

Supporting Information

Au-Cu-M (M=Pt, Pd, Ag) Nanorods with Enhanced Catalytic Efficiency by Galvanic Replacement Reaction

Xudong Wang,^a Shutang Chen,^a Gabriella Reggiano,^a Sravan Thota,^a Yongchen Wang,^a Peter Kerns,^a Steven L. Suib^{ab} and Jing Zhao^{*ab}

^a Department of Chemistry, University of Connecticut, 55 North Eagleville Road,
Storrs, CT 06269, United States

^b Institute of Material Science, University of Connecticut, Storrs, CT 06269, United States

* Address Correspondence to: jing.zhao@uconn.edu

Experiments

Materials:

Silver nitrate (AgNO_3 99%), oleylamine (OLA, 70%), toluene (>99.5%), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%), chloroform ($\geq 99.8\%$), palladium (II) acetylacetonate (99%), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ 99.9%), copper(II) acetylacetonate (97%), 1-octadecene (ODE 90%), 4-nitrophenol (p-nitrophenol $\geq 99\%$) and sodium borohydride (NaBH_4 , 98%) were all obtained from Sigma-Aldrich. Thiol terminated poly(ethylene glycol) methyl ether (PEG-SH, $M_w=5000$), amine terminated poly(ethylene glycol) methyl ether (PEG-NH₂, $M_w=5000$) were purchased from Polymer Source. Tetradecylamine (>96.0%) was bought from TCI America. Ethanol (200 proof) was got from J. T. Baker.

Preparation of silver precursor solution:

5 mg of AgNO_3 was dissolved in 1.0 ml of oleylamine and then diluted with 2.0 ml of toluene.

Preparation of platinum precursor solution:

5 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in 1.0 ml of chloroform and then diluted with 2.0 ml of toluene.

Preparation of palladium precursor solution:

5 mg of palladium (II) acetylacetonate was dissolved in 1.0 ml of chloroform. 2.0 ml of toluene was added afterwards.

Synthesis of AuCu_3 nanorods:

The synthesis of AuCu_3 nanorods was referred to previous reports^{1,2}. 19.7 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.05 mmol) was dissolved in 2.15 g of tetradecylamine (10mmol) at 50 °C under stirring. The solution was then heated up to 140 °C and maintained at 140 °C for 20 minutes. Next, 53.2 mg of copper (II) acetylacetonate (0.2 mmol) was added into the solution at 140 °C. Then the solution was heated up to 180 °C and the temperature was kept for another 20 minutes.

The AuCu_3 nanorods were separated by adding 5 ml of toluene and centrifugation at 3000 rpm for 2 minutes. The nanorods were redispersed in 8 ml of toluene and separated a second time by centrifugation at 3000 rpm for 2 minutes. The AuCu_3 nanotods were dispersed in 3 ml of toluene for storage.

Seed-mediated synthesis of Au-Cu-M nanorods:

1 mL of OLA and 2 ml of ODE were added to the AuCu_3 solution. AuCu_3 nanorods were dispersed in the mixture by sonication. For silver, the reaction solution was heated to 60 °C. Palladium and platinum trimetallic nanorods were synthesized at room temperature. After the desired temperature reached, 3 ml of the metal precursor solution was injected gradually into the reaction flask in 1 hour. The corresponding temperature was maintained during the synthesis and kept 5 more minutes after the injection.

The trimetallic nanorods were separated by adding 6 mL of ethanol, followed by centrifugation at 5000 rpm for 5 minutes. The resulting product was dispersed in toluene.

Ligand exchange for Au-Cu-M nanorods:

10 mg of PEG-SH/PEG-NH₂ was dissolved in 5 ml of chloroform in a 25 ml vial. The vial was capped with parafilm, covered with tin foil and stirred with a magnetic bar for 10 minutes at room temperature. 2 mL of the nanorod solution was added dropwise to the polymer solution while stirring. The solution was bubbled with nitrogen for 5 minutes and stirred overnight. The nanorods were then precipitated with hexane and washed with ethanol and water. The nanorods were first dispersed in ethanol. After evaporation of the solvent, the mass of the nanorods was determined. The nanorods were redispersed in DI water to a concentration of 1 mg/ mL.

Catalytic measurement of the reduction of p-nitrophenol:

1.4 mM p-nitrophenol and 0.42 M NaBH₄ were prepared separately as stock solutions. 0.5 mL of the p-nitrophenol stock solution was mixed with 7.0 ml of DI water. Then 1.0 ml of NaBH₄ stock solution was added during stirring. 200 microL of the nanorod solution at a concentration of 1 mg/mL was added to the solution. 2.0 mL of the reaction solution was immediately transferred to a quartz cuvette and absorption spectra were measured by UV-Vis spectrometer at different time intervals.

Characterization

UV-Vis spectra were measured with a Cary 60 (Agilent Technologies) UV-Vis spectrometer. Transmission electron microscopy (TEM) images, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray (EDX) mapping images were all obtained using a FEI-Talos microscope at an accelerating voltage of 200 kV.

The concentrations of metal elements were measured with an Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS) with a helium collision cell. Samples and standards were matrix matched with trace metal grade HNO₃ and HCl. Standards, QC checks and spike solutions were prepared from high purity standards (VHG Labs, Inc., Manchester, NH). Scandium, Indium and Bismuth were used as internal standards. QC samples, internal standards and spike recoveries were within 20 percent or better of expected values.

X-ray photoelectron spectroscopy (XPS) characterization of the synthesized materials were done on a PHI model Quantum 2000 spectrometer with scanning ESCA multiprobe (F Physical Electronics Industries Inc.), using Al K α radiation ($\lambda=1486.6$ eV) as the radiation source. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 187.85 eV and 29.35 eV for recording survey and high resolution spectra, respectively. The thin film sample was pressed onto double sided carbon tape, mounted on an Al coupon pinned to a sample stage with a wash and screw then placed in the analysis chamber. Binding energies (BE) were measured for Au 4f, Cu 2p, Ag 3d, Pd 3d and Pt 4f. The XPS spectra obtained were analyzed and fitted using CasaXPS software (version 2.3.16). Sample charging effects were eliminated by correcting the observed spectra with the C 1s BE value of 284.8 eV.

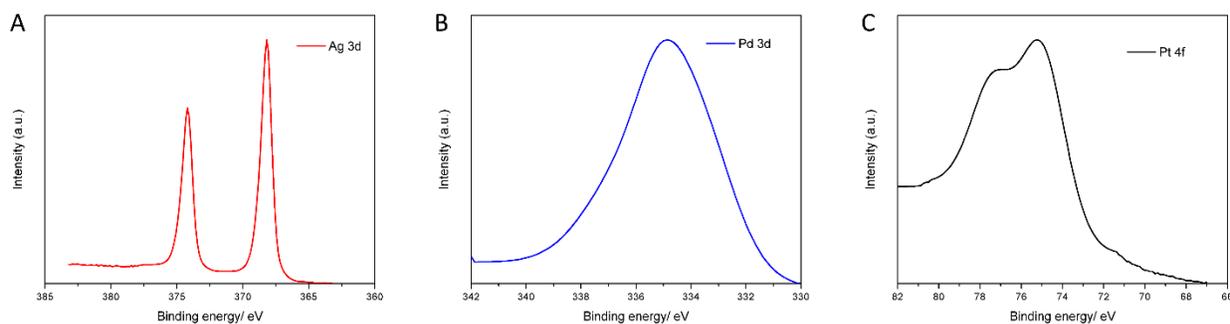


Figure S1. XPS spectra of Ag 3d in AuCuAg (A), Pd 3d in AuCuPd (B) and Pt 4f in AuCuPt (C) nanoalloys.

Table. S1 Atomic ratio of metal elements in PEG-SH capped alloyed metal nanoparticles derived from ICP-MS data.

Samples	Cu (%)	Au (%)	The third metal (%)
AuCu ₃ @PEG-SH	56.53	43.47	N/A
AuCuPt@PEG-SH	65.72	34.07	0.21 (Pt)
AuCuPd@PEG-SH	59.20	40.58	0.22 (Pd)
AuCuAg@PEG-SH	48.68	37.3	13.59 (Ag)

Table. S2 Catalytic property data of Au-Cu based multimetallic catalysts

Catalyst	Induction time/ min	Rate constant/ s ⁻¹	^b Mass activity/ s ⁻¹ mg ⁻¹	Contribution of AuCu/ s ⁻¹ mol ⁻¹	Mol activity of the third metal/s ⁻¹ mol ⁻¹
AuCu ₃ @PEG-SH	<1	0.0025	0.0125	1.73×10 ⁵	N/A
AuCuPt@PEG-SH	<1	0.0280	0.140	^a 1.73×10 ⁵	4.64×10 ⁷ (Pt)
AuCuPd@PEG-SH	<1	0.0293	0.146	^a 1.73×10 ⁵	5.21×10 ⁷ (Pd)
AuCuAg@PEG-SH	16	0.0057	0.0284	^a 1.73×10 ⁵	1.71×10 ⁶ (Ag)

^a assuming the mol activities of Au-Cu part in bimetallic and trimetallic nanoalloys are the same.

^b based on the mass of PEG-SH capped alloyed metal nanorods.

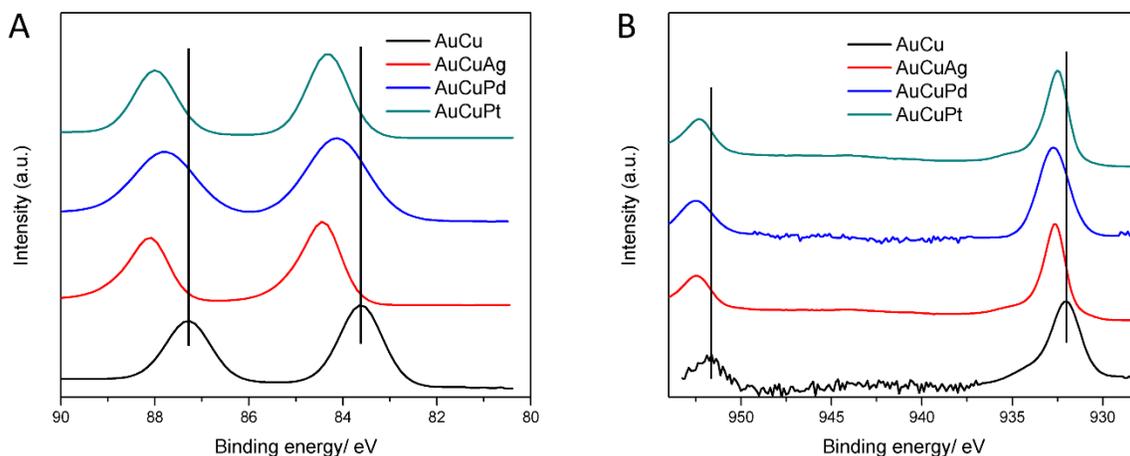


Figure. S2 XPS spectra of Au 4f (A) and Cu 2p (B) of AuCu, AuCuAg, AuCuPd and AuCuPt nanoalloys.

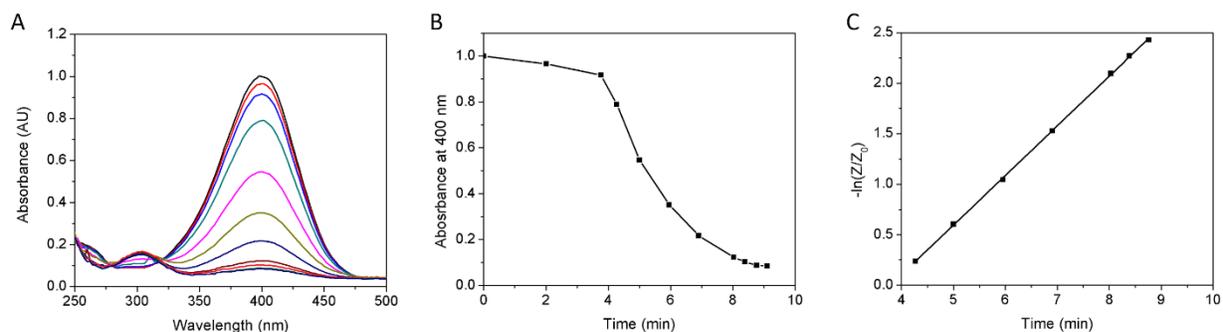


Figure. S3 (A) Time-dependent UV-Vis absorption spectra of p-nitrophenol reaction solution during the reduction with PEG-NH₂ capped Au-Cu-Ag nanorods, (B) normalized absorption of p-nitrophenol in presence of PEG-NH₂ capped Au-Cu-Ag nanorods vs. time, (C) the natural log of the normalized absorption of p-nitrophenol vs time of PEG-NH₂ capped Au-Cu-Ag nanorods.

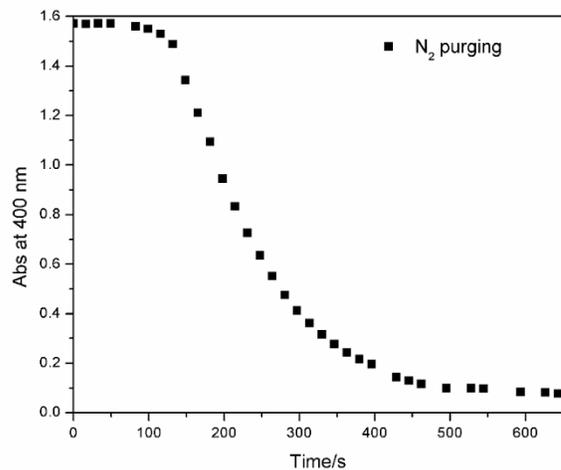


Figure. S4 Absorption of nitrophenol in the presence of PEG-SH capped Au-Cu-Ag nanorods vs. time in N₂ saturated DI water.

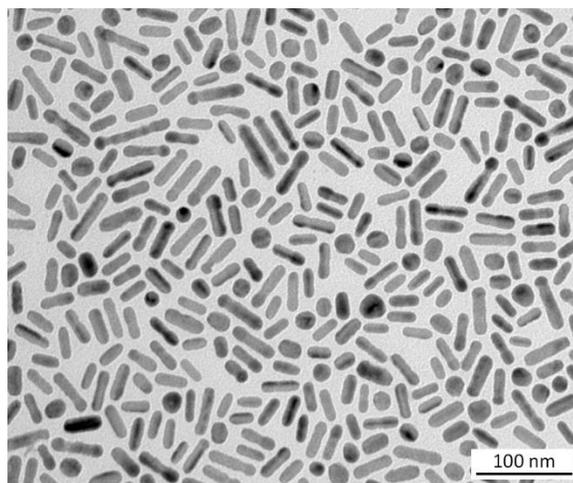


Figure. S5 TEM image of AuCu₃ nanorods.

Reference

1. S. Chen, S.V. Jenkins, J. Tao, Y. Zhu, J. Chen, *J. Phys. Chem. C*, 2013, **117**, 8924-8932.
2. S. Thota, S. Chen, Y. Zhou, Y. Zhang, S. Zou, J. Zhao, *Nanoscale*, 2015, **7**, 14652-14658.