Electronic Supplementary Information

Construction of kinked heteronanorods modified by metal nanoparticles with enhanced catalytic performance

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Experimental Section

Materials: Sodium diethyldithiocarbamate ($Na(S_2CNEt_2)$, 99%), $AgNO_3$ (99.9%), $Zn(NO_3)_2$ (99%), NaCl (99.5%), $HAuCl_4 \cdot 4H_2O$ (50%), KOH , $NaBH_4$ (96%), 4-nitrophenol (99.5%), hexane (97%), toluene (99.5%), methanol (99.5%), ethanol (99.7%), 1-dodecanethiol (DDT, 97%), oleic acid (OA, 85%), oleylamine (OLA, 80-90%), tri-n-butylphosphine (TBP, 99%), mercaptoacetic acid (TGA) and trichloromethane ($CHCl_3$) were purchased from the Shanghai Reagent Company (P. R. China). All chemicals were used as received without further purification.

Synthesis of $Zn(S_2CNEt_2)_2$ ($Zn(dedc)_2$) and $Ag(S_2CNEt_2)$ (Ag(dedc)). In a typical synthesis of $Zn(dedc)_2$, $ZnNO_3$ (1 mmol) and $Na(S_2CNEt_2)$ (2 mmol) were dissolved in deionized water (200 mL), respectively. Then, the two solutions were mixed together by dropwise addition of $ZnNO_3$ aqueous solution. And the resulting products were washed three times with deionized water and ethanol followed by drying. $AgNO_3$ (2 mmol) was used instead of $ZnNO_3$ (1 mmol) to prepare Ag(dedc).

Synthesis of Kinked ZnS Nanorods: Kinked Ag_2S-ZnS nanorods were prepared by our previously reported method**.** Typically, Ag(dedc) (0.05 mmol), $Zn(dedc)_2$ (0.5 mmol) and NaCl (0.5 mmol) were dissolved by 10 ml 1-dodecanethiol (DDT) in a three-neck flask with magnetic stirring and heated to 210 ^oC in 15 min. When the solution reacted for 5 min at 210 ^oC, 10 ml oleic acid (OA) was injected into the flask and the mixture color turned turbid gray. After keeping the reaction for 60 min, the resulting nanocrystals were collected and centrifuged at 8000 rpm for 5 min, and the upper clear solution was discarded. Then, the products were washed three times with hexane and ethanol.

Synthesis of Au Decorated Kinked ZnS Nanorods: As-prepared 10 mg of kinked ZnS

powder was dissolved by 5 mL oleylamine in a three-neck flask , and then different amount of Au stock solution was injected into this flask under vigorous stirring and heated to 100 ^{o}C in 20 min. The reaction was kept for 30 min. Purification of Au decorated kinked ZnS nanorods was similar to those of kinked ZnS nanorods.

Preparation of citrate-stabilized Au nanoparticles: A 50 mL flask was charged with 0.2 mL sodium citrate (1 wt%) and 14 mL aqueous solution of $HAuCl_4$ (0.3 mM). Then 0.6 mL of ice-cold $NaBH_4$ solution (0.1 M) was added with vigorous stirring. The solution turned from orange-yellow to brownish-red, indicating the formation of Au nanoparticles. The size of the resulting Au nanoparticles are about 3-5 nm.

Preparation of Au stock solution

For the Au stock solution, 1 g of $HAuCl_4$ was dissolved in the mixture of 20 mL of hexane and 20 mL of oleylamine. The suspension was sonicated for several minutes at ambient temperature until a luminous yellow solution was obtained. This mixture will be known as Au stock solution.

Phase Transfer of Au Decorated Kinked ZnS Nanorods from Hexane to Water

The hydrophobic Au decorated kinked ZnS nanorods could be further functionalized by other surfactants such as TGA, enabling the phase transfer from hydrophobic to hydrophilic media. In a typical process, 3 mL of ethanol solution containing 50 μL TGA and 50 mg KOH was added into a solution of 10 mg Au decorated kinked ZnS nanorods in 3 mL chloroform. The turbid solution was stirred for 3h, followed by centrifugation. The precipitate were washed with ethanol and re-dispersed in deionized water. Other hydrophobic nanocrystals can transferred to aqueous solution by the same method.

Catalysis Studies

Typically, freshly prepared aqueous solutions of $NaBH_4$ (0.1 mol/L, 2 mL) and 4-nitrophenol (1.0 mmol/L, 150 μL) were mixed together under magnetic stirring at ambient temperature for 10 min. Then, the aqueous solutions of Au decorated kinked ZnS nanorods (1 mg/mL, 50 μL) were added to the above solution. After addition the catalyst, the bright yellow solution gradually faded as the reaction proceeded. The reaction progress was monitored by measuring the UV-vis absorption spectra of the reaction solutions.

Characterizations

The X-ray diffraction patterns (XRD) were measured on a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite-monochromatized Cu KR radiation. UV-vis-NIR spectra were recorded on UV-2501PC/2550 at room temperature (Shimadzu Corporation, Japan). Nanocrystals dispersed in hexane were drop-casted on carbon-supported Cu grids for TEM and HRTEM observations, which were performed on Hitachi H-7650 and JEOL-2010F with an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) were determined on an ESCA Lab MKII X-ray photoelectron spectrometer with an excitation source of Mg $K\alpha$ radiation. Energy dispersive X-ray spectroscopy (EDS) and high-angle annular dark field scanning transmission electron microscopy (HAADF- STEM) were carried out using a JEM-ARM 200F Atomic Resolution Analytical Microscope operating at an accelerating voltage of 200 kV. Elemental mappings were collected by a Gatan GIF Quantum 965 instrument.

Supporting Figures

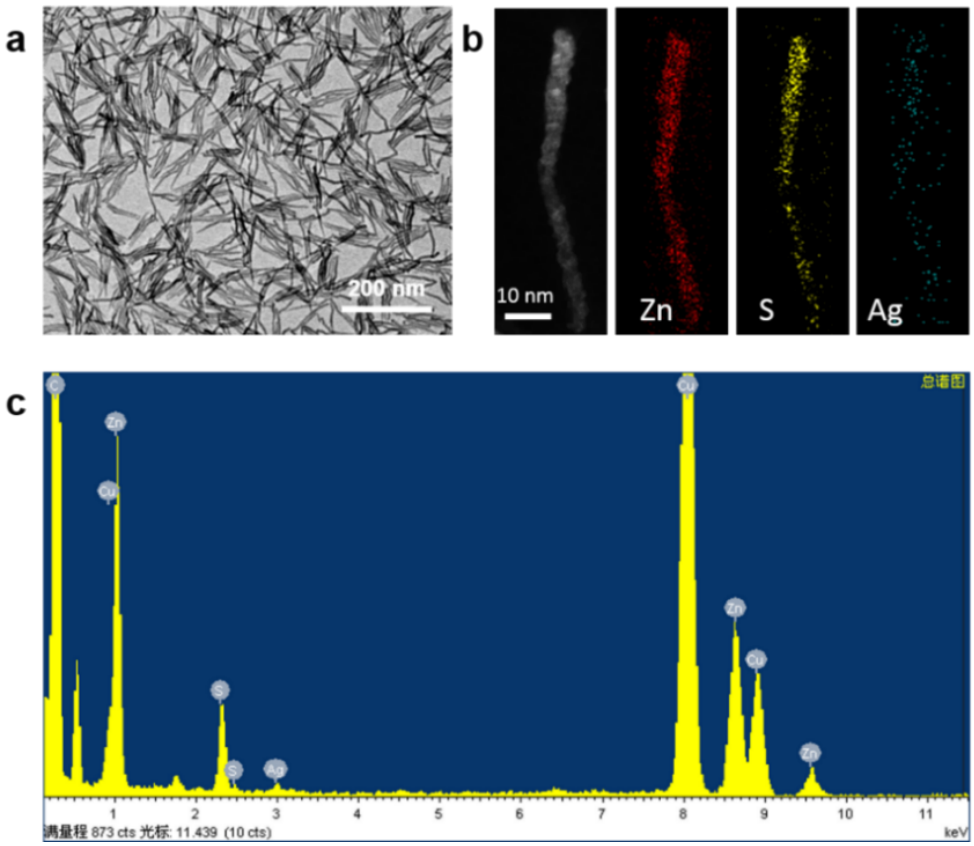

Fig. S1 (a) Representative TEM image of kinked ZnS nanorods synthesized using 0.5 mmol $Zn(dedc)_2$ and 0.5 mmol Ag(dedc) in the presence of 0.5 mmol NaCl at 210 °C for 60 min. (b) HAADF-STEM image and elemental mapping images of a single kinked Ag_2S-ZnS nanorods. (c) EDS spectra of the kinked Ag_2S-ZnS nanorods.

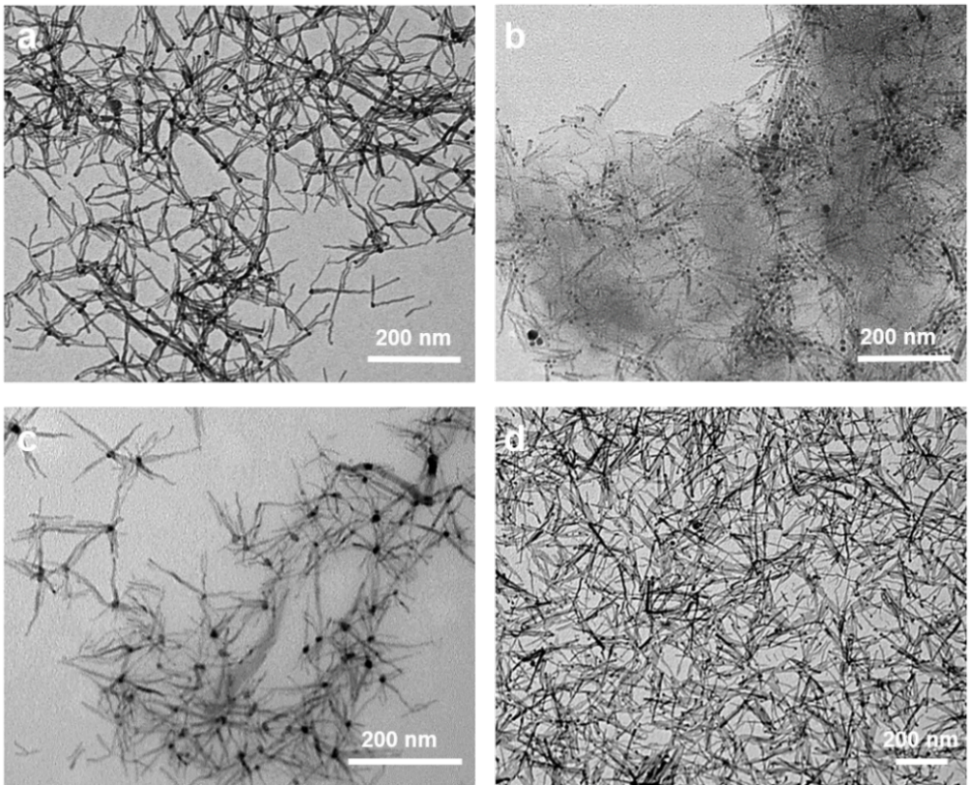

Fig. S2 TEM images of kinked nanostructures synthesized with 5 mL of OLA at 100 °C with different dose of Au stock solution, (a) 10 μL and (b) 1000 μL. (c) TEM image of kinked Ag_2S-ZnS heteronanostructures with 5 mL of OLA in the absence of Au stock solution. (d) Low magnification TEM image of the as-prepared Au/Ag_2S-ZnS with Au stock solution 100 μL.

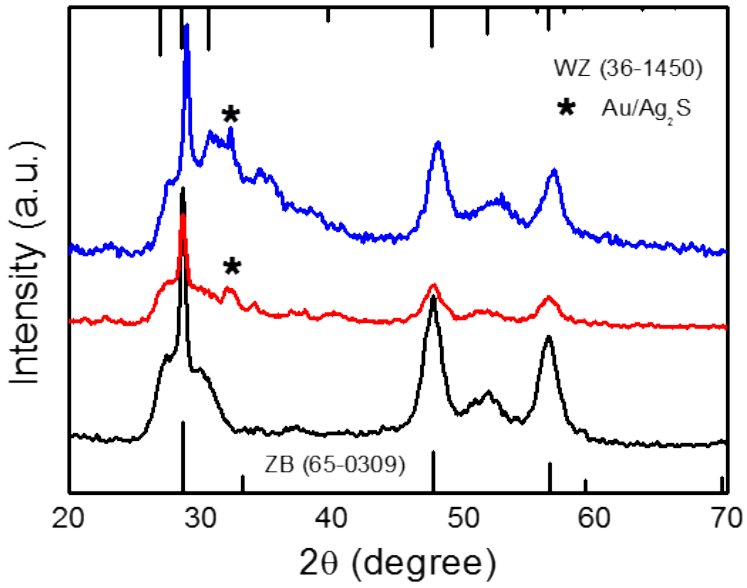

Fig. S3 XRD patterns of kinked Ag_2S-ZnS heteronanostructures (black), Au/Ag_2S-ZnS heteronanostructures (red) and Au/Ag_2S-ZnS/Au heteronanostructures (blue).

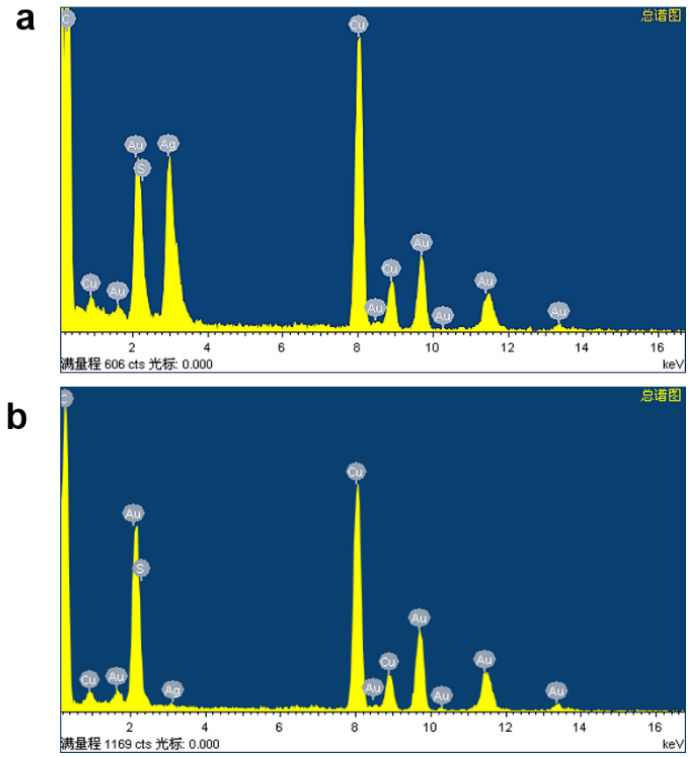

Fig. S4 EDS spectra of the kinked (a) Au/Ag_2S-ZnS and (b) Au/Ag_2S-ZnS/Au heteronanorods .The C and Cu elements are attributed to carbon film and copper grid, respectively.

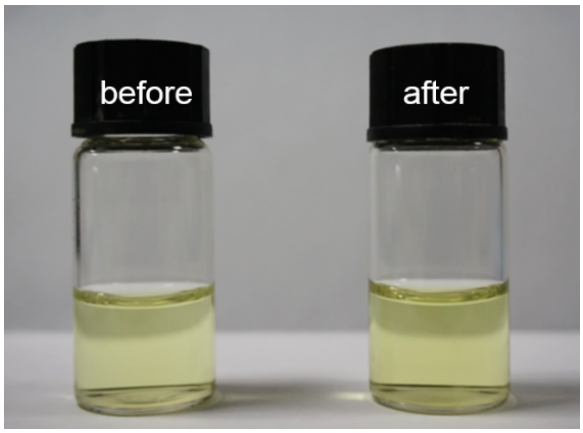

Fig. S5 Color changes during the reduction of 4-nitrophenol by $NaBH_4$ catalyzed by as prepared Au nanoparticles. Obviously, under the same circumstance, even after more than 24 h, the exiting solution had almost the same yellow color as the starting solution.