Greener Pathways to Organics and Nanomaterials: Sustainable Applications of Magnetic Nanocatalysts and Modified Graphitic Carbon Nitrides

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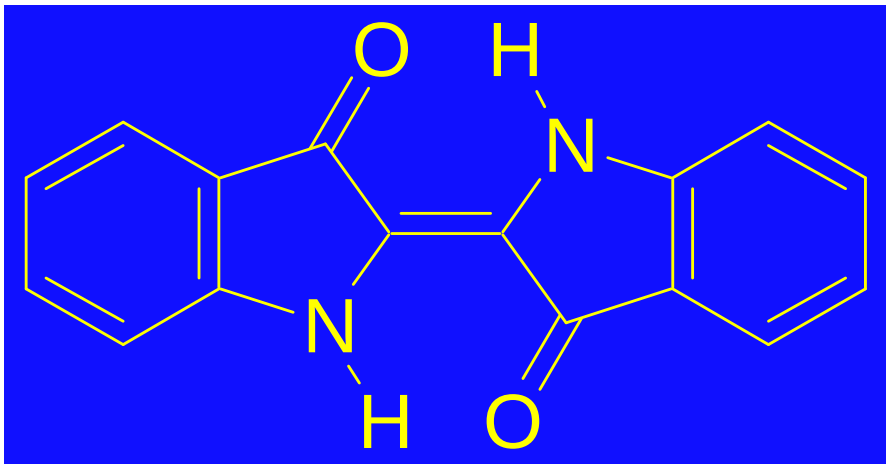
The Road To Sustainability
Impact Assessment
Risk Assessment
Risk Management
Benign by Design
WASTE MINIMIZATION
Green Chemistry
CLEAN CATALYSTS
SEPARATION CHNOLOGIES
Clean Products
CLEAN ENERGY
Renewable Sources
Solar, Biomass
Life Cycle Assessment (LCA)
Energy Efficiency
Minimum Chemical Waste
Benign Solvents
Atom Economy
Green Organic Chemistry
Efficient Isolation Processes
Renewable Feedstock
Safer Catalysts & Reagents
Sustainable Synthetic Method

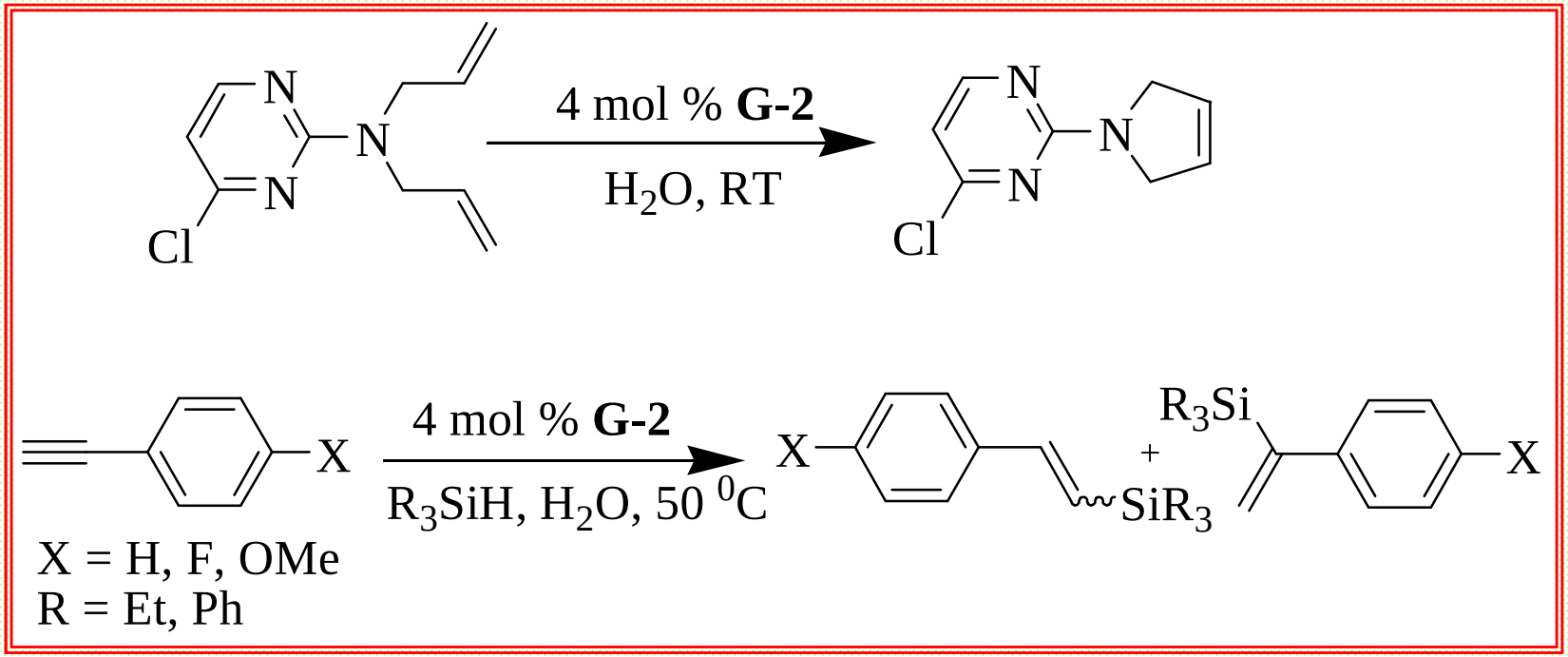
Adolf von Baeyer



Solventless Synthesis of Indigo
-1905 Nobel Chemistry Prize

Nobel Laureate
Bob Grubbs
Chemistry 2005

Ring Closing Metathesis (CRM) and Hydrosilylation Reactions in Water Using Grubbs 2nd Generation Catalyst



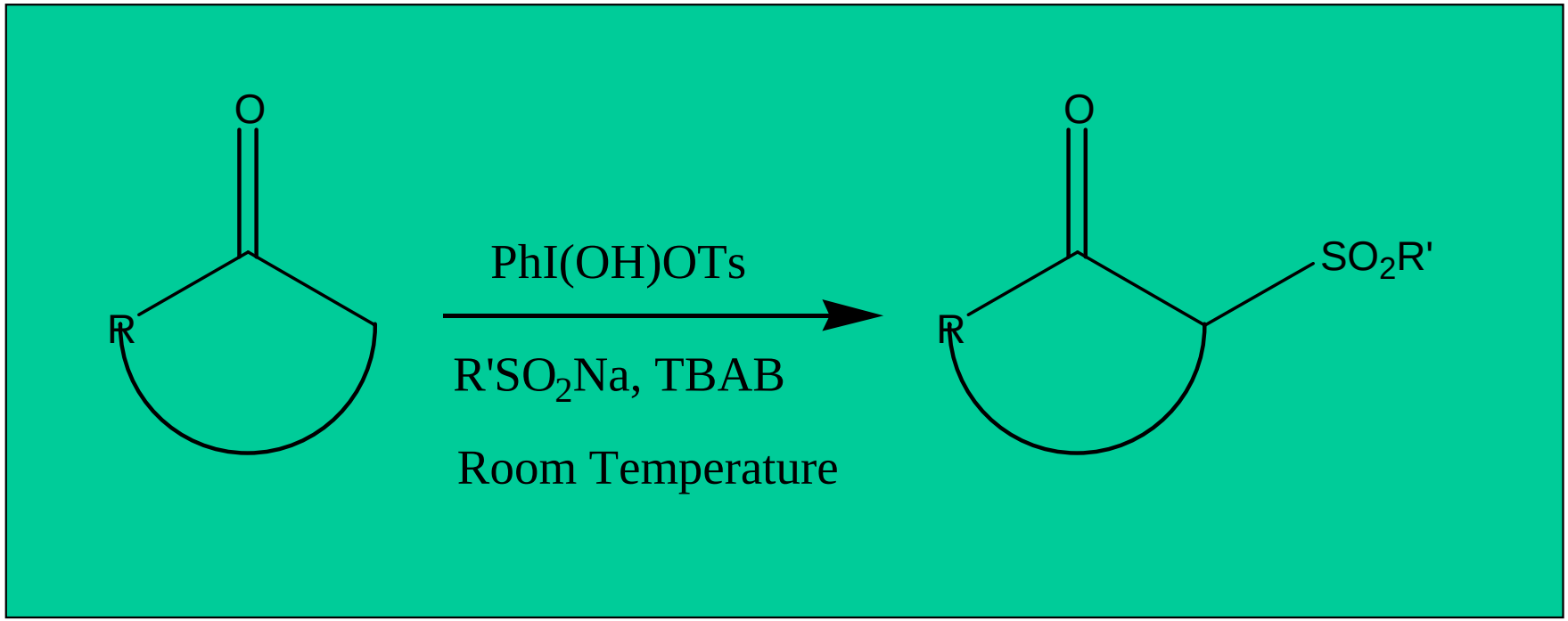
V. Polshettiwar & R. S. Varma, *J. Org. Chem.* **2008**, *73*, 7417

Solvent-free Mechanochemical Oxidative Preparation of Heterocycles

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4, *p*-$OCH_3C_6H_4$, *m*-$OCH_3C_6H_4$, *p*-$N(CH_3)_2C_6H_4$,

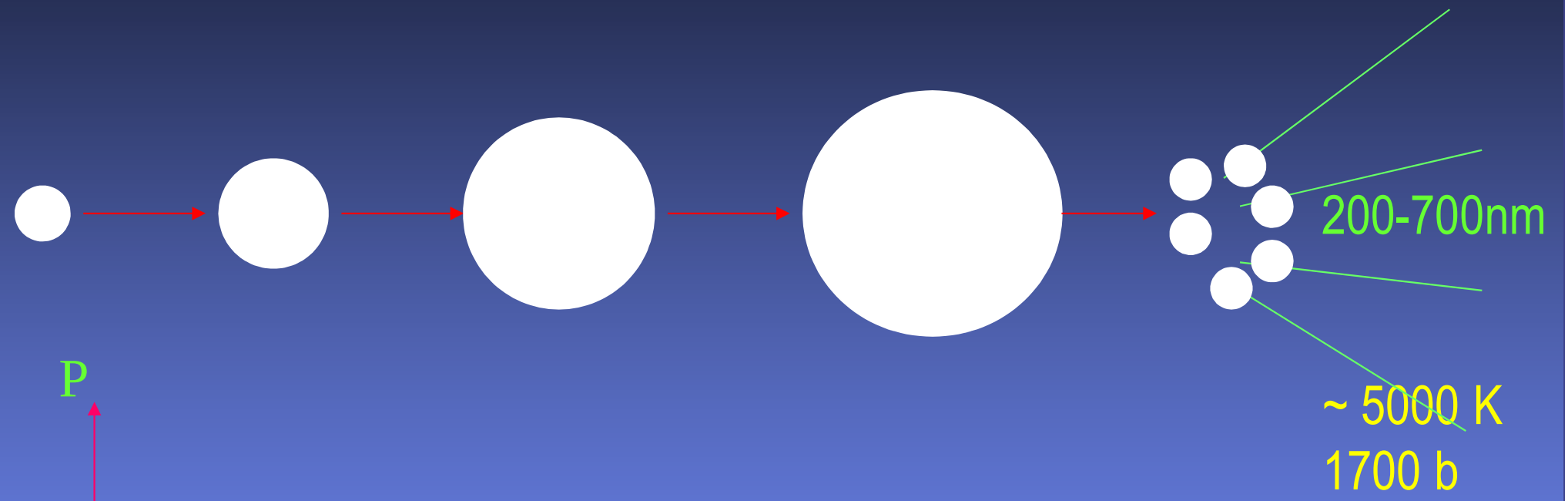
Kumar, Chandra Sekhar, Dhillon, Rao, and Varma, *Green Chem*., 2004, *6*, 156-157.

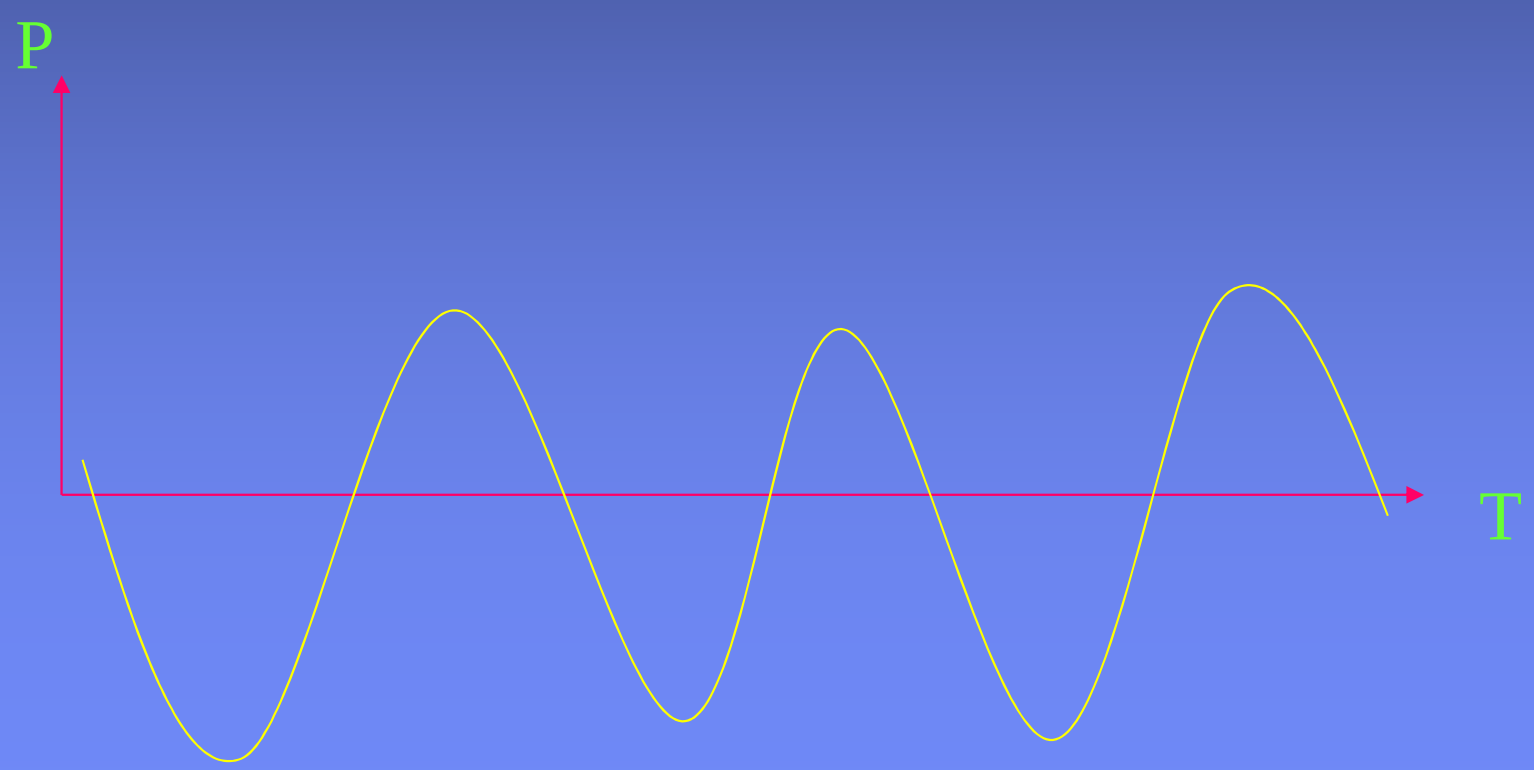
Solvent-free Synthesis of ß-Keto Sulfones from Ketones



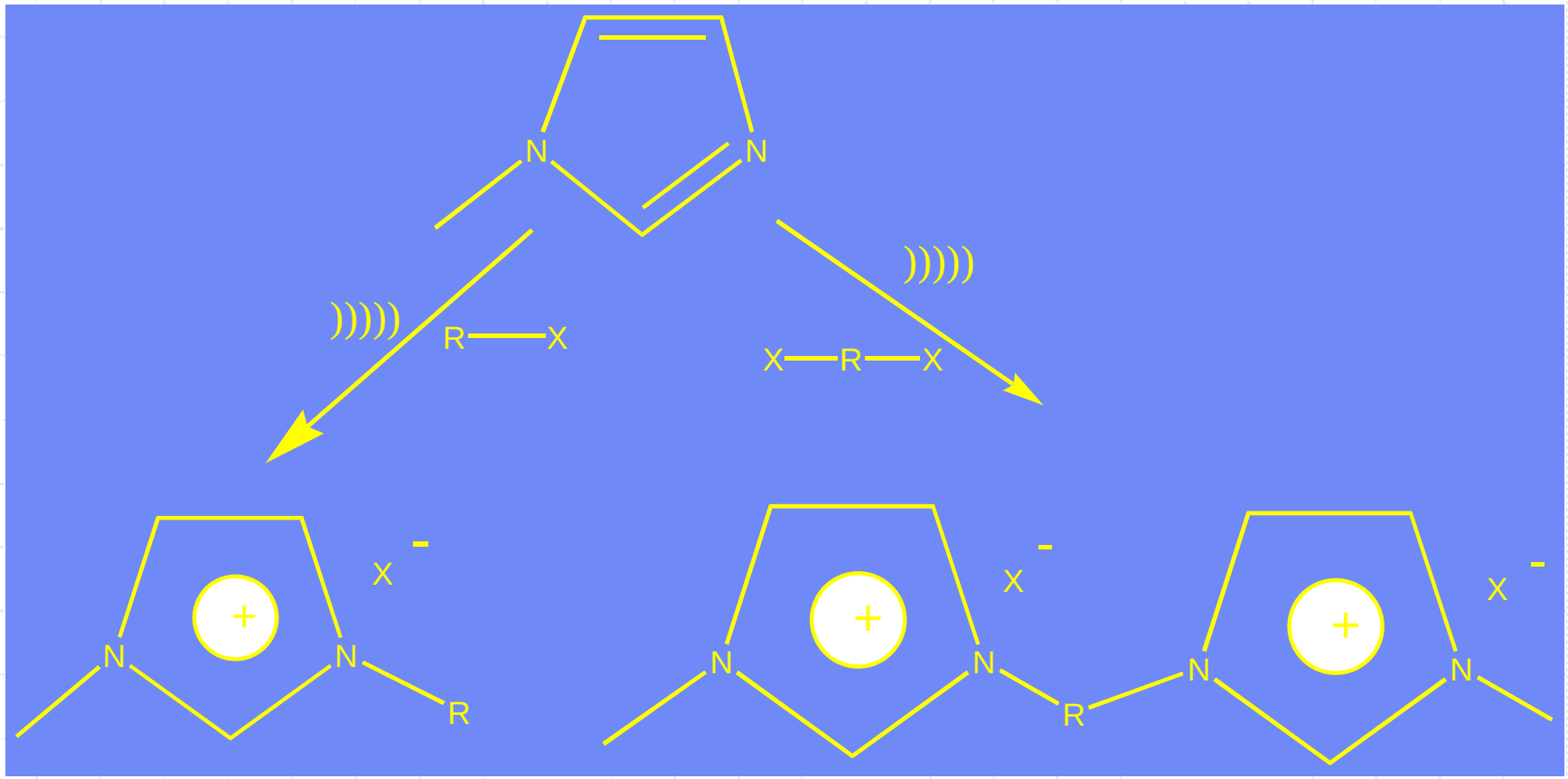
Kumar, Sundaree, Rao and Varma,
***Tetrahedron Letters*, 2006, *47*, 4197-4199.**

Dynamics of cavitation bubbles



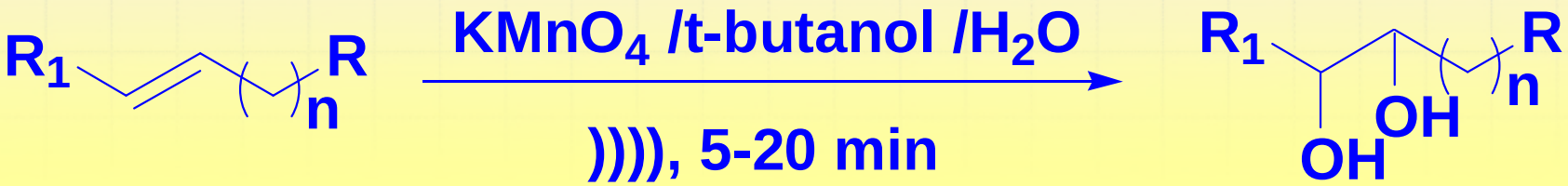


Solvent-free Sonochemical Preparation of Ionic Liquids



Varma, Namboodiri, *Org. Lett.*, *4*, 3161 (2002)

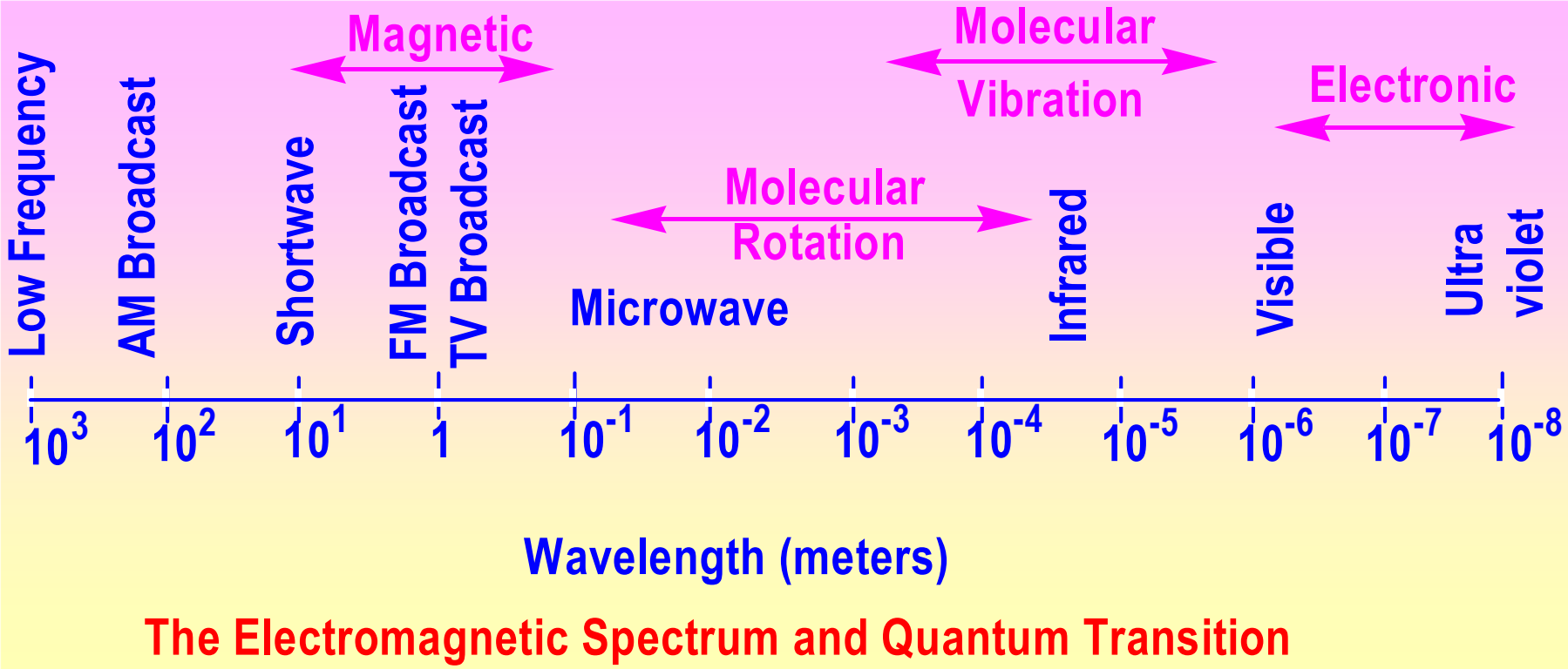
Ultrasound-accelerated Oxidation



R1 = H, C_6H_5, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4,
n = 0, 1 and R = H, Br

R. S. Varma, K. P. Naicker, *Tetrahedron Lett.*, 1998, *39*, 7463

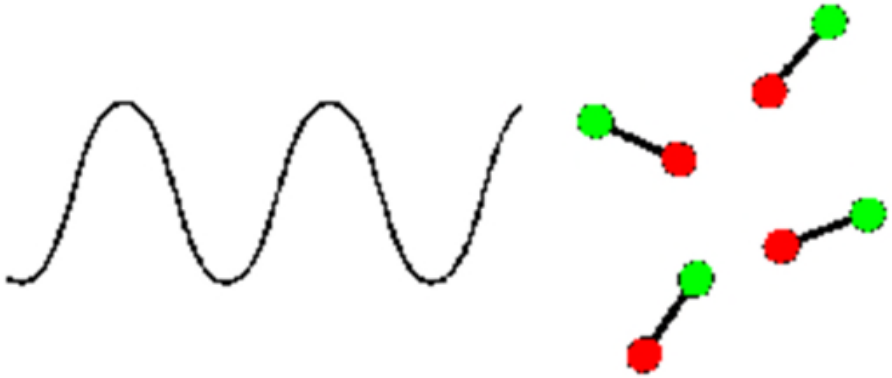
Microwaves



- **MW reactors operate at 2.45 GHz.**
- **Electric field oscillates at 4.9×10^9 times/sec – 10°C/sec heating rate.**

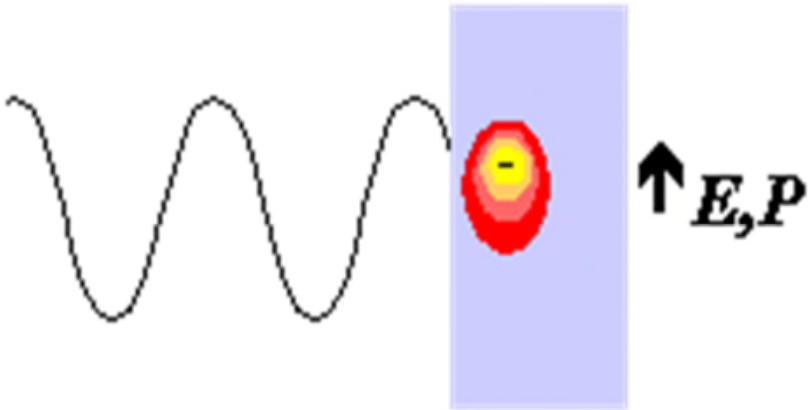
Microwave Dielectric Heating Mechanisms

Dipolar Polarization Mechanism



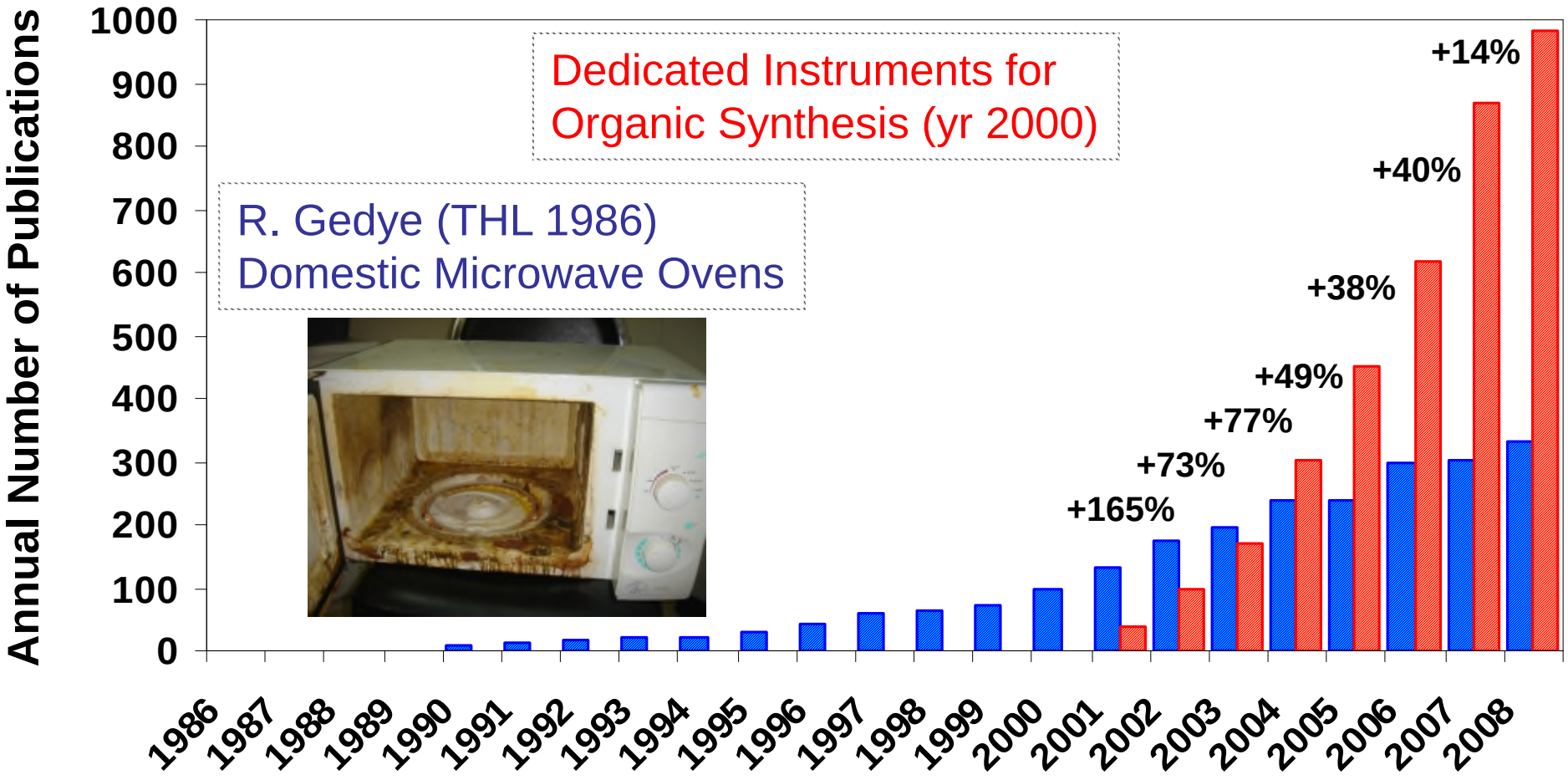
Dipolar molecules try to align to an oscillating field by rotation

Conduction Mechanism



Ions in solution will move by the applied electric field

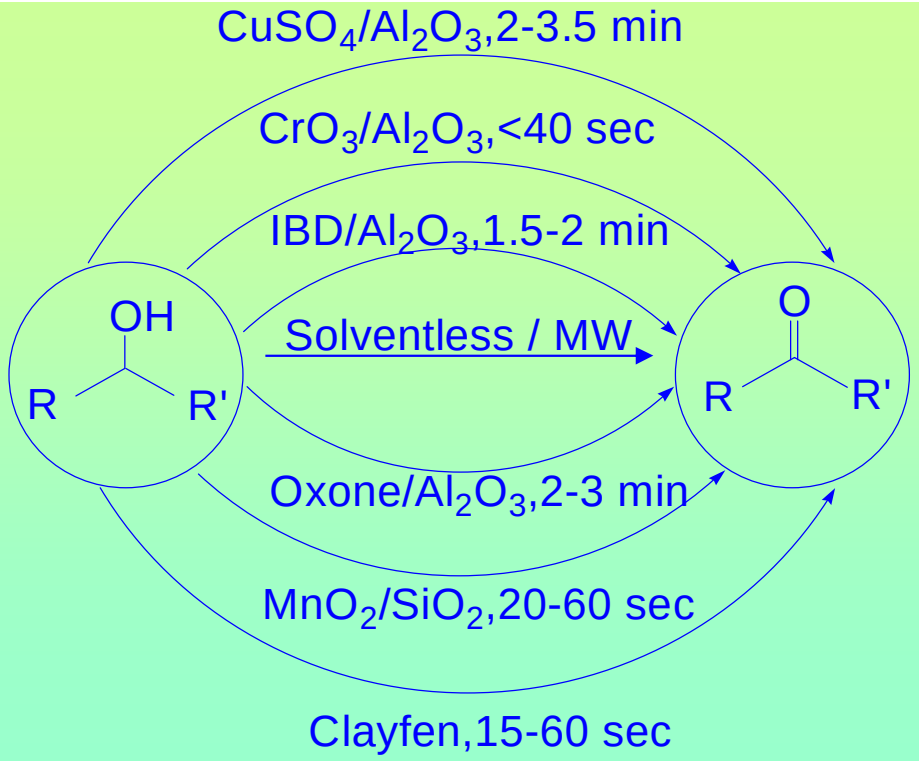
Number of Publications in Microwave-Assisted Organic Synthesis (1986-2008)

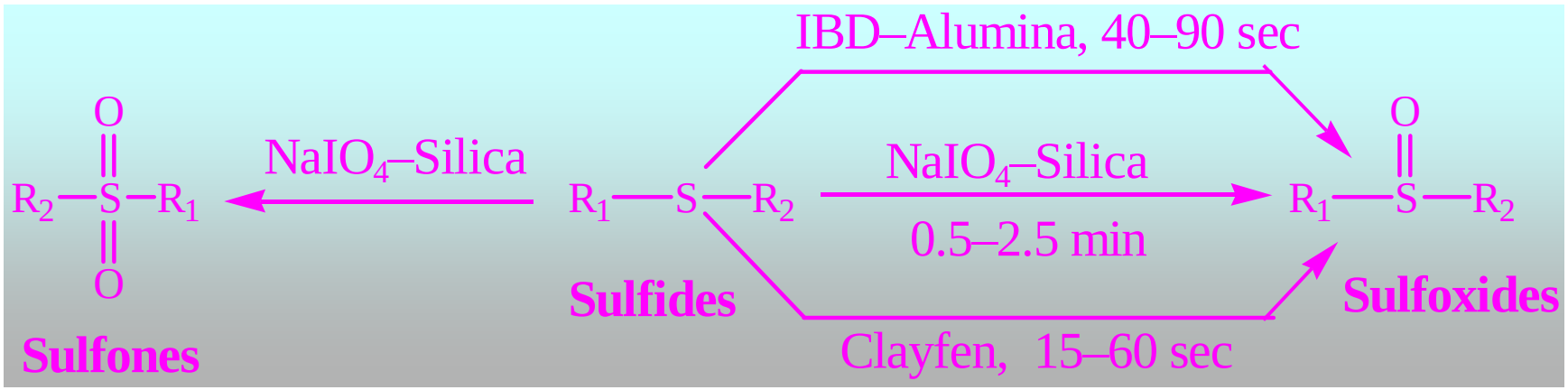


Keywords: 1986-2008, 7 synthetic chemistry journals (domestic and dedicated reactors)
Full Text: 2001-2008, all journals (dedicated reactors only)

Kappe, C. O.; Dallinger, D. *Mol .Diversity* **2009**, *13*, 71

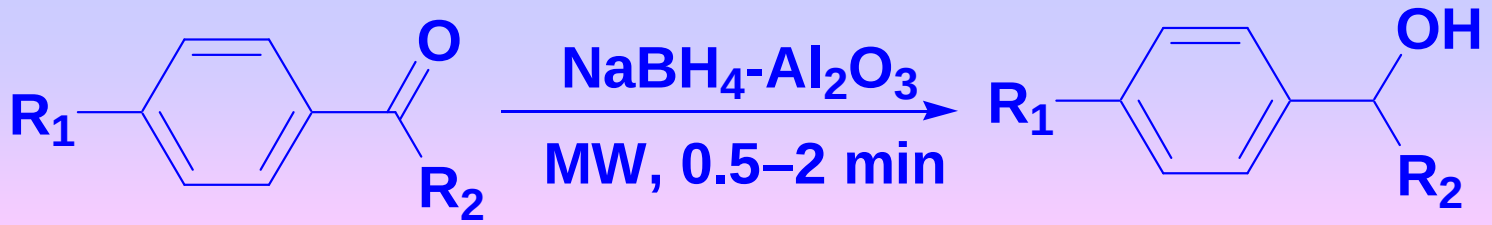
Oxidation Reactions





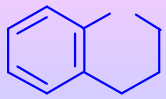
Varma, *Green Chem.*, *1*, 43 (1999)

Solvent-free Reduction Using MW



(62–93%)

Where R_1 = Cl, Me, NO_2 ; R_2 = H ; R_1 = H ; R_2 = Me, C_6H_5

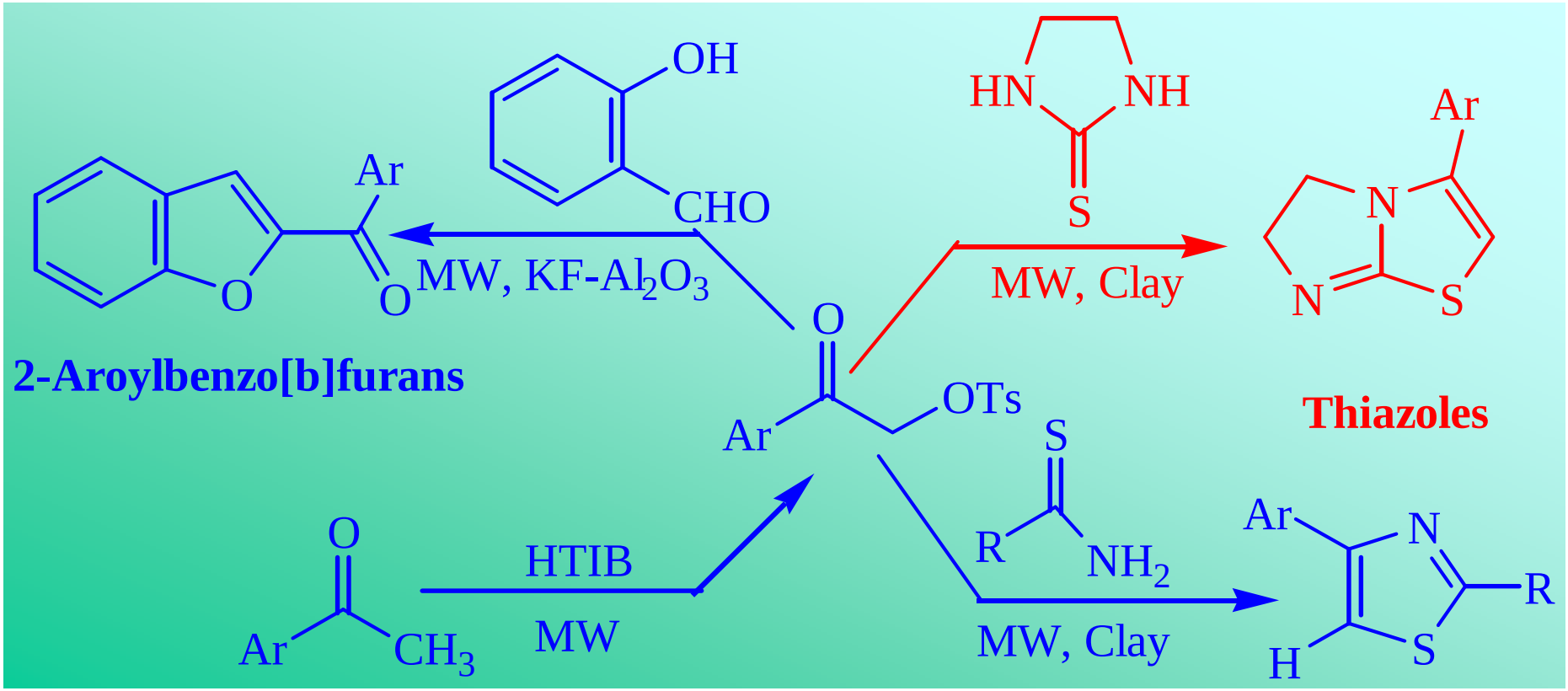
$R_1 = C_6H_5$; $R_2 = C_6H_5CH(OH)$; $R_1 = R_2$ = Me, 

R_1 = *p*-$MeOC_6H_4$; R_2 = *p*-$MeOC_6H_4CH(OH)$

Chemoselective reduction of *trans*-cinnamaldehyde: olefinic moiety remains intact and the aldehyde functionality is reduced in a facile reaction.

Varma *et al.*, *Tetrahedron Lett.*, 1997, *38*, 4337

Synthesis of Heterocyclic Compounds

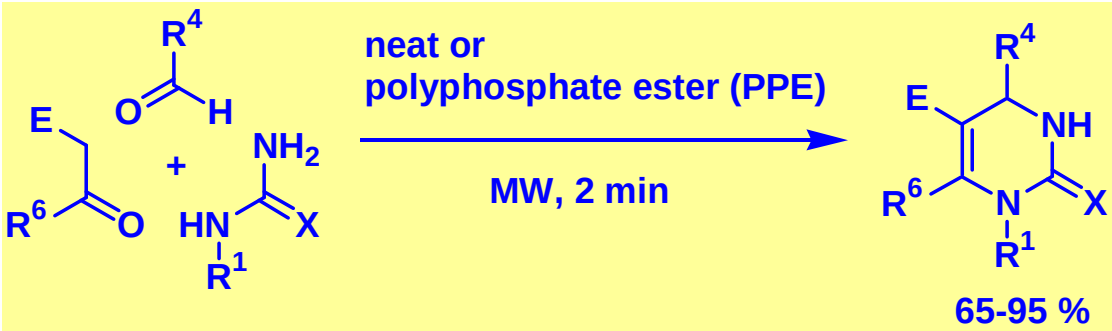


Varma *et al.*: *J. Chem. Soc. Perkin Trans. 1*, 4093 (1998)

Polshettiwar, Varma, *Pure Appl. Chem.*, *80*, 777 (2008)

Early Experiments Using Kitchen Microwaves (1998)

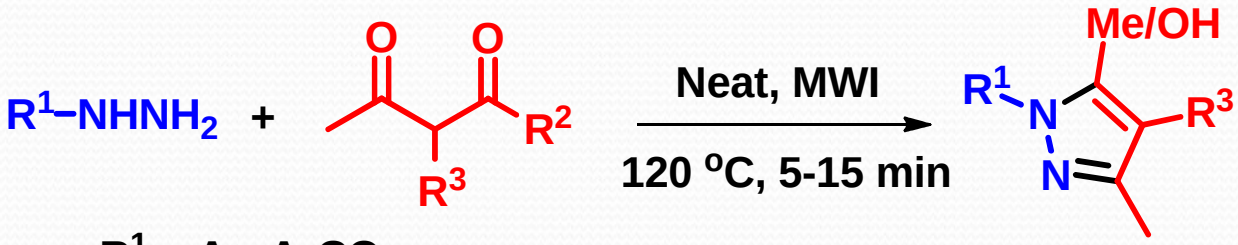
Biginelli Multicomponent Reaction



Kappe, O.; Kumar, D.; Varma, R. S. ***Synthesis*** **1999**, **1799**.

Riding The Microwave *Chemical & Engineering News,* Dec.13, **2004,** 82(50) p14

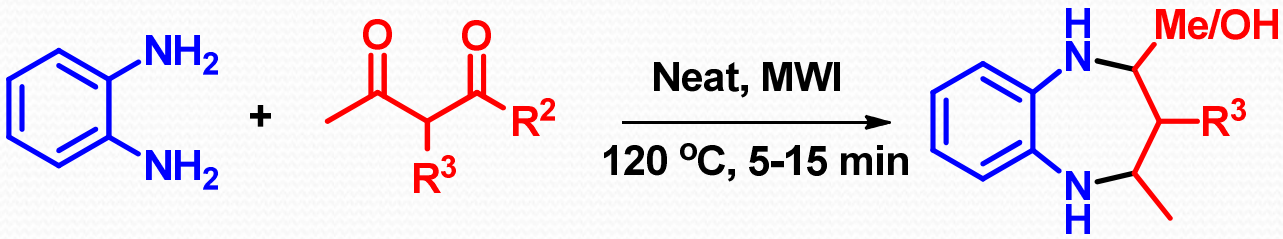
Microwave-assisted synthesis of pyrazoles under catalyst-free conditions



R^1 = Ar, ArCO-
R^2 = Me, OEt
R^3 = H, Cl, Et

% Yields: 95 - 99

Preparation of diazepines under neat conditions using microwaves

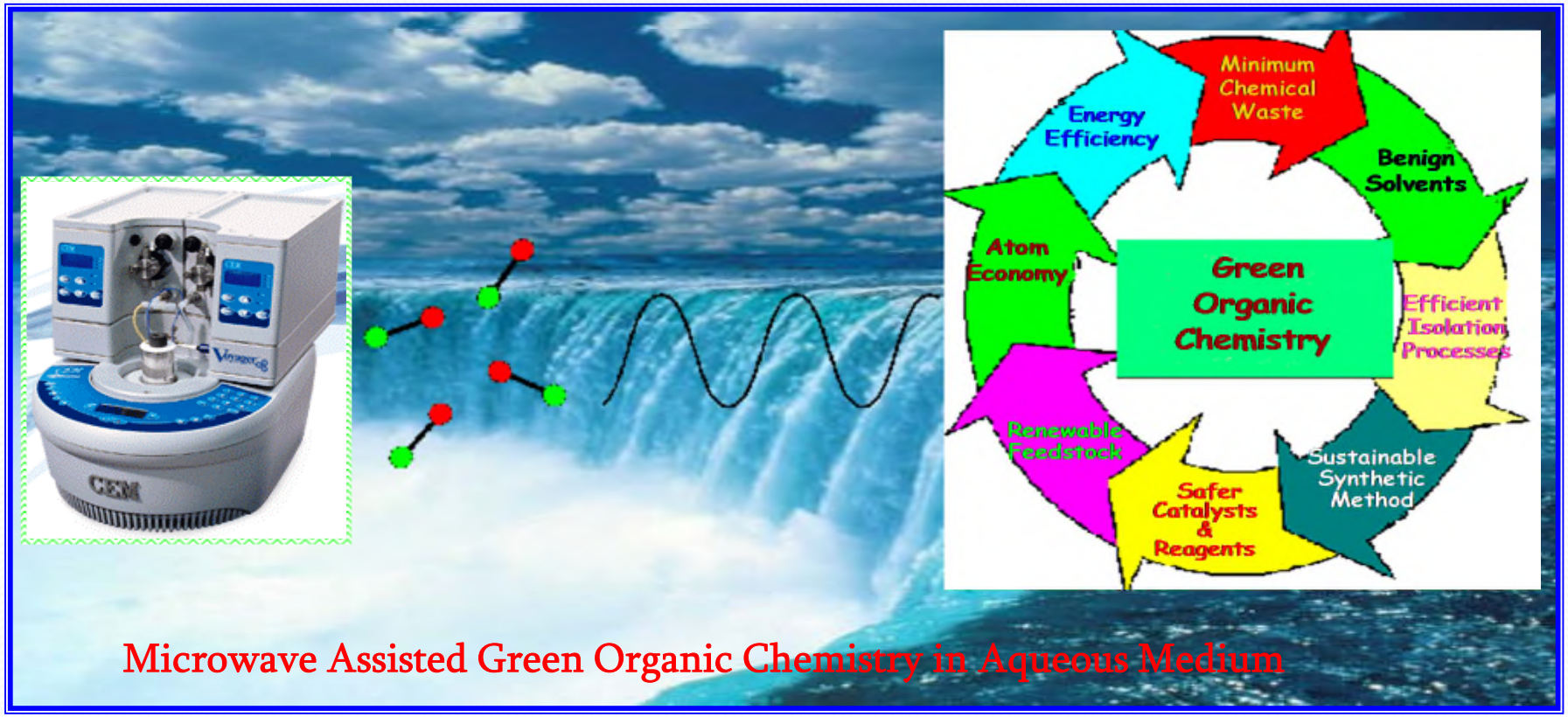


R^2 = Me, OEt
R^3 = H, Cl, Me, Et

% Yields: 93 - 96

Reddy, Varma, Leazer: *Tetrahedron Letters*, *54*, 1538-1541 (2013)

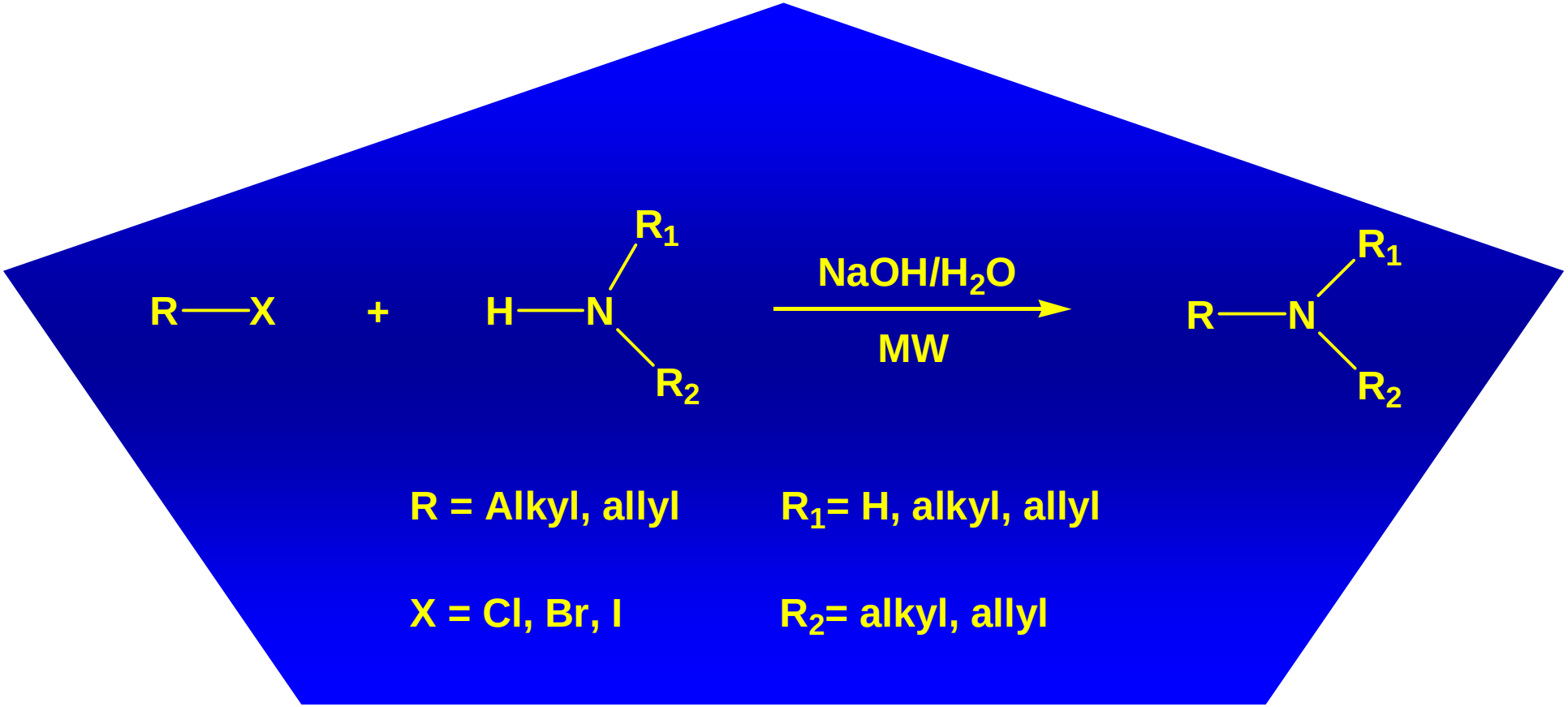
- Sustainable synthesis of chemical entities by microwave heating with nano-catalysis in water
- Green Chemistry principles are accommodated via multi-faceted approach



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

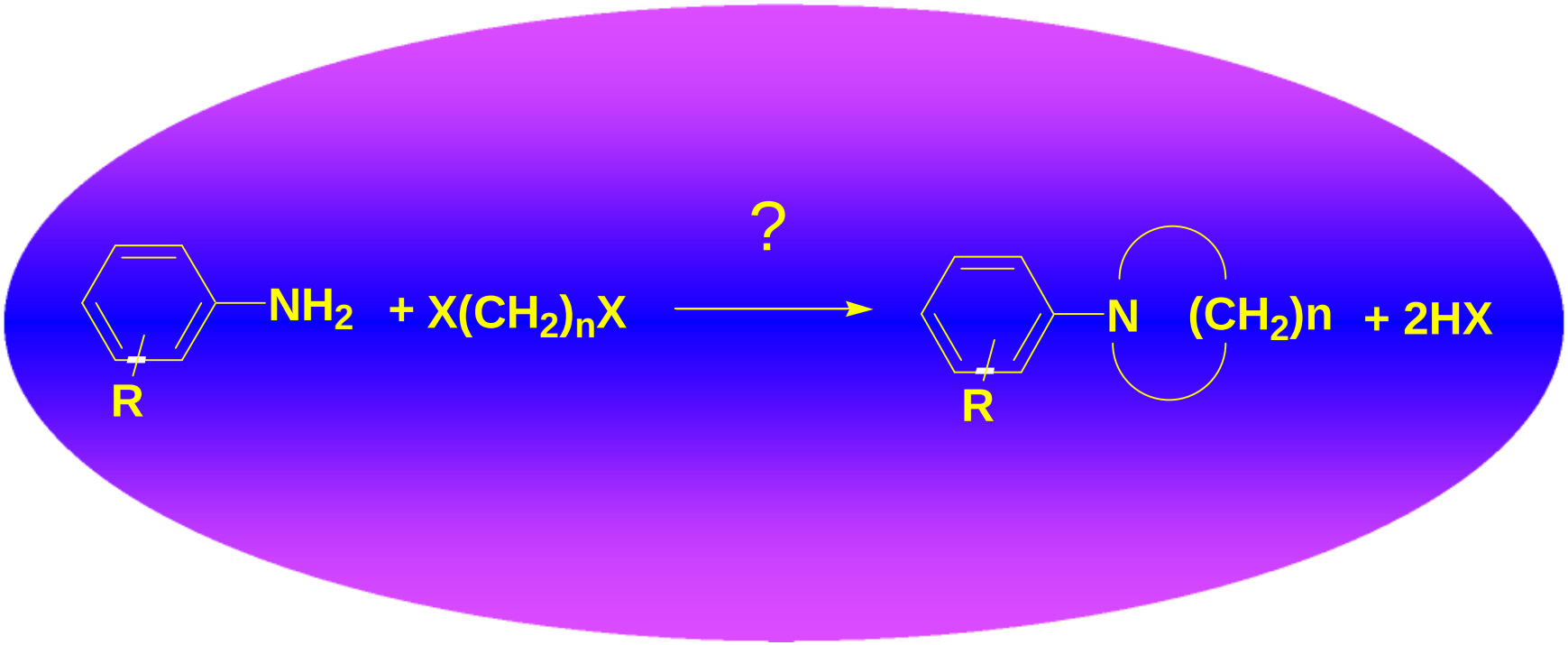
Acc. Chem. Res., 2008, *41*, 629; *Acc. Chem. Res.*, 2011, *44*, 469-478; *Acc. Chem. Res.*, 2014, *47*, 1338-1348
Chem. Soc. Rev., 2008, *37*, 1546-1557; *Chem. Soc. Rev.*, 2012, *41*, 1559-1584.
Pure App. Chem., 2008, *80*, 777-790; *Pure App. Chem.*, 2013, *85*, 1703-1710.
Curr. Opin. Drug Disc., 2007, *10*, 723-737.
Green Chem., 2010, *12*, 743-754; *Green Chem.*, 2014, *16*, 2027-2041.
Coord. Chem. Rev., 291, 68-94 (2015); *Coord. Chem. Rev.* 287, 137-156 (2015).

N-alkylation of Amines using Alkyl Halides

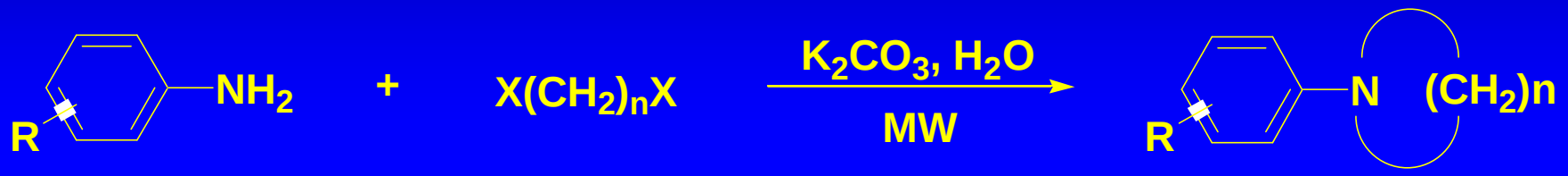


Ju, Y.; Varma, R. S., *Green Chem*. 2004, *6*, 219-221.

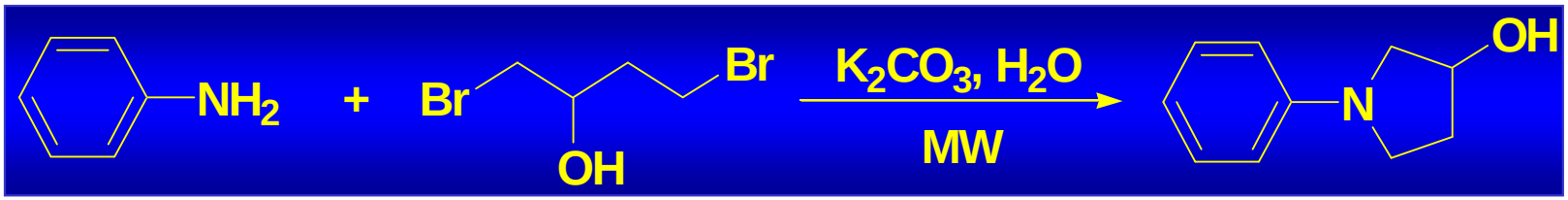
N-Heterocyclization of Aniline Derivatives (double alkylation)



MW Synthesis of *N*-Aryl Azacycloalkanes

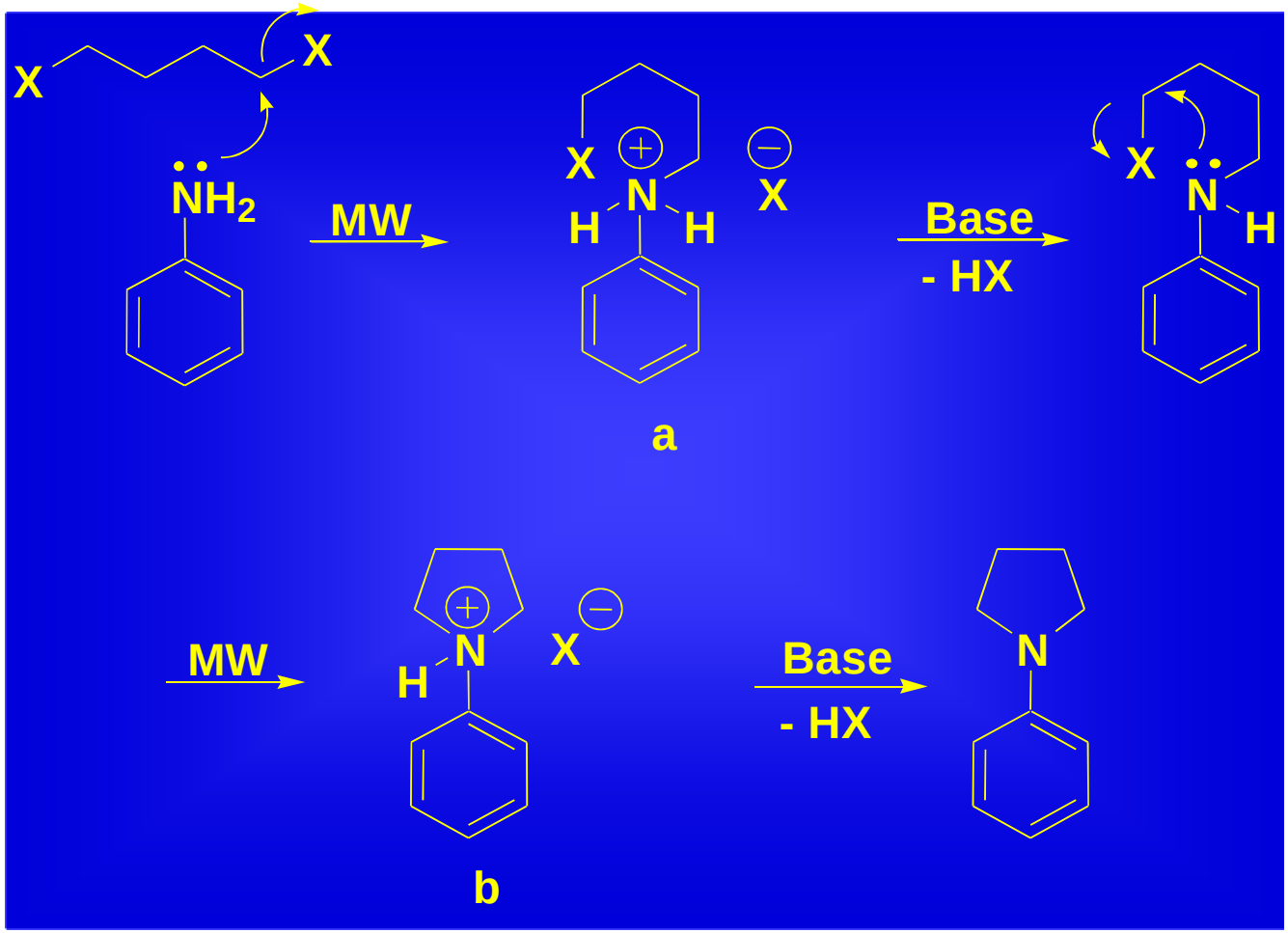


where R = H, CH_3, CH_2CH_3, Br, $COCH_3$, $COOCH_2CH_3$;
X = Br, I, OTs; n = 3, 4, 5, 6



Ju; Varma, *Tetrahedron. Lett.*, 2005, *46*, 6011.
Ju; Varma, *J. Org. Chem.*, 2006, *71*, 135.

Possible Reaction Mechanism



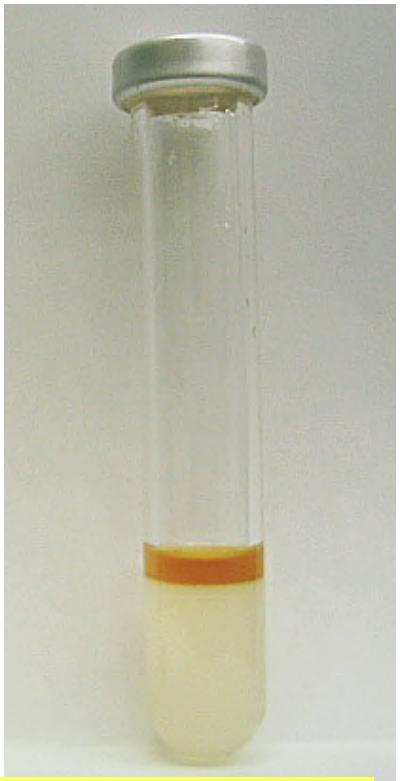
Specific MW effect observed as polarity is increased during the reaction from a neutral ground state to a dipolar transition (more polar) state

Phase separation

Before reaction

MW, 20 min

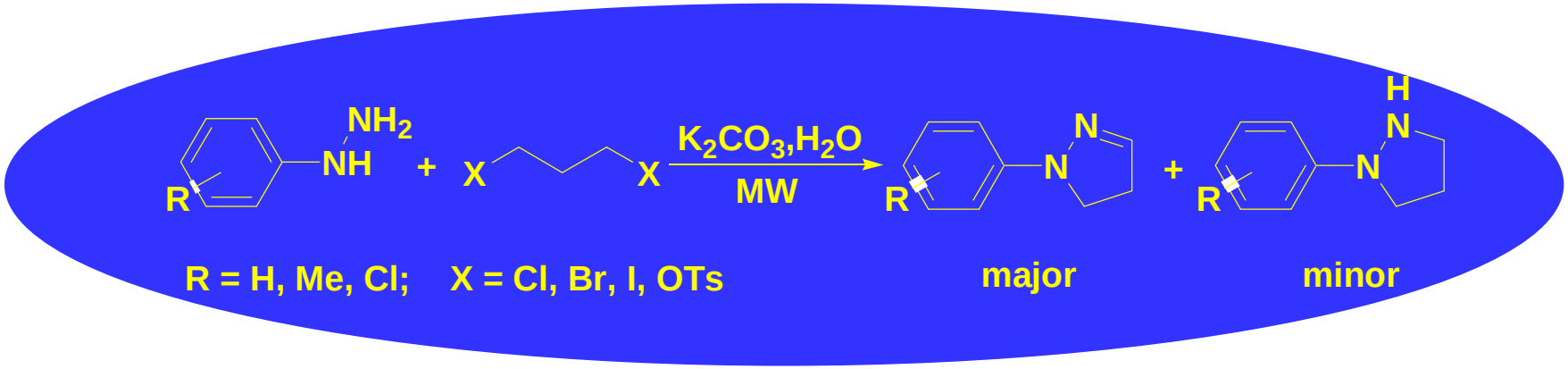
120 ^{o}C, 70-100W

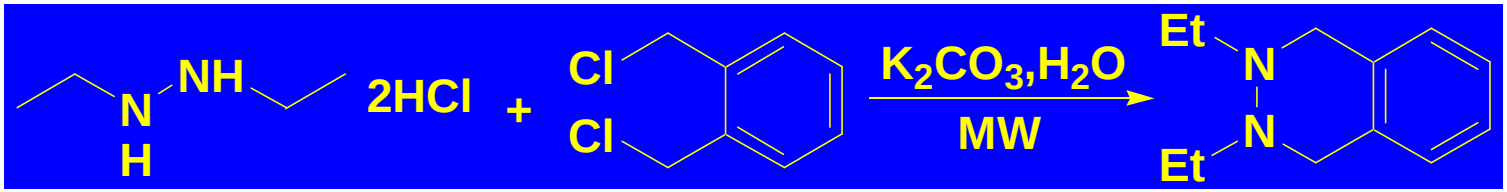


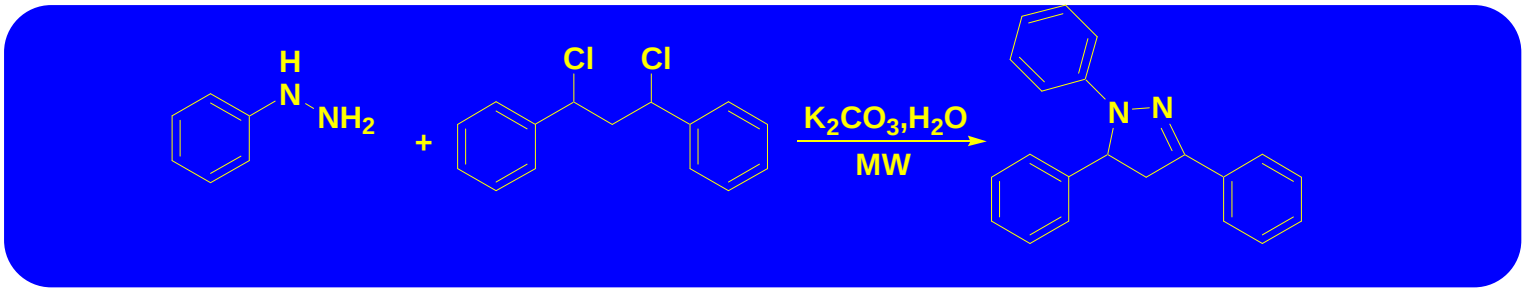
After reaction

Phase separation simplifies the product purification on large scale

Extension of Heterocyclization Reaction



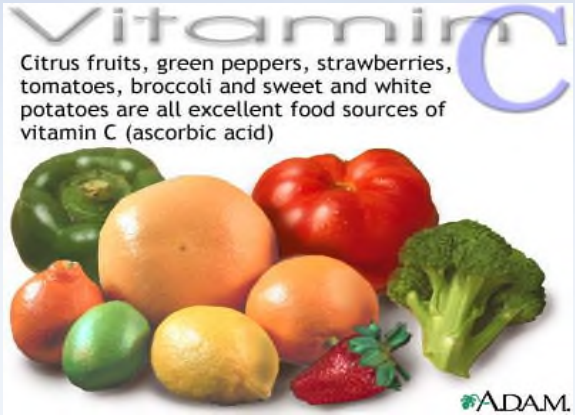




Ju, Y.; Varma, R. S. *Tetrahedron. Lett.* 2005, *46*, 6011.
Ju, Y.; Varma, R. S. *J. Org. Chem.* 2006, *71*, 135.

Plant Extract

Sugar



Vitamins

Tea

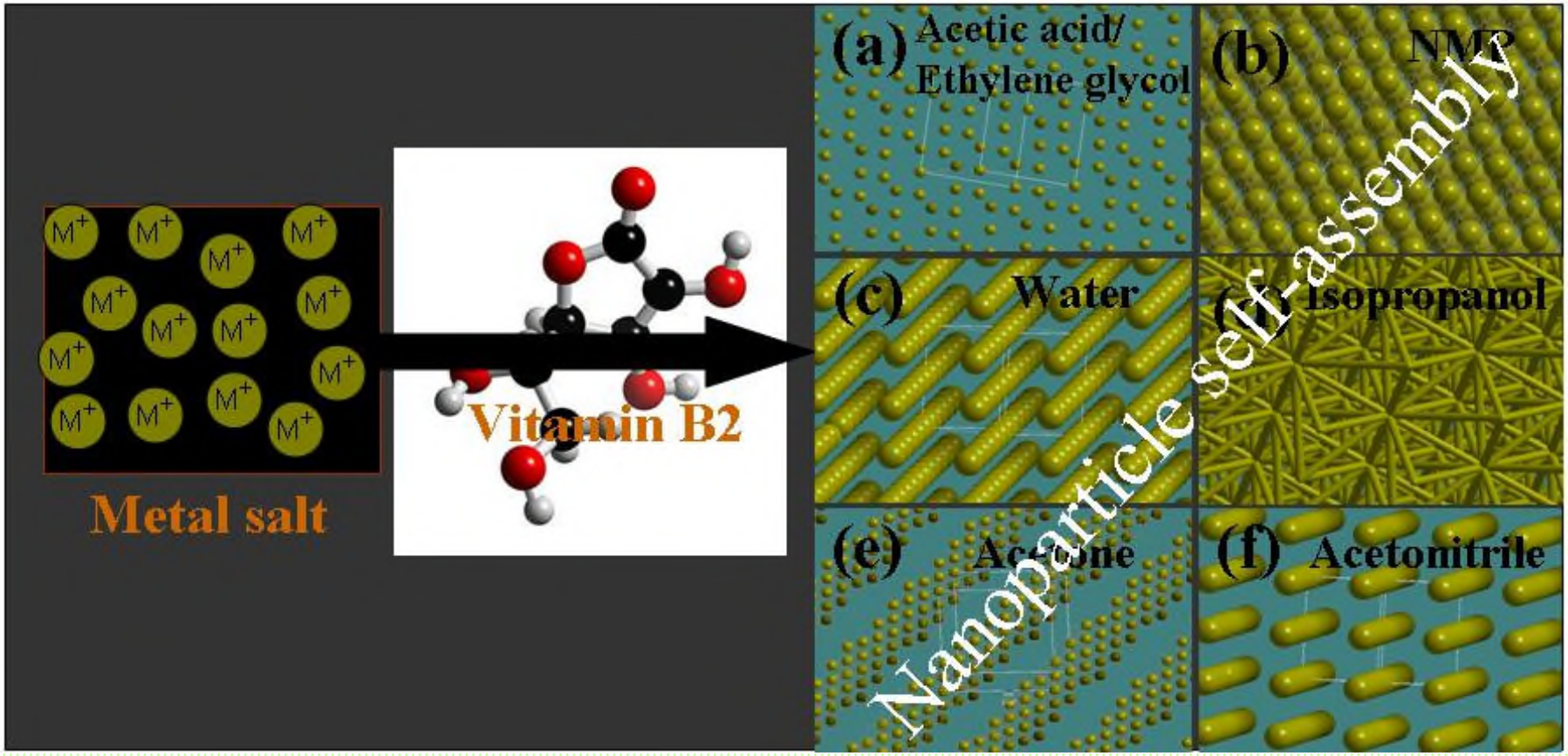
Wine

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



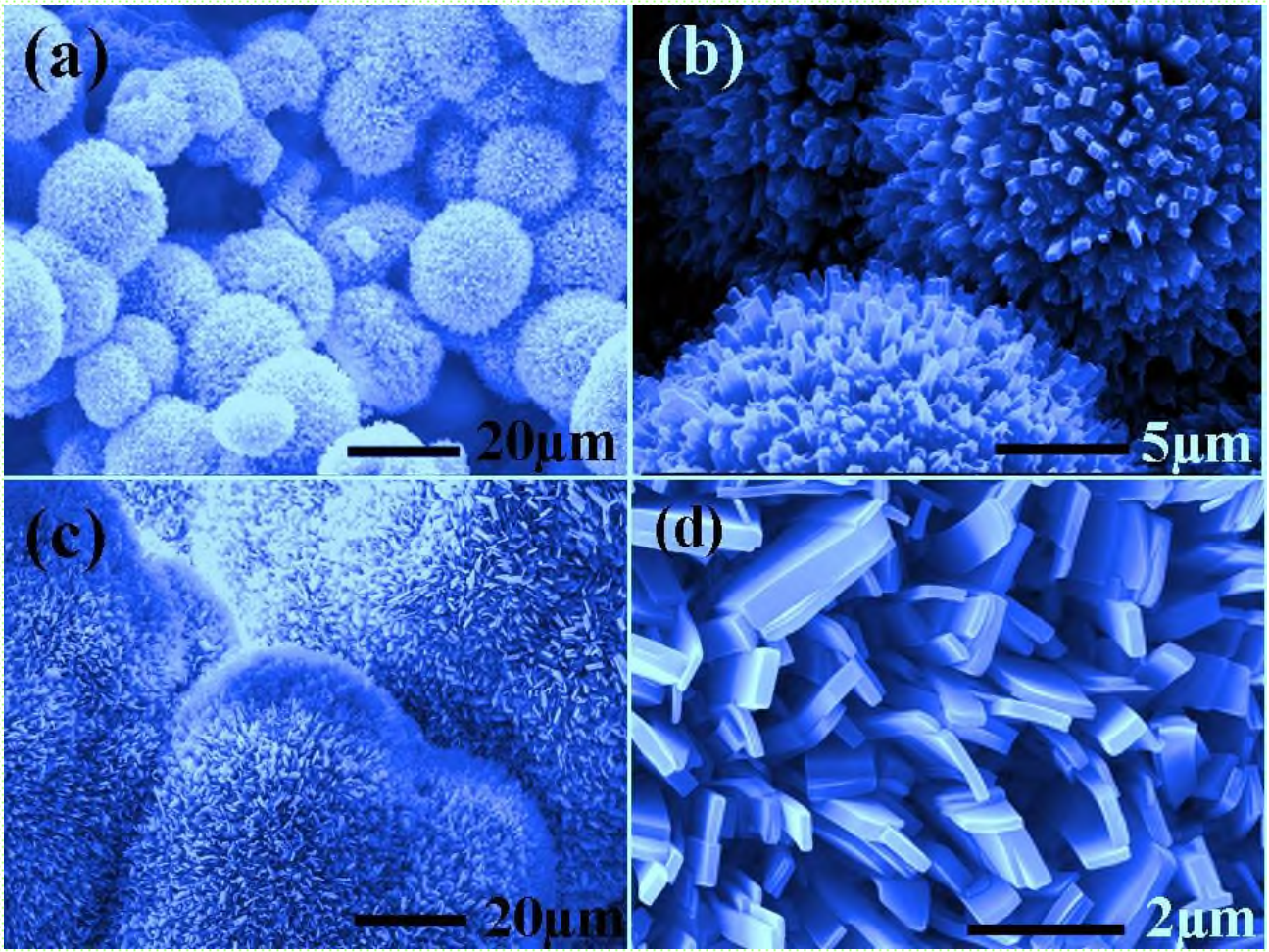
Nadagouda & Varma: *Green Chemistry*, *8*, 516, (2006)

Green Synthesis of Nanomaterials

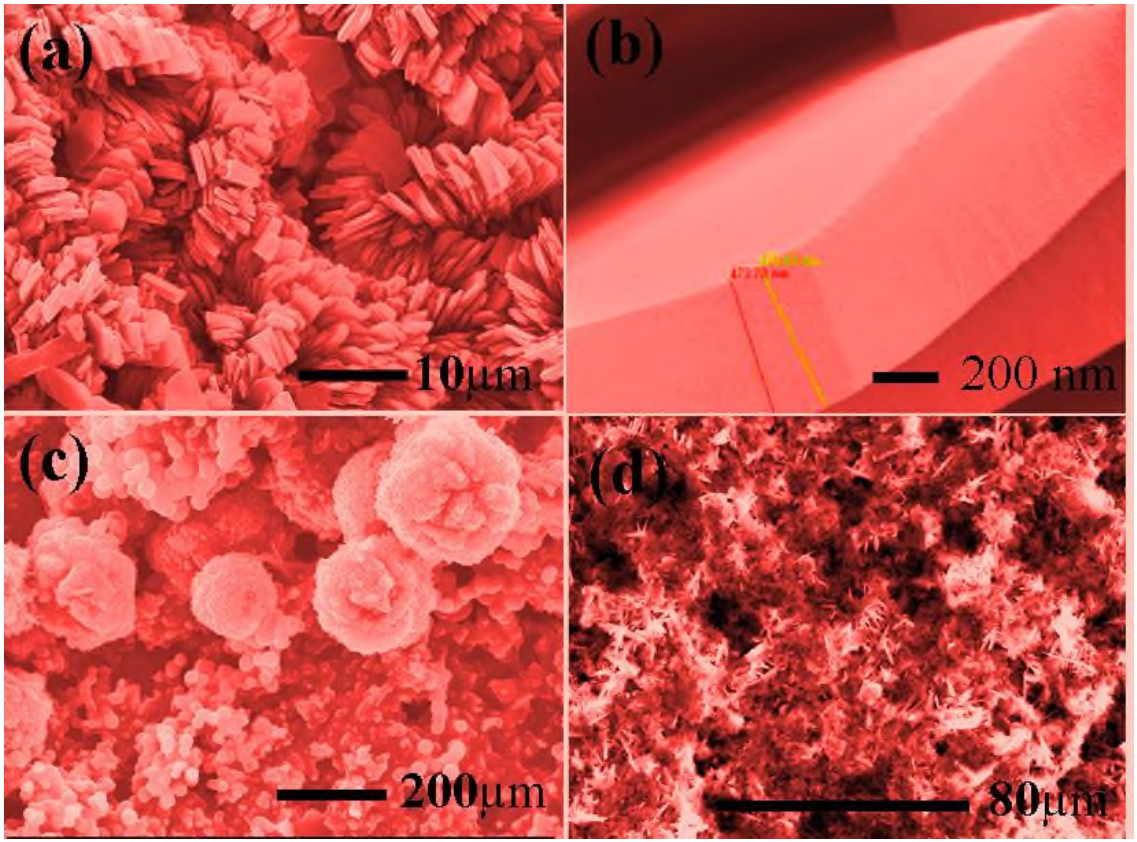
PROBLEM: Synthesize nanomaterials in a sustainable manner.

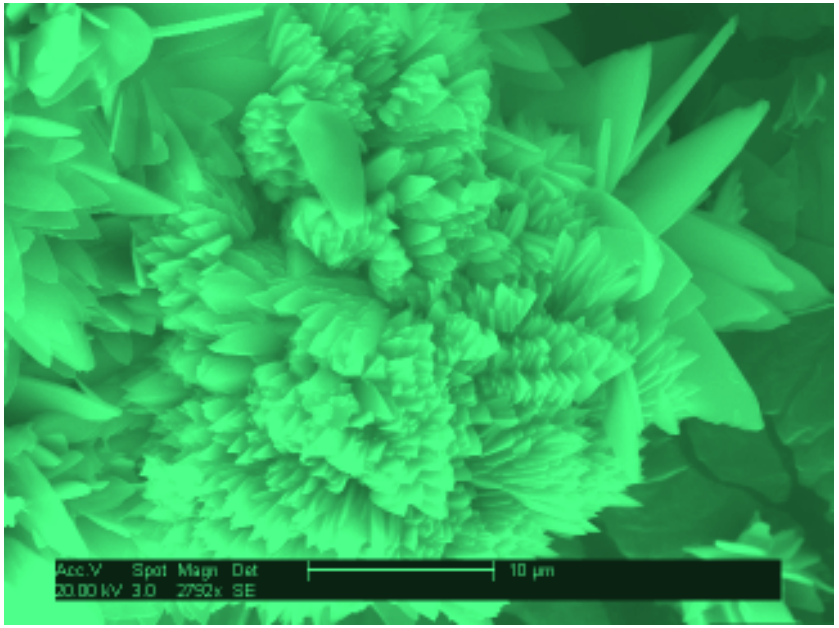
TECHNOLOGY SOLUTION: *Learning from Nature*- Use Vitamin B_1 in water to do the reduction and capping.

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)

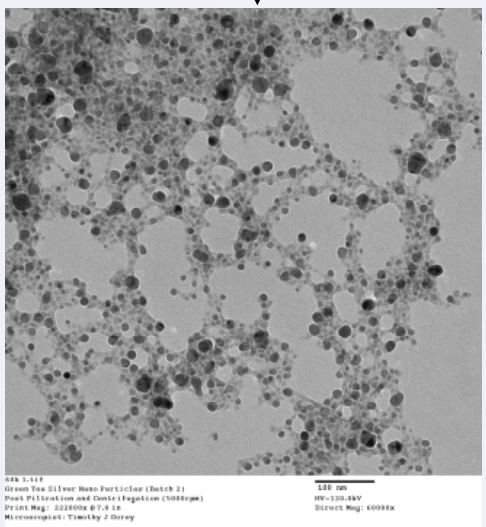
Tea for producing metal nanoparticles

Metal salt +

= Metal nanoparticle

(Ag, Au, Pd, Fe etc.)

Ag nanoparticle using green tea

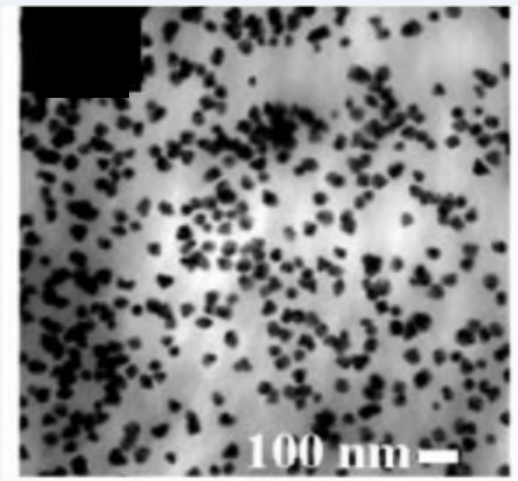


All particles are obtained at Room Temp.

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

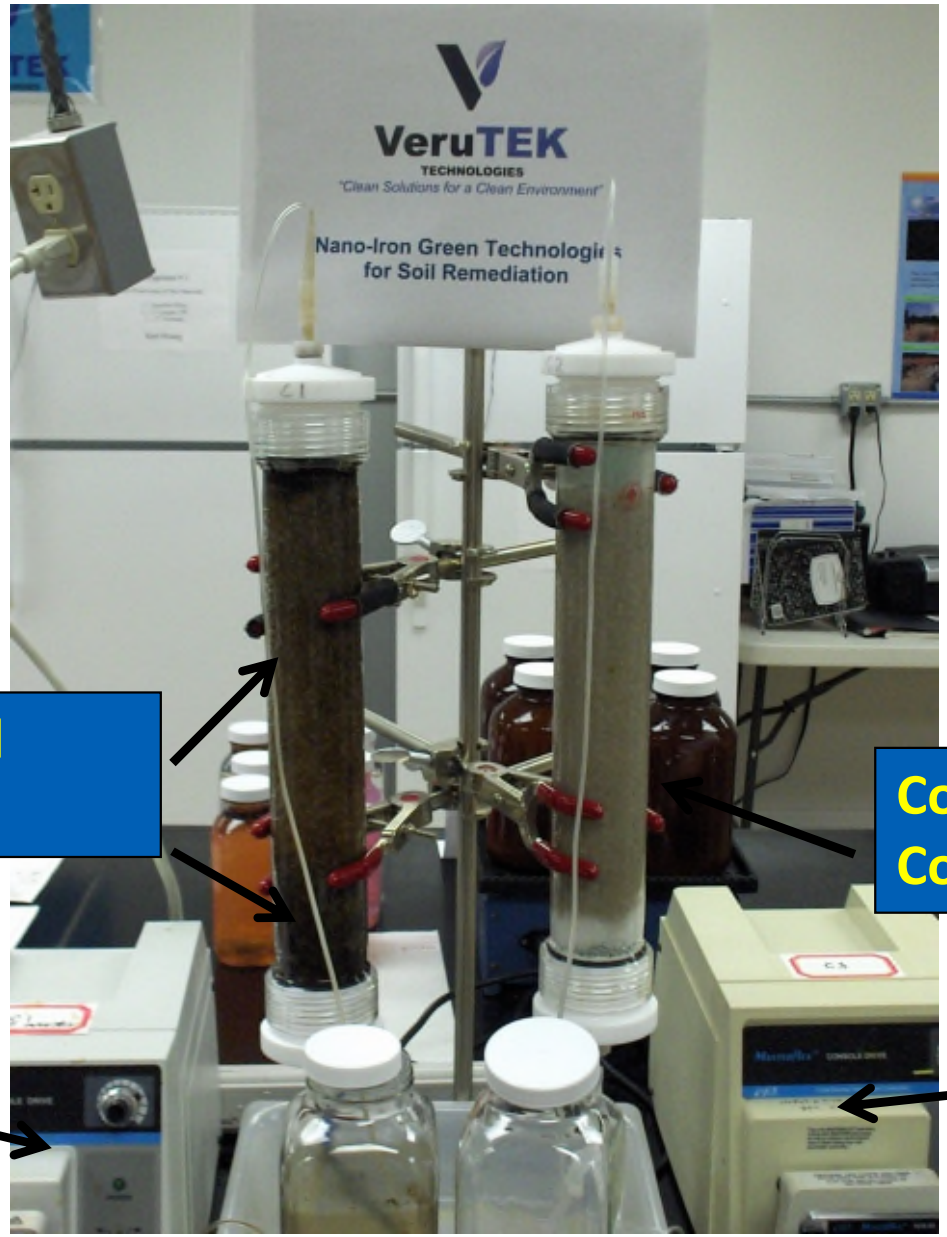
(*U S Patents*, 7,963,720, June 21, 2011; 8,057,682 B2, Nov. 15, 2011)

Pd nanoparticle using green tea



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

In Situ Formation of Iron Nanoparticle in Soils with Lemon Balm Extract and $Fe(NO_3)_3$



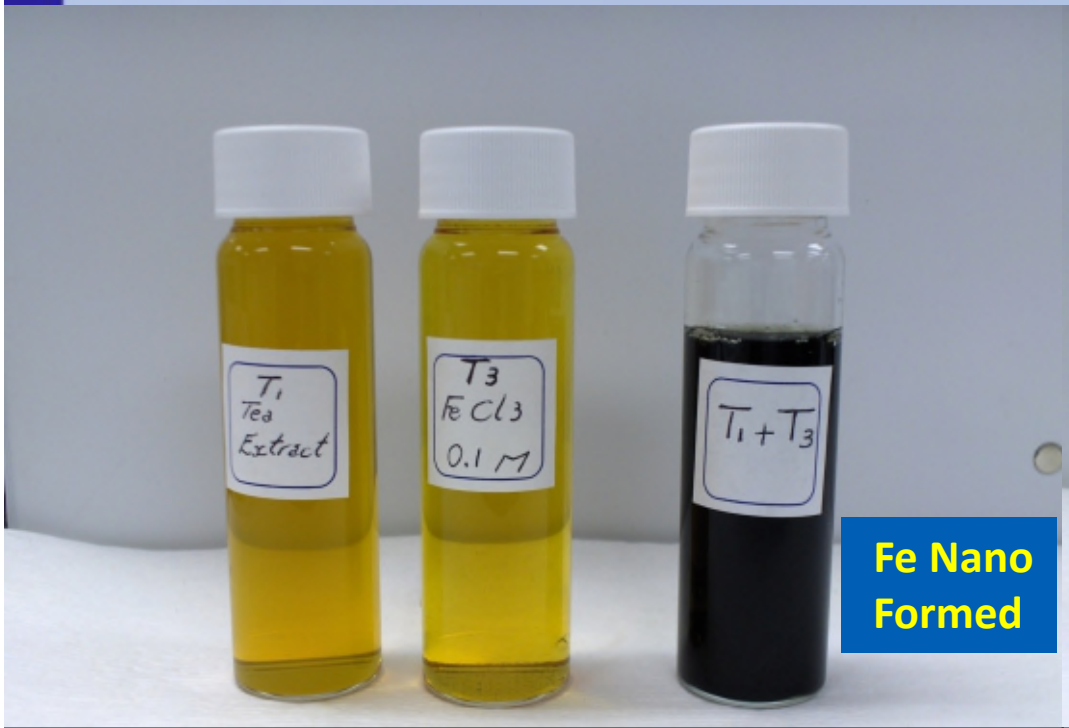
nZVI Formation in Soil Column

Control Column

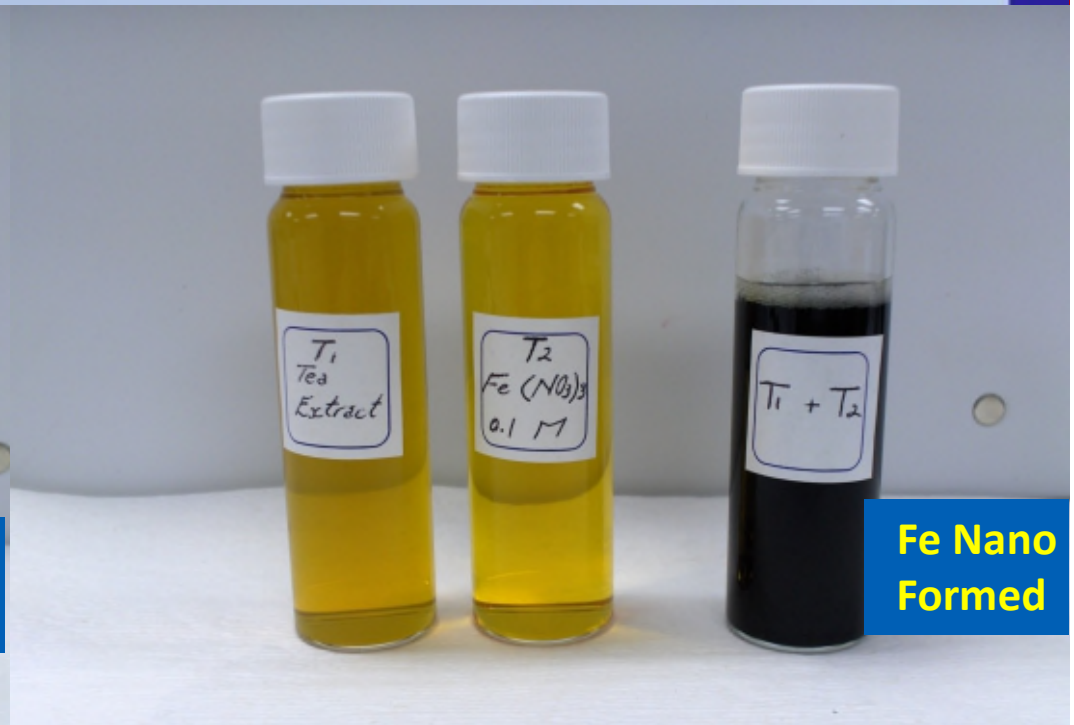
Lemon Balm Extract Feed Pump

$Fe(NO_3)_3$ Feed Pump

Manufacture of Nanoscale Iron Particles with Ferric Chloride and Ferric Nitrate using Green Tea



Formation of Nanoscale Iron
Green Tea Extract with Ferric Chloride



Formation of Nanoscale Iron
Green Tea Extract with Ferric Nitrate

Notes: Green Tea extract made by heating a 20 g/L solution of Dry Chumnee Tea for 20 minutes at 90 °C then filtering with paper filter.
Green Tea extract added to 0.1 M Ferric solutions on a 1:2 (v/v) basis.

Copyright VeruTEK 2011

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

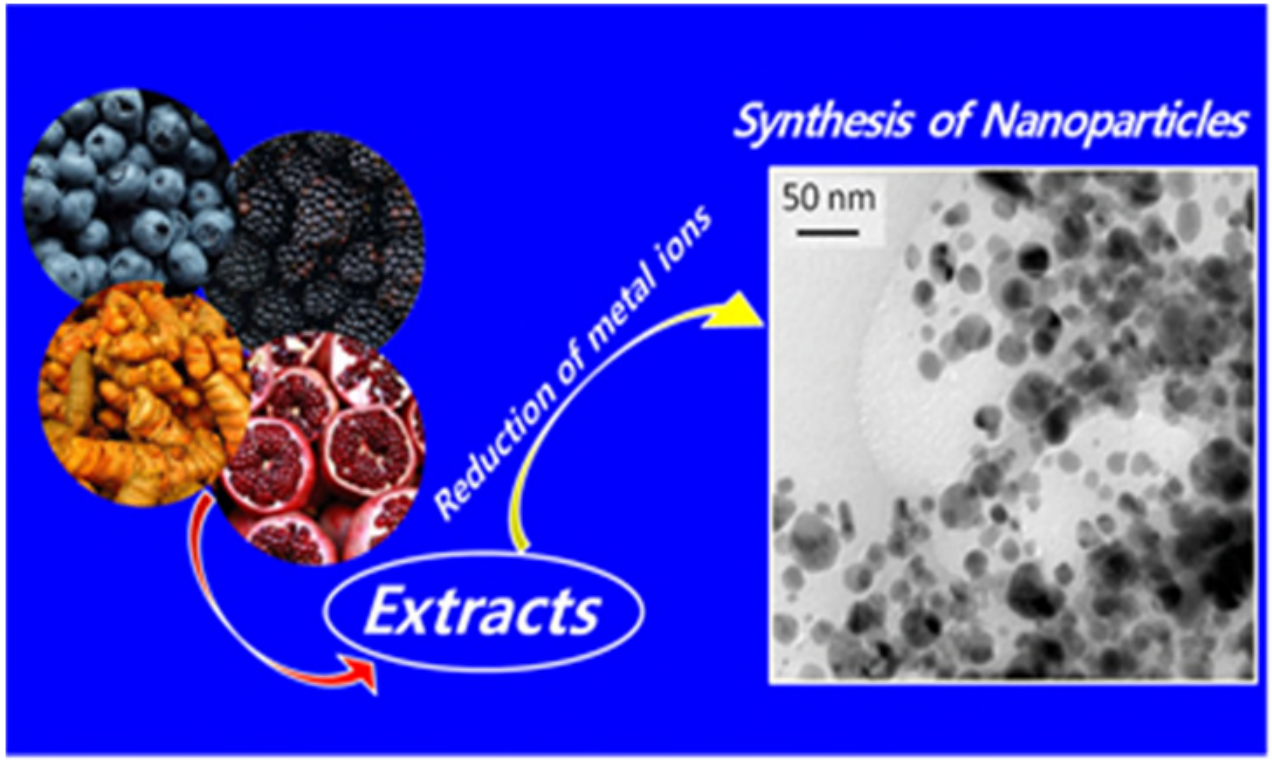
Several U.S. and Worldwide Patent Applications filed in 2008 -2010.

(*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

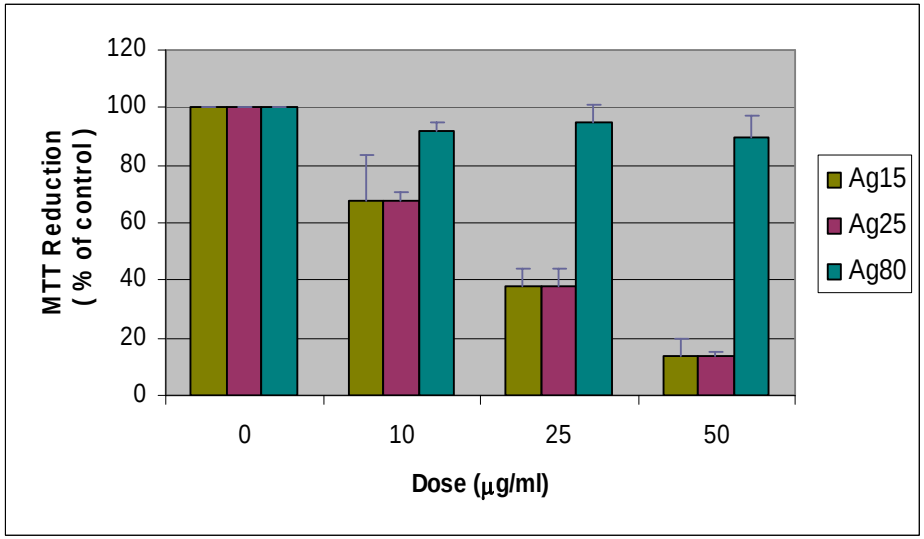
Greener synthesis of Ag and Au nanoparticles is described using antioxidants from blackberry, blueberry, pomegranate, and turmeric extracts; waste from fruit and juice industry can be utilized.



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

Toxicity of Silver NP in Mouse Keratinocytes: MTS Assay Viability

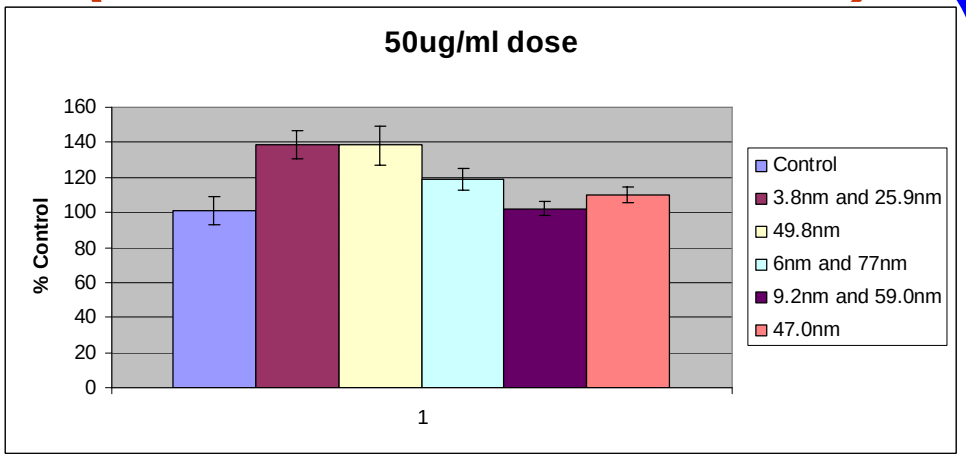
(Uncoated Silver)

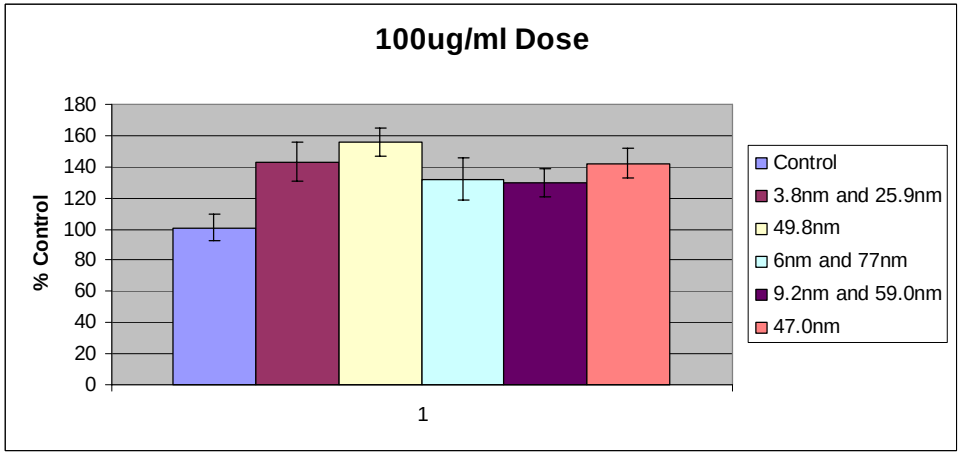


Collaboration with Dr. Saber Hussain, Air Force Research Laboratory, Dayton, Ohio

***Nanoscale*, 2, 763(2010)**

(Silver with Tea Extract)





***MTS measures mitochondrial function**

Dextron Templated Microwave-Assisted Synthesis of Porous Titanium Dioxide

- **The synthesis of carbon coated titania as well as spongy kind of titania by microwave combustion method**

- **The process is very simple and eco-friendly protocol which utilizes renewable polymer dextrose to create spongy kind of materials.**

Nadagouda & Varma: *J. Smart Materials and Structures*, *15*, 1260 (2006)

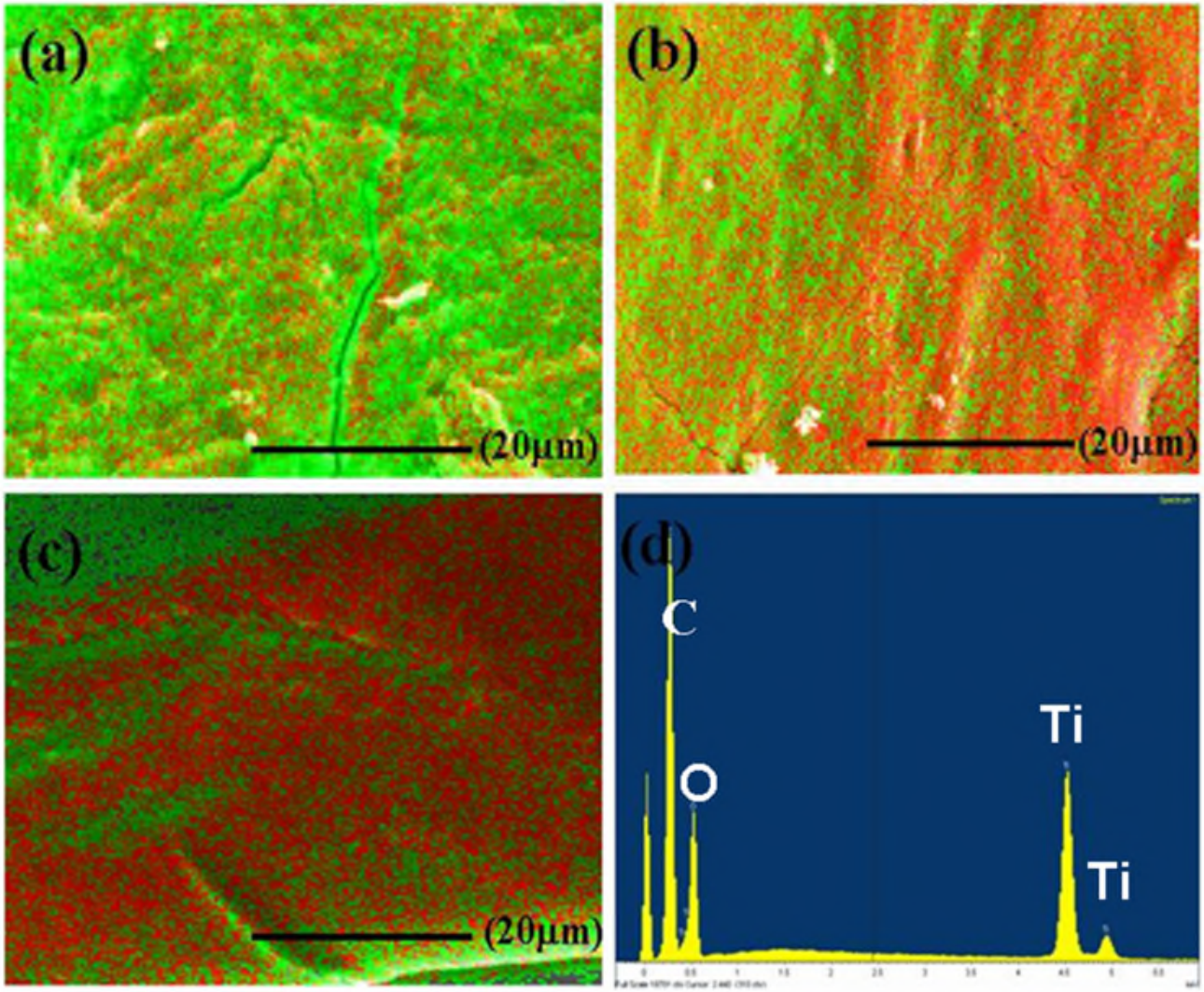
Objective

An alternative route to the preparation and formation of porous titania powders and carbon coated titania using microwave irradiation

☞ **Dextrose was used as a capping agent or a template for the following reasons:**

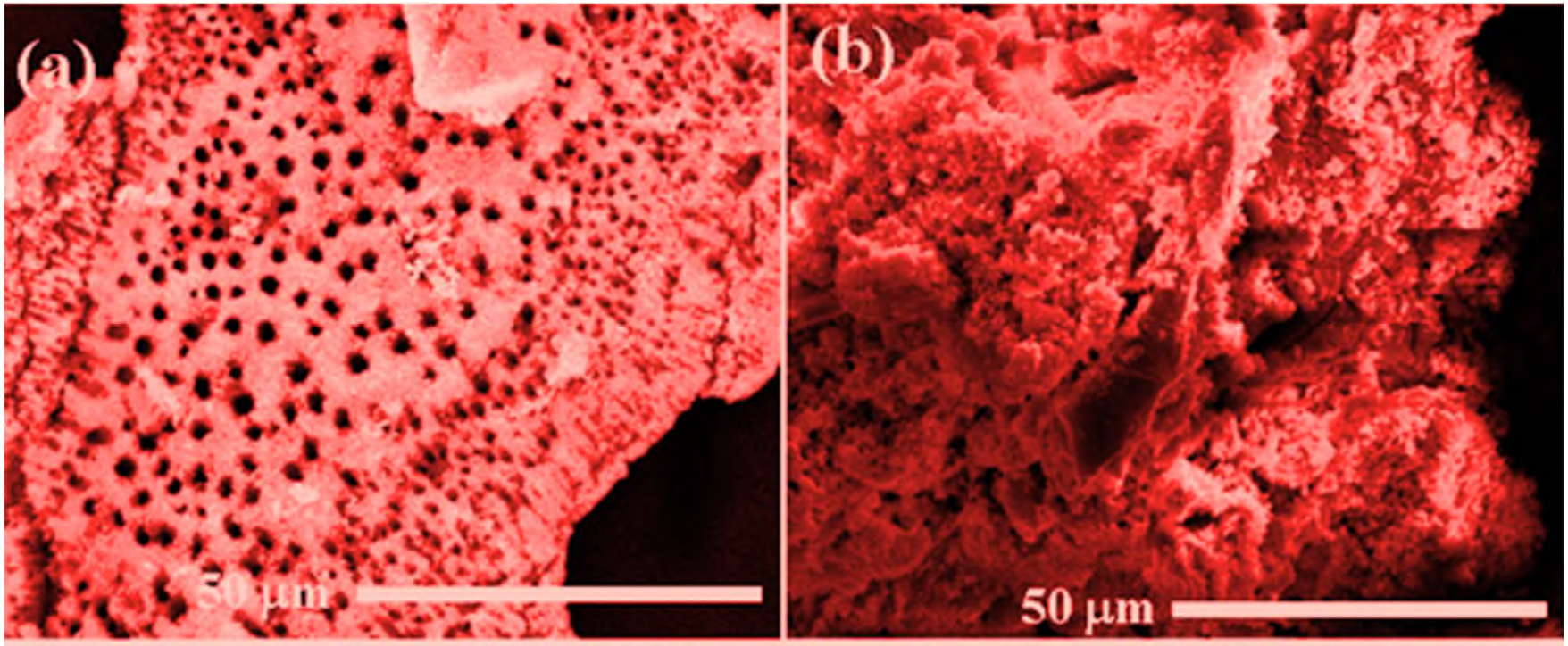
- High water solubility when compared to other sugar templates or capping agents
- Combustible material at low temperature
- Inexpensive material

Nadagouda & Varma: *J. Smart Materials and Structures*, *15*, 1260 (2006)



(a-c) X-ray mapping images of 1:1, 1:3 and 1:5 (titania: dextrose molar ratio) carbon coated titania synthesized using MW combustion synthesis.
Green region shows titania and red region shows carbon

Nadagouda & Varma: *J. Smart Materials and Structures*, *15*, 1260 (2006)



SEM images of ZrO_2 synthesized using:

(a) MW-initiated followed by conventional heat treatment at 850 ^{0}C for 1 h and (b) Only conventional heating furnace at 850 ^{0}C for 1 h

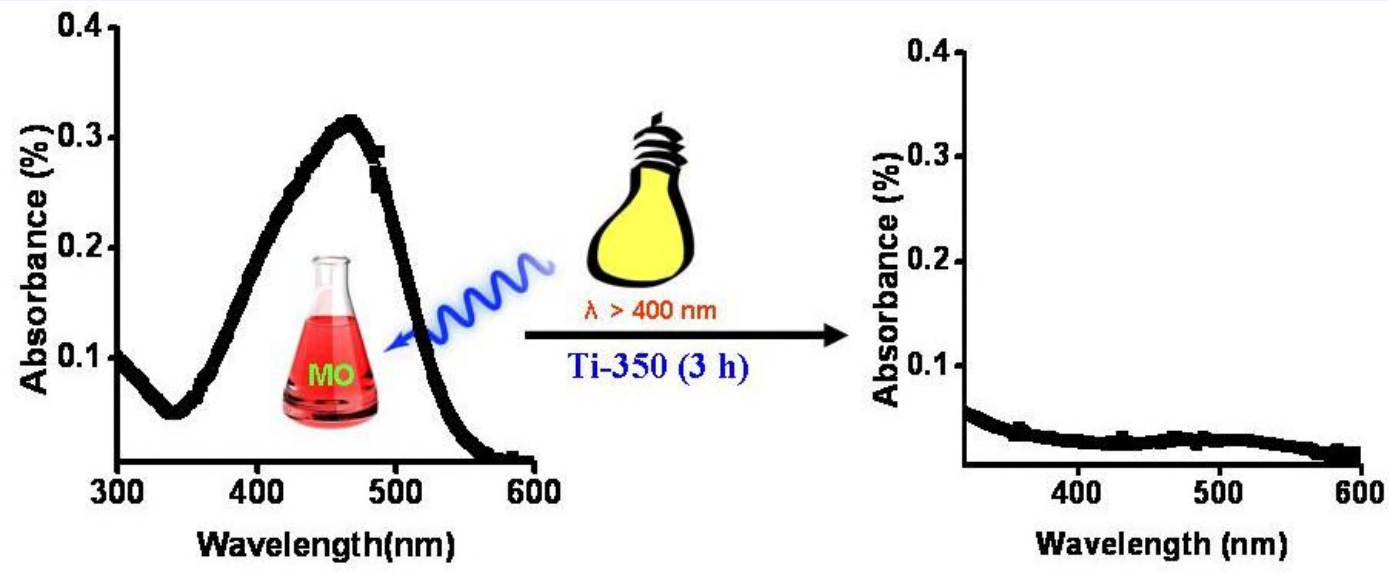
Nadagouda & Varma: *J. Smart Materials and Structures*, *15*, 1260 (2006)

US Patent 8791044, July 29, 2014

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



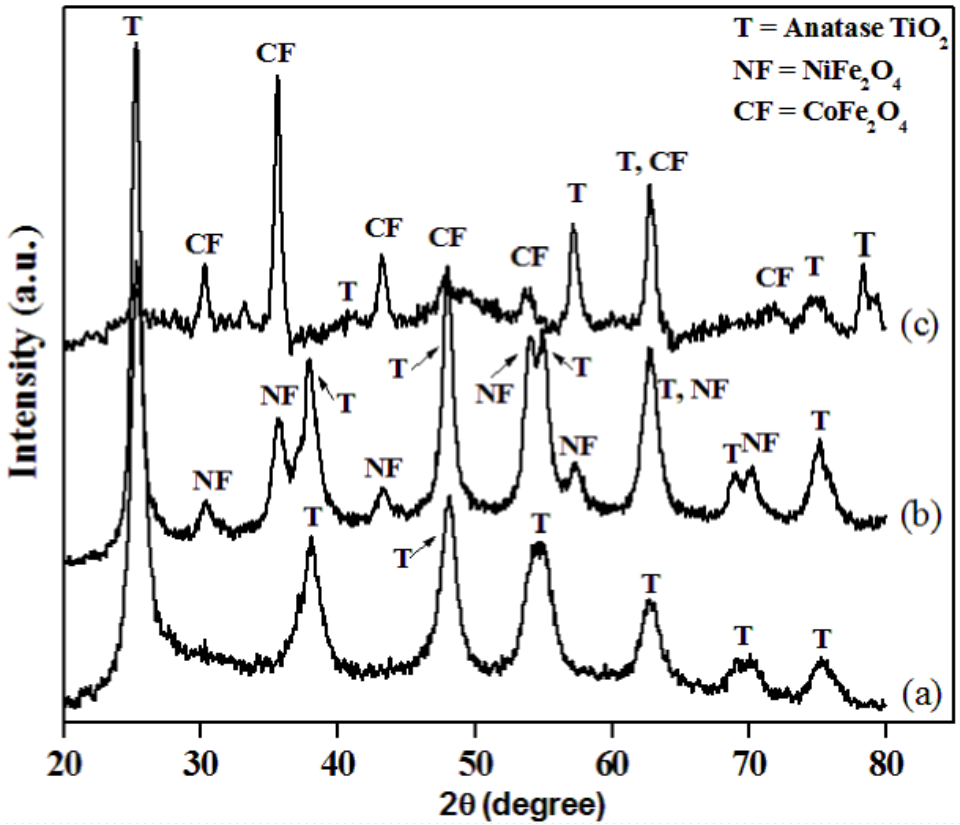
B. Baruwati, R. S. Varma, *J. Nanosci. Nanotech.*, *11*, 2036 (2010)

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)

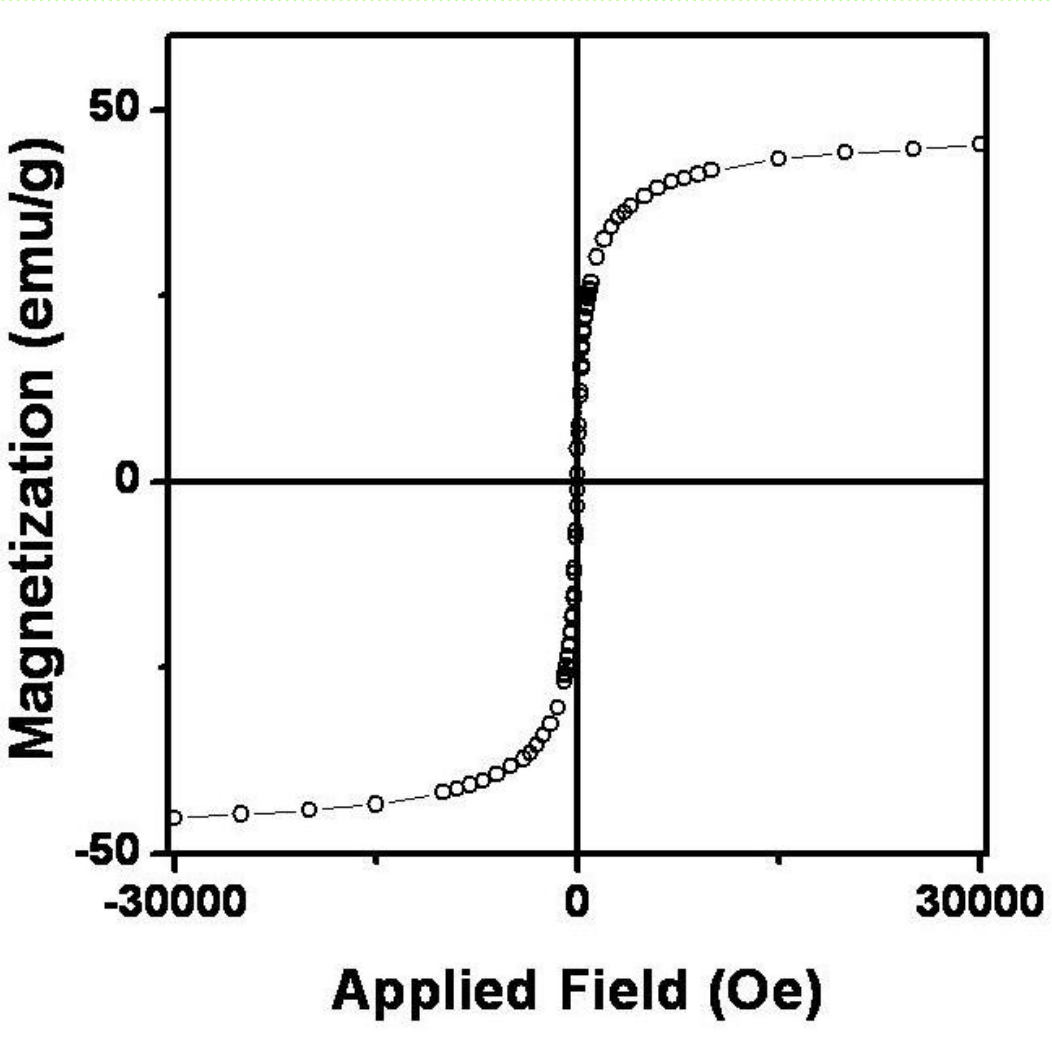
Doped TiO_2 Magnetically Separable Nano-catalysts



Material	d_p [a] (nm)	A_{BET} [b] ($m^2 g^{-1}$)	V_p [c] ($cm^3 g^{-1}$)
TiO_2 P25 (Aeroxide® P25)	21	50	0.30
TiO_2-G	5.0	280	0.35
TiO_2-G-$NiFe_2O_4$	4.9	217	0.30
TiO_2-G-$NiFe_2O_4$	5.8	200	0.31

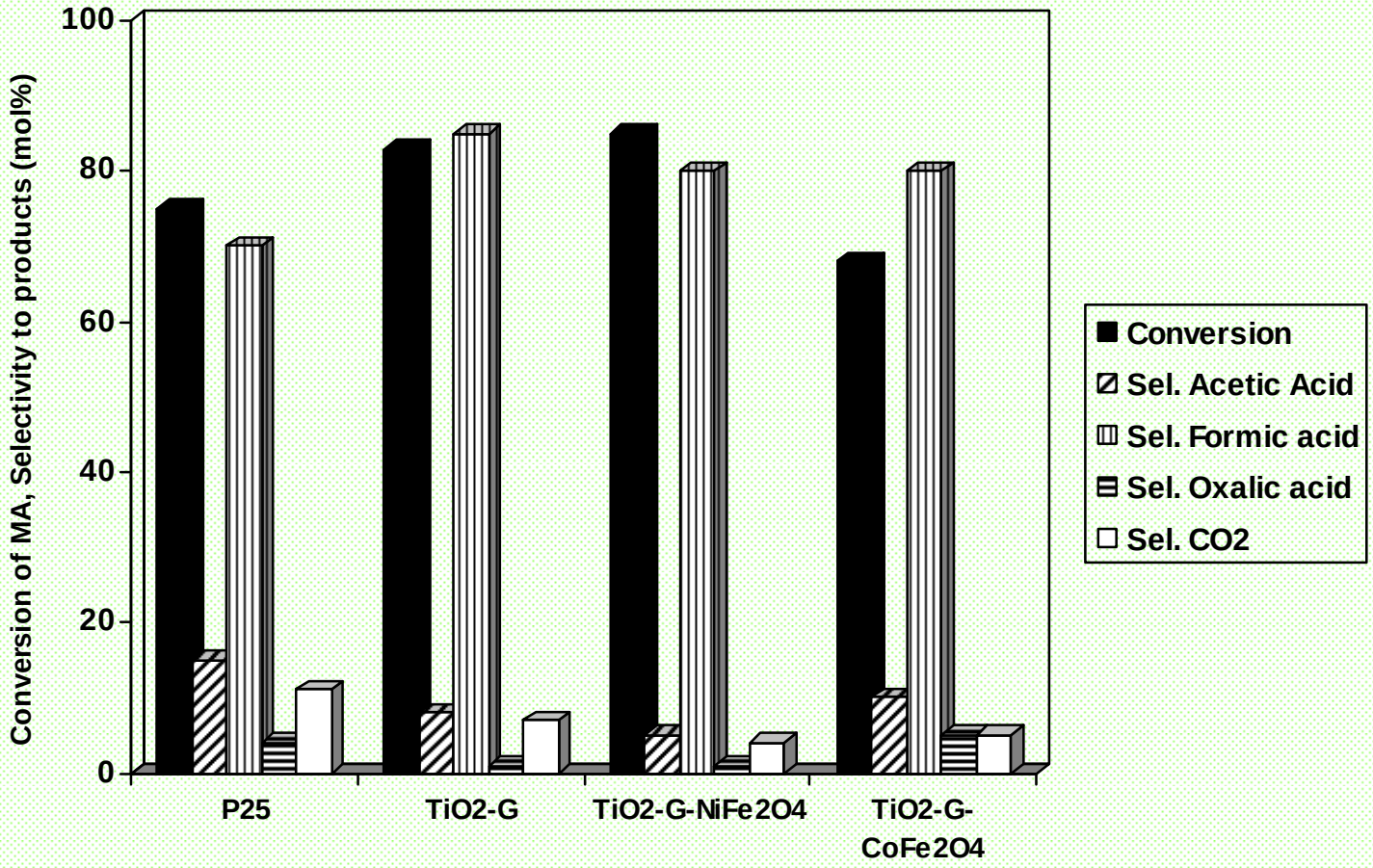
Baruwati, Luque, Varma et al.: *Green Chem.*, *13*, 2750 (2011)

Magnetic Properties of the TiO_2-G-($Ni,CoFe_2O_4$)



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

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

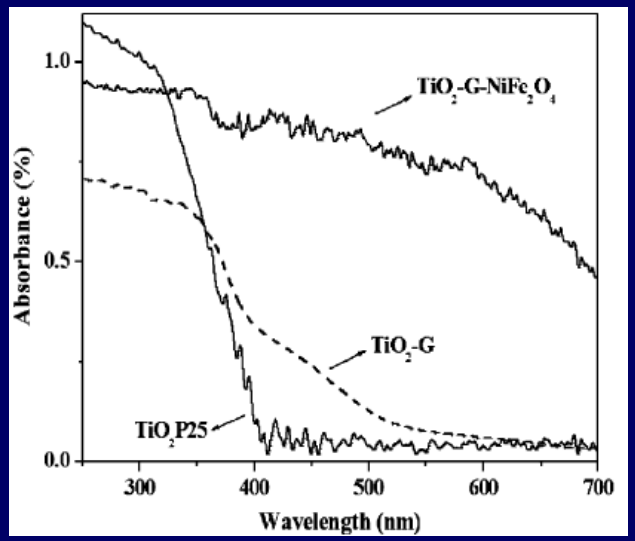


Baruwati, Luque, Varma et al.: *Green Chem.*, *13*, 2750 (2011)

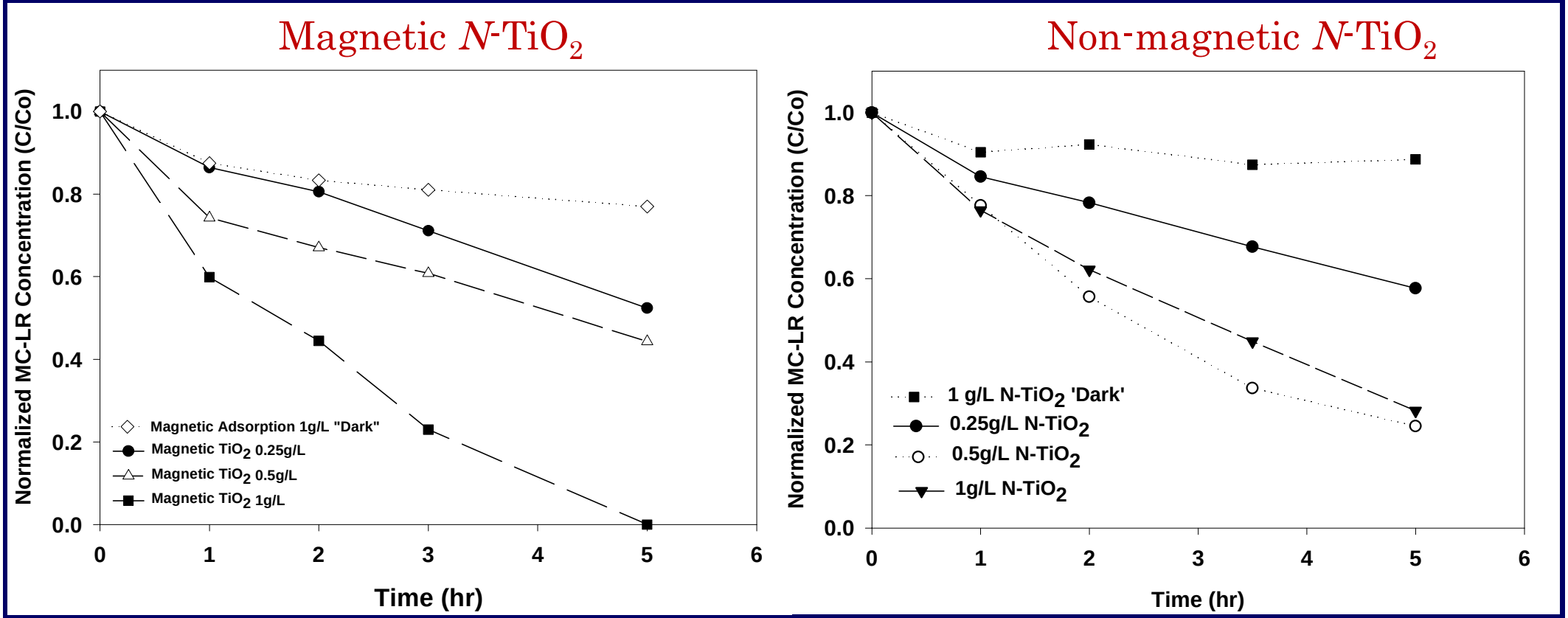
Microcystin-LR removal using Magnetically separable N-doped TiO_2

** 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)

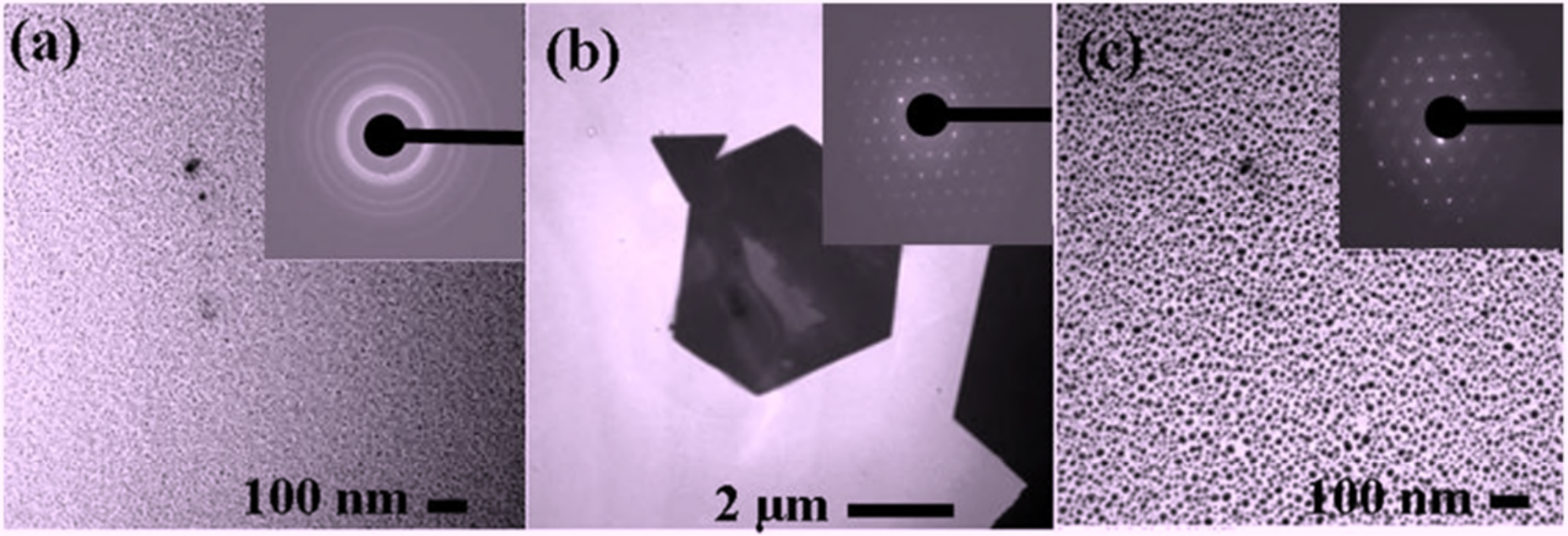
Microwave-Assisted Reactions Using Sugar Solutions

Noble salt (0.1 M) + Sugar $\xrightarrow[\text{30-40 sec}]{\text{MW}}$ Noble Nanostructures

Examples : Sucrose, Maltose, glucose etc.

Nadagouda & Varma: *International Microwave Power Institute Symposium Proceedings*, Boston, pp 217-219 (2006).

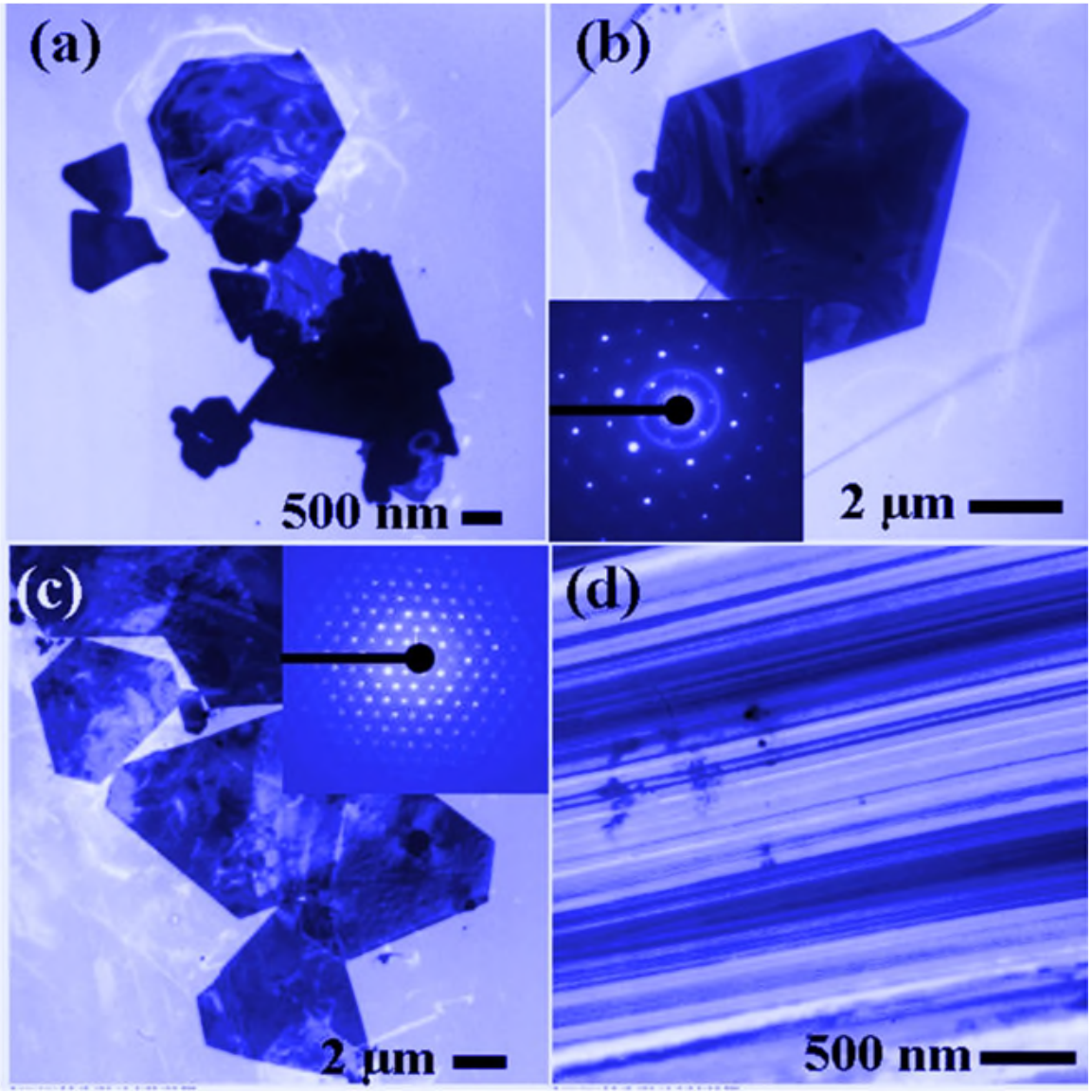
Gold Nanostructures



TEM image of gold nanostructures obtained using high concentration of sugars under microwave irradiation condition

(a) Glucose, (b) Maltose and (c) Sucrose

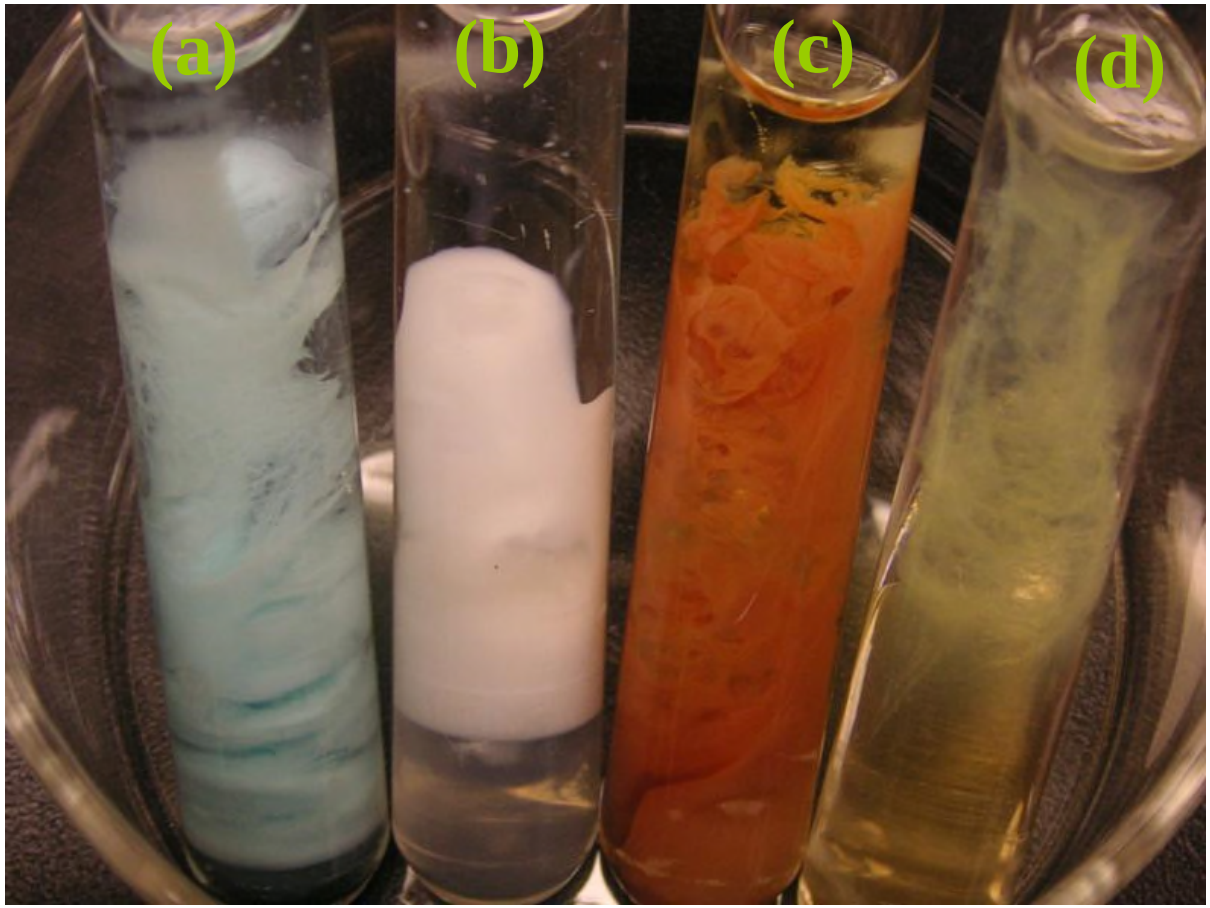
Nadagouda & Varma: *Crystal Growth and Design*, *7*, 686 (2007)



TEM image of (a-d) gold nanostructures obtained using low concentration of sugar solution under microwave irradiation

Nadagouda & Varma: *Crystal Growth and Design*, *7*, 686 (2007)

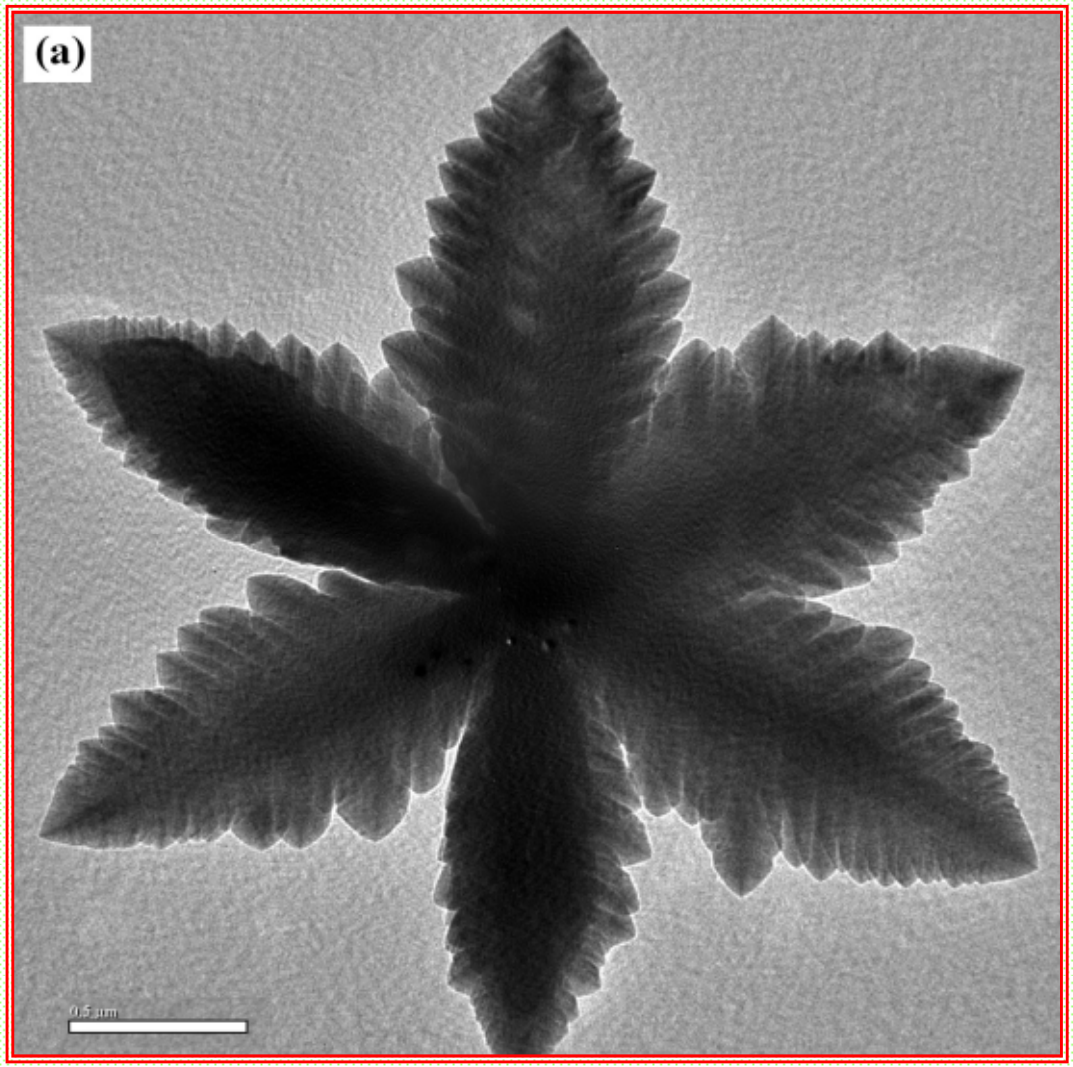
Synthesis of Thermally Stable Carboxymethyl Cellulose / Metal Biodegradable Nanocomposite Films for Potential Biological Applications



Carboxymethyl cellulose nanocomposites with (a) Cu, (b) In, (c) Fe and (d) Ag

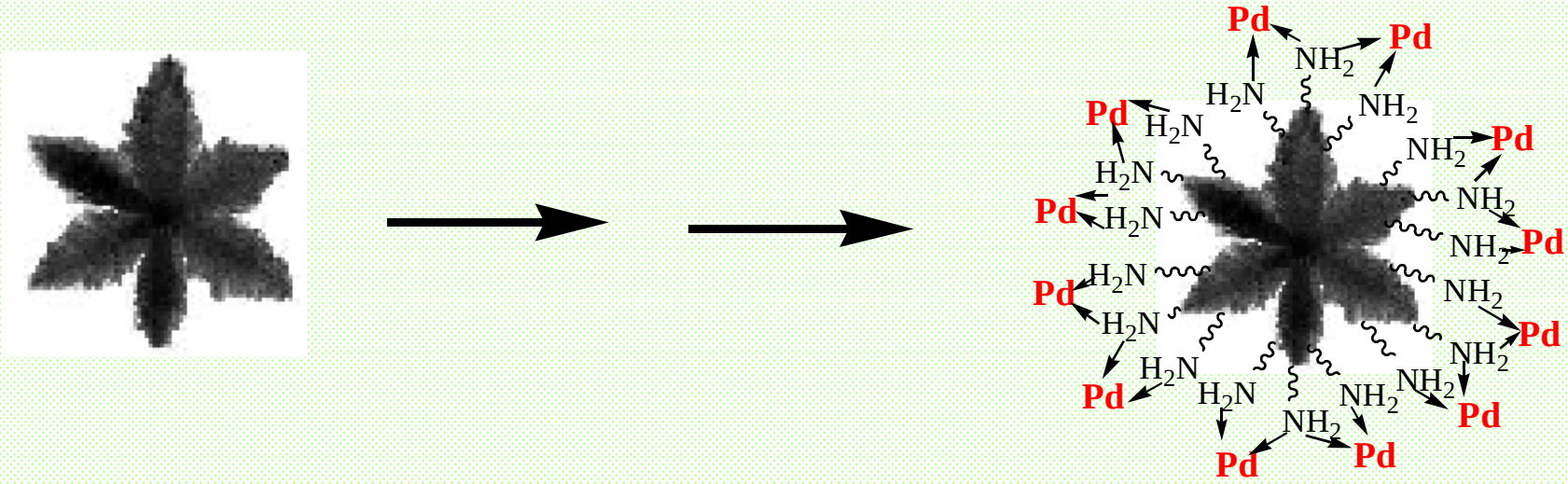
Nadagouda & Varma: *Biomacromolecules, 8*, 2762-2767 (2007)

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



Polshettiwar, Nadagouda & Varma, *Chem. Commun*. **2008**, *6318*

Synthesis of Catalyst



Convenient synthesis of single-crystal dendritic ferrite with micro-pine structuration under MW-irradiation conditions.

Materials were readily prepared from inexpensive starting materials in water without using any reducing or capping reagent.

Material was then functionalized and coated with Pd-metal which catalyzes various C-C coupling and hydrogenation reactions.

Polshettiwar, Nadagouda & Varma, *Chem. Commun.* **2008**, *6318*

Green Synthesis of Nanomaterials

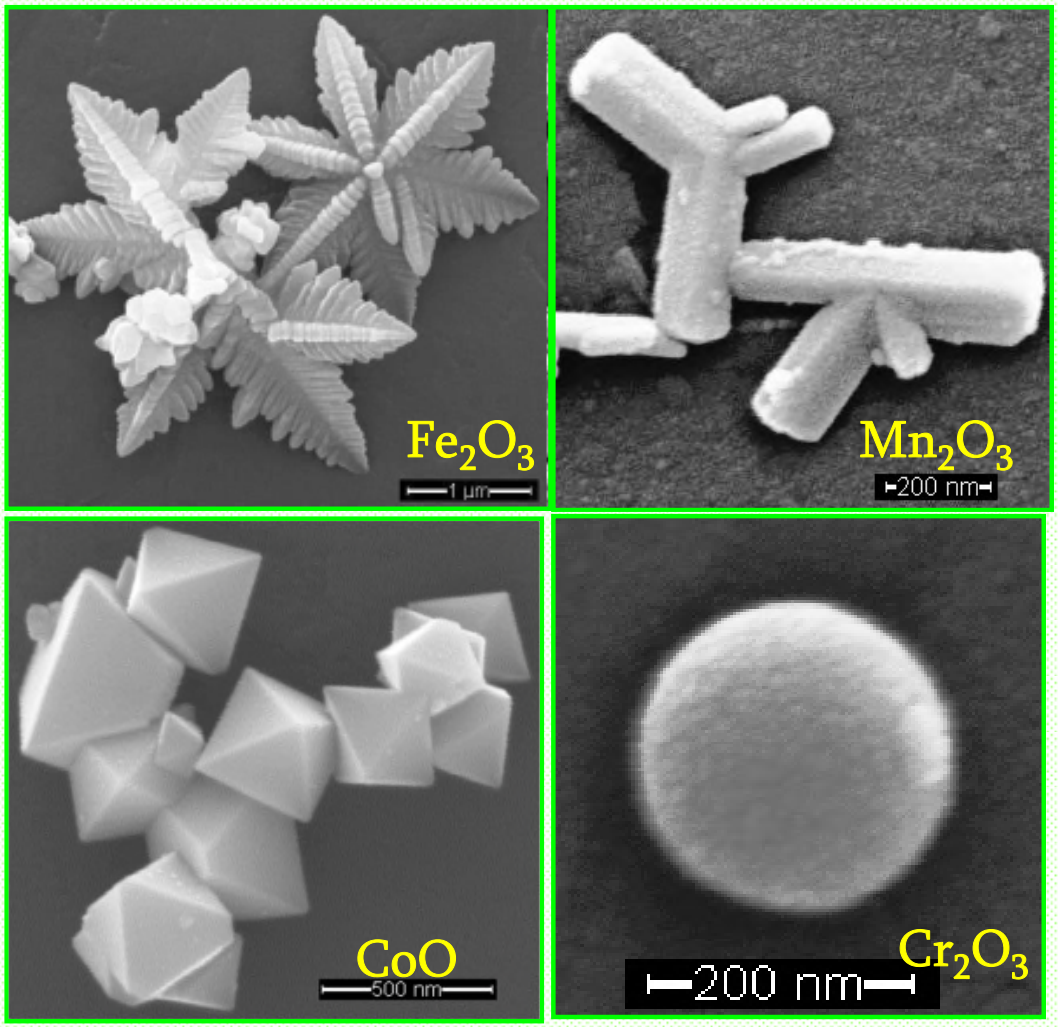
3D Nano-Metal Oxides

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.

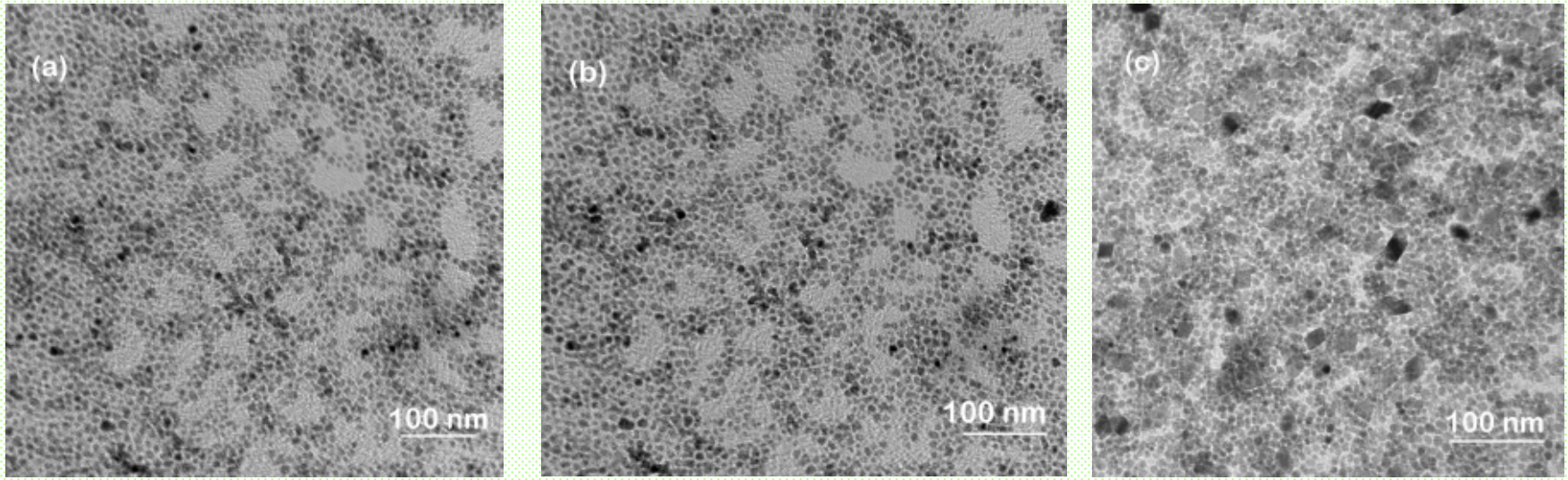


Polshettiwar, Baruwati & Varma, *ACS Nano*, *3*, 728 (2009)

Among the top 5 Most-Accessed Articles in 12 months

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

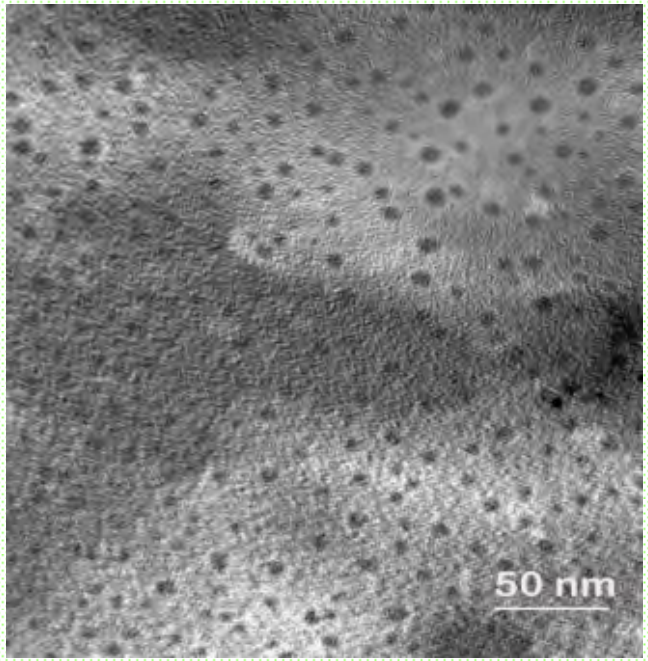
Monodispersed MFe_2O_4 (M=Fe, Mn, Co, Ni) nanoparticles have been synthesized via a water organic interface under both hydrothermal and MW conditions starting with readily available and inexpensive metal nitrate and halide precursors. The single phase particles are obtained at a temperature as low as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



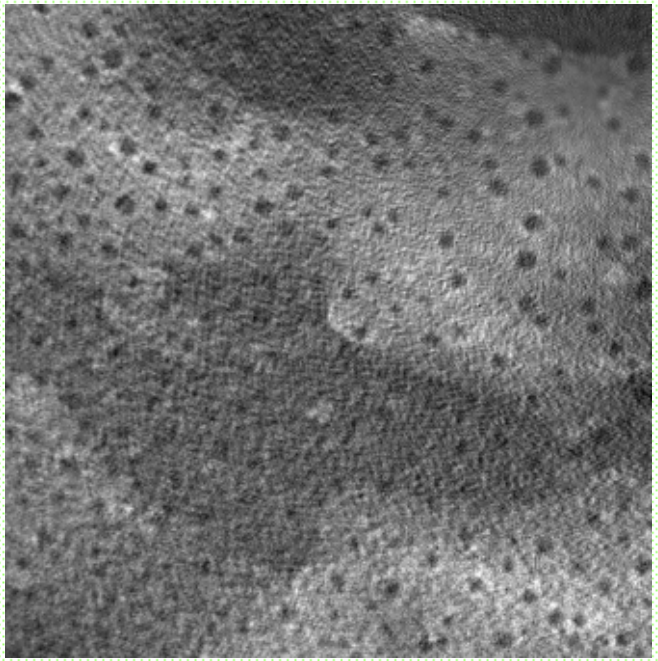
$NiFe_2O_4$ **$CoFe_2O_4$** γ-Fe_2O_3

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

Surface functionalization renders the particles dispersible in water



TEM of the particles dispersed in water



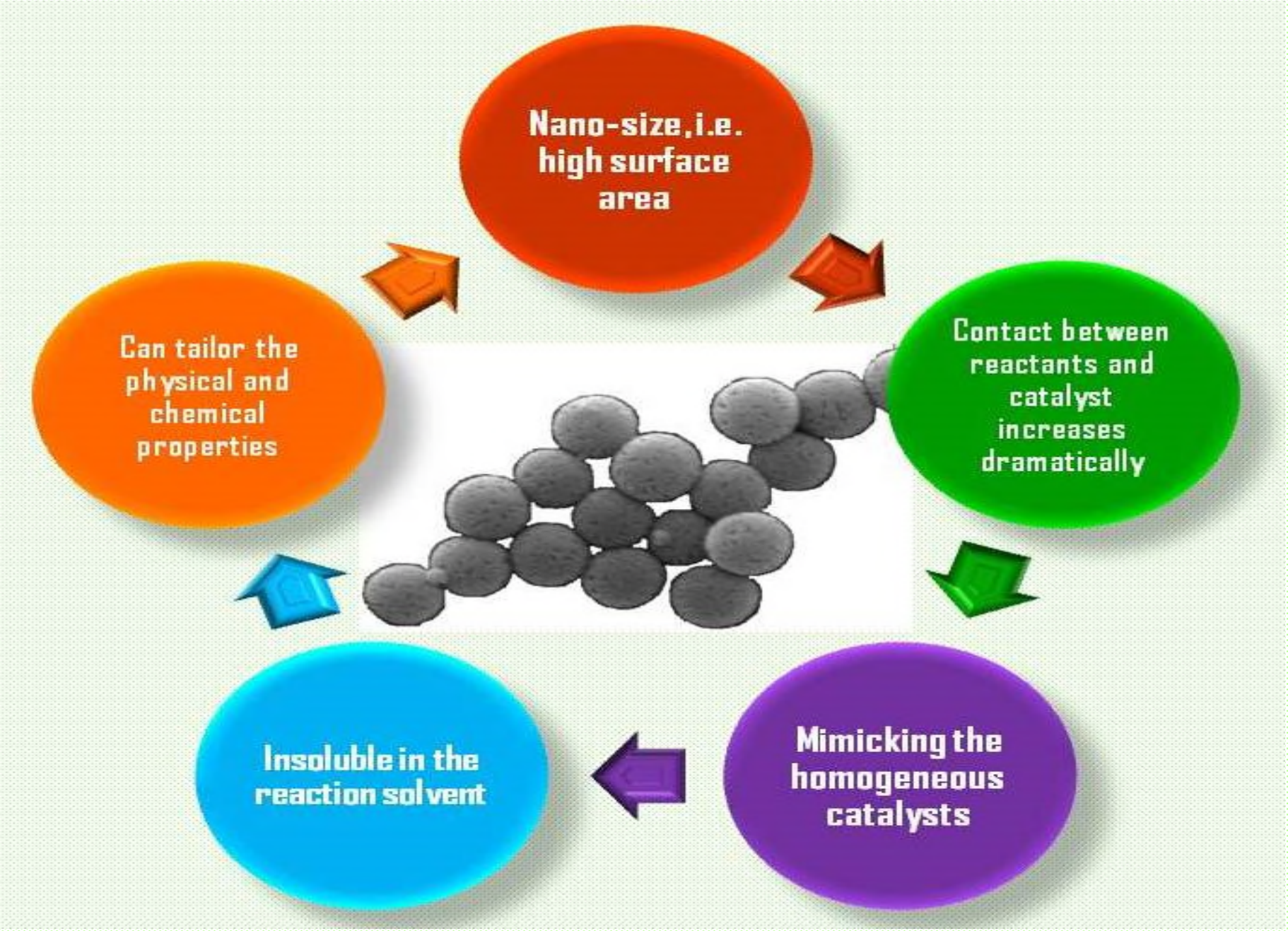
$NiFe_2O_4$

$CoFe_2O_4$

Photographic image of the particles in water and hexane

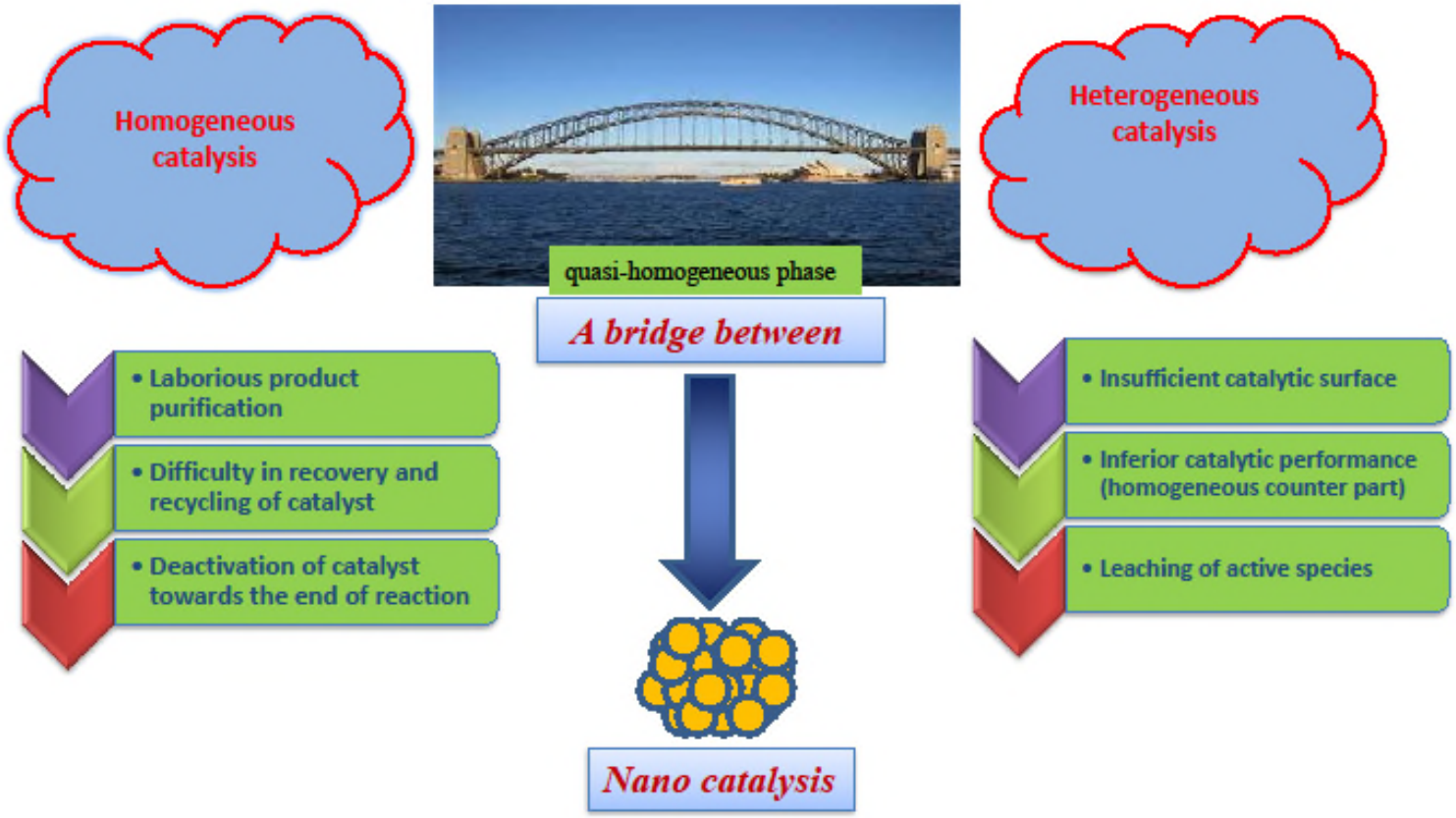
Baruwati, Nadagouda & Varma, *J. Phys. Chem. C*, *112*, 18399 (2008)

What is Nano-Catalysis?



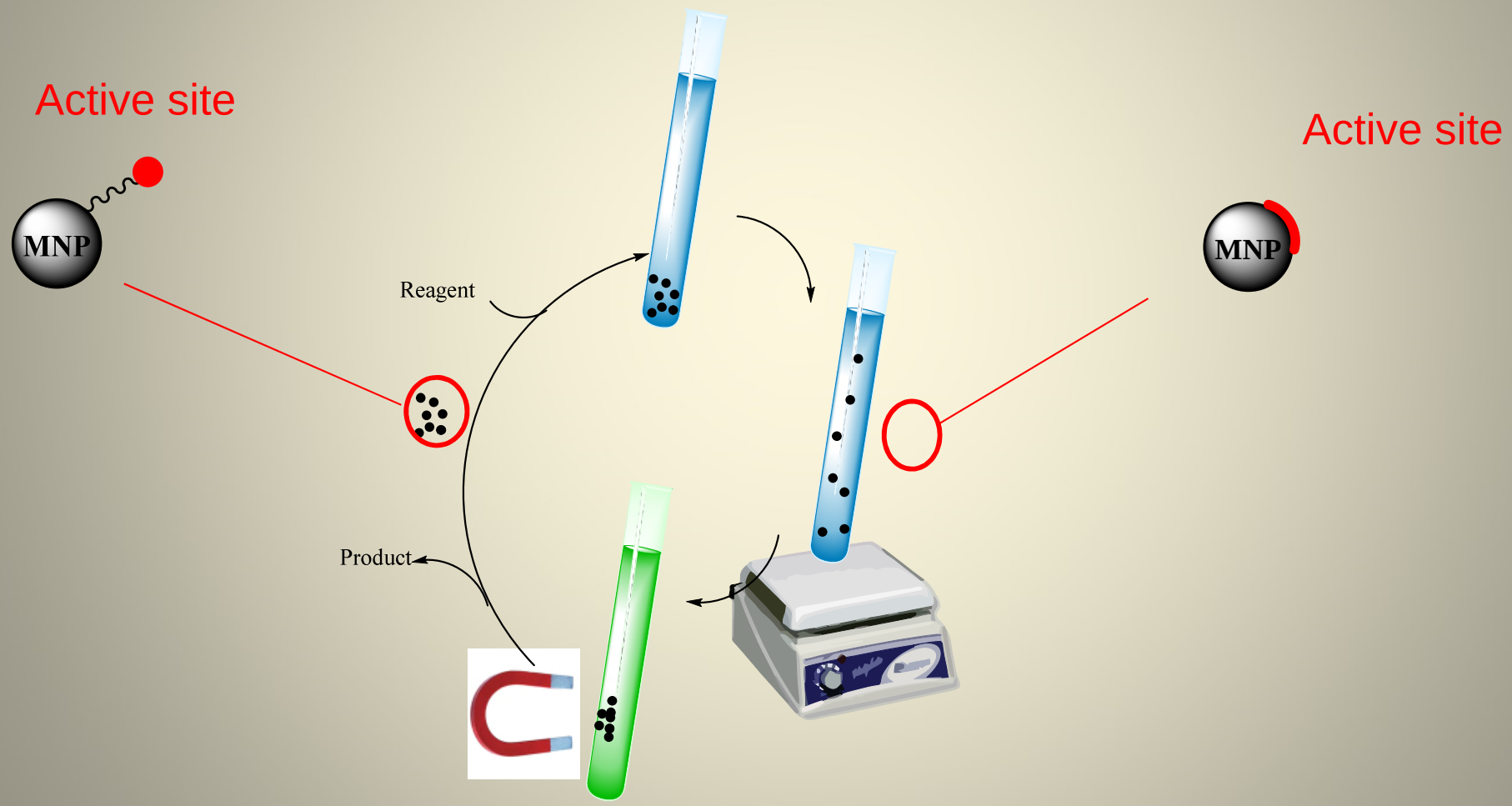
Nano catalyst acts as a quasi-homogeneous phase

A bridge between homogeneous and heterogeneous



Magnetic Nanoparticles in Catalysis

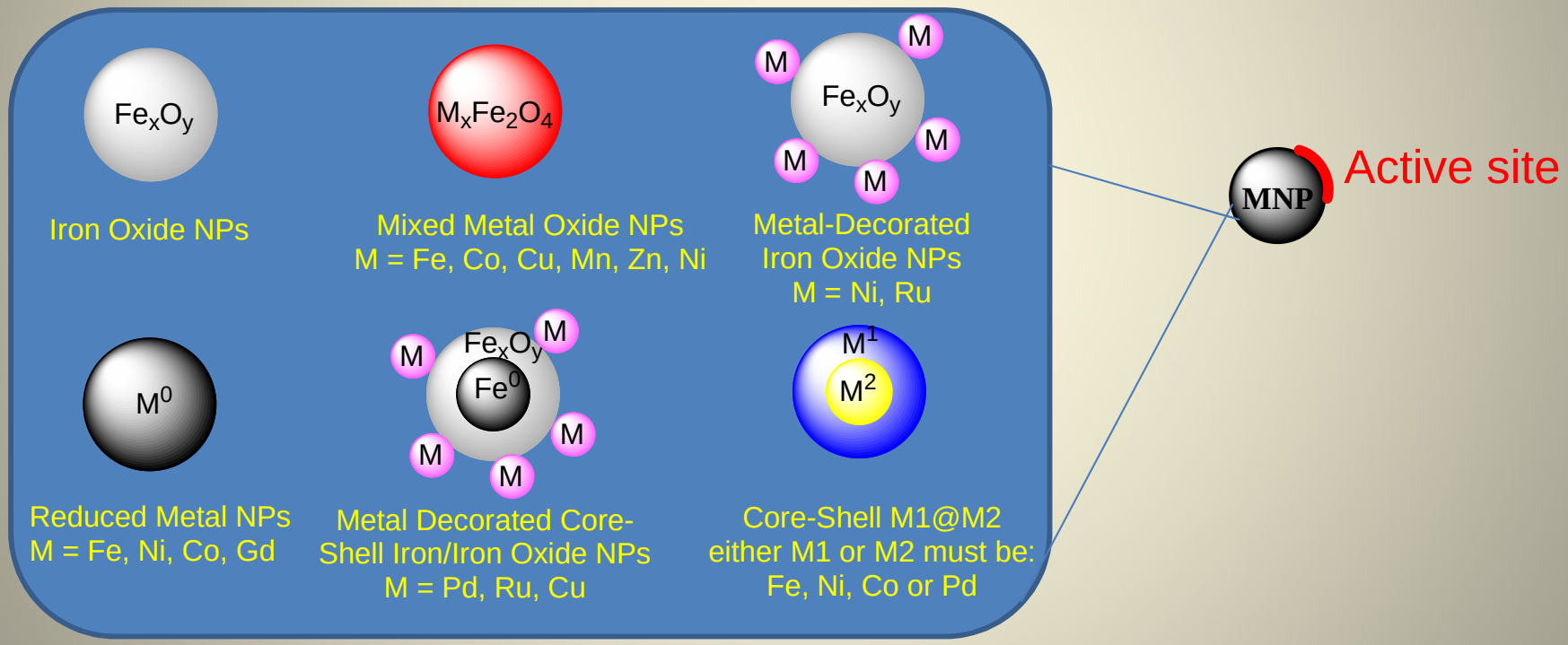
- **As simple magnetic anchors**
- **Catalytic bare magnetic nanoparticles**



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)

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

Magnetically Separable Nano-Catalyst

A Bridge Between

Homogeneous Catalysis

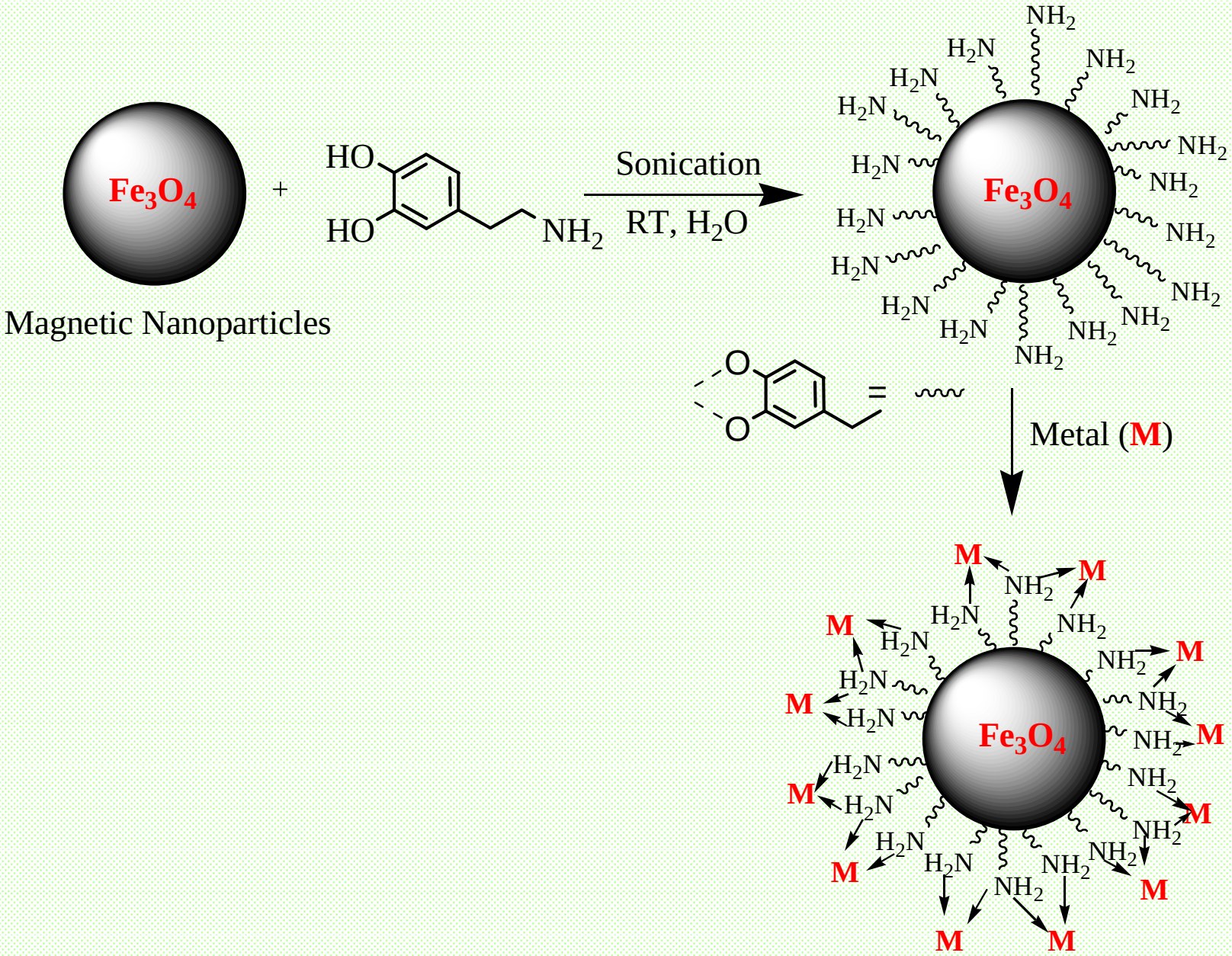
Heterogeneous Catalysis

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)
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)
Curr. Opin.Chem. Eng. *1*, 123 (2012)
Green Chem., *16*, p2027, p3494, p4137, p4333, p4493 (2014)

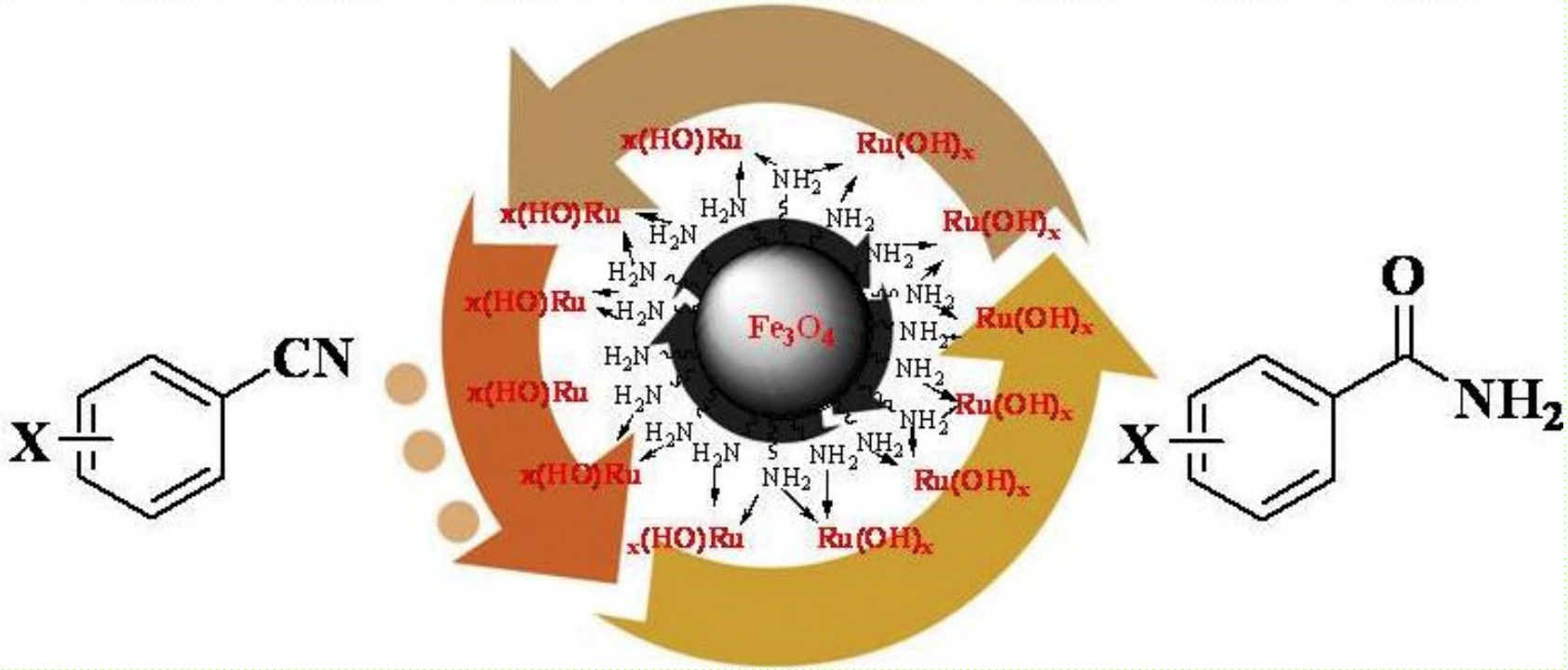
Coord. Chem. Rev., *287*, pp137-156 (2015)-Asymmetric Synthesis

Synthesis of Nano-Catalysts



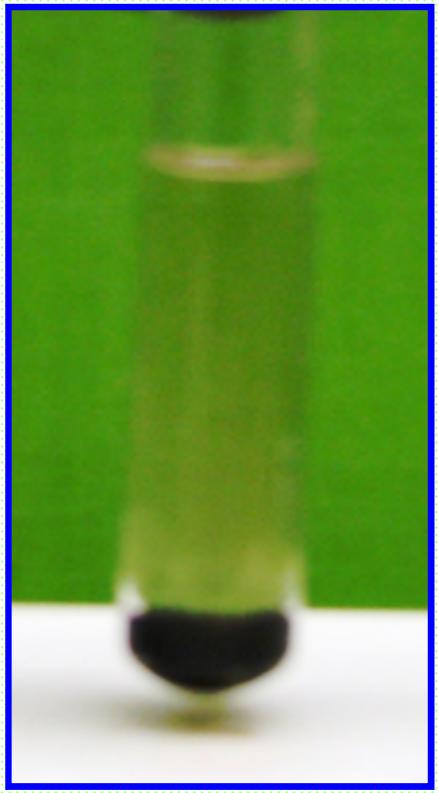
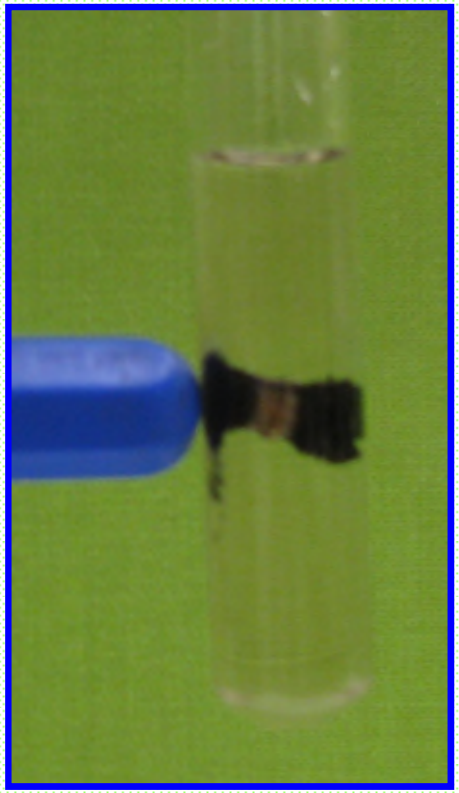
Polshettiwar, Nadaguda & Varma, *Chem. Commun*. 2008, 6318.

Magnetically Recoverable Ruthenium Hydroxide Nano-Catalyst



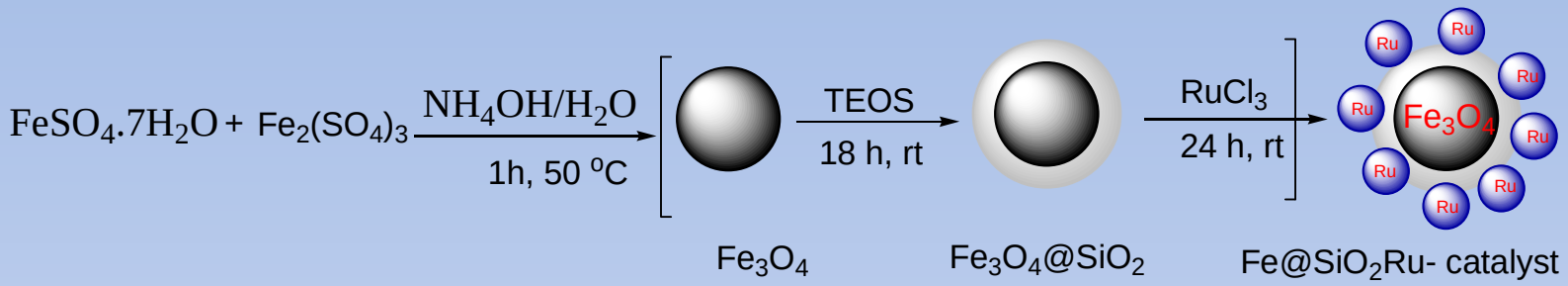
Polshettiwar & Varma, *Chem. Eur. J. 15*, 1582 (2009)

No Organic Solvent-
Even in the Work-Up Step

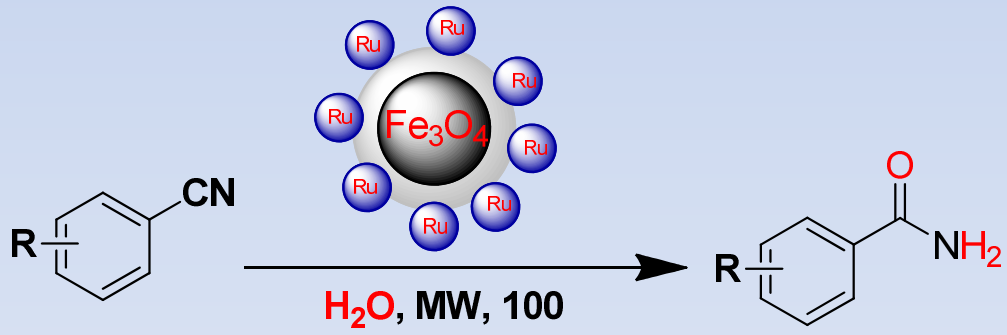
Reaction in Pure Aqueous Medium

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



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

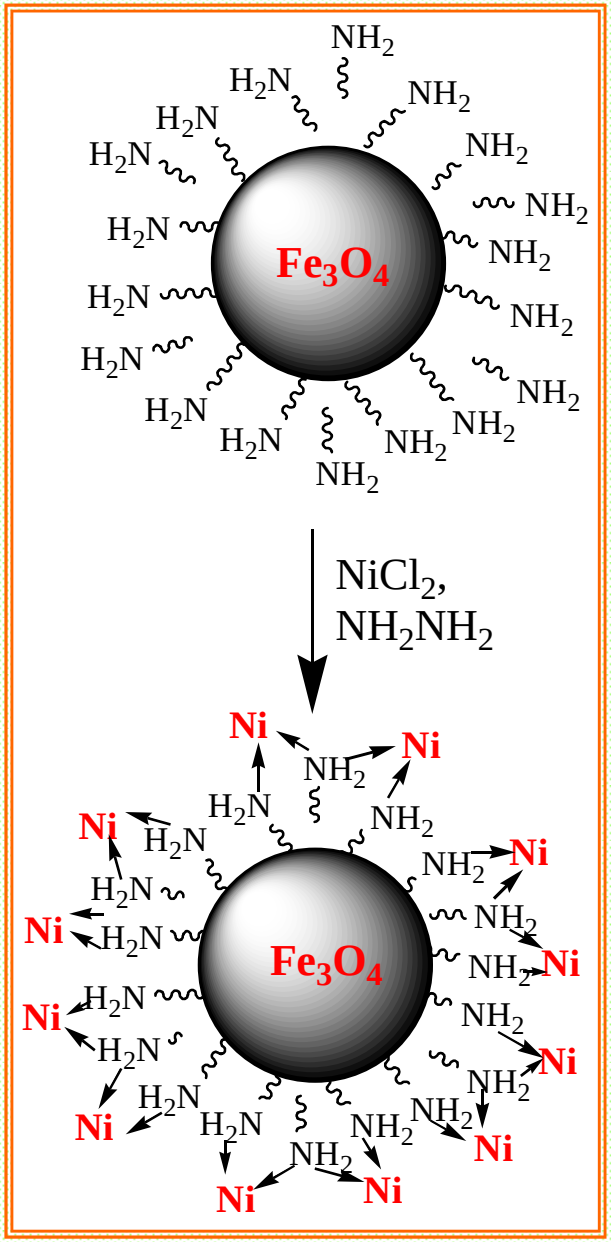
Aqueous Hydration of Nitriles Using Magnetic Silica Supported Ruthenium Hydroxide Nanoparticles

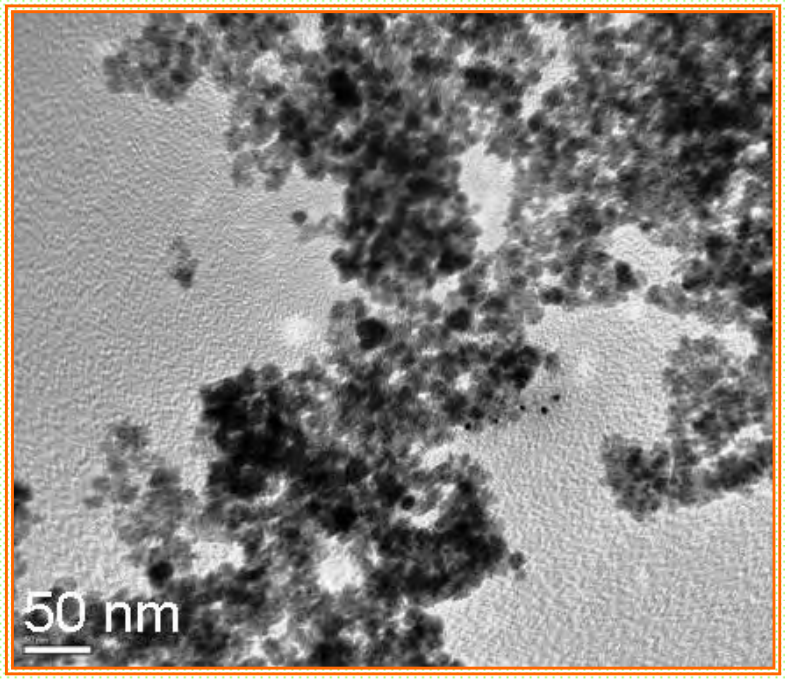


>99% conversion

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

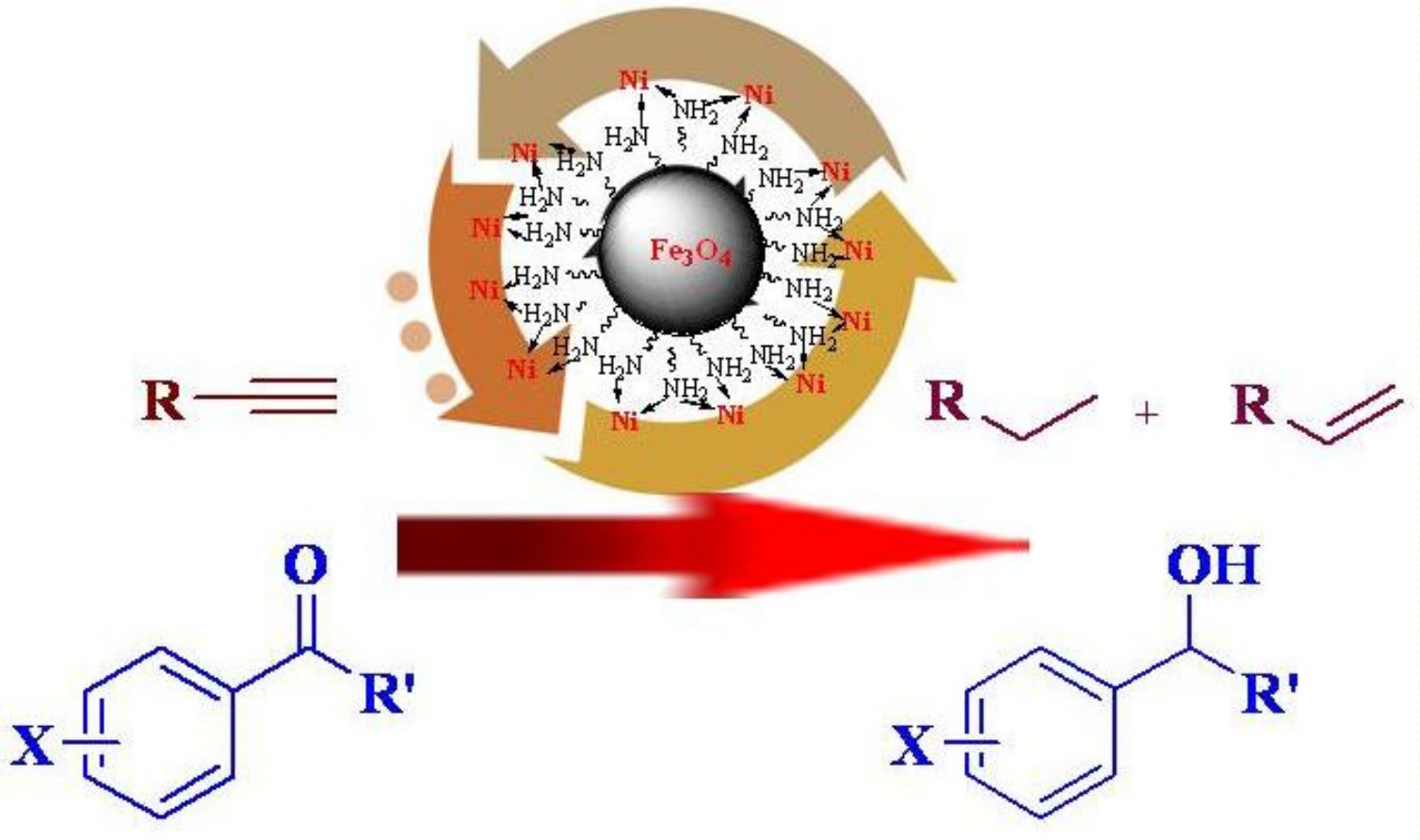
Synthesis of Ni-Nano-Catalysts





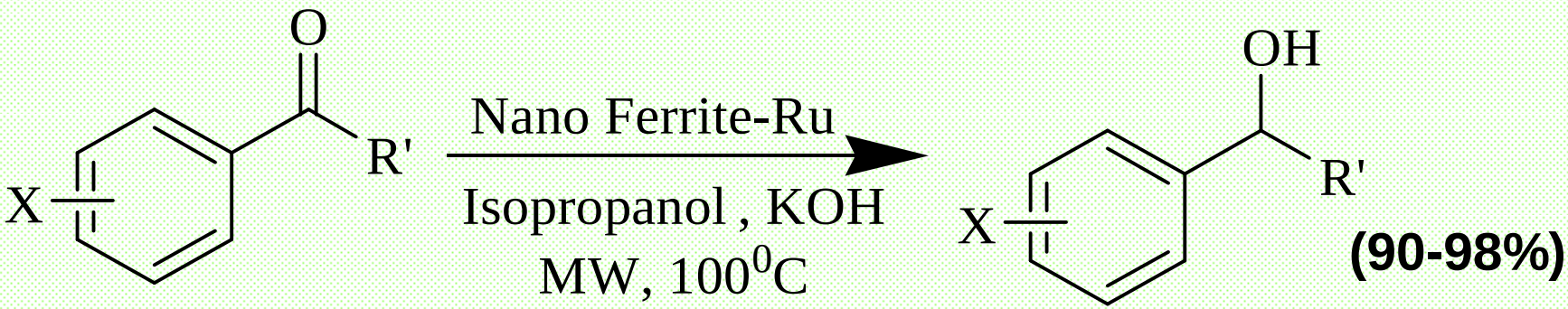
- Single-phase Fe_3O_4 nanoparticles
- Size range = 10-13 nm
- Nickel concentration = 8.3 % (ICP-AES)

Magnetically Recoverable Ni Nano-Catalyst for Reduction

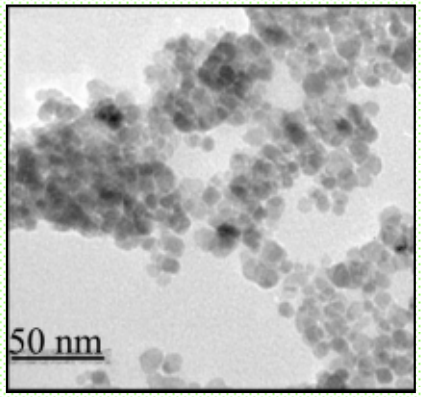


Polshettiwar, Baruwati & Varma, *Green Chem.*, *11*, 127 (2009)

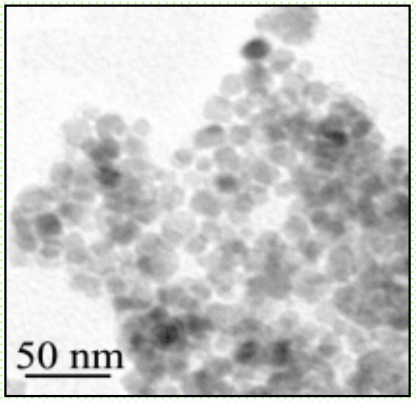
Transfer Hydrogenation of Carbonyl Compounds



R' - Me, Ph,H
X - Cl, Br, NO_2, NH_2



Catalyst before reaction

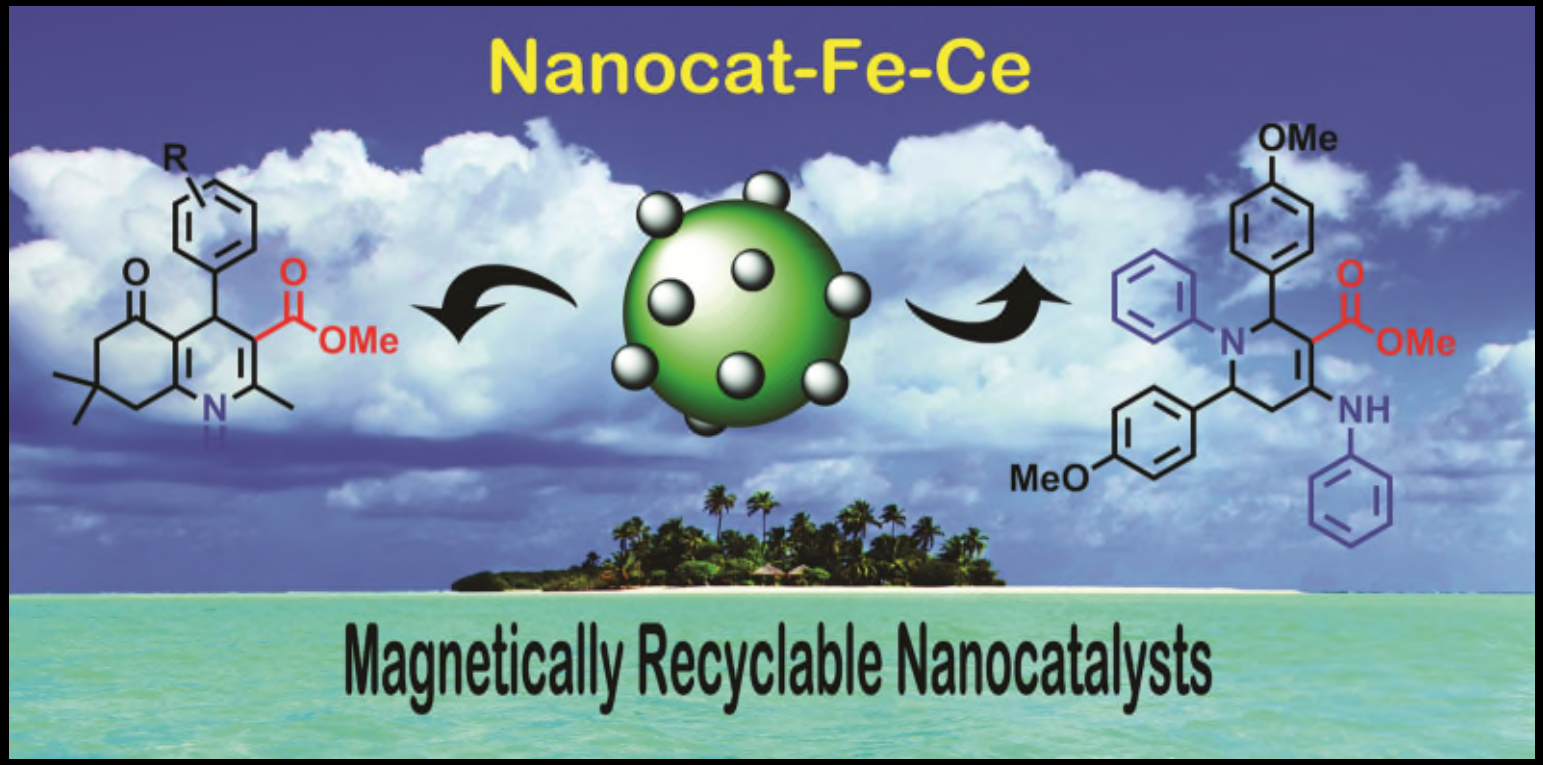


Catalyst after reaction

- **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

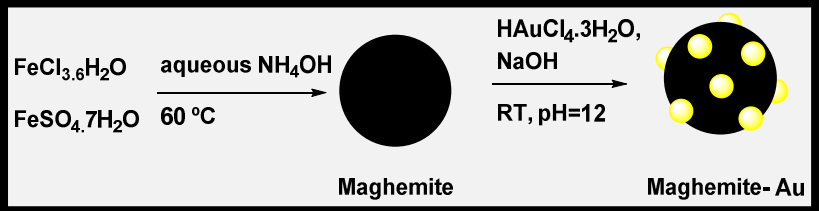


Gawande, Bonifácio, Varma, Branco, Nogueira, Bundaleski, Ghumman, Teodoro: *Green Chem.*, *15*, 1226 (2013)

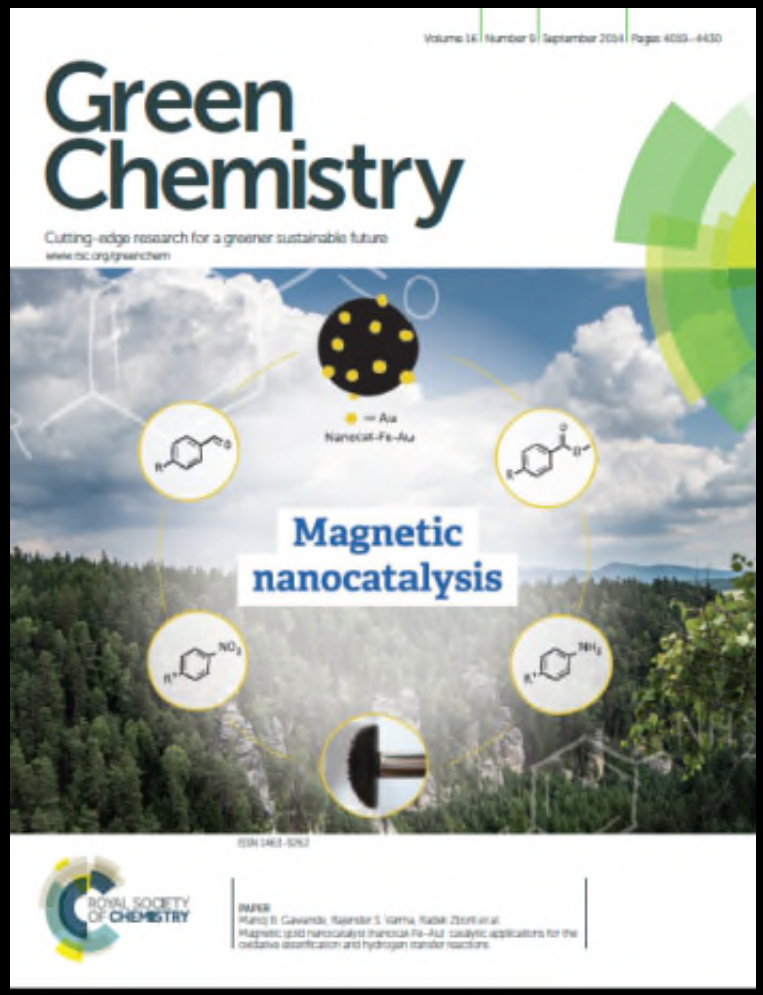
Iron Oxide-supported Copper Oxide Nanoparticles (Nanocat-Fe-CuO): Magnetically Recyclable Catalysts for the Synthesis of Pyrazole derivatives, 4-Methoxyaniline, and Ullmann-type Condensation Reactions

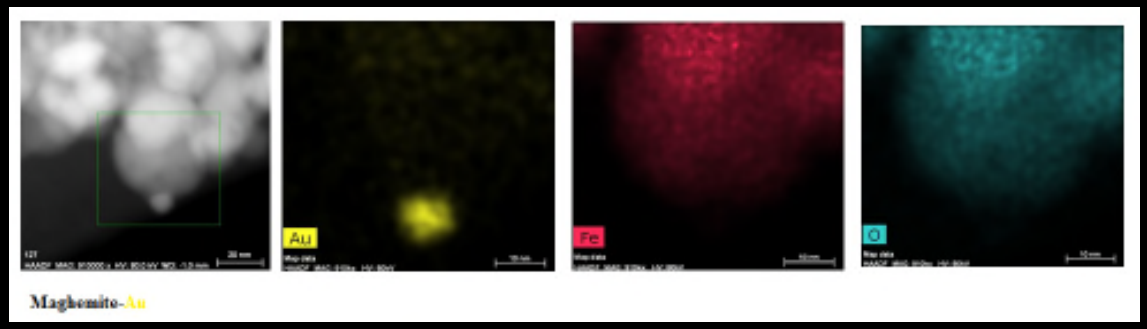
Shelke, Bankar, Mhaske, Kadam, Murade, Bhorkade, Rathi, Bundaleski, Teodoro, Varma, Zboril, Gawande*: ACS Sus. Chem. Eng*., 2, 1699 (2014)

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

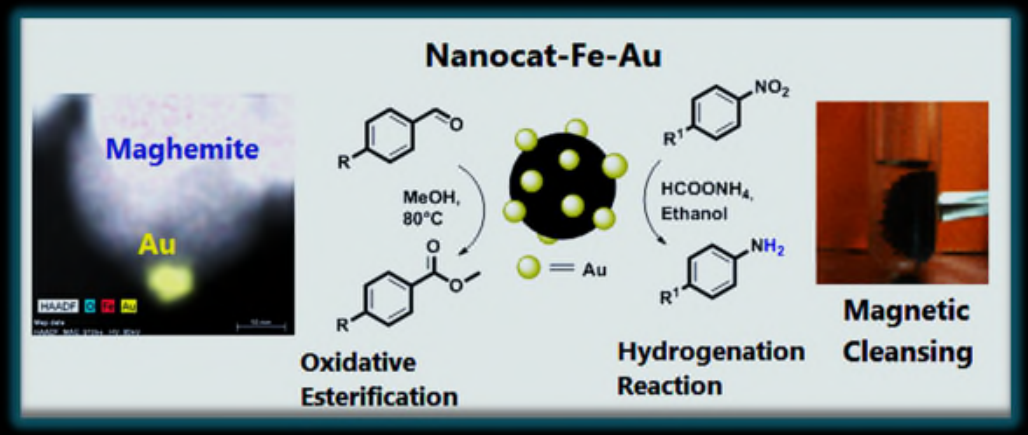


Synthesis of maghemite-Au





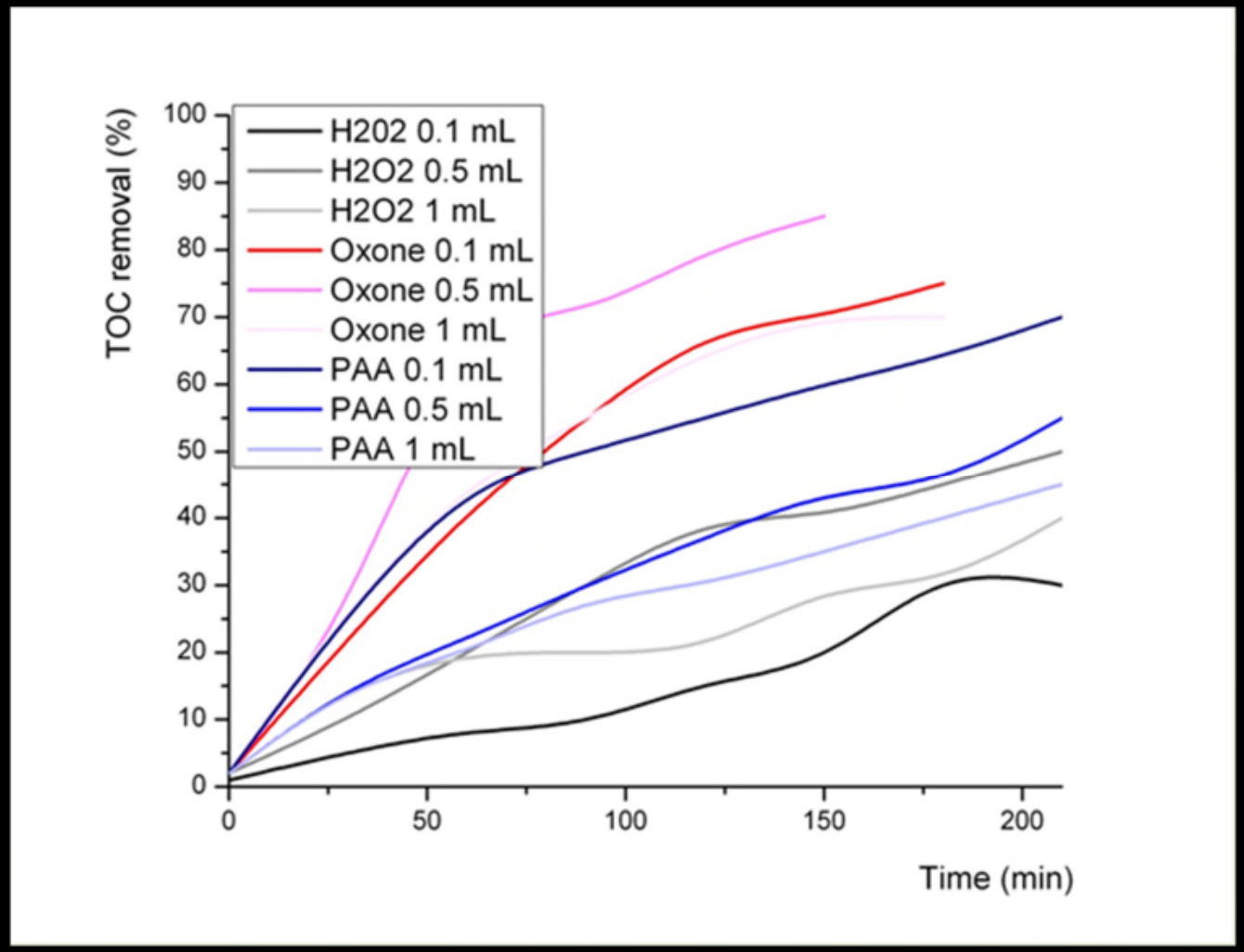
High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)



Application in oxidative esterification and reduction of aromatic nitro compounds

Green Chemistry, ,37, 4137 (2014)

Eco-friendly Magnetic Iron Oxide Pillared Montmorillonite for Advanced Catalytic Degradation of Dichlorophenol

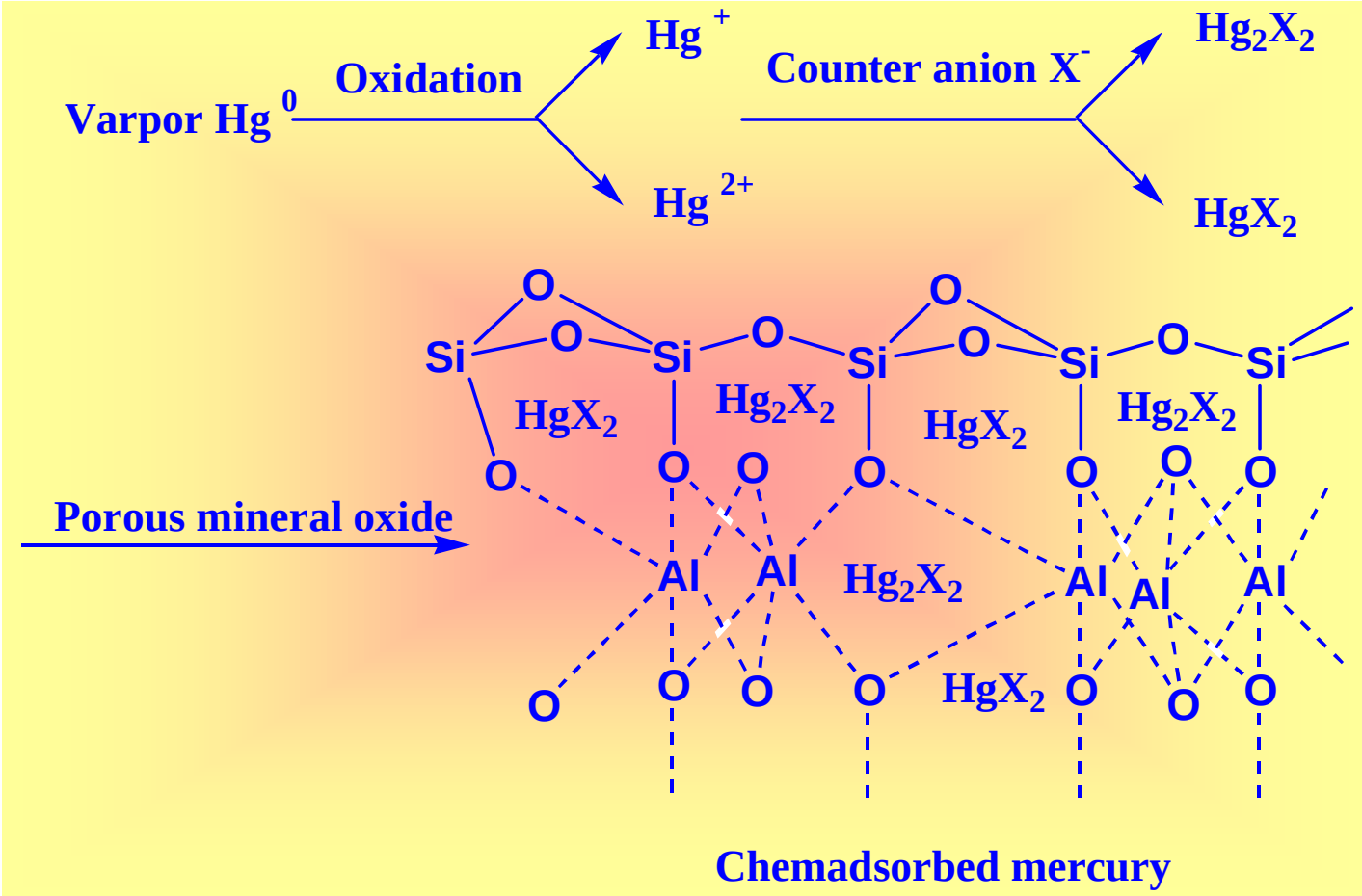


Clay-based iron oxide nanocomposite degrades dichlorophenol in presence of safer oxidants, H_2O_2, Oxone and Peracetic Acid.

Virkutyte and Varma*: ACS Sus. Chem. Eng*., 2, 1545 (2014)

A Novel Efficient and Cost-effective Adsorbents to Capture Vapor-phase Mercury from Coal-fired Power Plants

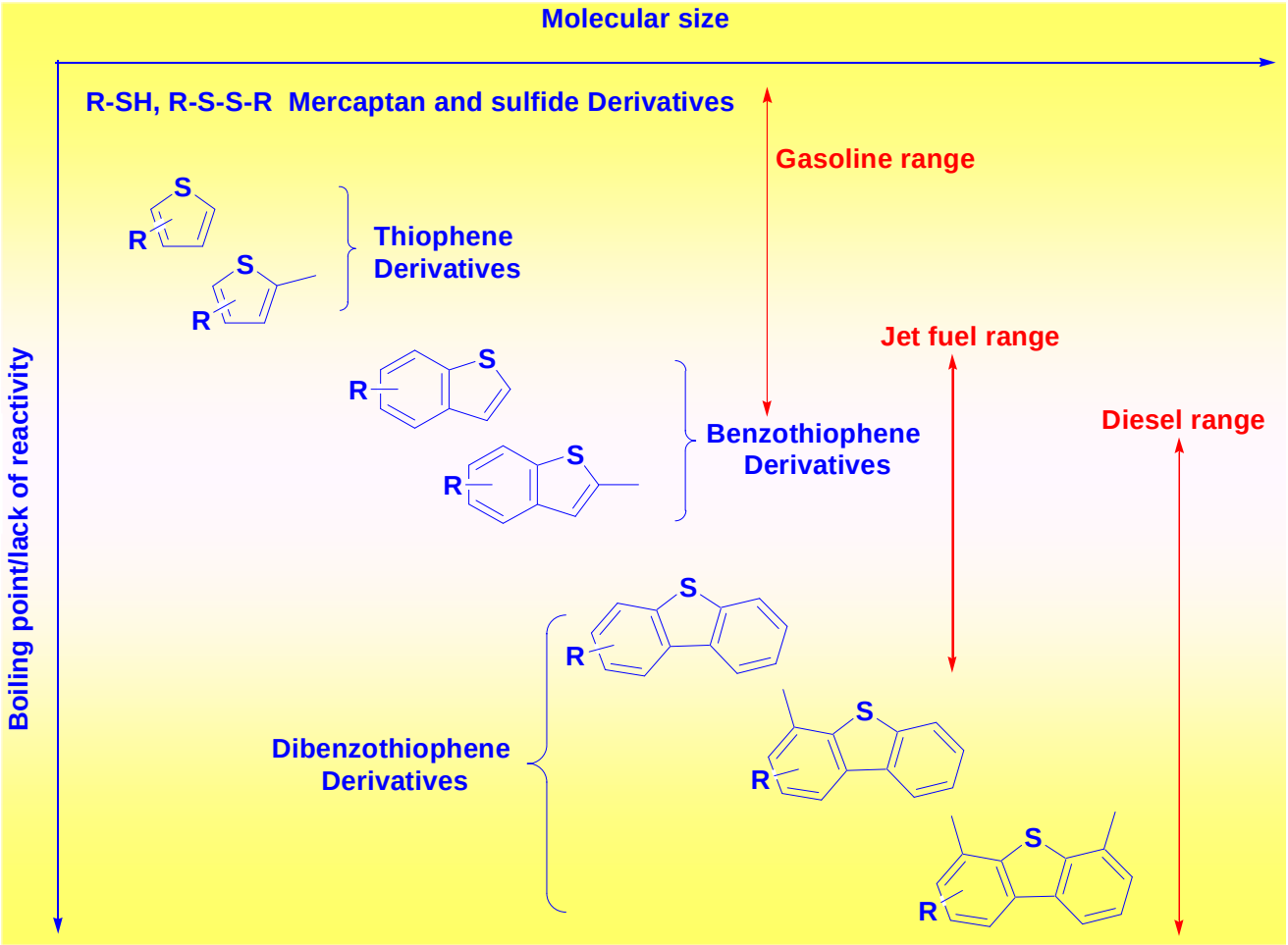
Rajender S. Varma et al.



U S Patent Number: 7, 858,061

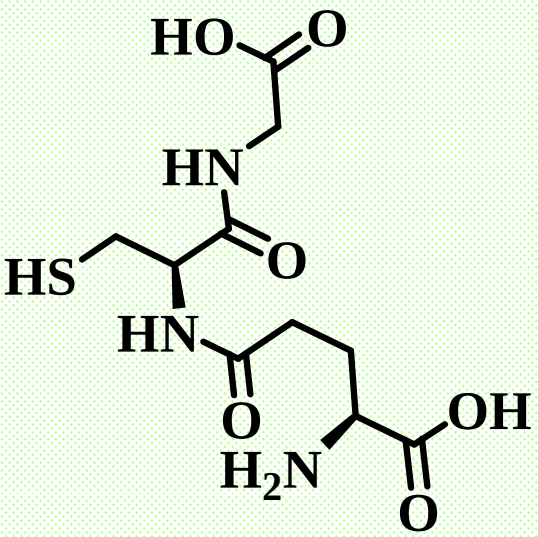
Metal Immobilized Porous Mineral Oxides as Sorbents for 'Deep' Desulfurization of Transportation Fuels

Rajender S. Varma et al.



U S Patent Number: 8, 029,662

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)

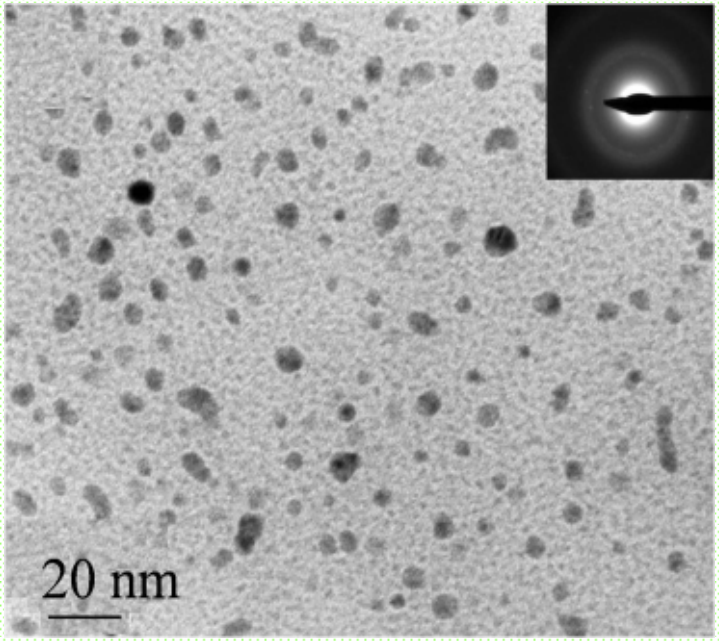
Baruwati, Polshettiwar, Varma, *Green Chem*. *11*, 926 (2009)

Metal nanoparticles in less than a minute under MW conditions

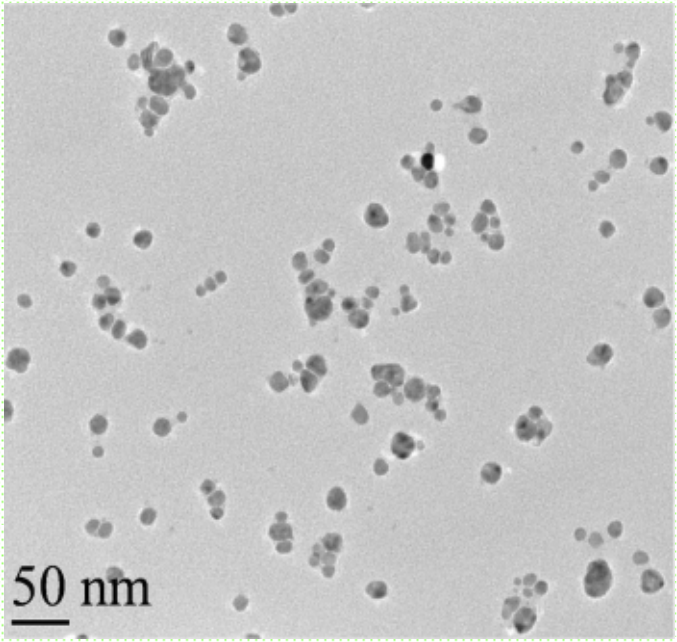
Optimized condition

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

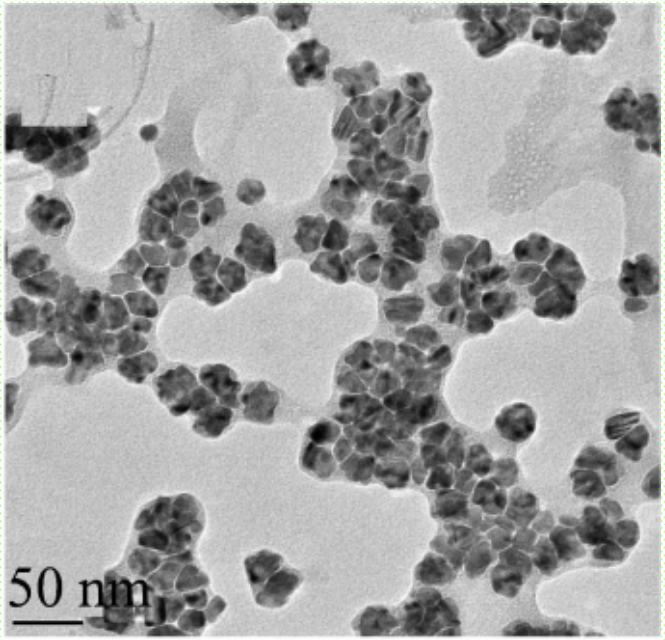
Silver Nanoparticles



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

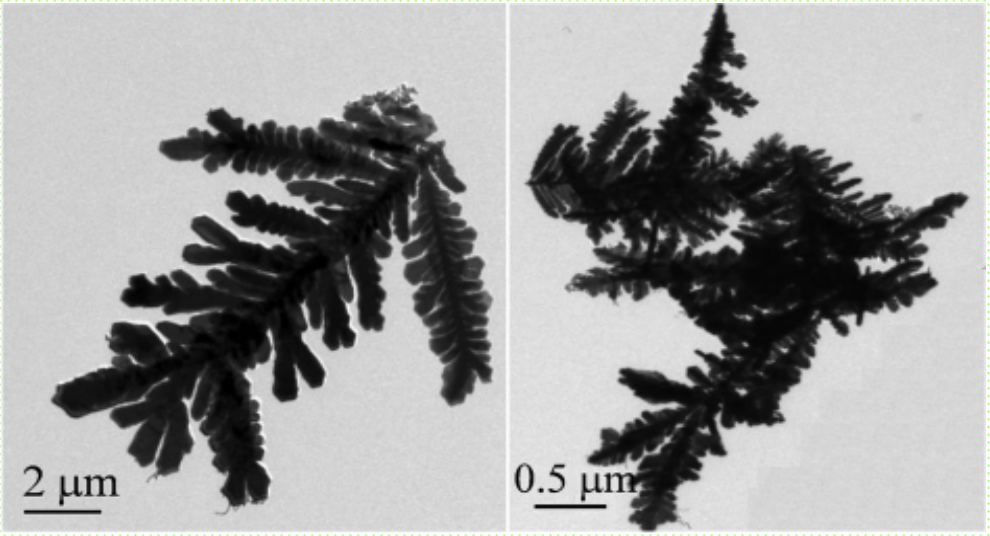


75 Watt, 60 seconds with mole ratio 1.0:0.15



100 Watt, 60 seconds with mole ratio 1.0:0.15

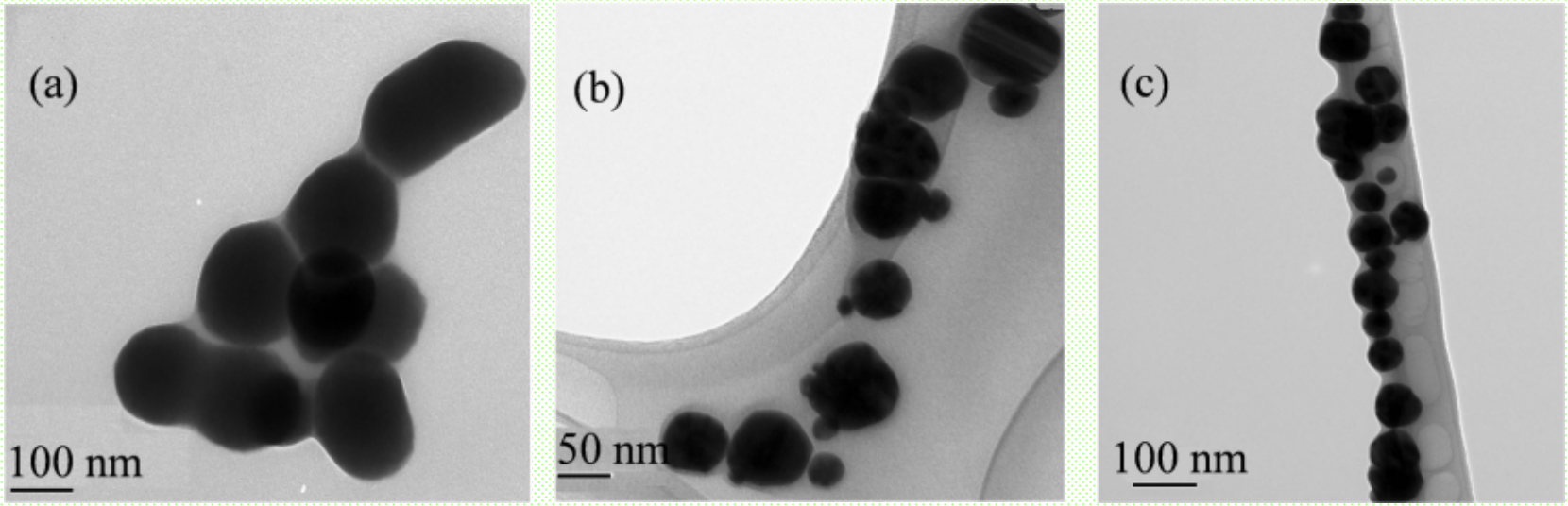
- Silver trees formed on the TEM grid when silver nitrate is not fully reduced
- Formation of dendritic structures are due to the carbon and copper in the TEM grid



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

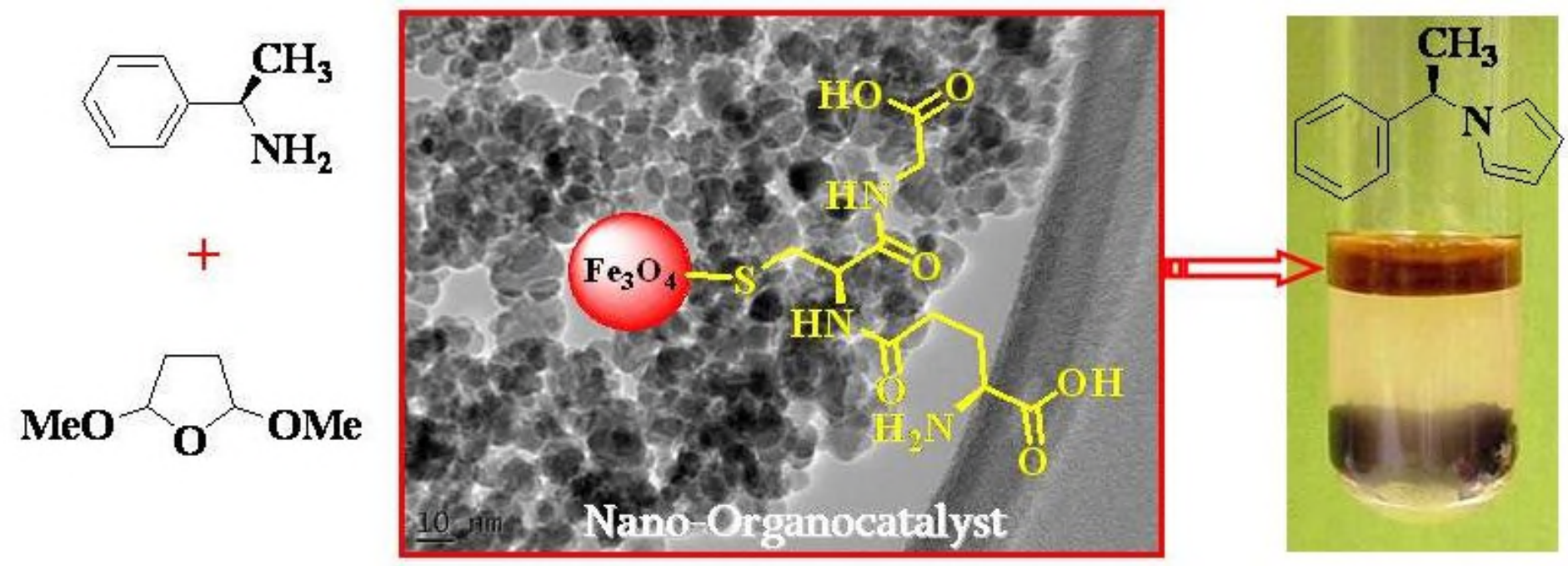
Gold, Platinum and Palladium Nanoparticles

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



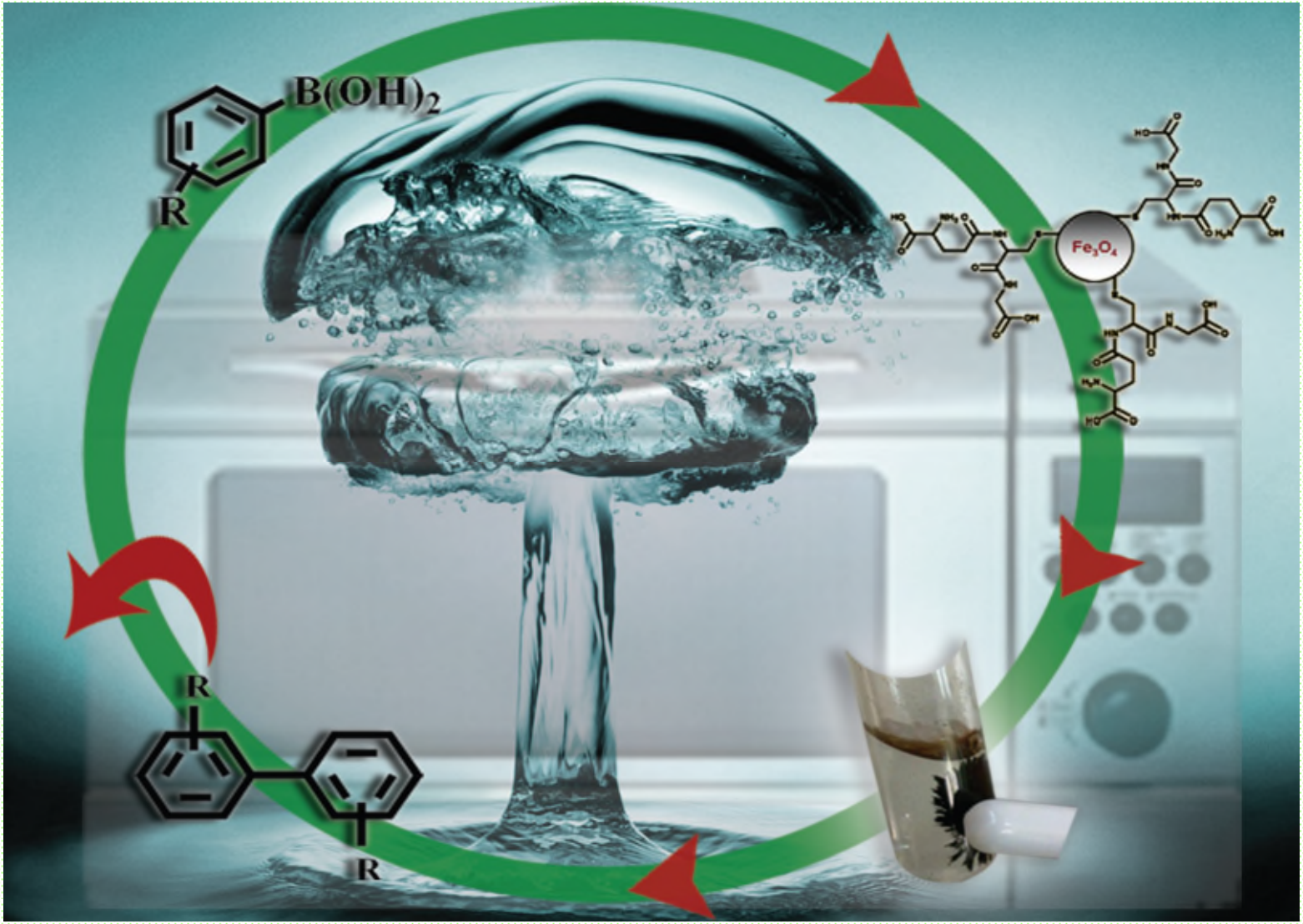
Polshettiwar &Varma: *Chem. Commun.*, 1837 (2009)

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

Green Chemistry

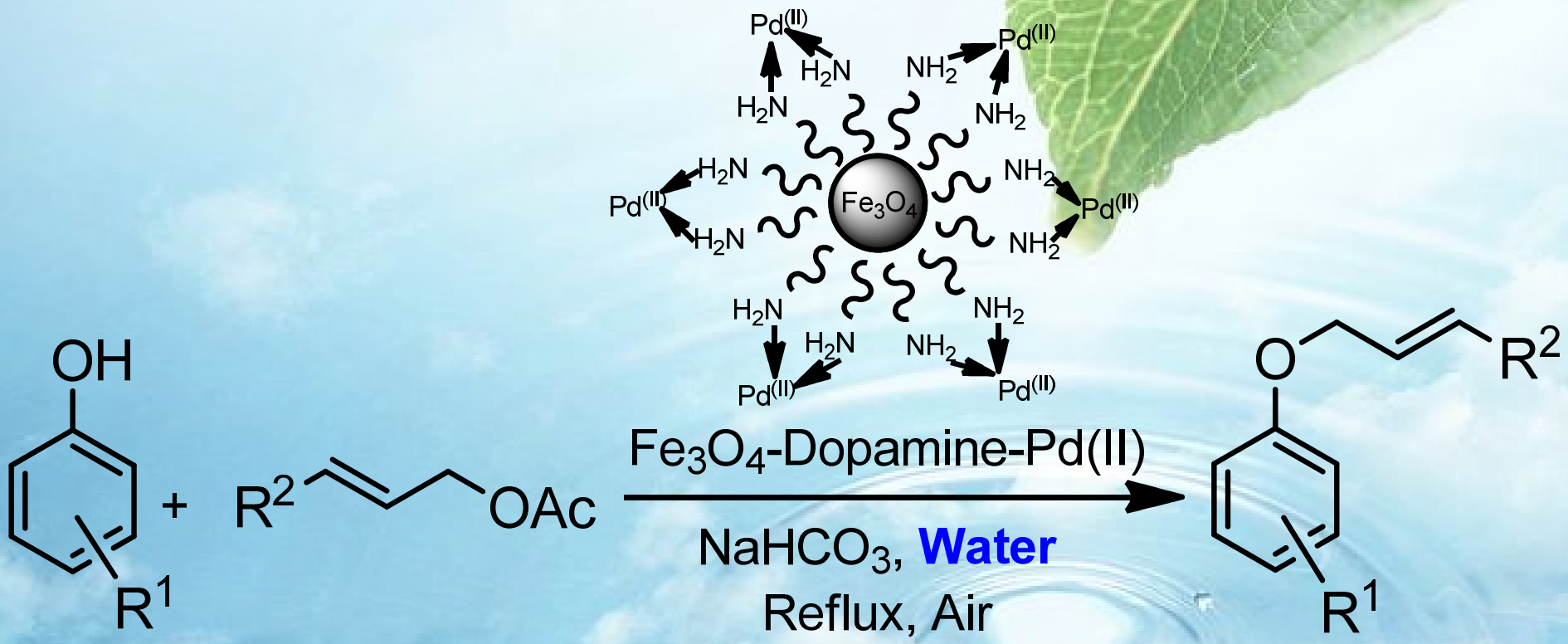
Cover page **Volume 12 | Number 9 | Sept. 2010**

Magnetically seperable organocatalyst for homocoupling of arylboronic acids



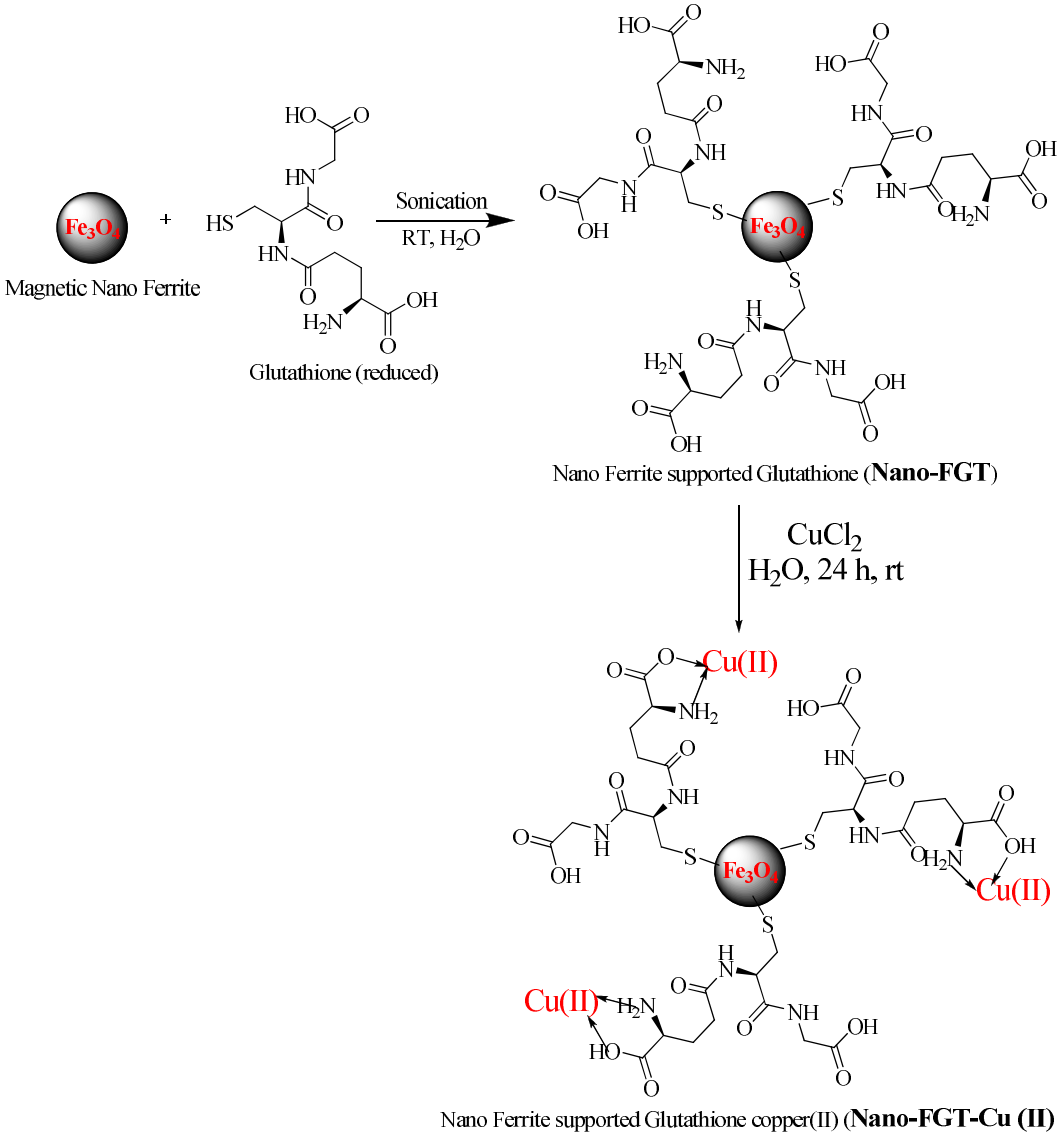
R. Luque, B. Baruwati, R. S. Varma: *Green Chem., 12*, 1540 (2010)

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



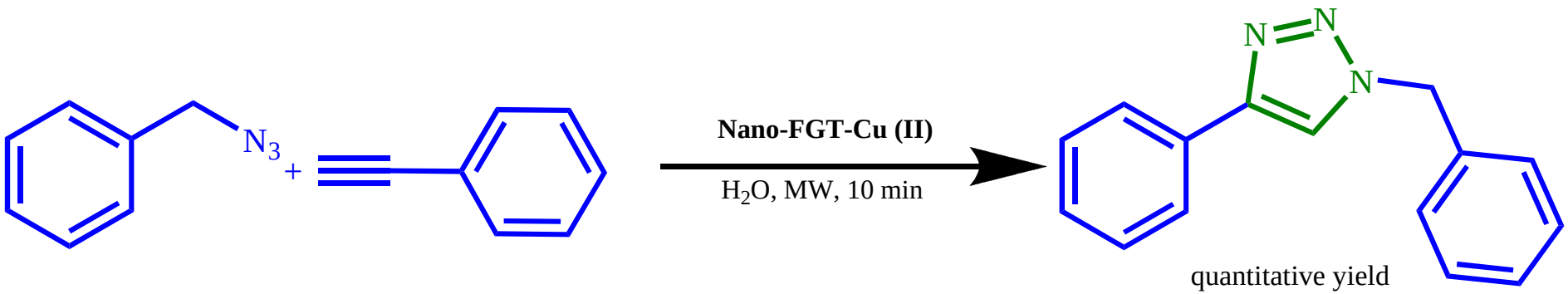
Saha, Leazer, Varma: *Green Chem.*, 14, 67-71 (2011)

Nano Ferrite supported-Glutathione copper(II) catalyst

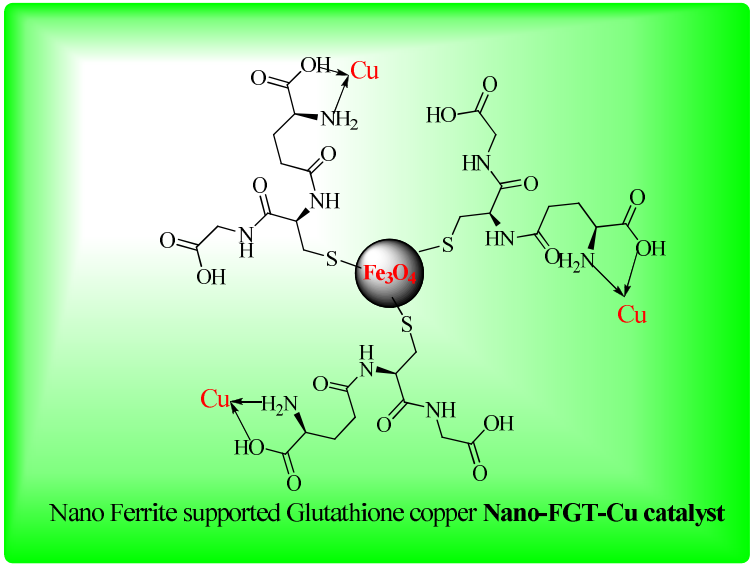


Baig, Varma: *Green Chem., 14, 625 (2012)*

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

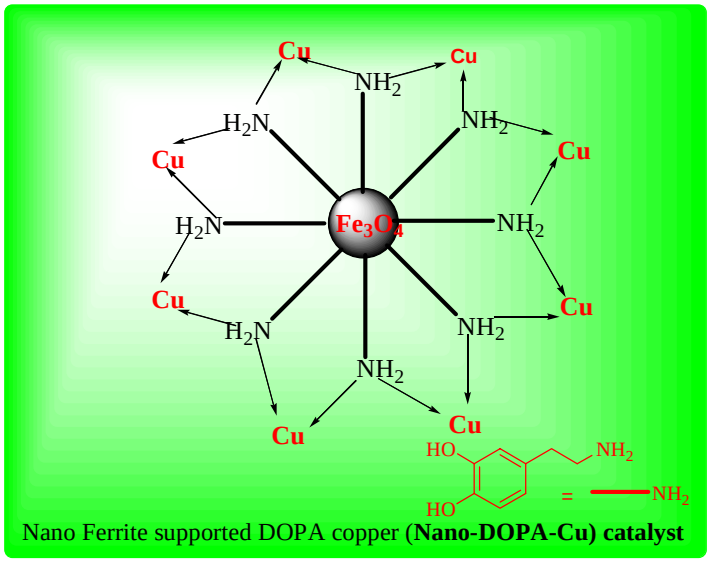


Baig, Varma: *Green Chem., 14, 625 (2012)*

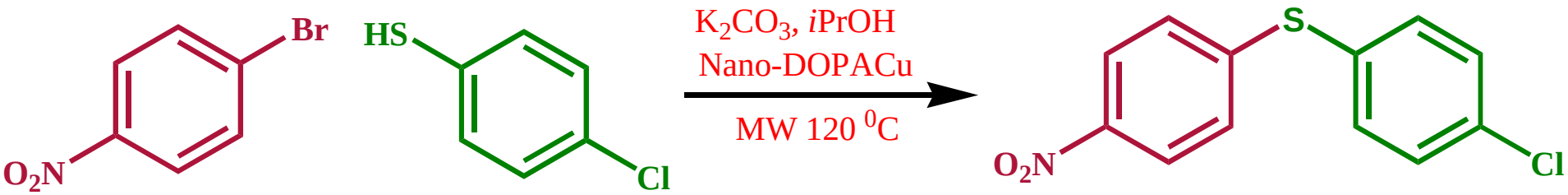


Nano Ferrite supported Glutathione copper **Nano-FGT-Cu catalyst**

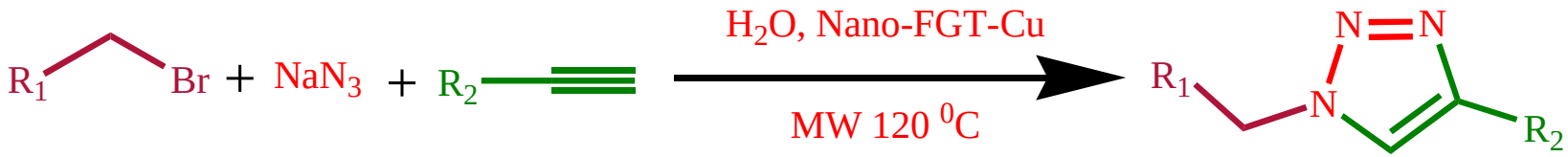
Ligands defines reactivity



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



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

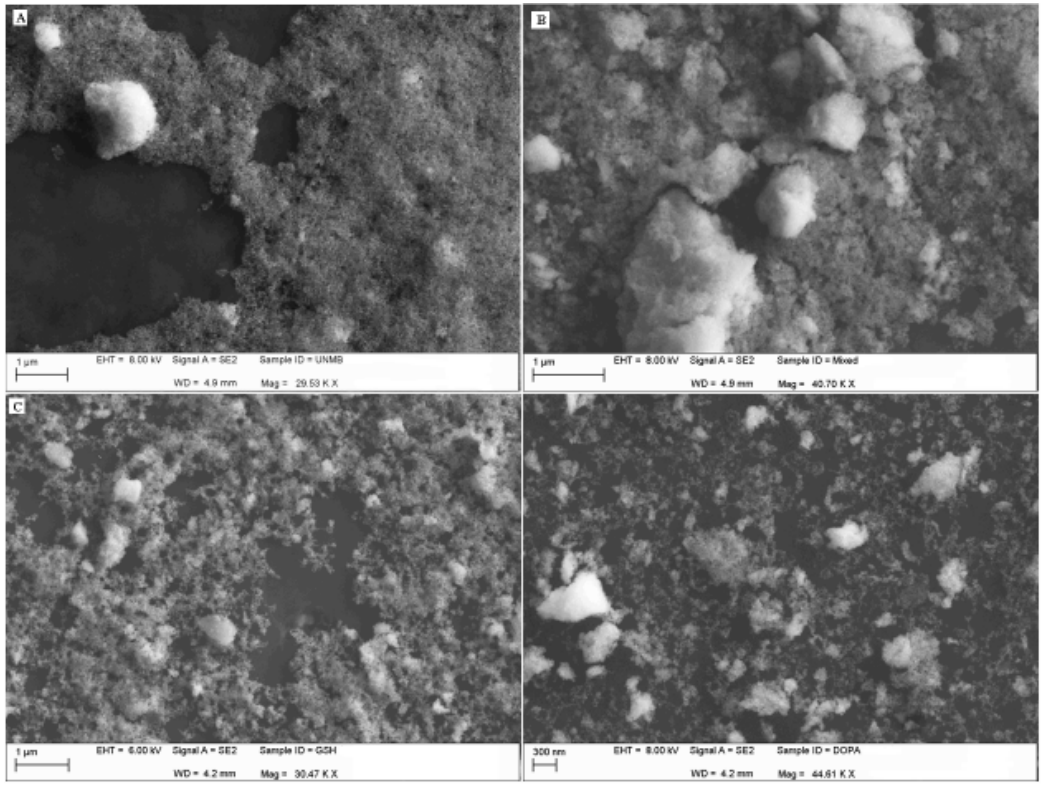


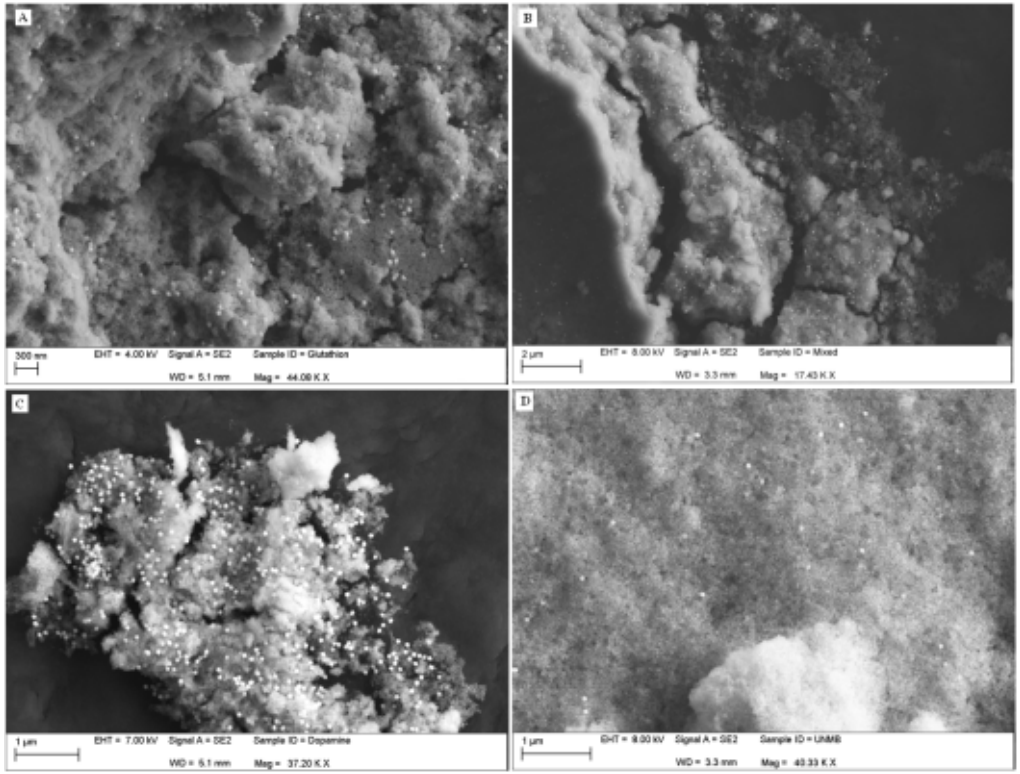
R = alkyl, aryl, heterocycle etc.

23 examples, yield up to 99%

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

Separation and Measurement of Silver Nanoparticles and Silver Ions Using Magnetic Particles





Environmental Samples

***Science of the Total Environment*: 472, 316-323 (2013)**

Sample	% AgNPs Captured by Magnetic particles
Distilled Water	99.01±0.21
Tap Water (Las Vegas)	98.05±0.33
Lake Hancock Water	98.18±0.29
San Francisco Bay Water	96.10±1.18

Bio-degradable & Bio-renewable Supports

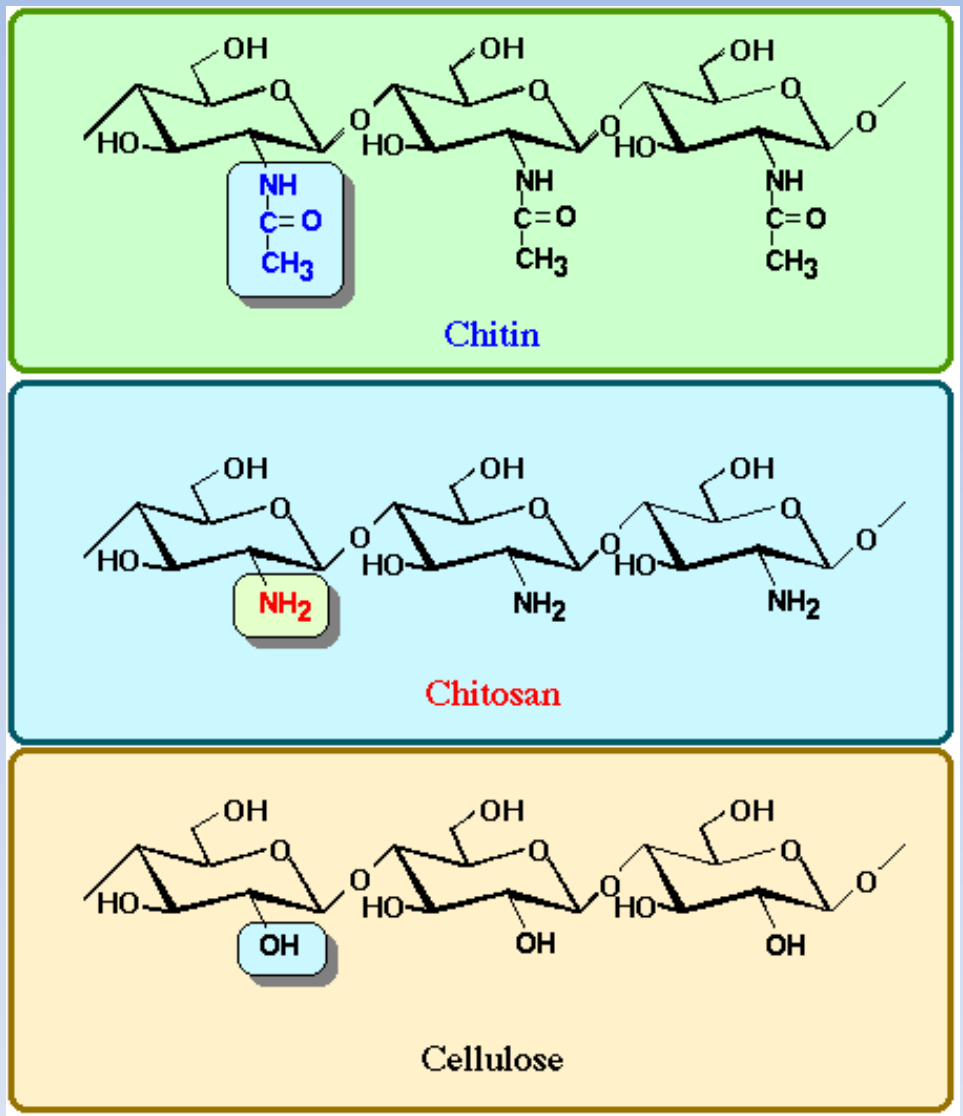
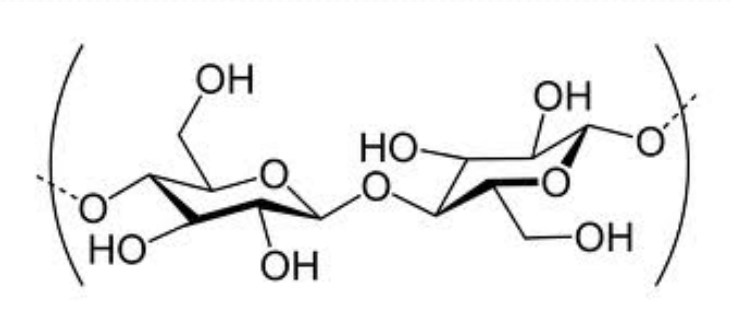


Fig. Structure of Chitin, Chitosan and Cellulose

Preparation of cellulose supported Pd-catalyst

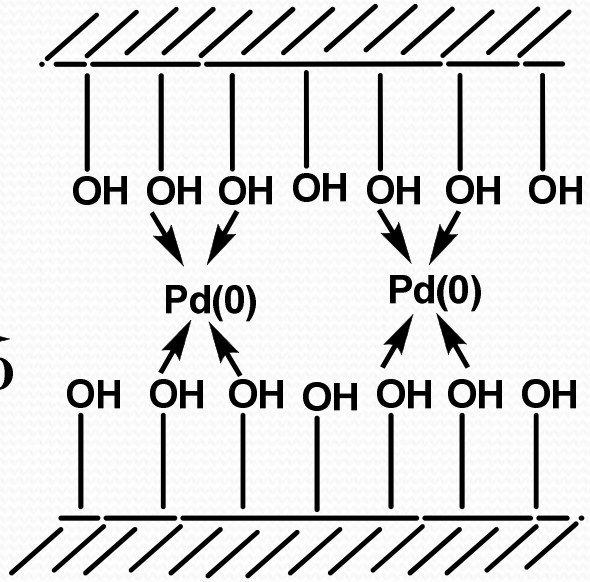


Cellulose

$PdCl_2$

$NaBH_4$, H_2O

rt, 15 h



Cellulose-Pd Catalyst