Metal Nanoparticles in Catalysis

María González Esguevillas
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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A microscopic particle of matter that is measured on the nanoscale

Nanoparticles along the time

<table>
<thead>
<tr>
<th>late Bronze Age</th>
<th>400-100 BC</th>
<th>4th Century BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>red glass</td>
<td>Celtic red enamels</td>
<td>Egyptian Blue</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>Cu NPs</td>
<td>PbS NPs</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>4th Century</th>
<th>9th Century</th>
<th>Middle Ages</th>
<th>Renaissance</th>
<th>1857</th>
<th>1970-80</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rome</td>
<td>Mesopotamia</td>
<td>Luster in glassy matrix of the ceramic glaze</td>
<td>Faraday</td>
<td>USA and Japan</td>
<td>1st fundamental studies with NPs</td>
<td></td>
</tr>
<tr>
<td>Alexandria</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lycurgus Cup</td>
<td>Glittering effect in Pottery</td>
<td>Ancient Stained-Glass</td>
<td>1st description of the optical properties of nanoscale-metals</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 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 environment
- **Incidental:** manmade industrial processes
- **Engineered:** milling or lithography etching of large sample, or by assembling smaller subunits

### Based on Composition

- **0D:** $(x,y,z)< 100 \text{ nm}$ clusters
- **1D:** (2 dimensions $< 100 \text{ nm}$) nanotubes, fibers and rods
- **2D:** (1 dimension $< 100 \text{ nm}$) films and coats
- **3D:** (0 dimension $< 100 \text{ nm}$) polycrystals, nanoflowers

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[www.nano.gov](http://www.nano.gov)
Introduction to Nanoparticles

Classification

Based on the Origin

- Carbon-based NPs
- Metallic NPs (Inorganic NPs)
- Organic-based NPs
- Composite-based NPs

Based on Composition

- Fullerenes
- Quantum Dots
- Gold NPs
- Dendrimers
- Hybrid nanofibers

Based on Dimensions

- spherical, ellipsoidal or tubular shape
- NPs of noble metals, metal oxides and semiconductors
- Organic matter excluding carbon-based and metallic
- multiphase: one NPs combine with other or with larger/bulk-type material

www.nano.gov
Synthesis of Metal-Nanoparticles

General Procedures

- Chemical Reduction of Metal Salts

\[ \text{AgNO}_3 + \text{reductor} \rightarrow \text{Ag}^{(0)} \text{(NPs)} \]

- reductor: \( H_2, \text{NaBH}_4, \text{alcohols, CO, sodium citrate, organosilanes} \)
- need stabilizing agents
- stable in water conditions
- controlled size and shape
- Au, Ag, Pd, Pt, Ir, Cu, Ru

- Displacement of Ligands from Organometallic Compounds

\[ \text{Pd}_2(\text{dba})_3 + \text{stabilizing agent} \rightarrow \text{Pd}^{(0)} \text{(NPs)} \]

- reductor: \( H_2, \text{organosilanes} \)
- soluble in water, DCM, THF
- polymers, imidazoles or ligands as stabilizing agents
- controlled size and shape
- Pd, Pt, Ru, Co, Cu, Au, Fe, Ni

Synthesis of Metal-Nanoparticles

General Procedures

- **Thermal, Photochemical or Sonochemical Decomposition**

  \[ \text{PtCl}_2 \xrightarrow{\Delta \text{ solvent}} \text{Pt}^{(0)} \text{(NPs)} \]

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

- **Condensation of Atomic Metal Vapor**

  \[ \text{Co}_2(\text{CO})_8 \xrightarrow{\Delta \text{ decomposition}} \text{Co}^{(0)} \text{(NPs)} \]

  - 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


Synthesis of Metal-Nanoparticles

General Procedures

- Reduction by Electrochemical Methods

\[
M \rightarrow M^{(0)} \text{(NPs)}
\]

- 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


Properties of Metal-Nanoparticles

- **Metal source**
- **Reducing agent, stabilizing and support**
- **Synthetic method of MNPs**
- **Size, shape and distribution (nano/surface)**

Special properties and essentially different from macroscale material

- 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
Metal-Nanoparticles: Applications

Electronic and optical fields

Data and Energy Storage

Photovoltaic solar cells

Chemical sensors

Air purification

Photocatalysis

Catalysis

Drug storage system

Drug delivery systems

Tissue nanoengineering

Covered Nanoparticles

Magnetic Nanoparticles

Metal-NPs

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

Why use Metal-Nanoparticles in catalysis instead homogeneous catalysis?

**Advantages**

- High atom efficiency
- Mild reaction conditions
- Simplified isolation of products
- Easy recovery and Recyclability

**Disadvantages**

- Each variable could change the nano formation
- Lower reproducibility control
- Each batch of NPs need to be characterized

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

**Synthetic Method**
- Reduction
- Decomposition
- Vapor Condensation
- Electrochemical

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

**Stabilizing reactants**
- Carbon supports
- Polymers
- Metal oxides

**Metal-NP vs Metal**
- High efficiency
- Recycling
- Green Conditions
- Simple isolation

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

\[ \text{nitro} \xrightarrow{\text{red.}} \text{nitroso} \xrightarrow{\text{red.}} \text{hydroxylamine} \xrightarrow{\text{red.}} \text{aniline} \]

- condensation
- \[ \text{azoxy} \xrightarrow{\text{red.}} \text{azo} \xrightarrow{\text{red.}} \text{hydrazo} \]
Hydrogenation of Nitroarenes

\[
\text{NO}_2 \xrightarrow{\text{H}_2, \text{catalyst}} \text{NH}_2
\]

**NanoParticles**

<table>
<thead>
<tr>
<th></th>
<th>Pt/C</th>
<th>Pt/N-CNF-H (N-doped-nanofiber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis</td>
<td>reduction: H\textsubscript{2}PtCl\textsubscript{6} with NaBH\textsubscript{4}</td>
<td>impregnation with Pt(dba\textsubscript{2})</td>
</tr>
<tr>
<td>Size and Shape</td>
<td>3 nm</td>
<td>1.8 nm</td>
</tr>
<tr>
<td>Reaction conditions</td>
<td>H\textsubscript{2}, 10\textdegree C</td>
<td>H\textsubscript{2} (7 -10 atm), 70\textdegree C</td>
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</table>

> 85 % yield < 4 hours

**no dehalogenation**

allow ketones and CN

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

**Hydrogenation of Nitroarenes**

![Chemical reaction diagram]

### NanoParticles

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<tr>
<th></th>
<th>Pt/C</th>
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<th>Silica Cat Pt&lt;sup&gt;0&lt;/sup&gt;</th>
</tr>
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<tr>
<td><strong>Synthesis</strong></td>
<td>reduction: H&lt;sub&gt;2&lt;/sub&gt;PtCl&lt;sub&gt;6&lt;/sub&gt; with NaBH&lt;sub&gt;4&lt;/sub&gt;</td>
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<td><strong>Size and Shape</strong></td>
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<td>1.7-3.1 nm</td>
</tr>
<tr>
<td><strong>Reaction conditions</strong></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, 10°C</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; (7-10 atm), 70°C</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, MeOH</td>
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<tr>
<th></th>
<th>&gt; 85% yield</th>
<th>&lt; 4 hours</th>
</tr>
</thead>
</table>

- **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**
- **Hydrophobic matrix ensures the selectivity of the most reactive NO<sub>2</sub>**
**Hydrogenation of Nitroarenes**

![Chemical reaction](image)

**NanoParticles**

<table>
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<tr>
<th></th>
<th>Pt/C</th>
<th>Pt/N-CNF-H (N-doped-nanofiber)</th>
<th>Silica Cat Pt⁰</th>
<th>Bimetallic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Synthesis</strong></td>
<td>reduction: H₂PtCl₆ with NaBH₄</td>
<td>impregnation with Pt(dba)₂</td>
<td>reduction K₂PtCl₂</td>
<td>double reduction</td>
</tr>
<tr>
<td><strong>Size and Shape</strong></td>
<td>3 nm</td>
<td>1.8 nm</td>
<td>1.7-3.1 nm</td>
<td>~ 2 nm</td>
</tr>
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<td>H₂, 10°C</td>
<td>H₂ (7-10 atm), 70°C</td>
<td>H₂, MeOH</td>
<td>H₂, solvent</td>
</tr>
</tbody>
</table>

- **NHOH**
  - > 85 % yield
  - < 4 hours
  - no dehalogenation
  - allow ketones and CN
  - high reactivity (99%), long reaction times (8h)

- **Silica Cat Pt⁰**
  - CN not tolerated
  - high selectivities
  - < 2 h

- **Bimetallic**
  - high reactivity
  - poor selectivity

Hydrogenation of Nitroarenes

New Metal-NanoParticles

\[
\begin{array}{c}
\text{FeNPs (3 equiv)} \\
\text{H}_2\text{O, rt}
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
\text{R} \\
\text{R}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{R} \\
\text{R}
\end{array}
\]

\[
\begin{array}{c}
\text{R} \\
\text{R}
\end{array}
\]

**Reduction of FeSO\(_4\).7H\(_2\)O in water using NaBH\(_4\) and citric acid as stabilizing agent**

Fe\(^{0}\)NPs
- 3-5 nm spheres
- nanotubes

\[
\begin{array}{c}
\begin{array}{c}
\text{MeOC} \\
\text{MeOC}
\end{array}
\end{array}
\]

intermediates was observed by MS

R = CHO, CO, COOH, CONHR
- CN, N\(_3\), SCN, halides
- 86-96% yield

R = OBn, OAllyl
- 90% yield

80% yield

Hydrogenation of Nitroarenes

Noble metal-free NanoParticles

\[
\begin{align*}
\text{BimetallicNPs} & \quad \text{BH}_3\cdot\text{NH}_3 \\
\text{methanolysis} & \\
\end{align*}
\]

\[
\begin{align*}
\text{co-reduction of} & \\
\text{Ni(acac)}_2 \text{ and Cu(acac)}_2 & \\
\text{with BBA in oleylamine} & \\
\text{and oleic acid} & \\
\rightarrow & \\
\text{monodisperse CuNiNPs} & \\
15 \text{ - } 16 \text{ nm} & \\
\text{Cu/Ni ratio 3:1 to 1:3} & \\
\text{graphene supported} & \\
\rightarrow & \\
\text{spheres} & \\
\end{align*}
\]

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

\[
\text{R} \quad \text{NO}_2 \quad \xrightarrow{\text{BimettalicNPs}} \quad \text{R} \quad \text{NH}_2
\]

\[
\text{BH}_3 \cdot \text{NH}_3
\]

\[
\text{methanolysis} \quad \text{H}_3\text{N} \cdot \text{BH}_3 + 4 \text{CH}_3\text{OH} \quad \xrightarrow{\text{G-Cu}_n\text{Ni}_m\text{NPs}} \quad \text{NH}_4 \cdot \text{B(OMe)}_4 + 3\text{H}_2
\]

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

Sun, S. *Chem. Mater.* 2017, 29, 1413
Hydrogenation of Nitroarenes

New Metal-NanoParticles

\[
\text{G-Cu}_{36}\text{Ni}_{64}\text{NPs}
\]

\[ \text{BH}_3\cdot\text{NH}_3, \text{MeOH, rt} \]

30 min > 97% yield

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

\[
\text{R} \equiv \text{R'} 
\]

8 - 10 group MNPs

\[
\text{H}_2 
\]

\[
\text{R} \equiv \text{R'} 
\]

\begin{itemize}
  \item Supported on \( \gamma\text{-Al}_2\text{O}_3 \)  
    (most used support for Au)
  
  \item Supported on an (IL)-hybrid \( \gamma\text{-Al}_2\text{O}_3 \)
  
  \item Avoid direct contact AuNPs and support
\end{itemize}
Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

Most plausible hydrogenation pathways

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

Ionic hydrogenation

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

Most plausible hydrogenation pathways

- Ionic hydrogenation

- Dissociative Chemisorption of \( H_2 \)

- by low-coordinated Au surface sites
- \( H \) atom formation in bridge positions sharing Au atoms
- no deformation of Au-Au distances

**Hydrogenation Reaction of Multiple Bonds**

Mechanistic Studies

\[
\text{AuNPs} \quad H_2 \rightarrow \text{diolefin}
\]

---

### Most plausible hydrogenation pathways

1. **Ionic hydrogenation**

   \[
   \text{Au-NPs/M}_x\text{O}_y
   \]

2. **Dissociative Chemisorption of \(H_2\)**

   \[
   \text{Au-NPs/M}_x\text{O}_y
   \]

- not yet been reported

- Au atoms or nanoclusters show better selectivity for butadienes, internal alkynes, carbonyl compounds

---

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

\[ R = C = C \rightarrow R' \]

\[ \text{AuNPs} \]

\[ H_2 \rightarrow R = C = C \]

Most plausible hydrogenation pathways

- Ionic hydrogenation

- Dissociative Chemisortion of \( H_2 \)

- \( H_2 \) activation with the ejection of Au-subnanometer cluster

- Outer-sphere: Disproportion

- not yet experimentally proved

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

**Catalytic Hydrogenation**

![Catalytic Hydrogenation Diagram]

- **Au-NPs**
- **H₂, n-hexane**
- **Au-γ-Al₂O₃**: 88% yield (50-100 °C)
- **Au-(IL)-γ-Al₂O₃**: 92-96% yield only at 100 °C

**Kinetic Isotopic Effect**

![Kinetic Isotopic Effect Diagram]

- **Au-NPs**
- **H₂ of D₂, n-hexane**
- **Au-γ-Al₂O₃**: $k_H/k_D = 1.1$
- **Au-(IL)-γ-Al₂O₃**: $k_H/k_D = 3.8 - 4.6$

**Different mechanisms**

- Activation of hydrogen is not the rate determining step in **Au-γ-Al₂O₃**
- 1,2- and 1,4-D addition were observed with **Au-(IL)-γ-Al₂O₃** suggests allyl intermediate

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

Hydrogenation Reaction of Multiple Bonds

Mechanistic Studies

Based on the experimental results, kinetic effects and kinetic models

- Ionic hydrogenation
- Dissociative Chemisorption of H$_2$
- Outer-sphere: Disproportion

Au-$\gamma$-Al$_2$O$_3$

Dissociative Chemisorption of H$_2$

homolytic activation based on the thickness of IL

Au-$(IL)\cdot\gamma$-Al$_2$O$_3$

Transfer Hydrogenation Reaction of Carbonyl Compounds

- Ni and Fe NPs
- Sreedhar, B. ChemCatChem. 2016, 8, 1139

- Metal mediated
- Metal hydrides of catalytic hydrogenation
- 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

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

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

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

- Pd and AuNPs require bases and benzylic substrates
- PtNPs (H₂, NaBH₄, ethanol) only 1 run (90 - 95% yield)

coordination and electronic properties of metal affect the activation of alcohol and oxygen
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 °C
recyclable reaction medium
low catalyst loading

NiNPs formed in situ and used in combination with micellar catalysis

96% yield
broad scope (more than 30 examples)

Lipshutz, B. H. Angew. Chem. Int. Ed. 2015, 54, 1194
C-C Bond Formation

Carbonylative Suzuki Cross-Coupling


- boronates, halides
- high temperature
- ligand
- excess coupling partner
- dry solvents
- high pressures
- mild conditions
- CuNPs or NiNPs
- recyclable reaction medium
- low catalyst loading

![Chemical Structures](image)

- 20 mol % CuNPs
- K₃PO₄, KF, tBuCOOH, PEG-400
- CO (balloon)

- 90% yield
- 38 examples, up to 95% yield

- 2 mol % NiCl₂
- K₃PO₄, PivOH, PEG-400, 80°C
- CO (balloon)

- 81% yield
- 36 examples, up to 93% yield

- insitu generated NiNPs
- efficient and recyclable
- no ligand
- PivOH to avoid C-C coupling
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  Leached homogeneous complex
produce active metal clusters

Chiral MNP catalysis

chiral Metal NP
- separable
- robust

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

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

R1OH

[Scheme: Au-Pd/PI and Rh/PI reactions with chiral ligand]

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

Kobayashi, S. *ACS Catal.* 2016, 6, 7979
C-N Bond Formation

Biogenic Cu-NanoParticles

Addition of CuSO$_4$ in the presence of leaf extracts of Ocimum Sanctum

CuONPs

< 5 nm spheres

bio-support

- pharmaceutical and biological interest
- metal catalyst (Pd, Ni, Fe, Co, Cu)
- low functional group tolerance

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

C-N Bond Formation

Biogenic Cu-NanoParticles

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N-Arylation and N-Vinylation of Amides
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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 demonstrated the potential use of AuNPs as photocatalyst for reduction of nitroarenes

\[ \text{MNPs serve as both the light absorber and host to the catalytic sites} \]

\[ \text{many potential materials (solids, polymers)} \]

Create new and better photocatalyst

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 $\rightarrow$ 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 mechanisms:
  - Photoelectric effect
  - Localized Surface Plasmon Resonance (LSPR)

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

- Size dependent:
  - Large NPs: stronger light absorption, not plasmon
  - Small NPs: plasmon resonance

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:
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- **Direct photocatalysis of metal nanoparticles**

Metal-Nanoparticles in Photocatalysis

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Semiconductor photocatalysis

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Direct photocatalysis of metal nanoparticles

- MNPs can intensely absorb visible light by two mechanism

  - Localized Surface Plasmon Resonance (LSPR)
  
  Size dependent:
  - Large NPs: stronger light absorption, not plasmon
  - Small NPs: plasmon resonance
Localized Surface Plasmon Resonance (LSPR) is 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.

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

- size
- shape
- material
- proximity to other NP

plasmon generate an absorption band in visible spectra

dipolar oscillation (t = 10^{-100} \text{ fs})

external stimulus \rightarrow distorsion (charge distribution) \rightarrow adquire kinetic energy instead equilibration


**Metal-Nanoparticles in Photocatalysis**

Localized Surface Plasmon Resonance

**LSPR** is 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.

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

- **AuNPs** (< 5 nm) not show LSPR absorption; good between 5-50 nm
- **Au clusters** (more than 300 atoms < 2nm) exhibit absorption
- Large particles: stronger light absorption

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

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 semiconductors
- Use as PCat: Good combination of plasmonic effects and catalysis effect

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 radioactive re-emission of photons
2. Non-radiative Landau-Damping: excitation of energetic electrons and holes in the metal particle
3. Interaction of excited surface plasmons with unpopulated adsorbate acceptor states

Inducing direct electron injection into the adsorbate (CID)

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

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


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

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

Plasmonic Photocatalytic Reactions

Reductions of Nitro Compounds

\[
\text{Cu}^{(0)}\text{NP}\text{/ Graphene (by reduction), 7 nm}
\]

- 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

Plasmonic Photocatalytic Reactions

Chemoselective reaction (alcohol vs amino)

Au/Zeolite

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

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.


Plasmonic Photocatalytic Reactions

Alcohol Oxidation

Chemoselective reaction (alcohol vs amino)

Supports:
- CeO₂,
- Zeolite
- no support

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 transfer and proton loss.


**Plasmonic Photocatalytic Reactions**

*Cross-Coupling Reaction*

\[
\text{Bimetallic NPs} \quad \xrightarrow{\text{base}} \quad \xrightarrow{\text{water conditions}}
\]

- **Au-Pd alloy NPs**
- **Au-Pd nanorods (25 nm), Au-Pd/TiO}_2 (82 nm)**

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

*Similar mechanism to homogeneous catalysis*

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Stevens, C. V. *Tetrahedron Lett.* **2012**, *53*, 1410
Metal Nanoparticles in Catalysis

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MacMillan Group Meeting
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