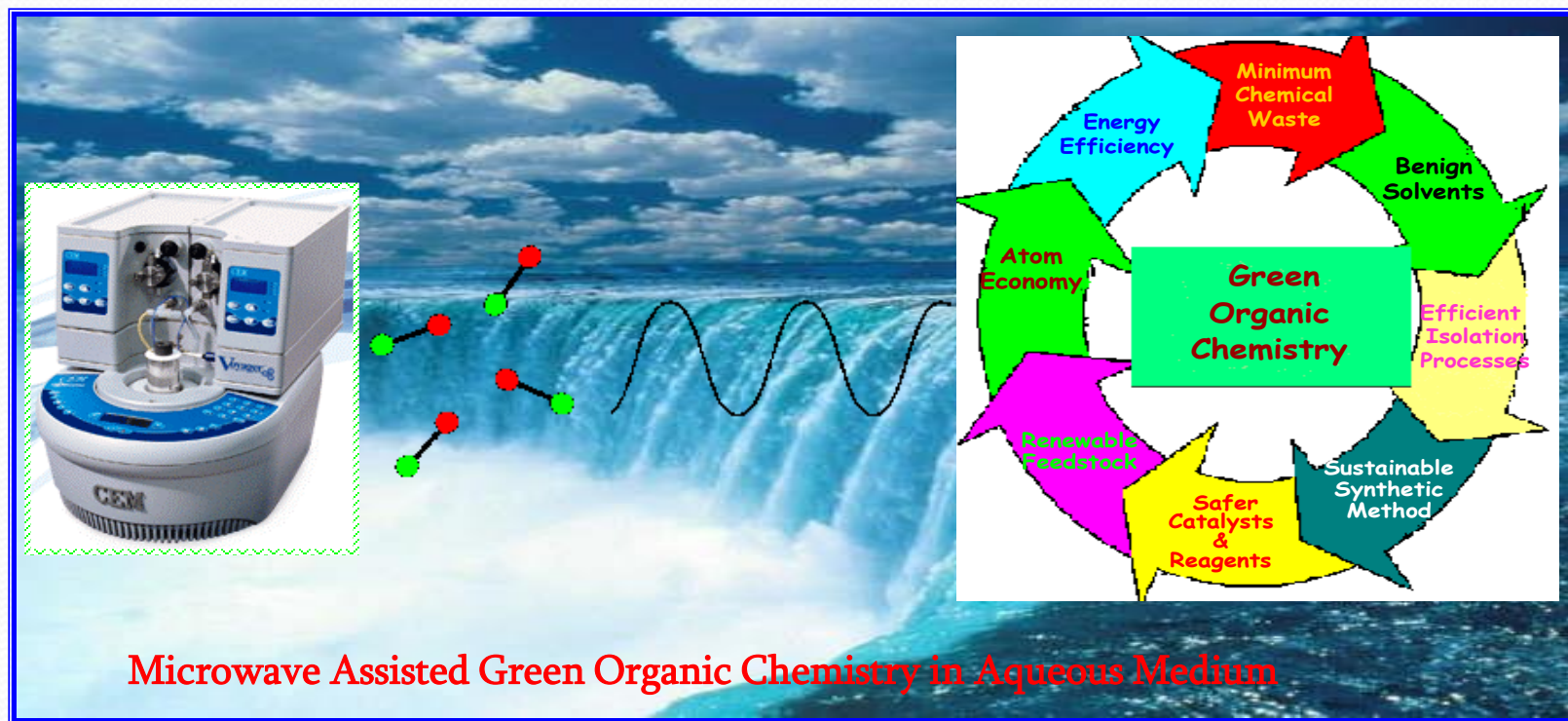


Sustainable Applications of Magnetic Nano-Catalysts and Graphitic Carbon Nitrides

Rajender S. Varma

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E-mail: Varma.Rajender@epa.gov**

- 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; *Acc. Chem. Res.*, 2011, 44, 469-478; *Acc. Chem. Res.*, 2014, 47, 1338-1348
Chem. Soc. Rev., 2008, 37, 1546-1557; *Chem. Soc. Rev.*, 2012, 41, 1559-1584
Chem. Rev., 2016, 116, 3722-3811; *ACS Sustain. Chem. & Eng.*, 2016, 4, 5866-5878
Pure App. Chem., 2008, 80, 777-790; *Pure App. Chem.*, 2013, 85, 1703-1710.
Curr. Opin. Drug Disc., 2007, 10, 723-737.
Green Chem., 1999, 1, 43-55; *Green Chem.*, 2010, 12, 743-754; *Green Chem.*, 2014, 16, 2027-2041.
Coord. Chem. Rev., 2015, 291, 68-94; *Coord. Chem. Rev.*, 2015, 287, 137-156.



Plant Extract



Sugar



Vitamins



Wine



Tea



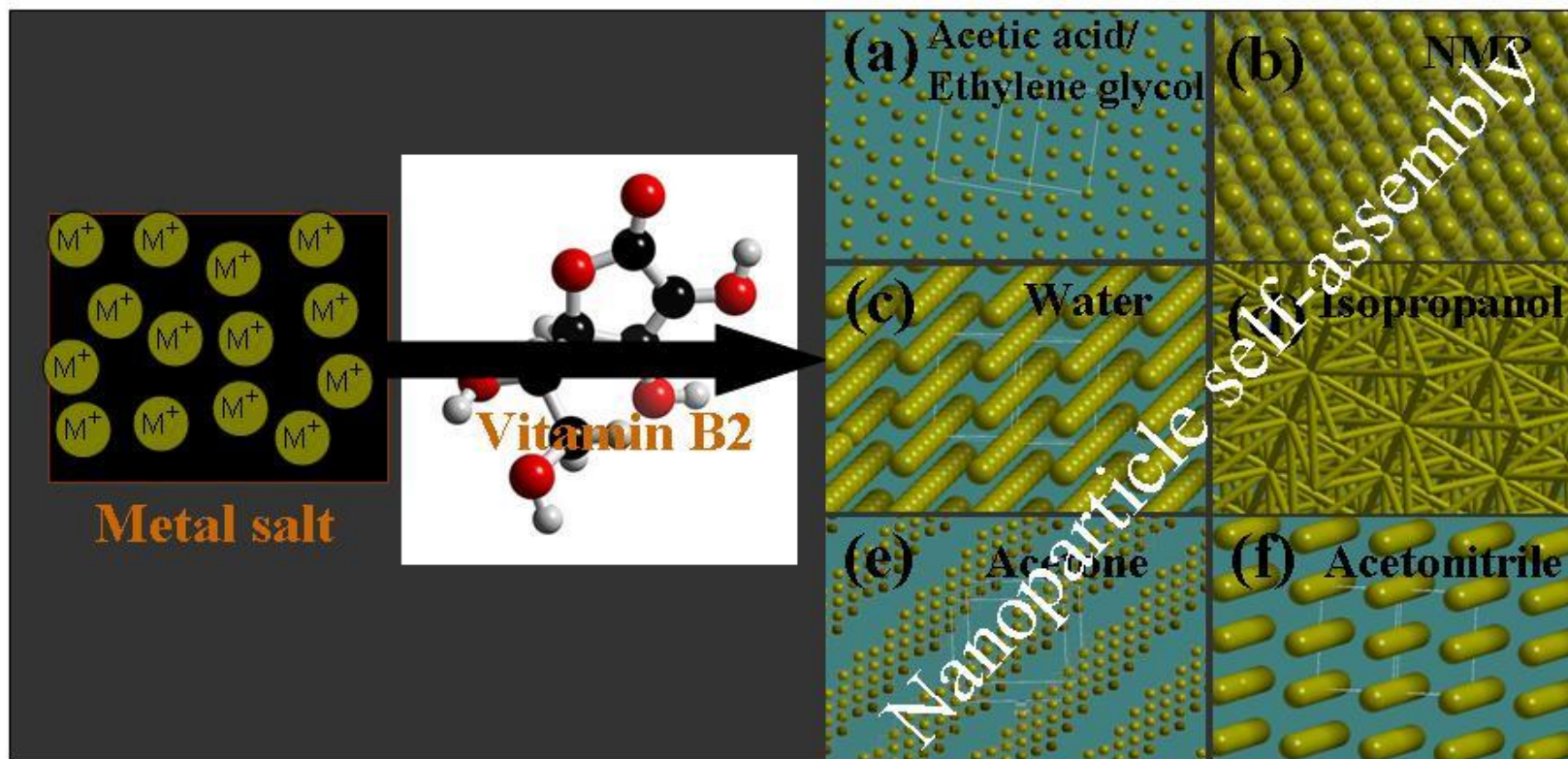
Water



Microwave

Green Synthesis of Nanomaterials

- **PROBLEM:** Synthesize nanomaterials in a sustainable fashion.
- **TECHNOLOGY SOLUTION:** *Learning from Nature-*
Use the elegance of Riboflavin (Vitamin B₂) for redox chemistry.
- **CURRENT STATUS:** Self-assembly of nanoparticles demonstrated

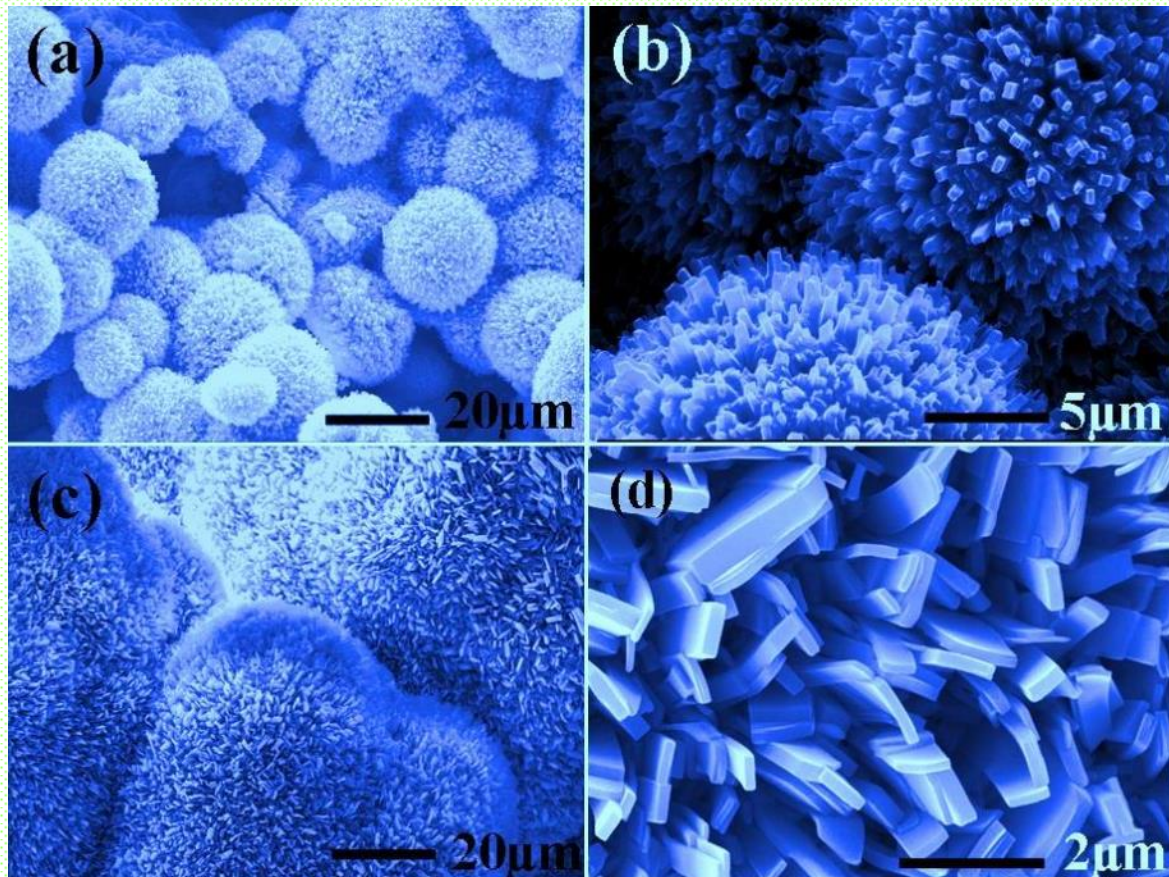


Green Synthesis of Nanomaterials

PROBLEM: Synthesize nanomaterials in a sustainable manner.

TECHNOLOGY SOLUTION: *Learning from Nature*- Use Vitamin B₁ in water to do the reduction and capping.

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



Tea for producing metal nanoparticles

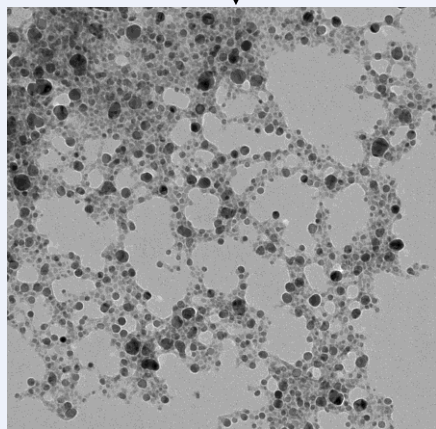
Metal salt +



= Metal nanoparticle

(Ag, Au, Pd, Fe etc.)

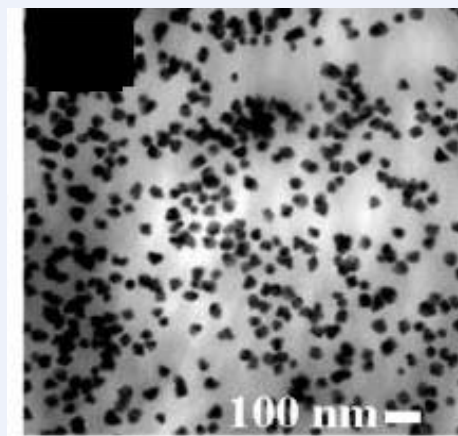
**Ag nanoparticle
using green tea**



408 1,512
Green Tea Silver Nano Particles (Batch 3)
Pure Filtration and Control (10000rpm)
Print Mag: 22000x @ 7.5 in
Micrograph: Timothy J. Grey

100 nm
HV: 120.0kV
Direct Mag: 65000x

**Pd 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)**

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

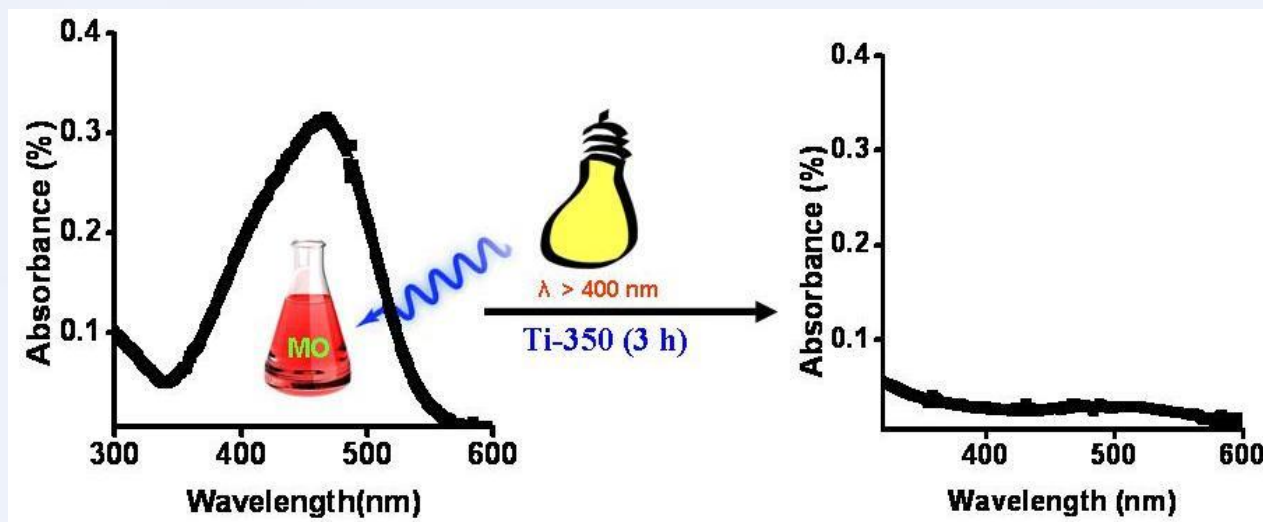
Greener synthesis of Ag and Au nanoparticles is described using antioxidants from blackberry, blueberry, pomegranate, and turmeric extracts; waste from fruit and juice industry can be utilized.



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)

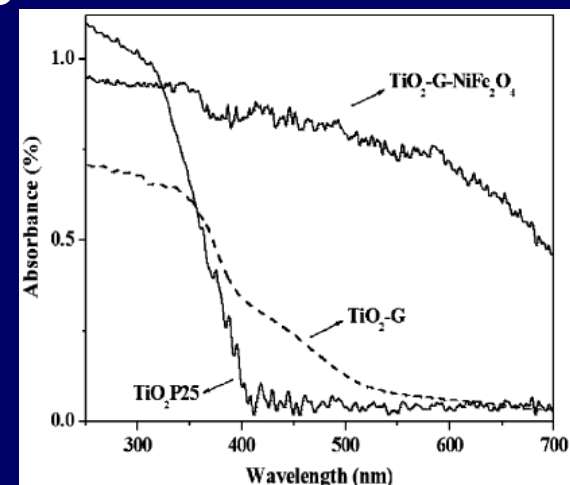
J. Virkutyte, R. S. Varma, *RSC Advances*, **2**, 1533 (2012); **2**, 2399 (2012)

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

Microcystin-LR removal using Magnetically separable N-doped TiO₂

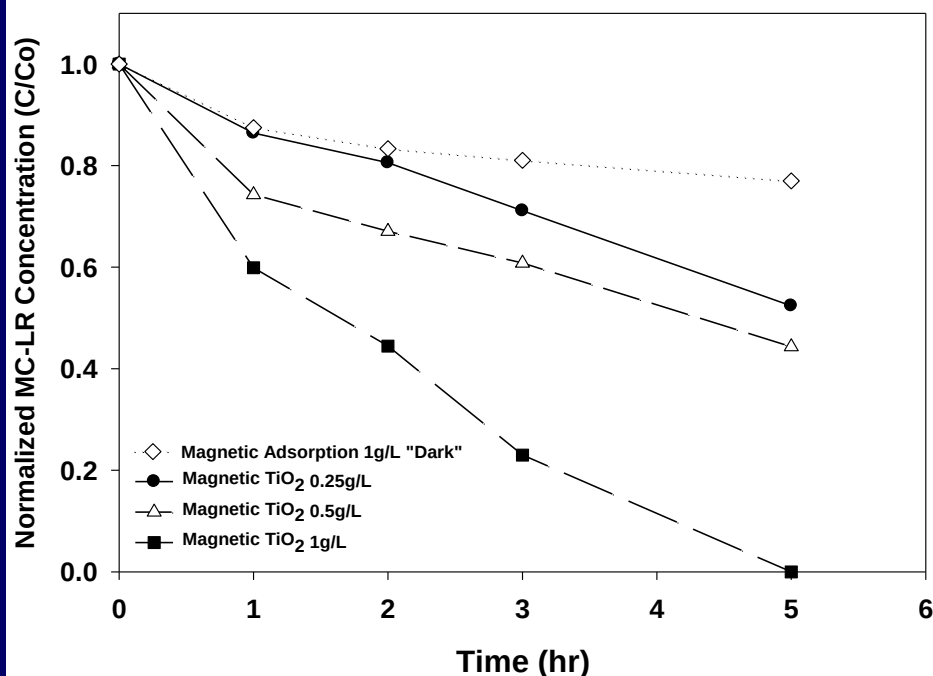
** In collaboration with Dr. Dionysious D. Dionysiou and Dr. Miguel Pelaez, Environmental Engineering and Science Program, University of Cincinnati, OH, USA*

- Microcystin-LR (MC-LR) is the most 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.
- TiO₂ 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 (TiO₂-G-NiFe₂O₄) and non-magnetic (TiO₂-G) nitrogen-doped TiO₂ nanoparticles have been previously synthesized.

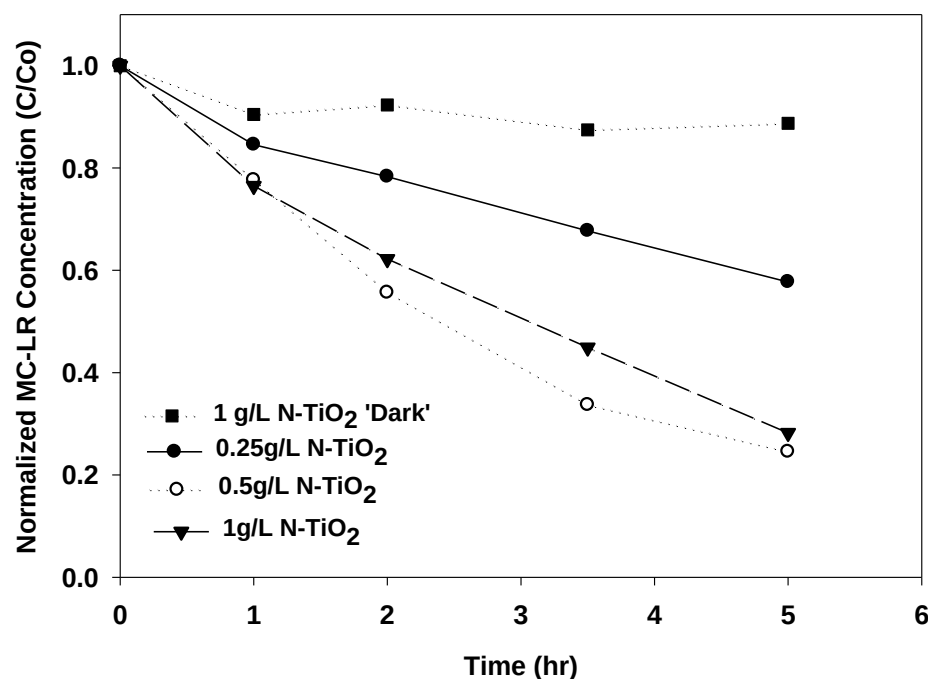


Balu, Baruwati, Serrano, Cot, Garcia-Martinez, Varma, Luque, Green Chemistry, 13, 2750-2758 (2013)

Magnetic $N\text{-TiO}_2$



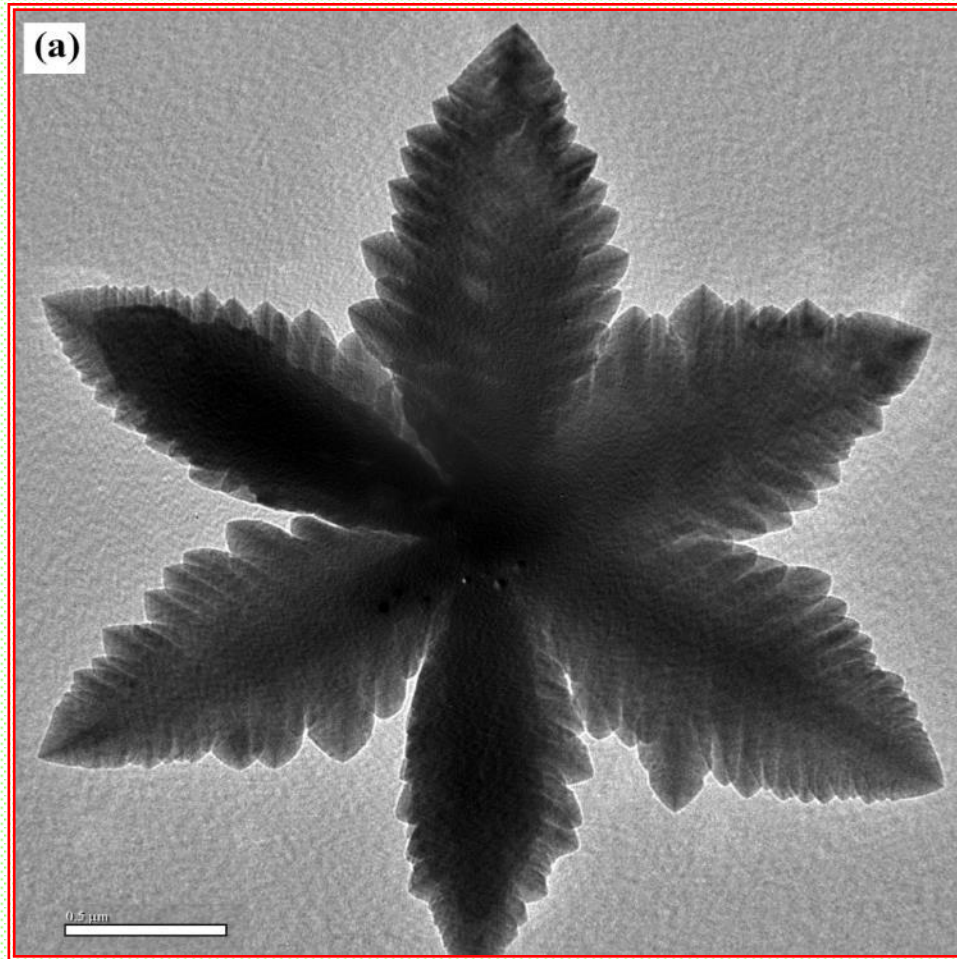
Non-magnetic $N\text{-TiO}_2$



Conditions: Visible light ($\lambda > 420$ nm). Initial MC-LR concentration: $450 \mu\text{g/L}$; pH solution 5.7.

- Non-magnetic and magnetic $N\text{-TiO}_2$ have proven highly active and efficient in the removal of MC-LR toxin from aqueous solutions at the conditions tested.
- In particular, magnetic $N\text{-TiO}_2$ exhibited a remarkable photodegradation activity, with complete removal of MC-LR after 5 h of irradiation.

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

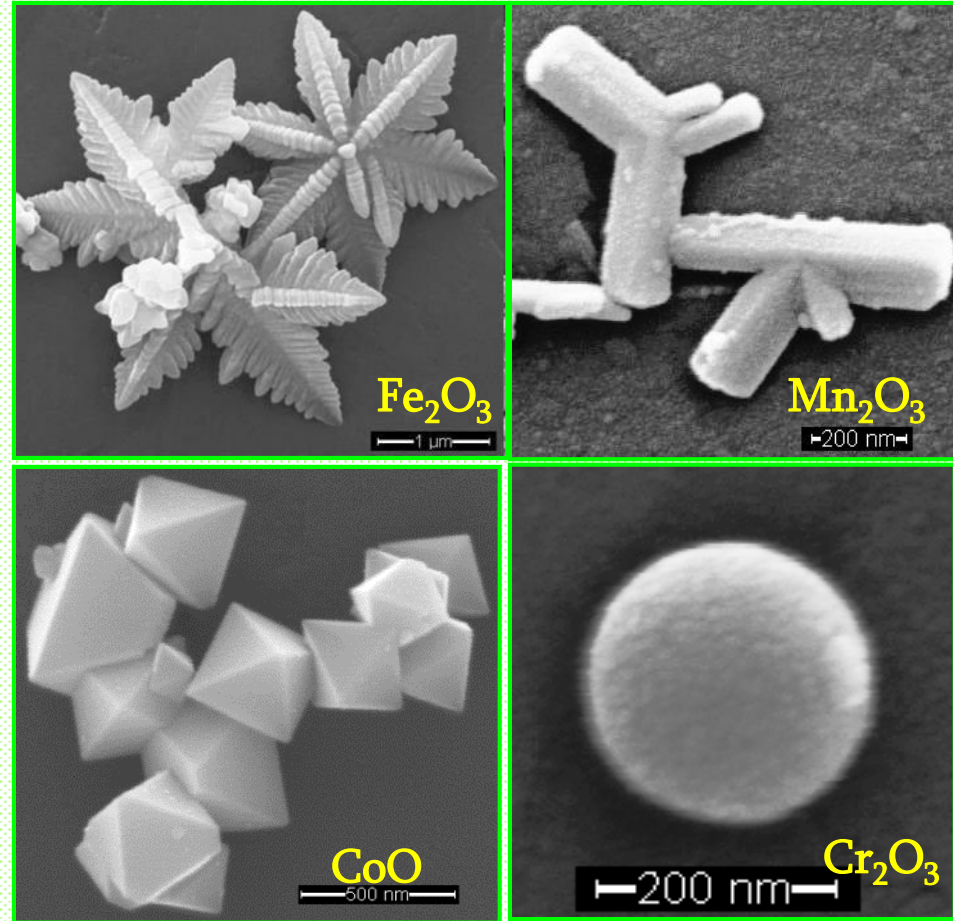
3D Nano-Metal Oxides

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.

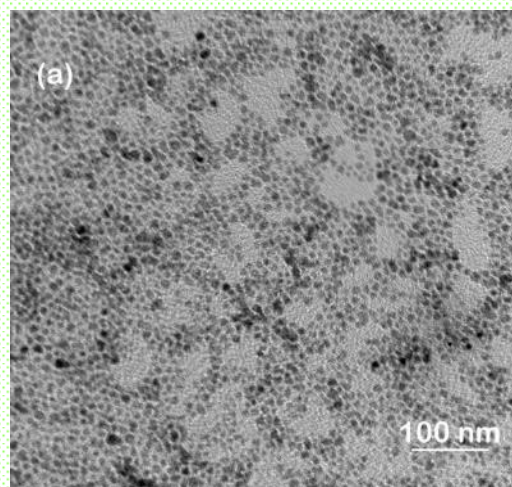


Polshettiwar, Baruwati & Varma: ACS Nano, 3, 728 (2009)

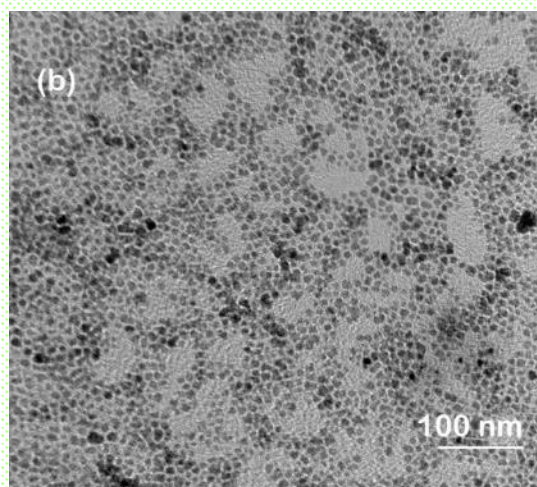
Among the top 5 Most-Accessed Articles in 12 months

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

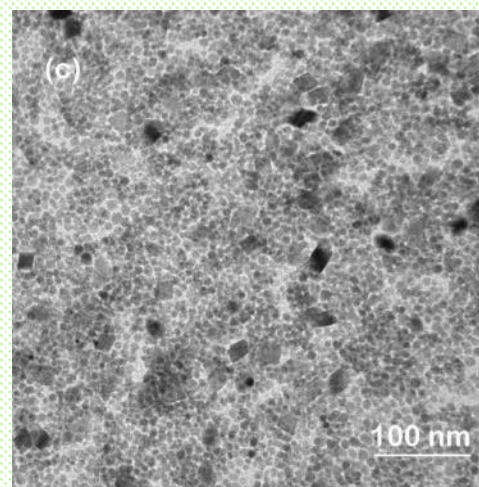
Monodispersed $M\text{Fe}_2\text{O}_4$ ($M=\text{Fe}$, Mn , Co , Ni) nanoparticles have been synthesized via a water organic interface under both hydrothermal and MW conditions starting with readily available and inexpensive metal nitrate and halide precursors. The single phase particles are obtained at a temperature as low as 150 °C under MW conditions. The as-synthesized particles are dispersible in nonpolar organic solvents.



NiFe_2O_4



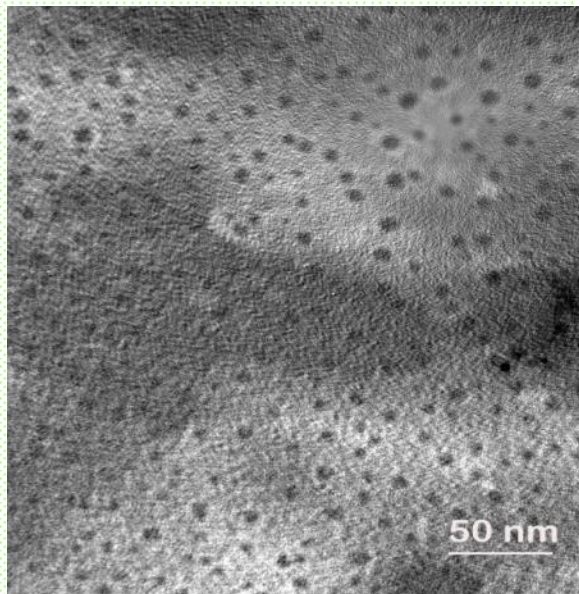
CoFe_2O_4



$\gamma\text{-Fe}_2\text{O}_3$

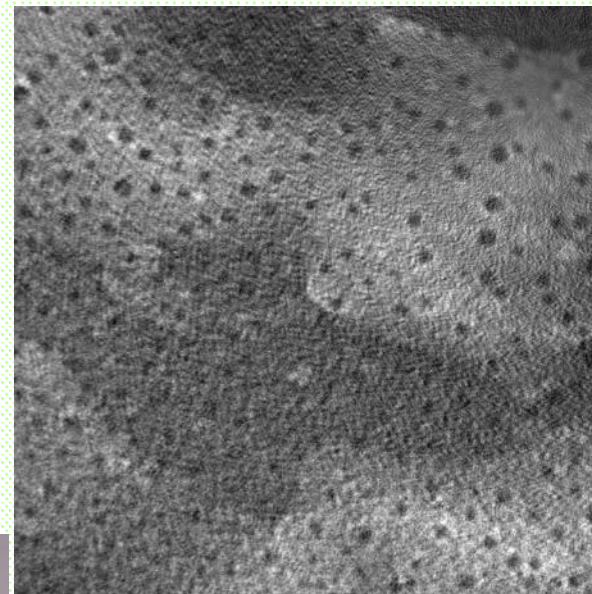
Baruwati, Nadagouda & Varma: *J. Phys. Chem. C*, 112, 18399 (2008)

Surface functionalization renders the particles dispersible in water



NiFe_2O_4

TEM of the particles dispersed in water

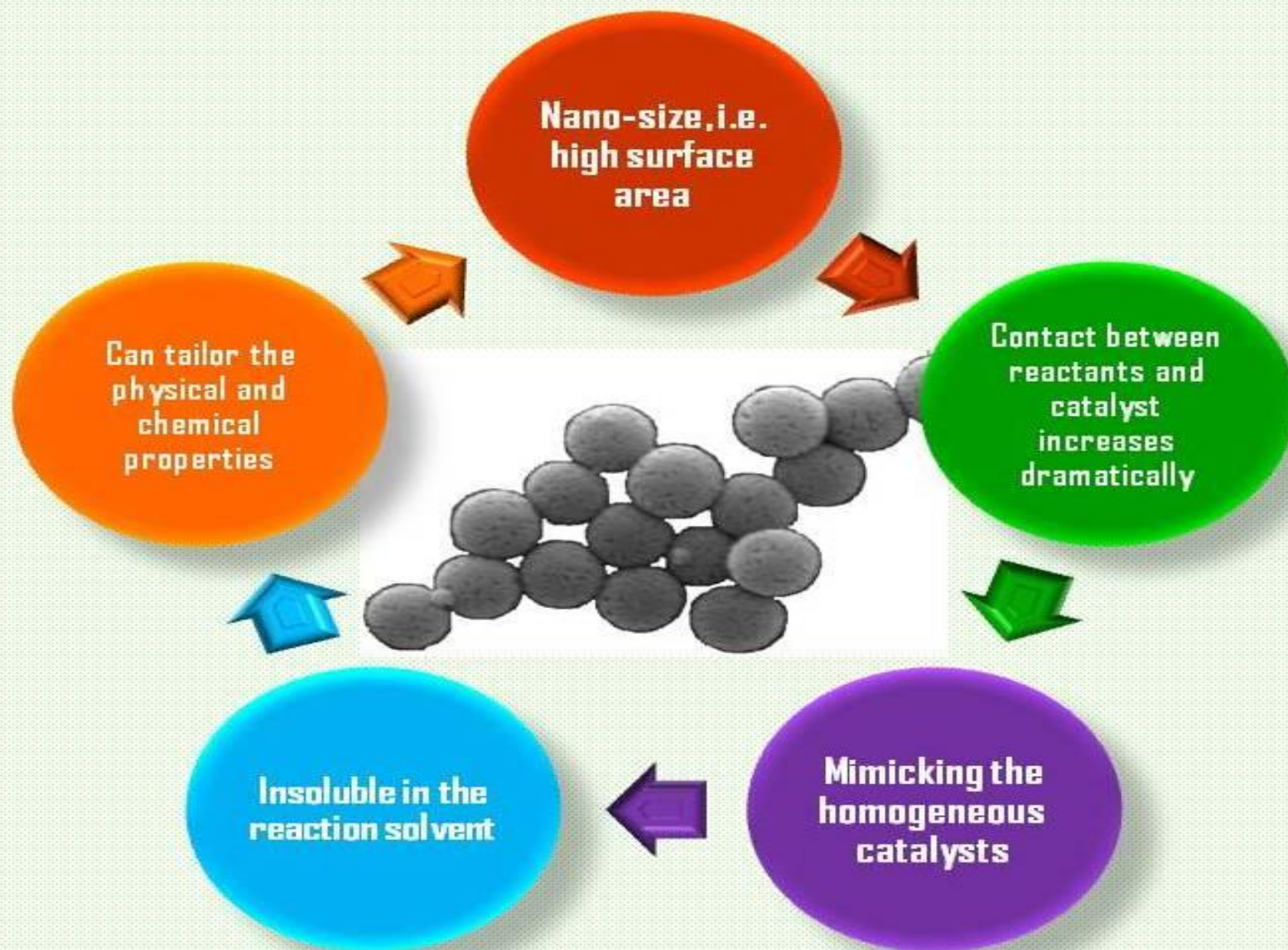


CoFe_2O_4



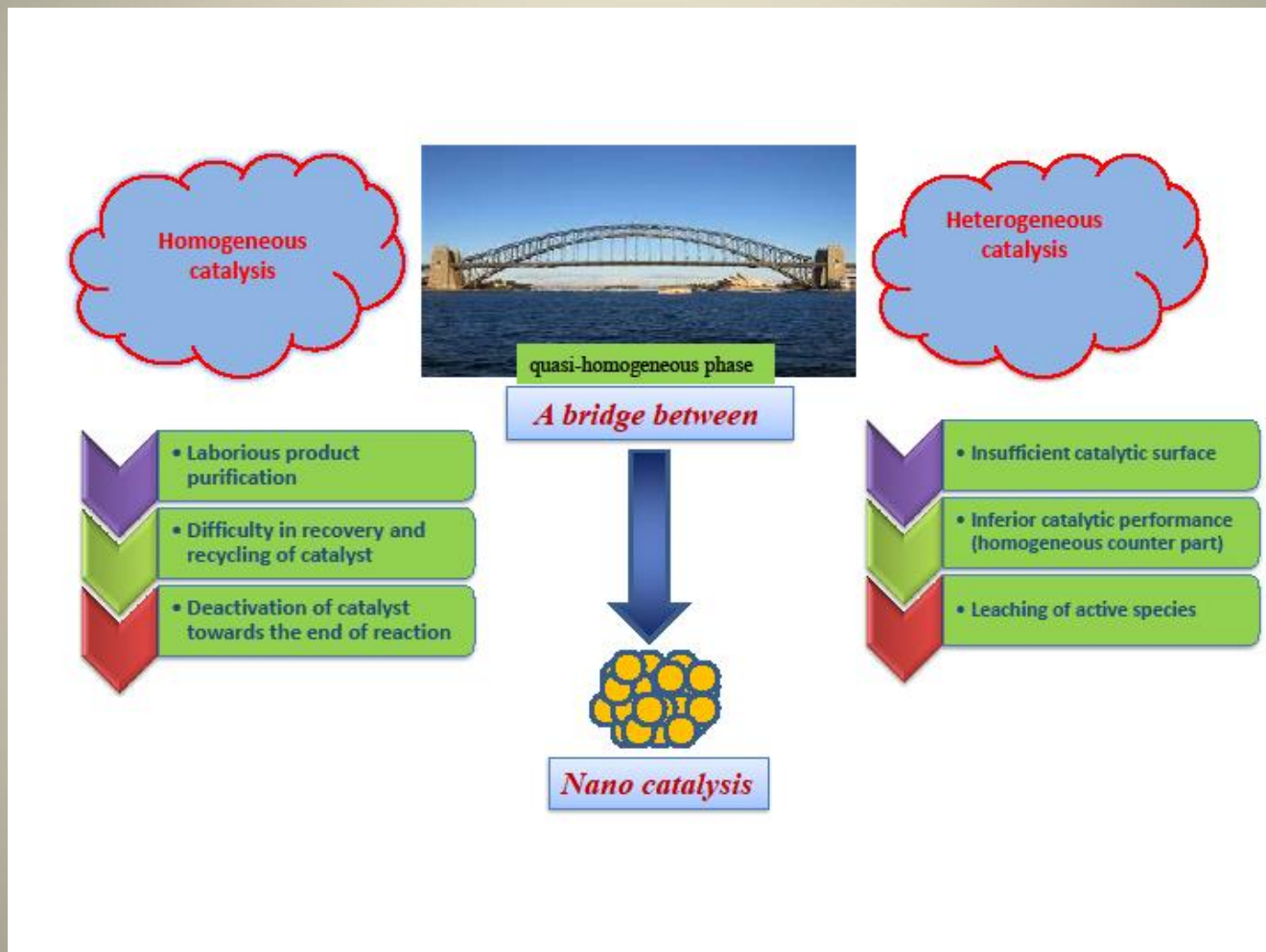
Photographic image of the particles in water and hexane

What is Nano-Catalysis?



Nano catalyst acts as a quasi-homogeneous phase

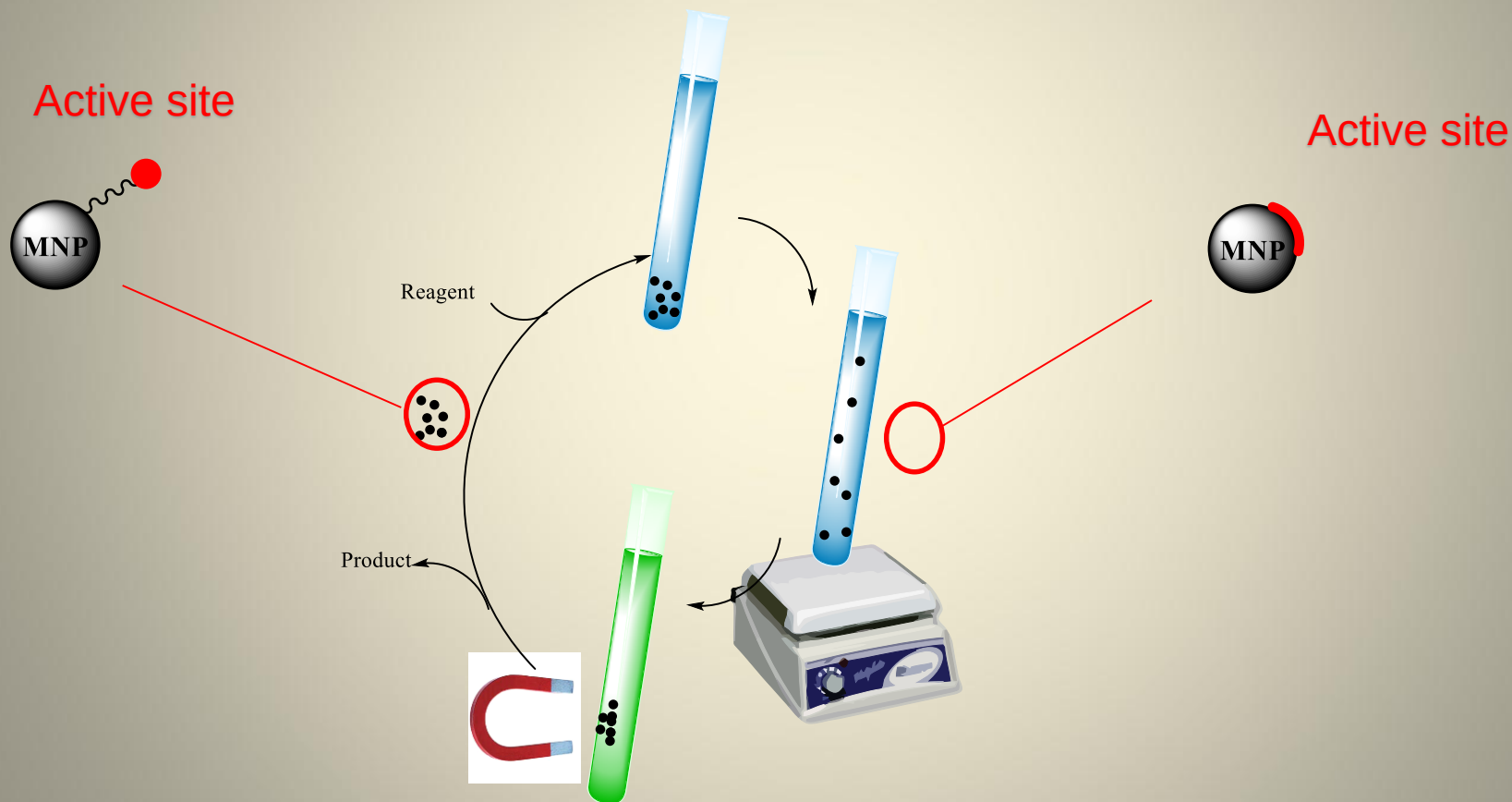
A bridge between homogeneous and heterogeneous



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

Magnetic Nanoparticles in Catalysis

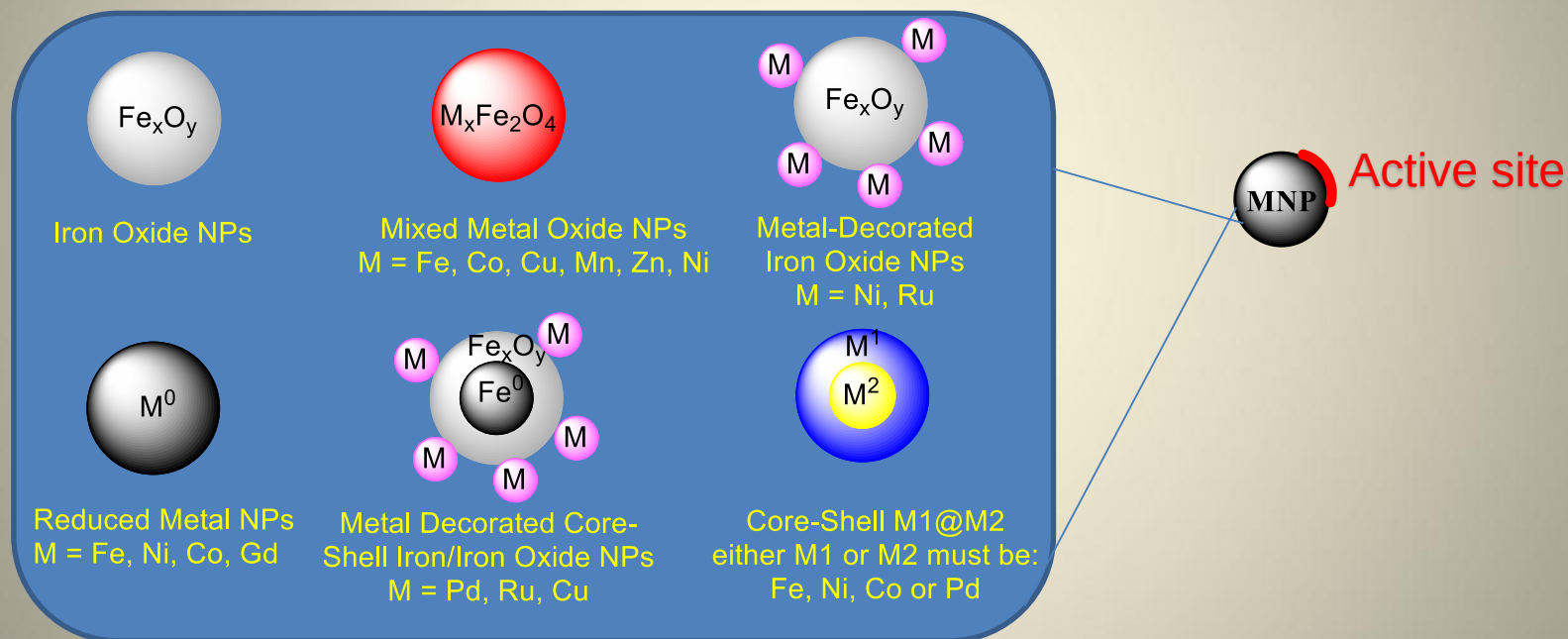
- As simple magnetic anchors
- Catalytic bare magnetic nanoparticles



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

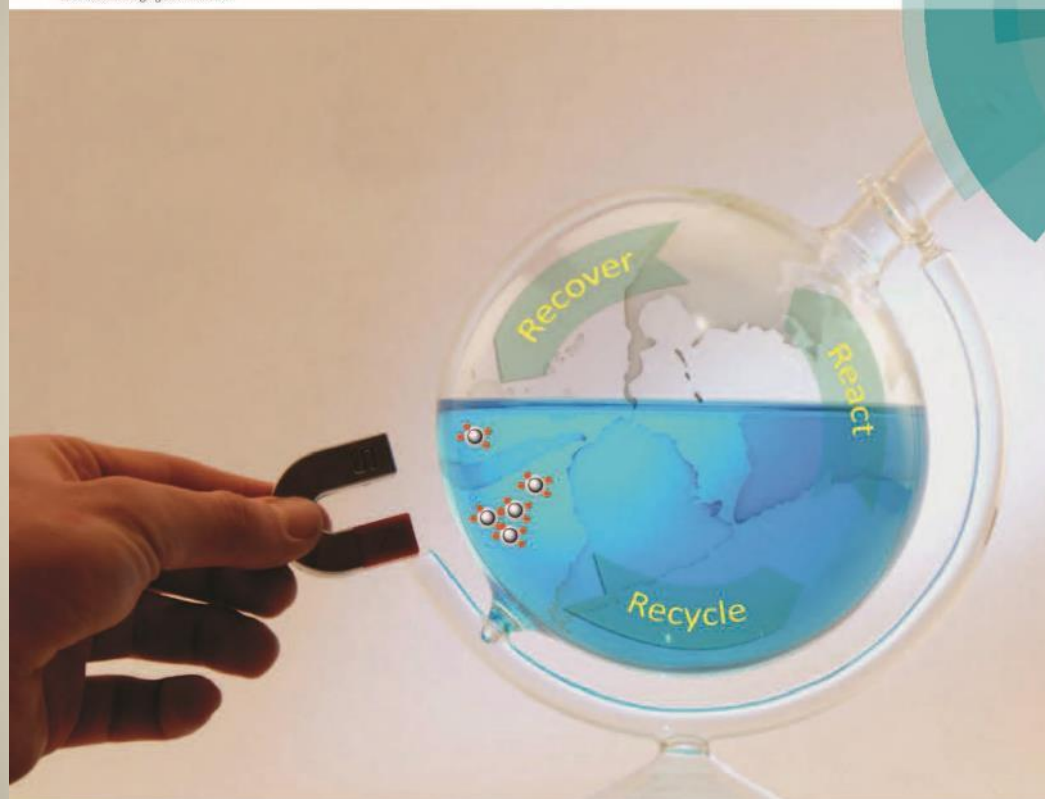
Magnetic Nanoparticles in Catalysis

- Catalytic bare magnetic nanoparticles



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TUTORIAL REVIEW
Audrey Moores et al.
Bare magnetic nanoparticles: sustainable synthesis and applications in catalytic organic transformations

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) *Green Chem.*, 16, p2027, p3494, p4137, p4333, p4493 (2014)

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)

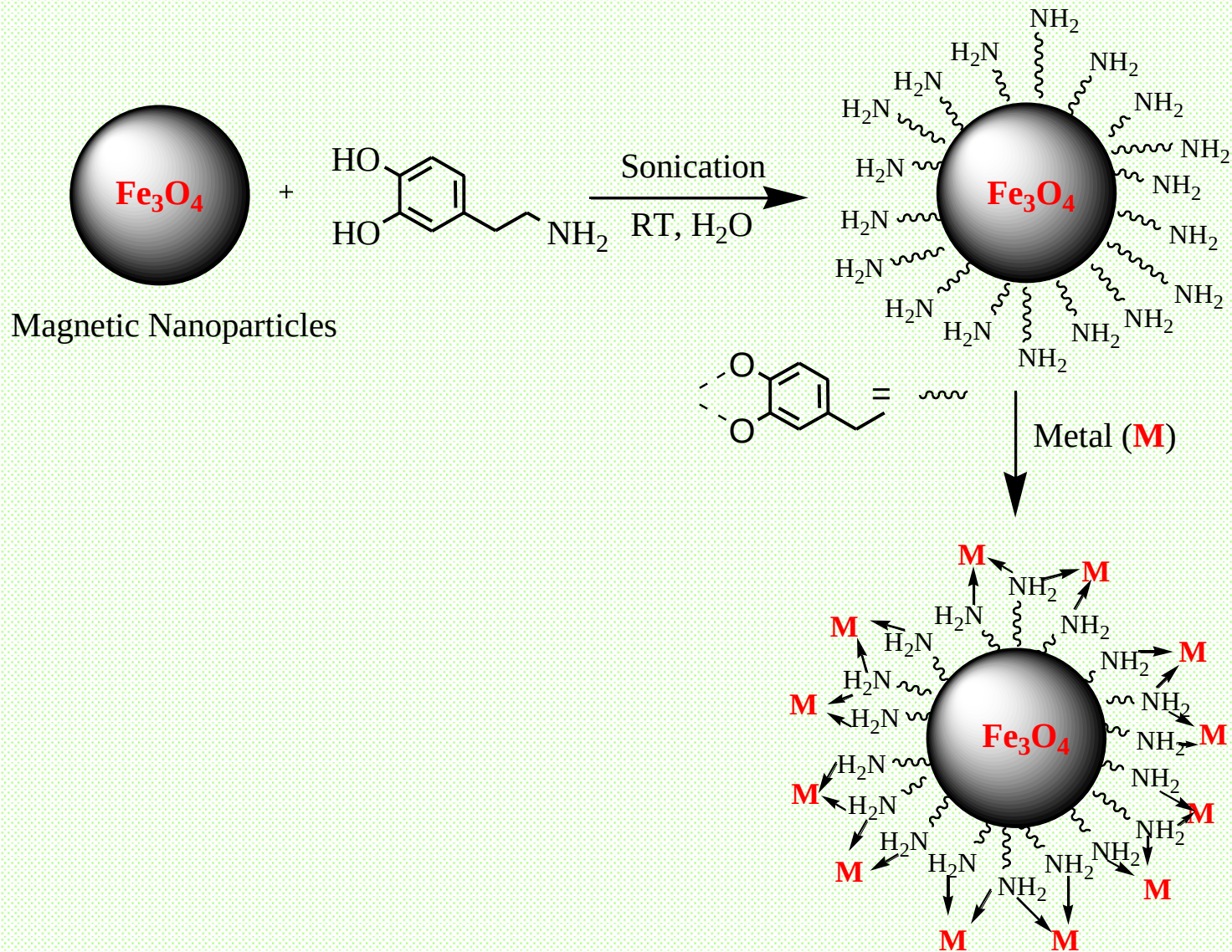
Chem. Soc. Reviews, 42, p3317 (2013)

RSC Advances, 3, p1050 (2013); 4, p6568 (2014)

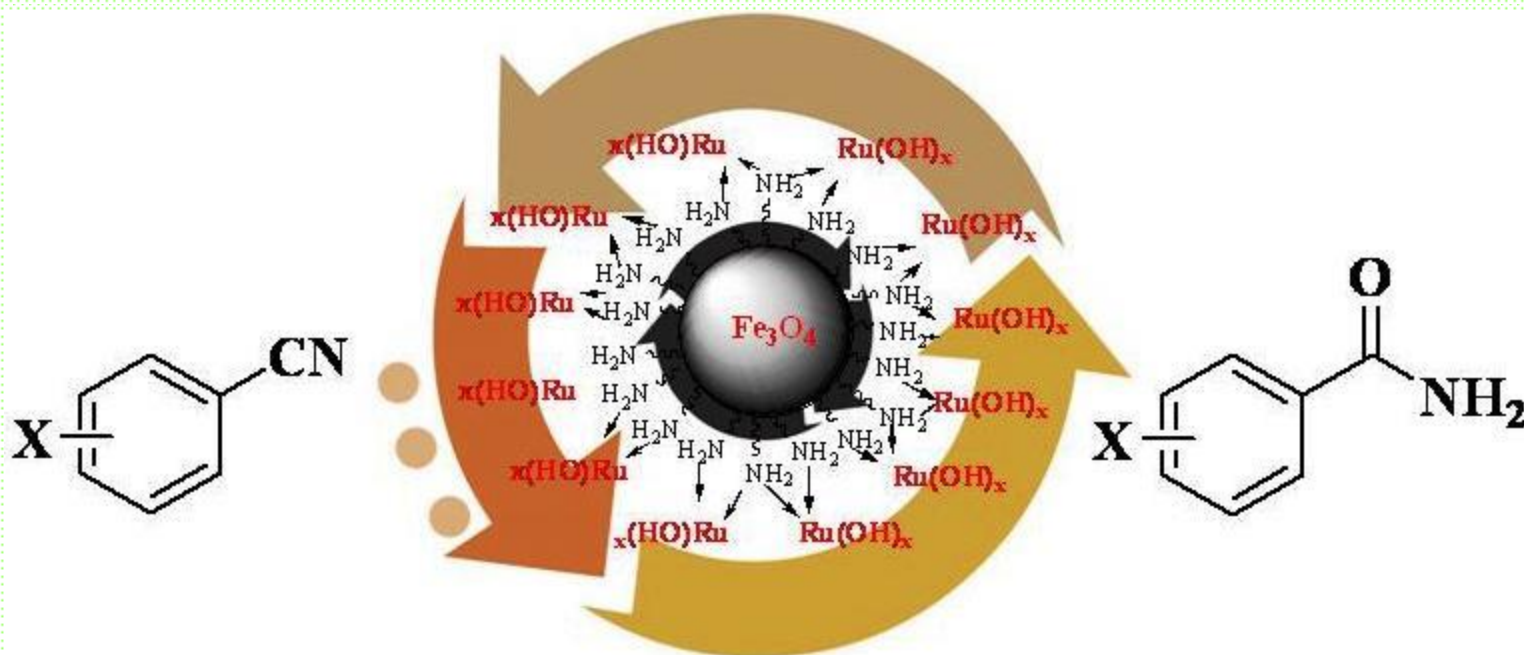
ACS Sust. Green Eng., 1, 805 (2013); 2, p1699; 2, p2155 (2014)

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

Synthesis of Nano-Catalysts

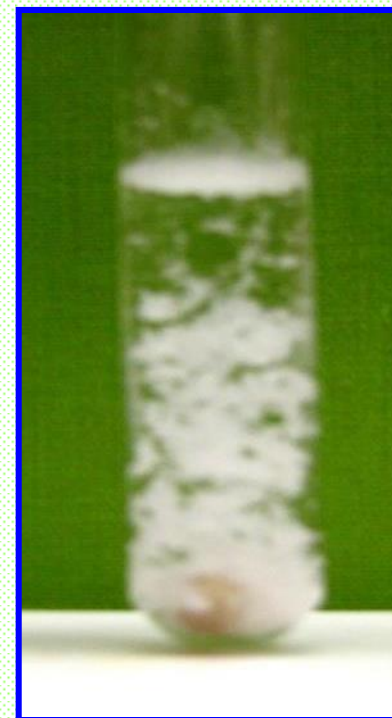
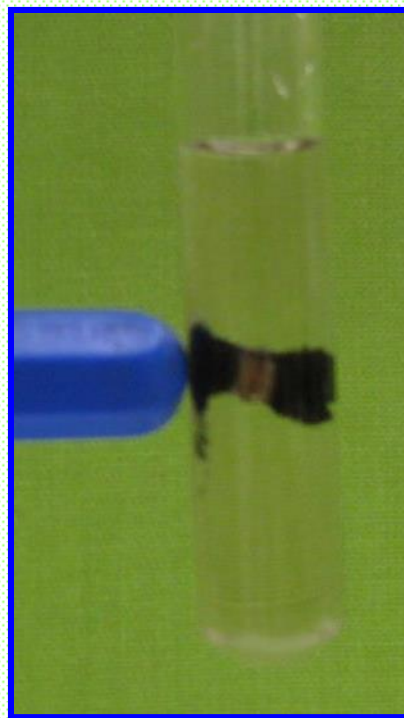
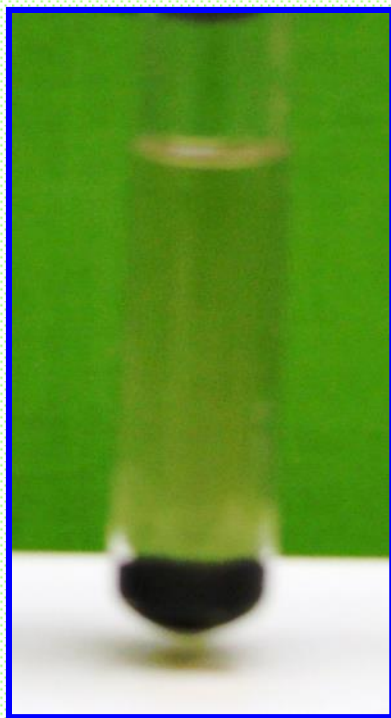


Magnetically Recoverable Ruthenium Hydroxide Nano-Catalyst



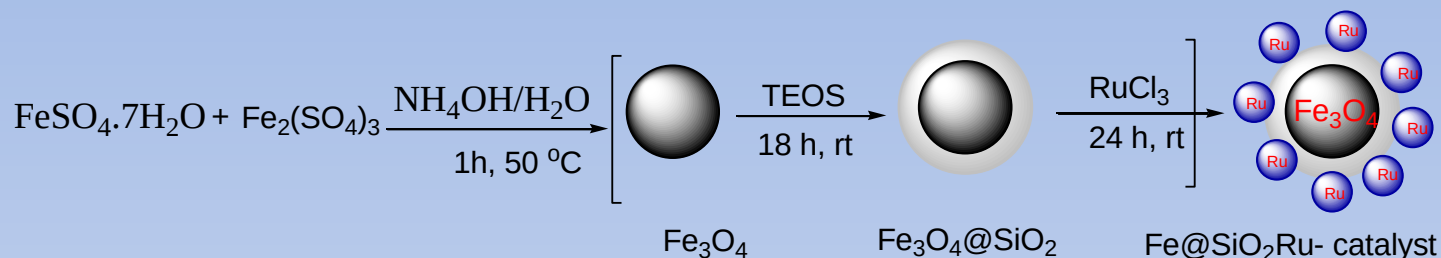
Polshettiwar & Varma: *Chem. Eur. J.* 15, 1582 (2009)

No Organic Solvent- Even in the Work-Up Step



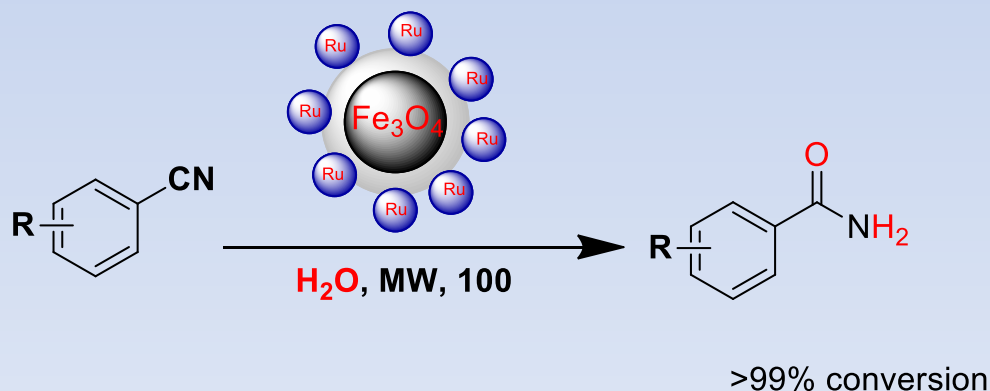
Reaction in Pure Aqueous Medium

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



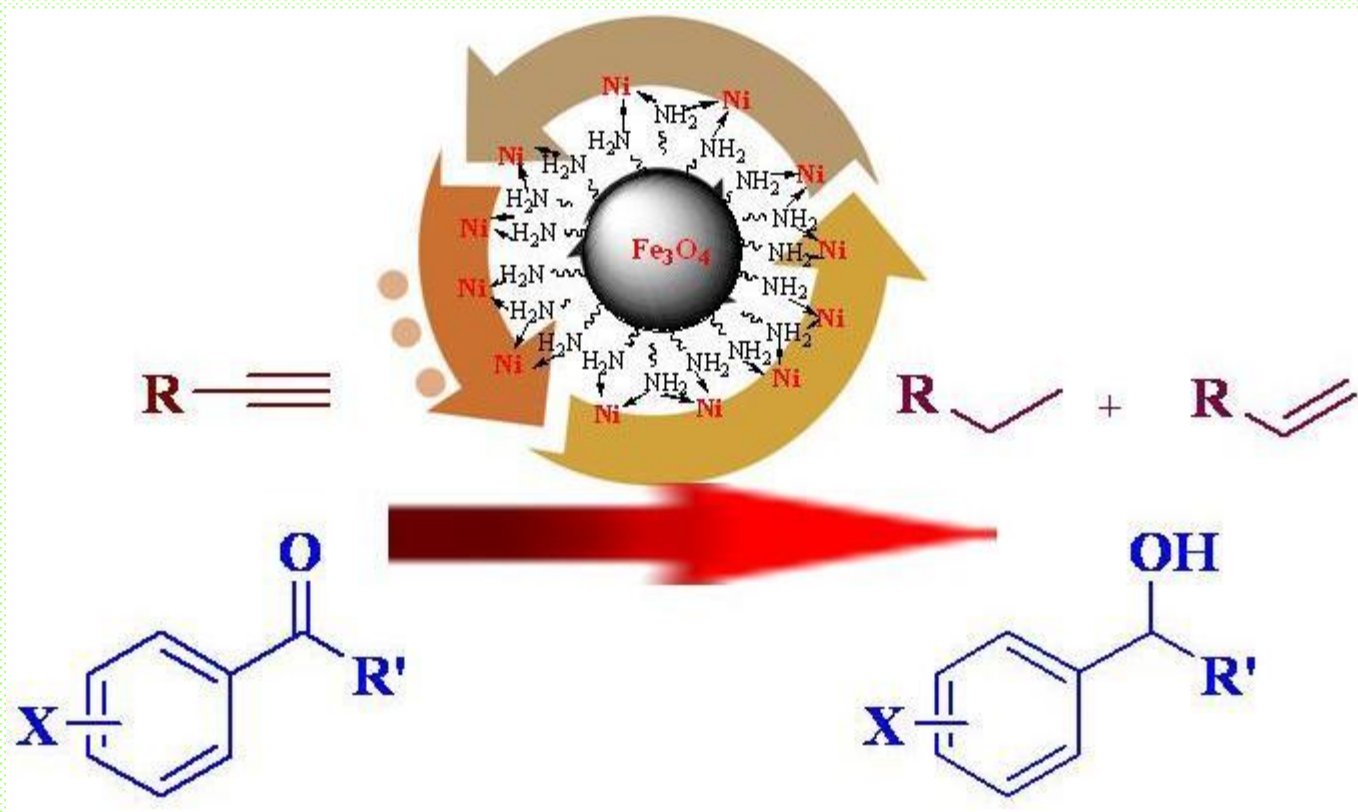
Scheme 1 One pot synthesis of nano- $\text{Fe@SiO}_2\text{Ru}$ catalyst

Aqueous Hydration of Nitriles Using Magnetic Silica Supported Ruthenium Hydroxide Nanoparticles



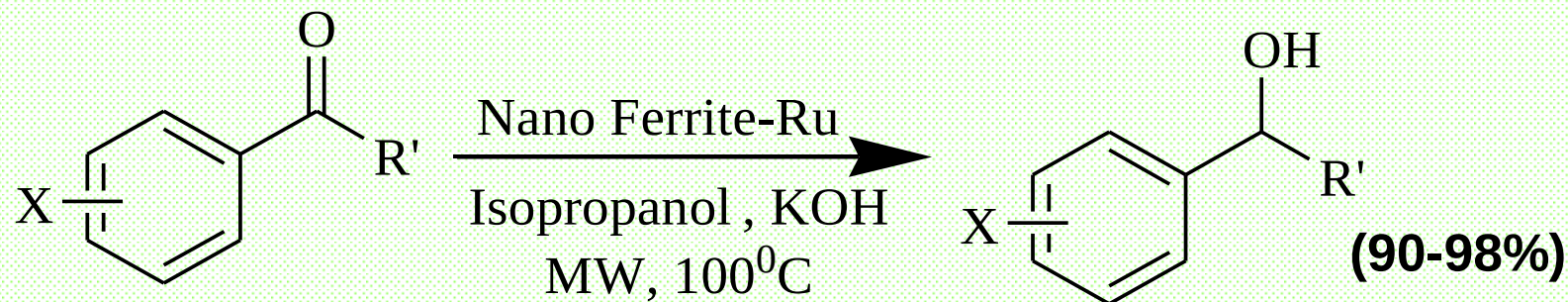
Baig, Varma: *Chem Commun.*, 48, 6220 (2012)

Magnetically Recoverable Ni Nano-Catalyst for Reduction



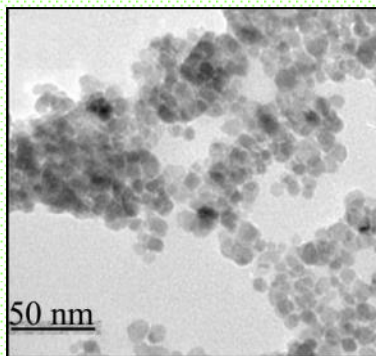
Polshettiwar, Baruwati & Varma: *Green Chem.*, 11, 127 (2009)

Transfer Hydrogenation of Carbonyl Compounds

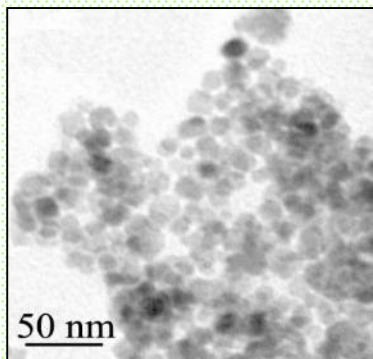


R' - Me, Ph, H

X - Cl, Br, NO₂, NH₂



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



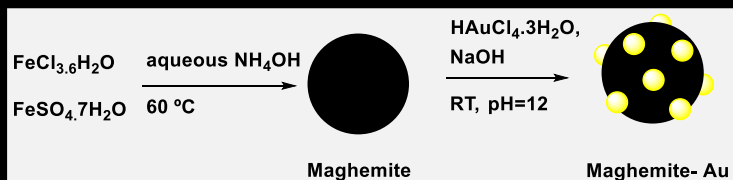
Gawande, Bonifácio, Varma, Branco, Nogueira, Bundaleski, Ghumman, Teodoro: *Green Chem.*, 15, 1226 (2013)

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

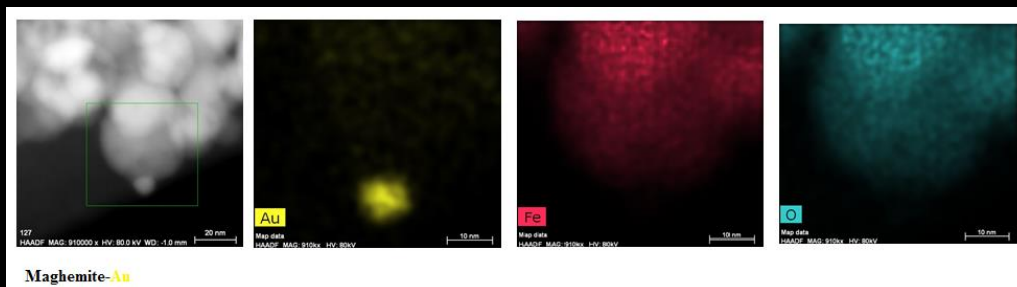


Shelke, Bankar, Mhaske, Kadam, Murade, Bhorkade, Rathi, Bundaleski, Teodoro, Varma, Zboril, Gawande: *ACS Sustain. Chem. Eng.*, 2, 1699 (2014)

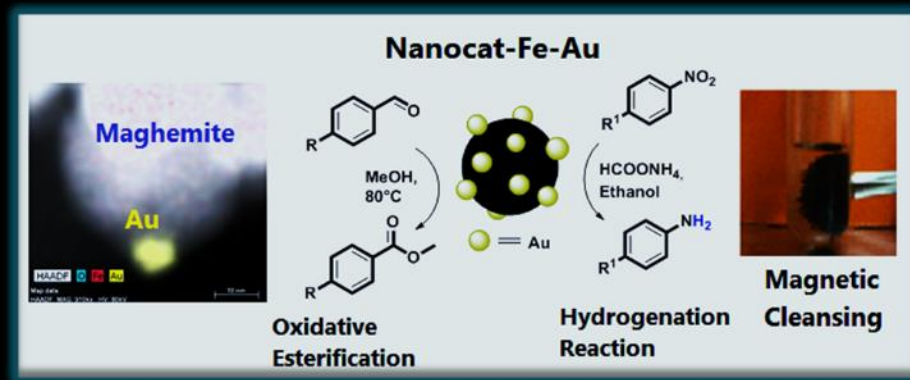
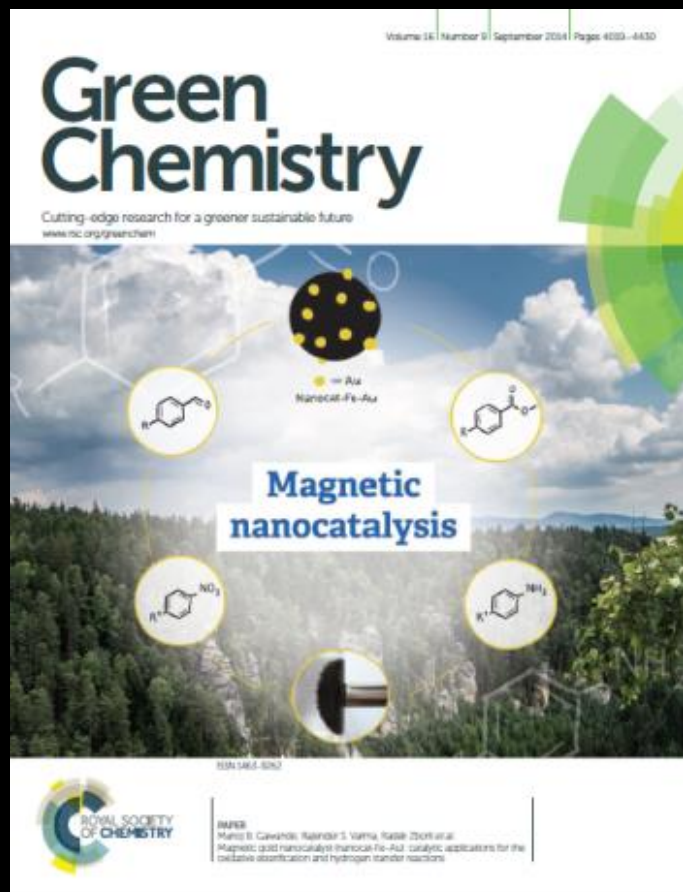
Maghemite-supported Gold ($\gamma\text{-Fe}_2\text{O}_3\text{-Au}$) Nanocatalyst Catalytic Applications in Organic Transformations



Synthesis of maghemite-Au



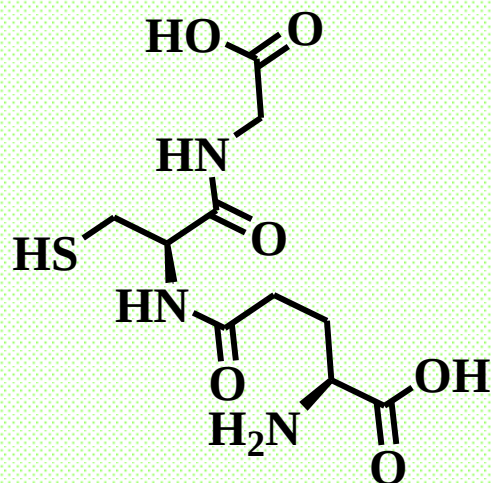
High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)



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

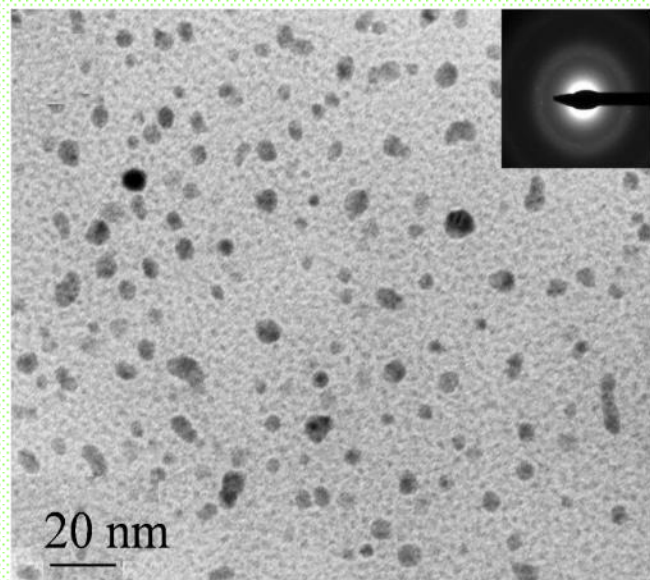
Baruwati, Polshettiwar, Varma: *Green Chem.*,11, 926 (2009)

Metal nanoparticles in less than a minute under MW conditions

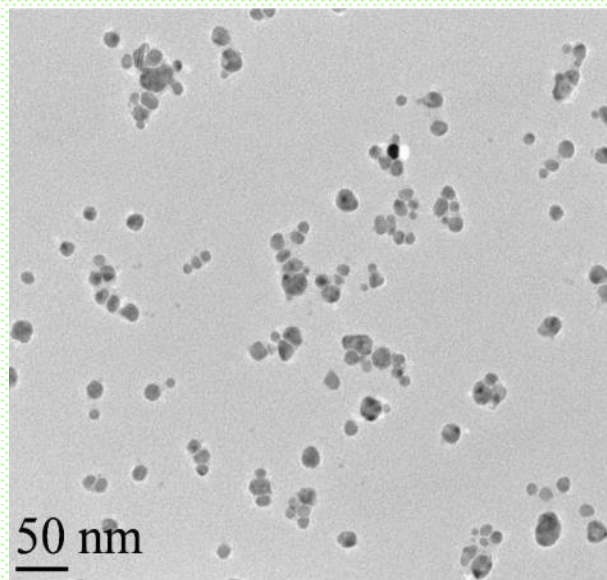
Optimized condition

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

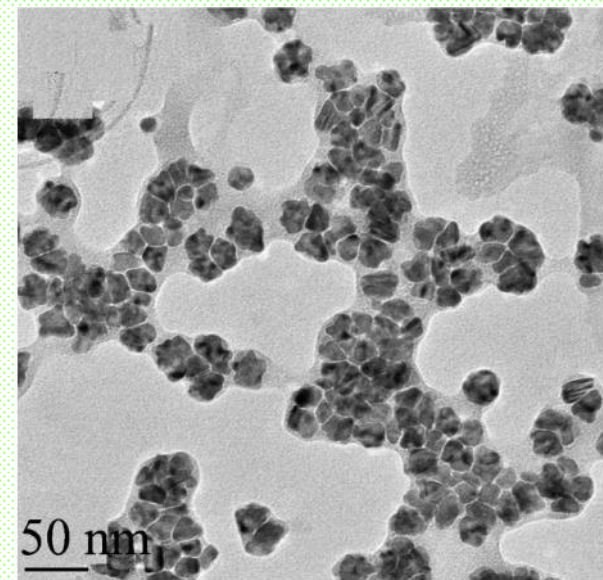
Silver Nanoparticles



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

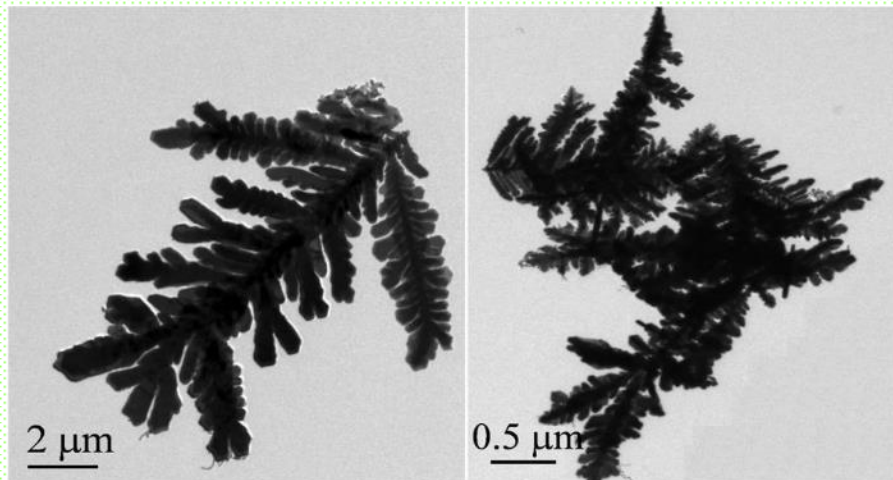


75 Watt, 60 seconds with mole ratio 1.0:0.15



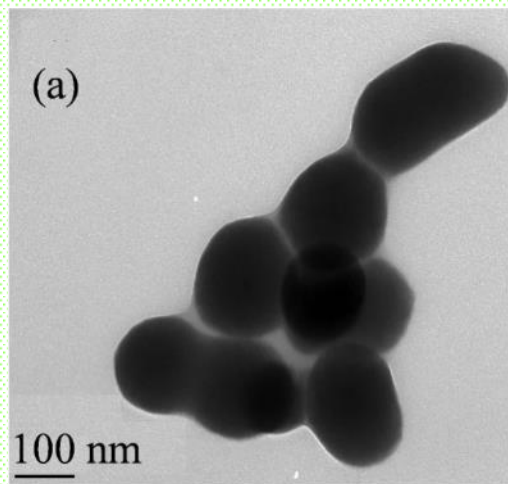
100 Watt, 60 seconds with mole ratio 1.0:0.15

- 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

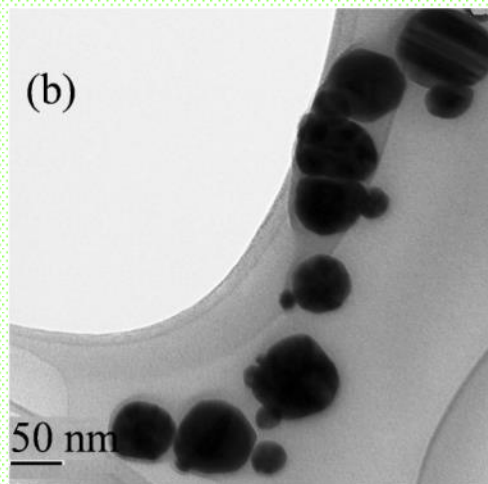


Silver trees: Dendritic nanostructures
Aus J. Chem., 62, 260 (2009)

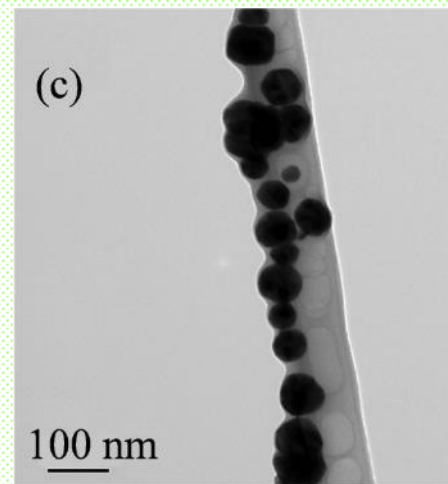
Gold, Platinum and Palladium Nanoparticles Varma et al., *Green Chem.* 11, 926 (2009)



Gold



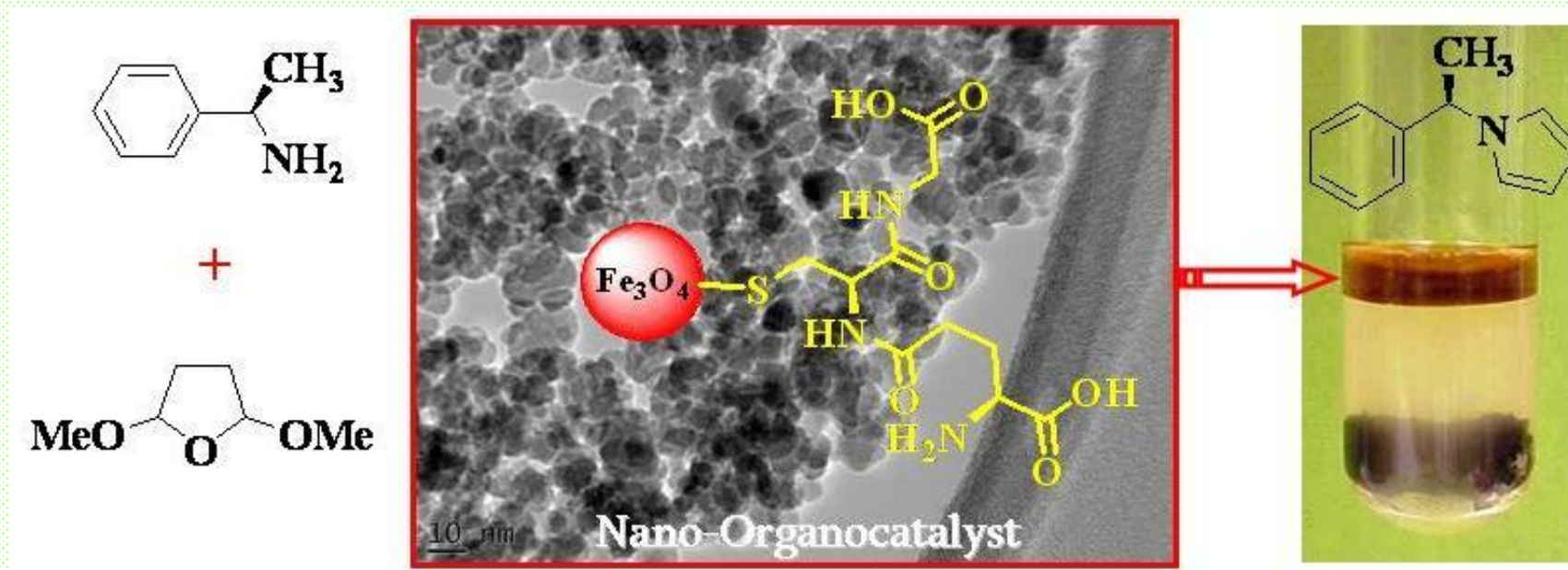
Platinum



Palladium

Nano-Organocatalyst

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



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

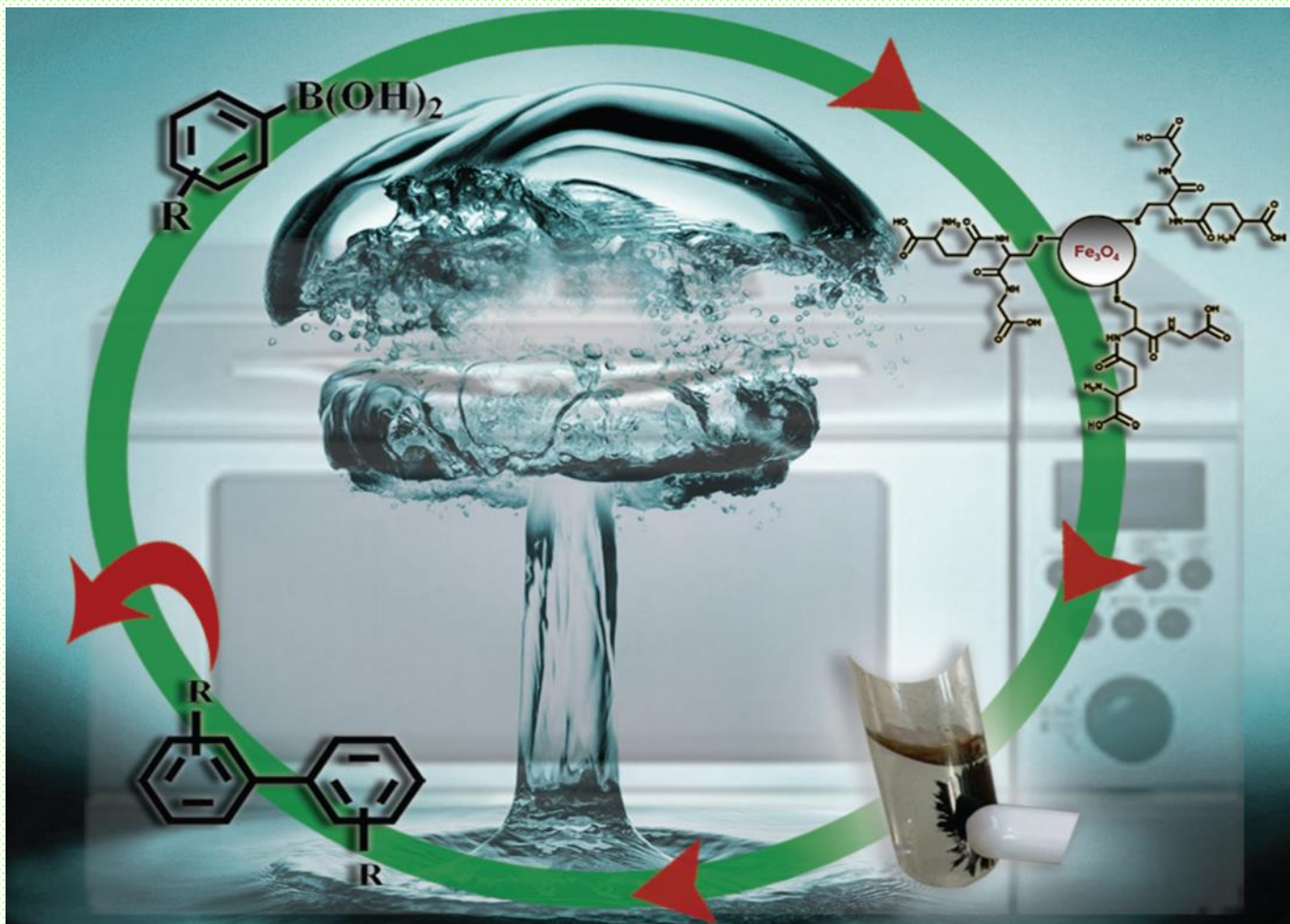
***Tetrahedron*, 66, 1091 (2010)**

Green Chemistry

Cover page

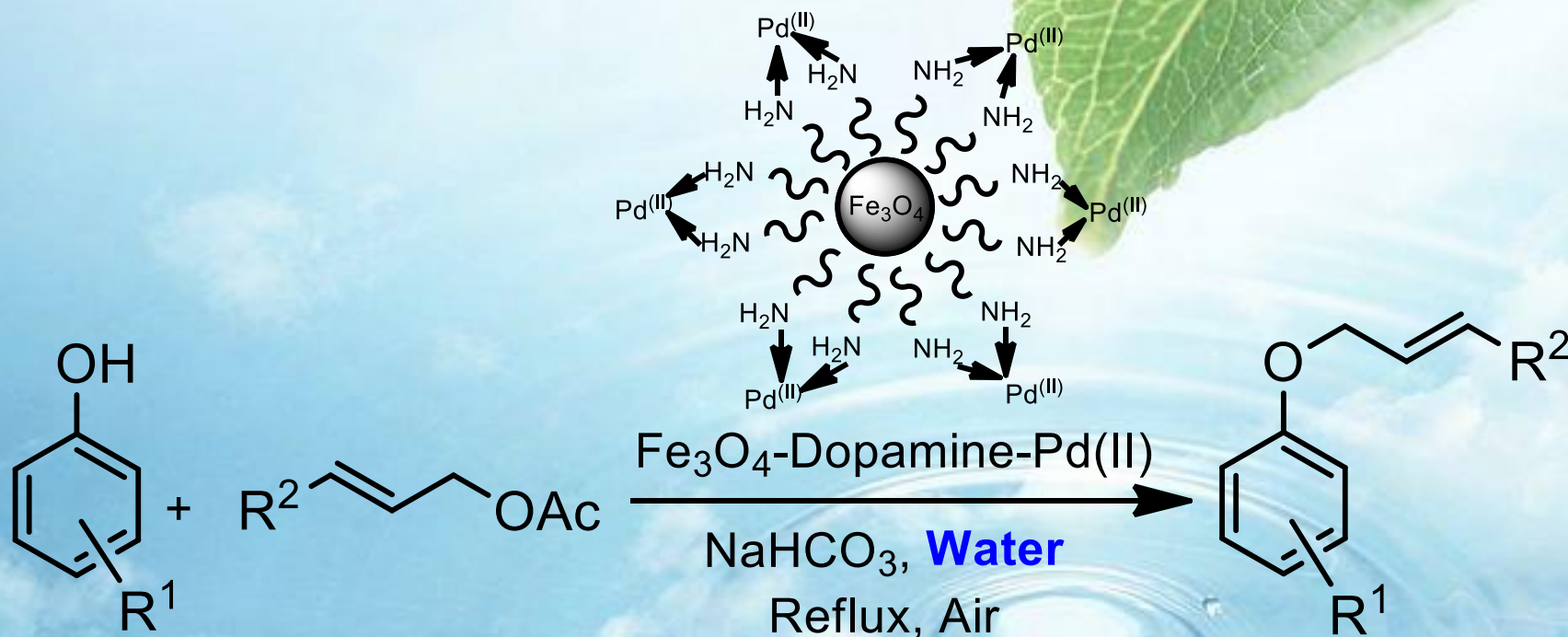
Volume 12 | Number 9 | Sept. 2010

Magnetically separable organocatalyst for homocoupling of arylboronic acids



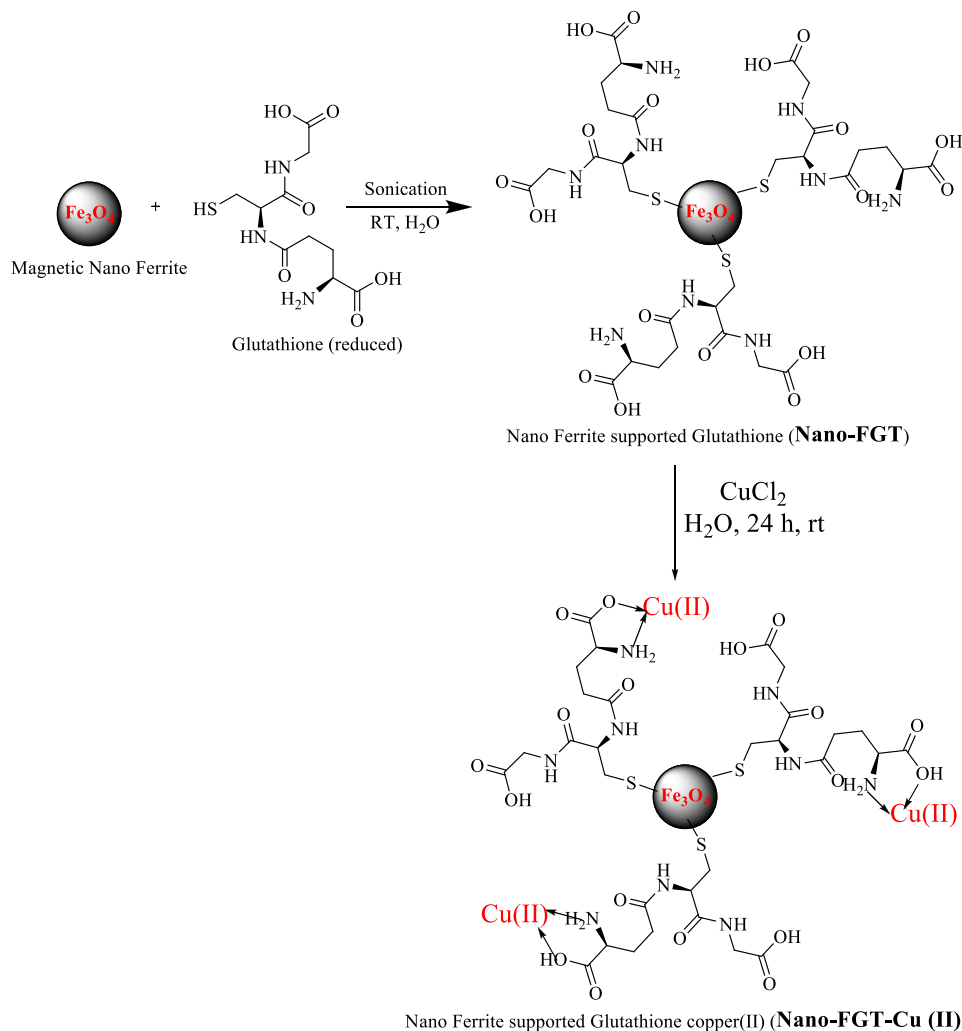
Luque, Baruwati, Varma: *Green Chem.*, 12, 1540 (2010)

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



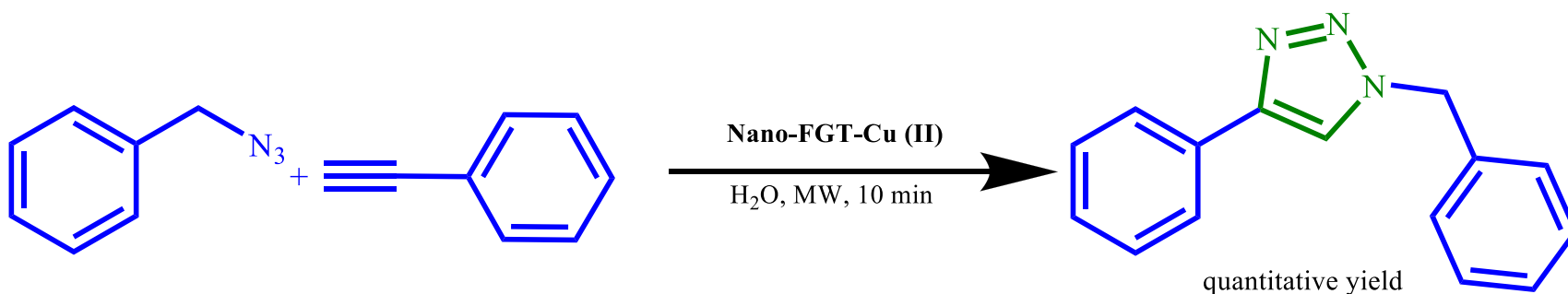
Saha, Leazer, Varma: *Green Chem.*, 14, 67-71 (2011)

Nano Ferrite supported-Glutathione copper(II) catalyst

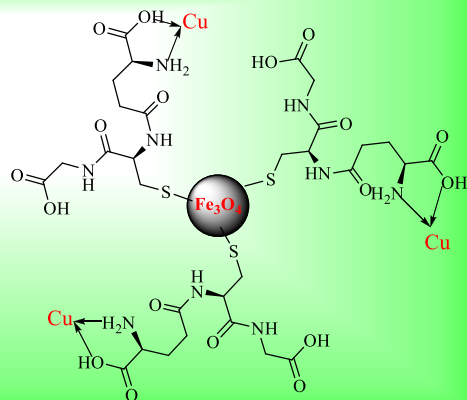


Baig, Varma: *Green Chem.*, 14, 625 (2012)

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

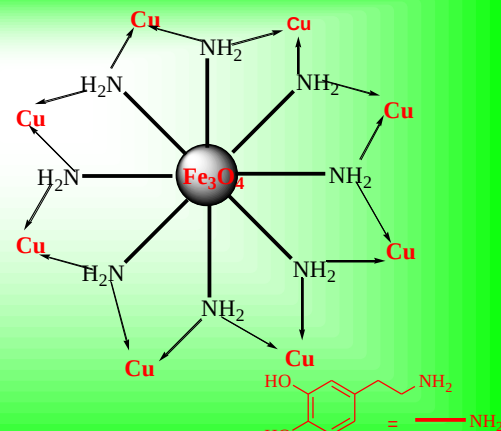


Baig, Varma: *Green Chem.*, 14, 625 (2012)

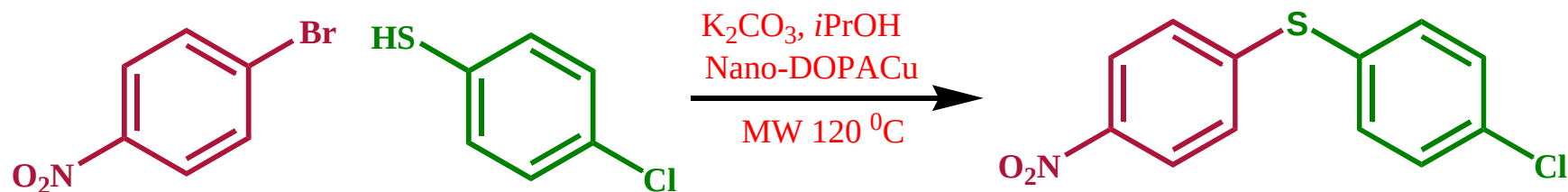


Nano Ferrite supported Glutathione copper **Nano-FGT-Cu** catalyst

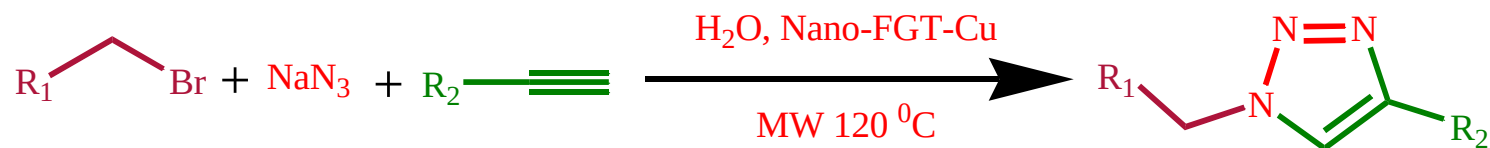
Ligands defines reactivity



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

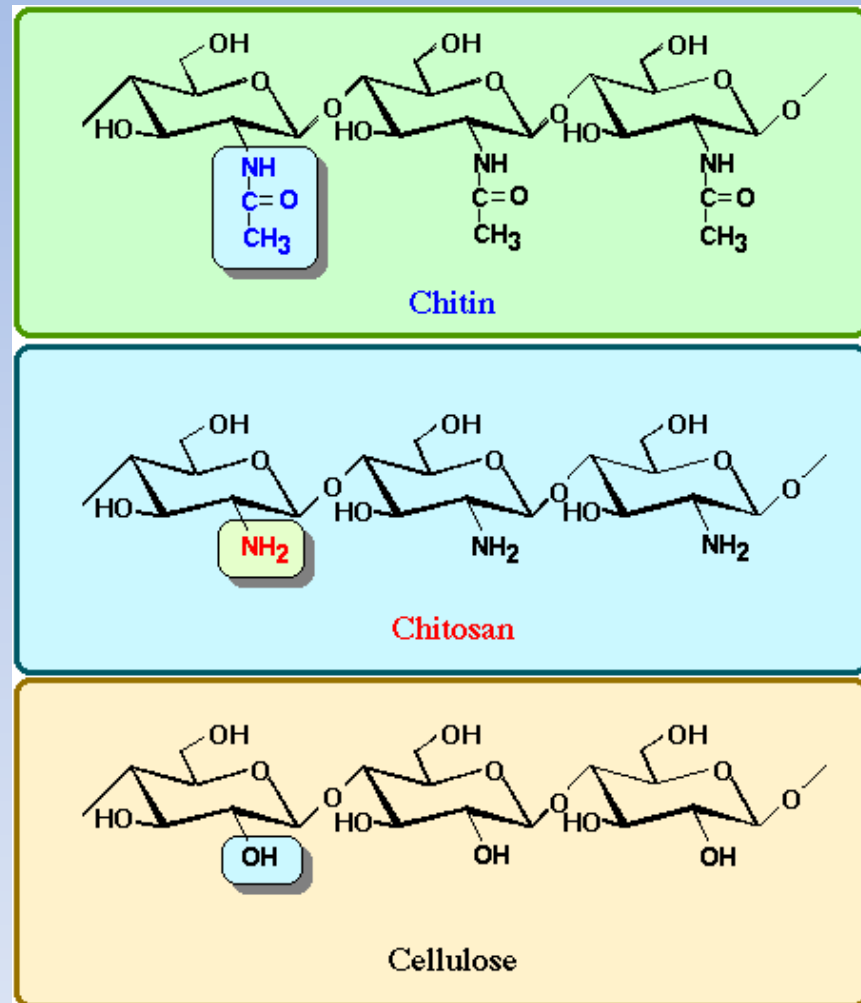
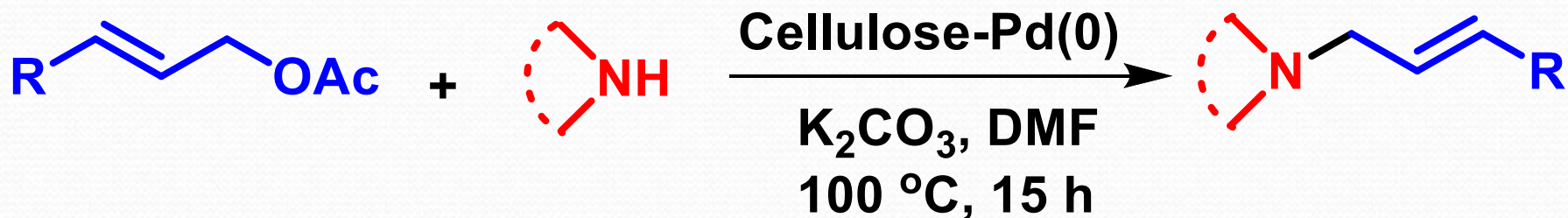


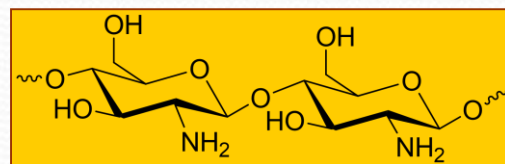
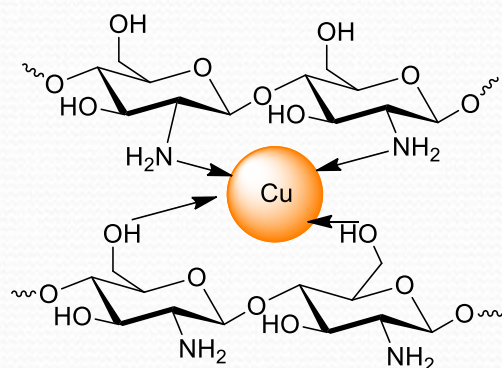
Fig. Structure of Chitin, Chitosan and Cellulose

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

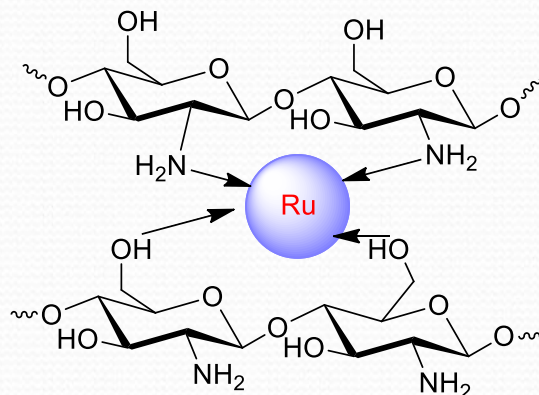
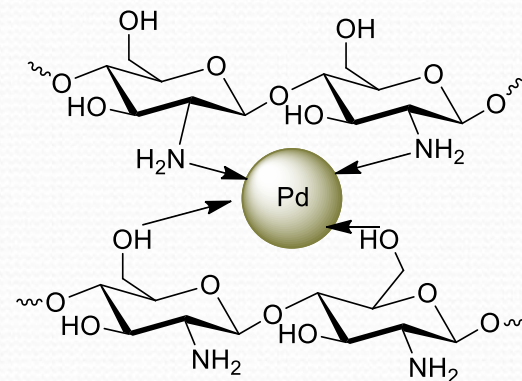


Reddy, Saha, Varma, Leazer: *Eur. J. Org. Chem.*, 6707 (2012)

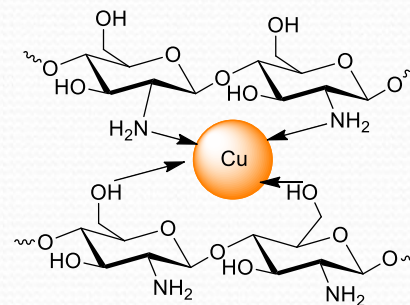
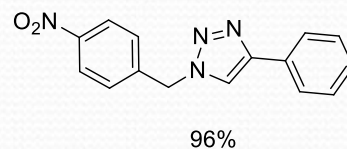
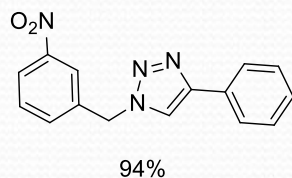
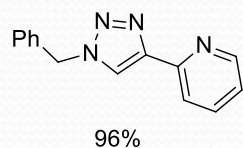
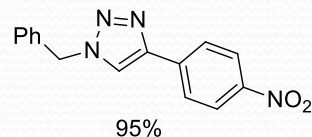
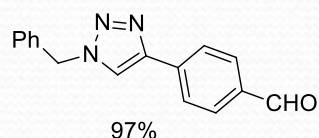
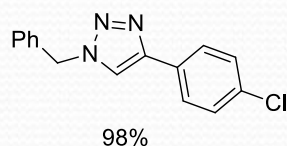
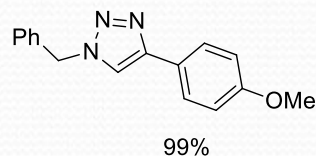
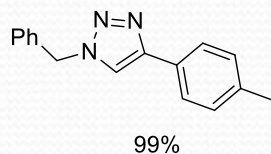
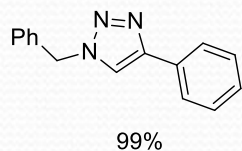
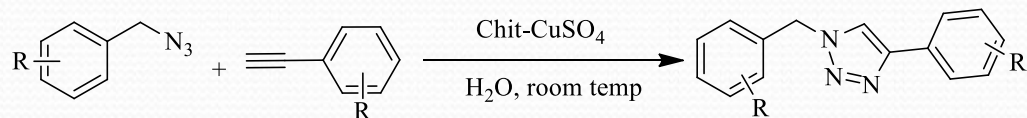
Synthesis of Chitosan-supported Catalysts



Chitosan polymer

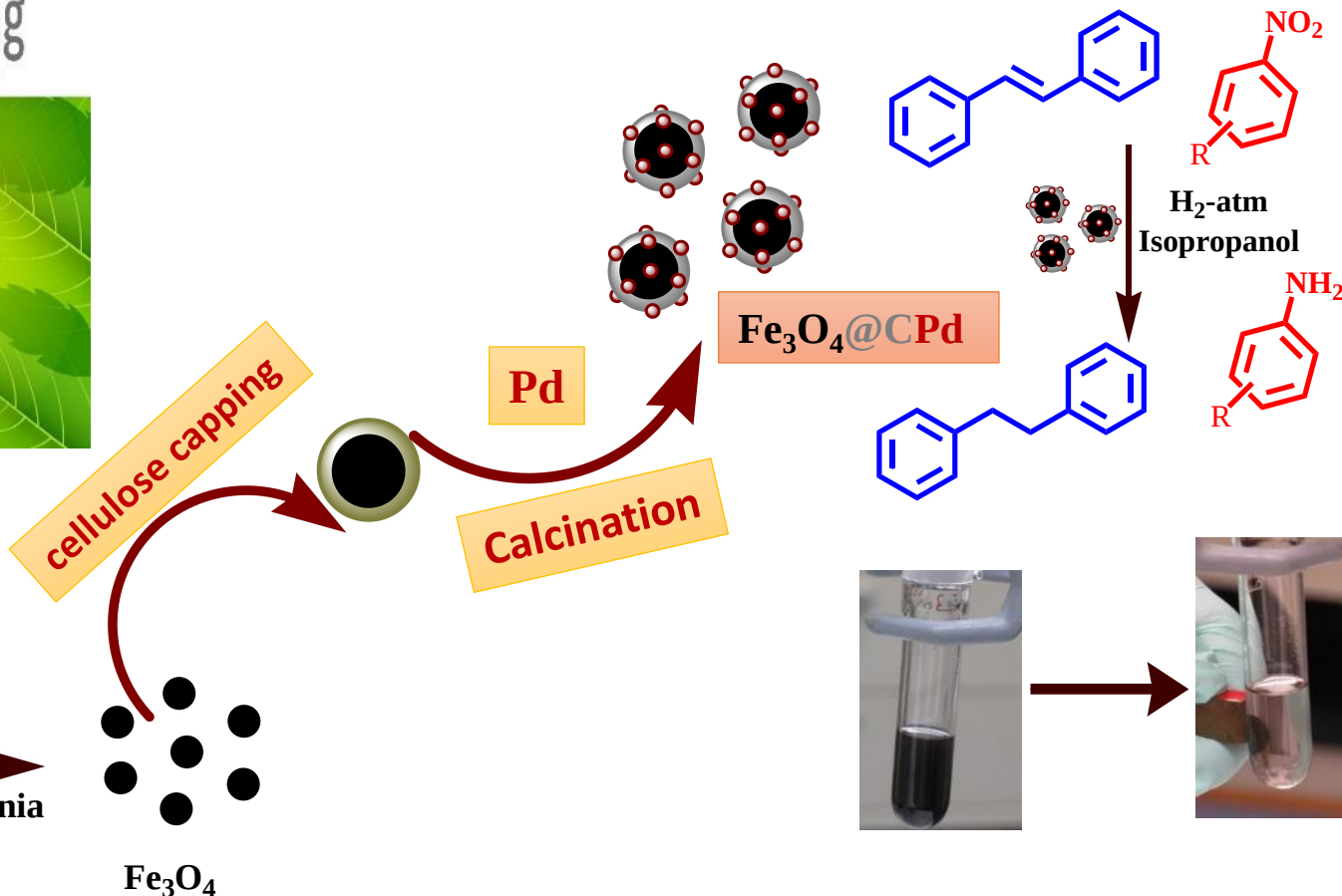
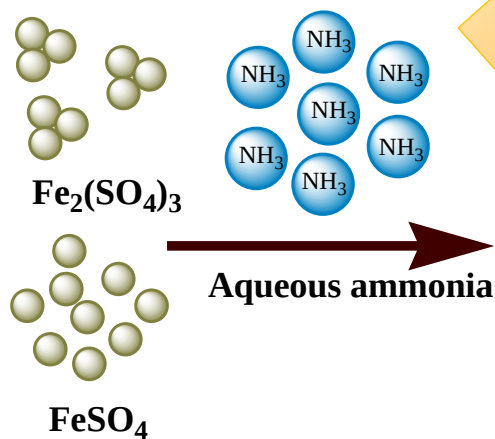


Chit-CuSO₄ Catalyzed Azide Alkyne Cycloaddition



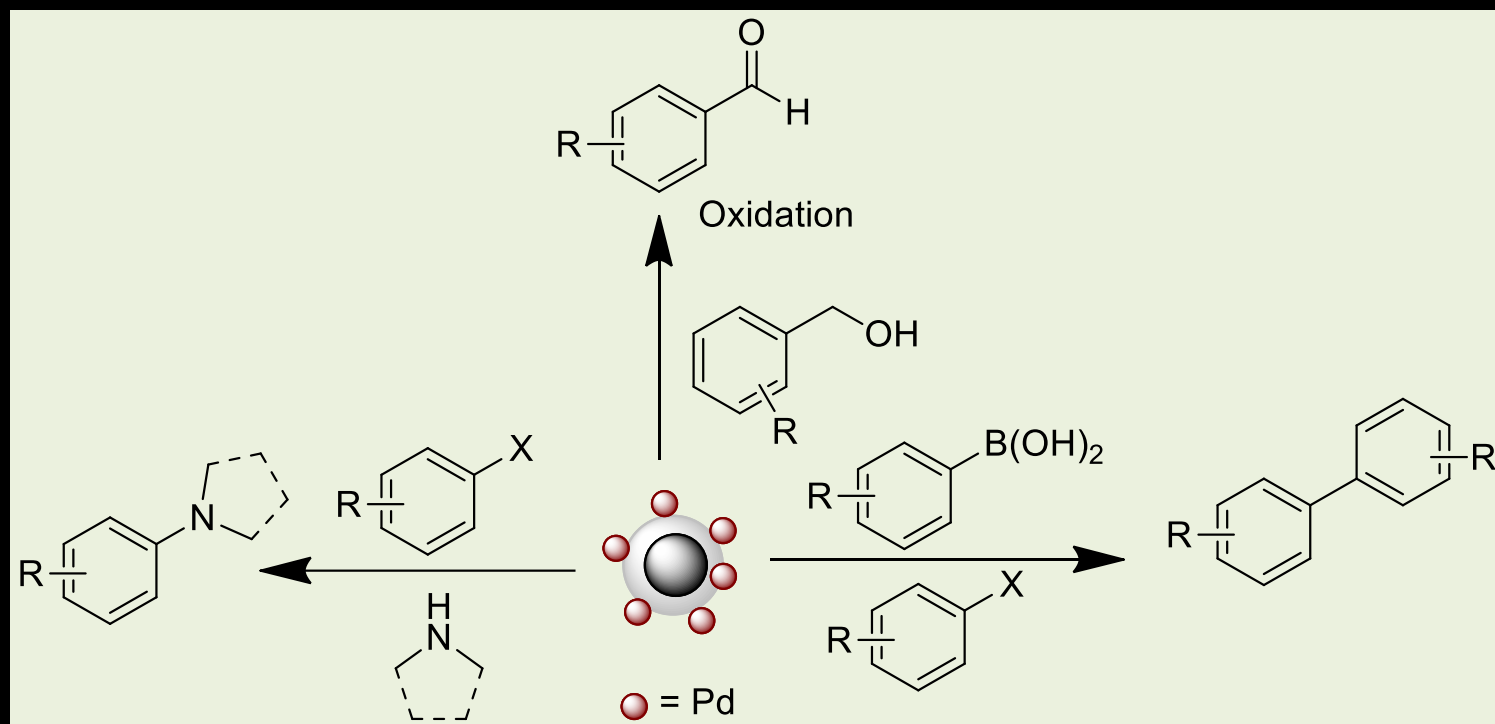
Baig, Varma: *Green Chem.*, 15, 1839-1843 (2013)

Magnetic Carbon-Supported Palladium Nanoparticles: Recyclable Catalyst for Hydrogenation



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

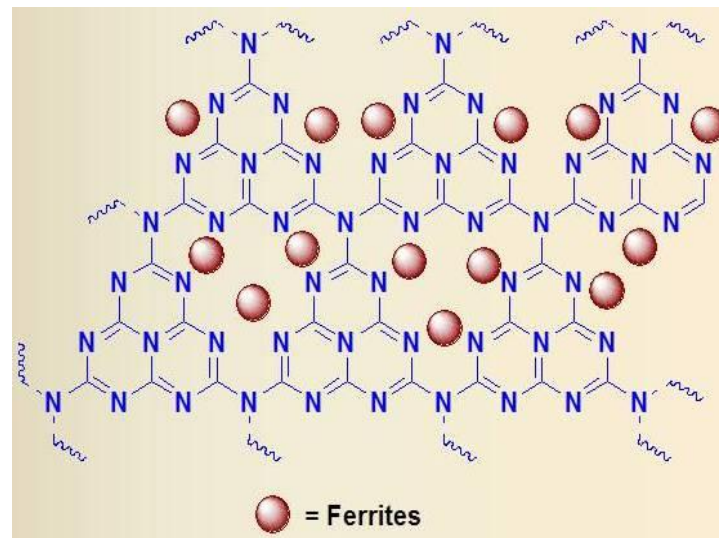
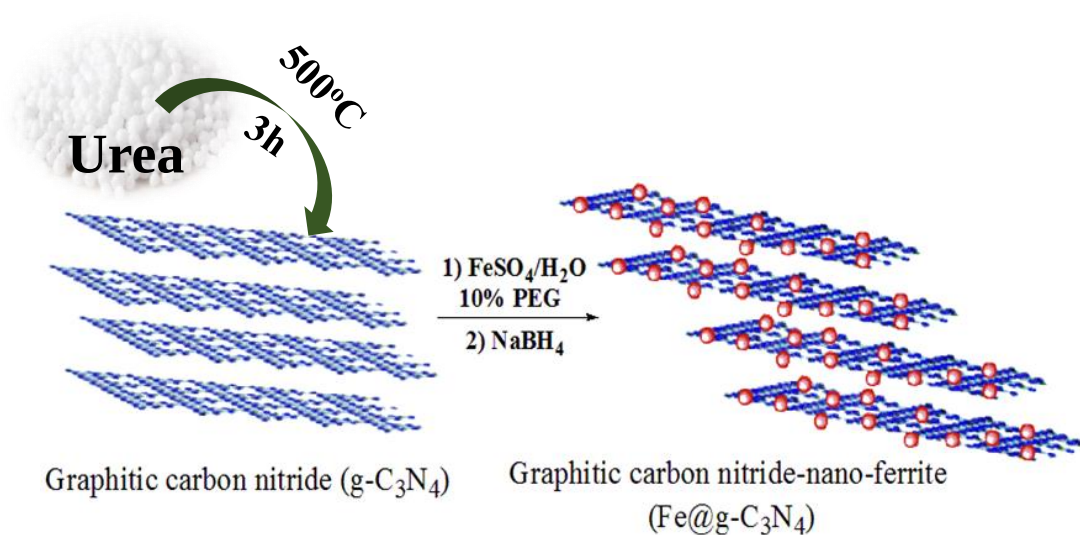
Carbon-Coated Magnetic Palladium: Applications in Partial Oxidation of Alcohols and Coupling Reactions



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

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

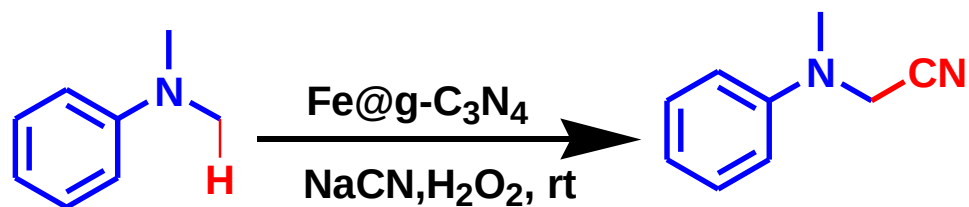
Synthesis of Magnetic $\text{Fe@g-C}_3\text{N}_4$



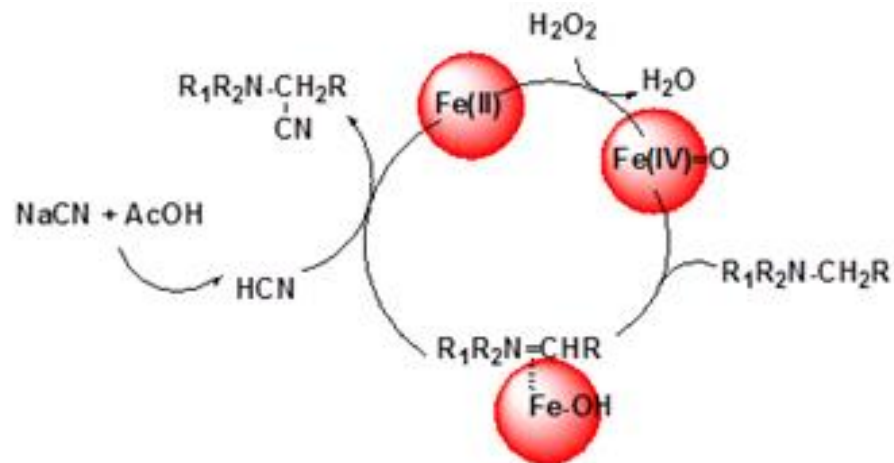
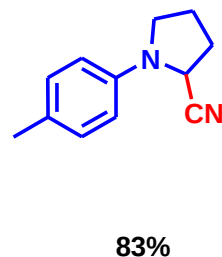
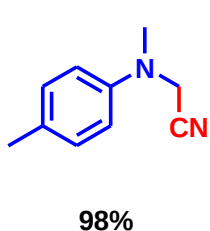
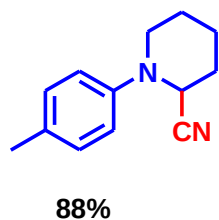
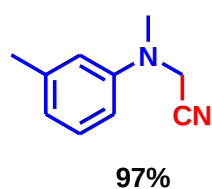
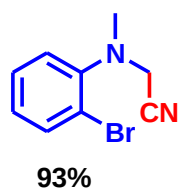
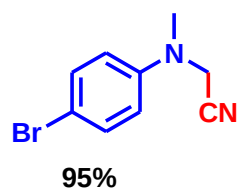
$\text{Fe@g-C}_3\text{N}_4$

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

C-H Activation and Synthesis of α -Amino Nitriles



Mechanism of α -amino nitrile synthesis

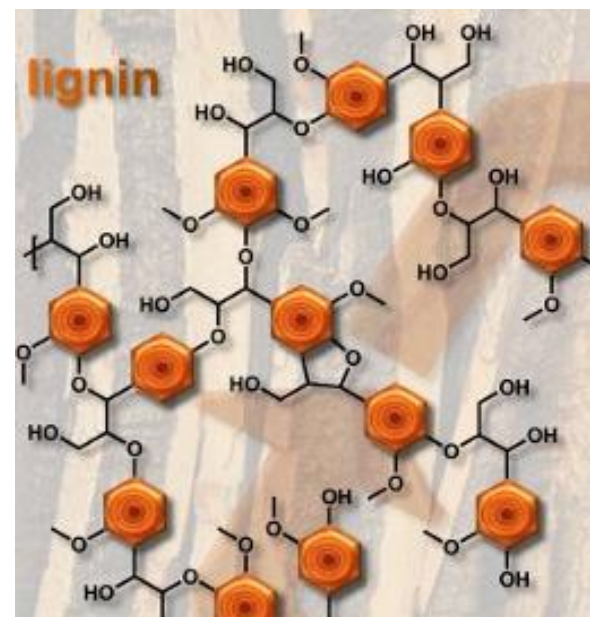
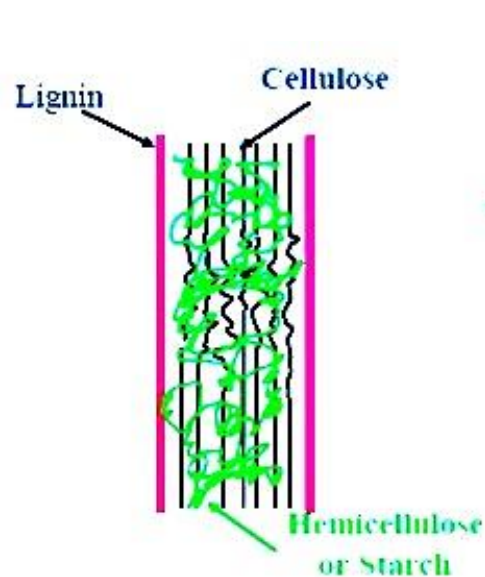


Verma, Baig, Han, Nadagouda and Varma: *Chem. Commun.*, 51, 15554 (2015)

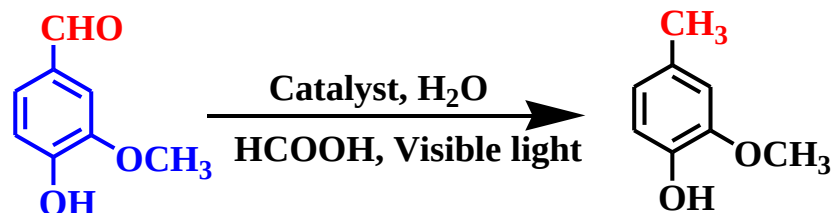
Visible Light Mediated Upgrading of Biomass to Biofuel using Formic Acid

Lignin: about 25% of the material in the plant cell wall. Hard to process and cannot be fermented into alternative fuel.

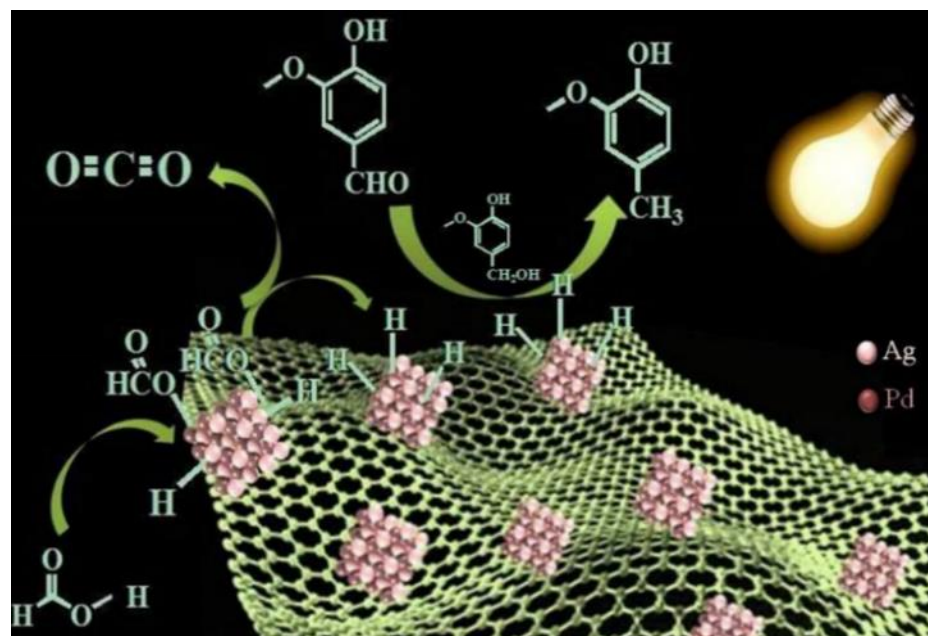
Cellulose: material that can be degraded into fermentable sugars which can be converted into biofuel.



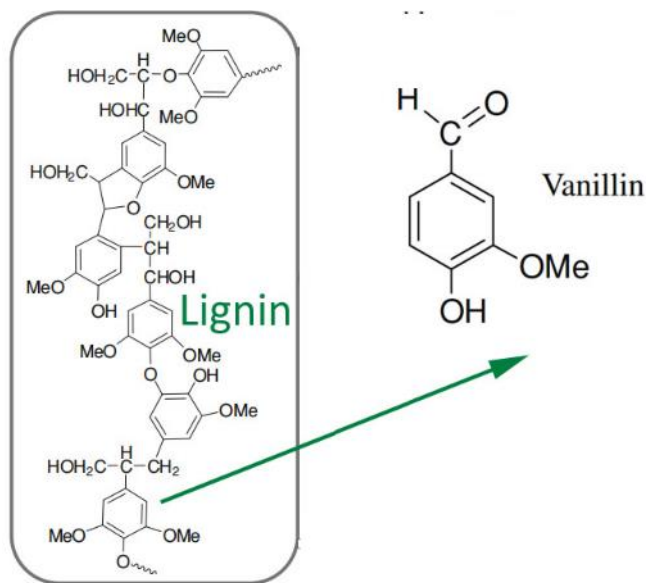
Visible Light Mediated Upgrading of Biomass to Biofuel using Formic Acid



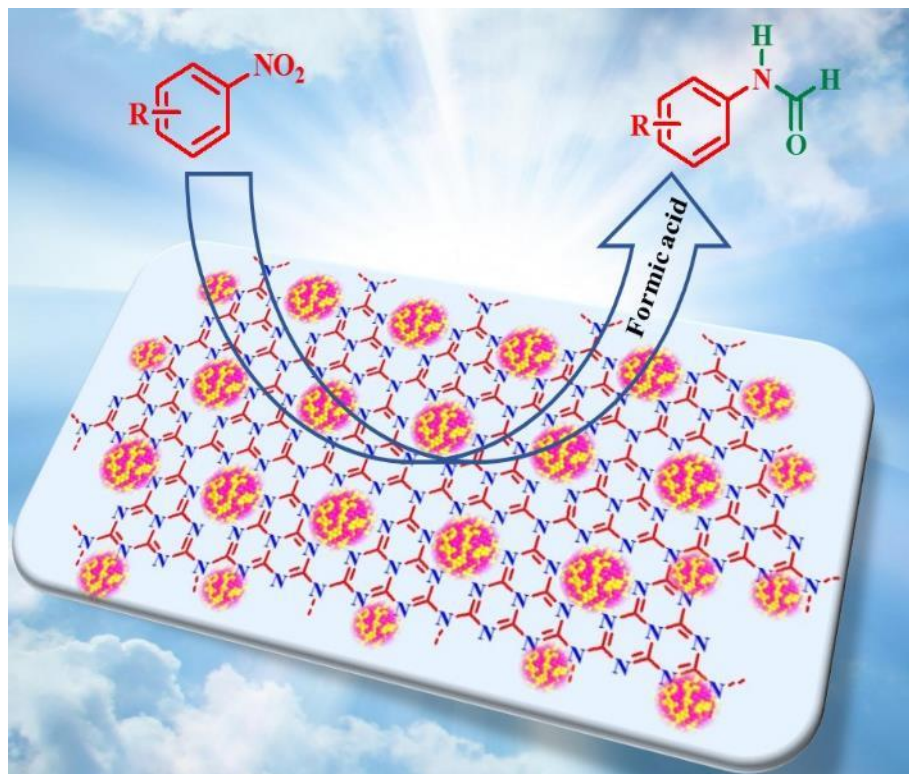
Reaction Pathway

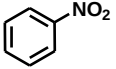
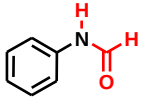
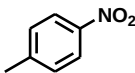
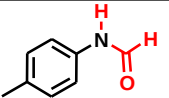
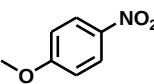
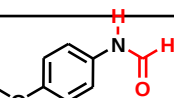
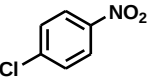
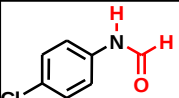
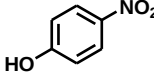
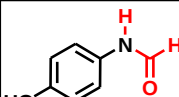
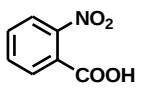
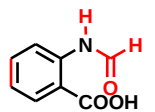
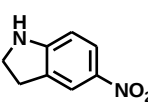
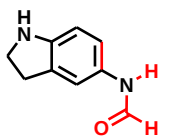
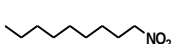


Vanillin and its derivatives as source of future biofuels

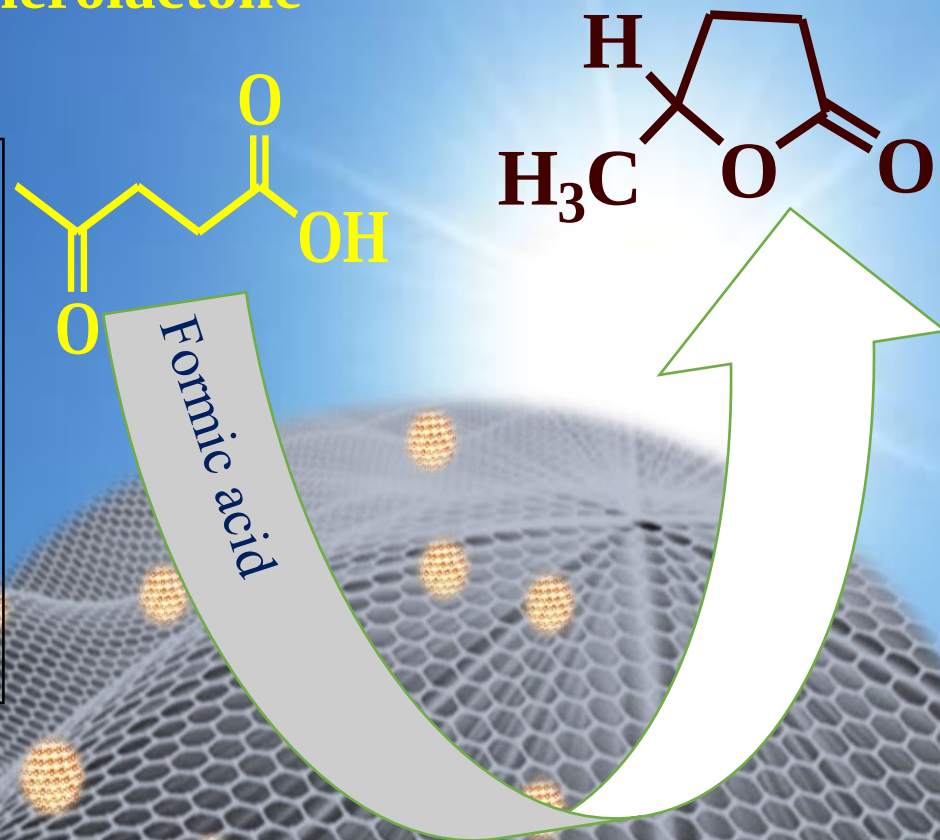
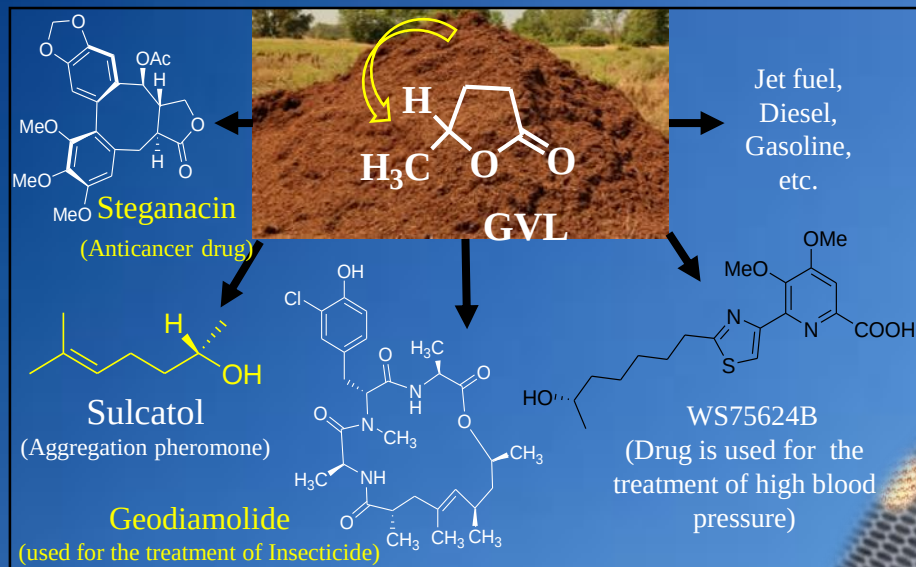


Direct Aminoformylation of Nitroarenes



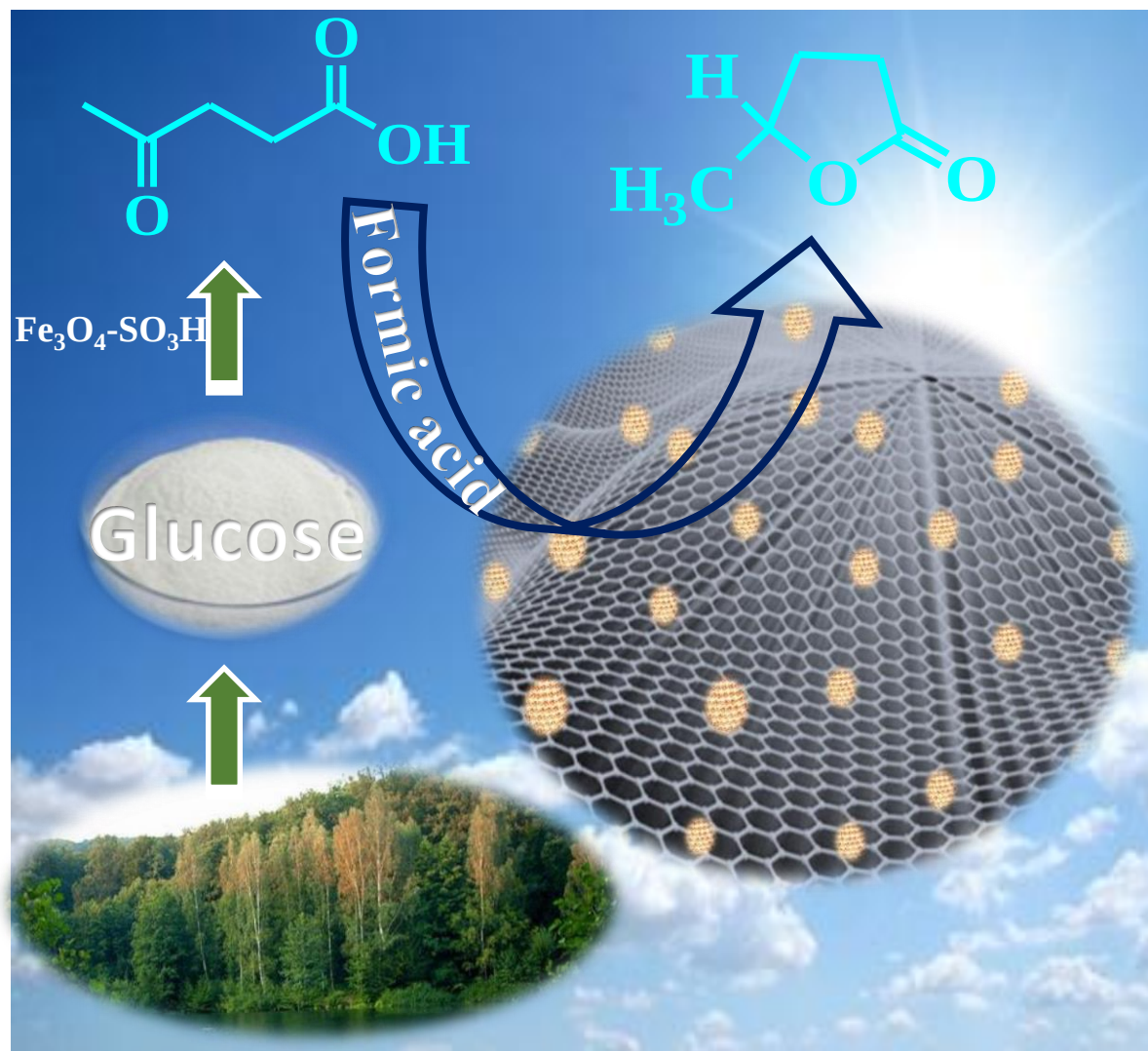
Entry	Reactant	Product	Time	Yield
1			2 h	99 %
2			2 h	98 %
3			2 h	96 %
4			2 h	97 %
5			2 h	97 %
6			2 h	96 %
7			3 h	76 %
8		-	12 h	-

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

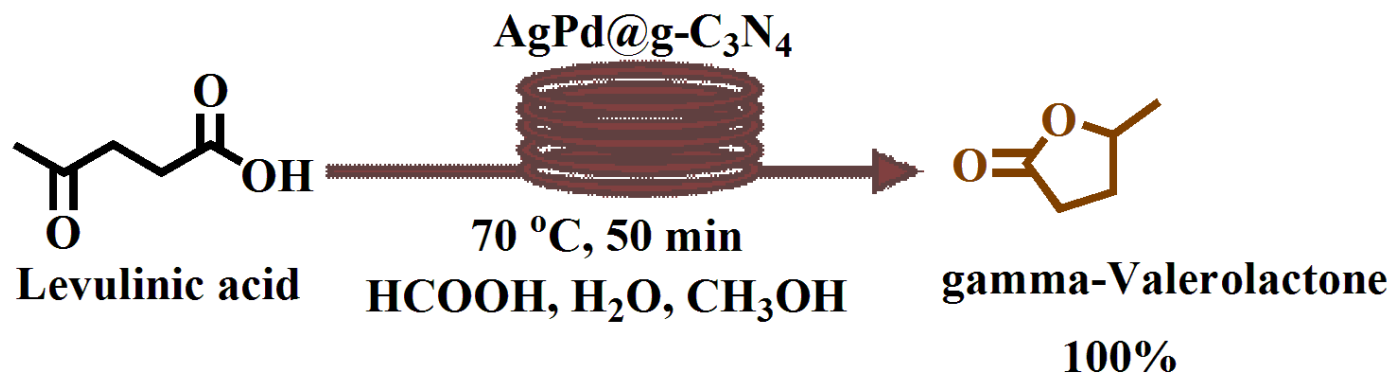
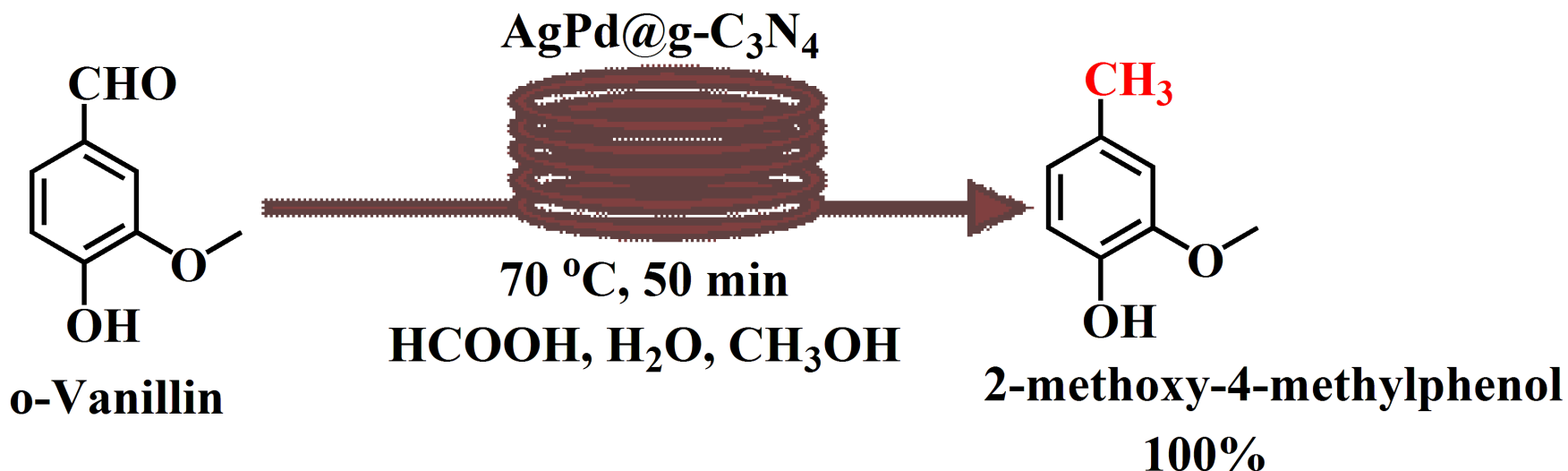


Verma, Baig, Nadagouda and Varma:
ChemCatChem, 8, 690-693 (2016)-Cover page

Visible Light-Mediated Synthesis of γ -Valerolactone from Biomass



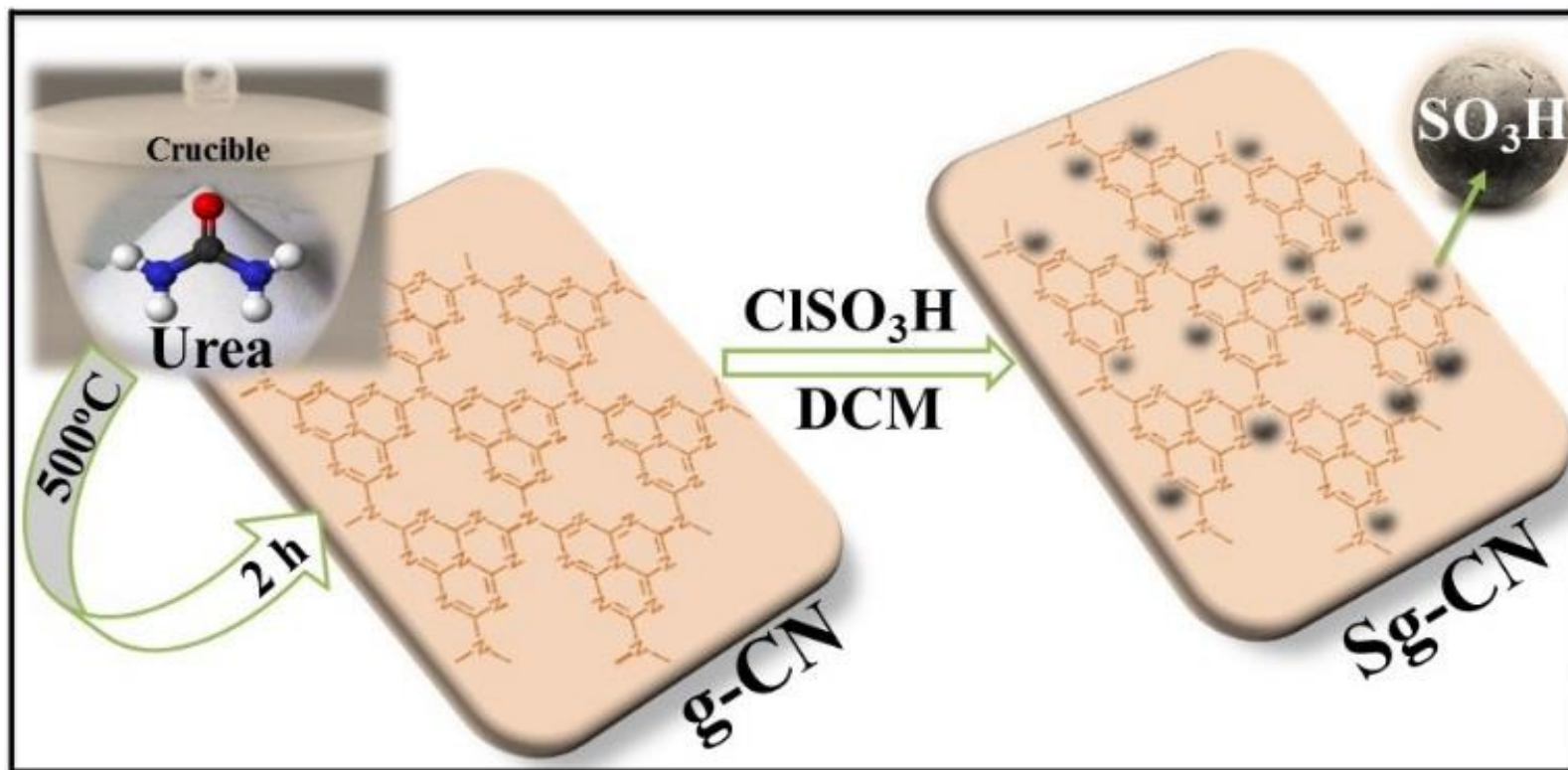
Sustainable Pathway to Empower Bio-based Future: Upgrading of Biomass *via* Process Intensification



Tadele, Verma, Gonzalez, Varma: *Green Chem.*, 19, Communicated (2017)

Sulfonated Graphitic Carbon Nitride (Sg-CN)

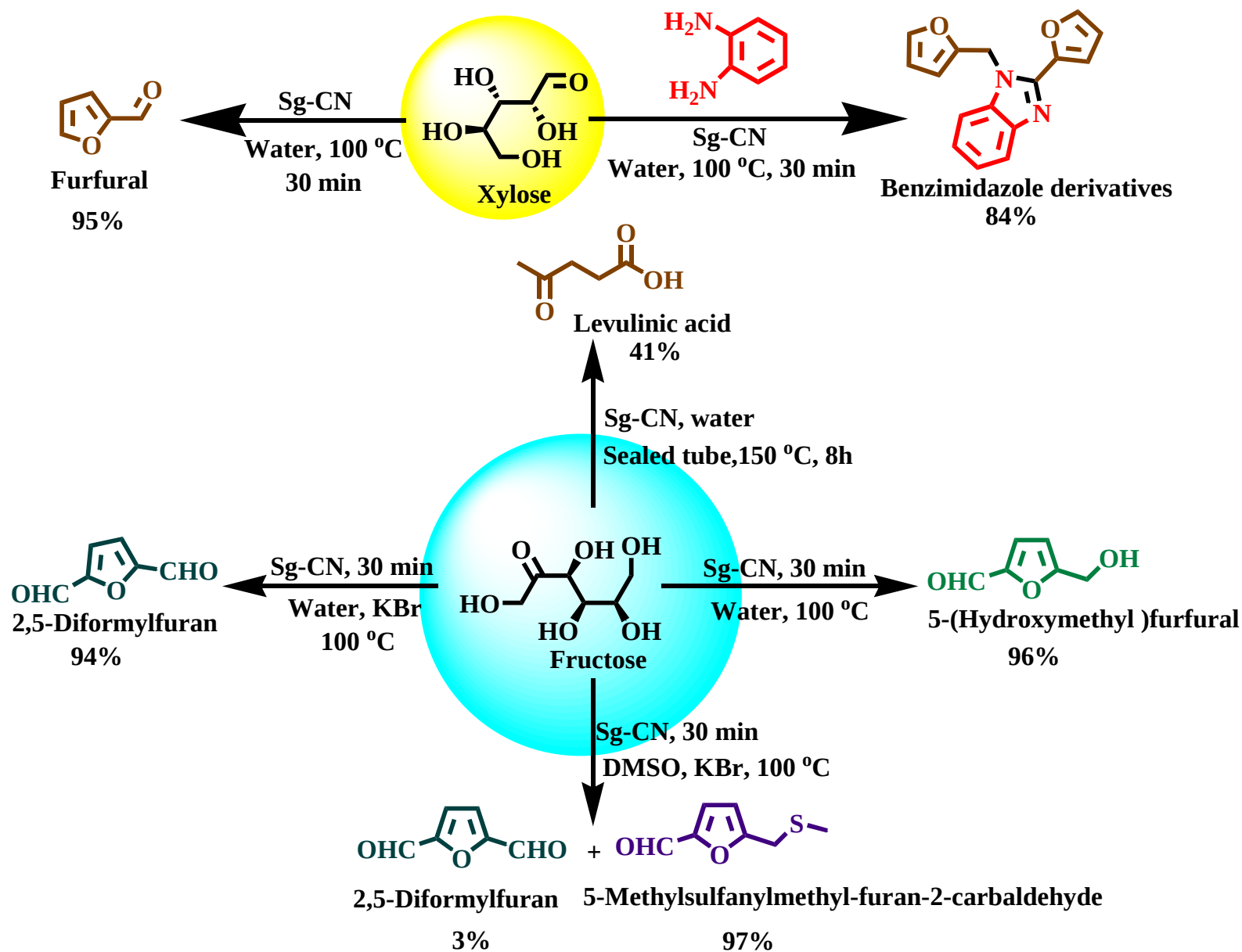
Simple synthesis from abundant and inexpensive materials



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

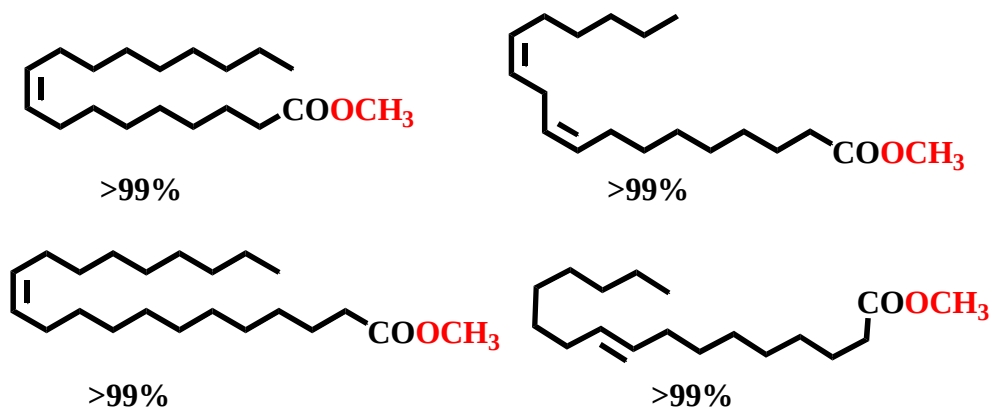
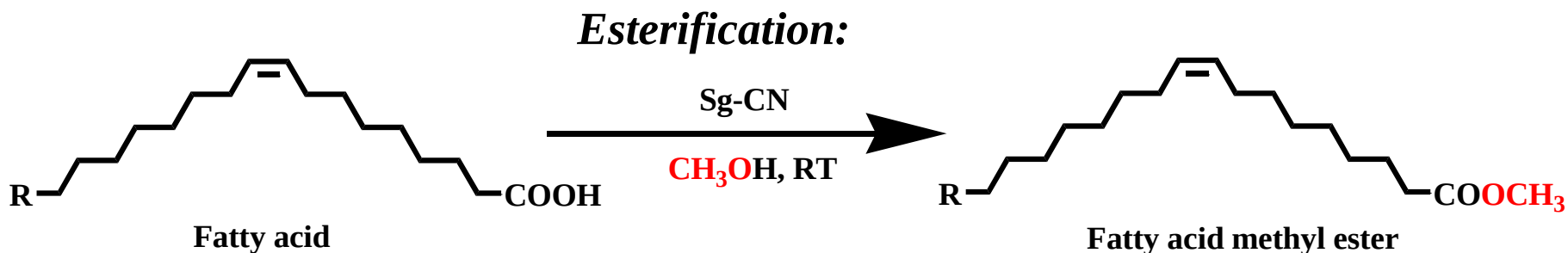
Baig, Verma, Nadagouda, Varma: *Nature Sci. Rpts.*, 2016, DOI:10.1038/srep39387

Sustainable Pathway to Furanics from Biomass

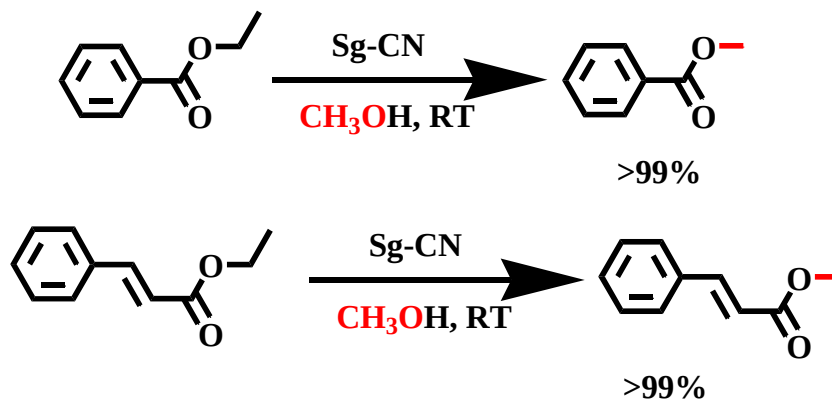


Verma, Baig, Nadagouda, Len, Varma: *Green Chem.*, 19, 164 (2017)

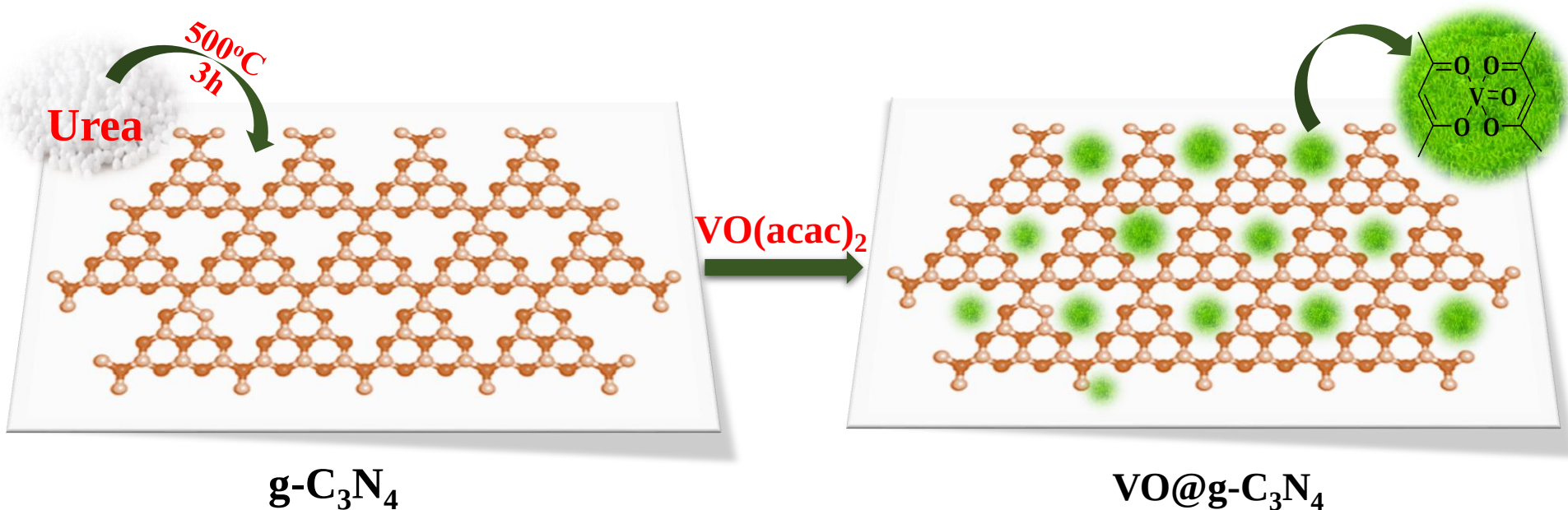
Synthesis of Biodiesel at Room Temperature



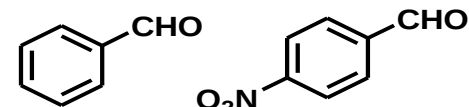
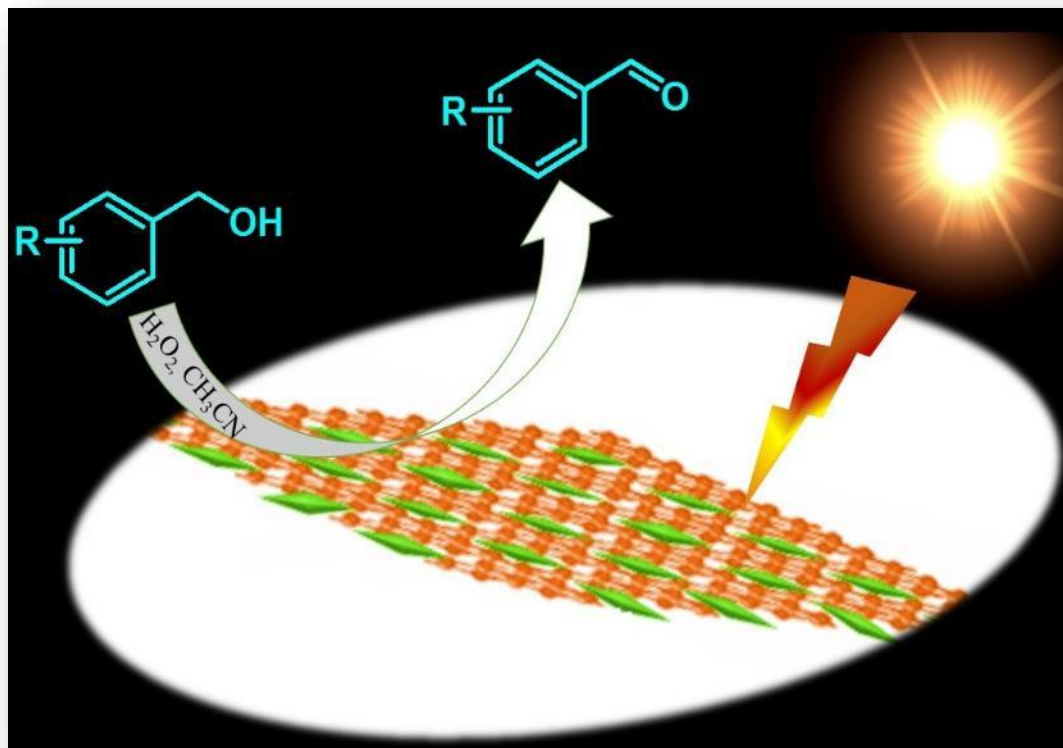
Transesterification:



Synthesis of Oxo-Vanadium Graphitic Carbon Nitride ($\text{VO}@g\text{-C}_3\text{N}_4$)

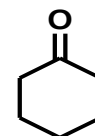


Selective Oxidation of Alcohols

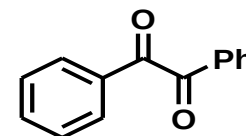


98%

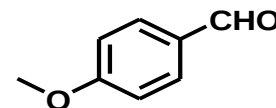
95%



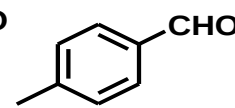
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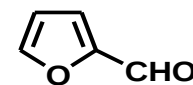
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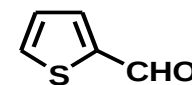
98%



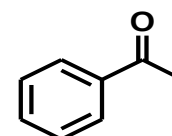
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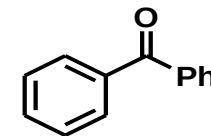
96%



96%



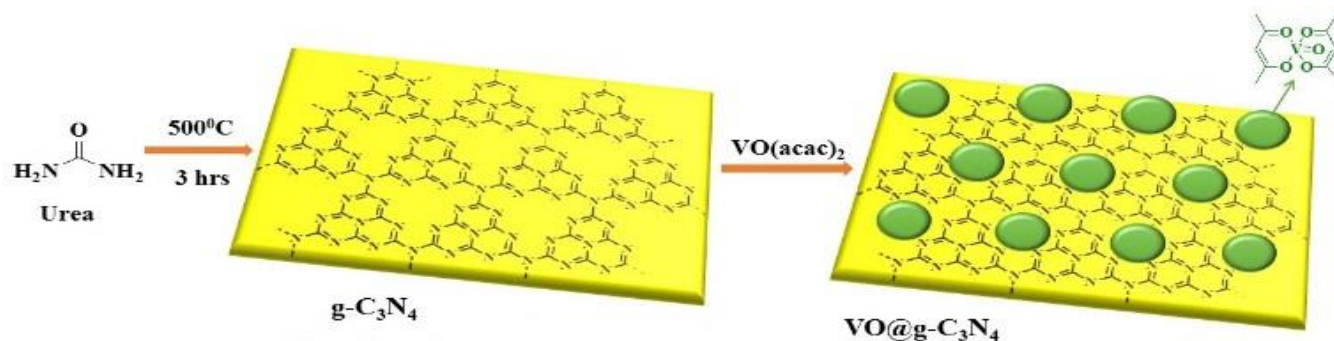
97%



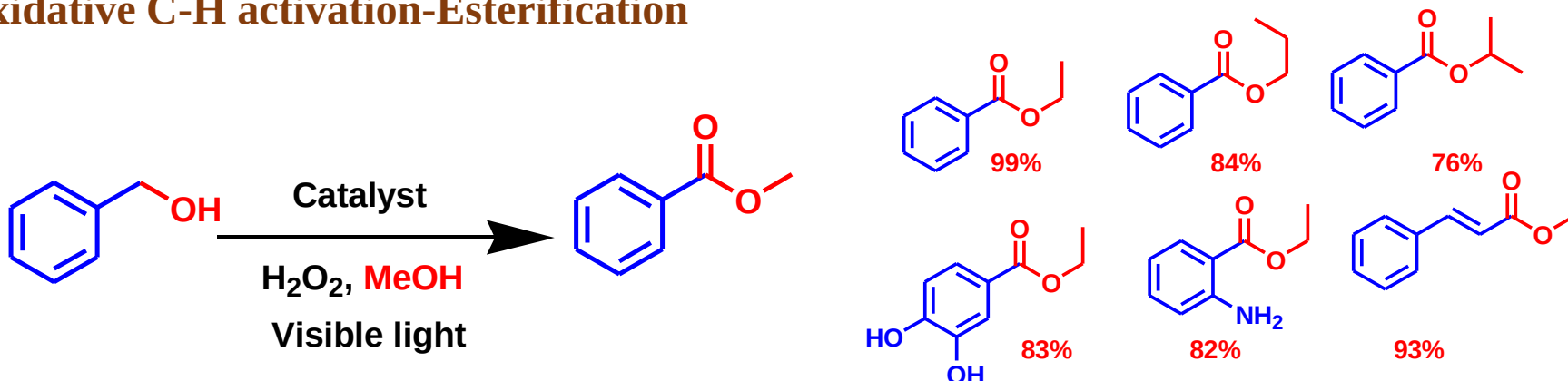
93%

Oxidative Esterification via Photocatalytic C-H Activation

Synthesis of Oxo Vanadium graphitic carbon nitride (VO@g-C₃N₄)



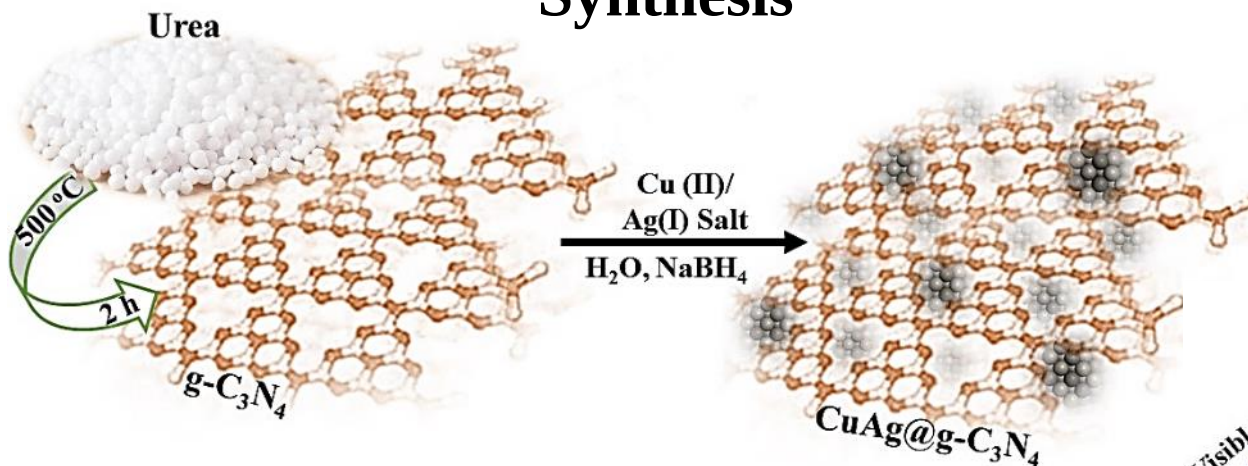
Oxidative C-H activation-Esterification



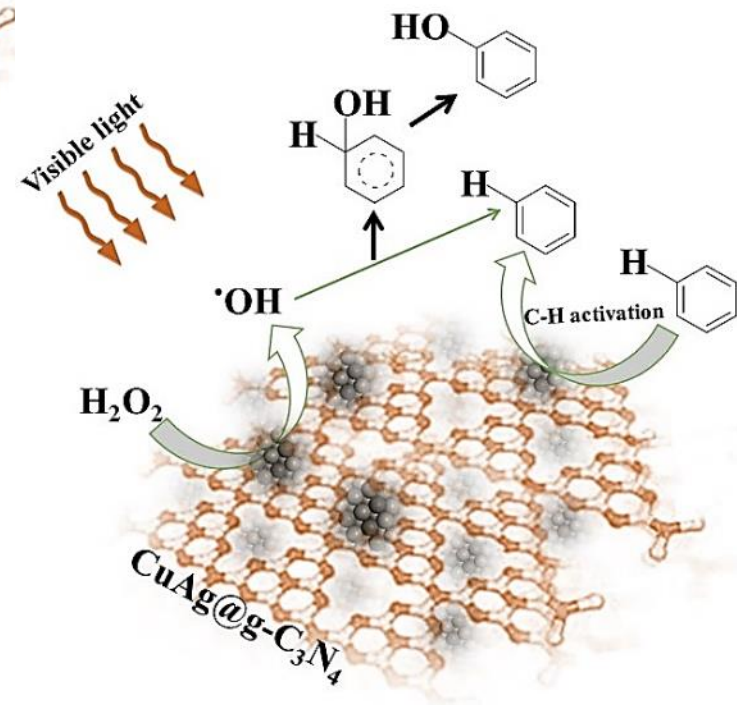
Verma, Baig, Han, Nadagouda, Varma: *Green Chem.* 18, 251, (2016)

Hydroxylation of Benzene via C-H Activation using Bimetallic CuAg@g-C₃N₄

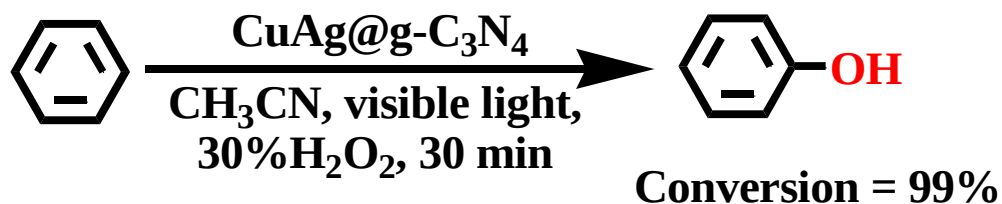
Synthesis



Mechanism

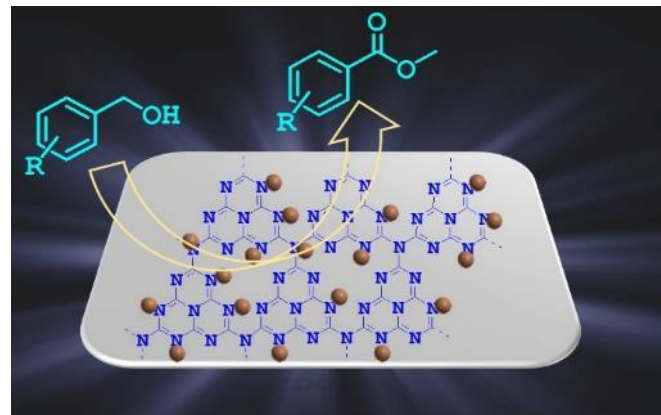
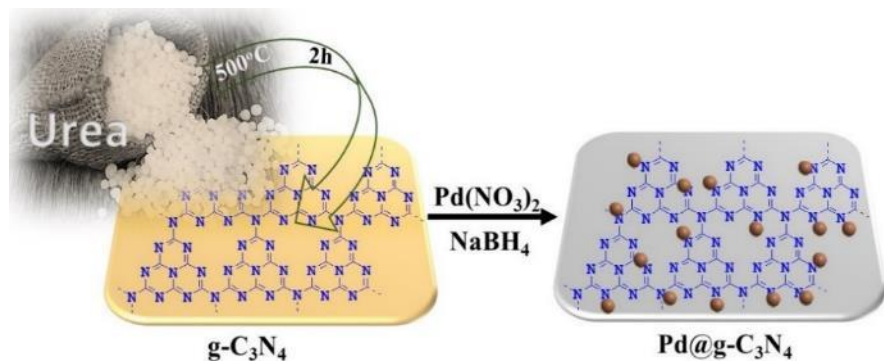


Application

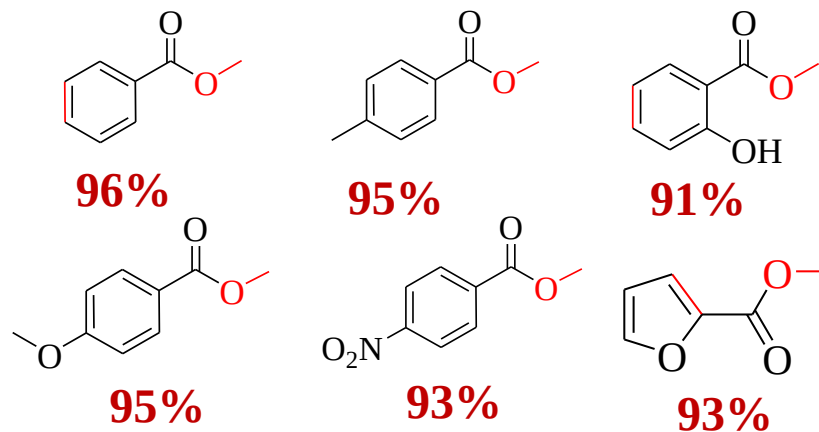
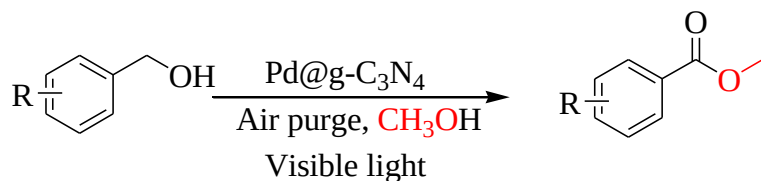


Photocatalytic C-H Activation and Oxidative Esterification Using Pd@g-C₃N₄

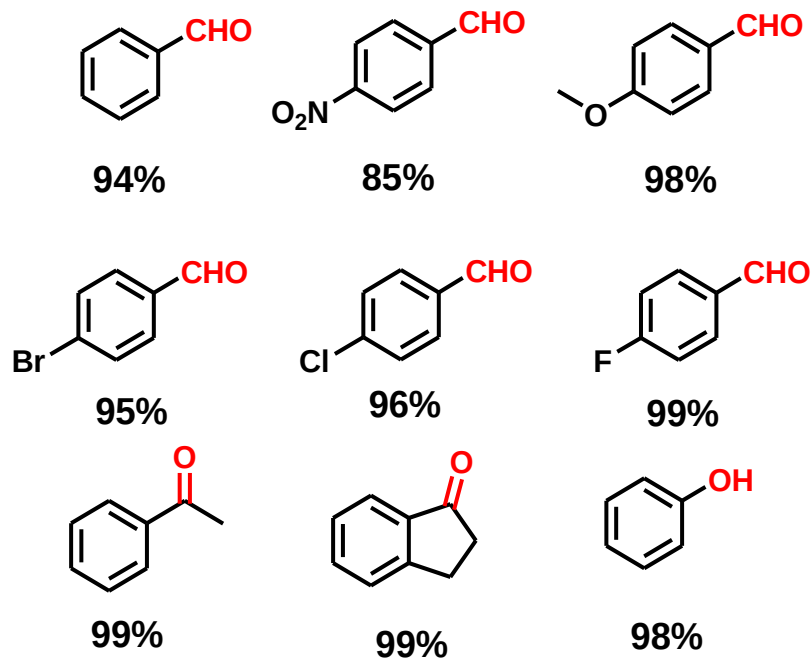
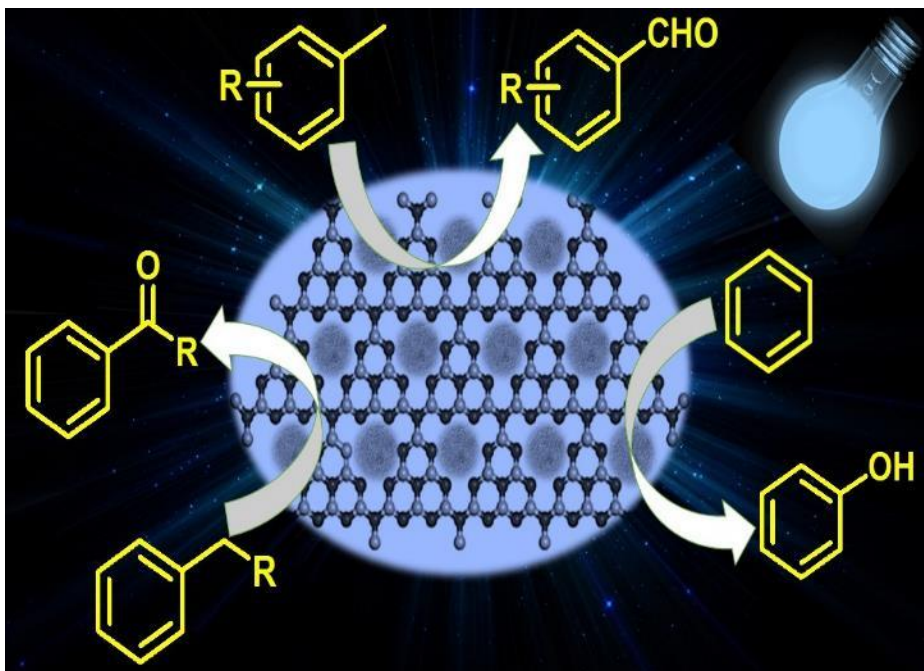
Synthesis of Pd@g-C₃N₄



Oxidative esterification of aromatic alcohols



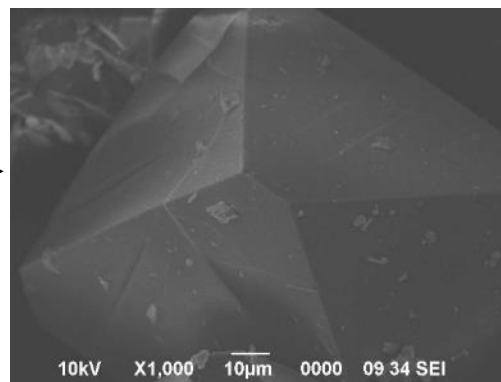
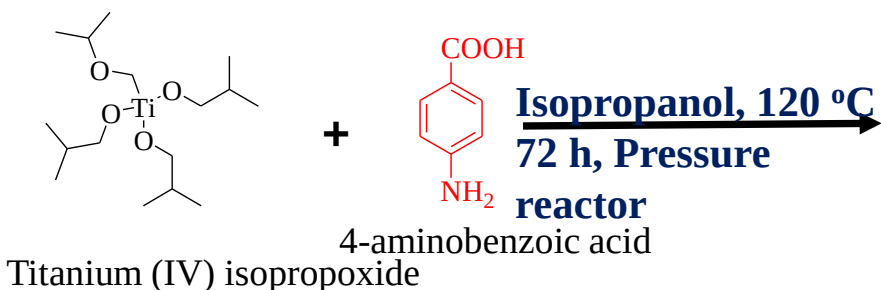
Photocatalytic C-H activation of Hydrocarbons



Verma, Baig, Nadagouda, Varma: *ACS Sustain. Chem. Eng.*, 4, 2333 (2016)

Aerobic Oxidation of Alcohols in Visible Light using Pd-Grafted Ti cluster

Synthesis of Pd@TiC



Ti cluster = $\text{Ti}_6\text{O}_6(\text{O}^i\text{Pr})_6(\text{abz})_6$

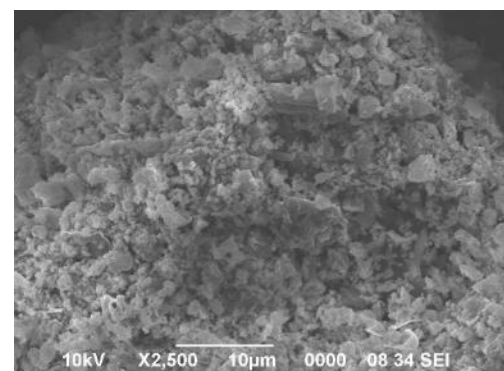
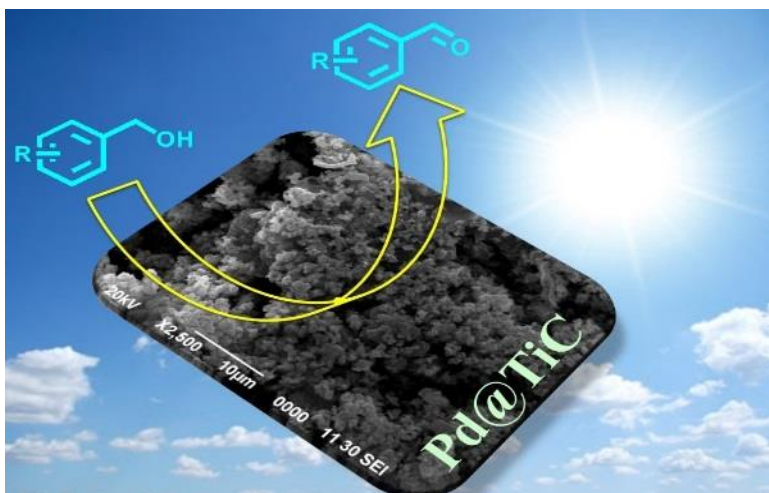
O^iPr = isopropoxide

abz = aminobenzoic acid

$\text{Pd}(\text{NO}_3)_2$

Isopropanol

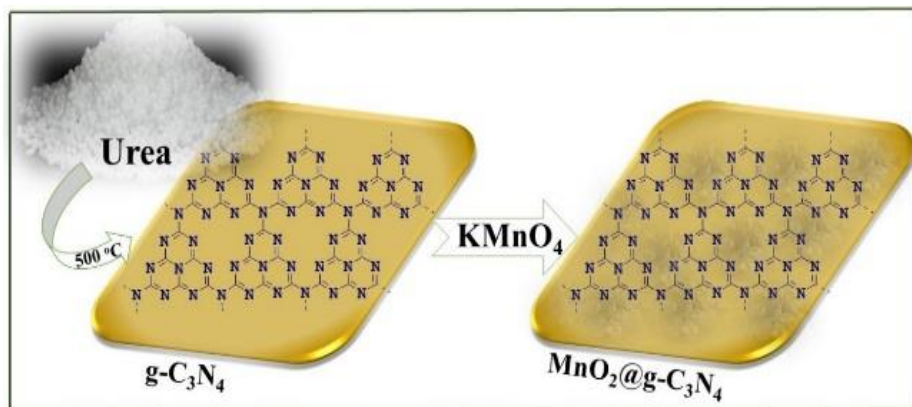
Pd@TiC



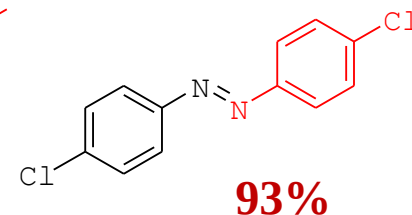
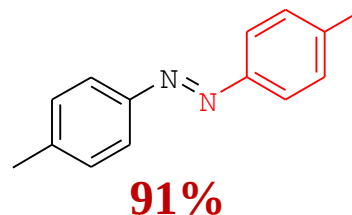
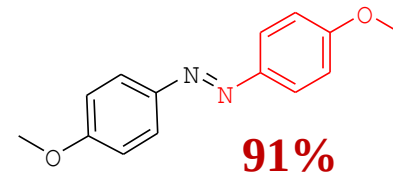
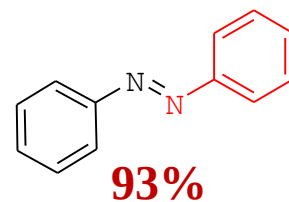
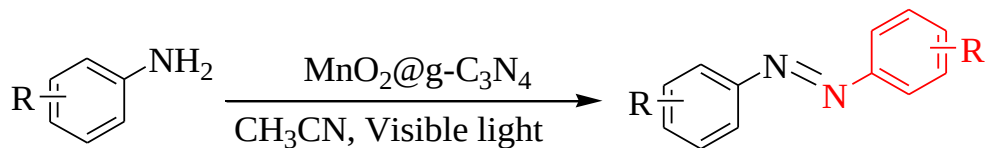
Verma, Baig, Nadagouda, Varma: *Tetrahedron* (Open Access)
<http://dx.doi.org/10.1016/j.tet.2016.07.070>

Photocatalytic Oxidation of Aromatic Amines using $\text{MnO}_2@\text{g-C}_3\text{N}_4$

Synthesis of $\text{MnO}_2@\text{g-C}_3\text{N}_4$

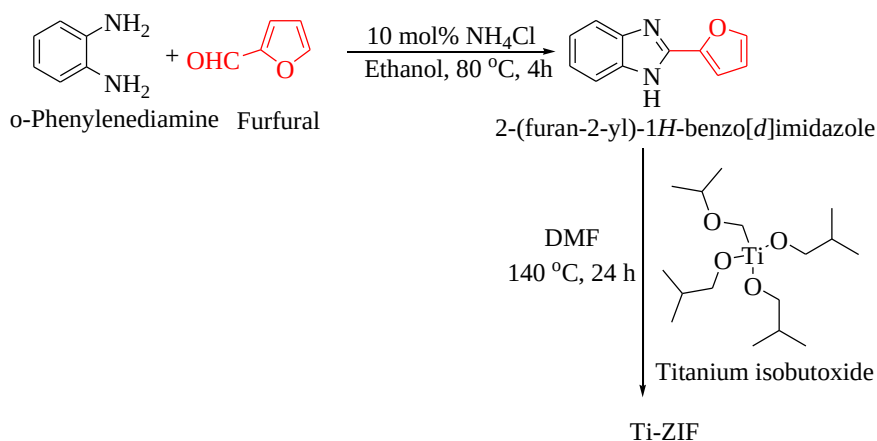


Oxidative Application

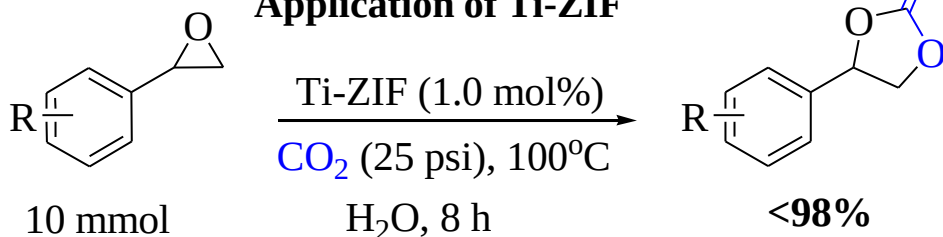


Titanium-based Zeolitic Imidazolate Framework for Chemical Fixation of Carbon dioxide

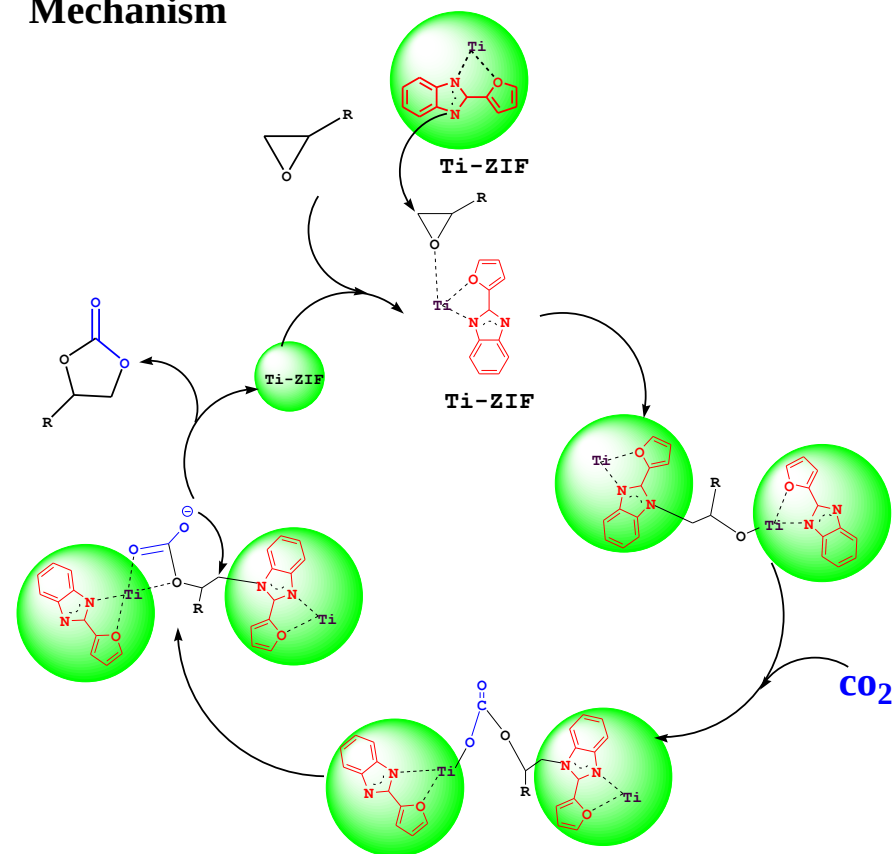
Synthesis of Ti-ZIF



Application of Ti-ZIF



Mechanism



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The use of trade names does not imply endorsement by the U.S. Government.