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Studying the Chemical, Optical and Catalytic Properties of Noble Metal (Pt, Pd, Ag, Au)/Cu_2O Core-Shell Nanostructures Grown via General Approach

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Experimental details

2.1 Materials

$HAuCl_4 \cdot 3H_2O$ (99.9%), $AgNO_3$ (99%), $Pd(NO_3)_2 \cdot 2H_2O$ (Pd ~40%), polyvinylpyrrolidone (PVP Mw=55,000), hexadecyltrimethylammonium bromide (CTAB, ≥99%), $NaBH_4$ (≥99%), ascorbic acid (99%), sodium ascorbate (≥99.0%), sodium dodecyl sulfate (SDS, 99%), NH_2OH*HCl (99%), sodium sulfide hydrate ($Na_2S \cdot xH_2O$, >= 60%) and trisodium citrate dihydrate (99%) were purchased from Sigma Aldrich. $H_2PtCl_2 \cdot 6H_2O$ (99.9%) and $CuCl_2$ (97%) were purchased from Strem. ethylene glycol (EG, 99%) was purchased from Alfa Aesar. All chemicals were used as received.

2.2 Synthesis of Pt Nanocubes

Pt Nanocubes coated with PVP with an edge length of ~8 nm were synthesized according to a known procedure with some modifications.[1] 2.5 mL of EG were refluxed for 5 min. After that, a total volume of 3 mL of 0.375 M PVP solution in EG, and 1.5 mL of 0.0625 M $H_2PtCl_2 \cdot 6H_2O$ solution in EG were added over a 16 min period, in 30 sec intervals. The mixture was then refluxed for another 5 min. The product was collected and triple amount of acetone was added in RT. The solution was then centrifuged at 3000 rpm for 10 min. The precipitation was re-dispersed in ethanol and a triple amount of hexane was added. The solution was centrifuged again at 3000 rpm for 10 min. The precipitation was re-dispersed in ethanol and the process was repeated. Finally, the product was dissolved in water for further use.

2.3 Synthesis of Au Nanorods

Au NR coated with CTAB were synthesized according to a procedure published elsewhere.[2] First, Au seeds were synthesized as followed: 0.125 mL of 0.01 M $HAuCl_4$ solution and 5 mL of 0.1 M CTAB solution in water were mixed at 30^{o}C. Then, 0.3 mL of 0.01 M ice cold $NaBH_4$ solution was added and the mixture was stirred for 5 min. The formed seeds were used as received. Secondly, 1 mL of 0.01 M $HAuCl_4$ solution, 0.2mL of 0.01 M $AgNO_3$ solution and 20mL of 0.1M CTAB solution in water were mixed at 30^{o}C. 0.4 mL of 1 M HCl solution was added in order to bring the solution to pH of about 3-4. Then, 0.16 mL of 0.1 M ascorbic acid solution and 48 µL of the seeds solution were added and the mixture was stirred for 2 hr. The product was collected by centrifuge at 8500 rpm for 15 min and redispersed in water. The cleaning procedure was repeated twice.

2.4 Synthesis of Pd Nanocubes

Pd nanocubes coated with CTAB with an average edge length of ~17 nm were synthesized according to a procedure published elsewhere.[3] 0.1820 g CTAB and 0.0099 g of sodium ascorbate were dissolved in 15 ml H_2O (18MΩ) and heated to 50^{o}C while stirring. Then, 0.0108 g $Pd(NO_3)_2 \cdot 2H_2O$ in 5 ml H_2O were added quickly and the solution was stirred at 50^{o}C for 30 min. after 30 min, the particles were centrifuged twice (7500 rpm, 15min) and redispersed in water.

2.5 Synthesis of Ag Spherical Nanoplates

Ag spherical nanoplates coated with CTAB were synthesized according to a known procedure with some modifications.[4] 0.2 ml of 0.01 M $AgNO_3$ solution and 8 ml of 0.00125 M solution of trisodium citrate were mixed in a glass vial. Then, 0.24 ml of 0.01 M $NaBH_4$ ice-cold solution was added dropwise to the soultion under vigorous stirring. The mixture was then stirred slowly for 3 min and left for 30 min. In order to passivate the formed Ag nanoparticles in CTAB, an excess amount of CTAB (~140 mg) was added to the reaction vial, resulting in the change of the solution's color from yellow to orange. The solution was heated slightly in order to dissolve the CTAB and stirred for ~10 min. The Ag nanoparticles were later used for Cu_2O growth without further cleaning.

2.6 Synthesis of Metal-Cu_2O Core-Shell Nanostructures

Core-shell nanostructures were synthesized based on a known procedure, with modifications.[5] In a typical synthesis, the following were added to the reaction vial: (9.55-X) mL of deionized water, 0.1 mL of $CuCl_2$ solution, 87 mg SDS, 0.1 mL of metal nanoparticles from stock solution, 0.25 mL NaOH 1 M, and X mL of 0.2 M $NH_2OH\cdot HCl$ solution. Concentration of the $CuCl_2$ solution varied from 0.001 M to 0.1 M. Value of X (represent the amount of reducing agent solution that was added) varied from 0.15 mL to 0.65 mL. The solution was aged for 2 hr to form the hybrid nanostructures. The product was collected by centrifuging the solution 4 times at 3000 rpm for 10 min, and redispersing the precipitation in either water or ethanol.

2.7 Synthesis of Metal-Cu_2S Core-Cage Nanostructures

The procedure for transforming metal-Cu_2O core-shell nanocrystals to metal-Cu_2S hollow core-cage nanocrystals is based on a known procedure.[6] 2 ml of metal-Cu_2O dispersed in ethanol were put in a glass vial and placed in an ice bath. The solution was stirred slowly while 5 µL of a 0.2 M $Na_2S\cdot H_2O$ solution were added. The mixture was left to stir for 30 sec, and the particles were separated by centrifugation (3000 rpm, 15 min) and redispersed in ethanol. Later, 10 µL of 2 M HCl solution were added, and the mixture was shaken for a few seconds. The particles were cleaned again by centrifugation and redispersed in ethanol.

2.8 Catalytic Measurements: Reduction of 4-Nitrophenol

240 µL of 0.01 M 4-nitrophenol solution were added to 24 ml of DI H_2O (18MΩ). Then, 960 µL of 0.1 M $NaBH_4$ solution were added, resulting in the change of the solution's color from color-less to bright yellow. Finally, Pt nanocubes or Pt@Cu_2O nanostructures were added from stock solutions and the mixture was stirred for a few seconds. Absorption measurements were conducted by taking 800 µL aliquots from the solution and recording their absorption spectrum between 200-600 nm. Time difference between the absorption measurements was 2 min.

2.9 Characterization Methods

Transmission Electron Microscopy (TEM) images were obtained by a Tecnai 12 TWIN (FEI) microscope. The microscope operated at 120 kV. High Resolution TEM images and Energy Filtered TEM images were obtained by a JEOL TEM 2100-F microscope operated at 200 kV. XRD data was collected using Philips 1050/70 diffractometer with CuKα radiation operating at 40 kV 30 mA. UV-Vis absorption spectra were taken by a Cary 5000 UV-Vis-NIR spectrophotometer

References

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S1

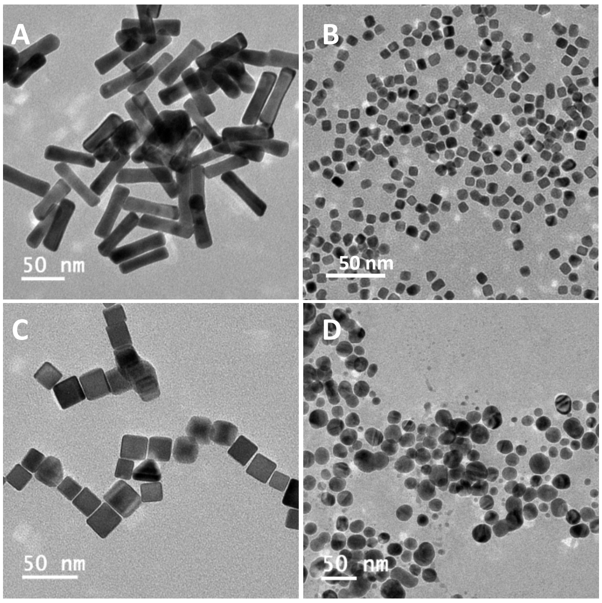

Figure S1. TEM images of the metals cores before the growth of Cu_2O shell, (A) Au nanorods capped with CTAB (B) Pt nanocubes capped with PVP (C) Pd nanocubes capped with CTAB (D) Ag spherical nanoplates capped with CTAB.

S2

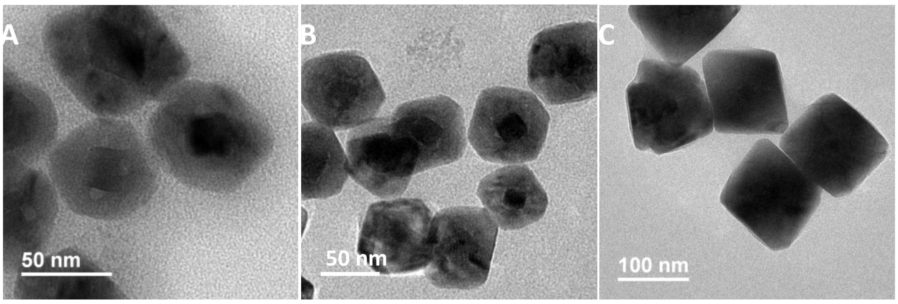

Figure S2. Thickness control of the Cu_2O shell on Pd-Cu_2O nanostructures. Average size of the Pd-Cu_2O hybrid nanocrytals is estimated as: (A) 60 nm (B) 70 nm (C) 155 nm. Ratio of the Cu salt amount in (A)-(C) is 1:2:20

S3

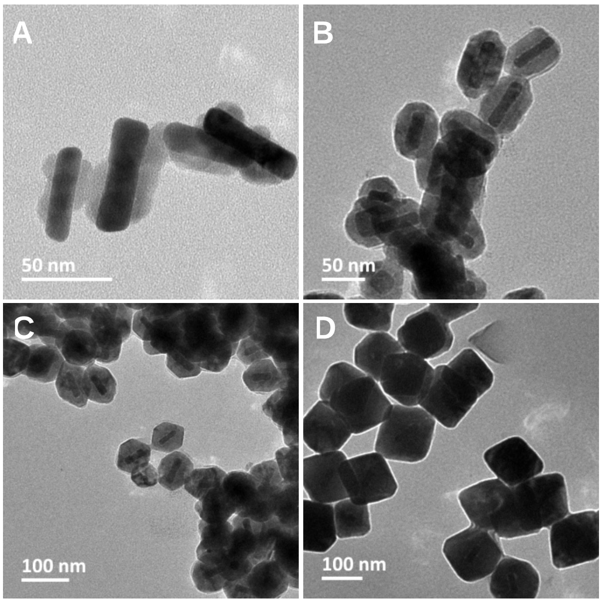

Figure S3. Thickness control of the Cu_2O shell on Au-Cu_2O nanostructures. Average thickness of the Cu_2O shell is estimated as: (A) 9 nm (B) 17 nm (C) 27 nm (D) 65 nm. Ratio of the Cu salt amount in (A)-(D) is 1:10:50:100