Greener Pathways to Nanomaterials and their Sustainable Applications

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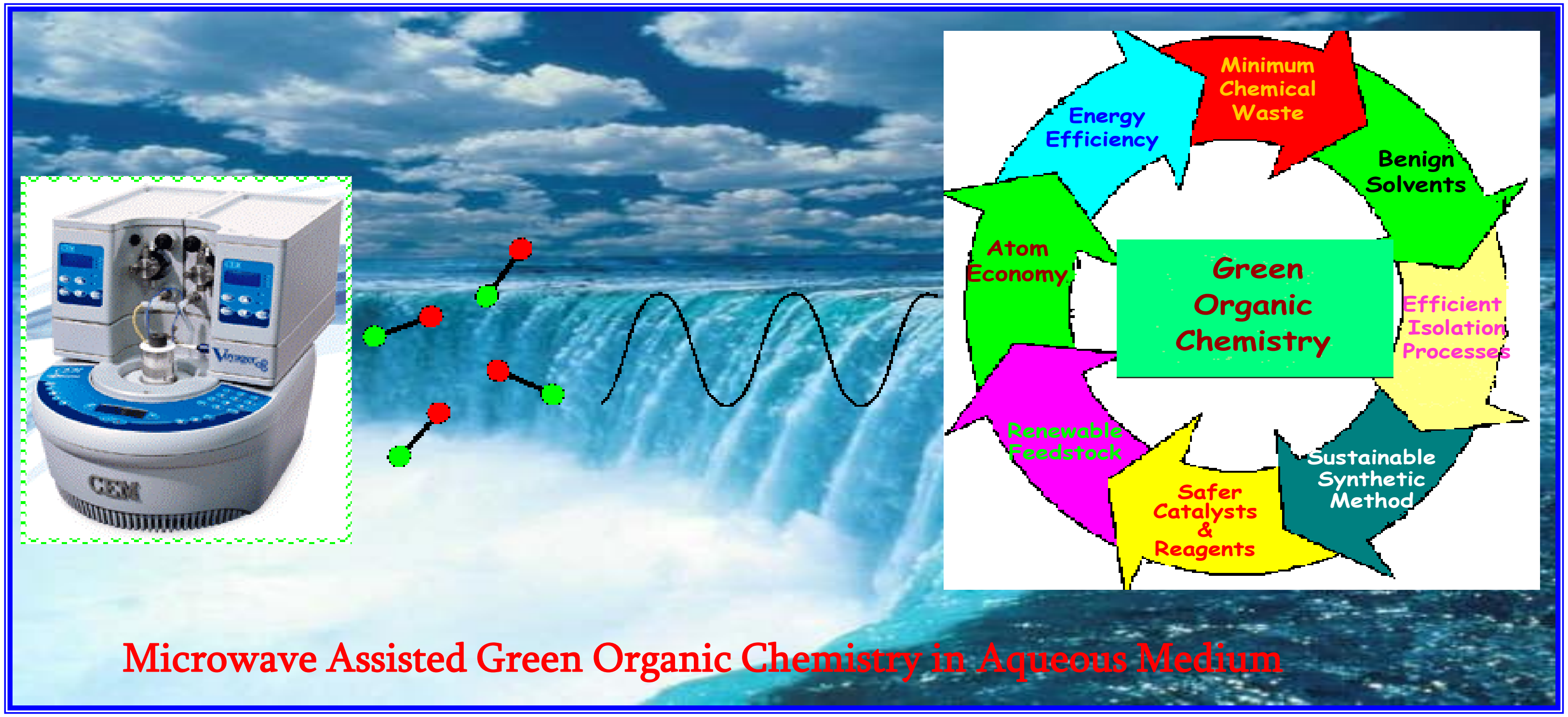
The Road To Sustainability
Impact Assessment
Risk Assessment
Risk Management
Benign by Design
WASTE MINIMIZATION
INTERSTATE
P2
Computer Modeling
Green Chemistry
CLEAN CATALYSTS
SEPARATION TECHNOLOGIES
Clean Products
Ecosystems Modeling
Credit Trading Design
CLEAN ENERGY
Renewable Sources
Electrochemistry
Solar, Wind, Biomass
Watershed Protection
Industrial Ecology
SLOW Roadwork Ahead
Systems Analysis
Life Cycle Assessment (LCA)
NRMRL/EPA

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

•CRADA's with the private companies: VeruTEK Technologies

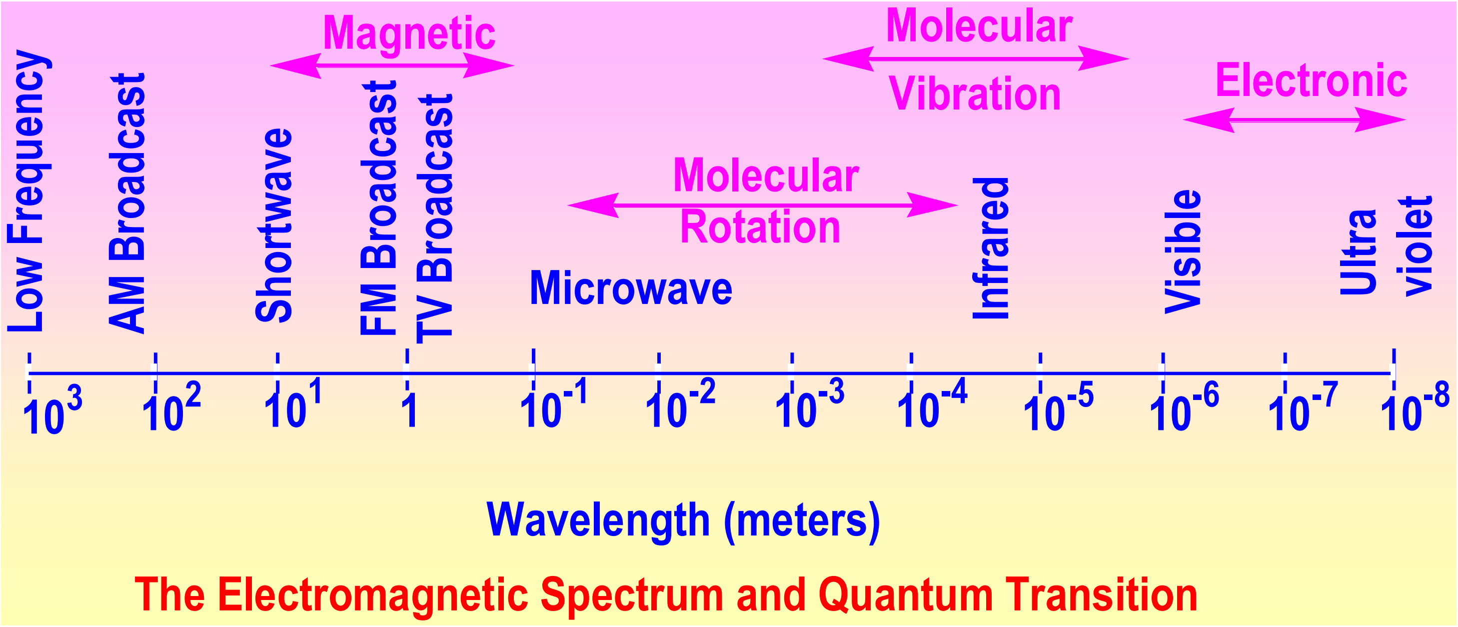
•Green Chemistry principles are accommodated via multi-faceted approach



Seminal Articles on these themes summarizing our in-house research: *Varma et al.*

1. *Acc. Chem. Res., 41*, 629-639 (2008) and *44*, 469-478 (2011);
2. *Chem. Soc. Rev.*, *37*, 1546-1557 (2008) and *41*, 1559-1584 (2012);
3. *Pure App. Chem.*, *73*, 193 (2007); *73*, 1309 (2007) and *80*, 777 (2008);
4. *Curr. Opinion Drug Disc.*, *10*, 723-737 (2007);
5. *Green Chem.*, *12*, 743-754 (2010)

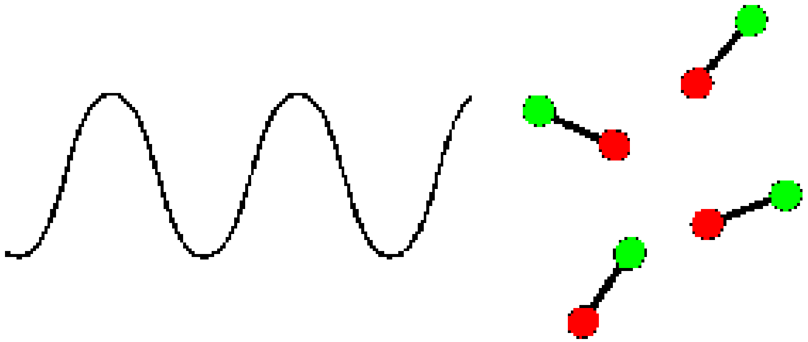
Microwaves



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

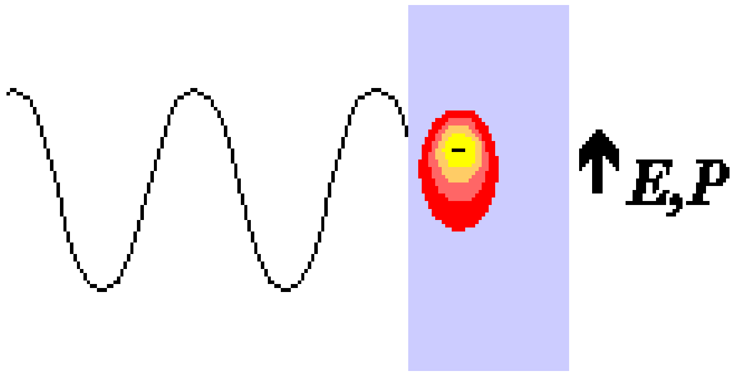
Microwave Dielectric Heating Mechanisms

Dipolar Polarization Mechanism



Dipolar molecules try to align to an oscillating field by rotation

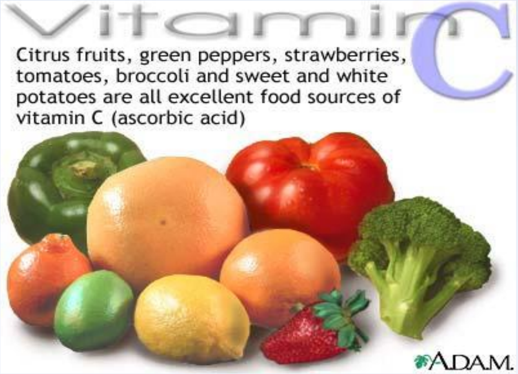
Conduction Mechanism



Ions in solution will move by the applied electric field

Plant Extract

Sugar



Vitamins

Tea

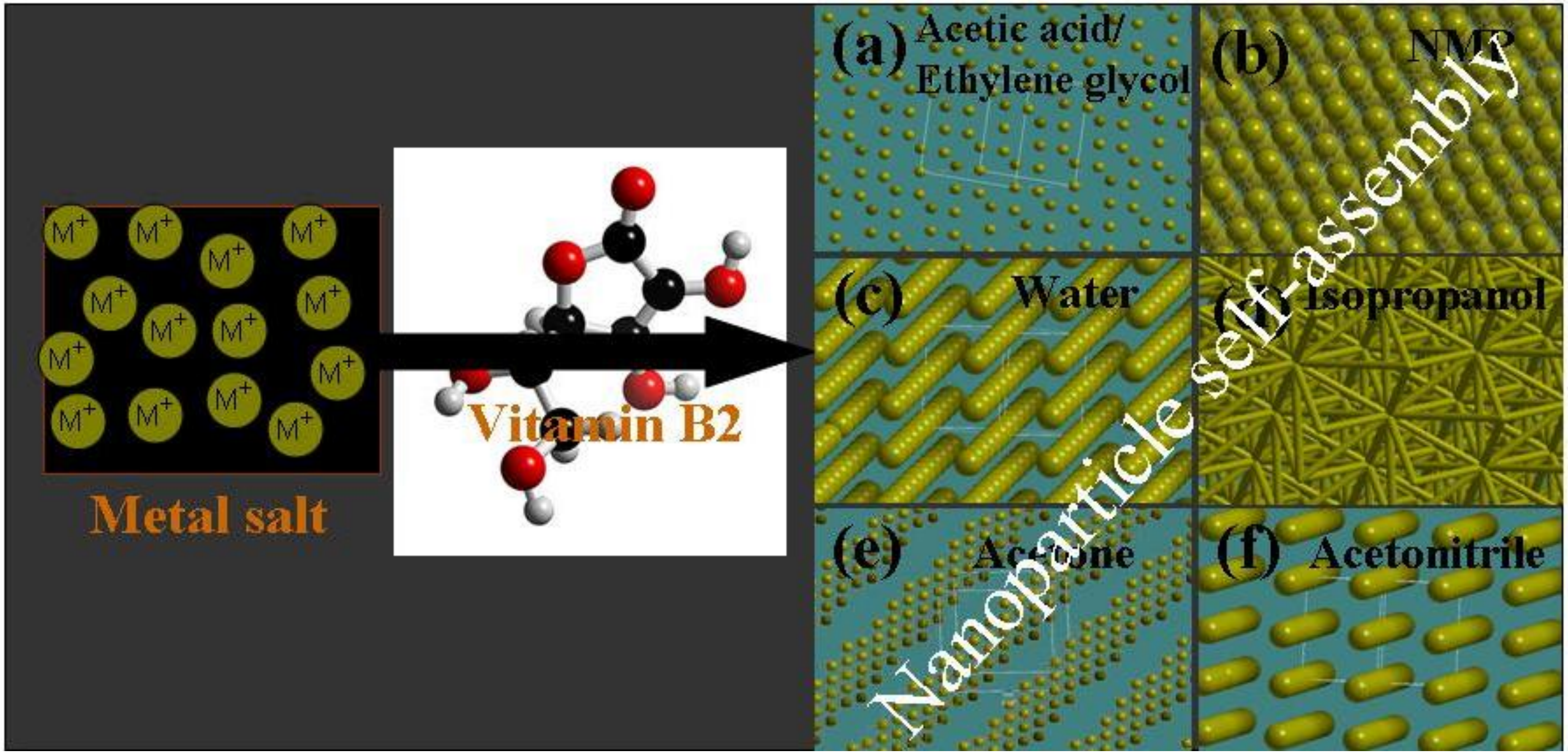
Wine

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:** Nanoparticle self-assembly demonstrated



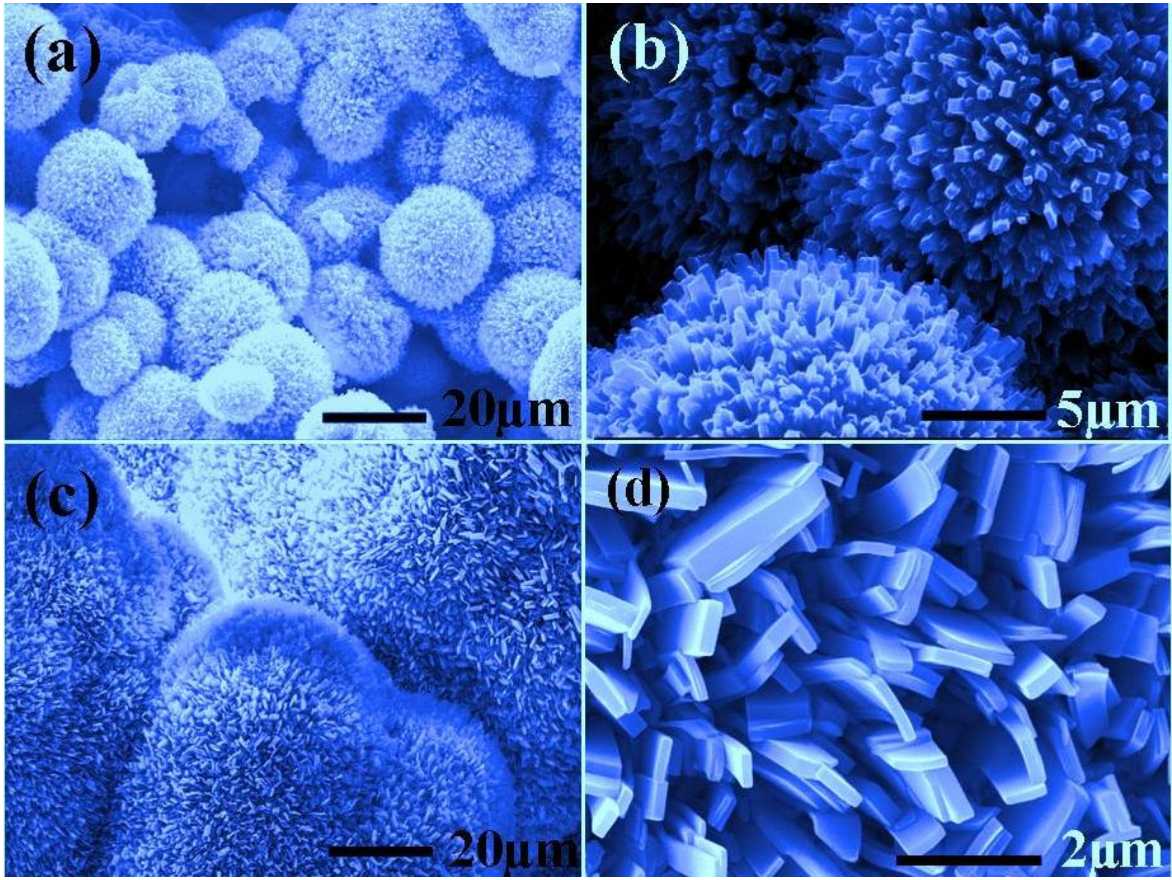
Nadagouda & Varma: *Green Chemistry*, *8*, 516, (2006)

Green Synthesis of Nanomaterials

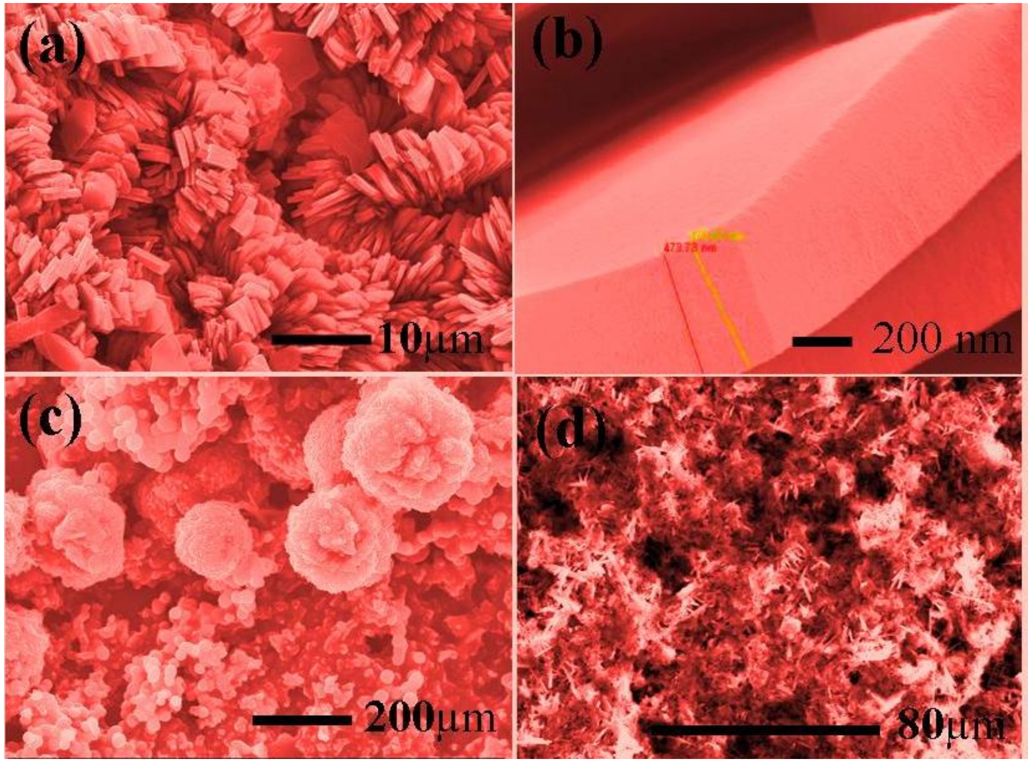
PROBLEM: Synthesize nanomaterials in a sustainable manner.

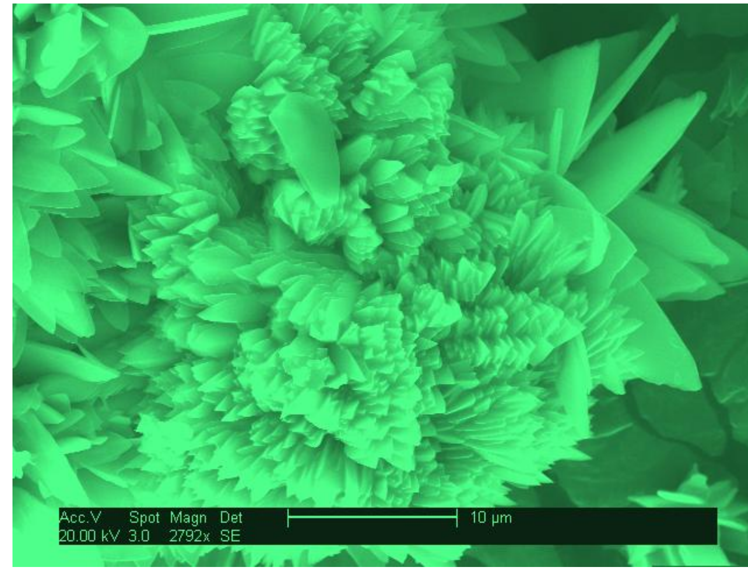
TECHNOLOGY SOLUTION: *Learning from Nature*- Use Vitamin B_1 in water to do the reduction and capping.

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

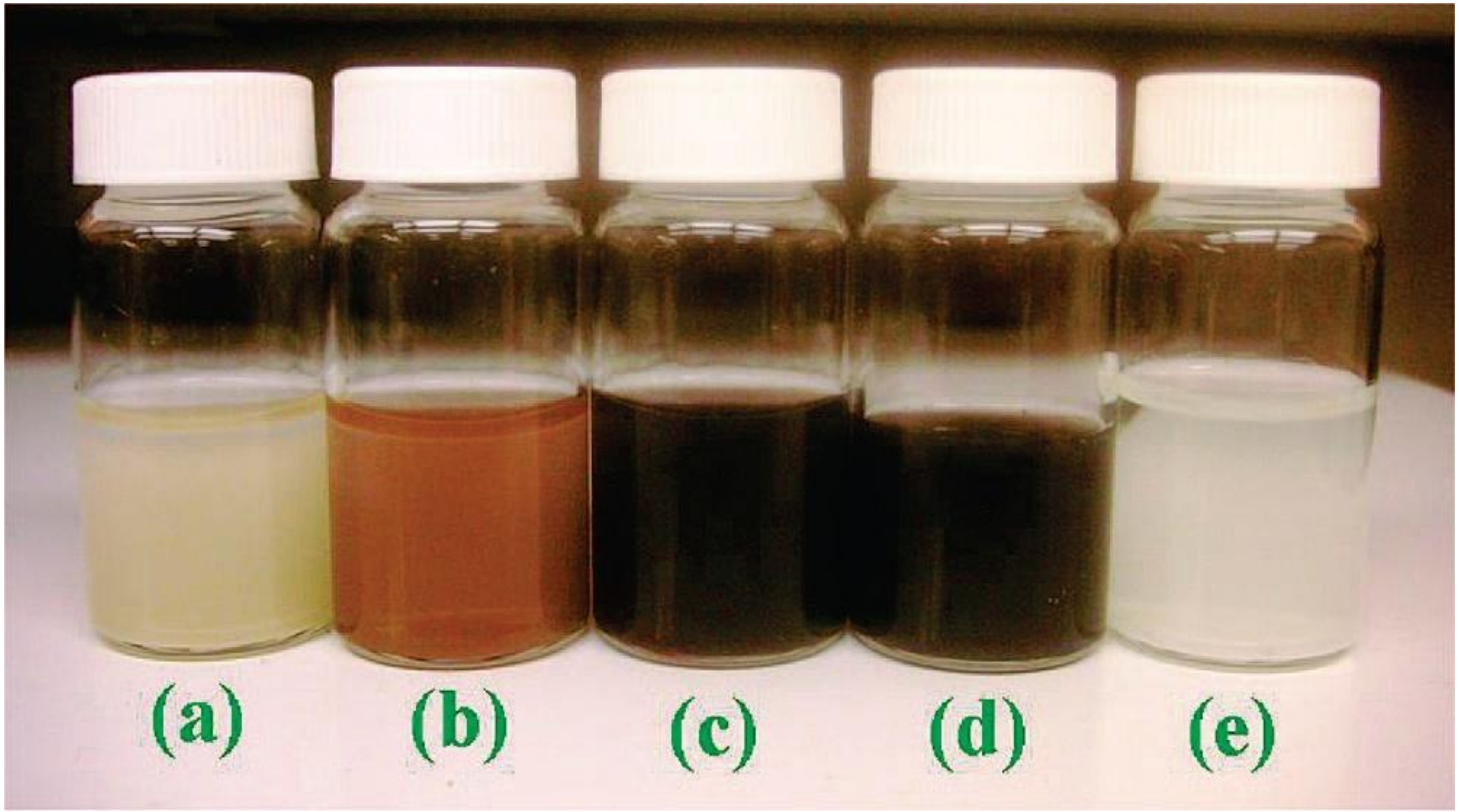
(c-d) Pd-catalyzed polypyrrole & polyaniline

Aligned platinum nanoflowers synthesized using vitamin B_1 in aqueous media

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

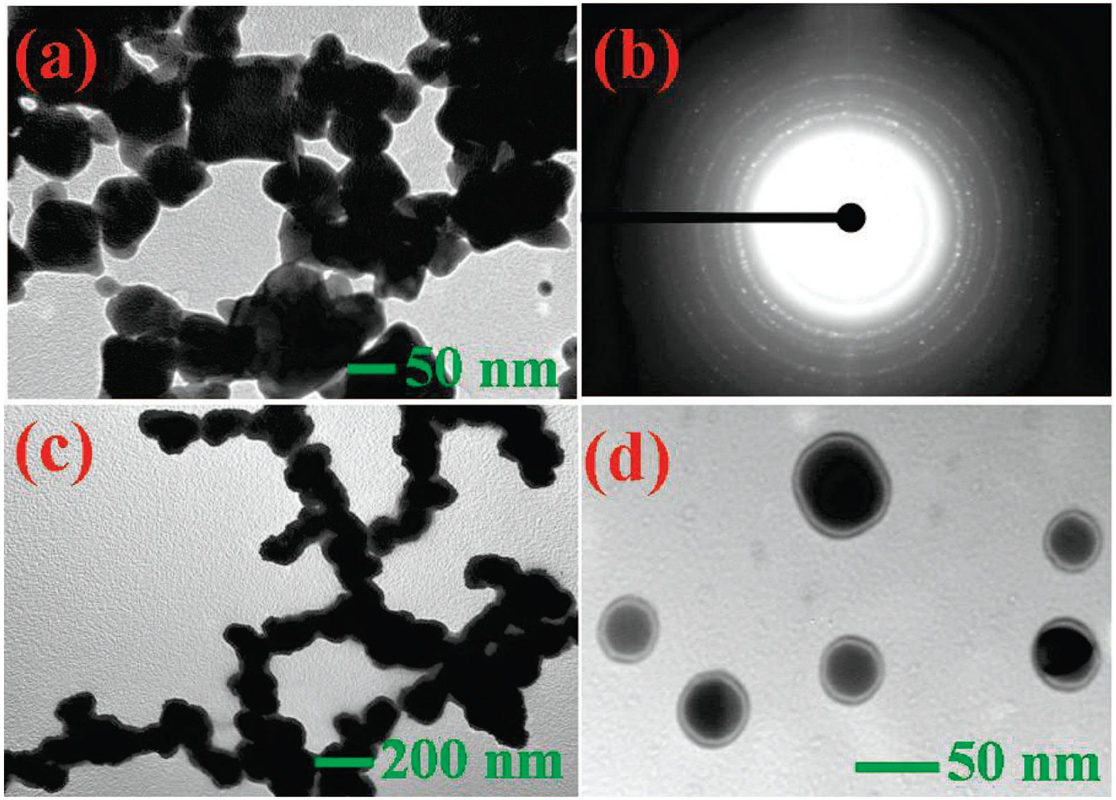
A Greener Synthesis of Core (Fe, Cu)-Shell (Au, Pt, Pd, and Ag) Nanocrystals Using Aqueous Vitamin C

Nadagouda & Varma: *Crystal Growth and Design*, *7*, 2582-2587 (2007)



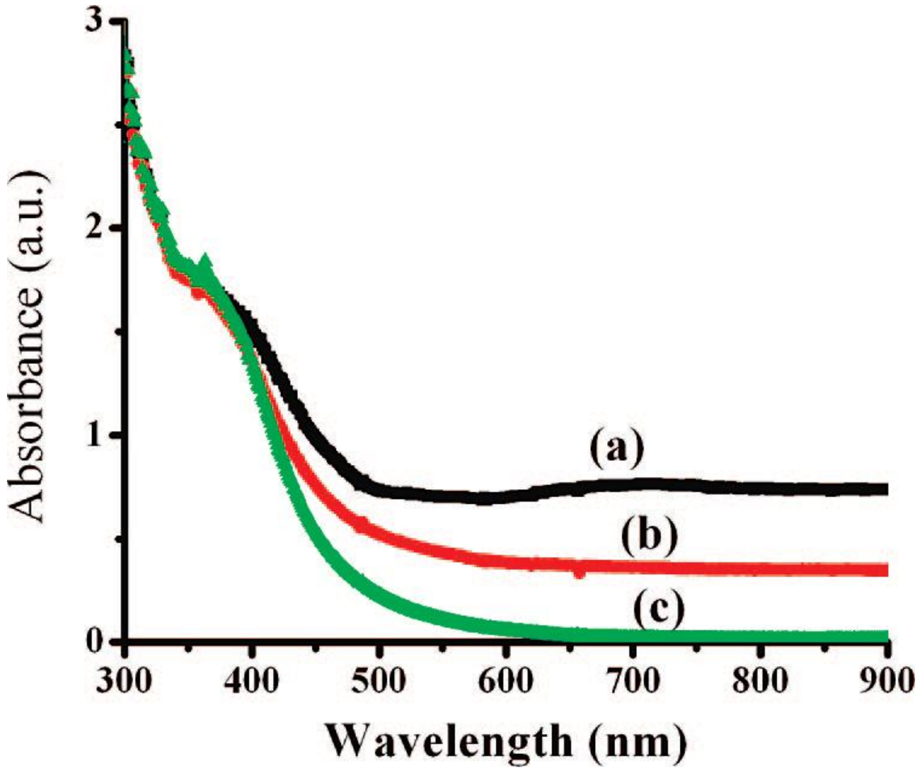
Photographic images of ascorbic acid reduced metallic nanostructures of (a) Ag, (b) Au, (c) Pd, (d) Pt, and (e) Cu.

Nadagouda & Varma: *Crystal Growth and Design*, *7*, 2582 (2007)



TEM images of core (Fe)-shell with (a) Au, (b) SAED of Au, (c) Pd, and (d) Pt core–shell bimetallic nanostructures.

Nadagouda & Varma: *Crystal Growth and Design*, *7*, 2582 (2007)



UV–visible spectra of core (Fe) shell with (a) Au, (b) Pd, and (c) Pt nanostructures synthesized using ascorbic acid.

Nadagouda & Varma: *Crystal Growth and Design*, *7*, 2582 (2007)

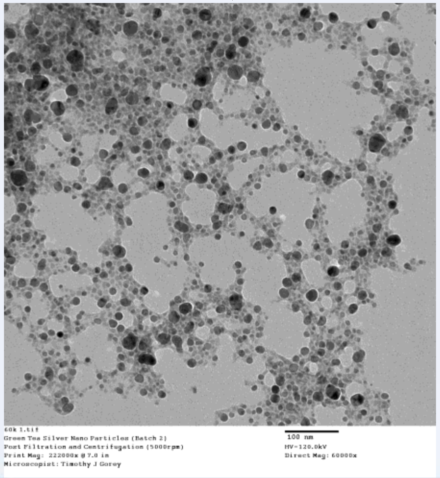
Tea for producing metal nanoparticles

Metal salt +

= Metal nanoparticle

(Ag, Au, Pd, Fe etc.)

Ag nanoparticle using green tea

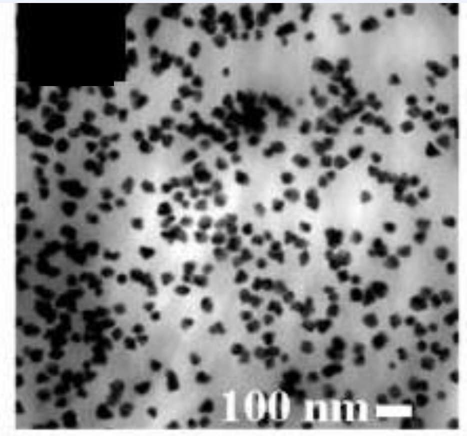


All particles are obtained at Room Temp.

Fe zero 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)

EPA United States Environmental Protection Agency

Green Remediation

VERUTEK TECHNOLOGIES

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)

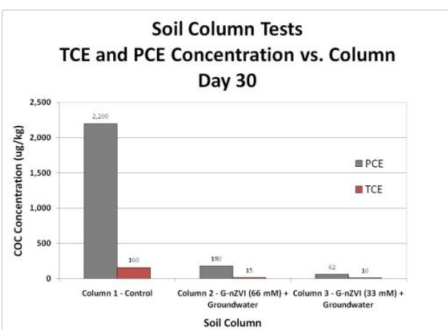
Nadagouda, Hoag, Collins, Varma: *Crystal Growth & Design*, *9*, 4979 (2009);
Remediation Application: *J. Mater. Chem*. 19, 8671 (2009);
Toxicity studies: *Green Chemistry*, *12*, 114 (2010)-Hot Article

Green Remediation CRADA–US EPA and VeruTEK Technologies (Connecticut Small Business)

(*U S Patents*, 7,963,720 & 8,057,682, and others pending)

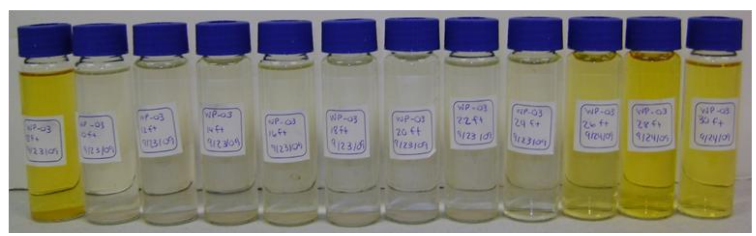
EPA United States Environmental Protection Agency

Nanoscale Zero Valent Iron Made By Combining Natural Plant Extracts Plus Dissolved Iron at Ambient Temperature



Reductive Treatment Tests for a Chlorinated Solvent Site in Europe

- Useful as Catalysts to Form Free Radicals to Destroy Nearly Any Organic Chemical Pollutant
- Can be Made On Site and In Situ (in the Subsurface)
- Directly Detoxifies Chlorinated Solvent, Chromium and Arsenic
- Complements VeruTEK's Green Emulsion and Oxidation Technologies now Used in U.S., Europe, Australia & Africa



Used to Help VeruTEK Develop Direct Free Radical Testing Kit for Water – Critical for Optimizing Use of Green Synthesized nZVI

VeruTEK TECHNOLOGIES

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)

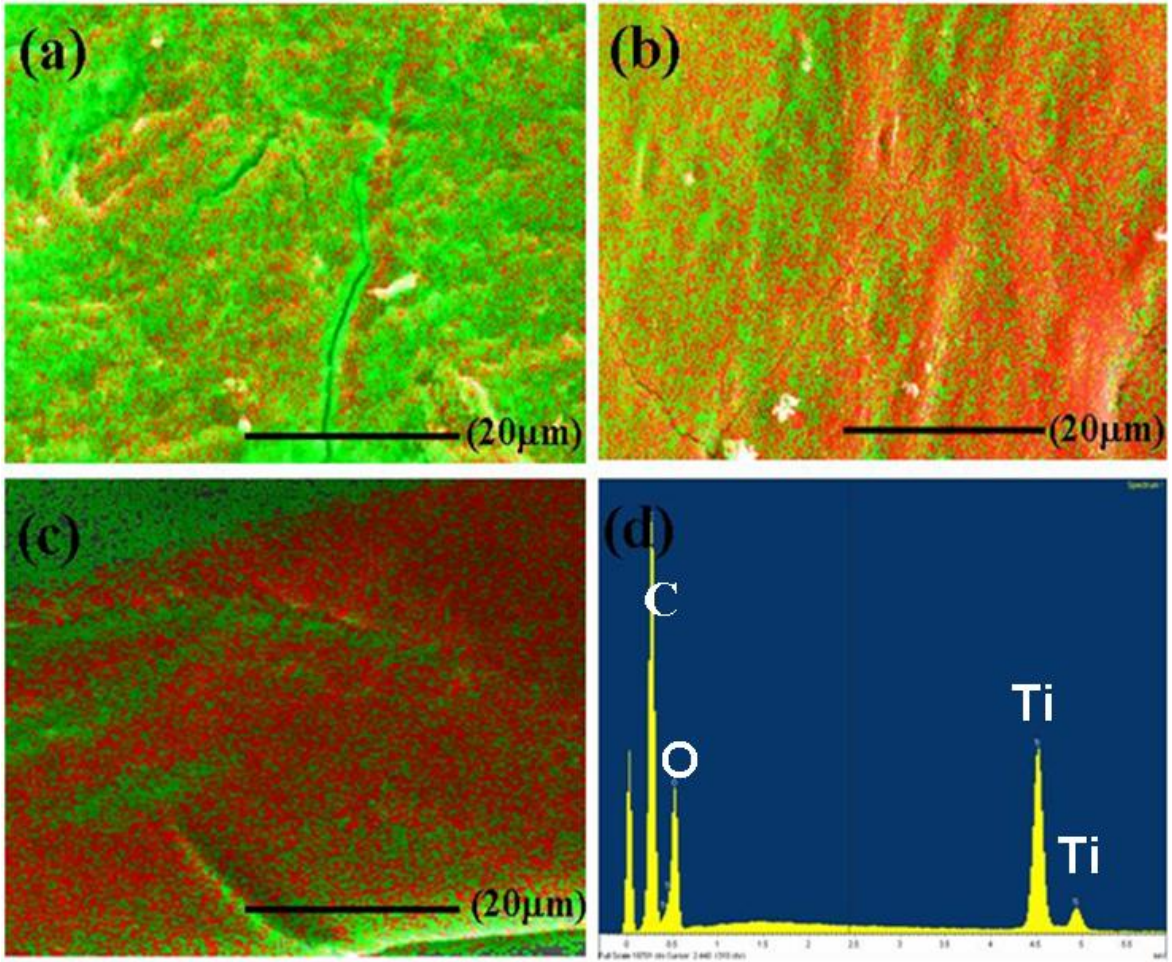
Objective

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

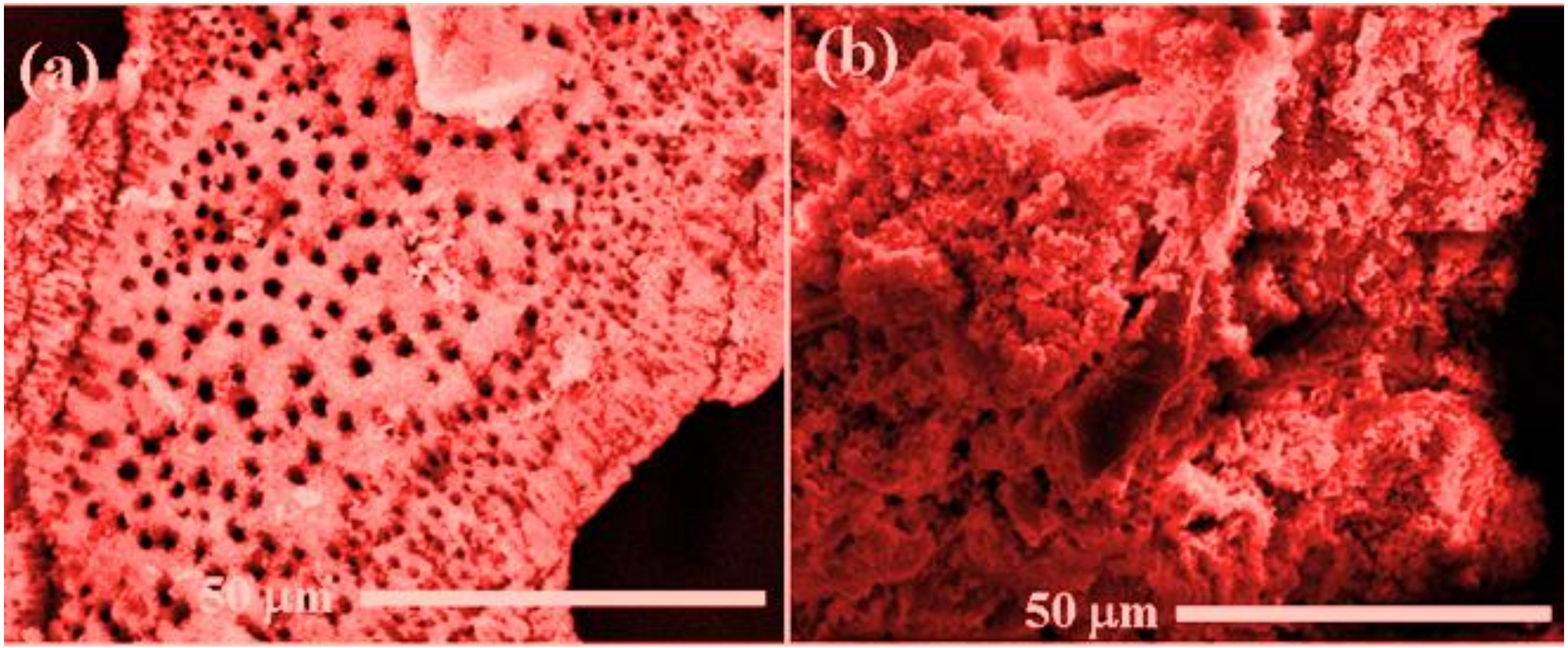
Nadagouda & Varma: *J. Smart Materials and Structures*, *15*, 1260 (2006)



(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:

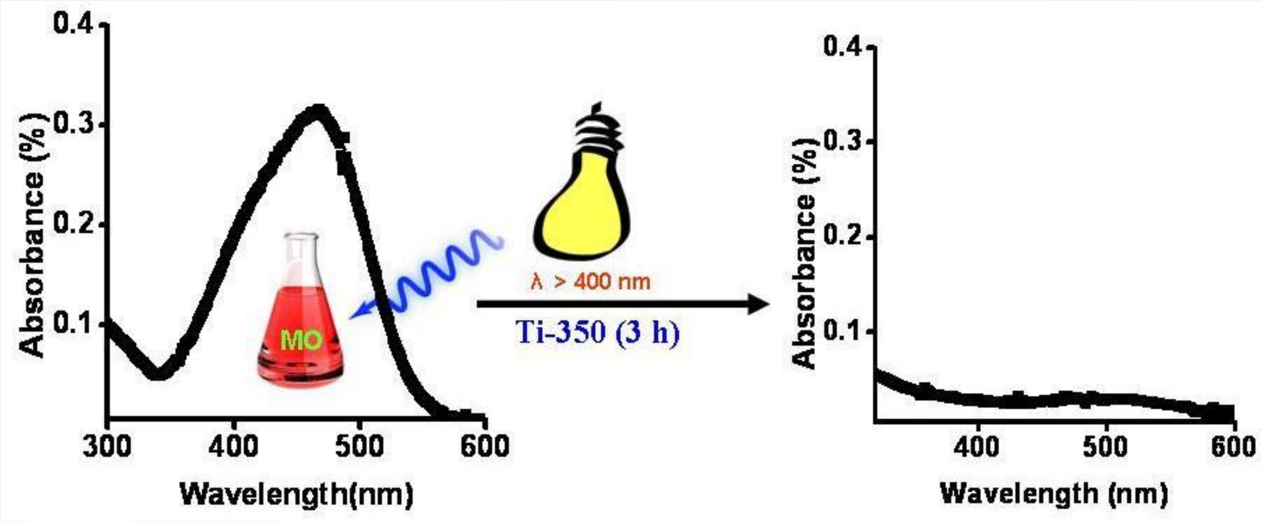
(a) MW-initiated followed by conventional heat treatment at 850 ^{0}C for 1 h and (b) Only conventional heating furnace at 850 ^{0}C for 1 h

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

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. Nanoscience and Nanotechnology, 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)

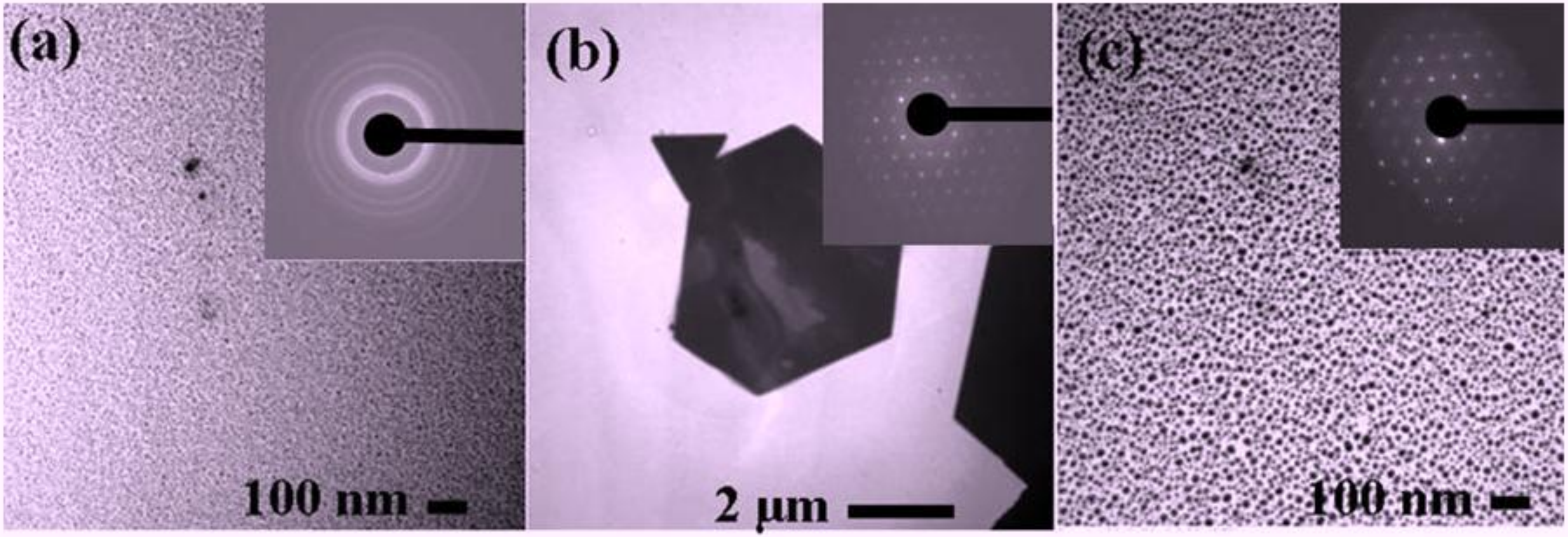
Microwave-Assisted Reactions Using Sugar Solutions

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).

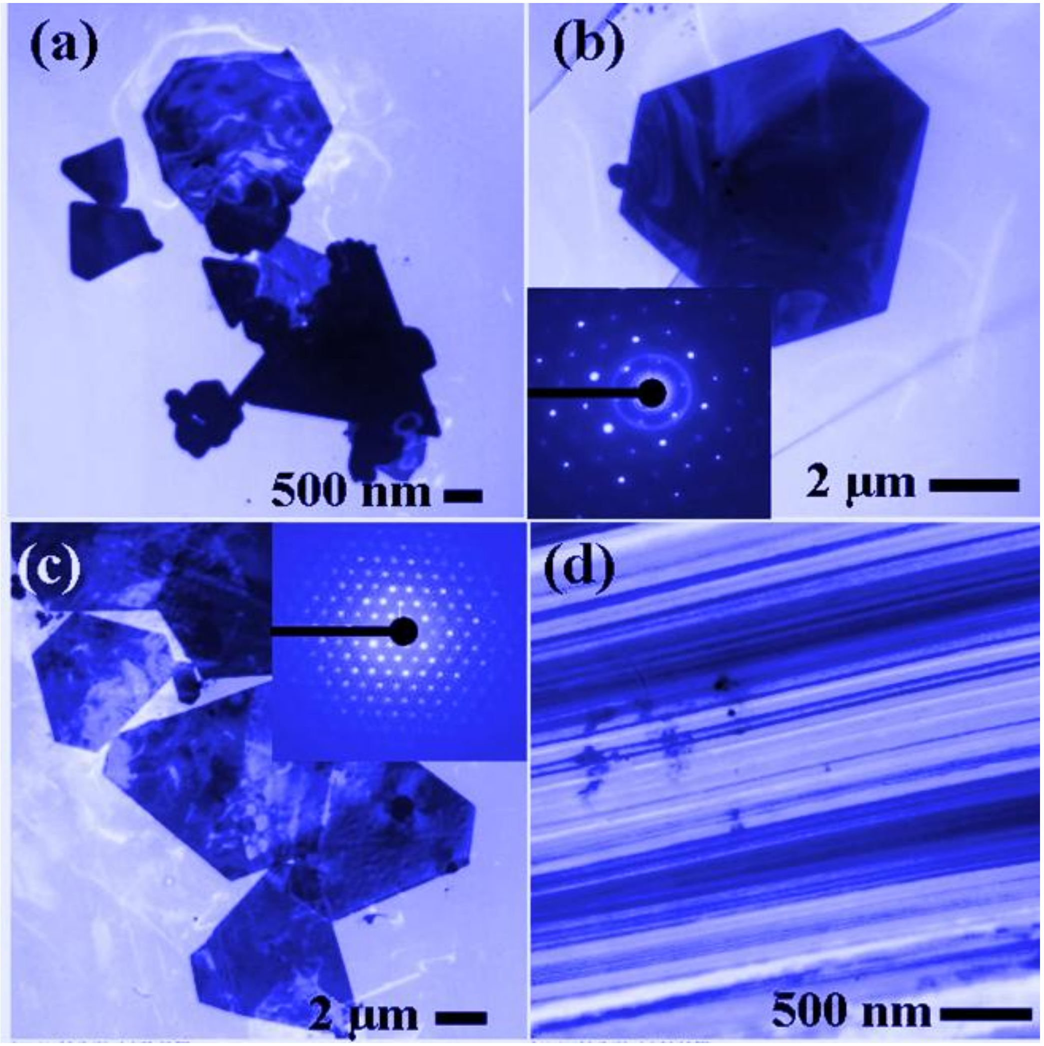
Gold Nanostructures



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)

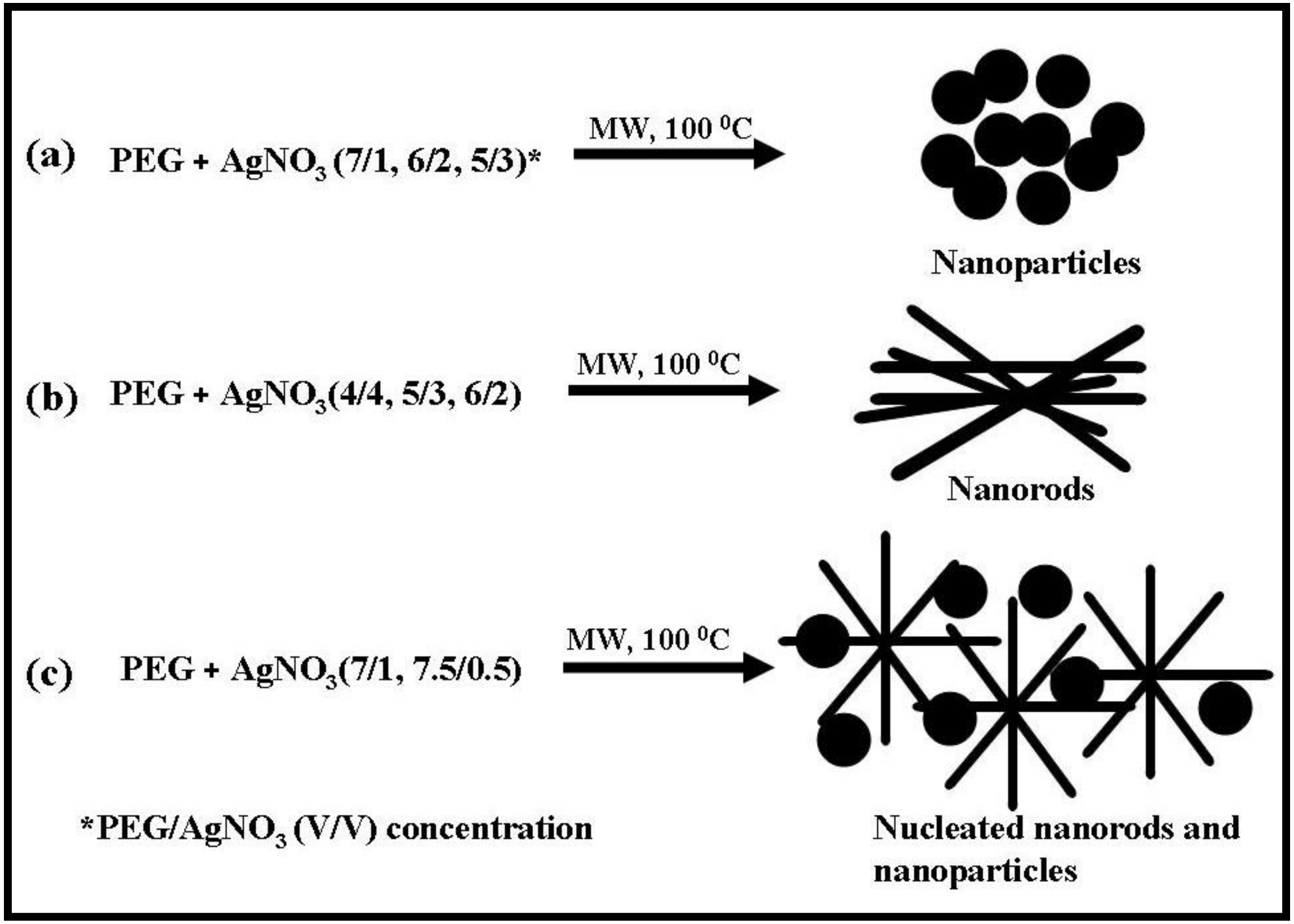


TEM image of (a-d) gold nanostructures obtained using low concentration of sugar solution under microwave irradiation

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

Bulk Synthesis of Silver Nanorods in Poly(ethylene glycol) using Microwave Irradiation

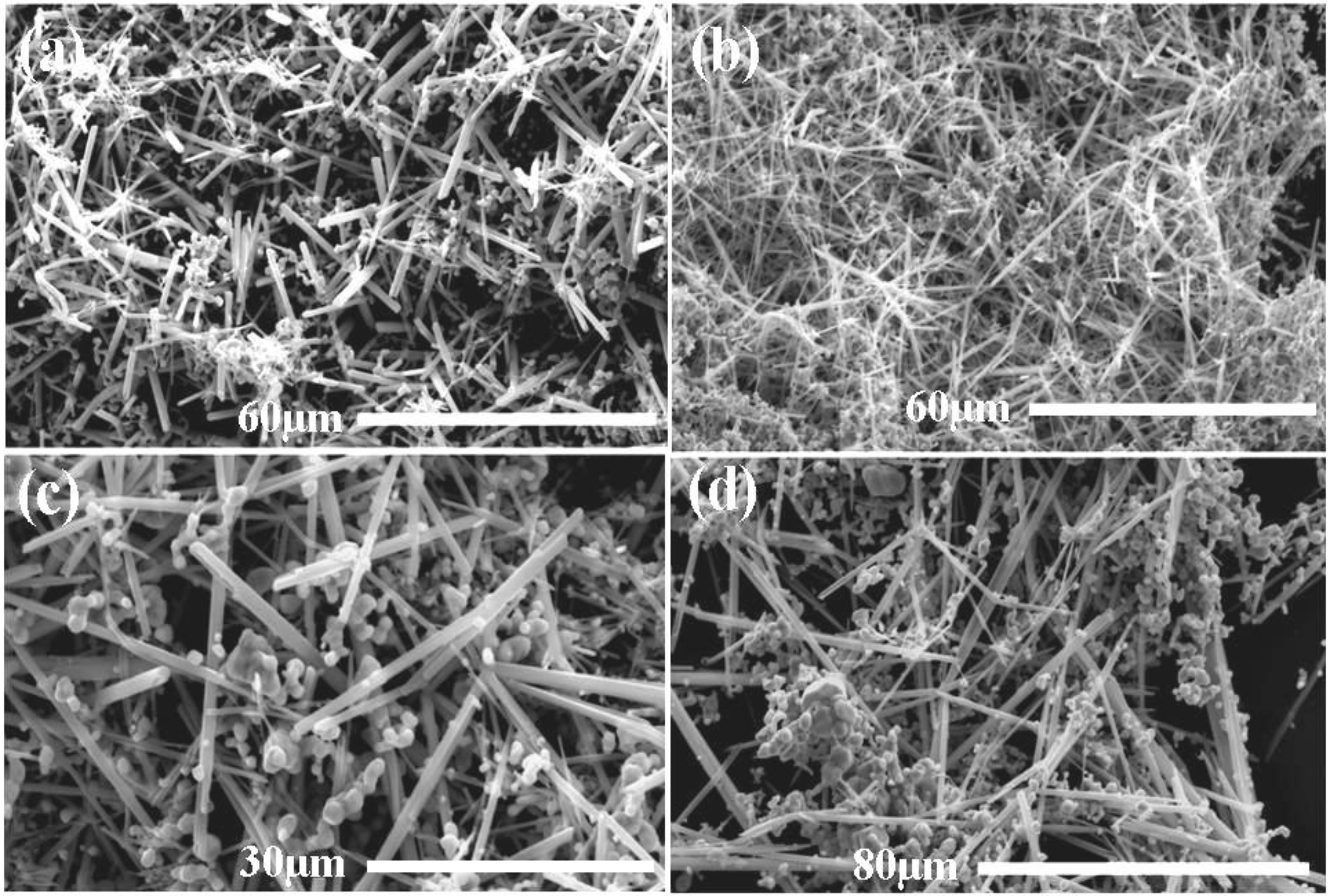
Nadagouda & Varma: *Crystal Growth and Design*, *8*, 291-295 (2008)



Schematic of experimental mechanisms that generate: Silver (a) Nanoparticles, (b) Nanorods, and (c) Nucleated Nanorods and Nanoparticles.

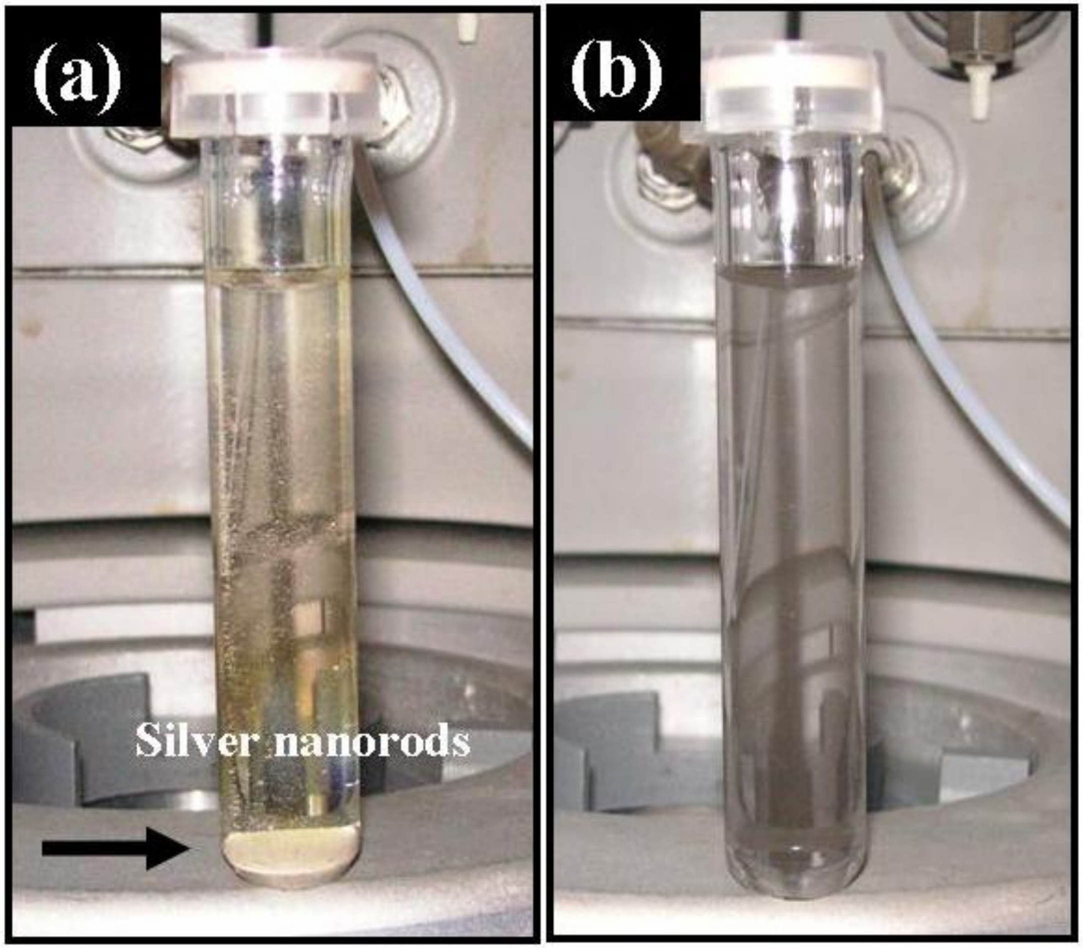
Nadagouda & Varma: *Crystal Growth and Design*, *8*, 291-295 (2008)

Bulk Synthesis of Silver Nanorods in Poly(ethylene glycol) using Microwave Irradiation



SEM images of silver nanorods synthesized via MW irradiation using (a) 4/4, (b) 5/3 , (c) 3/5 and (d) 2/6 PEG:$AgNO_3$ volume (mL) ratio

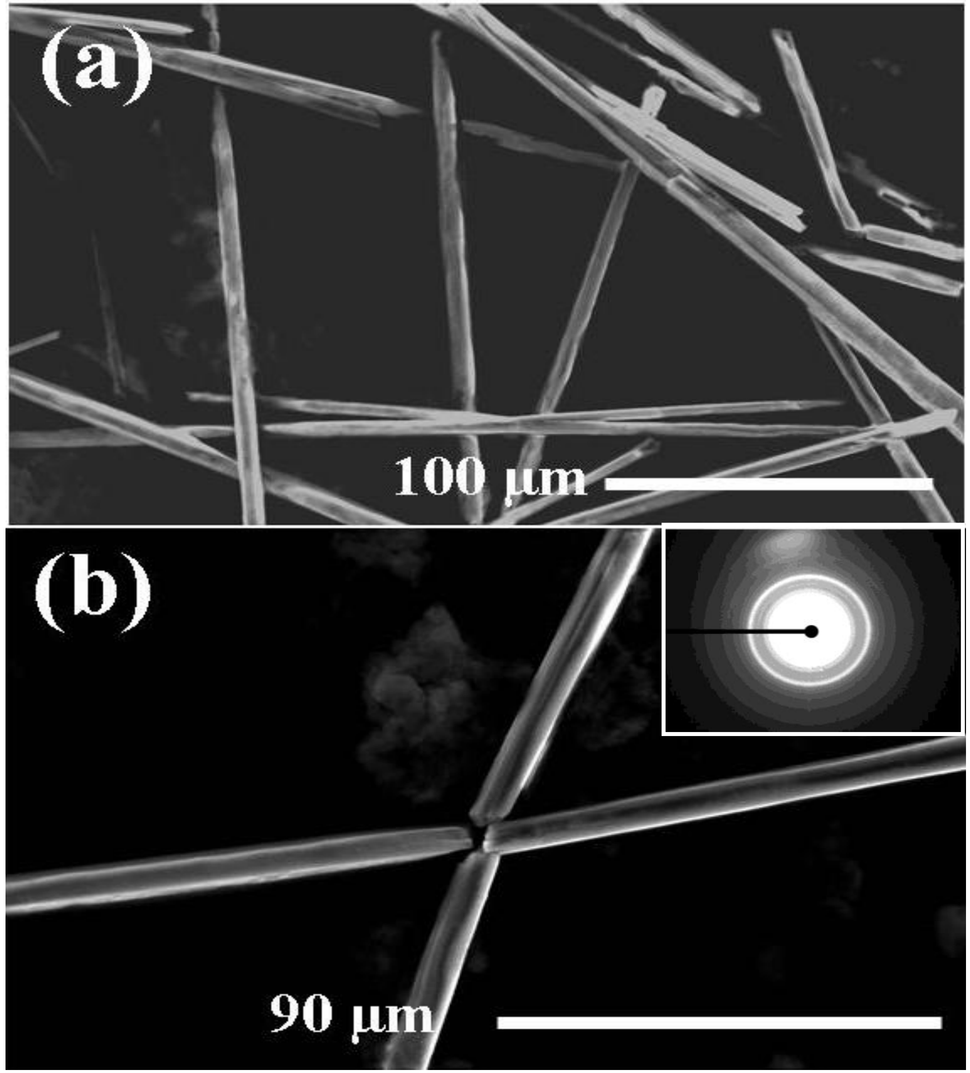
Nadagouda & Varma: *Crystal Growth and Design*, *8*, 291-295 (2008)



(a) Precipitated silver nanorods under MW irradiation for 2 min using PEG and

(b) Control reaction of the same reaction composition using oil bath at 100 ^{0}C for 1 hr.

Nadagouda & Varma: *Crystal Growth and Design*, *8*, 291-295 (2008)



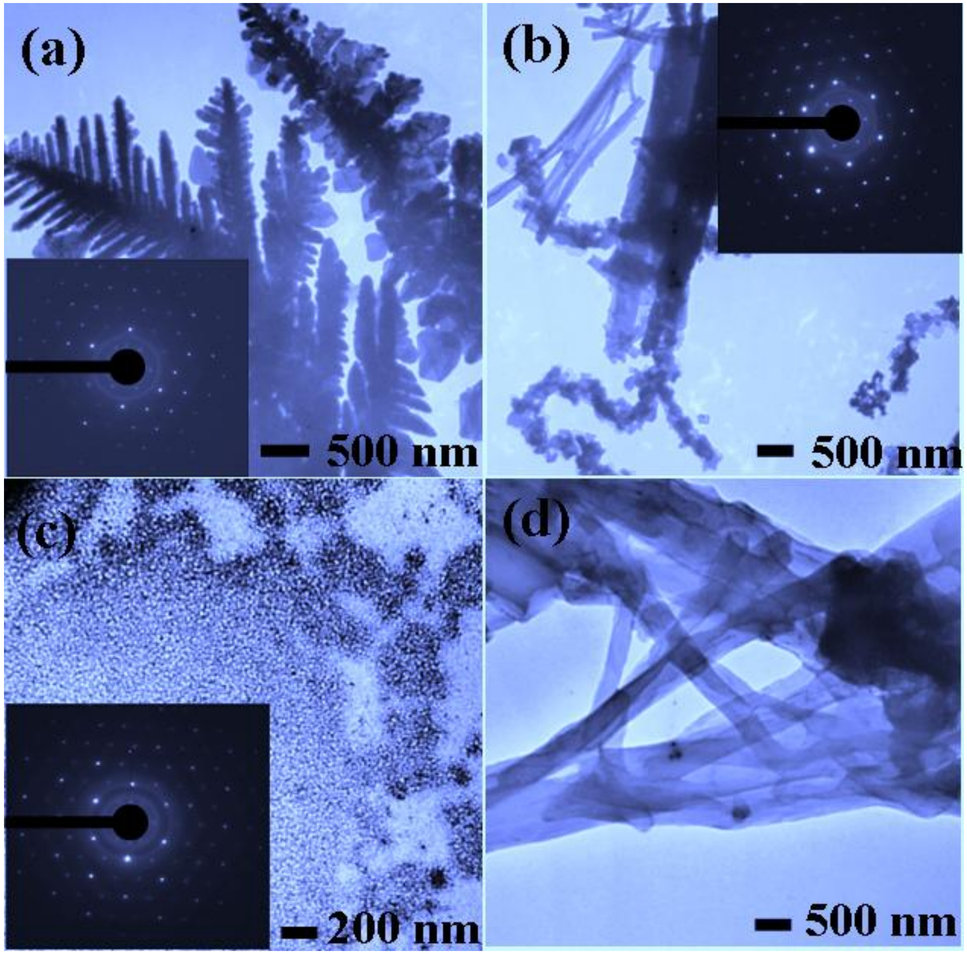
SEM images of Fe nanorods obtained from PG-12 composition (4 mL of PEG + 4 mL $Fe(NO_3)_3$ XH_2O) **under MW conditions; inset shows SAED pattern.**

Noble Metal Polymer Nanocomposites

Polymer nanocomposites are the class of reinforced polymers with low quantities of nanometric-sized metal nanoparticles.

Applications:

- **fire resistance and strength**
- **coating materials in automobile**
- **improved barrier properties**
- **civil and electrical engineering**
- **Packaging etc.**



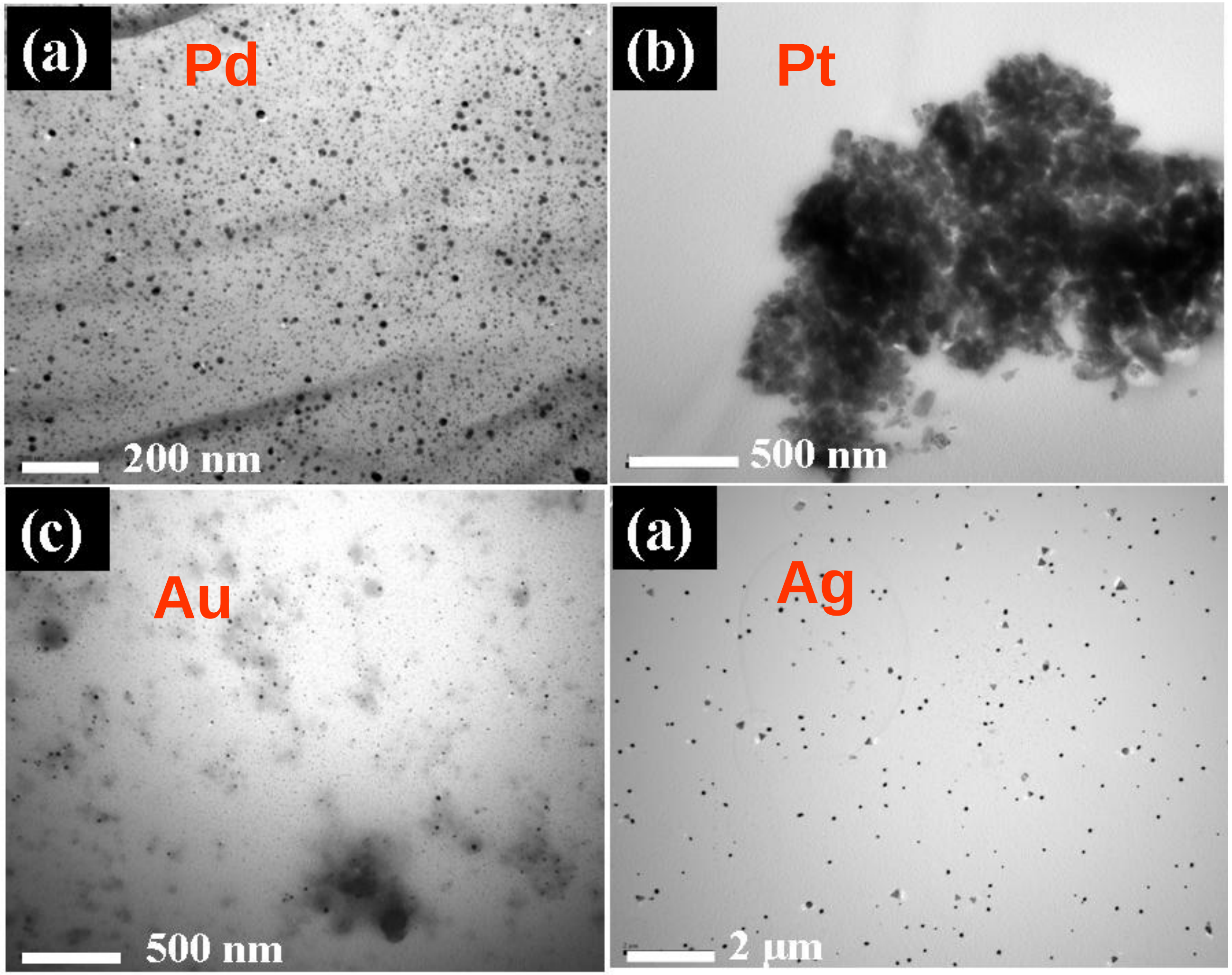
TEM images of different shape noble metal-polyaniline nanocomposites obtained from polyaniline nanofibers (synthesized using 1M acetic acid):

(a) Ag, (b) Pd, (c) Au and (d) Pt Nanocomposites.

(b) Inset shows corresponding electron diffraction patterns

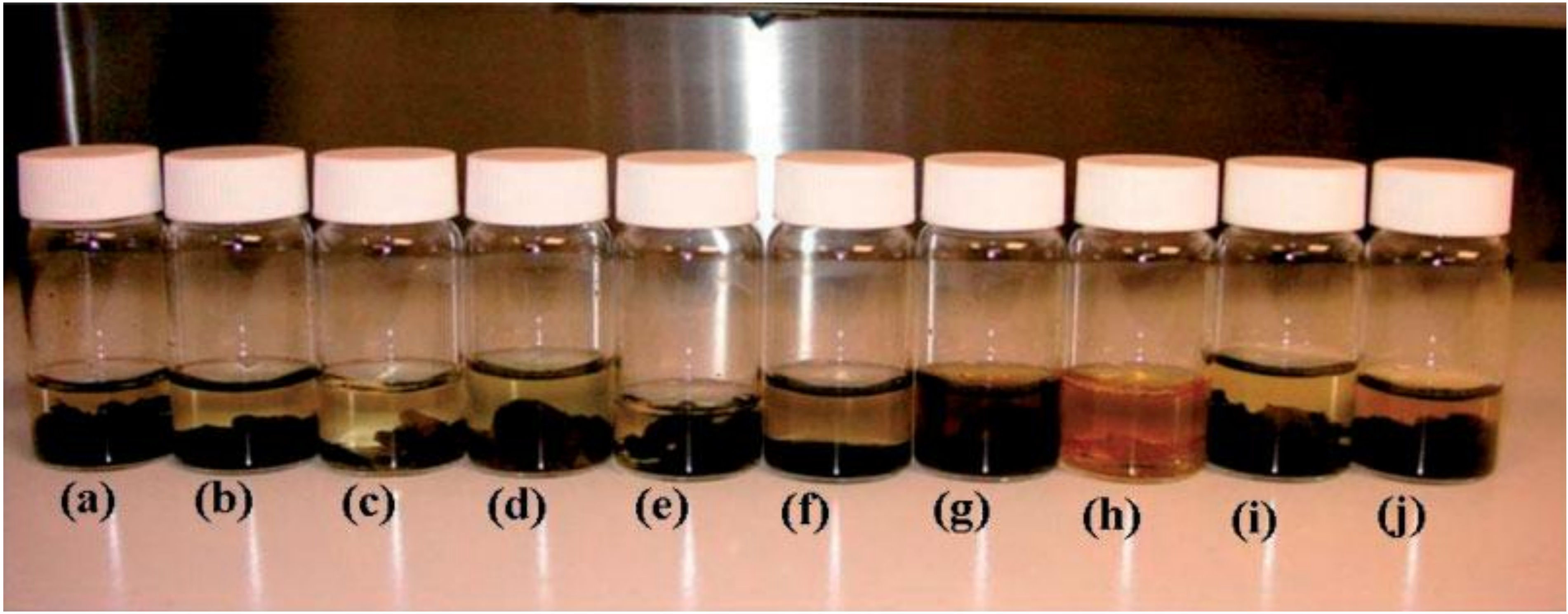
Nadagouda & Varma: *Green Chemistry*, *9*, 632-637, (2007)

Polypyrrole Nanocomposites



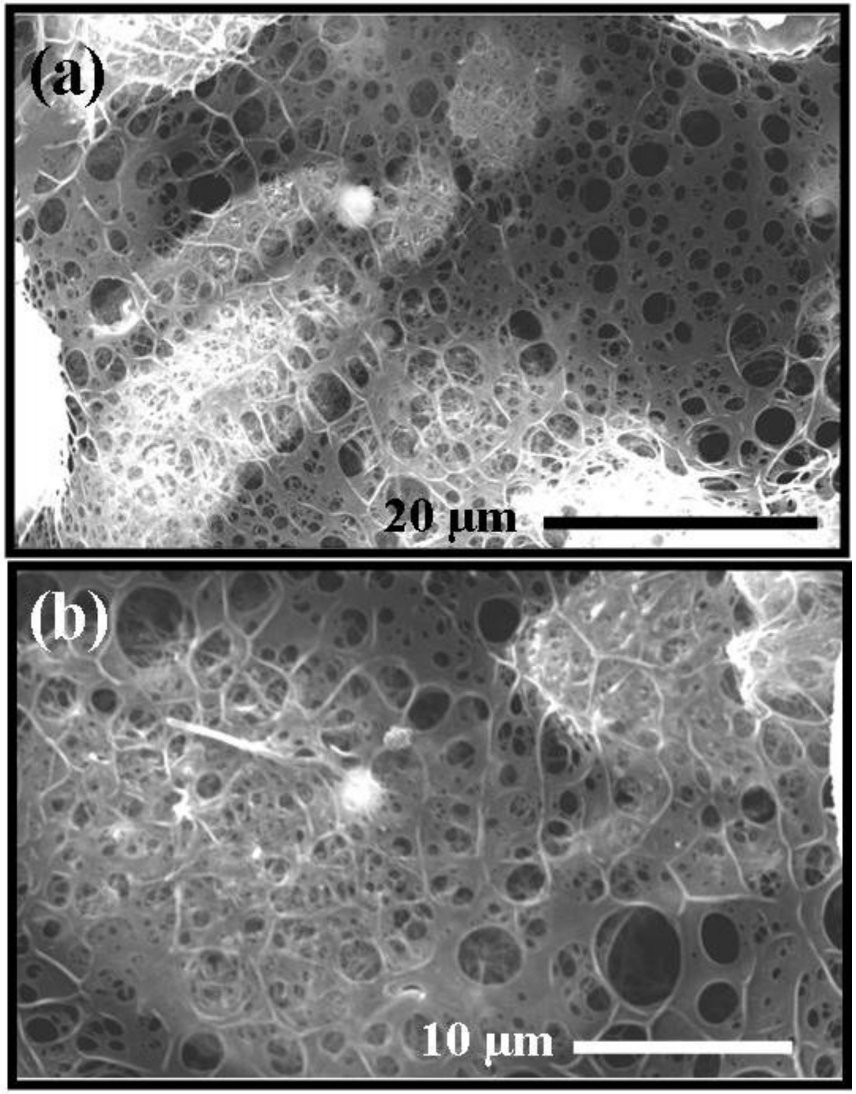
Nadagouda & Varma: *Green Chemistry*, *9*, 632-637, (2007)

Novel Metallic, Bimetallic Cross-Linked Poly(vinyl alcohol) Nanocomposites under MW Irradiation Conditions



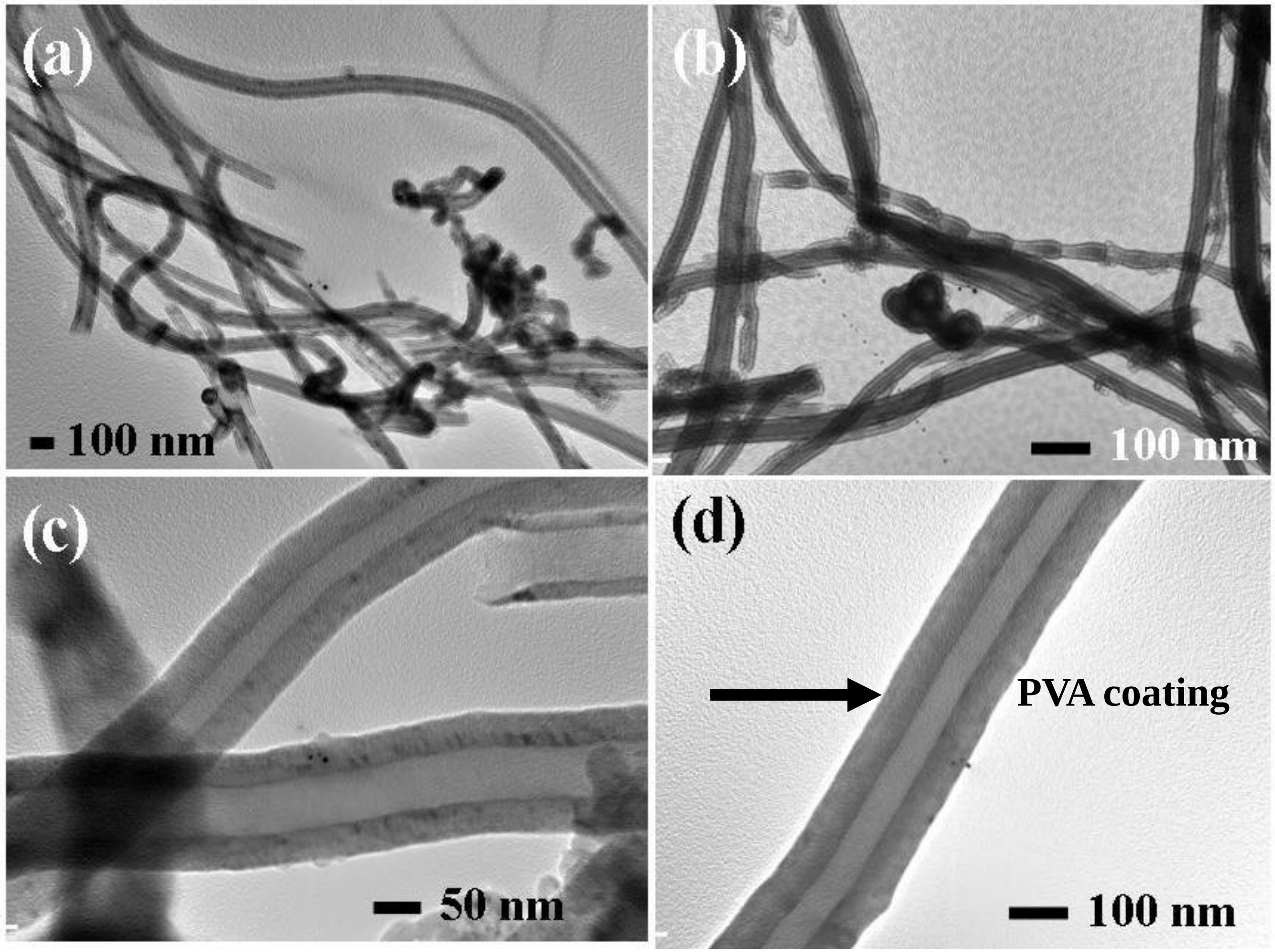
Cross-linked poly (vinyl alcohol)- with various metallic and bimetallic systems: (a) Pt, (b) Pt-In, (c) Ag-Pt, (d) Cu, (e) Pt-Fe, (f) Pt with higher concentration ratio, (g) Cu-Pd, (h) In, (i) Pt-Pd and (j) Pd-Fe.

Nadagouda & Varma: *Macromol. Rapid Commun*., *28*, 465 (2007)



SEM images of (a-b) 75 mg SWNT cross-linked PVA nanocomposites

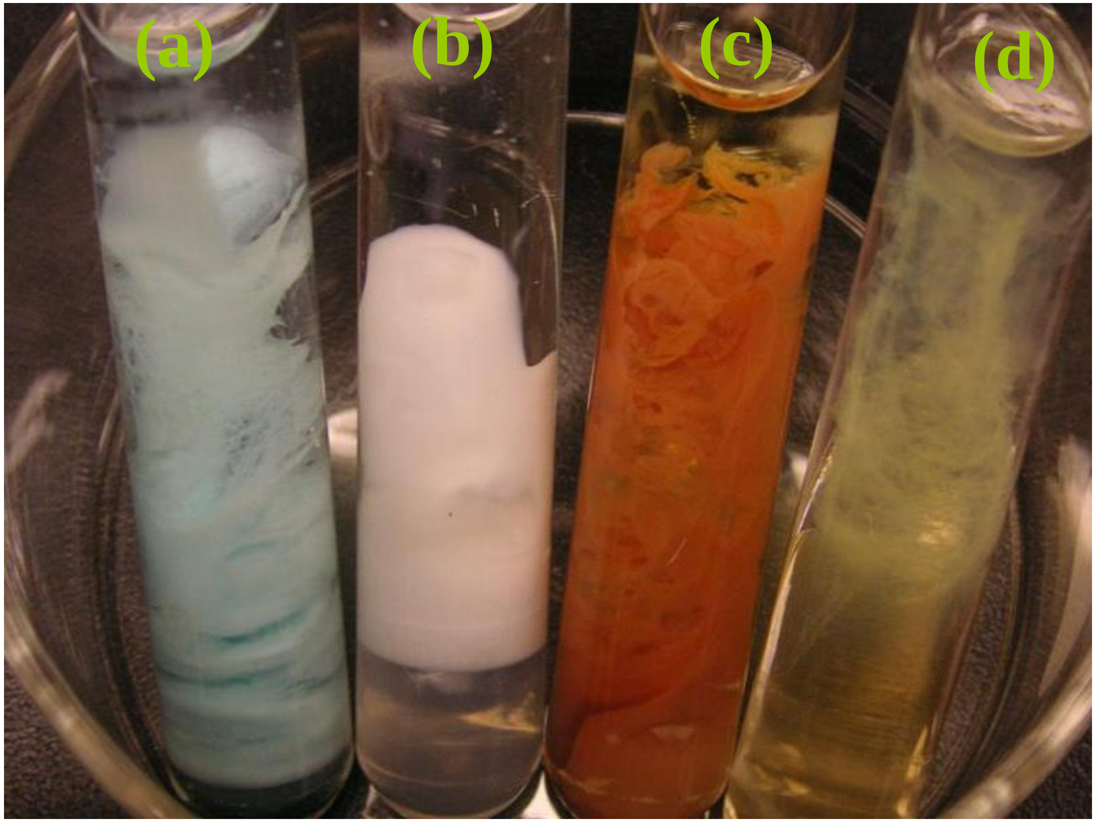
Nadagouda & Varma: *Macromol. Rapid Commun*., *28*, 842–847 (2007)



TEM images of (a) pure SWNT carbon nanotubes obtained from Bucky Inc., USA, (b) 25 (c) 50, (d) 75 mg SWNT cross-linked PVA nanocomposites.

Nadagouda & Varma: *Macromol. Rapid Commun*., *28*, 842–847 (2007)

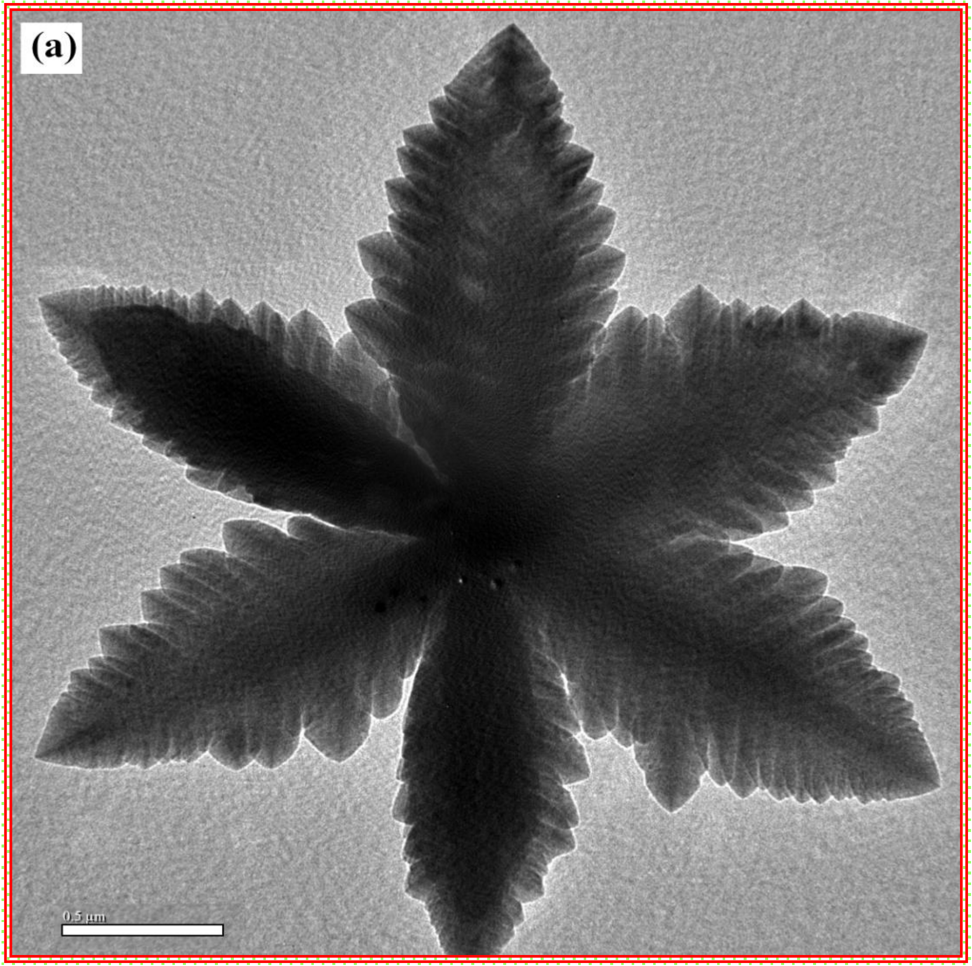
Synthesis of Thermally Stable Carboxymethyl Cellulose / Metal Biodegradable Nanocomposite Films for Potential Biological Applications



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

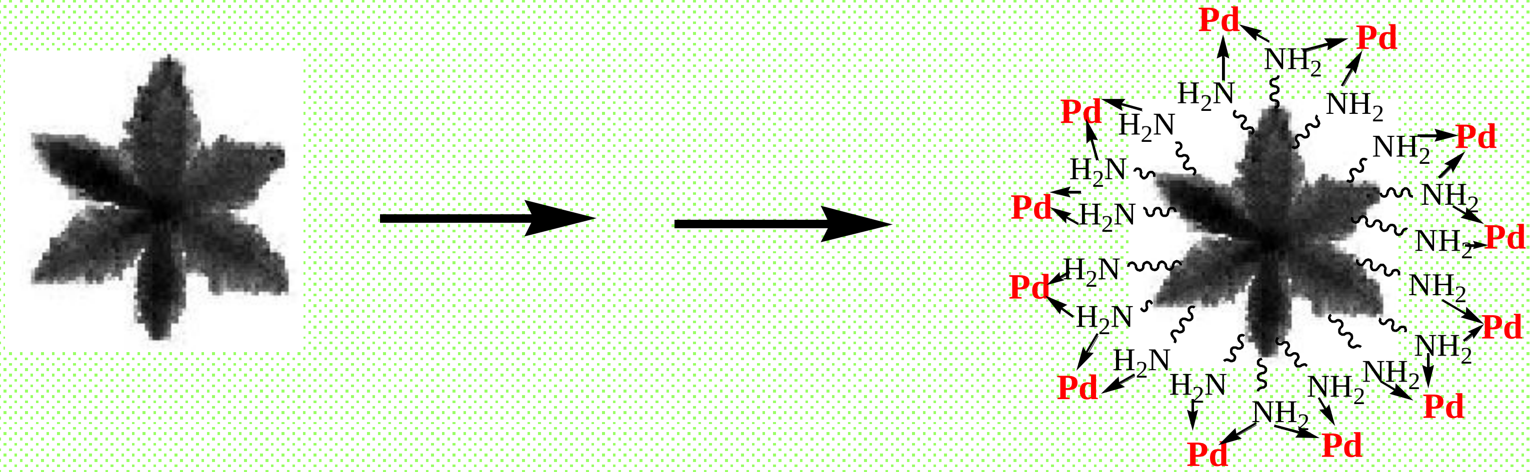
Nadagouda & Varma: *Biomacromolecules, 8*, 2762-2767 (2007)

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



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

Synthesis of Catalyst



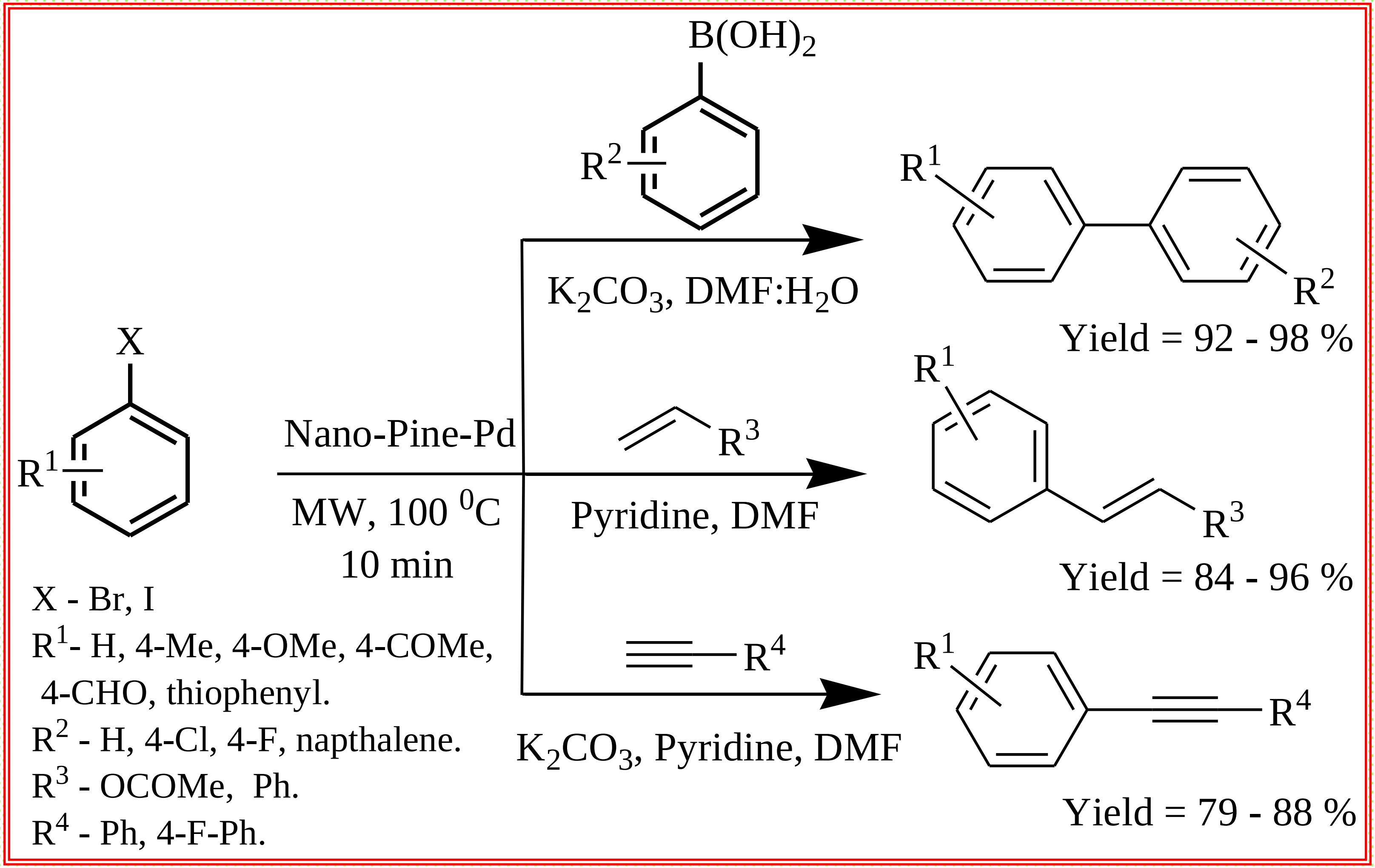
Convenient synthesis of single-crystal dendritic ferrite with micro-pine structuration under MW-irradiation conditions.

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*

Carbon-Carbon Coupling Reactions



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

EPA
United States
Environmental Protection
Agency

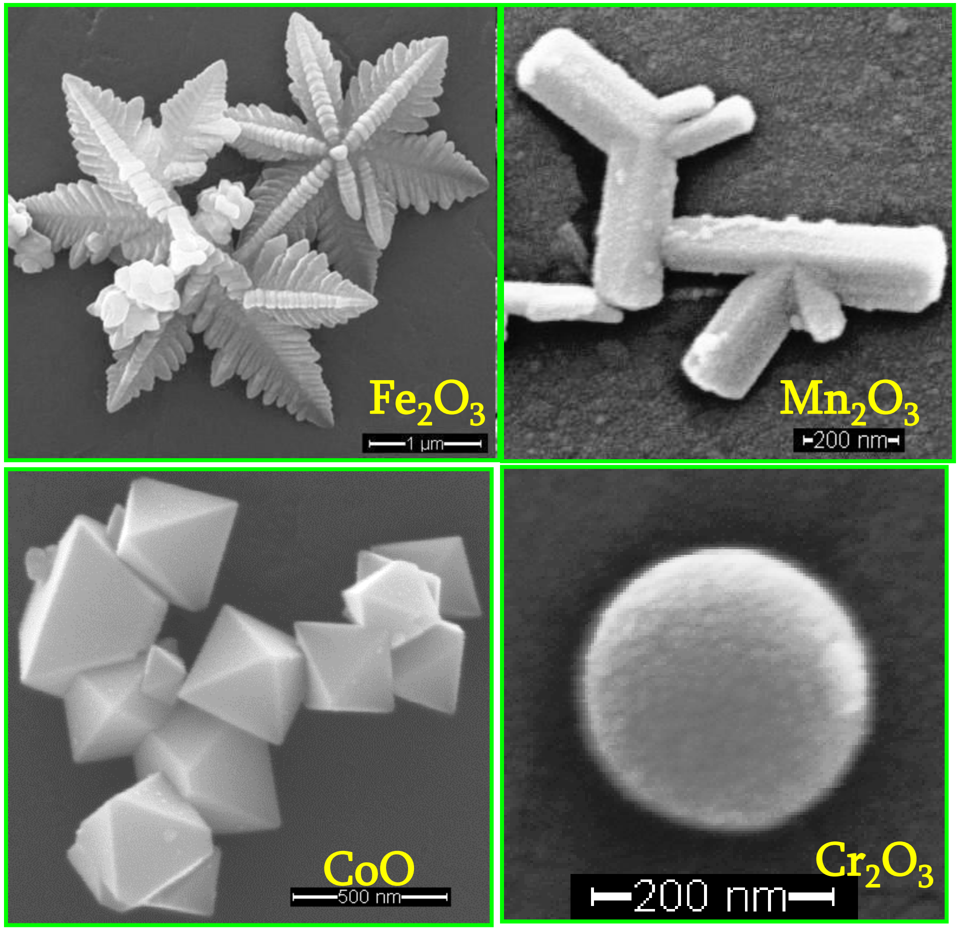
Green Synthesis of Nanomaterials

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.

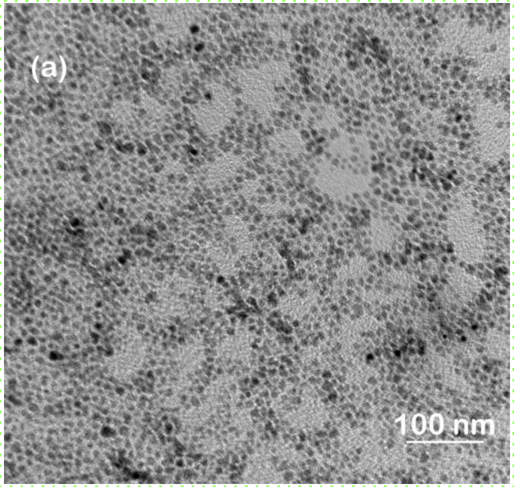


Polshettiwar, Baruwati & Varma, *ACS Nano, 3,* 728 (2009)

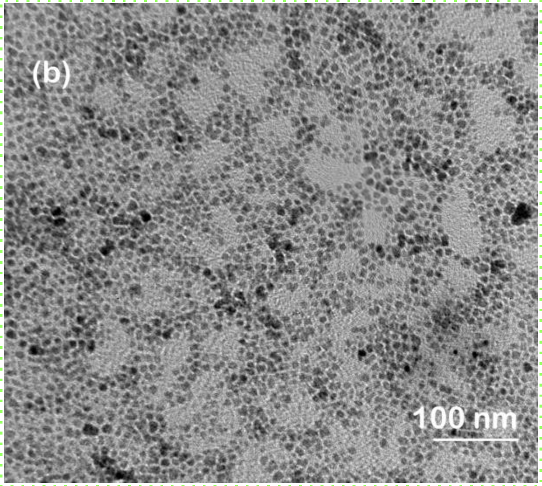
Among the top 5 Most-Accessed Articles in 12 months

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

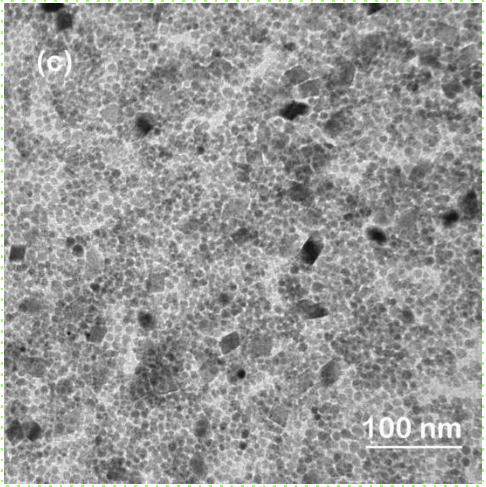
Monodispersed MFe_2O_4 (M=Fe, Mn, Co, Ni) nanoparticles have been synthesized via a water organic interface under both hydrothermal and MW conditions starting with readily available and inexpensive metal nitrate and halide precursors. The single phase particles are obtained at a temperature as low as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



$NiFe_2O_4$



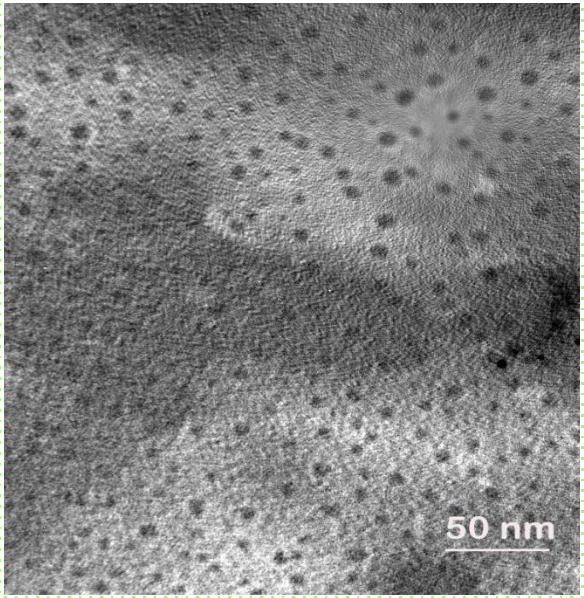
$CoFe_2O_4$



γ-Fe_2O_3

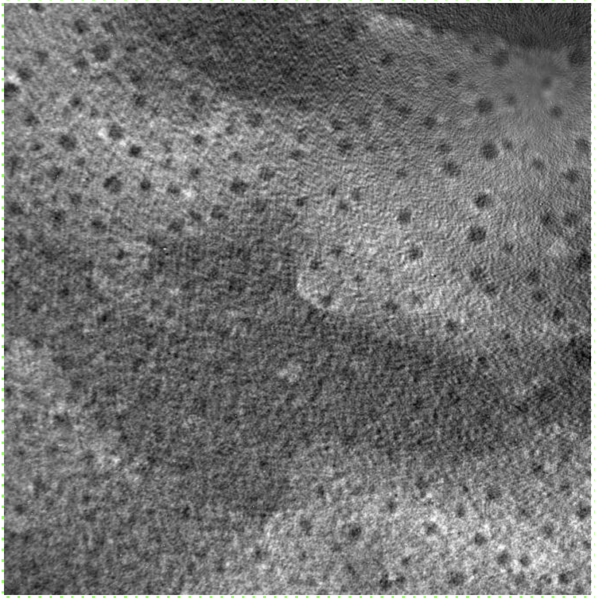
Baruwati, Nadagouda & Varma, *J. Phys. Chem. C*, *112*, 18399 (2008)

Surface functionalization renders the particles dispersible in water



$NiFe_2O_4$

TEM of the particles dispersed in water

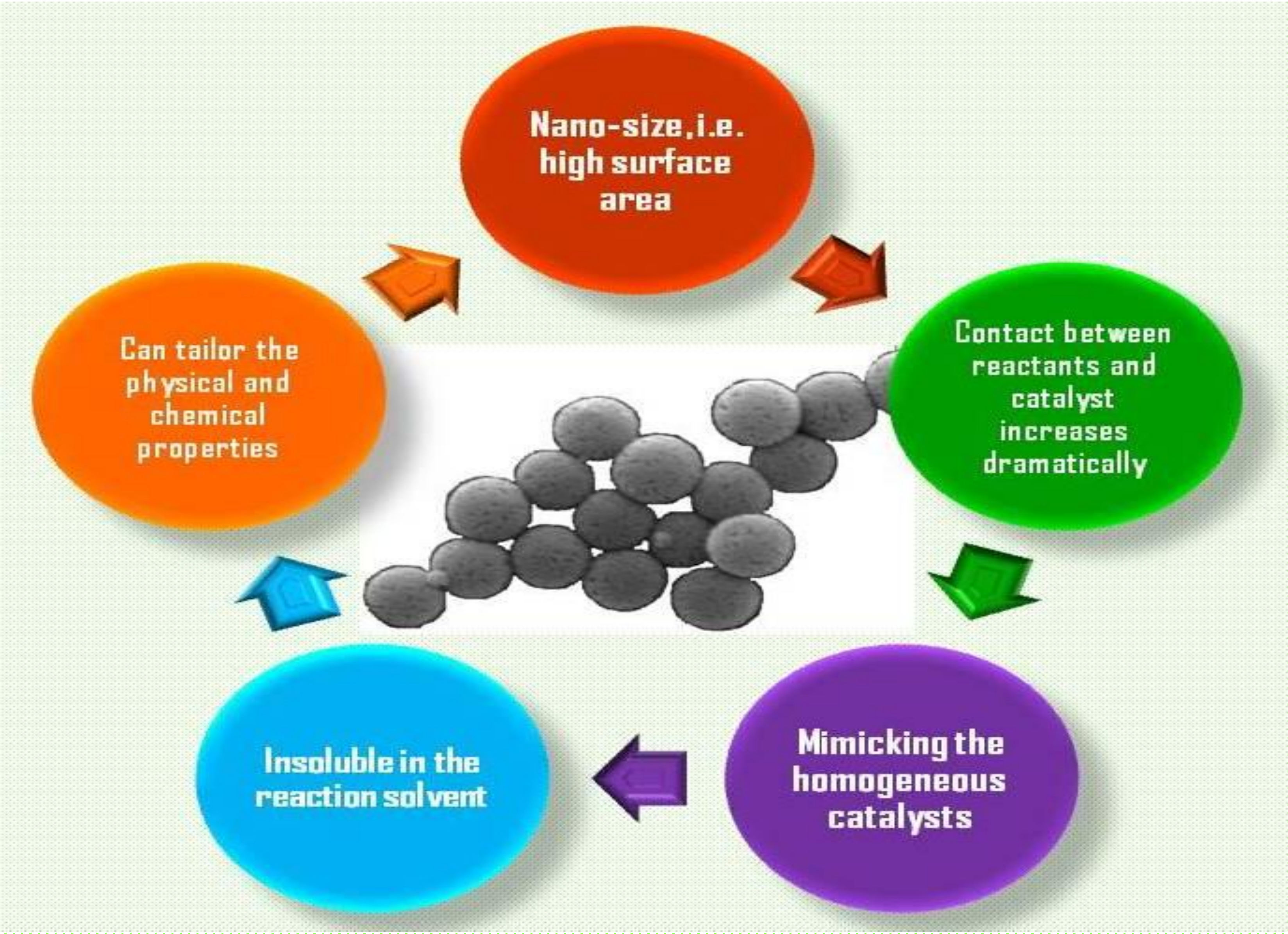


$CoFe_2O_4$

Photographic image of the particles in water and hexane

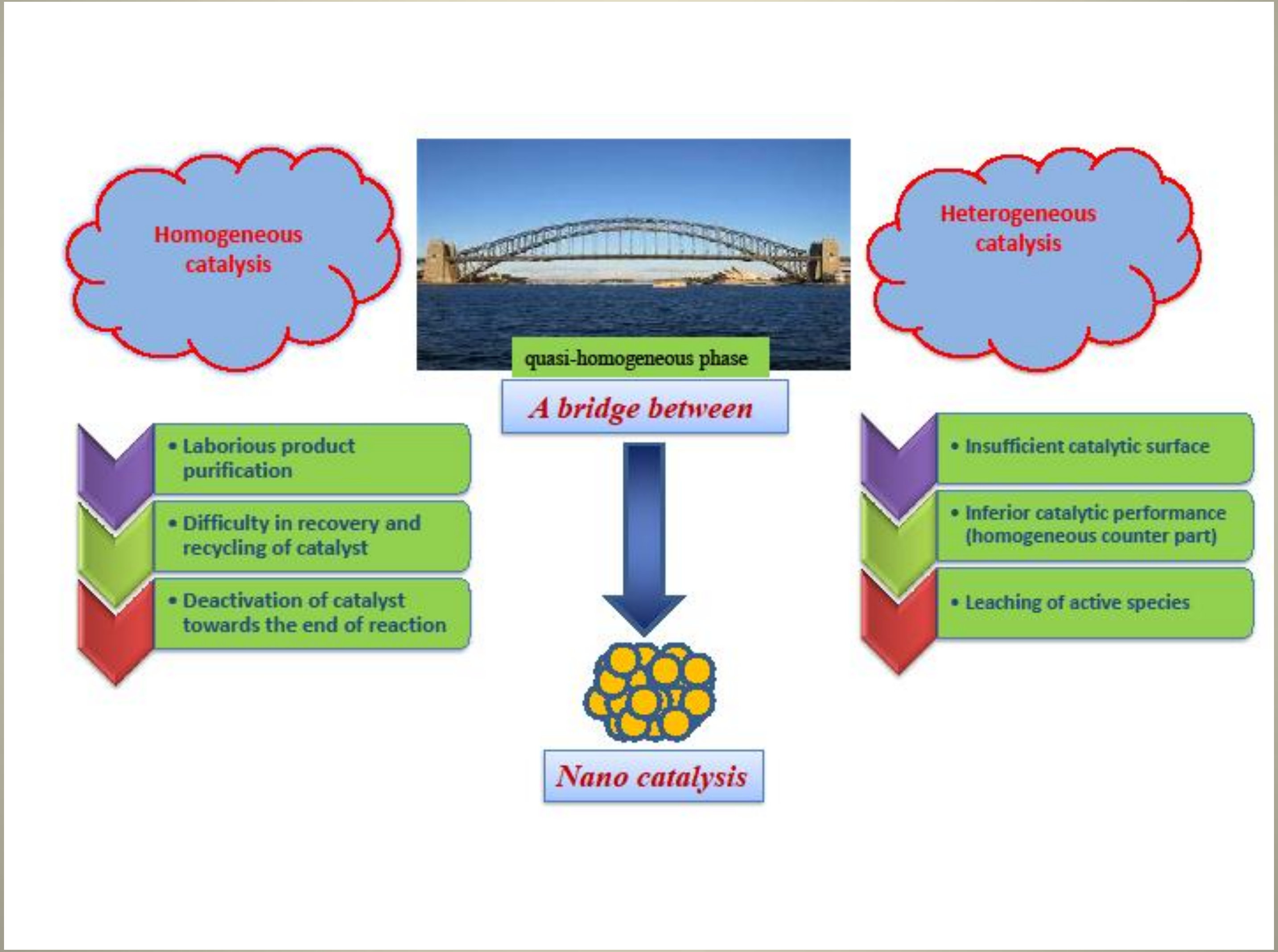
Baruwati, Nadagouda & Varma, *J. Phys. Chem. C*, *112*, 18399 (2008)

What is Nano-Catalysis?



Nano catalyst acts as a quasi-homogeneous phase

A bridge between homogeneous and heterogeneous



Magnetically Separable Nano-Catalyst

A Bridge Between

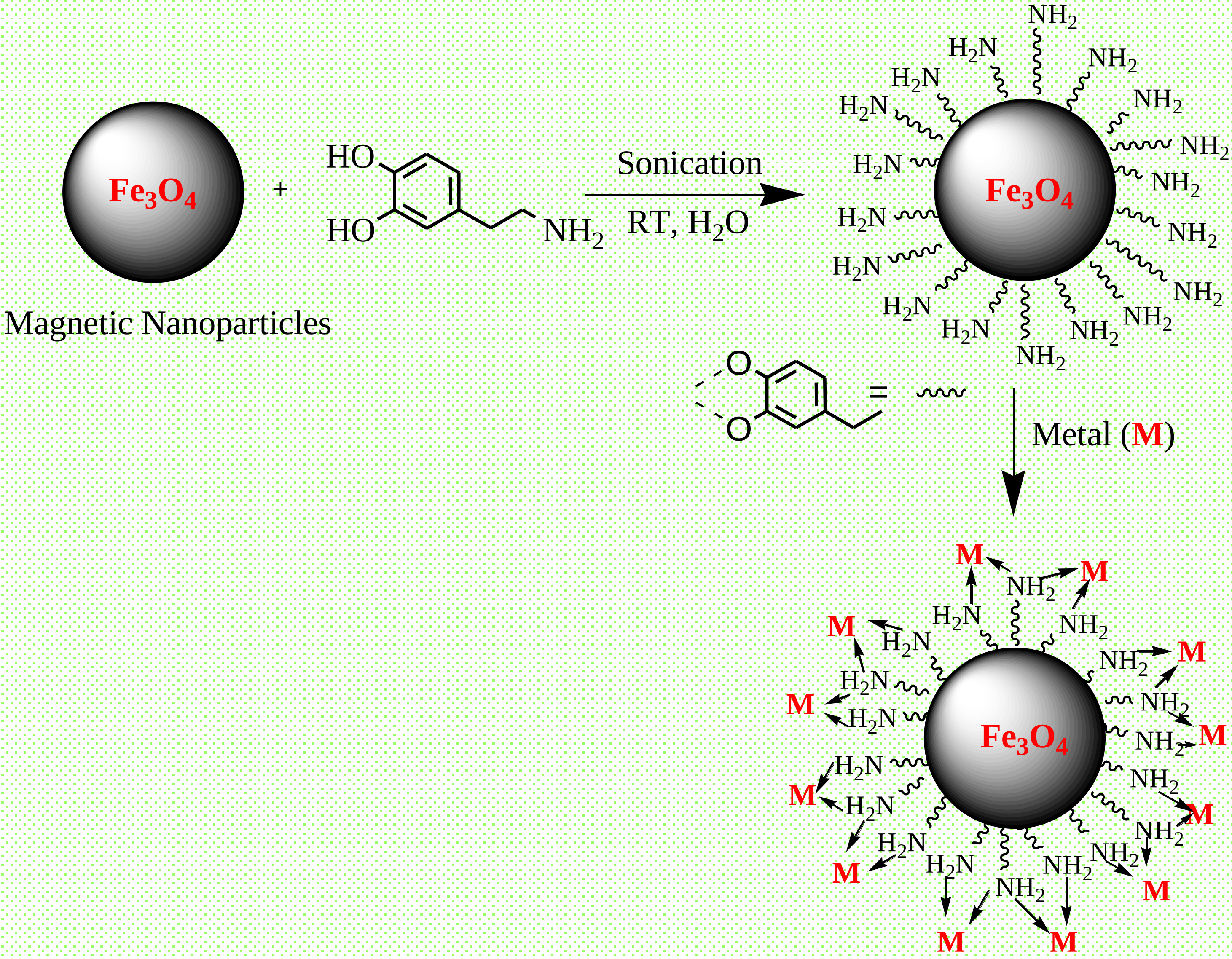
Homogeneous Catalysis

Heterogeneous Catalysis

Recent publications on this theme from our group:

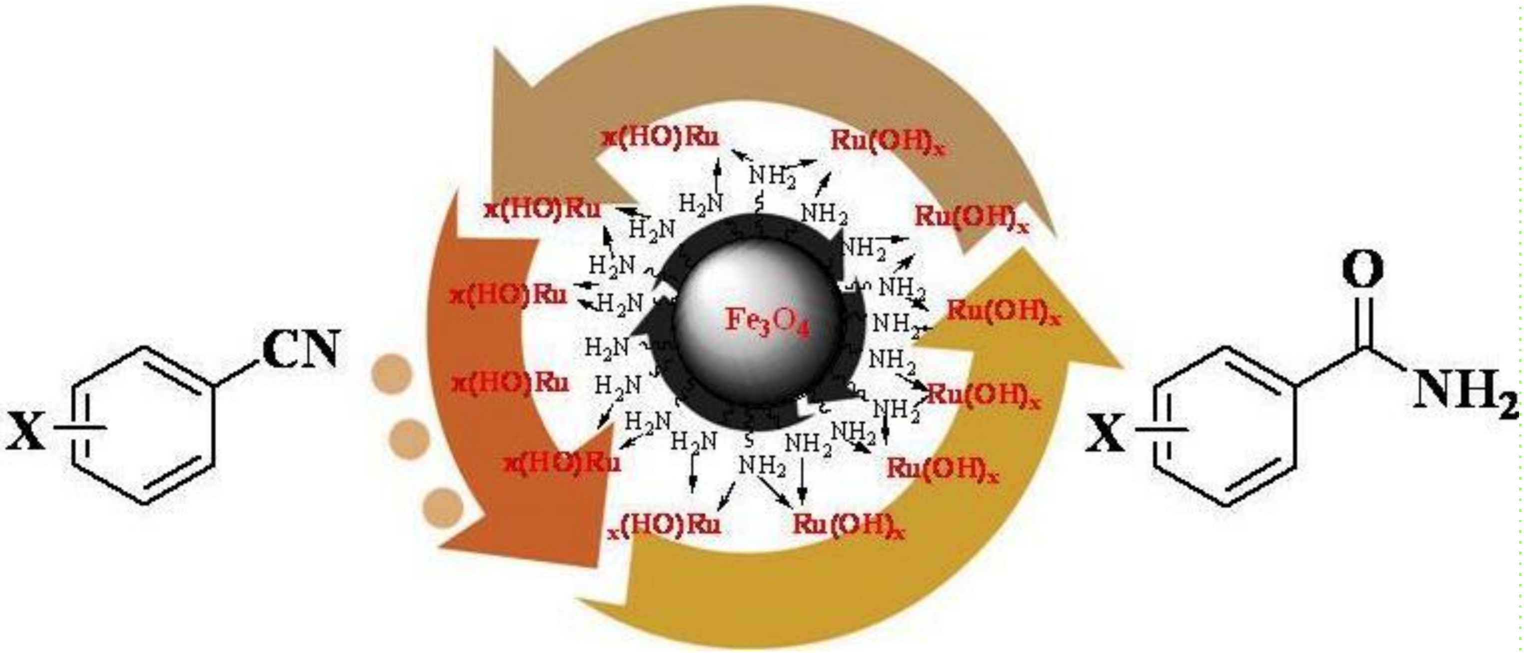
1. *Chem. Eur. J.*, *15*, 1582 (2009)
2. *Org. Biomol. Chem.*, *7*, 37 (2009)
3. *Green Chem.*, *11*, 127 (2009)
4. *Chem. Commun.*, 6318 (2008)
5. *Chem Commun.*, 1837 (2009)
6. *Tetrahedron*, *66*, 1091 (2010)
7. *Green Chem.*, *12*, 743 (2010)
8. *Green Chem.*, *13*, 2750 (2011)
9. *Curr. Opin.Chem. Eng. 1*, 123 (2012)
10. *Green Chem.*, *14*, 67 (2012)
11. *Chem. Commun.*, *48*, 2582 (2012)
12. *Green Chem.*, *14*, 625 (2012)
13. *Chem. Commun.*, *48*, 6220 (2012)
14. *Green Chem.*, *14*, 2133 (2012)

Synthesis of Nano-Catalysts



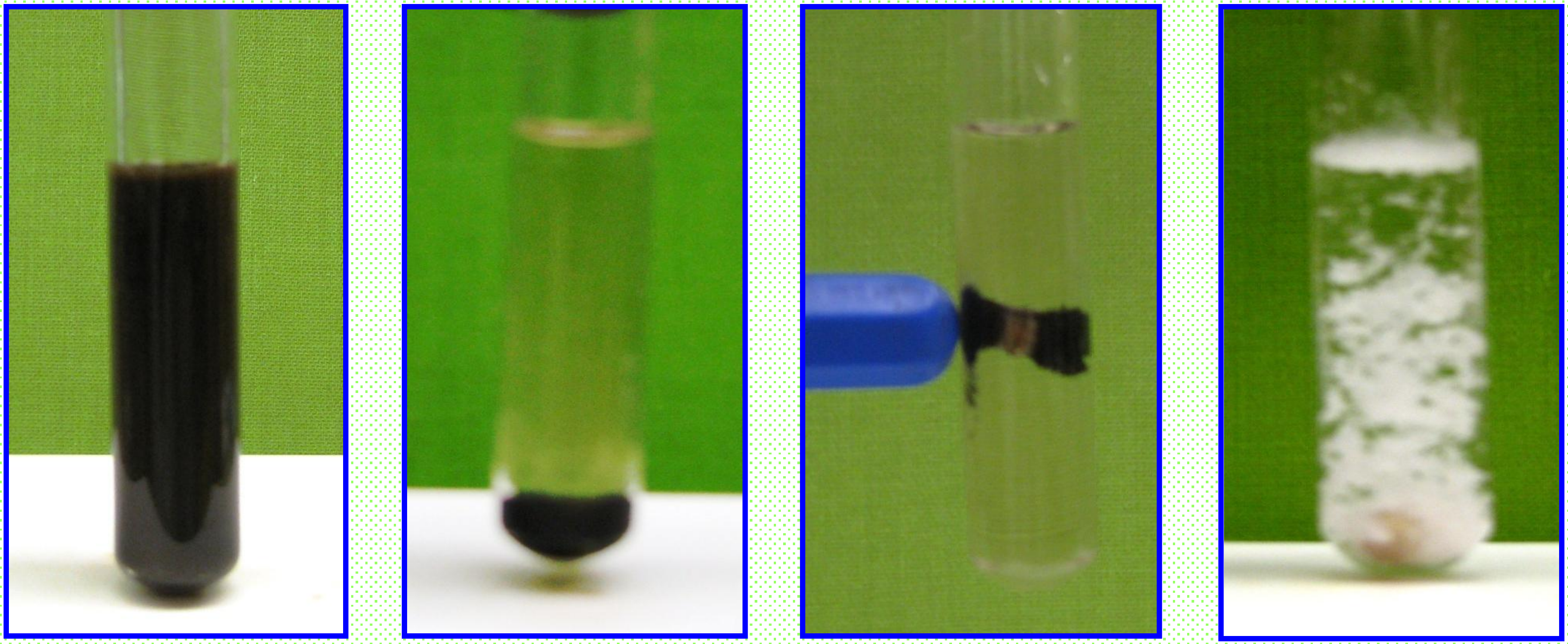
Polshettiwar, Nadaguda & Varma, ***Chem. Commun.*** **2008**, 6318.

Magnetically Recoverable Ruthenium Hydroxide Nano-Catalyst



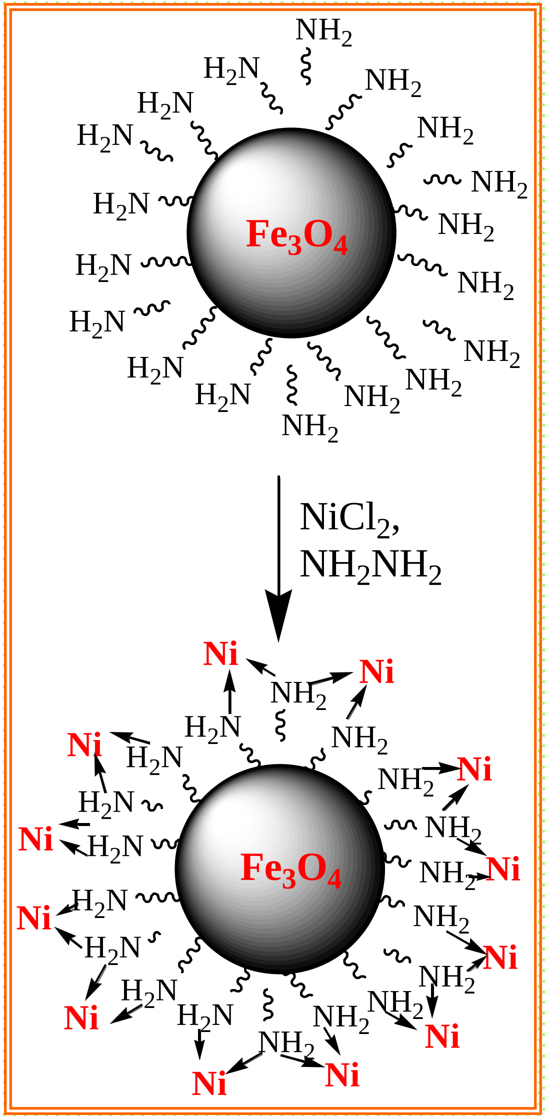
Polshettiwar & Varma, *Chem. Eur. J. 15*, 1582 (2009)

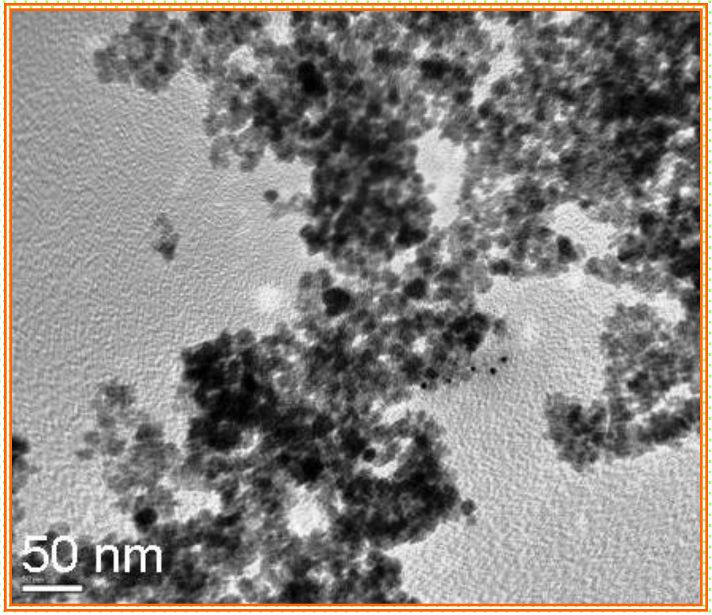
No Organic Solvent-
Even in the Work-Up Step



Reaction in Pure Aqueous Medium

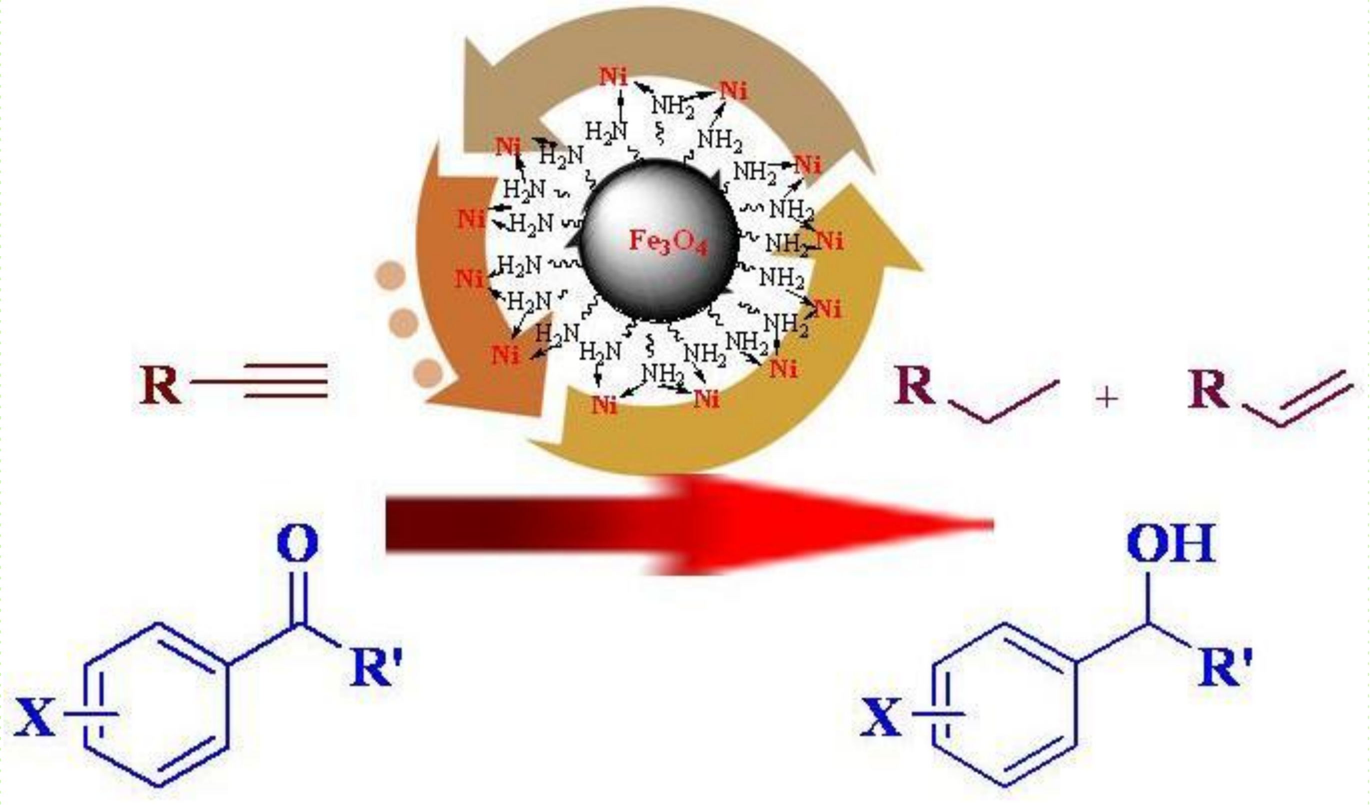
Synthesis of Ni-Nano-Catalysts





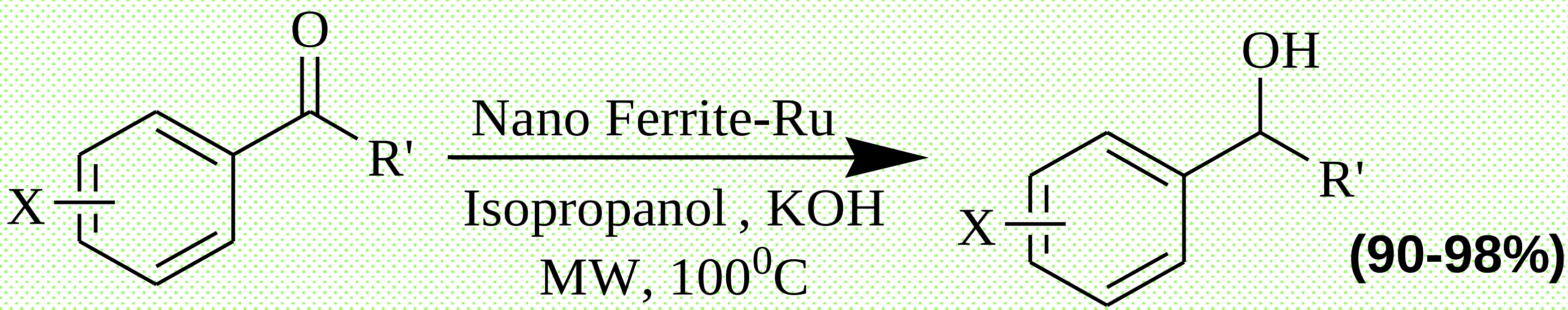
- Single-phase Fe_3O_4 nanoparticles
- Size range = 10-13 nm
- Nickel concentration = 8.3 % (ICP-AES)

Magnetically Recoverable Ni Nano-Catalyst for Reduction



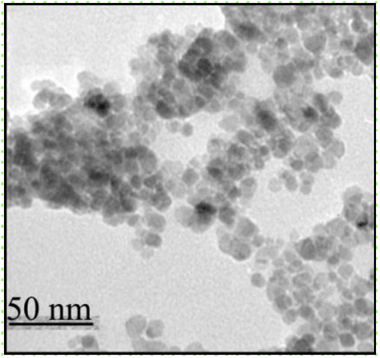
Polshettiwar, Baruwati & Varma, *Green Chem.*, *11*, 127 (2009)

Transfer Hydrogenation of Carbonyl Compounds

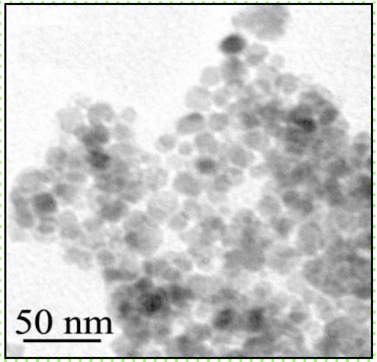


R' - Me, Ph,H

X - Cl, Br, NO_2, NH_2



Catalyst before reaction

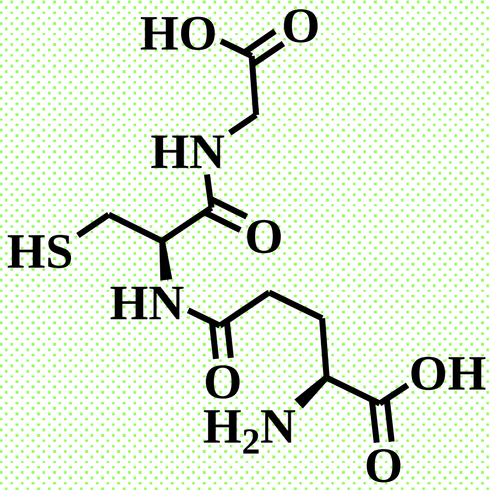


Catalyst after reaction

- 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)

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)

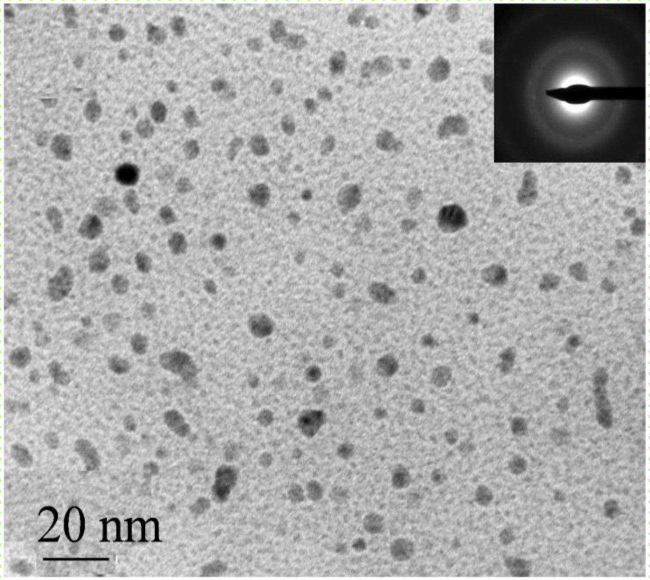
Baruwati, Polshettiwar, Varma, *Green Chem*. *11*, 926 (2009)

Metal nanoparticles in less than a minute under MW conditions

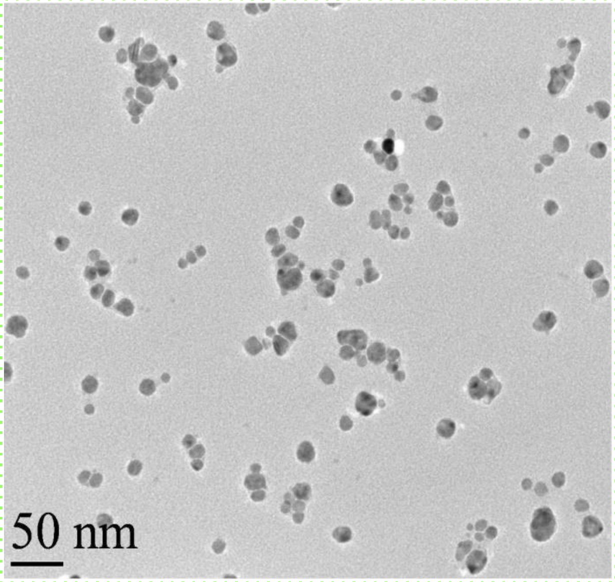
Optimized condition

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

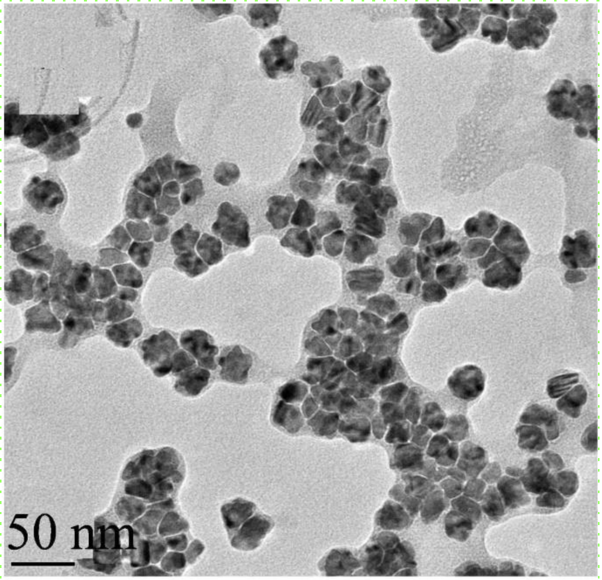
Silver Nanoparticles



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

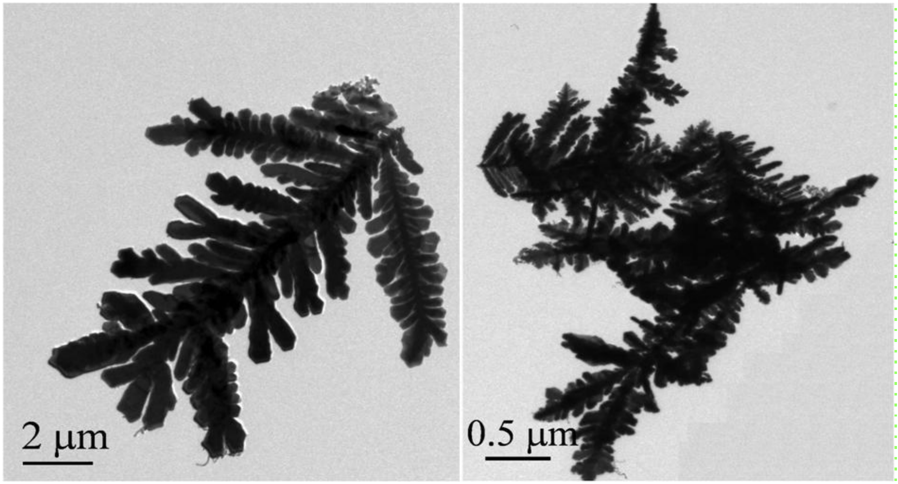


75 Watt, 60 seconds with mole ratio 1.0:0.15



100 Watt, 60 seconds with mole ratio 1.0:0.15

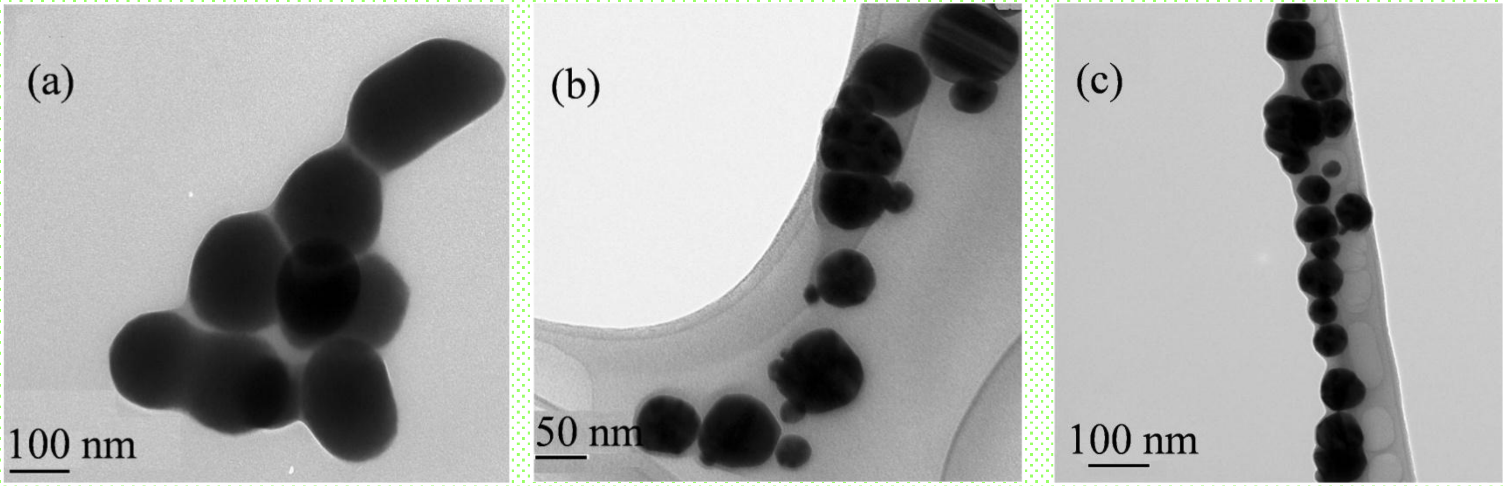
- Silver trees formed on the TEM grid when silver nitrate is not fully reduced
- Formation of dendritic structures are due to the carbon and copper in the TEM grid



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

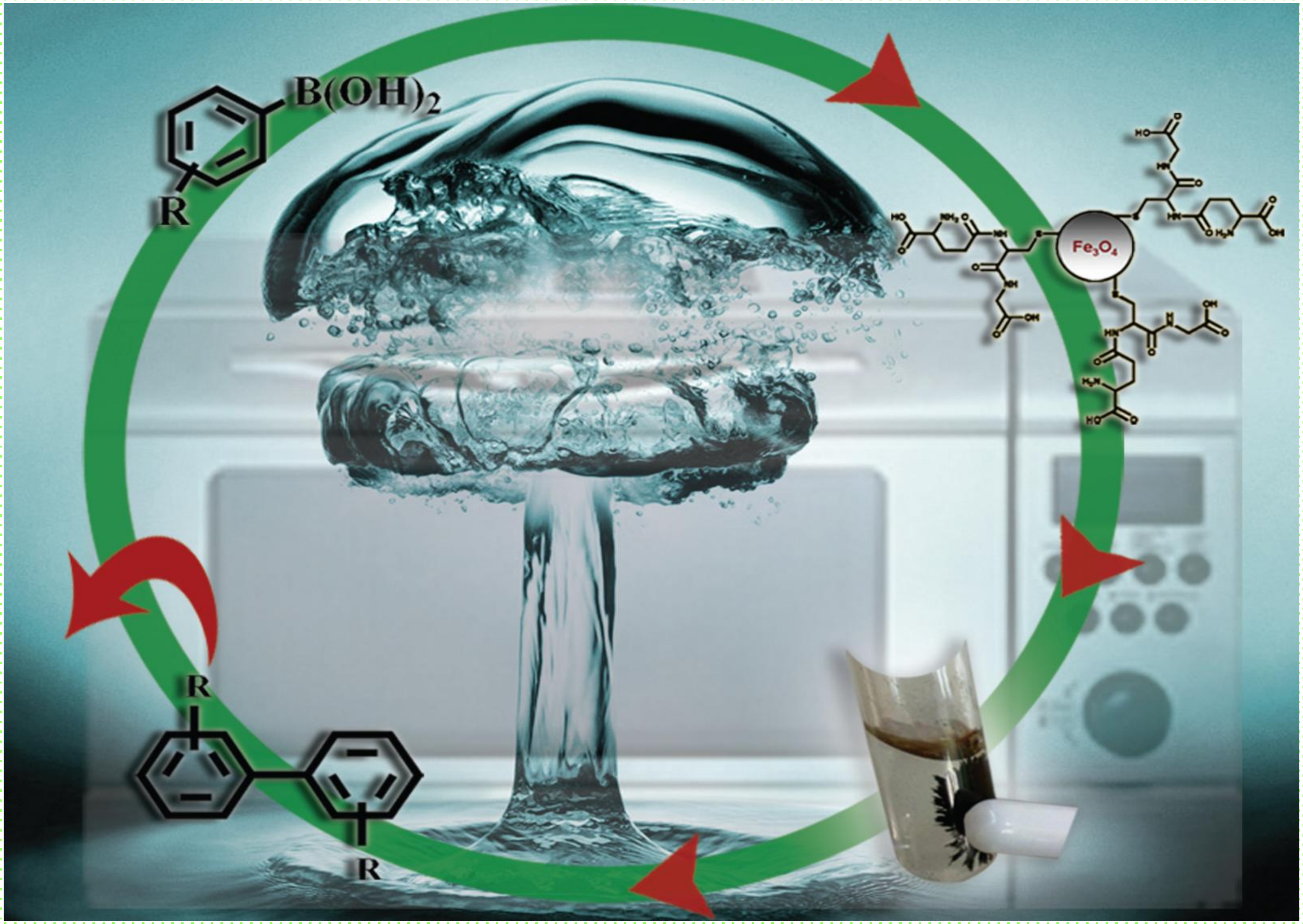
Polshettiwar &Varma, *Chem Commun.*, 1837 (2009)

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

Green Chemistry

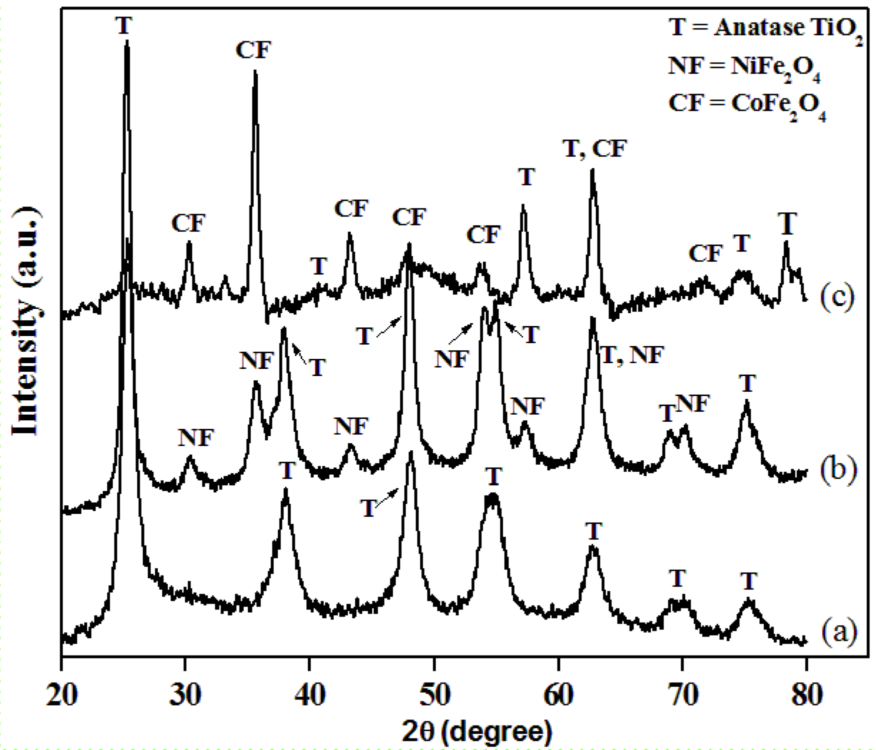
Cover page **Volume 12 | Number 9 | Sept. 2010**

Magnetically seperable organocatalyst for homocoupling of arylboronic acids



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

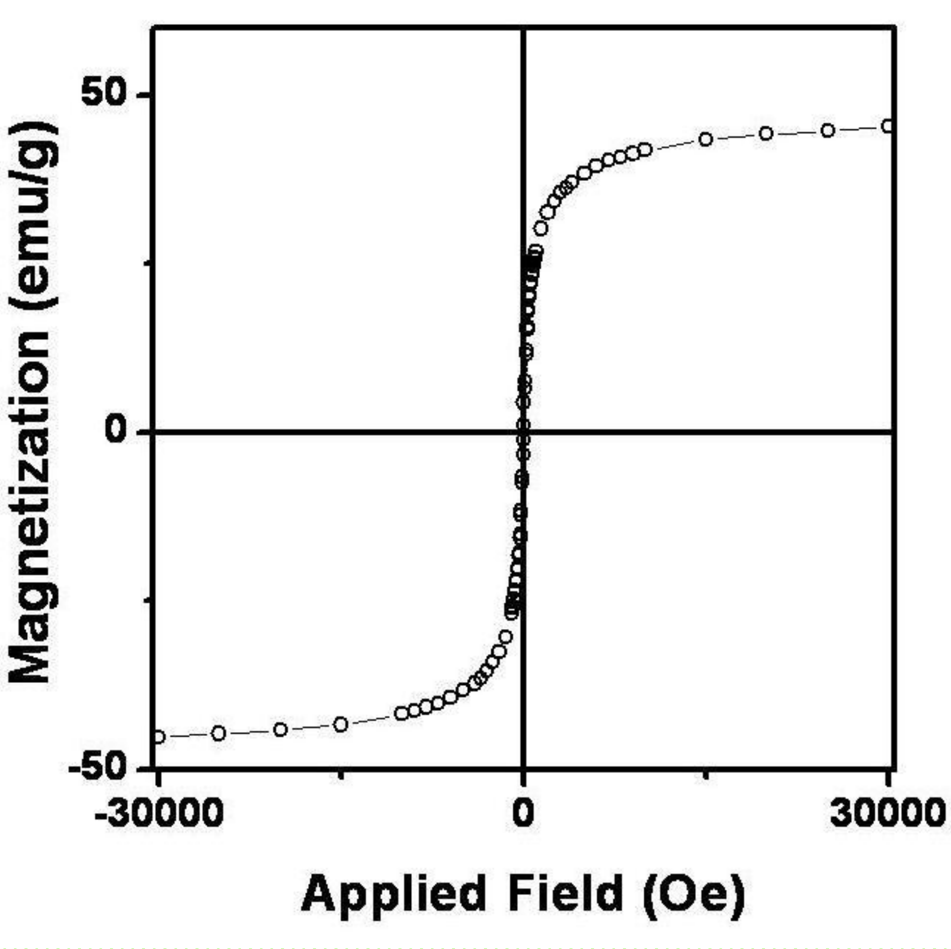
Doped TiO_2 Magnetically Separable Nano-catalysts



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

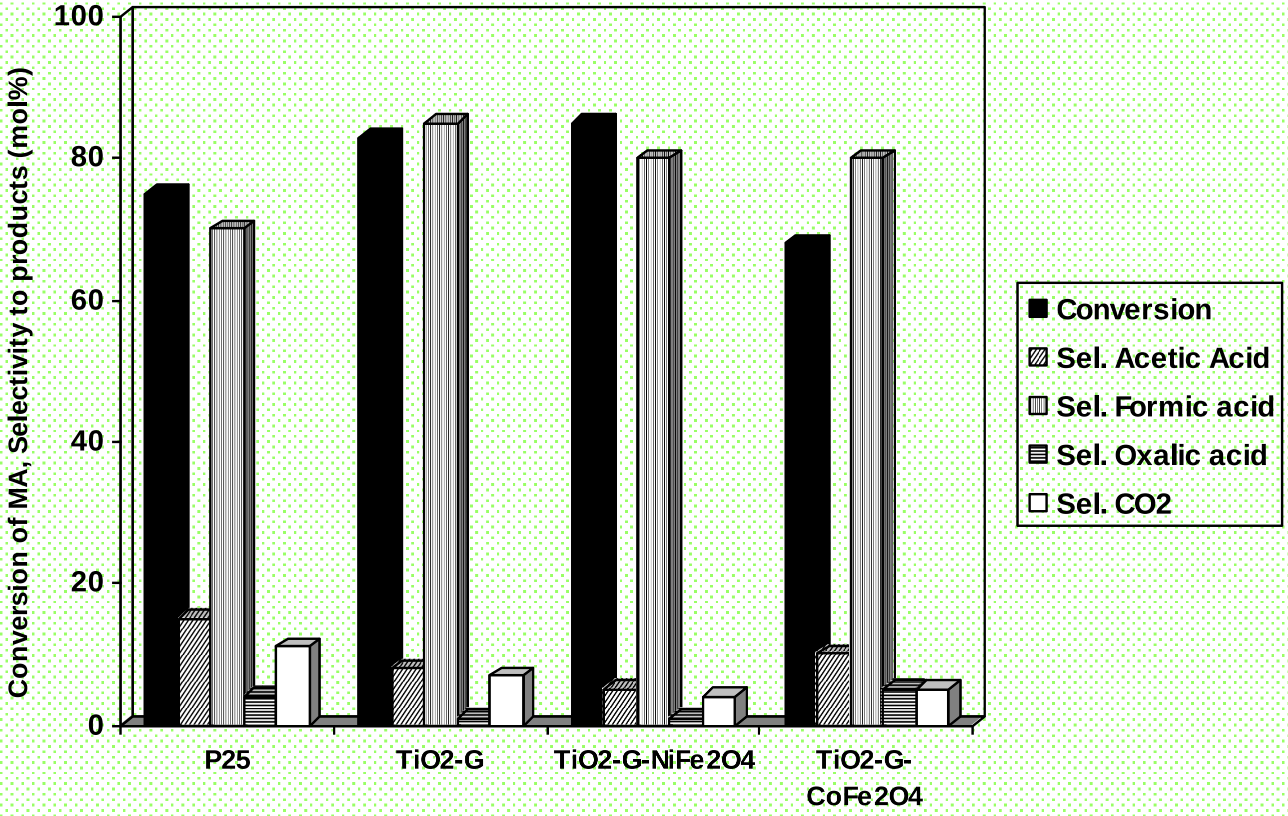
Baruwati, Luque, Varma et al. *Green Chem.* , 13, 2750 (2011)

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



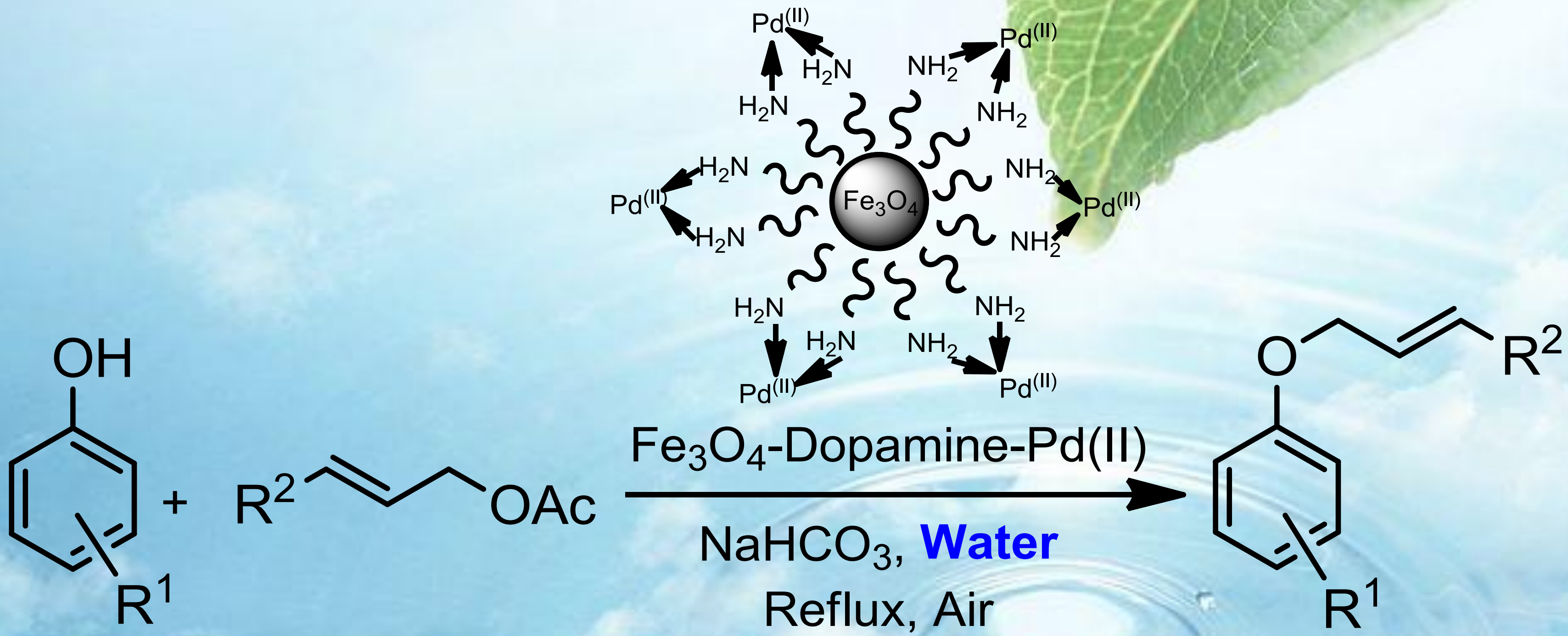
Baruwati, Luque, Varma et al. *Green Chem.* , 13, 2750 (2011)

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



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

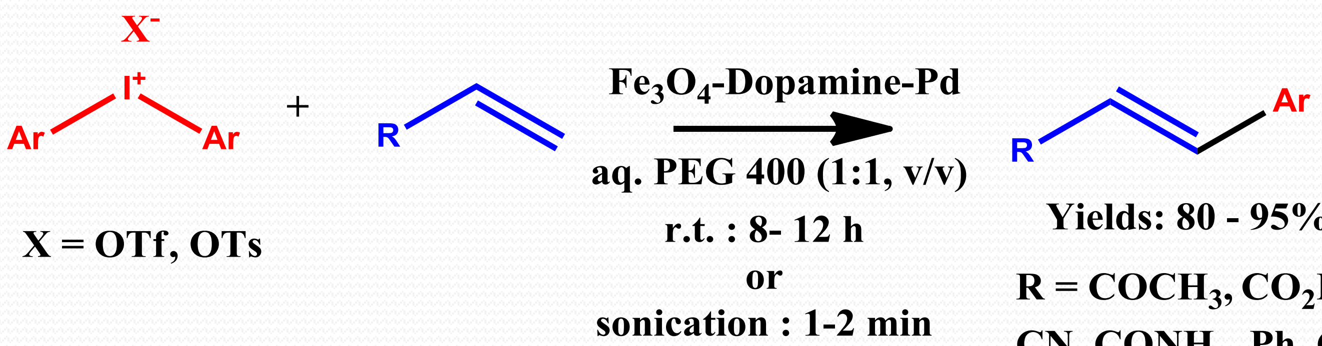
Magnetic Nano-ferrite Supported Heterogeneous Pd Catalyst for *O*-Allylation of Phenols in Water



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

Heck Reaction Using Magnetic Palladium Catalyst

- **Heck-type arylation was achieved using diaryliodonium salts with magnetically retrievable palladium catalyst under ultrasonic irradiation.**
- **The same transformation was also achieved at room temperature prolonging the reaction time duration.**

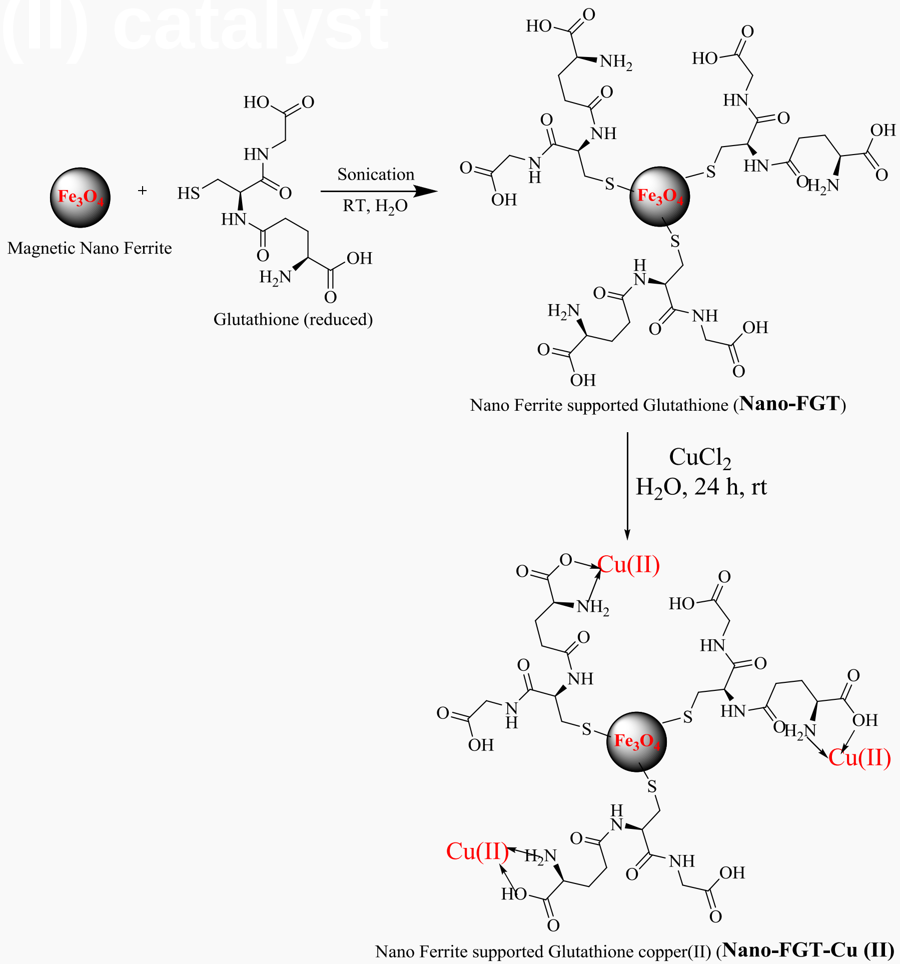


R = $COCH_3$, CO_2Me, $CO_2{}^{n}Bu$, CN, $CONH_2$, Ph, CH_2OAc, CH_2O-allyl

Ar = C_6H_5, 4-OMeC_6H_4, 3-$NO_2C_6H_4$, 2-thienyl, 4-$^{t}BuC_6H_4$

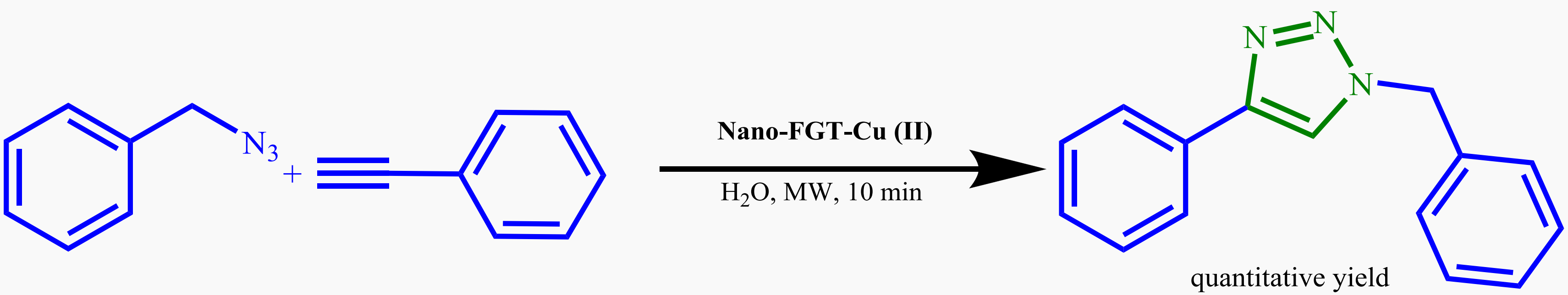
Reddy, Saha, Leazer, Varma; *Green Chem.*, *14*, 2133 (2012)

Nano Ferrite supported Glutathione-copper(II) catalyst



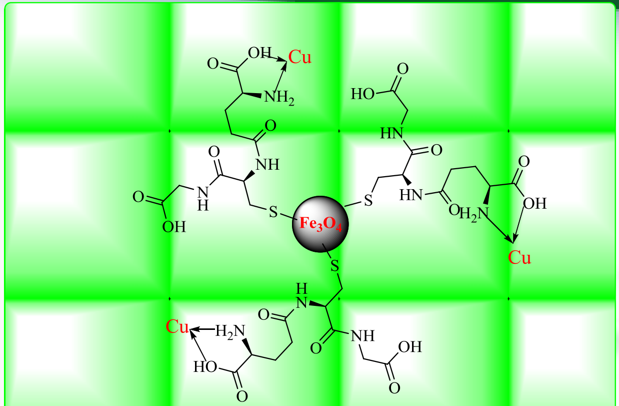
Baig, Varma: *Green Chem., 14, 625 (2012)*

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

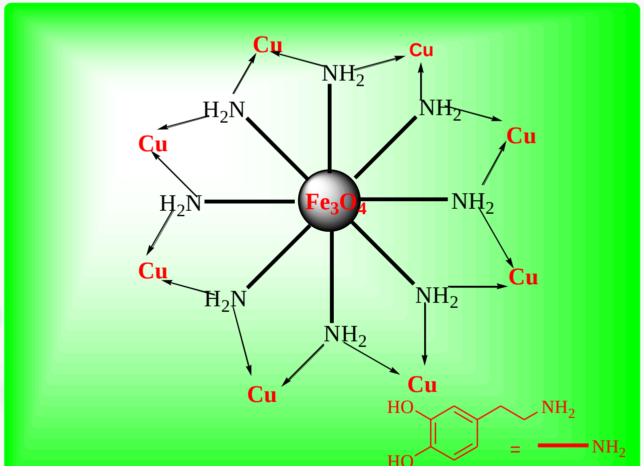


Baig, Varma: *Green Chem., 14, 625 (2012)*

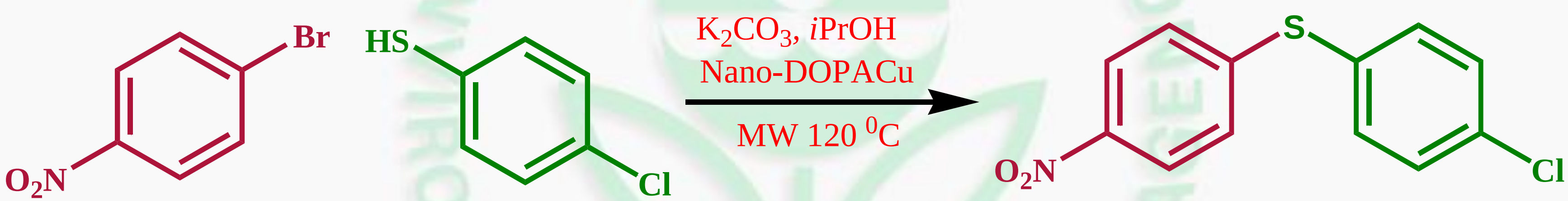
Ligands defines reactivity



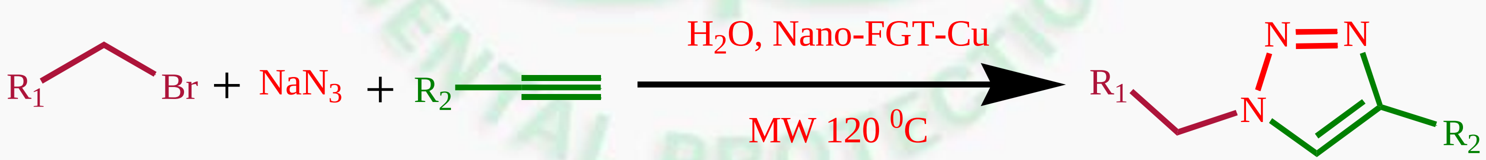
Nano Ferrite supported Glutathione copper **Nano-FGT-Cu catalyst**



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



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

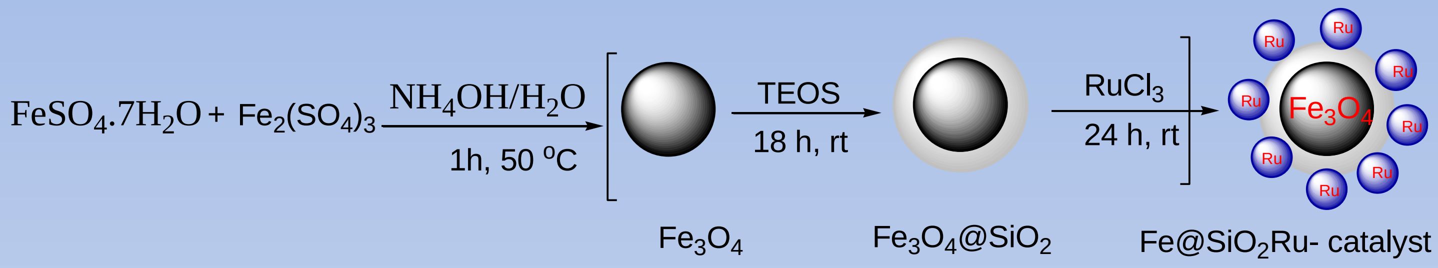


R = alkyl, aryl, heterocycle etc.

23 examples, yield up to 99%

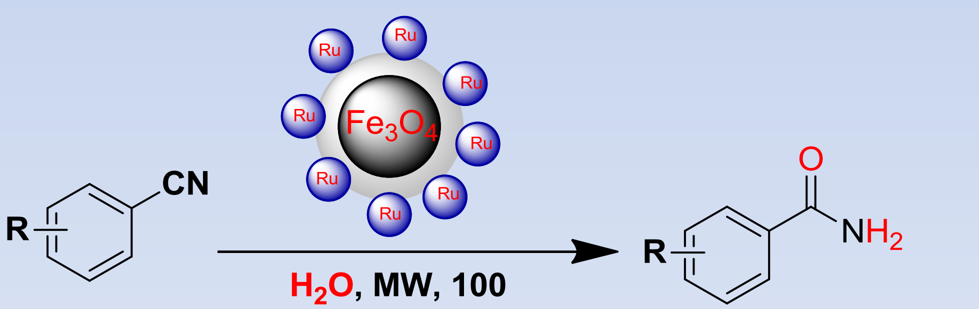
(Nano-FGT-Cu-active, Nano-DOPA-Cu-inactive) Baig, Varma: *Green Chem.*, 2012, *14*, 625

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



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

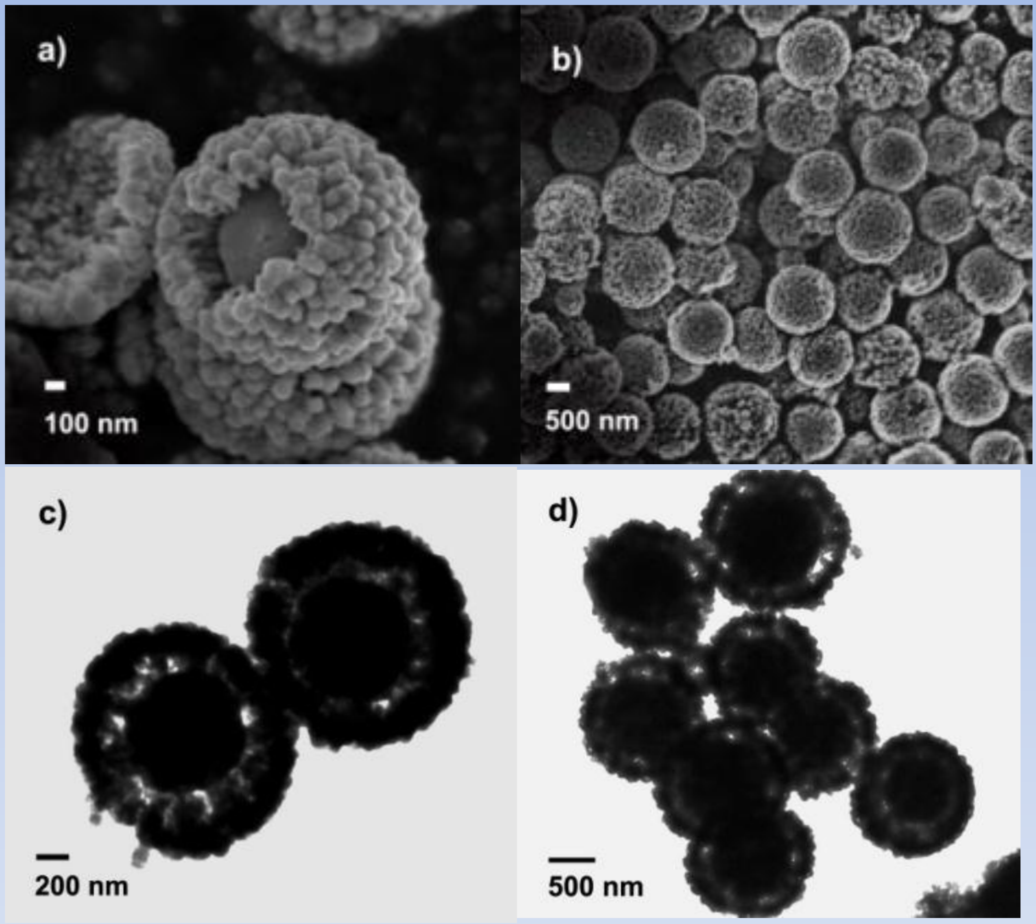
Aqueous Hydration of Nitriles Using Magnetic Silica Supported Ruthenium Hydroxide Nanoparticles

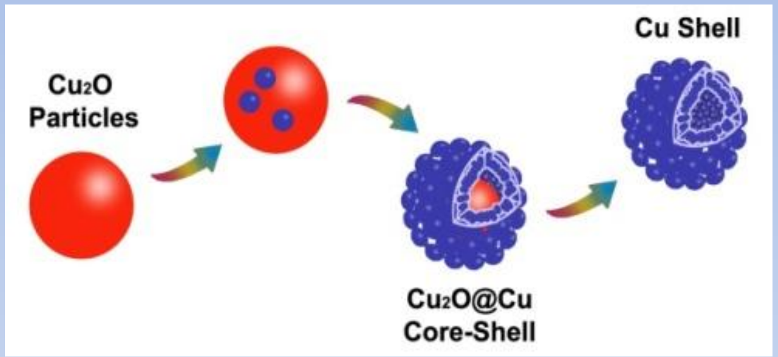


>99% conversion

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

Inside-Out Core-Shell Architecture Cu_2O@Cu Nanoparticles



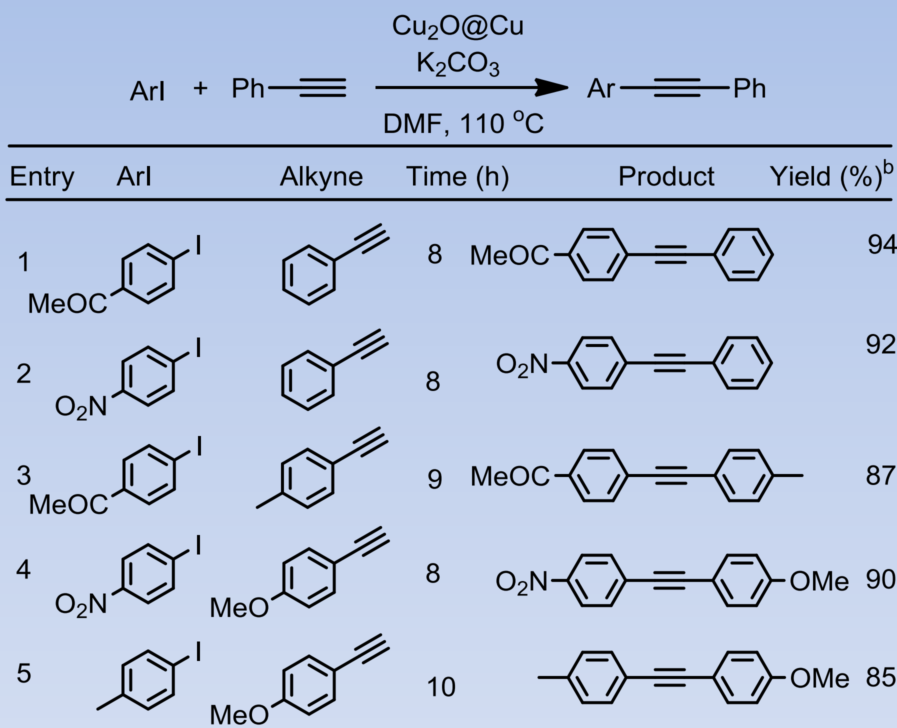


Images of typical core-shell Cu_2O@Cu.
a) and b) SEM image; c) and d) TEM image.

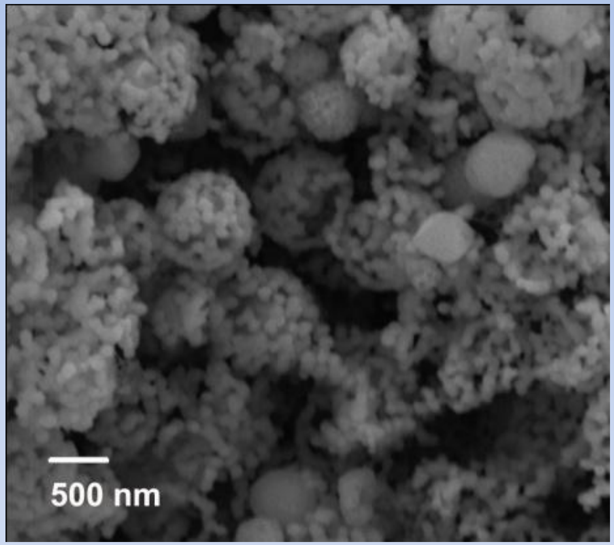
Kou, Saha, Varma*: Chem. Commun.*, 2012, *48*, 5862

Sonogashira Coupling Reaction Using $Cu_2O@Cu$

Cheaper substitute for expensive Pd



[a]A mixture of ArI (1 mmoml), alkyne (1 mmol), $Cu_2O@Cu$ (20 mg), K_2CO_3 (2 mmol) was heated at 110 °C in DMF (2 mL) for the required time period. [b]Yields refer to those of purified products characterized by IR and ^1H and ^{13}C NMR spectroscopic data.



SEM image of recycled sample

Kou, Saha, Varma: *Chem. Commun.*, 2012, *48*, 5862

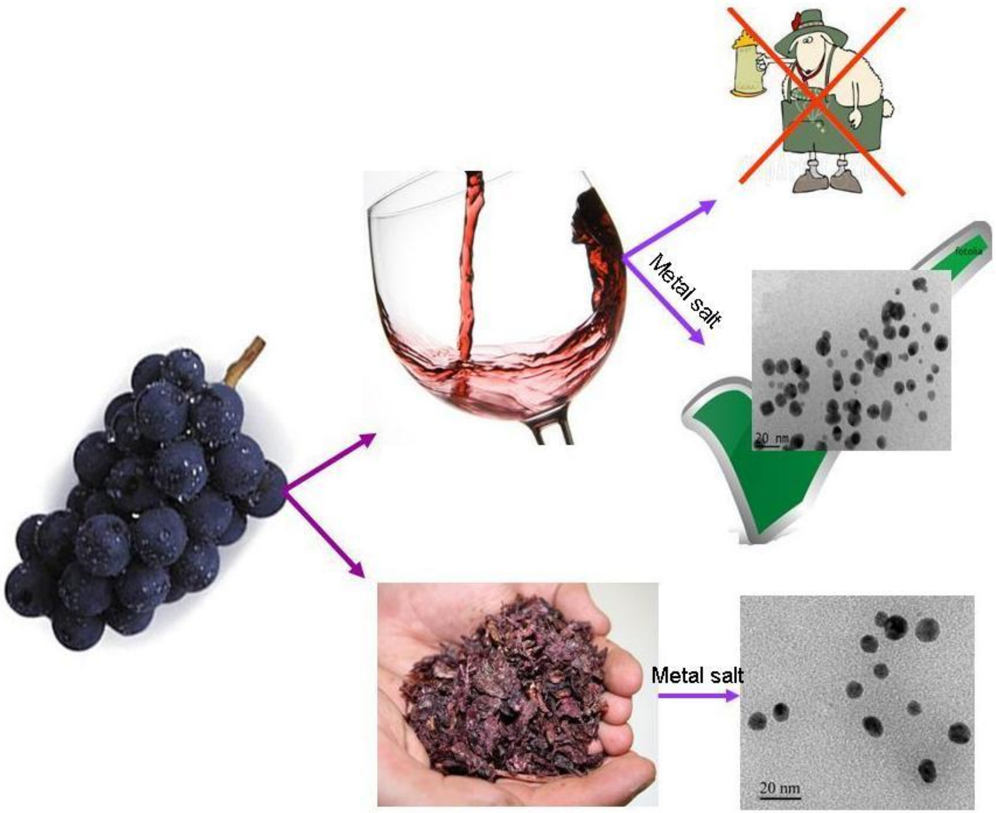
Green Synthesis of Nanomaterials

From Rag to Riches-Story of Red Grape Pomace

PROBLEM: ‘Green’ synthesis of nanoparticles using biorenewable sources.

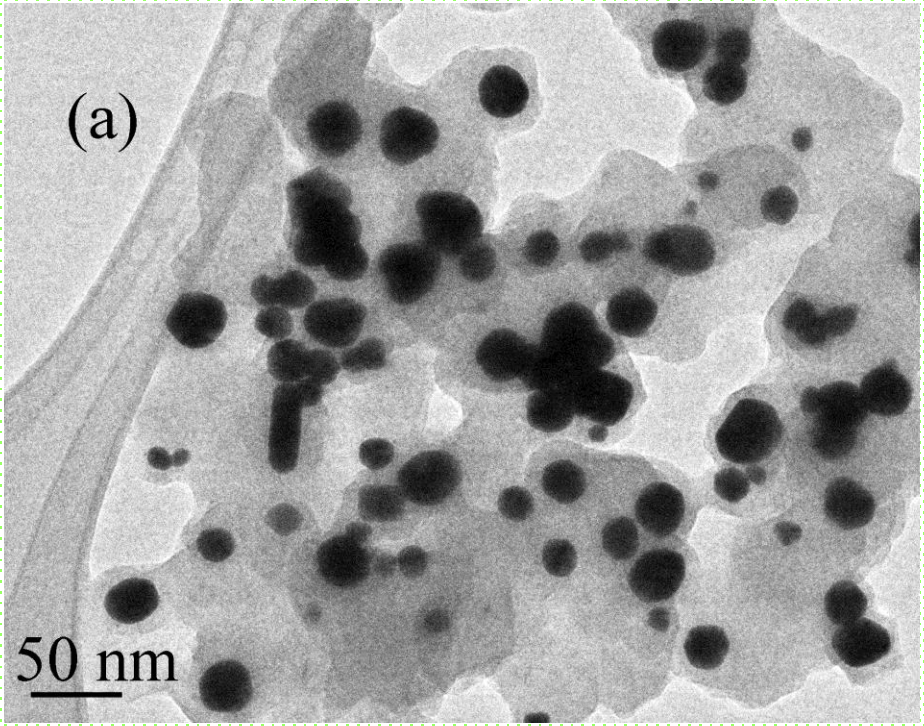
TECHNOLOGY SOLUTION: Utilize source of polyphenols from agricultural waste.

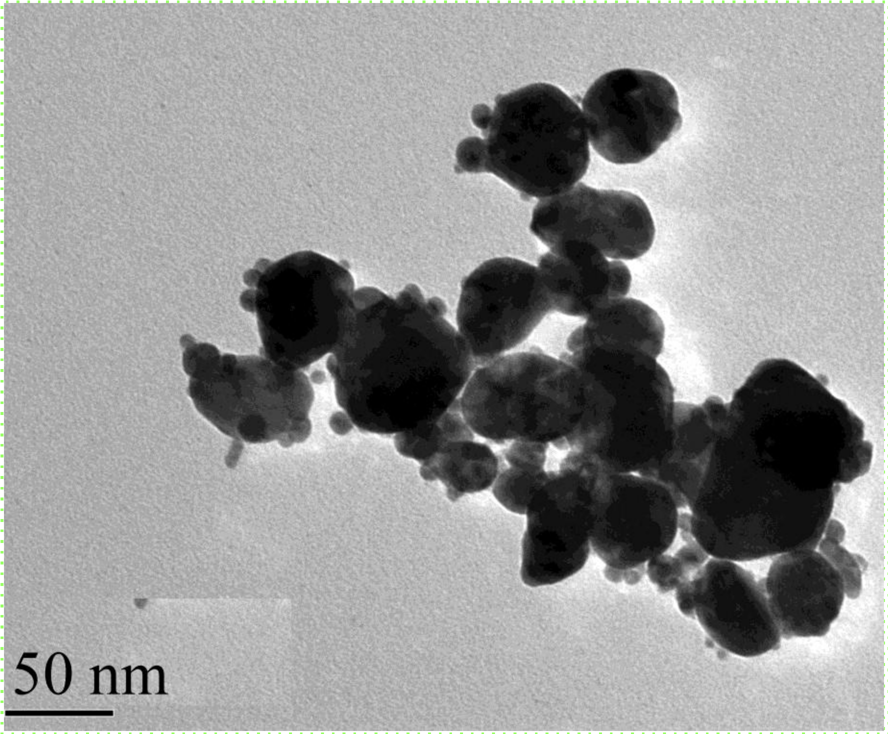
CURRENT STATUS: ‘Rags to riches’ story of nanoparticle generation using red wine and red grape pomace.



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

Gold Nanoparticles Using Wine



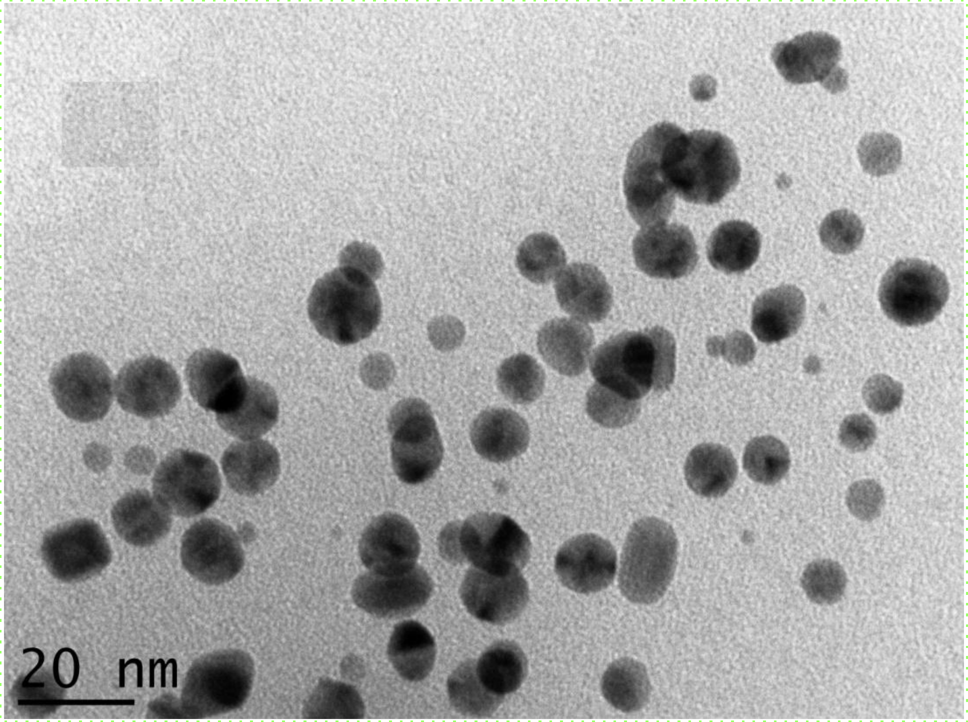


Red Wine **White Wine**

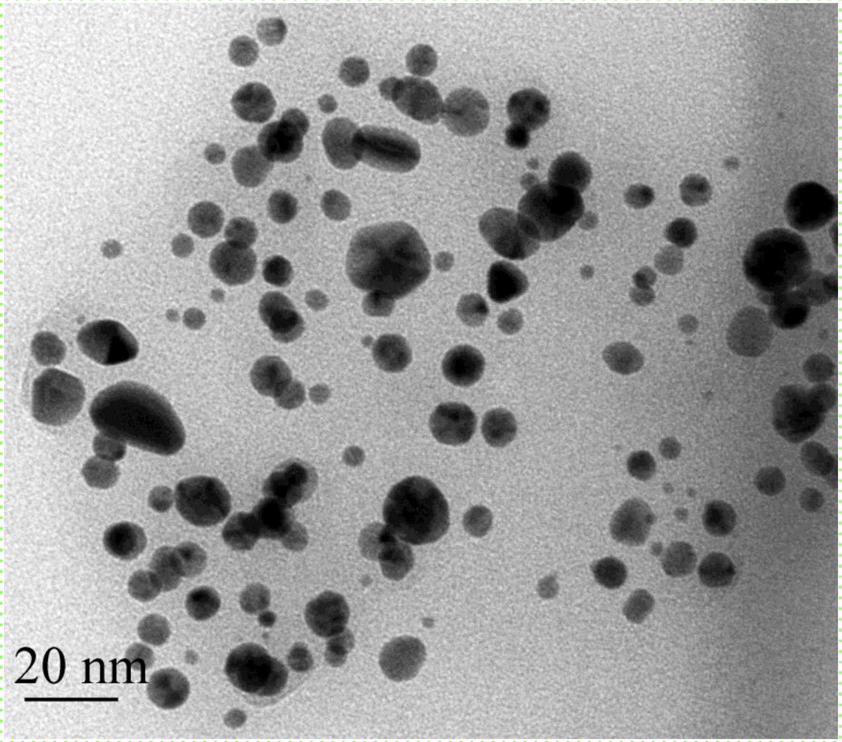
Baruwati, Varma, *ChemSusChem, 2*, 1041 (2009)

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

Gold Nanoparticles Using Red Grape Pomace



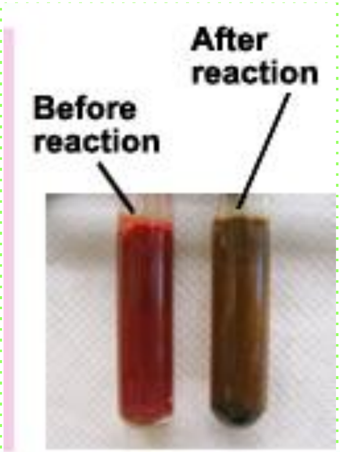
MW 50 W for 1 Minute

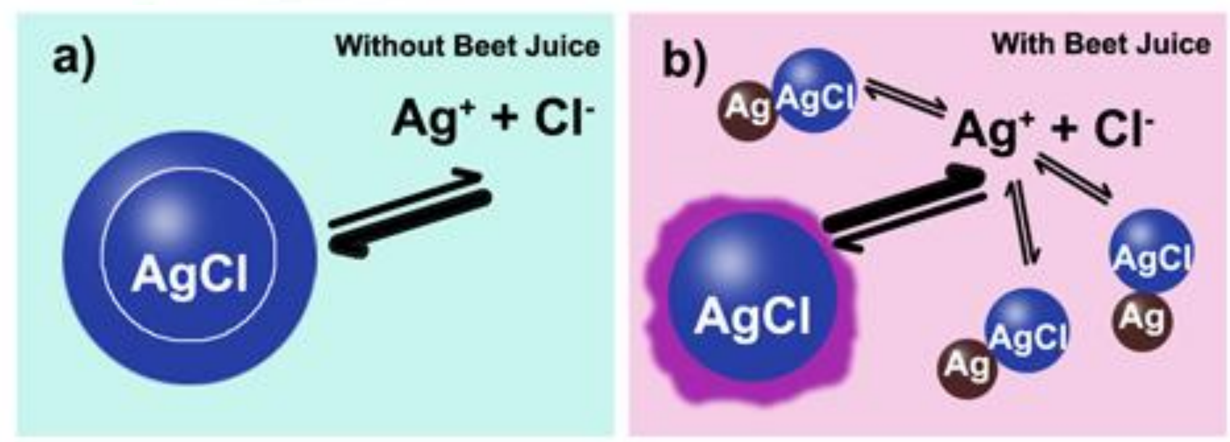


Room Temp. for 3 hours

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

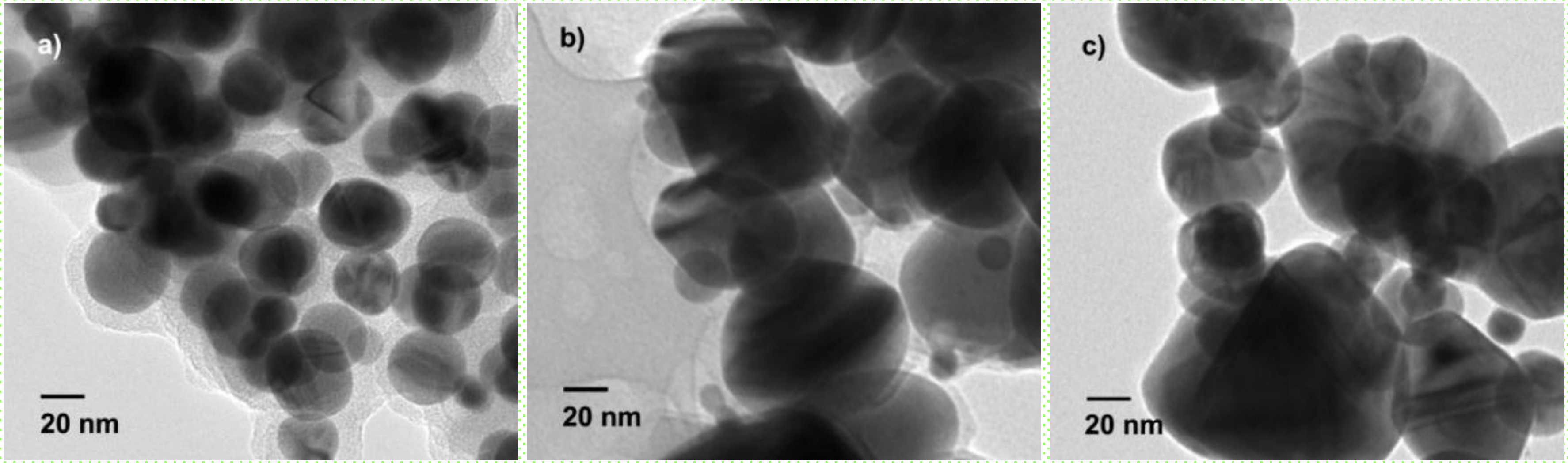
Beet Juice-induced Green Fabrication of Plasmonic AgCl/Ag Nanoparticles: Unusual Top-down Hydrothermal Synthesis





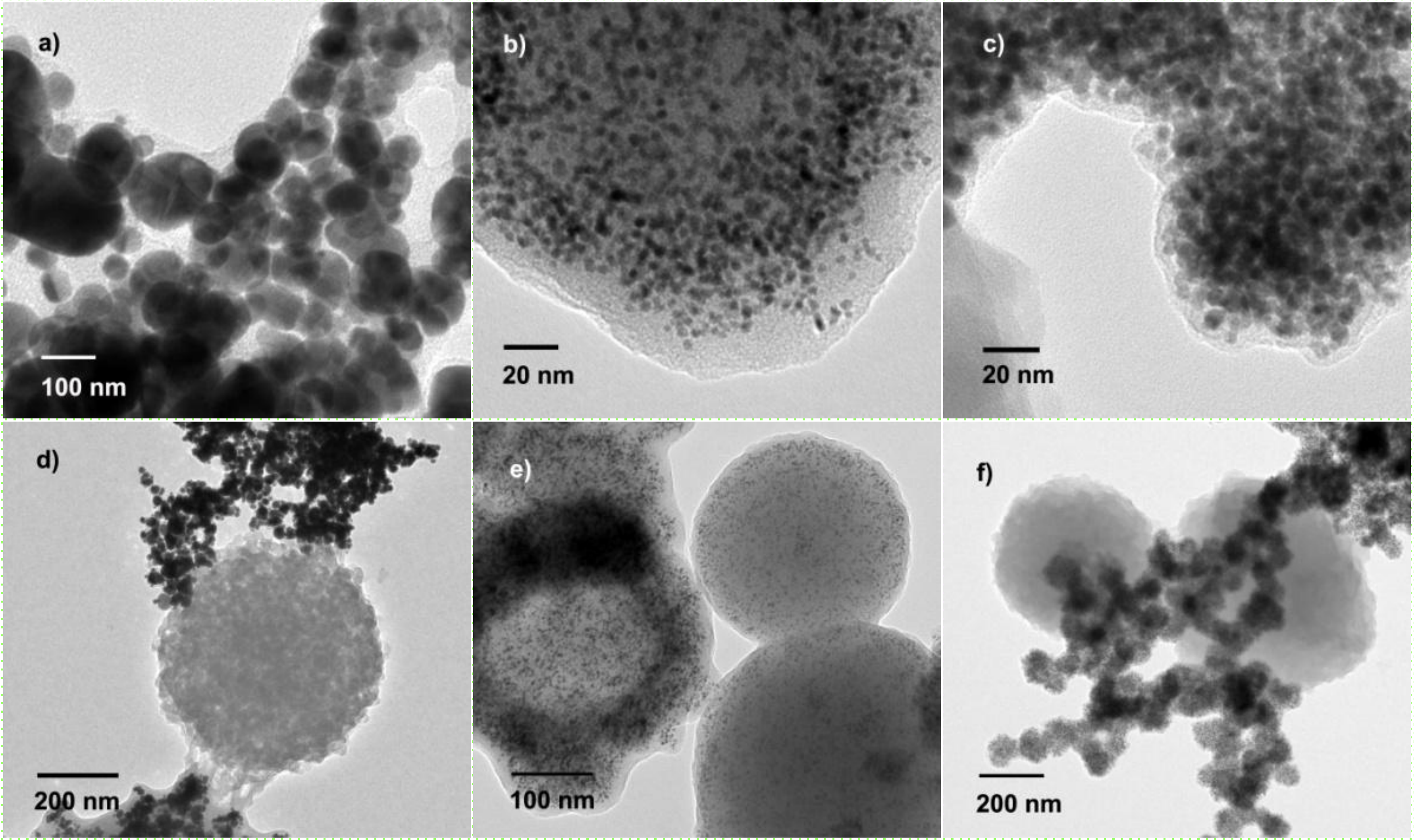
Kou, Varma: *ChemSusChem* (in press)

Ag Nanoparticles from Beet Juice: A Green Fabrication on Carbon Microsphere



TEM images of Ag nanoparticles obtained by using different beet juice content: a) 6 mL; b) 3 mL; c) 1 mL.

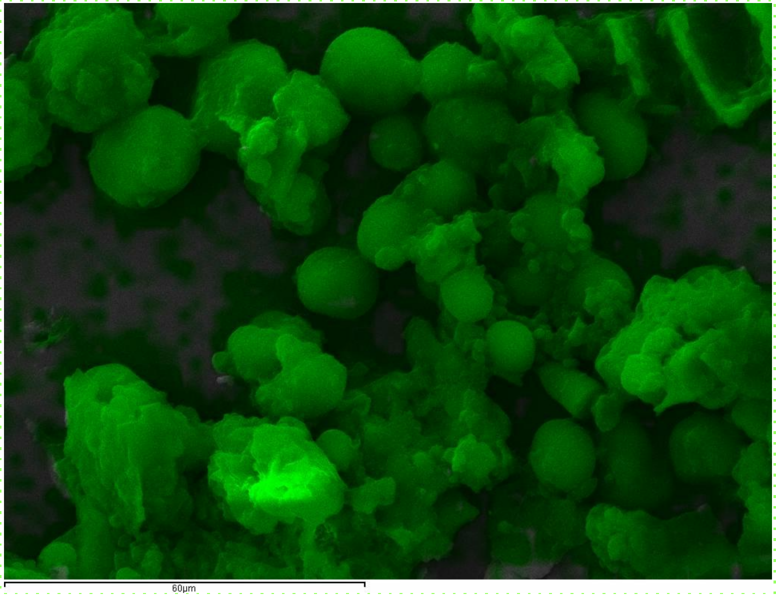
Kou, Varma: *RSC Advances* , *2*, 10283-10290 (2012)



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

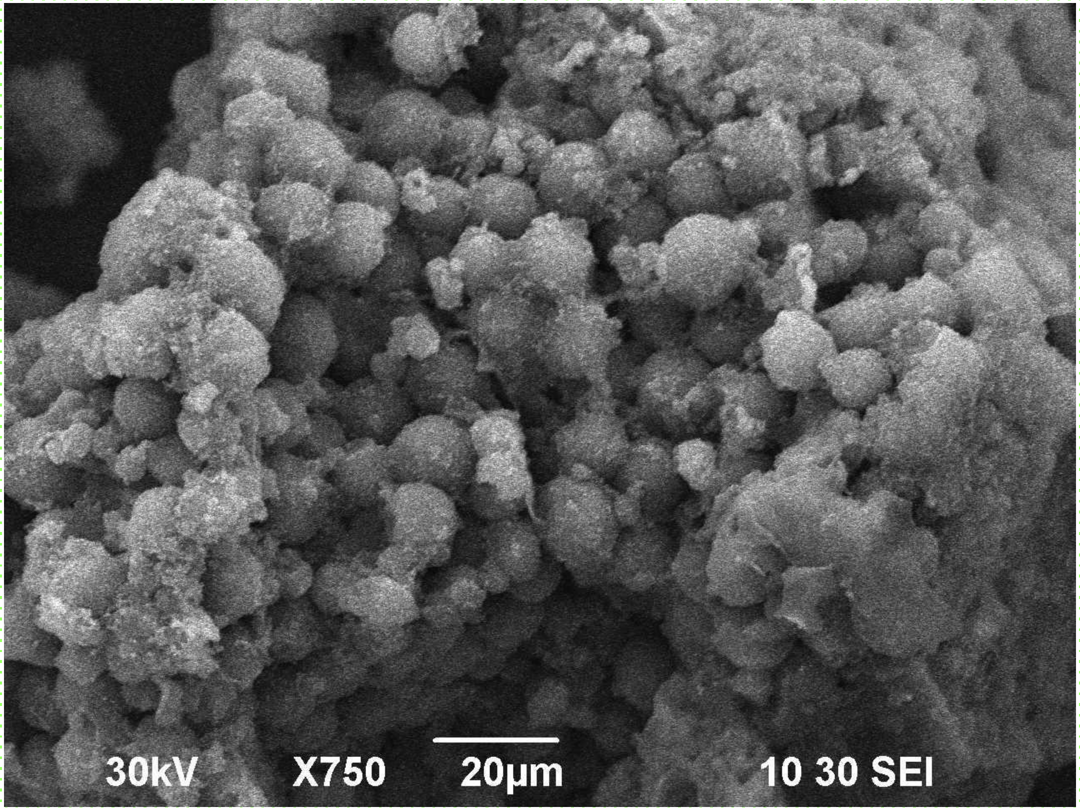
Kou, Varma: *RSC Advances* , *2*, 10283-10290 (2012)

X-Ray Mapping Images of Various Nanostructures Obtained Using Sorghum Bran

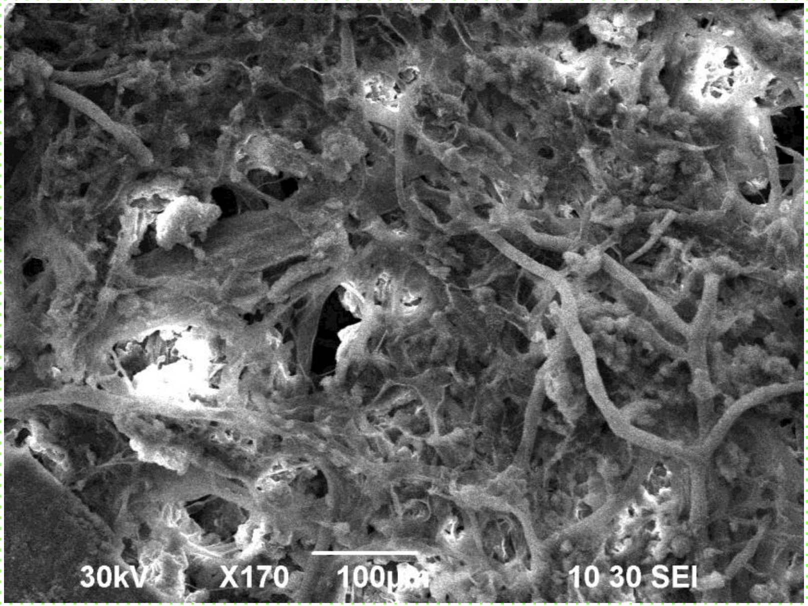


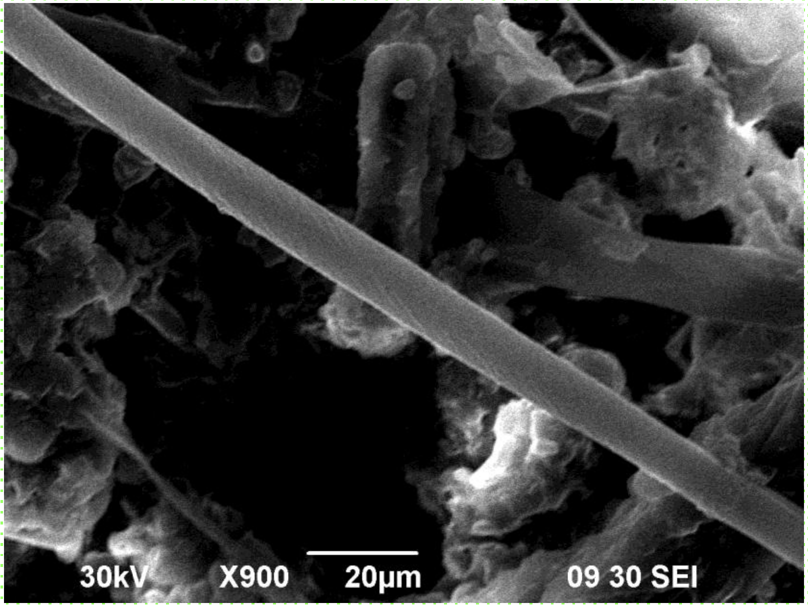
Pd Nanostructures (green)

Ag Nanostructures from Sorghum



Ag Nanoparticles from Sorghum Bran

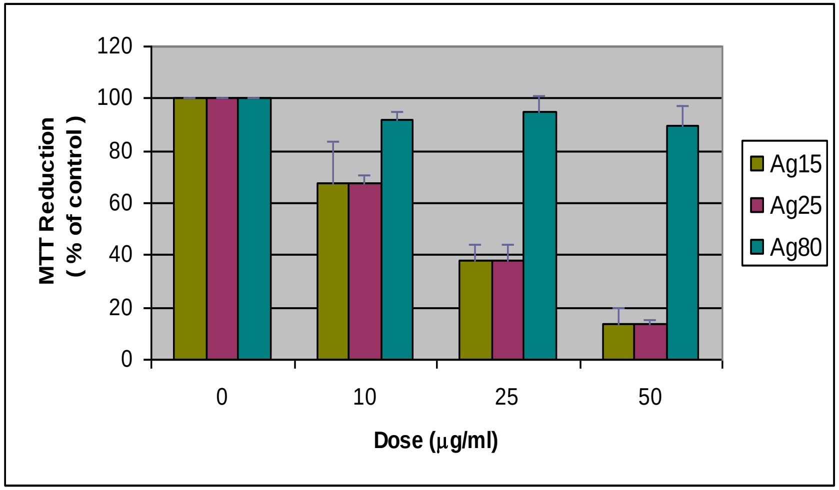




Au Nanowires from Sorghum Bran

Toxicity of Silver NP in Mouse Keratinocytes: MTS Assay Viability

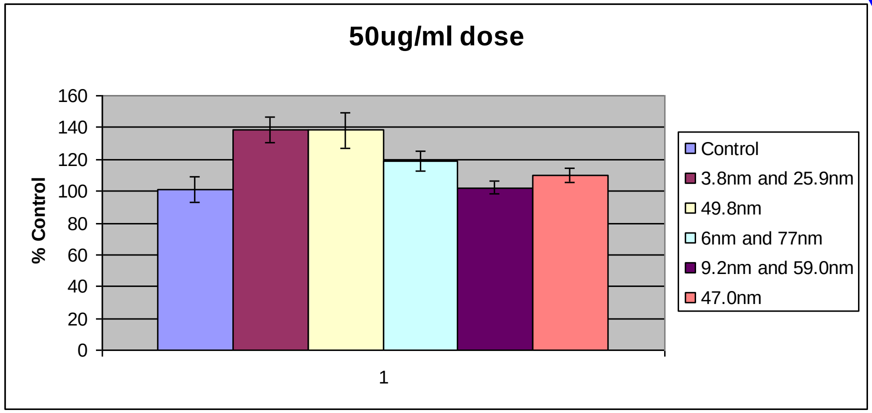
(Uncoated Silver)

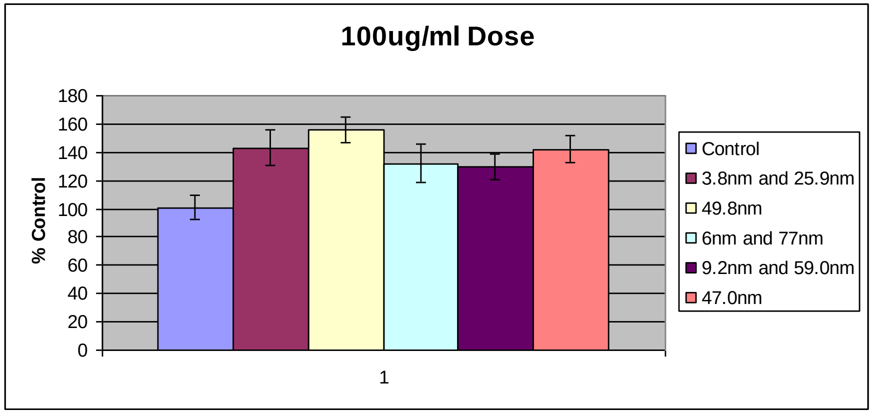


Collaboration with Dr. Saber Hussain, Air Force Research Laboratory, Dayton, Ohio

Nanoscale, 2, 763(2010)

(Silver with Tea Extract)



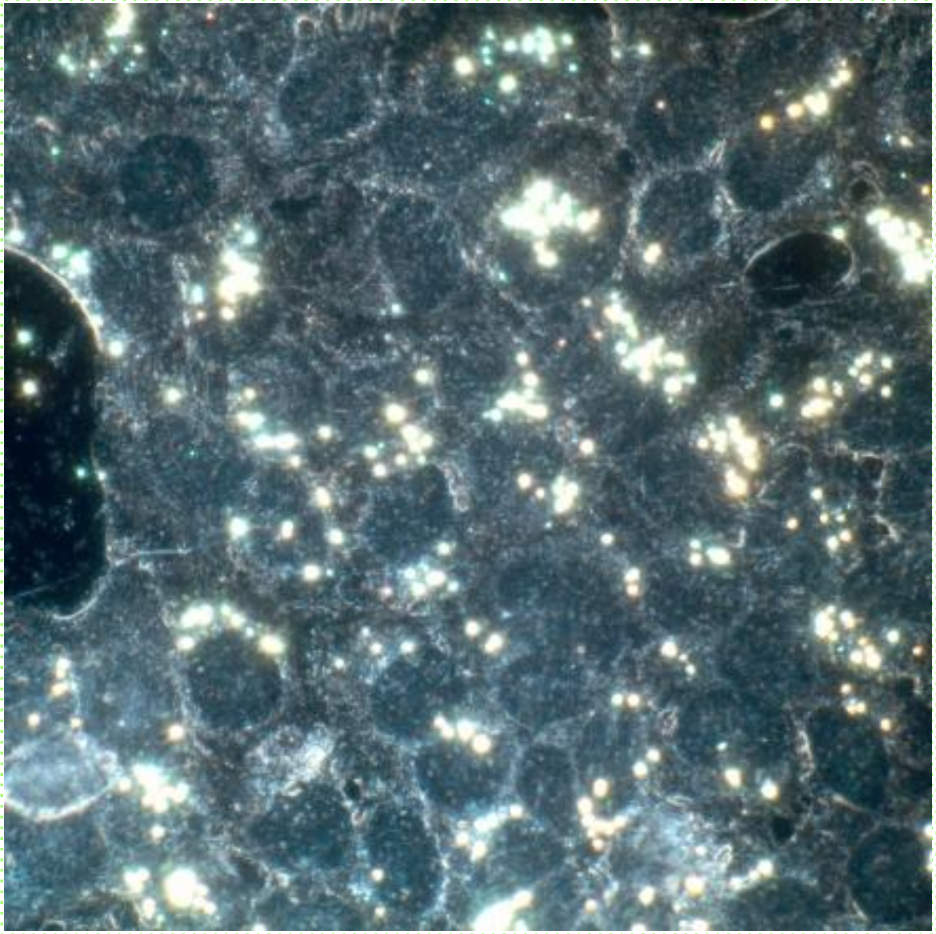


***MTS measures mitochondrial function**

Synthesis, Characterization and Biocompatibility of 'Green' Synthesized Silver Nanoparticles Using Tea Polyphenols

United States Air Force:
Michael C. Moulton,
Laura K. Braydich-Stolle,
Samantha Kunzelman,
And Saber M. Hussain

Environmental Protection Agency:
Mallikarjuna N. Nadagouda
and Rajender S. Varma*



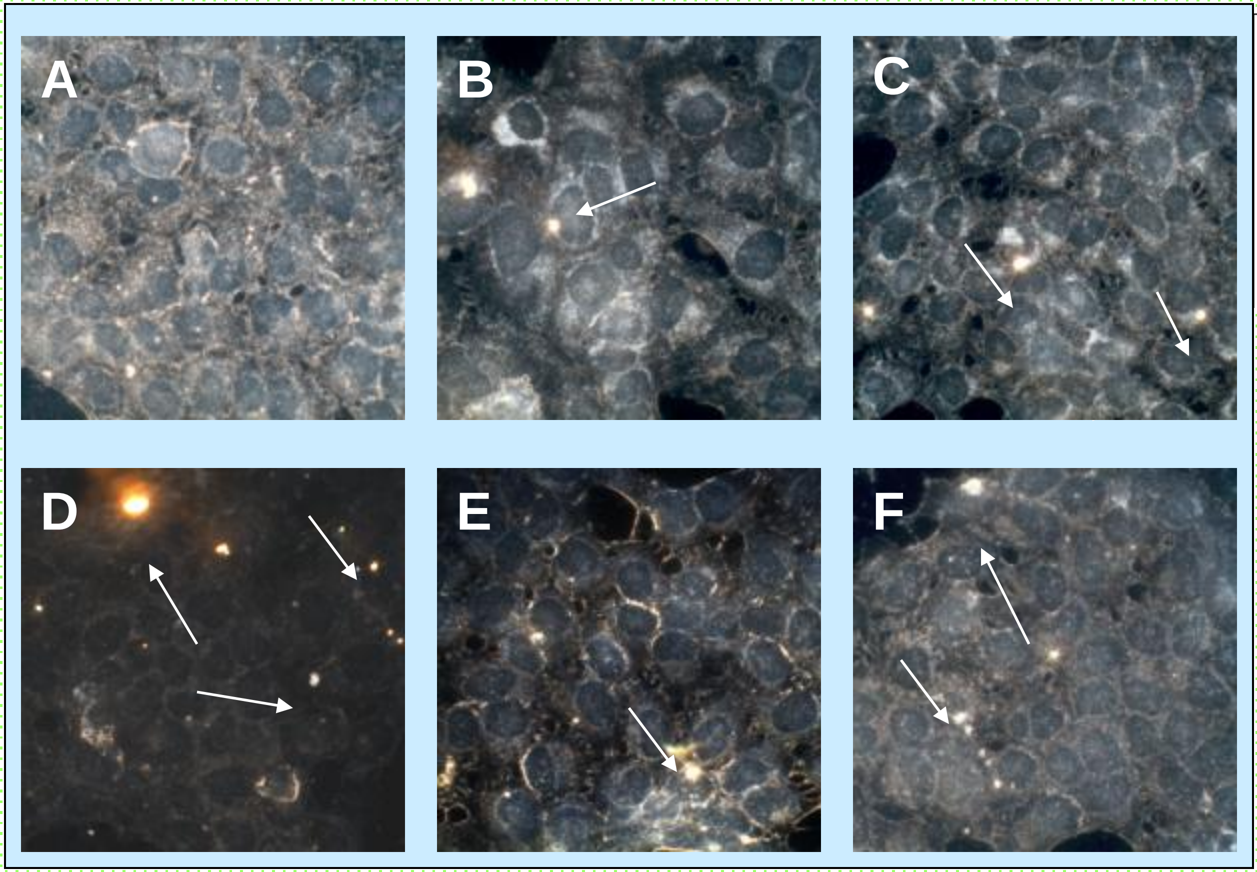
***Nanoscale*, *2*, 763 (2010)**

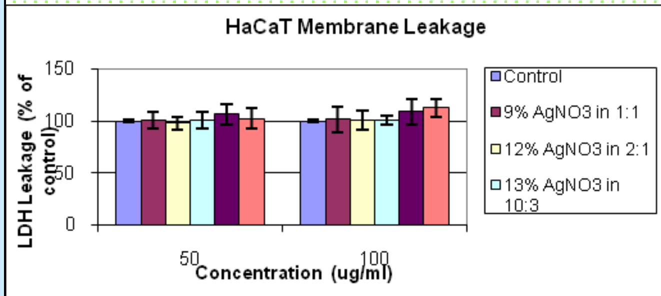
	Sample	Primary Particle Size (nm)	DLS Agglomerate Size (nm)		
			HEM	MEM	Water
Epicatechin	**9% AgNO3 in 1:1**	**11.5 4.7**	**6.51E+04**	**2980**	**3.05E+04**
	12% AgNO3 in 2:1	**25.8 15.8**	**5.30E+04**	**7650**	**4.78E+04**
	13% AgNO3 in 10:3	**11.9 3.9**	**3.29E+04**	**2.85E+04**	**4.48E+04**
	15% AgNO3 in 10:1	**17.3 7.0**	**1270**	**248**	**4640**
	16% AgNO3 in 20:1	**24.2 6.5**	**1320**	**2500**	**3.30E+04**
Tea Extract	**9% AgNO3 in 1:1**	**A. 91.3 20.9 B. 6.7 2.9**	**805**	**497**	**510**
	12% AgNO3 in 2:1	**A. 59.0 19.7 B. 9.2 1.9**	**1370**	**1010**	**611**
	13% AgNO3 in 10:3	**A. 71.1 22.3 B. 6.1 2.4**	**1340**	**735**	**661**
	15% AgNO3 in 10:1	**A. 49.8 14.7**	**1730**	**511**	**487**
	16% AgNO3 in 20:1	**A. 25.9 6.8 B. 3.8 0.88**	**1810**	**291**	**220**

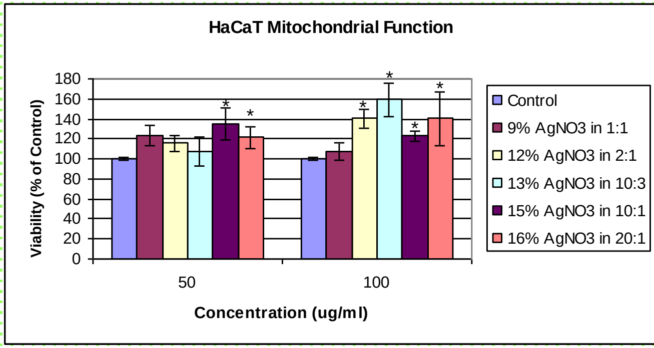
Characterization of epicatechin and tea extract synthesized Ag nanoparticles: Primary particle size evaluated with Transmission Electron Microscopy. Agglomerate size evaluated in HaCaT exposure media (HEM), MAC exposure media (MEM) and Millipore water, using dynamic light scattering (DLS). Estimate number of particles calculated using the TEM primary particle size distribution.

Biocompatibility of Epicatechin Synthesized Ag Nanoparticles

Nanoscale, 2, 763 (2010)





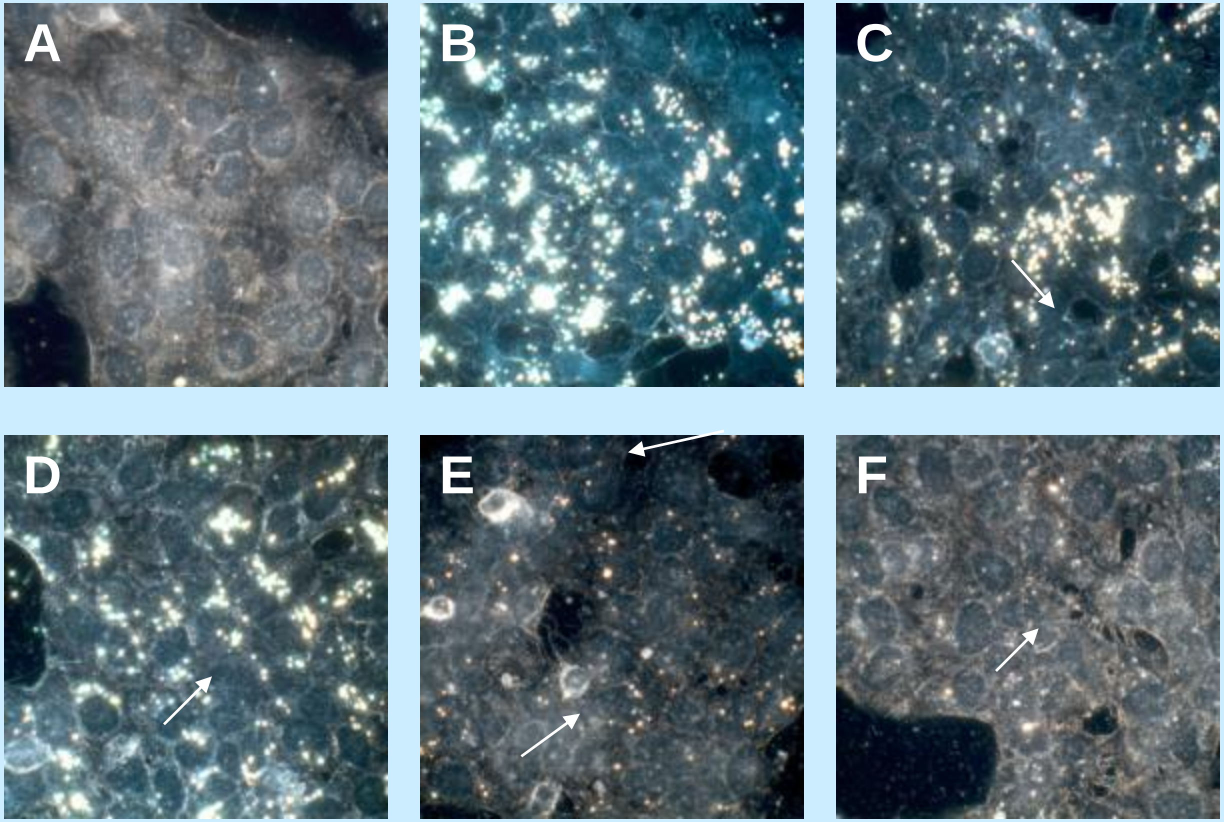


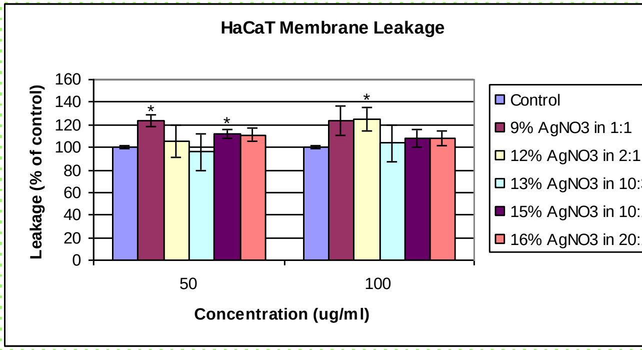
Morphological evaluation of HaCaT cells after treatment with Epi-Ag NP's. A) Control cells, B) 1:1 ratio of water to epicatechin, C) 2:1 ratio of water to epicatechin, D) 10:3 ratio of water to , E) 10:1 ratio of water to epicatechin, F) 20:1 ratio of water to epicatechin. Arrows indicate locations of nanoparticles.

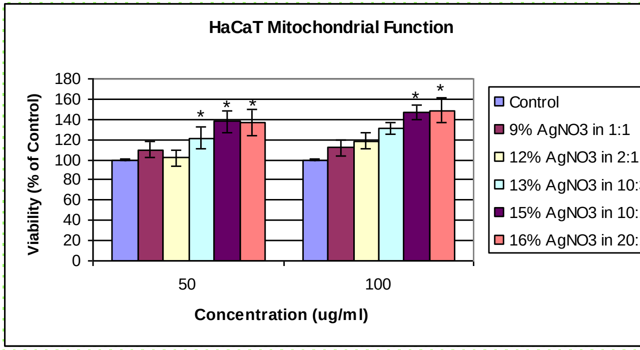
A. **Mitochondrial function of the HaCaT cell line exposed to Epicatechin synthesized Ag NP's,**
B. **Membrane leakage of the HaCaT cell line exposed to Epicatechin synthesized Ag NP's.**

Biocompatibility of Synthesized Ag Nanoparticles by Tea Polyphenols

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

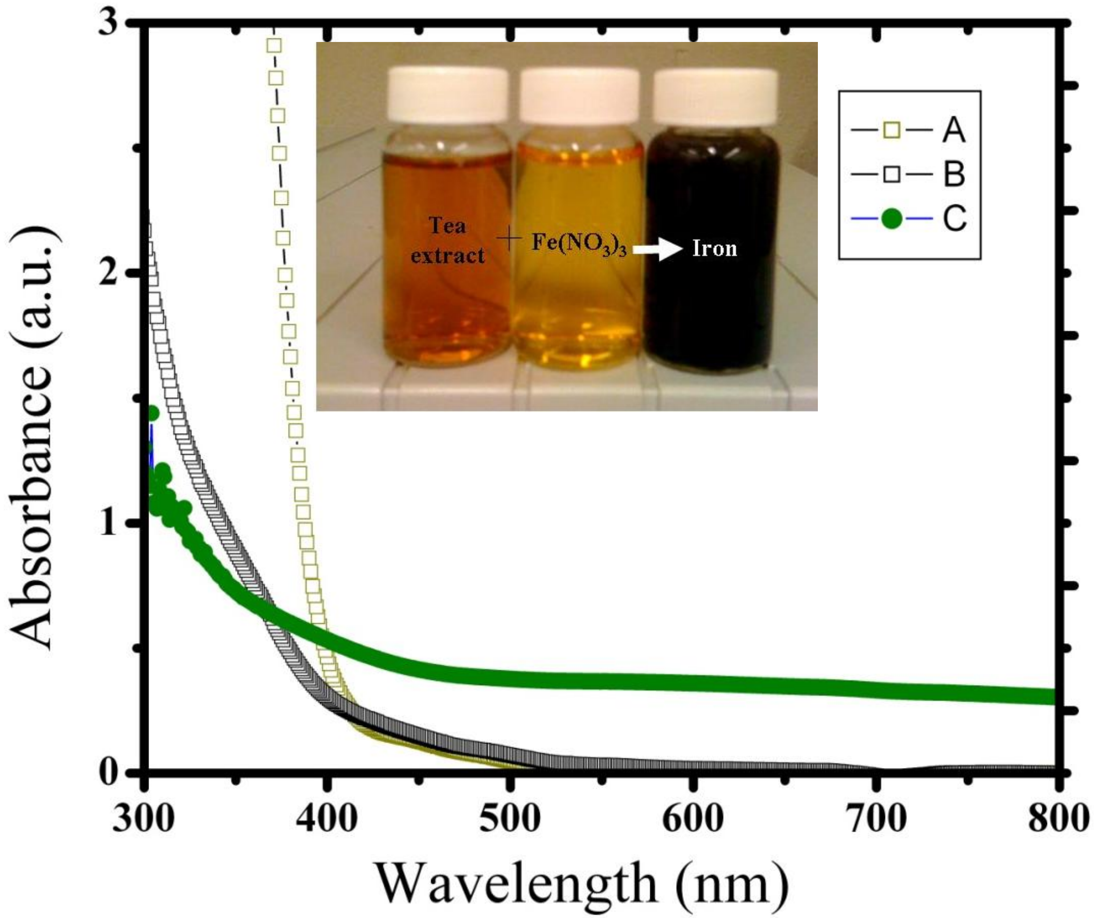






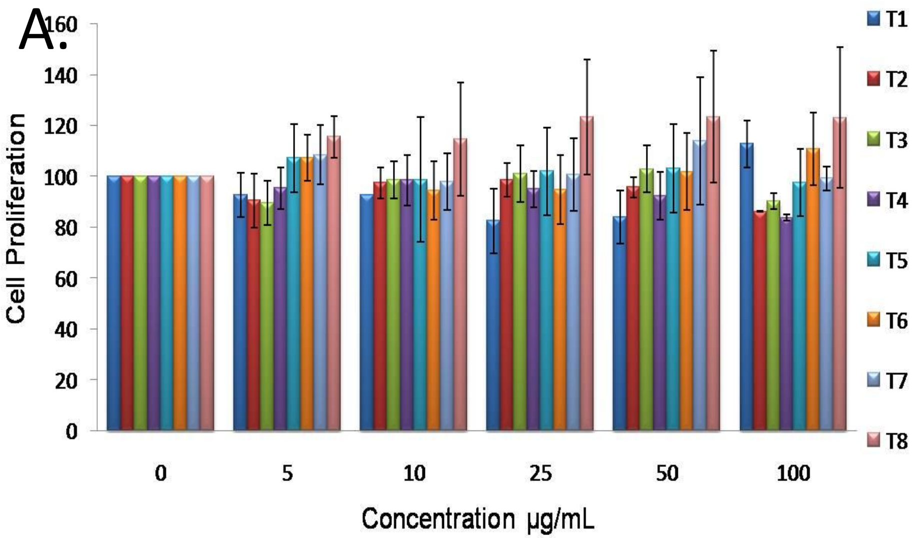
Morphological evaluation of HaCaT cells after treatment with Tea-Ag nanoparticles. A) Control cells B) 1:1 ratio of water to tea extract, C) 2:1 ratio of water to tea extract, D) 10:3 ratio of water to tea extract, E) 10:1 ratio of water to tea extract, F) 20:1 ratio of water to tea extract. Arrows indicate locations of nanoparticles.

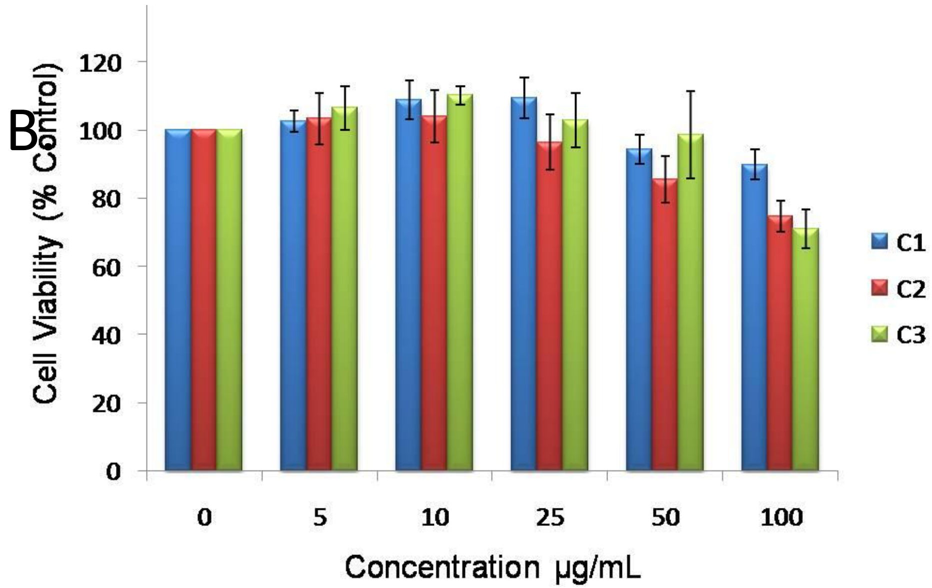
A. **Mitochondrial function of the HaCaT cell line exposed to tea extract synthesized Ag NP's,**
B. **Membrane leakage of the HaCaT cell line exposed to tea extract synthesized Ag NP's.**



UV spectra of (a) Fe, (b) tea extract and (c) reaction product of $Fe(NO_3)_3$ and tea extract. Inset shows the photographic image of the reaction.

Nadagouda, Castle, Murdock, Hussain & Varma: *Green Chemistry*, *12*, 114 (2010)-Hot Article





48h MTS results

- No significant decreases in cell proliferation after a 48h exposure to NZVI (Figure A.)

- No significant reductions in cell proliferation after a 48h exposure to control particles (Figure B.)

Nadagouda, Castle, Murdock, Hussain & Varma: *Green Chemistry*, *12*, 114 (2010)-Hot Article

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

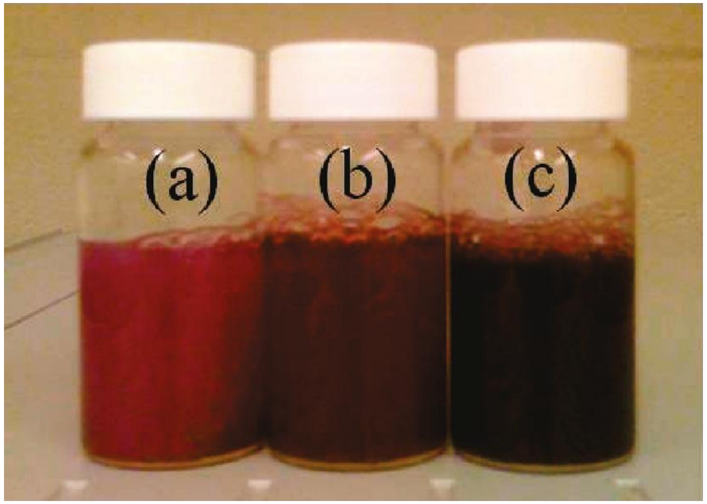
nZVI Formation in Soil Column

Control Column

Lemon Balm Extract Feed Pump

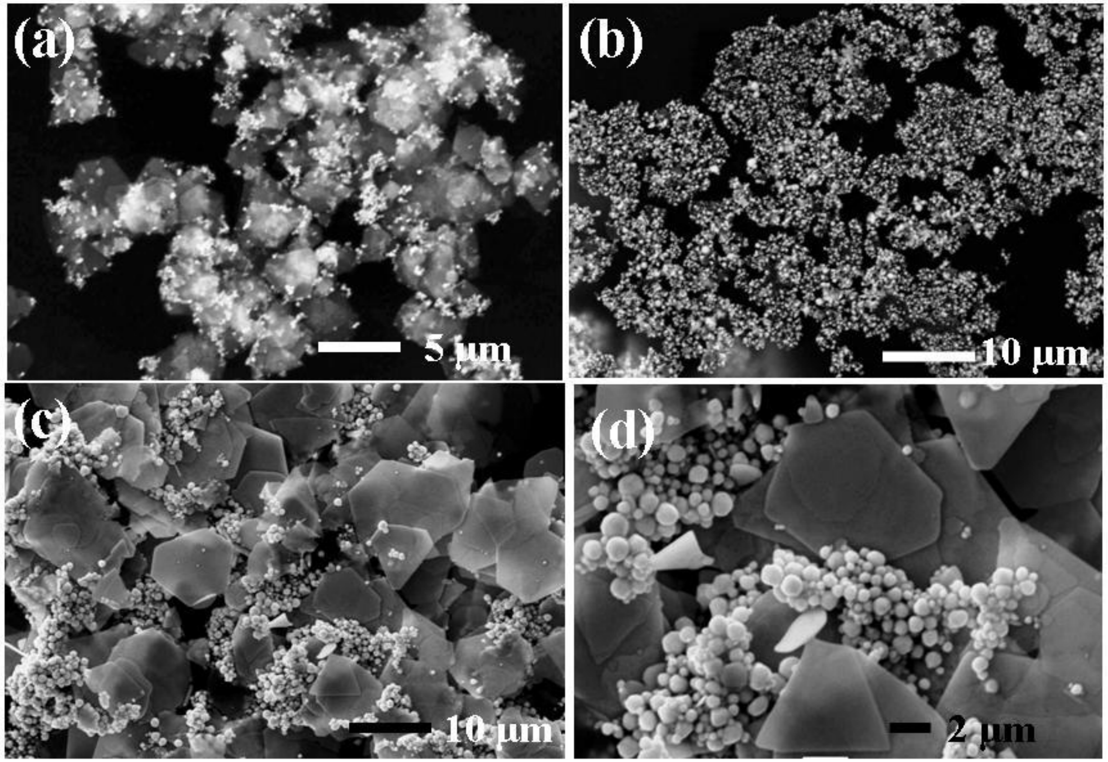
$Fe(NO_3)_3$ Feed Pump

Green Synthesis of Au Nanostructures at Room Temperature using Biodegradable Plant Surfactants



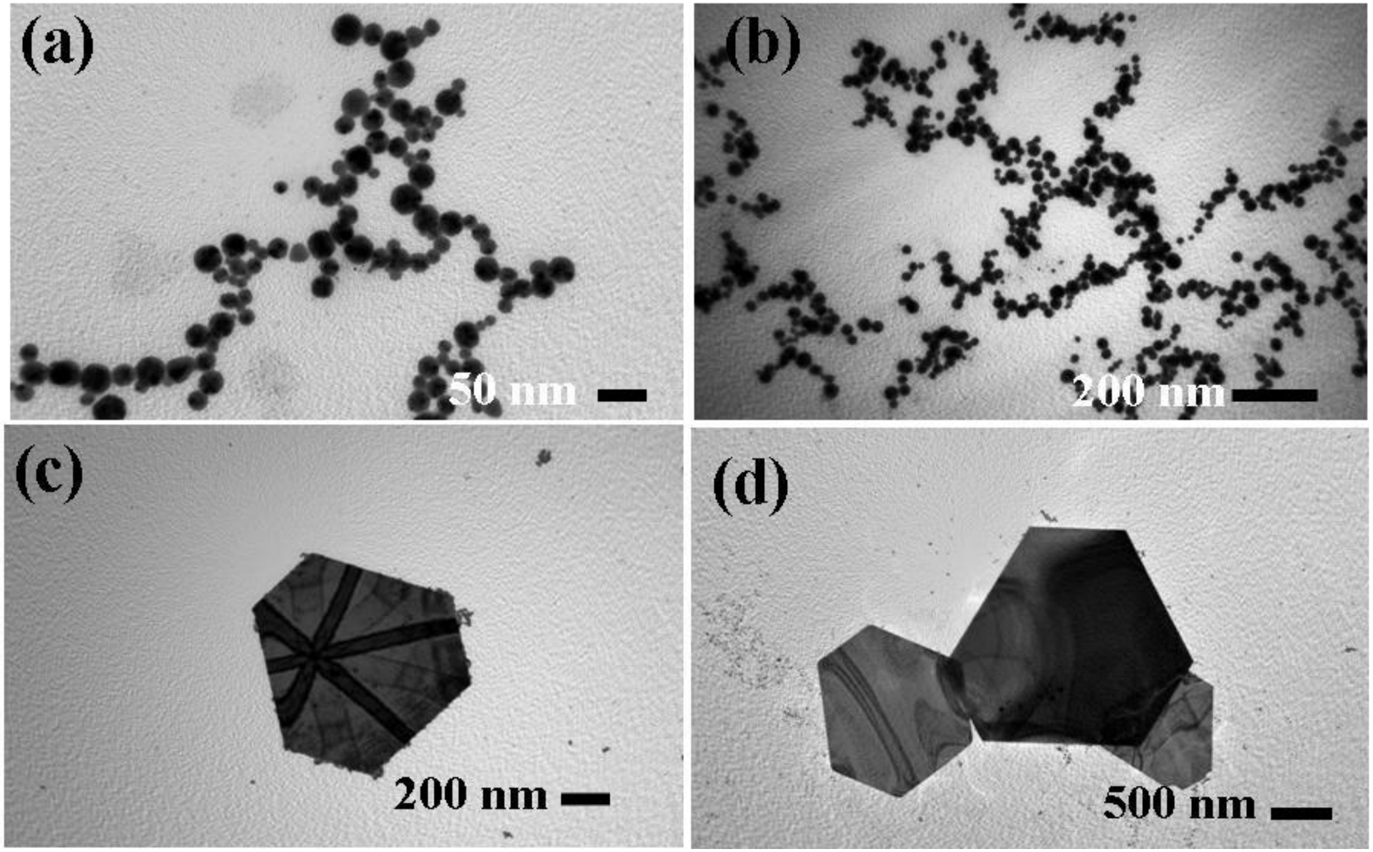
Representative photographic images of Au Nanostructures

Nadagouda, Hoag, Collins & Varma: *Crystal Growth & Design*, *9*, 4979 (2009)



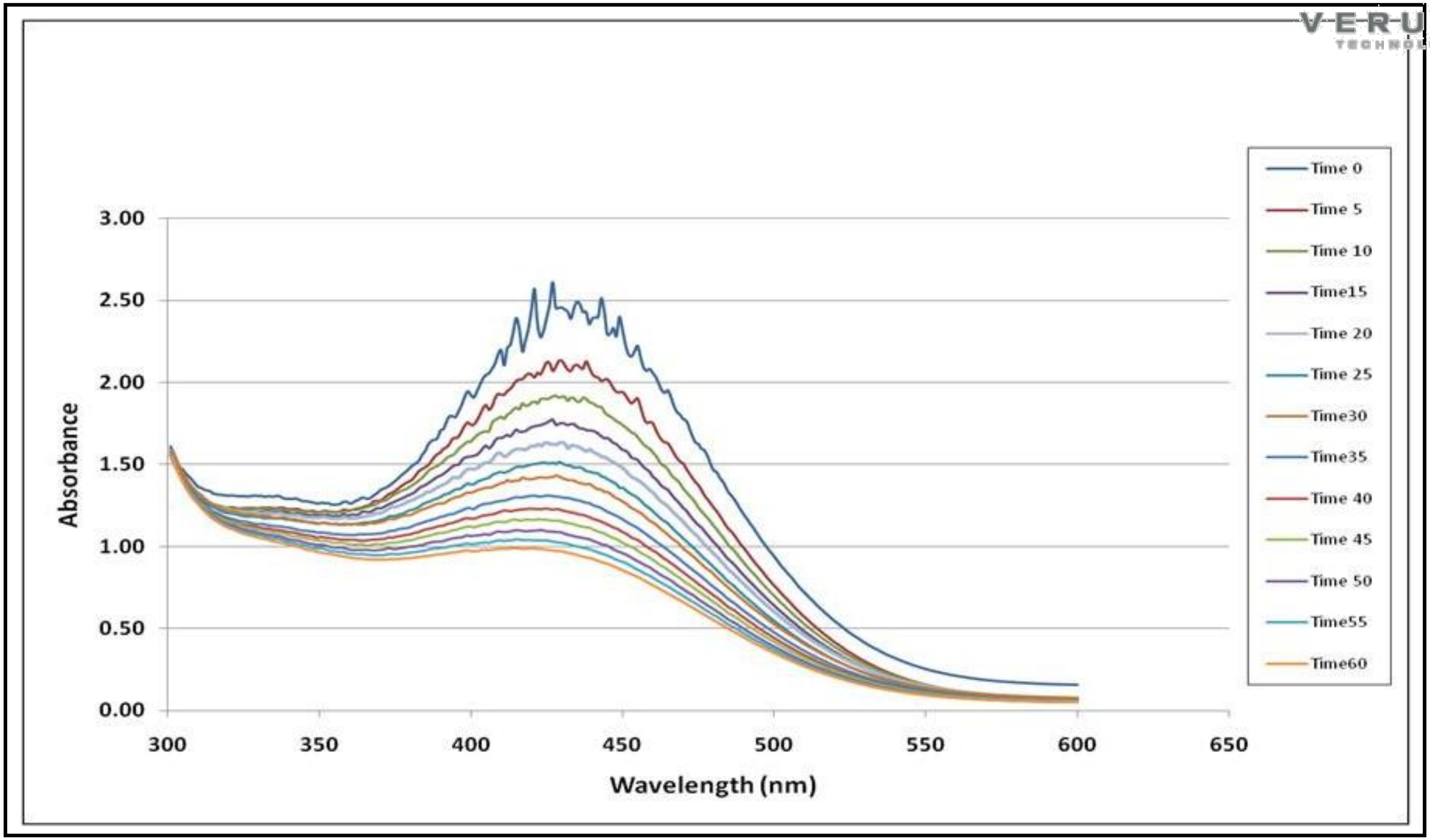
SEM Images of Au Nanostructures Synthesized Using Plant Surfactants

Nadagouda, Hoag, Collins & Varma: *Crystal Growth & Design*, *9*, 4979 (2009)



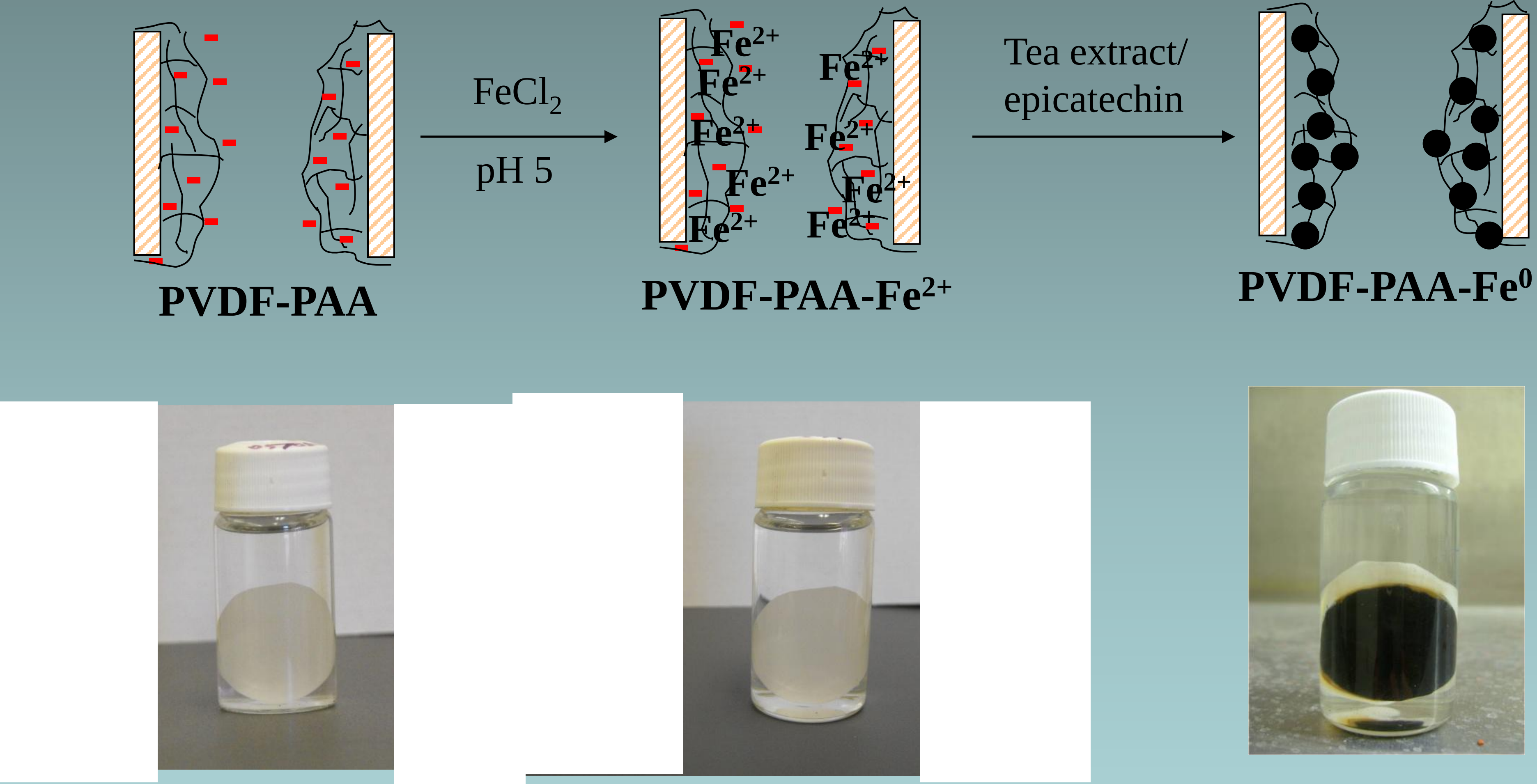
TEM Images of Au Nanostructures Synthesized Using Plant Surfactants

Nadagouda, Hoag, Collins & Varma: *Crystal Growth & Design*, *9*, 4979 (2009)

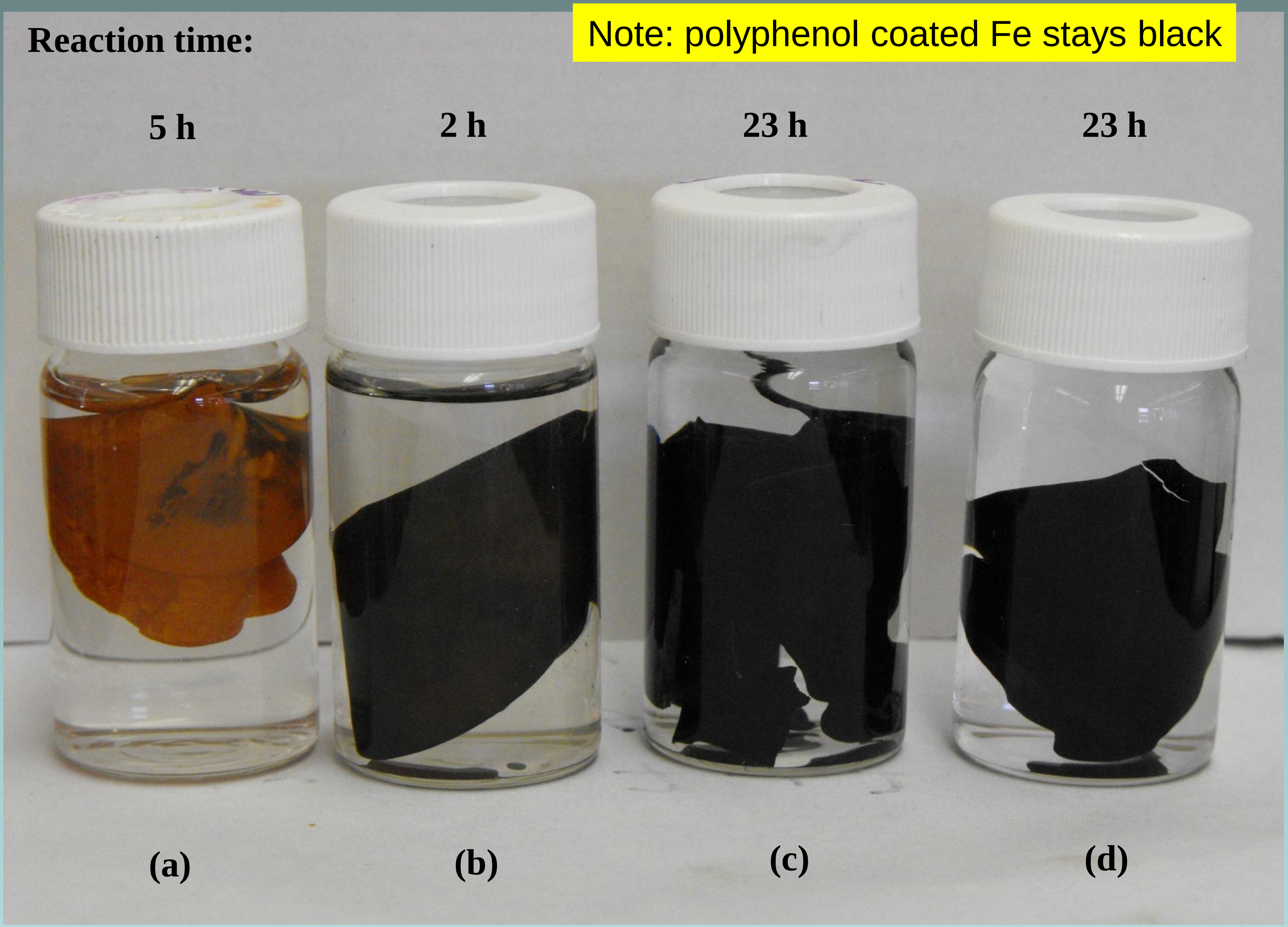


UV-Vis Spectra (Absorbance v Wavelength) of bromothymol blue over time for an initial solution containing 500 ppm bromothymol blue (pH 6), 2% H_2O_2, and 0.06 mM GT-nZVI.

J. Mater. Chem. **19**, 8671 (2009)



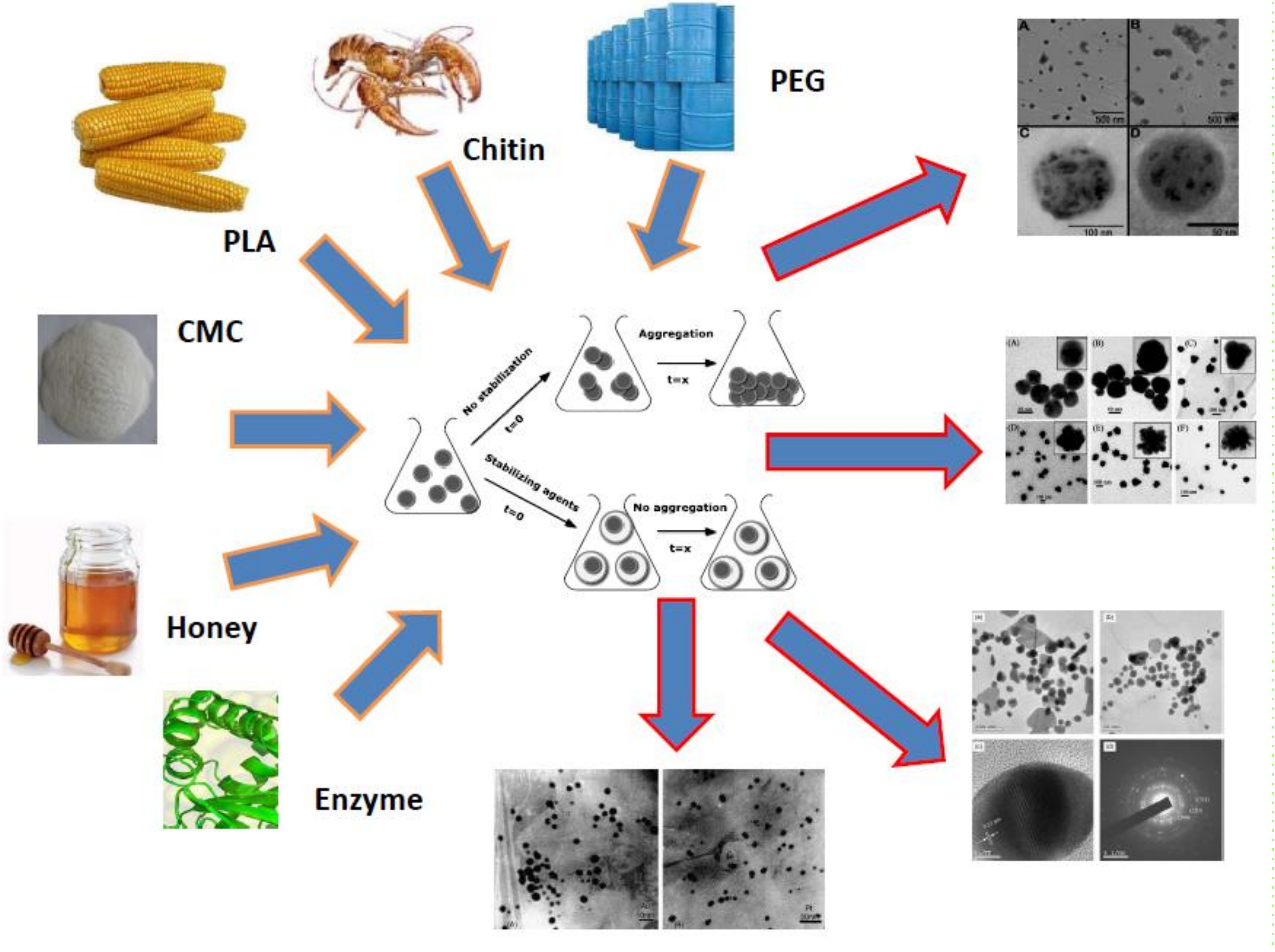
Schematic of Fe nanoparticle synthesis in PAA-coated PVDF membrane (using green tea extract as a reducing agent) and photos of the membrane after each step



NP-immobilized on PAA/PVDF membranes after TCE dechlorination

a) Fe and b) Fe/Pd (reduced by $NaBH_4$), c) Fe and b) Fe/Pd (reduced by tea extract)

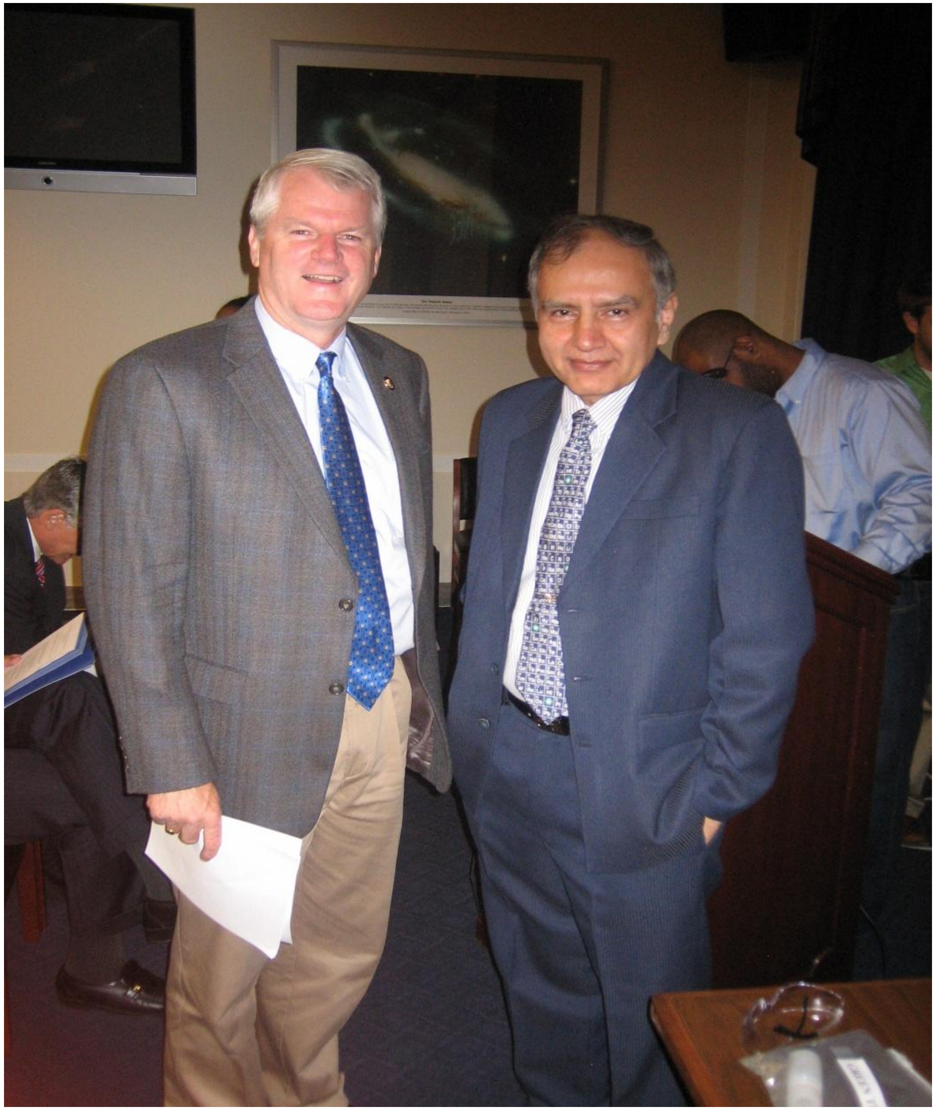
Biodegradable Polymers and Enzymes in Stabilization & Surface Functionalization



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

Presentation "Cool Science" at Capitol Hill, Oct. 13, 2010

(with Brian Baird, Chairman, Subcommittee on Energy and Environment)



Presenting to The Madam President of India in her Office, New Delhi, India

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- ***CRADA with University of Dayton***

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Dr. Saber Hussain (WP Air Force Base, Dayton, OH)
Dr. Rafael Luque (Cordoba, Spain)

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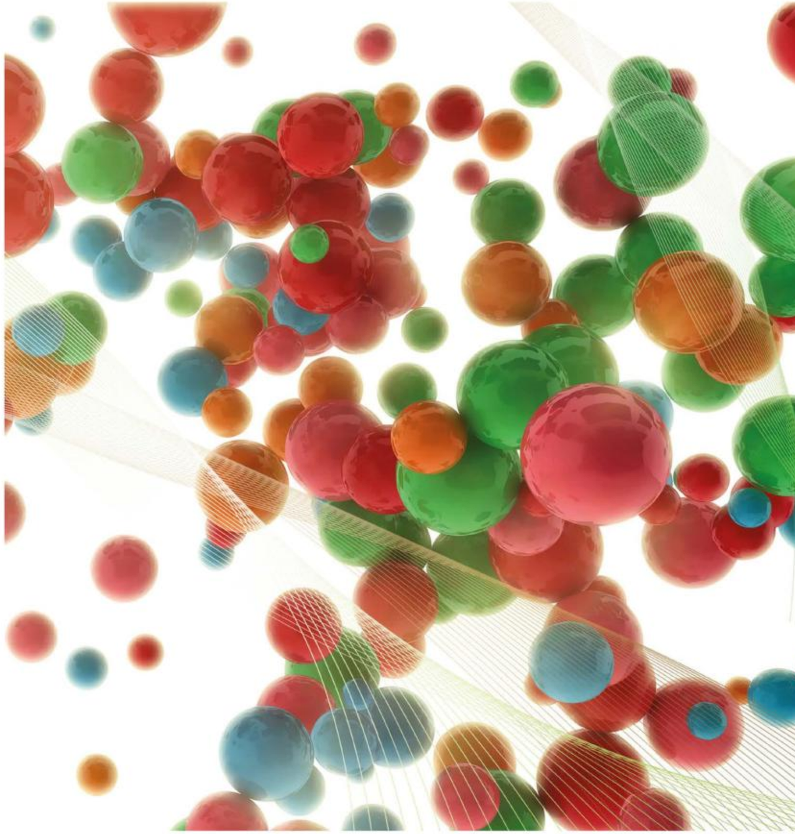
Methods and Applications



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