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Supporting Information

Phosphine ligands-mediated kinetics manipulation of aqueous cation exchange: a case study on synthesis of Au@SnS_x core-shell nanocrystals for photoelectrochemical water splitting

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1. Experimental Section

Synthesis of Au colloids in aqueous phase: The Au seed solution was prepared by firstly mixing $HAuCl_4 \cdot 4H_2O$ (1.25 mL, 1 mM) and cetyltrimethylammonium bromide (CTAB, 2.5 mL, 0.15 M) aqueous solutions into a 50 mL of centrifuge tube, followed by the addition of ice-cold $NaBH_4$ (0.3 mL, 0.01 M) under vigorous magnetic stirring for 2 min. The resulting mixture was kept at 25 ^{o}C for 1 hour. The Au growth solution was prepared by dissolving $HAuCl_4 \cdot 4H_2O$ (0.8 mL, 0.01 M) and CTAB (6.4 mL, 0.1 M) into deionized water (32 mL). Subsequently, the ascorbic acid (3.8 mL, 0.1 M) solution was introduced, followed by the addition of the seed solution (40 μL) immediately.

Synthesis of Au@Ag_2S core-shell HNCs in aqueous phase: The as-prepared Au colloids were washed by deionized water, collected by centrifugation at 7000 rpm for 10 min, and re-dispersed in CTAB aqueous solution (10 mL, 25 mM). Ascorbic acid (AA, 0.7 mL, 0.1 M), $AgNO_3$ (0.01 M, 0.3 mL), and NaOH aqueous solution (1 mL, 0.1 M) were sequentially added to the obtained Au colloids solution at room temperature to grow an uniform Ag layer surrounding the Au colloids. The aqueous sulfur precursor was prepared by adding Na_2S aqueous solution (11.7 mL, 50 mM) and sulfur powder (32 mg) into a 50 mL of centrifuge tube, which forms a bright yellow solution after ultrasonication treatment. The mixture was then transformed into an autoclave (15 mL) and was kept at 80 ºC for 12 h. A desired volume (100 μL) of the resulting sulfur precursor solution was added into the formed Au@Ag core-shell colloids solution under magnetic stirring for 10 min and was then kept at room temperature for 1 h. The final resulting Au@Ag_2S core-shell colloids were washed by deionized water, collected by centrifugation at 7000 rpm for 10 min, and re-dispersed in CTAB aqueous solution (10 mL, 50 mM) for subsequent usage.

Cation exchange in aqueous phase to produce Au@SnS$_x$ core-shell HNCs: For the preparation of Au@Sn$_2$S$_3$ core-shell HNCs, SnCl$_2$·2H$_2$O aqueous solutions (0.068 mL, 0.01 g mL^{-1}) were added to the prepared Au@Ag$_2$S aqueous suspension, followed by the adding of tri-*n*-butylphosphine (TBP, 0.05 mL) dissolved in a minor amount of methanol. After stirring for 1 min, the mixture was transferred to a water bath and was kept at 60 °C for 2 h. The final colloids solution was washed by deionized water, collected by centrifugation at 7000 rpm for 10 min, and re-dispersed in pure water. For the preparation of Au@SnS$_2$ core-shell HNCs, similar procedures were employed except for the replacement of TBP with tri-*n*-octylphosphine (TOP, 0.05 mL) ligand.

Characterizations: Low-resolution transmission electron microscopy (TEM) images of the samples were obtained by HITACHI H-7650 (accelerating voltage of 80 kV) electron microscopy. In this process, aqueous sol samples were dropped onto a copper mesh (300 mesh, carbon support film), and dried at room temperature. High-resolution transmission electron microscopy (HRTEM) characterization and energy dispersive X-ray spectroscopy (EDX) analysis were performed using transmission electron microscopy (FEI Tecnai G2 F20 S-Twin, acceleration voltage of 200 kV) equipped with X-ray energy-dispersive spectroscopy detector. The inductively coupled plasma optical emission spectroscopy (ICP-OES) measurement was conducted over ThermoFisher IRIS Intrepid II XPS spectrometer. The powder X-ray diffraction measurements were performed using a Bruker D8 multiply crystals X-ray diffratometer (5° per min). The UV-Vis measurements were carried out on a Shimadzu UV3600 UV-Vis spectrophotometer at room temperature. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a PerkinElmer Physics PHI 5300 spectrometer. The visible Raman spectra were collected on a Renishaw inVia Raman microscope with a 532 nm excitation laser (power 1 mW) which focused on the sample area with a diameter of 2-3 mm and an integration time of 30 s.

Photoelectrochemical (PEC) measurements: The PEC measurements were performed using a standard three-electrode potentiostat system (CHI760c, Chenghua, Shanghai, China) with a Pt counter electrode and a Ag/AgCl reference electrode. The working electrode was prepared by spray coating (at a speed of 0.05 mL min^{-1}) Au@SnS$_x$ core-shell HNCs on the FTO substrate (1 cm × 2 cm) that has been previously cleaned with ethanol and water. The surface area of the sample exposed to the electrolyte was fixed at 1 cm^2. Prior to PEC measurements, the resulting Au@SnS$_x$/FTO photoanode was annealed in a N_2 atmosphere at 200 ^{o}C for 1 h to strengthen the contact between the active material and the substrate. An aqueous solution containing 0.5 M of Na_2S and 0.5 M of Na_2SO_3 was used as the electrolyte to maintain the stability of the sulfide electrodes. The working electrode was illuminated from the front side with a 300 W Xe lamp (PLS-SXE300, Beijing Perfectlight Technology) equipped with an optical filter (PLS-CUT420, $\lambda > 420$ nm), and the illumination intensity near the photoelectrode surface was 200 mW cm^{-2}. The electrochemical impedance spectroscopy (EIS) measurements were conducted with a frequency range from 100 kHz to 50 mHz and the modulation amplitude of 10 mV under illumination.

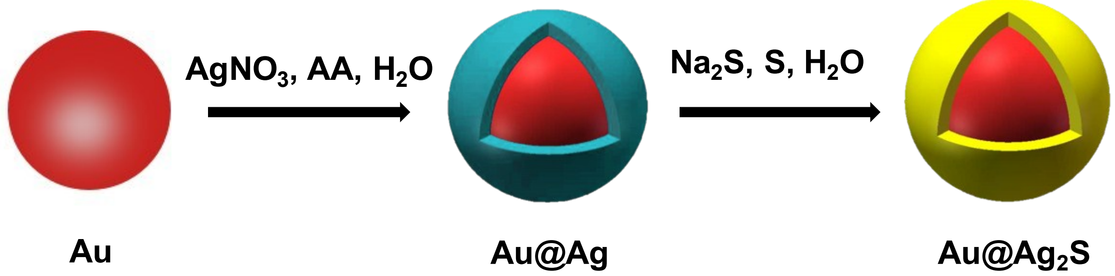
2. Supplementary Data

Table S1. Elemental composition of the core-shell HNCs determined by EDX elemental analysis.

Ligand	Atomic ratio (%)			
	Au	Sn	S	Sn : S
TBP	68.4	13.4	18.2	2.2 : 3.0
TOP	68.9	10.3	20.7	1.0 : 2.0

Table S2. Fitted binding energies and peak fwhm values (given in parentheses) of the Sn 3d core-levels for TBP and TOP-derived core-shell HNCs. All values are given in eV.

Ligand	Sn $3d_{3/2}$		Sn $3d_{5/2}$	
	Sn (II)	Sn (IV)	Sn (II)	Sn (IV)
TBP	494.1 (1.0)	494.7 (1.0)	485.6 (1.0)	486.2 (1.0)
TOP		494.9 (1.0)		486.5 (1.0)



Scheme S1 Schematic illustration for the synthetic process of Au@Ag_2S core-shell HNCs.

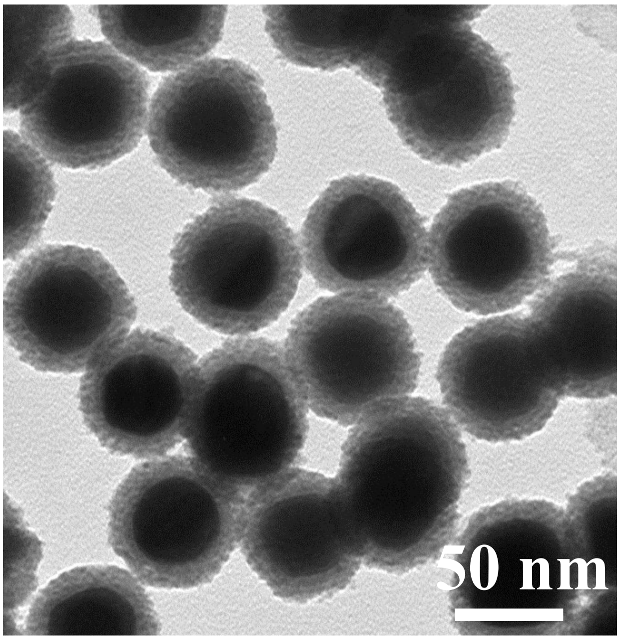


Figure S1 TEM image of the TBP-derived core-shell HNCs.

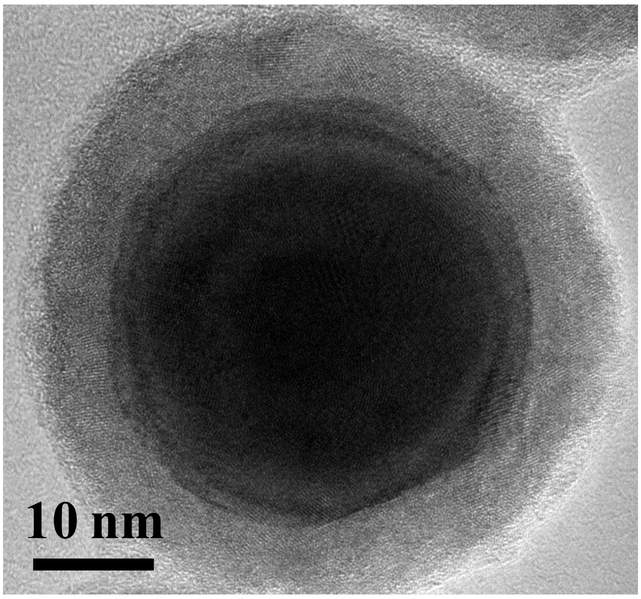


Figure S2 HRTEM image of the TOP-derived core-shell HNCs.

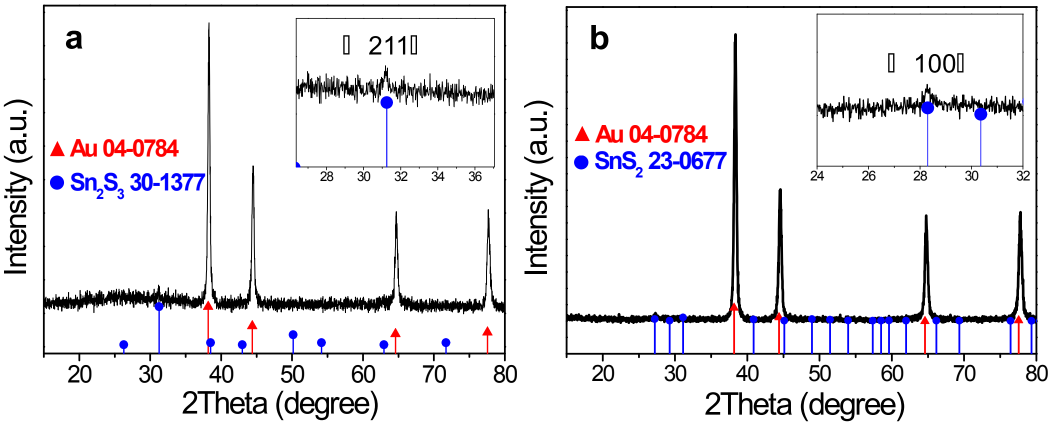


Figure S3 XRD patterns of the (a) TBP- and (b) TOP-derived core-shell HNCs.

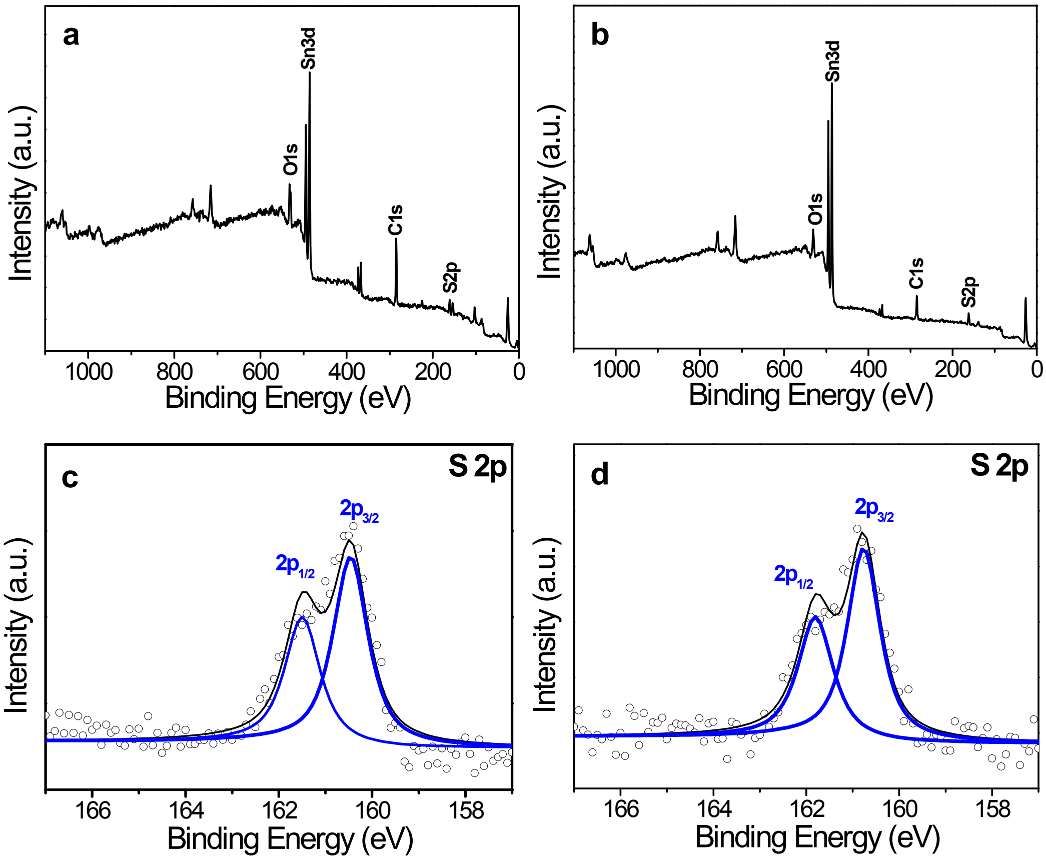


Figure S4 (a, b) XPS survey spectra and (c,d) high-resolution S 2p XPS spectra of the resultant core-shell HNCs using TBP (a,c) and TOP (b,d) as the ligands in cation exchange, respectively.