Electronic Supporting Information

Coalescence of Ag_2S and Au Nanocrystals at Room Temperature

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Experimental Procedures

1. General materials

The chemical reagents, including silver nitrate ($AgNO_3$, 99%), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.9%), hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, ACS reagent, ≥37.50% Pt basis), element sulfur (≥99.5%), sodium borohydride ($NaBH_4$, 98%), sodium citrate dehydrate (≥99%), dodecylamine (DDA, 98%), cadmium oxide (CdO, ≥99%), octadecylphosphonic acid (ODPA, 97%), oleylamine (OLA, technical grade, 70%), Se powder (≥99%), acetone (98%), and Nifion 117 solution (5% in a mixture of lower aliphatic alcohols and water) from Sigma-Aldrich, ethanol (ACS reagent, 99.5%), methanol (ReagentPlus, 99%), and toluene (ACS reagent, 99.5%) from Merck, bis(p-sulfonatophenyl) phenylphosphane dihydrate dipotassium salt (BSPP, 97%) from Strem Chemicals, aqueous $HClO_4$ solution (ACS reagent, 70%), and Vulcan XC-72 carbon powders (BET surface area of 250 m^2g^{-1} and average particle size of 40 ~ 50 nm) from Cabot, were used as received. All glassware and Teflon-coated magnetic stirring bars were cleaned with *aqua regia*, followed by copious rinsing with de-ionized water before drying in an oven.

2. Phase transfer of noble metal ions from water to toluene

In a typical experiment, 50 mL of 1 mM of aqueous metal salt solution ($AgNO_3$ or $HAuCl_4$) was mixed with 50 mL of ethanol containing 1 mL of dodecylamine. After 3 min of stirring, 50 mL of toluene was added, and stirred for another minute. Phase transfer of metal ions from water to toluene occurred rapidly and completely, as illustrated by the complete bleaching of the color in the aqueous phase. Assuming complete transfer of the ions from water, the metal ion concentration in toluene was 1 mM. The metal ions in toluene were separated from the aqueous phase, and kept for further experiments.

3. Synthesis of Ag_2S nanocrystals

7.5 mg of elemental sulfur was added to 50 mL of toluene solution of Ag^I ions in a 100 mL flat-bottomed flask. The mixture was stirred for 3 h at room temperature. The solution turned from colorless to dark brown, indicating the formation of Ag_2S

nanocrystals. TEM and HRTEM images of as-prepared Ag_2S nanocrystals were shown in Fig. S1a and b.

4. Synthesis of Au nanocrystals of different sizes

Approximately 13 nm Au nanocrystals were prepared by the citrate reduction of $HAuCl_4$. An aqueous solution of $HAuCl_4$ (1 mM, 20 mL) was refluxed at 110°C with stirring in an oil bath. 0.8 mL of 100 mM aqueous sodium citrate solution was added quickly, which resulted in a series of color changes before finally arriving at a wine red solution. The mixture was refluxed for another 15 min and allowed to cool to room temperature. The smaller 5 nm citrate-protected Au nanocrystals were prepared by a different procedure. Briefly, 20 mL of 1 mM aqueous solution of $HAuCl_4$ was mixed with 0.8 mL of 100 mM aqueous sodium citrate solution used as stabilizer. 0.6 mL of 100 mM aqueous solution of $NaBH_4$ was then added dropwise under vigorous stirring, giving rise to a red Au hydrosol. The Au hydrosol was only used after aging for 24 h to decompose residual $NaBH_4$.

5. Phase transfer of Au nanoparticles of different sizes

Au nanocrystals of 5 nm in diameter were transferred from water to toluene following the approach used for the phase transfer of Ag^I ions. Typically, the citrate-protected 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 to extract the Au nanocrystals. The TEM and HRTEM images of 5 nm Au nanoparticles after phase transfer were shown in Fig. S1c and d.

For the phase transfer of Au nanocrystals larger than 10 nm, 50 mg of solid BSPP were added to the Au hydrosol, and the mixture was aged for 30 min. Next, Au nanocrystals were transferred from water to toluene following the approach used for the phase transfer of Ag^I and Au^{III} ions. Typically, the BSPP-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. The TEM and HRTEM images of 13 nm Au nanocrystals after phase transfer were shown in Fig. S1e and f.

6. Synthesis of core-shell CdSe@CdS QDs

In total, 26 mg of CdO (0.2 mmol), 130 mg of ODPA (0.4 mmol), and 5 mL of

OLA were heated to 300°C under Ar flow until the reactants were completely dissolved, and then the solution was cooled to 240°C. The Se solution was prepared by dissolving 4 mg of Se powder (0.05 mmol) and 2 mg of $NaBH_4$ (0.05 mmol) in 2 mL of OLA. It was injected into the reaction mixture with rapid stirring. Next, the temperature for the reaction system was reduced to 220°C right away, where the mixture was kept for 1 min. The S solution was prepared by dissolving 1.5 mg of elemental sulfur (0.05 mmol) in 2 mL of OLA. It was injected into the reaction mixture dropwise with rapid stirring. The mixture was heated at 220°C for another 5 min and then cooled to room temperature. The resulting CdSe@CdS nanocrystals were precipitated, washed twice using acetone, and re-dispersed in 50 mL of chloroform (to obtain a nominal CdSe concentration of 1 mM).

7. Synthesis of QD-Au hybrids

For the preparation of QD-Au hybrids, 20 mL of core-shell CdSe@CdS QDs in toluene was mixed with 20 mL of Au^{III} ions in toluene. The mixture was aged for 1 h to complete the reaction. Additional reducing agent was not required; dodecylamine could reduce Au^{III} ions in toluene effectively in the presence of CdSe@CdS QDs.

8. Synthesis and phase transfer of alloy Au-Pt nanoparticles

For the synthesis of alloy Au-Pt nanoparticles with average size of 3 nm in diameter, 10 mL of 1 mM aqueous $HAuCl_4$ solution and 10 mL of 1 mM aqueous H_2PtCl_6 solution were mixed together. Then 0.8 mL of 100 mM aqueous solution of sodium citrate was added. Subsequently, under vigorous stirring, 0.6 mL of 100 mM aqueous $NaBH_4$ solution was added dropwise. The alloy Au-Pt hydrosol was only used after aging for 24 h to decompose residual $NaBH_4$.

The phase transfer of alloy Au-Pt nanoparticles followed the approach used for the transfer of 5 nm Au nanocrystals. The citrate-protected Au-Pt hydrosol was mixed with 20 mL of ethanol containing 0.4 mL of dodecylamine. After 3 min of stirring, 20 mL of toluene was added and stirred for another minute to extract the alloy Au-Pt nanoparticles, leaving behind a colorless aqueous solution.

9. Coalescence between Au and Ag_2S nanocrystals

Ag_2S nanocrystals in 10 mL of toluene were physically mixed with Au nanocrystals of different sizes in 10 mL of toluene at room temperature. TEM was applied to detect the coalescence process between Au and Ag_2S nanocrystals at different times.

10. Removal of Au from QD-Au hybrids using the coalescence between Au and Ag_2S nanocrystals

For the removal of Au from QD-Au hybrids using Ag_2S nanocrystals, 10 mL of CdSe@CdS-Au hybrid organosol in toluene was mixed with 10 mL of Ag_2S organosol in toluene. The mixture was aged for 48 h for completing the transfer of Au from QD-Au hybrids to the surface of Ag_2S nanocrystals. TEM and HAADF-STEM were adopted to determine the transfer of Au. EDX analysis under STEM mode was used to confirm the chemical components of different particles in the organosol.

11. Extraction of Au from alloy Au-Pt nanoparticles using the coalescence between Au and Ag_2S nanocrystals

10 mL of alloy Au-Pt organosol in toluene was mixed with 10 mL of Ag_2S organosol in toluene and the mixture was aged for 24 h for completing the extraction of Au from alloy Au-Pt nanoparticles by Ag_2S. EDX analysis under STEM mode was used to confirm the chemical components in alloy Au-Pt nanoparticles before and after Ag_2S treatment and heterodimers formed during the process.

12. Characterizations of the nanocrystals

Transmission electron microscopy (TEM) was performed on a FEI Tecnai G^2 F20 electron microscope operated at 200 kV with the software package for automated electron tomography. For TEM measurements, a drop of the nanocrystal solution was dispensed onto a 3-mm carbon-coated copper grid. Excess solution was removed by an absorbent paper, and the sample was dried under vacuum at room temperature. The average particle size and particle size distribution were obtained from a few randomly chosen areas in the TEM image containing ~200 nanocrystals each.

An energy-dispersive X-ray spectroscopy (EDX) analyzer attached to the FEI Tecnai G^2 F20 TEM operating in the scanning transmission electron microscopy (STEM) mode was used to analyze the components of different particles. The electron beam was only 0.7 nm in diameter, capable of providing a high-resolution analysis.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-3B diffractometer, using Cu K_α radiation (λ=1.54056Å). X -ray photoelectron spectra (XPS) analyses were conducted on an ESCALAB MKII spectrometer (VG Scientific) using Al-K_α radiation (1486.71 eV). Samples for XRD and XPS were concentrated from the toluene solution of different nanocrystals to 0.5 mL using flowing Ar. 10 mL of methanol were then added to precipitate the nanocrystals, which were recovered by centrifugation, and washed with methanol several times. They were then dried at room temperature in vacuum.

The emission spectra of all samples were obtained with a Jobin Yvon Horiba Fluorolog fluorescence spectrometer at an excitation wavelength of 362 nm.

13. Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode cell, which was connected to a PGSTAT 30 potentiostat. A leak-free Ag/AgCl (saturated with KCl) electrode was used as the reference. The counter electrode was a platinum mesh (1×1 cm^2) attached to a platinum wire.

13.1 Loading of alloy Au-Pt nanoparticles before and after Ag_2S treatment on carbon support

For the loading of the catalysts on Vulcan XC-72 carbon support, 9 mg of carbon powders was introduced into 10 mL of original alloy Au-Pt organosol in toluene and 10 mL of alloy Au-Pt organosol treated by Ag_2S, respectively. After 24 hours stirring of the mixtures, the alloy Au-Pt/C (~10 wt% Pt on carbon support) particles before and after treated by Ag_2S were collected using centrifugation and washed 3 times with methanol. They were then dried at room temperature in vacuum.

13.2 Preparation of working electrode

A thin layer of Nafion-impregnated catalyst cast on a vitreous carbon disk was used as the working electrode. The preparation of the catalyst ink followed a typical procedure in the literature with modification.[1] The alloy Au-Pt/C before and after Ag_2S treatment was ultrasonically dispersed in 10 mL of aqueous solution containing 4 mL of ethanol and 0.1 mL of the Nafion solution. A calculated volume of the ink was dispensed onto the 5 mm glassy carbon disk electrode to produce a nominal catalyst loading of 20 μg cm^{-2} (Pt base). The carbon electrode was then dried in a stream of warm air at 70ºC for 1 hour.

13.3 Methanol oxidation reaction (MOR)

The catalyst performance in room temperature methanol oxidation reaction (MOR) was evaluated by cyclic voltammetry. The potential window from 0 V to 1 V was scanned at 20 mV s^{-1} until a stable response was obtained before the voltammograms were recorded. The electrolyte was 1 M methanol in 0.1 M perchloric acid. For each catalyst (original alloy Au-Pt and alloy Au-Pt treated by Ag_2S), the current densities were normalized in reference to the geometric area of the glassy carbon electrode.

13.4 Oxygen reduction reaction (ORR)

The catalyst performance in room temperature oxygen reduction reaction (ORR) was evaluated in 0.1 M $HClO_4$ electrolyte solution using a glass carbon rotating disk electrode (RDE) at a rotation rate of 1600 rpm. Negative-going linear sweep voltammograms were recorded from 1 to 0 V at 20 mV·s^{-1} at room temperature in the presence of bubbling ultra-pure oxygen to maintain a saturated oxygen atmosphere near the working electrode. For each catalyst (original alloy Au-Pt and alloy Au-Pt treated by Ag_2S), the current densities were also normalized in reference to the geometric area of the glassy carbon electrode.

References

1. H. A. Gasteiger, S. S. Kocha, B. Sompalli and F. T. Wagner, *Appl. Catal. B*, 2005, **56**, 9.

Table S1 Electrochemical measurements of methanol oxidation on alloy Au-Pt nanoparticles before and after Ag_2S treatment. The data were obtained from Fig. S9a.

Materials	Forward scan peak potential (V)	Forward scan peak current density (mA cm^{-2})	Backward scan peak potential (V)	Backward scan peak current density (mA cm^{-2})
Au-Pt	0.74	45.8	0.53	39.4
Au-Pt treated by Ag_2S	0.70	62.1	0.46	47.9

Table S2 Comparison of the catalytic activity of alloy Au-Pt nanoparticles before and after Ag_2S treatment for the reduction of O_2 at room temperature. The data were obtained from Fig. S9b.

Materials	Half-wave potential at 1600 rpm (mV)	Kinetic current density at half-wave potential (mA cm^{-2})
Au-Pt	462	-1.88
Au-Pt treated by Ag_2S	409	-0.89

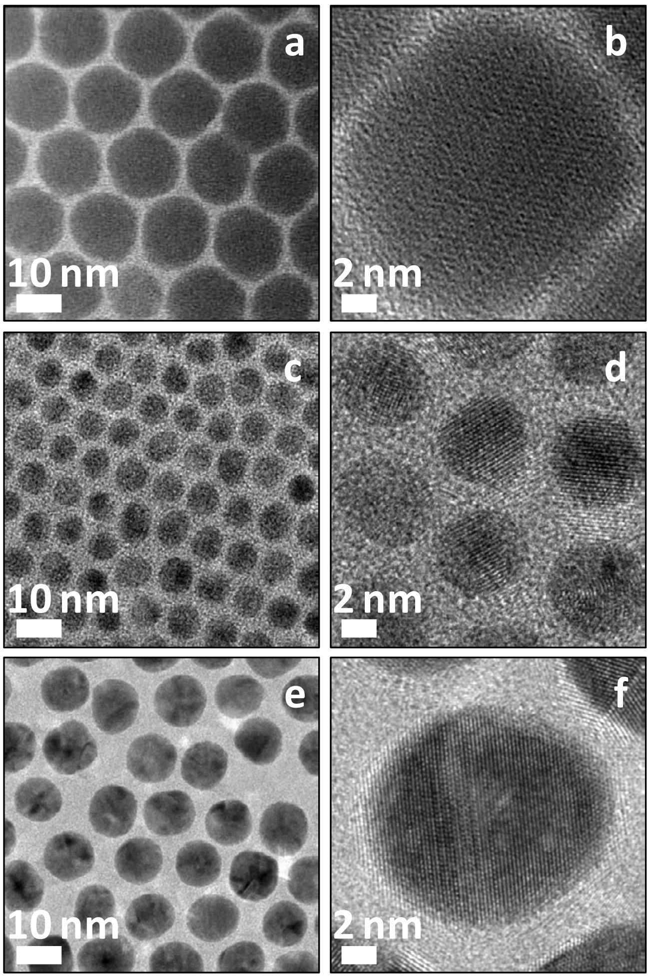

Fig. S1 a) TEM and b) HRTEM images Ag_2S nanocrystals with average size of ~15 nm in diameter, respectively; c) TEM and d) HRTEM images of Au nanocrystals with average size of ~5 nm in diameter, respectively; e) TEM and f) HRTEM image of Au nanocrystals with average size of ~13 nm in diameter, respectively.

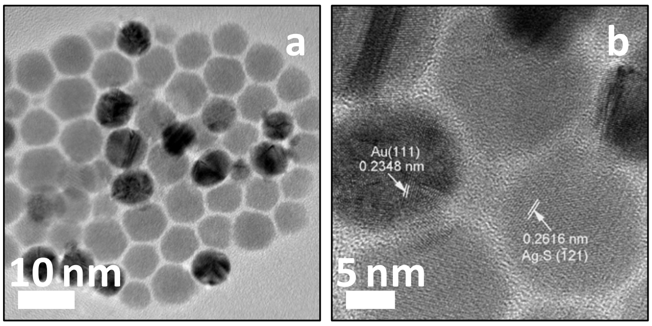

Fig. S2 Large area TEM image (a) and HRTEM image (b) of the physical mixture of Au and Ag_2S nanocrystals take at initial stage.

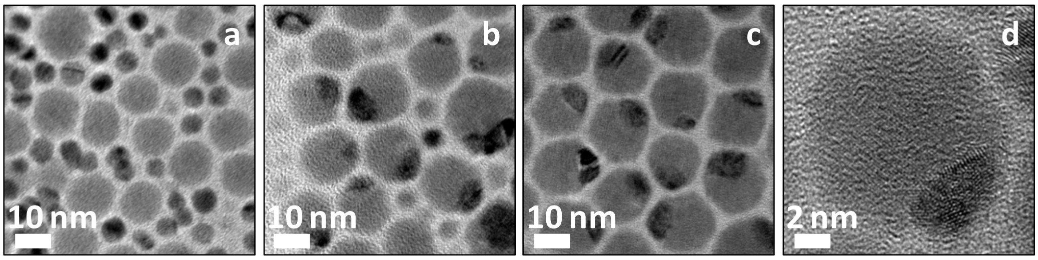

Fig. S3 a — c) TEM images of the physical mixture of Ag_2S and 5 nm Au nanocrystals taken at 0 h, 5 h, and 10 h, respectively; d) HRTEM image of a single Ag_2S-Au heterodimer.

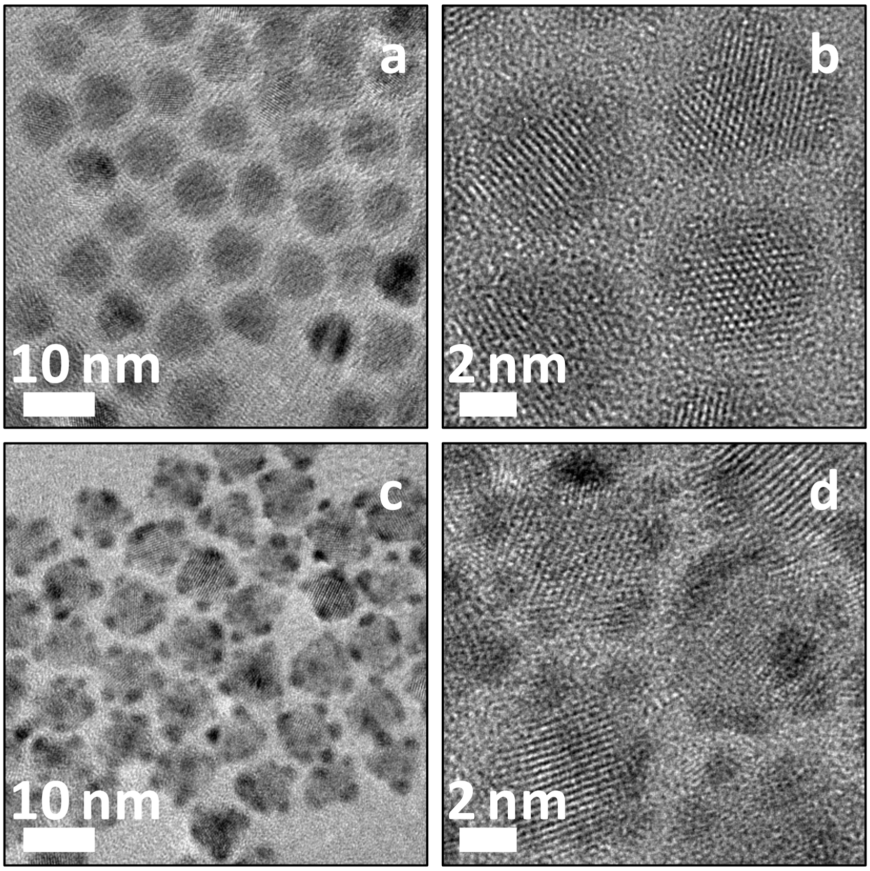

Fig. S4 a) TEM and b) HRTEM images of core-shell CdSe@CdS QDs, respectively; c) TEM and d) HRTEM images of CdSe@CdS-Au hybrids, respectively.

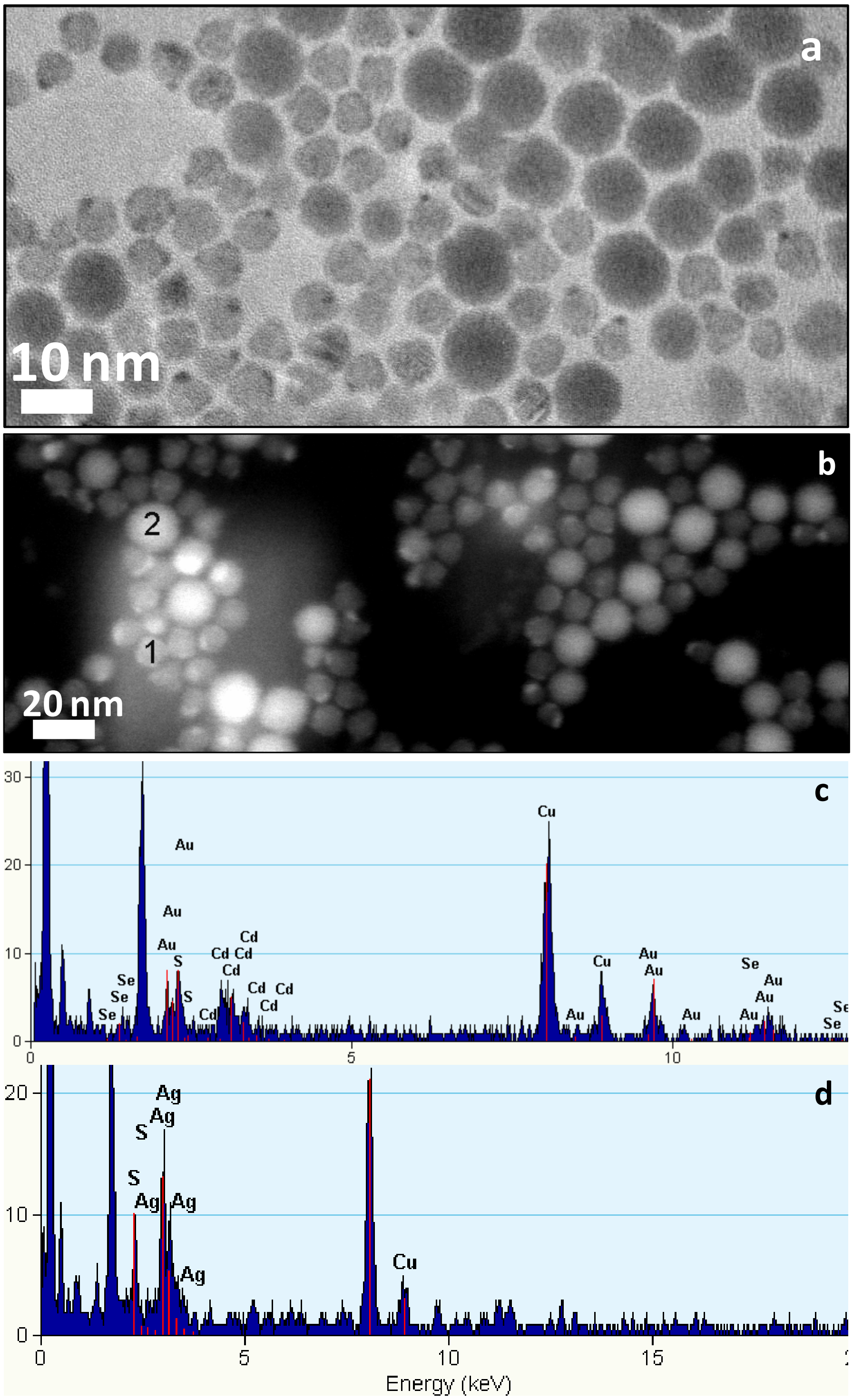

Fig. S5 a) Large-area TEM image of the mixture of Ag_2S nanocrystals and QD-Au hybrids at initial time; b) STEM image of the mixture of Ag_2S nanocrystals and QD-Au hybrids at initial time; c) EDX spectrum of the particle labeled as 1 in STEM image; d) EDX spectrum of the particle labeled as 2 in STEM image.

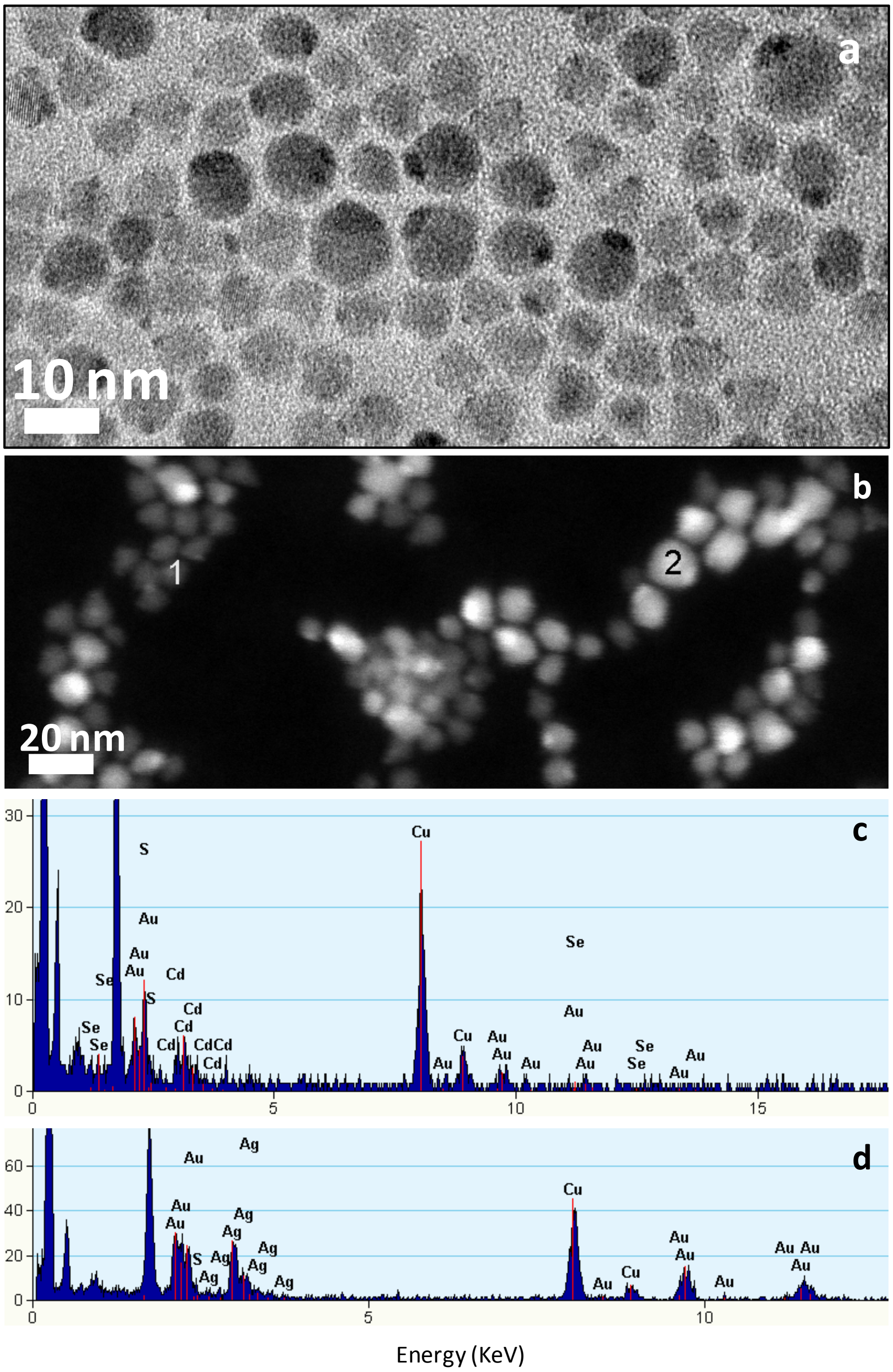

Fig. S6 a) Large-area TEM image of the mixture of Ag_2S nanocrystals and QD-Au hybrids at 24 h; b) STEM image of the mixture of Ag_2S nanocrystals and QD-Au hybrids at 24 h; c) EDX spectrum of the particle labeled as 1 in STEM image; d) EDX spectrum of the particle labeled as 2 in STEM image.

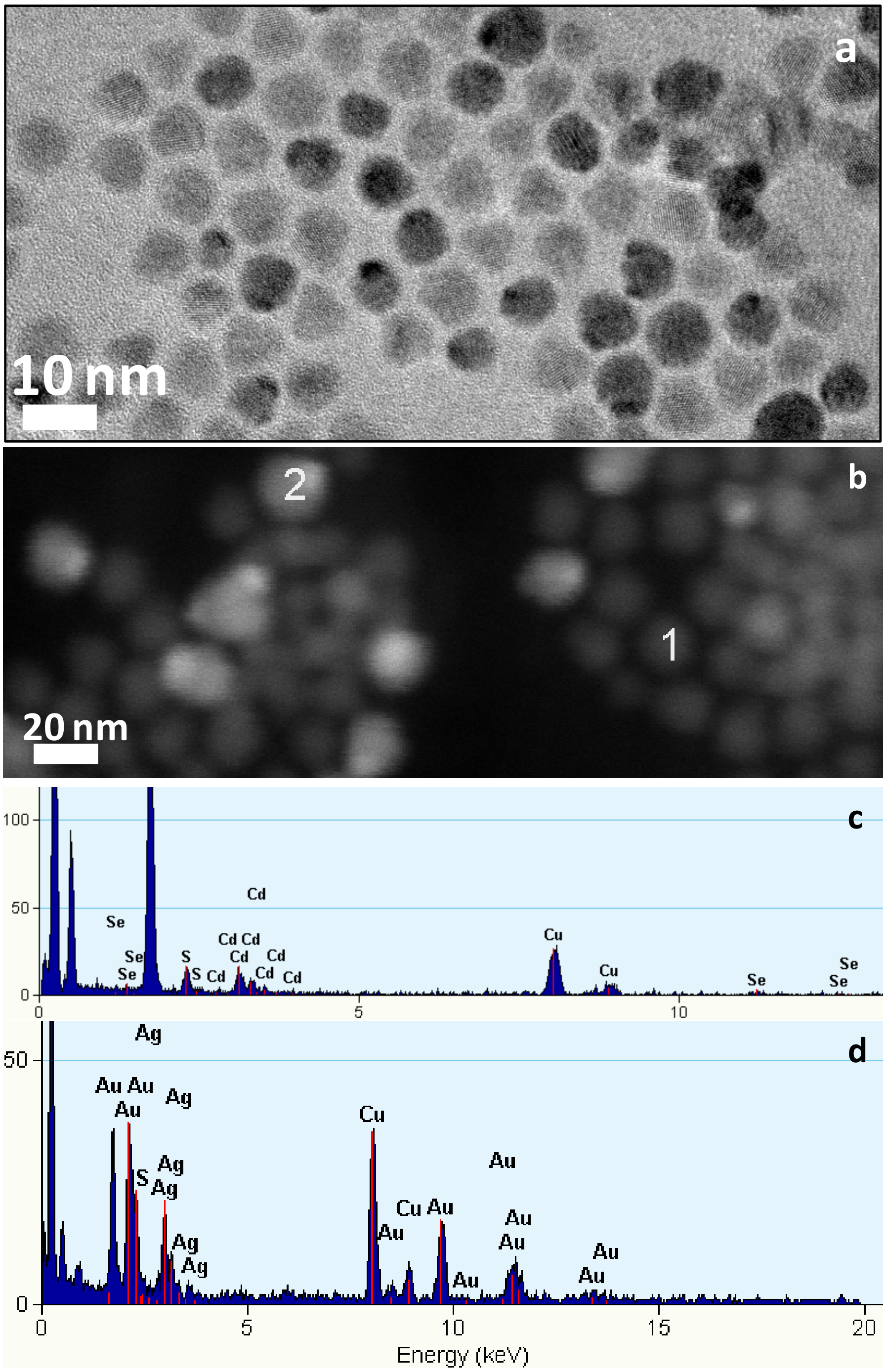

Fig. S7 a) Large-area TEM image of the mixture of Ag_2S nanocrystals and QD-Au hybrids at 48 h; b) STEM image of the mixture of Ag_2S nanocrystals and QD-Au hybrids at 48 h; c) EDX spectrum of the particle labeled as 1 in STEM image; d) EDX spectrum of the particle labeled as 2 in STEM image.

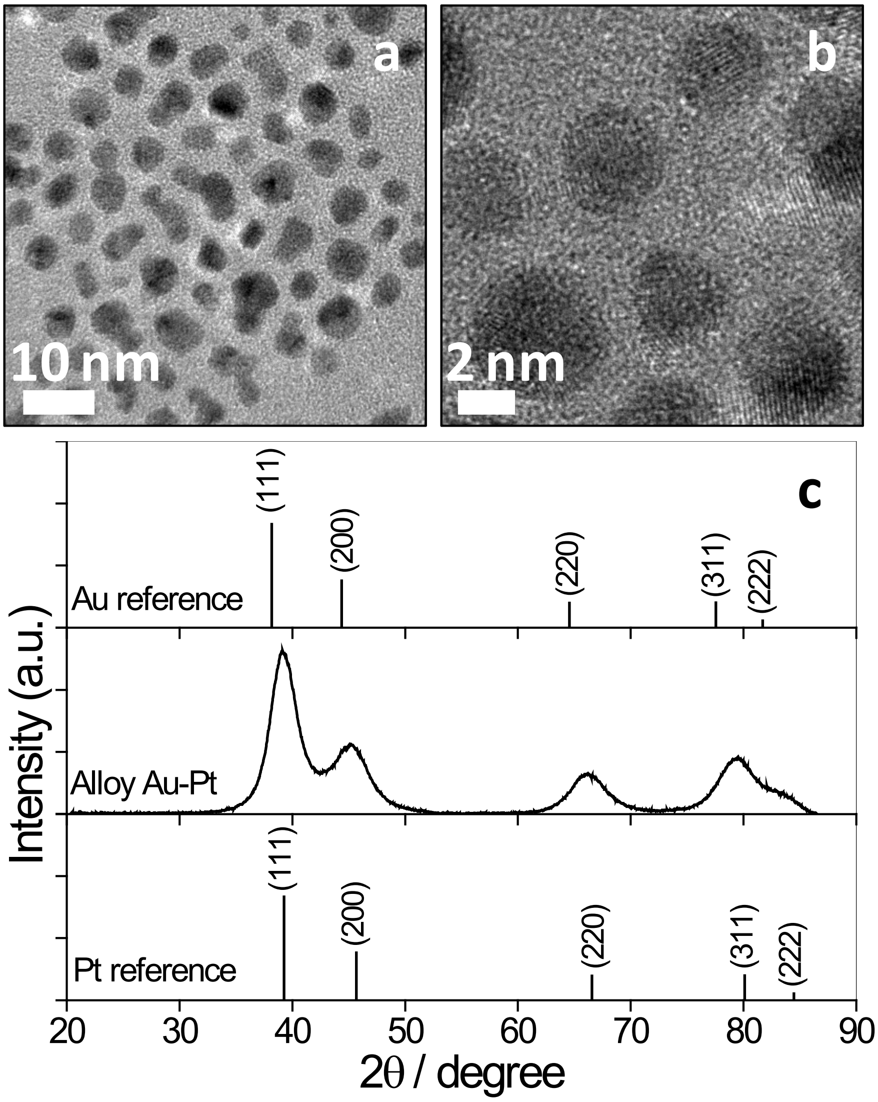

Fig. S8 a) TEM image, b) HRTEM image, and c) XRD pattern of alloy Au-Pt nanoparticles prepared by co-reduction of $HAuCl_4$ and H_2PtCl_6 using $NaBH_4$ as reducing agent.

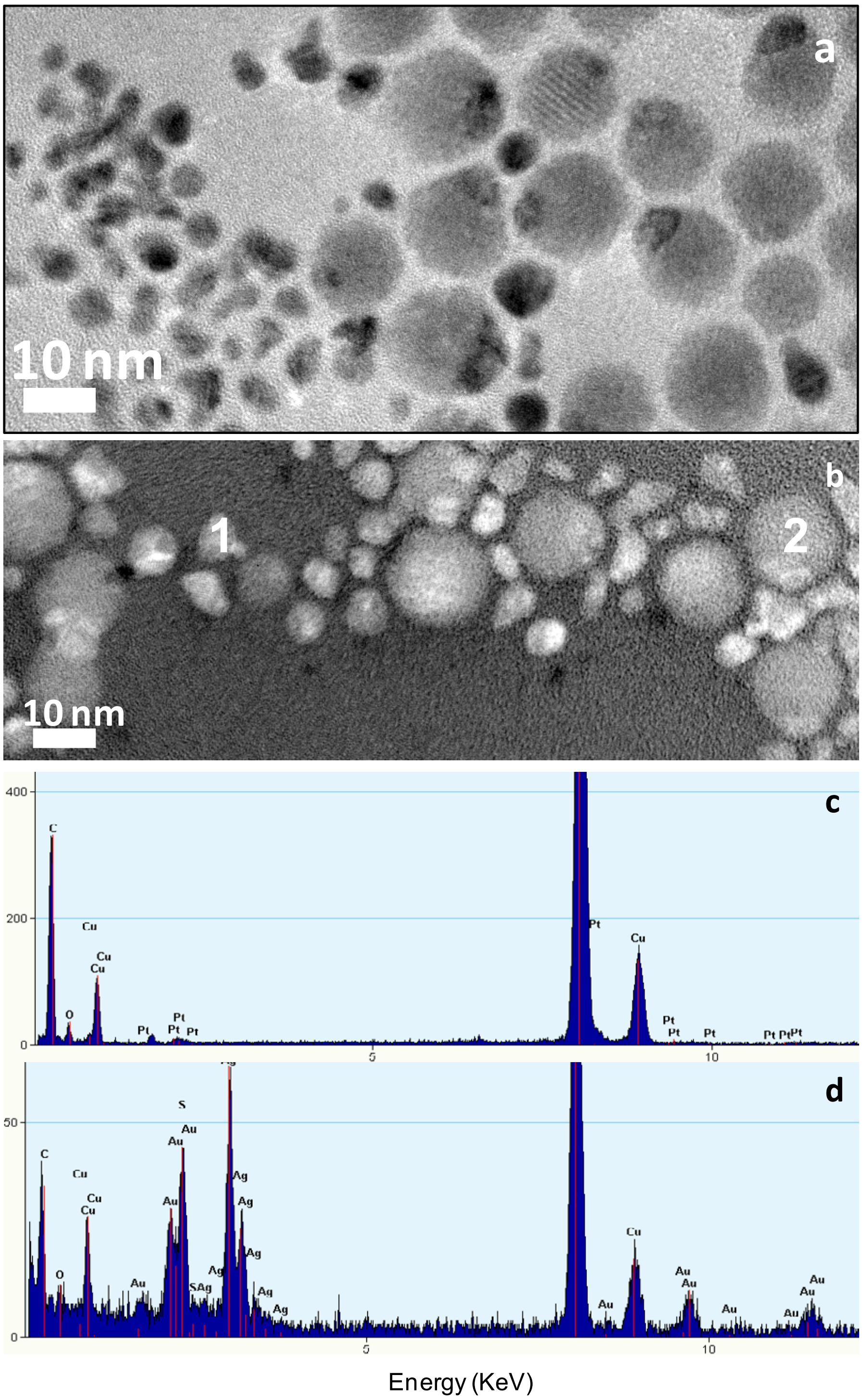

Fig. S9 a) Large-area TEM image of Ag_2S nanocrystals and alloy Au-Pt nanoparticles at 24 h; b) STEM image of the mixture of Ag_2S nanocrystals and alloy Au-Pt nanoparticles at 24 h; c) EDX spectrum of the particle labeled as 1 in STEM image; d) EDX spectrum of the particle labeled as 2 in STEM image.

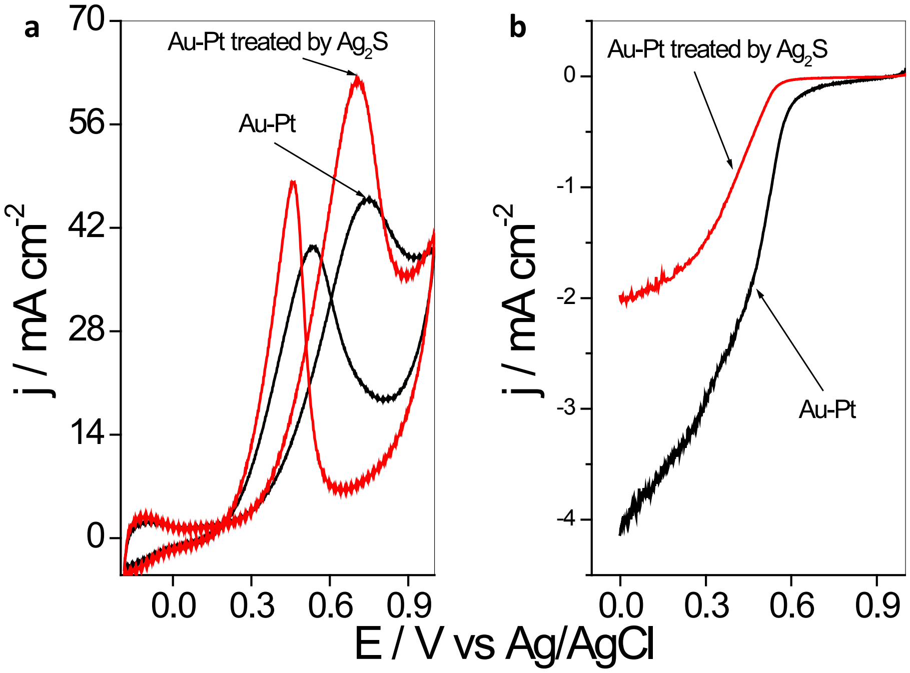

Fig. S10 Electrochemical measurements: a) Cyclic voltammograms of alloy Au-Pt nanoparticles before and after Ag_2S treatment in argon-purged $HClO_4$ (0.1M) with methanol (1 M). Sweep rate: 20 mV s^{-1}, room temperature; b) Polarization curve for ORR over alloy Au-Pt nano-particles before and after Ag_2S treatment in an O_2-saturated $HClO_4$ solution (1 M). Sweep rate: 20 mV s^{-1}, rotating speed: 1600 rpm, room temperature.