates, P.D., Franks, G.V., Biggs, S., and Jameson, G.J. 2005. Heteroaggregation with nanoparticles: effect of particle size ratio on optimum particle dose. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 255(1-3), 85-90.
510	Orthokinetic heteroaggregation with nanoparticles: Effect of particle size ratio on aggregate properties	Yates, P.D., Franks, G.V., and Jameson, G.J.	2008	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 326(1-2), 83-91	Published journal	Yates et al. (2008) investigated the strength of interaction between particles and consequently the strength of alumina aggregates by aggregating alumina colloids using polymer-alumina heteroaggregation, alumina-silica particle heteroaggregation, and alumina homoaggregation provoked by neutralization of surface charge by raising the pH (pH =9). The strongest particle interactions were achieved with alumina homoaggregation and alumina-silica heteroaggregation, with increasing particle-particle interactions at smaller sizes of silica nanoparticles. DLVO theory, which explains aggregation of aqueous materials, was used to model the strength of interactions between particles.	Yates, P.D., Franks, G.V., and Jameson, G.J. 2008. Orthokinetic heteroaggregation with nanoparticles: Effect of particle size ratio on aggregate properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 326(1-2), 83-91.
511	Interactions between natural organic matter and gold nanoparticles stabilized with different organic capping agents	Stankus, D.P., Lohse, S.E., Hutchison, J.E., and Nason, J.A.	2010	Environmental Science and Technology, 45(8), 3238-3244	Published journal	Stankus et al. (2010) studied the interaction and aggregation processes of different gold nanoparticles in the presence of humic acid. As expected, the addition of humic acid stabilizes nanoparticles by imparting a strong negative charge, as a result of the ubiquity of carboxyl and phenolic groups present in the humic acid molecules. This resulted in a strong negative charge across the pH range that kept the particles stabilized. However, in the presence of elevated concentrations of divalent cations (i.e. Ca^{2+} , Mg^{2+} , etc.), aggregation was enhanced with humic acid. This is possibly a result of cation bridging between humic acid molecules.	Stankus, D.P., Lohse, S.E., Hutchison, J.E., and Nason, J.A. 2010. Interactions between natural organic matter and gold nanoparticles stabilized with different organic capping agents. Environmental Science and Technology, 45(8), 3238-3244.

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512	Modeled environmental concentrations of engineered nanomaterials (TiO ₂ , ZnO, Ag, CNT, fullerenes) for different regions	Gottschalk, F., Sonderer, T., Scholz, R.W., and Nowack, B.	2009	Environmental Science and Technology, 43(24), 9216-9222	Published journal	Gottschalk et al. (2009) use a probabilistic materials flow analysis to determine predicted environmental concentrations (PECs) for various engineered nanomaterials. Many nanomaterials are expected to be released in concentrations of ng L ⁻¹ or less. The majority of ecotoxicological impact may occur from nanomaterials such as nano-Ag and nano-TiO ₂ released from sewage treatment plant effluent, considered to be a major sink for a variety of nanomaterials.	Gottschalk, F., Sonderer, T., Scholz, R.W., and Nowack, B. 2009. Modeled environmental concentrations of engineered nanomaterials (TiO ₂ , ZnO, Ag, CNT, fullerenes) for different regions. Environmental Science and Technology, 43(24), 9216-9222.
513	Exposure modeling of engineered nanoparticles in the environment	Mueller, N.C. and Nowack, B.	2008	Environmental Science and Technology, 42(12), 4447-4453	Published journal	Mueller and Nowack (2008) modeled the amount of nanomaterials (nano-Ag, nano-TiO ₂ , CNTs) released into the environment and compared the predicted environmental concentrations (PECs) to the predicted no-effect concentrations (PNEC) to understand potential risk of these materials. Whereas the PEC/PNEC ratio was greater than 1 for TiO ₂ , establishing possible risk, the PEC/PNEC ratios for nano-Ag and CNTs were less than 1. This quantitative approach may be used to understand environmental risk and establish life cycle assessments for engineered nanomaterials.	Mueller, N.C. and Nowack, B. 2008. Exposure modeling of engineered nanoparticles in the environment. Environmental Science and Technology, 42(12), 4447-4453.
514	Categorization framework to aid exposure assessment of nanomaterials in consumer products	Hansen, S., Michelson, E., Kamper, A., Borling, P., Stuer-Lauridsen, F., and Baun, A.	2008	Ecotoxicology, 17(5), 438-447	Published journal	Hansen et al. (2008) provide a framework to assess potential risk of nanomaterials to the environment. This framework was used to quantify possible consumer exposure to these materials but was hampered by the lack of information regarding ENP incorporation into commercial products and the lack of reliable sources containing the information needed to develop an accurate risk assessment.	Hansen, S., Michelson, E., Kamper, A., Borling, P., Stuer-Lauridsen, F., and Baun, A. 2008. Categorization framework to aid exposure assessment of nanomaterials in consumer products. Ecotoxicology, 17(5), 438-447.
515	Setting the limits for engineered nanoparticles in European surface waters - are current approaches appropriate?	Baun, A., Hartmann, N., Grieger, K., and Hansen, S.	2009	Journal of Environmental Monitoring, 11(10), 1774-1781	Published journal	Baun et al. (2009) review Europe's Water Framework Directive (WFD) and its relation to the eventual release of engineered nanomaterials into the environment. It was concluded that current information regarding ENP behavior, concentrations, and environmental impact is insufficient to set appropriate limits for ENPs in the environment. More work is needed to assess the environmental impacts of nanomaterials in order to accurately classify them as "priority substances" with regard to the WFD.	Baun, A., Hartmann, N., Grieger, K., and Hansen, S. 2009. Setting the limits for engineered nanoparticles in European surface waters - are current approaches appropriate?. Journal of Environmental Monitoring, 11(10), 1774-1781.
516	Potential scenarios for nanomaterial release and subsequent alteration in the environment	Nowack, B., Ranville, J., Diamond, S., Gallego-Urrea, J., Metcalfe, C., Rose, J., Horne, N., Koelmans, A., and Klaine, S.	2012	Environmental Toxicology and Chemistry, 31(1), 50-59	Published Journal	Nowack et al. (2012) discuss the release of engineered nanomaterials into the environment and the possible environmental processes that may alter the pristine state of the nanomaterial. Different case studies are presented to demonstrate the numerous processes that can affect ENMs in the environment and how these alterations may impact the chemistry, reactivity, and characterization of these materials in environmental samples. Attention was paid to the current knowledge gaps that need to be overcome in order to accurately assess the risk of these ENMs to environmental and human health, as well as the implications these alterations have with regard to environmental health and safety.	Nowack, B., Ranville, J., Diamond, S., Gallego-Urrea, J., Metcalfe, C., Rose, J., Horne, N., Koelmans, A., and Klaine, S. 2012. Potential scenarios for nanomaterial release and subsequent alteration in the environment. Environmental Toxicology and Chemistry, 31(1), 50-59.
517	Environmental Particles (Environmental Analytical and Physical Chemistry Series)	Buffle, J. and van Leeuwen, H.P.	1992	Lewis Publishers, International Union of Pure and Applied Chemistry (1992, 1st ed.)	Published Journal	Buffle and van Leeuwen (1992) compile various papers related to the sampling, monitoring, and reactivity of environmental colloids in both atmospheric and aqueous systems. Techniques such as filtration, centrifugation, and electron microscopy are discussed in their ability to characterize these materials; in addition, properties such as surface charge and elemental ratios are discussed in relation to their detection and characterization in environmental samples. Lastly, the role and processes these materials participate in in environmental samples are discussed.	Buffle, J. and van Leeuwen, H.P. 1992. Environmental Particles (Environmental Analytical and Physical Chemistry Series). Lewis Publishers, International Union of Pure and Applied Chemistry (1992, 1st ed.).

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518	Aquatic environmental nanoparticles	Wigginton, S., Haus, K., and Hochella, Jr., M.	2007	Journal of Environmental Monitoring, 9(12), 1306-1316	Published journal	Wigginton et al. (2007) discuss the formation of naturally occurring nanomaterials and give insight into their importance in environmental processes. In particular, the utility of iron oxide nanoparticles in the remediation of environmental contaminants is discussed. Possible tools and analytical techniques for the detection and characterization of these materials in the environment are also reviewed along with a case study showcasing the application of these techniques to the characterization of naturally occurring nanomaterials in an environmental sample.	Wigginton, S., Haus, K., and Hochella, Jr., M. 2007. Aquatic environmental nanoparticles. Journal of Environmental Monitoring, 9(12), 1306-1316.
519	Geochemical modeling of ZnS in biofilms: An example of ore depositional processes	Druschel, G., Labrenz, M., Thomsen-Ebert, T., Fowle, D., and Banfield, J.	2002	Economic Geology, 97(6), 1319-1329	Published Journal	Druschel et al. (2002) studied the formation of nanocrystalline ZnS (primarily sphalerite and wurtzite) within biofilms growing on mine timbers. The precipitation mechanism was driven by sulfate-reducing bacteria of the family Desulfobacteriaceae. The model proposed details the reduction of sulfate, followed by cluster formation (1-3 nm in size), subsequently followed by aggregation of these clusters. By identifying characteristics unique to these ZnS particles, nanocrystalline zinc sulfides of biogenic origin can be identified.	Druschel, G., Labrenz, M., Thomsen-Ebert, T., Fowle, D., and Banfield, J. 2002. Geochemical modeling of ZnS in biofilms: An example of ore depositional processes. Economic Geology, 97(6), 1319-1329.
520	Ultrastructure, aggregation-state, and crystal growth of biogenic nanocrystalline sphalerite and wurtzite	Moreau, J., Webb, R., and Banfield, J.	2004	American Mineralogist, 89(7), 950-960	Published Journal	Moreau et al. (2004) investigated the formation of nanocrystalline ZnS in neutral waters flowing from an abandoned Pb-Zn mine. High resolution TEM revealed the formation of spherical nanoparticles 1-3 nm in diameter that came together to form micron-sized aggregates. The crystal structure of the ZnS material was size-dependent, and the study shows some size-dependent phase stability in the biogenic formation of these nanomaterials.	Moreau, J., Webb, R., and Banfield, J. 2004. Ultrastructure, aggregation-state, and crystal growth of biogenic nanocrystalline sphalerite and wurtzite. American Mineralogist, 89(7), 950-960.
521	Reaction sequence of iron sulfide minerals in bacteria and their use as biomarkers	Pósfai, M., Buseck, P., Bazylinski, D., and Frankel, R.	1998	Science, 280(5365), 880-883	Published journal	Pósfai et al. (1998) studied the formation of various nanocrystalline iron-containing minerals (greigite (Fe ₃ S ₄), mackinawite (tetragonal FeS), and cubic FeS) formed intracellularly in magnetotactic many-celled prokaryotes (MMPs). The findings of this study may have implications for the presence of these iron sulfides in the Martian meteorite ALH8001.	Pósfai, M., Buseck, P., Bazylinski, D., and Frankel, R. 1998. Reaction sequence of iron sulfide minerals in bacteria and their use as biomarkers. Science, 280(5365), 880-883.
522	Characterization of Aquatic Colloids and Macromolecules	Buffie, J. and Leppard, G.G.	1995	Environmental Science and Technology, 29(9), 2169-2175	Published journal	Buffie and Leppard (1995) review important literature regarding the behavior, composition, and size distribution of naturally occurring colloids in environmental samples. In particular, the section on the size distribution of these colloids in the environment shows that environmental colloids tend to follow Pareto's Law in environmental samples, with a β value of 3. In addition, aggregation, sedimentation, and transport processes are also discussed.	Buffie, J. and Leppard, G.G. 1995. Characterization of Aquatic Colloids and Macromolecules. Environmental Science and Technology, 29(9), 2169-2175.
523	Subsurface transport of contaminants	McCarthy, J. and Zachara, J.	1989	Environmental Science and Technology, 23(5), 496-502	Published journal	McCarthy and Zachara (1989) discuss naturally occurring colloids and their potential for the transport of groundwater contaminants. In particular, they postulate that colloids act as a third highly mobile phase (aqueous (mobile) and sediment (immobile) being the other two). As a result of their mobility in aqueous systems and their high surface area for the adsorption of contaminants, these colloids play a major role in the fate and transport of contaminants in aqueous systems.	McCarthy, J. and Zachara, J. 1989. Subsurface transport of contaminants. Environmental Science and Technology, 23(5), 496-502.
524	Plutonium and neptunium speciation bound to hydrous ferric oxide colloids	Kalmykov, S., Kriventsov, V., Teterin, Y., and Novikov, A.	2007	Comptes Rendus Chimie, 10(10-11), 1060-1066	Published Journal	Kalmykov et al. (2007) studied the Mayak production site, investigating the speciation of plutonium and neptunium bound to the hydrous ferric oxide colloids that transport these contaminants into the far-field. It was discovered that near the source of contamination, intrinsic plutonium oxide colloids are formed that break down in the far-field to form pseudo-colloids through adsorption onto the iron oxide colloids.	Kalmykov, S., Kriventsov, V., Teterin, Y., and Novikov, A. 2007. Plutonium and neptunium speciation bound to hydrous ferric oxide colloids. Comptes Rendus Chimie, 10(10-11), 1060-1066.
525	Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site	Buddemeier, R. and Hunt, J.	1988	Applied Geochemistry, 3(5), 535-548	Published Journal	Buddemeier and Hunt (1988) collected groundwater samples within a nuclear detonation cavity and approximately 300 m away from the sampled cavity. It was discovered that all the transition metals of interest (Mn, Co) and lanthanides (Ce, Eu) were associated with the colloidal fraction of the sample. The results indicate that the transport from the cavity is assisted through colloidal transport.	Buddemeier, R. and Hunt, J. 1988. Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site. Applied Geochemistry, 3(5), 535-548.

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526	Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation	Phenrat, T., Saleh, N., Sirk, K., Kim, H.-J., Tilton, R., and Lowry, G.	2008	Journal of Nanoparticle Research, 10(5), 795-814	Published journal	Phenrat et al. (2008) prepared various dispersions of nanoscale zero-valent iron (NZVI) with different poly(styrene sulfonate), carboxymethyl cellulose and polyaspartate polymeric coatings to stabilize the particle and prevent aggregation. As these particles are used for groundwater remediation, the ability of these particles to remain dispersed will enhance their ability to remediate contaminants, as aggregation and settling reduce the reactive surface area. It was found that all polymers were able to stabilize the particles to a degree, but there is a fraction of particles that nevertheless aggregate and settle out of solution.	Phenrat, T., Saleh, N., Sirk, K., Kim, H.-J., Tilton, R., and Lowry, G. 2008. Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. Journal of Nanoparticle Research, 10(5), 795-814.
527	Nanomaterial enabled biosensors for pathogen monitoring-A review	Vikesland, P. and Wigginton, K.	2010	Environmental Science and Technology, 44(10), 3656-3669	Published journal	Vikesland and Wigginton (2010) explore the current state-of-the-art in pathogen monitoring using nanomaterial-enabled biosensors. Different signal transduction methods can be exploited in nanomaterials, such as electrochemical, fluorescence, surface-enhanced plasmon resonance and magnetic methods. By functionalizing a nanomaterial with the appropriate antibody or biomolecule, one can tailor it to be a very sensitive and specific sensor for a variety of water-borne pathogens.	Vikesland, P. and Wigginton, K. 2010. Nanomaterial enabled biosensors for pathogen monitoring-A review. Environmental Science and Technology, 44(10), 3656-3669.
528	Fe0 nanoparticles remain mobile in porous media after aging due to slow desorption of polymeric surface modifiers	Kim, H.J., Phenrat, T., Tilton, R., and Lowry, G.	2009	Environmental Science and Technology, 43(10), 3824-3830	Published journal	Kim et al. (2009) investigated the desorption of polymeric surface coatings that had modified zerovalent iron nanoparticles to prevent aggregation and subsequent sedimentation. It was found that many of the coatings remained adsorbed to the particles and subsequently remained mobile in porous media even after extensive aging (4 months). High molecular weight polyelectrolyte had greater adsorbed mass and slower desorption rates. It was concluded that the mobility of aged modified nanoparticles was similar to that of freshly modified particles, in contrast to the immobility of aged unmodified zero valent iron nanoparticles.	Kim, H.J., Phenrat, T., Tilton, R., and Lowry, G. 2009. Fe0 nanoparticles remain mobile in porous media after aging due to slow desorption of polymeric surface modifiers. Environmental Science and Technology, 43(10), 3824-3830.
529	Estimating attachment of nano- and submicrometer-particles coated with organic macromolecules in porous media: development of an empirical model	Phenrat, T., Song, J., Cisneros, C., Schoenfelder, D., Tilton, R., and Lowry, G.	2010	Environmental Science and Technology, 44(12), 4531-4538	Published journal	Phenrat et al. (2010) created an empirical correlation between nanoparticle properties and their sticking coefficients under a variety of electrolyte and flow conditions. It was discovered that semiempirical correlations that had been used to predict the attachment efficiency of electrostatically stabilized (uncoated) nanoparticles overestimate the attachment efficiency of nanoparticles coated with natural organic matter or polyelectrolytes. This is because these correlations fail to take into account the electrostatic repulsions and decreased friction afforded by these coatings. A dimensionless parameter (N_{EX}) is added to represent these steric repulsion and decreased friction forces that arise as a result of the adsorption of these molecules.	Phenrat, T., Song, J., Cisneros, C., Schoenfelder, D., Tilton, R., and Lowry, G. 2010. Estimating attachment of nano- and submicrometer-particles coated with organic macromolecules in porous media: development of an empirical model. Environmental Science and Technology, 44(12), 4531-4538.
530	Understanding biophysicochemical interactions at the nano-bio interface	Nel, A., Mädler, L., Velegol, D., Xia, T., Hoek, E., Somasundaran, P., Klaessign, F., Castranova, V., and Thompson, M.	2009	Nature Materials, 8(7), 543-557	Published Journal	Nel et al. (2009) review the current knowledge about the reactivity and interactions of nanomaterials at the biological interface. Different processes such as particle dissolution, intracellular uptake, and the formation of protein coronas on the surface of a nanomaterial are all discussed. The interactions with proteins, membranes, and organelles as well as various colloidal and biophysicochemical interactions will determine the extent of interaction between nanoparticles and biological systems. By understanding these interactions, one can develop predictive relationships that link nanoparticle properties such as size, shape, and surface coatings to potential biological interactions.	Nel, A., Mädler, L., Velegol, D., Xia, T., Hoek, E., Somasundaran, P., Klaessign, F., Castranova, V., and Thompson, M. 2009. Understanding biophysicochemical interactions at the nano-bio interface. Nature Materials, 8(7), 543-557.

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531	Effects of humic substances on precipitation and aggregation of zinc sulfide nanoparticles	Deonarine, A., Lau, B., Aiken, G., Ryan, J., and Hsu-Kim, H.	2011	Environmental Science and Technology, 45(8), 3217-3223	Published journal	Deonarine et al. (2011) investigated how the composition of natural organic matter (NOM) affected the aggregation of nanoparticulate zinc sulfides. Characteristics such as molecular weight, type of carbon, and ligand density were all studied to determine how well they correlated to the growth and aggregation of Zn-S-NOM nanoparticles, as monitored by dynamic light scattering. It was found that the composition of natural organic matter may contribute significantly to the stabilization of zinc sulfide nanoparticles in the environment.	Deonarine, A., Lau, B., Aiken, G., Ryan, J., and Hsu-Kim, H. 2011. Effects of humic substances on precipitation and aggregation of zinc sulfide nanoparticles. Environmental Science and Technology, 45(8), 3217-3223.
532	Thiolation of maghemite nanoparticles by dimercaptosuccinic acid	Fauconnier, N., Pons, J., Roger, J., and Bee, A.	1997	Journal of Colloid and Interface Science, 194(2), 427-433	Published journal	Fauconnier et al. (1997) investigated the adsorption of disulfide species onto maghemite nanoparticles in an effort to stabilize these particles for biological applications. It was found that the charge of the particles is modified in the presence of a chelating agent, such that the particles are stabilized between pHs of 3-11, allowing their use for biological application.	Fauconnier, N., Pons, J., Roger, J., and Bee, A. 1997. Thiolation of maghemite nanoparticles by dimercaptosuccinic acid. Journal of Colloid and Interface Science, 194(2), 427-433.
533	Secondary Organic Aerosol Coating of Synthetic Metal-Oxide Nanoparticles	Lee, J. and Donahue, N.	2011	Environmental Science and Technology, 45(11), 4689-4695	Published journal	Lee and Donahue (2011) studied the coating that formed on TiO ₂ and CeO ₂ metal oxide nanoparticles in smog-chamber experiments in the presence of α -pinene and ozone. They also compared the formation of this coating on bare metal oxide nanoparticles and those coated with poly(acrylic acid), and it was found that the organic vapors coat bare metal oxides more readily than those with the PAA coating.	Lee, J. and Donahue, N. 2011. Secondary Organic Aerosol Coating of Synthetic Metal-Oxide Nanoparticles. Environmental Science and Technology, 45(11), 4689-4695.
534	Understanding the nanoparticle-protein corona using methods to quantify exchange rates and affinities of proteins for nanoparticles	Cedervall, T., Lynch, I., Lindman, S., Berggård, T., Thulin, E., Nilsson, H., Dawson, K., and Linse, S.	2007	Proceedings of the National Academy of Sciences, 104(7), 2050-2055	Published journal	Cedervall et al. (2007) studied the nanoparticle-protein interactions that form the protein corona. Rates, affinities, and stoichiometries of protein association and dissociation from the particles were studied using isothermal titration calorimetry. Rates of protein association and dissociation were studied using thiol-linked gold nanoparticles, exploiting their surface plasmon resonance properties. The binding properties were found to depend on both protein identity and particle surface characteristics and size.	Cedervall, T., Lynch, I., Lindman, S., Berggård, T., Thulin, E., Nilsson, H., Dawson, K., and Linse, S. 2007. Understanding the nanoparticle-protein corona using methods to quantify exchange rates and affinities of proteins for nanoparticles. Proceedings of the National Academy of Sciences, 104(7), 2050-2055.
535	Nanoparticle size and surface properties determine the protein corona with possible implications for biological impacts	Lundqvist, M., Sigler, J., Elia, G., Lynch, I., Cedervall, T., and Dawson, K.	2008	Proceedings of the National Academy of Sciences, 105(38), 14265-14270	Published journal	Lundqvist et al. (2008) determined the composition of the "hard" protein corona surrounding polystyrene nanoparticles of different size and charge, following immersion of the particles in human plasma. (The hard corona is the portion of proteins that has a strong affinity for the nanoparticle, as opposed to the "soft" portion, which exhibits frequent exchange of proteins with the medium). The authors conducted a systematic investigation of neutral, negatively charged (carboxyl-associated), and positively charged (amine-associated) polystyrene particles 50 and 100 nm in diameter. Among neutral particles, size did not affect the corona composition. However, for charged particles, the particle size did appear to have an effect on the composition. The large particles showed more variation in protein composition than did the small particles. Results of additional tests indicate that surface charge, rather than overall particle charge, may be a driving factor behind protein corona composition.	Lundqvist, M., Sigler, J., Elia, G., Lynch, I., Cedervall, T., and Dawson, K. 2008. Nanoparticle size and surface properties determine the protein corona with possible implications for biological impacts. Proceedings of the National Academy of Sciences, 105(38), 14265-14270.
536	Protein-nanoparticle interactions	Lynch, I. and Dawson, K.	2008	Nano Today, 3(1), 40-47	Published Journal	Lynch and Dawson (2008) briefly review the state-of-the-art in protein-nanoparticle interactions, specifically the protein corona that forms on the surface of the nanoparticle in a biological medium. Various topics are discussed, such as the effects of protein conformation on binding to nanoparticles, methods for characterizing nanoparticle-protein interactions, and the role nanoparticles may play in the fibrillation of certain proteins. In addition, the utility that nanoparticles may have in probing protein-protein interactions is briefly discussed.	Lynch, I. and Dawson, K. 2008. Protein-nanoparticle interactions. Nano Today, 3(1), 40-47.

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537	Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: a critical review	Baalousha, M., Stolpe, B., and Lead, J.	2011	Journal of Chromatography A, 1218(27), 4078-4103.	Published journal	Baalousha et al. (2011) provide an extensive review of flow field flow fractionation (FIFFF) and its application in the separation and characterization of nanomaterials, both engineered and natural, in the environment. In addition to FI-FFF theory, the authors address experimental considerations such as calibration, detectors, and sample preparation. FIFFF is also compared to other sizing and fractionation techniques that have been commonly used in the analysis of nanoparticles in environmental samples.	Baalousha, M., Stolpe, B., and Lead, J. 2011. Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: a critical review. <i>Journal of Chromatography A</i> , 1218(27), 4078-4103.
538	Particle size distributions of silver nanoparticles at environmentally relevant conditions	Cumberland, S. and Lead, J.	2009	Journal of Chromatography A, 1216(52), 9099-9105.	Published journal	Cumberland and Lead (2009) study the aggregation of 15-nm silver nanoparticles using flow field-flow fraction to both fractionate and size the nanoparticles. They found that in the presence of high ionic strength, the particles aggregate and settle out of solution. The addition of humic substances stabilized the nanoparticles, as humic substances adsorbed onto the surfaces of the particles and provided a strong negative charge that prevented aggregation.	Cumberland, S. and Lead, J. 2009. Particle size distributions of silver nanoparticles at environmentally relevant conditions. <i>Journal of Chromatography A</i> , 1216(52), 9099-9105.
539	Characterization of structural and surface speciation of representative commercially available cerium oxide nanoparticles	Baalousha, M., Coustumer, P., Jones, I., and Lead, J.	2010	Environmental Chemistry, 7(4), 377-385.	Published Journal	Baalousha et al. (2010) characterized commercially available cerium oxide nanoparticles using high resolution transmission electron microscopy coupled with electron energy loss spectroscopy. It was found that nanoscale and bulk ceria have the same crystal structure and morphology; however, bulk ceria contain a higher proportion of Ce (IV), where as ceria nanoparticles are predominantly Ce (III). This difference in oxidation state may play a significant role in the toxicology of these particles.	Baalousha, M., Coustumer, P., Jones, I., and Lead, J. 2010. Characterization of structural and surface speciation of representative commercially available cerium oxide nanoparticles. <i>Environmental Chemistry</i> , 7(4), 377-385.
540	The effect of environmentally relevant conditions on PVP stabilized gold nanoparticles	Hitchman, A., Smith, G., Ju-Nami, Y., Sterling, M., and Lead, J.	2013	Chemosphere, 90(2), 410-416	Published journal	Hitchman et al. (2013) synthesized 7-nm gold nanoparticles stabilized with polyvinyl pyrrolidone (PVP). It was found that this sterically stabilized particle did not aggregate with changes to pH, ionic strength, calcium concentration, and in the presence of dissolved organic matter (fulvic acid). Even at relatively high calcium concentrations (0.1 M Ca ²⁺), these particles showed no aggregation. This suggests that sterically stabilized particles may be highly mobile, and subsequently bioavailable in the environment.	Hitchman, A., Smith, G., Ju-Nami, Y., Sterling, M., and Lead, J. 2013. The effect of environmentally relevant conditions on PVP stabilized gold nanoparticles. <i>Chemosphere</i> , 90(2), 410-416.
541	What the cell "sees" in bionanoscience	Walczyk, D., Bombelli, B., Monopoli, M., Lynch, I., and Dawson, K.	2010	Journal of the American Chemical Society, 132(16), 5761-5768	Published Journal	Walczyk et al. (2010) studied the protein corona that forms on dispersions of surface-carboxylated polystyrene nanoparticles, surface-sulfonated polystyrene nanoparticles, and silica particles by incubating them in human blood plasma. The subsequent protein corona that forms on the particles was studied using differential centrifugation sedimentation (DCS), dynamic light scattering (DLS), and TEM. The implications of the formation of a protein corona are discussed, for although a bare nanoparticle may have a stronger, non-specific affinity for cell membranes, those coated with a layer of proteins and biomolecules may have more significant interactions with biological cells.	Walczyk, D., Bombelli, B., Monopoli, M., Lynch, I., and Dawson, K. 2010. What the cell "sees" in bionanoscience. <i>Journal of the American Chemical Society</i> , 132(16), 5761-5768.
542	Analysis of gold nanoparticle mixtures: a comparison of hydrodynamic chromatography (HDC) and asymmetrical flow field-flow fractionation (AF4) coupled to ICP-MS	Gray, E., Bruton, T., Higgins, C., Halden, R., Westerhoff, P., and Ranville, J.	2012	Journal of Analytical Atomic Spectrometry, 27(9), 1532-1539	Published journal	Gray et al. (2012) compare two separation techniques for the detection and characterization of gold nanoparticles. It was found that AF4-ICP-MS held significantly greater resolution when separating mixtures of particle sizes. However, recoveries from HDC-ICP-MS were consistently higher than that of AF4, as the AF4 recoveries were much lower for the largest of the nanoparticle sizes. The limit of detection for this study was found to be approximately 5 ppb. In addition, HDC is able to separate dissolved signal from the particle signal, whereas the dissolved signal is lost in AF4-ICP-MS.	Gray, E., Bruton, T., Higgins, C., Halden, R., Westerhoff, P., and Ranville, J. 2012. Analysis of gold nanoparticle mixtures: a comparison of hydrodynamic chromatography (HDC) and asymmetrical flow field-flow fractionation (AF4) coupled to ICP-MS. <i>Journal of Analytical Atomic Spectrometry</i> , 27(9), 1532-1539.

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543	Effect of Chloride on the Dissolution Rate of Silver Nanoparticles and Toxicity to <i>E. coli</i>	Levard, C., Mitra, S., Yang, T., Jew, A., Badiereddy, A., Lowry, G., and Brown, Jr., G.	2013	Environmental Science and Technology, 47(11), 5738–5745	Published journal	Levard et al. (2013) studied the rate of silver dissolution in the presence of a chloride salt and the implications these dissolution rates hold for their toxicity to <i>E. coli</i> . The kinetics of silver nanoparticle dissolution were studied using a Float-A-Lyzer G2 dialysis device with a nominal molar mass cutoff of 8-10 kDa. It was found that the kinetics of silver nanoparticle dissolution was highly dependent on the chlorine/silver ratio, consistent with the thermodynamic speciation of silver in the presence of chloride. Toxicity to <i>E. coli</i> was also found to be dependent on the speciation of silver, suggesting that the toxicity is a result of the dissolved ions, rather than the silver nanoparticle itself.	Levard, C., Mitra, S., Yang, T., Jew, A., Badiereddy, A., Lowry, G., and Brown, Jr., G. 2013. Effect of Chloride on the Dissolution Rate of Silver Nanoparticles and Toxicity to <i>E. coli</i> . Environmental Science and Technology, 47(11), 5738–5745.
544	Environmental transformations of silver nanoparticles: impact on stability and toxicity	Levard C., Hotze, E., Lowry, G., and Brown, Jr., G.	2012	Environmental Science and Technology, 46(13), 6900-6914	Published journal	Levard et al. (2012) review the various processes that affect silver nanoparticles in the environment and how these processes affect nanoparticle toxicity. Processes such as the sulfidation of nanoparticles will result in a decrease in their toxicity due to the inherent lower solubility of silver sulfide complexes. In addition to the discussion of these various environmental processes, future needs and research outlooks are also discussed.	Levard C., Hotze, E., Lowry, G., and Brown, Jr., G. 2012. Environmental transformations of silver nanoparticles: impact on stability and toxicity. Environmental Science and Technology, 46(13), 6900-6914.
545	Transformation of four silver/silver chloride nanoparticles during anaerobic treatment of wastewater and post-processing of sewage sludge	Lombi, E., Donner, E., Taheri, S., Tavakkoli, E., Jämtning, Å., McClure, S., Naidu, R., Miller, B., Scheckel, K., and Vasilev, K.	2013	Environmental Pollution, 176, 193-197	Published journal	Lombi et al. (2013) studied the speciation of silver nanoparticles capped with different surface groups (polyvinylpyrrolidone, citrate, mercaptosuccinic acid) when exposed to a wastewater sludge. The results indicated that regardless of silver nanoparticle compositions and surface functionality, silver sulfide was formed for all particles. These results may have implications for the reactivity and behavior of silver nanoparticles in environmental samples.	Lombi, E., Donner, E., Taheri, S., Tavakkoli, E., Jämtning, Å., McClure, S., Naidu, R., Miller, B., Scheckel, K., and Vasilev, K. 2013. Transformation of four silver/silver chloride nanoparticles during anaerobic treatment of wastewater and post-processing of sewage sludge. Environmental Pollution, 176, 193-197.
546	Fate of zinc oxide nanoparticles during anaerobic digestion of wastewater and post-treatment processing of sewage sludge	Lombi, E., Donner, E., Tavakkoli, E., Turney, T., Naidu, R., Miller, B., and Scheckel, K.	2012	Environmental Science and Technology, 46(16), 9089-9096	Published journal	Lombi et al. (2012) investigated the speciation of ZnO nanoparticles during the anaerobic digestion of sewage sludge. It was found that the speciation of the zinc nanoparticles was the same as that of a dissolved zinc salt after postprocessing of sewage sludge, indicating that all zinc species regardless of composition conform to a similar end-product. These results may have implications for the fate of engineered nanomaterials in treatment processes.	Lombi, E., Donner, E., Tavakkoli, E., Turney, T., Naidu, R., Miller, B., and Scheckel, K. 2012. Fate of zinc oxide nanoparticles during anaerobic digestion of wastewater and post-treatment processing of sewage sludge. Environmental Science and Technology, 46(16), 9089-9096.
547	Sulfidation processes of PVP-coated silver nanoparticles in aqueous solution: impact on dissolution rate	Levard, C., Reinsch, B., Michel, F., Oumahi, C., Lowry, G., and Brown, Jr., G.	2011	Environmental Science and Technology, 45(12), 5260-5266	Published journal	Levard et al. (2011) used synchrotron XRD and EXAFS to study the formation of silver sulfide when silver nanoparticles are exposed to sulfur. It was found that the silver sulfide that forms creates bridges between nanoparticles leading to chain-like structures. In addition, the sulfidation of these particles reduces the dissolution of the silver nanoparticles, which may impact toxicity, as the toxicity of silver nanoparticles is dependent on the release of silver ions.	Levard, C., Reinsch, B., Michel, F., Oumahi, C., Lowry, G., and Brown, Jr., G. 2011. Sulfidation processes of PVP-coated silver nanoparticles in aqueous solution: impact on dissolution rate. Environmental Science and Technology, 45(12), 5260-5266.
548	Colloidal silver nanoparticles: photochemical preparation and interaction with O ₂ , CCl ₄ , and some metal ions	Henglein, A.	1998	Chemistry of Materials, 10(1), 444-450	Published journal	Henglein (1998) produced 7-nm silver nanoparticles by illuminating silver perchlorate in the presence of polyethyleneimine. The particles produced possessed a narrow surface plasmon resonance. The wavelength and peak width of the SPR band changed with the addition of oxygen and other metal ions such as cadmium, nickel, silver, and mercury, with the more electropositive metals resulting in the largest change to the SPR.	Henglein, A. 1998. Colloidal silver nanoparticles: photochemical preparation and interaction with O ₂ , CCl ₄ , and some metal ions. Chemistry of Materials, 10(1), 444-450.

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549	Silver nanoparticles: partial oxidation and antibacterial activities	Lok, C.-N., Ho, C.-M., Chen, R., He, Q.-Y., Yu, W.-Y., Sun, H., Tam, P., Chiu, J.-F., and Che, C.-M.	2007	Journal of Biological Inorganic Chemistry, 12(4), 527-534	Published journal	Lok et al. (2007) studied the antibacterial properties of partially oxidized silver nanoparticles that had been formed via reduction by sodium borohydride. It was found that the partial oxidation of silver nanoparticles led to a surface of chemisorbed silver ions, which correlated with higher toxicity to the bacterium. These results indicate that the toxicity of silver nanoparticles may be dependent on levels of chemisorbed Ag ⁺ , which is dependent on the oxygen levels in the system.	Lok, C.-N., Ho, C.-M., Chen, R., He, Q.-Y., Yu, W.-Y., Sun, H., Tam, P., Chiu, J.-F., and Che, C.-M. 2007. Silver nanoparticles: partial oxidation and antibacterial activities. Journal of Biological Inorganic Chemistry, 12(4), 527-534.
550	TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties	Liu, Y., Majetich, S., Tilton, R., Sholl, D., and Lowry, G.	2005	Environmental Science and Technology, 39(5), 1338-1345	Published journal	Liu et al. (2005) studied the rate of dechlorination of TCE (trichloroethylene) for both zero-valent iron produced by reduction of ferrous iron, and a commercially available zero valent iron nanoparticle. Different conditions were tested, including iron-limiting and TCE-limiting reactions. It is suggested that the more crystalline magnetite shell (Fe ₃ O ₄) present on the commercially available particle may be responsible for the slower dechlorination rates, as less reactive iron is available. The addition of hydrogen gas also increased the rate of dechlorination, suggesting that a catalytic pathway may exist.	Liu, Y., Majetich, S., Tilton, R., Sholl, D., and Lowry, G. 2005. TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. Environmental Science and Technology, 39(5), 1338-1345.
551	Redox-active radical scavenging nanomaterials	Karakoti, A., Singh, S., Dowding, J., Seal, S., and Self, W.	2010	Chemical Society Reviews, 39(11), 4422-4432	Published journal	Karakoti et al. (2010) discuss the potential of engineered nanomaterials to scavenge radical oxygen and nitrogen species, which are the cause of many neurodegenerative diseases. In particular the chemistry and action by which these nanomaterials are able to protect biological systems from reactive oxygen species damage is discussed. Of the several ENPs in production, cerium oxide and fullerene nanomaterials are expected to be promising materials for the purpose of radical species scavenging.	Karakoti, A., Singh, S., Dowding, J., Seal, S., and Self, W. 2010. Redox-active radical scavenging nanomaterials. Chemical Society Reviews, 39(11), 4422-4432.
552	Electrokinetic characteristics of some metal sulfide-water interfaces	Liu, J. and Huang, C.	1992	Langmuir, 8(7), 1851-1856	Published journal	Liu and Huang (1992) studied the electrokinetic potential for several metal sulfides and determined the isoelectric point for each material. They also investigated the role that crystal structure, crystal field stabilization energies, and the ratio of cationic charge to ionic radius play in the electrokinetic behavior of these materials. For some metal sulfides (CuS, ZnS) the concentration of their corresponding cations (Cu ²⁺ , Zn ²⁺) can play a large role in determining their electrokinetic potential.	Liu, J. and Huang, C. 1992. Electrokinetic characteristics of some metal sulfide-water interfaces. Langmuir, 8(7), 1851-1856.
553	The surface acidity of hydrous CdS (s)	Park, S. and Huang, C.	1987	Journal of Colloid and Interface Science, 117(2), 431-441	Published journal	Park and Huang (1987) studied the surface acidity and electrokinetic potential of cadmium sulfide using titration methods. They determined that two surface sites existed, Bronsted sites (where OH ⁻ and H ⁺ are potential determining ions) and Lewis sites (where Cd ²⁺ and S ²⁻ are potential determining ions). It was determined that pH plays a larger role in the ratio of Lewis and Bronsted sites than the concentration of cadmium ions in solution.	Park, S. and Huang, C. 1987. The surface acidity of hydrous CdS (s). Journal of Colloid and Interface Science, 117(2), 431-441.
554	Probing the cytotoxicity of semiconductor quantum dots	Derfus, A., Chan, W., and Bhatia, S.	2004	Nano Letters, 4(1), 11-18	Published journal	Derfus et al. (2004) used primary hepatocytes isolated from rats to investigate the cytotoxicity of cadmium selenide semiconductor quantum dots. The primary pathway for quantum dot toxicity was found to be the release of cadmium ions resulting from photo- and chemical oxidation of the quantum dot. The capping of these quantum dots with BSA (bovine serum albumin) or zinc sulfide was found to greatly reduce their toxicity, most likely by protecting the cadmium selenide lattice from deterioration.	Derfus, A., Chan, W., and Bhatia, S. 2004. Probing the cytotoxicity of semiconductor quantum dots. Nano Letters, 4(1), 11-18.
555	Photochemical transformation of aqueous C ₆₀ clusters in sunlight	Hou, W. and Jafvert, C.	2009	Environmental Science and Technology, 43(2), 362-367	Published journal	Hou and Jafvert (2009) investigated the photochemical transformation of C ₆₀ clusters under both sunlight and lamp light (300-400 nm). It was found that the C ₆₀ clusters degraded over time to form soluble byproducts, as quantified by TOC measurements. The presence of humic substances and varying pH resulted in little change in the decay of these clusters. It was also found that the smaller clusters (~150 nm) decayed at a faster rate than the larger clusters (500 nm). Lastly, the decay in deoxygenated water was much slower, indicating that the presence of oxygen is a necessary component in the photochemical oxidation of these materials.	Hou, W. and Jafvert, C. 2009. Photochemical transformation of aqueous C ₆₀ clusters in sunlight. Environmental Science and Technology, 43(2), 362-367.
556	Toxicity reduction of polymer-stabilized silver nanoparticles by sunlight	Cheng, Y., Yin, L., Lin, S., Wiesner, M., Bernhardt, E., and Liu, J.	2011	Journal of Physical Chemistry C, 115(11), 4425-4432	Published journal	Cheng et al. (2011) investigated the toxicity of 6- and 25-nm silver nanoparticles coated with both PVP and gum arabic to <i>Lolium multiflora</i> . It was found that exposure to UV irradiation resulted in irreversible aggregation of the nanoparticles, reducing their toxicity. It was concluded that sunlight would be the primary driving force by inducing a strong oscillating dipole-dipole interaction, resulting in particle-particle aggregation.	Cheng, Y., Yin, L., Lin, S., Wiesner, M., Bernhardt, E., and Liu, J. 2011. Toxicity reduction of polymer-stabilized silver nanoparticles by sunlight. Journal of Physical Chemistry C, 115(11), 4425-4432.

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557	Chemical transformations during aging of zerovalent iron nanoparticles in the presence of common groundwater dissolved constituents	Reinsch, B., Forsberg, B., Penn, R., Kim, C., and Lowry, G.	2010	Environmental Science and Technology, 44(9), 3455-3461	Published journal	Reinsch et al. (2010) studied the aging of zerovalent iron nanoparticles under a variety of groundwater constituent and dissolved oxygen concentrations. Both fresh and aged NZVI particles were analyzed using x-ray absorption near edge structure (XANES) to determine the oxidation state, while extended x-ray absorption fine structure (EXAFS) was used to quantify the different proportions of minerals present. Most anions resulted in oxidation of the NZVI surface, whereas nitrate passivated the surface, preventing oxidation to the surface. Waters saturated with dissolved oxygen resulted in a rapid loss of zero-valent iron, subsequently resulting in the evolution of magnetite and maghemite.	Reinsch, B., Forsberg, B., Penn, R., Kim, C., and Lowry, G. 2010. Chemical transformations during aging of zerovalent iron nanoparticles in the presence of common groundwater dissolved constituents. Environmental Science and Technology, 44(9), 3455-3461.
558	Nanoparticle aggregation: Challenges to understanding transport and reactivity in the environment	Hotze, E., Phenrat, T., and Lowry, G.	2010	Journal of Environmental Quality, 39(6), 1909-1924	Published journal	Hotze et al. (2010) review aggregation processes as they relate to nanomaterials fate and transport in the environment. Whereas DLVO has been capable of sufficiently describing particle-particle interactions in the past, nanoparticles provide new challenges to effectively utilizing this theory as their size, shape, and strong interactions with other molecules (i.e., humic substances) can greatly alter the behavior of these particles.	Hotze, E., Phenrat, T., and Lowry, G. 2010. Nanoparticle aggregation: Challenges to understanding transport and reactivity in the environment. Journal of Environmental Quality, 39(6), 1909-1924.
559	Theoretical framework for nanoparticle reactivity as a function of aggregation state	Hotze, E., Bottero, J., and Wiesner, M.	2010	Langmuir, 26(13), 11170-11175	Published journal	Hotze et al. (2010) develop a theoretical framework with which to describe reactive oxygen species (ROS) production in fullerene aggregates. In particular, their concern is to describe the paradox of higher ROS production in fullerol suspensions ($C_{60}(OH)_{22-24}$) than in aqueous fullerene aggregates (aqC60) despite C60 molecules having a greater quantum yield and thus greater potential for photosensitization. The authors' theoretical framework qualitatively predicts higher singlet oxygen production from the fullerol aggregates than from the compact C60 aggregates. It is determined that the compact nature of C60 aggregates may result in triplet-triplet state annihilation between fullerene molecules in close proximity, leading to aggregation-suppressed ROS production. Fullerol aggregates, on the other hand have looser, less-compact structures. Smaller aggregates and aggregates of lower fractal dimensions result in higher ROS production.	Hotze, E., Bottero, J., and Wiesner, M. 2010. Theoretical framework for nanoparticle reactivity as a function of aggregation state. Langmuir, 26(13), 11170-11175.
560	Impact of aggregate size and structure on the photocatalytic properties of TiO ₂ and ZnO nanoparticles	Jassby, D., Budarz, J., and Wiesner, M.	2012	Environmental Science and Technology, 46(13), 6934-6941	Published journal	Jassby et al. (2012) studied the generation of free radicals from two photoactive nanomaterials (TiO ₂ and ZnO) as they underwent aggregation. Light scattering was used to determine the rate of aggregation of these materials with increasing concentrations of electrolyte. The generation of radical species decreased with increasing aggregate size, most likely due to the reduced surface reactivity.	Jassby, D., Budarz, J., and Wiesner, M. 2012. Impact of aggregate size and structure on the photocatalytic properties of TiO ₂ and ZnO nanoparticles. Environmental Science and Technology, 46(13), 6934-6941.
561	Characterization of ZnS Nanoparticles Aggregation using Photoluminescence	Jassby, D. and Wiesner, M.	2011	Langmuir, 27(3), 902-908	Published journal	Jassby et al. (2011) studied the photoluminescence of ZnS nanoparticles that undergo aggregation with increasing concentration of electrolyte. It is suspected that the aggregation of particles results in the passivation of the electron-hole pairs of the surface, leading to an increase in photoluminescent intensity along the band edge as a result of a drop in surface tension. These findings show that temporal changes in aggregate formation can be monitored using photoluminescent techniques.	Jassby, D. and Wiesner, M. 2011. Characterization of ZnS Nanoparticles Aggregation using Photoluminescence. Langmuir, 27(3), 902-908.
562	Dissimilatory reduction of extracellular electron acceptors in anaerobic respiration	Richter, K., Schicklberger, M., and Gescher, J.	2012	Applied and Environmental Microbiology, 78(4), 913-921	Published journal	Richter et al. (2012) review the current knowledge of extracellular respiration. Their work shows that c-type chromosomes play an important role in the formation of extended respiratory chains. These chromosomes are non-specific electron acceptors and donors that are suited for electron transfer.	Richter, K., Schicklberger, M., and Gescher, J. 2012. Dissimilatory reduction of extracellular electron acceptors in anaerobic respiration. Applied and Environmental Microbiology, 78(4), 913-921.
563	Biodegradation of single-walled carbon nanotubes through enzymatic catalysis	Allen, B., Kichambare, P., Gou, P., Vlasova, I., Kapralov, A., Konduru, N., Kagan, V., and Star, A.	2008	Nano Letters, 8(11), 3899-3903	Published journal	Allen et al. (2008) demonstrate the biodegradability of carbon nanotubes using natural horseradish peroxidase (HRP) at low concentrations of hydrogen peroxide. The degradation of these materials was monitored using several techniques, such as transmission electron microscopy, UV-vis, mass spectrometry, and dynamic light scattering. These results indicate that the degradation of carbon nanotubes is possible in environmental systems.	Allen, B., Kichambare, P., Gou, P., Vlasova, I., Kapralov, A., Konduru, N., Kagan, V., and Star, A. 2008. Biodegradation of single-walled carbon nanotubes through enzymatic catalysis. Nano Letters, 8(11), 3899-3903.

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564	Express it in numbers: efforts to quantify engineered nanoparticles in environmental matrices advance	Plata, D., Ferguson, P., and Westerhoff, P.	2012	Environmental Science and Technology, 46(22), 12243-12245	Published journal	Plata et al. (2012) briefly overview the various new techniques being used to detect and characterize carbon nano-tubes in biological and environmental samples. Near-infrared spectroscopy and single particle ICP-MS are both discussed as feasible methods to detect CNTs in environmental samples.	Plata, D., Ferguson, P., and Westerhoff, P. 2012. Express it in numbers: efforts to quantify engineered nanoparticles in environmental matrices advance. Environmental Science and Technology, 46(22), 12243-12245.
565	Characterization and quantitative analysis of single-walled carbon nanotubes in the aquatic environment using near-infrared fluorescence spectroscopy	Schierz, A., Parks, A., Washburn, K., Chandler, G., and Ferguson, P.	2012	Environmental Science and Technology, 46(22), 12262-12271	Published journal	Schierz et al. (2012) discuss the utility of near infrared spectroscopy for the selective and quantitative detection of semi-conducting carbon nanotubes in environmental matrices. Using a set of known standards, the chirality and diameters of these carbon nanotubes can be determined. Detection limits for the instrument were determined to be in the ppb range in both aqueous and sediment environments.	Schierz, A., Parks, A., Washburn, K., Chandler, G., and Ferguson, P. 2012. Characterization and quantitative analysis of single-walled carbon nanotubes in the aquatic environment using near-infrared fluorescence spectroscopy. Environmental Science and Technology, 46(22), 12262-12271.
566	Microbial bioavailability of covalently bound polymer coatings on model engineered nanomaterials	Kirschling, T., Golas, P., Unrine, J., Matyjaszewski, K., Gregory, K., Lowry, G., and Tilton, R.	2011	Environmental Science and Technology, 45(12), 5253-5259	Published journal	Kirschling et al. (2011) demonstrated that stabilizing polymers (poly(ethylene oxide)) covalently attached to the surface of engineered nanomaterials are bioavailable. The nanomaterials used in this study were synthesized in such a way that biodegradation was the only feasible breakdown mechanism. The breakdown of the polymer coating was monitored by the protein and CO ₂ production of the PEO-degrading enrichment culture. The biodegradation of the polymer coating may be dependent on how the polymer is attached to the particle, as highly cross-linked polymer may be less available for degradation.	Kirschling, T., Golas, P., Unrine, J., Matyjaszewski, K., Gregory, K., Lowry, G., and Tilton, R. 2011. Microbial bioavailability of covalently bound polymer coatings on model engineered nanomaterials. Environmental Science and Technology, 45(12), 5253-5259.
567	Silver nanoparticle characterization using single particle ICP-MS (SP-ICP-MS) and asymmetrical flow field flow fractionation ICP-MS (AF4-ICP-MS)	Mitrano, D., Barber, A., Bednar, A., Westerhoff, P., Higgins, C., and Ranville, J.	2012	Journal of Analytical Atomic Spectrometry, 27(7), 1131-1142	Published journal	Mitrano et al. (2012) use both single particle ICP-MS and AF4-ICP-MS to characterize mixtures of silver nanoparticles. Though SP-ICP-MS is more sensitive than AF4-ICP-MS (ng/L vs. ug/L), AF4 provides greater size resolution, being able to size particles down to 2 nm (as opposed to 20 nm for SP-ICP-MS). The resolution between particle sizes is also demonstrated. In addition, the formation of silver complexes from the dissolution of silver nanoparticles was demonstrated using AF4-ICP-MS. Both techniques can be useful for the detection and characterization of ENPs in environmental samples.	Mitrano, D., Barber, A., Bednar, A., Westerhoff, P., Higgins, C., and Ranville, J. 2012. Silver nanoparticle characterization using single particle ICP-MS (SP-ICP-MS) and asymmetrical flow field flow fractionation ICP-MS (AF4-ICP-MS). Journal of Analytical Atomic Spectrometry, 27(7), 1131-1142.
568	Detection of single walled carbon nanotubes by monitoring embedded metals	Reed, R., Goodwin, D., Marsh, K., Capracotta, S., Higgins, C., Fairbrother, H., and Ranville, J.	2013	Environmental Science: Processes and Impacts (2013), 15	Published journal	Reed et al. (2012) used single particle ICP-MS (SP-ICP-MS) to detect carbon nanotubes by monitoring for metals that have been intercalated in the CNT as a result of the synthesis of these materials. Possible metals to monitor for include yttrium, molybdenum, nickel, and cobalt. A clear correlation is shown between the mass loading of CNTs and the number of detection events, and the applicability of this technique to monitor the release of CNTs from a polymer composite.	Reed, R., Goodwin, D., Marsh, K., Capracotta, S., Higgins, C., Fairbrother, H., and Ranville, J. 2013. Detection of single walled carbon nanotubes by monitoring embedded metals. Environmental Science: Processes and Impacts (2013), 15.

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569	Separation and characterization of nanoparticles in complex food and environmental samples by field-flow fractionation	von der Kammer, F., Legros, S., Larson, E., Loeschner, K., and Hoffmann, T.	2011	Trends in Analytical Chemistry, 30(3), 425-436	Published journal	von der Kammer et al. (2011) review the different ways that field flow fractionation (FFF) has been applied to the detection and characterization of engineered nanomaterials in food and environmental samples. The type of information that can be obtained through FFF analysis is dependent on the type of detector that it is coupled to. The applicability of this technique is hindered by the method development necessary to create conditions that allow for optimal resolution of the particles. However, this technique shows great promise and could be extremely useful in the detection of ENMs in complex matrices.	von der Kammer, F., Legros, S., Larson, E., Loeschner, K., and Hoffmann, T. 2011. Separation and characterization of nanoparticles in complex food and environmental samples by field-flow fractionation. Trends in Analytical Chemistry, 30(3), 425-436.
570	Critical aspects of sample handling for direct nanoparticle analysis and analytical challenges using asymmetric field flow fractionation in a multi-detector approach	Ulrich, A., Losert, S., Bendixen, N., Al-Kattan, A., Hagendorfer, H., Nowack, B., Adhart, C., Ebert, J., Lattuada, M., and Hungerbühler, K.	2012	Journal of Analytical Atomic Spectrometry, 27(7), 1120-1130	Published journal	Ulrich et al. (2012) discuss the potential problems associated with the handling and analysis of engineered nanomaterials samples. Many different processes and sample preparation steps can result in the aggregation of nanomaterials, resulting in false size information. Consequently, the authors recommend a fast-screening method for particle size such as dynamic light scattering prior to further analysis, to monitor the formation of aggregates during sample handling and preparation.	Ulrich, A., Losert, S., Bendixen, N., Al-Kattan, A., Hagendorfer, H., Nowack, B., Adhart, C., Ebert, J., Lattuada, M., and Hungerbühler, K. 2012. Critical aspects of sample handling for direct nanoparticle analysis and analytical challenges using asymmetric field flow fractionation in a multi-detector approach. Journal of Analytical Atomic Spectrometry, 27(7), 1120-1130.
571	Application of hydrodynamic chromatography-ICP-MS to investigate the fate of silver nanoparticles in activated sludge	Tiede, K., Boxall, A., Wang, X., Gore, D., Tiede, D., Baxter, M., David, H., Tear, S., and Lewis, J.	2010	Journal of Analytical Atomic Spectrometry, 25(7), 1149-1154	Published journal	In an earlier paper, Tiede et al. developed a method for using hydrodynamic chromatography coupled with plasma mass spectrometry (HDC-ICP-MS) to detect and size nanoparticles. In this paper (2010) they used the method to determine whether it could detect spiked silver nanoparticles in mixed liquor sewage sludge and to determine whether the size distribution of the nanoparticles changed as a result of contact with the sludge (silver nanoparticles are used for antibacterial purposes). The authors found that more than 90 percent of added silver was removed from the supernatant and was assumed to be partitioned to sludge. HDC-ICP-MS analysis indicated that the supernatant still contained silver nanoparticles (approximately 3 nm in diameter). The silver remaining in the supernatant could have ecological implications since it is likely to be discharged to surface waters after the treatment process.	Tiede, K., Boxall, A., Wang, X., Gore, D., Tiede, D., Baxter, M., David, H., Tear, S., and Lewis, J. 2010. Application of hydrodynamic chromatography-ICP-MS to investigate the fate of silver nanoparticles in activated sludge. Journal of Analytical Atomic Spectrometry, 25(7), 1149-1154.
572	Partial validation of cross flow ultrafiltration by atomic force microscopy	Liu, R. and Lead, J.	2006	Analytical Chemistry, 78(23), 8105-8112	Published journal	Liu and Lead (2006) investigated the efficacy of cross flow ultrafiltration for separating particle sizes by identifying the filtrate particle sizes using atomic force microscopy. The results recommend high cross flow values for optimum particle separation. Though AFM is useful for validating particle sizes, it may not be useful for determining changes in particle conformation as a result of cross flow ultrafiltration.	Liu, R. and Lead, J. 2006. Partial validation of cross flow ultrafiltration by atomic force microscopy. Analytical Chemistry, 78(23), 8105-8112.
573	Measuring colloidal and macromolecular properties by FFF	Giddings, J.	1995	Analytical Chemistry, 67(19), 592A-598A	Published journal	Giddings (1995) reviews the theory and application of field flow fractionation (FFF). The different types of FFF are discussed including flow, sedimentation, thermal, and electrical FFF, as well as the theory of FFF. In addition to particle size characterization, secondary measurements such as polymer molecular weight, surface characterization, and aggregation formation are also reviewed. This review makes apparent the wide applicability of FFF to the characterization of colloidal/particulate systems.	Giddings, J. 1995. Measuring colloidal and macromolecular properties by FFF. Analytical Chemistry, 67(19), 592A-598A.
574	Size fractionation and characterization of natural colloids by flow-field flow fractionation coupled to multi-angle laser light scattering	Baalousha, M., Kammer, F.V.D., Motelica-Heino, M., Hlal, H., and Coustumer, P.	2006	Journal of Chromatography A, 1104(1), 272-281	Published journal	Baalousha et al. (2006) use field-flow fractionation (FFF) coupled to multi-angle laser light scattering (MALLS) to size and characterize naturally occurring colloids. By obtaining the hydrodynamic diameter from FFF, and the radius of gyration from MALLS, and determining the ratio of the two, one can describe the deviation of the particle from a hard-sphere colloid. The applicability of this technique was demonstrated by studying a natural colloidal system, showing that the presence of calcium carbonate has the potential to act as a cement between particles, resulting in aggregation.	Baalousha, M., Kammer, F.V.D., Motelica-Heino, M., Hlal, H., and Coustumer, P. 2006. Size fractionation and characterization of natural colloids by flow-field flow fractionation coupled to multi-angle laser light scattering. Journal of Chromatography A, 1104(1), 272-281.

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575	Detection, separation, and quantification of unlabeled silica nanoparticles in biological media using sedimentation field-flow fractionation	Tadjiki, S., Assemi, S., Deering, C., Veranth, J., and Miller, J.	2009	Journal of Nanoparticle Research, 11(4), 981-988	Published journal	Tadjiki et al. (2009) utilized sedimentation field-flow fractionation (Sed-FFF) to characterize silica nanoparticles extracted from rat and human endothelial cells. The silica nanoparticles were extracted via acid digestion and analyzed using Sed-FFF, where the fraction collected at the peak maxima of the elution was further analyzed by transmission electron microscopy (TEM). Percent recoveries were also determined for this technique. These results indicated that sedimentation FFF can be a useful technique for the sizing and characterization of extracted nanoparticles.	Tadjiki, S., Assemi, S., Deering, C., Veranth, J., and Miller, J. 2009. Detection, separation, and quantification of unlabeled silica nanoparticles in biological media using sedimentation field-flow fractionation. Journal of Nanoparticle Research, 11(4), 981-988.
576	Separation of Protein Inclusion Bodies from <i>Escherichia coli</i> lysates using Sedimentation Field-flow Fractionation	Ratanathanawongs-Williams, S.K., Raner, G., Ellis, Jr., W., and Giddings, J.C.	1997	Journal of Microcolumn Separation, 9(3), 233-239	Published journal	Ratanathanawongs-Williams et al. (1997) studied the ability of sedimentation field-flow fractionation (Sed-FFF) to characterize myohemerythrin inclusion bodies amidst a background of growth media, soluble proteins, and unlysed cells in <i>E. coli</i> cell lysates. In addition to the identification of the inclusion bodies, the presence of unlysed cells can also be determined by allowing the field to operate for a longer time.	Ratanathanawongs-Williams, S.K., Raner, G., Ellis, Jr., W., and Giddings, J.C. 1997. Separation of Protein Inclusion Bodies from <i>Escherichia coli</i> lysates using Sedimentation Field-flow Fractionation. Journal of Microcolumn Separation, 9(3), 233-239.
577	Shape separation of nanometer gold particles by size-exclusion chromatography	Wei, G.-T., Liu, F.-K., and Wang, C.	1999	Analytical Chemistry, 71(11), 2085-2091	Published journal	Wei et al. (1999) demonstrated the ability of size exclusion chromatography to separate gold nanoparticles based on size. This was achieved by using a surfactant mixture of sodium dodecyl sulfate (SDS) and polyoxyethylene dodecanol, affecting the adsorption of the particles to the packing materials. The elution of the particles was then monitored using a diode-array detector, which produced a 3-D chromatogram. The fractions collected at the peak maxima of elution were further characterized by transmission electron microscopy (TEM) to further validate their shape.	Wei, G.-T., Liu, F.-K., and Wang, C. 1999. Shape separation of nanometer gold particles by size-exclusion chromatography. Analytical Chemistry, 71(11), 2085-2091.
578	Recycling size exclusion chromatography for the analysis and separation of nanocrystalline gold	Al-Somali, A., Krueger, K., Falkner, J., and Colvin, V.	2004	Analytical Chemistry, 76(19), 5903-5910	Published journal	Al-somali et al. (2004) show that a dramatic increase in particle resolution can be achieved in the separation of gold nanoparticles by applying an alternate recycling method to size exclusion chromatography. With alternate recycling, size resolution was increased to a point at which baseline separation between particles differing only 6Å in size could be achieved. It was demonstrated that the resolution ratio of separation increases with the square root of the cycle number, demonstrating the power of this technique to separate particles.	Al-Somali, A., Krueger, K., Falkner, J., and Colvin, V. 2004. Recycling size exclusion chromatography for the analysis and separation of nanocrystalline gold. Analytical Chemistry, 76(19), 5903-5910.
579	Characterization of nanoparticulate systems by hydrodynamic chromatography	Williams, A., Varela, E., Meehan, E., and Tribe, K.	2002	Journal of Pharmaceutics, 242(1), 295-299	Published journal	Williams et al. (2002) discuss the applicability of hydrodynamic chromatography (HDC) to the separation and sizing of polymers and particles. Separation is achieved through the retention of particles in a packed column where the inter-particle channels retain smaller particles more effectively than larger particles, resulting in an elution order of large to small particles. The dynamic range of this technique allows for the sizing of particles from the molecular size up to micron-sized materials.	Williams, A., Varela, E., Meehan, E., and Tribe, K. 2002. Characterization of nanoparticulate systems by hydrodynamic chromatography. Journal of Pharmaceutics, 242(1), 295-299.
580	Hydrodynamic chromatography a new approach to particle size analysis	Small, H., Saunders, F., and Solc, J.	1976	Advances in Colloid and Interface Science, 6(4), 237-266	Published journal	Small et al. (2009) introduce hydrodynamic chromatography (HDC) as a powerful tool for sizing nanoparticle systems. In their review, the different parameters that affect retention time such as colloid size, packing material size and ionic strength are discussed. In addition, the various properties that may affect transport such as the hydrodynamic effect, ionic strength effect and van der Waals forces are also reviewed. Lastly, the development, calibration, and application of HDC to nanoparticle systems are discussed, showcasing its versatility in the characterization of colloidal systems.	Small, H., Saunders, F., and Solc, J. 1976. Hydrodynamic chromatography a new approach to particle size analysis. Advances in Colloid and Interface Science, 6(4), 237-266.
581	Measurement of nanoparticles by light-scattering techniques	Brar, S. and Verma, M.	2011	Trends in Analytical Chemistry, 30(1), 4-17	Published journal	Brar and Verma (2011) review light scattering techniques as they apply to the detection and characterization of nanomaterials in food and environmental samples. The review discusses the theory and application of dynamic light scattering (DLS) and static light scattering (SLS) and present different case studies for the analysis of nanomaterials in environmental samples, such as samples from a wastewater treatment plant, and in food products, where materials such as nano-titanium dioxide are ubiquitous. The advantages of dynamic light scattering are the rapid analysis of the materials without the need for calibration.	Brar, S. and Verma, M. 2011. Measurement of nanoparticles by light-scattering techniques. Trends in Analytical Chemistry, 30(1), 4-17.

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582	Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals	Yu, W., Qu, L., Guo, W., and Peng, X.	2003	Chemistry of Materials, 15(14), 2854-2860	Published journal	Yu et al. (2003) determined the extinction coefficients for three different semi-conducting nanomaterials (CdSe, CdTe, and CdS) establishing a relationship between the size of the nanocrystal and its extinction coefficient. The relationship between nanocrystal size and extinction coefficient was found to fall between a square and cubic dependence. Other factors, such as surface ligands, the solvents refractive index, photoluminescent quantum yield, temperature, and synthesis methods were found to have a minimal effect on the extinction coefficient.	Yu, W., Qu, L., Guo, W., and Peng, X. 2003. Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals. Chemistry of Materials, 15(14), 2854-2860.
583	Surface plasmon resonance sensors: review	Homola, J., Yee, S., and Gauglitz, G.	1999	Sensors and Actuators B: Chemical, 54(1), 3-15	Published journal	Homola et al. (1999) review surface plasmon resonance technologies for the application of sensitive detection. Surface plasmon resonance is a charge density oscillation phenomenon that occurs at the interface of two media that have dielectric constants of opposite sign, such as a metal and a dielectric. The various applications of these materials are discussed, and their utility in the sensitive detection of chemicals (i.e., NO ₂) and biological contaminants are also reviewed.	Homola, J., Yee, S., and Gauglitz, G. 1999. Surface plasmon resonance sensors: review. Sensors and Actuators B: Chemical, 54(1), 3-15.
584	Evaluating aggregation of gold nanoparticles and humic substances using fluorescence spectroscopy	Pallem, V., Stretz, H., and Wells, M.	2009	Environmental Science and Technology, 43(19), 7531-7535	Published journal	Pallem et al. (2009) study the interactions between gold nanoparticles capped with different surface ligands (β-D-glucose and citrate) and humic acid. Using UV-vis and fluorescence spectroscopy, changes in humic acid fluorescence were monitored. The mixture of glucose-capped gold nanoparticles with humic acid showed a loss in fluorescence intensity, which was interpreted as the replacement of the glucose surface groups with humic acids. In contrast, the mixture of citrate-capped gold nanoparticles with humic acids saw an enhancement in fluorescence intensity, potentially showing an overcoating of the citrate surface groups by humic acid, leading to an increase in transfer distance for fluorescence resonance energy transfer and subsequent enhancement of the fluorescence signal.	Pallem, V., Stretz, H., and Wells, M. 2009. Evaluating aggregation of gold nanoparticles and humic substances using fluorescence spectroscopy. Environmental Science and Technology, 43(19), 7531-7535.
585	Shape effects in plasmon resonance of individual colloidal silver nanoparticles	Mock, J., Barbic, M., Smith, D., Schultz, D., and Schultz, S.	2002	Journal of Chemical Physics, 116, 6755	Published journal	Mock et al. (2002) investigated the effect that shape has on the surface plasmon resonance of colloidal silver particles. It was found that changes in shape lead to different spectral responses from the different shapes. Through careful synthesis of these materials, homogenous populations of shapes and sizes can be obtained, allowing for a suite of multi-color nanomaterials that differ only in shape. These findings indicate these particles may be useful in biological applications.	Mock, J., Barbic, M., Smith, D., Schultz, D., and Schultz, S. 2002. Shape effects in plasmon resonance of individual colloidal silver nanoparticles. Journal of Chemical Physics, 116, 6755.
586	Characterization of nanomaterials by physical methods	Rao, C. and Biswas, K.	2009	Annual Review of Analytical Chemistry, 2, 435-462	Published journal	Rao and Biswa (2009) review several physical methods for the characterization of nanomaterials such as electron microscopy, scanning probe microscopy / atomic force microscopy, x-ray and neutron diffraction, and various x-ray scattering techniques such as x-ray photoelectron spectroscopy and energy dispersive x-ray analysis. Other techniques such as raman spectroscopy or magnetic characterization techniques such as vibrating sample magnetometer (VSM) and superconducting quantum interference devices are also discussed. Case studies illuminating the application of these techniques to the characterization of nanomaterials are also presented, show-casing their ability to analyze a wide array of materials ranging from gold and ReO ₃ nanocrystals, to nickel and cobalt nanowires, carbon nanotubes, and two-dimensional graphene.	Rao, C. and Biswas, K. 2009. Characterization of nanomaterials by physical methods. Annual Review of Analytical Chemistry, 2, 435-462.
587	Characterization of carbon nanotubes by TEM and infrared spectroscopy	Branca, C., Frusteri, F., Magazú, V., and Mangione, A.	2004	Journal of Physical Chemistry B, 108(11), 3469-3473	Published journal	Branca et al. (2004) characterize industrially produced single-walled carbon nanotubes and catalytically synthesized multi-walled carbon nanotubes using transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The location of FTIR peaks can be sensitive to the diameter of the CNT, allowing for accurate characterization of these materials. The FTIR results produced are in good agreement with the TEM characterization that was also performed.	Branca, C., Frusteri, F., Magazú, V., and Mangione, A. 2004. Characterization of carbon nanotubes by TEM and infrared spectroscopy. Journal of Physical Chemistry B, 108(11), 3469-3473.
588	Solid C ₆₀ : a new form of carbon	Krätschmer, W., Lamb, L., Fostiropoulos, K., and Huffman, D.	1990	Nature, 347(6291), 354-358	Published journal	Krätschmer et al. (1990) describe the synthesis and characterization of C ₆₀ molecules formed from evaporating graphitic electrodes in an atmosphere of helium and subsequently subjecting the resulting soot to several extraction procedures intended to purify the material. The material was then characterized using infrared spectroscopy and x-ray diffraction. Mass spectrometry confirmed the presence of C ₆₀ molecules with only a few percent C ₇₀ molecules present.	Krätschmer, W., Lamb, L., Fostiropoulos, K., and Huffman, D. 1990. Solid C ₆₀ : a new form of carbon. Nature, 347(6291), 354-358.
589	Analysis of C ₆₀ and C ₇₀ fullerenes using high-performance liquid chromatography–Fourier transform infrared spectroscopy	Treubig, Jr., J. and Brown, P.	2002	Journal of Chromatography A, 960(1), 135-142	Published journal	Treubig Jr. and Brown (2002) coupled a Fourier transform infrared spectroscopy (FTIR) to high performance liquid chromatography (HPLC) for the characterization of C ₆₀ and C ₇₀ fullerenes. No changes were needed to modify the instrumental set-up from the typical HPLC-UV instrumental set-up, using an octadecylsilane (ODS) column with a 1:1 acetonitrile-toluene mobile phase. Online FTIR spectra were compared to literature results from offline IR spectra for these materials, showing good agreement. The results indicate HPLC-FTIR as an effective means of separation and characterization of these materials.	Treubig, Jr., J. and Brown, P. 2002. Analysis of C ₆₀ and C ₇₀ fullerenes using high-performance liquid chromatography–Fourier transform infrared spectroscopy. Journal of Chromatography A, 960(1), 135-142.

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590	Comparative analysis of two aqueous-colloidal solutions of C ₆₀ fullerene with help of FTIR reflectance and UV-Vis spectroscopy	Andrievsky, G., Klochkov, V., Boryuh, A., and Dovbeshko, G.	2002	Chemical Physics Letters, 364(1), 8-17	Published journal	Andrievsky et al. (2002) characterized two fullerene-water colloidal systems using several analytical techniques, specifically surface-enhanced infrared absorption (SEIRA) in FTIR reflectance mode. This technique revealed vibrational bands in the 400-900cm ⁻¹ range, which are forbidden in infrared spectra. The results showed that the molecular-colloidal system of C60 shows isolated C60 molecules in a hydrated state, with clusters of these C60 molecules.	Andrievsky, G., Klochkov, V., Boryuh, A., and Dovbeshko, G. 2002. Comparative analysis of two aqueous-colloidal solutions of C60 fullerene with help of FTIR reflectance and UV-Vis spectroscopy. Chemical Physics Letters, 364(1), 8-17.
591	Comprehensive study of surface chemistry of MCM-41 using ²⁹ Si CP/MAS NMR, FTIR, Pyridine-TPD, and TGA	Zhao, X., Lu, G., Whittaker, A., Millar, G., and Zhu, H.	1997	Journal of Physical Chemistry B, 101(33), 6525-6531	Published journal	Zhao et al. (1997) used several techniques to characterize a sample of a mesoporous MCM-41 material. Spectroscopic techniques revealed the presence of three silanol groups (single, hydrogen-bonded, and geminal groups). The number of silanol groups per area can be determined using silicon-29 magic angle spinning nuclear magnetic resonance. All silanol groups were shown to be active sites for pyridine adsorption, but possessed different desorption energy values. It was also determined that the hydrogen-bound silanol groups can be removed or transformed to geminal silanol groups through heat treatment.	Zhao, X., Lu, G., Whittaker, A., Millar, G., and Zhu, H. 1997. Comprehensive study of surface chemistry of MCM-41 using ²⁹ Si CP/MAS NMR, FTIR, Pyridine-TPD, and TGA. Journal of Physical Chemistry B, 101(33), 6525-6531.
592	Surface chemistry of gold nanoparticles produced by laser ablation in aqueous media	Sylvestre, J.-P., Poulin, S., Kabashin, A., Sacher, E., Meunier, M., and Luong, J.	2004	Journal of Physical Chemistry B, 108(43), 16864-16869	Published journal	Sylvestre et al. (2004) synthesized gold nanoparticles through the ablation of a gold rod with a Ti/sapphire femtosecond laser. The particles produced were monodispersed and highly reactive due to partial oxidation of the particle surface by oxygen present in the solution. As a result, anions greatly affected the net surface charge of the particles produced, allowing for strong electrostatic repulsion between particles, and subsequently small particle growth. These results indicate that the size of the particles can be controlled through the use of different salts such as potassium chloride, sodium chloride, and sodium hydroxide.	Sylvestre, J.-P., Poulin, S., Kabashin, A., Sacher, E., Meunier, M., and Luong, J. 2004. Surface chemistry of gold nanoparticles produced by laser ablation in aqueous media. Journal of Physical Chemistry B, 108(43), 16864-16869.
593	Characterization by ²⁷ Al NMR, X-ray Absorption Spectroscopy, and Density Functional Theory Techniques of the Species Responsible for Benzene Hydrogenation in Y Zeolite-Supported Carburized Molybdenum Catalysts	Rocha, A.S., da Silva, V., Eon, J., Menezes, S., Faro, Jr., A., and Rocha, A.B.	2006	Journal of Physical Chemistry B, 110(32), 15803-15811	Published journal	Rocha et al. (2006) investigated the capability and mechanism of benzene hydrogenation of three different carburized molybdenum catalysts that had been prepared from three different precursors (adsorption of molybdenum hexacarbonyl (5% and 10% Mo respectively) or impregnation of the aluminum substrate by aqueous ammonium heptamolybdate (5% Mo). Though each sample contained the carburized molybdenum catalyst, the activity of each catalyst toward benzene hydrogenation differed. Those catalysts with the most initial activity showed the least stability and vice versa. The structure and activity of these catalysts were studied using various spectroscopic techniques and were also described via density functional theory.	Rocha, A.S., da Silva, V., Eon, J., Menezes, S., Faro, Jr., A., and Rocha, A.B. 2006. Characterization by ²⁷ Al NMR, X-ray Absorption Spectroscopy, and Density Functional Theory Techniques of the Species Responsible for Benzene Hydrogenation in Y Zeolite-Supported Carburized Molybdenum Catalysts. Journal of Physical Chemistry B, 110(32), 15803-15811.
594	Characterization of Nanocrystalline Nanomaterials: NMR of Zinc Phosphate as a Case Study	Röming, M., Feldmann, C., Avadhut, Y., and Schmedt auf der Günne, J.	2008	Chemistry of Materials, 20(18), 5787-5795	Published journal	Röming et al. (2008) characterized zinc phosphate nanoparticles prepared through a polyol-mediated synthesis method, producing uniform, non-crystalline 20-nm particles. Various techniques were used to size and characterize these particles including x-ray diffraction, TEM, SEM, and BET. ¹ H, ¹³ C, and ³¹ P magic angle spinning nuclear magnetic resonance were also used to characterize these nanomaterials. In particular, ³¹ P(¹ H) rotational echo double resonance experiments were used to differentiate between particles of homogenous and core-shell composition.	Röming, M., Feldmann, C., Avadhut, Y., and Schmedt auf der Günne, J. 2008. Characterization of Nanocrystalline Nanomaterials: NMR of Zinc Phosphate as a Case Study. Chemistry of Materials, 20(18), 5787-5795.
595	Characterization of phosphonic acid capped SnO ₂ nanoparticles	Holland, G., Sharma, R., Agola, J., Amin, S., Solomon, V., Singh, P., Buttry, D., and Yarger, J.	2007	Chemistry of Materials, 19(10), 2519-2526	Published journal	Holland et al. (2007) synthesized and characterized phosphonic acid capped SnO ₂ nanoparticles that were either water-soluble when capped with 2-carboxyethanephosphonic acid (CEPA), or water-insoluble when capped with phenylphosphonic acid (PPA). Analysis by ¹ H NMR revealed an absence of acidic protons indicative of a P-O-Sn linkage between the ligand and the nanoparticle surface. The results of this study suggest a bi- and/or tri-dentate bonding configuration of the surface ligand to the tin oxide nanoparticle surface.	Holland, G., Sharma, R., Agola, J., Amin, S., Solomon, V., Singh, P., Buttry, D., and Yarger, J. 2007. Characterization of phosphonic acid capped SnO ₂ nanoparticles. Chemistry of Materials, 19(10), 2519-2526.

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596	High resolution NMR of water absorbed in single-wall carbon nanotubes	Sekhaneh, W., Kotecha, M., Dettlaff-Węglińska, U., and Veeman, W.	2006	Chemical Physics Letters, 428(1), 143-147	Published journal	Sekhaneh et al. (2006) utilized ¹ H magic angle spinning nuclear magnetic resonance spectroscopy to study the absorption of water into single-walled carbon nanotubes that had been synthesized via an iron catalyst. Using MAS NMR, two chemical shift regions were determined for water protons. Using temperature-controlled experiments, it was determined that these two regions represent water absorbed inside and outside the carbon nanotubes.	Sekhaneh, W., Kotecha, M., Dettlaff-Węglińska, U., and Veeman, W. 2006. High resolution NMR of water absorbed in single-wall carbon nanotubes. Chemical Physics Letters, 428(1), 143-147.
597	Analysis of environmental particles by atomic force microscopy, scanning and transmission electron microscopy	Mavrocordatos, D., Pronk, W., and Boiler, M.	2004	Water Science & Technology, 50(12), 9-18	Published journal	Mavrocordatos, Pronk and Boiler (2004) review available microscopy techniques for the analysis of naturally occurring nanomaterials, and their applicability to studying how environmental processes can affect these particles. Atomic force microscopy (AFM) has the ability to analyze these particles <i>in situ</i> , allowing for the direct observation of different transformation processes such as dissolution and aggregation. By coupling transmission electron microscopy to electron energy loss spectrometry, one can perform sensitive chemical analysis, allowing for the determination of surface adsorption of different elements. Though some of these techniques, particularly the electron microscopy methods that require vacuum, can introduce artifacts, these microscopy methods can be used to understand nanoparticle behavior beyond size characterization.	Mavrocordatos, D., Pronk, W., and Boiler, M. 2004. Analysis of environmental particles by atomic force microscopy, scanning and transmission electron microscopy. Water Science & Technology, 50(12), 9-18.
598	New approach to inter-technique comparisons for nanoparticle size measurements; using atomic force microscopy, nanoparticle tracking analysis and dynamic light scattering	Boyd, R., Pichaimuthu, S., and Cuenat, A.	2011	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 387(1), 35-42	Published journal	Boyd et al. (2011) compared various sizing techniques including single particle techniques (transmission electron microscopy and atomic force microscopy) as well as ensemble techniques (dynamic light scattering and nanoparticle tracking analysis). There is currently no standard sizing technique for size measurements, so this paper compares the different information that can be obtained from these sizing measurements.	Boyd, R., Pichaimuthu, S., and Cuenat, A. 2011. New approach to inter-technique comparisons for nanoparticle size measurements; using atomic force microscopy, nanoparticle tracking analysis and dynamic light scattering. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 387(1), 35-42.
599	Determination of size and concentration of gold nanoparticles from UV-vis spectra	Haiss, W., Thanh, K., Averyard, J., and Fernig, D.	2007	Analytical Chemistry, 79(11), 4215-4221	Published journal	Haiss et al. (2007) synthesized and characterized gold nanoparticles (5 nm to 100 nm in size) using transmission electron microscopy and UV-vis absorbance. Good agreement was found between instrumental measurements and multipole scattering theory describing the size of the nanomaterials. These results show that size and concentration of the gold nanoparticles can be determined by UV-vis.	Haiss, W., Thanh, K., Averyard, J., and Fernig, D. 2007. Determination of size and concentration of gold nanoparticles from UV-vis spectra. Analytical Chemistry, 79(11), 4215-4221.
600	Counting of particles in aqueous solutions by laser-induced photoacoustic breakdown detection	Scherbaum, F., Knopp, R., and Kim, J.	1996	Applied Physics B, 63(3), 299-306	Published journal	Scherbaum et al. (1996) demonstrates the ability of laser-induced photoacoustic breakdown detection as a technique for the detection of nanoparticles in aqueous media. The principles and application of this technique are reviewed and applied to the detection of polystyrene latex, alumina, and thoriaol nanoparticles.	Scherbaum, F., Knopp, R., and Kim, J. 1996. Counting of particles in aqueous solutions by laser-induced photoacoustic breakdown detection. Applied Physics B, 63(3), 299-306.
601	Sensors as tools for quantitation, nontoxicity and nanomonitoring assessment of engineered nanomaterials	Sadik, O., Zhou, A., Kikandi, S., Du, N., Wang, Q., and Varner, K.	2009	Journal of Environmental Monitoring, 11(10), 1782-1800	Published journal	Sadik et al. (2009) review the application of nano-enabled sensors to the detection of nanomaterials and other contaminants in the environment. Nanosensors are typically divided into two broad classes: (i) nanotechnology-enabled sensors that are either nanomaterials themselves, or contain nanosized components, and (ii) nanoproperty quantifiable sensors, those that measure nanoscale properties and phenomena. As a great deal of literature is present on category I sensors, this review instead focuses on category II sensors, providing case studies in the detection of fullerenes and quantum dots.	Sadik, O., Zhou, A., Kikandi, S., Du, N., Wang, Q., and Varner, K. 2009. Sensors as tools for quantitation, nontoxicity and nanomonitoring assessment of engineered nanomaterials. Journal of Environmental Monitoring, 11(10), 1782-1800.
602	Determination of size and concentration of gold nanoparticles from extinction spectra	Khlebstov, N.	2008	Analytical Chemistry, 80(17), 6620-6625	Published journal	Khlebstov (2008) discusses how size and concentration of gold nanoparticles can be determined from the extinction coefficient, which generally agrees with theoretical Mie theory calculations. However, noticeable deviations are found when the nanoparticles deviate from a monodispersed spherical shape. These results indicate that there are limitations to the applicability of using the extinction spectra for the characterization of nanomaterials.	Khlebstov, N. 2008. Determination of size and concentration of gold nanoparticles from extinction spectra. Analytical Chemistry, 80(17), 6620-6625.

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603	Extinction coefficient of gold nanoparticles with different sizes and different capping ligands	Liu, X., Atwater, M., Wang, J., and Huo, Q.	2007	Colloids and Surfaces B: Biointerfaces, 58(1), 3-7	Published journal	Liu et al. (2007) studied the extinction coefficients of gold nanoparticles of varying sizes capped with one of three capping agents (citrate, oleyamide, or decanethiol). The particles were characterized using high resolution transmission electron microscopy (HRTEM) and UV-visible absorption spectroscopy. It was found that the extinction spectra of the nanoparticles is independent of the capping agent and the solvent these nanomaterials are measured in, allowing for a linear relationship between extinction coefficient and diameter of the nanoparticles.	Liu, X., Atwater, M., Wang, J., and Huo, Q. 2007. Extinction coefficient of gold nanoparticles with different sizes and different capping ligands. Colloids and Surfaces B: Biointerfaces, 58(1), 3-7.
604	Characterization of silver nanoparticles using flow-field flow fractionation interfaced to inductively coupled plasma mass spectrometry	Poda, A., Bednar, A., Kennedy, A., Hull, M., Mitrano, D., Ranville, J., and Stevens, J.	2011	Journal of Chromatography A, 1218(27), 4219-4225	Published journal	Poda et al. (2011) utilized flow-field flow fractionation coupled to ICP-MS to characterize silver nanoparticles extracted from <i>Lumbriculus variegatus</i> . The nanoparticles were also characterized using transmission electron microscopy (TEM) and the hydrodynamic diameter results from FFF were compared to measurements obtained from dynamic light scattering (DLS). Silver nanoparticles extracted from <i>L. variegatus</i> show an increase in primary particle size from 31 nm to 46 nm, indicating a change in particle size as a result of exposure. Overall, FFF-ICP-MS is a sensitive and selective method for the characterization of nanomaterials in biological samples.	Poda, A., Bednar, A., Kennedy, A., Hull, M., Mitrano, D., Ranville, J., and Stevens, J. 2011. Characterization of silver nanoparticles using flow-field flow fractionation interfaced to inductively coupled plasma mass spectrometry. Journal of Chromatography A, 1218(27), 4219-4225.
605	Overcoming challenges in analysis of polydisperse metal-containing nanoparticles by single particle inductively coupled plasma mass spectrometry	Reed, R., Higgins, C., Westerhoff, P., Tadjiki, S., and Ranville, J.	2012	Journal of Analytical Atomic Spectrometry, 27(7), 1093-1100	Published journal	Reed et al. (2012) used single particle inductively coupled plasma mass spectrometry (spICP-MS) to characterize a variety of nanomaterials such as silver nanowires, titanium dioxide, and cerium oxide nanoparticles. Zinc oxide nanoparticle analysis was also attempted, but dissolution was too rapid for accurate analysis. This technique allows for sensitive and accurate characterization of engineered nanomaterials, but can be hindered by a large concentration of particles, resulting in coincidence. Coincidence is reduced and characterization is optimized when the percentage of particle readings is approximately 2.5%. Particle sizes determined from spICP-MS were compared to Sedimentation-FFF to validate accurate size measurement.	Reed, R., Higgins, C., Westerhoff, P., Tadjiki, S., and Ranville, J. 2012. Overcoming challenges in analysis of polydisperse metal-containing nanoparticles by single particle inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry, 27(7), 1093-1100.
606	Nanomaterials for environmental studies: classification, reference material issues, and strategies for physico-chemical characterization	Stone, V., Nowack, B., Baun, A., van den Brink, N., von der Kammer, F., Dusinska, M., Handy, R., Hankin, S., Hasselöv, M., Joner, E., and Fernandes, T.	2010	Science of the Total Environment, 408(7), 1745-1754	Published journal	Stone et al. (2010) sought to address several questions regarding nanomaterials in the environment, including the determination of which nanomaterial properties are relevant to environmental studies, the development of reference standards for environmental studies, and the classification of nanomaterials with respect to their environmental impact. The workshop determined that properties such as aggregation, size, dissolution, surface charge, surface area and surface composition might be the most important properties with relevance to environmental studies, assuming chemical composition is known. Some possible reference materials are titanium dioxide nanoparticles, polystyrene beads labeled with fluorescent dyes, and silver nanoparticles, though more work is required to standardize these materials for environmental use. Though no consensus was reached on an appropriate classification system, it was generally accepted that a classification scheme based on chemistry is a likely starting point.	Stone, V., Nowack, B., Baun, A., van den Brink, N., von der Kammer, F., Dusinska, M., Handy, R., Hankin, S., Hasselöv, M., Joner, E., and Fernandes, T. 2010. Nanomaterials for environmental studies: classification, reference material issues, and strategies for physico-chemical characterization. Science of the Total Environment, 408(7), 1745-1754.
607	Characterizing manufactured nanoparticles in the environment: multimethod determination of particle sizes	Domingos, R., Baalousha, M., Ju-Nam, Y., Reid, M., Tufenkji, N., Lead, J., Leppard, G., and Wilkinson, K.	2009	Environmental Science and Technology, 43(19), 7277-7284	Published journal	Domingos et al. (2009) compared several sizing techniques for the characterization of nanomaterials. Techniques such as transmission electron microscopy, fluorescence correlation spectroscopy, nanoparticle tracking analysis, flow field-flow fractionation, atomic force microscopy, and dynamic light scattering are all reviewed and discussed. It was determined that no single technique is most effective at sizing and characterizing nanomaterials, as each has its own inherent advantages and limitations. The techniques that are most commonly used (DLS and TEM) also happen to introduce the most artifacts during analysis.	Domingos, R., Baalousha, M., Ju-Nam, Y., Reid, M., Tufenkji, N., Lead, J., Leppard, G., and Wilkinson, K. 2009. Characterizing manufactured nanoparticles in the environment: multimethod determination of particle sizes. Environmental Science and Technology, 43(19), 7277-7284.

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608	Comparison of centrifugation and filtration techniques for the size fractionation of colloidal material in soil suspensions using sedimentation field-flow fractionation	Gimbert, L., Haygarth, P., Beckett, R., and Worsfold, P.	2005	Environmental Science and Technology, 39(6), 1731-1735	Published journal	Gimbert et al. (2005) used sedimentation field-flow fractionation (SdFFF) with a UV detector to compare both centrifugation and filtration for the size fractionation of a clay soil suspension. The results show that membrane filtration underestimated the total mass of the particulate matter compared to centrifugation. This may have implication for accurately determining the colloidal and soluble fractions of naturally occurring colloids.	Gimbert, L., Haygarth, P., Beckett, R., and Worsfold, P. 2005. Comparison of centrifugation and filtration techniques for the size fractionation of colloidal material in soil suspensions using sedimentation field-flow fractionation. Environmental Science and Technology, 39(6), 1731-1735.
609	Cloud point extraction as an advantageous preconcentration approach for analysis of trace silver nanoparticles in environmental waters	Liu, J.-F., Chao, J.-B., Liu, R., Tan, Z.-Q., Yin-Y.-G., Wu, Y., and Jiang, G.-B.	2009	Analytical Chemistry, 81(15), 6496-6502	Published journal	Liu et al. (2009) demonstrate the ability of cloud point extraction with Triton X-114 to preconcentrate silver nanoparticles while still preserving their sizes and morphology. The most efficient extraction occurs on the zero point charge pH and can be enhanced through the addition of salts such as sodium nitrate and sodium thiosulfate. The concentrated silver nanoparticles were characterized by electron microscopy and UV-vis absorbance to demonstrate the preservation of size and shape. This technique allows for the concentration of nanoparticles found in environmental samples, particularly as humic acid does not affect the extraction efficiency of the nanoparticles.	Liu, J.-F., Chao, J.-B., Liu, R., Tan, Z.-Q., Yin-Y.-G., Wu, Y., and Jiang, G.-B. 2009. Cloud point extraction as an advantageous preconcentration approach for analysis of trace silver nanoparticles in environmental waters. Analytical Chemistry, 81(15), 6496-6502.
610	Physicochemical and microbial preservation of colloid characteristics of natural water samples I: Experimental conditions	Chen, Y.-W. and Buffle, J.	1996	Water Research, 30(9), 2178-2184	Published journal	Chen et al. (1996) examine the difficulties that may arise in the analysis of colloids in environmental samples. Particular attention is paid to the development of sample handling procedures that minimize sample perturbation such that accurate analysis can be performed while minimizing artifacts. The different contaminants that can arise are also described; these include artifacts introduced by filtration membranes, vessel and tubing walls, and atmospheric contaminants. Appropriate stabilizing compounds, apparatus, and experimental conditions for accurate analysis of environmental colloids are also discussed.	Chen, Y.-W. and Buffle, J. 1996. Physicochemical and microbial preservation of colloid characteristics of natural water samples I: Experimental conditions. Water Research, 30(9), 2178-2184.
611	Imaging of engineered nanoparticles and their aggregates under fully liquid conditions in environmental matrices	Tiede, K., Tear, S., David, H., and Boxall, A.	2009	Water Research, 43(13), 3335-3343	Published journal	Tiede et al. (2009) characterize nanomaterials using WetSEM technology, which allows for <i>in situ</i> imaging of the nanomaterials by scanning electron microscopy. By using a capsule that uses a membrane coating to attract the sample to the walls of the capsule, images can be obtained under fully liquid conditions. The results are apparent when using energy dispersive x-ray spectroscopy (EDS) for elemental determination, as conventional SEM is subject to several of the other interferences present in the sample, whereas WetSEM is able to accurately determine the composition of the nanomaterial.	Tiede, K., Tear, S., David, H., and Boxall, A. 2009. Imaging of engineered nanoparticles and their aggregates under fully liquid conditions in environmental matrices. Water Research, 43(13), 3335-3343.
612	Selective identification, characterization and determination of dissolved silver (I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry	Laborda, F., Jiménez-Lamana, J., Bolea, E., and Castillo, J.	2011	Journal of Analytical Atomic Spectrometry, 26(7), 1362-1371	Published journal	Laborda et al. (2011) present single particle inductively coupled plasma mass spectrometry (spICP-MS) as a selective and sensitive technique for the analysis of engineered nanoparticles. The use of ICP-MS allows for mass detection limits at environmentally relevant concentrations of 10^{-8} g/L, and the method can detect as few as 1×10^{-4} particles / L. The various means by which one may fit the data (i.e., Poisson, lognormal) are also discussed, as are suggestions on how this technique can be improved.	Laborda, F., Jiménez-Lamana, J., Bolea, E., and Castillo, J. 2011. Selective identification, characterization and determination of dissolved silver (I) and silver nanoparticles based on single particle detection by inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry, 26(7), 1362-1371.

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613	Synthesis of isotopically modified ZnO nanoparticles and their potential as nontoxicity tracers	Dybowska, A., Croteau, M.-N., Misra, S., Berhanu, D., Luoma, S., Christian, P., O'Brien, P., and Valsami-Jones, E.	2011	Environmental Pollution, 159(1), 266-273	Published journal	Dybowska et al. (2011) evaluate the use of a stable isotope zinc oxide nanoparticle tracer to further understand the uptake and behavior of nanoparticles. For this study ⁶⁷ ZnO nanoparticles were exposed to <i>L. stagnalis</i> via amended diatoms. Using this tracer, the exposure concentration was found to be in the lower concentration range (below 15 µg/g), which is a vast improvement over the naturally occurring zinc exposure concentration of 5000 µg/g. The use of these isotopically modified tracers may provide an option to study environmentally relevant exposure concentrations.	Dybowska, A., Croteau, M.-N., Misra, S., Berhanu, D., Luoma, S., Christian, P., O'Brien, P., and Valsami-Jones, E. 2011. Synthesis of isotopically modified ZnO nanoparticles and their potential as nontoxicity tracers. Environmental Pollution, 159(1), 266-273.
614	Isotopically modified nanoparticles for enhanced detection in bioaccumulation studies	Misra, S., Dybowska, A., Berhanu, D., Croteau, M., Luoma, S., Boccaccini, A., and Valsami-Jones, E.	2011	Environmental Science and Technology, 46(2), 1216-1222	Published journal	Misra et al. (2011) synthesized isotopically enriched copper oxide nanoparticles (65Cu) for use in ecotoxicological studies. The copper oxide nanomaterials were synthesized as rods (7x40 nm) and spheres (7 nm) and were characterized by transmission electron microscopy, atomic force microscopy, and zeta potentiometry. The use of a stable isotope tracer allowed for determining exposure concentration close to that of the ambient concentration in freshwater systems (0.2-30 µg/L), whereas the detection of newly accumulated 63Cu is problematic even at exposure concentrations greater than 1 mg/L.	Misra, S., Dybowska, A., Berhanu, D., Croteau, M., Luoma, S., Boccaccini, A., and Valsami-Jones, E. 2011. Isotopically modified nanoparticles for enhanced detection in bioaccumulation studies. Environmental Science and Technology, 46(2), 1216-1222.
615	Evaluation of Stable Isotope Tracing for ZnO Nanomaterials--New Constraints from High Precision Isotope Analyses and Modeling	Larner, F. and Rehkämper, M.	2012	Environmental Science and Technology, 46(7), 4149-4158	Published journal	Larner et al. (2012) evaluate the use of stable zinc isotopes for the study of nanomaterial toxicology and behavior. Initial experiments investigated the ratio of zinc isotopes in commercially available zinc oxide nanoparticles compared to the natural abundance and found no discernible difference. Consequently, inexpensive isotopically modified zinc oxide nanomaterials were used. The results indicate that an extremely low concentration of these modified nanoparticles (5 ng/g) can be identified amidst a Zn background (100 µg/g). In addition, the use of these isotopically modified materials allows for differentiation between nanoparticles and their dissolved constituents.	Larner, F. and Rehkämper, M. 2012. Evaluation of Stable Isotope Tracing for ZnO Nanomaterials--New Constraints from High Precision Isotope Analyses and Modeling. Environmental Science and Technology, 46(7), 4149-4158.
616	Parameter Identifiability in Application of Soft Particle Electrokinetic Theory to Determine Polymer and Polyelectrolyte Coating Thicknesses on Colloids	Louie, S.; Pehhart, T.; Small, M.; Tilton, R. and Lowry, G.	2012	Langmuir, 28(28), 10334-10347	Published journal	Louie et al. (2012) undergo an investigation of the parameters necessary to correctly apply soft particle electrokinetic theory in determining the thickness of a polymer/polyelectrolyte coating on a particle. Specifically, this paper compares fitted parameters (layer charge density, layer thickness, and permeability) to analytical and numerical electrokinetic models. Different particle sizes and particle coating types were investigated, showing good agreement with the analytical model for particle having thin, lower-charged coatings, opposed to a greater uncertainty in particle with thick, highly-charged coatings.	Louie, S.; Pehhart, T.; Small, M.; Tilton, R. and Lowry, G. 2012. Parameter Identifiability in Application of Soft Particle Electrokinetic Theory to Determine Polymer and Polyelectrolyte Coating Thicknesses on Colloids. Langmuir, 28(28), 10334-10347.
617	Fate of Zinc Oxide and Silver Nanoparticles in a Pilot Wastewater Treatment Plant and in Processed Biosolids	Ma, R.; Levard, C.; Judy, J.; Unrine, J.; Durenkamp, M.; Martin, B.; Jefferson, B. and Lowry, G.	2014	Environmental Science & Technology, 48(1), 104-112	Published Journal	Ma et al. (2014) utilized x-ray absorption spectroscopy to determine the chemical speciation of silver and zinc in sludge produced from a pilot wastewater treatment plant. Sources of silver and zinc included PVP-coated 50nm silver nanoparticles, 30nm ZnO nanoparticles and their respective dissolved salt counterparts. In addition to examining the effects of activated sludge, additional treatment processes such as lime and heat treatment were also investigated. It was determined that regardless of silver ion origin, all silver was converted to silver sulfide (Ag ₂ S). Zinc on the other hand was converted to three different zinc species (zinc sulfide, zinc phosphate, and zinc associated with iron oxy/hydroxides). The ratio of these three zinc species depend on the redox state and water content available in the biosolids. Regardless of the Zn and Ag input (nanoparticulate or dissolved) all ions were transformed into similar chemical forms in the waste water treatment process.	Ma, R.; Levard, C.; Judy, J.; Unrine, J.; Durenkamp, M.; Martin, B.; Jefferson, B. and Lowry, G. 2014. Fate of Zinc Oxide and Silver Nanoparticles in a Pilot Wastewater Treatment Plant and in Processed Biosolids. Environmental Science & Technology, 48(1), 104-112.

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618	CuO and ZnO Nanoparticles: Phytotoxicity, Metal Speciation, and Induction of Oxidative Stress in Sand-Grown Wheat	Dimkpa, C.; McLean, J.; Latta, D.; Manangon, E.; Britt, D.; Johnson, W.; Boyanov, M. and Anderson, A.	2012	Journal of Nanoparticle Research, 14(9), 1-15	Published journal	Dimkpa et al. (2012) studied the impact of commercial copper oxide and zinc oxide nanoparticles on wheat plants (<i>Triticum aestivum</i>) grown in sand. Analytical techniques such dynamic light scattering and atomic force microscopy were used to investigate the aggregation of these materials, as well as the transformation of ZnO particles into elongated rods in the aqueous phase of the sand. Bulk equivalents of copper and zinc added to the sand matrix were also investigated and showed significant reduction of root growth. Of the nanomaterials, only CuO impaired shoot growth, yet these growth reductions were less than that of the bulk materials. Bioaccumulation of these materials in the form of copper(II)-sulfur and zinc-phosphate complexes were detected in the shoots of plants that had been exposed to the nanomaterials. Oxidative stress was also present in nanoparticle treated plants, indicating increased production of reactive oxygen species.	Dimkpa, C.; McLean, J.; Latta, D.; Manangon, E.; Britt, D.; Johnson, W.; Boyanov, M. and Anderson, A. 2012. CuO and ZnO Nanoparticles: Phytotoxicity, Metal Speciation, and Induction of Oxidative Stress in Sand-Grown Wheat. <i>Journal of Nanoparticle Research</i> , 14(9), 1-15.
619	Synchrotron Micro-XRF and Micro-XANES Confirmation of the Uptake and Translocation of TiO ₂ Nanoparticles in Cucumber (<i>Cucumis sativus</i>) Plants	Servin, A.; Castillo-Michel, H.; Hernandez-Viezcas, J.; Dias, B.; Peralta-Videa, J. and Gardea-Torresdey, J.	2012	Environmental Science and Technology, 46(14), 7637-7643	Published journal	Servin et al. (2012) evaluated the uptake and impact of titanium dioxide nanoparticles on hydroponically grown cucumber (<i>Cucumis sativus</i>) plants. Concentrations of TiO ₂ nanoparticles ranging from 0 to 4000ppm were applied to seven day old seedlings. The plants were then harvested and the sizes of the roots and shoots were measured, and micro-XRF and micro-XAS were used to track the presence and speciation of TiO ₂ within the plant. All TiO ₂ concentration significantly increased root length, and micro-XRF indicated the transport of Ti to the leaf trichomes. Micro-XANES indicated that the titanium present in the plant tissues was in the form of TiO ₂ , as opposed to another biotransformed chemical species.	Servin, A.; Castillo-Michel, H.; Hernandez-Viezcas, J.; Dias, B.; Peralta-Videa, J. and Gardea-Torresdey, J. 2012. Synchrotron Micro-XRF and Micro-XANES Confirmation of the Uptake and Translocation of TiO ₂ Nanoparticles in Cucumber (<i>Cucumis sativus</i>) Plants. <i>Environmental Science and Technology</i> , 46(14), 7637-7643.
620	International Perspective on Government Nanotechnology Funding in 2005	Roco, M.	2005	Journal of Nanoparticle Research, 7(6), 707-712	Published journal	Roco (2005) details the extent of government nanotechnology funding and its implications for the continued research and development of nanotechnology. The findings indicate the significant growth (approximately nine-fold) of investment in nanotechnology research and development in the 8 years prior to 2005. This analysis was performed using the National Nanotechnology Initiative definition of nanotechnology, using information ascertained from managers of nanotechnology research and development in the various countries.	Roco, M. 2005. International Perspective on Government Nanotechnology Funding in 2005. <i>Journal of Nanoparticle Research</i> , 7(6), 707-712.
621	Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-size-related Properties, and Applications Toward Biology, Catalysis, and Nanotechnology	Daniel, M.-C. and Astruc, D.	2004	Chemical Reviews, 104(1), 293-346	Published journal	Daniel and Astruc (2004) extensively reviewed various information pertaining to gold nanoparticles. Topics covered included synthesis, properties, and applications to catalysis, biomedical, and nano-electronics. The various structures and properties of gold nanomaterials inform the variety of applications they are used for, and ensure their continued use in research and industry.	Daniel, M.-C. and Astruc, D. 2004. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-size-related Properties, and Applications Toward Biology, Catalysis, and Nanotechnology. <i>Chemical Reviews</i> , 104(1), 293-346.
622	A Review of the Antibacterial Effects of Silver Nanomaterials and Potential Implications for Human Health and the Environment	Marambio-Jones, C. and Hoek, E.	2010	Journal of Nanoparticle Research, 12(5), 1531-1551	Published journal	Marambio-Jones and Hoek (2010) review the antibacterial effects of silver nanomaterials, as well as their potential toxicity to higher organisms and humans. Several nanomaterials are discussed including nanoparticles, polymer composites, and activated carbon materials. Though some bactericidal effects are nanoparticle-specific, the main toxic action for most materials is a result of silver ion release which results in potential increased membrane permeability, disruption of DNA replication, and other biological effects. The various factors governing particle characteristics (size, shape, capping agents) are also discussed within the context of their stability and bioavailability.	Marambio-Jones, C. and Hoek, E. 2010. A Review of the Antibacterial Effects of Silver Nanomaterials and Potential Implications for Human Health and the Environment. <i>Journal of Nanoparticle Research</i> , 12(5), 1531-1551.
623	Zero-valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects	Li, X.-Q.; Ellitt, D. and Zhang, W.-X.	2006	Critical Reviews in Solid State and Materials Sciences, 31(4), 111-122	Published journal	Li et al. (2006) reviewed various aspects of zero-valent iron nanoparticles, specifically their applicability to the remediation of environmental pollutants. Topics covered include the synthesis and characterization of these materials in addition to their application toward organic contaminants (i.e. TCE) and inorganic contaminants (i.e. uranium, arsenic). The fate and transport of these materials are also discussed within the context of their environmental impact.	Li, X.-Q.; Ellitt, D. and Zhang, W.-X. 2006. Zero-valent Iron Nanoparticles for Abatement of Environmental Pollutants: Materials and Engineering Aspects. <i>Critical Reviews in Solid State and Materials Sciences</i> , 31(4), 111-122.

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624	Slurry Compositions and Method for the Chemical-Mechanical Polishing of Copper and Copper Alloys	Mahulikar, D.; Mravic, B.; Pasqualoni, A.	2000	US Patent 5840629	Patent	Mahulikar et al. (2000) detail a method for polishing copper layer with high removal rates and reducing the amount of defects and erosion generated. This procedure uses two slurries, one comprised of a bulk copper removal slurry that removes the majority of copper. The second slurry is a 1:1:1 mixture of copper/tantalum silicon dioxide that reduces the amount of dishing and erosion that occurs in the copper arrays. The abrasive phase of the slurries is comprised of particles ranging from 10-800nm, where the liquid phase contains carboxylic acid and an oxidizer capable of removing copper at a rate greater than 3000Å/min.	Mahulikar, D.; Mravic, B.; Pasqualoni, A. 2000. Slurry Compositions and Method for the Chemical-Mechanical Polishing of Copper and Copper Alloys. US Patent 5840629.
625	Titanium Dioxide and Zinc Oxide Nanoparticles in Sunscreens: Focus on their Safety and Effectiveness	Smijs, T. and Pavel, S.	2011	Nanotechnology, Science and Application, 4, 95	Published journal	Smijs and Pavel (2011) review the efficacy of TiO ₂ and ZnO nanoparticles in protection against UVA and UVB radiation, in addition to the safety considerations these materials present. The extent of protection against UVA and UVB radiation can be modified by altering the ratio of micro- and nano-sized ZnO and TiO ₂ nanoparticles in the sunscreen formulation. The most pressing safety issue is the generation of free-radicals due to their photocatalytic activity. In addition, alteration to these particles can be generated from particle-particle, particle-skin, and skin-particle-light interactions that may result in additional toxic effects.	Smijs, T. and Pavel, S. 2011. Titanium Dioxide and Zinc Oxide Nanoparticles in Sunscreens: Focus on their Safety and Effectiveness. Nanotechnology, Science and Application, 4, 95.
626	Experimental Investigations on the Effects of Cerium Oxide Nanoparticle Fuel Additives on Biodiesel	Sajith, V.; Sobhan, C. and Peterson, G.	2010	Advances in Mechanical Engineering, 2010, 1-6	Published journal	Sajith et al. (2010) investigate the influence on the addition of cerium oxide nanoparticles on the properties and performance of biodiesel. The viscosity and flash point of the biodiesel was found to increase with the inclusion of the cerium oxide nanoparticles in relation to the concentration of nanoparticles added. The addition of these material also showed an increase in the efficiency of the engine tested. Lastly, the emission levels of hydrocarbon and NO _x are reduced upon addition of the cerium oxide nanoparticles.	Sajith, V.; Sobhan, C. and Peterson, G. 2010. Experimental Investigations on the Effects of Cerium Oxide Nanoparticle Fuel Additives on Biodiesel. Advances in Mechanical Engineering, 2010, 1-6.
627	Luminescent Quantum Dots for Multiplexed Biological Detection and Imaging	Chan, W.; Maxwell, D.; Gao, X.; Bailey, R. Han, M. and Nie, S.	2002	Current Opinion in Biotechnology, 13(1), 40-46	Published journal	Chan et al. (2002) review advances in the synthesis of semiconductor quantum dots modified with biorecognition molecules which can be used as fluorescent labels. These labels are water-soluble and biocompatible which is advantageous over previously used organic dyes and lanthanide probes. The narrow emission wavelength of these materials, achieved by altering the size of the core nanocrystal, make it particularly attractive for the utilization of multiple quantum dot types fluorescing upon excitation from a single light source. These properties make these materials particularly attractive for molecular biotechnology and biomedical applications.	Chan, W.; Maxwell, D.; Gao, X.; Bailey, R. Han, M. and Nie, S. 2002. Luminescent Quantum Dots for Multiplexed Biological Detection and Imaging. Current Opinion in Biotechnology, 13(1), 40-46.
628	Carbon Nanotubes-The Route Toward Applications	Baughman, R.; Zakhidov, A. and de Heer, W.	2002	Science, 297(5582), 787-792	Published journal	Baughman et al. (2002) review the synthesis, properties, and applications of carbon nanotubes. Their high electrical conductivity and tensile strength make them highly attractive for use in a variety of applications such as hydrogen storage, energy conversion, and semiconductors. Though current cost and processing limitations hinder the wide-scale application of these materials, their novel properties ensure their continued development and application in consumer and industrial products.	Baughman, R.; Zakhidov, A. and de Heer, W. 2002. Carbon Nanotubes-The Route Toward Applications. Science, 297(5582), 787-792.
629	Nanomaterials for Hydrogen Storage Applications: A Review	Niemann, M.; Srinivasan, S.; Phani, A.; Kumar, A.; Goswami, D. and Stefanakos, E.	2008	Journal of Nanomaterials, 2008, 1-9	Published journal	Niemann et al. (2008) review the application of nanomaterials for the purposes of hydrogen storage. The inherent high surface area to volume ratio of nanomaterials make them ideal candidates for hydrogen and energy storage. Examples of such materials include carbon nanotubes, magnesium hydrides, and metal -organic frameworks have all shown to be strong candidates for hydrogen storage. The various properties pertaining to hydrogen storage and the efficacy of these materials is discussed within.	Niemann, M.; Srinivasan, S.; Phani, A.; Kumar, A.; Goswami, D. and Stefanakos, E. 2008. Nanomaterials for Hydrogen Storage Applications: A Review. Journal of Nanomaterials, 2008, 1-9.
630	Dendrimers as Therapeutic Agents: A Systematic Review	Gajbhiye, V.; Palanirajan, V.; Tekade, R. and Jain, N.	2009	Journal of Pharmacy and Pharmacology, 61, 989-1003	Published journal	Gajbhiye et al. (2009) review the application of dendritic macromolecules as therapeutic agents. Their highly branched nature and low polydispersity make them ideal nanoscale container and excellent drug delivery agents. Their properties prevent the formation of amyloid fibrils and viral adhesion which would reduce their efficacy as drug carriers. They have currently been demonstrated to be effective against prion diseases, Alzheimer's, HIV and cancer.	Gajbhiye, V.; Palanirajan, V.; Tekade, R. and Jain, N. 2009. Dendrimers as Therapeutic Agents: A Systematic Review. Journal of Pharmacy and Pharmacology, 61, 989-1003.
631	Turkevich Method for Gold Nanoparticle Synthesis Revisited	Kimling, J.; Maier, M.; Okenve, B.; Kotaidis, V.; Ballot, H. and Plech, A.	2006	Journal of Physical Chemistry B, 110(32), 15700-15707	Published journal	Kimling et al. (2006) revisit the Turkevich method (citrate reduction) for the synthesis of gold nanoparticles. Specifically, the gold-to-reductant ratio is investigated, showing a clear relationship between the ratio of these reagents and the final gold nanoparticle size, irrespective of absolute concentrations. Control over various parameters of this synthesis process can result in well-defined particle shapes and sizes. Application of this procedure is also possible for the formation of platinum and palladium nanomaterials.	Kimling, J.; Maier, M.; Okenve, B.; Kotaidis, V.; Ballot, H. and Plech, A. 2006. Turkevich Method for Gold Nanoparticle Synthesis Revisited. Journal of Physical Chemistry B, 110(32), 15700-15707.

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632	Some Recent Advances in Nanostructure Preparation from Gold and Silver Nanoparticles: A Short Topical Review	Burst, M. and Kiely, C.	2002	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 202(2), 175-186	Published journal	Burst and Kiely (2002) briefly review several aspects of gold and silver nanostructure self-assembly. An overview of the history and preparation of self-organized gold and silver superlattices are discussed. Other nano-architectures such as those created from various templates and DNA base pair recognition are also discussed. The surface chemistry, optical properties, and potential for molecular recognition are also reviewed in addition to current and future applications of these materials.	Burst, M. and Kiely, C. 2002. Some Recent Advances in Nanostructure Preparation from Gold and Silver Nanoparticles: A Short Topical Review. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 202(2), 175-186.
633	Sol-Gel Template Synthesis of Semiconductor Nanostructures	Lakshmi, B.; Dorhout, P. and Martin, C.	1997	Chemistry of Materials, 9(3), 857-862	Published journal	Lakshmi et al. (1997) describes the use of sol-gel chemistry to prepare TiO ₂ , WO ₃ , and ZnO semiconductor nanomaterials. The TiO ₂ nanofibrils that formed were found to be single-crystalline anatase with diameters of 22nm. Bundles of these fibrils were also found to be crystalline suggesting highly organized arrangement of these fibrils. The application of these nanomaterials was demonstrated through the photocatalytic decomposition of salicylic acid using a 200nm TiO ₂ fibril.	Lakshmi, B.; Dorhout, P. and Martin, C. 1997. Sol-Gel Template Synthesis of Semiconductor Nanostructures. Chemistry of Materials, 9(3), 857-862.
634	A Review on Nano-TiO ₂ Sol-Gel Type Syntheses and Its Applications	Macwan, D.; Dave, P. and Chaturvedi, S.	2011	Journal of Materials Science, 46(11), 3669-3686	Published journal	Macwan et al. (2011) discuss the various sol-gel technique employed for the purposes of nano-TiO ₂ preparation. In this review various sol-gel techniques are discussed in addition to colloidal synthesis, solvothermal synthesis, and supersonically expanded plasma jet methods of synthesis. In addition to the preparation of these materials, their various applications are also reviewed.	Macwan, D.; Dave, P. and Chaturvedi, S. 2011. A Review on Nano-TiO ₂ Sol-Gel Type Syntheses and Its Applications. Journal of Materials Science, 46(11), 3669-3686.
635	(CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites	Dabbousi, B.; Rodriguez-Viejo, J.; Mikulec, F.; Heine, J.; Mattoussi, H.; Ober R.; Jensen, K. and Bawendi, M.	1997	Journal of Physical Chemistry B, 101(46), 9463-9475	Published journal	Dabbousi et al. (1997) synthesis several cadmium selenide-zinc sulfide composite quantum dots with core diameters ranging from 23-55 Å. As expected, these materials possess a narrow photoluminescence spanning the visible range, with quantum yields of approximately 30-50% at room temperature. X-ray spectroscopy, XPS, and TEM were used to characterize their chemical composition, size, size distribution, shape, and structure. This research also investigated the growth of the zinc sulfide shell on the core to determine how the structure of the ZnS shell influences the photoluminescent properties of the quantum dots.	Dabbousi, B.; Rodriguez-Viejo, J.; Mikulec, F.; Heine, J.; Mattoussi, H.; Ober R.; Jensen, K. and Bawendi, M. 1997. (CdSe)ZnS Core-Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites. Journal of Physical Chemistry B, 101(46), 9463-9475.
636	Carbon Nanotubes: Synthesis, Integration, and Properties	Dai, H.	2002	Accounts of Chemical Research, 35(12), 1035-1044	Published journal	Dai (2002) reviewed the various synthetic routes for the preparation of carbon nanotubes. It was demonstrated that patterned growth of these materials is possible with catalytic nanoparticles, with the potential to be scaled up for industrial application. The potential application of these materials in a variety of products is also reviewed.	Dai, H. 2002. Carbon Nanotubes: Synthesis, Integration, and Properties. Accounts of Chemical Research, 35(12), 1035-1044.
637	Vapor-phase Synthesis of Nanoparticles	Swihart, M.	2003	Current Opinion in Colloid and Interface Science, 8(1), 127-133	Published journal	Swihart (2003) reviews various methods for the preparation of nanomaterials through the vapor-phase synthesis. The principle behind this synthetic route is that conditions are achieved where the vapor phase mixture is thermodynamically unstable, instead resorting to a more stable nanoparticulate form (typically achieved at chemical supersaturation). Various means of achieving these conditions are discussed including laser pyrolysis, thermal plasma synthesis, and flame spray pyrolysis.	Swihart, M. 2003. Vapor-phase Synthesis of Nanoparticles. Current Opinion in Colloid and Interface Science, 8(1), 127-133.
638	Nanoparticle-cored Dendrimers: Synthesis and Characterization	Gopidas, K.; Whitesell, J. and Fox, M.	2003	Journal of the American Chemical Society, 125(21), 6491-6502	Published journal	Gopidas et al. (2003) synthesize nanoparticle-cored dendrimers. These materials are prepared through the synthesis of a gold nanoparticle core (via reduction of chloroauric acid) follow by the self-assembly of disulfide dendrimer wedges as the nanoparticle is formed. These materials were then characterized by TEM, TGA, UV-vis, IR, and NMR spectroscopy. As a large fraction of the surface area is not passivated, these materials may still be suitable for catalytic activity.	Gopidas, K.; Whitesell, J. and Fox, M. 2003. Nanoparticle-cored Dendrimers: Synthesis and Characterization. Journal of the American Chemical Society, 125(21), 6491-6502.
639	Silver Nanoparticle Protein Corona Composition in Cell Culture Media	Shannahan, J.; Lai, X.; Ke, P.; Podila, R. and Brown, J.	2013	PLoS One, 8(9), 1-10	Published journal	Shannahan et al. (2013) studied the formation and composition of the protein corona that formed around a set of four different silver nanoparticles. To investigate the protein corona, a label-free mass spectrometry-based proteomic approach was utilized. The form a protein corona, all silver nanoparticles were incubated in DMEM that had been supplemented with fetal bovine serum. The proteins were then identified and quantified, showing that all silver nanoparticles associated with 11 proteins. The larger citrate and PVP-stabilized nanoparticles were found to bind the greatest number of proteins, suggesting that protein corona formation may be based on surface curvature.	Shannahan, J.; Lai, X.; Ke, P.; Podila, R. and Brown, J. 2013. Silver Nanoparticle Protein Corona Composition in Cell Culture Media. PLoS One, 8(9), 1-10.

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640	Comparative Eco-Toxicity of Nanoscale TiO ₂ , SiO ₂ , and ZnO Water Suspensions	Adams, L.; Lyon, D. and Alvarez, P.	2006	Water Research, 40(19), 3527-3532	Published journal	Adams et al. (2006) investigated the eco-toxicity of titanium dioxide, silicon dioxide, and zinc oxide nanoparticle suspension to gram positive and gram negative bacteria. It was determined that silicon had the highest antibacterial activity with zinc oxide having the lowest, and the gram positive B. subtilis being the most susceptible to these effects. The most significant bacterial growth inhibition occurred under light conditions, suggesting the role of reactive oxygen species.	Adams, L.; Lyon, D. and Alvarez, P. 2006. Comparative Eco-Toxicity of Nanoscale TiO ₂ , SiO ₂ , and ZnO Water Suspensions. Water Research, 40(19), 3527-3532.
641	Size-controlled Dissolution of Organic-Coated Silver Nanoparticles	Ma, R.; Levard, C.; Marinakos, S.; Cheng, Y.; Liu, J.; Michel, F.; Brown, Jr., G. and Lowry, G.	2012	Environmental Science & Technology, 46(2), 752-759	Published journal	Ma et al. (2012) measured the solubility of different sizes of silver nanoparticles (diameters ranging from 5-80nm) that were synthesized using various methods and possessing different organic polymer coatings. Transmission electron microscopy was used to characterize the size of the nanomaterials, where x-ray absorption spectroscopy (XAFS) and x-ray scattering were used to study the structure and changes in the crystal lattice of the silver nanoparticle as a function of size. It was determined that lattice parameter does not change with particle size, down to a diameter of 6nm, indicating that particle solubility can be estimated using a modified Kelvin equation for particles with sizes between 5-40nm.	Ma, R.; Levard, C.; Marinakos, S.; Cheng, Y.; Liu, J.; Michel, F.; Brown, Jr., G. and Lowry, G. 2012. Size-controlled Dissolution of Organic-Coated Silver Nanoparticles. Environmental Science & Technology, 46(2), 752-759.
642	Low Concentrations of Silver Nanoparticles in Biosolids Cause Adverse Ecosystem Responses Under Realistic Field Scenario	Colman, B.; Arnaout, C.; Anciaux, S.; Gunsch, C.; Hochella Jr., M.; Kim, B.; Lowry, G.; McGill, B.; Reinsch, B.; Richardson, C.; Unrine, J.; Wright, J.; Yin, L. and Bernhardt, E.	2013	PLoS One, 8(2), e57189		Colman et al. (2013) performed a long-term terrestrial mesocosm field experiment entailing the application of silver nanoparticles via a likely exposure route (sewage biosolids). At low concentrations of silver (0.14 mg Ag kg ⁻¹ soil), the microorganism community was different in slurries that contained silver nanoparticles as determined by T-RLFP analysis of 16s-rRNA genes. The N ₂ O flux was also higher in the silver nanoparticle and slurry treatment than the slurry by itself, but both the N ₂ O flux and bacterial community composition converged to similar values after 50 days. In addition, it was demonstrated that these responses were larger in magnitude when compared to a positive control of silver nitrate which had been added at a concentration four times higher than the mass concentration of nanoparticles.	Colman, B.; Arnaout, C.; Anciaux, S.; Gunsch, C.; Hochella Jr., M.; Kim, B.; Lowry, G.; McGill, B.; Reinsch, B.; Richardson, C.; Unrine, J.; Wright, J.; Yin, L. and Bernhardt, E. 2013. Low Concentrations of Silver Nanoparticles in Biosolids Cause Adverse Ecosystem Responses Under Realistic Field Scenario. PLoS One, 8(2), e57189.
643	Presence of Nanoparticles in Wash Water from Conventional Silver and Nano-Silver Textiles	Mitrano, D.; Rimmel, E.; Wichser, A.; Erni, R.; Height, M. and Nowack, B.	2014	ACS Nano, 8(7), 7208-7219	Published journal	Mitrano et al. (2014) simulated the house-hold laundering of nano-enabled textiles that had been prepared with known silver and silver nanoparticle treatments. Serial filtration separated various size fractions of nanomaterials which were then characterized by TEM and EDX. Ionic silver showed the most release of total silver than those incorporating silver nanoparticles. Of the silver nanoparticle-enabled textiles, those incorporated into the fabric, as opposed to surface treatment, saw less silver being released during the fabric washing process. Silver was found in various forms such as metallic silver, silver chloride, and silver sulfide particles, which depended on the initial speciation of silver in the sock fabric.	Mitrano, D.; Rimmel, E.; Wichser, A.; Erni, R.; Height, M. and Nowack, B. 2014. Presence of Nanoparticles in Wash Water from Conventional Silver and Nano-Silver Textiles. ACS Nano, 8(7), 7208-7219.
644	Langendorff heart: a model system to study cardiovascular effects of engineered nanoparticles	Stampfl, A.; Maier, M.; Radykewicz, R.; Reitmair, P.; Göttlicher, M. and Niessner, R.	2011	ACS Nano, 5(7), 5345-5353	Published journal	Stampfl et al. (2011) studied the cardiovascular effects of ENPs on physiological systems by utilizing an isolated beating heart (Langendorff heart) as the model system. Using this model, a significant correlation between heart rate and material type and concentration was found, with increased heart rate and arrhythmia occurring for all particle types aside from flame derived SiO ₂ (Aerosil) and monodisperse polystyrene. The sensitivity of the Langendorff Heart to these effect may make it a suitable test model for studying ENP toxicity.	Stampfl, A.; Maier, M.; Radykewicz, R.; Reitmair, P.; Göttlicher, M. and Niessner, R. 2011. Langendorff heart: a model system to study cardiovascular effects of engineered nanoparticles. ACS Nano, 5(7), 5345-5353.
645	Distinguishing Between Interlayer and External Sorption Sites of Clay Minerals Using X-ray Absorption Spectroscopy	Papelis, C. and Hayes, K.	1996	Colloids and Surfaces A: Physicochemical and Engineering Aspects, 107, 89-96	Published journal	Papelis and Hayes (1996) utilized x-ray absorption spectroscopy to study the adsorption of cobalt onto smectite-clay minerals. It was demonstrated that at low pH and low concentrations of sodium, the cobalt will form an outer-sphere surface complex. However at increasing pH and sodium ion concentration, these interlayer sites are taken, resulting in polynuclear, external surface-hydroxyl complexes with cobalt. This research demonstrates the utility of XAS in differentiating the interlayer and external site sorption of trace metals on clay minerals.	Papelis, C. and Hayes, K. 1996. Distinguishing Between Interlayer and External Sorption Sites of Clay Minerals Using X-ray Absorption Spectroscopy. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 107, 89-96.

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646	Cerium Oxidation State in Ceria Nanoparticles Studied with X-ray Photoelectron Spectroscopy and Absorption Near Edge Spectroscopy	Zhang, F.; Wang, P.; Koberstein, J.; Khalid, S. and Chan, S.-W.	2004	Surface Science, 563(1-3), 74-82	Published journal	Zhang et al. (2004) investigated the cerium oxidation state of ceria nanoparticles using both CPS and XANES. A comparison of the results revealed that x-ray photoelectron spectroscopy overestimated the concentration of cerium 3+ present inside the nanoparticles. It was suggested that surface reduction could occur within the XPS vacuum chamber. Additionally the fast reduction dynamics of ceria nanoparticles and the diffuse depth profile of these materials may have also contributed to this error. This work highlights the importance of orthogonal analytical techniques in the characterization of nanomaterials.	Zhang, F.; Wang, P.; Koberstein, J.; Khalid, S. and Chan, S.-W. 2004. Cerium Oxidation State in Ceria Nanoparticles Studied with X-ray Photoelectron Spectroscopy and Absorption Near Edge Spectroscopy. Surface Science, 563(1-3), 74-82.
647	Long-Term Transformation and Fate of Manufactured Ag Nanoparticles in a Simulated Large Scale Freshwater Emergent Wetland.	Lowry, G.; Espinasse, B.; Badireddy, A.; Richardson, C.; Reinsch, B.; Bryant, L.; Bone, A.; Deonarine, A.; Chae, S.; Therezien, M.; Colman, B.; Hsu-Kim, H.; Bernhardt, E.; Matson, C. and Wiesner, M.	2012	Environmental Science & Technology, 46(13), 7027-7036	Published journal	Lowry et al. (2012) studied the long-term behavior of PVP-capped silver nanoparticles in freshwater mesocosms to study their impact on an emergent wetland environment. The silver nanoparticles were applied to either the water column or the soils, and the distribution of silver characterized after 18 months. It was determined that over 70 wt. % of the silver resided in the soils, and while most remained in their initial dosing compartment, some exchange between soil and sediment was determined. Most of the silver was transformed into silver sulfides or silver-sulphydryl compounds, and despite this sulfidation, a fraction of silver was found to be bioaccumulated in plant biomass and some of the organisms present.	Lowry, G.; Espinasse, B.; Badireddy, A.; Richardson, C.; Reinsch, B.; Bryant, L.; Bone, A.; Deonarine, A.; Chae, S.; Therezien, M.; Colman, B.; Hsu-Kim, H.; Bernhardt, E.; Matson, C. and Wiesner, M. 2012. Long-Term Transformation and Fate of Manufactured Ag Nanoparticles in a Simulated Large Scale Freshwater Emergent Wetland.. Environmental Science & Technology, 46(13), 7027-7036.
648	Characterization of Synthesized Titanium Oxide Nanoclusters by MALDI-TOF Mass Spectrometry	Guan, B.; Lu, W.; Fang, J. and Cole, R.	2007	Journal of the American Society for Mass Spectrometry, 18(3), 517-524	Published journal	Guan et al. (2007) demonstrated the utility of MALDI-TOF-MS and LDI-TOF-MS for the characterization of titanium dioxide nanoparticles. The peak maxima obtained from these methods was found to correlate with particle size, demonstrating their potential as particle sizing techniques. In addition, the particle size distribution obtained from these two mass spectrometry techniques was found to be in good agreement with the distribution obtained from transmission electron microscopy.	Guan, B.; Lu, W.; Fang, J. and Cole, R. 2007. Characterization of Synthesized Titanium Oxide Nanoclusters by MALDI-TOF Mass Spectrometry. Journal of the American Society for Mass Spectrometry, 18(3), 517-524.
649	Exposure to engineered nanoparticles: Model and measurements for accident situations in laboratories.	Walser, T.; Hellweg, S.; Juraske, R.; Luechinger, N.; Wang, J. and Fierz, M.	2012	Science of the Total Environment, 420, 119-126	Published journal	Walser et al. (2012) simulated three scenarios of equipment failure for processes used in gas phase production of nanomaterials to model potential nanomaterial exposure to workers. Release of nanomaterials was monitored with high spatial and temporal resolution using nine charge-based aerosol samplers (MiniDiSC) that were compared to a conventional condensation particle counter (CPC). Worst case release scenarios show that a very rapid dispersal event (60s) occurs with nanoparticle concentrations up to 10^6 particle / cm^3 in a 300m^2 work area. Particle number concentrations drop rapidly after this even with proper ventilation, suggesting appropriate safety measures after accidental release.	Walser, T.; Hellweg, S.; Juraske, R.; Luechinger, N.; Wang, J. and Fierz, M. 2012. Exposure to engineered nanoparticles: Model and measurements for accident situations in laboratories. Science of the Total Environment, 420, 119-126.
650	Toxicity and penetration of TiO2 nanoparticles in hairless mice and porcine skin after subchronic dermal exposure	Wu, J.; Liu, W.; Xue, C.; Zhou, S.; Lan, F.; Bi, L.; Xu, H.; Yang, X. and Zeng, F.	2009	Toxicology Letters, 191(1), 1-8	Published journal	Wu et al. (2009) studied the penetration of toxicity of titanium dioxide nanoparticles to hairless mice and porcine skin following dermal exposure. In vitro results showed no penetration of titanium dioxide through the stratum corneum. However, in vivo, TiO2 nanoparticles can penetrate through the horny layer of the porcine skin and reach the deep layer of epidermis. In the hairless mice, the TiO2 nanoparticle can penetrate the skin and translocate to different tissue. The implications show that there may be a human health risk to TiO2 after prolonged dermal exposure.	Wu, J.; Liu, W.; Xue, C.; Zhou, S.; Lan, F.; Bi, L.; Xu, H.; Yang, X. and Zeng, F. 2009. Toxicity and penetration of TiO2 nanoparticles in hairless mice and porcine skin after subchronic dermal exposure. Toxicology Letters, 191(1), 1-8.
651	Multi-walled carbon nanotube interactions with human epidermal keratinocytes	Monteiro-Riviere, N.; Nemanich, R.; Inman, A.; Wang, Y. and Riviere, J.	2005	Toxicology Letters, 155(3), 377-384	Published journal	Monteiro-Riviere et al.(2005) investigated the toxicity of carbon nanotubes to human epidermal keratinocytes, which were exposed to different concentrations of multi-walled carbon nanotubes. Transmission electron microscopy measurements indicated the presence of MWCNTs in the cytoplasmic vacuoles of the cells at all time points. In addition, the MWCNTs resulted in the release of interleukin 8 (a proinflammatory cytokine) indicating an irritative response from cell.	Monteiro-Riviere, N.; Nemanich, R.; Inman, A.; Wang, Y. and Riviere, J. 2005. Multi-walled carbon nanotube interactions with human epidermal keratinocytes. Toxicology Letters, 155(3), 377-384.

Doc ID	Title	Authors	Year	Journal Title, Vol. No., and Page No. (or Year)	Document Type	Article Summary	Complete Citation
652	Estimation of cumulative aquatic exposure and risk due to silver. Contribution of nano-functionalized plastics and textiles	Blaser, S.; Scheringer, M.; MacLeod, M. and Hungerbühler, K.	2008	Science of the Total Environment, 390(2-3), 396-409	Published journal	Blaser et al. (2008) performed risk analysis on the impact of nanosilver originating from biocidal plastics and textiles to freshwater ecosystems. Risk analysis was performed in several steps including the assessment of silver fate, toxicity evaluation, estimation of predicted environmental concentrations (PECs), and predicted no-effect concentrations (PNECs), as well as risk characterization. Though the amount of silver that truly reaches a freshwater ecosystem will depend on the ability of waste water treatment facilities to treat nanosilver, PEC/PNEC ratios greater than one are a distinct possibility.	Blaser, S.; Scheringer, M., MacLeod, M. and Hungerbühler, K. 2008. Estimation of cumulative aquatic exposure and risk due to silver. Contribution of nano-functionalized plastics and textiles. Science of the Total Environment, 390(2-3), 396-409.
653	Characterization of silver release from commercially available functional (nano)textiles	Lorenz, C.; Windler, L.; von Goetz, N.; Lehmann, R.; Schuppler, M.; Hungerbühler, K.; Heuberger, M.; Nowack, B.	2012	Chemosphere, 89(7), 817-824	Published journal	Lorenz et al. (2012) investigated the release of silver nanomaterials during a washing and rinsing cycle from several different (nano)functional textiles. The silver collected was size fractionated and characterized using electron microscopy and EDX. The antimicrobial behavior of these silver nanomaterials was also investigated before and after a wash cycle. It was determined that the silver released after a wash cycle can come in several different forms including a Ti/Si-AgCl nanocomposite, silver chloride and metallic silver nanoparticles, and silver sulfide particles. One textile in particular showed a reduction in microbial toxicity after washing, which had been attributed to the formation of the less bioavailable silver sulfide, reducing its toxicity.	Lorenz, C.; Windler, L.; von Goetz, N.; Lehmann, R.; Schuppler, M.; Hungerbühler, K.; Heuberger, M.; Nowack, B. 2012. Characterization of silver release from commercially available functional (nano)textiles. Chemosphere, 89(7), 817-824.
654	Use of Nanoparticles in Swiss Industry: A Targeted Survey	Schmid, K. and Riediker, M.	2008	Environmental Science and Technology, 42(7), 2253-2260	Published journal	Schmid and Riediker (2008) evaluated the use of nanomaterials, the safety measures taken to protect workers, and the number of workers currently exposed to engineered nanomaterials in the Swiss Industry. The research was performed by a targeted telephone survey of 197 different Swiss companies. It was determined that several of these companies had been creating or using engineered nanomaterials, and that some import and trade prepackaged goods containing nanomaterials. The use of nanomaterials extends beyond companies specifically in the nanotechnology field, and has entered into some traditional industries such as paints. Some of the most commonly used nanomaterials (>1000 kg / yr / company) are silver, aluminum and iron oxides, silica, and titania.	Schmid, K. and Riediker, M. 2008. Use of Nanoparticles in Swiss Industry: A Targeted Survey. Environmental Science and Technology, 42(7), 2253-2260.
655	Nanopesticides: Guiding principles for regulatory evaluation of environmental risks	Kookana, R.; Boxall, A.; Reeves, P.; Ashauer, R.; Beulke, S.; Chaudry, Q.; Cornelis, G.; Fernandes, T.; Gan, J.; Kah, M.; Lynch, I.; Ranville, J.; Sinclair, C.; Spurgeon, D.; Tiede, K. and Van den Brink, P.	2014	Journal of Agricultural and Food Chemistry, 62(19), 4227-4240	Published journal	Kookana et al. (2014) review the current approaches for the environmental risk assessment of pesticides and their applicability to an emerging class of nano-pesticides. These new materials show promise in increasing the efficacy of pesticides while simultaneously preserving human and ecological health. However, there are still several issues that need to be addressed. Among these are a clear definition of what constitutes a nano-pesticide, improved analytical methodology to characterize these materials, and an adaptive regulatory framework to respond to the continued development of these nanomaterials.	Kookana, R.; Boxall, A.; Reeves, P.; Ashauer, R.; Beulke, S.; Chaudry, Q.; Cornelis, G.; Fernandes, T.; Gan, J.; Kah, M.; Lynch, I.; Ranville, J.; Sinclair, C.; Spurgeon, D.; Tiede, K. and Van den Brink, P. 2014. Nanopesticides: Guiding principles for regulatory evaluation of environmental risks. Journal of Agricultural and Food Chemistry, 62(19), 4227-4240.
656	Improvements in the detection and characterization of engineered nanoparticles using spICP-MS with microsecond dwell times	Montaño, M.; Baidei, H.; Bazargan, S. and Ranville, J.	2014	Environmental Science: Nano, 1, 338-346	Published journal	Montaño et al. (2014) demonstrate the utility of microsecond dwell times in the analysis of engineered nanomaterials by spICP-MS. Their findings indicate a significantly improved working range from a particle number concentration stand-point, as well as an improved ability to discern nanoparticulate and dissolved signals at proportionally high dissolved background concentrations. In addition, the utilization of these short data acquisitions times may open the door for multi-element analysis on a particle-by-particle basis, resulting in a potential way to differentiate naturally occurring and engineered nanomaterials.	Montaño, M.; Baidei, H.; Bazargan, S. and Ranville, J. 2014. Improvements in the detection and characterization of engineered nanoparticles using spICP-MS with microsecond dwell times. Environmental Science: Nano, 1, 338-346.
657	Simultaneous mass quantification of nanoparticles of different composition in a mixture by microdroplet generator-ICPTOFMS	Borovinskya, O.; Gschwind, S.; Hattendorf, B.; Tanner, M. and Günther, D.	2014	Analytical Chemistry	Published journal	Borovinskya et al. (2014) investigated the use of an inductively coupled plasma time-of-flight mass spectrometer for the analysis of gold, silver, and gold core-silver shell nanomaterials. The utilization of the time-of-flight allowed for simultaneous mass quantification of the different nanoparticles. By utilizing these high temporal resolution of this technique, these three particles can be differentiated from one another. In addition, the limits-of-detection for this technique were also discussed, along with the demonstration of using this technique to investigate differences in vaporization behavior.	Borovinskya, O.; Gschwind, S.; Hattendorf, B.; Tanner, M. and Günther, D. 2014. Simultaneous mass quantification of nanoparticles of different composition in a mixture by microdroplet generator-ICPTOFMS. Analytical Chemistry.

Doc ID	Title	Authors	Year	Journal Title, Vol. No., and Page No. (or Year)	Document Type	Article Summary	Complete Citation
658	A prototype of a new inductively coupled plasma time-of-flight mass spectrometer providing temporally resolved, multi-element detection of short signals generated by single particles and droplets	Borovinskya, O.; Hattendorf, B.; Tanner, M.; Gschwind, S. and Günther, D.	2013	Journal of Analytical Atomic Spectrometry, 28, 226-233	Published journal	Borovinskya et al. (2014) demonstrated the use of a prototype ICP-TOF-MS for the characterization of single nanoparticles. The quasi-simultaneous detection (acquisition time 33 microseconds) allows for the monitoring of the short temporal signals originating from the nanoparticle. The size detection limits for silver, gold and uranium nanoparticles are determined. This analytical technique also allows for the monitoring of multiple elements within a given particles.	Borovinskya, O.; Hattendorf, B.; Tanner, M.; Gschwind, S. and Günther, D. 2013. A prototype of a new inductively coupled plasma time-of-flight mass spectrometer providing temporally resolved, multi-element detection of short signals generated by single particles and droplets. Journal of Analytical Atomic Spectrometry, 28, 226-233.

Image library in support of:

**Detection and characterization of engineered nanomaterials in the environment:
current state-of-the-art and future directions**
Report, annotated bibliography, and image library

Image library in support of:
**Detection and characterization of engineered nanomaterials in the environment:
current state-of-the-art and future directions**

EPA Contract EP-C-11-039
Task Order 5

Steven P. Gardner

U.S. Environmental Protection Agency
Office of Research and Development
National Environmental Research Laboratory
Environmental Sciences Division
Characterization and Monitoring Branch
944 E. Harmon Ave.
Las Vegas, NV 89119

Manuel Montañó¹
James F. Ranville, Ph.D.¹
Julie Blue, Ph.D.²
Nupur Hiremath²
Clare Stankwitz²
Gregory V. Lowry, Ph.D.³

¹Colorado School of Mines
1500 Illinois Street
Golden, CO 80401

²The Cadmus Group, Inc.
100 5th Avenue, Suite 100
Waltham, MA 02451

³Carnegie Mellon University
5000 Forbes Avenue
Pittsburgh, PA 15213

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U.S. Environmental Protection Agency
Office of Research and Development
Washington DC 20460

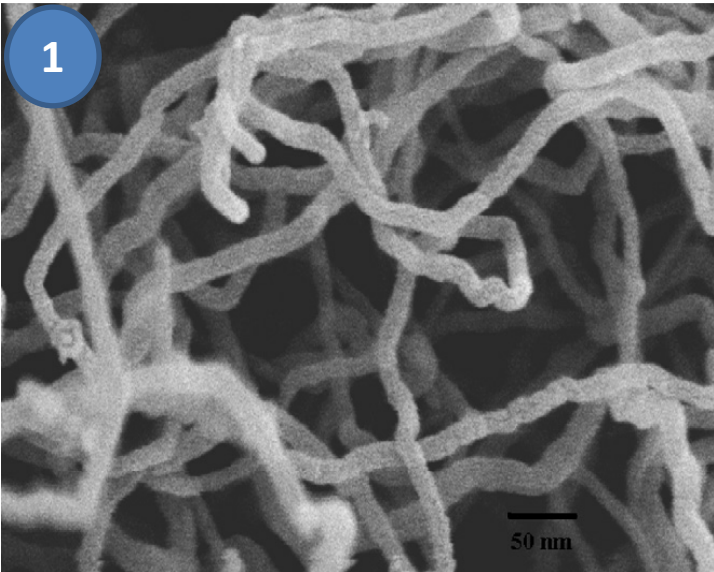
Disclaimer

The United States Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been peer reviewed by the EPA and approved for publication.

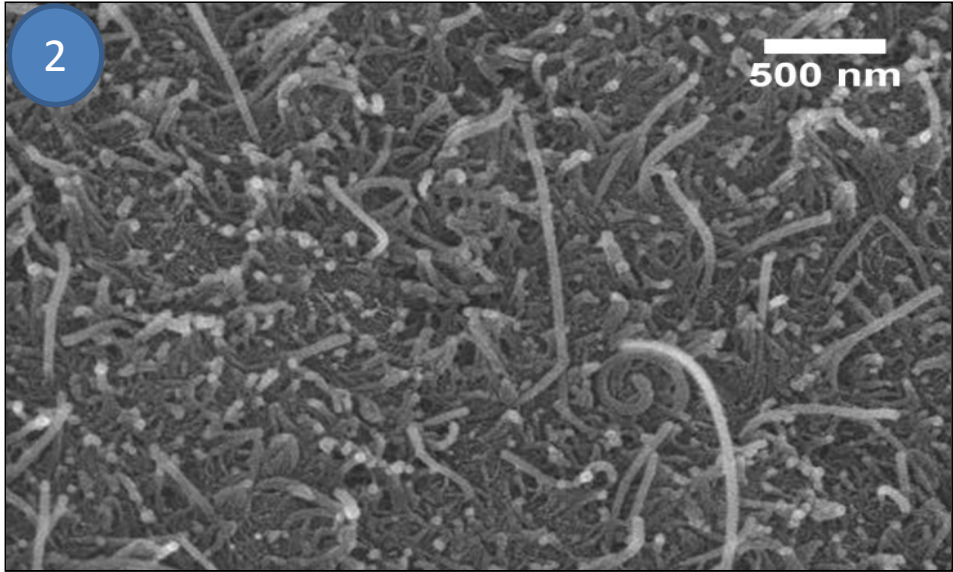
Current Status and Future Directions for Examining Engineered Nanoparticles in Natural Systems - Image Library Appendix

- The purpose of this image library is to provide examples of engineered nanoparticles and contrast them to images of their naturally occurring and/or biogenically produced counterparts. Images are provide (where possible) of the engineered particles in a product and in some cases, an image of an engineered particle that demonstrates obvious weathering effects.
- Apparent in most images is the similarity between the engineered nanomaterial and it's naturally occurring analogue. Though the engineered particles showed a greater degree of monodispersity, most particles both manufactured and natural have similar morphologies. The similarity between these images show the need for corroborative measurements to verify the identity and origin of these materials.
- There are some engineered materials that will possess very unique morphologies and surface coatings that are noticeably different than naturally occurring materials of the same composition (Slide 40). However, alterations made to these features upon entry into the environment is still a topic of research and not well understood. It is possible these highly-engineered material properties may be changed and altered to reflect materials more similar to those found in the environment as a result of chemical changes and weathering that may occur.
- It should be noted that imaging alone may not be sufficient to determine the origin and identity of nanomaterials. Other techniques that exploit key physio-chemical differences between these particles are necessary to detect and characterize these engineered nanomaterials upon entry into the environment.

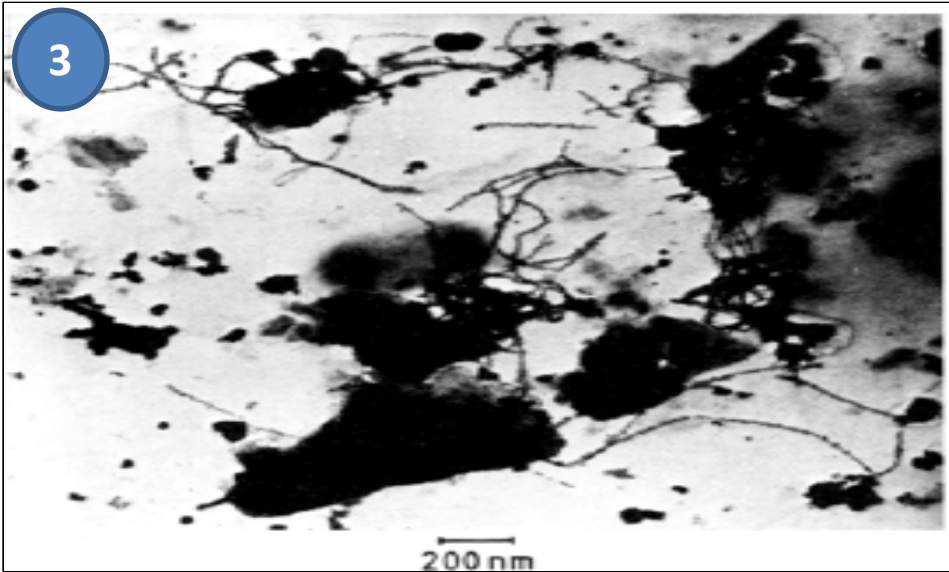
Carbon nanotubes - Images



SEM image of Purified CNTs (Lu et al., 2006)



5 % CNTs in PVOH (Fairbrother, unpublished data)



Organic filaments in lake (Buffle and Leppard, 1995)

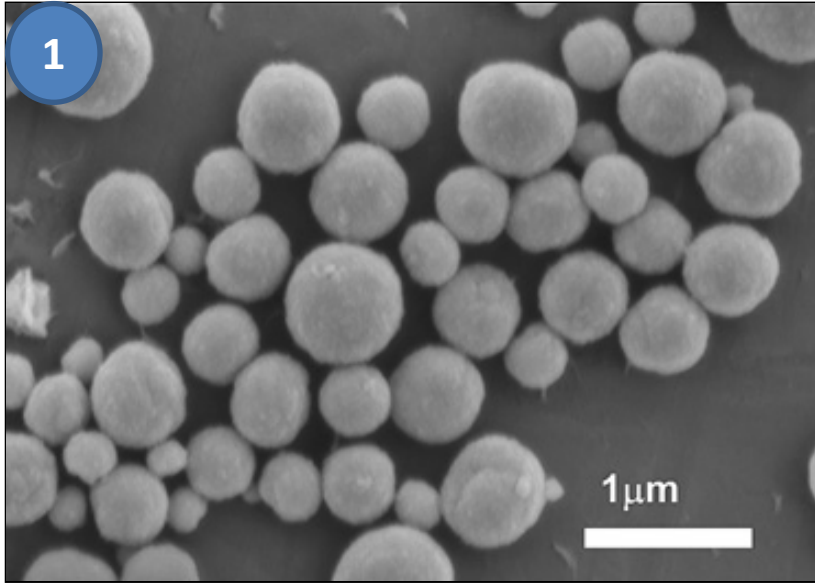
Carbon nanotubes – References (Clockwise from top left)

- 1) Scanning electron microscope image of purified multi-walled carbon nanotubes.
 - 1) Imaged by SEM.
 - 2) Lu, C.; Chung, Y.-L.; Chang, K.-F. Adsorption thermodynamic and kinetic studies of trihalomethanes on multiwalled carbon nanotubes. *Journal of Hazardous Materials B*. **2006**, 138, pp. 304-310

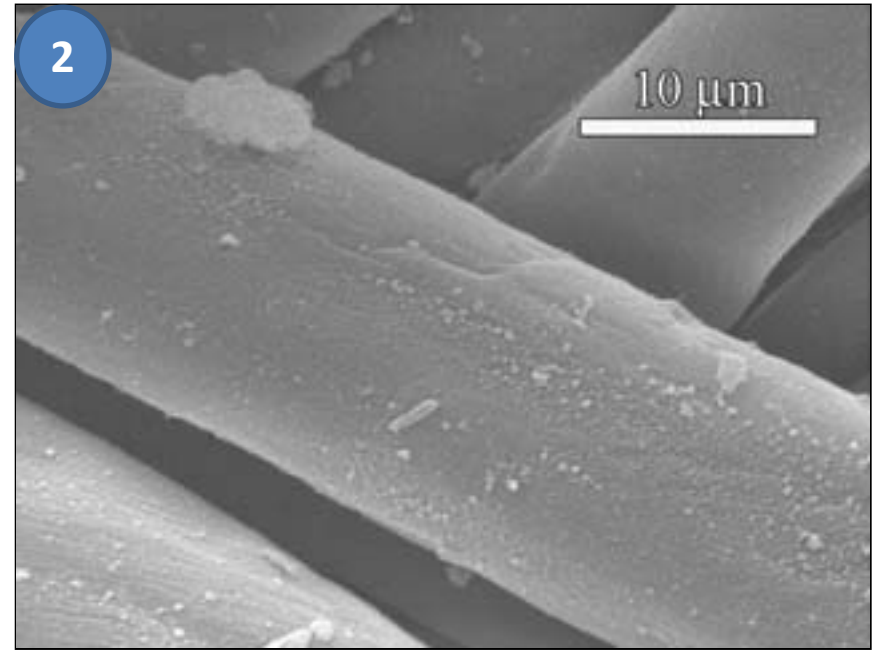
- 2) 5% CNTs in polyvinyl alcohol.
 - 1) Imaged by SEM
 - 2) Howard Fairbrother. John Hopkins University. *Unpublished Data*

- 3) Organic filaments in lake water.
 - 1) Observed by transmission electron microscopy.
 - 2) Buffle, J.; Leppard, G. G. Characterization of aquatic colloids and macromolecules. 1. Structure and Behavior of Colloidal Material. *Environmental Science and Technology*. **1995**, 29, pp. 2169-2175.

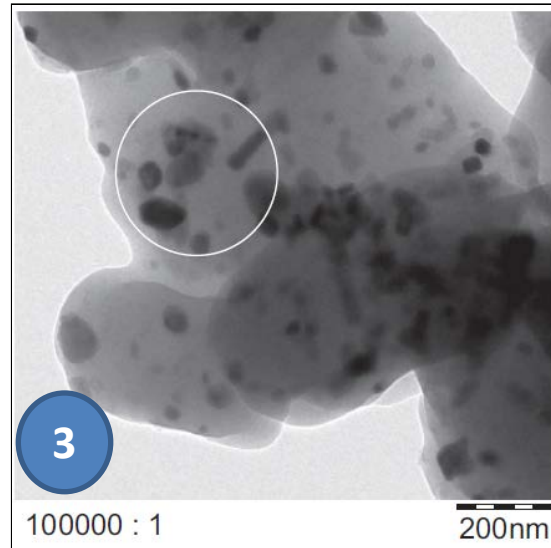
ZnO nanoparticles- Images



ZnO nanoparticles imaged by SEM (Dybowska et al., 2011)



ZnO applied to a cotton textile (Behceri et al. 2008)

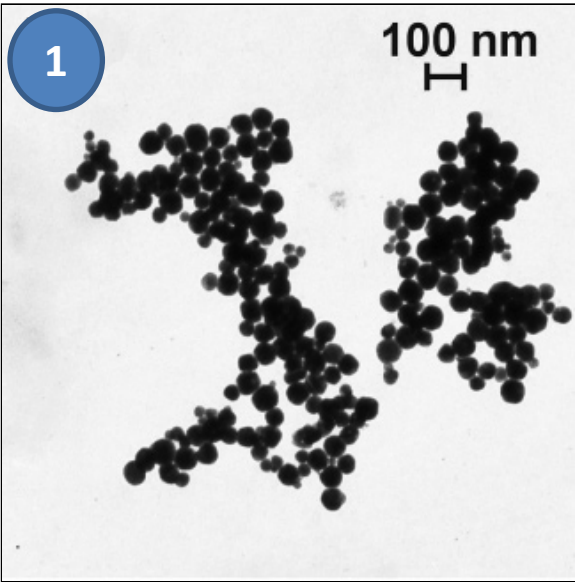


ZnO nanoparticles contained in a surface coating (Vorbau et al., 2009)

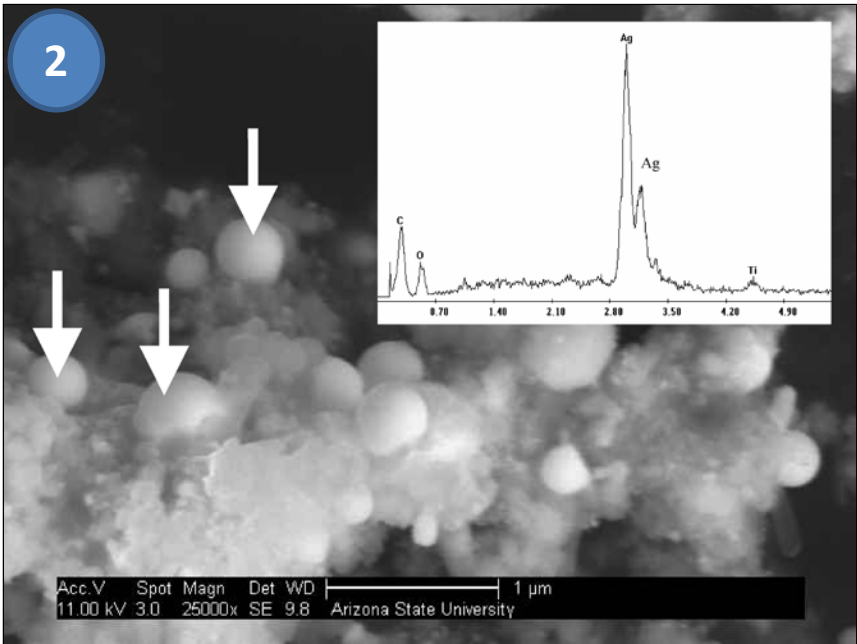
ZnO nanoparticles– References (Clockwise from top left)

- 1) Images of isotopically modified ZnO nanoparticles
 - 1) Imaged by SEM (at micron scale)
 - 2) Dybowska, A.; Croteau, M-N.; Misra, S.; Berhanu, D.; Luoma, S.; Christian, P.; O'Brien, P.; Valsami-Jones, E. Synthesis of isotopically modified ZnO nanoparticles and their potential as nanotoxicity tracers. *Environmental Pollution*, **2011**, 159, pp. 266-273.
- 2) ZnO nanoparticles applied to a cotton textile
 - 1) Imaged by SEM (at micron scale)
 - 2) Becheri, A.; Dürr, M.; Lo Nostro, P.; Baglioni, P. Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers. *Journal of Nanoparticle Research*, **2008**, 10, pp. 679-689.
- 3) ZnO nanoparticles released from a surface coating via abrasion.
 - 1) Imaged by TEM.
 - 2) Vorbau, M.; Hillemann, L.; Stintz, M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *Aerosol Science*, **2009**, 40, pp. 209-217.

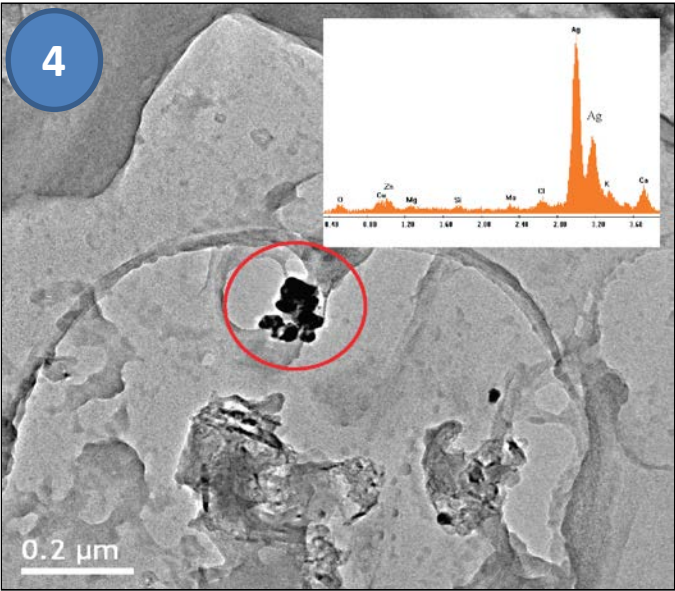
Ag nanoparticles- Images



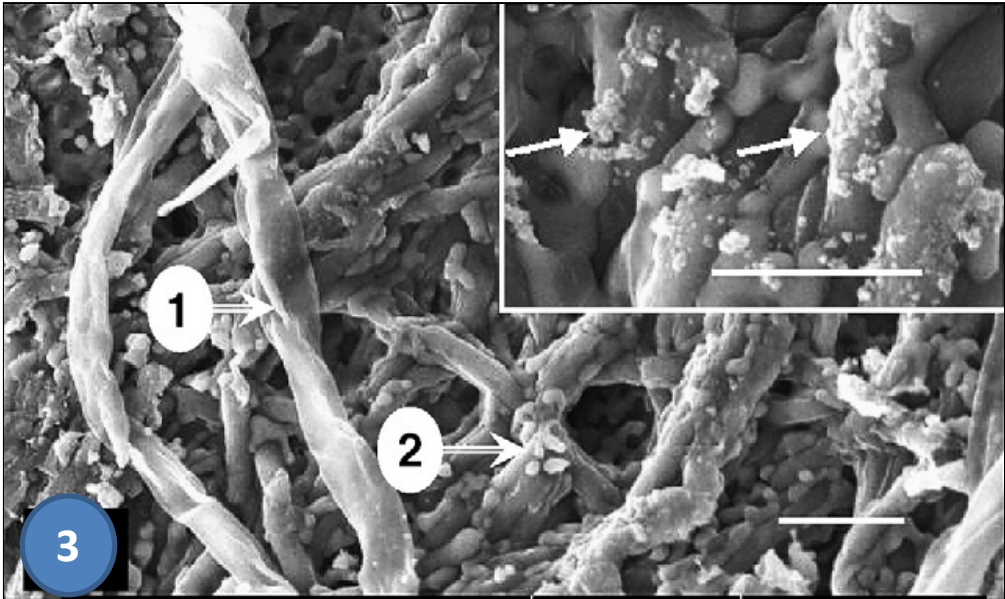
Ag nanoparticles prepared by silver ammonia reduction (Panacek et al., 2006)



Ag nanoparticles found in sock fabric (Benn and Westerhoff, 2008)



Ag nanoparticles found in wash water (Benn and Westerhoff, 2007)

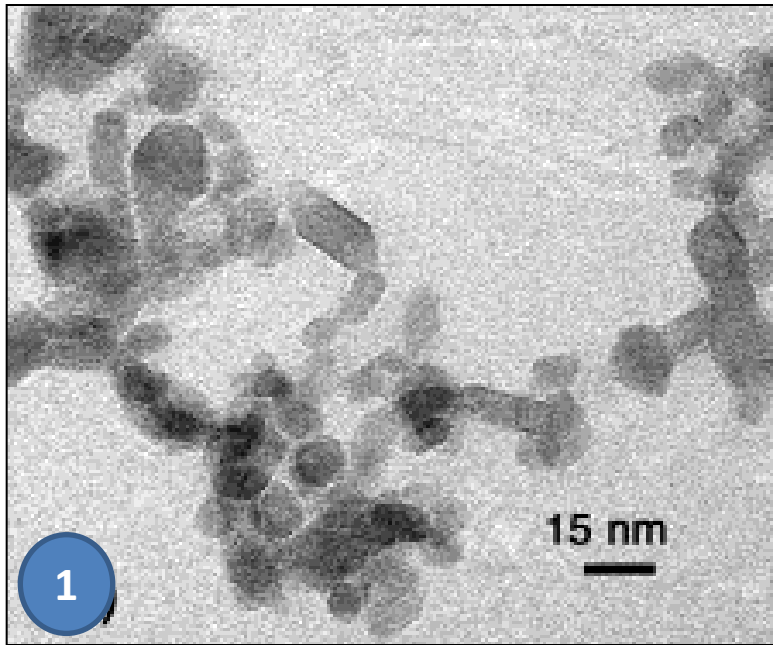


Ag nanoparticles synthesized by *Aspergillus flavus* (Vigneshwaran et al., 2007)

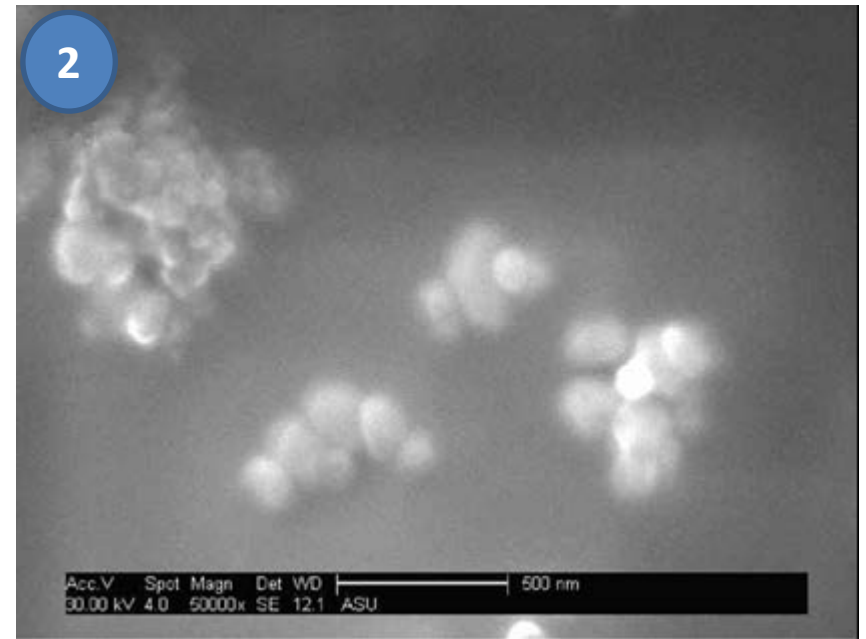
Ag nanoparticles– References (Clockwise from top left)

- 1) Ag nanoparticles formed via the reduction of silver ammoniate by glucose
 - 1) Imaged by TEM
 - 2) Panáček, A.; Kvitek, L.; Prucek, R.; Kolář, M.; Večeřová, R.; Pizúrová, N.; Sharma, V.; Nevěčná, T.; Zbořil, R. Silver Colloid Nanoparticles: Synthesis, Characterization, and Their Antibacterial Activity. *Journal of Physical Chemistry B*, **2006**, *110*, pp. 16248-16253.
- 2) Ag nanoparticles found in ashed sock fabric (EDX inset)
 - 1) Imaged by SEM (at micron scale)
 - 2) Benn, T.; Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environmental Science and Technology*, **2008**, *42*, pp. 4133-4139.
- 3) Silver nanoparticles formed from the reduction of silver nitrate by *Aspergillus flavus*
 - 1) Imaged by SEM
 - 2) Vigneshwaran, N.; Ashtaputre, N.; Varadarajan, P.; Nachane, R.; Paralikar, K.; Balasubramanya, R. Biological synthesis of silver nanoparticles using the fungus *Aspergillus flavus*. *Materials Letters*, **2007**, *61*, pp. 1413-1418.
- 4) Ag nanoparticles found in wash water from sock fabrics (inset is EDX)
 - 1) Imaged by TEM
 - 2) Benn, T.; Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environmental Science and Technology*, **2008**, *42*, pp. 4133-4139.

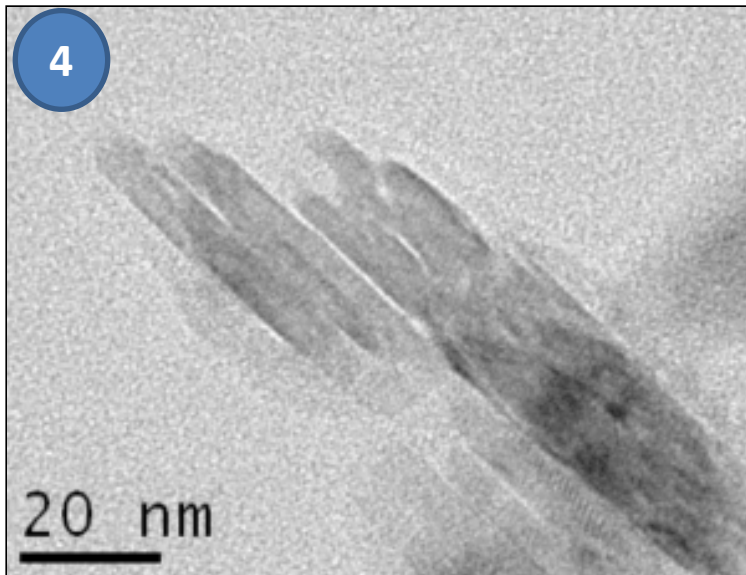
TiO₂ nanoparticles- Images



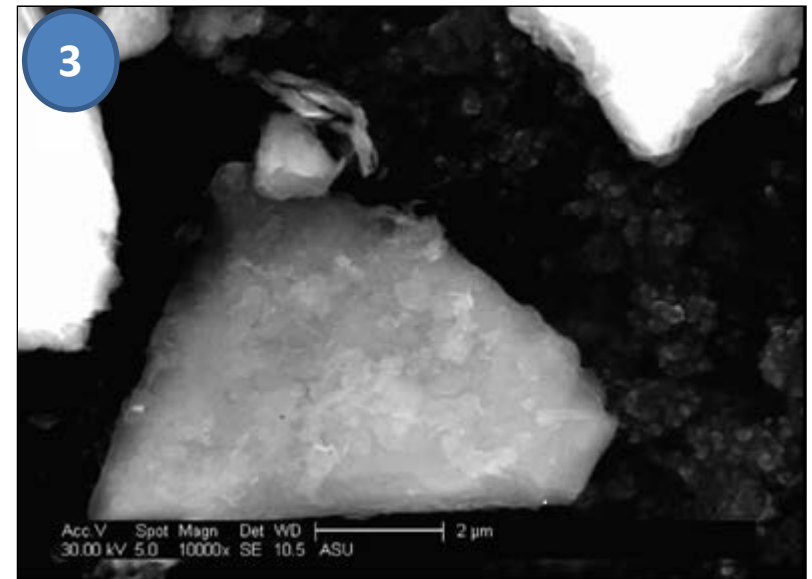
TiO₂ nanoparticles imaged by TEM (Oskam et al., 2003)



TiO₂ nanoparticles in toothpaste (Kiser et al., 2008)



Weathered TiO₂ particle in sunscreen (Nowack et al., 2012)

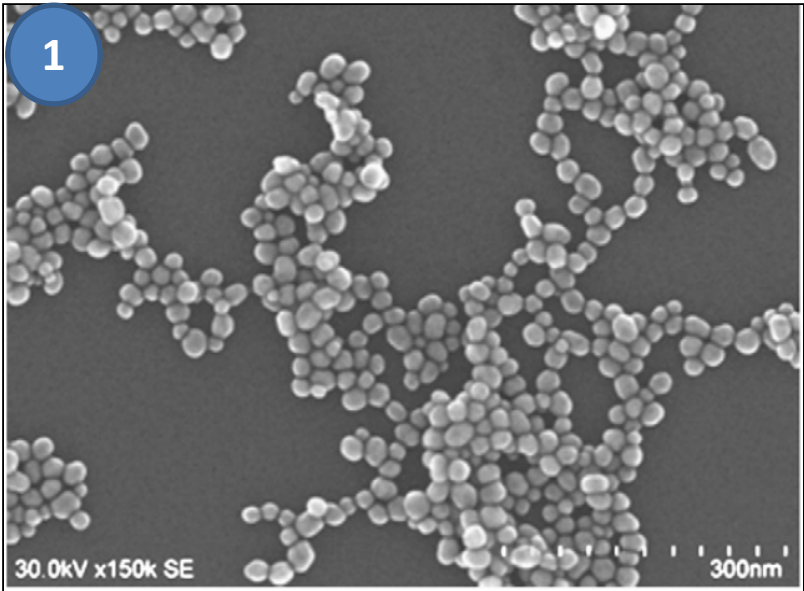


Ti-containing mineral in a biosolid (Kiser et al., 2008)

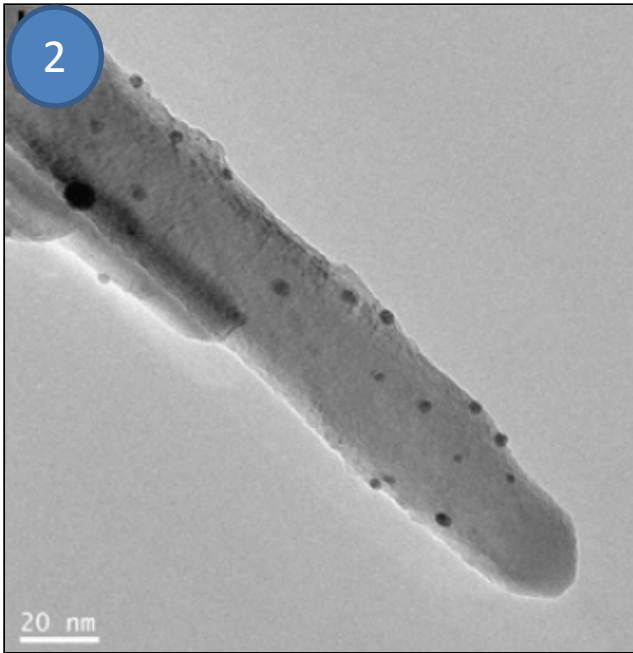
TiO₂ nanoparticles– References (Clockwise from top left)

- 1) Image of TiO₂ nanoparticles prepared from titanium (IV) isopropoxide
 - 1) Imaged by TEM
 - 2) Oskam, G.; Nellore, A.; Penn, R. L.; Searson, P. The Growth Kinetics of TiO₂ Nanoparticles from Titanium (IV) Alkoxide at High Water/Titanium Ratio. *Journal of Physical Chemistry B*. **2003**, *107*, pp. 1734-1738.
- 2) TiO₂ nanoparticles in toothpaste
 - 1) Imaged by SEM
 - 2) Kiser, M.; Westerhoff, P.; Benn, T.; Wang, Y.; Pérez-Rivera, J.; Hristovski, K. Titanium Nanomaterial Removal and Release from Wastewater Treatment . *Environmental Science and Technology*. **2008**, *43*, pp. 6757-6763.
- 3) Titanium containing mineral in a biosolid
 - 1) Observed by SEM (at micron scale)
 - 2) Kiser, M.; Westerhoff, P.; Benn, T.; Wang, Y.; Pérez-Rivera, J.; Hristovski, K. Titanium Nanomaterial Removal and Release from Wastewater Treatment . *Environmental Science and Technology*. **2008**, *43*, pp. 6757-6763.
- 4) Weathered titania nanoparticle released from sunscreen
 - 1) Observed by TEM
 - 2) Nowack, B.; Ranville, J.; Diamond, S.; Gallego-Urrea, J.; Metcalfe, C.; Rose, J.; Horne, N.; Koelmans, A.; Klaine, S. Potential Scenarios for Nanomaterial Release and Subsequent Alteration in the Environment. *Environmental Toxicology and Chemistry*, **2012**, *31*, pp. 50-59.

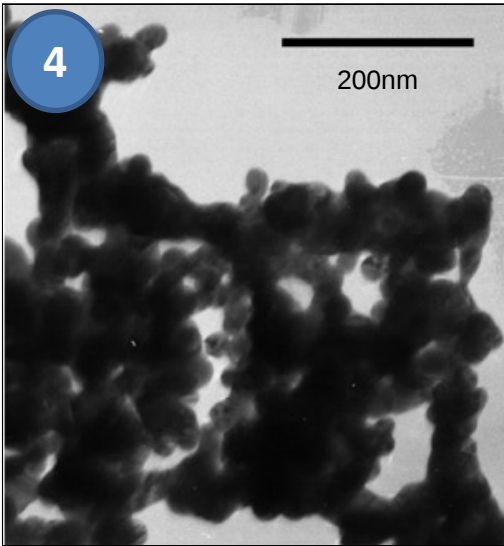
Au nanoparticles- Images



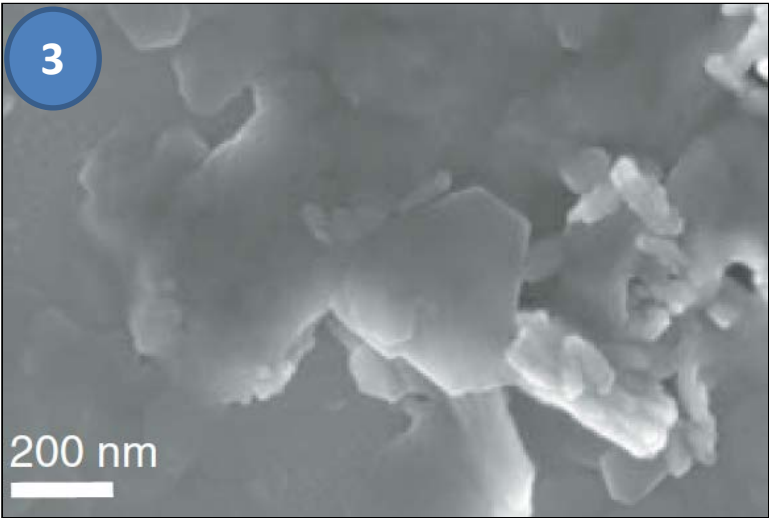
Gold nanoparticles synthesized by reduction of chloroauric acid (Cichomski et al., 2011)



Catalytic gold nanoparticles deposited on a ZnO support (Catillejos et al., 2012)



Aggregated acrylate capped gold nanoparticles at pH=2 (Diegoli et al., 2008)

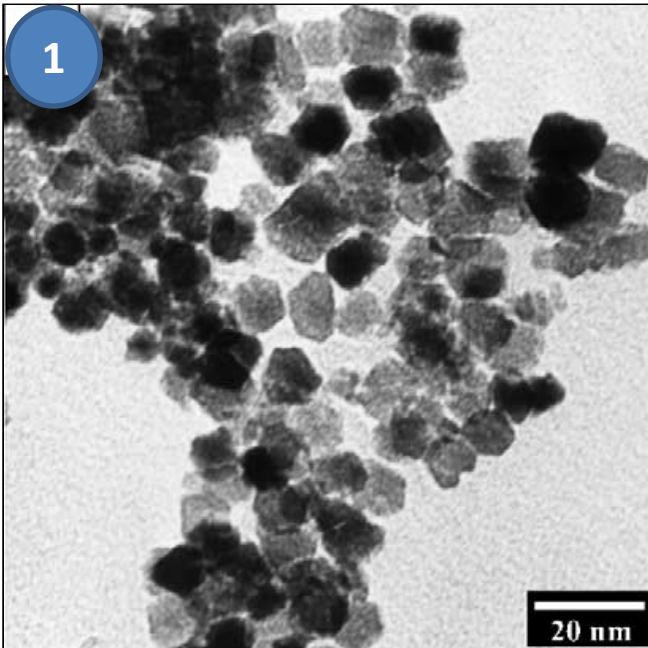


Gold nanoparticles found in weathered gold deposits (Hough et al., 2008)

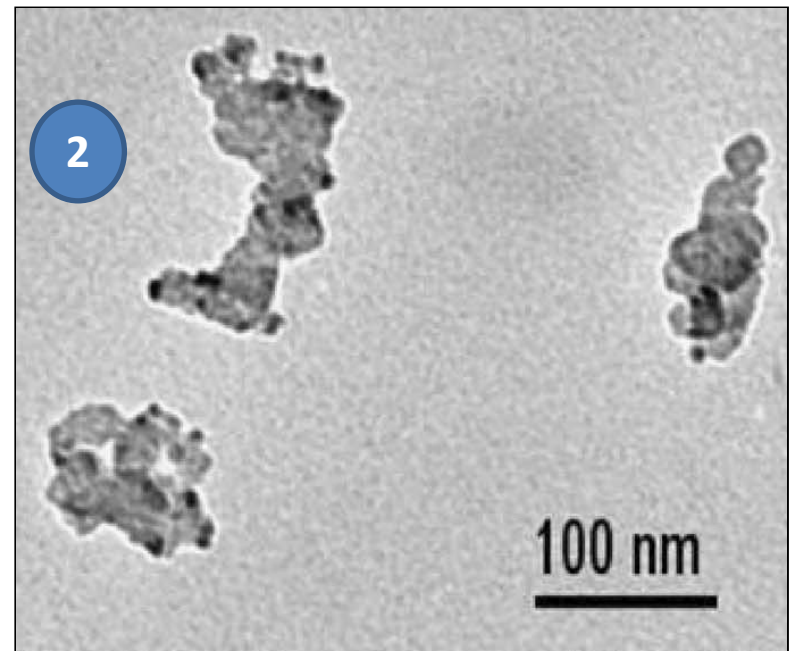
Au nanoparticles– References (Clockwise from top left)

- 1) Gold nanoparticles synthesized via reduction of chloroauric acid by trisodium citrate
 - 1) Imaged by SEM
 - 2) Cichomski, M.; Tomaszewska, E.; Kośla, K.; Kozłowski, W.; Kowalczyk, P.; Grobelny, J. Study of dithiol monolayer as the interface for controlled deposition of gold nanoparticles. *Materials Characterization*, **2011**, 42, pp. 268-274.
- 2) Catalytic gold nanoparticles deposited on a ZnO support
 - 1) Imaged by TEM
 - 2) Castillejos, E.; Gallegos-Suarez, E.; Bachiller-Baeza, B.; Bacsa, R.; Serp, P.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. Deposition of gold nanoparticles on ZnO and their catalytic activity for hydrogenation applications. *Catalysis Communications*, **2012**, 22, pp. 79-82.
- 3) Gold nanoparticles found in weather gold deposits
 - 1) Imaged by SEM
 - 2) Hough, R.; Noble, R.; Hitchen, G.; Hart, R.; Reddy, S.; Saunders, M.; Clode, P.; Vaughan, D.; Lowe, J.; Gray, D.; Anand, R.; Butt, C.; Verrall, M. Naturally occurring gold nanoparticles and nanoplates. *Geology*, **2008**, 36, pp. 571-574.
- 4) Aggregated acrylate-capped gold nanoparticles at pH=2.
 - 1) Imaged by TEM
 - 2) Diegoli, S.; Manciuola, A.; Begum, S.; Jones, I.; Lead, J.; Preece, J. Interaction between manufactured gold nanoparticles and naturally occurring macromolecules. *Science of the Total Environment*, **2008**, 402, pp. 51-61.

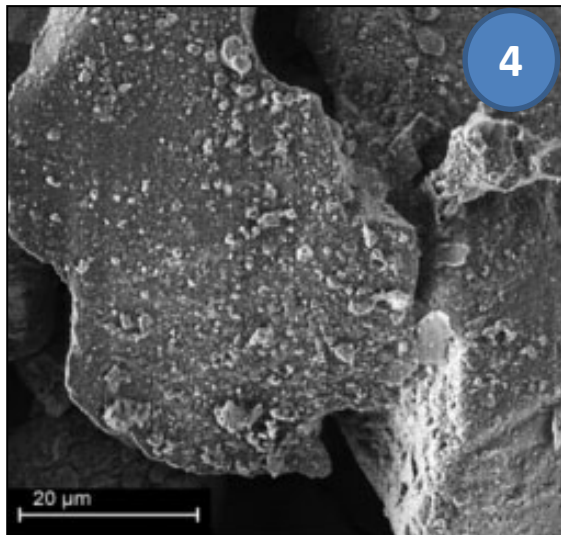
1) CeO₂ nanoparticles- Images



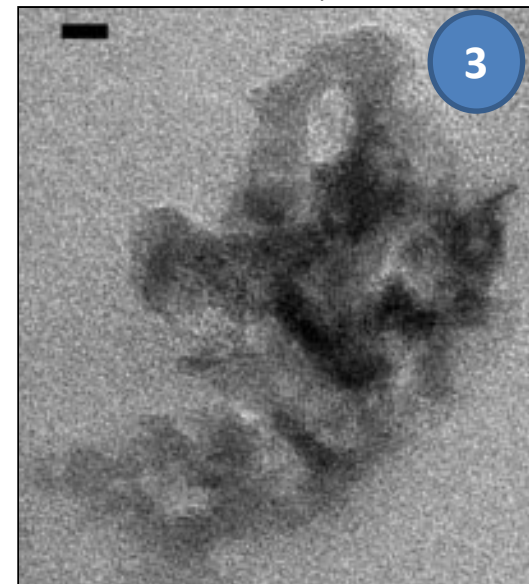
Cerium oxide nanoparticles prepared at 70°C (Chen and Chang, 2005)



Cerium oxide adhered to diesel particles in fuel additive (Jung et al., 2005)



CeO₂ particles adhered to a silty loam (von der Kammer et al., 2012)

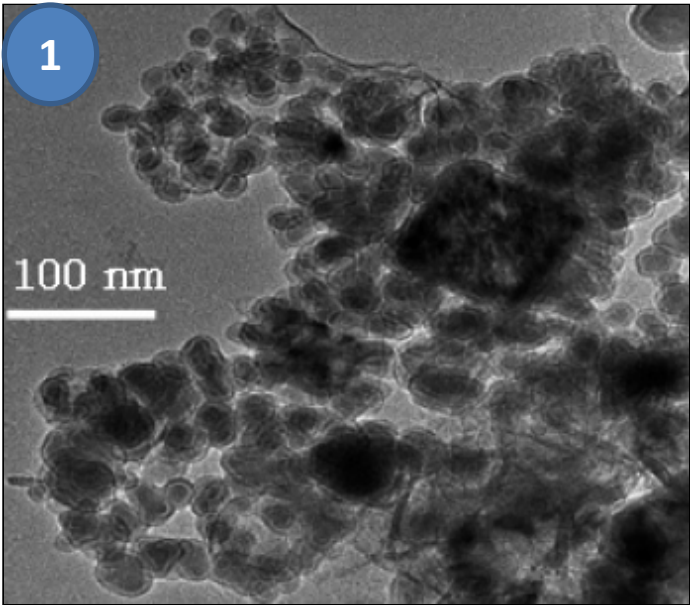


CeO₂ nano-cluster found in a floodplain (von der Kammer et al., 2012)

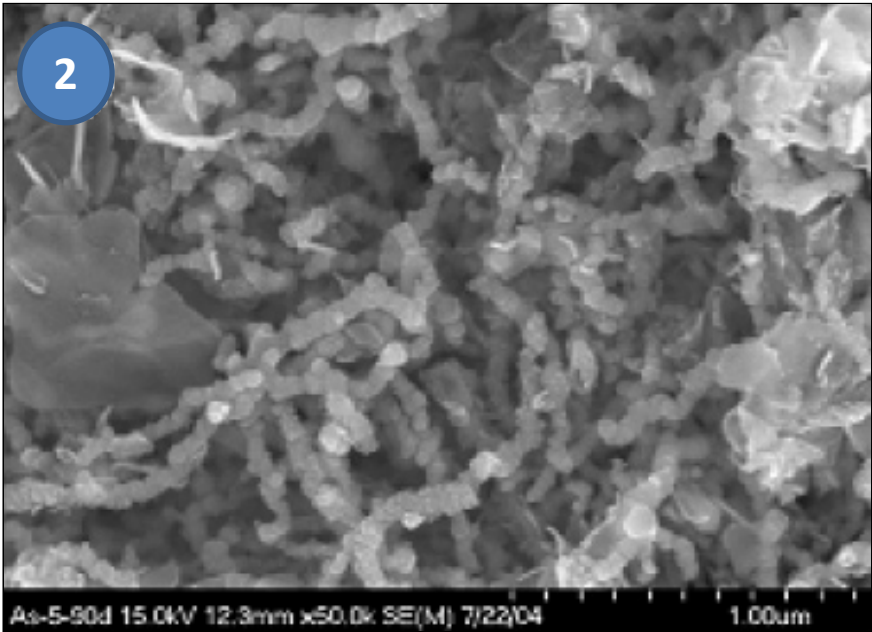
CeO₂ nanoparticles– References (Clockwise from top left)

- 1) Cerium oxide nanoparticles prepared from the oxidation of cerium ammoniate at 70⁰ C.
 - 1) Imaged by TEM
 - 2) Chen, H.; Chang, H. Synthesis of nanocrystalline cerium oxide particles by the precipitation method. *Ceramic International*, **2005**, 31, pp. 795-802.
- 2) Cerium oxide nanoparticles found on diesel particles
 - 1) Imaged by TEM
 - 2) Jung, H.; Kittelson, D.; Zachariah, M. The influence of a cerium additive on ultrafine diesel particle emissions and kinetics of oxidation. *Combustion and Flame*, **2005**, 142, pp. 276-288.
- 3) Natural Ce-containing nanoparticle cluster from the floodplain of Clark Fork River, Montana, USA
 - 1) Imaged by TEM (scale not specified)
 - 2) von der Kammer, F.; Ferguson, P.; Holden, P.; Mason, A.; Rogers, K.; Klaine, S.; Koelmans, A.; Horne, N.; Unrine, J. Analysis of Engineered Nanomaterials in Complex Matrices (Environment and Biota): General Consideration and Conceptual Case Studies. *Environmental Toxicology and Chemistry*, **2012**, 31, pp. 32-49.
- 4) Cerium dioxide nanoparticles adhered to the surface of a silty loam
 - 1) Imaged by SEM (at micron scale)
 - 2) von der Kammer, F.; Ferguson, P.; Holden, P.; Mason, A.; Rogers, K.; Klaine, S.; Koelmans, A.; Horne, N.; Unrine, J. Analysis of Engineered Nanomaterials in Complex Matrices (Environment and Biota): General Consideration and Conceptual Case Studies. *Environmental Toxicology and Chemistry*, **2012**, 31, pp. 32-49.

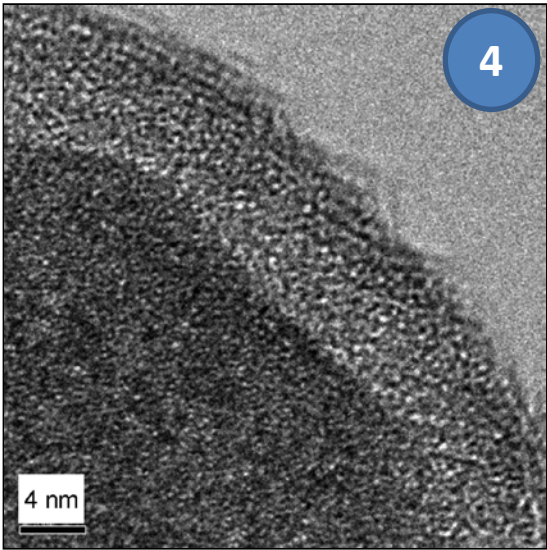
Zero valent iron nanoparticles- Images



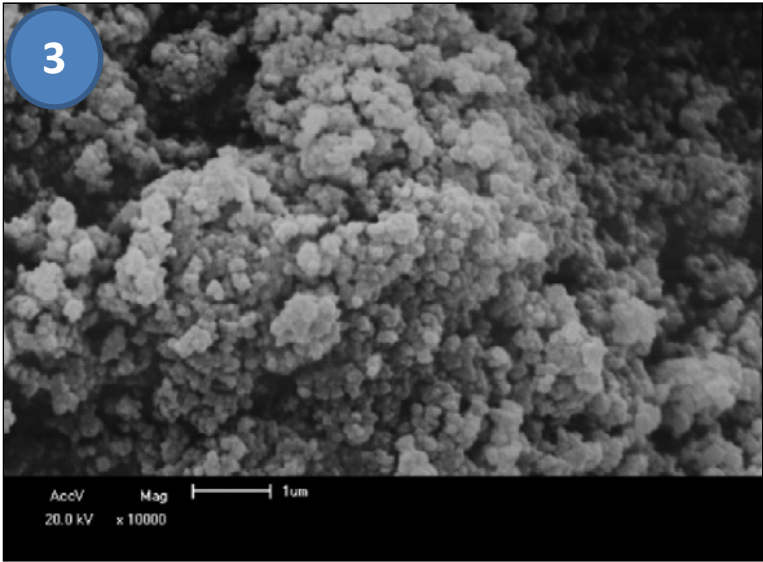
Pristine zero valent iron NP (Kanel et al., 2006)



As(V) adsorbed to a ZVI reactive barrier (Kanel et al., 2006)



Zero valent iron NP with an oxide shell (Ramos et al., 2009)

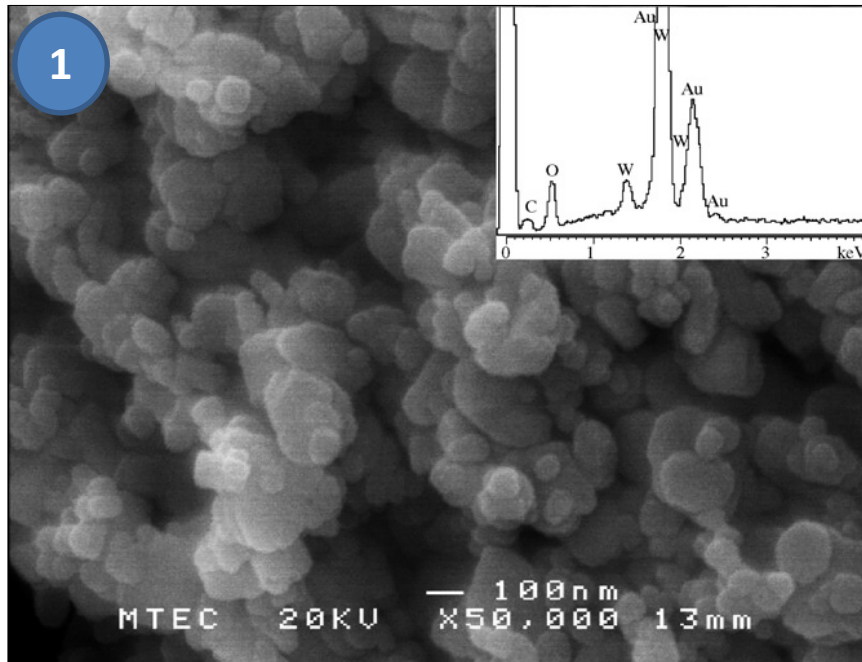


Magnetite particles formed from photooxidation (Silva et al., 2012)

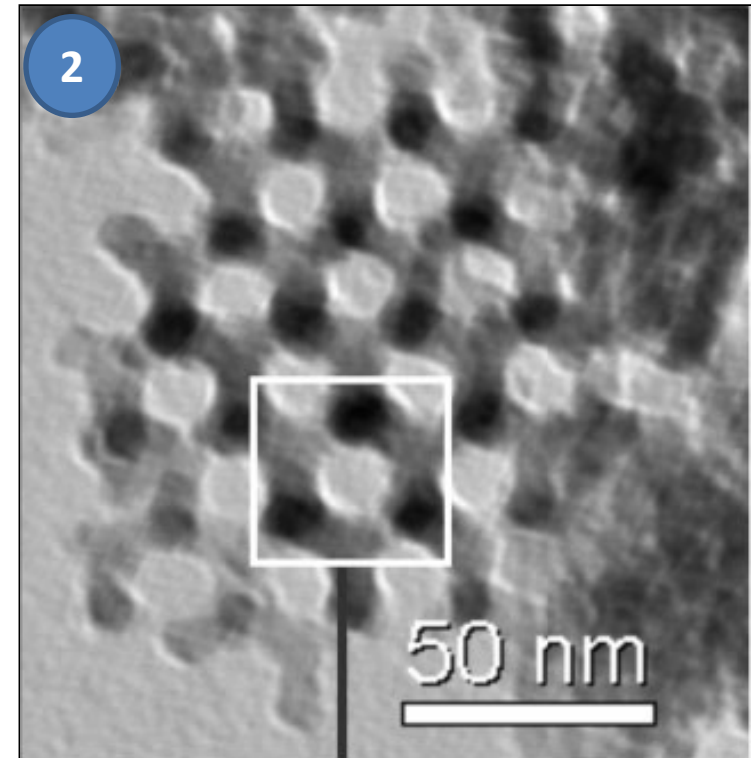
Zero valent iron nanoparticles– References (Clockwise from top left)

- 1) Pristine zero valent iron nanoparticles
 - 1) Imaged by TEM
 - 2) Kanel, S.; Greneche, J.; Choi, H. Arsenic (V) Removal from Groundwater Using Nano Scale Zero-Valent Iron as a Colloidal Reactive Barrier Material. *Environmental Science and Technology*, **2006**, 40, pp. 2045-2050.
- 2) Arsenic (V) adsorbed onto a reactive barrier of zero valent iron nanoparticles
 - 1) Imaged by SEM (at micron scale)
 - 2) Kanel, S.; Greneche, J.; Choi, H. Arsenic (V) Removal from Groundwater Using Nano Scale Zero-Valent Iron as a Colloidal Reactive Barrier Material. *Environmental Science and Technology*, **2006**, 40, pp. 2045-2050.
- 3) Magnetite particles formed from the precipitation and photooxidation of acid mine drainage
 - 1) Imaged by SEM (at micron scale)
 - 2) Silva, R.; Castro, C.; Vigânico, E.; Petter, C.; Schneider, I. Selective precipitation/UV production of magnetite particles obtained from the iron recovered from acid mine drainage. *Minerals Engineering*, **2012**, 29, pp. 22-27.
- 4) Zero valent iron nanoparticle with a formed oxide coating
 - 1) Imaged by TEM
 - 2) Ramos, M.; Yan, W.; Li, X.; Koel, B.; Zhang, W. Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the Core-Shell Structure. *Journal of Physical Chemistry C Letters*, **2009**, 113, pp. 14591-14594.

WO₃ nanoparticles- Images



WO₃ nanoparticles prepared by acid precipitation (Supothina et al. 2007)

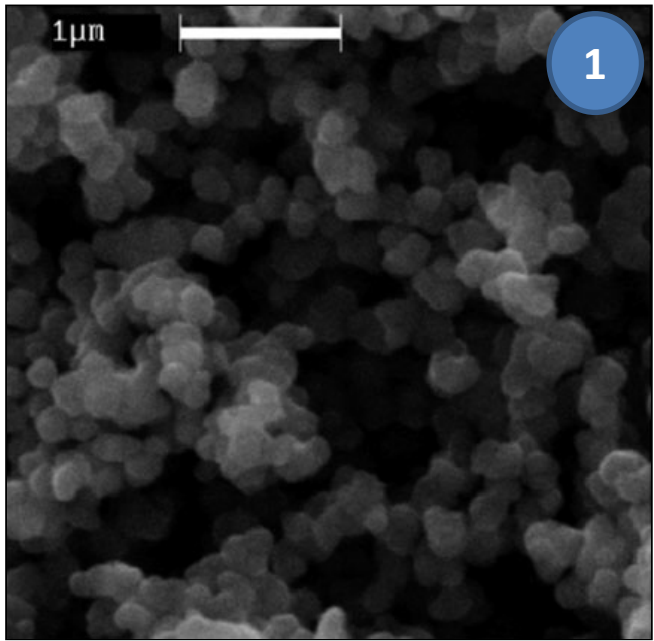


Tungsten oxide nanoparticles used for NO₂ gas sensing (Rossinyol et al., 2007)

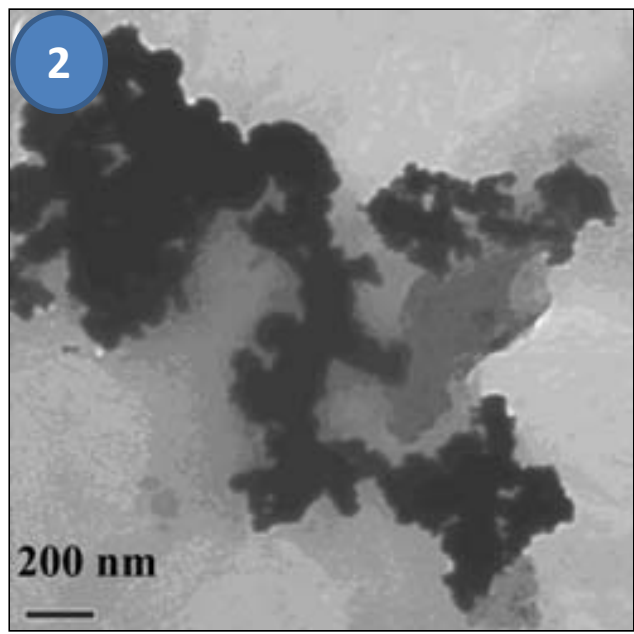
Zero valent iron nanoparticles– References (Clockwise from top left)

- 1) Pristine tungsten oxide (WO_3) nanoplates
 - 1) Imaged by SEM
 - 2) Supothina, S.; Seeharaj, P.; Yoriya, S.; Sriyudthsak, M. Synthesis of tungsten oxide nanoparticles by acid precipitation method. *Ceramics International*, **2007**, 33, pp. 931-936.
- 2) Tungsten oxide nanoparticles templated on a KIT-6 structure for gas-sensing applications
 - 1) Imaged by TEM
 - 2) Rossinyol, E.; Prim, A.; Pellicer, E.; Arbio, J.; Hernández-Ramírez, F.; Peiró, F.; Cornet, A.; Morante, J.; Solovyov, L.; Tian, B.; Bo, T; Zhao, D. Synthesis and Characterization of Chromium-Doped Mesoporous Tungsten Oxide for Gas-sensing Applications. *Advanced Functional Materials*, **2007**, 17, pp. 1801-1806.

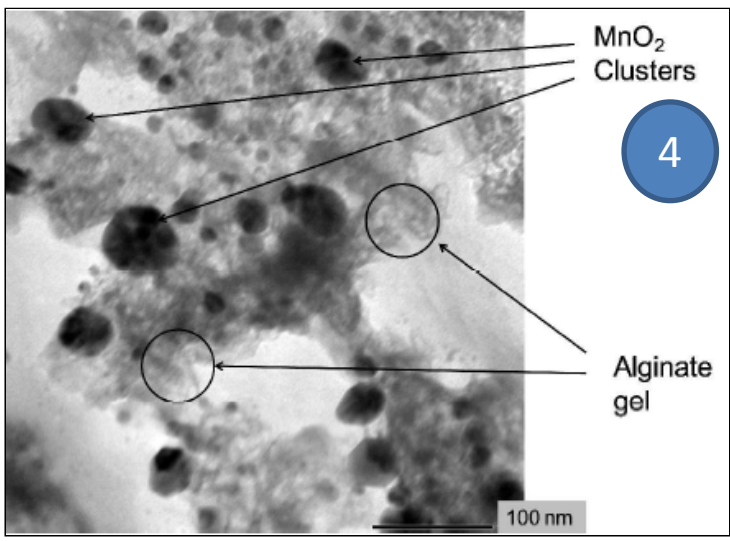
MnO₂ nanoparticles- Images



Pristine MnO₂ nanoparticles (Ching et al., 2011)



Carbon coated MnO₂ nanoparticles for catalysis (Roche et al., 2008)



MnO₂ aggregation in the presence of biomolecules and divalent cations (Huangfu et al., 2013)

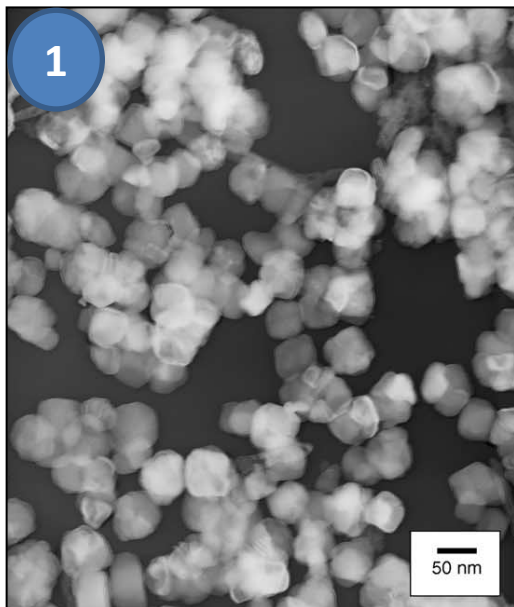


Biogenically synthesized manganese oxides (Miyata et al., 2007)

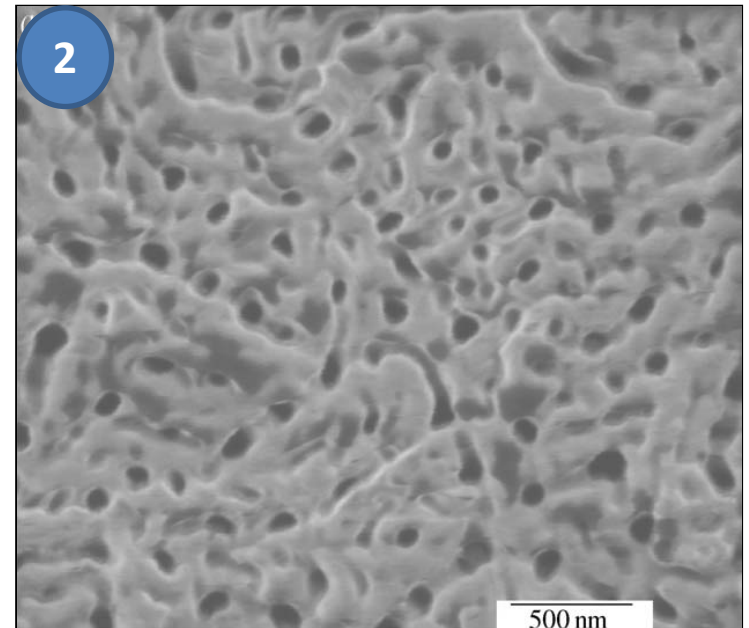
MnO₂ – References (Clockwise from top left)

- 1) Pristine manganese oxide (MnO₂) nanoparticles
 - 1) Imaged by SEM (at micron scale)
 - 2) Ching, S.; Kriz, D.; Luthy, K.; Njagi, E.; Suib, S. Self-assembly of manganese oxide nanoparticles and hollow spheres. Catalytic activity in carbon monoxide oxidation. *Chemical Communications*, **2011**, 47, pp. 8286-8288.
- 2) Manganese oxide / carbon electrocatalysts
 - 1) Imaged by TEM
 - 2) Roche, I.; Chaînet, E.; Chatenet, M.; Vondrák, J. Durability of carbon-supported manganese oxide nanoparticles for the oxygen reduction reaction (ORR) in alkaline medium. *Journal of Applied Electrochemistry*, **2008**, 38, pp. 1195-1201.
- 3) Manganese (II) oxidation by *Acremonium* sp. Strain KR21-2 to form manganese oxides
 - 1) Imaged by TEM
 - 2) Miyata, N.; Tani, Y.; Sakata, M.; Iwahori, K. Microbial Manganese Oxide Formation and Interaction with Toxic Metal Ions. *Journal of Bioscience and Bioengineering*, **2007**, 104, pp.1-8.
- 4) Aggregated Mn₂ nanoparticles in the presence of 10mM calcium nitrate and 2 mg/L alginate
 - 1) Imaged by TEM
 - 2) Huangfu, X.; Jiang, J.; Ma, J.; Yongze, L.; Jing, Y. Aggregation Kinetics of Manganese Dioxide Colloids in Aqueous Solution: Influence of Humic Substances and Biomacromolecules. *Environmental Science and Technology*, **2013**, Just Accepted.

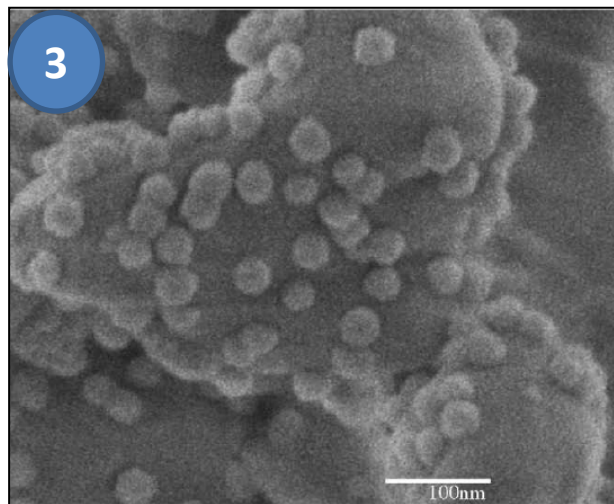
Al₂O₃ nanoparticles- Images



α -Al₂O₃ nanoparticles formed in the presence of Na(AOT) (Park et al., 2005)



Nano-porous anodised alumina coating on titanium (Briggs et al., 2004)

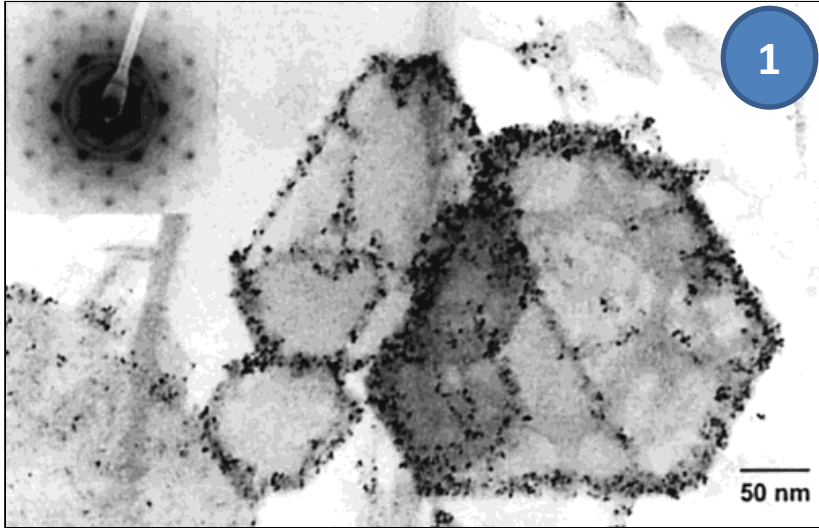


Silica-alumina nanoparticle heteroaggregation (Garcia-Perez et al., 2006)

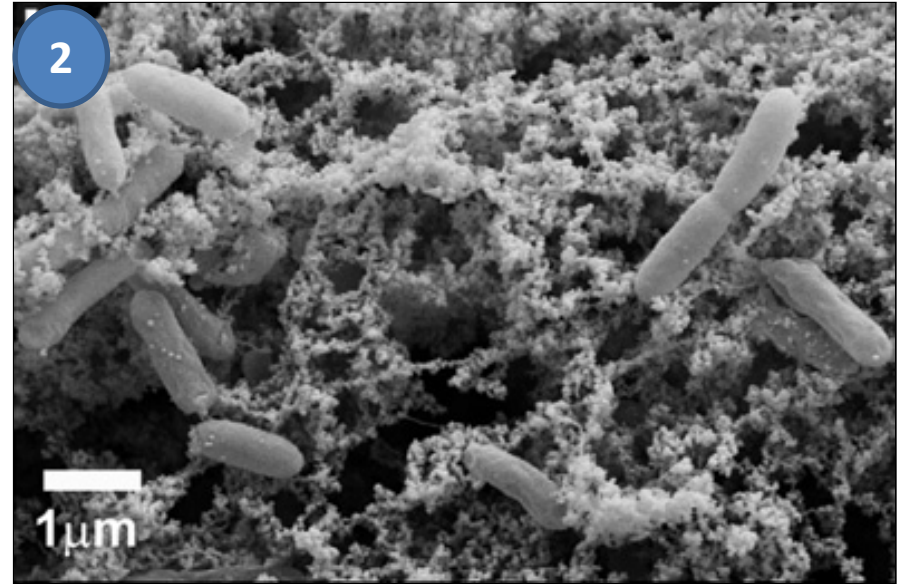
Al₂O₃ – References (Clockwise from top left)

- 1) α -Al₂O₃ nanoparticles form in the presence of sodium bis(2-ethylhexyl) sulfosuccinate
 - 1) Imaged by SEM
 - 2) Park, Y.; Tadd, E.; Zubris, M.; Tannenbaum, R. Size-controlled synthesis of alumina nanoparticles from aluminum alkoxides. *Materials Research Bulletin*, **2005**, 40, pp.1506-1512.
- 2) Nano-porous anodised alumina coating on titanium for surgical implants
 - 1) Imaged by SEM
 - 2) Briggs, E.; Walpole, A.; Wilshaw, P.; Karlsson, M.; Pålsgård, E. Formation of highly adherent nano-porous alumina on Ti-based substrates: a novel bone implant coating. *Journal of Materials Science: Materials in Medicine*, **2004**, 15, pp. 1021-1029.
- 1) Alumina colloids heteroaggregated with silica nanoparticles
 - 1) Imaged by Cryo-FEG-SEM
 - 2) Garcia-Perez, P.; Pagnoux, C.; Rossignol, F.; Baumard, J. Heterocoagulation between SiO₂ nanoparticles and Al₂O₃ submicronparticles; influence of the background electrolyte. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, **2006**, 281, pp. 58-66.

UO₂ nanoparticles- Images



Uraninite nanoparticles precipitated on green rusts
(O'Loughlin et al., 2003)

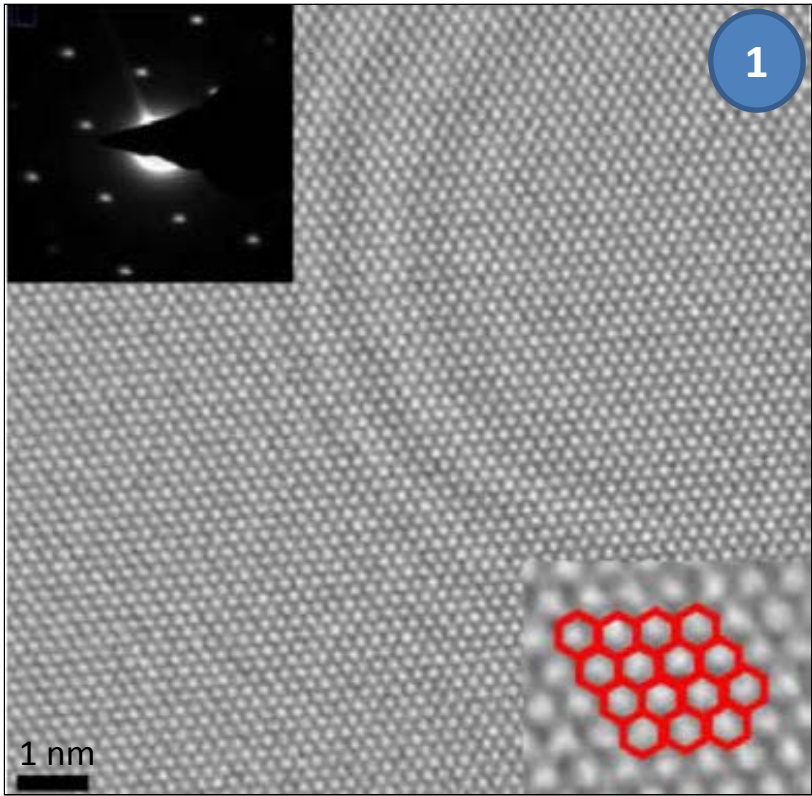


Uranium nanoparticles precipitated from bio-reduction of U(VI)
by *Shewanella oneidensis* (Burgos et al., 2008)

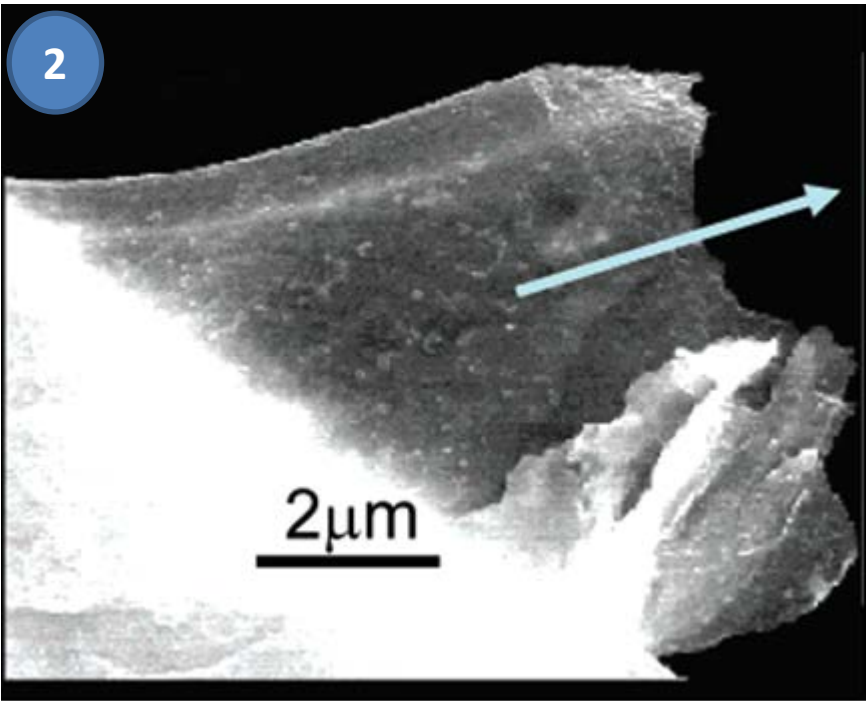
UO₂ – References (Clockwise from top left)

- 1) Uraninite nanoparticles precipitated on mixed Fe(II)/Fe(III) hydroxides
 - 1) Imaged by TEM
 - 2) O'Loughlin, E.; Kelly, S.; Cook, R.; Csencsits, R.; Kemner, K. Reduction of Uranium (VI) by Mixed Iron (II)/ Iron(III) Hydroxide (Green Rusts: Formation of U₂ Nanoparticles. *Environmental Science and Technology*, **2003**, 37, pp. 721-727.
- 2) Uraninite nanoparticles precipitated from soluble U(VI) by *Shewanella oneidensis* MR-1 strain
 - 1) Imaged by SEM (at micron scale)
 - 2) Burgos, W.; McDonough, J.; Senko, J.; Zhang, G.; Dohnalkova, A.; Kelly, S.; Gorby, Y.; Kemner, K. Characterization of uraninite nanoparticles produced by *Shewanella oneidensis* MR-1. *Geochimica et Cosmochimica Acta*, **2008**, 72, pp. 4901-4915.

Graphene - Images



Graphene layer produced by chemical vapor deposition
(Park et al., 2010)

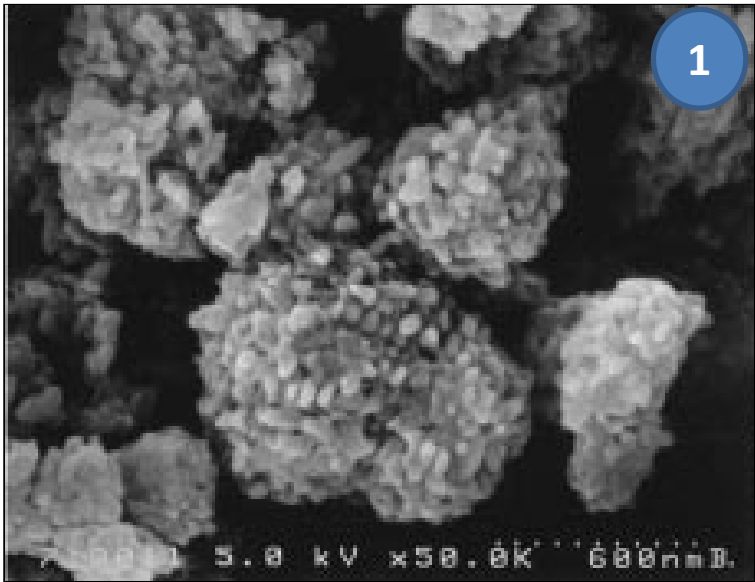


Graphene sheets with embedded gold nanoparticles
(Muszynski et al., 2008)

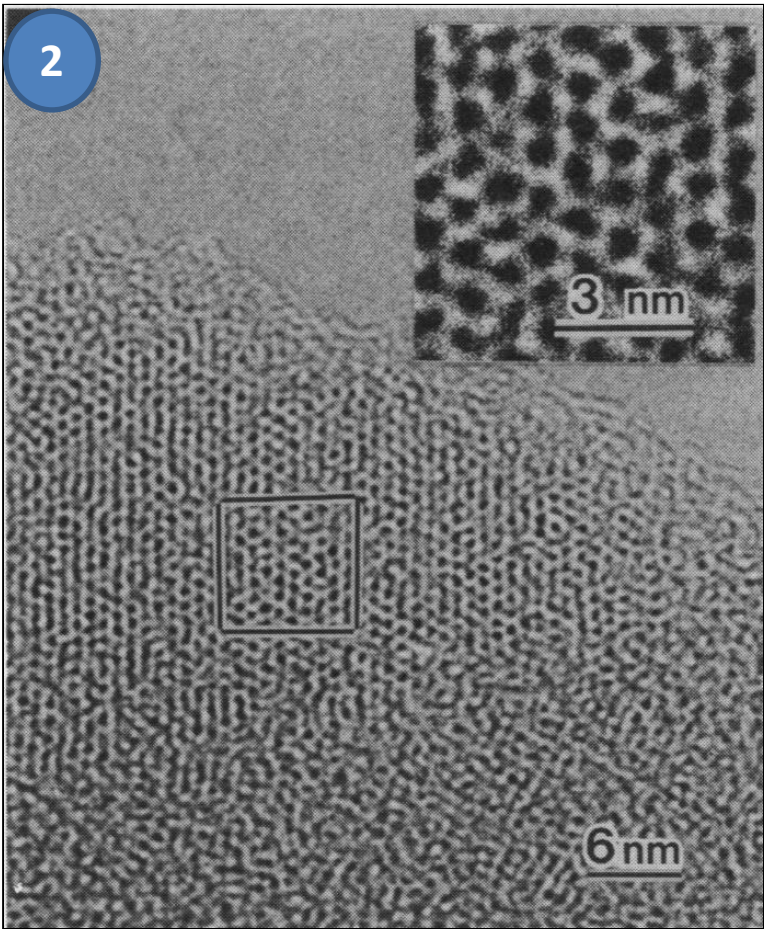
Graphene – References (Clockwise from top left)

- 1) Graphene prepared by chemical vapor deposition
 - 1) Imaged by TEM
 - 2) Park, H.; Meyer, J.; Rother, S.; Skákalová, V. Growth and properties of few-layer graphene prepared by chemical vapor deposition. *Carbon*, **2010**, 48, pp. 1088-1094.
- 2) Graphene sheets with embedded gold nanoparticles for catalysis applications
 - 1) Imaged by SEM (at micron scale)
 - 2) Muszynski, R.; Seger, B.; Kamat, P. Decorating Graphene Sheets with Gold Nanoparticles. *Journal of Physical Chemistry C Letters*, **2008**, 112, pp. 5263-5266.

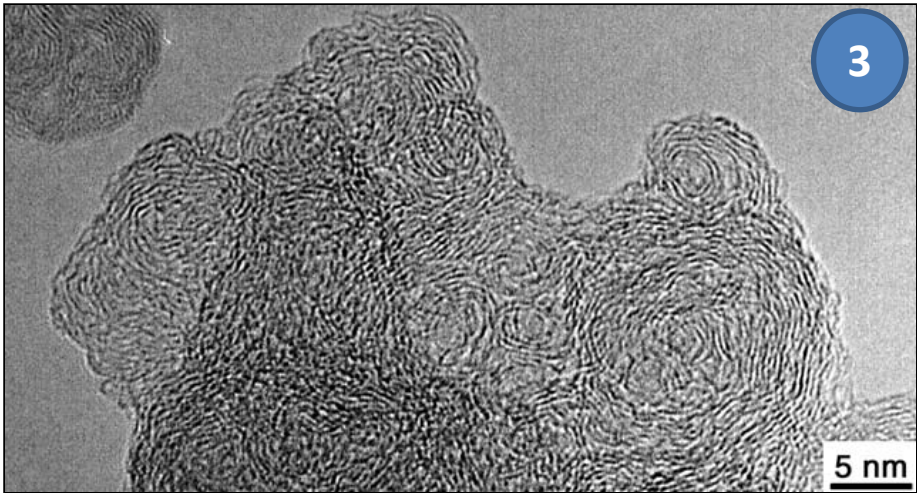
Fullerenes- Images



SEM image of C₆₀ powder (Gusev et al., 1999)



Fullerene particles found in precambrian rocks from Russia (Buseck et al., 1992)

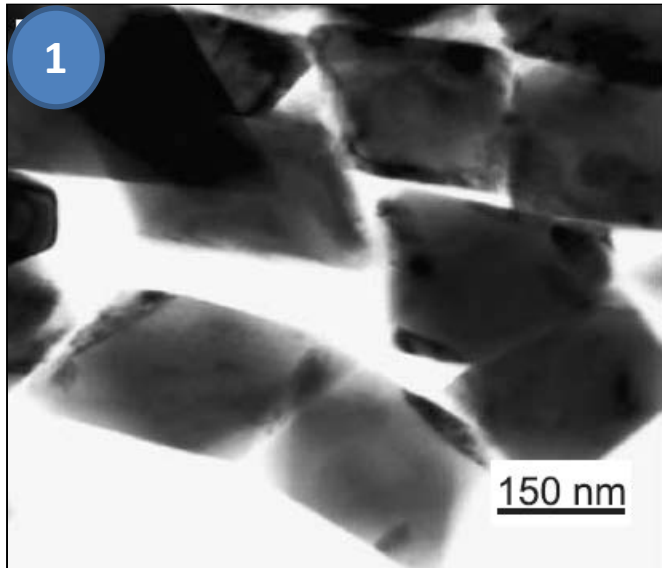


Fullerene-like soot from a EuroIV diesel engine (Su et al., 2004)

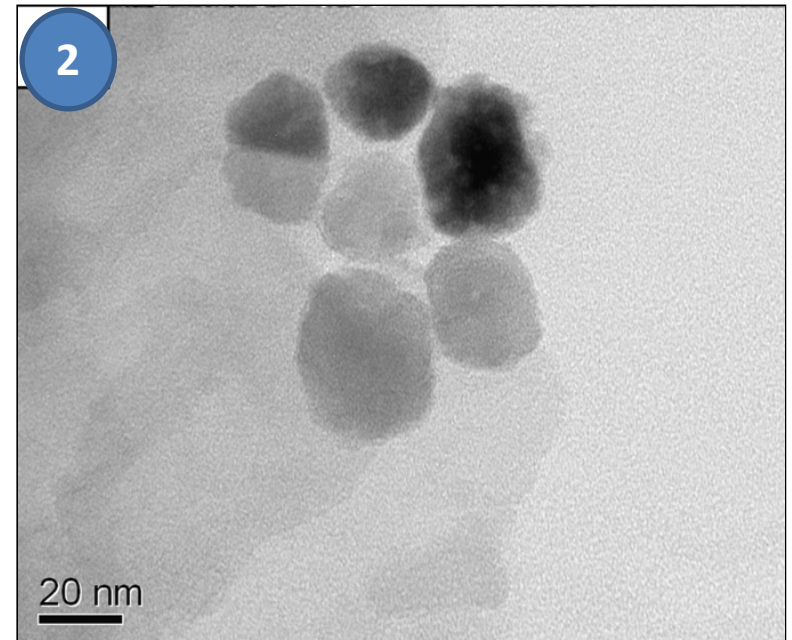
Fullerenes– References (Clockwise from top left)

- 1) SEM image of C₆₀ powder
 - 1) Imaged by SEM
 - 2) Gusez, Y.; Ruetsch, S.; Popeko, L.; Popeko, I. Nitrogen and Argon Adsorption and SEM Characterization of C₆₀ And C_{60/70} Fullerenes: Comparison with Graphite. *Journal of Physical Chemistry B*, **1999**, *103*, pp. 6498-6503.
- 2) TEM images of fullerenes found in a precambrian rock from Russia
 - 1) Imaged by TEM
 - 2) Buseck, P.; Tsipursky, S.; Hettich, R. Fullerenes from the Geological Environment. *Science*, **1992**, *257*, pp. 215-217.
- 3) TEM image of fullerene-like soot from EuroIV diesel engine
 - 1) Imaged by TEM
 - 2) Su, D.; Müller, J.-O; Jentoft, R.; Rothe, D.; Jacob, E.; Schlögl, R. Fullerene-like soot from EuroIV diesel engine: consequences for catalytic automotive pollution control. *Topics in Catalysis*, **2004**, *30/31*, pp. 241-245.

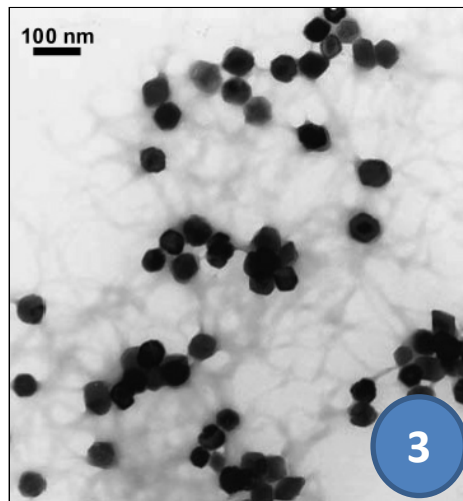
1) Fe₂O₃- Images



TEM image of hematite nanoparticles coated with HPC (Jing and Wu, 2004)



Hematite nanoparticles found in free-drifting icebergs (Shaw et al., 2011)

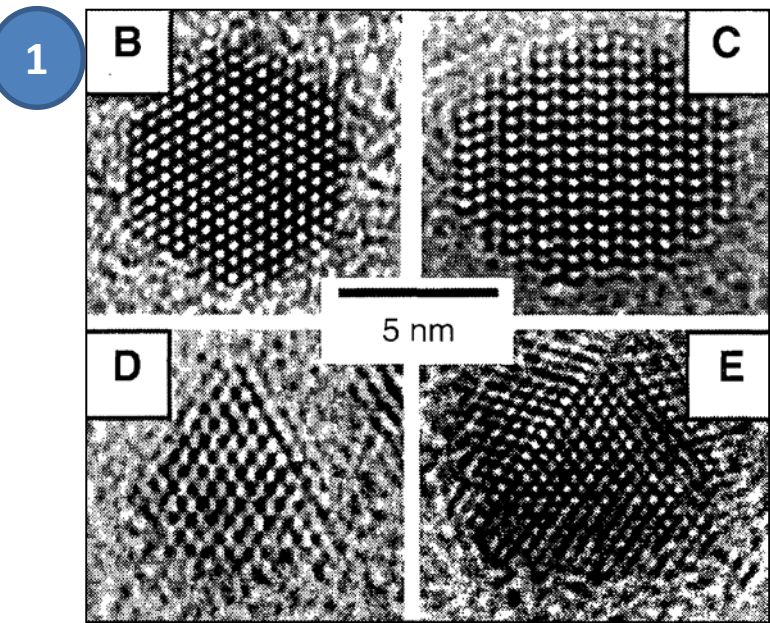


Aggregated alginate-coated hematite nanoparticles (Chen et al., 2006)

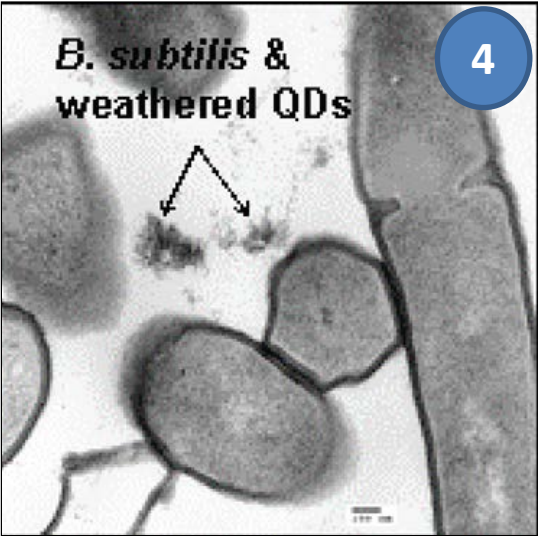
Graphene – References (Clockwise from top left)

- 1) TEM image of hematite nanoparticles coated with hexadecylpyridinium chloride (HPC)
 - 1) Imaged by TEM
 - 2) Jing, Z.; Wu, S. Synthesis and characterization of monodisperse hematite nanoparticles modified by surfactants via hydrothermal approach. *Materials Letters*, **2004**, 58, pp.3637-3640.
- 2) N/A hematite nanoparticle in a product
- 3) Hematite nanoparticles found in free-drifting icebergs
 - 1) Imaged by TEM
 - 2) Shaw, T.; Raiswell, R.; Hexel, C.; Vu, H.; Moore, W.; Dudgeon, R.; Smith Jr., K. Input, composition, and potential impact of terrigenous material from free-drifting icebergs in the Weddell Sea. *Deep-Sea Research II*, **2011**, 58, pp. 1376-1383.
- 4) Aggregated alginate-coated hematite nanoparticles in the presence of divalent salts
 - 1) Imaged by TEM
 - 2) Chen, K.; Mylon, S.; Elimelech, M. Aggregation Kinetics of Aligned-Coated Hematite Nanoparticles in Monovalent and Divalent Electrolytes. *Environment Science and Technology*, **2006**, 40, pp. 1516-1523.

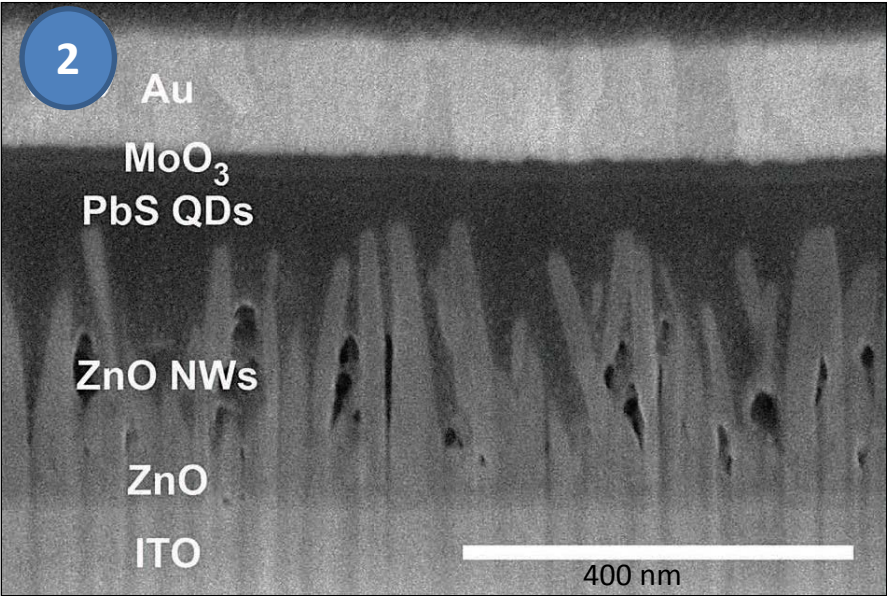
Quantum dots - Images



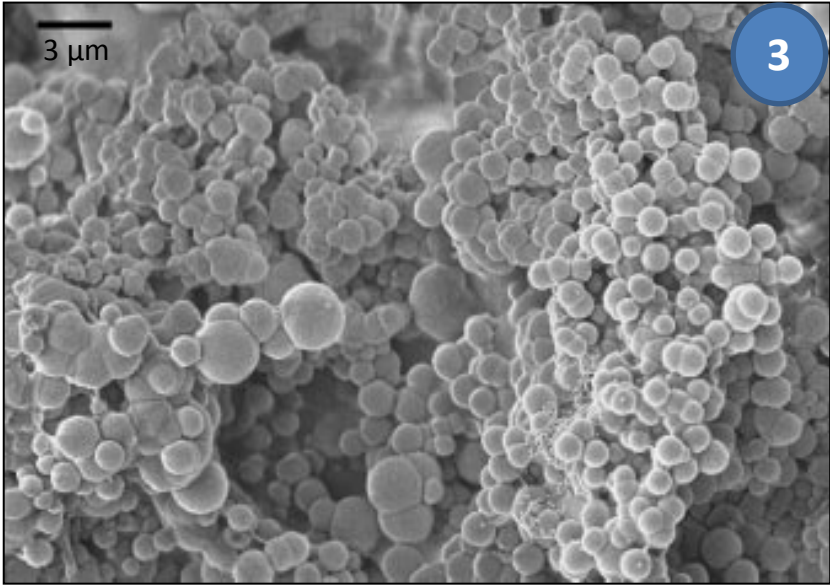
TEM images of various quantum dots (Alivisatos, 1996)



TEM images of weathered quantum dot clusters (Mahendra et al., 2008)



PbS Quantum dots in solar cells (Jean et al., 2013)

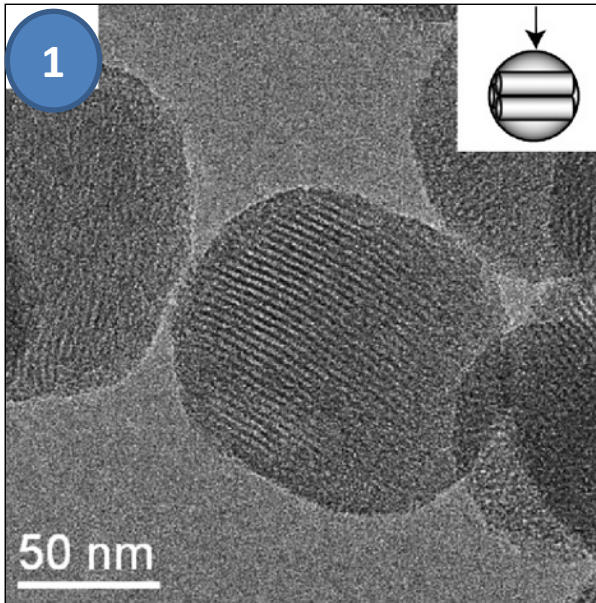


Spherical aggregates of ZnS nanoparticles formed in a biofilm (Labrenz et al., 2000)

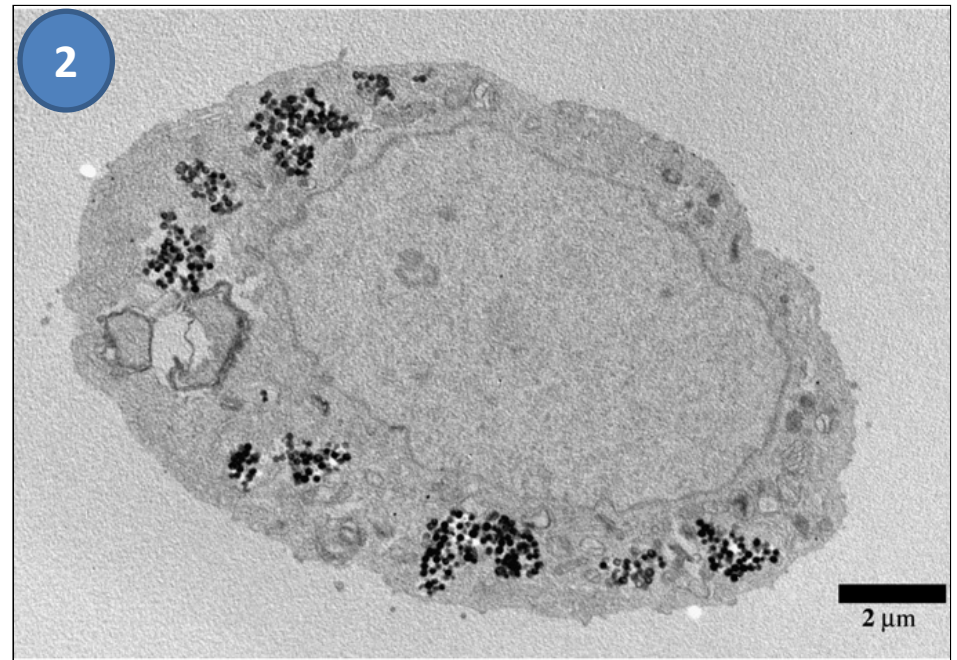
Quantum dots – References (Clockwise from top left)

- 1) TEM images of various quantum dots lattices
 - 1) Imaged by TEM
 - 2) Alivisatos, A. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science*, **1996**, 271, pp. 933-937.
- 2) Lead sulfide quantum dots in solar cells
 - 1) Imaged by SEM
 - 2) Jean, J.; Chang, S.; Brown, P.; Cheng, J.; Rekemeyer, P.; Bawendi, M.; Gradečak, S.; Bulović, V. ZnO Nanowire Arrays for Enhanced Photocurrent in PbS Quantum Dot Solar Cells. *Advanced Materials*, **2013**, 25, pp. 2790-2796.
- 3) Spherical aggregates of ZnS nanoparticles formed in a biofilm
 - 1) Imaged by SEM (at micron scale)
 - 2) Labrenz, M.; Druschel, G.; Thomsen-Ebert, T.; Gilbert, B.; Welch, S.; Stasio, G.; Bond, P.; Lai, B.; Kelly, S.; Banfield, J. Formation of Sphalerite (ZnS) Deposits in Natural Biofilms of Sulfate-Reducing Bacteria. *Science*, **2000**, 290, pp. 1744-1747.
- 4) Weathered quantum dots clusters with *Bacillus subtilis*
 - 1) Imaged by TEM
 - 2) Mahendra, S.; Zhu, H.; Colvin, V.; Alvarez, P. Quantum Dot Weathering Results in Microbial Toxicity. *Environmental Science and Technology*, **2008**, 42, pp. 9424-9430.

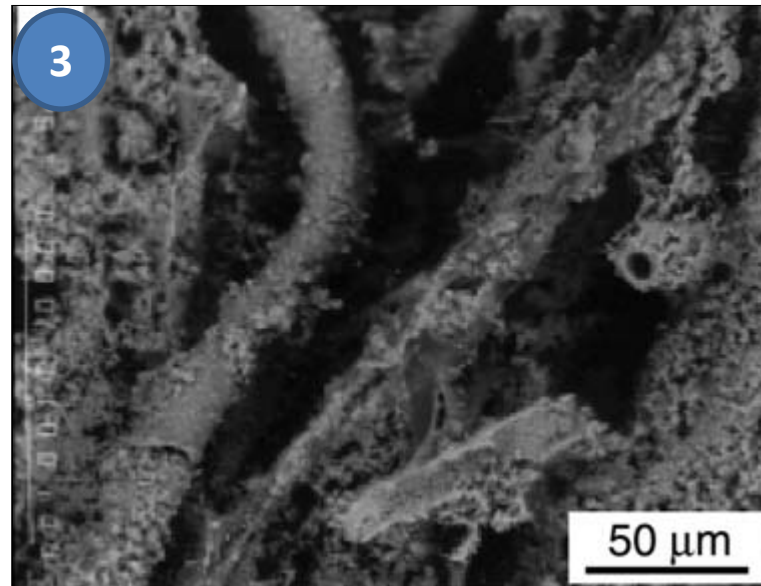
SiO₂ nanoparticles - Images



TEM image of mesoporous silica (Slowing et al., 2008)



Endocytosed mesoporous silica in a HeLa cell (Slowing et al., 2008)



Silicified filamentous microbes in geothermal waters (Inagaki et al., 2003)

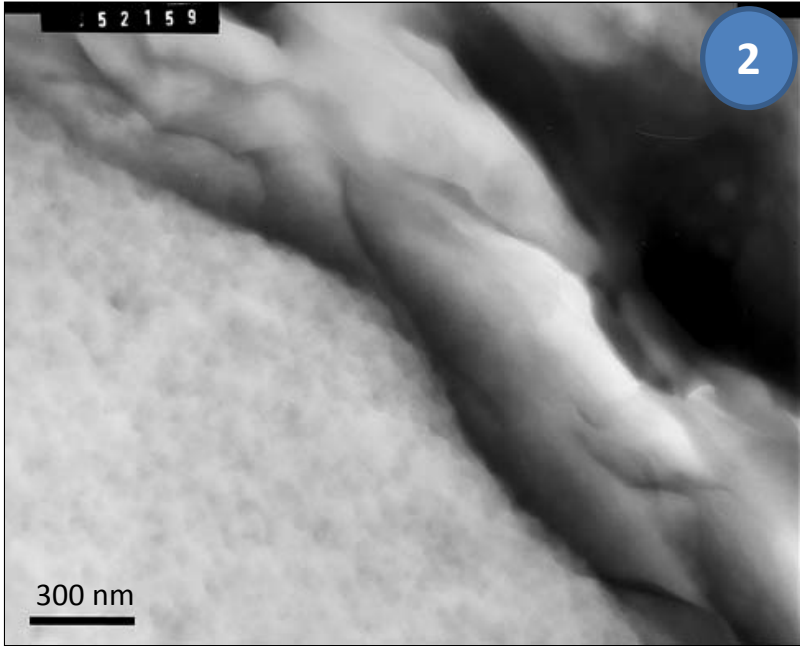
SiO₂ nanoparticles – References (Clockwise from top left)

- 1) Mesoporous silica imaged perpendicular to pores
 - 1) Imaged by TEM
 - 2) Slowing, I.; Vivero-Escoto, J.; Wu, C.; Lin, V. Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers. *Advanced Drug Delivery Review*, **2008**, 60, pp. 1278-1288.
- 2) Mesoporous silica endocytosed by HeLa cells
 - 1) Imaged by TEM (at micron scale)
 - 2) Slowing, I.; Vivero-Escoto, J.; Wu, C.; Lin, V. Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers. *Advanced Drug Delivery Review*, **2008**, 60, pp. 1278-1288.
- 3) Silicified filamentous microbes found in geothermal waters
 - 1) Imaged by SEM (at micron scale)
 - 2) Inagaki, F.; Motomura, Y.; Ogata, S. Microbial silica deposition in geothermal hot waters. *Applied Microbiology and Biotechnology*, **2003**, 60, pp. 605-611.

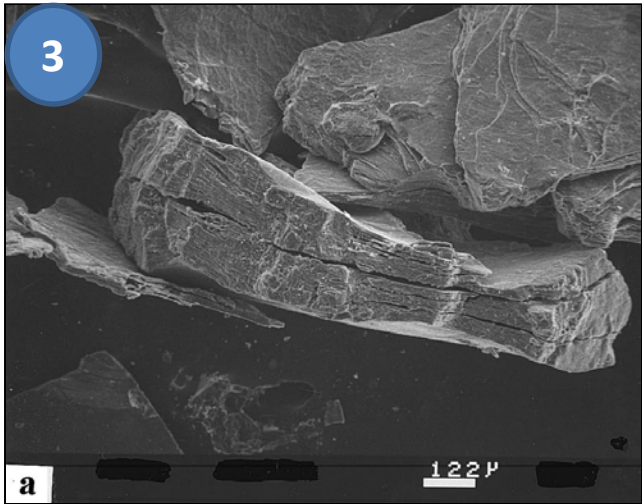
Nanoclay composites - Images



TEM of HDPE/nanoclay composite (Faruk et al., 2008)



TEM image of silicone/montmorillonite composite containing siloxane-modified montmorillonite clay (Simon et al., 2008)

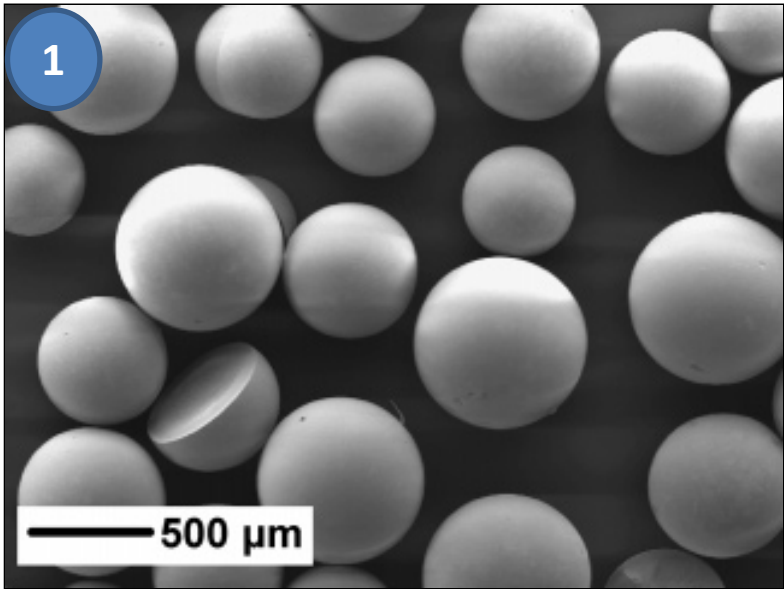


SEM image of phyllosilicate grains from regolith (Murphy et al., 1998)

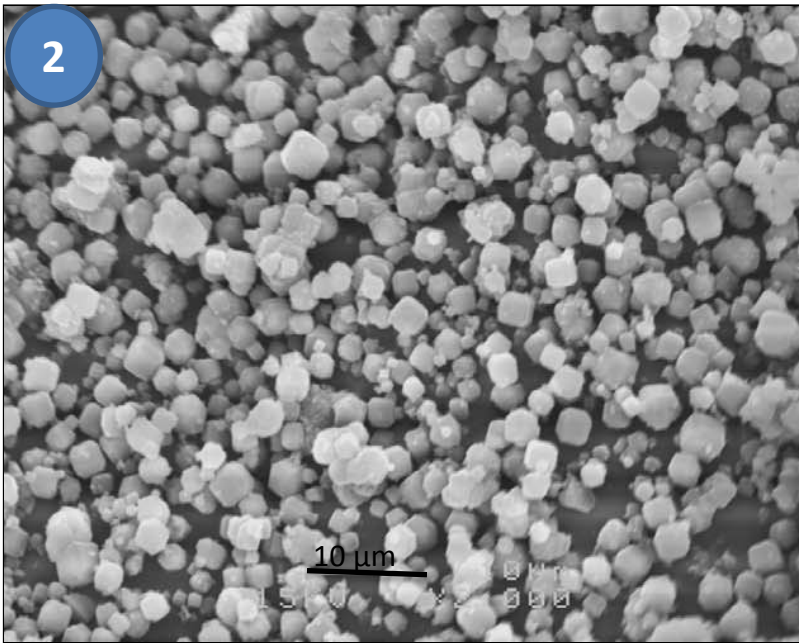
Nanoclay composites – References (Clockwise from top left)

- 1) TEM image of HDPE/nanoclay composites
 - 1) Imaged by TEM
 - 2) Faruk, O.; Matuana, L. Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Composites Science and Technology*, **2008**, 68, pp. 2073-2077.
- 2) TEM micrograph of silicone/montmorillonite composite containing 5 wt% siloxane-modified montmorillonite clay
 - 1) Imaged by TEM
 - 2) Simon, M.; Stafford, K.; Ou, D. Nanoclay Reinforcement of Liquid Silicone Rubber. *Journal of Inorganic and Organometallic Polymers and Materials*, **2008**, 18, pp. 364-373.
- 3) Regolith grain consisting of biotite and kaolinite clay.
 - 1) Imaged by SEM (at micron scale)
 - 2) Murphy, S.; Brantley, S.; Blum, A.; White, A.; Dong, H. Chemical weathering in a tropical watershed, Liguillo Mountains, Puerto Rico: II. Rate and mechanism of biotite weathering. *Geochimica et Cosmochimica Acta*, **1998**, 62m pp. 227-243.

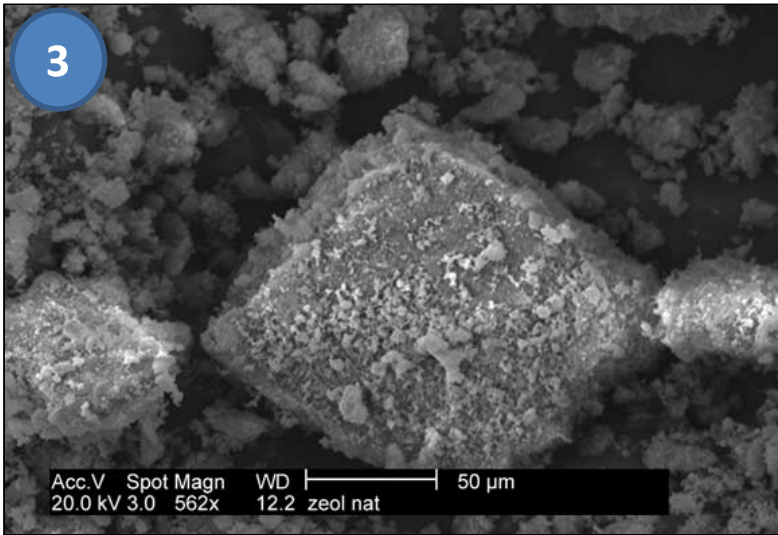
Zeolites - Images



Solid zeolite particles from resin templating (Tosheva et al., 2005)



Zeolite 4A for use as a detergent builder (Hui and Chao, 2006)



SEM image of a naturally occurring Chilean zeolite (Englert and Rubio, 2005)

Zeolites – References (Clockwise from top left)

- 1) Solid zeolite particle from resin templating
 - 1) Imaged by SEM (at micron scale)
 - 2) Tosheva, L.; Valtchev, V. Nanozeolites: Synthesis, Crystallization Mechanisms, and Applications. *Chemistry of Materials*, **2005**, 17, pp. 2494-2513.
- 2) Zeolite 4A synthesized from coal fly ash
 - 1) Imaged by SEM (at micron scale)
 - 2) Hui, K.; Chao, C. Pure, single phase, high crystalline, camfered-edge zeolite 4A synthesized from coal fly ash for use as a builder in detergents. *Journal of Hazardous Materials B*, **2006**, 137, pp. 401-409.
- 3) Image of a grain of a naturally occurring Chilean zeolite
 - 1) Imaged by SEM (at micron scale)
 - 2) Englert, A.; Rubio, J. Characterization and environmental application of a Chilean natural zeolite. *International Journal of Mineral Processing*, **2005**, 75, pp. 21-29.

Chitosan nanoparticles - Images

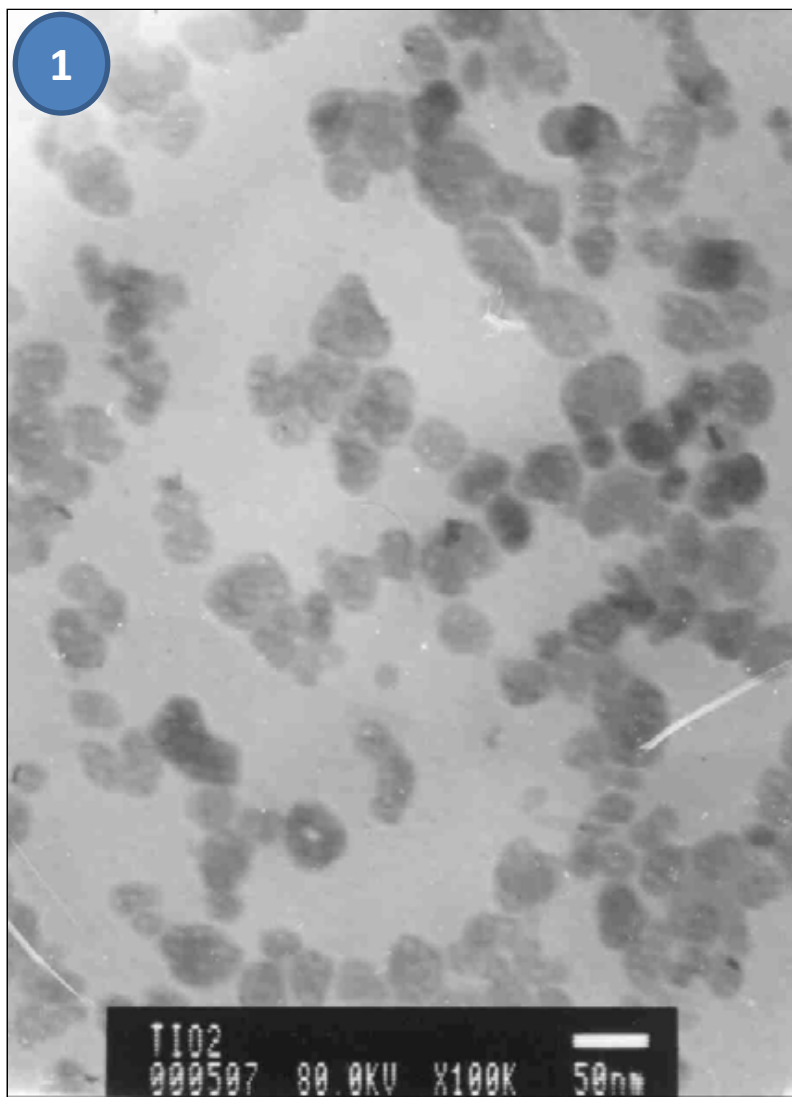
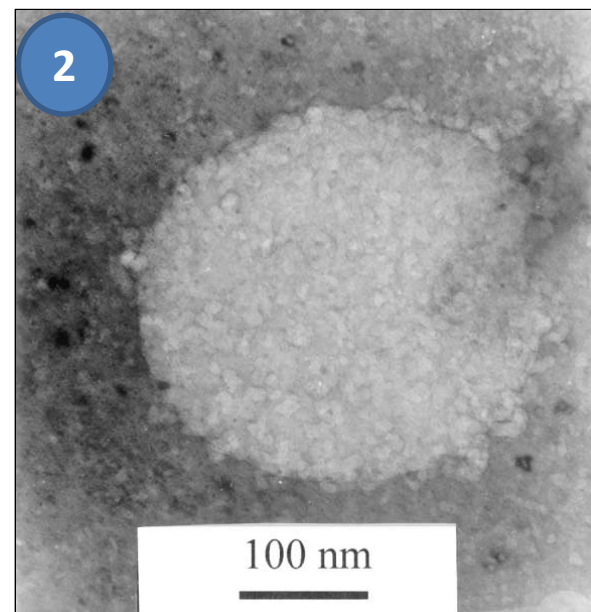


Image of 10% cross-linked chitosan nanoparticles
(Banerjee et al., 2002)

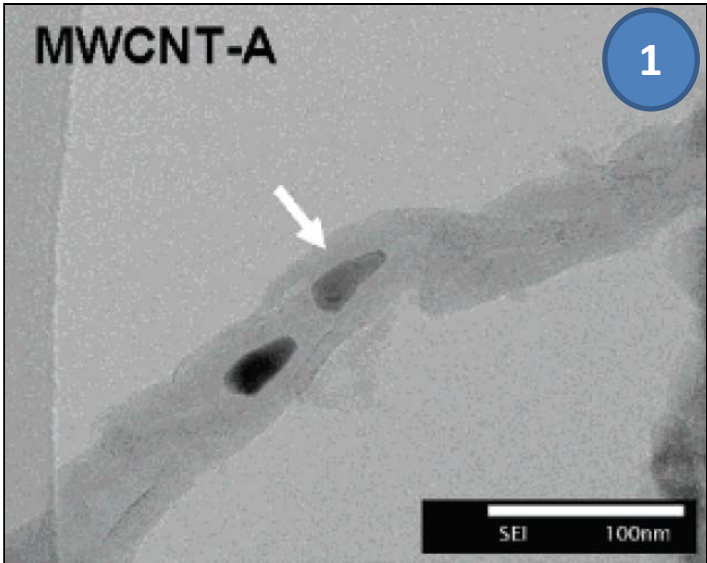


Chitosan nanoparticle loaded with cyclosporin A
(De Campos et al., 2001)

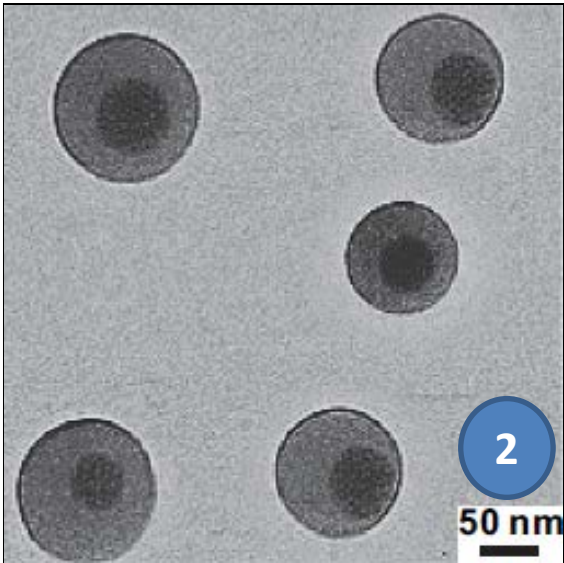
Chitosan nanoparticles – References (Clockwise from top left)

- 1) 10% cross-linked chitosan nanoparticles
 - 1) Imaged by TEM
 - 2) Banerjee, T.; Mitra, S.; Singh, A.; Sharma, R.; Maitra, A. Preparation, characterization and biodistribution of ultrafine chitosan nanoparticles. *International Journal of Pharmaceutics*, **2002**, 243, pp. 93-105.
- 2) Chitosan nanoparticle loaded with cyclosporin A
 - 1) Imaged by TEM
 - 2) De Campos, A.; Sánchez, A.; Alonso, M. Chitosan nanoparticles: a new vehicle for the improvement of the delivery of drugs to the ocular surface. Application to cyclosporin A. *International Journal of Pharmaceutics*, **2001**, 224, pp. 159-168.

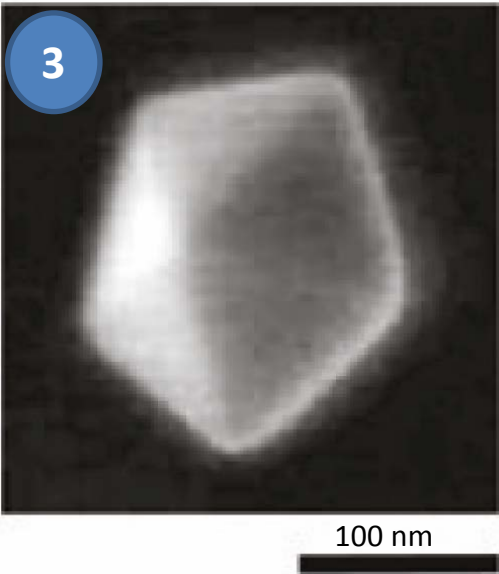
Highly functionalized nanoparticles - Images



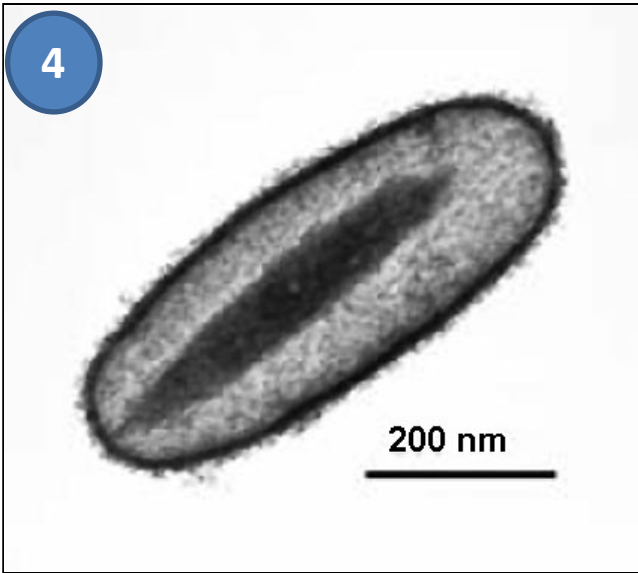
Residual metal catalyst embedded in carbon nanotube (Pumera, 2007)



Quantum dot nanoparticle surrounded by a PLGA shell to form a core-shell nanocomposite (Lee et al., 2010)



Silver nanoparticle decahedron formed in DMF (Tsuji et al., 2010)



Double-walled SnO₂ nano-cocoon with an α -Fe₂O₃ spindle embedded inside (Lou et al., 2007)

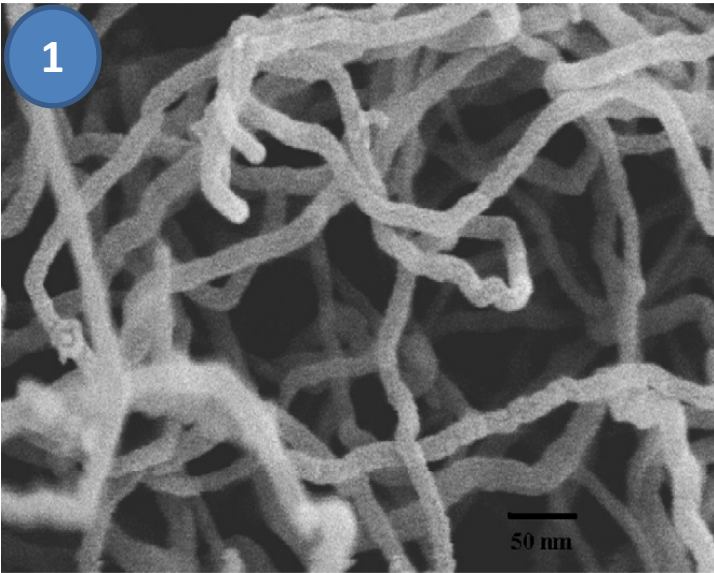
Highly functionalized nanoparticles – References (Clockwise from top left)

- 1) Residual metal catalyst embedded in carbon nanotube
 - 1) Imaged by TEM
 - 2) Pumera, M. Carbon Nanotubes Contain Residual Metal Catalyst Nanoparticles even after Washing with Nitric Acid at Elevated Temperature Because These Metal Nanoparticles Are Sheathed by Several Graphene Sheets. *Langmuir*, **2007**, 23, pp. 6453-6458.
- 2) Quantum dot nanoparticle surrounded by a PLGA shell to form a core-shell nanocomposite
 - 1) Imaged by TEM
 - 2) Lee, P.-W.; Hsu, S.-H.; Tsai, J.-S.; Chen, F.-R.; Huang, P.-J.; Ke, C.-J.; Liao, Z.-X.; Hsiao, C.-W.; Lin, H.-J.; Sung, H.-W. Multifunctional core-shell polymeric nanoparticles for transdermal DNA delivery and epidermal Langerhans cells tracking. *Biomaterials*, **2010**, 31, pp. 2425-2434.
- 3) Silver nanoparticle decahedron formed in DMF
 - 1) Imaged by SEM
 - 2) Tsuji, M.; Ogino, M.; Matsuo, R.; Kumagae, H.; Hikino, S.; Kim, T.; Yoon, S.-H. Stepwise Growth of Decahedral and Icosahedral Silver Nanocrystals in DMF. *Crystal Growth & Design*, **2010**, 10, pp. 296-301.
- 4) Double-walled SnO₂ nano-cocoon with an α -Fe₂O₃ spindle embedded inside
 - 1) Imaged by TEM
 - 2) Lou, X.; Yuan, C.; Archer, L. Double-walled SnO₂ Nano-Cocoons with Movable Magnetic Cores. *Advanced Materials*, **2007**, 19, pp. 3328-3332.

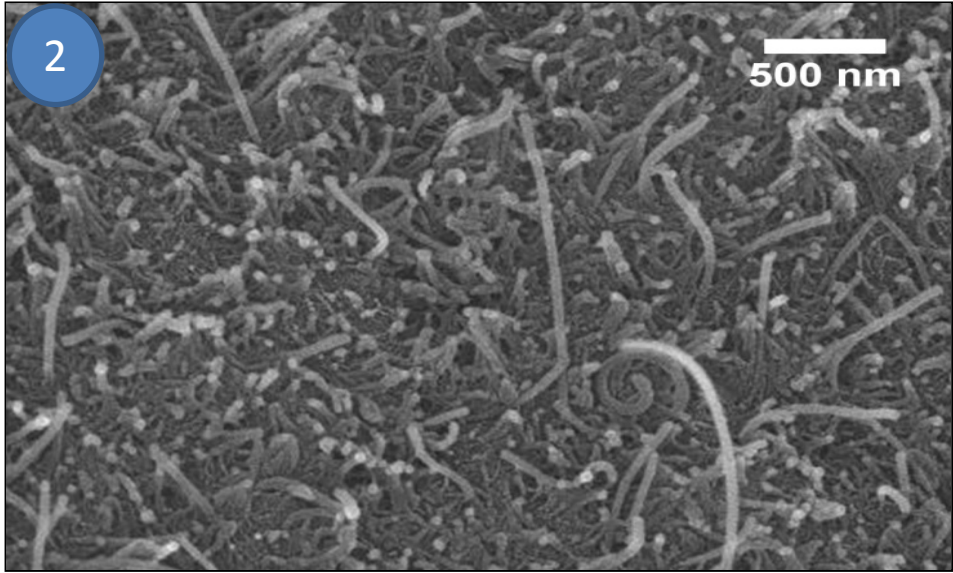
Current Status and Future Directions for Examining Engineered Nanoparticles in Natural Systems - Image Library Appendix

- The purpose of this image library is to provide examples of engineered nanoparticles and contrast them to images of their naturally occurring and/or biogenically produced counterparts. Images are provide (where possible) of the engineered particles in a product and in some cases, an image of an engineered particle that demonstrates obvious weathering effects.
- Apparent in most images is the similarity between the engineered nanomaterial and it's naturally occurring analogue. Though the engineered particles showed a greater degree of monodispersity, most particles both manufactured and natural have similar morphologies. The similarity between these images show the need for corroborative measurements to verify the identity and origin of these materials.
- There are some engineered materials that will possess very unique morphologies and surface coatings that are noticeably different than naturally occurring materials of the same composition (Slide 40). However, alterations made to these features upon entry into the environment is still a topic of research and not well understood. It is possible these highly-engineered material properties may be changed and altered to reflect materials more similar to those found in the environment as a result of chemical changes and weathering that may occur.
- It should be noted that imaging alone may not be sufficient to determine the origin and identity of nanomaterials. Other techniques that exploit key physio-chemical differences between these particles are necessary to detect and characterize these engineered nanomaterials upon entry into the environment.

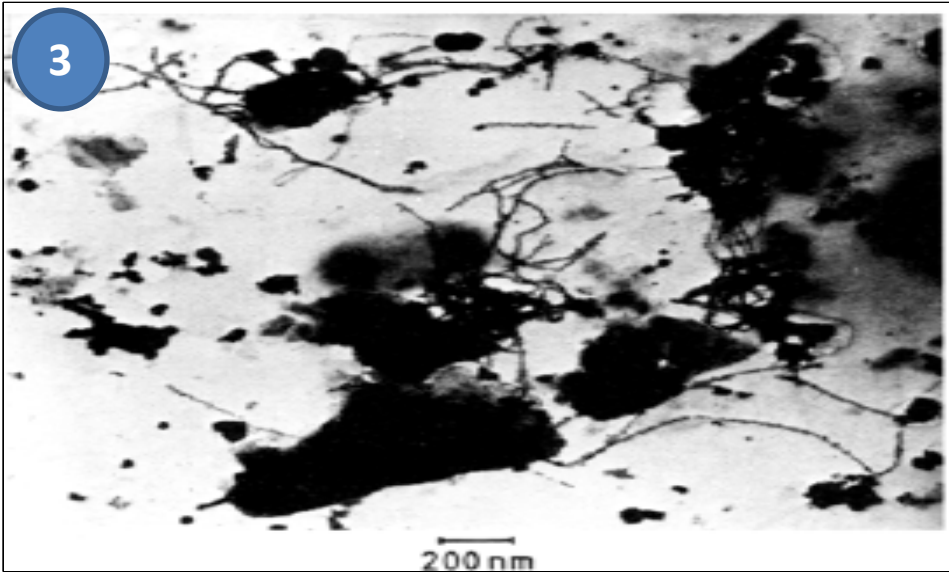
Carbon nanotubes - Images



SEM image of Purified CNTs (Lu et al., 2006)



5 % CNTs in PVOH (Fairbrother, unpublished data)



Organic filaments in lake (Buffle and Leppard, 1995)

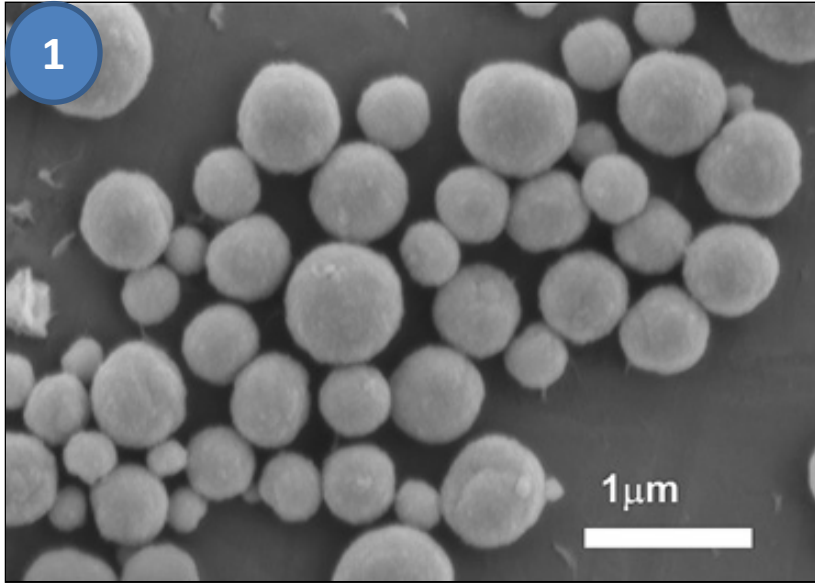
Carbon nanotubes – References (Clockwise from top left)

- 1) Scanning electron microscope image of purified multi-walled carbon nanotubes.
 - 1) Imaged by SEM.
 - 2) Lu, C.; Chung, Y.-L.; Chang, K.-F. Adsorption thermodynamic and kinetic studies of trihalomethanes on multiwalled carbon nanotubes. *Journal of Hazardous Materials B*. **2006**, 138, pp. 304-310

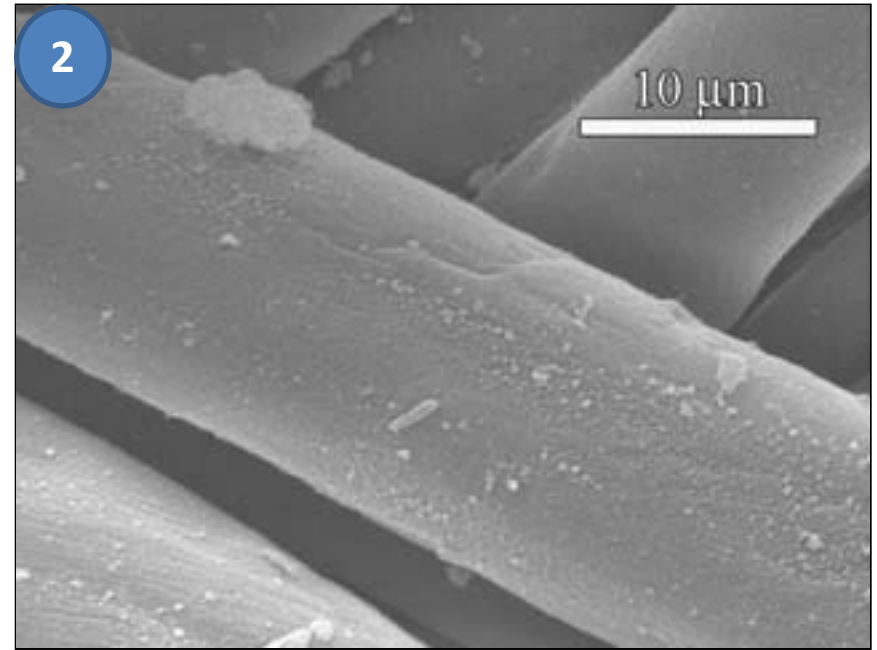
- 2) 5% CNTs in polyvinyl alcohol.
 - 1) Imaged by SEM
 - 2) Howard Fairbrother. John Hopkins University. *Unpublished Data*

- 3) Organic filaments in lake water.
 - 1) Observed by transmission electron microscopy.
 - 2) Buffle, J.; Leppard, G. G. Characterization of aquatic colloids and macromolecules. 1. Structure and Behavior of Colloidal Material. *Environmental Science and Technology*. **1995**, 29, pp. 2169-2175.

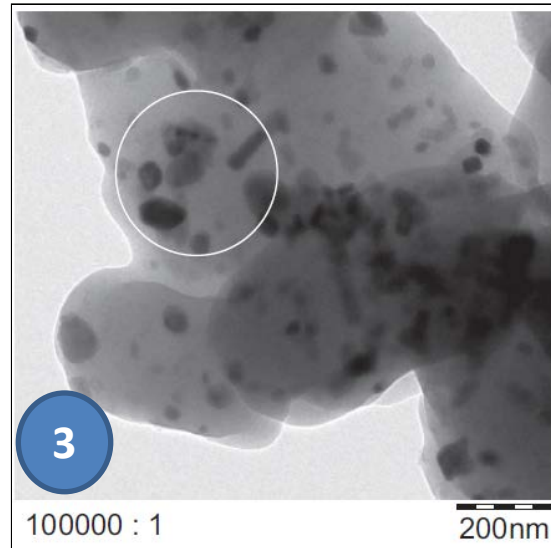
ZnO nanoparticles- Images



ZnO nanoparticles imaged by SEM (Dybowska et al., 2011)



ZnO applied to a cotton textile (Behceri et al. 2008)

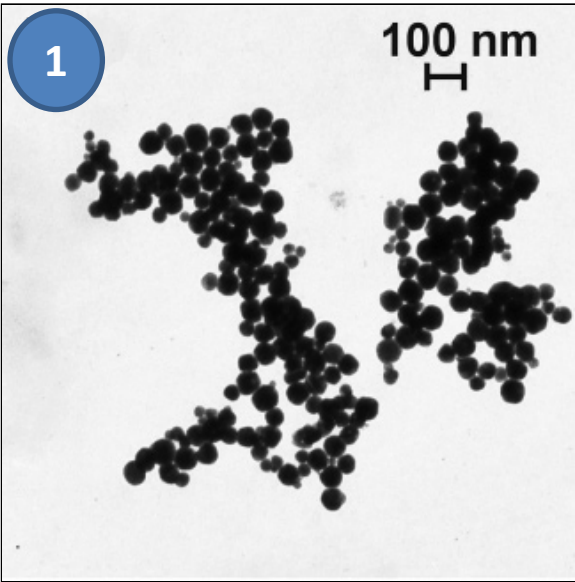


ZnO nanoparticles contained in a surface coating (Vorbau et al., 2009)

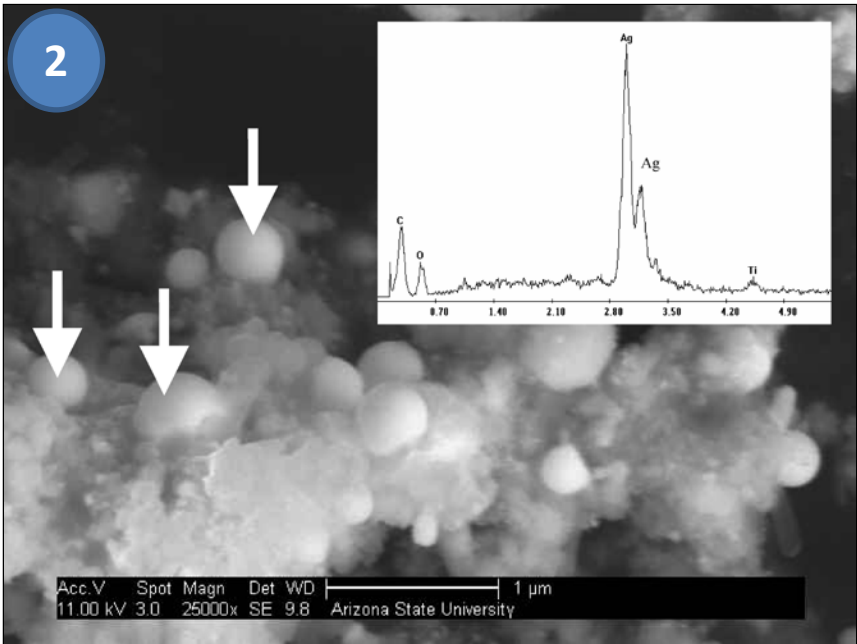
ZnO nanoparticles– References (Clockwise from top left)

- 1) Images of isotopically modified ZnO nanoparticles
 - 1) Imaged by SEM (at micron scale)
 - 2) Dybowska, A.; Croteau, M-N.; Misra, S.; Berhanu, D.; Luoma, S.; Christian, P.; O'Brien, P.; Valsami-Jones, E. Synthesis of isotopically modified ZnO nanoparticles and their potential as nanotoxicity tracers. *Environmental Pollution*, **2011**, 159, pp. 266-273.
- 2) ZnO nanoparticles applied to a cotton textile
 - 1) Imaged by SEM (at micron scale)
 - 2) Becheri, A.; Dürr, M.; Lo Nostro, P.; Baglioni, P. Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers. *Journal of Nanoparticle Research*, **2008**, 10, pp. 679-689.
- 3) ZnO nanoparticles released from a surface coating via abrasion.
 - 1) Imaged by TEM.
 - 2) Vorbau, M.; Hillemann, L.; Stintz, M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *Aerosol Science*, **2009**, 40, pp. 209-217.

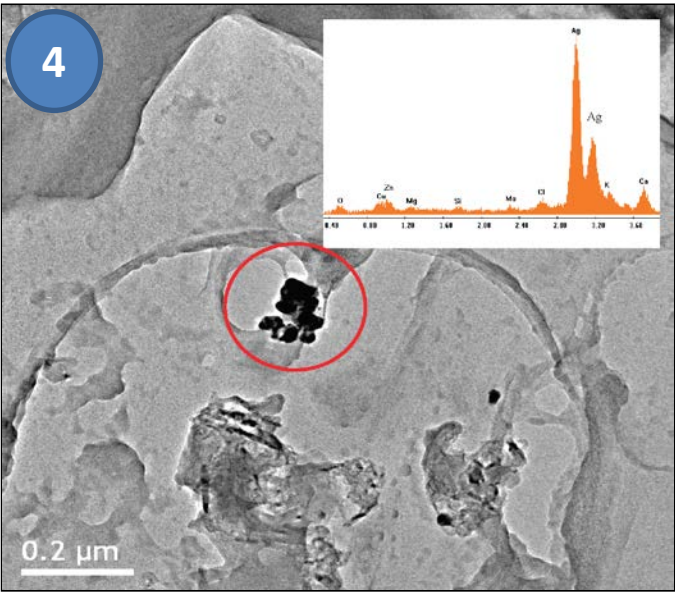
Ag nanoparticles- Images



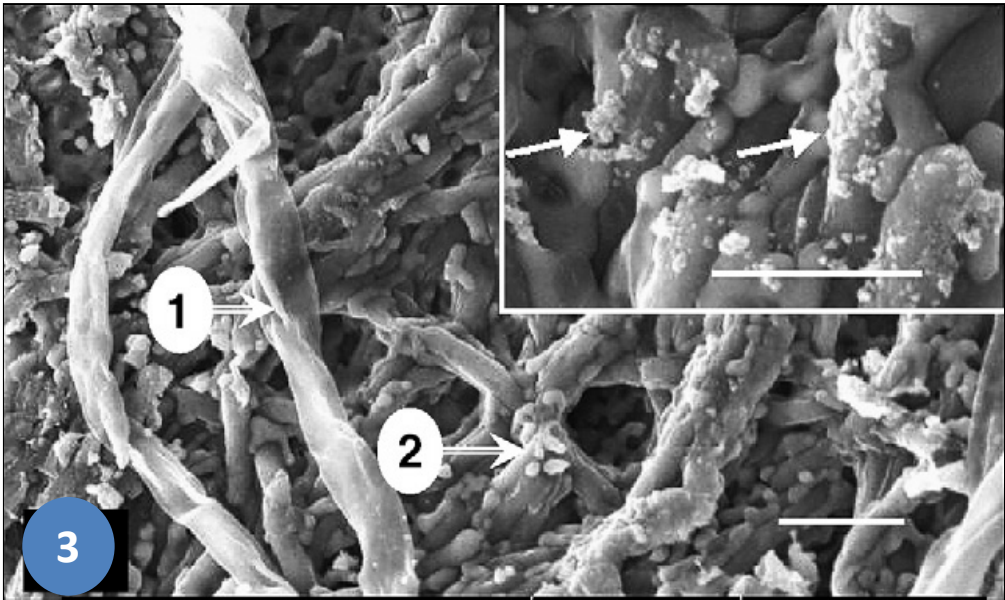
Ag nanoparticles prepared by silver ammonia reduction (Panacek et al., 2006)



Ag nanoparticles found in sock fabric (Benn and Westerhoff, 2008)



Ag nanoparticles found in wash water (Benn and Westerhoff, 2007)

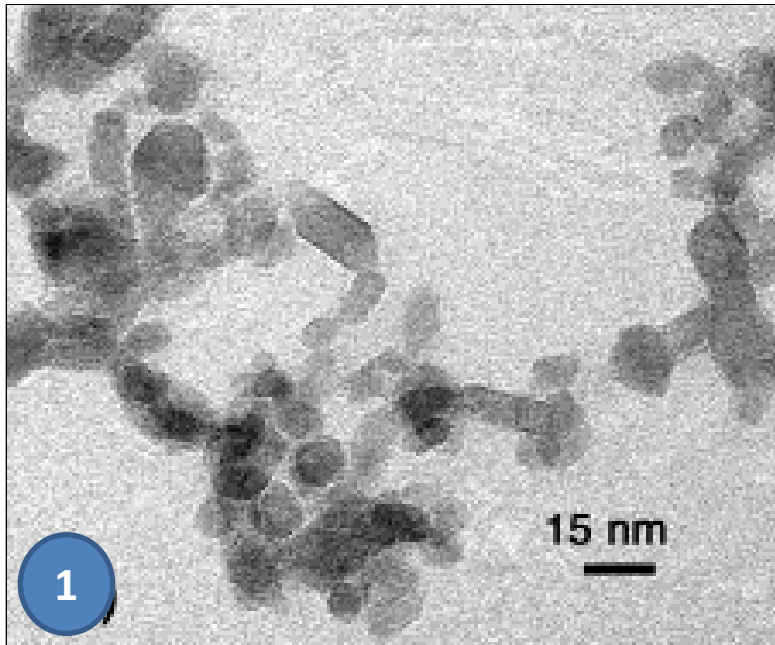


Ag nanoparticles synthesized by *Aspergillus flavus* (Vigneshwaran et al., 2007)

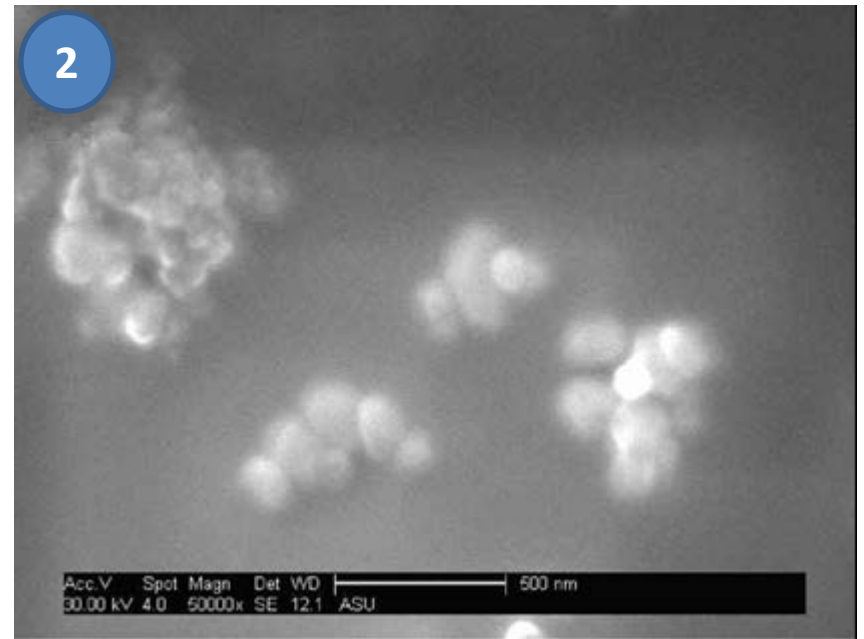
Ag nanoparticles– References (Clockwise from top left)

- 1) Ag nanoparticles formed via the reduction of silver ammoniate by glucose
 - 1) Imaged by TEM
 - 2) Panáček, A.; Kvitek, L.; Prucek, R.; Kolář, M.; Večeřová, R.; Pizúrová, N.; Sharma, V.; Nevěčná, T.; Zbořil, R. Silver Colloid Nanoparticles: Synthesis, Characterization, and Their Antibacterial Activity. *Journal of Physical Chemistry B*, **2006**, *110*, pp. 16248-16253.
- 2) Ag nanoparticles found in ashed sock fabric (EDX inset)
 - 1) Imaged by SEM (at micron scale)
 - 2) Benn, T.; Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environmental Science and Technology*, **2008**, *42*, pp. 4133-4139.
- 3) Silver nanoparticles formed from the reduction of silver nitrate by *Aspergillus flavus*
 - 1) Imaged by SEM
 - 2) Vigneshwaran, N.; Ashtaputre, N.; Varadarajan, P.; Nachane, R.; Paralikar, K.; Balasubramanya, R. Biological synthesis of silver nanoparticles using the fungus *Aspergillus flavus*. *Materials Letters*, **2007**, *61*, pp. 1413-1418.
- 4) Ag nanoparticles found in wash water from sock fabrics (inset is EDX)
 - 1) Imaged by TEM
 - 2) Benn, T.; Westerhoff, P. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. *Environmental Science and Technology*, **2008**, *42*, pp. 4133-4139.

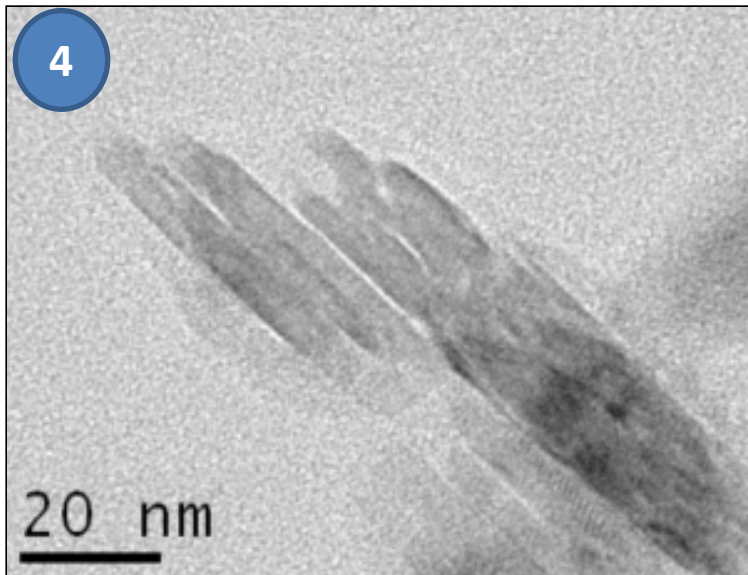
TiO₂ nanoparticles- Images



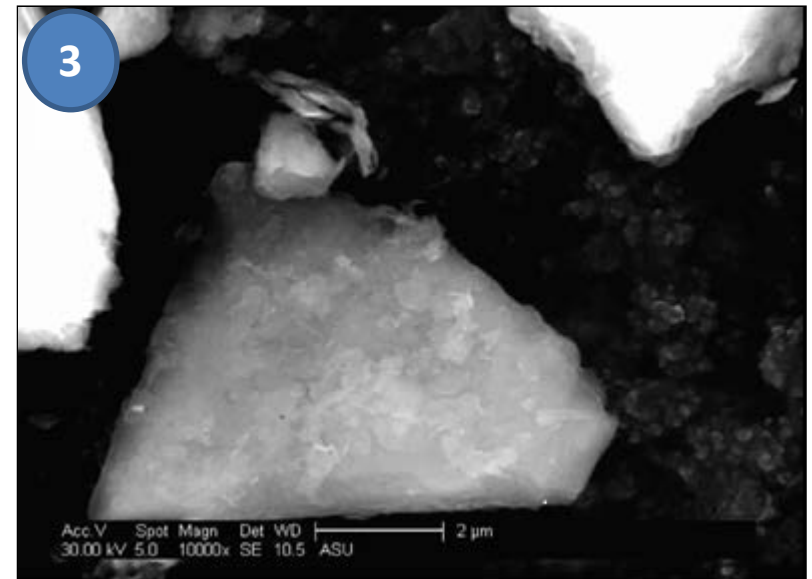
TiO₂ nanoparticles imaged by TEM (Oskam et al., 2003)



TiO₂ nanoparticles in toothpaste (Kiser et al., 2008)



Weathered TiO₂ particle in sunscreen (Nowack et al., 2012)

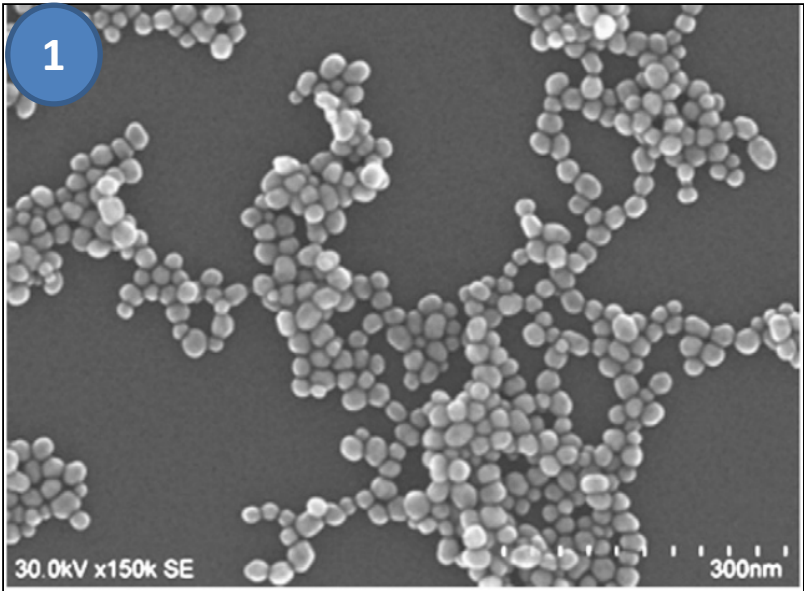


Ti-containing mineral in a biosolid (Kiser et al., 2008)

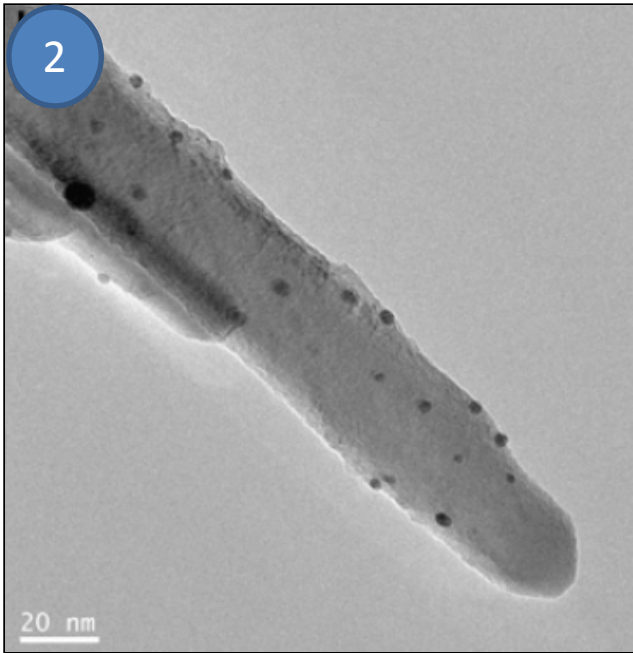
TiO₂ nanoparticles– References (Clockwise from top left)

- 1) Image of TiO₂ nanoparticles prepared from titanium (IV) isopropoxide
 - 1) Imaged by TEM
 - 2) Oskam, G.; Nellore, A.; Penn, R. L.; Searson, P. The Growth Kinetics of TiO₂ Nanoparticles from Titanium (IV) Alkoxide at High Water/Titanium Ratio. *Journal of Physical Chemistry B*. **2003**, *107*, pp. 1734-1738.
- 2) TiO₂ nanoparticles in toothpaste
 - 1) Imaged by SEM
 - 2) Kiser, M.; Westerhoff, P.; Benn, T.; Wang, Y.; Pérez-Rivera, J.; Hristovski, K. Titanium Nanomaterial Removal and Release from Wastewater Treatment . *Environmental Science and Technology*. **2008**, *43*, pp. 6757-6763.
- 3) Titanium containing mineral in a biosolid
 - 1) Observed by SEM (at micron scale)
 - 2) Kiser, M.; Westerhoff, P.; Benn, T.; Wang, Y.; Pérez-Rivera, J.; Hristovski, K. Titanium Nanomaterial Removal and Release from Wastewater Treatment . *Environmental Science and Technology*. **2008**, *43*, pp. 6757-6763.
- 4) Weathered titania nanoparticle released from sunscreen
 - 1) Observed by TEM
 - 2) Nowack, B.; Ranville, J.; Diamond, S.; Gallego-Urrea, J.; Metcalfe, C.; Rose, J.; Horne, N.; Koelmans, A.; Klaine, S. Potential Scenarios for Nanomaterial Release and Subsequent Alteration in the Environment. *Environmental Toxicology and Chemistry*, **2012**, *31*, pp. 50-59.

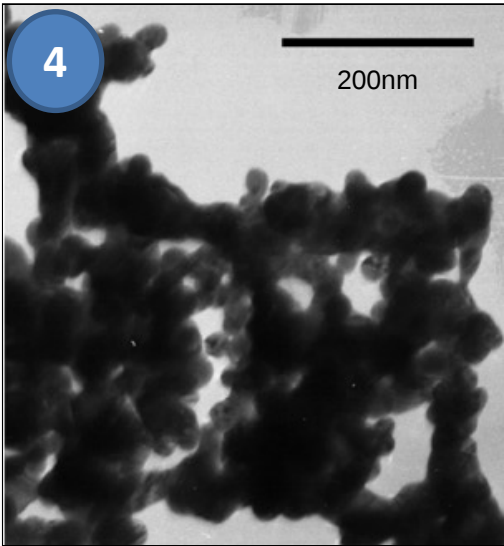
Au nanoparticles- Images



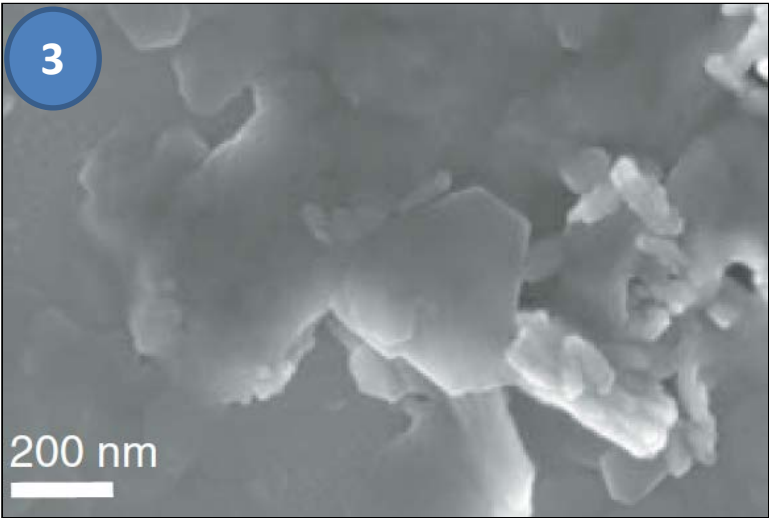
Gold nanoparticles synthesized by reduction of chloroauric acid (Cichomski et al., 2011)



Catalytic gold nanoparticles deposited on a ZnO support (Catillejos et al., 2012)



Aggregated acrylate capped gold nanoparticles at pH=2 (Diegoli et al., 2008)

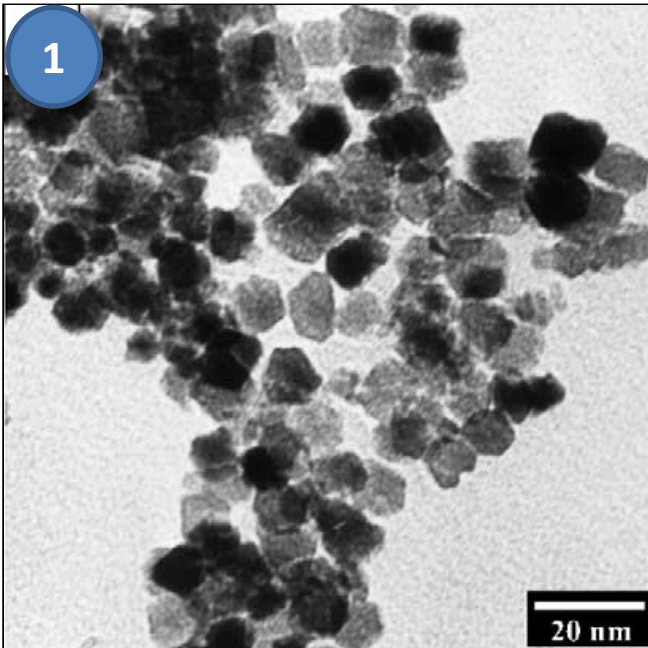


Gold nanoparticles found in weathered gold deposits (Hough et al., 2008)

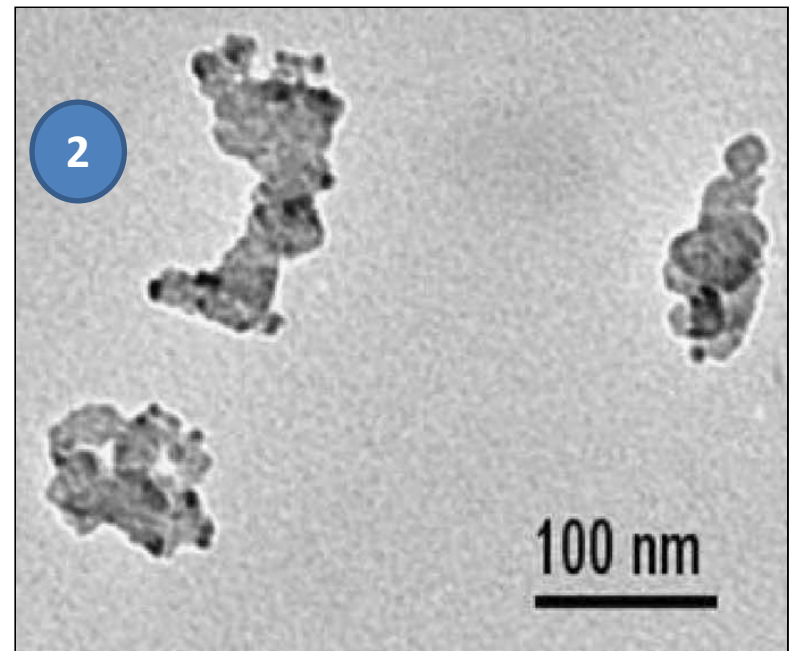
Au nanoparticles– References (Clockwise from top left)

- 1) Gold nanoparticles synthesized via reduction of chloroauric acid by trisodium citrate
 - 1) Imaged by SEM
 - 2) Cichomski, M.; Tomaszewska, E.; Kośla, K.; Kozłowski, W.; Kowalczyk, P.; Grobelny, J. Study of dithiol monolayer as the interface for controlled deposition of gold nanoparticles. *Materials Characterization*, **2011**, 42, pp. 268-274.
- 2) Catalytic gold nanoparticles deposited on a ZnO support
 - 1) Imaged by TEM
 - 2) Castillejos, E.; Gallegos-Suarez, E.; Bachiller-Baeza, B.; Bacsa, R.; Serp, P.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. Deposition of gold nanoparticles on ZnO and their catalytic activity for hydrogenation applications. *Catalysis Communications*, **2012**, 22, pp. 79-82.
- 3) Gold nanoparticles found in weather gold deposits
 - 1) Imaged by SEM
 - 2) Hough, R.; Noble, R.; Hitchen, G.; Hart, R.; Reddy, S.; Saunders, M.; Clode, P.; Vaughan, D.; Lowe, J.; Gray, D.; Anand, R.; Butt, C.; Verrall, M. Naturally occurring gold nanoparticles and nanoplates. *Geology*, **2008**, 36, pp. 571-574.
- 4) Aggregated acrylate-capped gold nanoparticles at pH=2.
 - 1) Imaged by TEM
 - 2) Diegoli, S.; Manciuola, A.; Begum, S.; Jones, I.; Lead, J.; Preece, J. Interaction between manufactured gold nanoparticles and naturally occurring macromolecules. *Science of the Total Environment*, **2008**, 402, pp. 51-61.

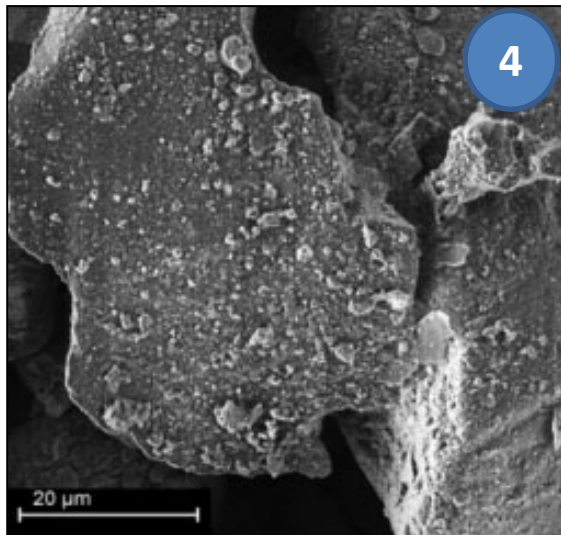
1) CeO₂ nanoparticles- Images



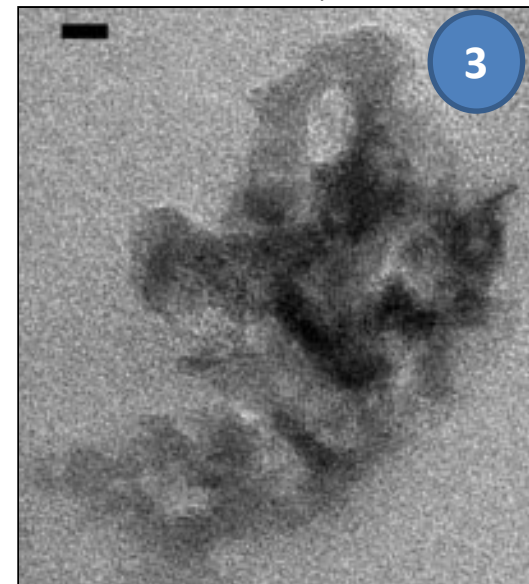
Cerium oxide nanoparticles prepared at 70°C (Chen and Chang, 2005)



Cerium oxide adhered to diesel particles in fuel additive (Jung et al., 2005)



CeO₂ particles adhered to a silty loam (von der Kammer et al., 2012)

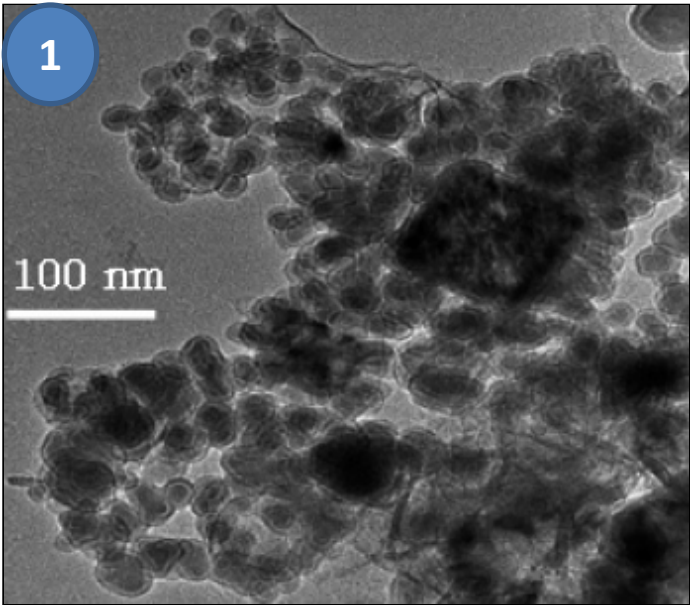


CeO₂ nano-cluster found in a floodplain (von der Kammer et al., 2012)

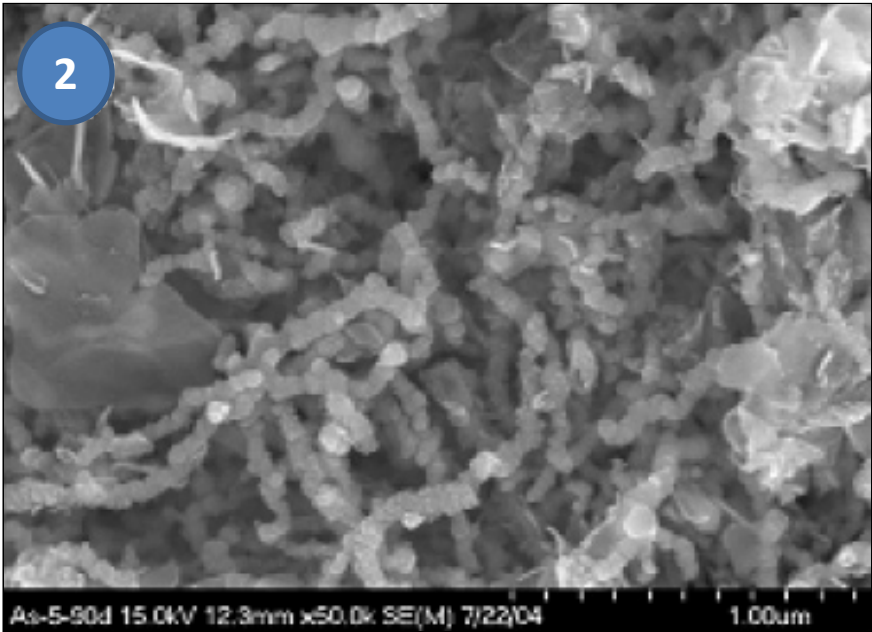
CeO₂ nanoparticles– References (Clockwise from top left)

- 1) Cerium oxide nanoparticles prepared from the oxidation of cerium ammoniate at 70⁰ C.
 - 1) Imaged by TEM
 - 2) Chen, H.; Chang, H. Synthesis of nanocrystalline cerium oxide particles by the precipitation method. *Ceramic International*, **2005**, 31, pp. 795-802.
- 2) Cerium oxide nanoparticles found on diesel particles
 - 1) Imaged by TEM
 - 2) Jung, H.; Kittelson, D.; Zachariah, M. The influence of a cerium additive on ultrafine diesel particle emissions and kinetics of oxidation. *Combustion and Flame*, **2005**, 142, pp. 276-288.
- 3) Natural Ce-containing nanoparticle cluster from the floodplain of Clark Fork River, Montana, USA
 - 1) Imaged by TEM (scale not specified)
 - 2) von der Kammer, F.; Ferguson, P.; Holden, P.; Mason, A.; Rogers, K.; Klaine, S.; Koelmans, A.; Horne, N.; Unrine, J. Analysis of Engineered Nanomaterials in Complex Matrices (Environment and Biota): General Consideration and Conceptual Case Studies. *Environmental Toxicology and Chemistry*, **2012**, 31, pp. 32-49.
- 4) Cerium dioxide nanoparticles adhered to the surface of a silty loam
 - 1) Imaged by SEM (at micron scale)
 - 2) von der Kammer, F.; Ferguson, P.; Holden, P.; Mason, A.; Rogers, K.; Klaine, S.; Koelmans, A.; Horne, N.; Unrine, J. Analysis of Engineered Nanomaterials in Complex Matrices (Environment and Biota): General Consideration and Conceptual Case Studies. *Environmental Toxicology and Chemistry*, **2012**, 31, pp. 32-49.

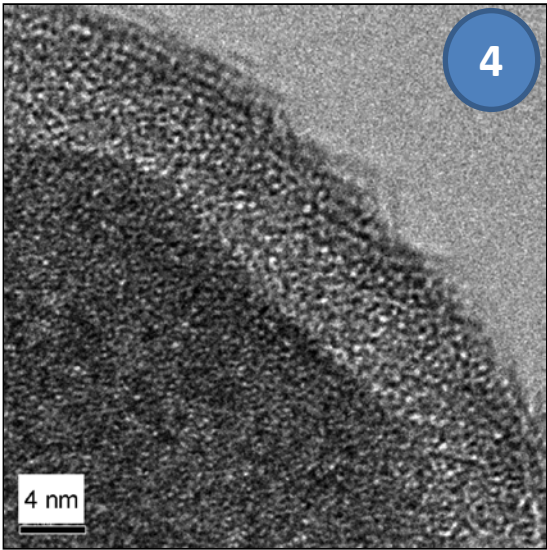
Zero valent iron nanoparticles- Images



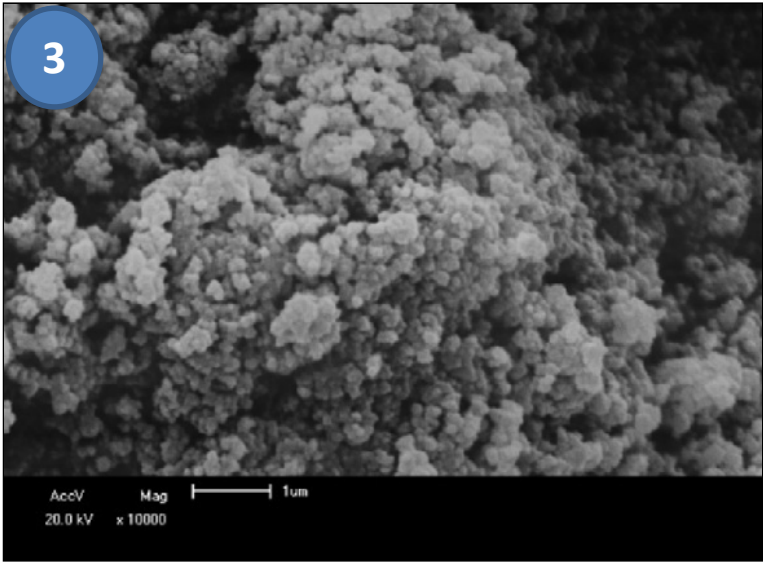
Pristine zero valent iron NP (Kanel et al., 2006)



As(V) adsorbed to a ZVI reactive barrier (Kanel et al., 2006)



Zero valent iron NP with an oxide shell (Ramos et al., 2009)

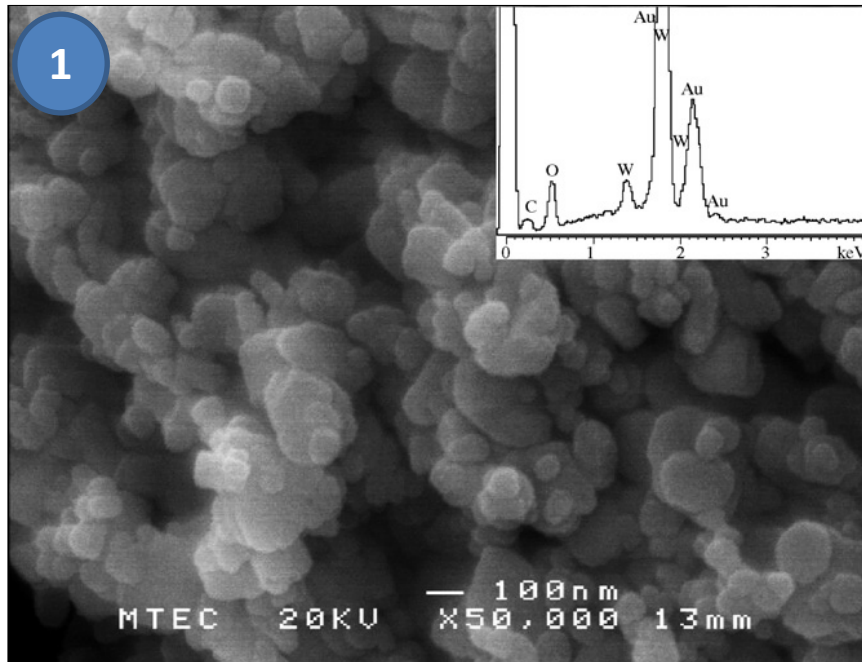


Magnetite particles formed from photooxidation (Silva et al., 2012)

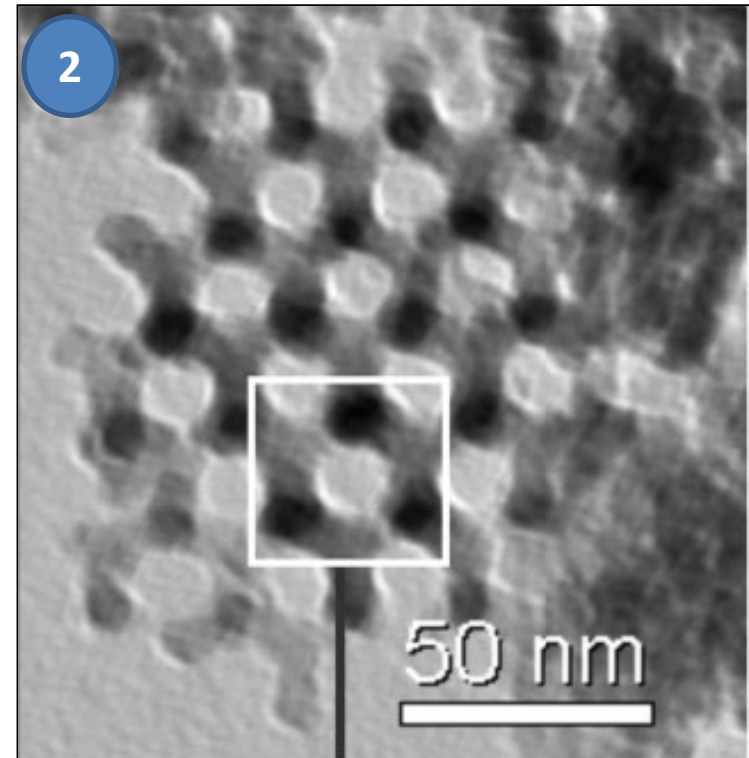
Zero valent iron nanoparticles– References (Clockwise from top left)

- 1) Pristine zero valent iron nanoparticles
 - 1) Imaged by TEM
 - 2) Kanel, S.; Greneche, J.; Choi, H. Arsenic (V) Removal from Groundwater Using Nano Scale Zero-Valent Iron as a Colloidal Reactive Barrier Material. *Environmental Science and Technology*, **2006**, *40*, pp. 2045-2050.
- 2) Arsenic (V) adsorbed onto a reactive barrier of zero valent iron nanoparticles
 - 1) Imaged by SEM (at micron scale)
 - 2) Kanel, S.; Greneche, J.; Choi, H. Arsenic (V) Removal from Groundwater Using Nano Scale Zero-Valent Iron as a Colloidal Reactive Barrier Material. *Environmental Science and Technology*, **2006**, *40*, pp. 2045-2050.
- 3) Magnetite particles formed from the precipitation and photooxidation of acid mine drainage
 - 1) Imaged by SEM (at micron scale)
 - 2) Silva, R.; Castro, C.; Vigânico, E.; Petter, C.; Schneider, I. Selective precipitation/UV production of magnetite particles obtained from the iron recovered from acid mine drainage. *Minerals Engineering*, **2012**, *29*, pp. 22-27.
- 4) Zero valent iron nanoparticle with a formed oxide coating
 - 1) Imaged by TEM
 - 2) Ramos, M.; Yan, W.; Li, X.; Koel, B.; Zhang, W. Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent Iron Nanoparticles: Understanding the Significance of the Core-Shell Structure. *Journal of Physical Chemistry C Letters*, **2009**, *113*, pp. 14591-14594.

WO₃ nanoparticles- Images



WO₃ nanoparticles prepared by acid precipitation (Supothina et al. 2007)

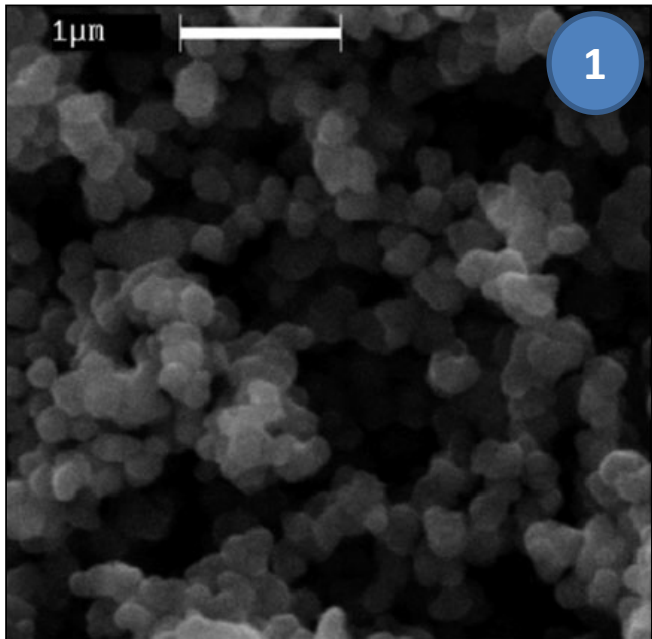


Tungsten oxide nanoparticles used for NO₂ gas sensing (Rossinyol et al., 2007)

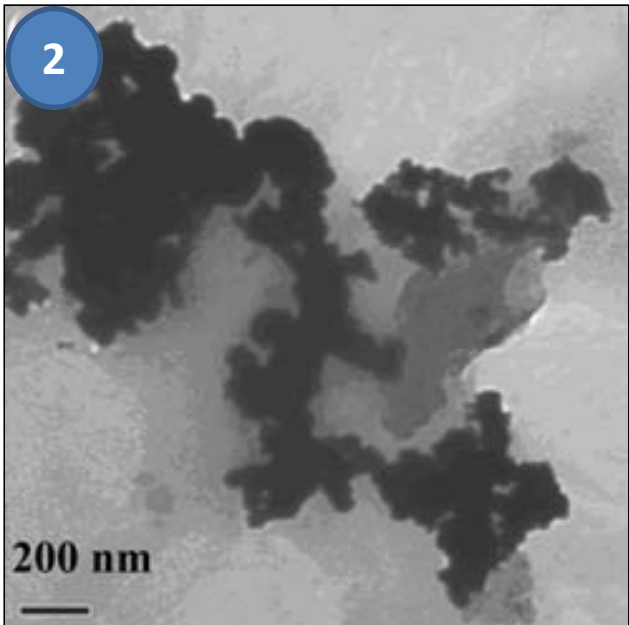
Zero valent iron nanoparticles– References (Clockwise from top left)

- 1) Pristine tungsten oxide (WO_3) nanoplates
 - 1) Imaged by SEM
 - 2) Supothina, S.; Seeharaj, P.; Yoriya, S.; Sriyudthsak, M. Synthesis of tungsten oxide nanoparticles by acid precipitation method. *Ceramics International*, **2007**, 33, pp. 931-936.
- 2) Tungsten oxide nanoparticles templated on a KIT-6 structure for gas-sensing applications
 - 1) Imaged by TEM
 - 2) Rossinyol, E.; Prim, A.; Pellicer, E.; Arbio, J.; Hernández-Ramírez, F.; Peiró, F.; Cornet, A.; Morante, J.; Solovyov, L.; Tian, B.; Bo, T; Zhao, D. Synthesis and Characterization of Chromium-Doped Mesoporous Tungsten Oxide for Gas-sensing Applications. *Advanced Functional Materials*, **2007**, 17, pp. 1801-1806.

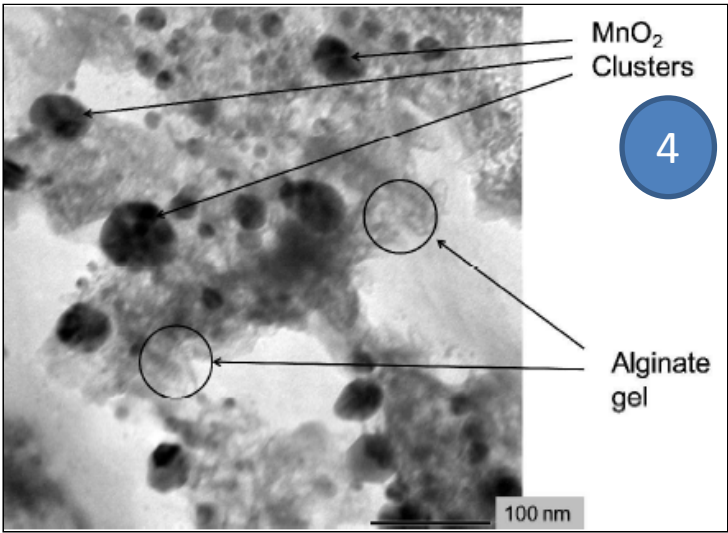
MnO₂ nanoparticles- Images



Pristine MnO₂ nanoparticles (Ching et al., 2011)



Carbon coated MnO₂ nanoparticles for catalysis (Roche et al., 2008)



MnO₂ aggregation in the presence of biomolecules and divalent cations (Huangfu et al., 2013)

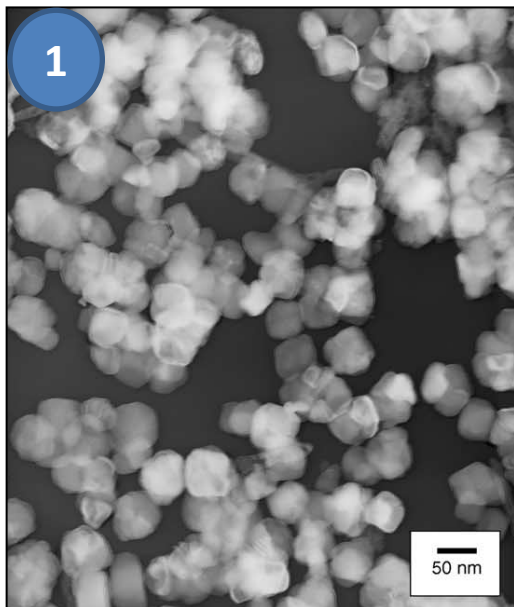


Biogenically synthesized manganese oxides (Miyata et al., 2007)

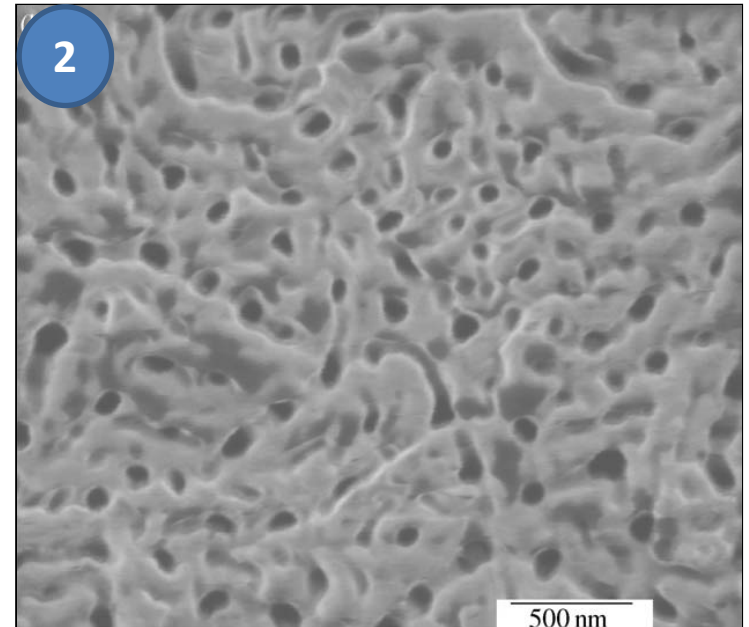
MnO₂ – References (Clockwise from top left)

- 1) Pristine manganese oxide (MnO₂) nanoparticles
 - 1) Imaged by SEM (at micron scale)
 - 2) Ching, S.; Kriz, D.; Luthy, K.; Njagi, E.; Suib, S. Self-assembly of manganese oxide nanoparticles and hollow spheres. Catalytic activity in carbon monoxide oxidation. *Chemical Communications*, **2011**, 47, pp. 8286-8288.
- 2) Manganese oxide / carbon electrocatalysts
 - 1) Imaged by TEM
 - 2) Roche, I.; Chaînet, E.; Chatenet, M.; Vondrák, J. Durability of carbon-supported manganese oxide nanoparticles for the oxygen reduction reaction (ORR) in alkaline medium. *Journal of Applied Electrochemistry*, **2008**, 38, pp. 1195-1201.
- 3) Manganese (II) oxidation by *Acremonium* sp. Strain KR21-2 to form manganese oxides
 - 1) Imaged by TEM
 - 2) Miyata, N.; Tani, Y.; Sakata, M.; Iwahori, K. Microbial Manganese Oxide Formation and Interaction with Toxic Metal Ions. *Journal of Bioscience and Bioengineering*, **2007**, 104, pp.1-8.
- 4) Aggregated Mn₂ nanoparticles in the presence of 10mM calcium nitrate and 2 mg/L alginate
 - 1) Imaged by TEM
 - 2) Huangfu, X.; Jiang, J.; Ma, J.; Yongze, L.; Jing, Y. Aggregation Kinetics of Manganese Dioxide Colloids in Aqueous Solution: Influence of Humic Substances and Biomacromolecules. *Environmental Science and Technology*, **2013**, Just Accepted.

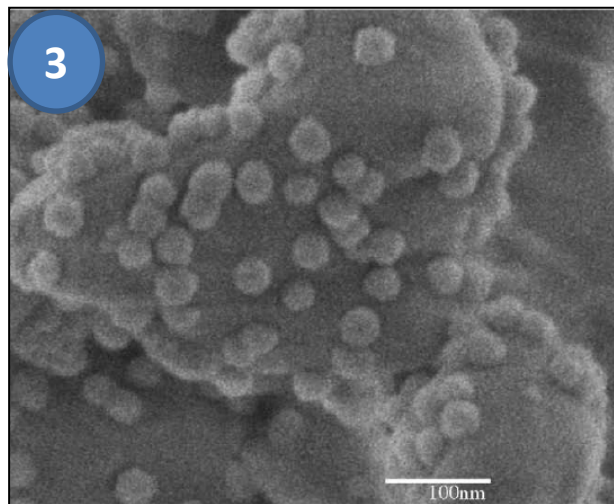
Al₂O₃ nanoparticles- Images



α -Al₂O₃ nanoparticles formed in the presence of Na(AOT) (Park et al., 2005)



Nano-porous anodised alumina coating on titanium (Briggs et al., 2004)

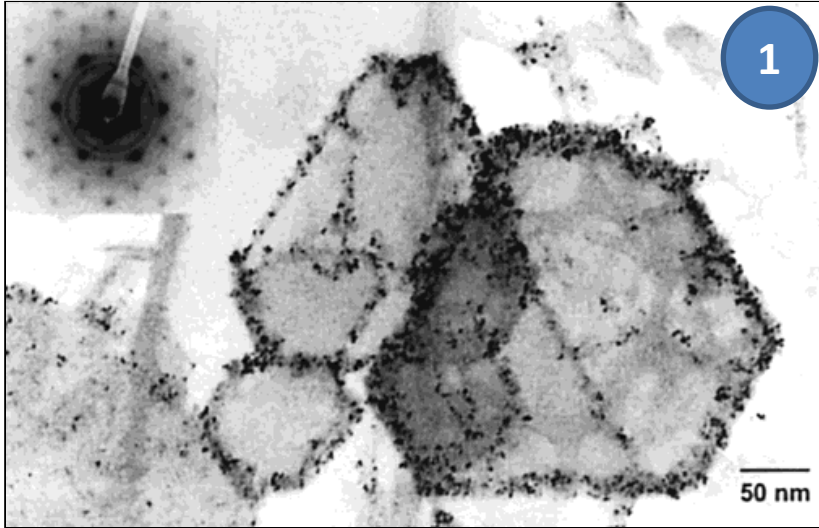


Silica-alumina nanoparticle heteroaggregation (Garcia-Perez et al., 2006)

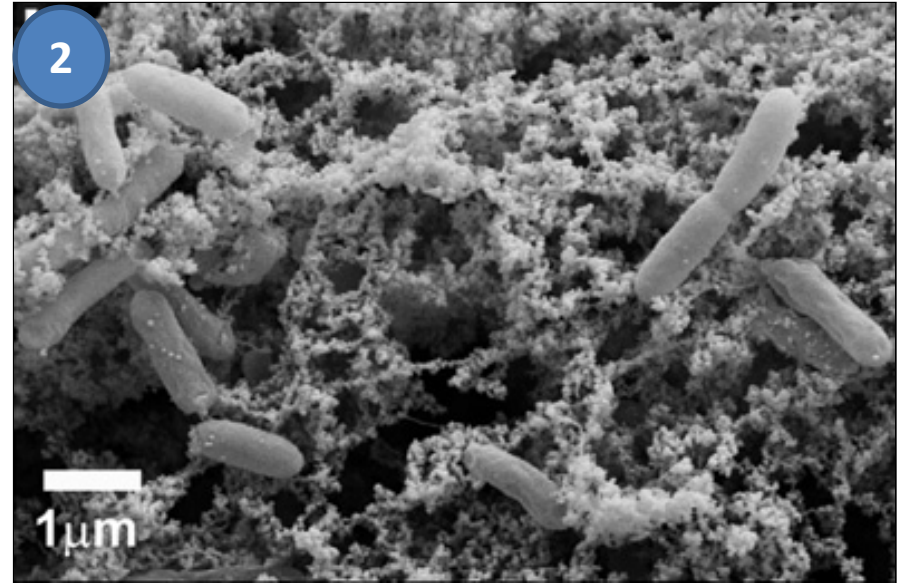
Al₂O₃ – References (Clockwise from top left)

- 1) α -Al₂O₃ nanoparticles form in the presence of sodium bis(2-ethylhexyl) sulfosuccinate
 - 1) Imaged by SEM
 - 2) Park, Y.; Tadd, E.; Zubris, M.; Tannenbaum, R. Size-controlled synthesis of alumina nanoparticles from aluminum alkoxides. *Materials Research Bulletin*, **2005**, 40, pp.1506-1512.
- 2) Nano-porous anodised alumina coating on titanium for surgical implants
 - 1) Imaged by SEM
 - 2) Briggs, E.; Walpole, A.; Wilshaw, P.; Karlsson, M.; Pålsgård, E. Formation of highly adherent nano-porous alumina on Ti-based substrates: a novel bone implant coating. *Journal of Materials Science: Materials in Medicine*, **2004**, 15, pp. 1021-1029.
- 1) Alumina colloids heteroaggregated with silica nanoparticles
 - 1) Imaged by Cryo-FEG-SEM
 - 2) Garcia-Perez, P.; Pagnoux, C.; Rossignol, F.; Baumard, J. Heterocoagulation between SiO₂ nanoparticles and Al₂O₃ submicronparticles; influence of the background electrolyte. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, **2006**, 281, pp. 58-66.

UO₂ nanoparticles- Images



Uraninite nanoparticles precipitated on green rusts
(O'Loughlin et al., 2003)

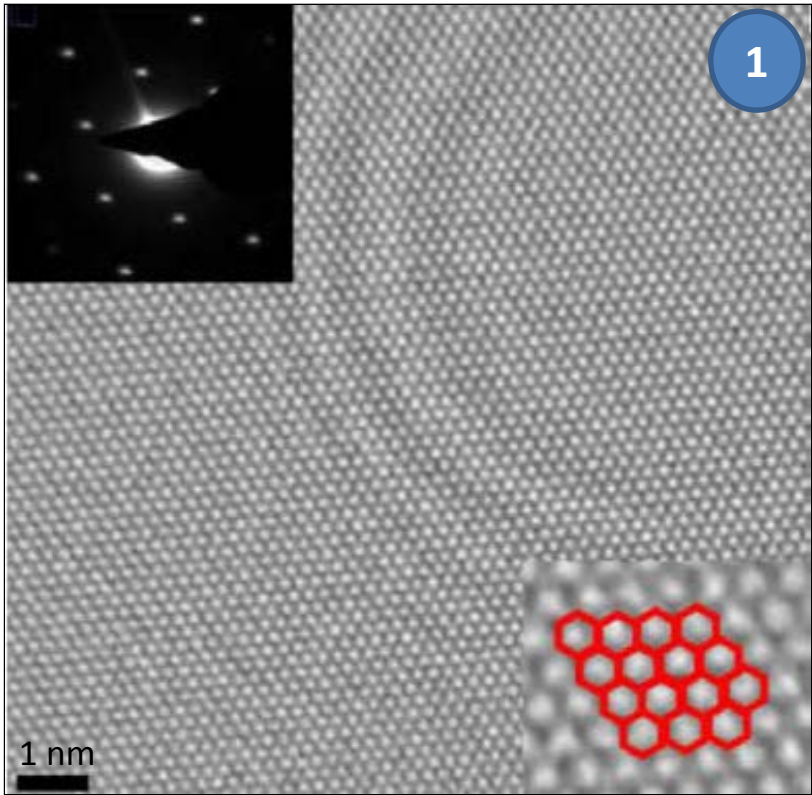


Uranium nanoparticles precipitated from bio-reduction of U(VI)
by *Shewanella oneidensis* (Burgos et al., 2008)

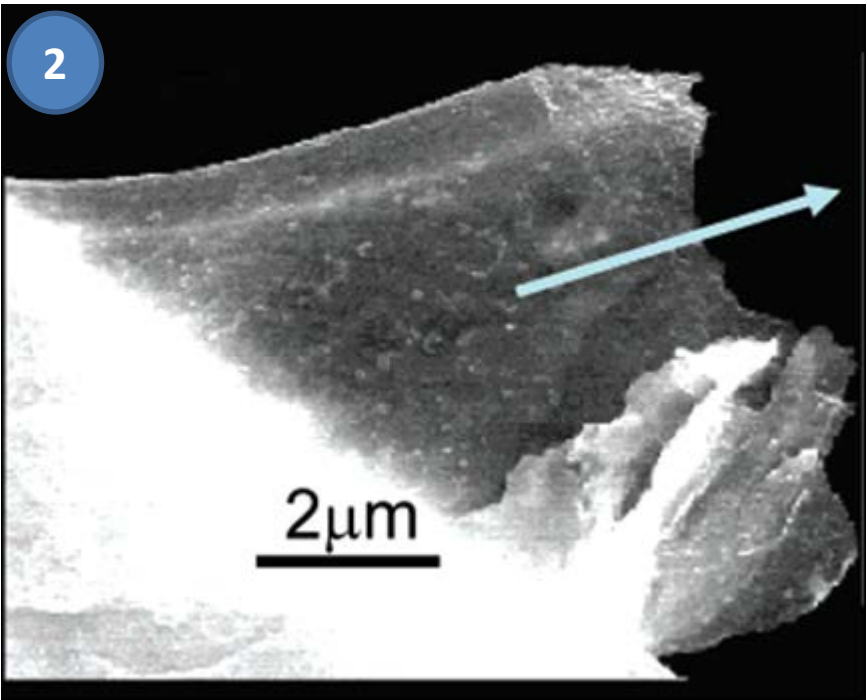
UO₂ – References (Clockwise from top left)

- 1) Uraninite nanoparticles precipitated on mixed Fe(II)/Fe(III) hydroxides
 - 1) Imaged by TEM
 - 2) O'Loughlin, E.; Kelly, S.; Cook, R.; Csencsits, R.; Kemner, K. Reduction of Uranium (VI) by Mixed Iron (II)/ Iron(III) Hydroxide (Green Rusts: Formation of U₂ Nanoparticles. *Environmental Science and Technology*, **2003**, 37, pp. 721-727.
- 2) Uraninite nanoparticles precipitated from soluble U(VI) by *Shewanella oneidensis* MR-1 strain
 - 1) Imaged by SEM (at micron scale)
 - 2) Burgos, W.; McDonough, J.; Senko, J.; Zhang, G.; Dohnalkova, A.; Kelly, S.; Gorby, Y.; Kemner, K. Characterization of uraninite nanoparticles produced by *Shewanella oneidensis* MR-1. *Geochimica et Cosmochimica Acta*, **2008**, 72, pp. 4901-4915.

Graphene - Images



Graphene layer produced by chemical vapor deposition
(Park et al., 2010)

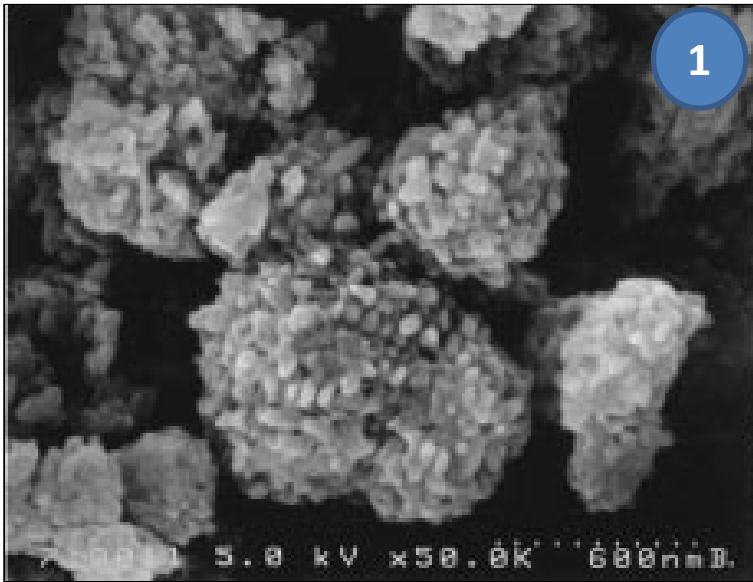


Graphene sheets with embedded gold nanoparticles
(Muszynski et al., 2008)

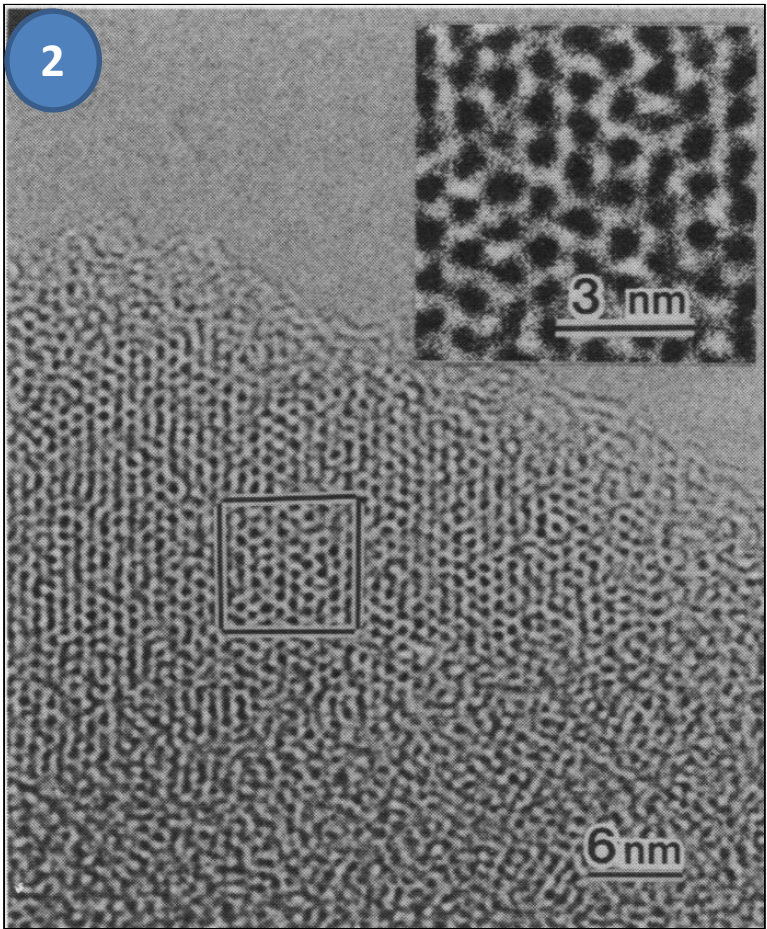
Graphene – References (Clockwise from top left)

- 1) Graphene prepared by chemical vapor deposition
 - 1) Imaged by TEM
 - 2) Park, H.; Meyer, J.; Rother, S.; Skákalová, V. Growth and properties of few-layer graphene prepared by chemical vapor deposition. *Carbon*, **2010**, 48, pp. 1088-1094.
- 2) Graphene sheets with embedded gold nanoparticles for catalysis applications
 - 1) Imaged by SEM (at micron scale)
 - 2) Muszynski, R.; Seger, B.; Kamat, P. Decorating Graphene Sheets with Gold Nanoparticles. *Journal of Physical Chemistry C Letters*, **2008**, 112, pp. 5263-5266.

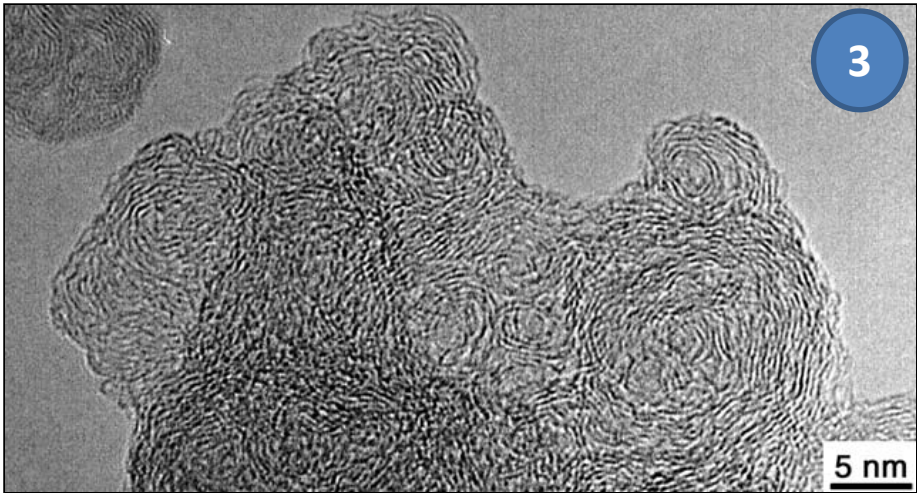
Fullerenes- Images



SEM image of C₆₀ powder (Gusev et al., 1999)



Fullerene particles found in precambrian rocks from Russia (Buseck et al., 1992)

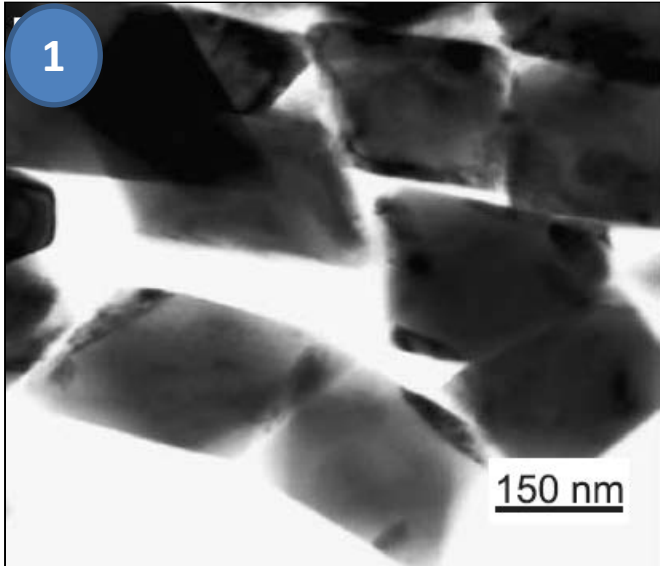


Fullerene-like soot from a EuroIV diesel engine (Su et al., 2004)

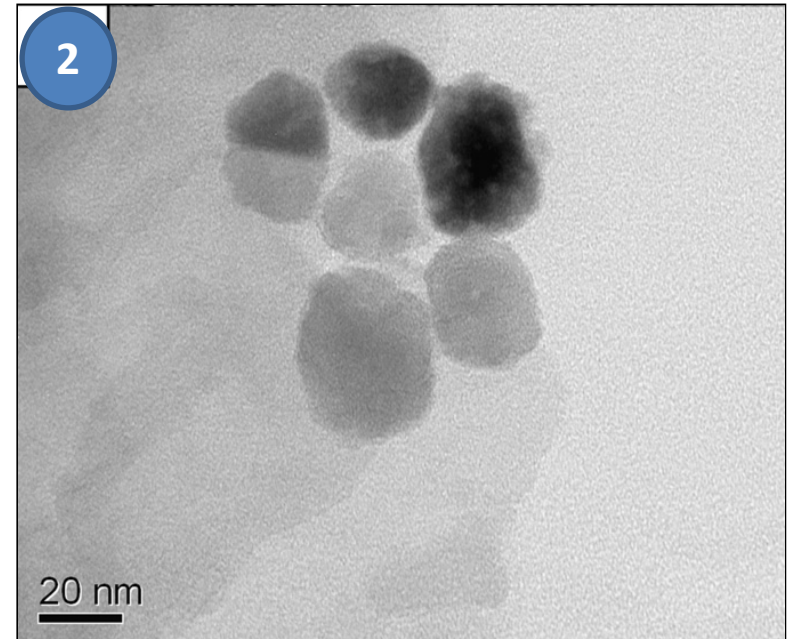
Fullerenes– References (Clockwise from top left)

- 1) SEM image of C₆₀ powder
 - 1) Imaged by SEM
 - 2) Gusez, Y.; Ruetsch, S.; Popeko, L.; Popeko, I. Nitrogen and Argon Adsorption and SEM Characterization of C₆₀ And C_{60/70} Fullerenes: Comparison with Graphite. *Journal of Physical Chemistry B*, **1999**, *103*, pp. 6498-6503.
- 2) TEM images of fullerenes found in a precambrian rock from Russia
 - 1) Imaged by TEM
 - 2) Buseck, P.; Tsipursky, S.; Hettich, R. Fullerenes from the Geological Environment. *Science*, **1992**, *257*, pp. 215-217.
- 3) TEM image of fullerene-like soot from EuroIV diesel engine
 - 1) Imaged by TEM
 - 2) Su, D.; Müller, J.-O; Jentoft, R.; Rothe, D.; Jacob, E.; Schlögl, R. Fullerene-like soot from EuroIV diesel engine: consequences for catalytic automotive pollution control. *Topics in Catalysis*, **2004**, *30/31*, pp. 241-245.

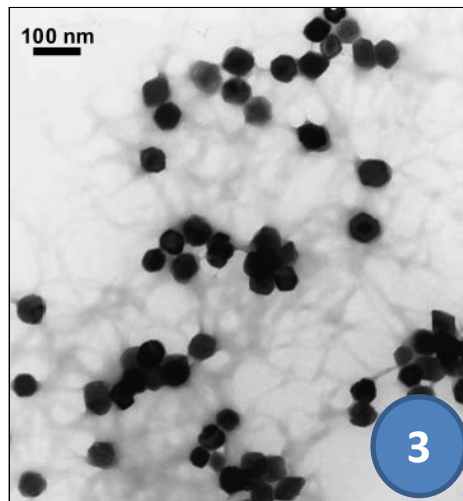
1) Fe₂O₃- Images



TEM image of hematite nanoparticles coated with HPC (Jing and Wu, 2004)



Hematite nanoparticles found in free-drifting icebergs (Shaw et al., 2011)

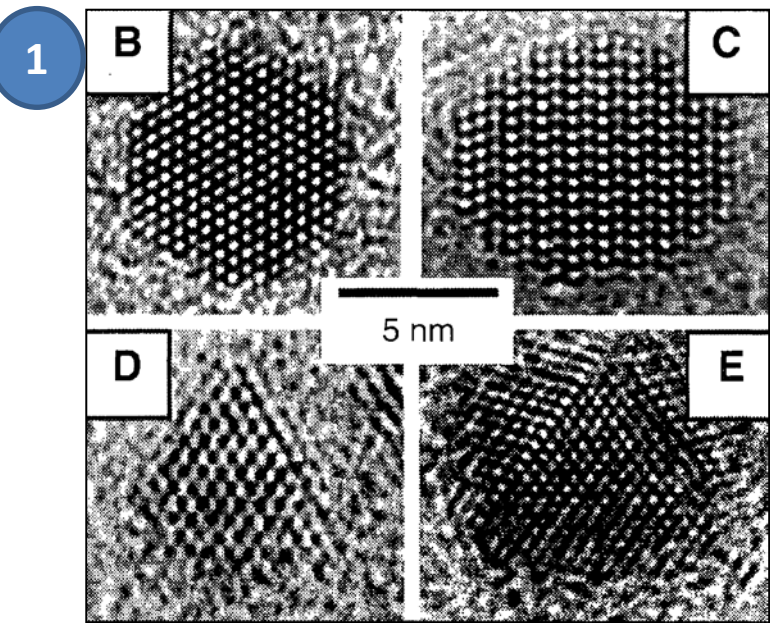


Aggregated alginate-coated hematite nanoparticles (Chen et al., 2006)

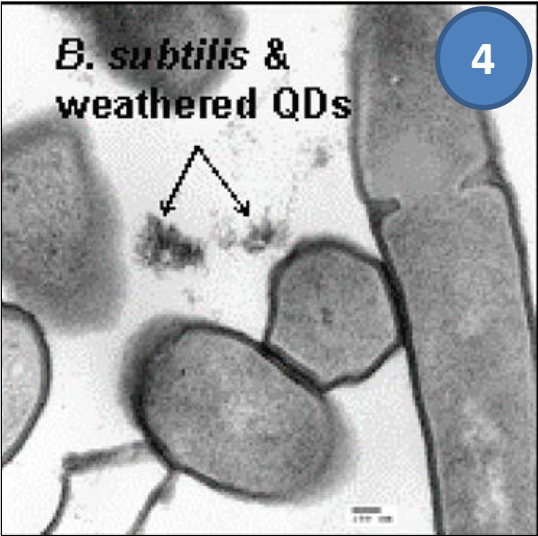
Graphene – References (Clockwise from top left)

- 1) TEM image of hematite nanoparticles coated with hexadecylpyridinium chloride (HPC)
 - 1) Imaged by TEM
 - 2) Jing, Z.; Wu, S. Synthesis and characterization of monodisperse hematite nanoparticles modified by surfactants via hydrothermal approach. *Materials Letters*, **2004**, 58, pp.3637-3640.
- 2) N/A hematite nanoparticle in a product
- 3) Hematite nanoparticles found in free-drifting icebergs
 - 1) Imaged by TEM
 - 2) Shaw, T.; Raiswell, R.; Hexel, C.; Vu, H.; Moore, W.; Dudgeon, R.; Smith Jr., K. Input, composition, and potential impact of terrigenous material from free-drifting icebergs in the Weddell Sea. *Deep-Sea Research II*, **2011**, 58, pp. 1376-1383.
- 4) Aggregated alginate-coated hematite nanoparticles in the presence of divalent salts
 - 1) Imaged by TEM
 - 2) Chen, K.; Mylon, S.; Elimelech, M. Aggregation Kinetics of Aligned-Coated Hematite Nanoparticles in Monovalent and Divalent Electrolytes. *Environment Science and Technology*, **2006**, 40, pp. 1516-1523.

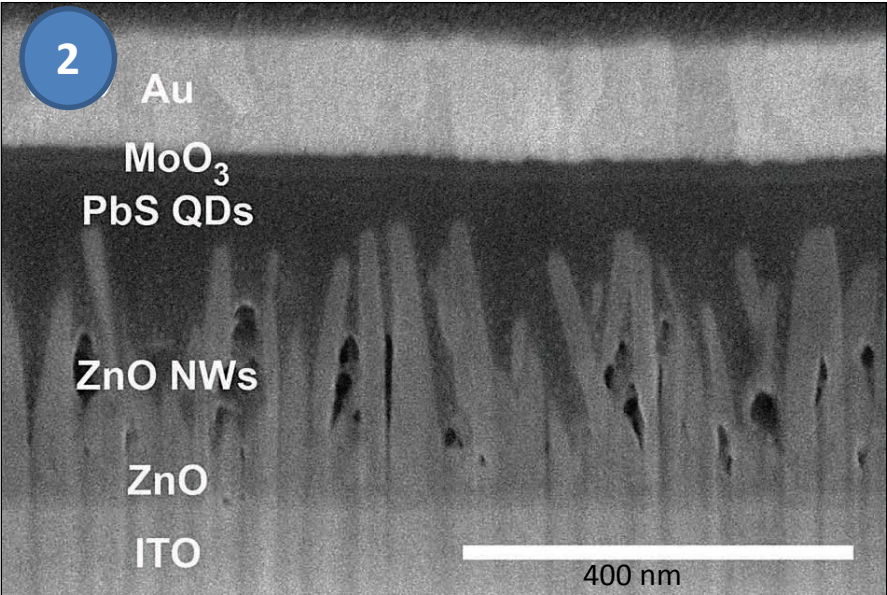
Quantum dots - Images



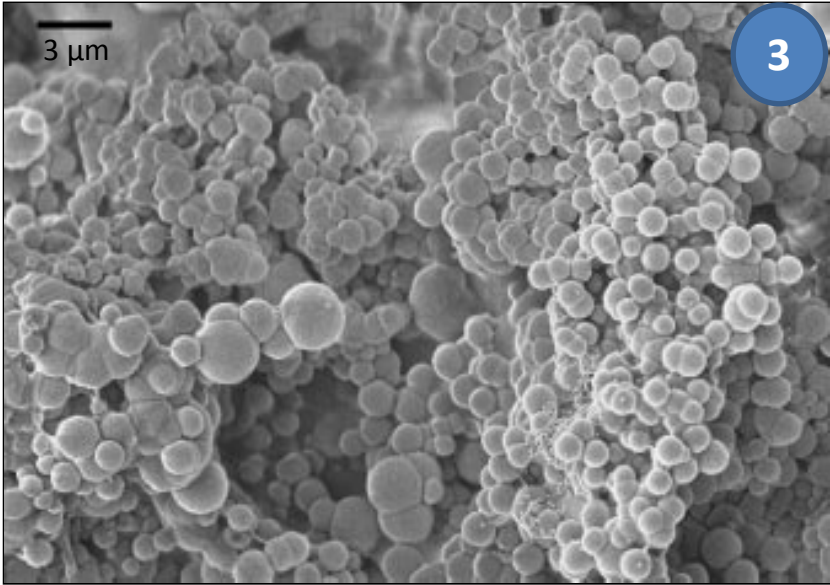
TEM images of various quantum dots (Alivisatos, 1996)



TEM images of weathered quantum dot clusters (Mahendra et al., 2008)



PbS Quantum dots in solar cells (Jean et al., 2013)

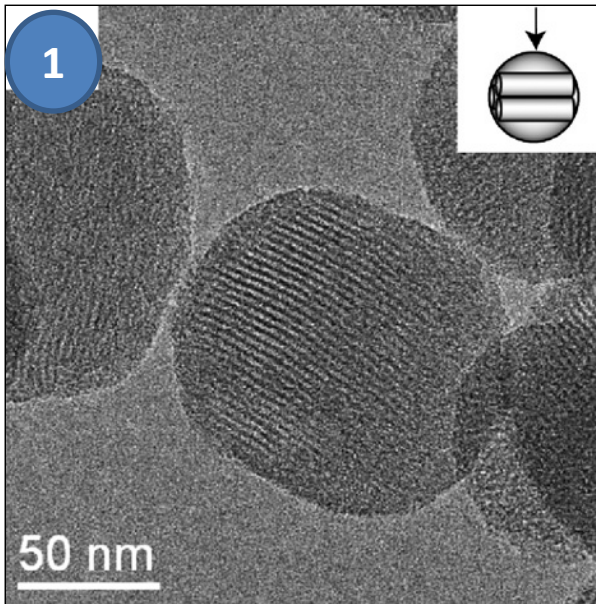


Spherical aggregates of ZnS nanoparticles formed in a biofilm (Labrenz et al., 2000)

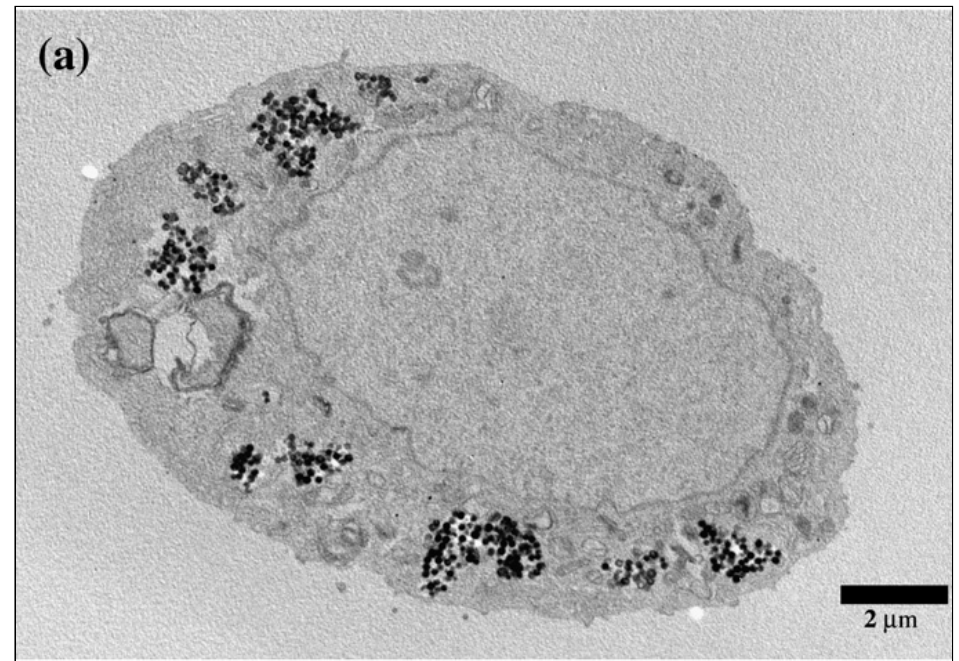
Quantum dots – References (Clockwise from top left)

- 1) TEM images of various quantum dots lattices
 - 1) Imaged by TEM
 - 2) Alivisatos, A. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science*, **1996**, 271, pp. 933-937.
- 2) Lead sulfide quantum dots in solar cells
 - 1) Imaged by SEM
 - 2) Jean, J.; Chang, S.; Brown, P.; Cheng, J.; Rekemeyer, P.; Bawendi, M.; Gradečak, S.; Bulović, V. ZnO Nanowire Arrays for Enhanced Photocurrent in PbS Quantum Dot Solar Cells. *Advanced Materials*, **2013**, 25, pp. 2790-2796.
- 3) Spherical aggregates of ZnS nanoparticles formed in a biofilm
 - 1) Imaged by SEM (at micron scale)
 - 2) Labrenz, M.; Druschel, G.; Thomsen-Ebert, T.; Gilbert, B.; Welch, S.; Stasio, G.; Bond, P.; Lai, B.; Kelly, S.; Banfield, J. Formation of Sphalerite (ZnS) Deposits in Natural Biofilms of Sulfate-Reducing Bacteria. *Science*, **2000**, 290, pp. 1744-1747.
- 4) Weathered quantum dots clusters with *Bacillus subtilis*
 - 1) Imaged by TEM
 - 2) Mahendra, S.; Zhu, H.; Colvin, V.; Alvarez, P. Quantum Dot Weathering Results in Microbial Toxicity. *Environmental Science and Technology*, **2008**, 42, pp. 9424-9430.

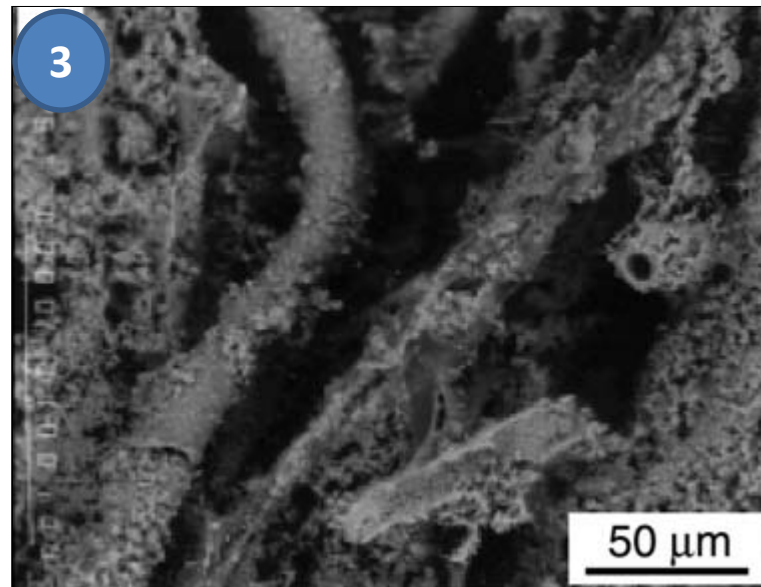
SiO₂ nanoparticles - Images



TEM image of mesoporous silica (Slowing et al., 2008)



Endocytosed mesoporous silica in a HeLa cell (Slowing et al., 2008)



Silicified filamentous microbes in geothermal waters (Inagaki et al., 2003)

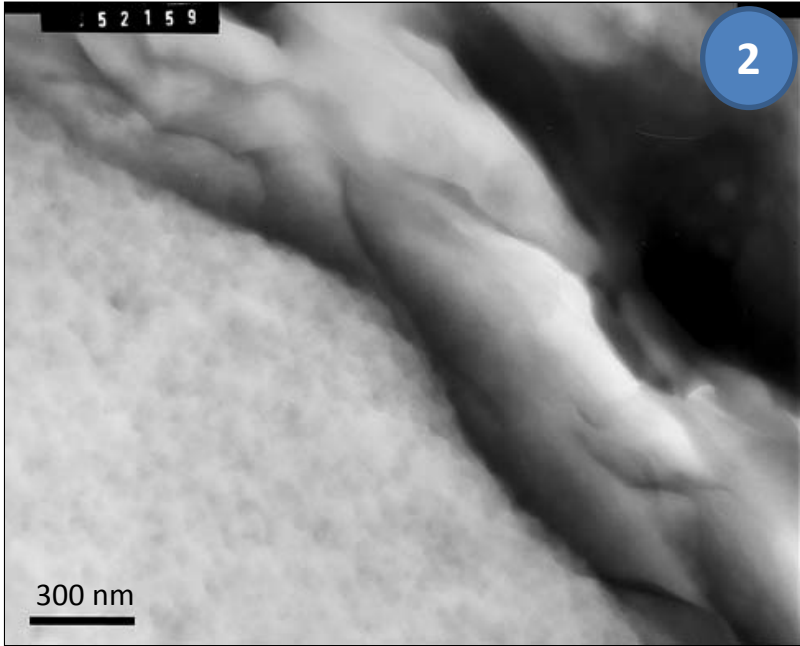
SiO₂ nanoparticles – References (Clockwise from top left)

- 1) Mesoporous silica imaged perpendicular to pores
 - 1) Imaged by TEM
 - 2) Slowing, I.; Vivero-Escoto, J.; Wu, C.; Lin, V. Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers. *Advanced Drug Delivery Review*, **2008**, 60, pp. 1278-1288.
- 2) Mesoporous silica endocytosed by HeLa cells
 - 1) Imaged by TEM (at micron scale)
 - 2) Slowing, I.; Vivero-Escoto, J.; Wu, C.; Lin, V. Mesoporous silica nanoparticles as controlled release drug delivery and gene transfection carriers. *Advanced Drug Delivery Review*, **2008**, 60, pp. 1278-1288.
- 3) Silicified filamentous microbes found in geothermal waters
 - 1) Imaged by SEM (at micron scale)
 - 2) Inagaki, F.; Motomura, Y.; Ogata, S. Microbial silica deposition in geothermal hot waters. *Applied Microbiology and Biotechnology*, **2003**, 60, pp. 605-611.

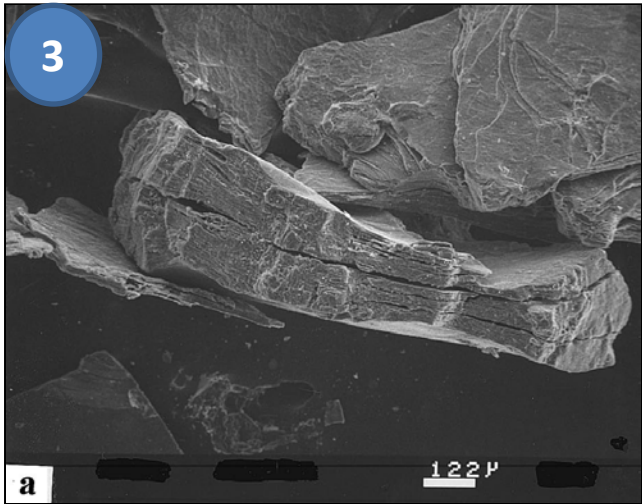
Nanoclay composites - Images



TEM of HDPE/nanoclay composite (Faruk et al., 2008)



TEM image of silicone/montmorillonite composite containing siloxane-modified montmorillonite clay (Simon et al., 2008)

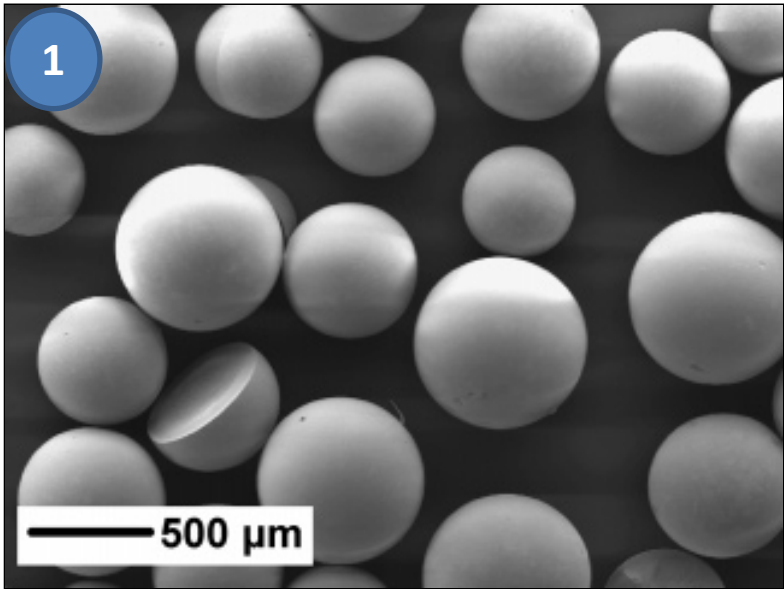


SEM image of phyllosilicate grains from regolith (Murphy et al., 1998)

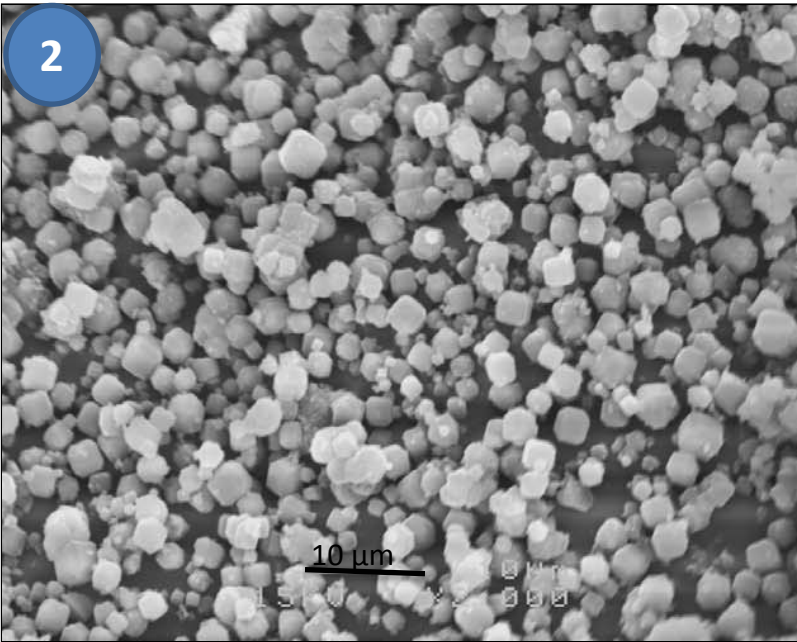
Nanoclay composites – References (Clockwise from top left)

- 1) TEM image of HDPE/nanoclay composites
 - 1) Imaged by TEM
 - 2) Faruk, O.; Matuana, L. Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Composites Science and Technology*, **2008**, 68, pp. 2073-2077.
- 2) TEM micrograph of silicone/montmorillonite composite containing 5 wt% siloxane-modified montmorillonite clay
 - 1) Imaged by TEM
 - 2) Simon, M.; Stafford, K.; Ou, D. Nanoclay Reinforcement of Liquid Silicone Rubber. *Journal of Inorganic and Organometallic Polymers and Materials*, **2008**, 18, pp. 364-373.
- 3) Regolith grain consisting of biotite and kaolinite clay.
 - 1) Imaged by SEM (at micron scale)
 - 2) Murphy, S.; Brantley, S.; Blum, A.; White, A.; Dong, H. Chemical weathering in a tropical watershed, Liguillo Mountains, Puerto Rico: II. Rate and mechanism of biotite weathering. *Geochimica et Cosmochimica Acta*, **1998**, 62m pp. 227-243.

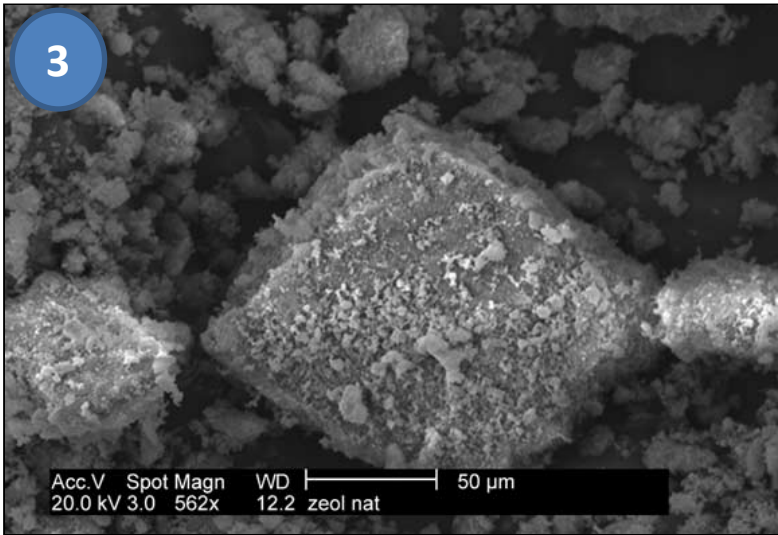
Zeolites - Images



Solid zeolite particles from resin templating (Tosheva et al., 2005)



Zeolite 4A for use as a detergent builder (Hui and Chao, 2006)



SEM image of a naturally occurring Chilean zeolite (Englert and Rubio, 2005)

Zeolites – References (Clockwise from top left)

- 1) Solid zeolite particle from resin templating
 - 1) Imaged by SEM (at micron scale)
 - 2) Tosheva, L.; Valtchev, V. Nanozeolites: Synthesis, Crystallization Mechanisms, and Applications. *Chemistry of Materials*, **2005**, 17, pp. 2494-2513.
- 2) Zeolite 4A synthesized from coal fly ash
 - 1) Imaged by SEM (at micron scale)
 - 2) Hui, K.; Chao, C. Pure, single phase, high crystalline, camfered-edge zeolite 4A synthesized from coal fly ash for use as a builder in detergents. *Journal of Hazardous Materials B*, **2006**, 137, pp. 401-409.
- 3) Image of a grain of a naturally occurring Chilean zeolite
 - 1) Imaged by SEM (at micron scale)
 - 2) Englert, A.; Rubio, J. Characterization and environmental application of a Chilean natural zeolite. *International Journal of Mineral Processing*, **2005**, 75, pp. 21-29.

Chitosan nanoparticles - Images

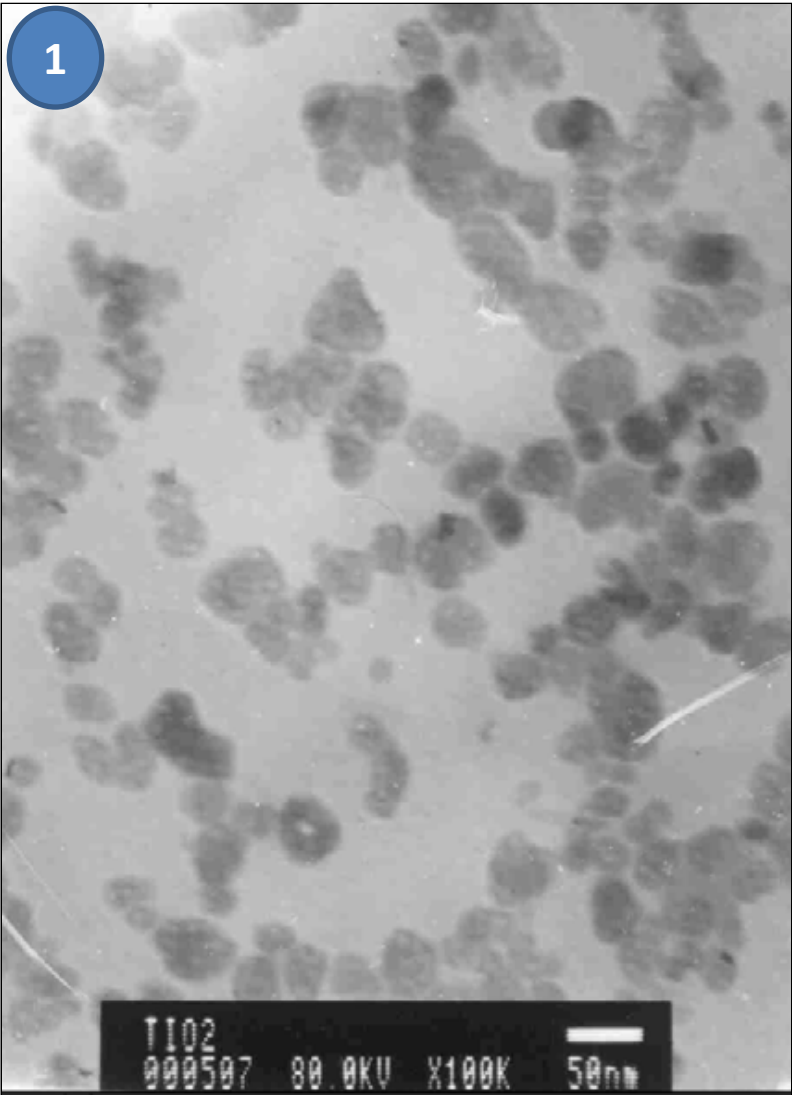
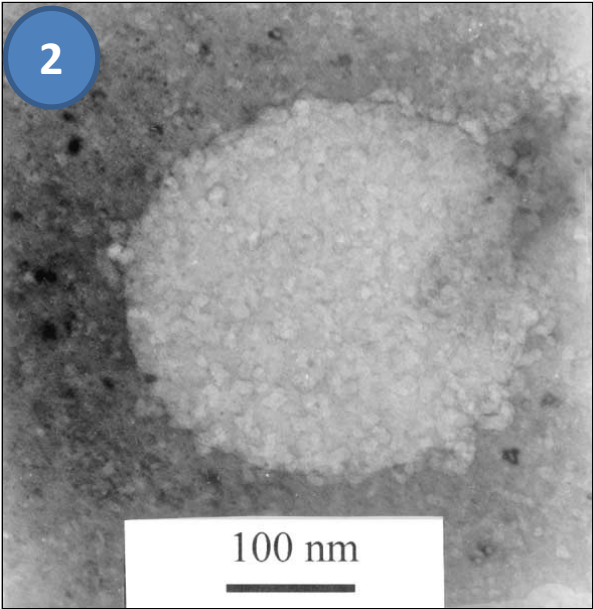


Image of 10% cross-linked chitosan nanoparticles
(Banerjee et al., 2002)

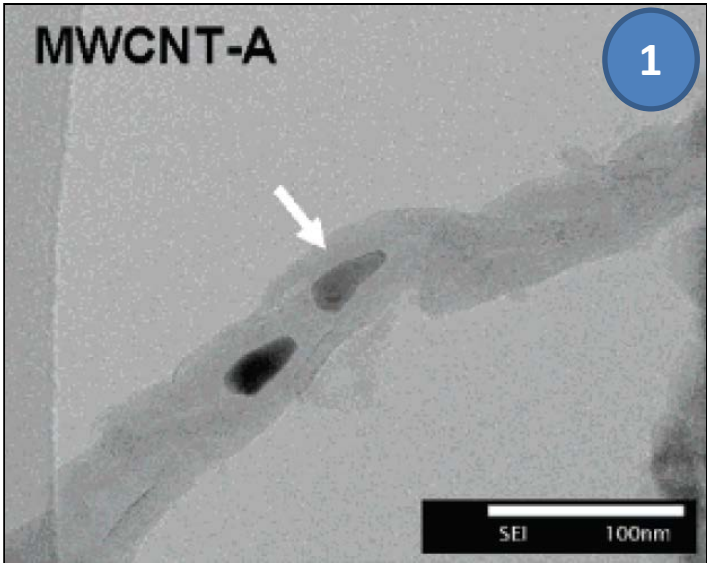


Chitosan nanoparticle loaded with cyclosporin A
(De Campos et al., 2001)

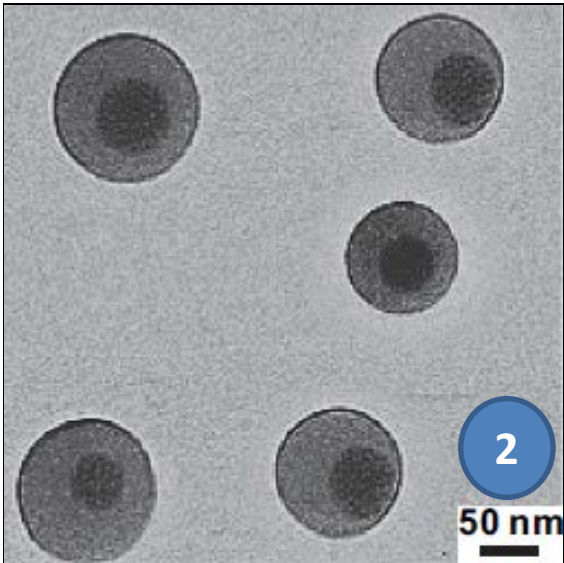
Chitosan nanoparticles – References (Clockwise from top left)

- 1) 10% cross-linked chitosan nanoparticles
 - 1) Imaged by TEM
 - 2) Banerjee, T.; Mitra, S.; Singh, A.; Sharma, R.; Maitra, A. Preparation, characterization and biodistribution of ultrafine chitosan nanoparticles. *International Journal of Pharmaceutics*, **2002**, 243, pp. 93-105.
- 2) Chitosan nanoparticle loaded with cyclosporin A
 - 1) Imaged by TEM
 - 2) De Campos, A.; Sánchez, A.; Alonso, M. Chitosan nanoparticles: a new vehicle for the improvement of the delivery of drugs to the ocular surface. Application to cyclosporin A. *International Journal of Pharmaceutics*, **2001**, 224, pp. 159-168.

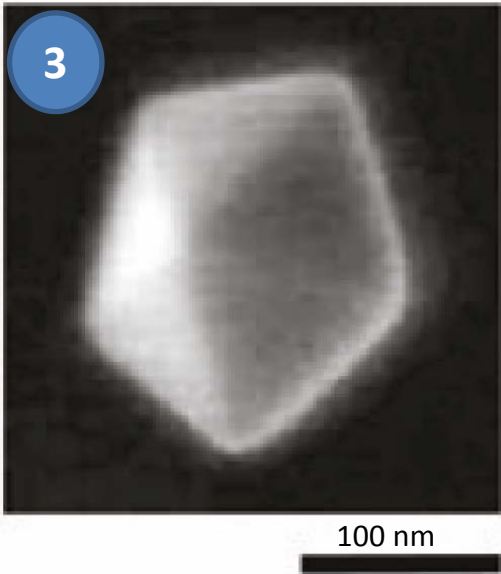
Highly functionalized nanoparticles - Images



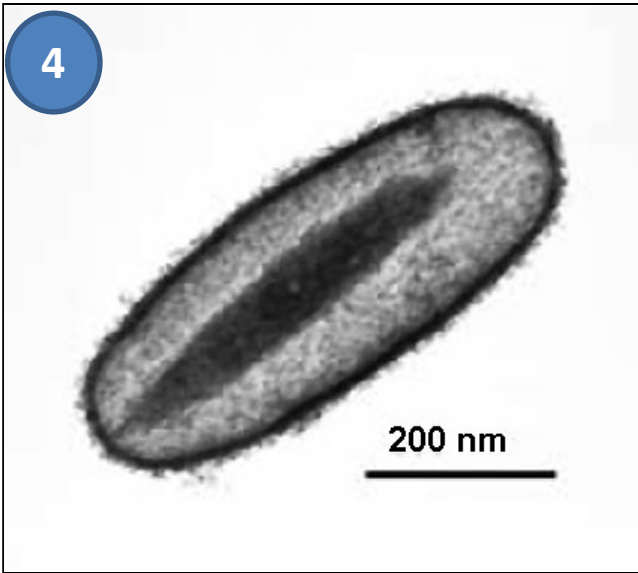
Residual metal catalyst embedded in carbon nanotube (Pumera, 2007)



Quantum dot nanoparticle surrounded by a PLGA shell to form a core-shell nanocomposite (Lee et al., 2010)



Silver nanoparticle decahedron formed in DMF (Tsuji et al., 2010)



Double-walled SnO_2 nano-cocoon with an $\alpha\text{-Fe}_2\text{O}_3$ spindle embedded inside (Lou et al., 2007)

Highly functionalized nanoparticles – References (Clockwise from top left)

- 1) Residual metal catalyst embedded in carbon nanotube
 - 1) Imaged by TEM
 - 2) Pumera, M. Carbon Nanotubes Contain Residual Metal Catalyst Nanoparticles even after Washing with Nitric Acid at Elevated Temperature Because These Metal Nanoparticles Are Sheathed by Several Graphene Sheets. *Langmuir*, **2007**, 23, pp. 6453-6458.
- 2) Quantum dot nanoparticle surrounded by a PLGA shell to form a core-shell nanocomposite
 - 1) Imaged by TEM
 - 2) Lee, P.-W.; Hsu, S.-H.; Tsai, J.-S.; Chen, F.-R.; Huang, P.-J.; Ke, C.-J.; Liao, Z.-X.; Hsiao, C.-W.; Lin, H.-J.; Sung, H.-W. Multifunctional core-shell polymeric nanoparticles for transdermal DNA delivery and epidermal Langerhans cells tracking. *Biomaterials*, **2010**, 31, pp. 2425-2434.
- 3) Silver nanoparticle decahedron formed in DMF
 - 1) Imaged by SEM
 - 2) Tsuji, M.; Ogino, M.; Matsuo, R.; Kumagae, H.; Hikino, S.; Kim, T.; Yoon, S.-H. Stepwise Growth of Decahedral and Icosahedral Silver Nanocrystals in DMF. *Crystal Growth & Design*, **2010**, 10, pp. 296-301.
- 4) Double-walled SnO₂ nano-cocoon with an α -Fe₂O₃ spindle embedded inside
 - 1) Imaged by TEM
 - 2) Lou, X.; Yuan, C.; Archer, L. Double-walled SnO₂ Nano-Cocoons with Movable Magnetic Cores. *Advanced Materials*, **2007**, 19, pp. 3328-3332.



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