

Supporting Information for

Cu₂ZnSnS₄-CdS heterostructured nanocrystals for enhanced photocatalytic hydrogen production

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Experimental Details

Chemicals and Reagents

Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$), nano-zinc oxide (ZnO , $\geq 99.9\%$), tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\geq 99.0\%$), tert-Dodecanethiol (t-DDT, 97%), 1-dodecanethiol (DDT, $\geq 98\%$), cadmium oxide (CdO , $\geq 99.0\%$), S powder ($\geq 99.99\%$), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\geq 96\%$), sodium sulfite (Na_2SO_3 , $\geq 97\%$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 99.0\%$), 1-octadecene (ODE, $\geq 90\%$), oleic acid (OA, $\geq 90\%$), oleylamine (OLA, $\geq 90\%$) and ammonium sulfide solution [$(\text{NH}_4)_2\text{S}$, 20% in H_2O] were purchased from Aladdin. Chloroform, isopropanol, tetrahydrofuran (THF), formamide, toluene and acetone were analytical grade and used as received without any further purification.

Synthesis of wurtzite CZTS nanocrystals

The synthesis of wurtzite CZTS nanocrystals was similar as previous report [S1]. In a typical synthesis, 5.4 mmol (0.920 g) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 4.8 mmol (0.391 g) of ZnO , 1.8 mmol (0.630 g) of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in a minimum amount of tetrahydrofuran (THF). Then, 24 mmol (6.43 g) of OLA and 20 g of ODE were loaded in the above prepared reaction mixture in a three-neck round-bottom flask. The solution was heated under flow of argon to 175 °C and maintained at this temperature for 1 hour to remove low boiling point impurities and water. The main reason for using THF as co-solvent is not only to facilitate the metal salts dissolution, but also to remove water from the reaction mixture. After purging, the mixture was cooled to 100 °C, and then 50 mmol (10.12 g) of tert-dodecylmercaptan and 5 mmol (1.012 g) of dodecanethiol were added using a syringe. Then the solution was heated to 250 °C and maintained at this temperature for one hour. The obtained CZTS nanocrystals were thoroughly purified by multiple precipitation and redispersion steps using isopropanol and chloroform. Finally, the poorly soluble unreacted metal complexes and large Zn-rich particles were precipitated using low speed centrifugation. The obtained wurtzite CZTS nanocrystals were collected and stored in chloroform for later use.

Synthesis of CZTS-CdS heterostructured nanocrystals

Previously, oleic acid and cadmium oxide were loaded into a reaction flask and kept at 240 °C for 30 min under flow of argon to obtain Cd precursor solution. In another flask, 1-octadecene and

S power were mixed at 150 °C for 30 min under flow of argon to obtain S precursor solution. These two precursor solutions were sealed before further use.

In a typical synthesis of CZTS-CdS heterostructured nanocrystals, 130 mg wurtzite CZTS nanocrystals seeds in 6 mL chloroform was introduced to a mixed solution composed of 4 mL oleylamine and 10 mL 1-octadecene in a three-neck round-bottom flask. This mixture was heated at 90 °C under argon flow to get rid of chloroform. After removal of chloroform, the temperature was increased to 110 °C to remove other low boiling point impurities and water, then the temperature was further increased to 170 °C. After Cd precursor solution was added to the above mixture and maintained at 170 °C for 20 min, S precursor solution was added to this mixture rapidly and also maintained at 170 °C for 20 min. Cd precursor solution and S precursor solution were alternately injected into CZTS seeds solution and maintained at 170 °C for 20 min for x cycles to obtain CZTS-CdS heterostructured nanocrystals, which are denoted as CZTS-xCdS. After the reaction system was cooled to room temperature, the final products were precipitated by centrifugation and washed with chloroform and isopropanol for four times before characterizations and use.

Photocatalytic hydrogen production

In order to get water-soluble photocatalyst, the obtained CZTS-CdS heterostructured nanocrystals were rendered water soluble by replacing the initial hydrophobic surfactants with $(\text{NH}_4)_2\text{S}$. In a typical ligand-exchange procedure, the dispersion of 50 mg CZTS-CdS heterostructured nanocrystals in 10 mL chloroform and toluene mixture (1:1, V:V) was mixed with 2 v% of $(\text{NH}_4)_2\text{S}$ solution in 9 mL formamide. The biphasic system was vigorously shaken for 2 hours until CZTS-CdS heterostructured nanocrystals completely moved into the upper formamide phase. The clear chloroform solution was discarded and the formamide phase was cleaned several times with fresh chloroform. CZTS-CdS heterostructured nanocrystals were precipitated with acetone and dried under vacuum overnight. Prior to the photocatalytic H_2 evolution reaction, 0.5 wt % Pt was loaded on the CZTS-CdS heterostructured nanocrystals by in situ photodeposition method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as the Pt source. In a typical photocatalyst evolution experiments, 50 mg of CZTS-CdS heterostructured nanocrystals was dispersed in 50 mL of aqueous solution, containing 0.4 mol/L Na_2S and 0.3 mol/L Na_2SO_3 as hole scavengers. The whole reaction was carried out at 6 °C in a gas-closed circulation and evacuation system with a Pyrex cell connected to water bath. Before irradiating the solution, the reactor was thoroughly

purged with argon to remove all oxygen in the headspace of the reactor and dissolved in water. The irradiation was visible light ($\lambda \geq 420$ nm) that supplied by the Xenon lamp with a cut-off filter. The reaction product was monitored by sampling the gas phase from glass chamber using a gastight syringe and analyzing by a gas chromatograph (Agilent 7890A, thermal conductivity detector, NaX zeolite column, and Ar carrier).

Characterizations

Transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) were recorded on a JEOL JEM-2010 TEM (JEOL, Japan) with an accelerating voltage of 200 kV. The crystallographic phases of the samples were performed on a D8 Advance X-ray powder diffraction (Germany, Bruck) with diffraction angle 2θ ranging from 20 to 70 °. Raman spectrum was performed using a LabRAM-1B confocal laser Raman spectrometer with an excitation wavelength of 632.5 nm. UV-vis spectra were obtained using a UV-vis spectrometer (Lambda 950, PerkinElmer, USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS ULTRA spectrometer using Al K α X-ray as the excitation source.

REFERENCES:

[S1] Shavel A, Ibanez M, Luo ZS, Roo JD, Carrete A, Dimitrievska M, Genc A, Meyns M, Perez-Rodriguez A, Kovalenko MV, Arbiol J and Cabot A, *Chem. Mater.*, 2016, **28(3)**, 720.

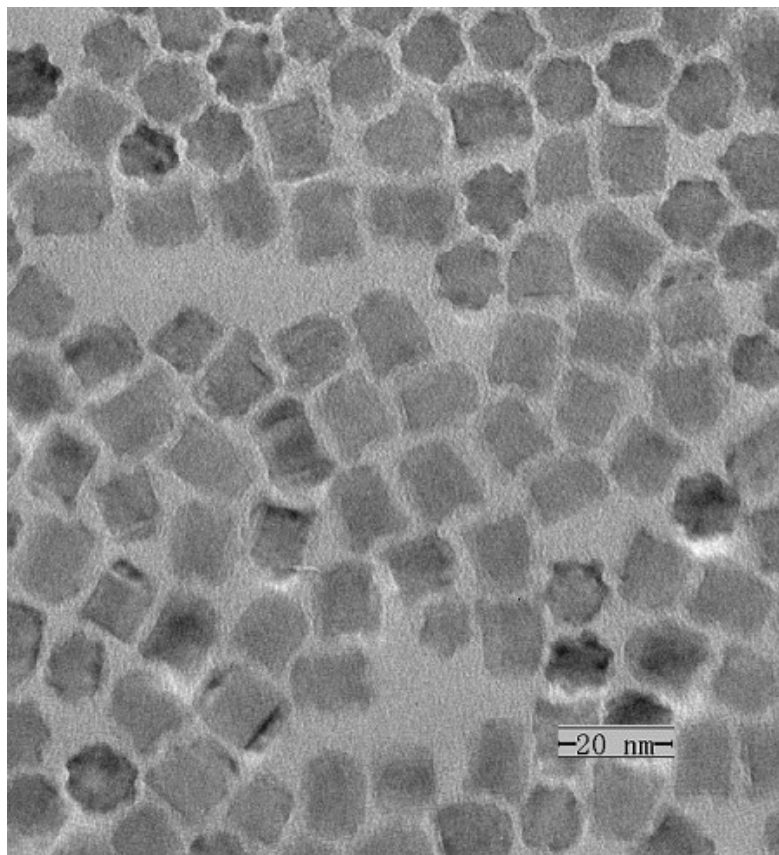


Fig. S1. TEM image of CZTS-3CdS heterostructured nanocrystals after photocatalytic hydrogen production reaction.

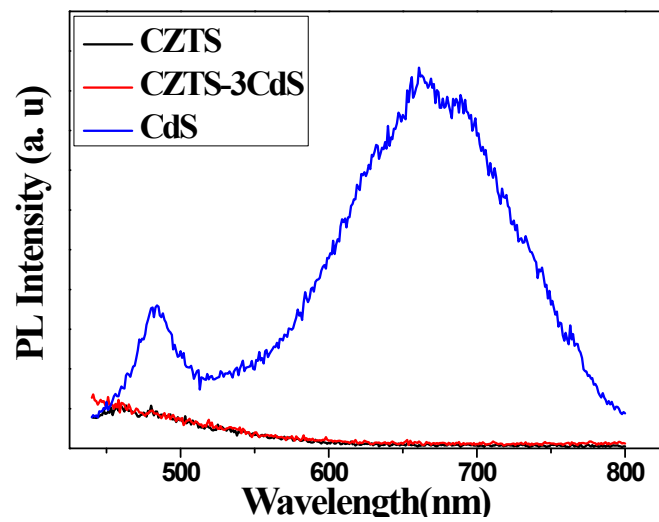


Fig. S2. The fluorescence spectra of CZTS, CZTS-3CdS and CdS nanocrystals.

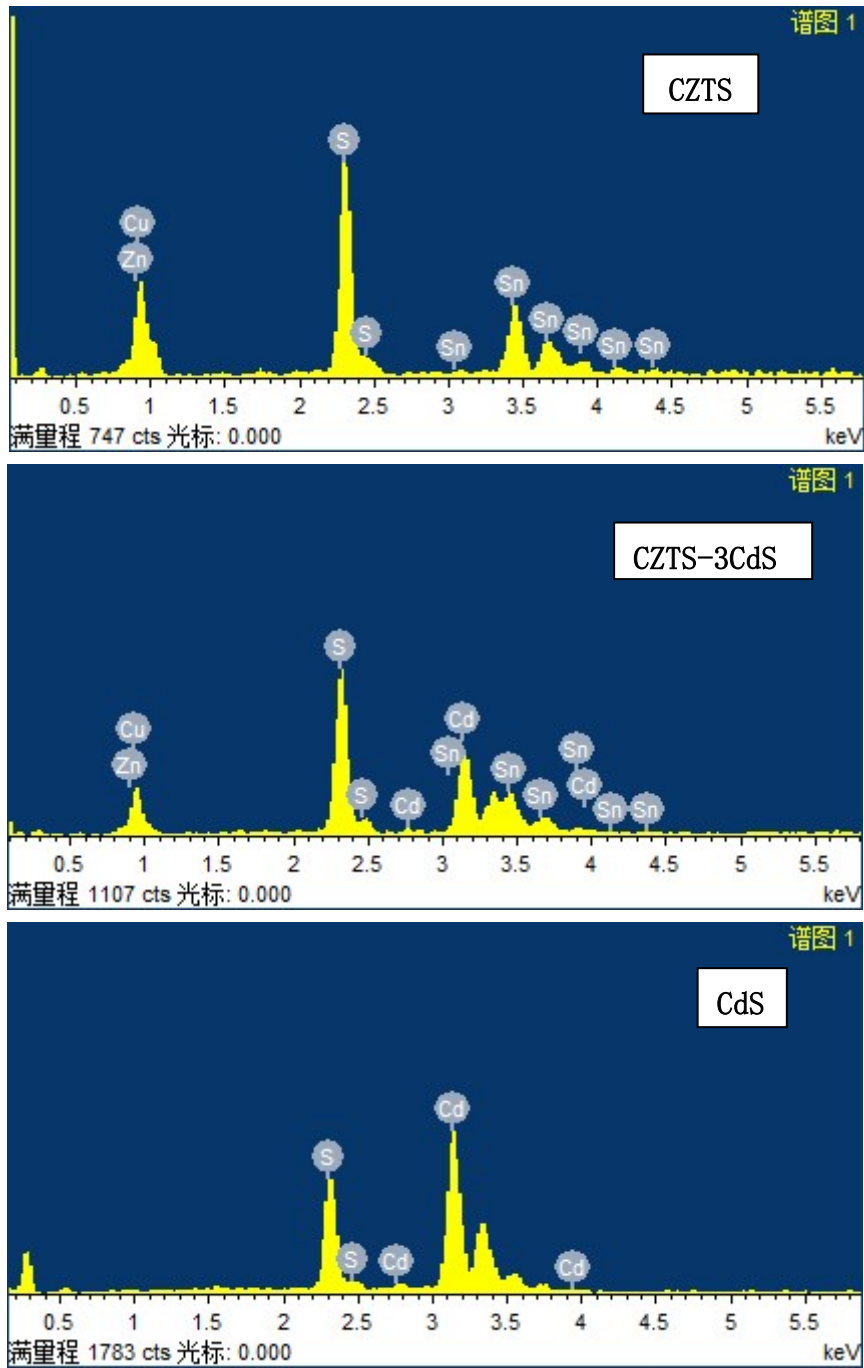


Fig. S3. The elemental analysis spectrum of CZTS, CZTS-3CdS and CdS nanocrystals.