Supporting Information

Structural evolution induced by Au atom diffusion in Ag₂S

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Experiment section

Materials.
Silver nitrate (AgNO₃, 99%), hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 99.9%), element sulfur (≥99.5%), sodium borohydride (NaBH₄, 98%), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O, ≥99%), dodecylamine (DDA, 98%) were obtained from Shanghai Chemical Reagents, China. Oleylamine (>70%), 1,2,3,4-tetrahydronaphthalene (tetralin) and borane t-butylamine complex (TBAB) were purchased from Sigma Aldrich. All reagents were of analytical grade and used without further purification.

Synthesis.

Phase transfer of Ag ions from water to toluene: The transfer of Ag ions from water to toluene were according to the previously reported methods. [1] In a typical experiment, 50 mL of aqueous AgNO₃ solution (1 mM) were mixed with 50 mL of ethanol containing 1 ml of dodecylamine. After 3 min of stirring, 50 mL of toluene were added, and stirred for another minute. The Ag ion concentration in toluene assuming complete transfer of the ions from water was 1 mM. The Ag ions in toluene were separated from the aqueous phase, and kept for further experiments.

Synthesis of 5.0 nm Au seed nanoparticles and phase transfer from water to toluene: 5.0 nm Au were synthesized as reported. [1] Au nanoparticles were transferred from water to toluene following the approach used for the phase transfer of Ag ions. Typically, the citrate-stabilized Au hydrosol was mixed with 20 mL of ethanol containing 0.4 mL of dodecylamine. After 3 min of stirring, 20 mL of toluene were added and stirred for another minute.

Synthesis of core-shell Au@Ag₂S nanoparticles and the diffusion of Au in Ag₂S: The synthesis of Au@Ag₂S was reported with a minor modified. [1] 10 mL of Ag (I) ions in toluene were mixed with 4 mL of Au organosol in toluene. Next, 2 mg of elemental sulfur were added under vigorous stirring; stirring was continued for another 8 h. For the synthesis of Ag₆Au₅S₃-AuAgₓ, 10 mL of Ag (I) ions in toluene were mixed with 2 mL of Au organosol. The core-shell Au@Ag₂S organosol in toluene was then hydrothermal treatment at 60°C for 90 minutes to complete the diffusion process.

Synthesis of Ag₂S nanocrystals: 5 mL of Ag (I) ions in toluene and 2 mg of elemental sulfur were mixed with stirring for 8 h.

Characterization.

X-ray photoelectron spectroscopy (XPS) spectra were taken on a Thermo ESCALAB MKIII instrument equipped with a Mg Kα (hv =1253.6 eV) X-ray source. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.6 eV. Transmission electron microscopy (TEM) images were acquired on a Hitachi H7700 transmission electron microscope at...
an acceleration voltage of 100 kV. Aberration-corrected High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEOL JEM-2010 LaB6 high-resolution transmission electron microscope operated at 200 kV. The in situ X-ray diffraction (XRD) patterns of samples were recorded on a diffractometer (Rigaku, Smartlab, Pt film as the base) operating at 45 kV voltage and 200 mA current with Cu Kα radiation (λ = 1.5418 Å).

**Water Splitting.**

All the electrochemical experiments were conducted on the electrochemical workstation (CHI660E, Chen Hua Instruments, China) in a three-electrode system in 0.2M Na$_2$SO$_4$ solution at room temperature. Samples were tested on the glassy carbon electrode (GCE, 0.07065 cm$^2$ in area) as the working electrode, Ag/AgCl as the reference electrodes and a Pt wire as the counter electrode. 2 mg catalysts were dispersed in 400 µL of water/ethanol/Nafion solution (v/v/v=196/196/8) by sonication for 30 min. Then, 5 µL well-dispersed catalysts (0.35 mg/cm$^2$) were dropped on the glassy carbon electrode with drying naturally for test. The 300 W Xenon lamp light source (PLS-SXE 300, Beijing Perfect Light Co. Ltd, China) with a 420 nm cutoff filter was used to provide the visible light illumination.

**Figure S1.** TEM images of (a) Au and (b) Au@Ag$_2$S NPs. XRD patterns of (c) Au and (d) Au@Ag$_2$S NPs.
Figure S2. Atomic resolution aberration corrected HAADF-STEM image (a) and TEM images (b) of AuAgS-AuAg₅.

Figure S3. The simulated (a) and standard (b) XRD of AuAgS.

Figure S4. In-situ XRD patterns of structure evolution of Au@Ag₂S from 78 min to 114 min.
**Figure S5.** XPS spectra of (a) Au, (b) Au@Ag$_2$S and (c) AuAgS-AuAg$_x$ NPs.

**Figure S6.** TEM image (a), and XRD pattern (c) of AuAgS-AuAg$_x$ NPs. TEM image (b) and XRD pattern (d) of Ag$_3$AuS$_2$-AuAg$_x$ NPs.
Figure S7. Particle size average histograms for 1.7 ± 0.4 nm Au (a), 3.1 ± 0.3 nm Au (e), 5.0 ± 0.3 nm Au (i); TEM images for 1.7 ± 0.4 nm Au (b), 3.1 ± 0.3 nm Au (f), 5.0 ± 0.3 nm Au (g); TEM images of AuAgS-AuAg\textsubscript{x} hybrid NCs obtained by 1.7 ± 0.4 nm Au (c), 3.1 ± 0.3 nm Au (g), 5.0 ± 0.3 nm Au (k); XRD patterns of AuAgS-AuAg\textsubscript{x} hybrid NCs obtained by 1.7 ± 0.4 nm Au (d), 3.1 ± 0.3 nm Au (h), 5.0 ± 0.3 nm Au (l).

Figure S8. The UV-vis diffuse reflectance spectra (DRS) of Ag\textsubscript{2}S, Ag\textsubscript{2}AuS\textsubscript{2}-AuAg\textsubscript{x} and AuAgS-AuAg\textsubscript{x}.
Figure S9. Time-dependent photocurrent measurement at an applied voltage of 0.4 V under the visible light illumination.

References