Supporting Information

Structural evolution induced by Au atom diffusion in Ag_2S

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Experiment section

Materials.

silver nitrate ($AgNO_3$, 99%), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), element sulfur (≥99.5%), sodium borohydride ($NaBH_4$, 98%), sodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, ≥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 $AgNO_3$ 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@Ag_2S nanoparticles and the diffusion of Au in Ag_2S: The synthesis of Au@Ag_2S 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 Ag_3AuS_2-$AuAg_x$, 10 mL of Ag (I) ions in toluene were mixed with 2 mL of Au organosol. The core-shell Au@Ag_2S organosol in toluene was then hydrothermal treatment at 60°C for 90 minutes to complete the diffusion process.

Synthesis of Ag_2S 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 MKⅡinstrument equipped with a Mg K_a (hν =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 K_a radiation (I = 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_2SO_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 uL of water/ethanol/Nafion solution (v/v/v=196/196/8) by sonication for 30 min. Then, 5 uL 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.

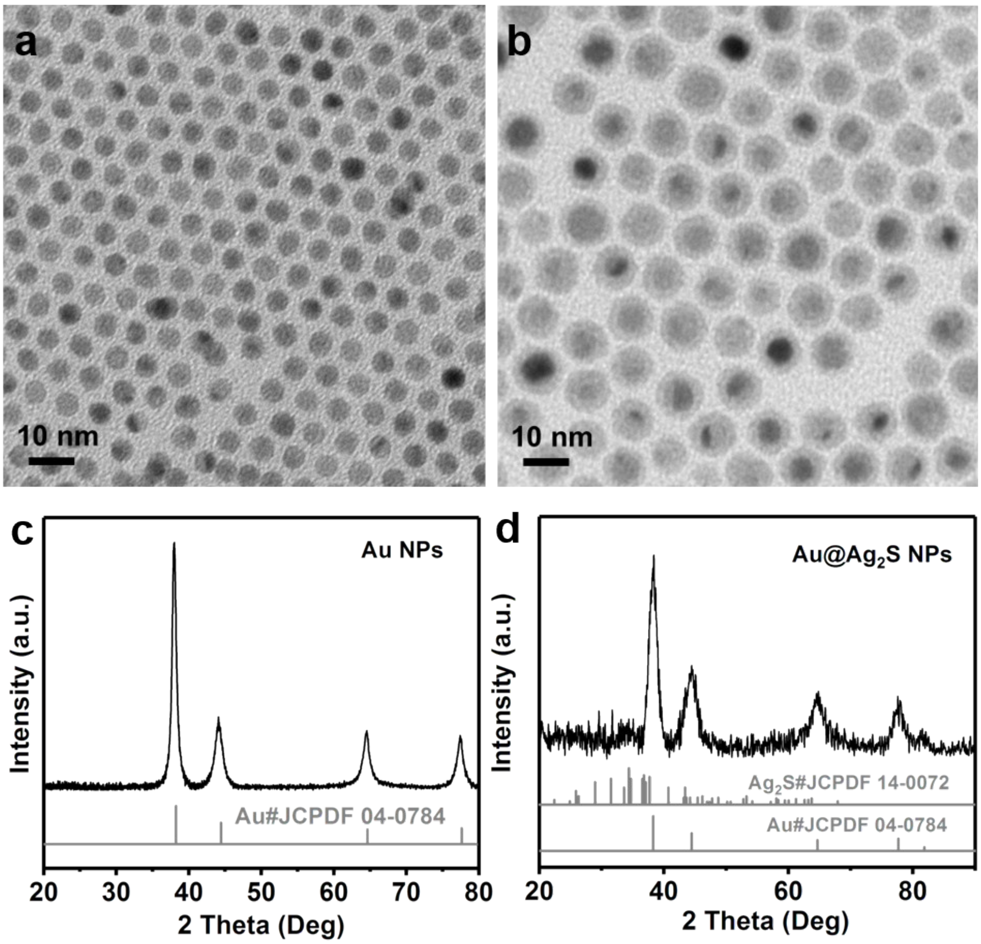

Figure S1. TEM images of (a) Au and (b) Au@Ag_2S NPs. XRD patterns of (c) Au and (d) Au@Ag_2S NPs.

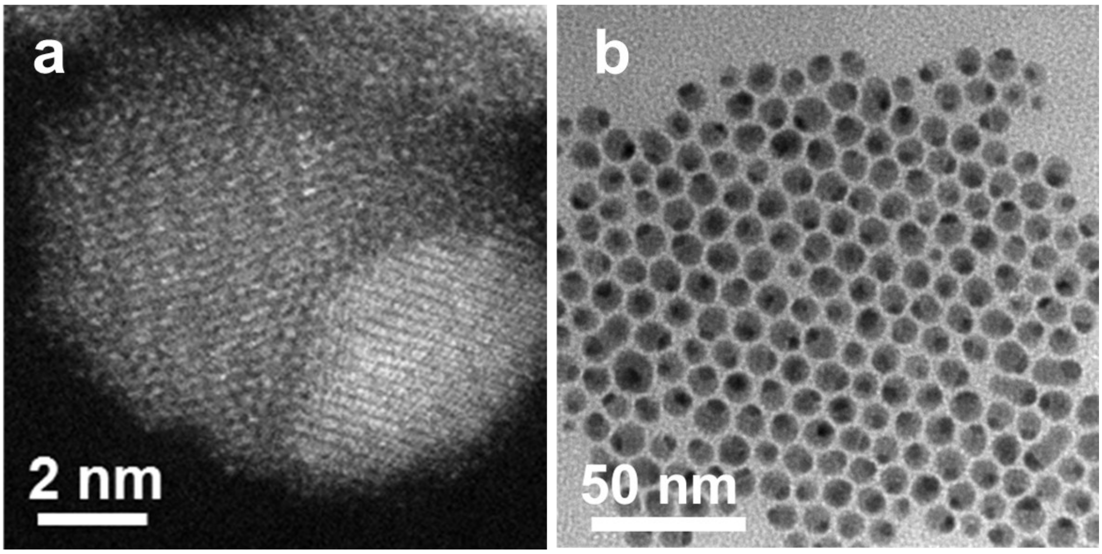

Figure S2. Atomic resolution aberration corrected HAADF-STEM image (a) and TEM images (b) of AuAgS-AuAg$_x$.

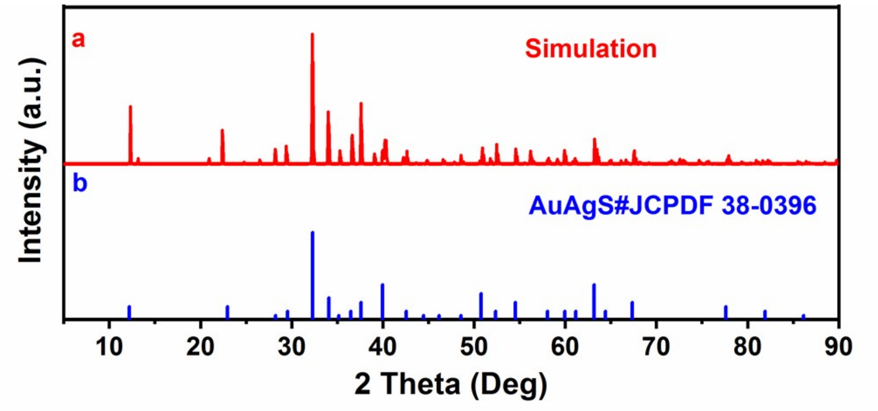

Figure S3. The simulated (a) and standard (b) XRD of AuAgS.

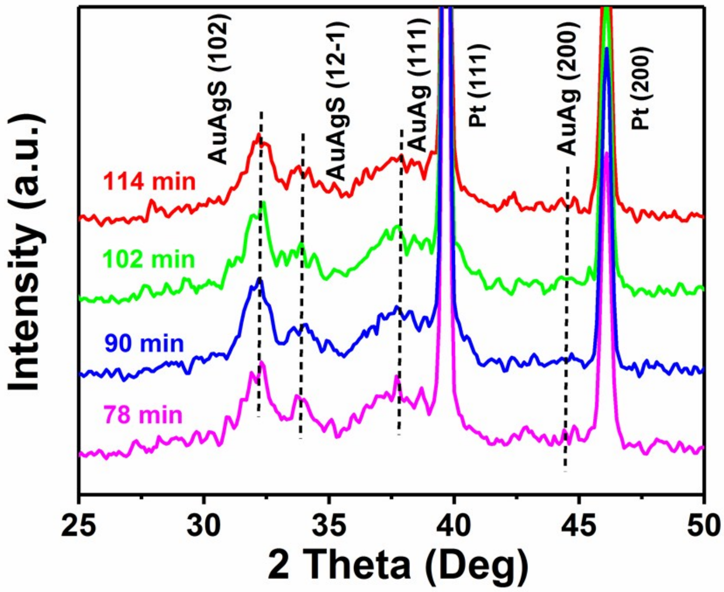

Figure S4. *In-situ* XRD patterns of structure evolution of Au@Ag$_2$S from 78 min to 114 min.

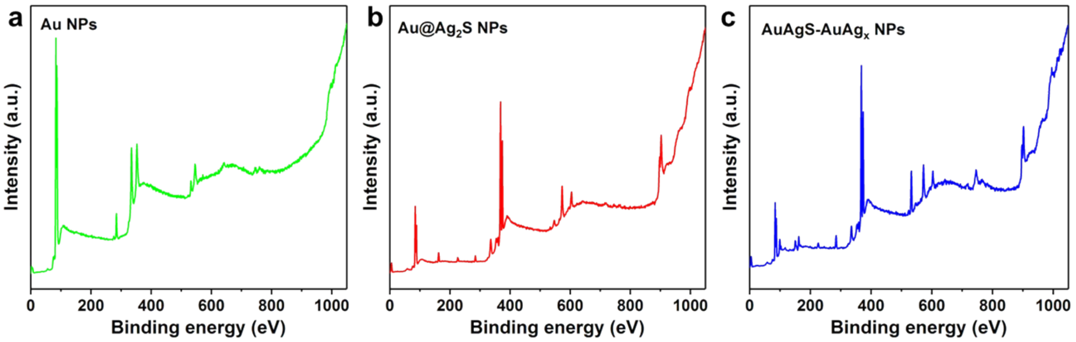

Figure S5. XPS spectra of (a) Au, (b) Au@Ag_2S and (c) AuAgS-$AuAg_x$ NPs.

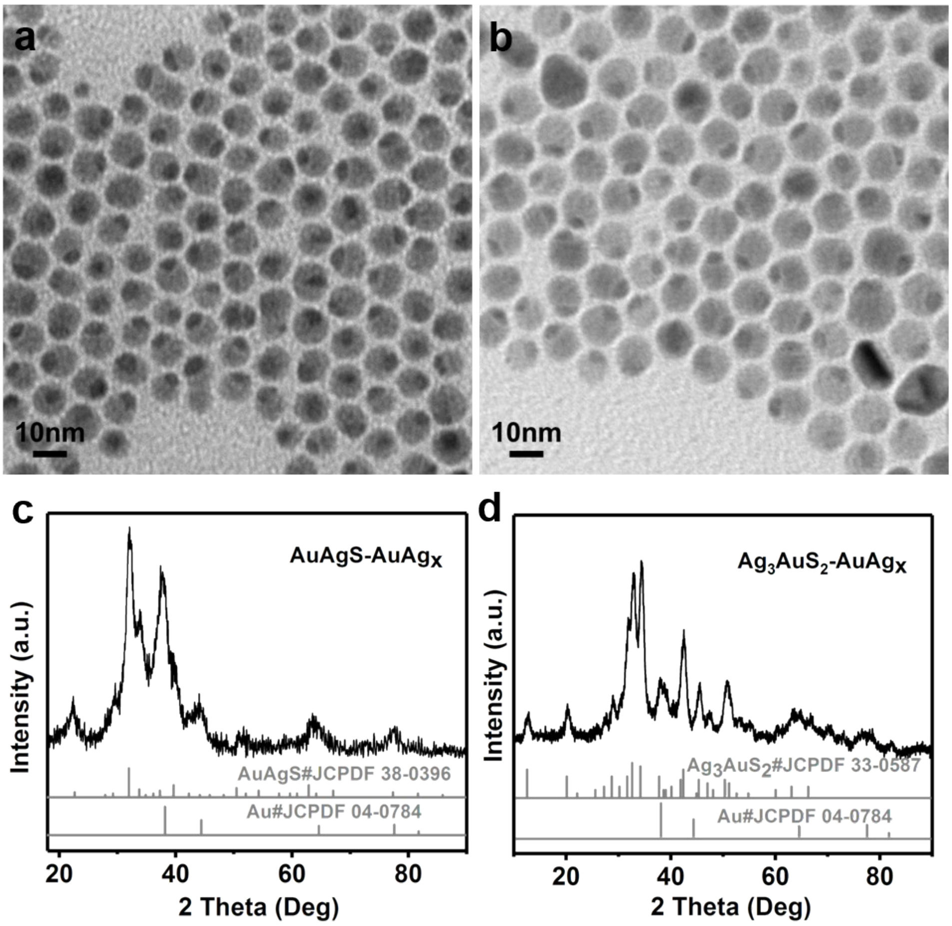

Figure S6. TEM image (a), and XRD pattern (c) of AuAgS-$AuAg_x$ NPs. TEM image (b) and XRD pattern (d) of Ag_3AuS_2-$AuAg_x$ NPs.

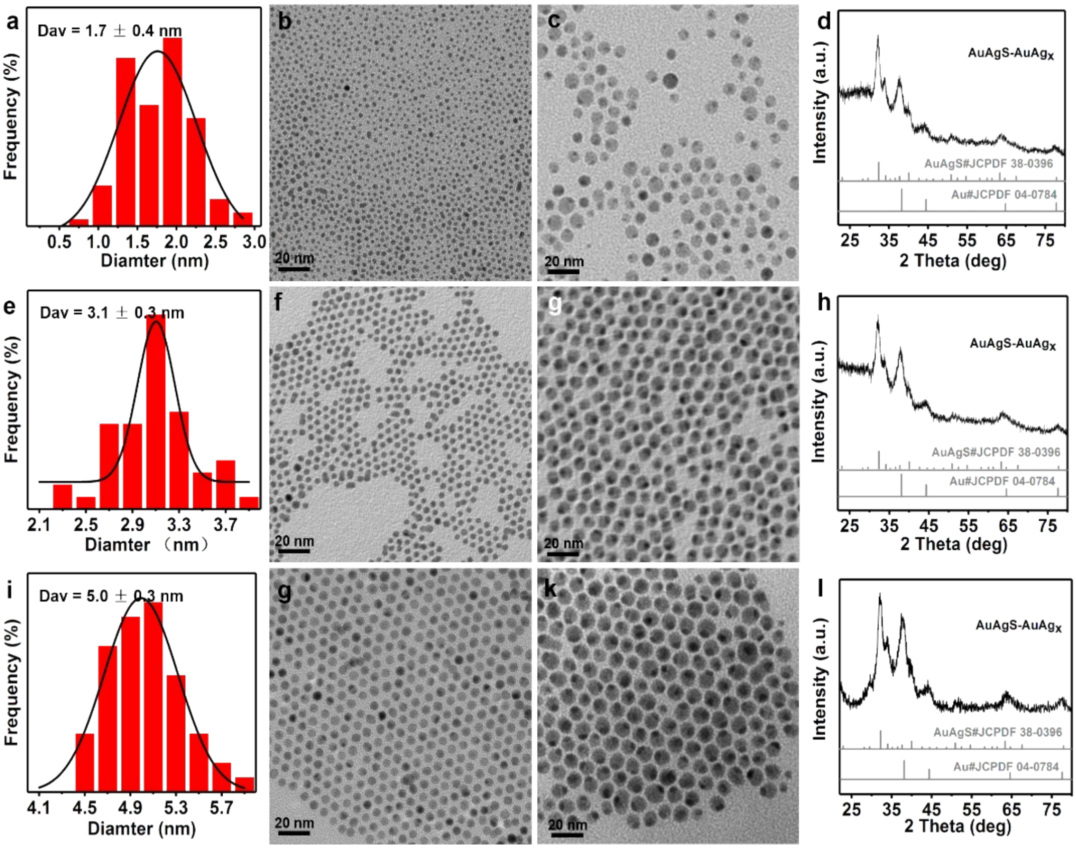

Figure S7. Particle size average histograms for 1.7 ± 0.4 nm Au (a), 3.1 ± 0.3 nm Au (e), 5.0 ± 0.3 nm Au (i); TEM images for 1.7 ± 0.4 nm Au (b), 3.1 ± 0.3 nm Au (f), 5.0 ± 0.3 nm Au (g); TEM images of $AuAgS$-$AuAg_x$ hybrid NCs obtained by 1.7 ± 0.4 nm Au (c), 3.1 ± 0.3 nm Au (g), 5.0 ± 0.3 nm Au (k); XRD patterns of $AuAgS$-$AuAg_x$ 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).

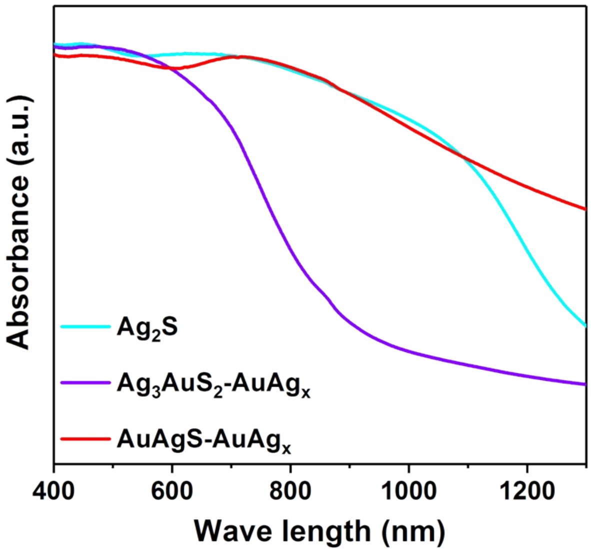

Figure S8. The UV-vis diffuse reflectance spectra (DRS) of Ag_2S, Ag_3AuS_2-$AuAg_x$ and $AuAg_S$-$AuAg_x$.

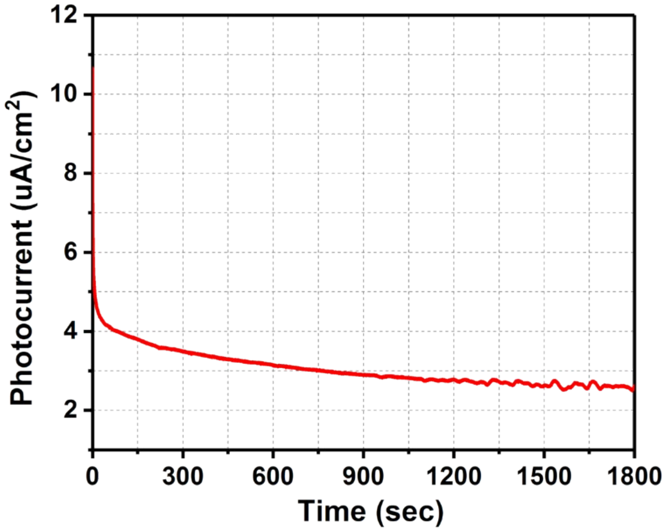

Figure S9. Time-dependent photocurrent measurement at an applied voltage of 0.4 V under the visible light illumination.

References

1. Yang, J.; Ying, J. Y. *J. Am. Chem. Soc.* **2010,** *132*, 2114-2115.