Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Heterostructure of AuAg Nanoparticle Tipping on Ag_2S Quantum Tube

Experimental section

1. Synthesis of ZnS NRs

All the reagents were analytical grade and used without further purification. In a typical synthesis of ZnS NRs, 0.5mmol $Zn(NO_3)_3.6H_2O$ (ACROS) and 0.5 mmol C_2H_5NS (ACROS) was dissolved into 4.0 mL octylamine (ACROS), 12.0 mL octanol (Tianjin Reagents Inc.) under agitation for 15 min at room temperature. After formation of a homogeneous solution, it was transformed into a Teflon bottle (20 mL). The Teflon bottle was sealed in a stainless autoclave and put into an oven at 220 °C for 3 h. After cooling to the ambient temperature, white precipitates at the bottom were separated by centrifugation with a speed of 5500 rpm, and washed by ethanol. The obtained precipitate was dried at 60 °C for further use.

2. Synthesis of HS1

ZnS NR powder of 22.8 mg was dispersed in 100 ml of cyclohexane to form a colloid solution. Otcylamine of 1.5 ml was added into 4 mL ZnS NR colloid solution with stirring for about 5 min at room temperature. Then, 60.8 mg of $AuCl_3$ (0.2 mmol) was dissolved in 100 ml ethanol to formation of gold growth solution (2 $mmol \cdot L^{-1}$). 4 mL of the gold growth solution was added in the above mixture solution, and the resulted mixture was stirred for about 10 min. After that, the mixture was transferred into a Teflon-lined autoclave. It's worth noting that the above procedures were carried out with avoiding light. The autoclave was sealed and maintained 100 ºC for 40min in an oven to obtain HS1. Then the autoclave containing HS1 was cooled to room temperature without any other treatment for the further synthesis of HS2. The yield of this synthesis is approximately 1.7 mg per autoclave.

3. Synthesis of HS2

5.3 μmol $AgNO_3$ (0.9mg) and 8mL cyclohexane were added into the Teflon bottle containing HS1 that obtained in the above step with agitation for 30 min at room temperature. Then the Teflon bottle was sealed in a stainless autoclave and put into an oven at 100 °C for 20min. After cooling to the ambient temperature, the precipitates at the bottom were separated by centrifugation with a speed of 5500 rpm, and washed by ethanol. The obtained HS2 product was dispersed in cyclohexane for posterior characterization. The yield of this synthesis is approximately 1.8 mg per autoclave.

4. Synthesis of Ag2S nanotubes for the contrast of photoelectrochemical (PEC) activity

ZnS NR powder of 22.8 mg was dispersed in 100 ml of cyclohexane to form a colloid solution. Then 4 mL ZnS NR colloid solution was added in a vessel and cooled to 0 °C. Then, 68 mg of $AgNO_3$ was dissolved in 100 ml ethanol to formation of silver solution (4 $mmol \cdot L^{-1}$). The 4 mL silver solution was added in the above 4 mL ZnS colloid vessel at 0 °C with stiring for 60 min. Then the mixture solution were centrifuged with a speed of 5500 rpm, and the precipitate were washed by ethanol. The procedures were carried out under avoiding light.

5. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2200 PC diffractometer with Cu Kα radiation (λ=1.5418Å) and graphite monochromator from 20º to 80º. The particle size and morphology of the resulting nanoparticles were characterized on a transmission electron microscopy (TEM, JEM100-CXII) equipped with selected area electron diffraction (SAED). The intrinsic crystallography of nanocrystals was observed by high-resolution TEM (HRTEM, FEI Tecnai G2 F30) fitted with scanning transmission electron microscopy (STEM) capability. X-ray photoelectron spectroscopy (XPS) analyses were applied to characterize the nanocrystals' components and surface. The XPS spectra were recorded on a PHI-5300 ESCA spectrometer (Perkin–Elmer) with its energy analyzer working in the pass energy mode at 35.75 eV, and the Al Ka line was used as excitation source. After subtraction of X-ray satellites and inelastic background (Shirley-type), peak deconvolution was carried out. Full width at half maximum (FWHM) was kept the same for chemical components within the same core level of an element, and all component peaks were set to be Gaussian-type. The steady-state absorption spectra were measured on a Shimidazu UV-3600 UV-VIS-NIR spectrophotometer. For measuring temporally and spectrally resolved fluorescence spectra, the second harmonic (400 nm, 120 fs, 1 kHz) of a regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) was used to excite the samples (liquid sample in a 10 mm cuvette) at the front surface with an incidence angle of 45°. Fluorescence collected along the direction normal to the sample surface was dispersed by a polychromator (250is, Chromex) and detected with a streak camera (C5680, Hamamatsu Photonics). The spectral resolution was 1.0 nm, and the temporal resolution at the desired time-delay range was about 200 ps. For twophoton pumped single-crystal lasing experiments, the excitation light came directly from the fundamental

(800 nm, 120 fs, 1 kHz) of the regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) with the excitation fluence adjusted by using a set of neutral density filters. Zeta potential was tested by Zetasizer nano ZS instrument (Malvern).

6. Fabrication of HS2 film on Fluorine doped Tin Oxide (FTO) glass

FTO glass substrates (1 cm × 2 cm) were cleaned with acetone and water, and dried by pure nitrogen. HS2 sample (0.5 μg) was dispersed in the ethanol (30 μL) with the assistance of sonication (at least 30 min) to form a homogeneous ink. Then, the catalyst ink were dropped onto on the surface of a washed FTO slide, afterwards, the HS2-coated FTO-glasses were heated at 65 ºC for 30 min to volatilize the solvent .

7. PEC measurement

The PEC experiment was carried out in air by measuring the photocurrent correlated with the water dissociation. To measure the photocurrent, an electrochemical workstation (CHI 660D) was employed with a three-electrode configuration (HS2/FTO, AgCl/Ag electrode and Pt-gauze electrode were used as the working, reference and counter electrodes, respectively) in 1.0 M CH_3OH (pH = 7.0). The CH_3OH electrolyte was purged with N_2 for 30 min prior to the measurement. A 350 W Xe lamp light source (80 $mWcm^{-2}$, DOLAN JENNER Model 150 Illuminator) coupled with an optical filter (λ> 400 nm) was used to provide the visible illuminationon the HS2/FTO. All the measurements were conducted in the ambient conditions.

Discussion of the process and mechanism

The process and mechanism of HS1 transferring to HS2 were investigated in this work. The ~5 nm diameter of AuAg alloy nanoparticles in HS2 was larger than that of gold nanoparticles in HS1 (~2 nm). So we believed that the AuAg alloy nanoparticles formed by ripening growth of gold nanoparticles with Ag$^+$ in the solution. On the other hand, the evolution from ZnS NR to Ag$_2$S QT is believed to be driven by Kirkendall effect, which has produced many hollow nanostructures.[1] It means that atomic diffusion occurs through vacancy exchange (not the direct interchange of atoms) at a solid/gas or solid/liquid interface, leading to the hollow nanostructure. Here, the Ag$^+$ ions adsorbed on the NRs surface, and reacted with ZnS to form an Ag$_2$S thin layer, made possible because Ag$_2$S is much more stable than ZnS. The inner S^{2-} ions in the ZnS NRs were separated from the outside Ag$^+$ in the bulk solution due to the Ag$_2$S thin layer, which blocked direct cation exchange between Ag$^+$ and ZnS. However, the Ag$^+$ ions diffused inward to react further with the outward S^{2-} ions to form Ag$_2$S at the solid/liquid interface motivated by the Kirkendall effect, resulting in a void formation in ZnS NR. Scheme 1b depicts the top-view of ZnS NR along the axial direction. There are only two or three layers of ZnS in the range of their ultrasmall diameter. Thus, S^{2-} diffusion from the inner layers to the surface of ZnS NR occurs quickly through vacancy exchange (Kirkendall effect) for the ultrashort diffusion distance. This intermediate mechanism is illustrated in Scheme 1c.

Fig. S1. XRD Pattern of ZnS NRs, and the bottom shows ZnS standard peaks (JCPDS card NO. 36-1450)

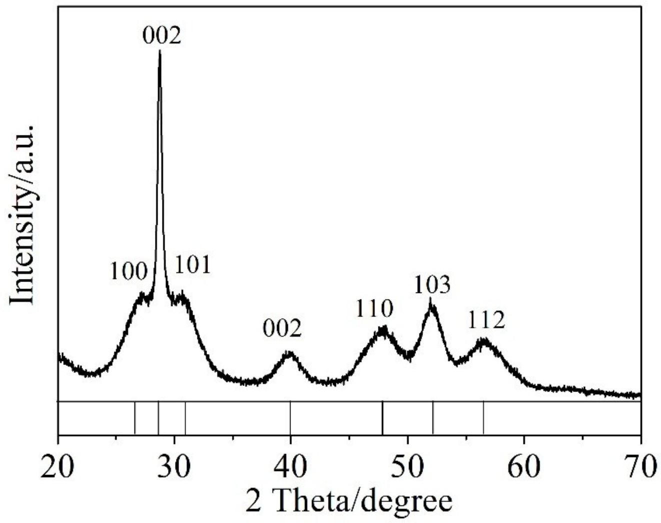


Fig. S2. XRD Pattern of HS1, and the bottom shows ZnS standard peaks (JCPDS card NO. 36-1450) and gold standard peaks (JCPDS card No.04-0784).

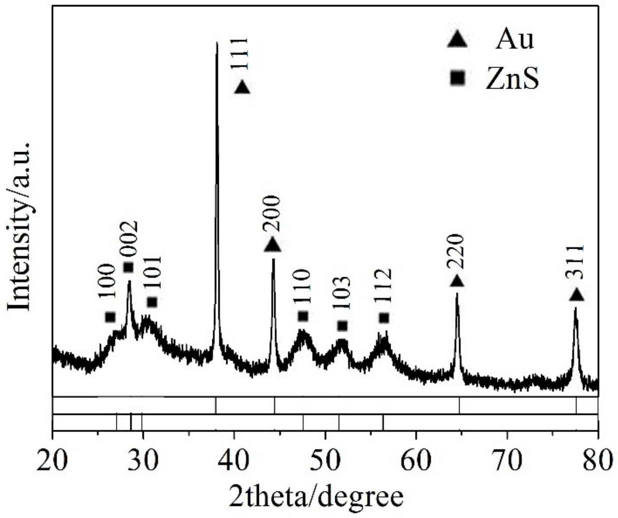


Fig. S3. XRD pattern of the prepared AuAg-Ag_2S heterostructure

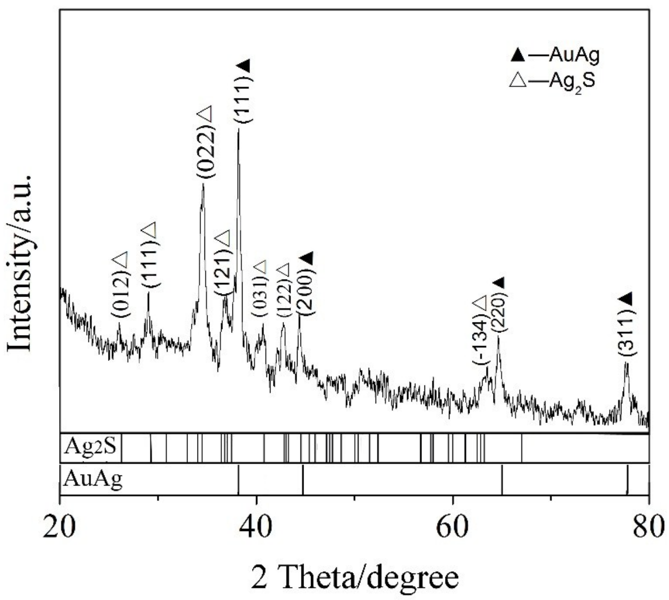


Fig. S4. HRTEM image of the gold nanoparticles tipping on ZnS nanorod

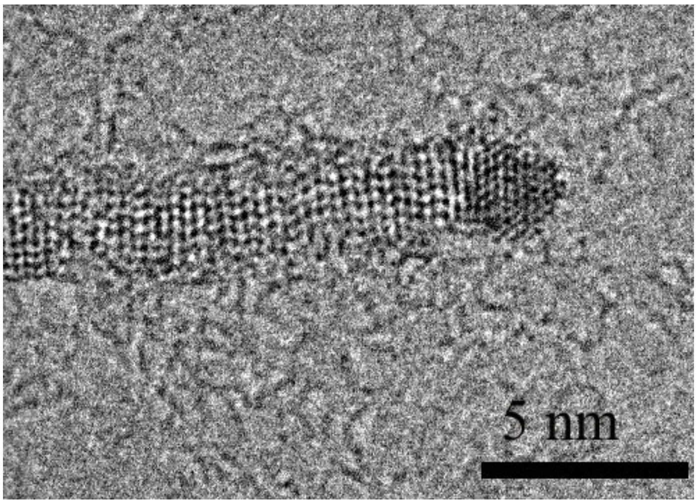


Fig. S5. XPS patterns of survey (a), Au 4f (b), Ag 3d (c), and S 2p (d)

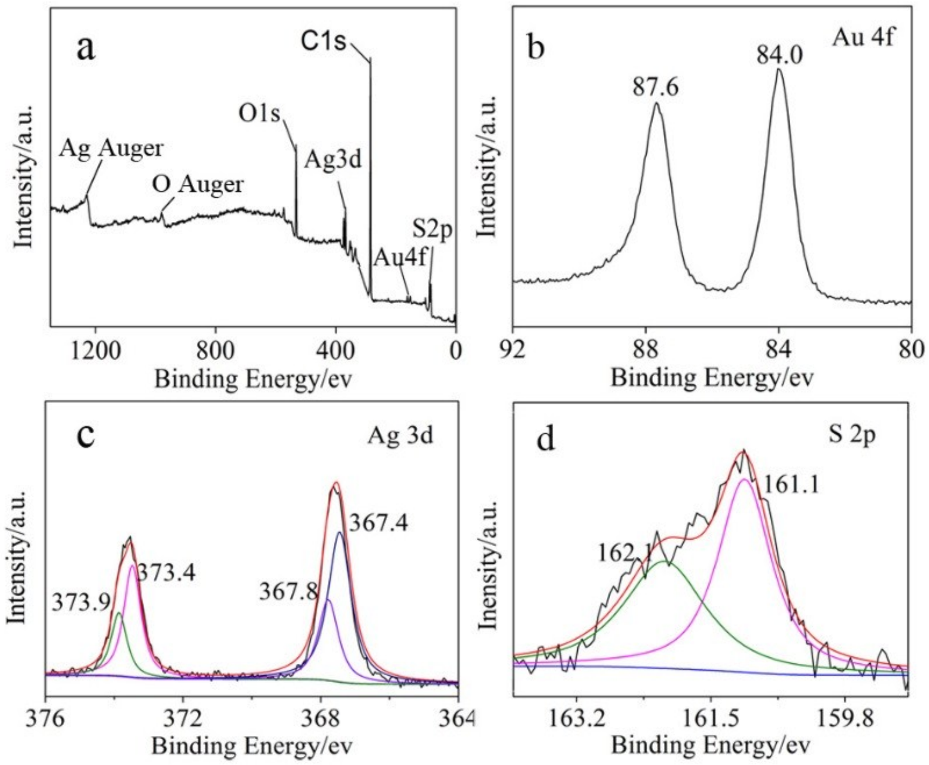


Fig. S6. UV−Vis-NIR absorption spectrum (a); PL spectrum at room temperature (λ_{ex} = 470 nm) (b); the inset is the fluorescence decay curves of HS2.

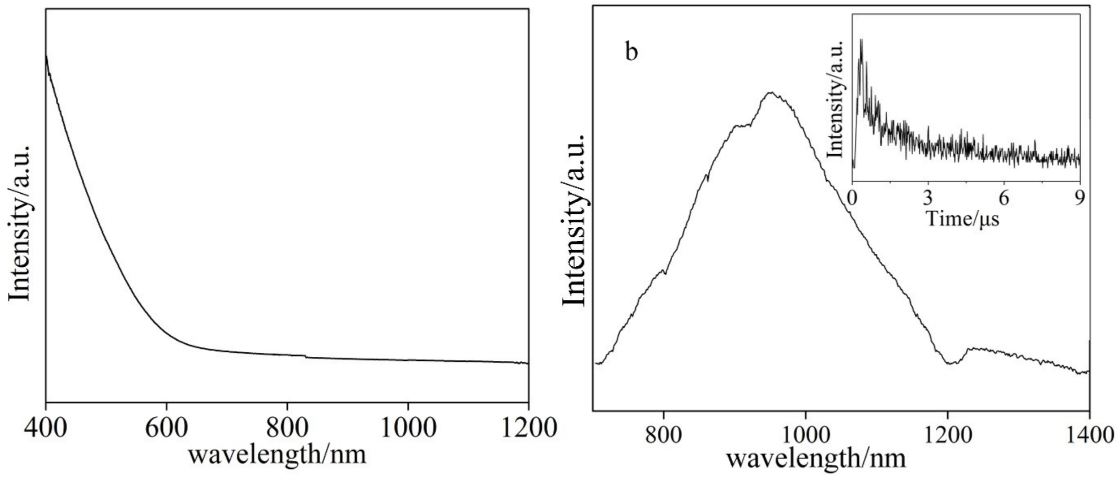
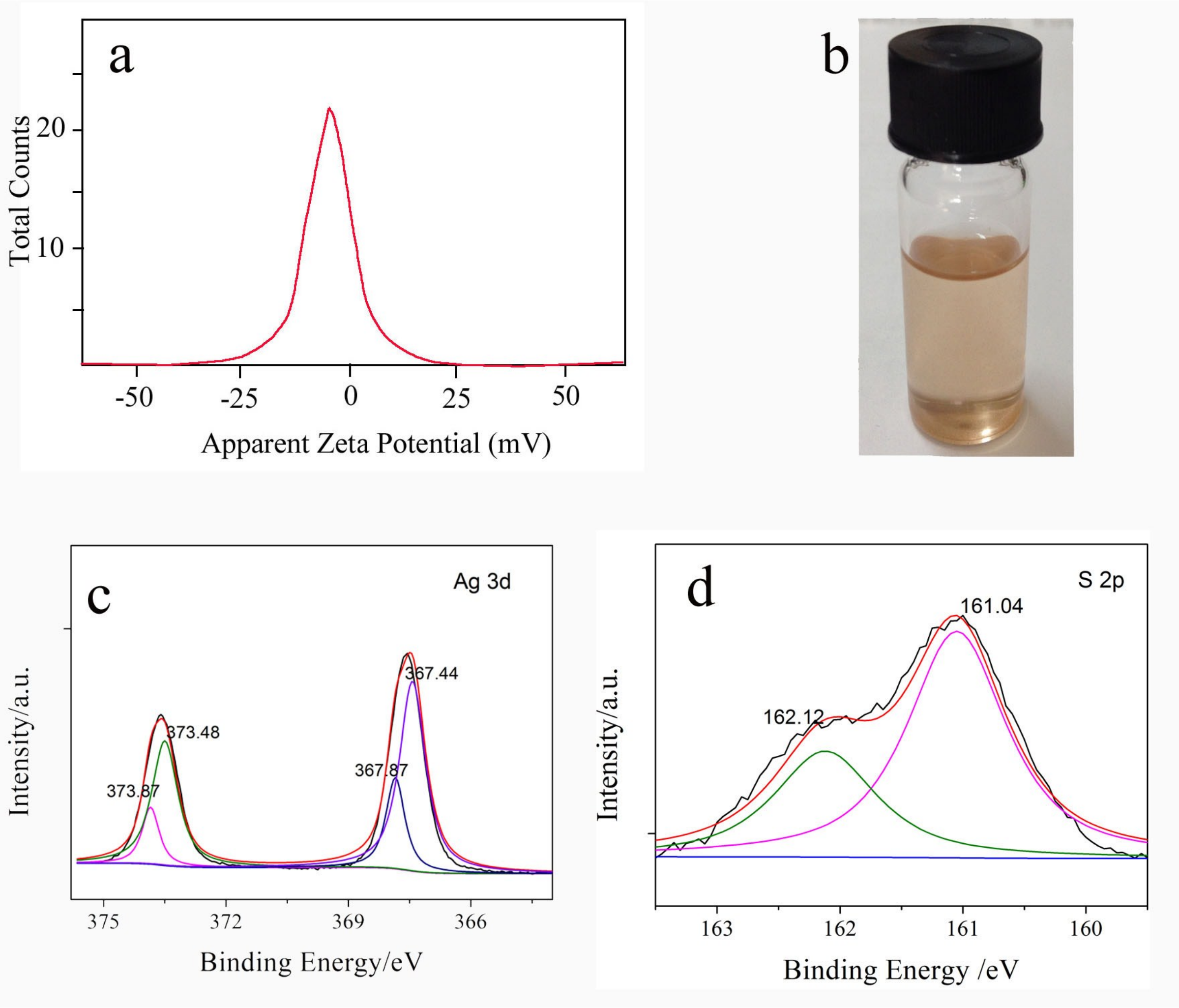


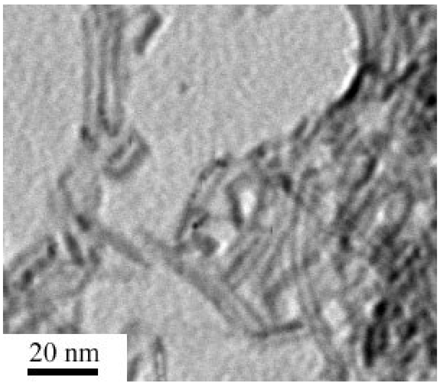
Fig. S7. (a) Zeta potential of the prepared HS2 dispersed in water; (b) Optical Photograph of the prepared HS2 dispersed in cyclohexane; (c) XPS spectrum of Ag element in the HS2 sample that was kept for 2 weeks after preparation; (d) XPS spectrum of S element in the HS2 sample that was kept for 2 weeks after preparation.



Discussion of stability and oxidation of the HS2 product:

The prepared HS2 sample precipitates quickly in water. This can be explained by its zeta potential characterization (Fig. S7a), which showed weak negative surface charges. However, the prepared HS2 was able to disperse in cyclohexane for at least two weeks without precipitate (Fig. S7b). This could be induced by the surface capping with organic molecules (octylamine) during the synthesis. Furthermore, the XPS measurement indicated the obtained HS2 had a good stability without oxidation. Fig. S7c and 7d are the XPS spectra of S and Ag elements in the HS2 sample that was kept for 2 weeks after preparation. They show the same binding energy as that of the fresh sample (Fig. S5) within low error for Ag(0), Ag(I) and S in the samples.

Fig. S8. TEM image of the prepared Ag_2S nanotubes



Reference:

1 (a) L. Shi and Y. Dai, *J. Mater. Chem. A*, 2013, **1**, 12981; (b) Z. Fei, S. He, L. Li, W. Ji and C.-T. Au, *Chem. Commun.*, 2012, **48**, 853