Magnetic and Carbonaceous Nano-Catalysts in Sustainable Chemical Transformations

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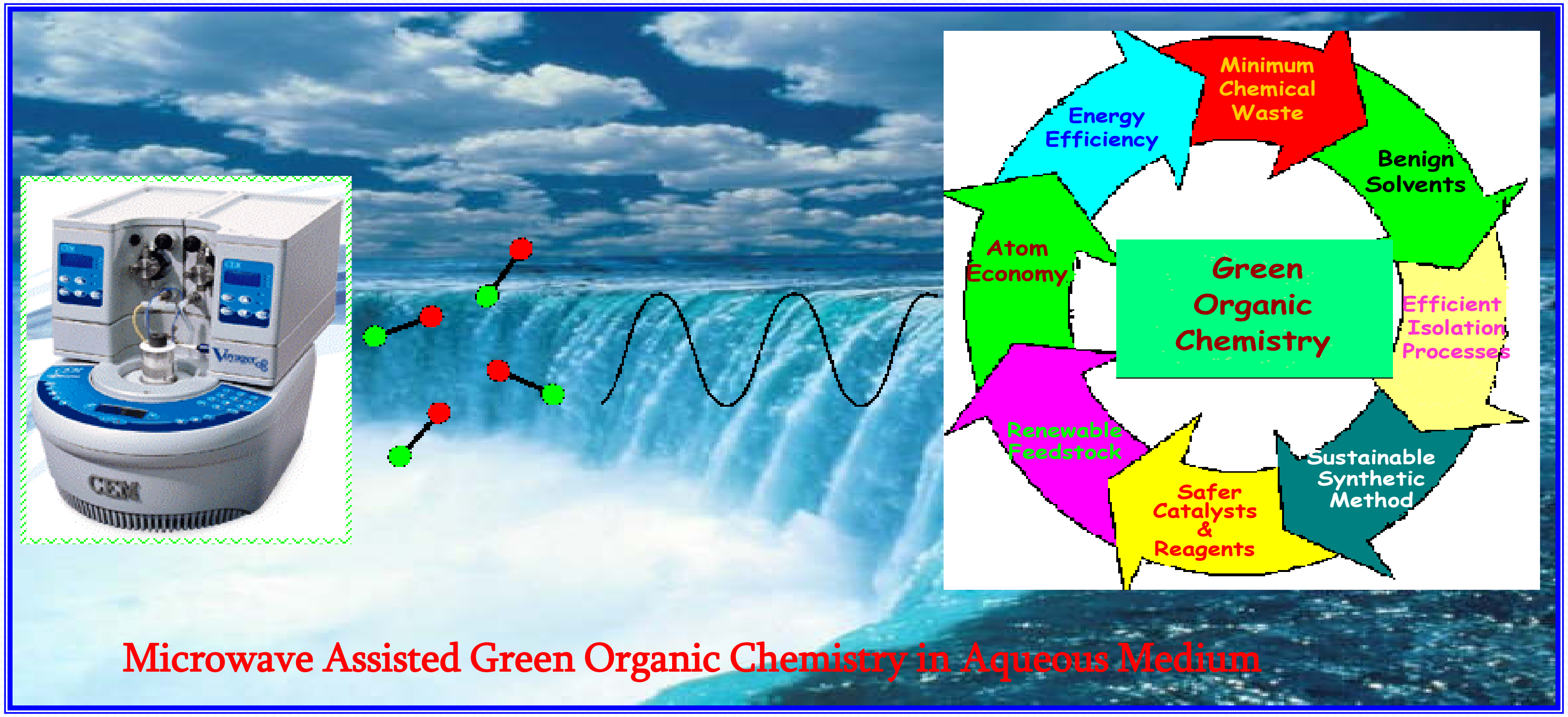
•Sustainable synthesis of chemical entities by microwave heating with nano-catalysis in water

•Green Chemistry principles are accommodated via multi-faceted approach



Seminal Review Articles on these themes summarizing our in-house research:

Acc. Chem. Res., (2008), *41*, 629; (2011), *44*, 469-478; (2014), *47*, 1338-1348; (2015), *48*, 182-191.

Chem. Soc. Rev., (2008) *37*, 1546; (2012) *41*, 1559; (2013) *42*, 3371; *42*, 5522; (2015) *44*, 7540; (2015) *44*, 8410; (2017) *46*, 6675.

Chem. Rev., (2017), *117*,1445-1514; (2016),*116*, 3722-3811; *ACS Sustain. Chem. & Eng.,* (2016), *4*, 5866-5878

Pure App. Chem., (2001) *73*, 193-198; *73*, 1309-1313; (2008), *80*, 777-790; (2013), *85*, 1703-1710.

Curr. Opin. Drug Disc., (2007), *10*, 723-737; *Curr. Opin. Chem. Eng.*, (2012) *1*, 123; *ChemSusChem*, (2014) *7*, 24-44.

Green Chem., (1999), *1*, 43-55; (2010), *12*, 743-754; (2014), *16*, 2027-2041.

Coord. Chem. Rev., (2015), *287*, 64-78; (2015), *291*, 68-94; (2015), 287, 137-156; (2017), *347*, 48-76.

Plant Extract

Sugar

Vitamins

Tea

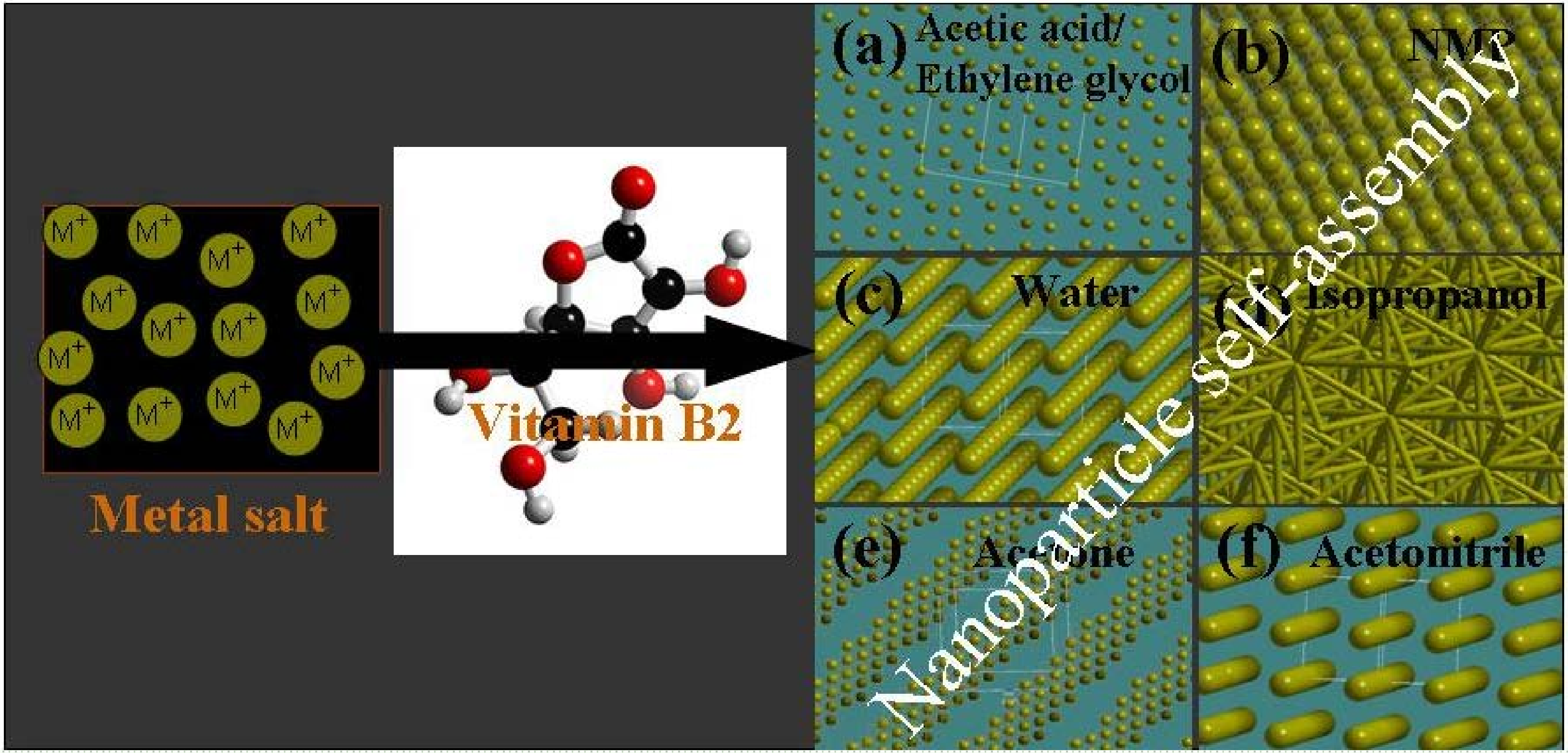
Wine

Water

Microwave

Green Synthesis of Nanomaterials

- **PROBLEM:** Synthesize nanomaterials in a sustainable fashion.
- **TECHNOLOGY SOLUTION:** *Learning from Nature-*
  Use the elegance of Riboflavin (Vitamin B_2) for redox chemistry.
- **CURRENT STATUS:** Self-assembly of nanoparticles demonstrated



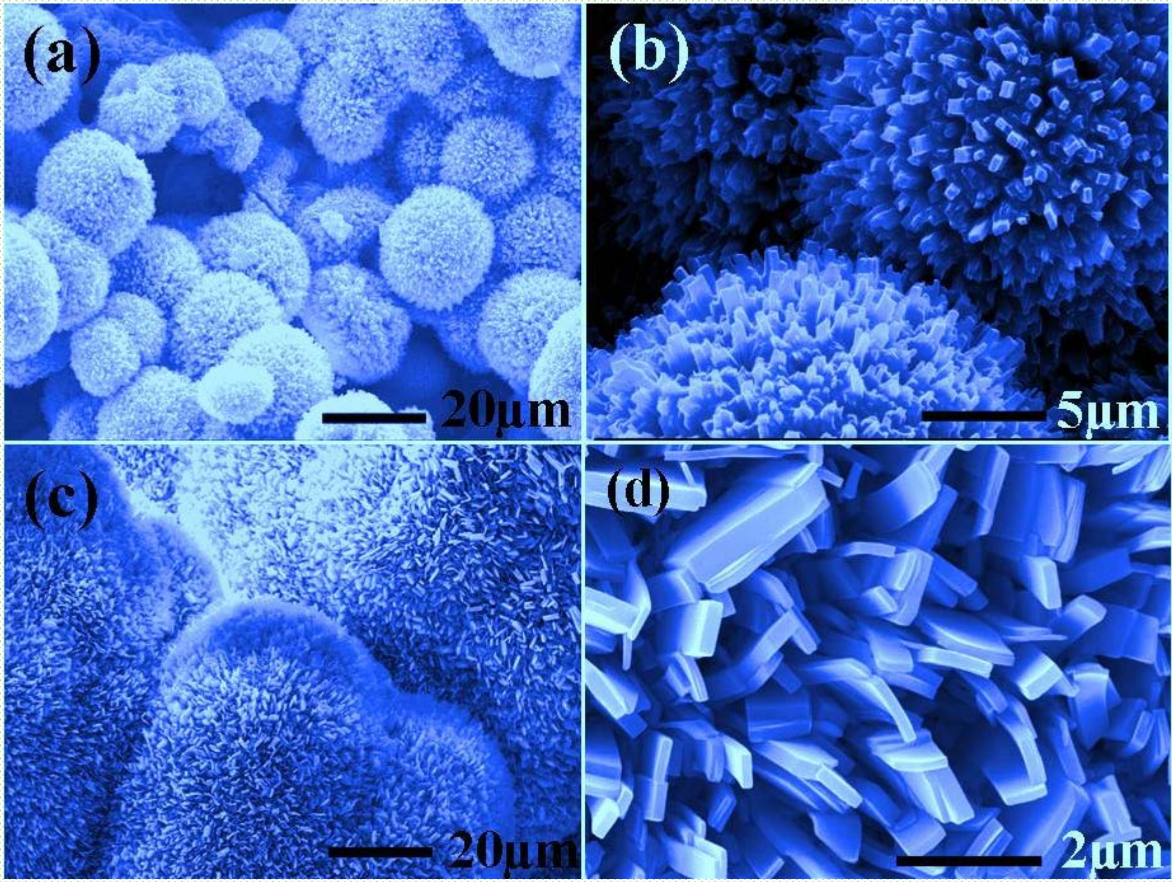
Nadagouda & Varma: *Green Chemistry*, *8*, 516, (2006)

Green Synthesis of Nanomaterials

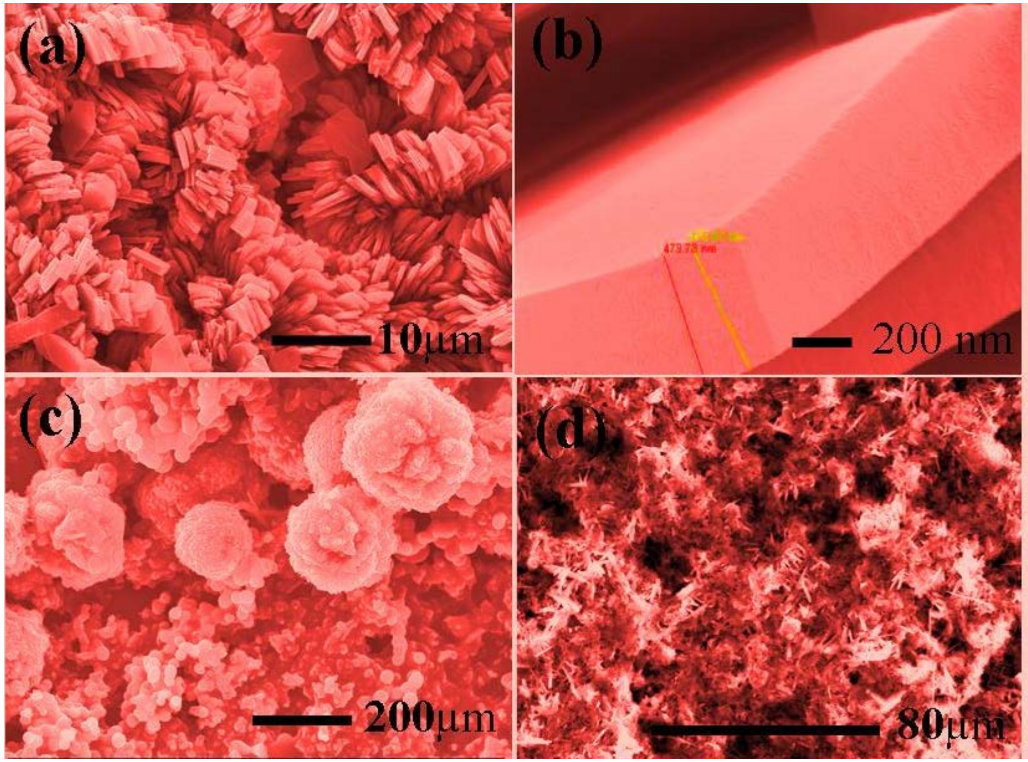
PROBLEM: Synthesize nanomaterials in a sustainable manner.

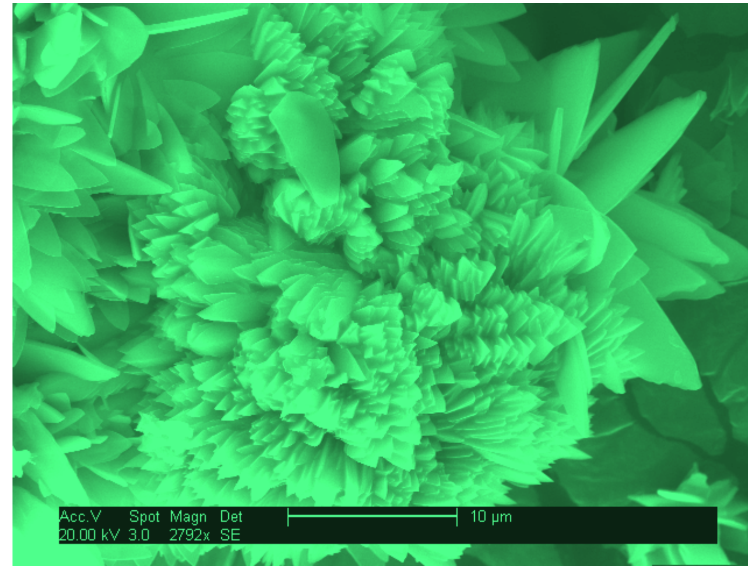
TECHNOLOGY SOLUTION: *Learning from Nature*- Use Vitamin B_1 in water to do the reduction and capping.

CURRENT STATUS: Aligned palladium nanoplates synthesized and toxic reducing and capping agents avoided.



Nadagouda, Polshettiwar & Varma: *J. Mat. Chem.*, 19, 2026 (2009)





(a-b) Pd nanoplates and

(c-d) Pd-catalyzed polypyrrole & polyaniline

Aligned platinum nanoflowers synthesized using vitamin B_1 in aqueous media

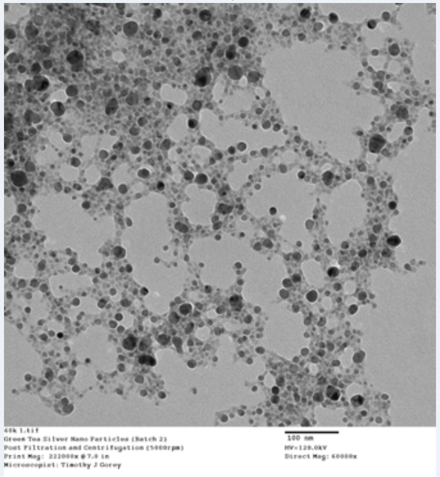
Nadagouda, Polshettiwar & Varma: *J. Mat. Chem.*, 19, 2026 (2009)

Tea for producing metal nanoparticles

Metal salt +  = Metal nanoparticle

(Ag, Au, Pd, Fe etc.)

Ag nanoparticle using green tea

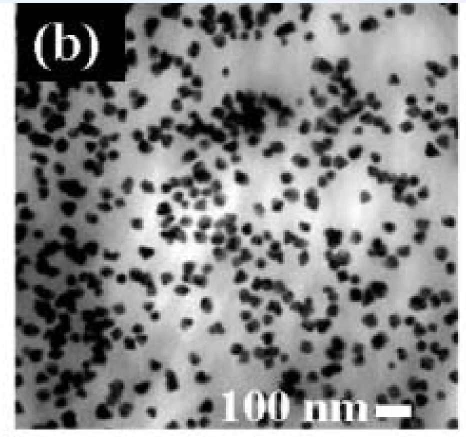


All particles are obtained at Room Temp.

Fe nanoparticles produced by this method are used by VeruTEK for soil remediation

(*U S Patents*, 7,963,720, June 21, 2011; 8,057,682 B2, Nov. 15, 2011)

Pd nanoparticle using green tea



Nadagouda & Varma: *Green Chemistry*, *10*, 859 (2008)

Green Remediation

PROBLEM: There are ~ 500,000 contaminated sites across the USA. Current cleanup technology requires excavation and may even generate toxic by-products. Remediating various environmental toxins in the subsurface and in water at or around these sites is a complex challenge.

TECHNOLOGY SOLUTION: Through a CRADA (445-08) between EPA's National Risk Management Research Laboratory (NRMRL) and the private company VeruTEK in Bloomfield, Connecticut, EPA green-synthesis technology is being used to further improve VeruTEK's green remediation and treatment technologies used in environmental cleanup. This project combines EPA's expertise in green synthesis of nanoparticles with VeruTEK's expertise with surfactant enhanced in situ chemical oxidation and reduction methods. The benefits from the new green-synthesis methods over conventionally used processes are: only natural materials are used; no hazardous waste is produced; reduced processing is required; materials are more stable, easily stored, and transported; and, materials can be more easily produced around the world.

Current Status:

Demonstrated destruction of contaminated soils

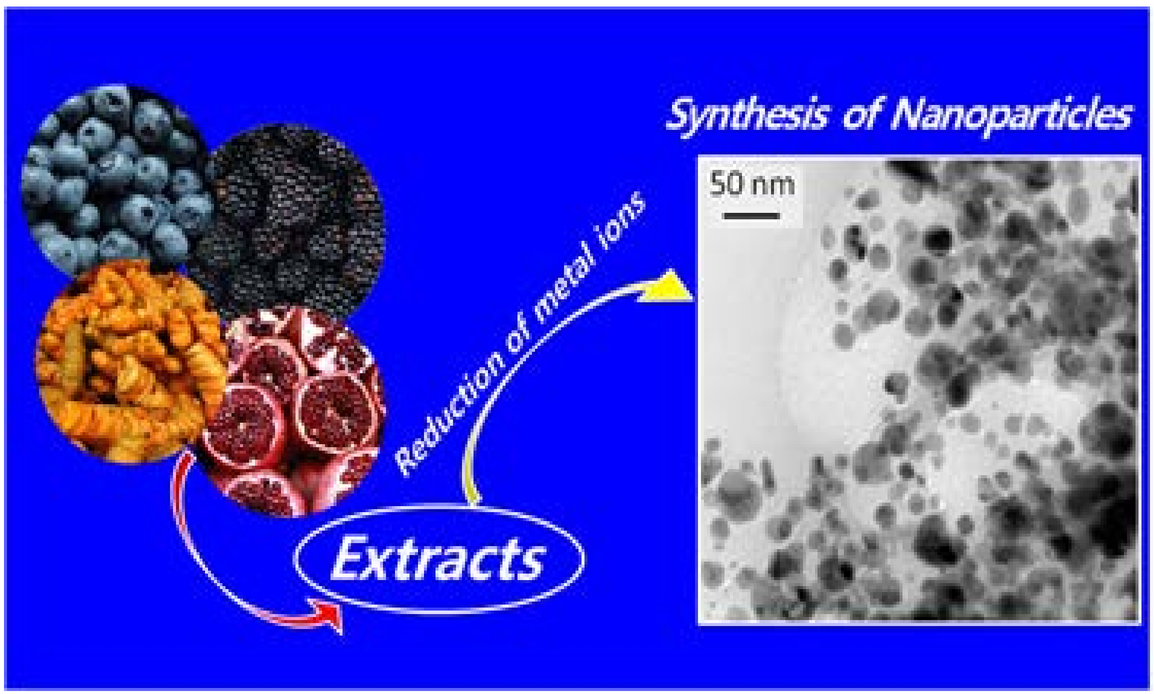
Several U.S. and Worldwide Patent Applications filed in 2008 -2010.

(*U S Patents*, 7,963,720, June 21, 2011; 8,057,682, Nov. 15, 2011)

Nadagouda, Hoag, Collins, Varma: *Crystal Growth & Design*, *9*, 4979 (2009);
Remediation Application: *J. Mater. Chem*. 19, 8671 (2009);
Toxicity studies: *Green Chemistry*, *12*, 114 (2010)-Hot Article

Synthesis of Silver and Gold Nanoparticles Using Antioxidants from Blackberry, Blueberry, Pomegranate and Turmeric Extracts

Greener synthesis of Ag and Au nanoparticles is described using antioxidants from blackberry, blueberry, pomegranate, and turmeric extracts; waste from fruit and juice industry can be utilized.



Nadagounda, Iyanna, Lalley, Han, Dionysiou, Varma: *ACS Sus. Chem. Eng.*, *2*, 1717 (2014)

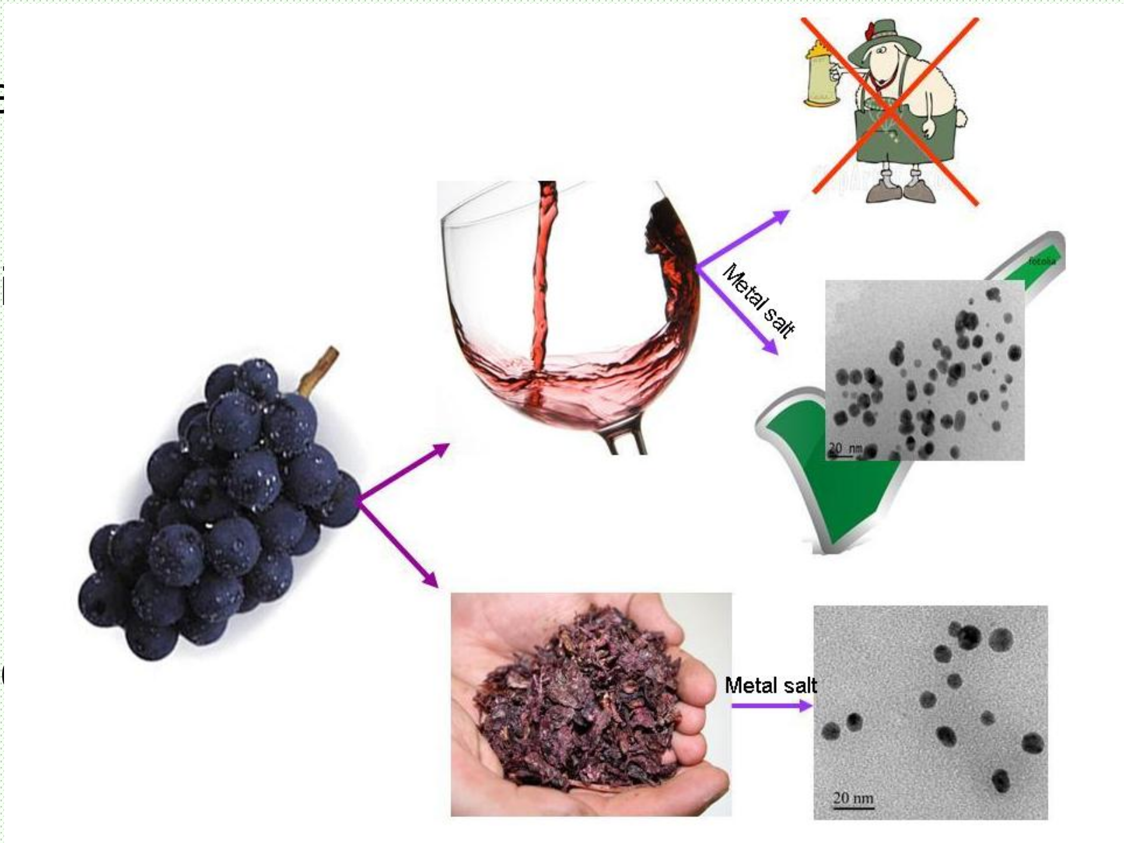
Green Synthesis of Nanomaterials

From Rag to Riches-Story of Red Grape Pomace

PROBLEM: 'Green' synthesis of nanoparticles using biorenewabl sources.

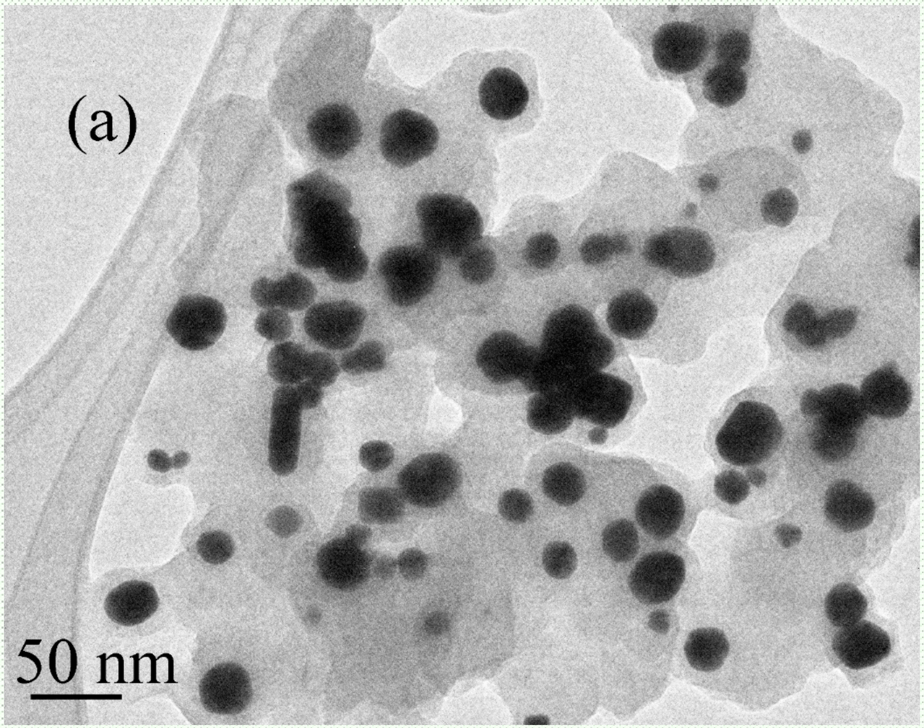
TECHNOLOGY SOLUTION: Utili source of polyphenols from agricultural waste.

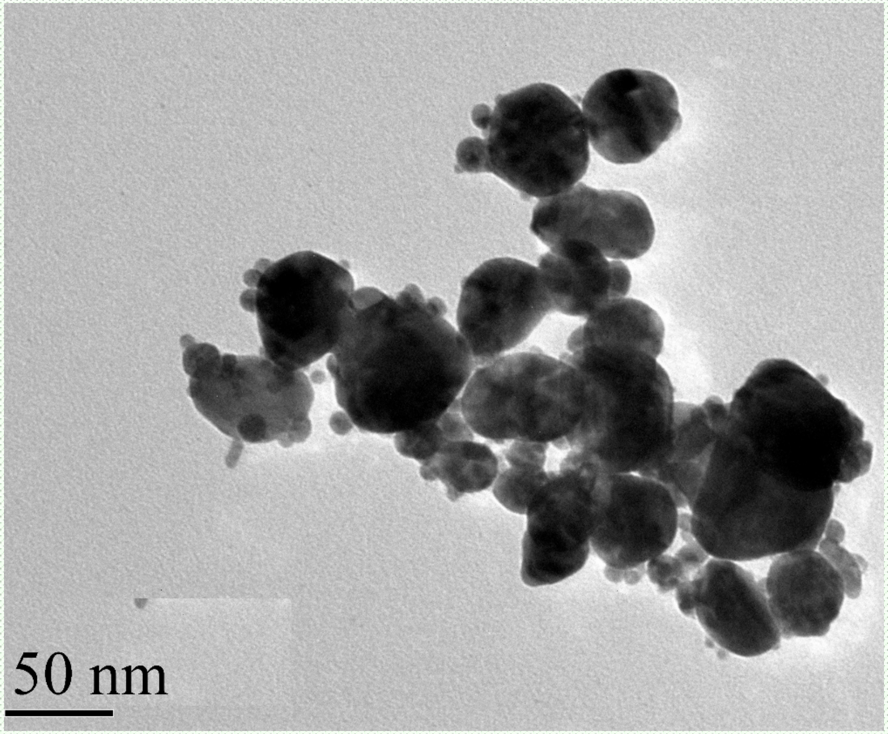
CURRENT STATUS: 'Rags to riches' story of nanoparticle generation using red wine and re grape pomace.



Baruwati, Varma: *ChemSusChem, 2*, 1041 (2009)

Gold Nanoparticles Using Wine



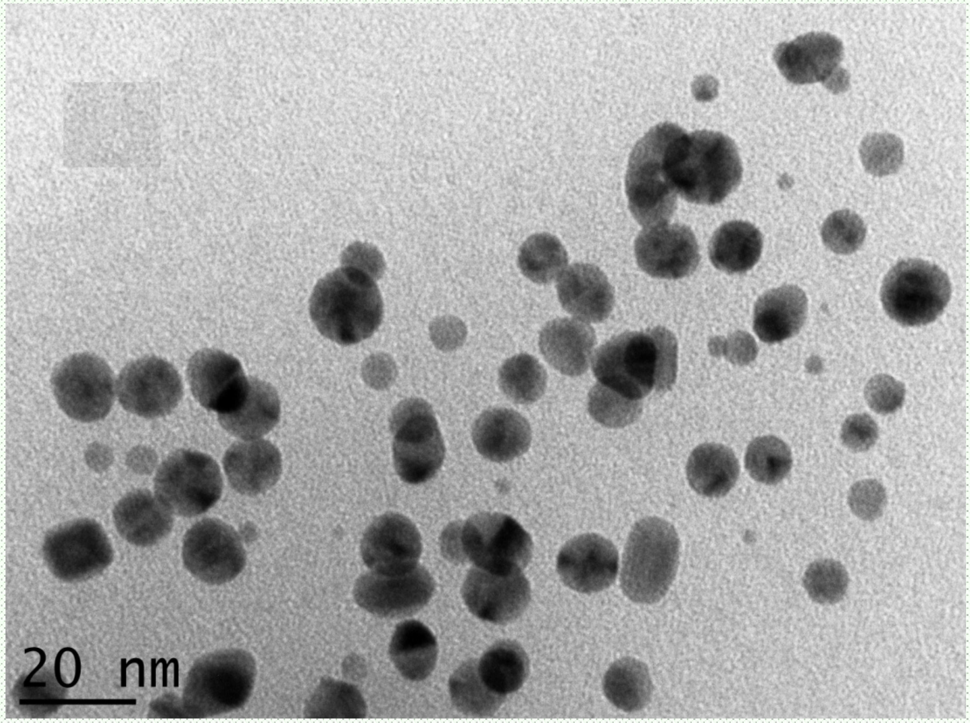


Red Wine **White Wine**

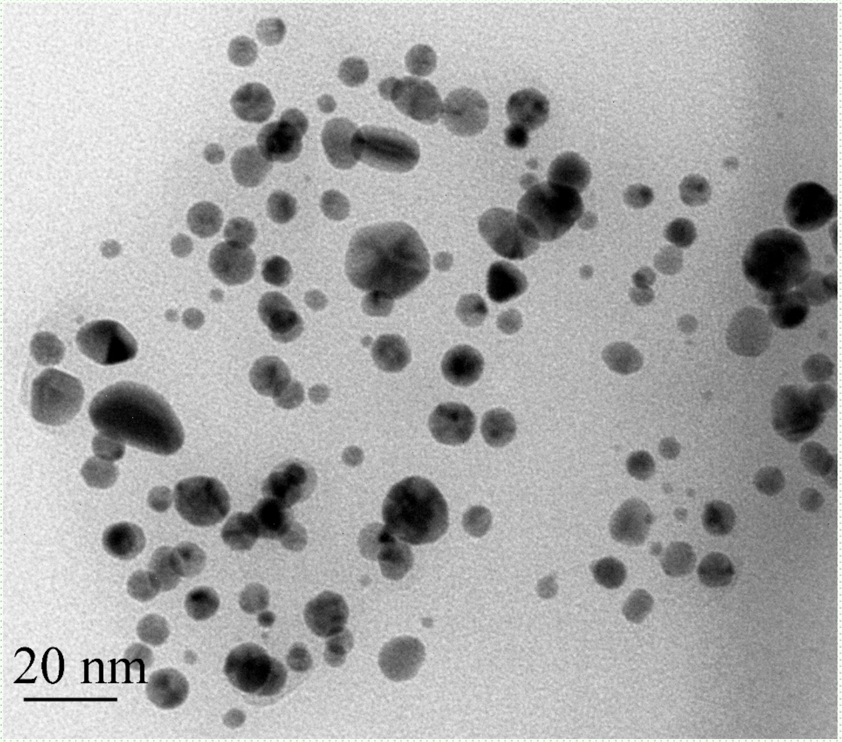
Baruwati, Varma: *ChemSusChem, 2*, 1041 (2009)

Chemistryworldblog: http://prospect.rsc.org/blogs/cw/?p=2337

Gold Nanoparticles Using Red Grape Pomace



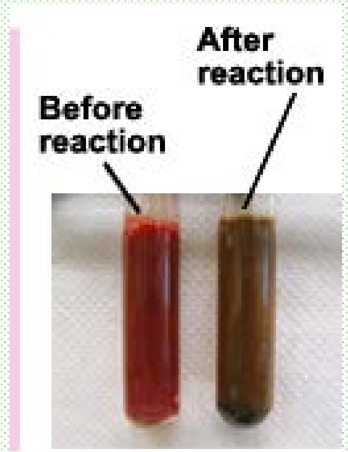
MW 50 W for 1 Minute



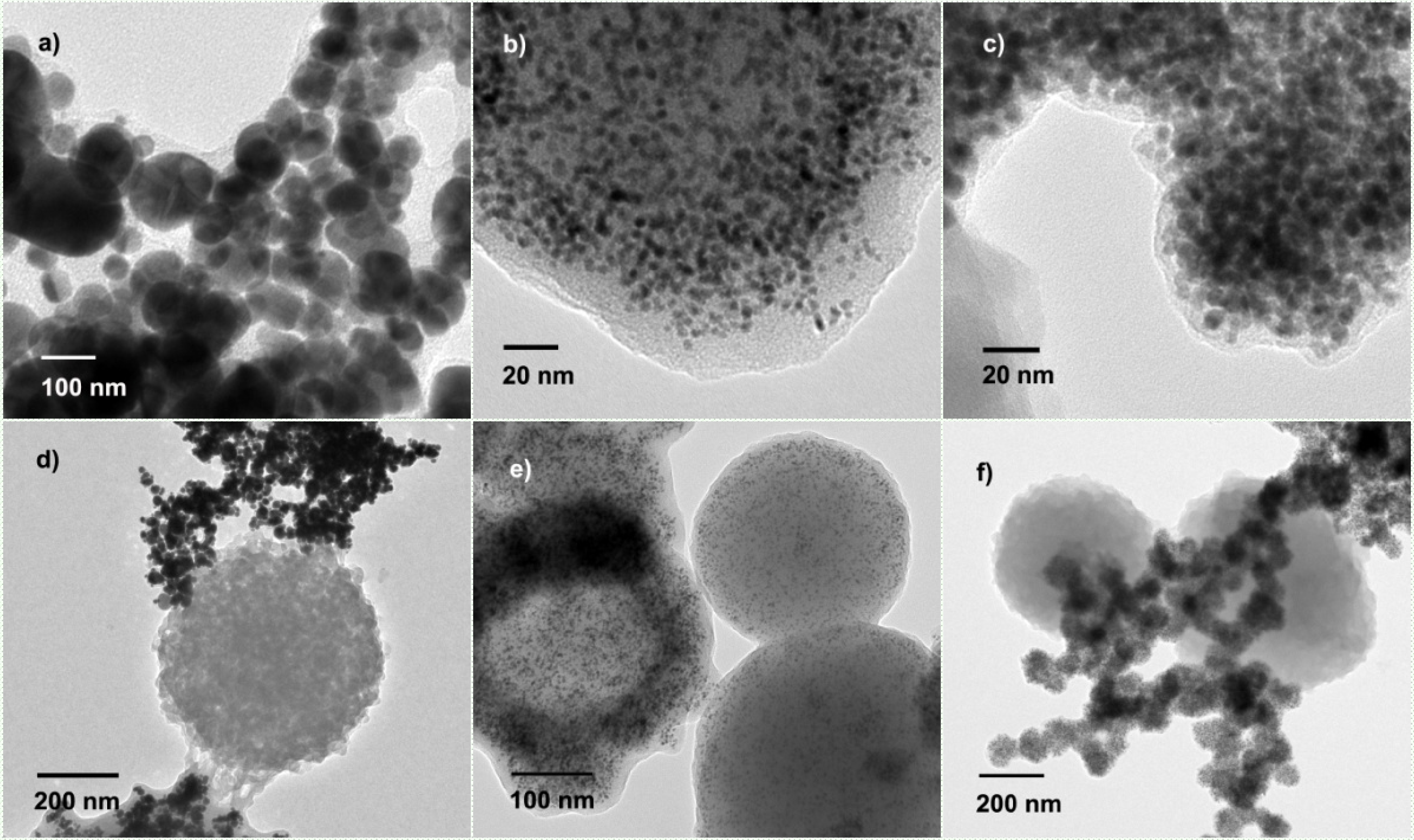
Room Temp. for 3 hours

Baruwati, Varma: *ChemSusChem, 2*, 1041 (2009)

Beet Juice-induced Green Fabrication of Plasmonic AgCl/Ag Nanoparticles: Unusual Top-down Hydrothermal Synthesis



Kou, Varma: *ChemSusChem* , *5*, 2435-2441 (2012)



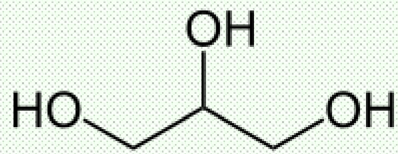
TEM images of typical Au, Pt, and Pd samples with Beet Juice: a) Au with capping; b) Pt with capping; c) Pd with capping; d) Au with organic microspheres; e) Pt with organic microspheres, and f) Pd with organic microspheres.

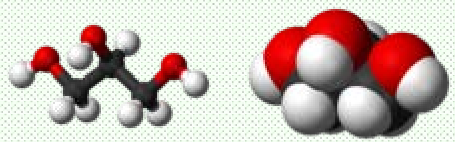
Kou, Varma: *RSC Advances*, *2*, 10283-10290 (2012)

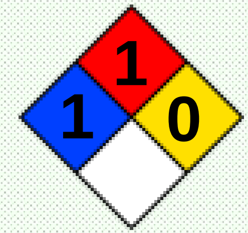
Utilization of Glycerol: Introduction

Glycerol

co-product of biodiesel
(approximately 10 wt %)







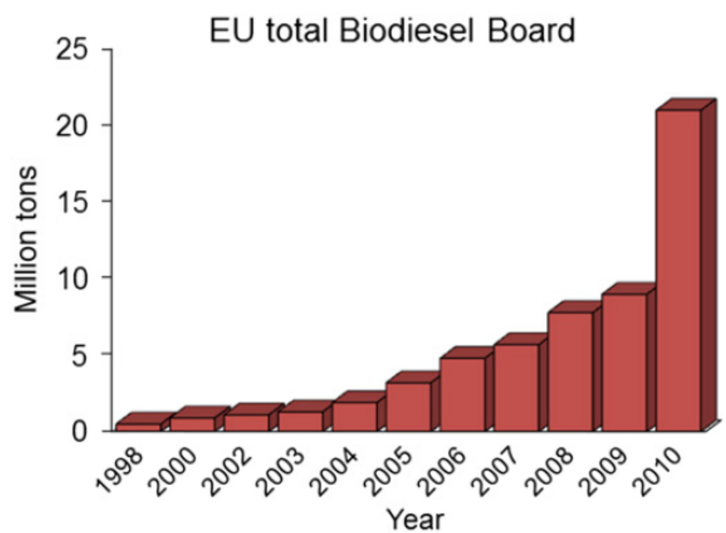


Fig. 1. Total biodiesel production of EU member states among the years (European Biodiesel Board, 2010).

S. Abad, X. Turon / Biotechnology Advances 30 (2012) 733–741

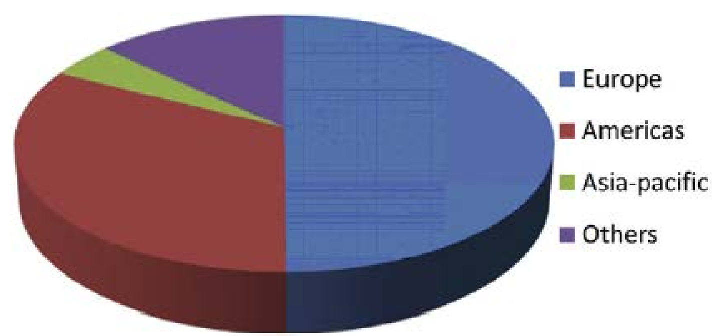
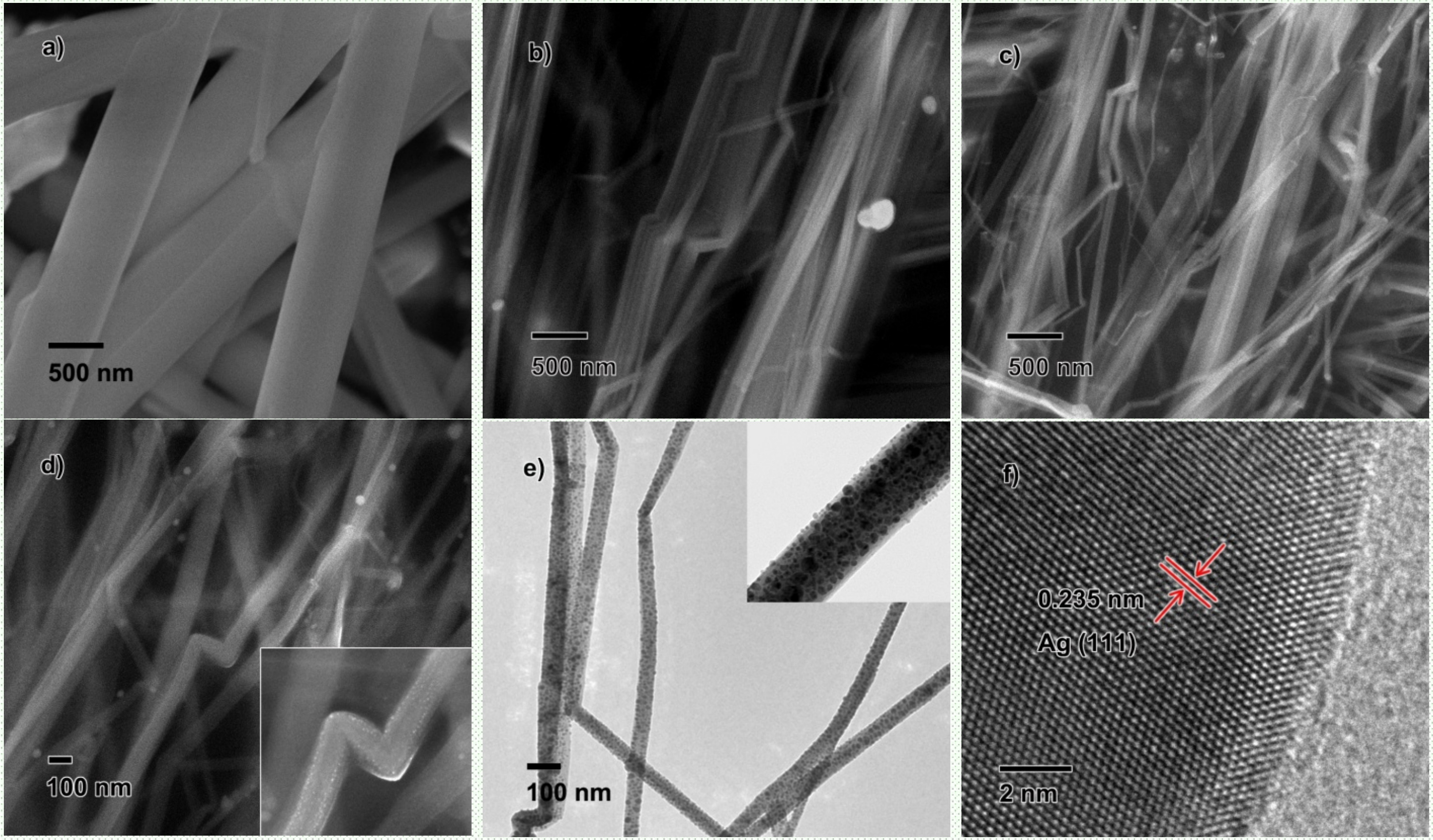


Fig. 3 – **Global biodiesel production share of different geographic regions of the world till 2009 [20].**

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 6473–6490

Diameter-controlled Ag Nanowires-Glycerol



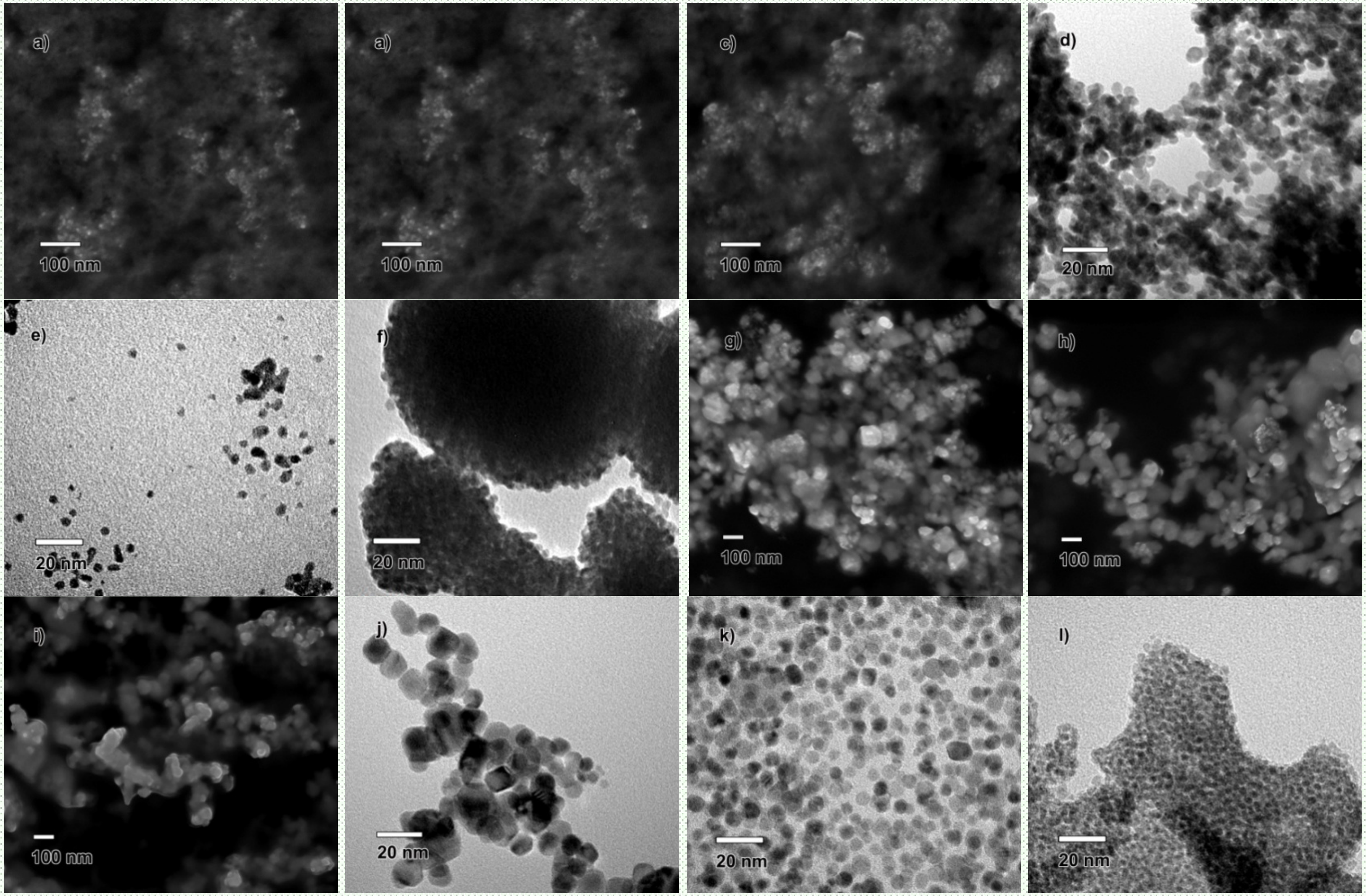
SEM Ag nanowires with different sodium dodecyl sulfate (SDS) amount

a) no SDS; b) 0.1 mmol SDS; c) 0.2 mmol SDS; d) 0.3 mmol SDS.

b) e) TEM and f) HRTEM images of typical Ag nanowires.

Kou, Varma: *Chem Commun*., *49*, 692 (2013)

Utilization of Glycerol: Nanometals (Pt, Pd)



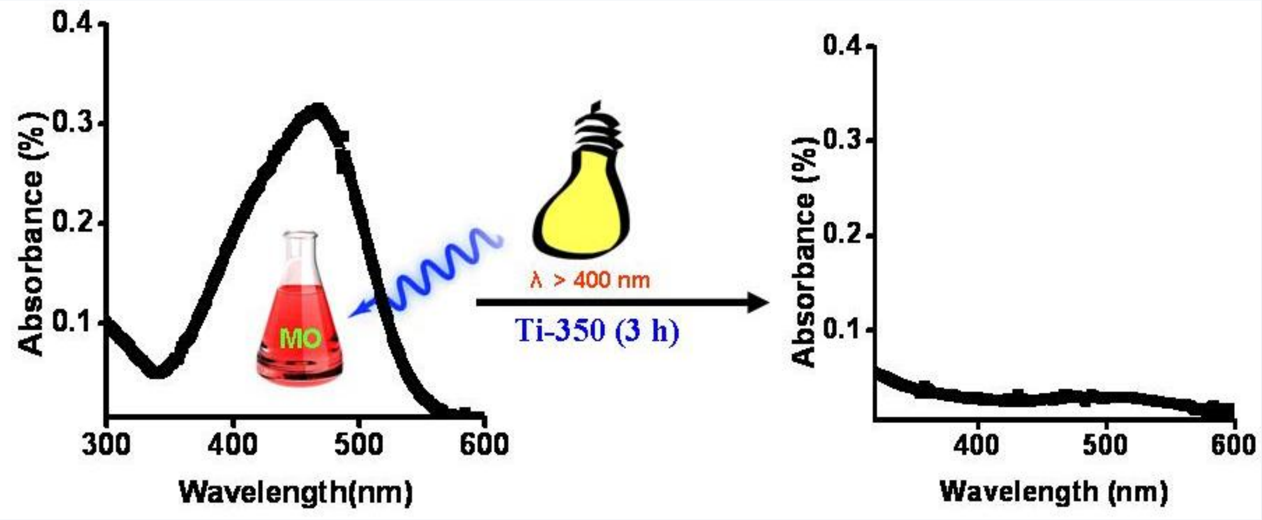
a) SEM image of Pt, 2 min; b) SEM image of Pt, 30 min; c) SEM image of Pt, 2 min with SDS; d) TEM image of Pt, 2 min; e) TEM image of Pt, 2 min with PVP; f) TEM image of Pt, 2 min with CTAB; g) SEM image of Pd, 2 min; h) SEM image of Pd, 30 min; i) SEM image of Pd, 2 min with SDS; j) TEM image of Pd, 2 min; k) TEM image of Pd, 2 min with PVP; l) TEM image of Pd, 2 min with CTAB.

Kou, Varma *et al.: ACS Sustain. Chem. Eng.*, *1*, 810 (2013)

Visible Light Active TiO_2 Photo Catalyst

Conventional TiO_2 is UV active. Band Gap 3.2 eV

Tailoring the band gap for red shift, it is possible to make TiO_2 active in visible light facilitating economic and green pathway for various remediation process



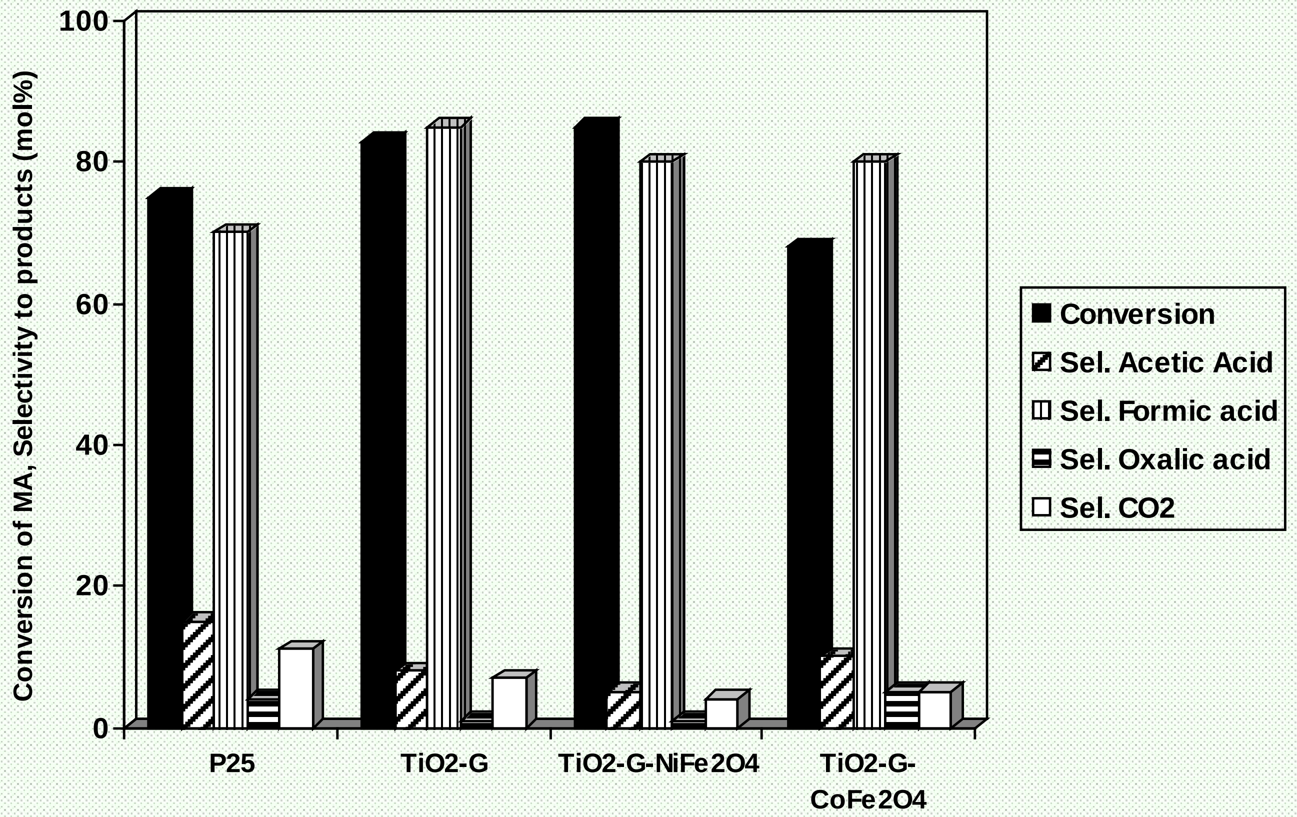
B. Baruwati, R. S. Varma, *J. Nanosci. Nanotech., 11*, 2036 (2010)

J. Virkutyte, B. Baruwati, R. S. Varma, *Nanoscale*, *2*, 1109 (2010)

J. Virkutyte, R. S. Varma, *RSC Advances*, *2*, 1533 (2012); *2*, 2399 (2012)

TiO_2 Films: *Coordination Chem. Reviews*, 306, 43-64 (2016)

Photocatalytic Transformation Studies of Malic acid under Visible Light Irradiation using Various Titania Catalysts



Baruwati, Luque, Varma et al.: *Green Chem.*, *13*, 2750 (2011)

Microcystin-LR removal using Magnetically separable N-doped TiO_2

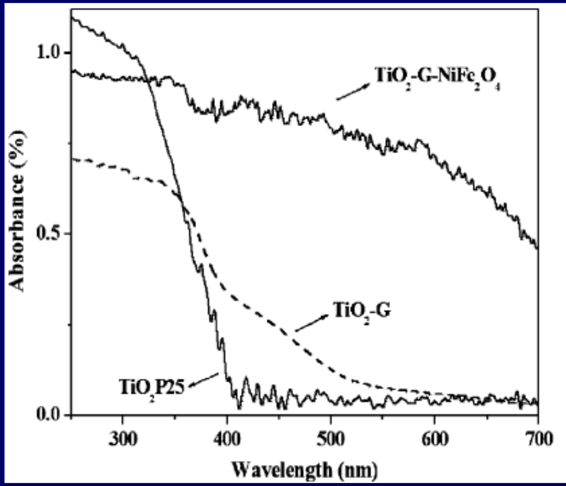
** In collaboration with Dr. Dionysious D. Dionysiou and Dr. Miguel Pelaez, Environmental Engineering and Science Program, University of Cincinnati, OH, USA*

- **Microcystin-LR (MC-LR) is themost commonly cyanotoxin released from cyanobacteria harmful algal blooms (Cyano-HABs - favored by eutrophication).**

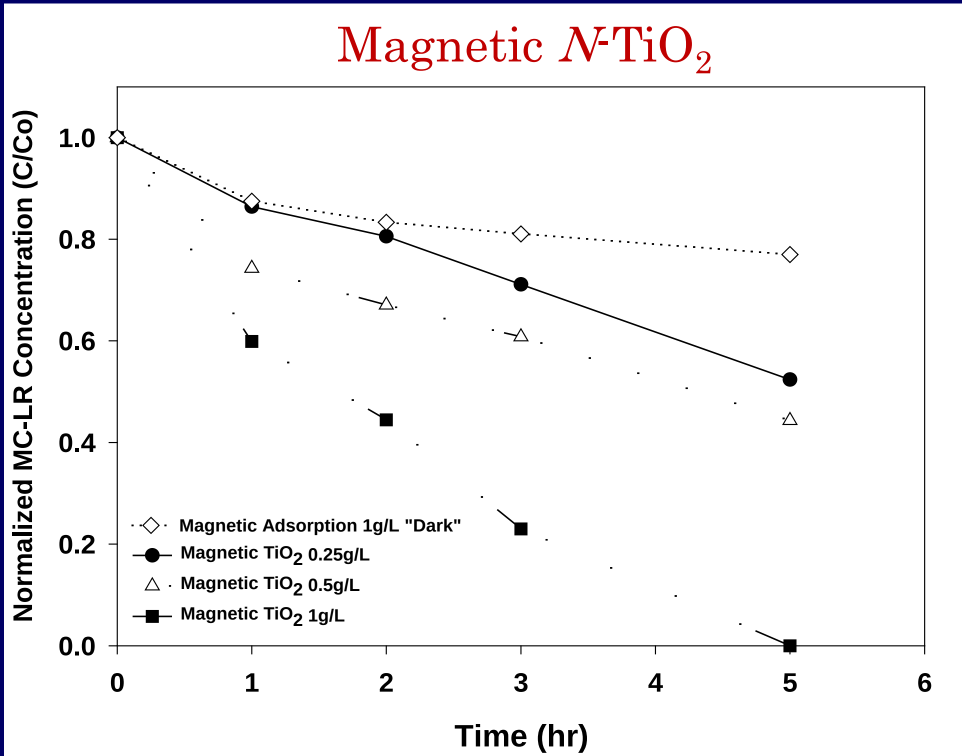
- **Conventional treatment processes and chemical oxidation technologies have been evaluated for the treatment of cyanotoxins with various results.**
  Lawton and Robertson, Chem. Soc. Rev. 1999, 28, 217; Liu et al., Environ. Sci. Technol, 2003, 37 3214.

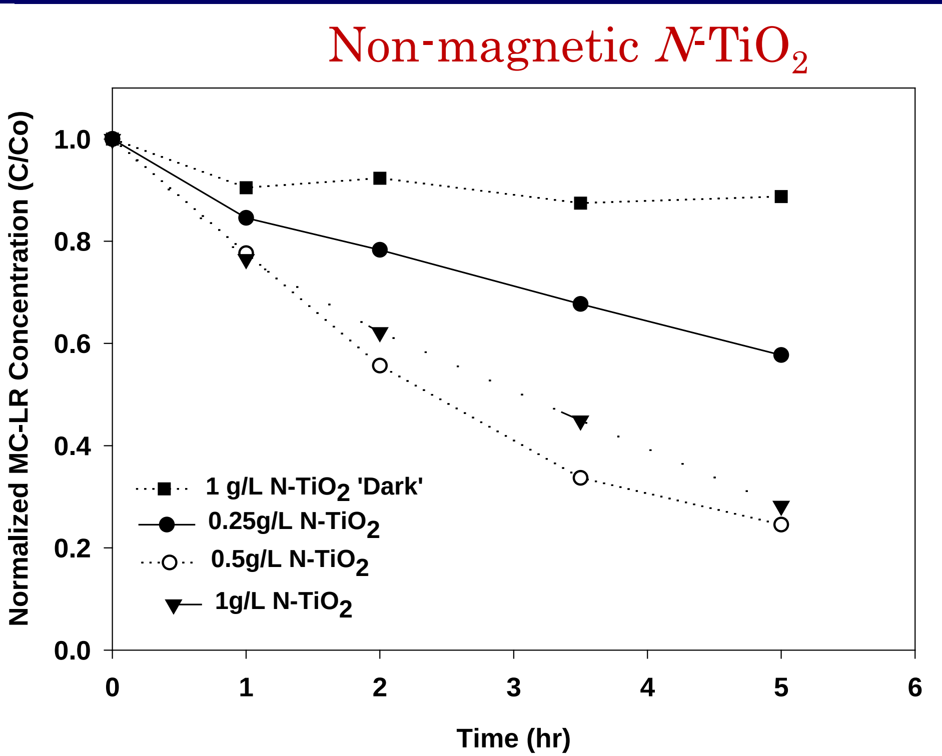
- **TiO_2 photocatalysis has been proven effective to remove MC-LR in water.**
  Antoniou et al., Toxicon 2008; Pelaez et al., Appl. Cat. B 2010 & 2012.

- **Magnetic (TiO_2-G-$NiFe_2O_4$) and non-magnetic (TiO_2-G) nitrogen-doped TiO_2 nanoparticles have been previously synthesized.**



Balu, Baruwati, Serrano, Cot, Garcia-Martinez, Varma, Luque, Green Chemistry, 13, 2750-2758 (2013)





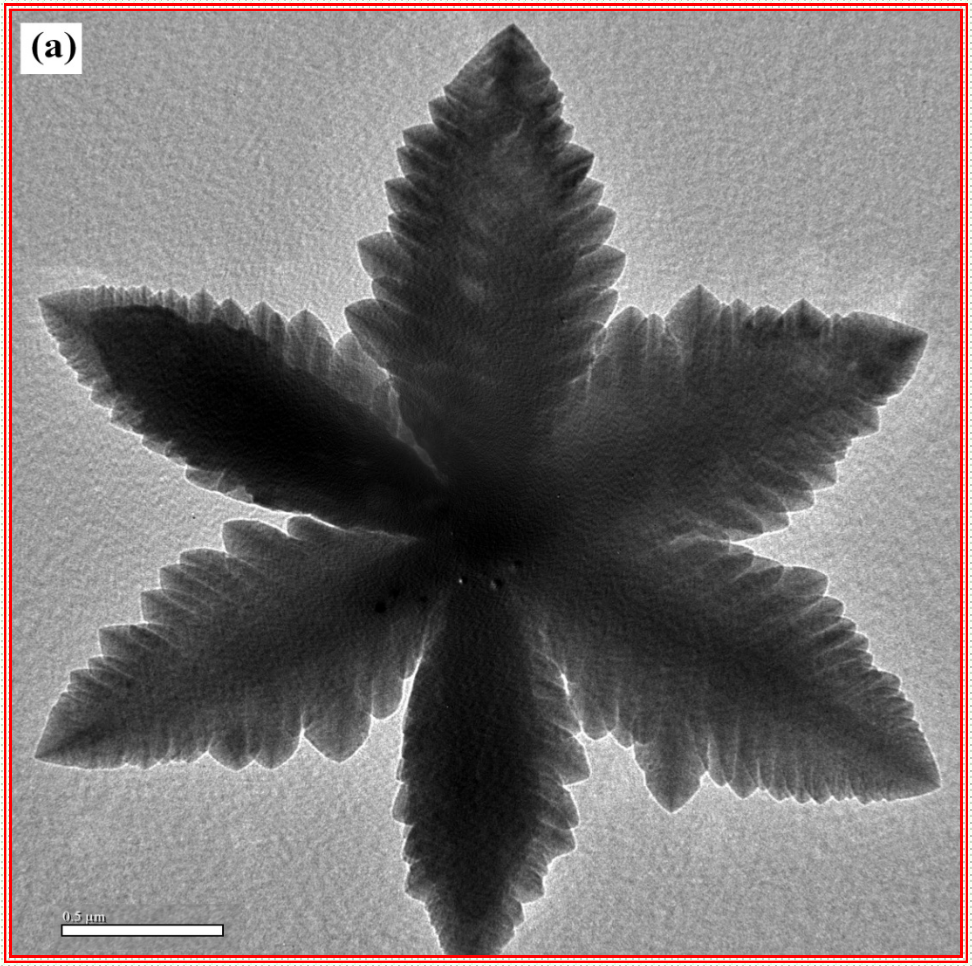
Conditions: Visible light (λ >420 nm). Initial MC-LR concentration: 450 μg/L; pH solution 5.7.

- Non-magnetic and magnetic *N*-TiO_2 have proven highly active and efficient in the removal of MC-LR toxin from aqueous solutions at the conditions tested.

- In particular, magnetic *N*-TiO_2 exhibited a remarkable photodegradation activity, with complete removal of MC-LR after 5 h of irradiation.

Pelaez, Baruwati, Varma, Luque, Dionysiou: *Chem. Commun., 49*, 10118 (2013)

Synthesis of Single-Crystal Micro-Pine Structured Nano-Ferrites and Their Application in Catalysis



Polshettiwar, Nadagouda & Varma: *Chem. Commun*., 6318 (2008)

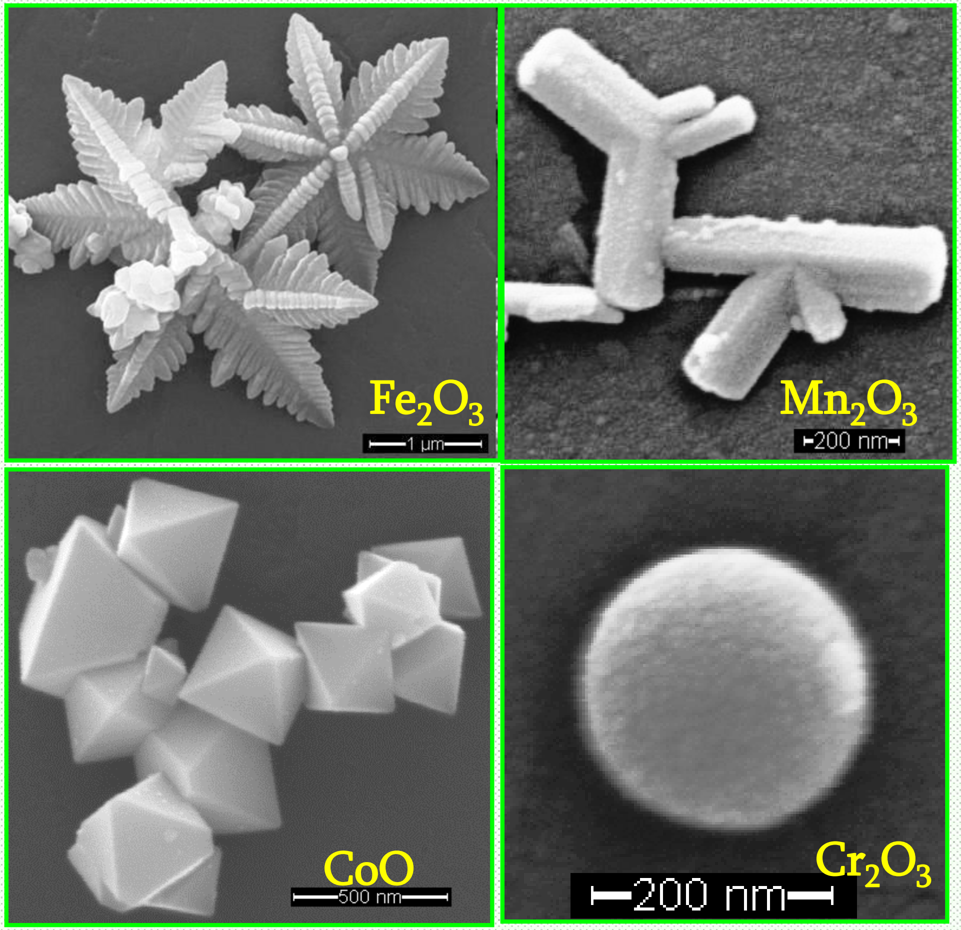
Green Synthesis of Nanomaterials

3D Nano-Metal Oxides
MW Synthesis in Water from Simple Salts

PROBLEM: Shape-selective ‘green’ synthesis of nano-metal oxides.

TECHNOLOGY SOLUTION: Utilize alternative form of microwave energy in water to do the hydrolysis of common salts.

CURRENT STATUS: Shape-selective oxides synthesized.

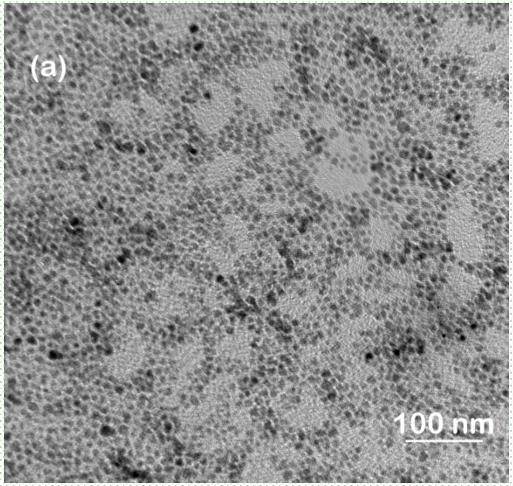


Polshettiwar, Baruwati & Varma: ***ACS Nano*, *3*, 728 (2009)**

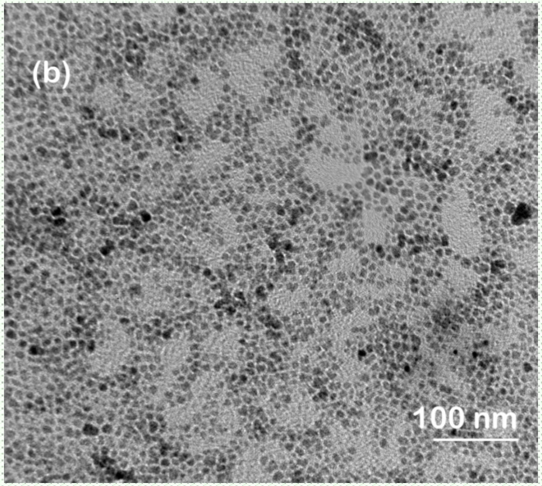
Among the Most-Accessed Articles in 12 months and ~10 years

Synthesis of Monodispersed Ferrite Nanoparticles at Water-Organic Interface Under Conventional/MW Hydrothermal Conditions

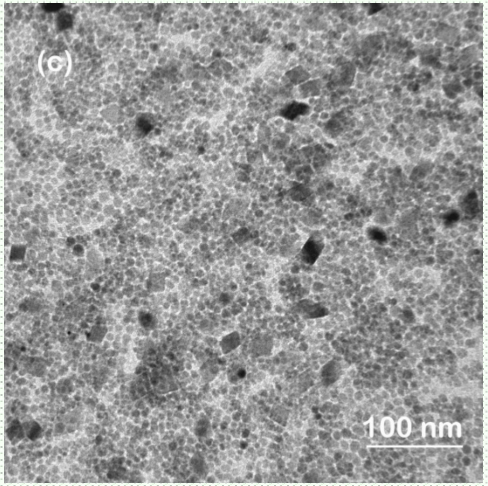
Monodispersed MFe_2O_4 (M=Fe, Mn, Co, Ni) nanoparticles have been synthesized via a water organic interface under both hydrothermal and MW conditions starting with readily available and inexpensive metal nitrate and halide precursors. The single phase particles are obtained at a temperature as low as 150 ^{o}C under MW conditions. The as-synthesized particles are dispersible in nonpolar organic solvents.



$NiFe_2O_4$



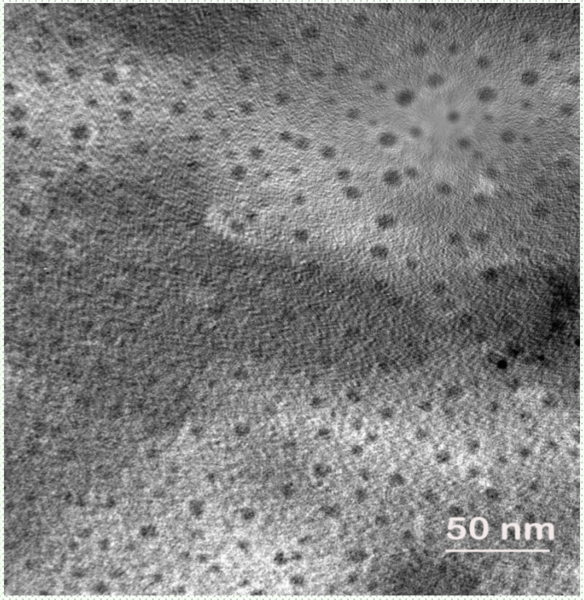
$CoFe_2O_4$



γ-Fe_2O_3

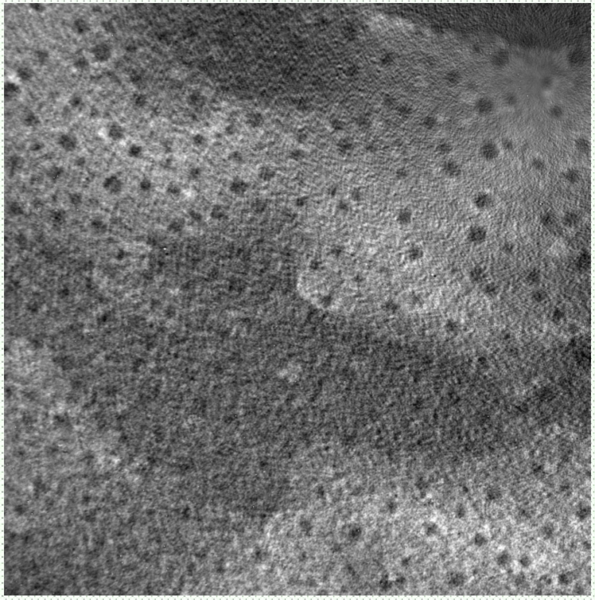
Baruwati, Nadagouda & Varma: *J. Phys. Chem. C, 112*, 18399 (2008)

Surface functionalization renders the particles dispersible in water



$NiFe_2O_4$

TEM of the particles dispersed in water

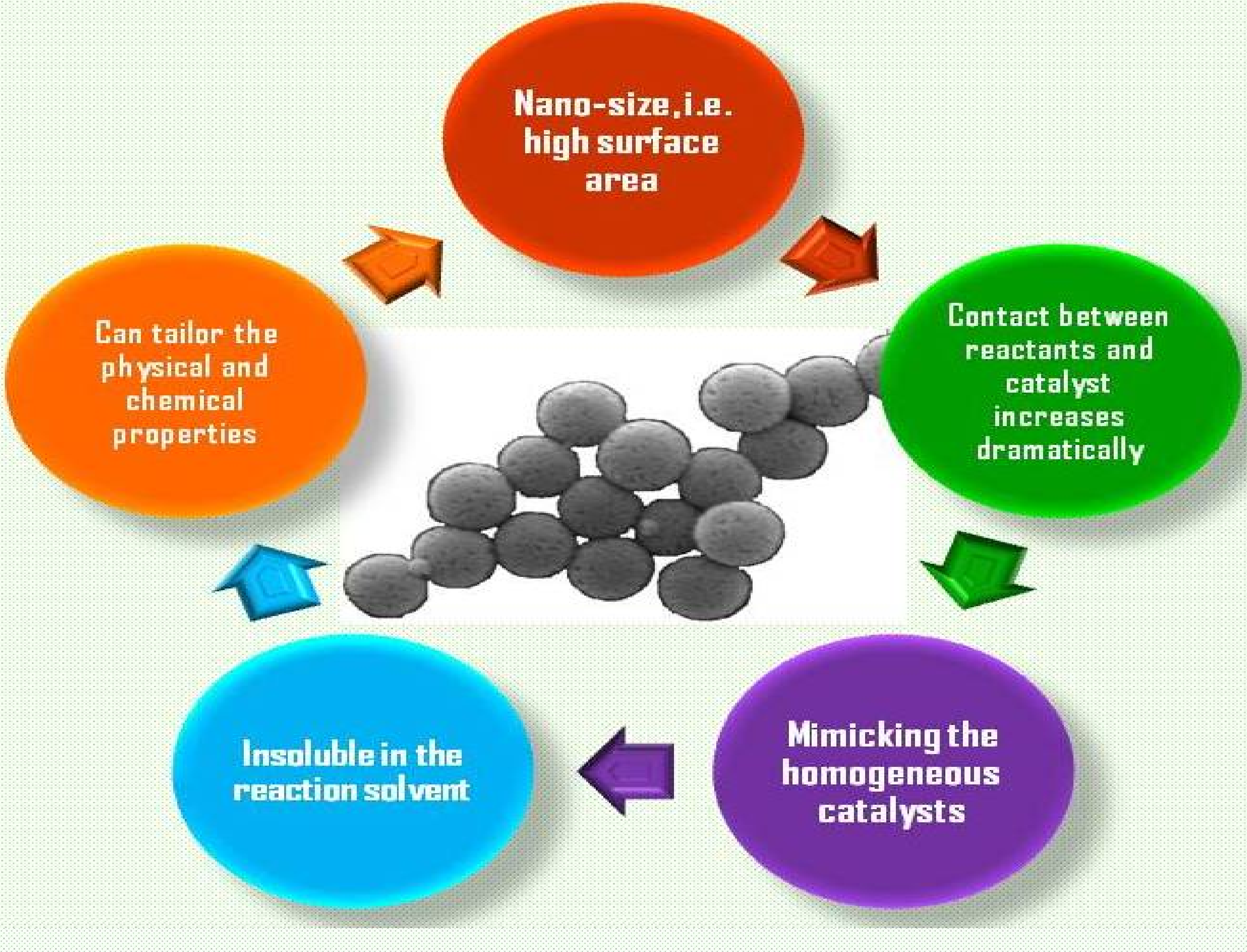


$CoFe_2O_4$

Photographic image of the particles in water and hexane

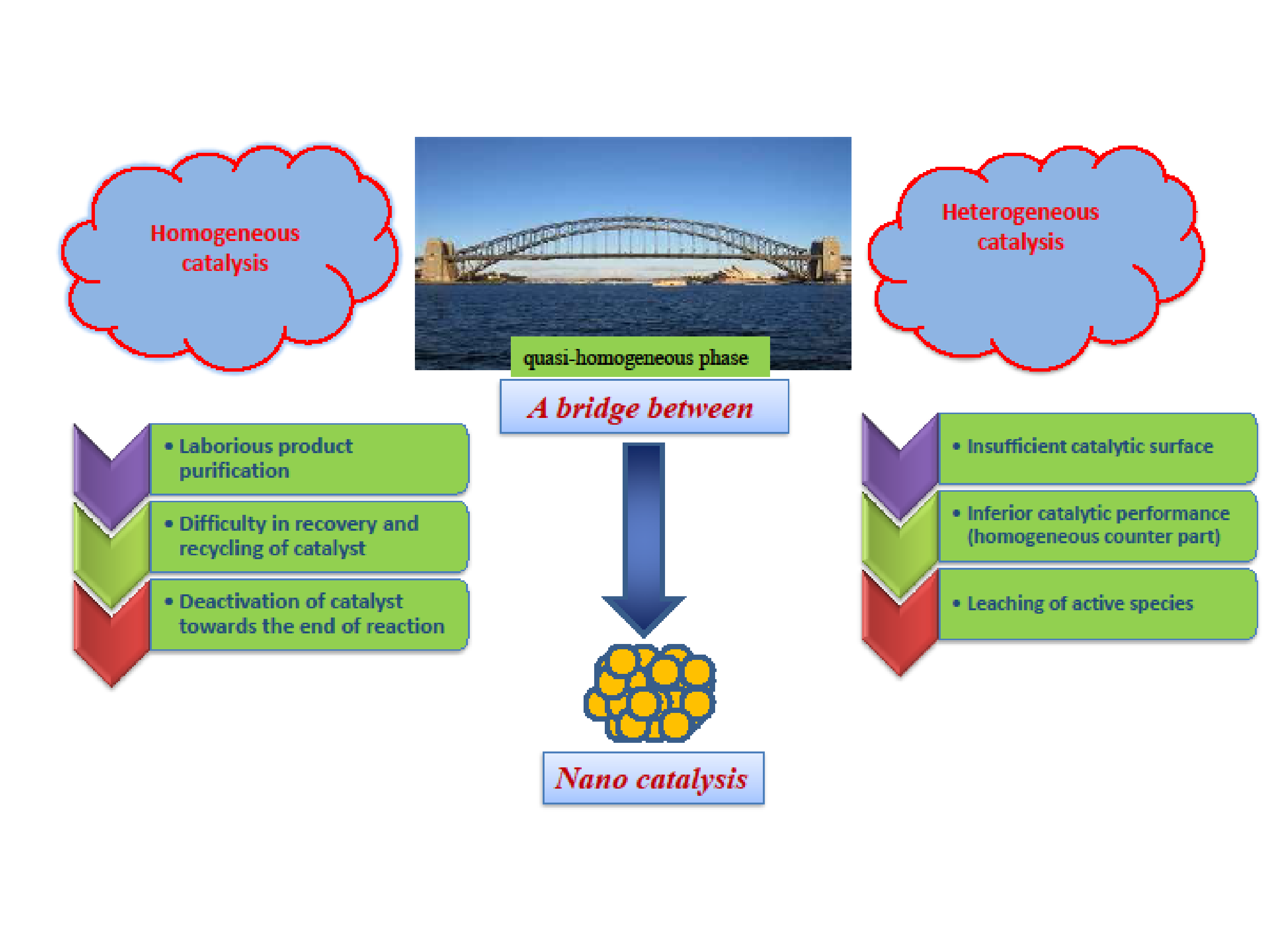
Baruwati, Nadagouda & Varma, *J. Phys. Chem. C*, *112*, 18399 (2008)

What is Nano-Catalysis?



Nano catalyst acts as a quasi-homogeneous phase

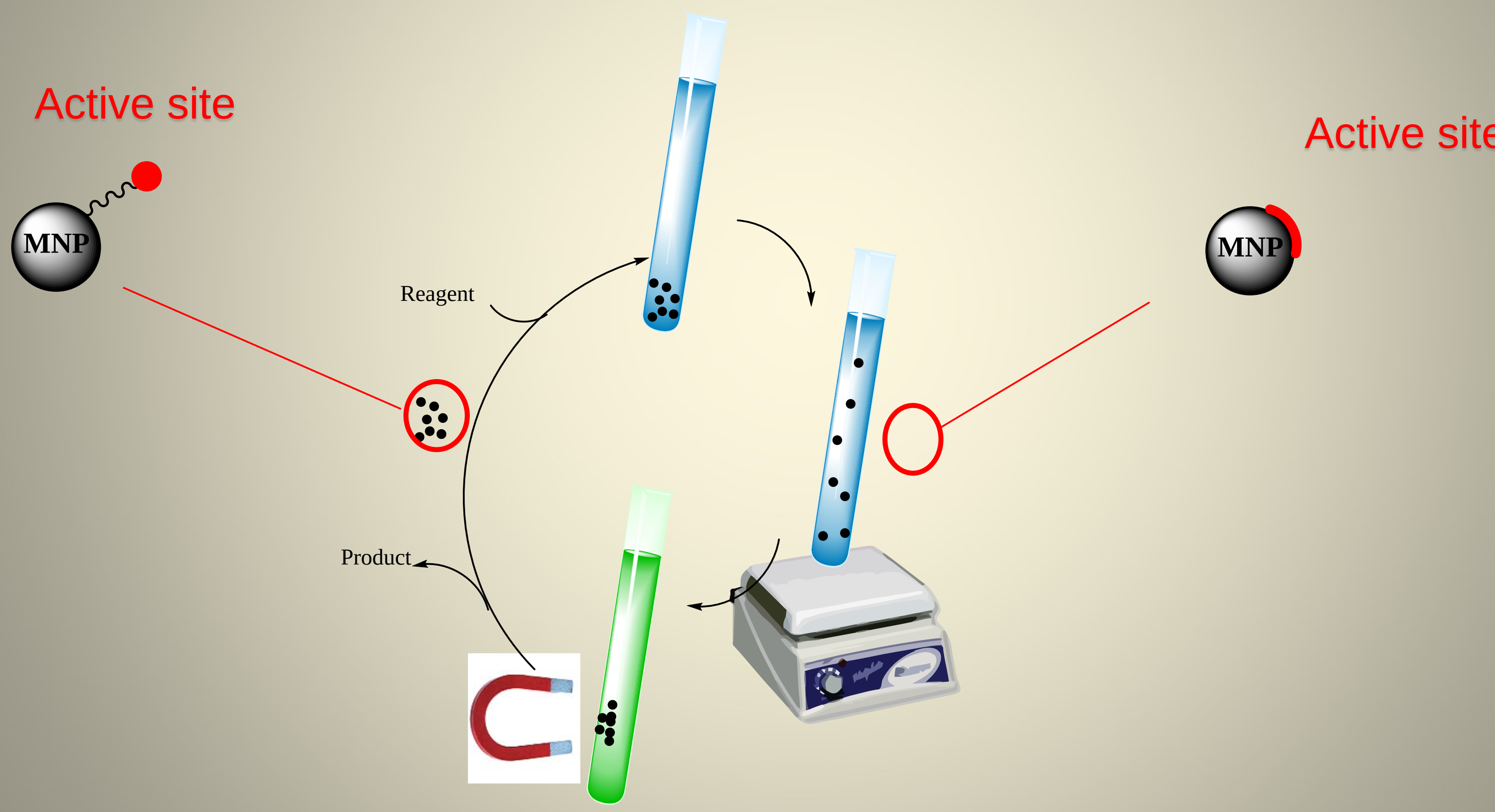
A bridge between homogeneous and heterogeneous



Varma: *Green Chemistry*, *16*, 2027-2041 (2014);
Varma: *ACS Sustain. Chem. & Eng.*, *4*, 5866-5878 (2016)

Magnetic Nanoparticles in Catalysis

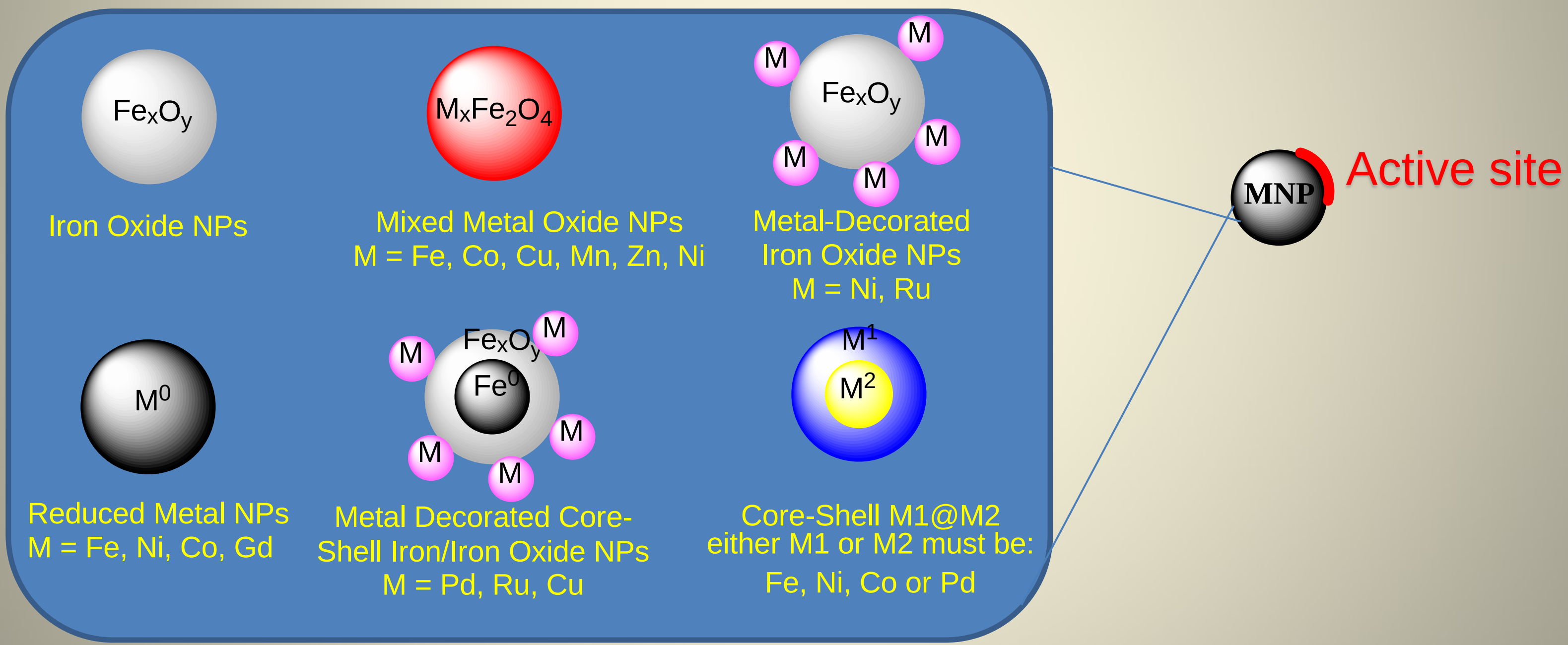
- As simple magnetic anchors
- Catalytic bare magnetic nanoparticles



Magnetically Retrievable Catalysts for Asymmetric Synthesis
Baig, Nadagouda, Varma: *Coord. Chem. Rev.* 287, pp137-156 (2015)

Magnetic Nanoparticles in Catalysis

- **Catalytic bare magnetic nanoparticles**



Hudson, Feng, Varma, Moores: *Green Chem.*, *16*, 4493-4505 (2014)-Tutorial Review

Hudson, Feng, Varma, Moores: *Green Chem.*, *16*, 4493-4505 (2014)-Tutorial Review

Magnetically Separable Nano-Catalyst

A Bridge Between

Homogeneous Catalysis

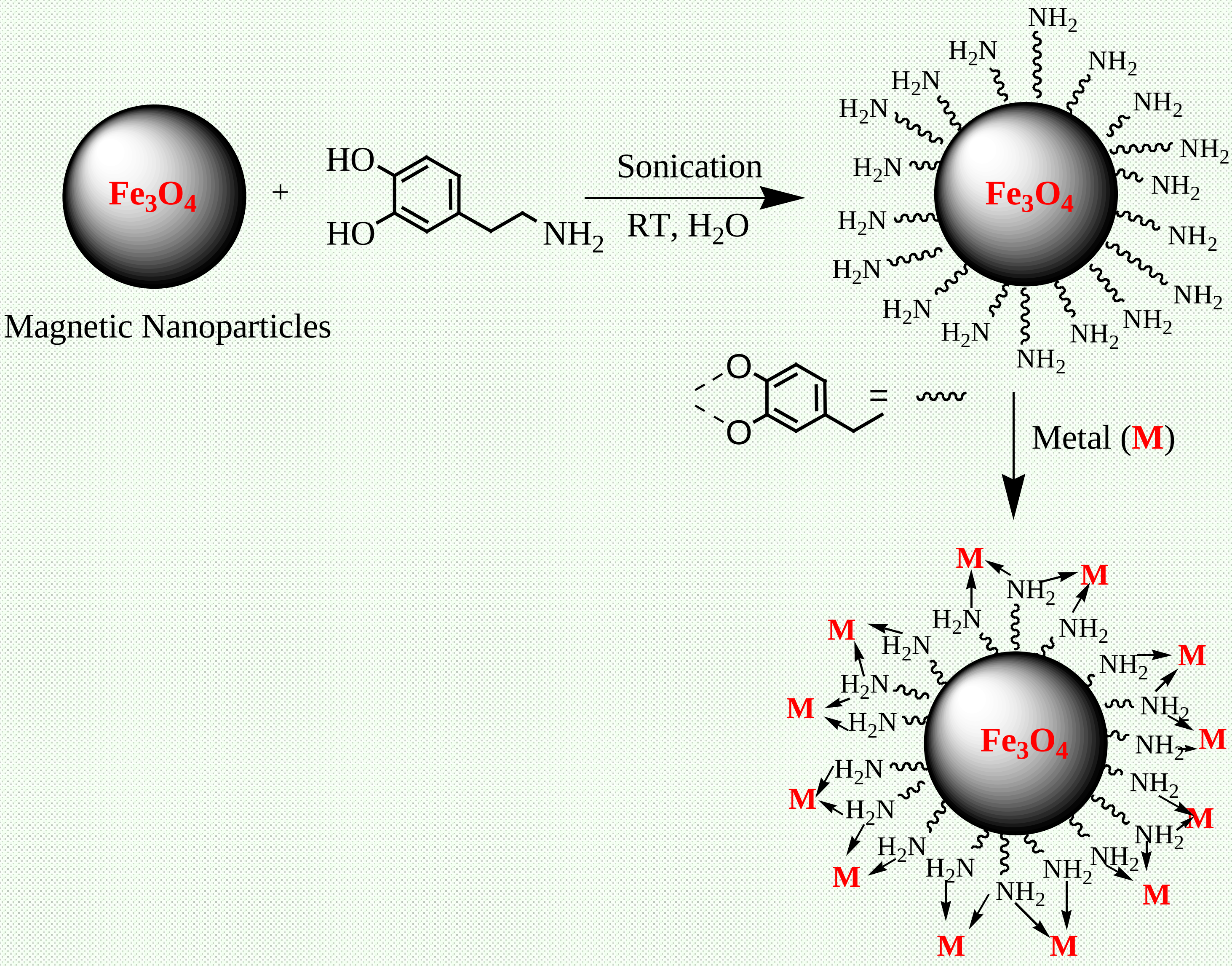
Heterogeneous Catalysis

Recent publications on this theme from our group:

Chem. Eur. J., 15, 1582 (2009)
Org. Biomol. Chem., 7, 37 (2009)
Green Chem., 11, 127 (2009)
Chem. Commun., 6318 (2008)
Chem Commun., 1837 (2009)
Tetrahedron, 66, 1091 (2010)
Green Chem., 12, 743 (2010)
Green Chem., 13, 2750 (2011)
Green Chem., 14, 67 (2012)
Curr. Opin.Chem. Eng. 1, 123 (2012)
Chem. Commun., 48, 2582 (2012)
Green Chem., 14, 625 (2012)
Chem. Commun., 48, 6220 (2012)
Green Chem., 14, 2133 (2012)
Chem. Commun., 49, 752 (2013)
Green Chem., 15, p392 (2013); *15,* p1226 (2013)
Chem. Soc. Reviews, 42, p3317 (2013)
RSC Advances, 3, p1050 (2013); *4,* p6568 (2014)
ACS Sust. Green Eng., 1, 805 (2013); *2,* p1699; *2,* p2155 (2014)
Green Chem., 16, p2027, p3494, p4137, p4333, p4493 (2014)

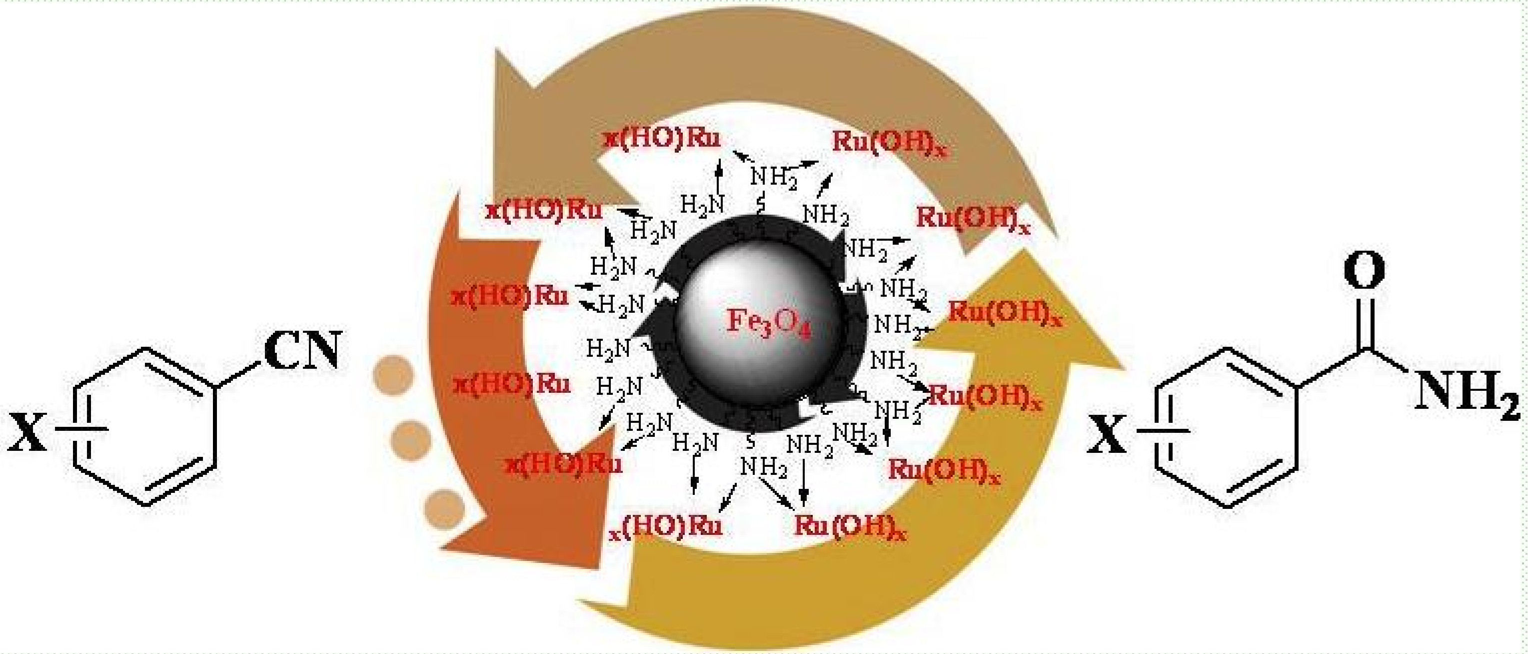
Coord. Chem. Rev., 287, **pp137-156 (2015)-Asymmetric Synthesis**

Synthesis of Nano-Catalysts



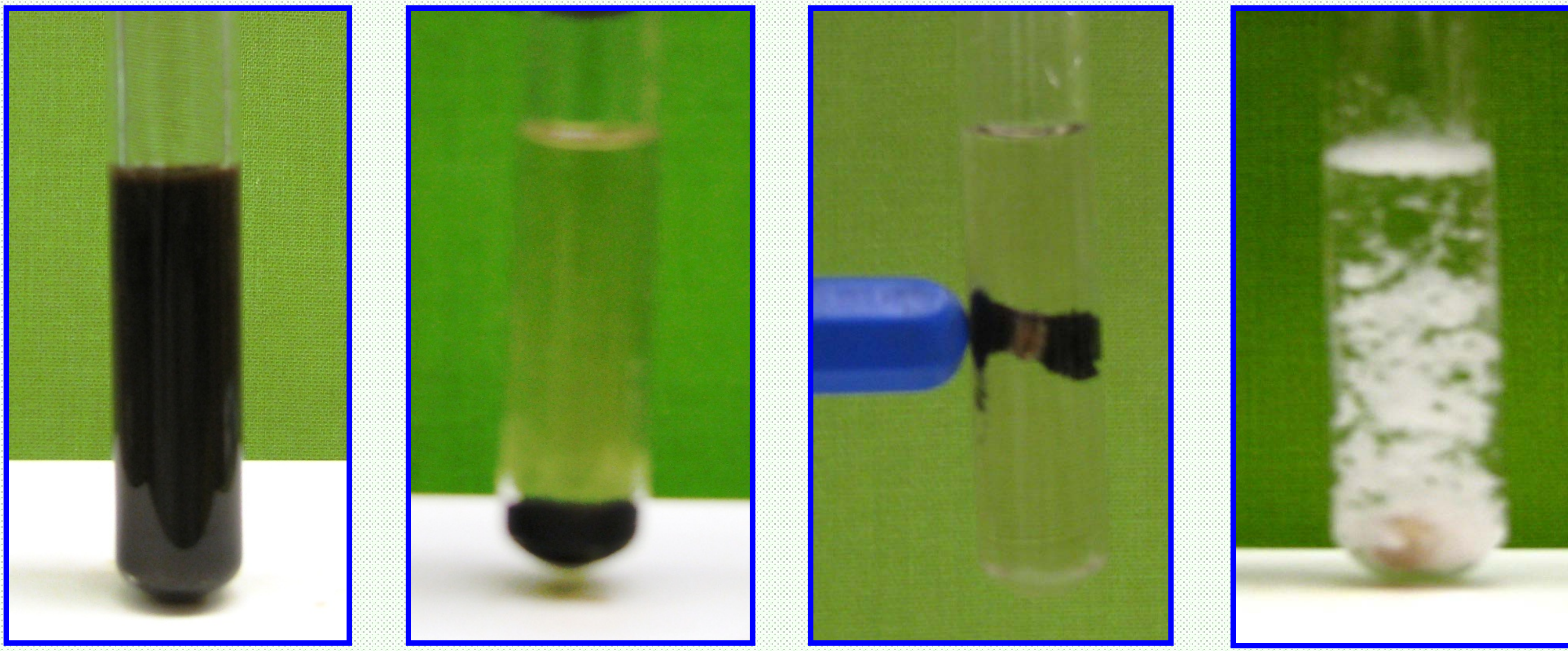
Polshettiwar, Nadagouda & Varma: *Chem. Commun.*, 6318 (2008)

Magnetically Recoverable Ruthenium Hydroxide Nano-Catalyst



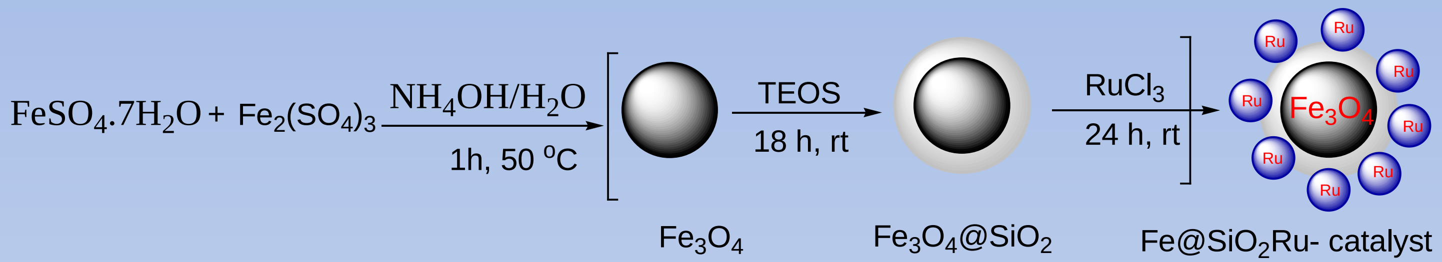
Polshettiwar & Varma: *Chem. Eur. J. 15*, 1582 (2009)

No Organic Solvent-
Even in the Work-Up Step



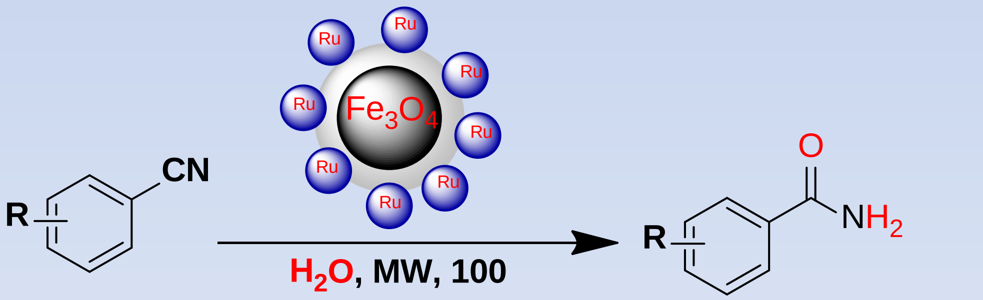
Reaction in Pure Aqueous Medium

Facile One-pot Synthesis of Ruthenium Hydroxide Nanoparticles on Magnetic Silica



Scheme 1 One pot synthesis of nano-$Fe@SiO_2Ru$ catalyst

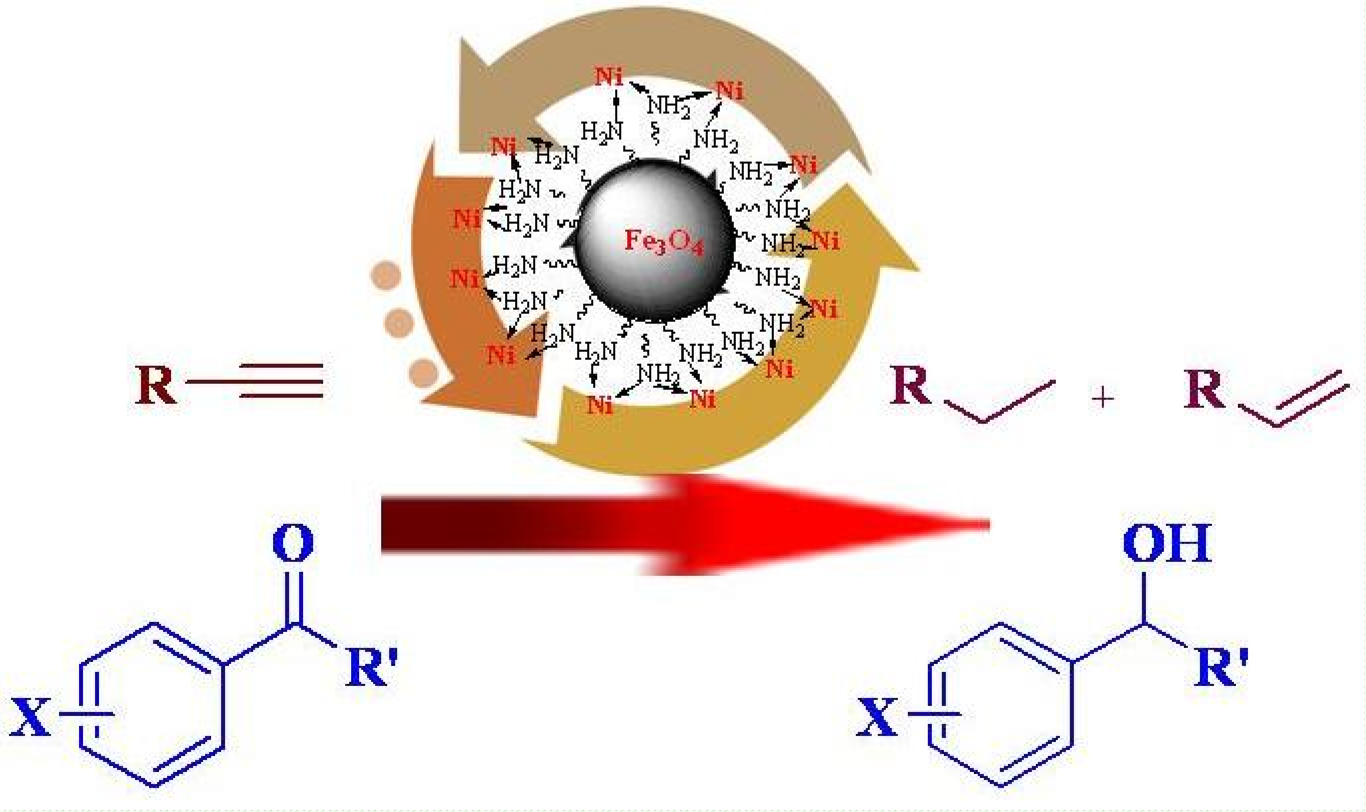
Aqueous Hydration of Nitriles Using Magnetic Silica Supported Ruthenium Hydroxide Nanoparticles



>99% conversion

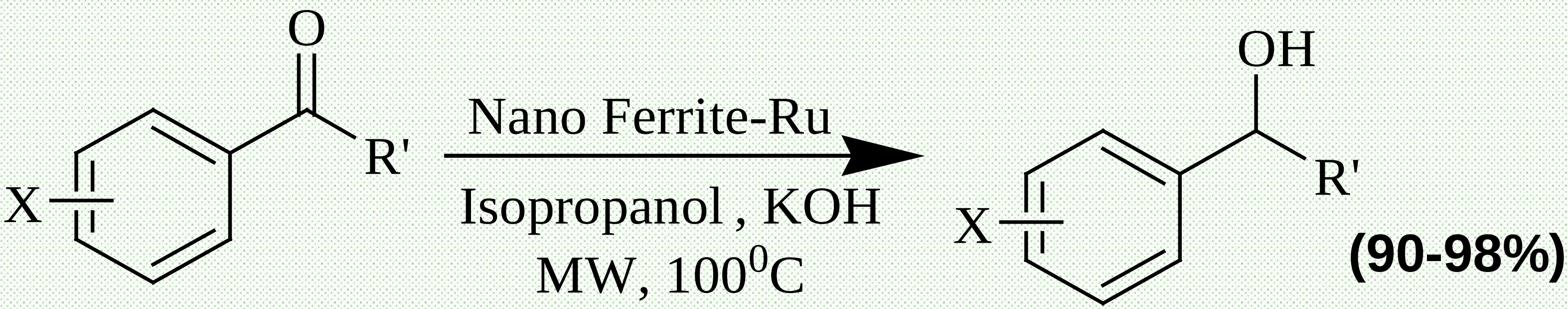
Baig, Varma: *Chem Commun., 48*, 6220 (2012)

Magnetically Recoverable Ni Nano-Catalyst for Reduction



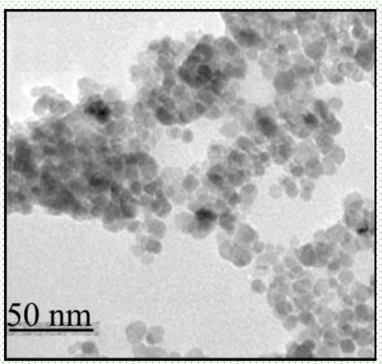
Polshettiwar, Baruwati & Varma: *Green Chem.*, *11*, 127 (2009)

Transfer Hydrogenation of Carbonyl Compounds

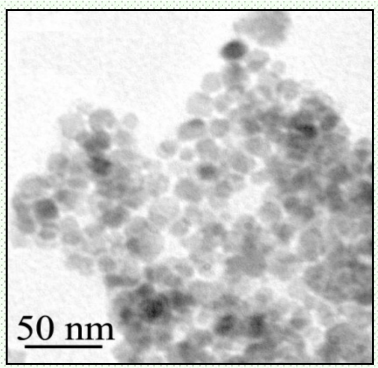


R' - Me, Ph,H

X - Cl, Br, NO_2, NH_2



Catalyst before reaction

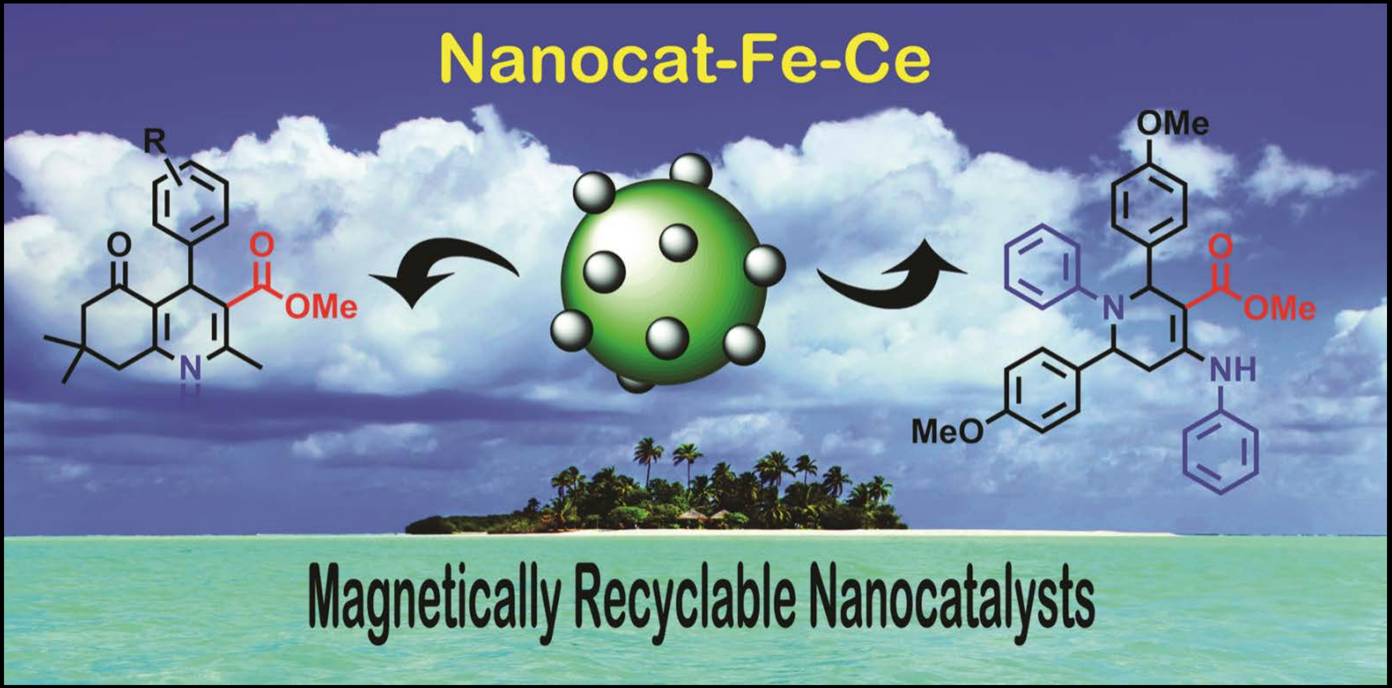


Catalyst after reaction

- **Magnetically separable**
- **Catalyst shows excellent efficiency even after 3 uses**
- **Negligible metal leaching as confirmed by ICP-AES**

Baruwati, Polshettiwar & Varma: *Tetrahedron Letters, 50, 1215* (2009)

Magnetically Recyclable Magnetite-Ceria (Nanocat-Fe-Ce) Nanocatalyst - Applications in Multicomponent Reactions under Benign Conditions

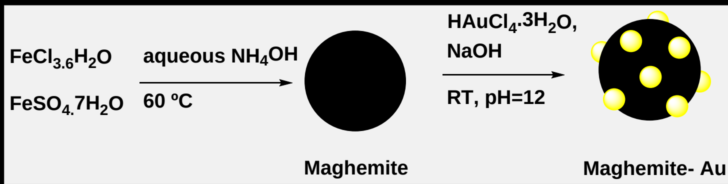


Gawande, Bonifácio, Varma, Branco, Nogueira, Bundaleski, Ghumman, Teodoro: *Green Chem., 15,* 1226 (2013)

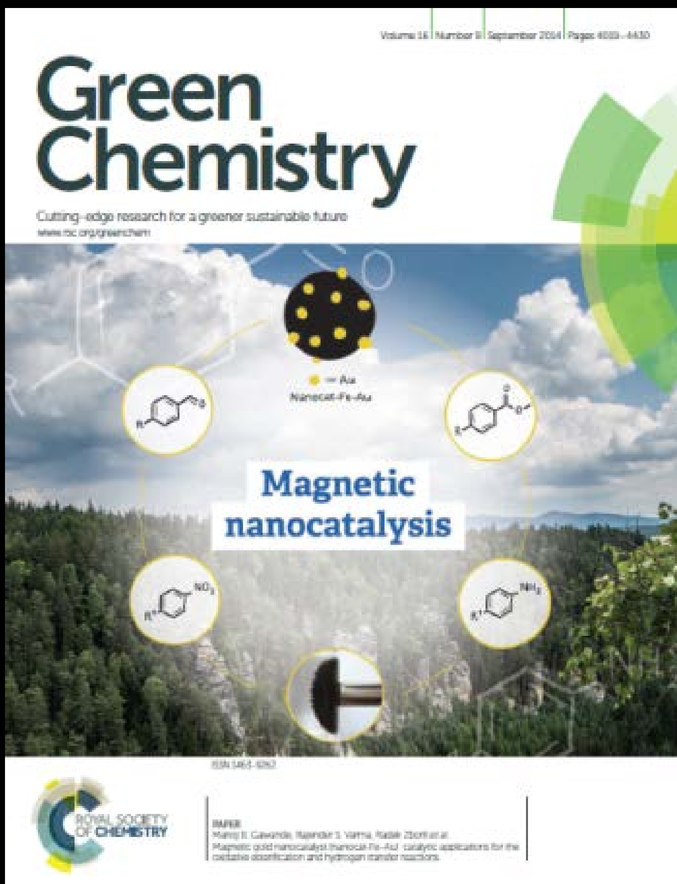
Iron Oxide-supported Copper Oxide Nanoparticles (Nanocat-Fe-CuO): Magnetically Recyclable Catalysts for the Synthesis of Pyrazole derivatives, 4-Methoxyaniline, and Ullmann-type Condensation Reactions

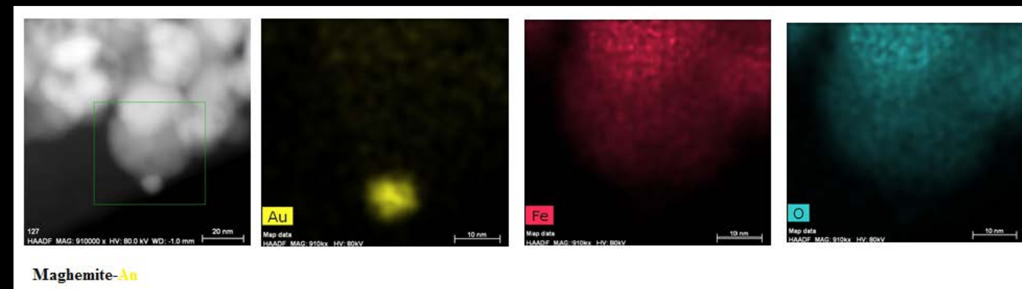
Shelke, Bankar, Mhaske, Kadam, Murade, Bhorkade, Rathi, Bundaleski, Teodoro, Varma, Zboril, Gawande: *ACS Sustain. Chem. Eng*., 2, 1699 (2014)

Maghemite-supported Gold (γ-Fe_2O_3-Au) Nanocatalyst Catalytic Applications in Organic Transformations

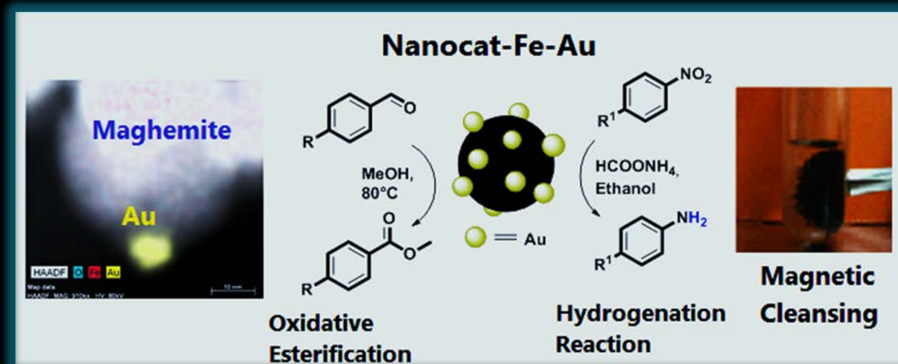


Synthesis of maghemite-Au





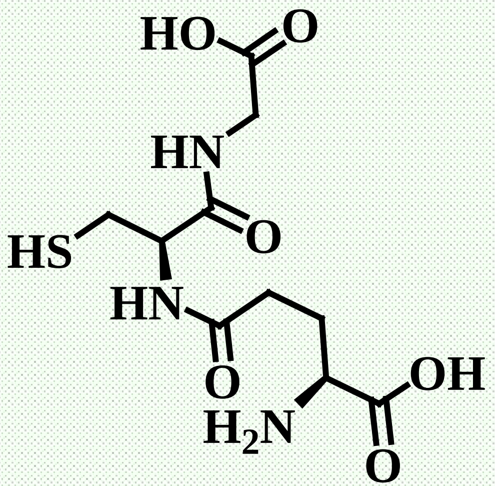
High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)



Application in oxidative esterification and reduction of aromatic nitro compounds

***Green Chemistry, 16*, 4137-4143 (2014)**

Glutathione as a Reducing and Capping agent for the Synthesis of Metal Nanoparticles



Glutathione reduced

Choice of Glutathione because …

- An ubiquitous tripeptide and antioxidant present in human and plant cells
- Presence of a highly reactive thiol group that can be used to reduce the metal salts
- Completely benign nature

Baruwati, Polshettiwar, Varma:*Green Chem*.,*11*, 926 (2009)

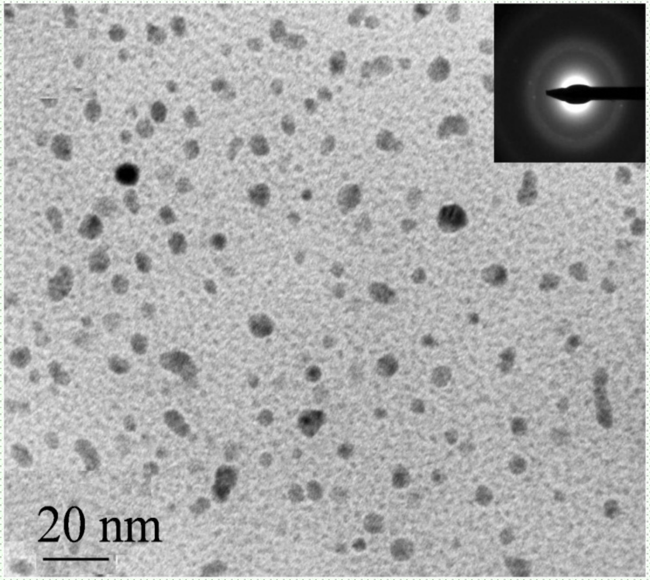
Baruwati, Polshettiwar, Varma, *Green Chem*. *11*, 926 (2009)

Metal nanoparticles in less than a minute under MW conditions

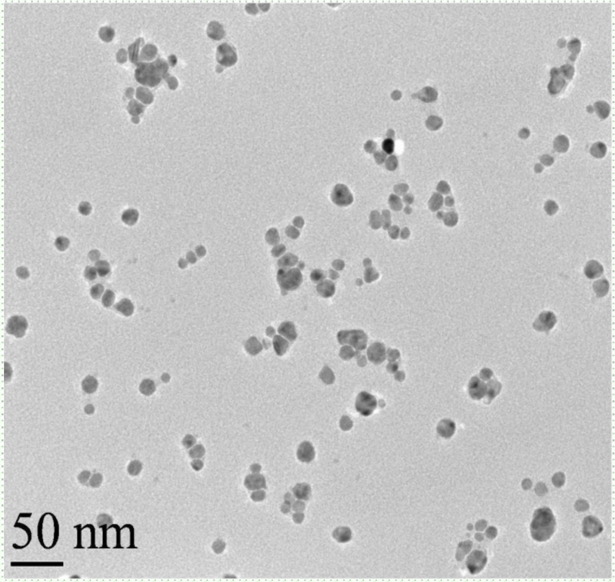
Optimized condition

- 50 W power level
- 45-60 seconds exposure time
- 1:0.15 silver nitrate to glutathione mole ratio

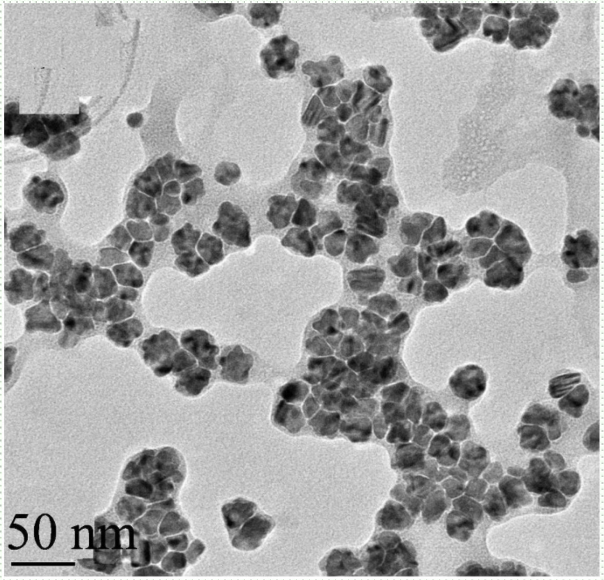
Silver Nanoparticles



50 Watt, 60 seconds with silver nitrate to glutathione mole ratio 1.0:0.15

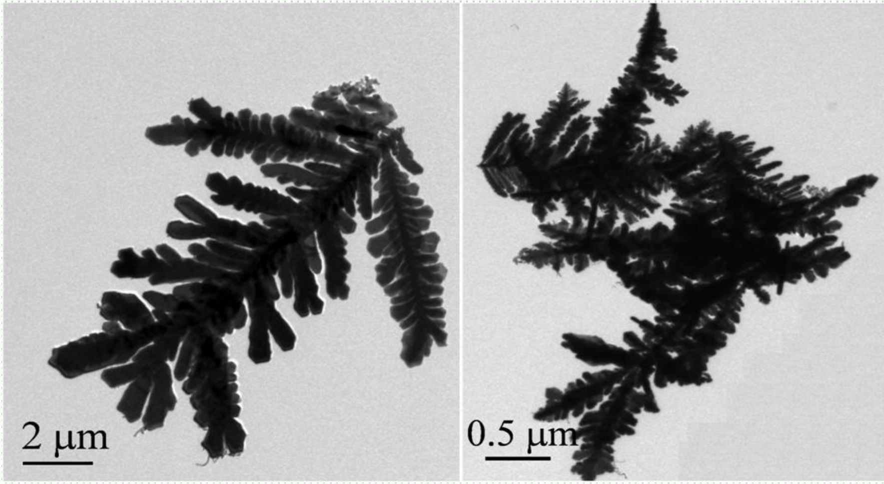


75 Watt, 60 seconds with mole ratio 1.0:0.15



100 Watt, 60 seconds with mole ratio 1.0:0.15

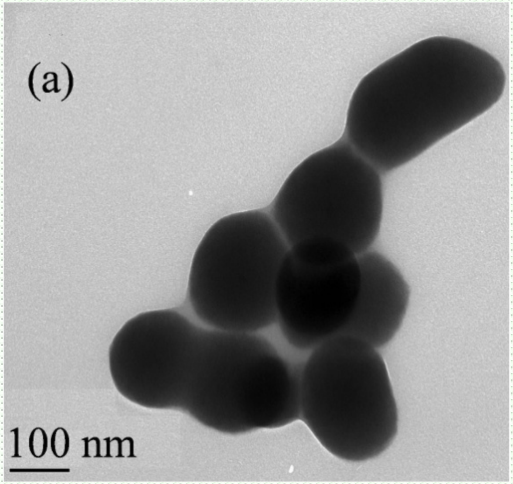
- Silver trees formed on the TEM grid when silver nitrate is not fully reduced
- Formation of dendritic structures are due to the carbon and copper in the TEM grid



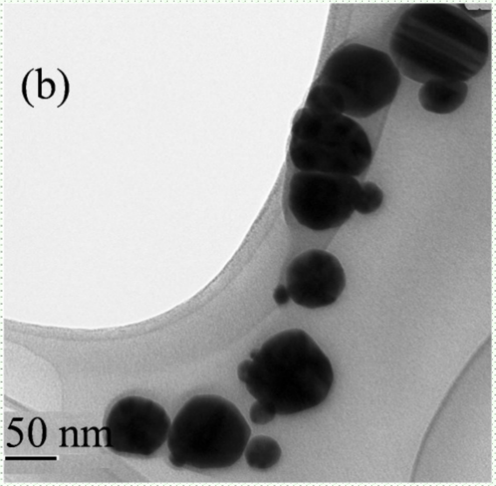
Silver trees: Dendritic nanostructures
***Aus J. Chem*., *62*, 260 (2009)**

Gold, Platinum and Palladium Nanoparticles

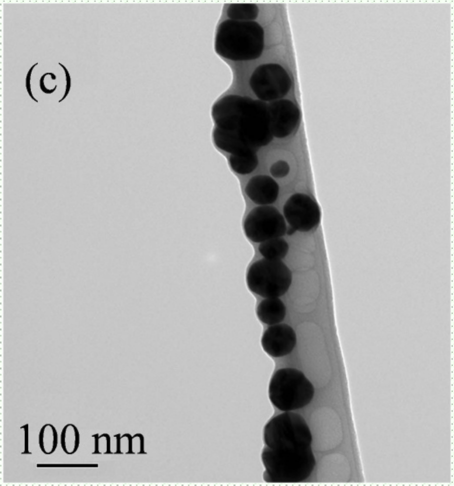
Varma et al., *Green Chem*. *11*, 926 (2009)



Gold



Platinum



Palladium

Nano-Organocatalyst
Truly Sustainable Protocol with
No Use of Organic Solvent-Even in Work-up

Polshettiwar &Varma: *Chem. Commun.*, 1837 (2009)

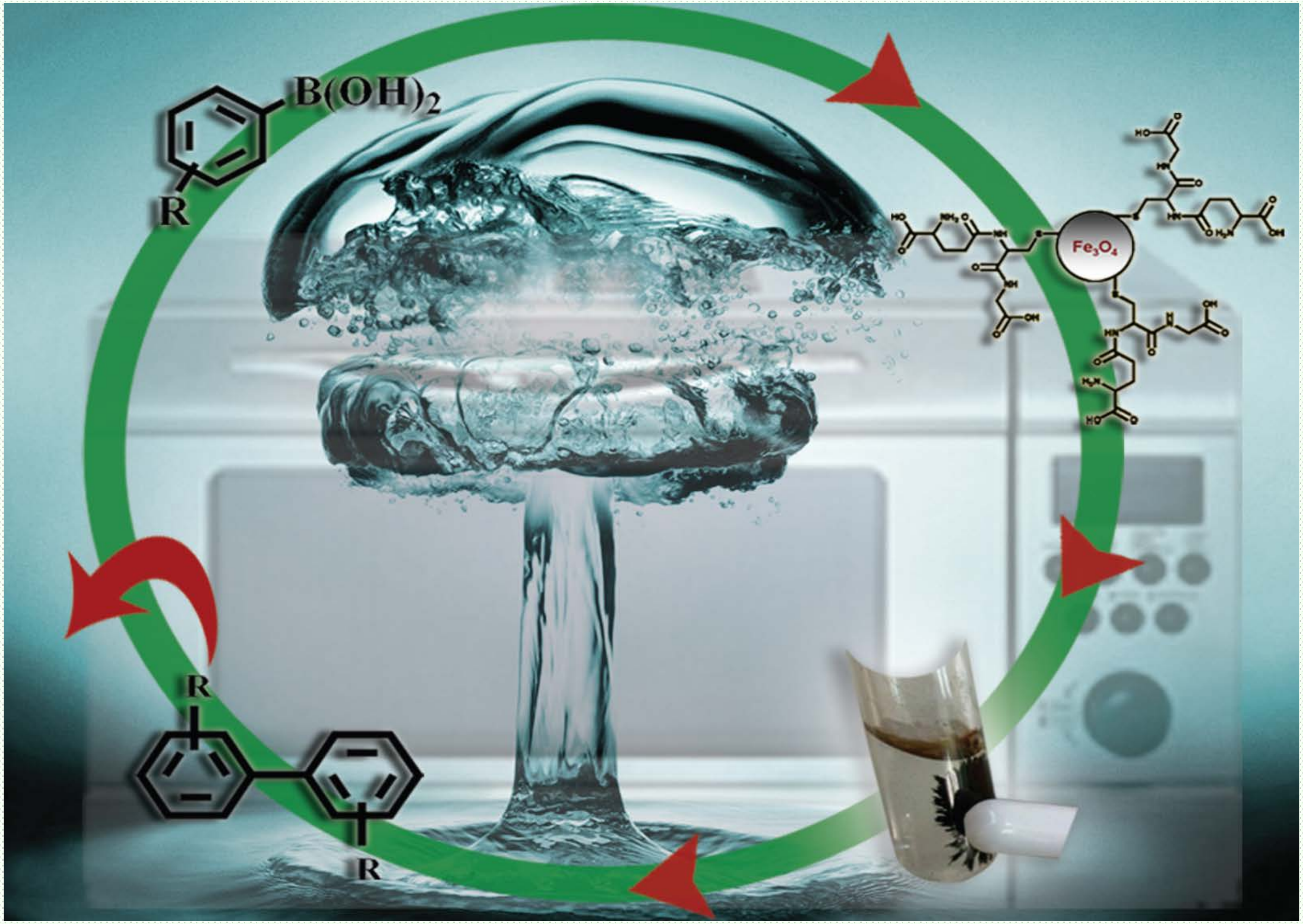
***Tetrahedron*, *66*, 1091 (2010)**

Green Chemistry

Cover page

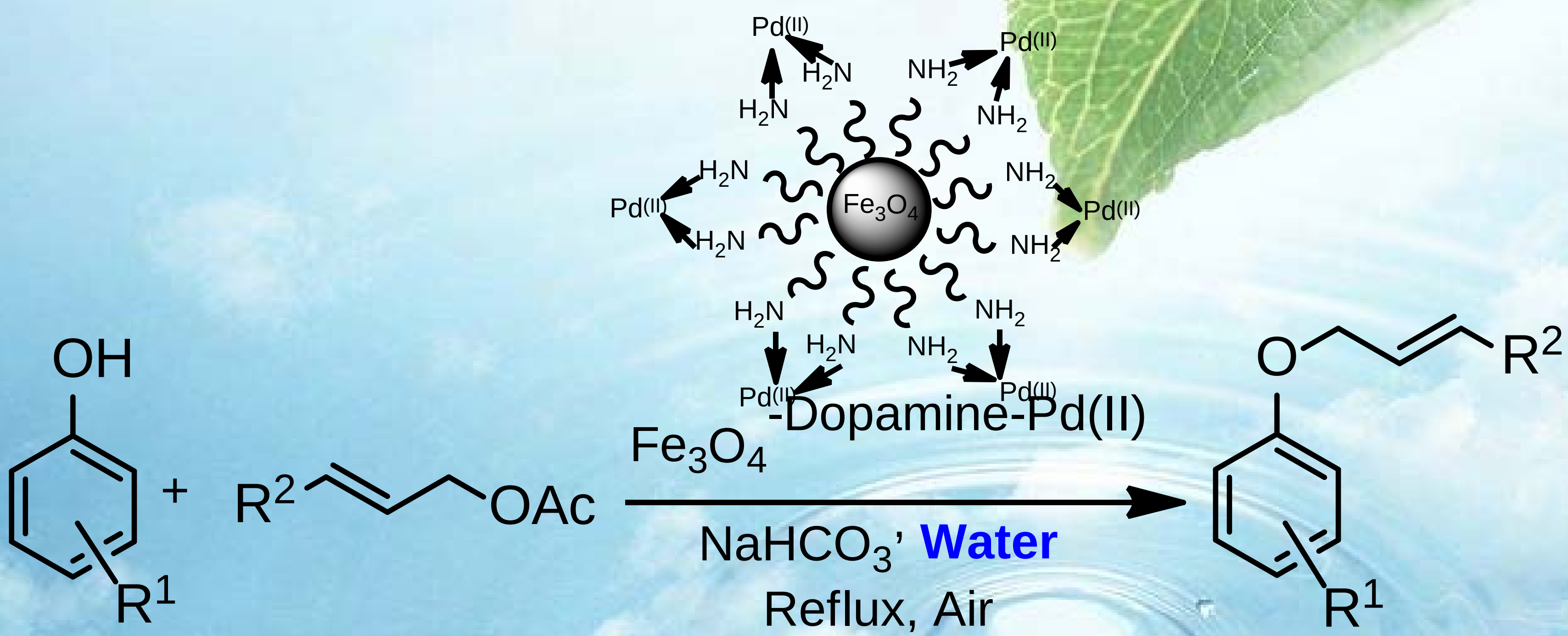
Volume 12 | Number 9 | Sept. 2010

Magnetically seperable organocatalyst for homocoupling of arylboronic acids



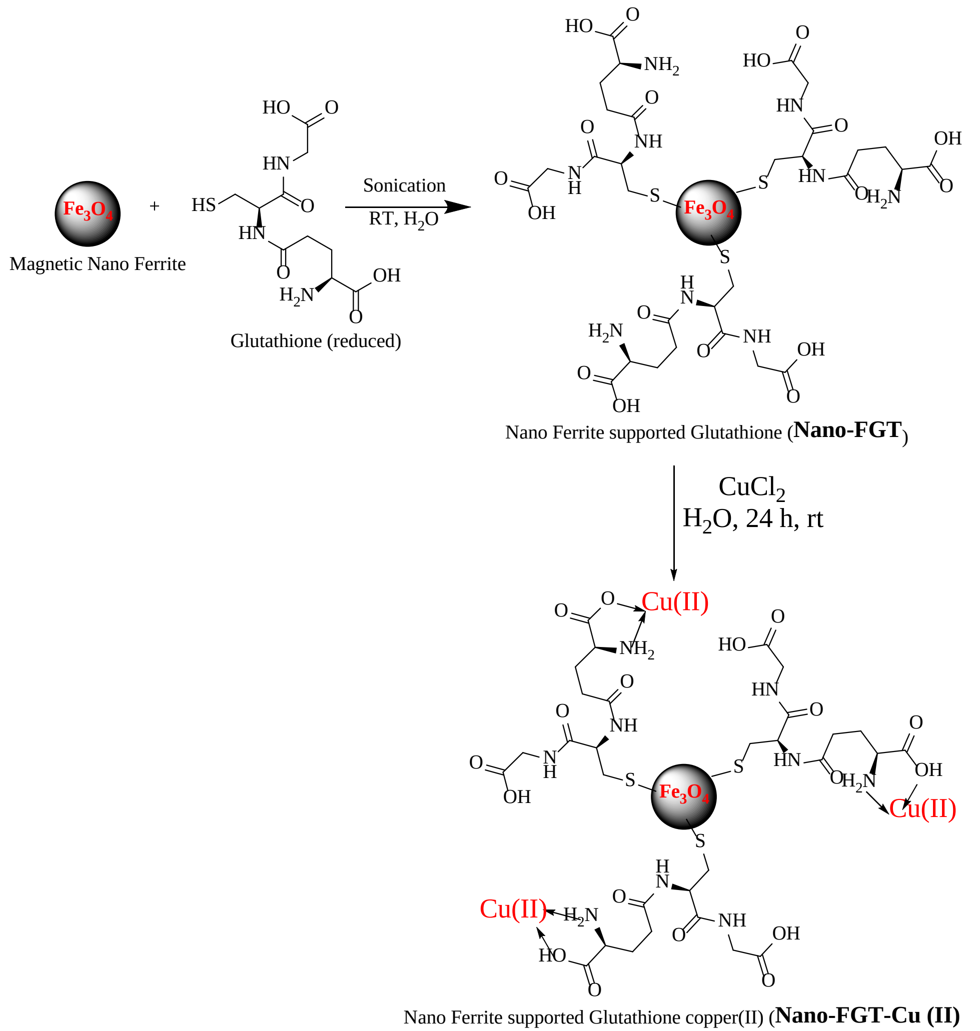
Luque, Baruwati, Varma: *Green Chem., 12*, 1540 (2010)

Magnetic Nano-ferrite Supported Heterogeneous Pd Catalyst for *O*-Allylation of Phenols in Water



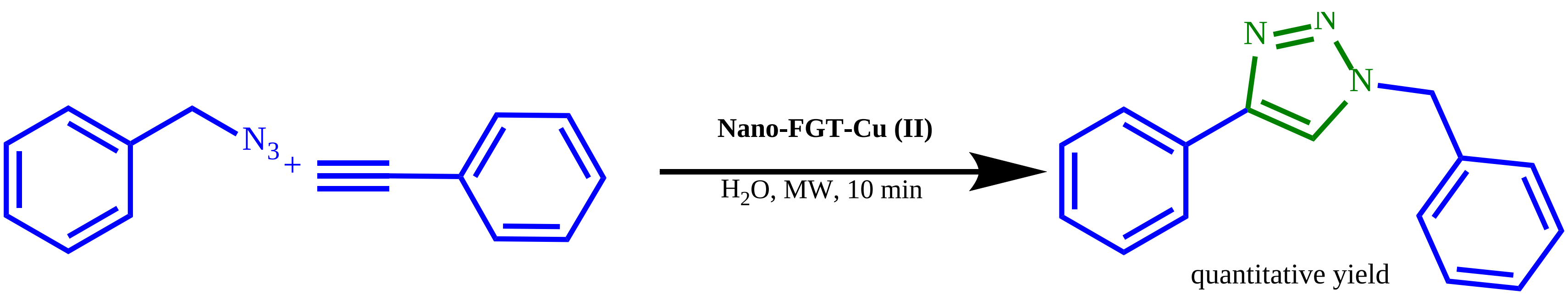
Saha, Leazer, Varma: *Green Chem.,* 14, 67-71 (2011)

Nano Ferrite supported-Glutathione copper(II) catalyst

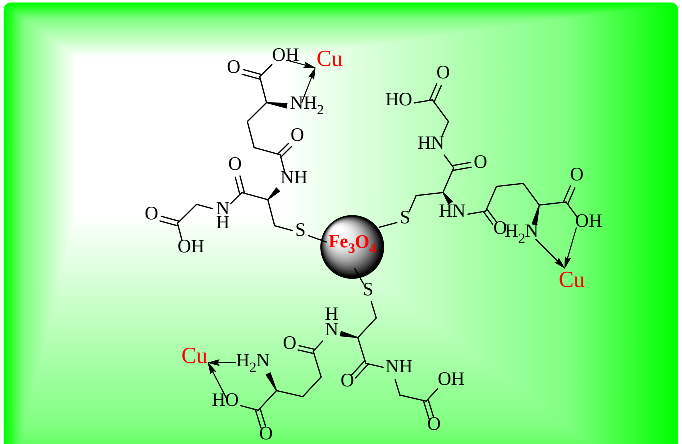


Baig, Varma: *Green Chem., 14, 625 (2012*)

1,3 Dipolar Cycloaddition Reaction Catalyzed by Magnetic Nano-FGT-Cu (II)

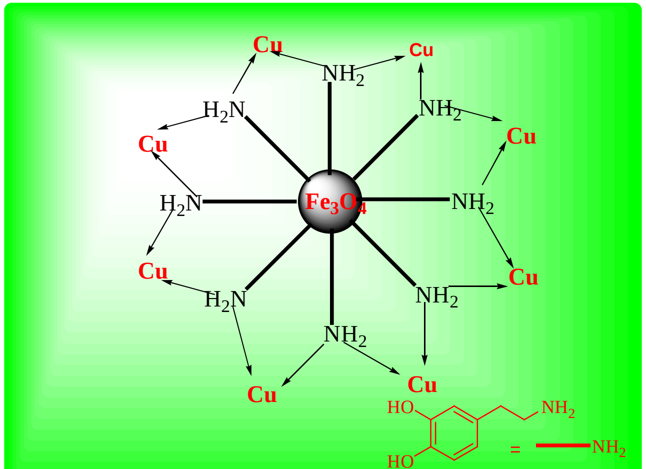


Baig, Varma: *Green Chem., 14, 625 (2012*)

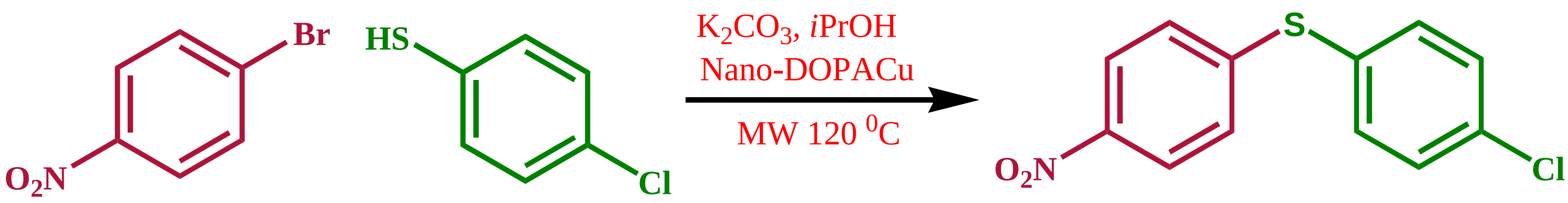


Nano Ferrite supported Glutathione copper **Nano-FGT-Cu catalyst**

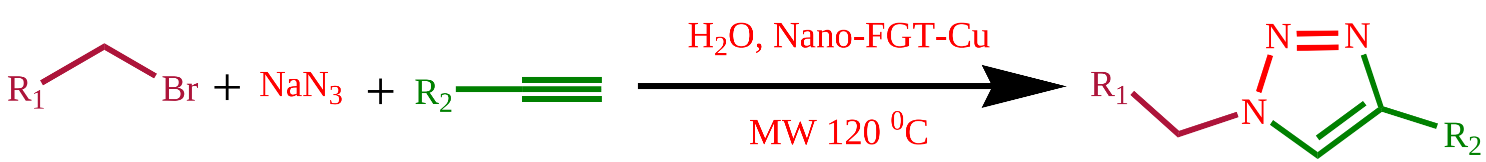
Ligands defines reactivity



Nano Ferrite supported DOPA copper (**Nano-DOPA-Cu) catalyst**



(Nano-DOPA-Cu-active, Nano-FGT-Cu-inactive) Baig, Varma: *Chem Commun.*, 2012, *48*, 2582



R = alkyl, aryl, heterocycle etc.

23 examples, yield up to 99%

(Nano-FGT-Cu-active, Nano-DOPA-Cu-inactive) Baig, Varma: *Green Chem.*, 2012, *14*, 625

Bio-degradable & Bio-renewable Supports

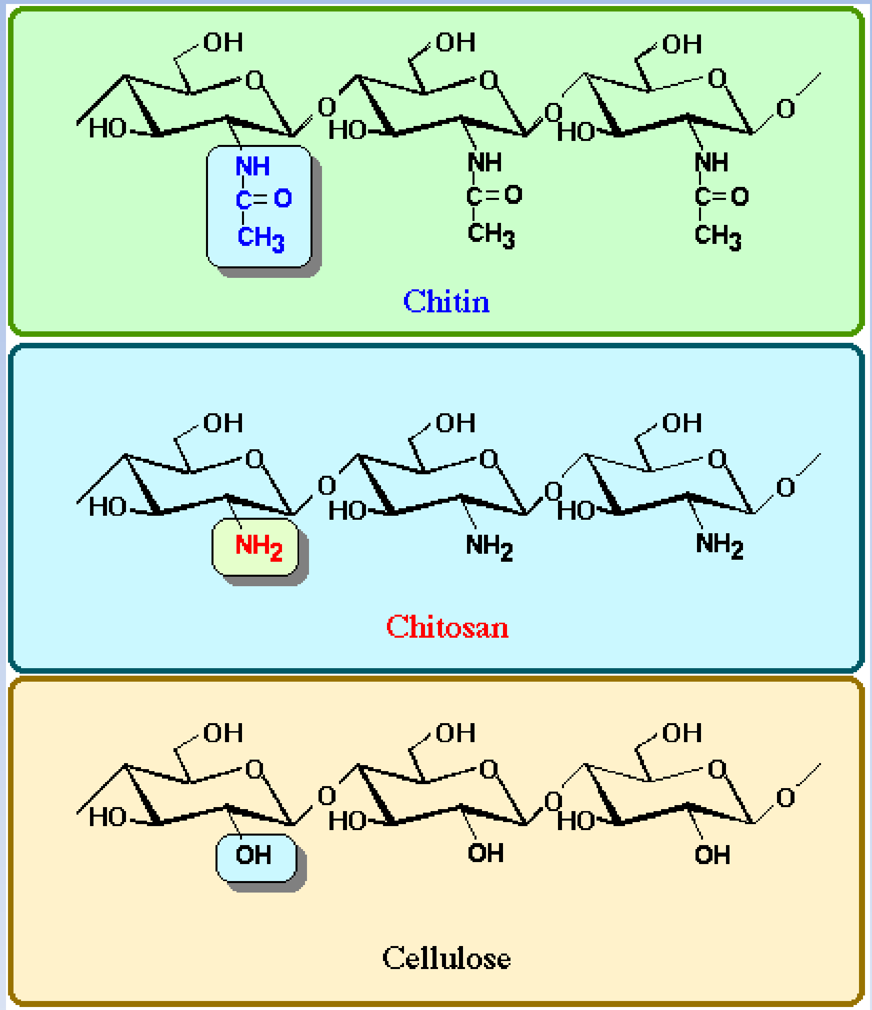
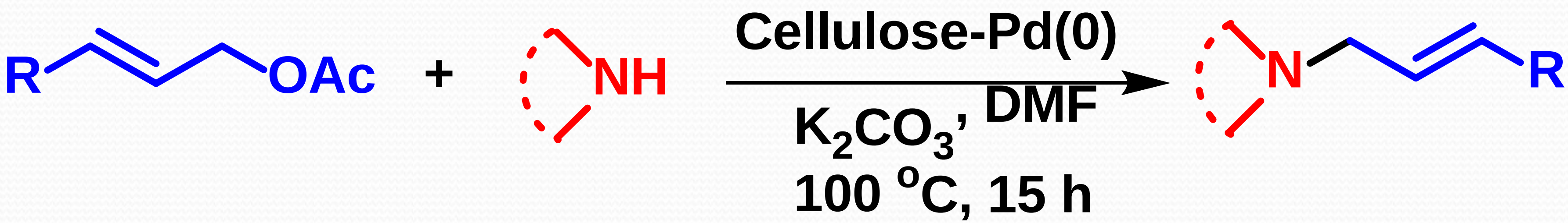


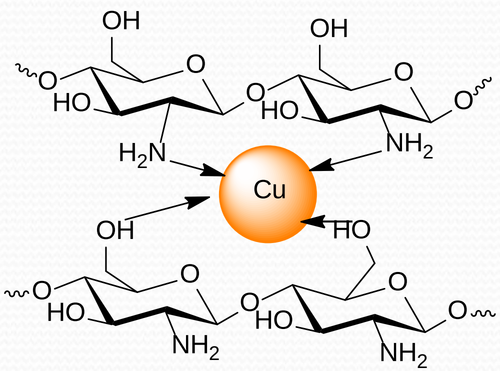
Fig. Structure of Chitin, Chitosan and Cellulose

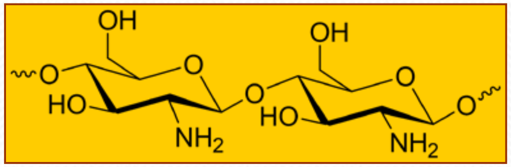
Tsuji-Trost *N*-allylation with allylic acetates using cellulose-Pd catalyst



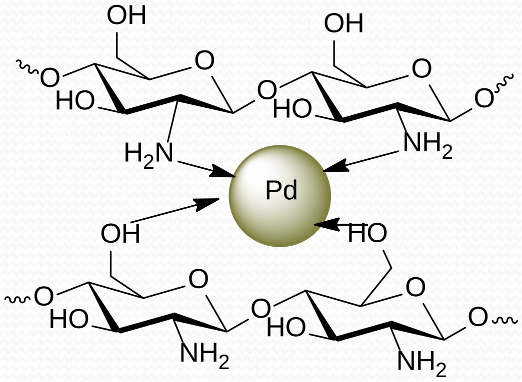
Reddy, Saha, Varma, Leazer: *Eur. J. Org. Chem.*, 6707 (2012)

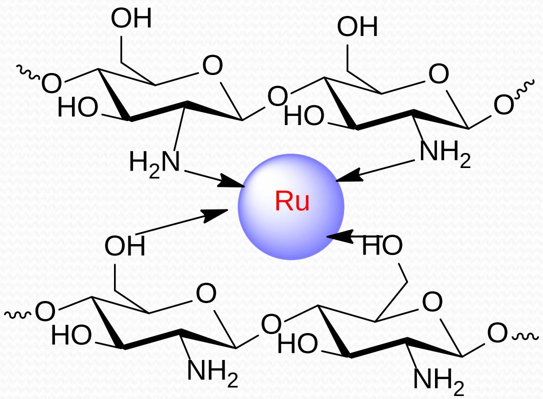
Synthesis of Chitosan-supported Catalysts





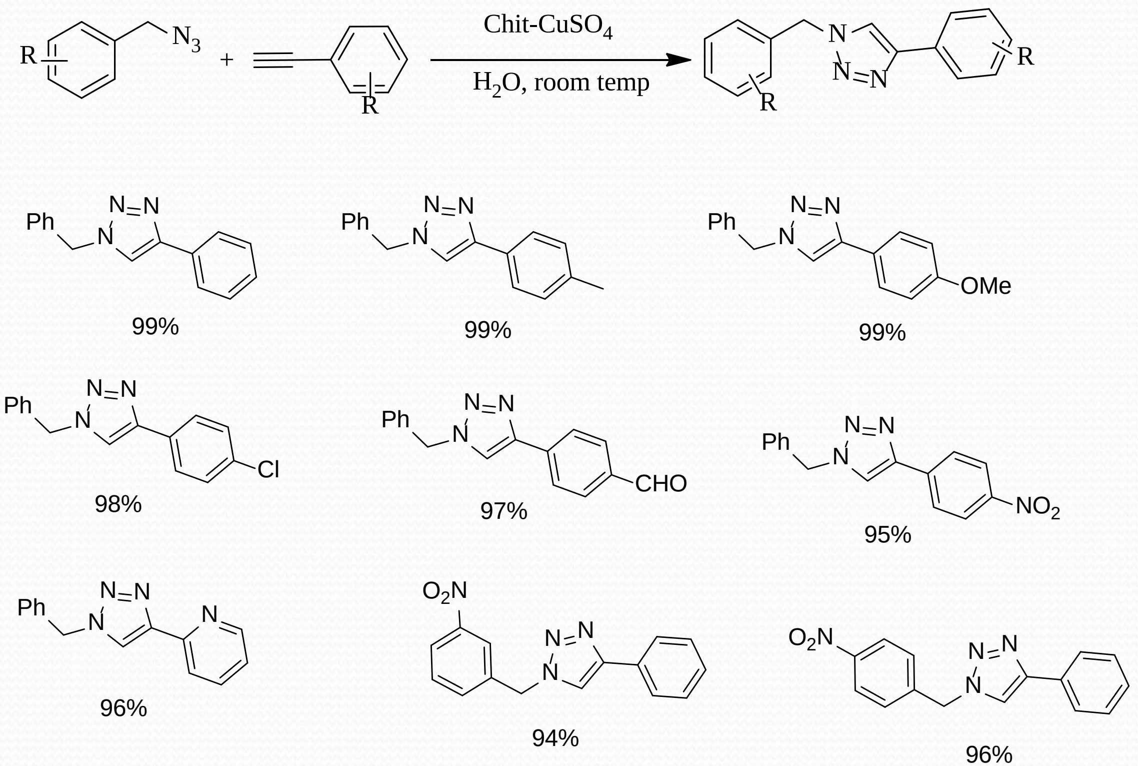
Chitosan polymer

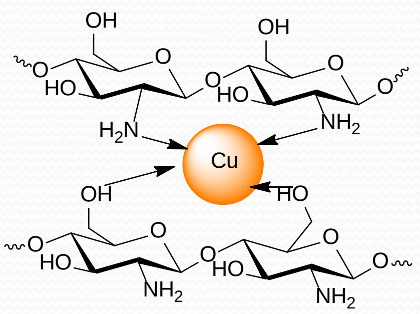




Varma: *ACS Sustain. Chem. & Eng., 4*, 5866-5878 (2016)

Chit-$CuSO_4$ Catalyzed Azide Alkyne Cycloaddition

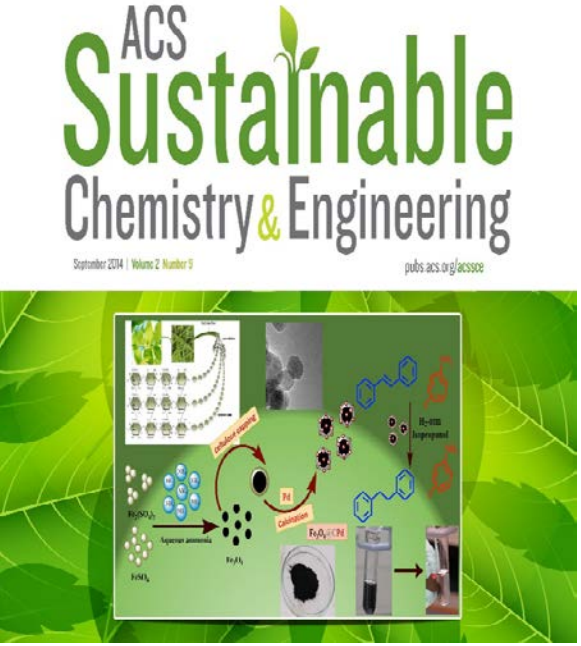


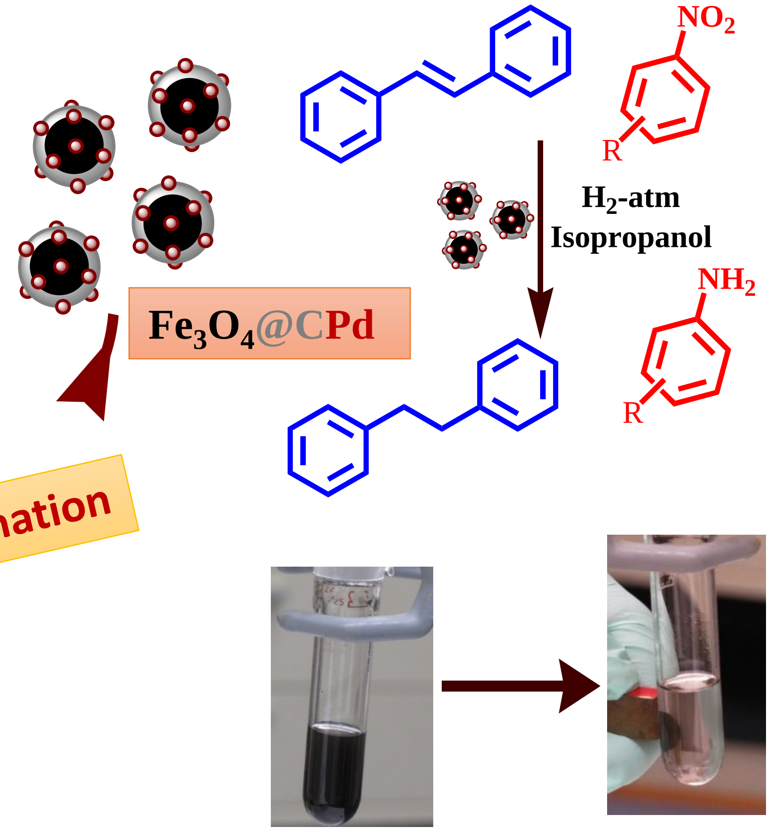


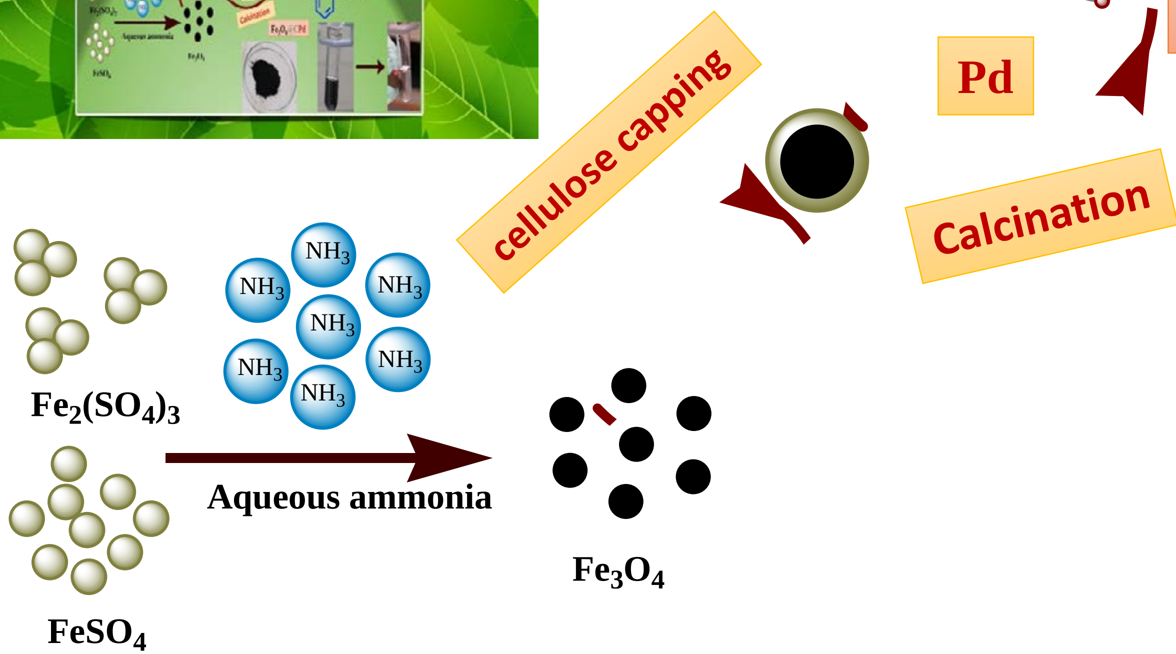
Chit-CuSO4 catalyst

Baig, Varma: *Green Chem., 15*, 1839-1843 (2013)

Magnetic Carbon-Supported Palladium Nanoparticles: Recyclable Catalyst for Hydrogenation

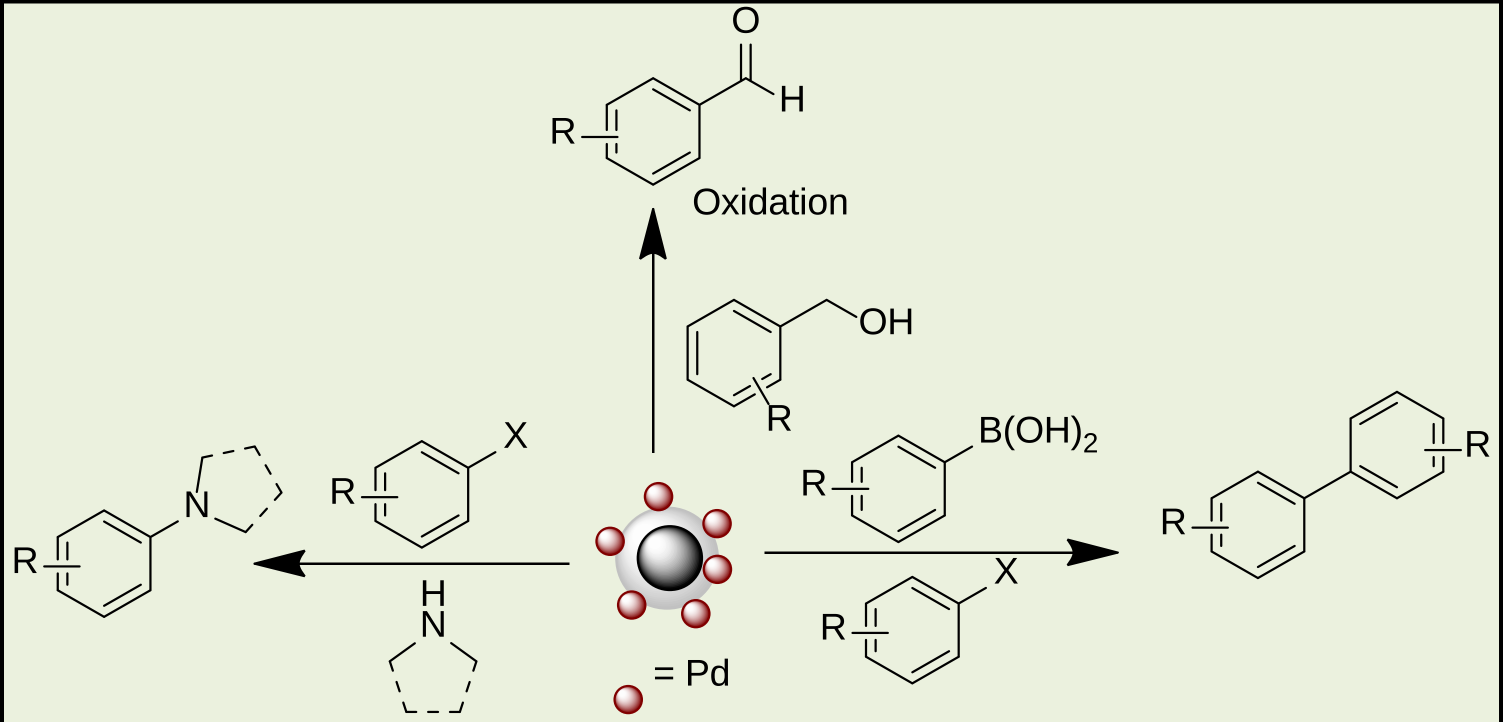






Baig, Varma: *ACS Sustain. Chem. Eng.*, *2* , 2155 (2014)

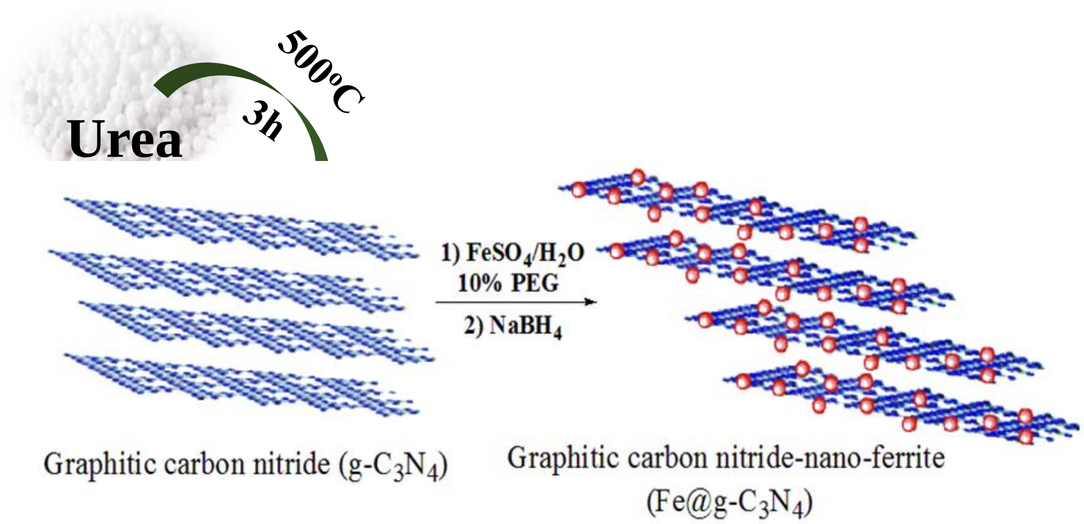
Carbon-Coated Magnetic Palladium: Applications in Partial Oxidation of Alcohols and Coupling Reactions

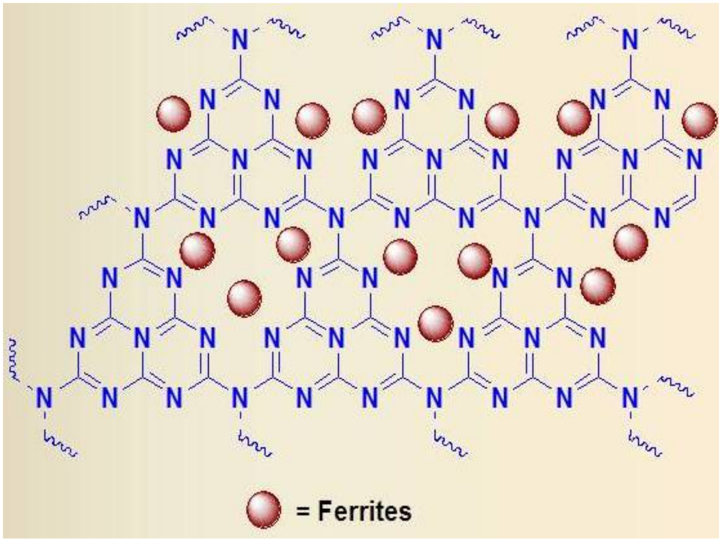


Baig, Nadagouda, Varma: *Green Chem.*, *16*, 4333 (2014)

Magnetic Graphitic Carbon Nitride: Application in C-H activation of Amines

Synthesis of Magnetic Fe@g-C_3N_4

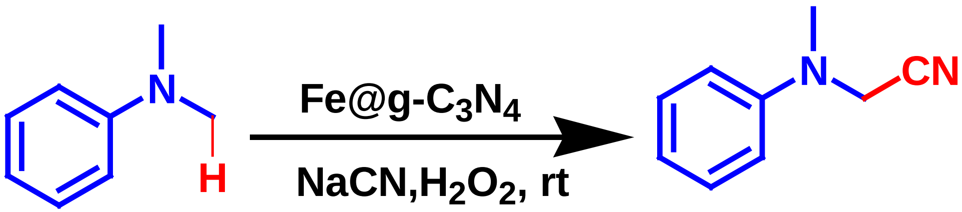


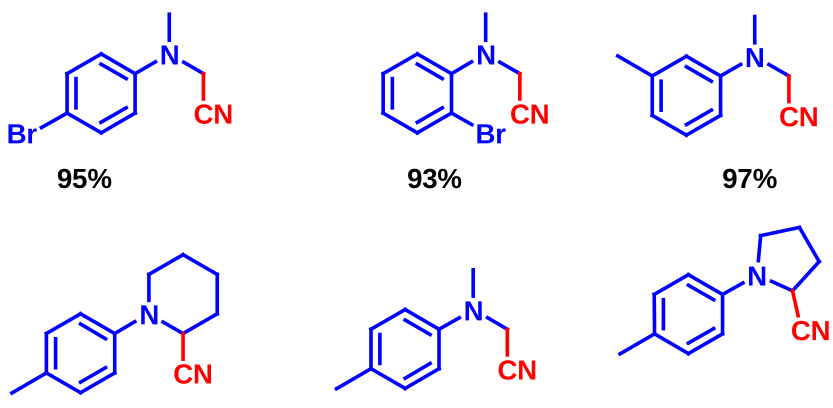


Fe@g-C_3N_4

Verma, Baig, Han, Nadagouda and Varma: *Chem. Commun.*, *51*, 15554 (2015)

C-H Activation and Synthesis of α-Amino Nitriles

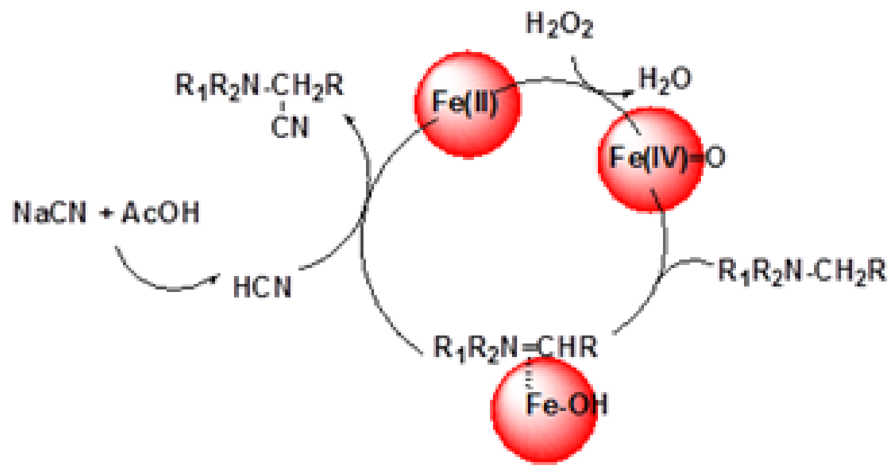




95% 93% 97%

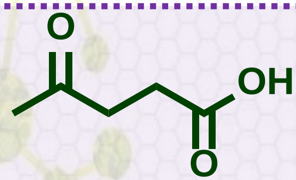
88% 98% 83%

Mechanism of α-amino nitrile synthesis



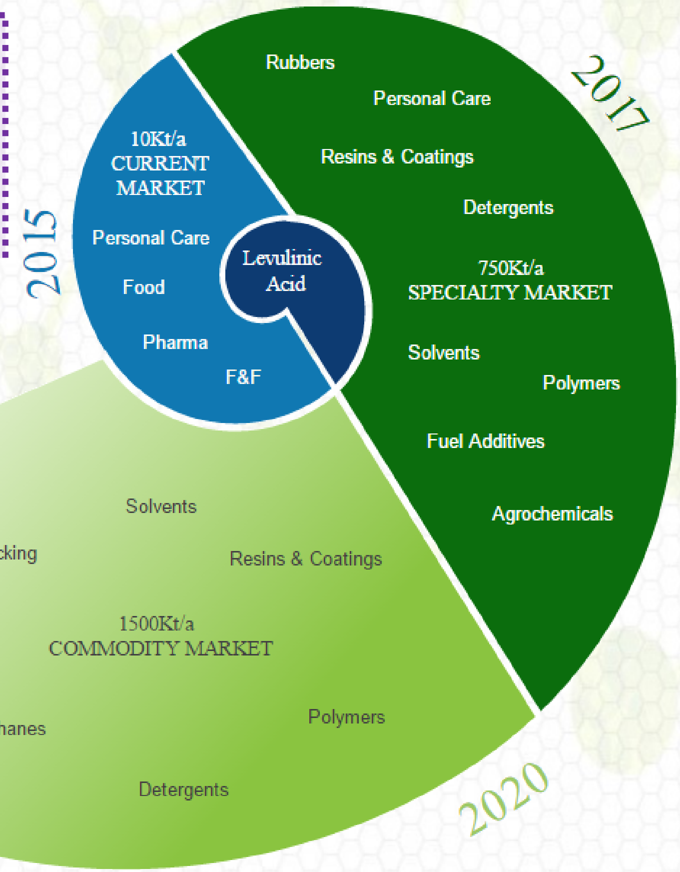
Verma, Baig, Han, Nadagouda and Varma: *Chem. Commun.*, *51*, 15554 (2015)

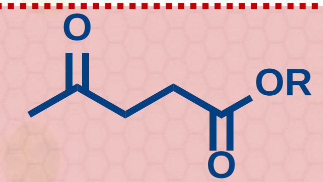
Platform Chemicals from Biomass



Levulinic Acid

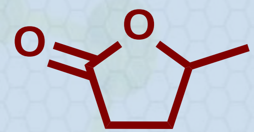
Highlighted by the United States Department of Energy a promising building block for chemistry





Alkyl Levulinates

- ✓ Solvent
- ✓ Additive
- ✓ Precursor to GVL



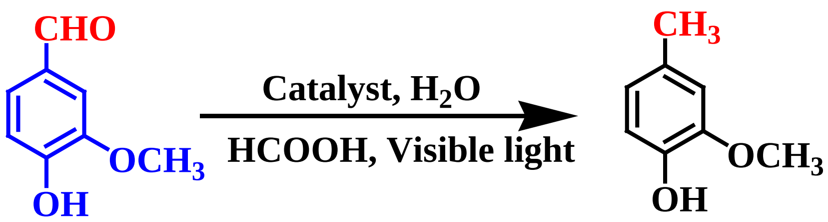
γ-valerolactone

- ✓ F&F
- ✓ Solvent
- ✓ Fuel Additive
- ✓ Precursor to liquid alkanes

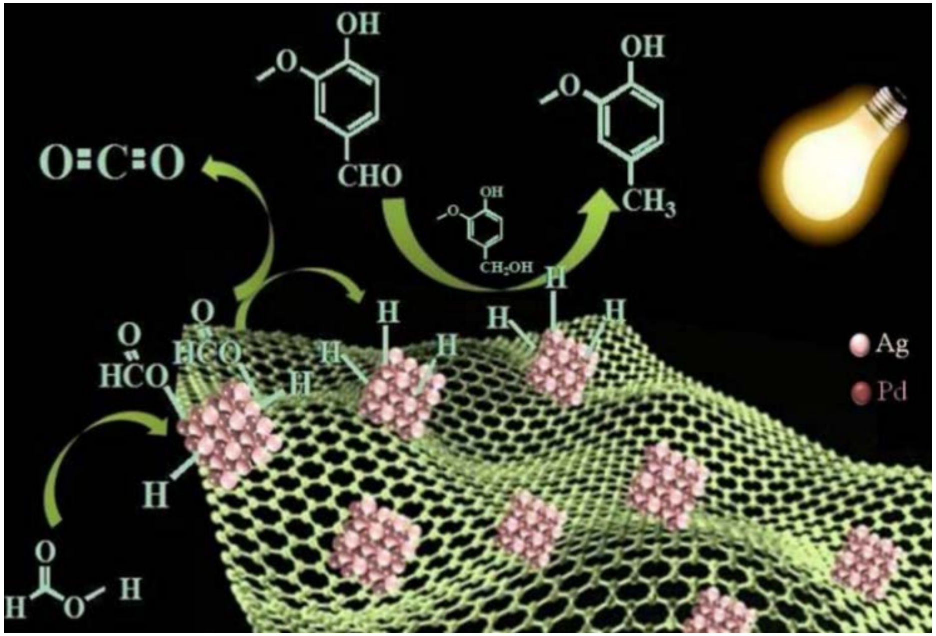
Conventional methods still employ mineral acids as catalysts, high pressures and temperatures

ACS Sustainable Chem. Eng. **2014, *2*, 1338. Website: www.gfbiochemicals.com/products/**

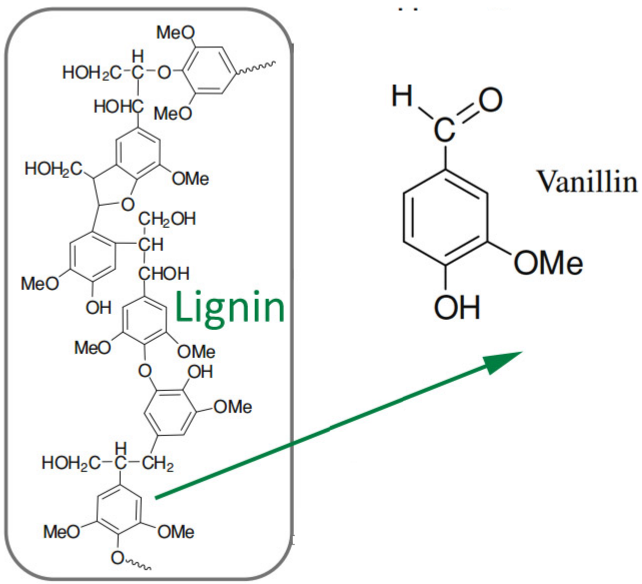
Visible Light Mediated Upgrading of Biomass to Biofuel using Formic Acid



Reaction Pathway

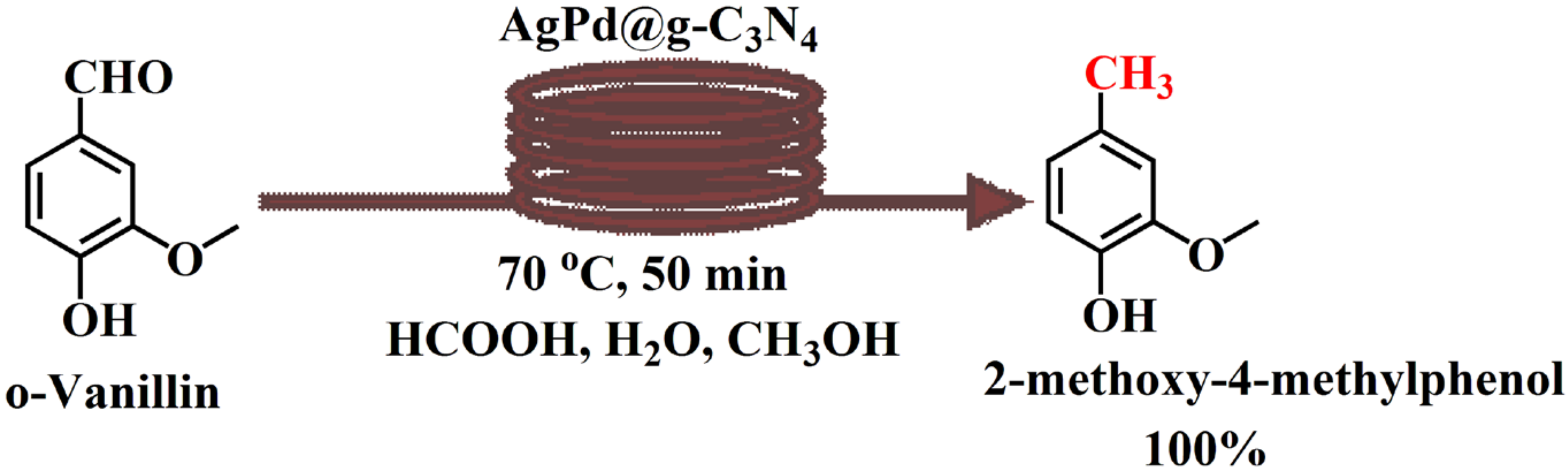


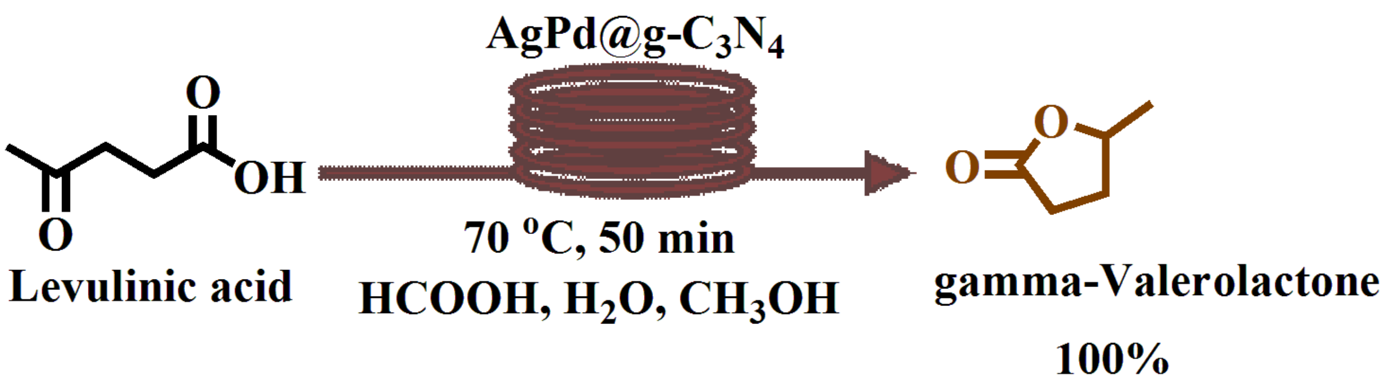
Vanillin and its derivatives as source of future biofuels



Verma, Baig, Nadagouda, Varma: *Green Chem.*, *18*, 1327-1333, (2016)-Cover page

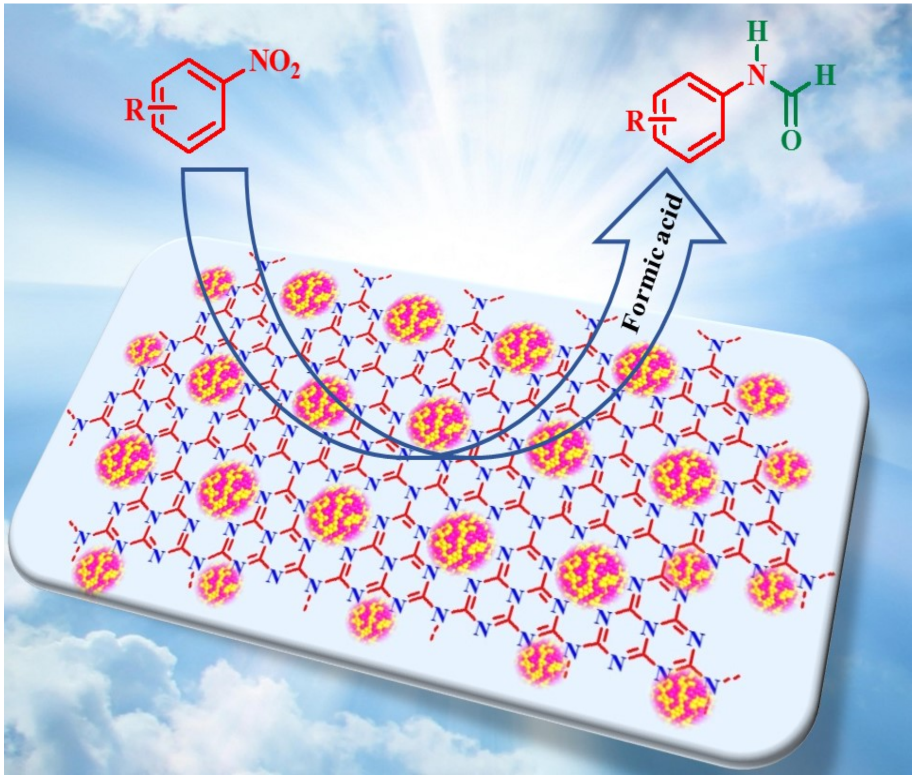
Sustainable Pathway to Empower Bio-based Future: Upgrading of Biomass *via* Process Intensification

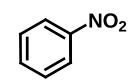
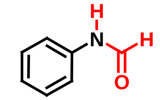
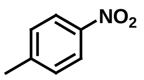
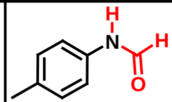
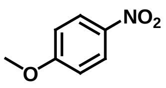
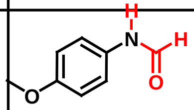
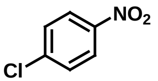
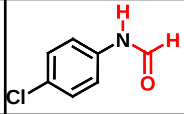
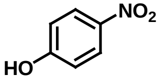
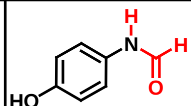
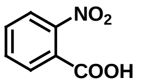
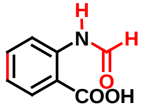
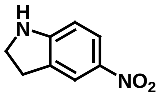
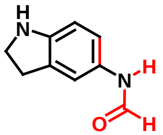
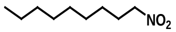




Tadele, Verma, Gonzalez, Varma: *Green Chem.*, *19*, 1624 (2017)-Cover page

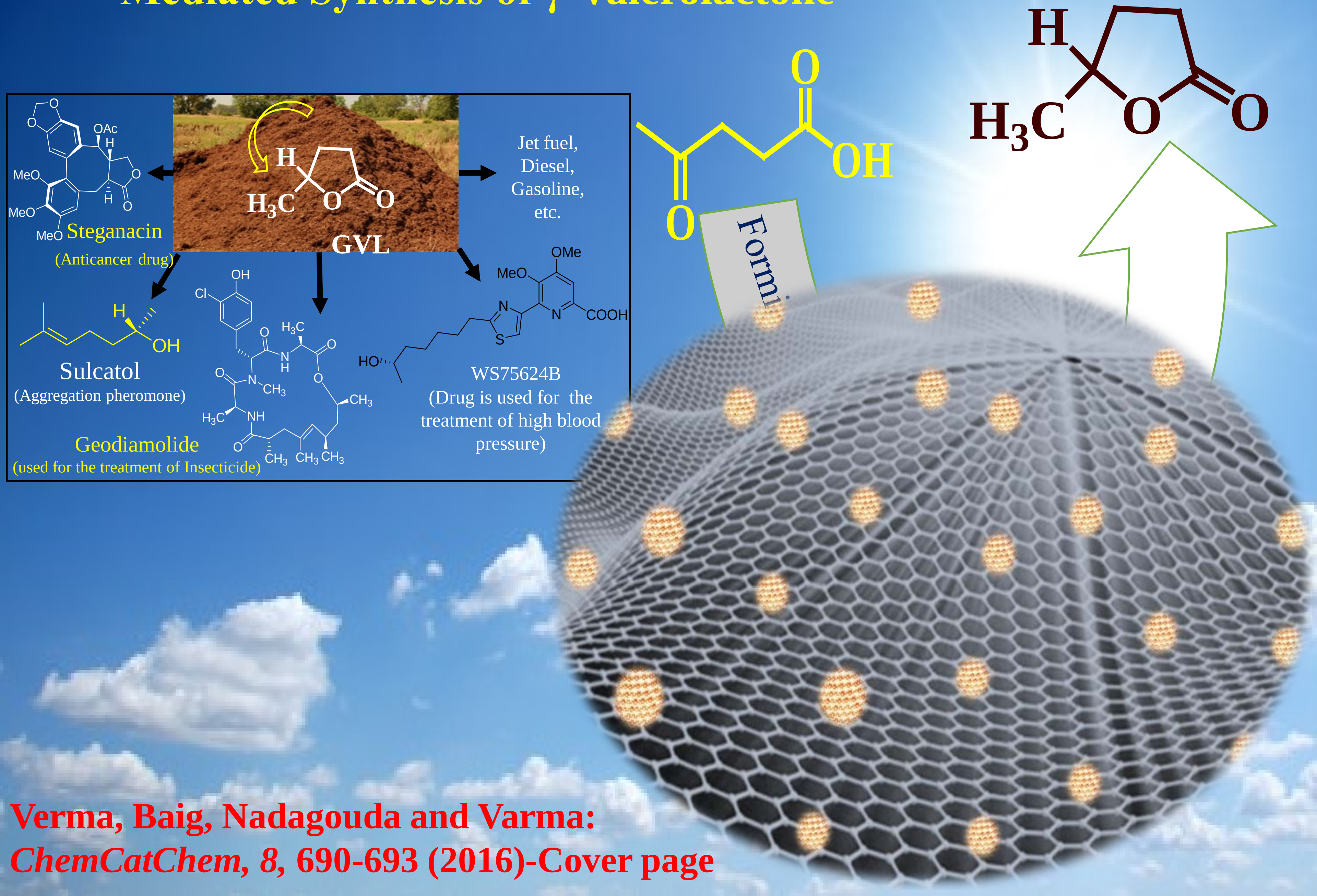
Direct Aminoformylation of Nitroarenes



Entry	Reactant	Product	Time	Yield
1			2 h	99 %
2			2 h	98 %
3			2 h	96 %
4			2 h	97 %
5			2 h	97 %
6			2 h	96 %
7			3 h	76 %
8		-	12 h	-

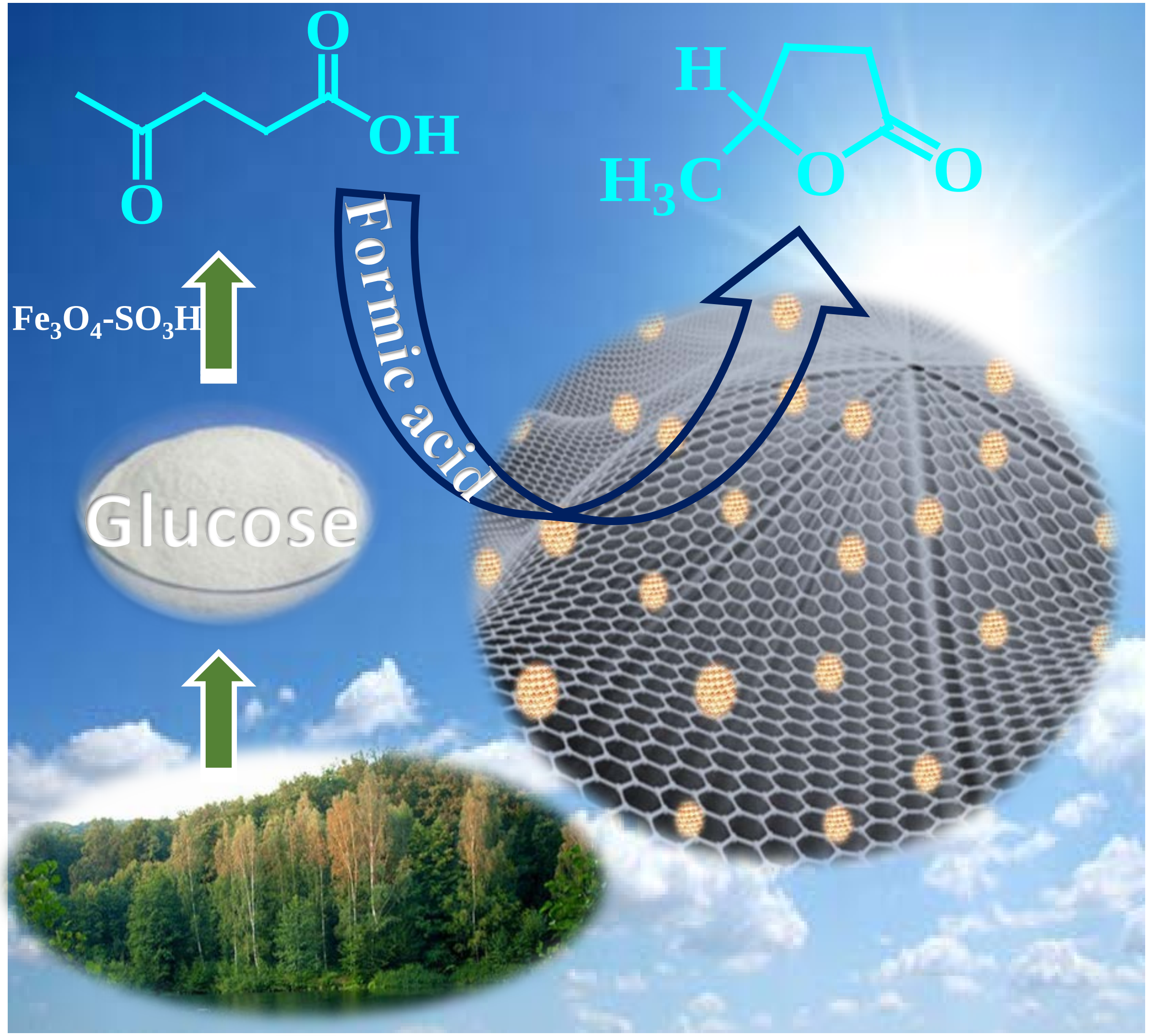
Baig, Verma, Nadagouda, Varma: *Green Chem., 18*, 1019 (2016)-Cover page

Sustainable Strategy Utilizing Biomass: Visible Light-Mediated Synthesis of γ-Valerolactone



Verma, Baig, Nadagouda and Varma:
***ChemCatChem*, *8*, 690-693 (2016)-Cover page**

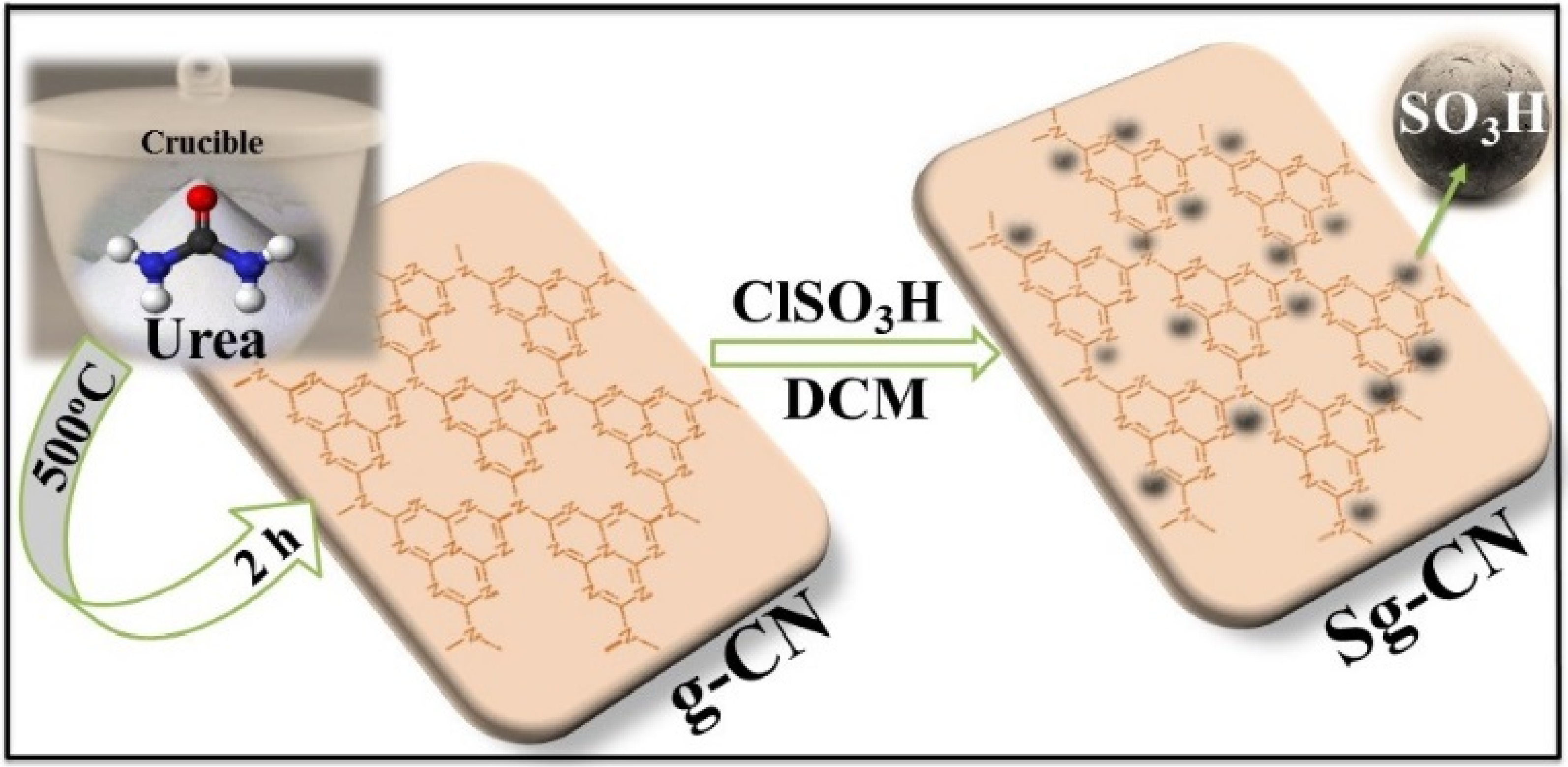
Visible Light-Mediated Synthesis of γ-Valerolactone from Biomass



Verma, Baig, Nadagouda, Varma: *ChemCatChem*, *8*, 690 (2016)-Cover page

Sulfonated Graphitic Carbon Nitride (Sg-CN)

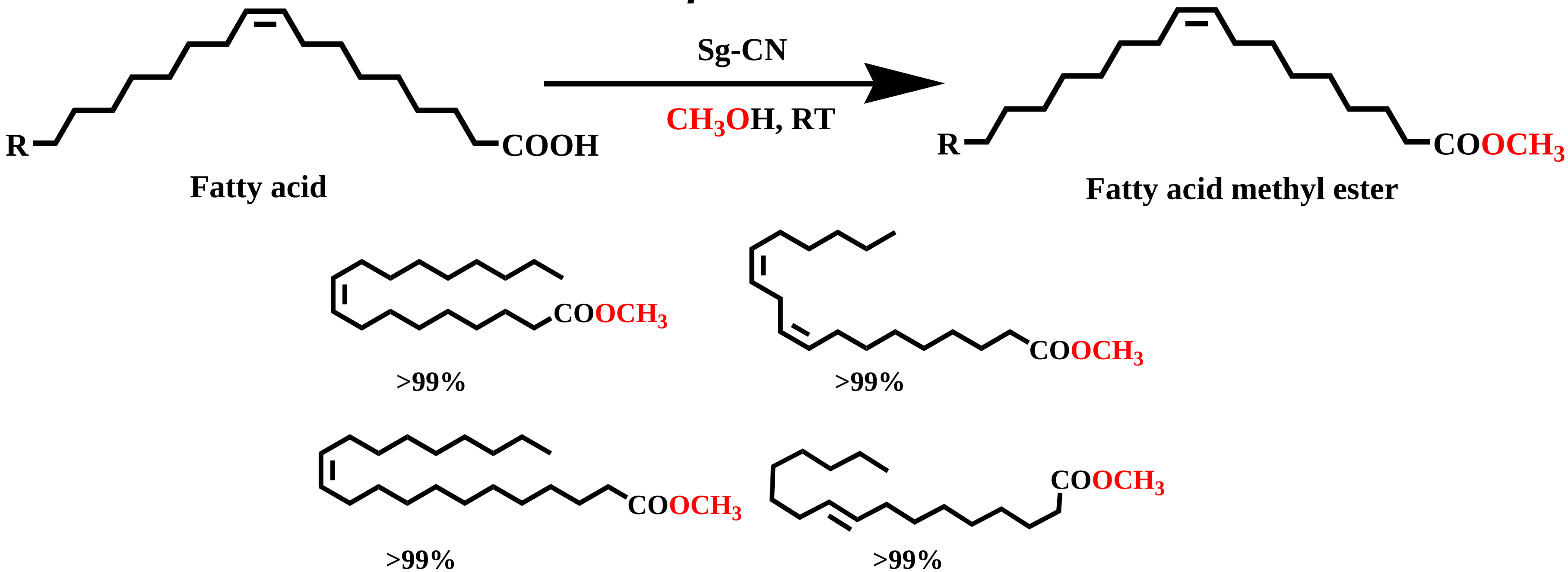
Simple synthesis from abundant and inexpensive materials



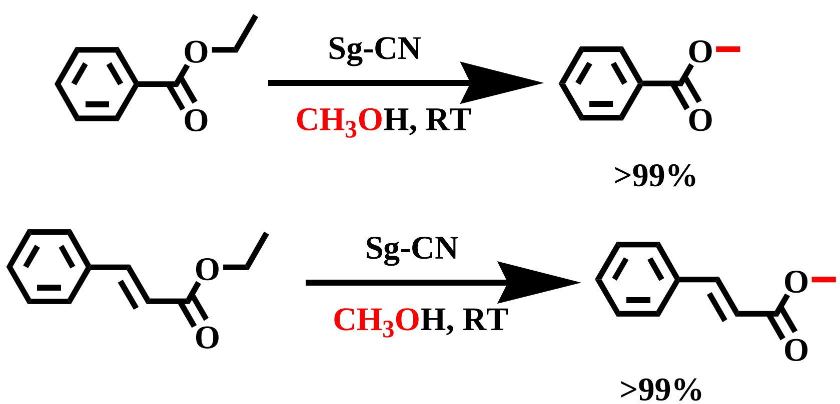
Verma, Baig, Nadagouda, Len, Varma: *Green Chem.*, *19*, 164 (2017)
Baig, Verma, Nadagouda, Varma: *Sci. Rpts.*, *6*, 39387 (2016), DOI:10.1038/srep39387

Synthesis of Biodiesel at Room Temperature

Esterification:

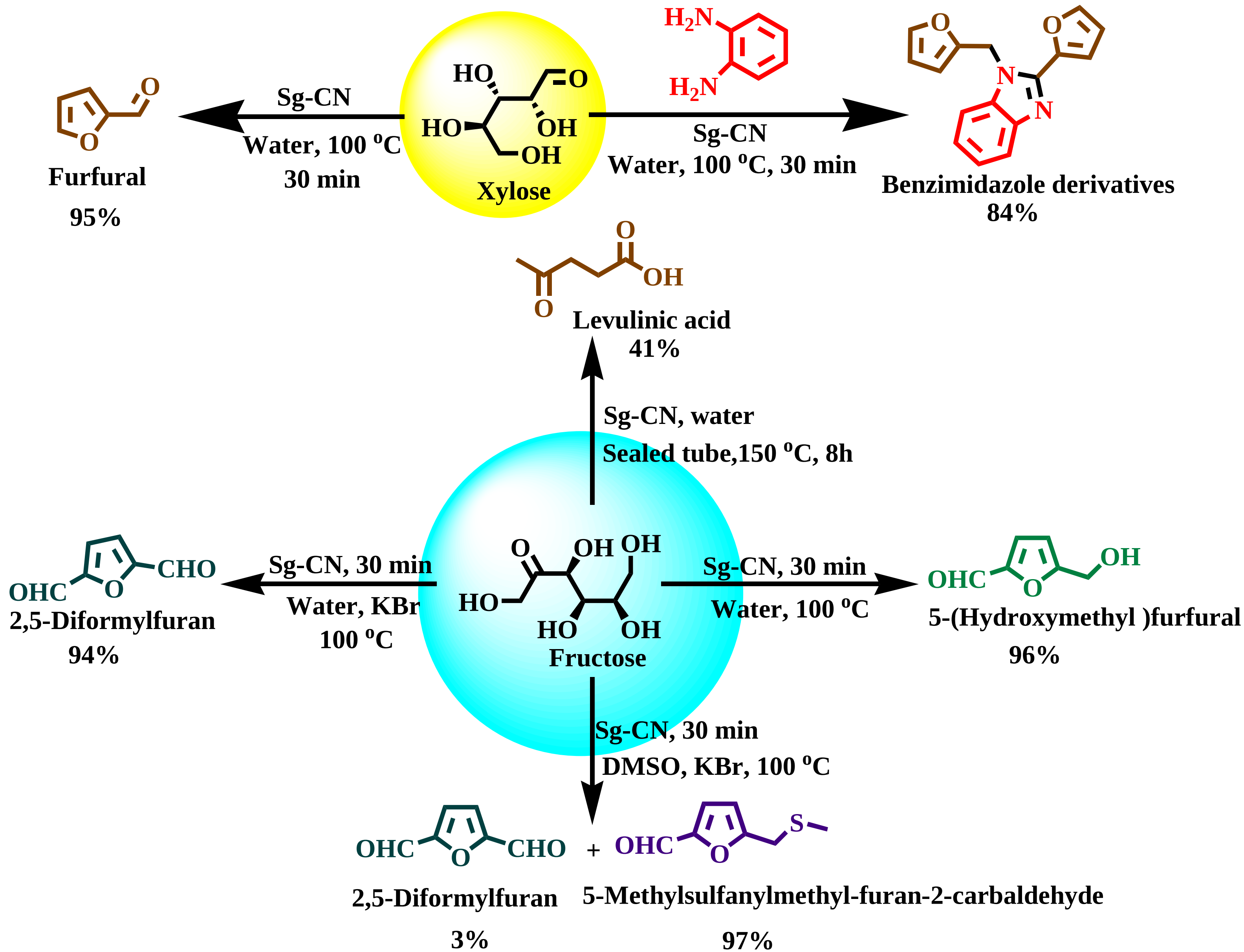


Transesterification:



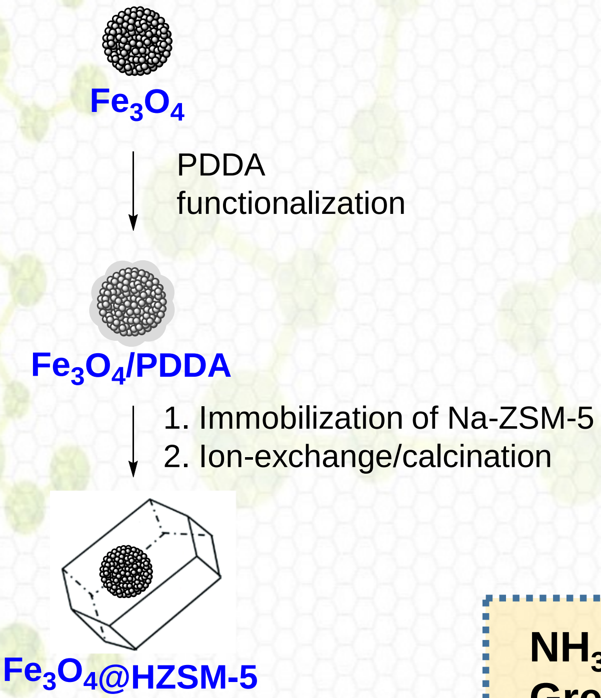
Baig, Verma, Nadagouda, Varma: *Scientific Reports*, *6*, 39387 (2016)

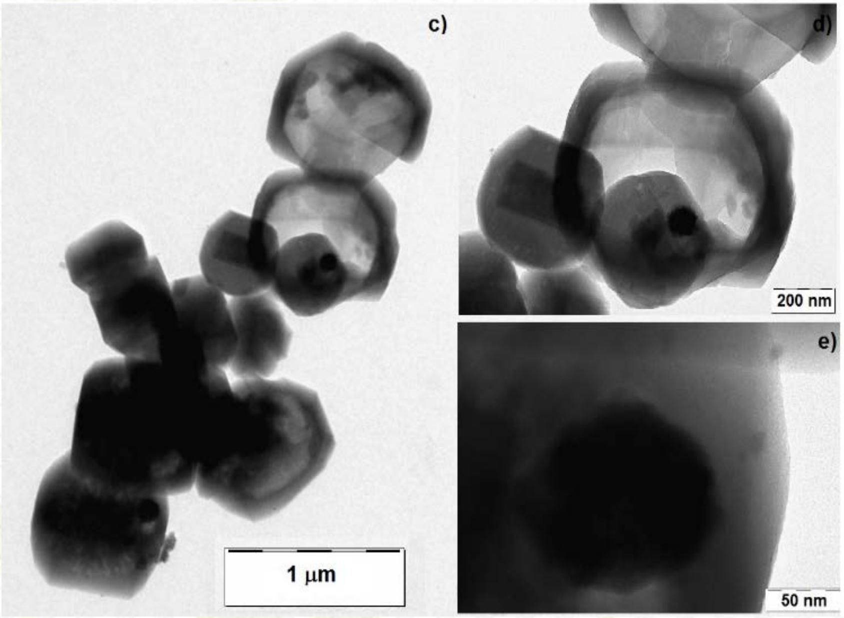
Sustainable Pathway to Furanics from Biomass *via* Heterogeneous Organo-Catalysis



Verma, Baig, Nadagouda, Len, Varma: *Green Chem.*, *19*, 164 (2017)

Magnetically Recoverable HZSM-5 Zeolite: Catalyst Characterization



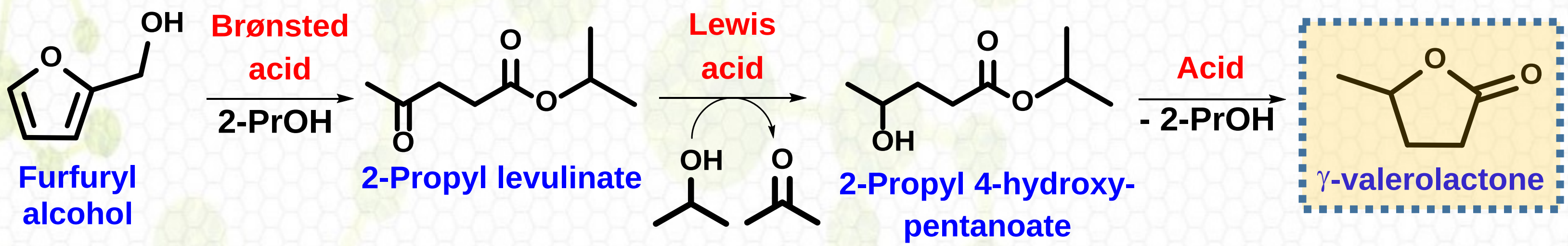


NH_3-TPD and FTIR of absorbed pyridine:
Great amount of moderate to strong acid sites
-both Lewis and Brønsted in nature

Lima, Lima, Rathi, Gawande, Tucek, Urquieta-González, Zbořil , Paixão, Varma. *Green Chem.*, 2016, *18*, 5586.

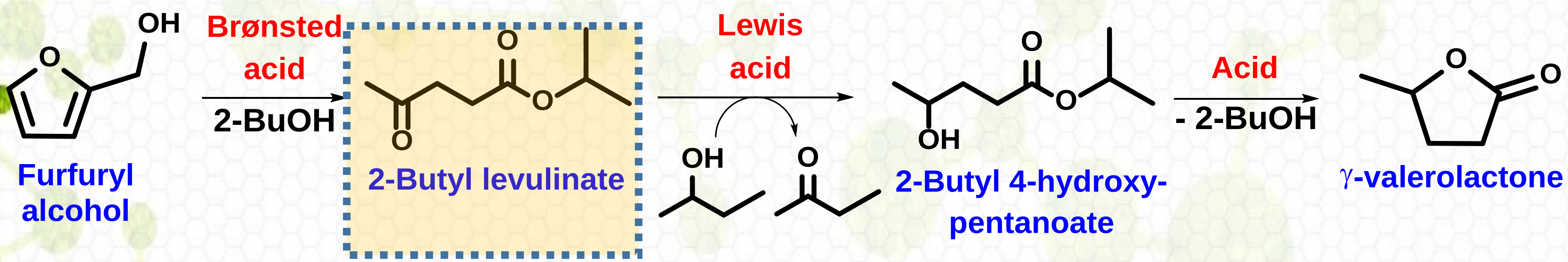
Magnetically Recoverable HZSM-5 Zeolite: Catalytic Utility

Reaction in 2-propanol



Evaluation of the reaction parameters: temperature, catalyst loading and molar ratio FA:2-PrOH

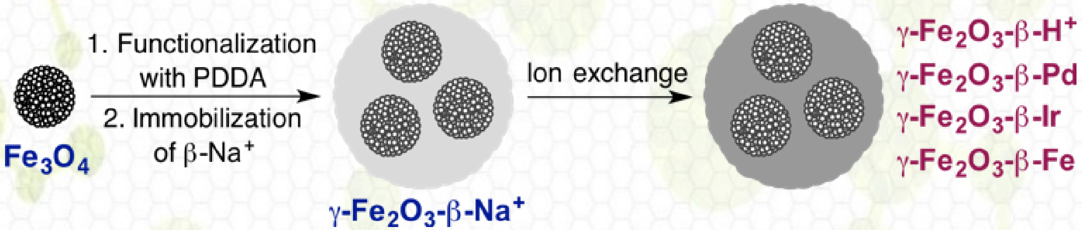
Reaction in 2-butanol

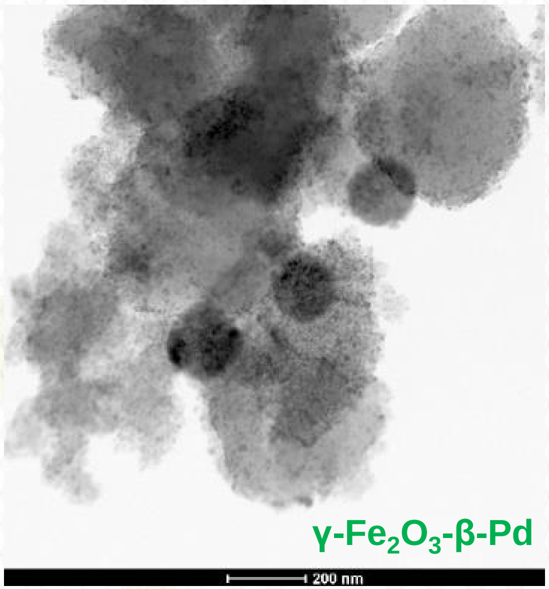


With 5% (%v/v) water in 2-butanol: **levulinic acid** is the main product

Lima, Lima, Rathi, Gawande, Tucek, Urquieta-González, Zbořil , Paixão, Varma. *Green Chem.*, 2016, *18*, 5586.

Magnetically Recoverable Metal-exchanged β-zeolites: Catalyst Characterization





DRX with Rietveld refinement

19, 3856-3868

Maghemite (5.5%), β-zeolite (60.5 %), ZSM-12 (34%)

XPS

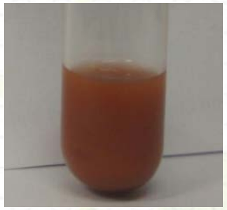
γ-Fe_2O_3-β-Pd
γ-Fe_2O_3-β-Ir
γ-Fe_2O_3-β-Fe

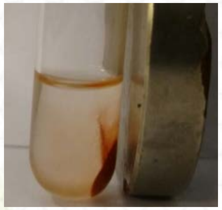
Superficial oxides

Metals exchanged into the zeolite

SQUID magnetization

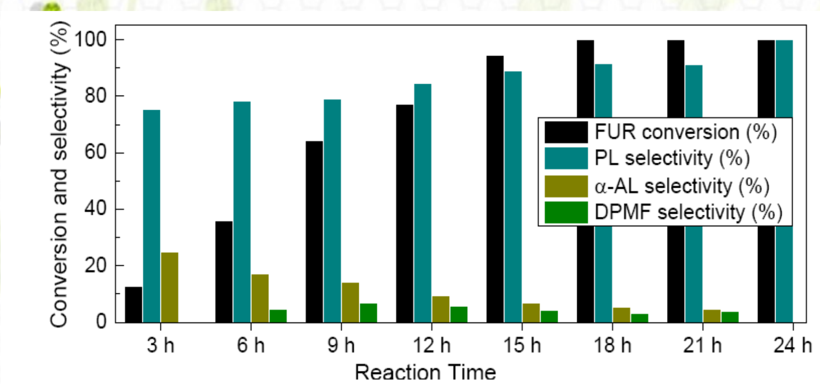
Magnetic support with high magnetization: 64.2 emu/g
γ-Fe_2O_3-β-Pd: 6 emu/g



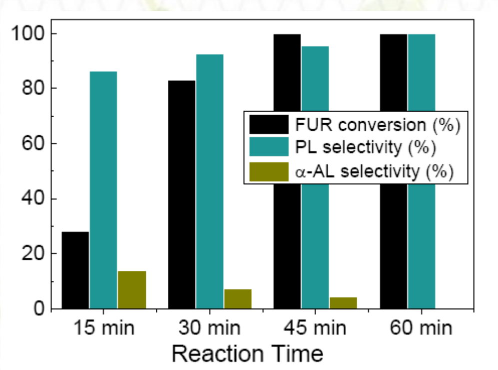


Jorge, Lima, Lima, Marchini, Castelblanco, Rivera, Urquieta-González, Varma, Paixão, *Green Chem., 19,* 3856 (2017)

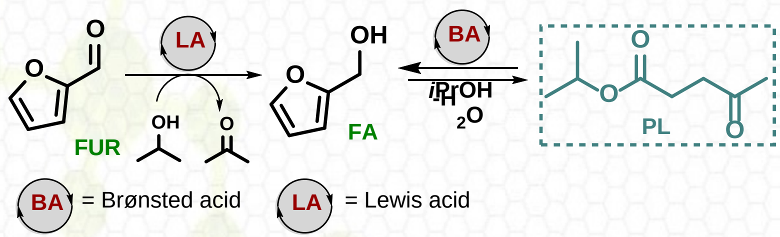
Magnetically Recoverable Metal-exchanged *β*-Zeolites: Catalytic Applications

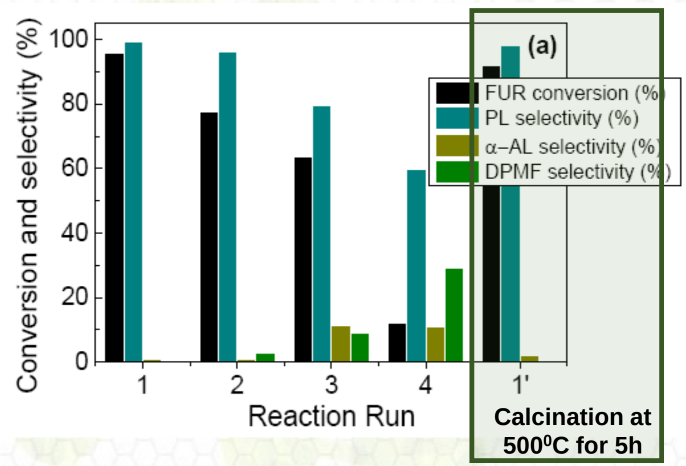


Conventional Heating



MW Heating

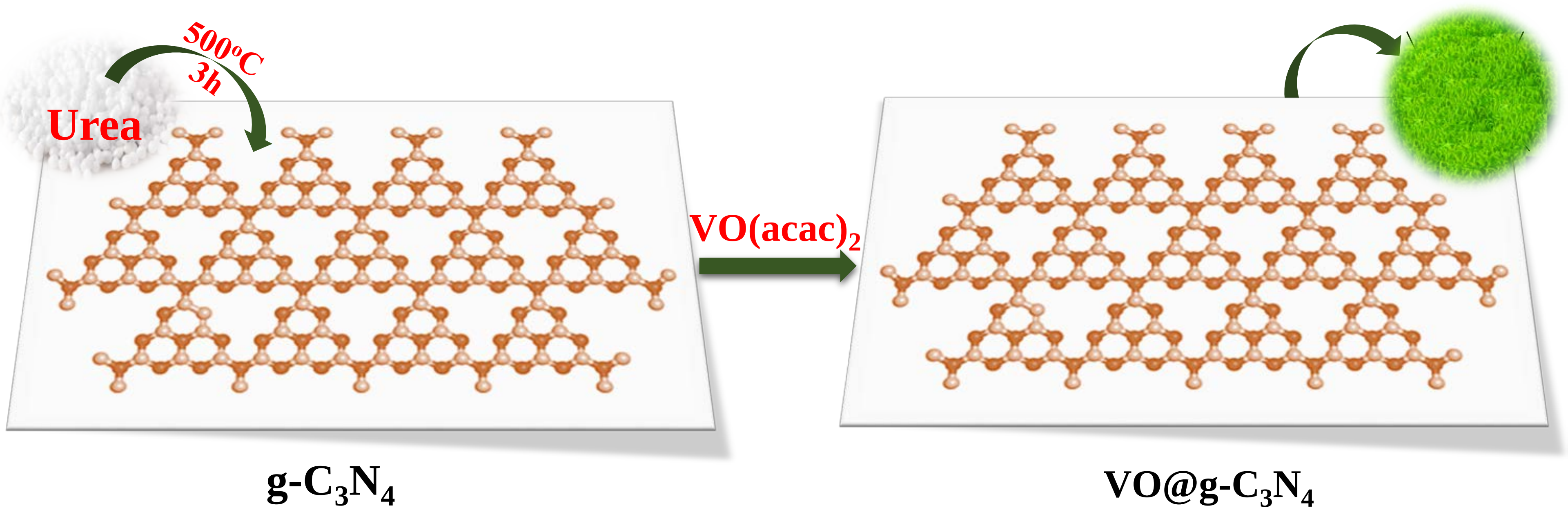




n_{FA} = 0.3 mmol, m_{cat} = 75 mg, V_{iPrOH} = 460 μL, T = 130˚C, t = 24h

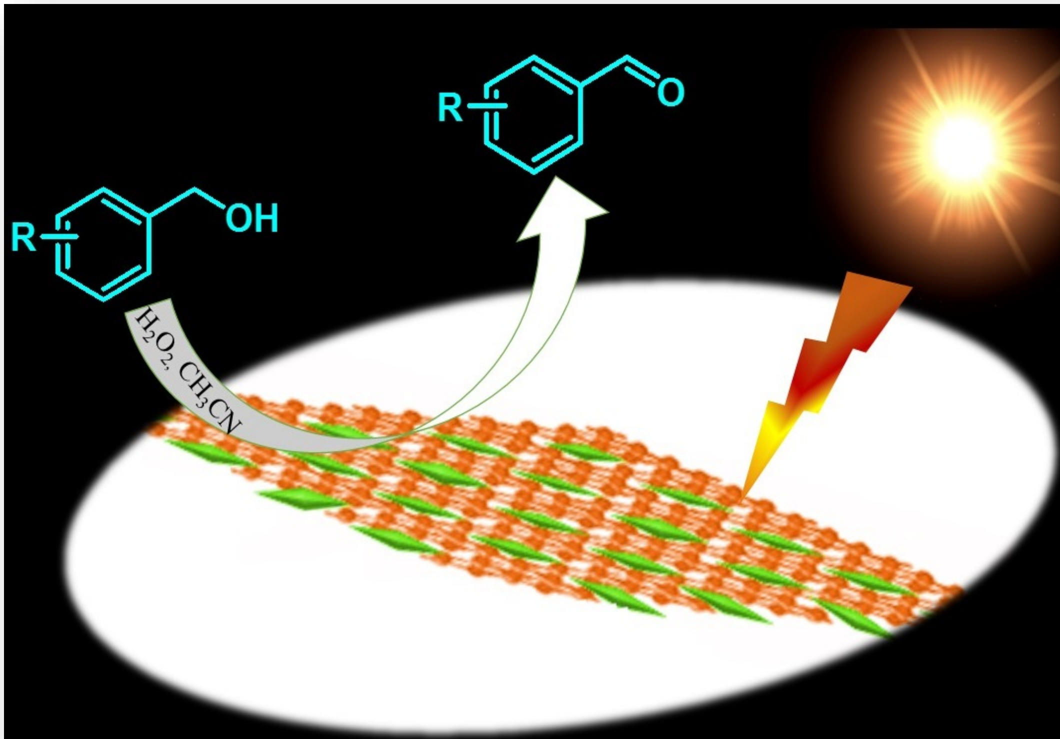
Jorge, Lima, Lima, Marchini, Castelblanco, Rivera, Urquieta-González, Varma, Paixão, *Green Chem.*, *19*, 3856 (2017)

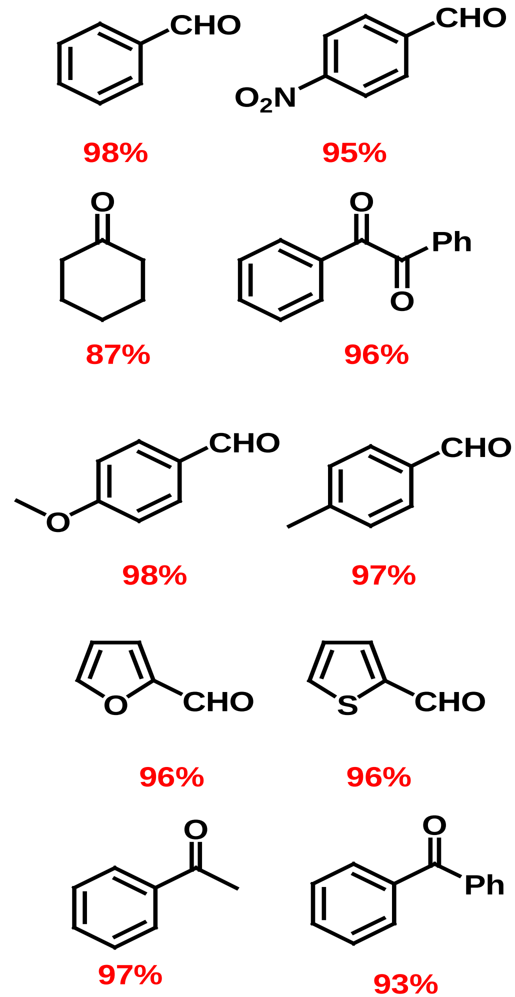
Synthesis of Oxo-Vanadium Graphitic Carbon Nitride ($VO@g\text{-}C_3N_4$)



Verma, Baig, Nadagouda, Varma: *ACS Sustain. Chem. Eng., 4,* 1094 *(*2016)- Open Access

Selective Oxidation of Alcohols

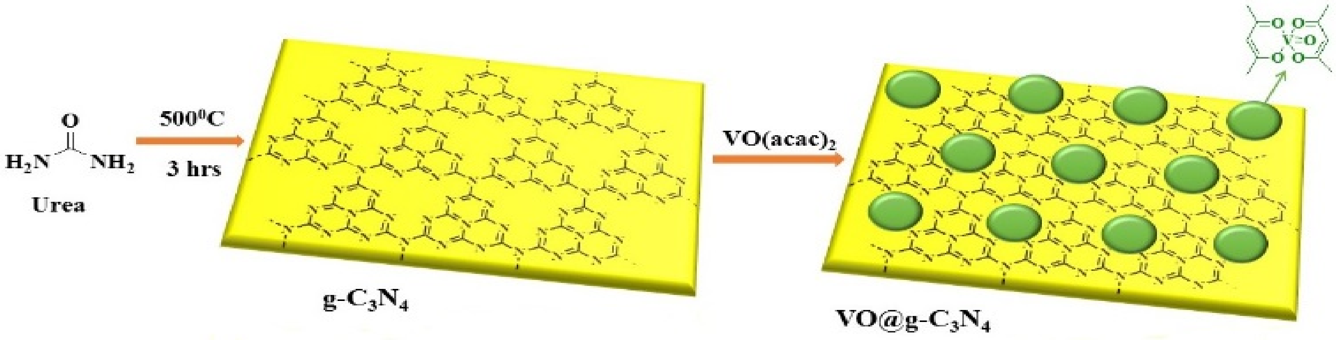




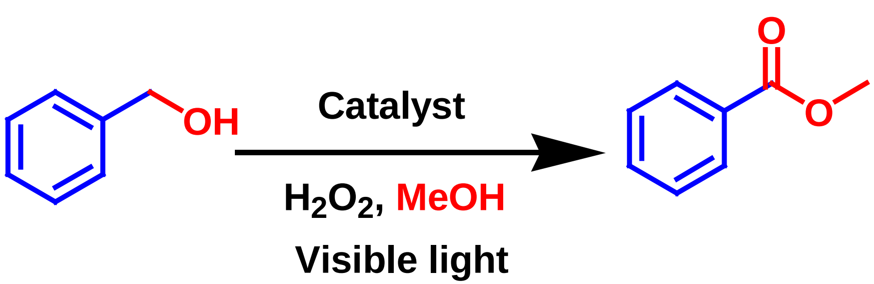
Verma, Baig, Nadagouda, Varma: *ACS Sustain. Chem. Eng.*, *4*, 1094 (2016)- Open Access

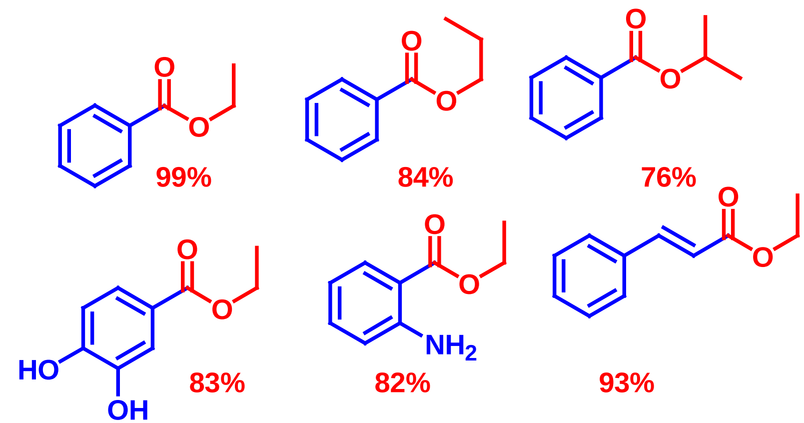
Oxidative Esterification via Photocatalytic C-H Activation

Synthesis of Oxo Vanadium graphitic carbon nitride (VO@g-C_3N_4)



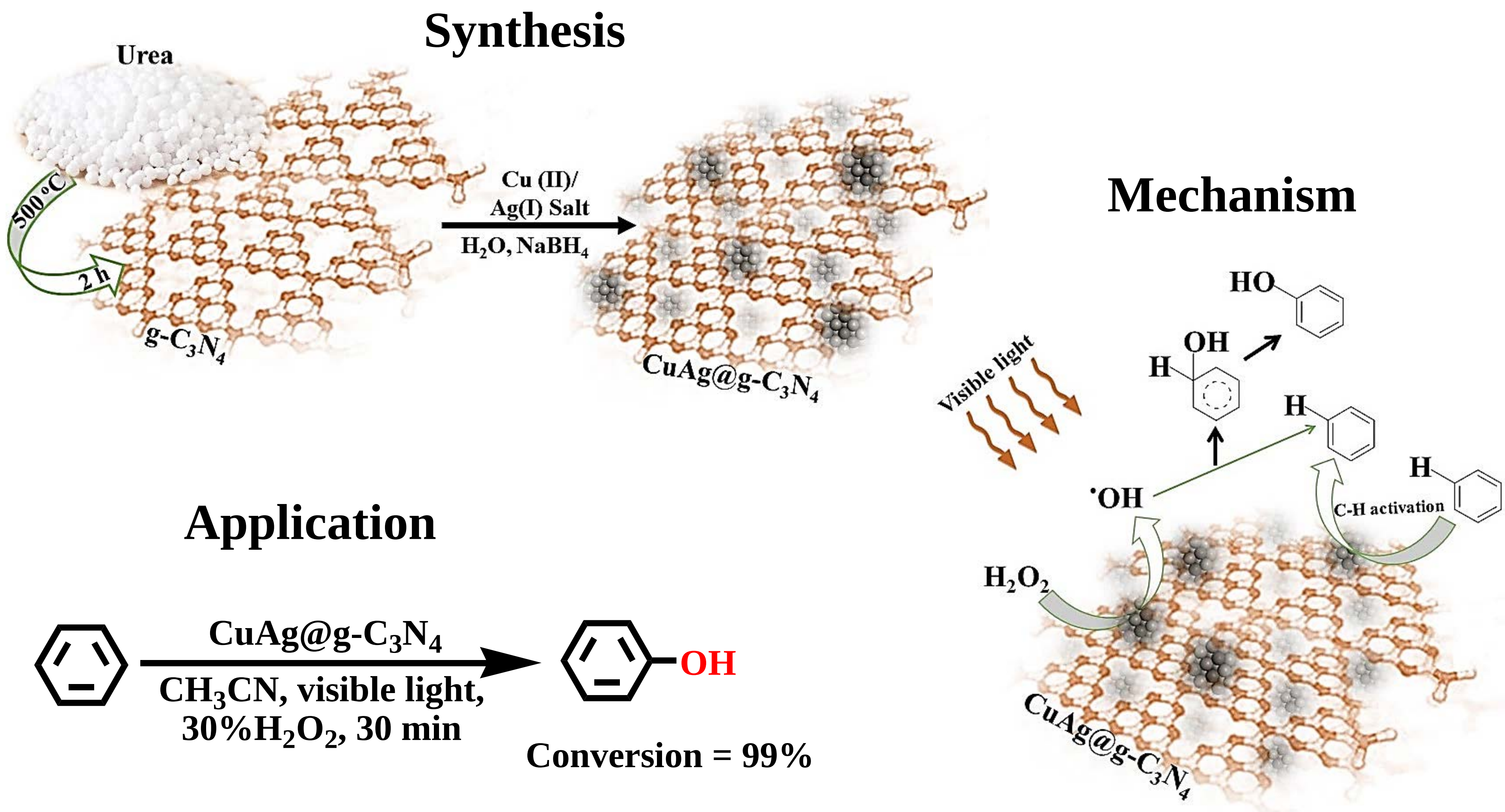
Oxidative C-H activation-Esterification





Verma, Baig, Han, Nadagouda, Varma: *Green Chem. 18*, 251, (2016)

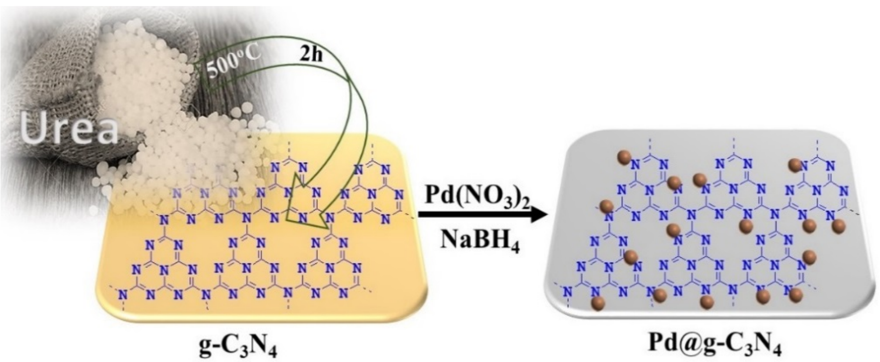
Hydroxylation of Benzene *via* C-H Activation using Bimetallic CuAg@g-C_3N_4

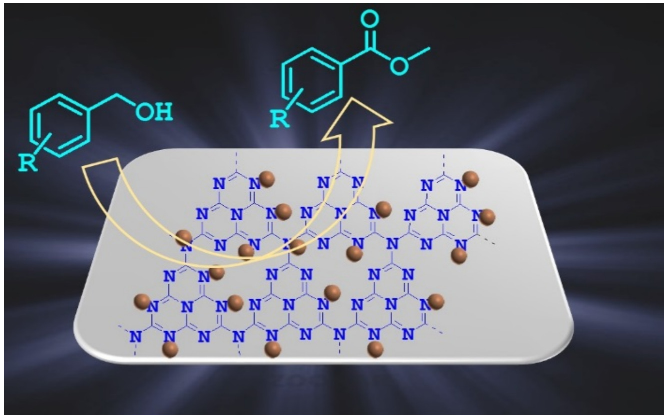


Verma, Baig, Nadagouda, Varma: ACS *Sustain. Chem. Eng.*, *5*, 3637 (2017)-Open Access

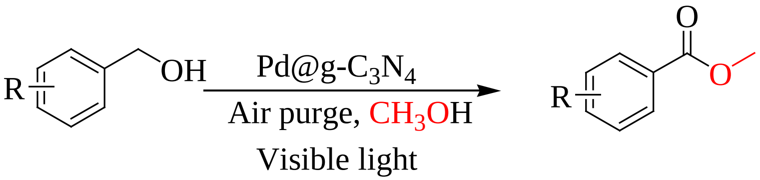
Photocatalytic C-H Activation and Oxidative Esterification Using Pd@g-C_3N_4

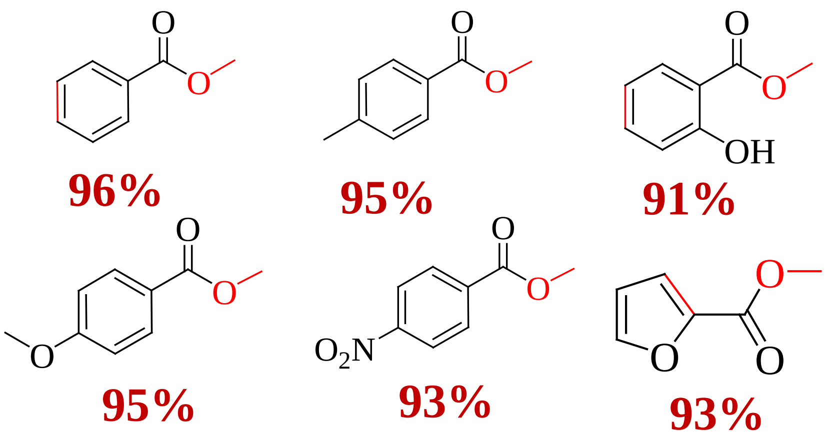
Synthesis of Pd@g-C_3N_4





Oxidative esterification of aromatic alcohols

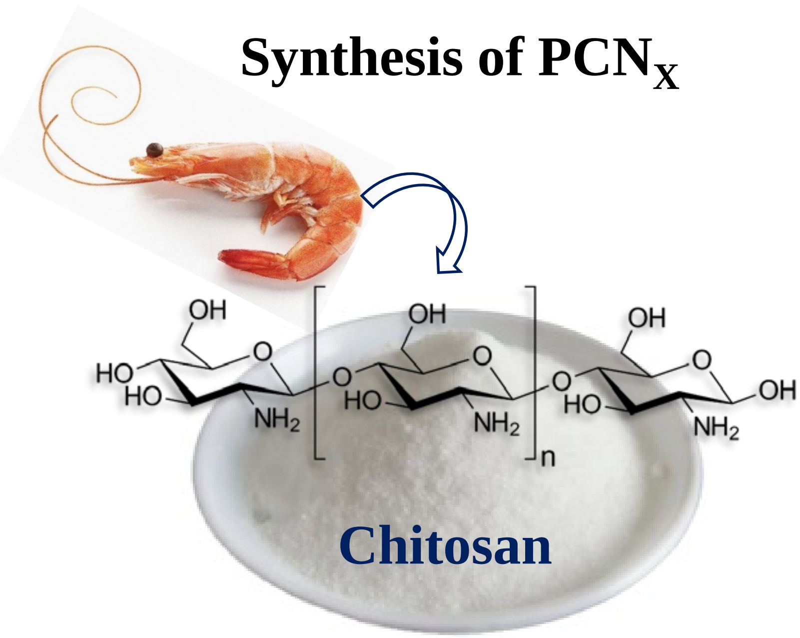




Verma, Baig, Nadagouda, Varma: *Catalysis Today* (in press) 2018

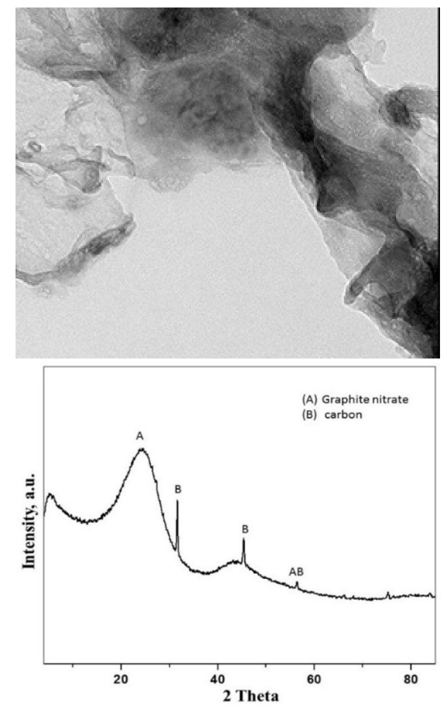
Porous *N*-Enriched Carbonaceous Material from Marine Waste: Chitosan-derived Carbon Nitride Catalyst for Aerial Oxidation of HMF to 2,5-furandicarboxylic acid (FCDA)

Synthesis of PCN_X



300 °C

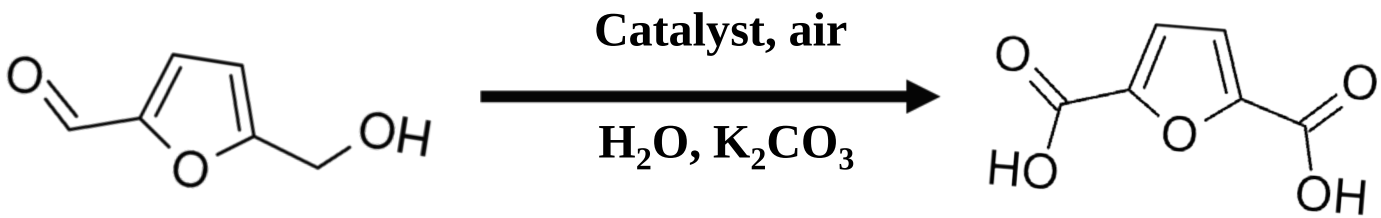
N_2, 4 h



Porous carbon nitride catalyst (PCN_x)

Verma, Nadagouda, Varma: *Scientific Reports*, 7, 13596 (2017)
DOI:10.1038/s41598-017-14016-5

Aerial Oxidation of HMF to Furandicarboxylic acid FDCA



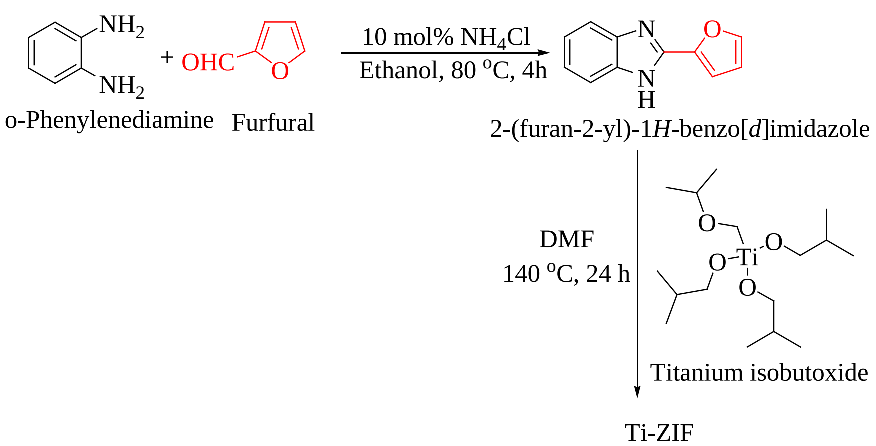
5-hydroxymethylfurfural **2,5-furandicarboxylic acid**

Entry	Catalyst	Time	Temperature	Yield
1	Graphite	36 h	70 ^oC	-
2	Graphene oxide	36 h	70 ^oC	-
3	Carbon nanotube	36 h	70 ^oC	-
4	Carbon nanofibers	36 h	70 ^oC	-
5	*N*-doped graphene	36 h	70 ^oC	5 %
6	g-C_3N_4	36 h	70 ^oC	15%
7	**PCN_X**	**36 h**	**70 ^oC**	**83%**

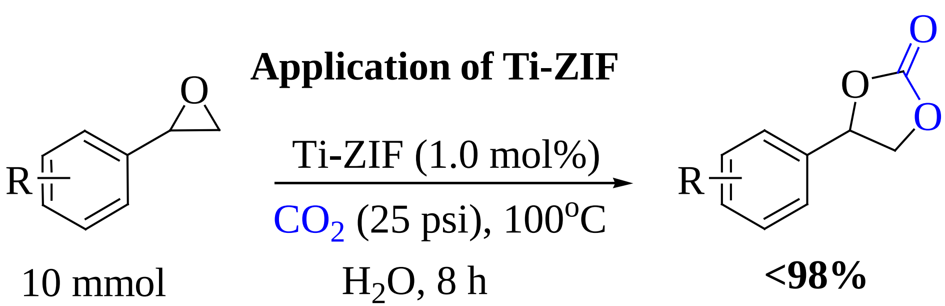
Verma, Nadagouda, Varma: *Scientific Reports*, 7, 13596 (2017)
DOI:10.1038/s41598-017-14016-5

Titanium-based Zeolitic Imidazolate Framework for Chemical Fixation of Carbon dioxide

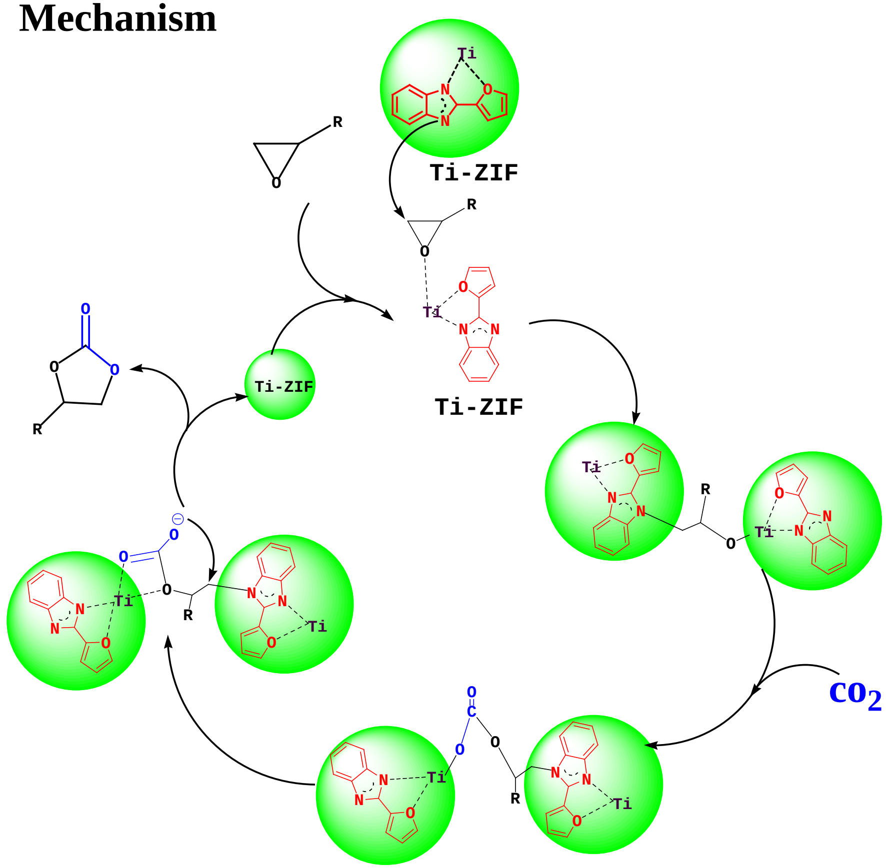
Synthesis of Ti-ZIF



Application of Ti-ZIF



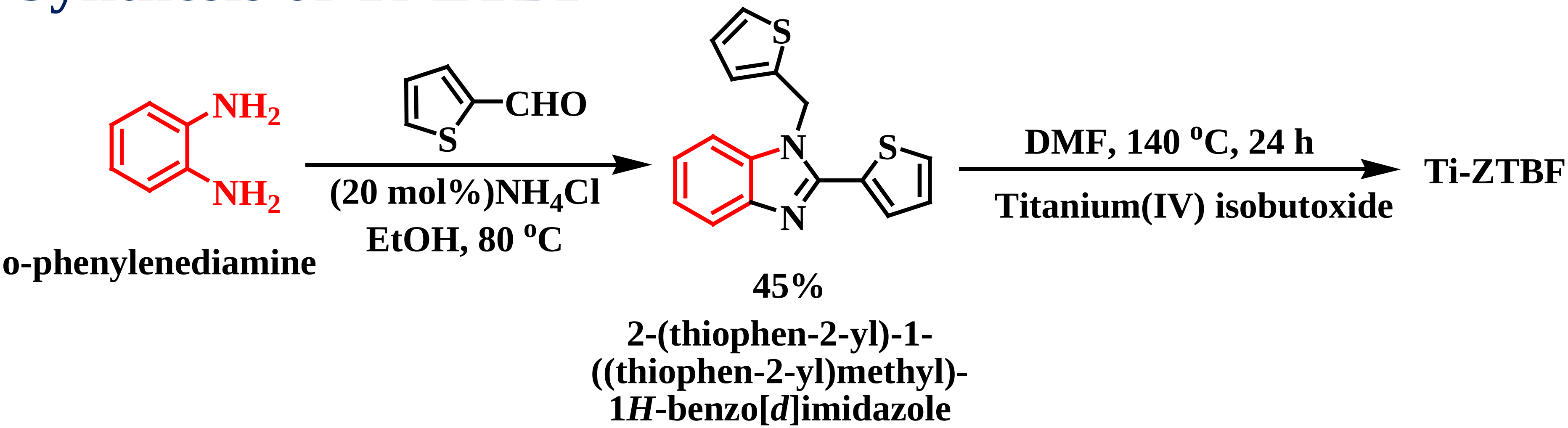
Mechanism



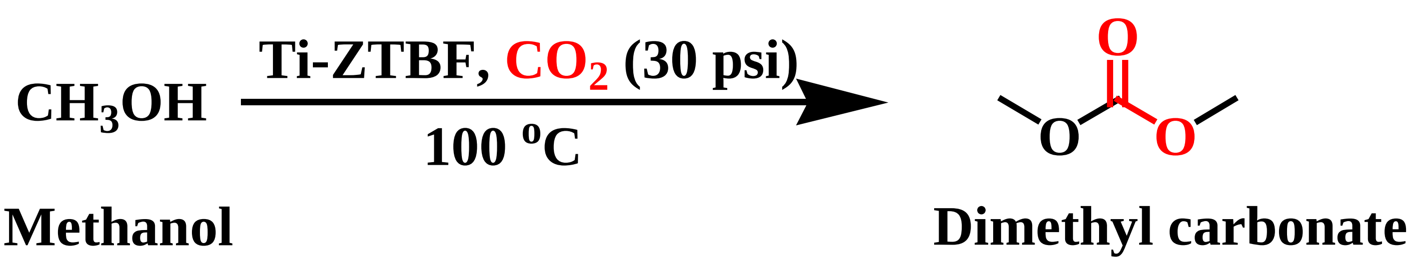
Verma, Baig, Nadagouda, Varma: *Green Chem.*, 2016, 18 , 4855 (Cover Page)

Fixation of Carbon Dioxide into Dimethyl Carbonate

Synthesis of Ti-ZTBF



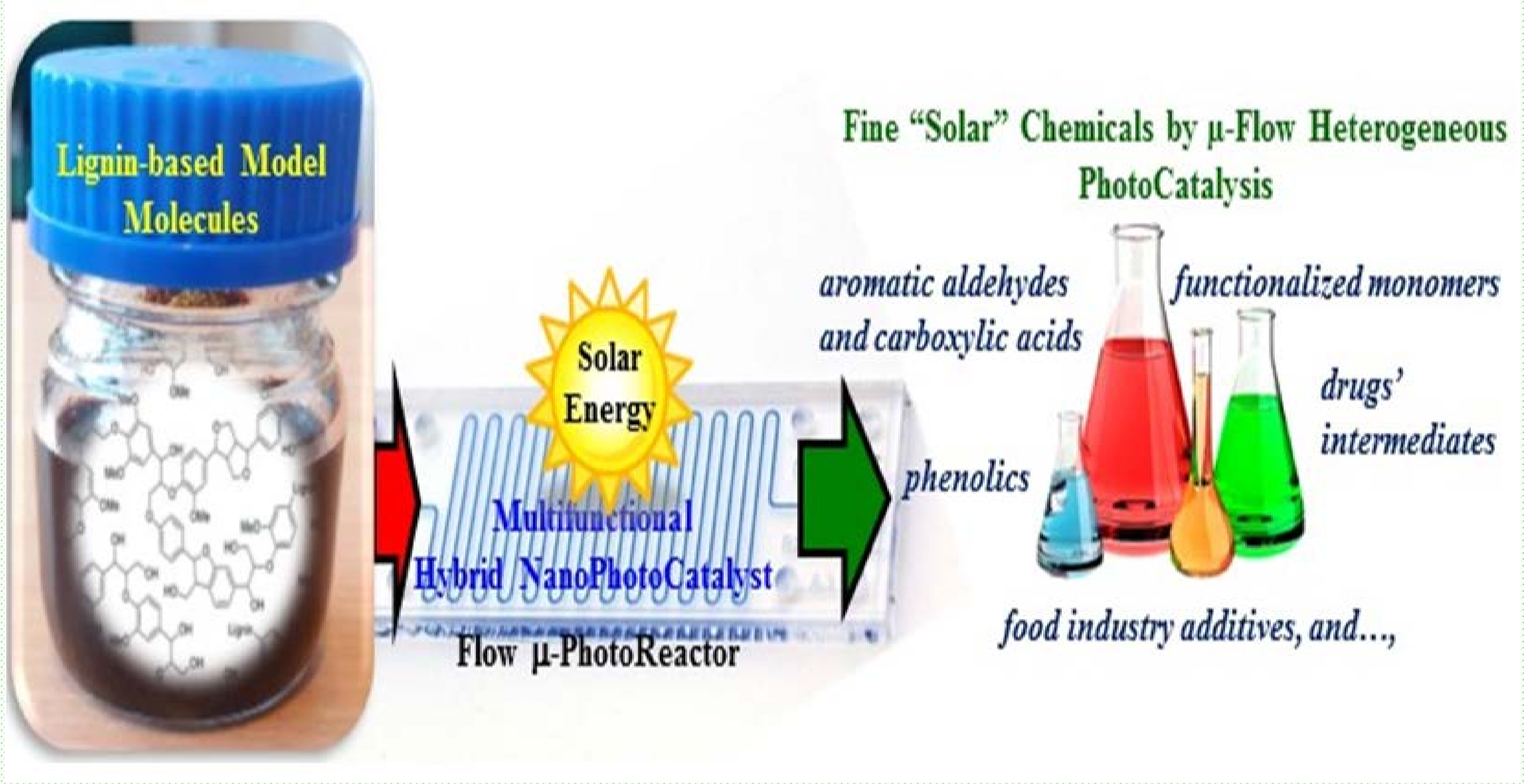
Application of Ti-ZTBF: Synthesis of DMC



Varma *et al*. *Scientific Reports*, 7: 655 (2017), DOI:10.1038/s41598-017-00736-1

Selective Photocatalysis of Lignin-inspired Chemicals by Integrating Hybrid Nanocatalysis in Microfluidic Reactors A Critical Review

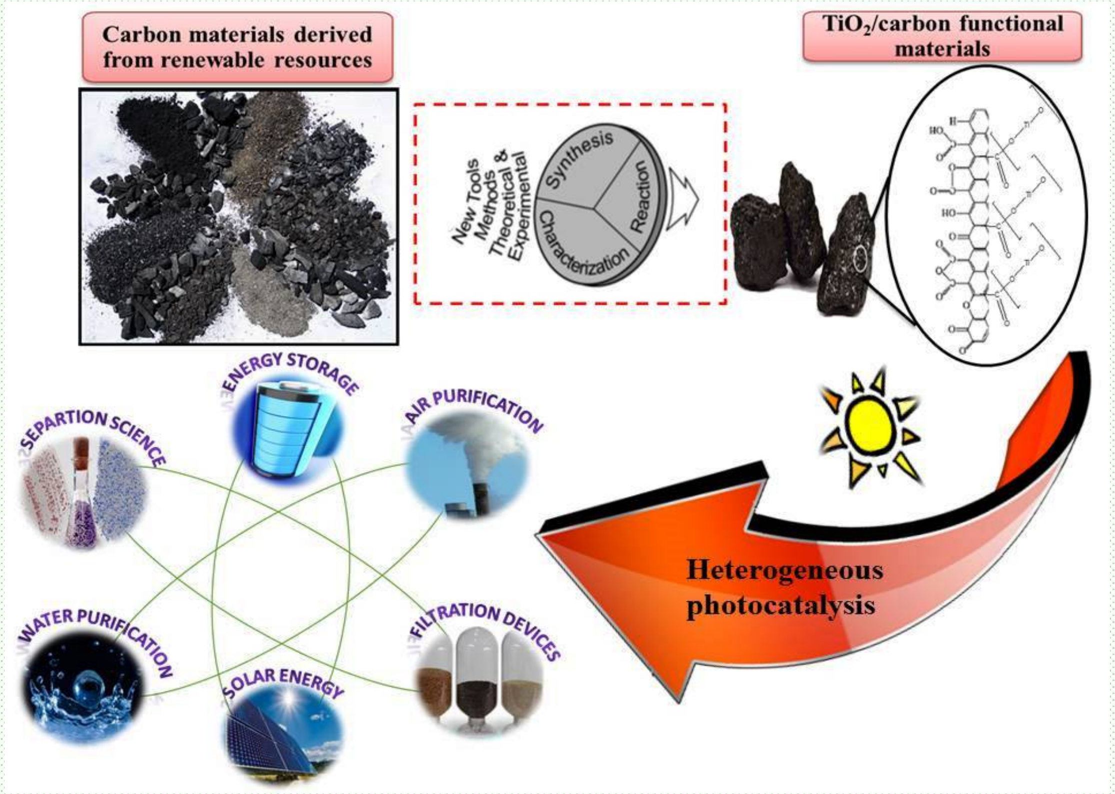
New proof-of-concept for upgrading lignin-based chemicals via the synergistic coupling of nanophotocatalysis with microfluidic systems.



Colmenares, Varma, Nair: *Chem. Soc. Rev., 46*, 6675-6686 (2017)

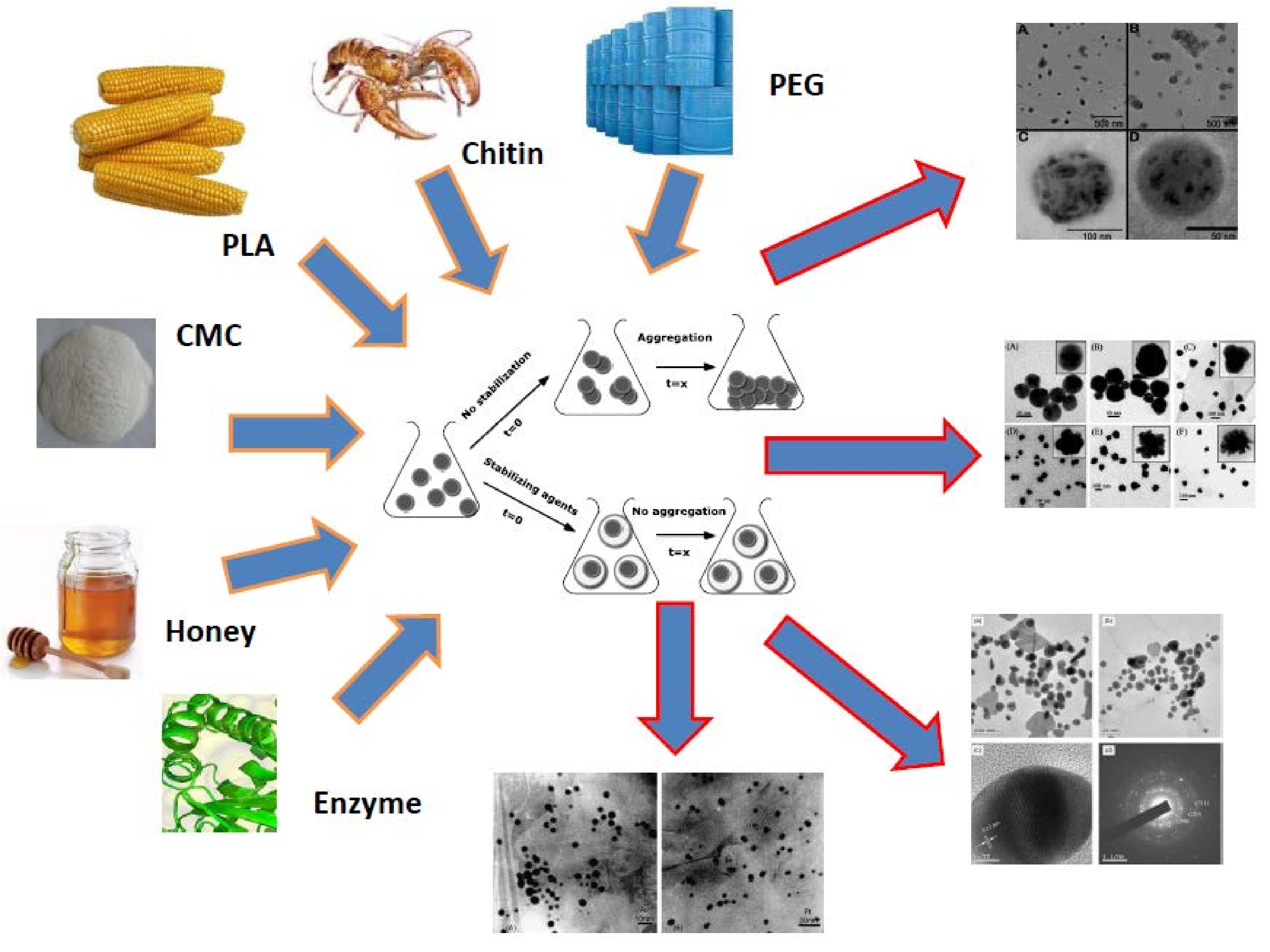
Sustainable Hybrid Photocatalysts: Titania Immobilized on Carbon Materials Derived from Renewable and Biodegradable Resources A Critical Review

Preparation, properties and heterogeneous photocatalytic applications of TiO2 immobilized on carbon materials derived from earth-abundant, renewable and biodegradable agricultural residues and sea food waste resources, are reviewed.



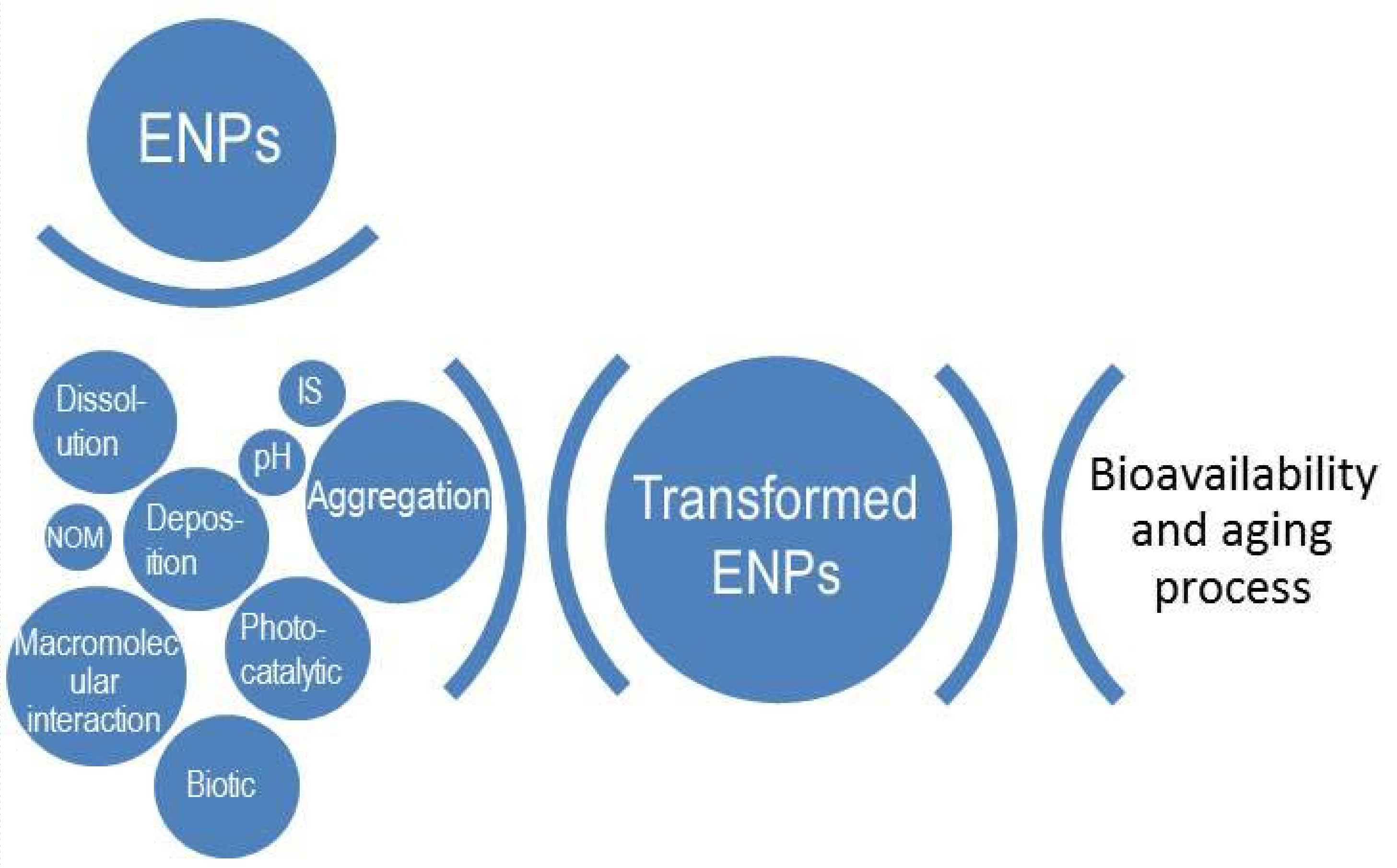
Colmenares, Varma, Lisowski: *Green Chem., 18*, 5736-5750 (2016)

Biodegradable Polymers and Enzymes in Stabilization & Surface Functionalization



Virkutyte, Varma: *Chem. Sci.*, 2, 837 (2011)

Fate of Engineered Nanoparticles: Implications in the Environment



Dwivedi, Dubey, Sillanpää, Kwon, Lee, Varma: *Coord. Chem. Rev.* 287, 64-78 (2015)

Acknowledgements

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Dr. Babita Baruwati   Dr. Jurate Virkutyte
Prof. Jiahui Kou; Dr. Buchi Reddy, Prof. Amit Saha; Prof. Dalip Kumar

Dr. Harshadas Meshram   Dr. Rajender Dahiya   Dr. Rajesh Saini
Dr. Vasu Namboodiri   Dr. Unnikrishnan R. Pillai
Dr. Yuhong Ju   Dr. Yong-Jin Kim

Prof. Virender Sharma (Texas A & M, TX); Prof. Dion Dionysiou (Cincinnati, OH)
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