Electronic Supplementary Information

Synthesis of Ultrathin CdS Nanosheets as Efficient Visible-light-driven Water Splitting Photocatalysts for Hydrogen Evolution

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Experimental Details

1. Material Synthesis.

1.1 Chemicals: All chemicals are analytical grade and used as received without further purification.

1.2 Synthesis of inorganic-organic hybrid CdS-DETA nanosheets: In a typical synthesis procedure, $CdCl_2 \cdot 2.5H_2O$ (0.0732g), S powder (0.064g), and diethylenetriamine (DETA, 12 mL) were added to a Teflon-lined autoclave with a capacity of 20 mL. The mixture was vigorously stirred for 30 min to form a homogeneous suspension. The autoclave was then sealed and heated at 80 °C for 48 h. After being cooled to room temperature, the light yellow precipitate was collected by centrifugation and washed with ethanol and the distilled water for three times, respectively. The final product was dried in a vacuum oven at 40 °C for 6 h.

1.3 Synthesis of ultrathin CdS nanosheets. In a typical procedure, CdS-DETA (20 mg), L-cysteine (10 mg), DETA (0.1 mL), and H_2O (40 mL) were added into a flat bottomed beaker with a 100 mL capacity. These samples were then sonicated continuously for 2 h at a low-power sonic bath. The resultant dispersions were centrifuged at 800 rpm for 10 min to remove aggregates. After centrifugation, the dispersions become almost transparent; the supernatant (top four-fifth of the centrifuged dispersion) was collected by pipette.

1.4 Synthesis of CdS nanosheet-based aggregates. In a typical procedure, CdS-DETA (50 mg) and H_2O (50 mL) were added to a single-necked round bottom flask with a capacity of 100 mL. The round bottom flask containing the samples was then stirred in a 80 °C water bath for 10 h to lead to the release the DETA component from the hybrid precursor. After cooling to room temperature, the precipitate was collected by centrifugation and washed with ethanol and the distilled water for three times, respectively. The final product was dried in a vacuum oven at 40 °C for 6 h.

2. Characterization

The scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopic (EDX) analysis were taken with a Hitachi S-4800 scanning electron microscope (SEM, 5 kV) equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. Transmission electron microscopy (TEM) and higher-resolution transmission electron microscopy (HRTEM) images were obtained with JEOL-2100F system equipped with EDAX Genesis XM2. Atomic force microscopy (AFM) study was preformed by means of a Bruker MultiMode 8 AFM. Inductively coupled plasma mass spectrometry analysis (7700X, Aglilent) was conducted to detect the concentration of CdS in the dispersion. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Focus Diffraction System using a Cu K α source (λ = 0.154178 nm). FTIR spectra were recorded on a MAGNA-IR 750 (Nicolet Instrument Co) FTIR spectrometer. Thermogravimetric analysis was made with a Mettler Toledo TGA/DSC 1 STARe system equipped with a gas controller (GC 200) and a recirculating stage cooling bath set at 22 °C (Julabo). The Uv-vis absorption spectra were recorded on a UV-vis spectrophotometer (TU-1901). Photoluminescence (PL) measurement was carried out on a Jobin Yvon Fluorolog 3-21 fluorescence photometer. Zeta potential measurements were carried out on a Malvern Zetasizer Nano ZS.

3. Photocatalytic Reaction. The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Typically, 15 mL of CdS colloidal dispersion was diluted by 15 mL of aqueous solution containing 0.5 M Na₂S and 0.5 M Na₂SO₃ to obtain 30 mL of aqueous solution. Thus, the mass amount of CdS in the aqueous solution is calculated to be 1.425 mg according to the concentration of CdS in the dispersion determined by ICP-MS. For comparison, the amounts of CdS-DETA, CdS aggregates, and CdS nanoparticles used in each photocatalytic reaction were also controlled to be 1.425 mg. The catalysts were then mixed with 30 mL aqueous solution containing 0.25 M Na₂S and 0.25 M Na₂SO₃. The solution was then degassed for 30 min, followed by irradiation with a 300 W Xe lamp equipped with a 420 nm-cut-off filter. The reactant solution was stirred and maintained at room temperature by a flow of cooling water during the photocatalytic reaction. The amount of evolved H₂ was determined with an on-line Agilent 7890A gas chromatography equipped with a TCD detector.

The apparent quantum efficiency (QE) for H_2 evolution was measured under the same photocatalytic reaction condition with irradiation light at 420 nm by using combined band-pass and cut-off filters. The intensity and number of photons of the light source at 420 nm were measured by an irradiate-meter. The QE was finally calculated according to Eq. (1):

$$QE [\%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$
$$= \frac{\text{number of evolved H}_2 \text{ molecules x 2}}{\text{number of incident photons}} \times 100$$
(1)



Fig. S1 (a) XRD pattern, (b) FTIR spectra, (c) EDX spectrum, and (d) TG profile of the inorganic-organic hybrid CdS-DETA nanosheets. The XRD pattern is similar to those obtained from some previously reported CdS-amine hybrid materials, such as $(Cd_2S_2)(pa)$ (pa = n-propylamine), $(Cd_2S_2)(ba)$ (ba = n-butylamine), $(Cd_2S_2)(ha = n$ -hexylamine)(*J. Am. Chem. Soc.*, **2007**, *139*, 3157.) , and CdS· 0.5en (en = ethylenediamine) (*Inorg. Chem.*, **2003**, *42*, 2331.). The FTIR spectrum of sample confirms the presence of DETA molecules in the hybrid materials. EDX analysis showed that Cd, S, C, and N were the major elements included in the resulting products after the solvothermal reaction. This result further suggests that inorganic-organic hybrid CdS-DETA nanometrials were produced. In the TG profile, it was found that ~1.3 % weight loss occurred before 200 °C, which can be attributed to the loss of water, and the distinct weight loss in the range of 200-350 °C originates from the release of DETA with the hybrid nanosheets. These results unambiguously indicate the inorganic-organic hybrid CdS-DETA nanosheets are sensitive unambiguously indicate the inorganic-organic hybrid CdS-DETA nanosheets. These results unambiguously indicate the inorganic-organic hybrid CdS-DETA nanosheets can be synthesized through the solvothermal reaction.



Fig. S2 SEM image of the CdS samples obtained after exfoliation suggesting the well-dispersed 2D sheet-like morphology. This image suggests that the large-area CdS ultrathin nanosheets can be fabricated via an L-cysteine-assisted ultrasonication-induced aqueous exfoliation approach.



Fig. S3 (a) Photographs and (b) UV-vis spectra of the CdS dispersion at the initial stage (collected after exfoliation) and stored under ambient conditions for 3 weeks. It was found the obtained dispersion showed no precipitation and no obvious change in the UV-vis spectrum even after three weeks under ambient condition, indicating its high stability with the L-cysteine as the stabilizing agent.



Fig. S 4 (a) UV-vis spectrum of the as-obtained ultrathin CdS nanosheet dispersion. (b) PL spectrum of the as-obtained ultrathin CdS nanosheet dispersion under irradiation at 380 nm.



Fig. S5 (a) UV-vis spectra of CdS ultrathin nanosheet colloid dispersion, L-cysteine aqueous solution and DETA aqueous solution. (b) UV-vis spectra of CdS ultrathin nanosheet dispersion (blue line), CdS-DETA disersion (cyan line) and CdS nanosheet aggregate solution (red line; for SEM image, please see Figure S14). To compare their UV-vis spectra, the CdS-DETA and CdS nanosheet aggregates were dispersed in water to form a suspension with the same concentration of CdS to that of the ultrathin CdS nanosheets dispersion, which is determined by ICP. From the (a) image, it can be seen that the absorbance in the UV-vis spectrum of the CdS ultrathin nanosheet dispersion originated from CdS rather than L-cysteine and DETA. From the (b) image, it was found that the big specific surface area and high percentage of disordered surface atoms of ultrathin CdS nanosheets enabled them to harvest remarkably increased visible light compared with the CdS-DETA nanosheets and CdS aggregates.



Fig. S6 Illustration of the change in the molecular structure of L-cysteine under different pH conditions (*Anal. Methods*, 2013, *5*, 1695.).



Fig. S7 Zeta potential test of the CdS ultrathin nanosheet dispersion. The sample was measured for three times. It was found that the zeta potential was about -20 mV, suggesting their good stability through electrostatic repulsion due to the adsorption of L-cysteine.



Fig. S8 Photograph of the stability test of the dispersion containing the as-prepared ultrathin CdS nanosheets stabilized by L-cysteine under constantly strong stirring.



Fig. S9 Photographs of the ultrathin CdS nanosheet dispersion prepared in the absence/presence of L-cysteine after stirring for different time.



Fig. S10 (a) Photograph of the CdS dispersion in water obtained in the absence of L-cysteine at the initial stage and stored under ambient conditions for 24 h. (b) The Zeta potential of the CdS dispersion in the absence of L-cysteine. Figure S8a suggests the stablitily of CdS ultrathin nanosheet dispersion is weaker than that prepared in the presence of L-cysteine. ICP-MS suggested that the concentration of CdS in the dispersion was about 0.019 mg/mL, which is much lower that that (~0.095 mg/mL) obtained in the presence of L-cysteine with other conditions were kept unchanged.. These results not only indicate that L-cysteine plays a key role in keeping the stability of the obtain CdS dispersion, but also imply that the addition can facilitate the exfoliation process and thus increase the concentration of CdS in the dispersion.



Fig. S11 (a) Photograph of the Tyndall effect of the dispersion containing ultrathin ZnS nanosheets stabilized by L-cysteine. (b) Photographs of the dispersion containing ultrathin ZnS nanosheets before and after constant stirring for 96 h. It was found that no aggregates or precipitate can be observed after constantly strong stirring for 4 days, indicating the good stability of the dispersion. This futher demonstrates that the L-cysteine-assisted aqueous exfoliation approach may make the L-cysteine-assisted ultrasonication strategy to be developed to a generalized method to obtain stable dispersion of inorganic ultrathin nanosheets. The ultrathin ZnS nanosheets were synthesized through the similar procedure to the preparation of ultrathin CdS nanosheets by using the $2D-[(Zn_2S_2)(pa)]$ (*pa* stands for *n*-propylamine) nanostructures as the starting precursors for the ultrasonication. The $2D-[(Zn_2S_2)(pa)]$ precursors were obtained according to the reference (*J. Am. Chem. Soc.*, **2007**, *129*, 3157.).



Fig. S12 (a) Photographs and (b) UV-vis spectra of the CdS dispersion at the initial stage (pH=10) and after adding acid (pH=5). It was found that the changes in the pH changed the molecular structure of L-cysteine and then further influence the stability of the CdS dispersion.



Fig. S13 (a) UV-vis spectrum and (b) Zeta potential measurement of the CdS dispersion when L-cysteine was replaced by mercaptoacetie acid at pH=10. The inset of (a) is the photograph of the obtained dispersion.



Fig. S14 (a) UV-vis spectrum and (b) Zeta potential measurment of the CdS dispersion when L-cysteine was replaced by 3-mercaptopropionic acids at pH=10. The inset of (a) is the photograph of the obtained dispersion.



Fig. S15 Illustration of the change in the molecular structure of (a) mercaptoacetie acid and (b) 3-mercaptopropionic acids under different pH conditions.



Fig. S16 (a,b) SEM images of the bulk CdS obtained after heating the CdS-DETA in water at 80 °C for 10 h. It was found that many aggregates composed of sheet-like building blocks generated after the release of DETA component from the hybrid precursors.



Fig. S17 (a) SEM image and (b) XRD pattern of CdS nanoparticles prepared according to the reference (*J. Phys. Chem. C*, 2009, 113, 3617.).

Tab. S1 Photocatalytic H₂ ecolution over CdS and loading with PdS (1 wt%).

Catalyst	H_2 evolution rate(µmol h^{-1})	QE (%)
CdS	58.56	1.38
PdS/CdS ^a	421.9	9.62

^a the loading of PdS on CdS producing PdS/CdS was realized by in-situ deposition according to the reference (*J. Catal.* 2009, 266, 165.).



Fig. S18 SEM image and XRD pattern of the CdS collected after a 12h photocatalytic test. It was found the 2D sheet-like morphology and the wurtzite phase structure can be maintained after 12 h photocatalysis.



Fig. S19 (a) Photograph of the CdS collected after a 12h photocatalytic test. The laser light beam is incident from the side to demonstrate the Tyndall effect. (b) UV-vis spectra of the CdS ultrathin nanosheet dispersion diluted using equal volume aqueous solution containing 0.5 M Na₂S and 0.5 M Na₂SO₃ and after photocatalysis for 12 h. These results (Fig. S18-19) indicated that the ultrathin CdS nanosheets had a good stability during the photocatalytic measurement.