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Regiospecific growth of Au on a concave PtZn nanocube to form an Au-PtZn surface mosaic nanocube and an Au-PtZn octapod

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Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology and a JEOL ARM200F Cs STEM. The SERS spectra were recorded using a Horiba Aramis Raman spectrometer coupled to a Olympus microscope with 100x objectives (N.A.=0.90). The 633 nm excitation (17 mW at the sample) was from a Helium-Neon laser and used with D1(Transmission 10%) filter having a grating of 1800 lines per millimeter. The backscattered Raman signals were collected on a multichannel air cooled (-70 °C) CCD detector. The scattering spectra were recorded in the range of 1000-1700 cm⁻¹, and collected after 60 s of accumulation in one acquisition. Fourier transform infrared (FT-IR) spectra of all the sample solutions were measured by using a Varian 640-IR spectrometer in the range of 1200-3400 cm⁻¹ with a 1 cm⁻¹ resolution. The sample spectra were background corrected by subtracting the spectra of the reference solutions from those of the sample solutions. All FT-IR spectra were measured at 19.0 °C

Experimental Section

Preparation of PtZn concave cube structure. (Figure 1a)

A slurry of Pt(acac)² (0.02 mmol, Aldrich, 97%), Zn(OAc)² (0.01 mmol, Aldrich, 99.99%), stearic acid (0.49 mmol, Aldrich, 95%) and ocatdecylamine (15.0 mmol, Aldrich, 97%)) was prepared in a 100 mL Schlenk tube with a magnetic stirring bar. The tube was placed in the oil bath and heated to 90 °C. After 10 min, the Schlenk

tube was evacuated for another 10 min and purged with CO gas. Resulting reaction mixture was heated up to 260 °C and kept at that temperature for 15 min under CO gas. Finally, dark black precipitates could be obtained by cooling down the solution to room temperature and then by centrifugation with added methanol/toluene (v/v = 10 mL/15 mL).

Preparation of filled-concave Au-PtZn cube structure. (Figure 1b)

A slurry of PtZn concave cube as prepared (~10 mg), HAuCl₄·xH₂O (0.01 mmol, Aldrich, 99.999%) and oleylamine 2 mL (Aldrich, 70%) was prepared in a 100 mL Schelenk tube with a magenetic sirring at 90 °C for 10 min. Then, the tube was evacuated for another 10 min and purged with Ar gas. Resulting reaction mixture was heated up to 70 °C and kept that temperature for 8 hours Ar condition. Finally, dark black precipitates was obtained by cooling down to room temperature and centrifugation with metahanol and toluene (v/v = 10 mL/15 mL).

Preparation of Au-PtZn octapods structure. (Figure 2)

A slurry of PtZn concave cube as prepared (~10 mg), HAuCl₄·xH₂O (0.02 mmol, Aldrich, 99.999%) and oleylamine 2 mL (Aldrich, 70%) was prepared in a 100 mL Schelenk tube with a magenetic sirring at 90 °C for 10 min. Then, the tube was evacuated for another 10 min and purged with CO gas. Resulting reaction mixture was heated up to 70 °C and kept that temperature for 8 hours CO condition. Finally, dark black precipitates was obtained by cooling down to room temperature and centrifugation with metahanol and toluene (v/v = 10 mL/15 mL).

Preparation of conjoined Au-PtZn octapods structure. (Figure 3c)

A slurry of PtZn concave cube as prepared (~10 mg), $HAuCl_4 \cdot xH_2O$ (0.04 mmol, Aldrich, 99.999%) and oleylamine 2 mL (Aldrich, 70%) was prepared in a 100 mL Schelenk tube with a magenetic sirring at 90 °C for 10 min. Then, the tube was evacuated for another 10 min and purged with CO gas. Resulting reaction mixture was heated up to 70 °C and kept that temperature for 8 hours CO condition. Finally, dark black precipitates was

obtained by cooling down to room temperature and centrifugation with metahanol and toluene (v/v = 10 mL/15 mL).

Preparation of substrate for SERS.

A slurry of a nanostructure (5 mg), 4-aminothiophenol (2.5×10^{-3} mmol. Aldrich, 97%), and toluene (20 mL, DAEJUNG, 99.5%) was prepared in a 100 mL Schlenk tube with a magnetic stirring at the room temperature. After purged with Ar gas, the mixture was strring for 12 hour. Finally, dark black precipitate was and then by centrifugation with added ethanol/toluene (v/v = 10 mL/15 mL), and then was redispersed in 10 mL toluene. 5 mL aliquot of the 4-ATP-loaded AuPtZn nanostructures was placed onto the 0.5 x 0.5 cm Si wafer drop-by-drop, allowing the slow evaporation of toluene. The Si substrate was finally further dried in vaccum chamber at room temperature for 24 h.



Fig. S1. (a) Low and (b) high resolution TEM images of PtZn concave cube. i) Corresponding FFT patterns along the zone axis of [110].



Fig. S2. TEM images of poorly defined Pt nanocrystals prepared under the same reaction condition without using Zn.



Fig. S3. Size distribution of PtZn concave cube, filled-concave Au-PtZn, and Au-PtZn octapod structures.



Fig. S4. Energy dispersive X-ray spectra of a) filled-concave Au-PtZn structure and b) Au-PtZn octapods (inset: corresponding HAADF STEM images. scale bar indicates 20 nm.).



Fig. S5. FT-IR spectra of PtZn concave cube, filled-concave Au-PtZn, and Au-PtZn octapod structures.



Fig. S6. TEM images of Au-PtZn structures formed at different reaction temperature a) 60 °C, b) 70 °C, c) 80 °C and d) 90 °C.



Figure S7. TEM images of Au-PtZn structures formed with different amounts of Au precuirsor a) 0.010 mmol, b) 0.015 mmol, c) 0.020 mmol, d) 0.025 mmol, e) 0.030 mmol, and f) 0.040 mmol.