Metal Nanoparticles in Catalysis

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MacMillan Group Meeting

May 15, 2018

Outline

General Concepts

Metal-NPs as catalyst in organic chemistry

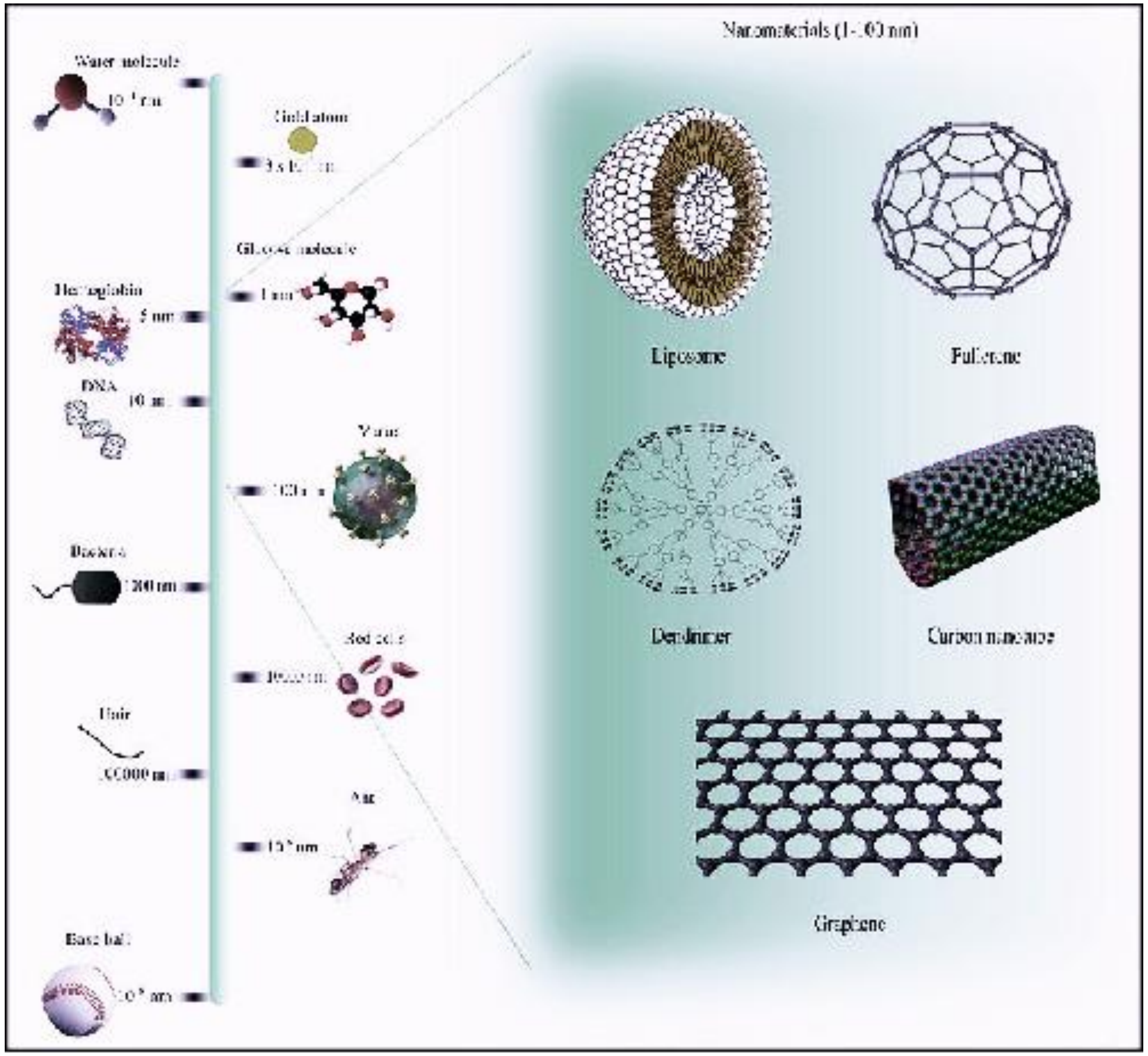
Metal-NPs in Photocatalysis

Introduction to Nanoparticles

Nanoparticle:

A particle with dimensions less than 100 nm

A microscopic particle of matter that is measured on the nanoscale



Introduction to Nanoparticles

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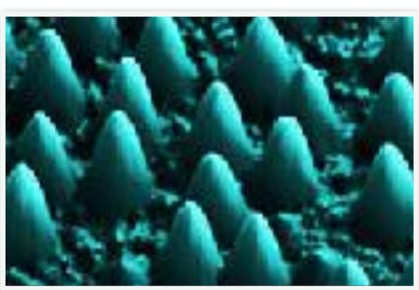
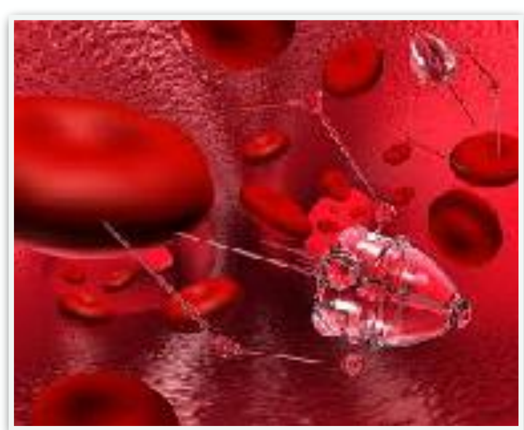


NanoScience ***NanoTechnology***

Introduction to Nanoparticles

Nanoparticle:

A particle with dimensions less than 100 nm

A microscopic particle of matter that is measured on the nanoscale

Nanoparticles along the time

late Bronze Age	400-100 BC	4th Century BC
red glass	*Celtic red enamels*	*Egypcian Blue*
Cu NPs	***Cu NPs***	**PbS NPs**

Introduction to Nanoparticles

Nanoparticle:

A particle with dimensions less than 100 nm

A microscopic particle of matter that is measured on the nanoscale

Nanoparticles along the time

4th Century

Rome

Alexandria

Lycurgus Cup

9th Century

Mesopotamia

Glittering effect in Pottery

Middle Ages — **Renaissance**

Luster in glassy matrix of the ceramic glaze

Ancient Stained-Glass

1857

Faraday

1st description of the optical properties of nanoscale-metals

1970-80

USA and Japan

1st fundamental studies with NPs

Present

- *AgNPs, 100 nm, Sphere*
- *AuNPs, 25 nm, Sphere*
- *AgNPs, 40 nm, Sphere*
- *AgNPs, 100 nm, Prism*
- *AuNPs, 50 nm, Sphere*
- *AuNPs, 100 nm, Sphere*

Introduction to Nanoparticles

Classification

Based on the Origin

- *Natural:*

occur in the enviroment

- *Incidental:*

manmade industrial processes

- *Engineered:*

milling or lithography etching of large sample, or by assembling smaller subunits

Based on Composition

Based on Dimensions

- *0D: (x,y,z)< 100 nm*

clusters

- *1D: (2 dimensions < 100 nm)*

nanotubes, fibers and rods

- *2D: (1 dimension < 100 nm)*

films and coats

- *3D: (0 dimension < 100 nm)*

polycrystals, nanoflowers

Danquah, M. K. *et al. Beilstein J. Nanotechnol.* **2018,** *9,* 1050

www.nano.gov

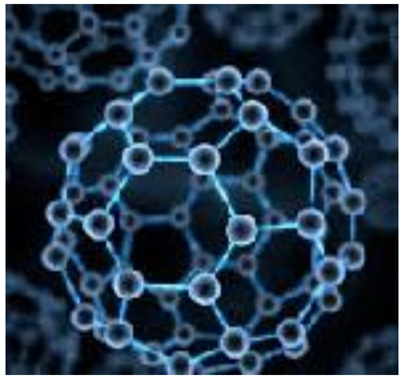
Introduction to Nanoparticles

Classification

Based on the Origin | **Based on Composition** | **Based on Dimensions**

- *Carbon-based NPs*

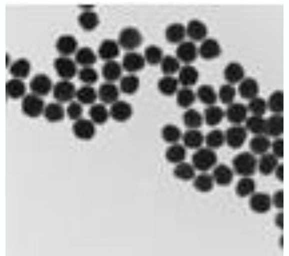
spherical, ellipsoidal or tubular shape



Fullerenes

- *Metallic NPs (Inorganic NPs)*

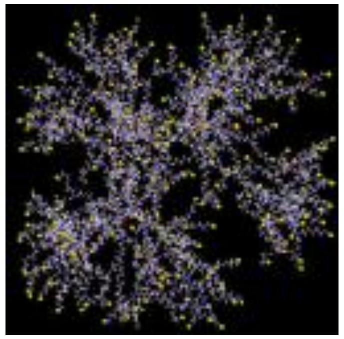
Quantum Dots
NPs of noble metals, metal oxides and semiconductors



Gold NPs

- *Organic-based NPs*

Organic matter excluding carbon-based and metallic



Dendrimers

- *Composite-based NPs*

multiphase: one NPs combine with other or with larger/bulk-type material

Hybrid nanofibers

Danquah, M. K. *et al. Beilstein J. Nanotechnol.* **2018,** *9,* 1050

www.nano.gov

Synthesis of Metal-Nanoparticles

General Procedures

Chemical Reduction of Metal Salts

$$AgNO_3 \xrightarrow[\text{ethylene glycol}]{\text{reductor}} Ag^{(0)}\ (NPs)$$

- *reductor: H_2, $NaBH_4$, alcohols, CO, sodium citrate, organosilanes*
- *controled size and shape*
- *need stabilizing agents*
- *stable in water conditions*
- *Au, Ag, Pd, Pt, Ir, Cu, Ru*

Displacement of Ligands from Organometallic Compounds

$$Pd_2(dba)_3 \xrightarrow[\text{solvent}]{\text{stabilizing agent}} Pd^{(0)}\ (NPs)$$

- *reductor: H_2, organosilanes*
- *soluble in water, DCM, THF*
- *controled size and shape*
- *polymers, imidazoles or ligands as stabilizing agents*
- *Pd, Pt, Ru, Co, Cu, Au, Fe, **Ni***

Ghorbani, H. R. *Arabian J. of Chemistry* . **2014,** DOI: 10.1016/j.arabjc.2014.12.014

Patin, H. *Chem. Rev.* ***2002***, *102,* 3757

Synthesis of Metal-Nanoparticles

General Procedures

■ Thermal, Photochemical or Sonochemical Decomposition

$$PtCl_2 \xrightarrow[\text{solvent}]{\Delta} Pt^{(0)}\text{ (NPs)}$$

- *solvents with high boiling points, IL*
- *no controled size distribution*
- *hazardous conditions*
- *no stabilizing agents*
- *Pt, Pd, Fe (thermal), Ag, Au, Ir (photo), Ni, Cu, Fe (sono)*

■ Condensation of Atomic Metal Vapor

$$Co_2(CO)_8 \xrightarrow[\text{decomposition}]{\Delta} Co^{(0)}\text{ (NPs)}$$

- *volatile ketones as stabilizing agents*
- *High temperatures to generate the metal vapor*
- *small nanoparticles, good size control*
- *complex reactors*
- *Co, Fe, Au, Pd, Cu, Ni, Pt, Pr, Yb, Er*

von Wangelin, A. J. *Current Org. Chem.* **2012,** *17*, 326

Ghorbani, H. R*. Arabian J. of Chemistry .* **2014,** DOI: 10.1016/j.arabjc.2014.12.014

Patin, H. *Chem. Rev.* ***2002***, *102,* 3757

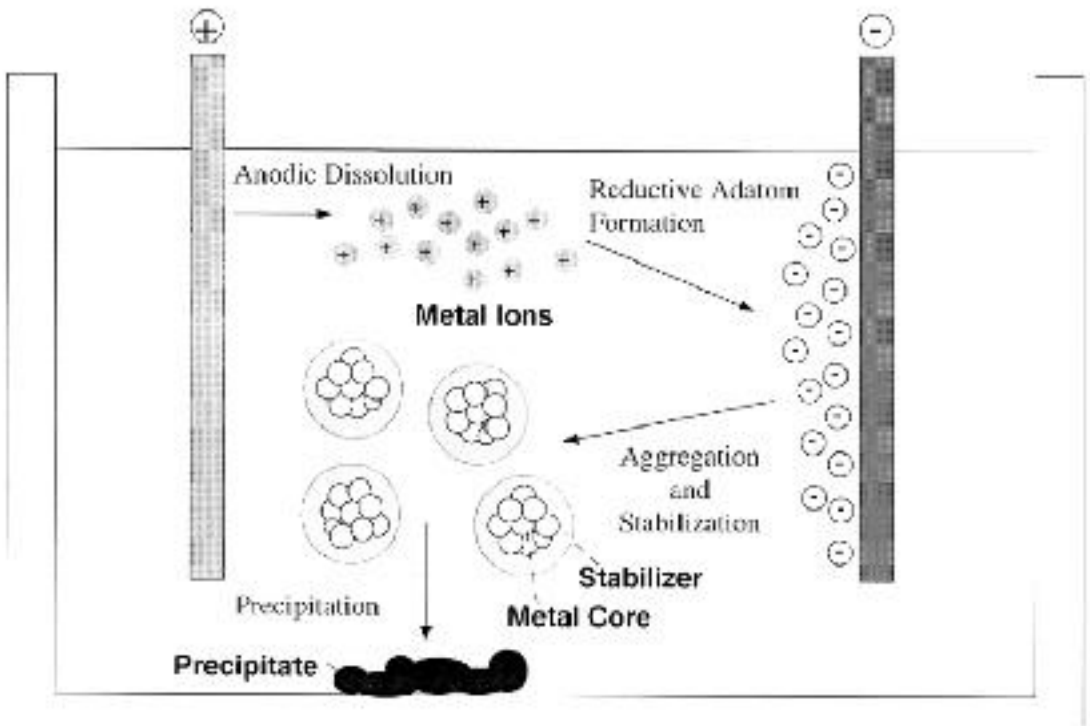
Synthesis of Metal-Nanoparticles

General Procedures

Reduction by Electrochemical Methods

M ⟶ $M^{(0)}$ (NPs)

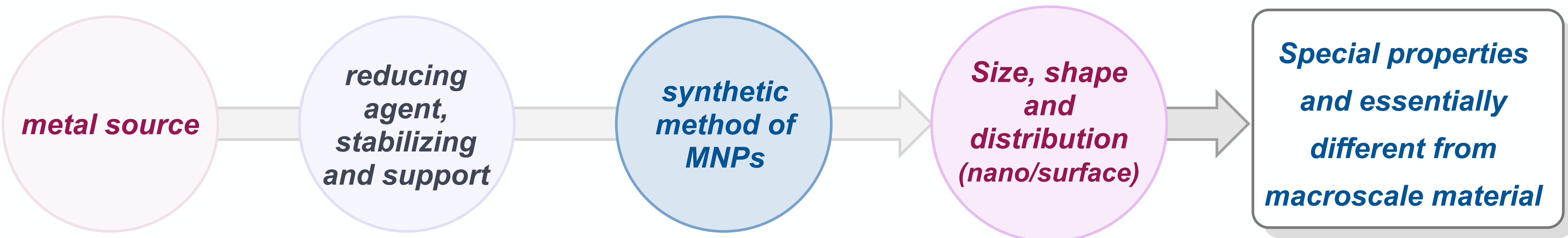
- *sacrificial anode as metal source*
- *Pt, Pd, Rh, Ru (transition metal salt as precursor)*
- quaternary *ammonium salt as both electrolyte and stabilizing agent*
- ***Ni, Cu***



Ghorbani, H. R. *Arabian J. of Chemistry* . **2014,** DOI: 10.1016/j.arabjc.2014.12.014

Patin, H. *Chem. Rev.* ***2002****, 102,* 3757

Properties of Metal-Nanoparticles



- *Thermal or electrical conductivity*
- *Melting Point*
- *Light absorption*
- *Highest reactivity*
- *New electronic and optical properties*
- *Better elasticity and resistance*

Mpourmpakis, G. *ACS Cat.* **2015,** *5*, 6296

Islam, Sk. M. *ACS Sustainable Chem. Eng.* ***2017****, 5,* 648

Metal-Nanoparticles: Applications

Catalysis

Electronic and optical fields

Drug storage system

Data and Energy Storage

Drug delivery systems

Metal-NPs

Photovoltaic solar cells

Tissue nanoengineering

Chemical sensors

Covered Nanoparticles

Air purification

Magnetic Nanoparticles

Photocatalysis

Mpourmpakis, G. *ACS Cat.* **2015,** *5*, 6296

Islam, Sk. M. *ACS Sustainable Chem. Eng.* ***2017****, 5,* 648

Outline

General Concepts

Metal-NPs as catalyst in organic chemistry

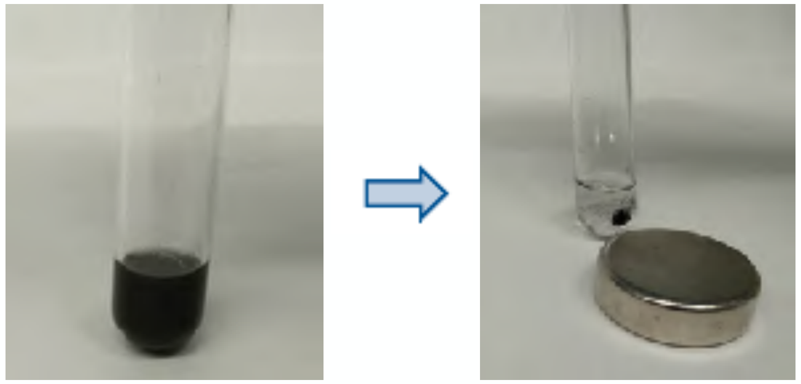
Metal-NPs in Photocatalysis

Metal-Nanoparticles in Catalysis

Why use Metal-Nanoparticles in catalysis instead homogeneous catalysis?

Advantages

- *High atom efficiency* ⇨ wide reactive surface
- *Mild reaction conditions* ⇨ lower T, green solvents
- *Simplied isolation of products*
- *Easy recovery and Recyclability*



Disadvantages

- *Each variable could change the nano formation* ⇨ *metal source, support, stabilizing species, synthesis* ⇨ *properties*
- *Lower reproducibily control*
- *Each batch of NPs need to be characterized* ⇨ TEM, ICP-MS or TGA

Islam, Sk. M. *ACS Sustainable Chem. Eng.* ***2017***, *5,* 648

Metal-Nanoparticles in Catalysis

How many posibilities can we choose to make MNPs? Can I predict the catalytic effect?

Synthetic Method

- *Reduction*
- *Decomposition*
- *Vapor Condensation*
- *Electrochemical*

⇩

Reactants

Properties

- *Size*
- *Shape*
- *Surface properties*
- *Crystalline structure*

⇩

Aggregation Problems

Stabilizing reactants

Immobilization

- *Carbon supports*
- *Polymers*
- Metal oxides

⇩

Interactions. No inert

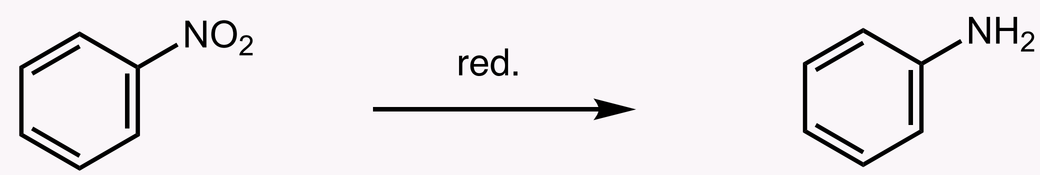
Metal-NP vs Metal

- *Hight efficiency*
- *Recycling*
- *Green Conditions*
- *Simple isolation*

Islam, Sk. M. *ACS Sustainable Chem. Eng.* ***2017****, 5,* 648

Hydrogenation of Nitroarenes

Reaction and Mechanism

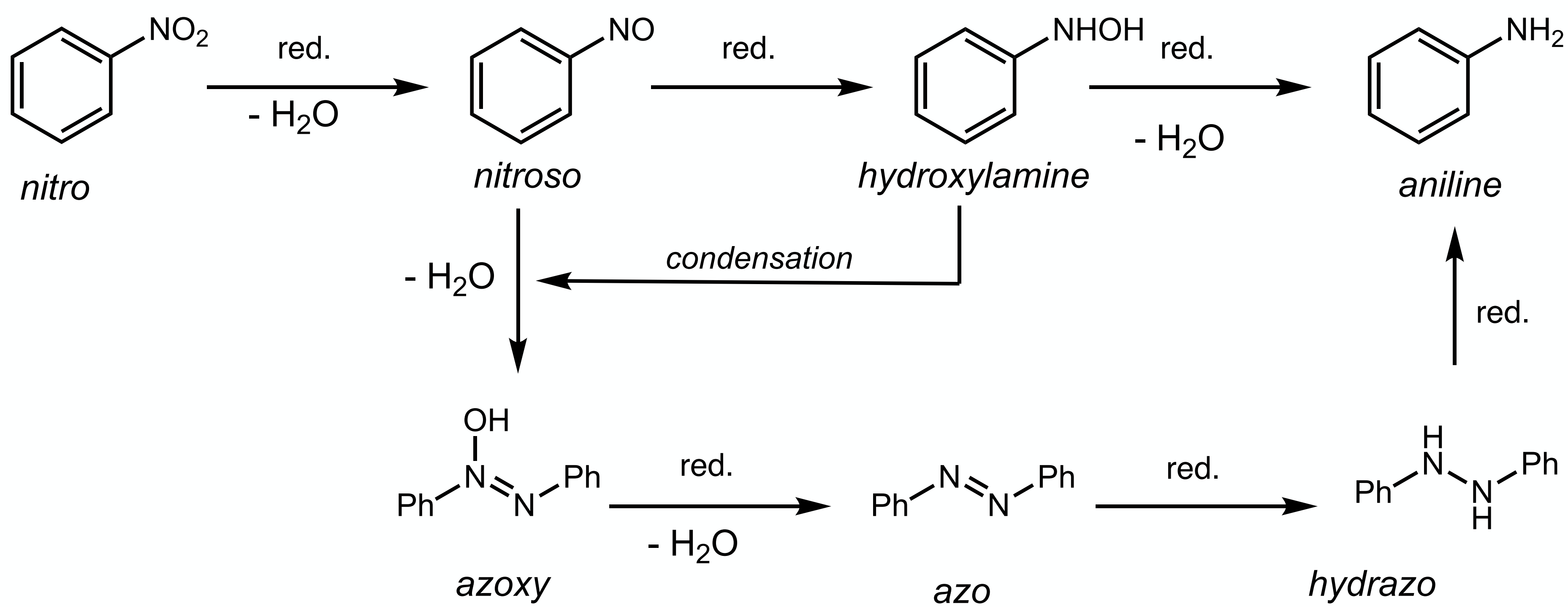


- *metal, sulfides as reductant*
- *low catalytic activity*
- *difficult chemoselective reduction*

NPs reaction

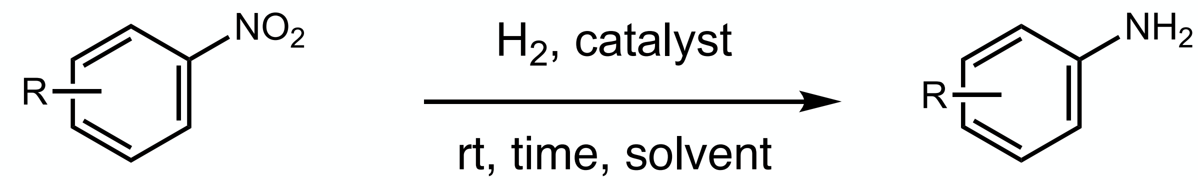
- *size, shape dependents*
- *choice of support*
- *high specific surface*
- *more reactive sites*

Accepted Mechanism

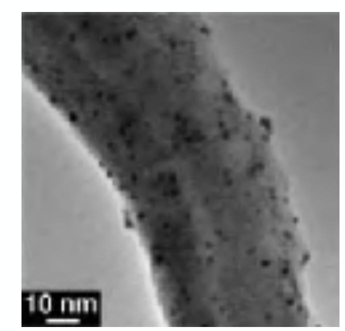


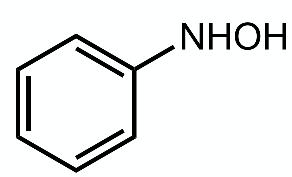
Philippot, K. *Catal. Sci. Technol.* ***2014****, 4,* 2445

Hydrogenation of Nitroarenes



NanoParticles	Pt/C	Pt/N-CNF-H (N-doped-nanofiber)
Synthesis	reduction: H_2PtCl_6 with $NaBH_4$	impregnation with $Pt(dba)_2$
Size and Shape	**3 nm**	**1.8 nm**
Reaction conditions	H_2, 10°C	H_2 (7 -10 atm), 70°C





> 85 % yield
< 4 hours

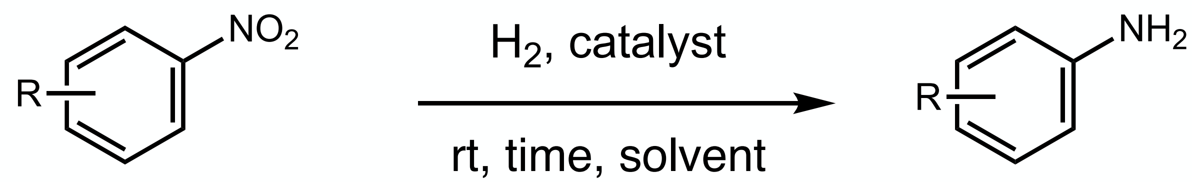
no dehalogenation

allow ketones and CN

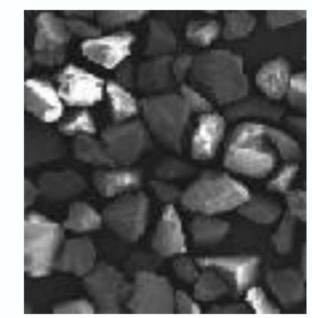
high reactivity (99%),
long reaction times (8h)

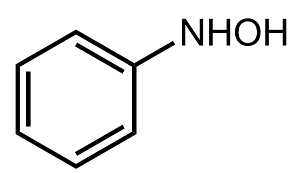
Philippot, K. *Catal. Sci. Technol.* ***2014****, 4,* 2445

Hydrogenation of Nitroarenes



NanoParticles	*Pt/C*	*Pt/N-CNF-H (N-doped-nanofiber)*	*Silica Cat Pt^0*
Synthesis	reduction: H_2PtCl_6 with $NaBH_4$	impregnation with $Pt(dba)_2$	reduction K_2PtCl_2
Size and Shape	**3 nm**	**1.8 nm**	**1.7-3.1 nm**
Reaction conditions	H_2, 10ºC	H_2 (7 -10 atm), 70ºC	H_2 , MeOH





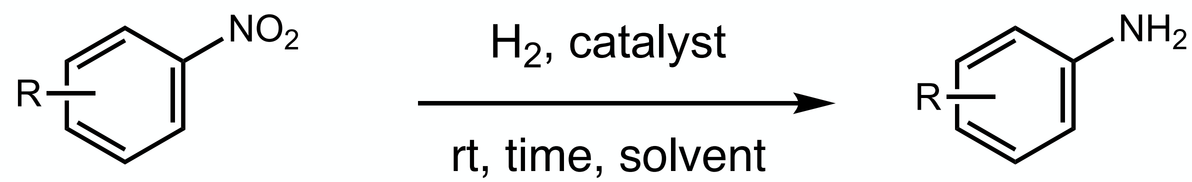
> 85 % yield
< 4 hours

no dehalogenation
allow ketones and CN
high reactivity (99%), long reaction times (8h)

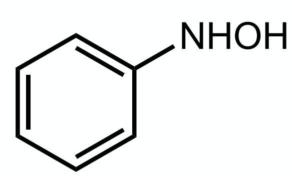
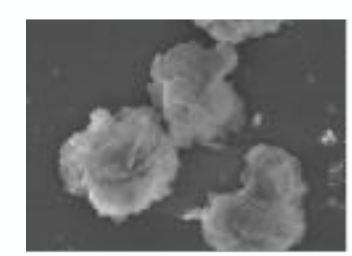
dehalogenation (-I)
CN not tolerated
high selectivities
< 2 h

encapsulation ensures stabilization of catalyst
absence of water
hydrofobic matrix ensures the selectivity of the most reactive NO_2

Hydrogenation of Nitroarenes



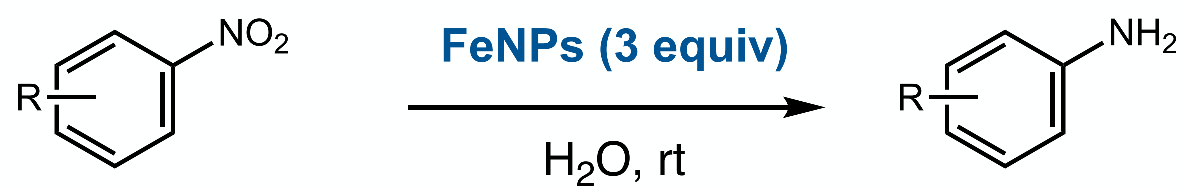
NanoParticles	***Pt/C***	***Pt/N-CNF-H (N-doped-nanofiber)***	***Silica Cat Pt⁰***	**Bimettalic**
Synthesis	reduction: H_2PtCl_6 with $NaBH_4$	impregnation with $Pt(dba)_2$	reduction K_2PtCl_2	double reduction
Size and Shape	**3 nm**	**1.8 nm**	**1.7-3.1 nm**	**~ 2 nm**
Reaction conditions	H_2, 10°C	H_2 (7 -10 atm), 70°C	H_2 , MeOH	H_2 , solvent

 *> 85 % yield < 4 hours*	*no dehalogenation* *allow ketones and CN* *high reactivity (99%), long reaction times (8h)*	*dehalogenation (-I)* *CN not tolerated* *high selectivities < 2 h*	*high reactivity* *poor selectivity* 

Philippot, K. *Catal. Sci. Technol.* ***2014**, 4,* 2445

Hydrogenation of Nitroarenes

New Metal-NanoParticles



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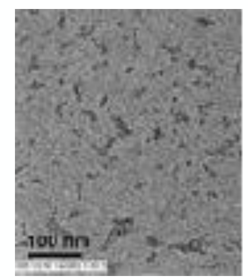
reduction of $FeSO_4.7H_2O$ in water using $NaBH_4$ and citric acid as stabilizing agent

5 min ⇨

$Fe^{(0)}$NPs

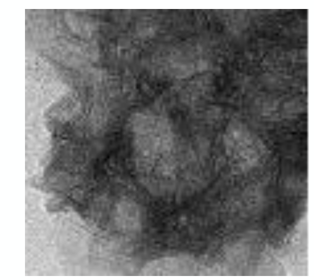
3-5 nm spheres

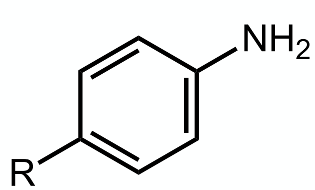


⇨

(Fe_2O_3)NPs

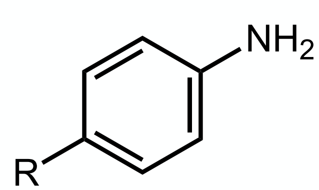
nanotubes





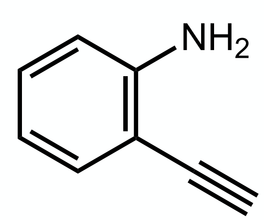
R = CHO, CO, COOH, CONHR CN, N_3, SCN, halides

86-96% yield

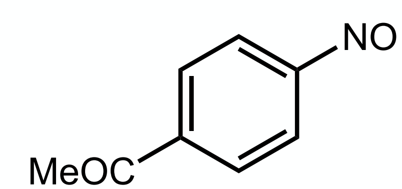


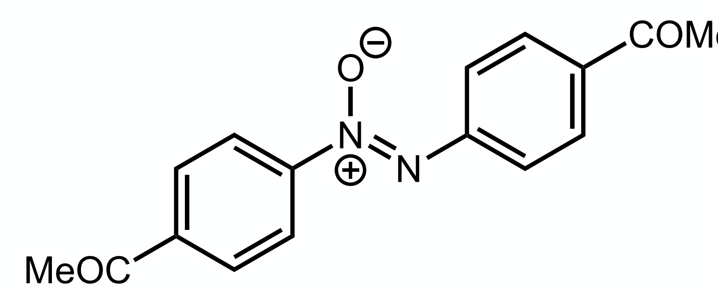
R = OBn, OAllyl

90% yield



80% yield



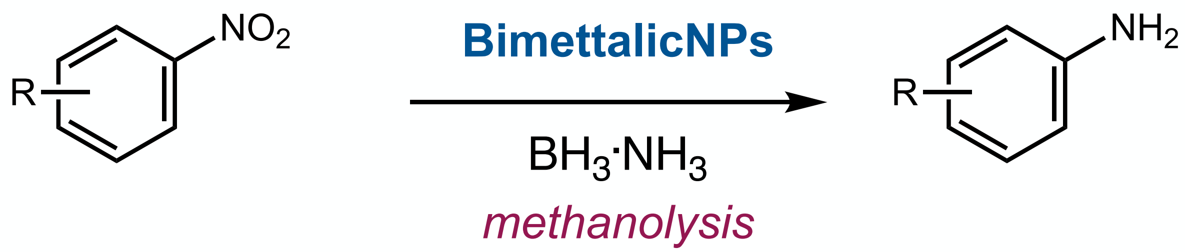


intermediates was observed by MS

Ranu, B. C. *Chem. Commun.* ***2012****, 48,* 7982

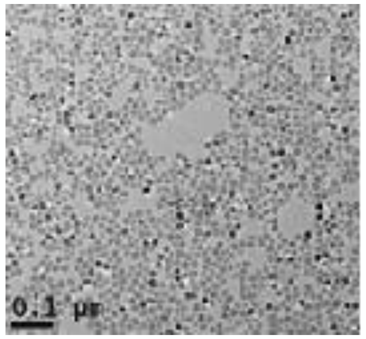
Hydrogenation of Nitroarenes

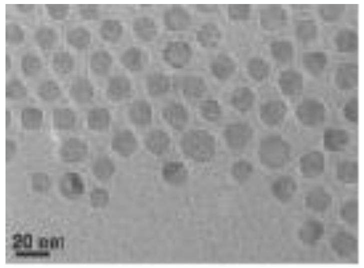
Noble metal-free NanoParticles



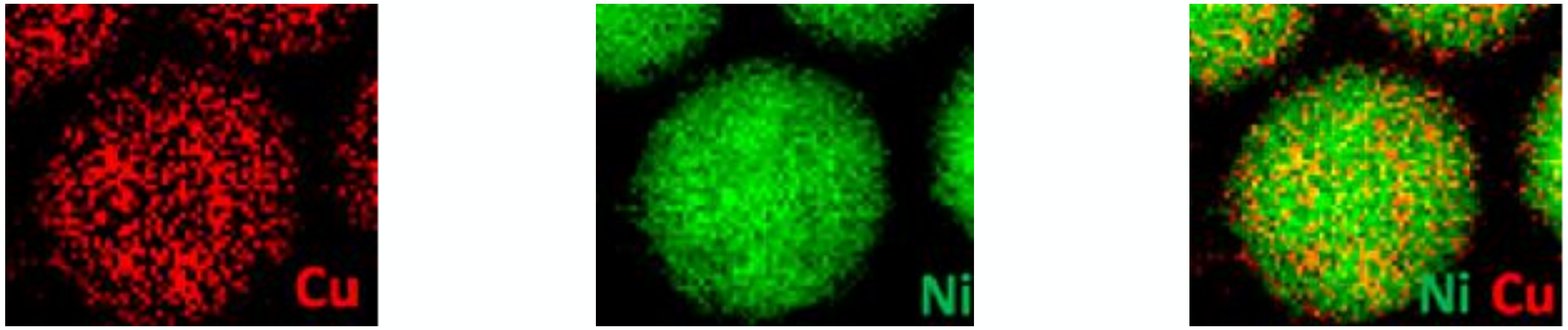
co-reduction of
$Ni(acac)_2$ and $Cu(acac)_2$
with BBA in oleylamine
and oleic acid

monodisperse CuNiNPs
15 - 16 nm
Cu/Ni ratio 3:1 to 1:3
graphene supported





spheres

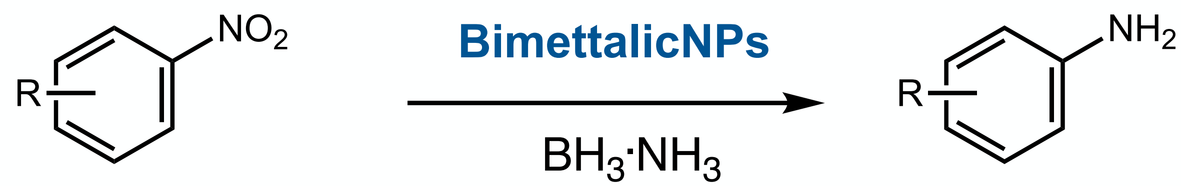


BBA = borane-*t*-butyl amine

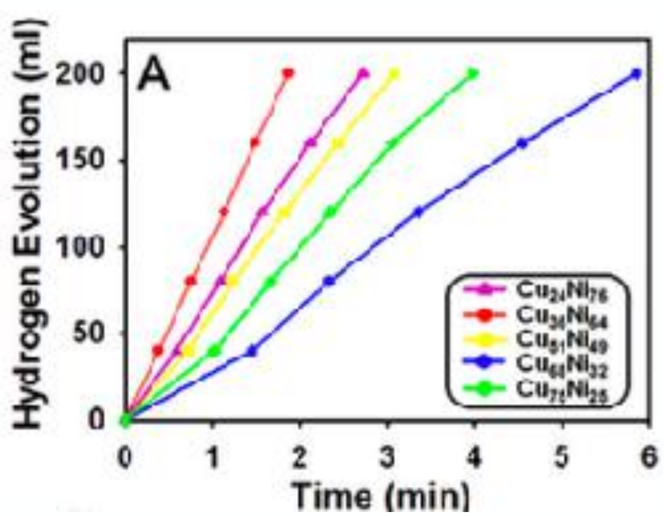
Sun, S. *ACS Catal.* ***2012****, 2,* 1290
Sun, S. *Chem. Mater.* ***2017****, 29,* 1413

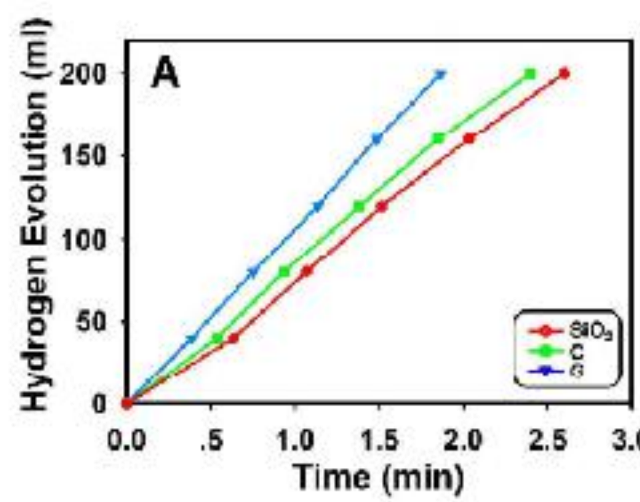
Hydrogenation of Nitroarenes

New Metal-NanoParticles



methanolysis $H_3N{\cdot}BH_3$ + 4 CH_3OH $\xrightarrow{\text{G-Cu}_n\text{Ni}_m\text{NPs}}$ $NH_4{\cdot}B(OMe)_4$ + $3H_2$

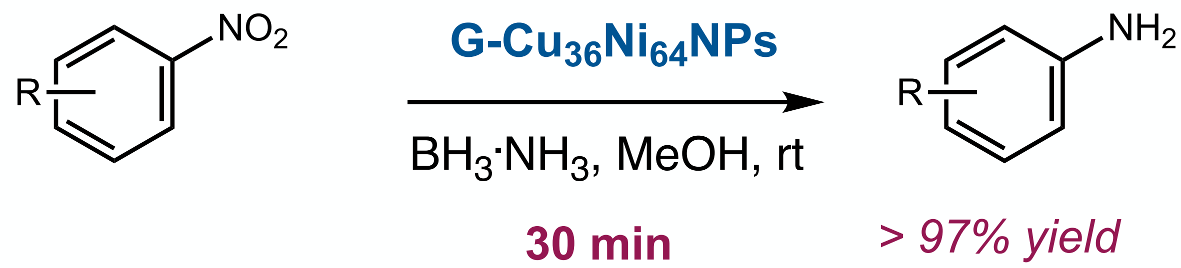


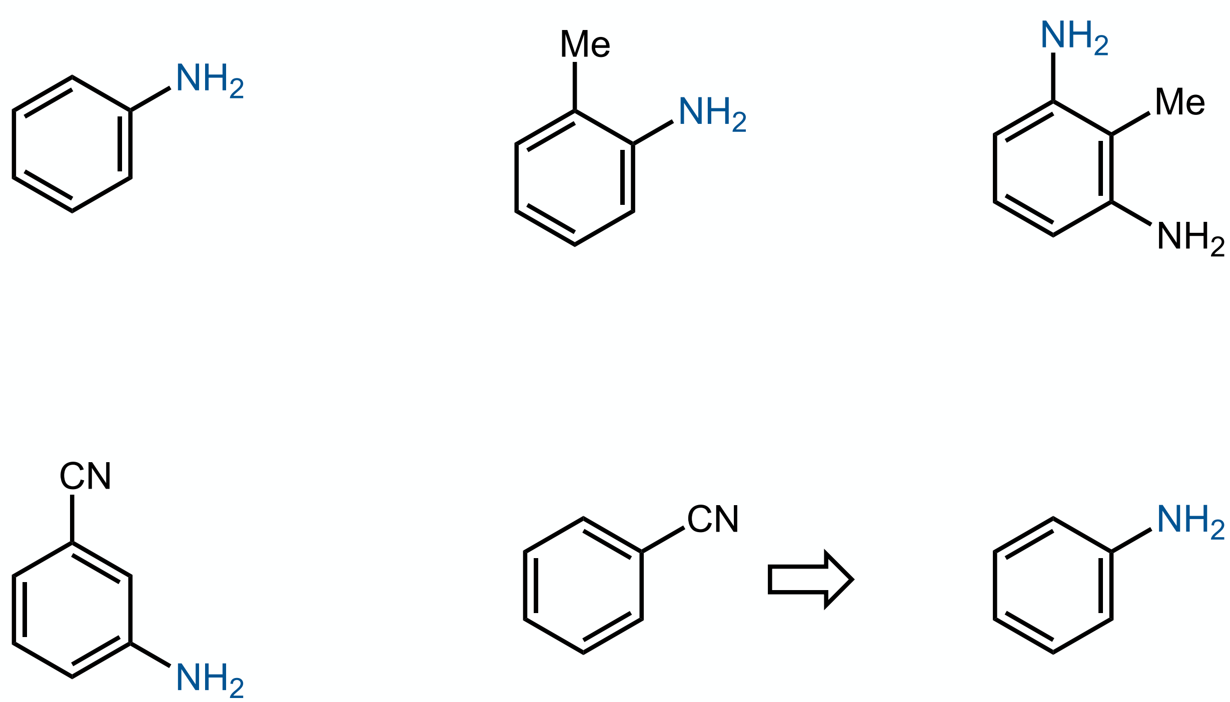


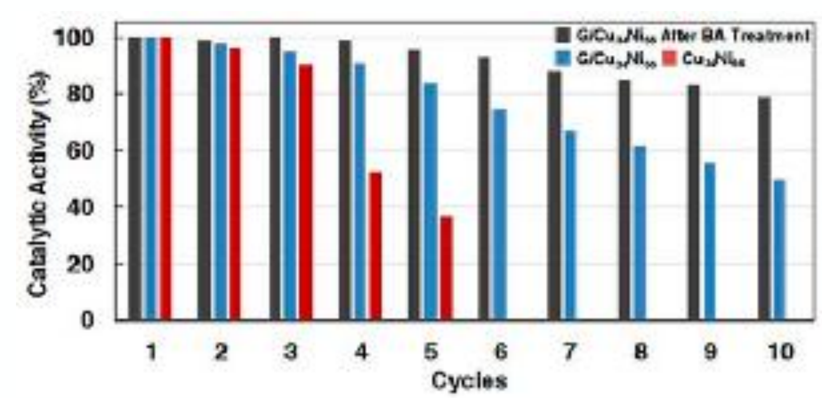
Sun, S. *ACS Catal.* ***2012***, *2,* 1290
Sun, S. *Chem. Mater.* ***2017***, *29,* 1413

Hydrogenation of Nitroarenes

New Metal-NanoParticles







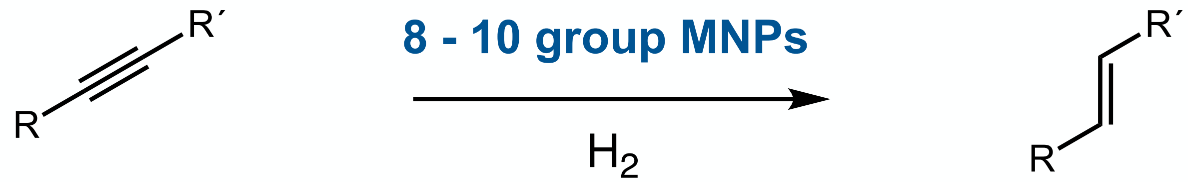
long durability, retaining 80% of its activity after the 10th cycle

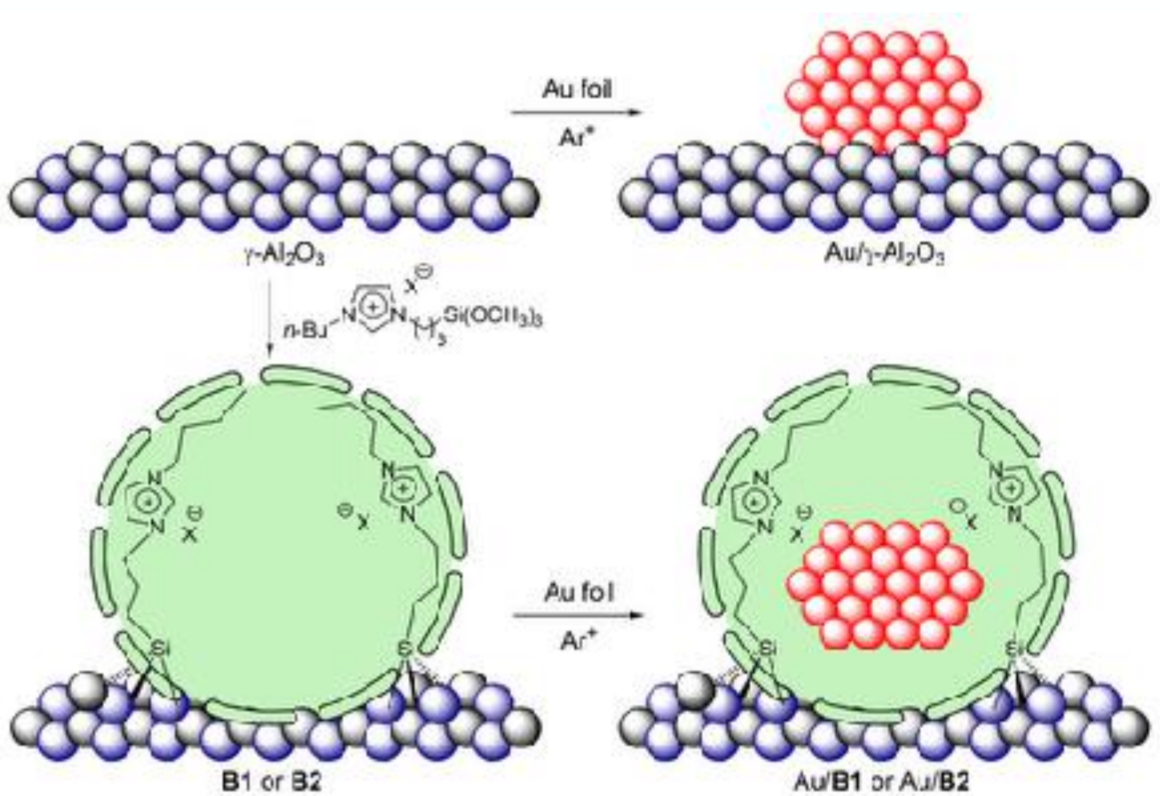
Sun, S. *ACS Catal.* ***2012****, 2,* 1290

Sun, S. *Chem. Mater.* ***2017****, 29,* 1413

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies





■ Supported on γ-Al_2O_3
(most used support for Au)

⇩

Strong interaction support-metal

■ *Supported on an (IL)-hybrid* γ-Al_2O_3

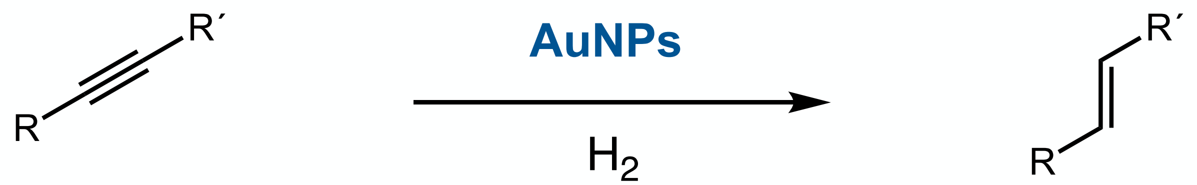
⇩

Avoid direct contact AuNPs and support

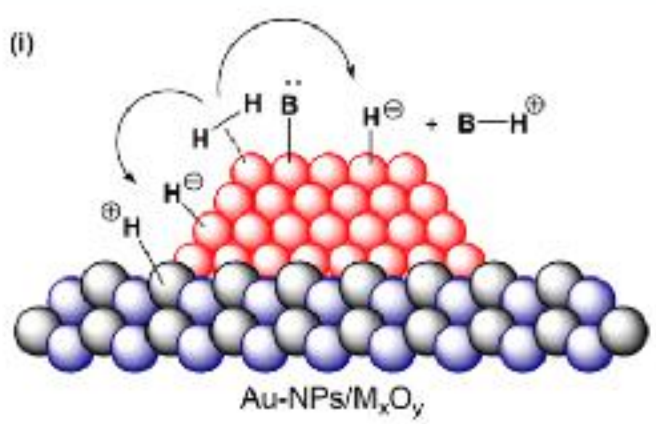
Dupont, J. *ACS Catal.* ***2017***, *7,* 2791

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies



Most plausible hydrogenation pathways



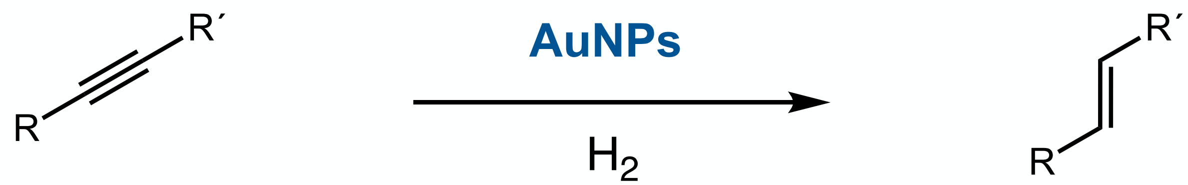
Ionic hydrogenation

- *support, additive, substrate collaborate with Au surface*
- *direct heterolytic activation of H_2*
- *transfer of one H^+ to form metal hydride*

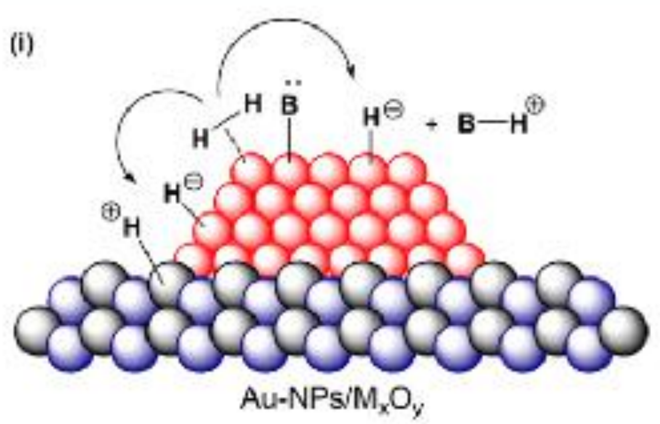
Dupont, J. *ACS Catal.* ***2017***, *7,* 2791

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies



Most plausible hydrogenation pathways



Ionic hydrogenation

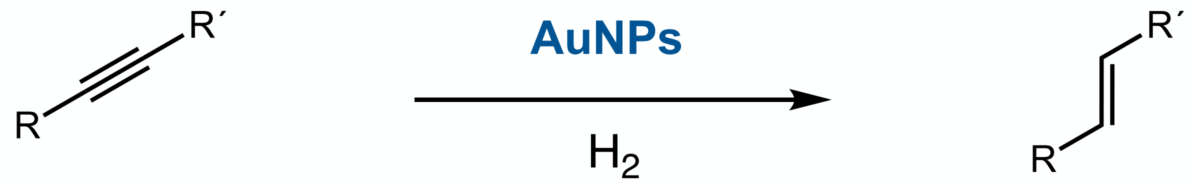
- *by low-coordinated Au surface sites*
- *H atom formation in brigde positions sharing Au atoms*
- *no deformation of Au-Au distances*

Dissociative Chemisortion of H_2

Dupont, J. *ACS Catal.* ***2017***, *7,* 2791

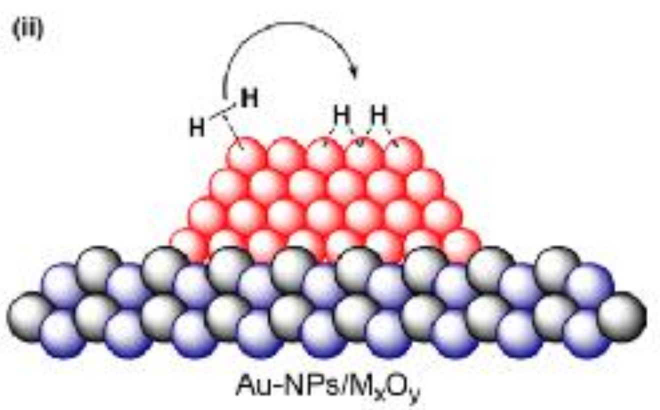
Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

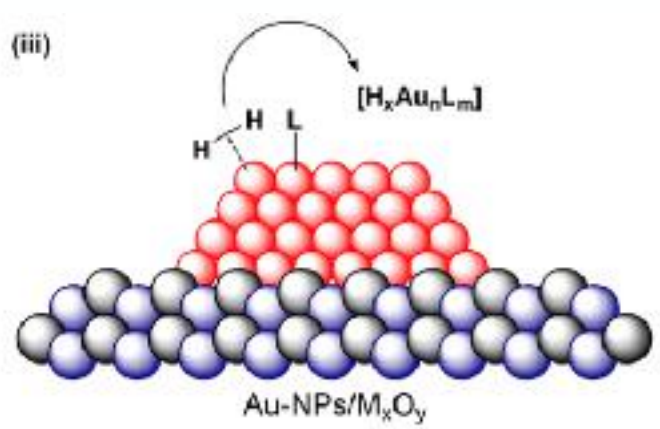


Most plausible hydrogenation pathways

Ionic hydrogenation



Dissociative Chemisortion of H_2



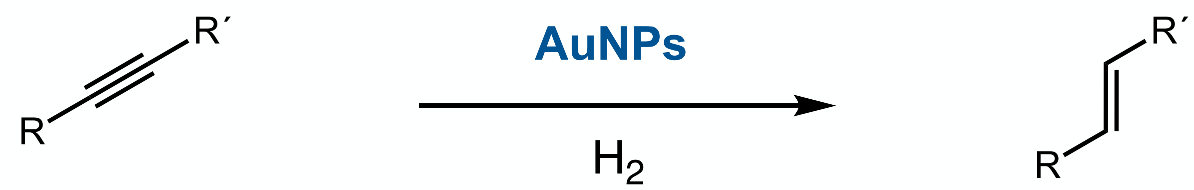
H_2 activation with the ejection of Au-subnanometer cluster

- *not yet been reported*
- *Au atoms or nanoclusters shows better selectivity for butadienes, internal alkynes, carbonyl compounds*

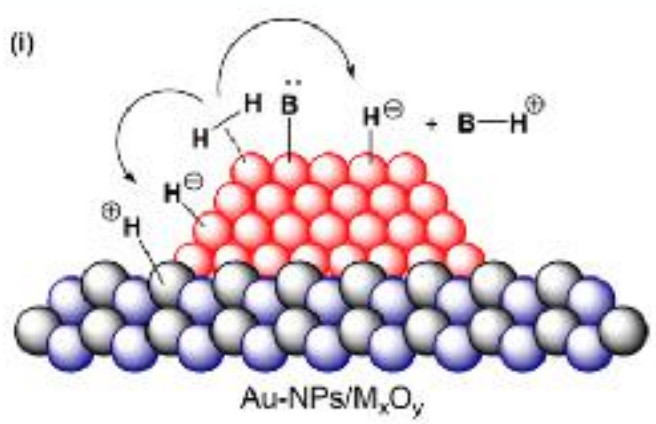
Dupont, J. *ACS Catal.* ***2017***, *7,* 2791

Hydrogenation Reaction of Multiple Bonds

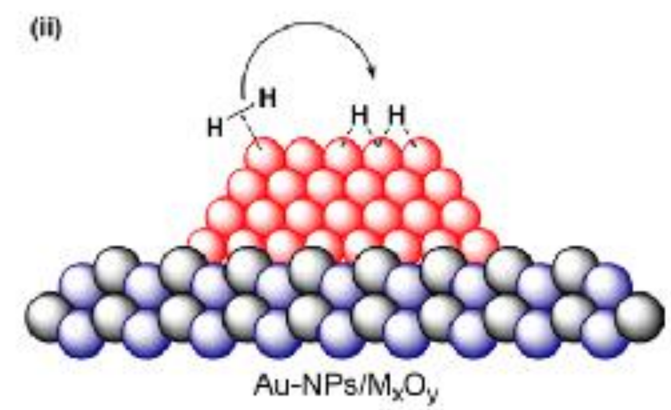
Mechanistic Studies



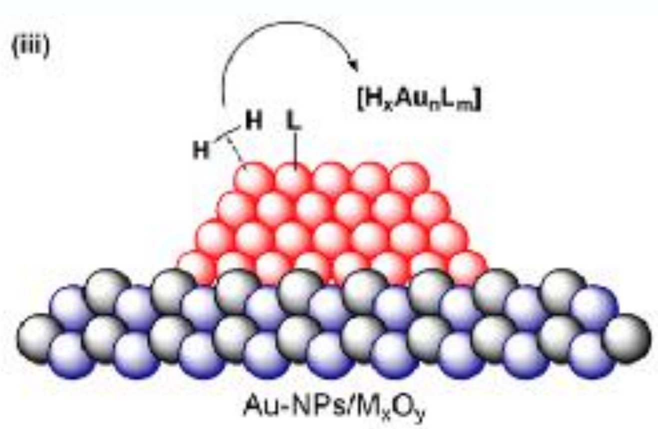
Most plausible hydrogenation pathways



Ionic hydrogenation

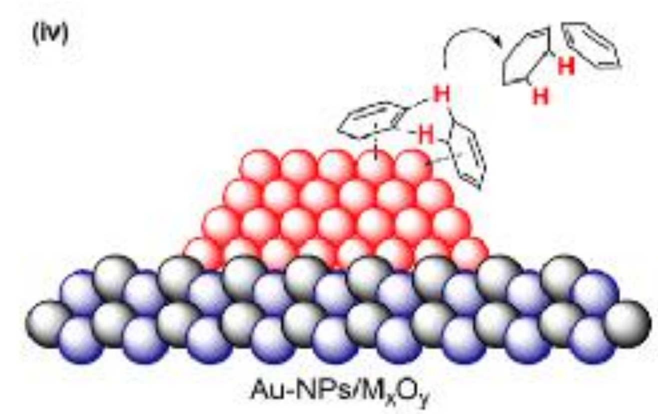


Dissociative Chemisortion of H_2



H_2 activation with the ejection of Au-subnanometer cluster

■ *not yet experimentally proved*



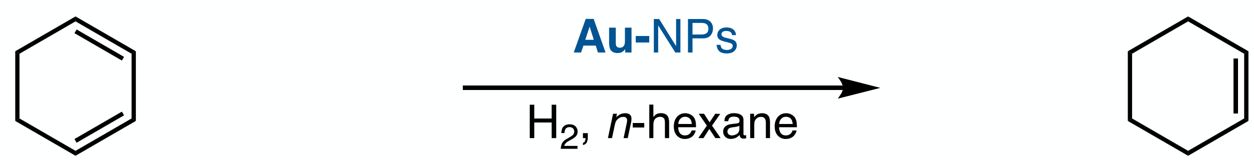
Outer-sphere: Disproportion

Dupont, J. *ACS Catal.* ***2017***, *7,* 2791

Hydrogenation Reaction of Multiple Bonds

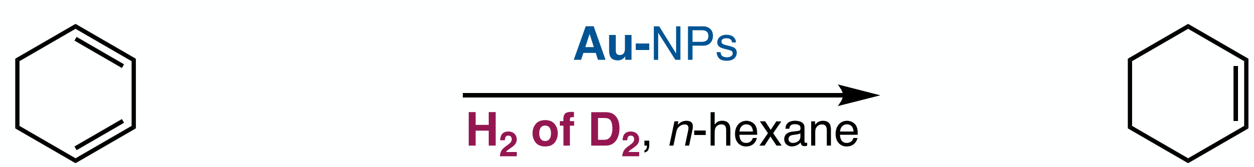
Mechanistic Studies

Catalytic Hydrogenation



- **Au-**γ-Al_2O_3 : *88% yield (50-100 °C)*
- **Au-**(IL)-γ-Al_2O_3 : *92-96% yield only at 100 °C*

Kinetic Isotopic Effect



- **Au-**γ-Al_2O_3 : $k_H/k_D = 1.1$
- **Au-**(IL)-γ-Al_2O_3 : $k_H/k_D = 3.8 - 4.6$

- *Different mechanisms*
- *Activation of hydrogen is not the rate determining step in **Au-**γ-Al_2O_3*
- *1,2- and 1,4-D addition were observed with **Au-**(IL)-γ-Al_2O_3 suggests allyl intermediate*

Hydrogenation pathways (heterolytic, homolytic or outer sphere) are directly related to the nature of support

Dupont, J. *ACS Catal.* ***2017***, *7*, 2791

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

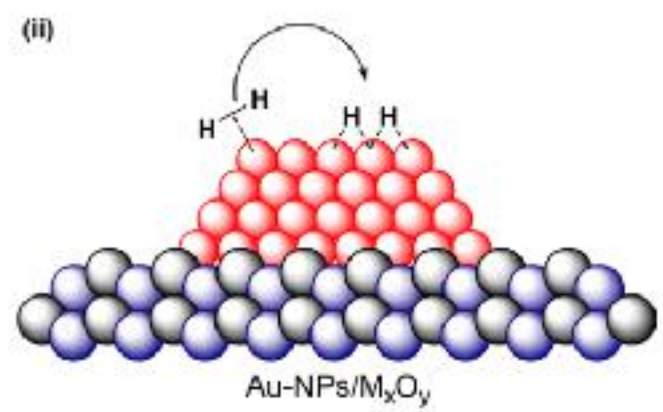
- Based on the experimental results, kinetic effects and kinetic models

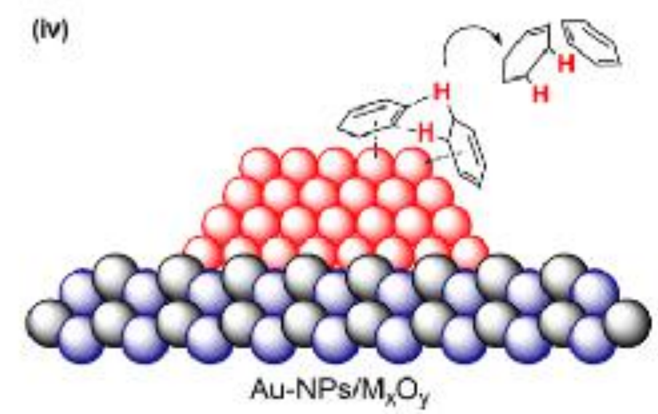
Au-γ-Al_2O_3

Ionic hydrogenation

heterolytic activation

***Au**-(IL)-γ-Al_2O_3*





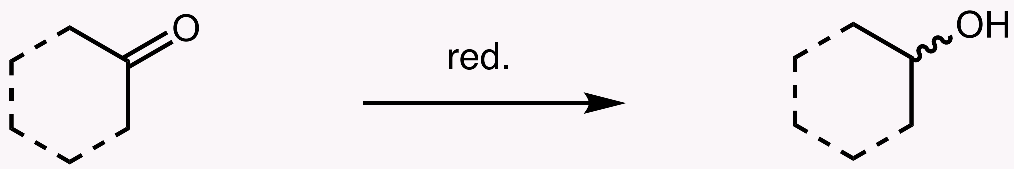
Dissociative Chemisortion of H_2

Outer-sphere: Disproportion

homolytic activation based on the thickness of IL

Dupont, J. *ACS Catal.* ***2017**, 7,* 2791

Transfer Hydrogenation Reaction of Carbonyl Compounds



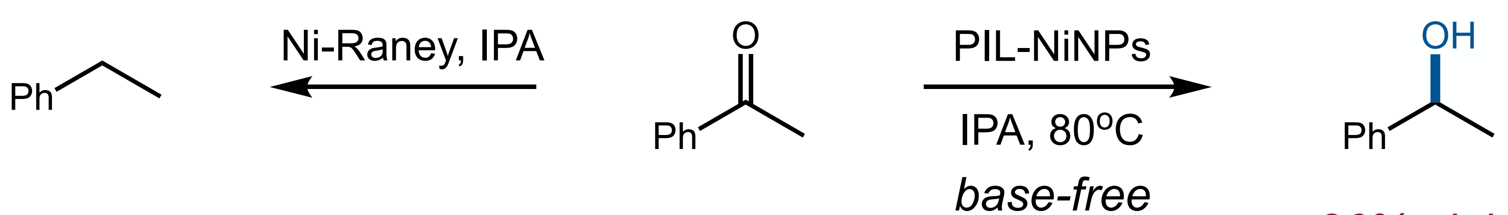
- *metal hydrides of catalytic hydrogenation*
- *metal mediated*

TH Reaction

- *mild conditions*
- *easy handling*
- *environmental friendliness*

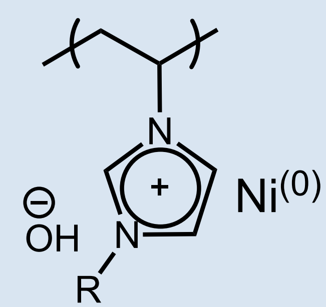
IPA as H donor, KOH as base

- Ni source as an alternative of Pt, Pd, Ir, Os and Ru: Ni complexes, Ni-Raney and NiNPs



86% yield

- *pH controlled by IL*
- *good reactivity*
- *higher size lower activity*
- *good group tolerance (benzyl, alkyl, alkenes)*
- *Magnetic separation & Recycled*



R = C_2H_5, C_4H_9, C_5H_{11}

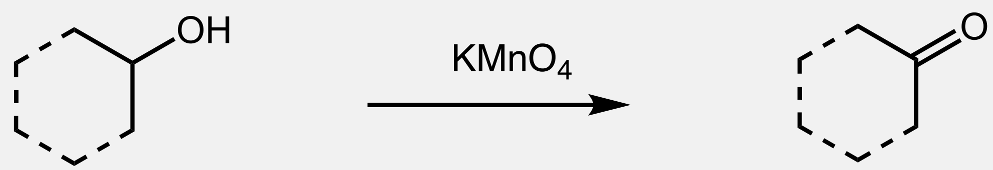
PIL-Ni-NPs

7-40 nm

Sreedhar, B. *ChemCatChem.* **2016,** *8*, 1139

von Wangelin, A. J. *Current Org. Chem.* ***2013***, *17*, 326

Aerobic Alcohol Oxidation



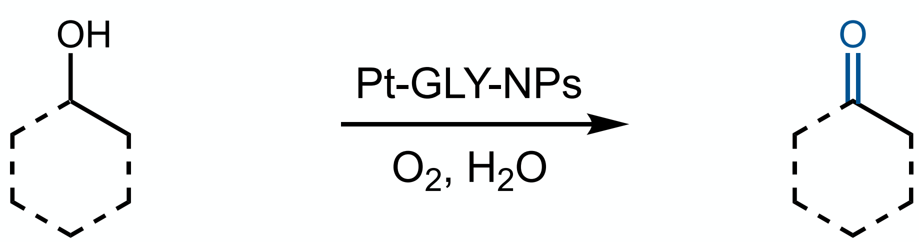
- *stoichiometric amounts noxious oxidants*
- *non-green organic solvents*
- *hazardous conditions*

Green alternative

- *industry process*
- *water as solvent*
- *base-free reaction*

Water soluble NPs

Pt NPs stabilizing with PVP (1.5 nm)



up to 99%

- *mild conditions*
- *good reactivity*
- *activated and non-activated*
- *Good recycling*

- *Pd and AuNPs require bases and benzylic substrates*
- *PtNPs (H_2, $NaBH_4$, ethanol) only 1 run (90 - 95% yield)*

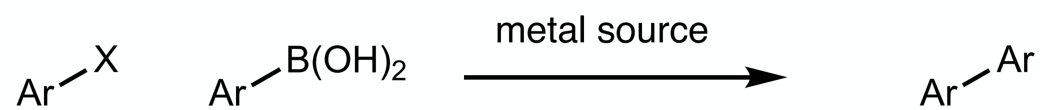
⇩

coordination and electronic properties of metal affect the activation of alcohol and oxygen

Liu. H. *Chem. Commun.* ***2007***, 4375

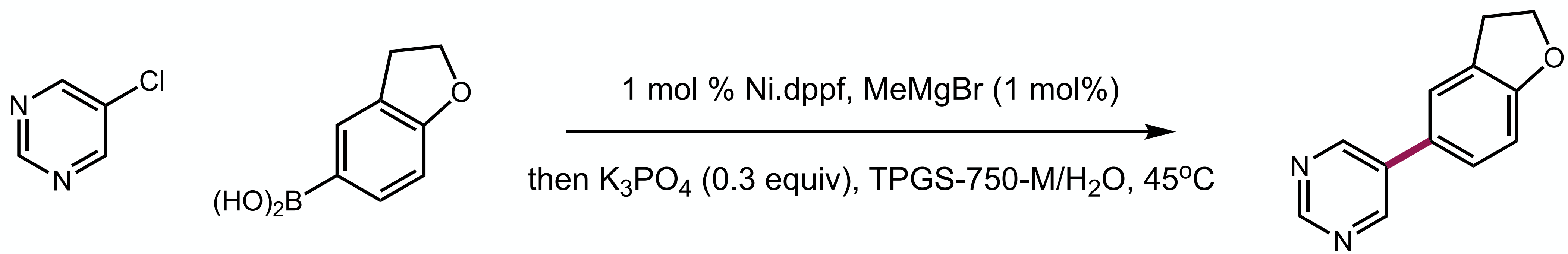
C-C Bond Formation

Suzuki Cross-Coupling



- *boronates, halides*
- *ligand*
- *excess coupling partner*
- *high temperature*
- *dry solvents*

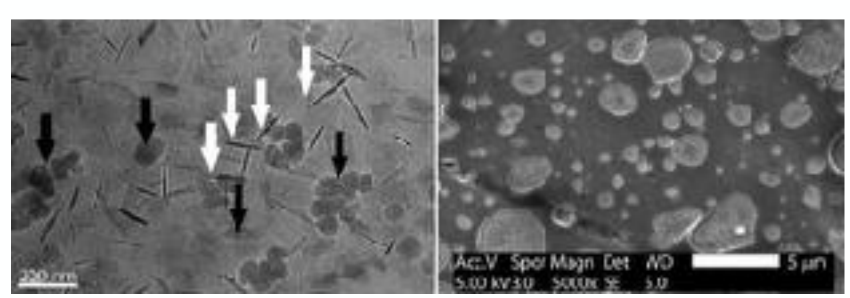
- *water as solvent*
- *mild conditions: rt to 45 ^oC*
- *recyclabe reaction medium*
- *low catalyst loading*



96% yield

broad scope
(more than 30 examples)

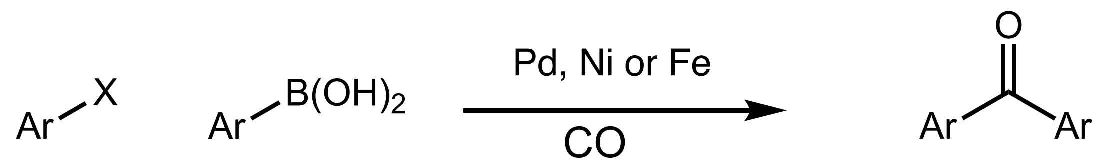
NiNPs formed in situ and used in combination with micellar catalysis



Lipshutz, B. H. *Angew. Chem. Int. Ed.* ***2015****, 54,* 1194

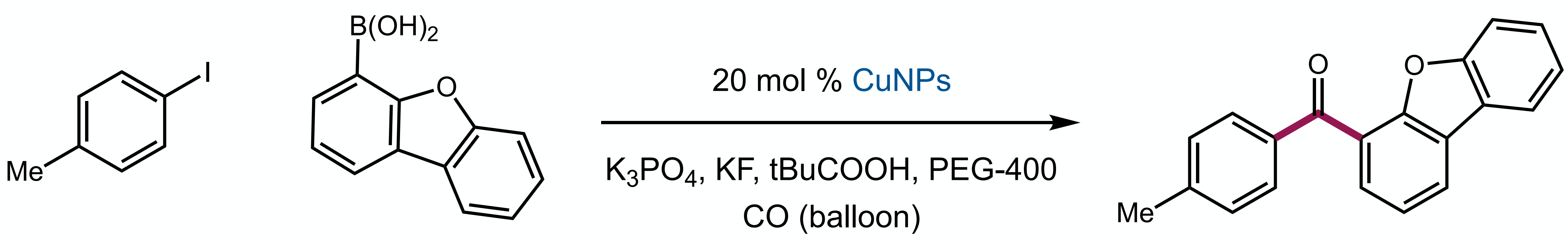
C-C Bond Formation

Carbonylative Suzuki Cross-Coupling



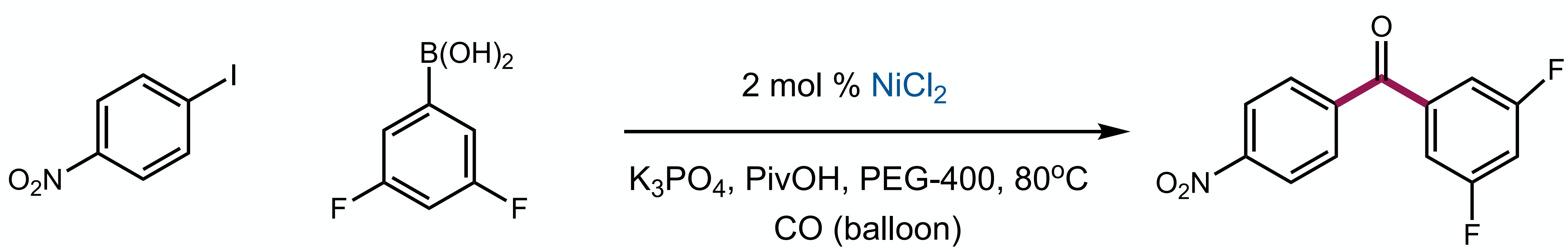
- *boronates, halides*
- *ligand*
- *excess coupling partner*
- *high temperature*
- *dry solvents*
- *high pressures*

- *mild conditions*
- *CuNPs or NiNPs*
- *recyclabe reaction medium*
- *low catalyst loading*



90% yield

38 examples, up to 95% yield



81% yield

36 examples, up to 93% yield

- *insitu generated NiNPs*
- *efficient and recyclable*
- *no ligand*
- *PivOH to avoid C-C coupling*

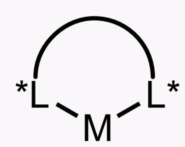
Wu, X.-F. *Chem. Rev.* ***2018***, DOI: 10.1021/acs.chemrev.8b00068

C-C Bond Formation

Chiral Metal-NanoParticles

Could we use Metal Nanoparticles in asymmetric catalysis?

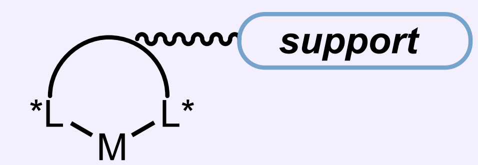
Homogeneous catalysis



chiral metal-complex

- *high activity*
- *not recoverable*

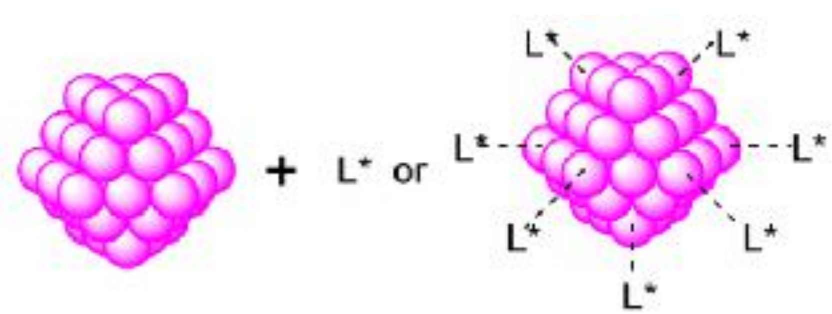
Immobilized catalysis



immobilized chiral metal-complex

- *separable*
- *lower activity*
- *reusable*
- *complicated synthesis*

Chiral MNP catalysis



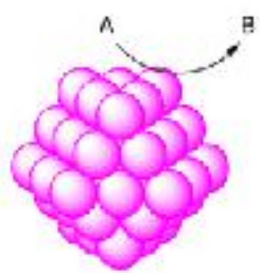
chiral Metal NP

- *separable*
- *robust*

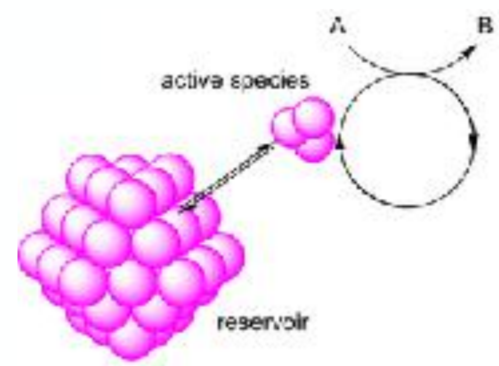
Kobayashi, S. *ACS Catal.* ***2016***, *6*, 7979

C-C Bond Formation

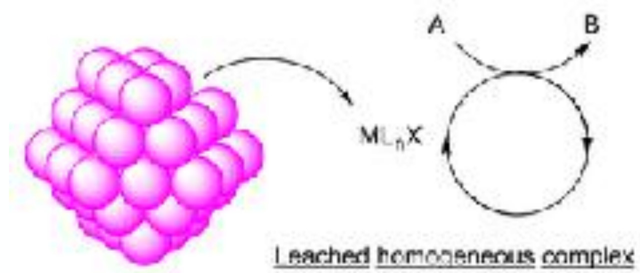
Chiral Metal-NanoParticles



Reaction on surface

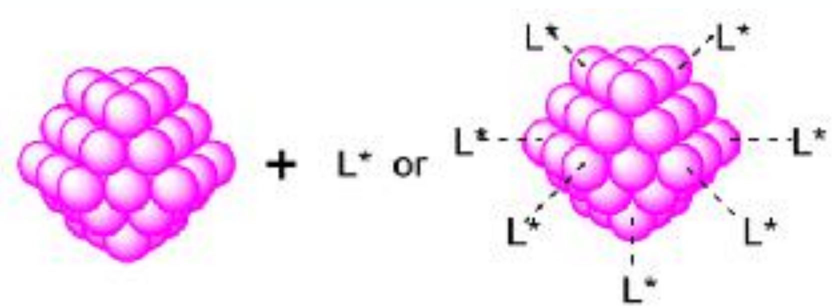


NPs as reservoir
produce active metal clusters



Leached homogeneous complex

Chiral MNP catalysis



chiral Metal NP

- *separable*
- *robust*

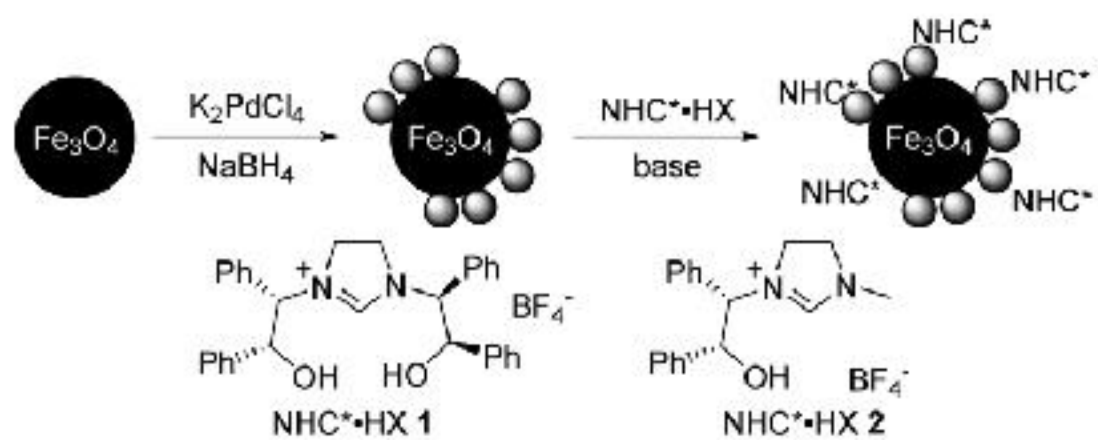
Kobayashi, S. *ACS Catal.* ***2016****, 6*, 7979

C-C Bond Formation

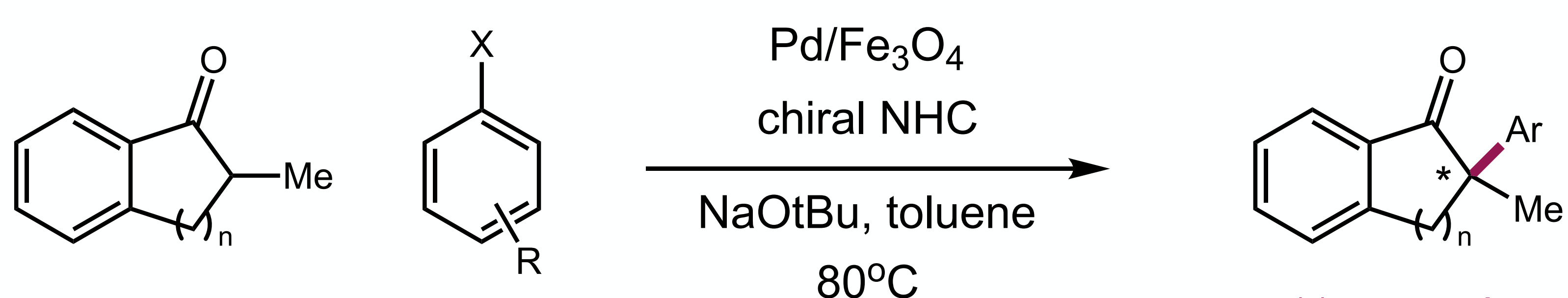
Chiral Metal-NanoParticles

Desing a bifunctional chiral modifier

- *coordination to the surface of NPs* ⇨ *active species and excellent chiral environment*
- *interaction with substrates* ⇨ *facilitate reaction between substrate and active sites*



Glorius, 2010. *Asymmetric α-arylation*



11 examples,
up to 91% yield, up to 85% ee

Kobayashi, S. *ACS Catal.* ***2016***, *6*, 7979

C-C Bond Formation

Chiral Metal-NanoParticles

Desing a bifunctional chiral modifier

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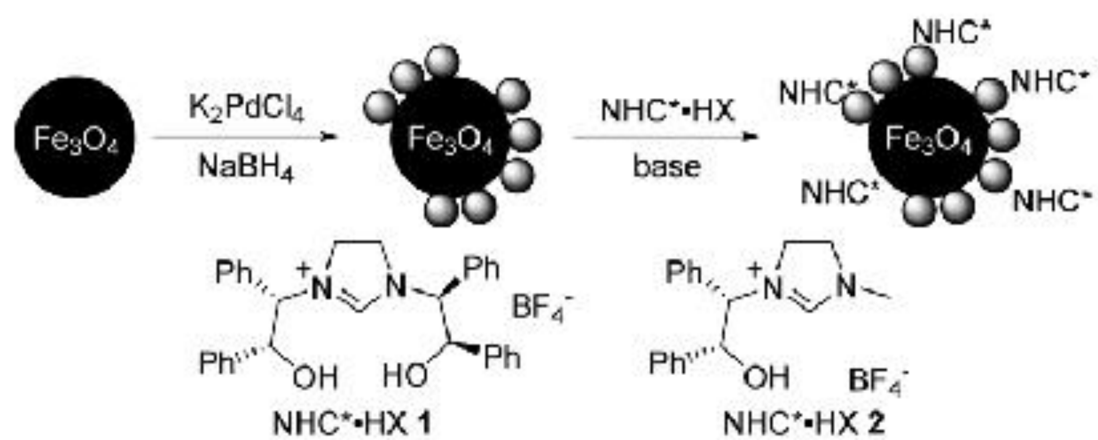
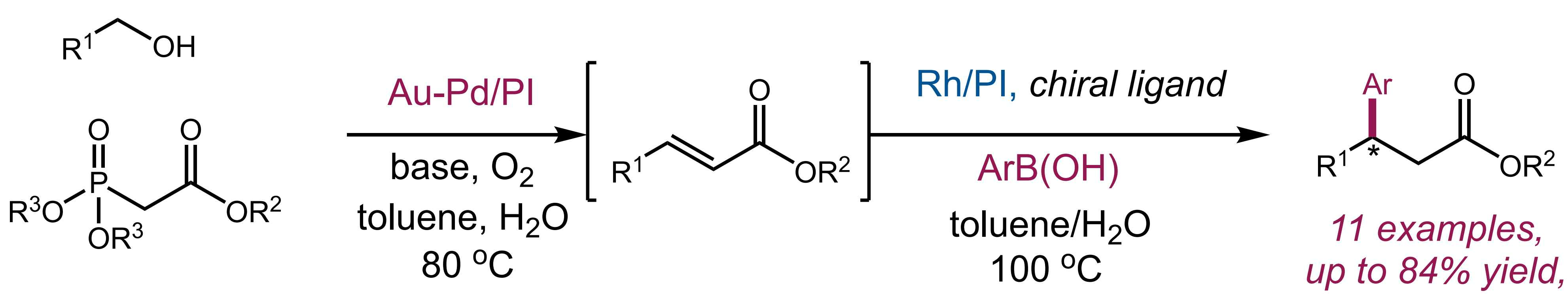


Kobayashi, 2015. *Oxidation- HWE olefination - Asymmetric 1,4-Addition*

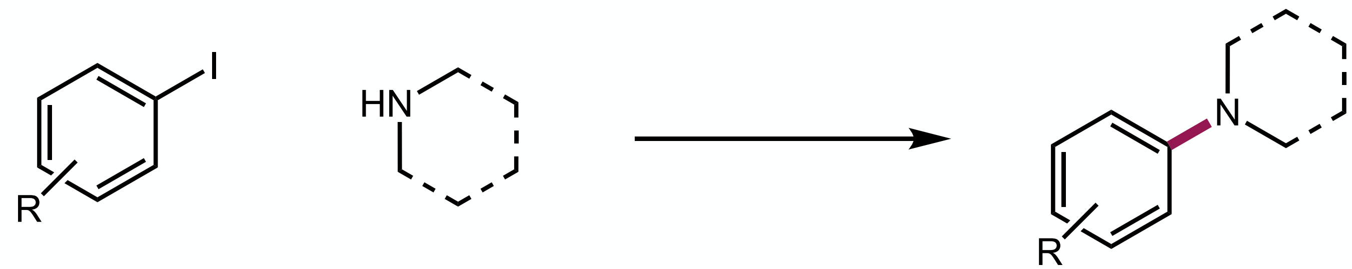


11 examples,
up to 84% yield,
up to >99% ee

Kobayashi, S. *ACS Catal.* ***2016***, *6*, 7979

C-N Bond Formation

Biogenic Cu-NanoParticles



■ *pharmaceutical and biological interest*

■ *metal catalyst (Pd, Ni, Fe, Co, Cu)*

■ *low functional group tolerance*

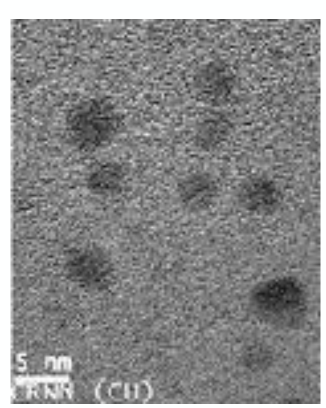
Addition of $CuSO_4$ in the presence of leaf extracts of Ocimum Sanctum

CuONPs

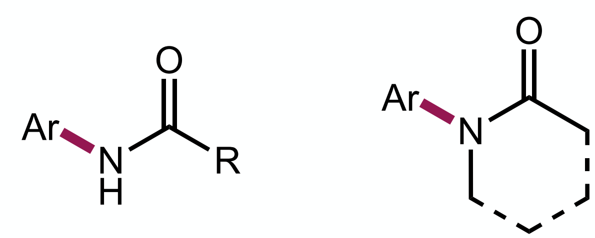
< 5 nm

spheres

bio-support

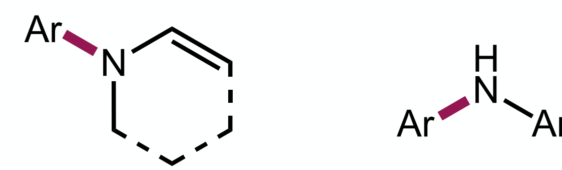


N-Arylation and N-Vinylation of Amides



23 examples, up to 96% yield

N-Arylation of N-Heterocycles and Aryl-amines

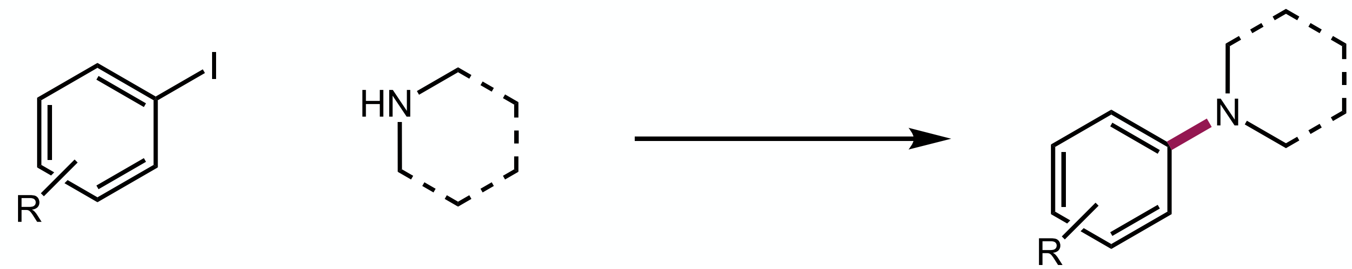


16 examples, up to 91% yield

Islam, Sk. M. *ACS Sustainable Chem. Eng.* ***2017***, *5*, 648

C-N Bond Formation

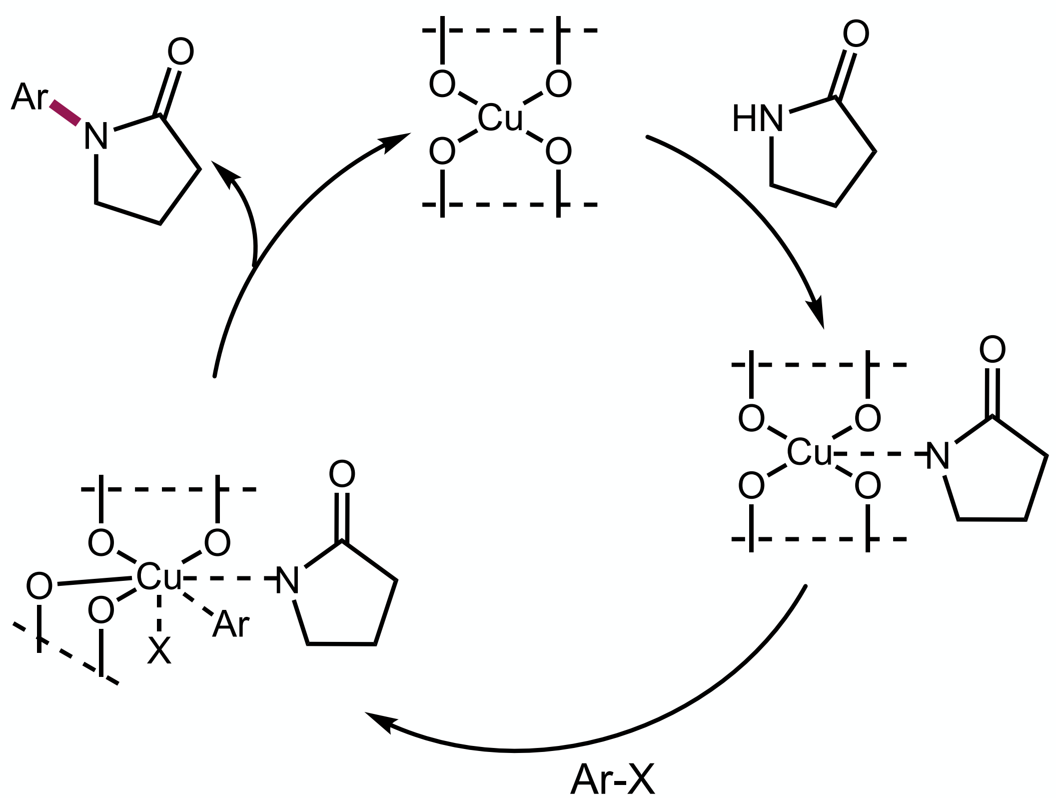
Biogenic Cu-NanoParticles



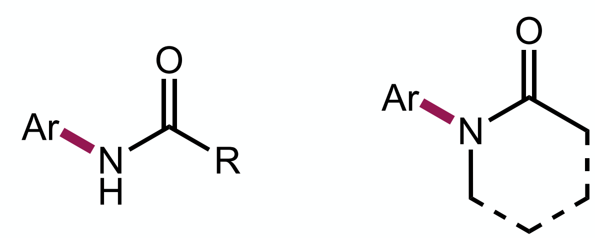
■ *pharmaceutical and biological interest*

■ *metal catalyst (Pd, Ni, Fe, Co, Cu)*

■ *low functional group tolerance*



N-Arylation and N-Vinylation of Amides



23 examples,
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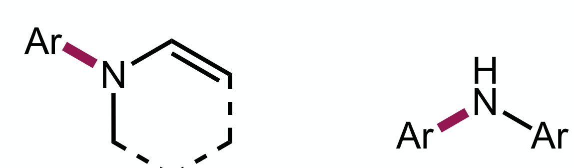

16 examples,
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Islam, Sk. M. *ACS Sustainable Chem. Eng.* ***2017****, 5*, 648

Outline

General Concepts

Metal-NPs as catalyst in organic chemistry

Metal-NPs in Photocatalysis

Metal-Nanoparticles in Photocatalysis

Introduction

- *Metal nanoparticles (Au and Ag) have optical properties: Lycurgus Cup*
- Zhu demostred the potencial use of AuNPs as photocatalyst for reduction of nitroarenes

MNPs serve as both the **light absorber** and **host** to the catalytic sites

many potencial materials (solids, polymers)

⇩

Create new and better photocatalyst

Ye, J. *Nature Sci. Rev.* ***2017***, *4,* 761

Zhu, H.-Y. *Chem. Asian J.* ***2014***, *9,* 3046

Zhu, H.-Y. *Catal. Sci, Technol.* ***2016***, *6,* 320

Metal-Nanoparticles in Photocatalysis

Based on the nature of photocatalysis

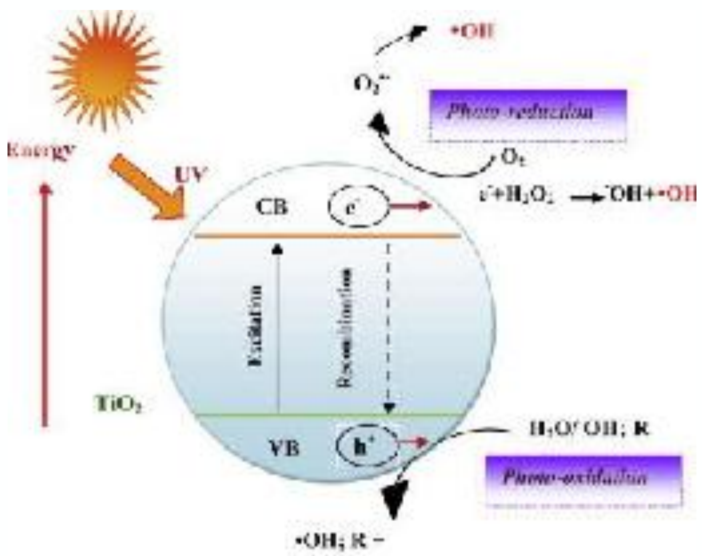
Semiconductor photocatalysis

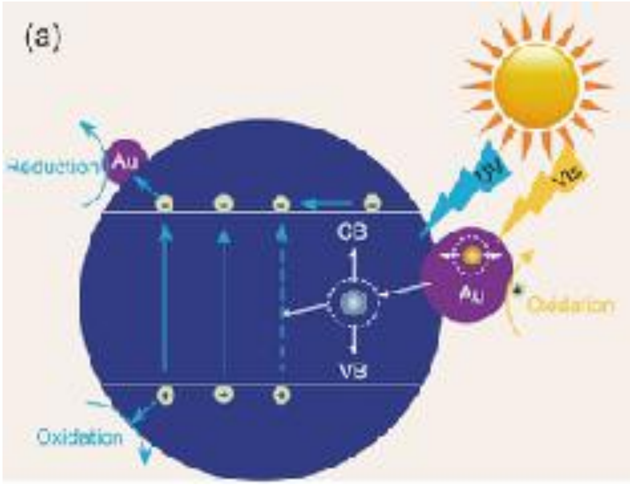
- TiO_2: Absorb photons in UV (wide band gap = 3.2 eV)
- Doping TiO_2 with metal ions, oxides, clusters:

high probability of electron-hole recombination ⇨ *decrease the efficiency*

energy lost during charge transfer *weak affinity toward many organic reactants*

low concentration of active sites





Ye, J. *Nature Sci. Rev.* ***2017***, *4,* 761

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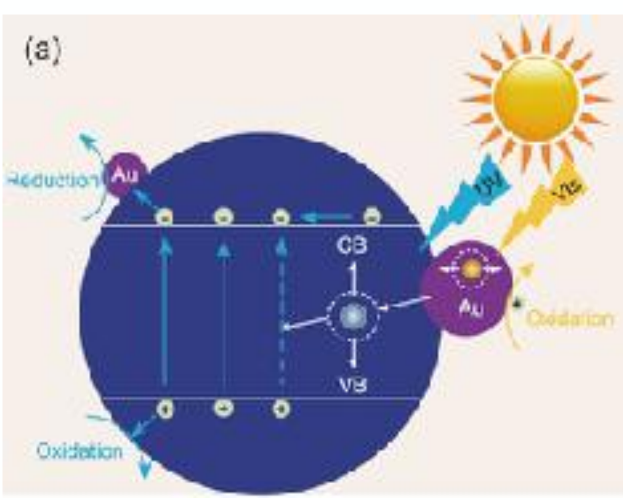
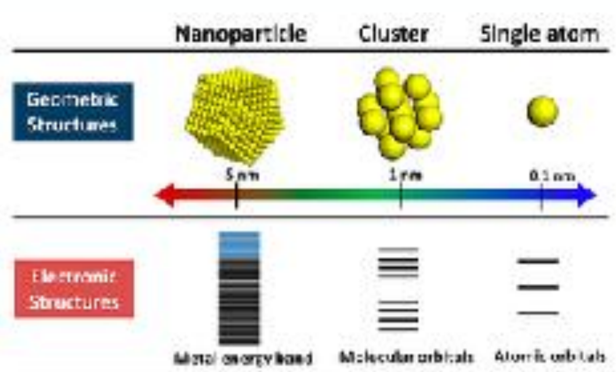
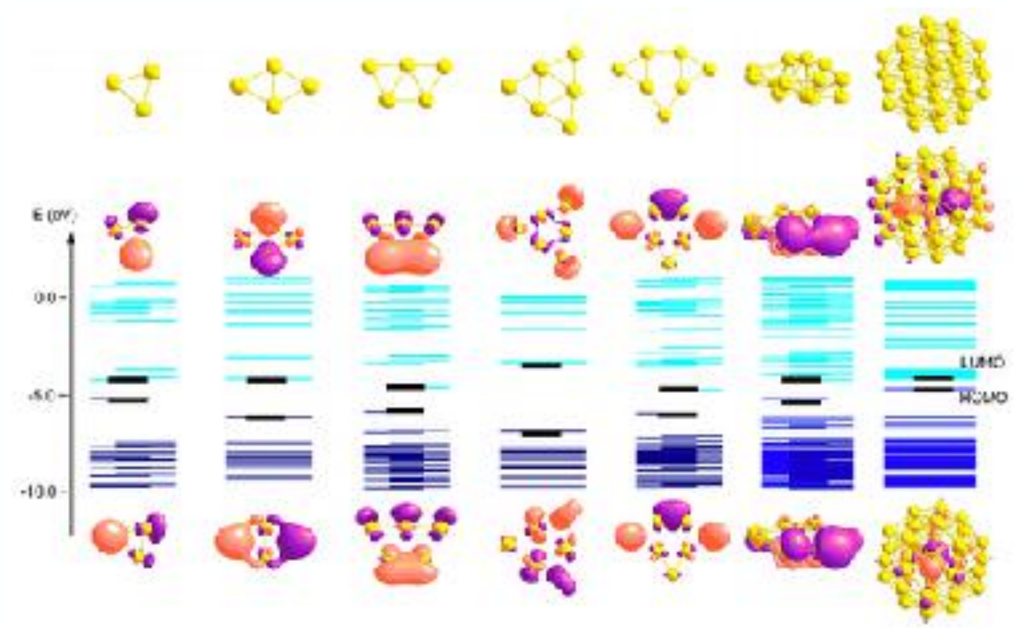
Direct photocatalysis of metal nanoparticles







Zhu, H.-Y. *Catal. Sci, Technol.* ***2016***, *6*, 320

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Based on the nature of photocatalysis

Semiconductor photocatalysis

- TiO_2: Absorb photons in UV (wide band gap = 3.2 eV)
- Doping TiO_2 with metal ions, oxides, clusters:

high probability of electron-hole recombination ⇨ *decrease the efficiency*

energy lost during charge transfer *weak affinity toward many organic reactants*

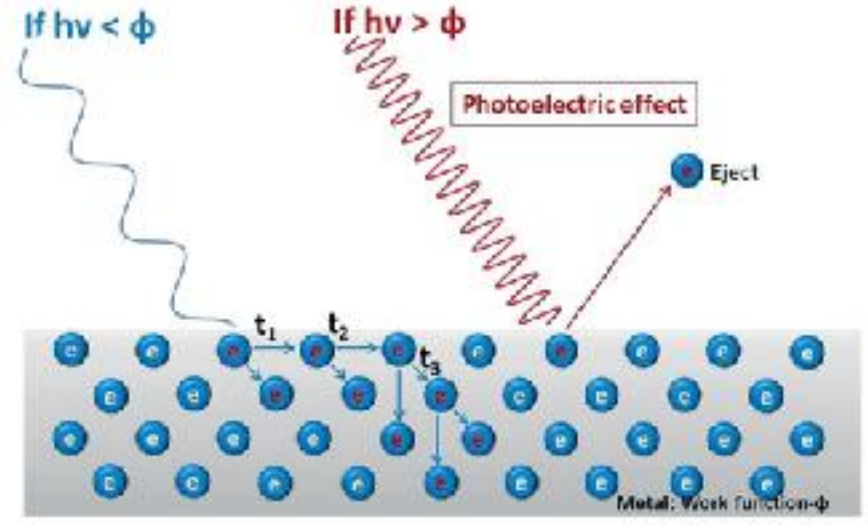
low concentration of active sites

Direct photocatalysis of metal nanoparticles

- MNPs *can intensely absorb visible light by two mechanism*

Photoelectric effect

Energy dependent:
ejection of electron or
hot electron with low energy (by subsequent electron-electron collision)



Metal-Nanoparticles in Photocatalysis

Based on the nature of photocatalysis

- Semiconductor photocatalysis
  - TiO_2: Absorb photons in UV (wide band gap = 3.2 eV)
  - Doping TiO_2 with metal ions, oxides, clusters:

high probability of electron-hole recombination ⇨ *decrease the efficiency*

energy lost during charge transfer *weak affinity toward many organic reactants*

low concentration of active sites

- Direct photocatalysis of metal nanoparticles
  - MNPs *can intensely absorb visible light by two mechanism*

Localized Surface Plasmon Resonance (LSPR)

Size dependent:

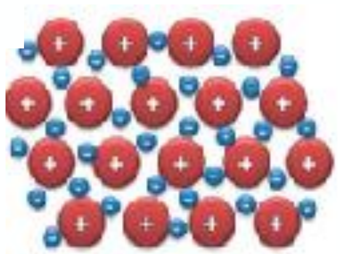
Large NPs: stronger ligh absortion, not plasmon

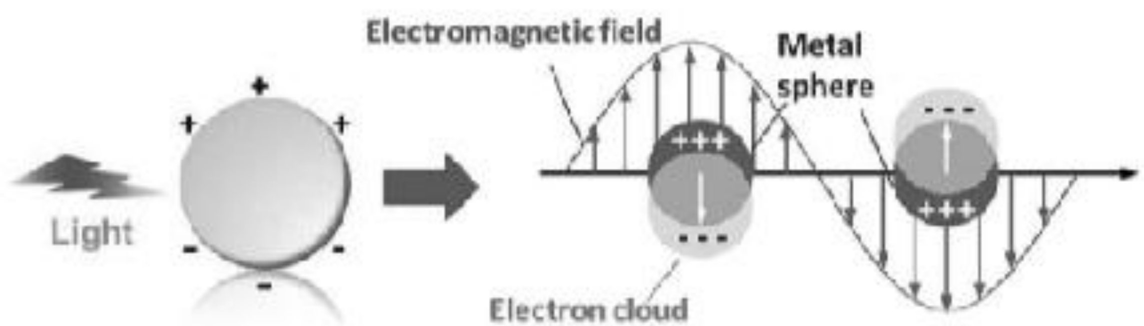
Small NPs: plasmon resonance

Metal-Nanoparticles in Photocatalysis

Localized Surface Plasmon Resonance

LSPR i*s an optical phenomena that occurs when light is incident on a conductive NP that is smaller than the wavelength of incident light, which* ***produce a strong interaction*** *between the incident* ***electric field*** *and the* ***free conduction electrons of the metal NPs****.*





dipolar oscillation (t = 10 -100 fs)

plasmon generate an absortion band in visible spectra

external stimulus ⇨ *distorsion (charge distribution)* ⇨ *adquire kinetic energy instead equilibration*

Frequency and strength depends on the intrinsic dielectric properties. Plasmon resonance can be tuned:

- size
- shape
- material
- proximity to other NP

Zhu, H.-Y. *Chem. Asian J.* ***2014****, 9,* 3046

Zhu, H.-Y. *Catal. Sci, Technol.* ***2016****, 6,* 320

Metal-Nanoparticles in Photocatalysis

Localized Surface Plasmon Resonance

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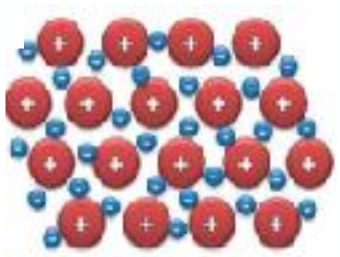
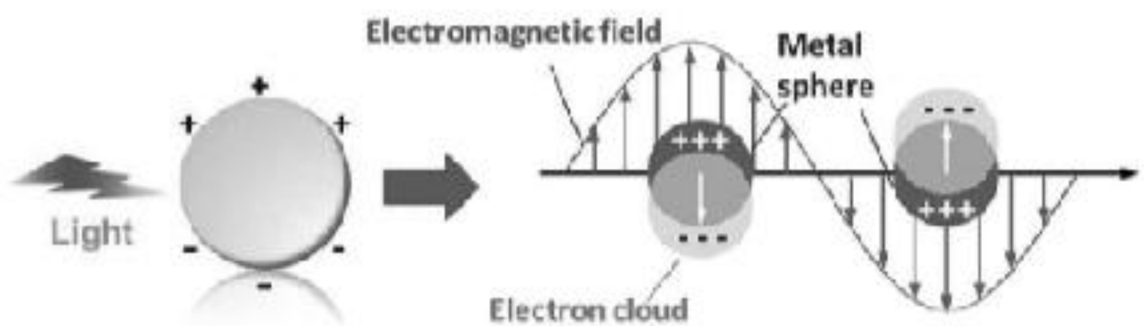




dipolar oscillation (t = 10 -100 fs)

plasmon generate an absorption band in visible spectra

external stimulus ⇨ *distorsion (charge distribution)* ⇨ *adquire kinetic energy instead equilibration*

Frequency and strength depends on the intrinsic dielectric properties. Plasmon resonance can be tuned:

- size

AuNPs (< 5 nm) not show LSPR absorption; good between 5-50 nm

Au clusters (more than 300 atoms < 2nm) exhibit absorption

⇨ Small particles have larger specific surface (more active sites)
Large particles: stronger light absorption

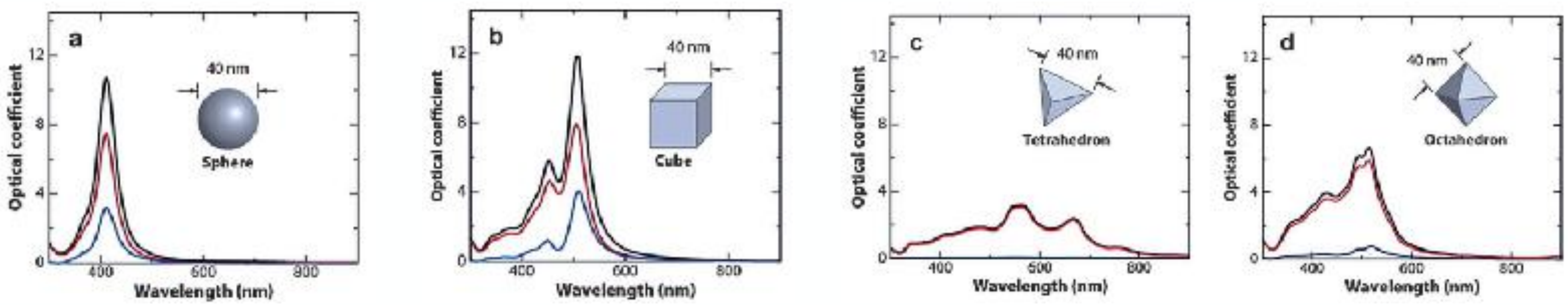
Zhu, H.-Y. *Chem. Asian J.* ***2014****, 9,* 3046

Zhu, H.-Y. *Catal. Sci, Technol.* ***2016****, 6,* 320

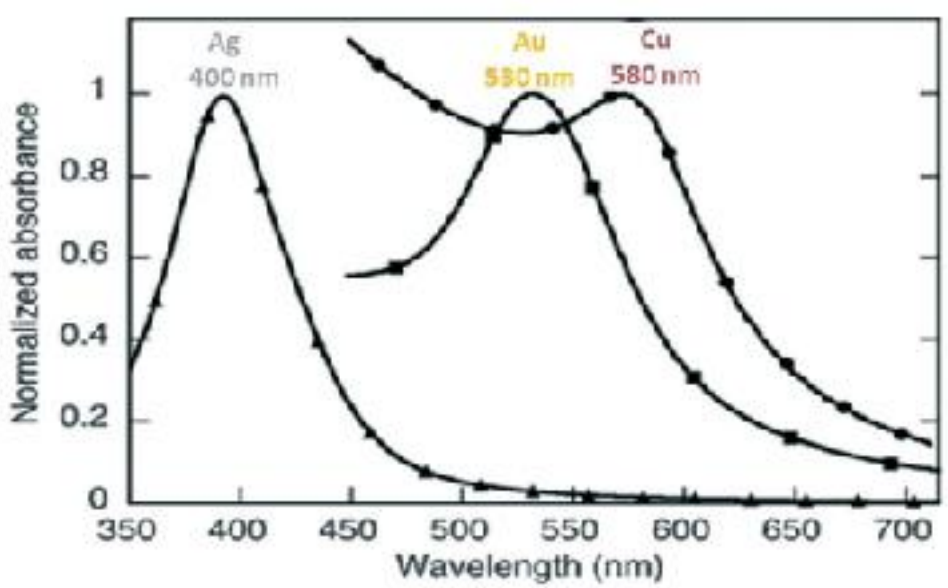
Metal-Nanoparticles in Photocatalysis

Localized Surface Plasmon Resonance

■ Calculated LSPR spectra of various AgNPs



■ LSPR absorbance spectra of Au, Ag and Cu spherical NPs (20 nm)



- MNPs can absorb the incident light in their vicinity
- MNPs absorb more light than seminconductors
- *Use as PCat: Good combination of plasmonic effects and catalysis effect*

Zhu, H.-Y. *Chem. Asian J.* ***2014****, 9,* 3046

Zhu, H.-Y. *Catal. Sci, Technol.* ***2016****, 6,* 320

Metal-Nanoparticles in Photocatalysis

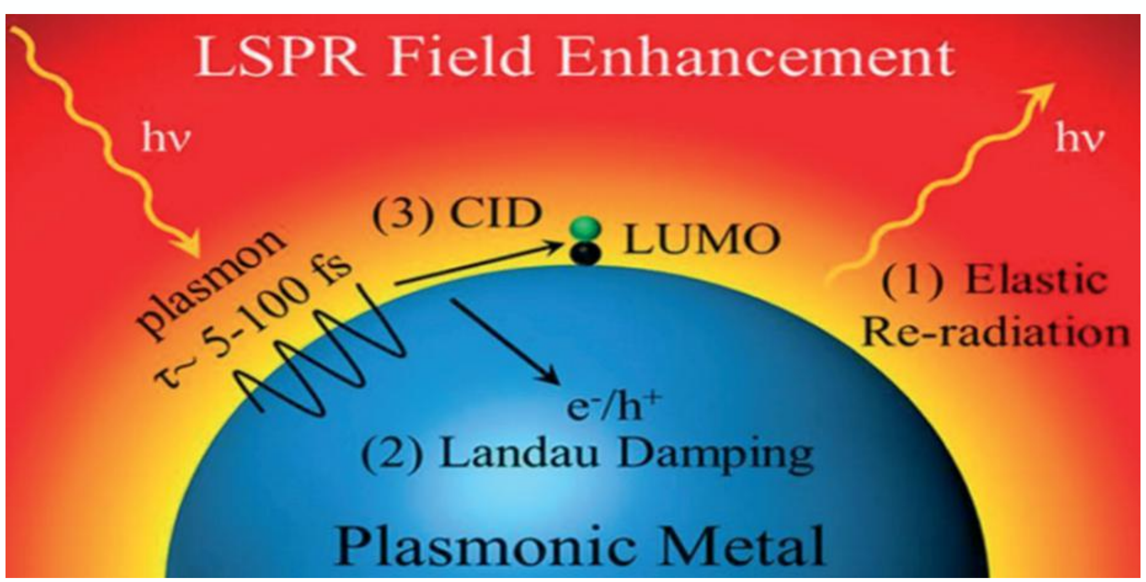
Direct Photocatalysis on Plasmonic-Metal NPs

Plasmonic MNPs act simultaneously as light absorbers and catalytic sites when irradiated with visible light.

⇩

Charge transfer between the plasmonic metal and support (observed Metal/semiconductor) is not required for catalysis to occur

- Three processes can transfer light energy into the adsorbed reactants:



(1) Elastic radiactive re-emission of photons

(2) Non-radiactive Landau-Damping: excitation of energetic electrons and holes in the metal particle

(3) Interaction of excited surface plasmons with unpopulated adsobate acceptor states

⇩

Inducing direct electron injection into the adsorbate (CID)

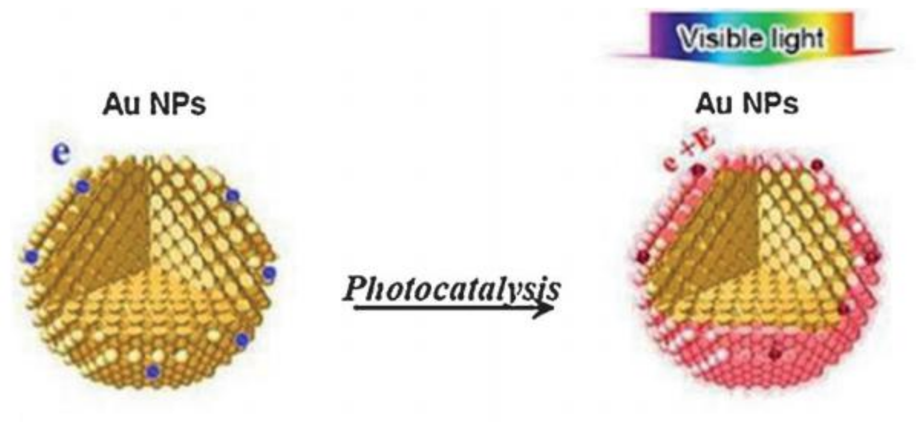
- Size
- Shape
- Metal
- Proximity (local electric field enhancement)
- Surface

Zhu, H.-Y. *Catal. Sci, Technol.* ***2016***, *6,* 320

Metal-Nanoparticles in Photocatalysis

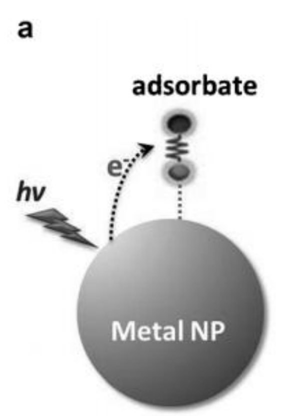
Direct Photocatalysis on Plasmonic-Metal NPs

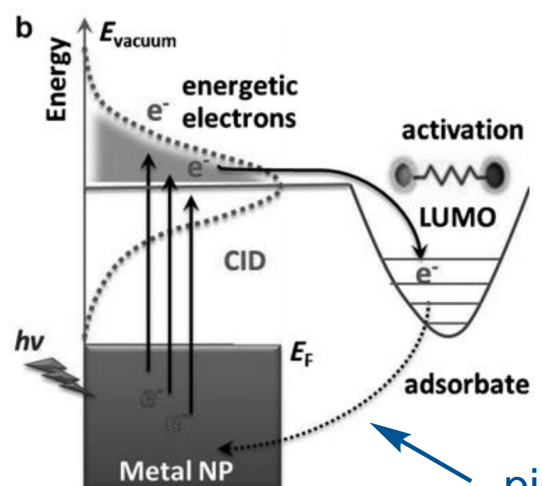
- Direct interaction between excited state and reactant



- *Light energy is economically utilized: it is efficiently channeled into the reactant molecules.*
- *No dispersion to other components of the reaction system*

- Proposed mechanism of direct charge injection from metal to adsorbate





pico seconds as average ⇨ *chemical transformations*

Corma, A. *Chem. Rev.* ***2018***, DOI: 10.1021/acs.chemrev.7b00776

Zhu, H.-Y. *Chem. Asian. J.* ***2014***, *9,* 3046

Metal-Nanoparticles in Photocatalysis

Direct Photocatalysis on Plasmonic-Metal NPs

■ The effect of the support

■ *Free-standing plasmonic NPs without support are **not stable** under visible light irradiation*

■ *Support should be **inert***

■ ***Support metal oxides**: similar structure to semiconductor photocatalyst modified with NPs*
Different active sites, electron transfer is not required
Acid-base properties can facilitate the formation of products

■ *Plasmonic NPs ⇨ double functionality ⇨ **any support material** (carbon, polymers)*

■ *Good dispersion*

■ *Enable the recovery ad recycling*

■ *Mesoporosity may affect product selectivity due to steric restriction*

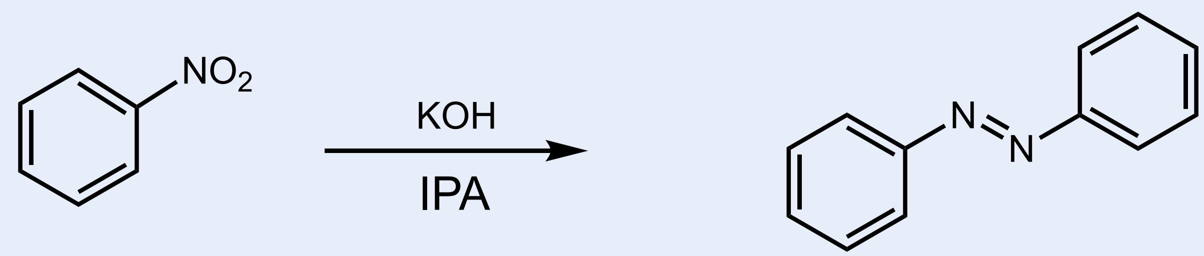
To understand the functionality of plasmonic PCat ⇨ Plasmonic NPs + support

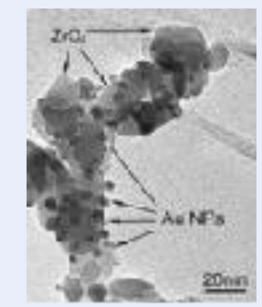
Corma, A. *Chem. Rev.* ***2018***, DOI: 10.1021/acs.chemrev.7b00776

Zhu, H.-Y. *Chem. Asian. J.* **2014**, *9,* 3046

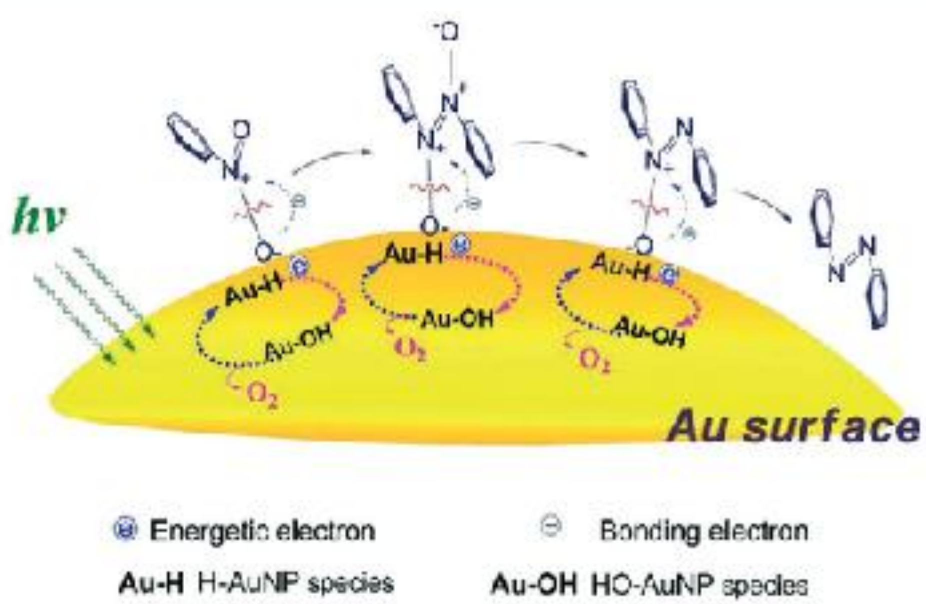
Plasmonic Photocatalytic Reactions

Reductions of Nitro Compounds





- **AuNP**/ ZrO_2 *(by reduction)*, 6 nm



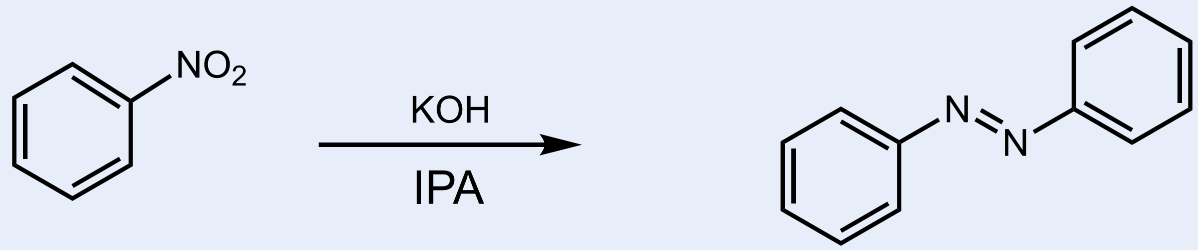
- Surface Hydrogen species is formed by abstraction of H from the solvent
- H-Au can combine with N-O bonds to give OH-AuNP
- excited electron can provide the required energy for the cleavage of N-O bond
- O_2 as byproduct

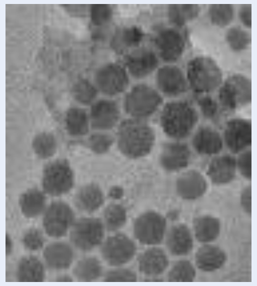
Guo, X. Y. *Angew. Chem. Int. Ed.* **2014**, *53,* 1973

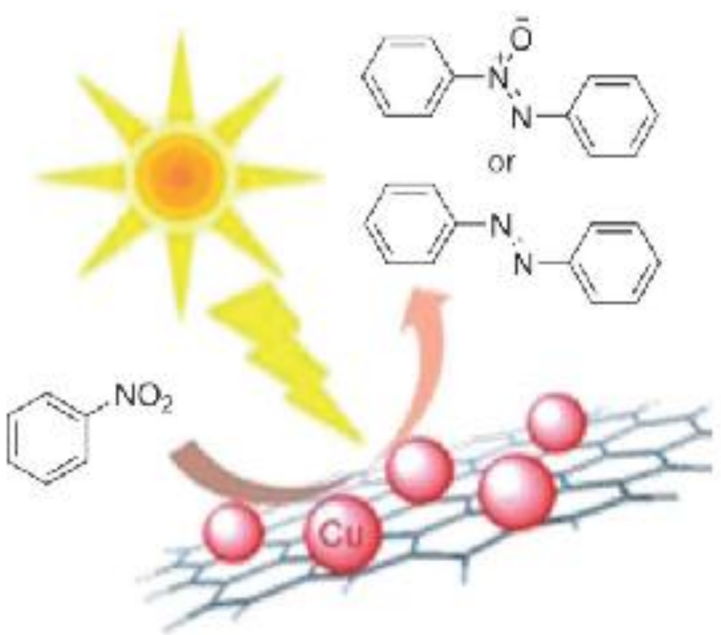
Liu, W. *Angew. Chem. Int. Ed.* **2010**, *49,* 9657

Plasmonic Photocatalytic Reactions

Reductions of Nitro Compounds







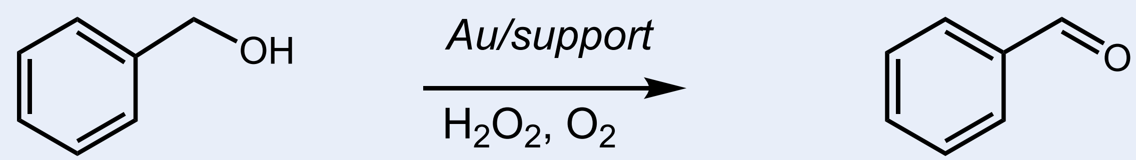
- **$Cu^{(0)}$NP**/ Graphene (*by reduction*), 7 nm

- Electrons gain the energy of the incident light through the LSPR of CuNPs
- Excited energetic electrons facilitate the cleavage of N-O bonds
- Graphene stabilize NPs susceptible to oxidation
- high yields

Guo, X. Y. *Angew. Chem. Int. Ed.* **2014**, *53,* 1973
Liu, W. *Angew. Chem. Int. Ed.* **2010**, *49,* 9657

Plasmonic Photocatalytic Reactions

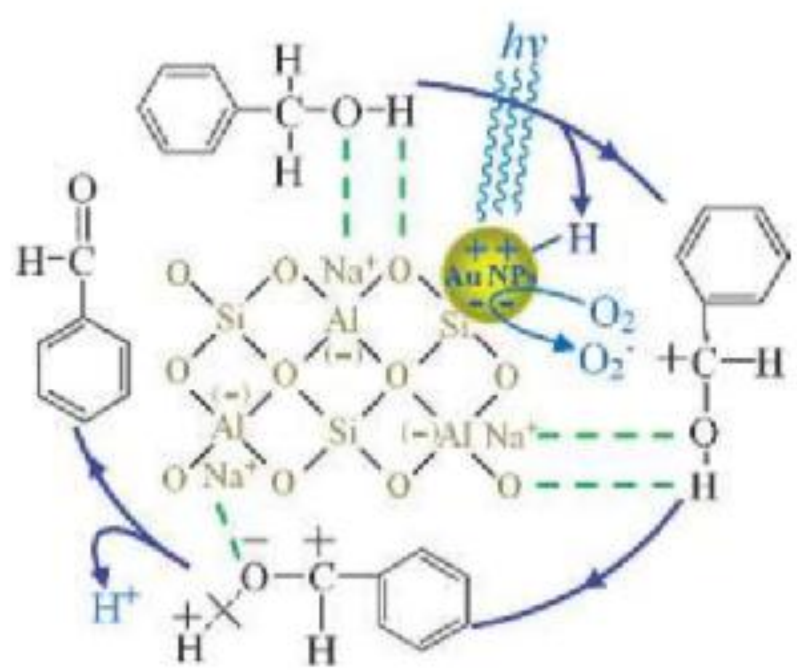
Alcohol Oxidation



- Chemoselective reaction (alcohol vs amino)

Supports:
- CeO_2,
- Zeolite
- no support

Au/Zeolite

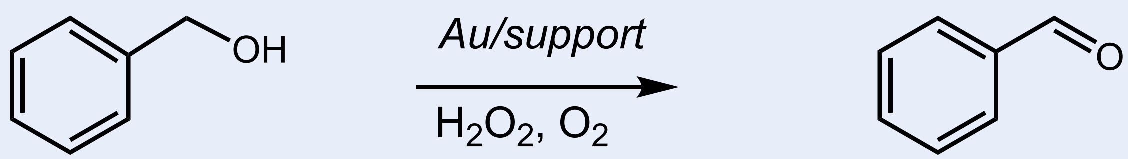


- Zeolite supports could concentrate reactants
- Catalytic activity are influenced by the adsorptive properties of support, size of Au, LSPR effect and surface areas of NPs.

Scaiano, J. C. *J. Phys. Chem. C* **2011**, *115,* 10784
Zhu, H. Y. *Chem. Eur. J.* **2012**, *18,* 8048

Plasmonic Photocatalytic Reactions

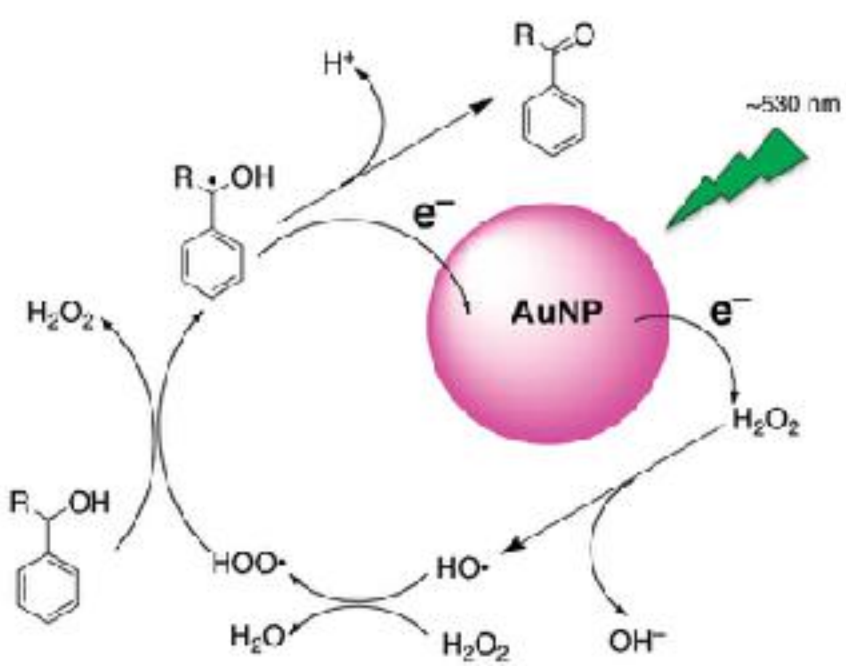
Alcohol Oxidation



Supports:
- CeO$_2$,
- Zeolite
- no support

- Chemoselective reaction (alcohol vs amino)

- **AuNPs**



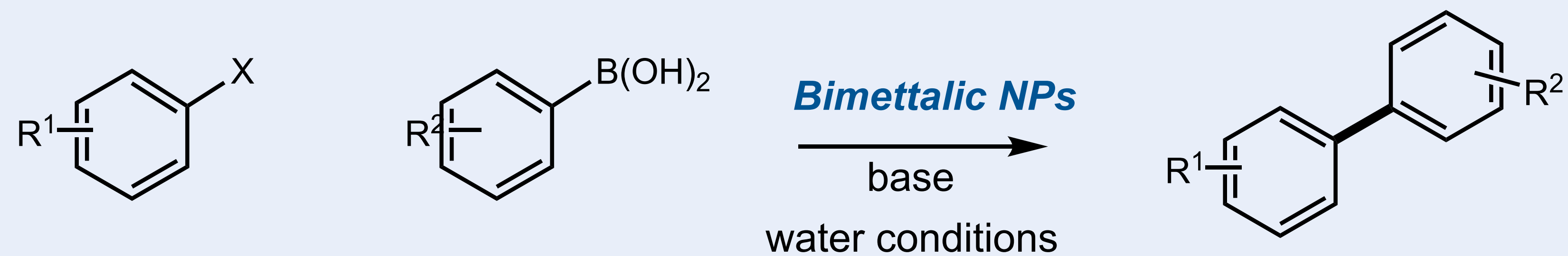
- SET from AuNP and ketyl radical formation are initiated primarily through interaction of the NP surface with the light incident on the sample
- sequential back electron tranfer and proton loss.

Scaiano, J. C. *J. Phys. Chem. C* **2011**, *115,* 10784

Zhu, H. Y. *Chem. Eur. J.* **2012**, *18,* 8048

Plasmonic Photocatalytic Reactions

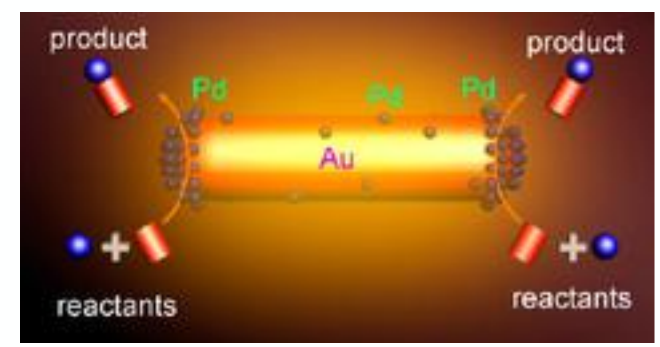
Cross-Coupling Reaction

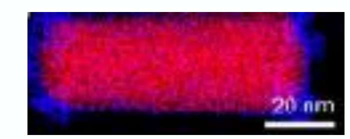


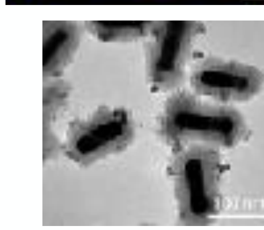
■ Au-Pd alloy NPs

similar mechanism to homogeneous catalysis

■ Au-Pd nanorods (25 nm), Au-Pd/TiO_2 (82 nm)







- ■ high reactivity (up to 99%)
- ■ under visible light and laser ilumination
- ■ In one nanostructure the light energy absorbed by plasmonic component to be directly transferred to the catalytic component

Yan, J., *J. Am. Chem. Soc.* **2013**, *135,* 5588

Stevens. C. V. *Tetrahedron Lett.* **2012**, *53,* 1410

Metal Nanoparticles in Catalysis

María González Esguevillas

MacMillan Group Meeting

May 15, 2018