Generation of anisotropic gold and gold-palladium bimetallic nanoparticles on functionalized surfaces

Veronica L. Gerios

Organization

In situ Generated Metal Nanoparticles

- ⊙ AuPd Bimetallic Nanoparticles on Surface (catalyst)
- ⊙ Au Nanorods on Surface (catalyst)

Bimetallic NPs Overview

Background

Hong, Y. ACS Sustainable Chem. Eng. 2014, 2, 1752-1759.

Wang, J. ACS Catal. 2015, 5, 3575-3587

Lenueau, M. Chem. Mater. 2019, 31, 15, 5759-5768

In-situ Generation of NPs on Surfaces

Surface Morphology with AFM

Au:Pd Ratio	Particle Size (nm)
1:0	2.45
1:0.5	2.99
1:1	1.62
0.5:1	2.63
0:1	3.01

Monitoring Surface Plasmons

Au:Pd Ratio	Wavelength Maximum (nm)
1:0	567
1:0.5	540
1:1	561
0.5:1	598
0:1	616

Potential Nanoparticle Structure

Bimetallic NP Size > Au NP Size of 2.45 nm

Bimetallic NP Wavelength < Au NP Wavelength of 567 nm

1:0.5 Au:Pd

Size = 2.99 nm

$\lambda = 540$ nm

**Core Shell
Supported**

1:1 Au:Pd

Size = 1.62 nm

$\lambda = 561$ nm

**Core Shell
Partially
Supported**

0.5:1 Au:Pd

Size = 2.63 nm

$\lambda = 598$ nm

**Core Shell
Supported**

Chemical Composition of NPs

Impedance change in the presence of a redox probe

Proposed equivalent circuit

Impedance response in presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as redox probe

Impedance response in presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as redox probe

ITO + Monolayer + $[\text{AuCl}_4]^-$
 $R_{\text{ct}} = 26.3 \, \Omega$

ITO + Monolayer + $[\text{AuCl}_4]^-$ + $[\text{PdCl}_4]^{2-}$
 $R_{\text{ct}} = 1805 \, \Omega$

ITO + Monolayer + $[\text{PdCl}_4]^{2-}$
 $R_{\text{ct}} = 26050 \, \Omega$

Analysis of Electrocatalytic Behavior

Au:Pd Ratio	$K_{app} \times 10^{-4} (1/s)$
1:0	1.69
1:0.5	3.17
1:1	2.57
0.5:1	2.28
0:1	5.69

Most Pd Exposure

Moderate Pd Exposure

Least Pd Exposure

Analysis of Electrocatalytic Properties

0:1 Au:Pd NPs with MeOH

1:0 Au:Pd NPs with EtOH

0:1 Au:Pd NPs with Propanol

1:0 Au:Pd NPs with Glycerol

0:1 Au:Pd NPs with Ethylene Glycol

Analysis of Electrocatalytic Properties

	Alcohol	Methanol	Ethanol	Propanol	Ethylene glycol	Glycerol
Au:Pd Ratio	1:0	4.07	4.11	3.95	1.15	4.92
	1:0.5	0.90	1.06	1.60	1.65	3.20
	1:1	1.42	1.01	2.04	1.03	1.90
	0.5:1	3.48	1.45	3.74	2.43	2.59
	0:1	4.27	1.10	4.09	2.68	2.71

Summary of Electrocatalytic Properties

**Current Ratio is
near the value for
Pd NPs.**

**Current Ratio is
near the value for
Au NPs.**

More Pd Exposed

More Au Exposed

Summary of Electrocatalytic Properties

0.5:1 Au:Pd

Ethylene glycol
ratio was near the
Pd ratio.

0.5:1 Au:Pd

EtOH ratio was
near the Pd ratio.

0.5:1 Au:Pd

Glycerol ratio was
near the Pd ratio.

0.5:1 Au:Pd

Propanol ratio was
near the Au ratio.

1:1 Au:Pd

EtOH ratio was
near the Pd ratio.

1:1 Au:Pd

Ethylene glycol
ratio was near the
Au ratio.

1:0.5 Au:Pd

EtOH ratio was
near the Pd ratio.

More Pd Exposed

More Au Exposed

Summary

1:0.5 Au:Pd

Size = 2.99 nm

$\lambda = 540$ nm

**More Pd
Exposure**

K Value

EtOH Ratio

**Well formed Pd shell
with Au core**

1:1 Au:Pd

Size = 1.62 nm

$\lambda = 561$ nm

**More Pd
Exposure**

K Value

EtOH Ratio

**More Au
Exposure**

Ethylene
glycol ratio

**Poor Pd shell with Au
core**

0.5:1 Au:Pd

Size = 2.63 nm

$\lambda = 598$ nm

**More Pd
Exposure**

K Value
EtOH,
ethylene
glycol, &
glycerol ratio

**More Au
Exposure**

Propanol
ratio

**Moderate Pd shell with
Au core**

Nanorods

Au Nanorods Overview

Background

Mieszawska, A. J. AM. CHEM. SOC. 2006, 128, 5622-5623

Guo, J. Appl. Organometal. Chem. 2019, 33, 4791

Murphy, C. Chem. Mater. 2005, 17, 1325-1330

Seed Synthesis

Rod Synthesis

Seed treatment

- Soak in 0.2 M CTAB for ~10 minutes

Growth Solution A (GSA) from colloid paper

- 0.10 g of CTAB
- 5 mL of 1.5×10^{-1} M BDAC
- 0.20 mL of 4×10^{-3} M AgNO_3
- 5 mL of 1×10^{-3} M HAuCl_4
- 0.070 mL of 7.78×10^{-2} M Ascorbic Acid

Why surfactants?

Why silver?

Monitoring Surface Plasmons

Type of ITO	Seeded ITO					Monolayer ITO		Cleaned ITO	
Time in GSA	Seeds	15 min	30 min	45 min	60 min	30 min	60 min	30 min	60 min
$\lambda_{\max 1}$ (nm)	417	420	421	409	414	456	486	449	450
$\lambda_{\max 2}$ (nm)	-	600	619	633	644	-	-	-	-

Nanorod Size with SEM

Type of ITO	Seeded ITO				Monolayer ITO
Time in GSA	15 min	30 min	45 min	60 min	60 min
Average Length, L (μm)	34.8	46.5	104	61.1	61.9
Average Width, W (μm)	10.9	11.3	12.6	10.1	10.6
Average Aspect Ratio, L/W	4.79	5.56	9.11	7.04	7.20

Morphology with SEM

Analysis of Electrocatalytic Ability

Surface		Average Current Ratio	
ITO Type	Time in GSA	Ethylene Glycol	Ethanol
Seeded ITO	Seeds	2.60	5.22
	15 min	1.34	2.23
	30 min	3.53	2.56
	45 min	5.50	3.63
	60 min	2.05	4.54
Monolayer ITO	60 min	-	-
Cleaned ITO	60 min	-	-

Summary

Thank You!

- Shout out to my subgroup: Diana Paicu, Aileen Peer, & Ian Smith
- Rackham School of Graduate Studies, UM-Ann Arbor
- Office of Research & Sponsored Programs, UM-Dearborn
- NSF-MRI (0619267, 0923023, & 1039817)
- Office of the Vice President for Research, UM-Ann Arbor
- ACS-PRF Grant

Questions?

Types of Nanoparticle Assemblies

Oxidation Pathways of Alcohols