Engineering the Morphology and Configuration of Ternary Heterostructures for Improving Their Photocatalytic Activity

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Supporting Information

ABSTRACT: Heteronanomaterials composed of suitable semiconductors enable the direct conversion from solar power into clean and renewable energy. Ternary heterostructures with appropriate configuration and morphology possess rich and varied properties, especially for improving the photocatalytic activity and stability synchronously. However, suitable ternary heterostructure prototypes and facile while effective strategy for modulating their morphology and configuration are still scarce. Herein, various ternary ZnS-Cds-Zn$_{1-x}$Cd$_x$S heterostructures with tunable morphology (0 to 2 D) and semiconductor configurations (randomly distributed, interface mediated, and quantum dots sensitized core@shell heterostructures) were facilely synthesized via one-pot hydrothermal method resulting from the different molecular structures of the amine solvents. Semiconductor morphology, especially configuration of the ternary heterostructure, shows dramatic effect on their photocatalytic activity. The CdS sensitized porous Zn$_{1-x}$Cd$_x$S@ZnS core@shell takes full advantage of ZnS, Zn$_{1-x}$Cd$_x$S and CdS and shows the maximal photocatalytic H$_2$-production rate of 100.2 mmol/h/g and excellent stability over 30 h. This study provides some guidelines for the design and synthesis of high-performance ternary heterostructure via modulation of semiconductor configuration and morphology using one-pot method.

KEYWORDS: ternary heterostructure, morphology, configuration, photocatalytic activity, core–shell

1. INTRODUCTION

Semiconductor heteronanomaterial with appropriate configuration and morphology enables the direct conversion from solar power into clean and renewable hydrogen energy via photocatalytic water splitting. However, most of the heterostructures are based on two semiconductors, the binary heterostructure, which may suffer from the drawbacks including poor band structure matching and large lattice stress due to the distinct intrinsic parameters of the two semiconductors. The noble metal cocatalysts (such as Pt, Pd, Au) were adopted to further facilitate the separation and transport of photogenerated charge carriers. Embedding a cost-effective semiconductor with suitable parameter and feature into the traditional binary heterostructure could improve the separation and transport efficiency of charge carriers, thus increasing the photocatalytic activity and stability simultaneously. Additionally, rational design of ternary heterostructure could bring out rich and varied properties via modulating the configuration. To the best of our knowledge, suitable ternary heterostructure prototypes are still scarce, and the modulation of their configuration and morphology with facile method is still a grand challenge.

To date, most of the semiconductor heterostructures are fabricated at least by two steps using surface modification process, that is, one semiconductor is fabricated on the surface of another one, which largely restricts the scale-up synthesis of heterostructure photocatalysts and decreases the number of active sites. One-pot method, which involves the reconstruction of the precursors and bulk fabrication of heterostructure could facilitate the thoroughgoing reaction of the reactants and increases the heterostructure active sites. Moreover, the modulation of the morphology and semiconductor configuration of the heterostructures could increase the number of exposed active sites and enhance the separation and transport efficiency of charge carriers, respectively. Nevertheless, the fabrication of heterostructures, especially the ternary heterostructures, and the modulation of their morphology and configuration using one-pot method are rarely reported.

ZnS with a wide bandgap possesses negligible visible light photocatalytic activity and excellent stability, whereas CdS shows excellent photocatalytic activity but very poor lifetime. Zn$_{1-x}$Cd$_x$S, the “alloy” of ZnS and CdS, possesses continuously tunable bandgap ($E_g$) ranging from 3.66 (ZnS) to 2.4 eV (CdS) and lattice constant between 0.331 (ZnS) and 0.359 nm (CdS). Also, Zn$_{1-x}$Cd$_x$S exhibits a better photocatalytic activity than that of single CdS, even loaded with Pt as cocatalyst. Constructing the ternary...
heterostructure of ZnS-CdS-Zn$_{1-x}$Cd$_S$ with suitable configuration via a facile one-pot method could not only relieve the structure mismatch, but also improve the photocatalytic stability due to the different characteristics of ZnS, CdS, and Zn$_{1-x}$Cd$_S$. In this regard, rational design of the morphology and configuration of the ternary ZnS-CdS-Zn$_{1-x}$Cd$_S$ heterostructure via a simple method for completely utilizing the features of these semiconductors is of special importance from both the scientific and practical viewpoints. Although all these semiconductors and the heterostructures between ZnS and CdS have been extensively investigated as photocatalysts, the Zn$_{1-x}$Cd$_S$ based heterostructures, especially the ZnS-CdS-Zn$_{1-x}$Cd$_S$ ternary heterostructure as photocatalysts, have been researched scarcely.

Herein, ZnS, CdS, and Zn$_{1-x}$Cd$_S$ were adopted for constructing the ternary heterostructures to take advantage of the different merits of these semiconductors. Both the morphology (0D to 2D) and semiconductor configurations (randomly distributed, interface mediated, and quantum dots sensitized core@shell heterostructures) were facilely modulated via a one-pot hydrothermal method using different solvents (ethylenediamine, EDA; 1,2-diaminopropane, DAP; diethylethlenetriamine, DETA; deionized water, DIW) with different molecular structures as templates. The photocatalytic activity was found to be dominated by the morphology, especially the semiconductor configuration. The rational designed CdS sensitized porous Zn$_{1-x}$Cd$_S$@ZnS core@shell heterostructure completely utilizes the features of the semiconductors and shows the maximal photocatalytic rate of 100.2 mmol/h/g (apparent quantum efficiency = 38.4%) and excellent stability. This value is 143- and 911-times higher than that of CdS prepared with DETA and DIW as solvents, respectively.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. In a typical synthesis of the ZnS-DETA hybrid nanomaterial precursor, 1.5 mmol of ZnCl$_2$ and 3.0 mmol of CN$_2$H$_4$S (thiourea) were dissolved in 30 mL of pure DETA under reflux. Both the morphology and configuration of the ternary ZnS-DETA ternary heterostructure was modulated by the distinct molecular structures of the amines (as shown in the inset). The morphology of these hybrid nanomaterials could be modulated by the different solvents as templates.

2.2. Characterization. X-ray diffraction (XRD) patterns were recorded on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu K$_\alpha$ radiation (\(\lambda = 1.54060\ \AA\)) with different Cd$_x$(Zn+Cd) molar ratios (0, 10, 30, and 50 at%) were dissolved in DIW (2.8 mL) and then dropped into the aforementioned solution quickly under mild stirring. After several minutes, the obtained solution was transferred into 15 mL autoclave and maintained at 180 °C for 21 h. The final white products were rinsed and dried at 60 °C overnight. Thirty milligrams of the as-prepared ZnS-DETA precursor was washed in 10 mL of DIW under ultrasound for a few minutes. Given contents of Cd(NO$_3$)$_2$.5H$_2$O with different Cd$_x$(Zn+Cd) molar ratios (0, 10, 20, 30, and 50 at%) were dissolved in DIW (2.8 mL) and then dropped into the aforementioned solution quickly under mild stirring. After several minutes, the obtained solution was transferred into 15 mL autoclave and maintained at 140 °C for different times (2, 3, 4, 6, 8, 10, 15, 20, 24, and 30 h). The final products were rinsed and dried at 60 °C overnight in the vacuum oven to evaporate the solvent. The heterostructures (the Cd content of 30 at%, reaction time of 10 h) derived from EDA, DAP, and DIW were fabricated with the same parameters using different solvents as templates.

2.3. Photocatalytic Hydrogen Production. The photocatalytic H$_2$-production experiments were performed via a photocatalytic H$_2$-production activity evaluation system (CEL-SPH2N, CEALight, China) in a 300 mL Pyrex flask, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp through a UV-cutoff filter with a wavelength range of 420–1000 nm. The focused intensity on the flask was about 200 mW cm$^{-2}$. In a typical photocatalytic H$_2$-production experiment, 5 mg of the prepared photocatalyst was suspended in mixed solution containing Na$_2$S (0.55 M) and Na$_2$SO$_3$ (0.25 M). Before irradiation, the system was evacuated for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. The evolved H$_2$ content was analyzed by gas chromatography. Twenty milligrams of catalyst was used to measure the apparent quantum efficiency under the similar photocatalytic reaction conditions to the above-mentioned system using a filter at 420 nm (420 ± 8 nm).

3. RESULTS AND DISCUSSION

Various solvents (DAP, EDA, DETA, and DIW) were adopted to fabricate the ZnS precursors. Both the morphology and configuration of the ternary heterostructures (Cd$_x$(Zn+Cd) = 30 at%) were modulated via a one-pot hydrothermal process for 10 h, and the corresponding samples were abbreviated as ZC-DAP, ZC-EDA, ZC-DETA, and ZC-DIW, respectively. All the heteronanomaterials show obvious ZnS, CdS, and Zn$_{1-x}$Cd$_S$ phases and similar bandgap corresponding to CdS phase (Figures S1 and S2). Figure 1, panels a–c exhibit the TEM images of the distinct morphology of the ternary heterostructures derived from the different molecular structures of the amines (as shown in the inset). The morphology of these samples was further confirmed by SEM (Figure S3). In contrast to the nanoparticle morphology with a radius of about 2 µm of ZCS-DIW, the morphology of the heteronanomaterials could be modulated by the distinct molecular structures of the amines owing to the formation of ZnS-amines inorganic–organic hybrid templates. The ZnS-EDA was sculpted layer by layer, and nanoframe morphology formed. The side chain in DAP facilitates the formation of heterostructure with small nanoparticle morphology. Notably, the heteronanomaterial...
observed in single nanoparticle (inset of Figure 1g), and the ternary heterostructure in ZC-DAP is composed of the random distribution of the nanoparticles with different phases. As reported in our previous investigation, the lattice fringe of Zn1−xCdS could be observed between ZnS and CdS phases, indicating its configuration of ZnS/Zn1−xCdS/CdS. As depicted in Figure 1, panel i, CdS quantum dots (CdS QDs) with a diameter of approximately 5 nm are embedded in the highly porous ZnS shell, while only the Zn1−xCdS lattice fringe is observed in core region. Moreover, all the heteronanomaterials derived from organic amines show higher N2-adsorption volume and S BET (Figure S6) than that of ZC-DIW. Characterizations for the composition of the samples derived from different amines via XPS and ICP (Figure S7) demonstrate that all the samples derived from different amines showed close Cd content, whereas ZC-DIW shows the much smaller Cd content (Figure S8) due to the incomplete reaction resulting from the larger particle size of ZnS (Figure S9).

Scheme 1 illustrates the evolution of morphology and configuration of the ternary heterostructures derived from different templates with increased reaction time. ZnS derived from ZnS-DETA hybrid nanomaterials shows the porous morphology after the rapid dissolution of DETA molecules. This preformed porous ZnS, acting as shell and Zn and S sources, reacted with CdCl2 and generated the Zn1−xCdS, which was surrounded by the remnant porous ZnS shell. Continuous reaction of ZnS and CdCl2 decreased the thickness of ZnS shell in longer reaction time, and the in situ formed CdS phase distributed in the matrix of ZnS porous shell through the cation exchange reaction between Cd2+ and ZnS. Significantly, the larger radius of Cd2+ than that of Zn2+ is another reason for the formation of CdS phase. ZnS derived from DETA and EDA exhibited quantum dots sensitized core@shell heterostructures derived from DETA, EDA, and DAP, respectively. Consequently, the corresponding ZnS-CdS-Zn1−xCdS heterostructures derived from DETA, EDA, and DAP exhibited quantum dots sensitized core@shell nanostructures, interface mediated nanoframe, and randomly distributed nanoparticle heterostructure, respectively.

The photocatalytic H2-production via water splitting was chosen for evaluating the effect of morphology and configuration on the photocatalytic performance (Figure 1).
Notably, the semiconductor morphology, especially configuration of the ternary heterostructure, showed distinct effect on their photocatalytic activity. All the heterostructures derived from amines possess much larger H\textsubscript{2}-production activity than that of ZC-DIW (3.1 mmol/h/g) (Figure S11) because of their modulated morphology and more active sites as confirmed by the EDX results.\(^{38}\) The Zn\textsubscript{1−x}Cd\textsubscript{x}S interface-mediated heterostructure derived from EDA shows a better photocatalytic activity of 23.5 mmol/h/g because of its Cd\textsubscript{0.5}S\textsubscript{0.5} nanorod morphology with very limited Cd content. Notably, ZC30 with appropriate amount of Cd possesses nanorod core and considerable amount of porous shell owing to the rapid and complete reaction between the small amount of Cd and sufficient ZnS; ZC50 shows nanorod morphology with very flimsy porous shell due to the large Cd content. Notably, ZC30 with appropriate amount of Cd possesses nanorod core and considerable amount of porous shell (Figure S15). A composition variation is observed in ZC10 and ZC30 due to the complex ternary heterostructure (Figure S16). Moreover, ZC30 possesses considerable large S\textsubscript{BET} of 81.5 m\textsuperscript{2}/g and the maximum water vapor adsorption volume (Figure S17). Consequently, ZC30 possesses the maximum H\textsubscript{2}-production rate (Figure S18) because of its Zn\textsubscript{1−x}Cd\textsubscript{x}S@porous ZnS core–shell structure and large amount of CdS sensitized highly porous ZnS shell. The separation and transport efficiency were further confirmed by EIS spectra as shown in Figure S19.

To modulate the thickness of porous shell in the core–shell heterostructure derived from DETA, a series of samples (ZC30) with different reaction times were prepared and labeled as ZC30-\(n\) (\(n = 2, 4, 6, 8, 10, 12, 15,\) and 20 h). Figure 2, panels a–e demonstrate the TEM images of ZC30 with different reaction times. First, Cd\textsuperscript{2+} reacted with the sufficient ZnS for a short time of 2 h, forming an irregular Zn\textsubscript{1−x}Cd\textsubscript{x}S nanoregion, which would become nanorod morphology in ZC30-6. The thickness of porous shell reduces with the increased reaction time, and ZC30-10 possesses a shell thickness of about 45 nm. However, the sample with longer reaction time (ZC30-15) shows very limited thickness of porous shell. Corresponding to the evolution of morphology, the content of Cd first increases with the reaction time increasing to 8 h owing to the decreased ZnS shell, while then it does not change dramatically in longer reaction time (Figure S20).

Effect of reaction time on the band structure of the heterostructure samples with 30 at\% Cd was investigated by the UV–vis diffuse reflection spectra (Figure 2f). All the samples with different reaction times show two band edges in the UV and visible region, respectively. The \(E_{g}\) values corresponding to the absorption in visible region were calculated by the Kubelka–Munk (KM) method and demonstrated in the inset of Figure 2, panel f.\(^{27}\) and no dramatic variation of band structure for CdS phase can be
observed in the heterostructure samples prepared with different reaction times. However, the \( E_g \) corresponding to the absorption in the UV region keeps a constant value first and then decreases strongly owing to the disappearance of ZnS (Figure S21). The Zn content of the solid solution core of ZC30-10 was specified to be 48.5 at% (Figure S22).

Dependence of shell thickness on the photocatalytic \( \text{H}_2 \) evolution rate in the samples is exhibited in Figure 2, panel h. ZC30-10 shows the maximum value of 100.2 mmol/h/g and excellent apparent quantum efficiency (AQE) of 38.4\% owing to the considerable amount of CdS and suitable thickness of shell.\(^39\) This \( \text{H}_2 \)-production rate is 143- and 911-times higher than that of CdS prepared using DETA and DIW as the solvents, respectively (Figure S23). In addition, the result is better than that of the previously reported CdS-based photocatalysts.\(^40\) It is noteworthy that the photocatalytic \( \text{H}_2 \)-production rate shows a sharp decline from 100.2 mmol/h/g in ZC30-10 to 9.2 mmol/h/g in ZC30-15, indicating the extremely momentous role of CdS sensitized porous ZnS shell in improving the photocatalytic \( \text{H}_2 \)-production activity. Moreover, ZC30-10 shows excellent photocatalytic stability over a period of 30 h (Figure 2i), which is much better than that of \( \text{Zn}_1\text{x}_{\text{Cd}}\text{S} \text{CdS} \) interface mediated heterostructure (less than 20 h) because of the protective role of ZnS shell.\(^30\) No obvious morphology variation is seen after the photocatalytic reaction of 30 h (Figure S24), which confirms that the CdS QDs sensitization could improve the photocatalytic activity of the shell without deteriorating its stability.\(^43\) Interfacial electron transfer of the samples with different heterostructure configurations is investigated by EIS spectra (Figure S25). All the heterostructure samples show a much smaller semicircle in the middle-frequency region than that of CdS. Significantly, the smallest semicircle in the middle-frequency region in ZC30-10 indicates its highest efficiency of interfacial electron transfer stemming from its considerable amount of CdS/ZnS active sites.\(^39\) Moreover, the core@shell heterostructure can also be obtained in ZC10 and ZC50 with reaction time of 24 and 3 h, respectively (Figure S26). However, the CdS phase is very weak, and the \( \text{H}_2 \)-productin rate is lower than that of ZC30-10 (Figure S27). These results further confirm the growth manchansim of the core–shell morphology and the important role of CdS sensitized core@shell on the photocatalytic activity.

The transport and separation among ZnS, CdS, and \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) are very important to evaluate the effect of semiconductor configuration on the photocatalytic activity. It was reported that the ZnS/CdS heterostructure exhibits the quasi-type II characteristics because of the acceptor states (\( I_\text{V} \), \( V_{\text{Zn}} \)) in ZnS.\(^{17,31,44,45}\) The defect states related acceptor levels in ZnS and \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) were characterized by the PL spectra (Figure S28). All the heterostructure samples and the solid solution samples prepared via thermolysis method\(^27\) with different amounts of Cd show the similar emission peak position derived from different defect states (such as \( V_{\text{Zn}} \)) to that in ZnS. These results were consistent with the previous publications,\(^{37-46}\) which reported that the peak position of the emission derived from the defect states (such as \( V_{\text{Zn}} \)) in \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) is similar to that in ZnS and will not change with the variation of \( E_g \) values derived from the different amounts of Cu\(^2+\) dopant. Consequently, the semiconductor with lower CB edge possesses lower defect (such as \( I_\text{V} \) and \( V_{\text{Zn}} \)) related acceptor level.

The excellent photocatalytic \( \text{H}_2 \)-production in CdS QDs sensitized porous \( \text{Zn}_{1-x}\text{Cd}_x\text{S}@\text{ZnS} \) core–shell heterostructure under visible light irradiation can be exhibited by the schematic illustrations in Scheme 2. The photogenerated holes transferred from the CdS to the acceptor states (\( V_{\text{Zn}} \) and \( I_\text{V} \) defect states) in porous ZnS shell.\(^37,41\) On the other hand, the charge transport and separation among three components (\( \text{Zn}_{1-x}\text{Cd}_x\text{S}@\text{ZnS} \)) near the core is demonstrated in the left side of Scheme 2. The photogenerated holes were transferred from CdS and \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) to the local acceptor states in ZnS shell due to the lower acceptor states in \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) than that in ZnS.\(^46\) In this regard, this core–shell heterostructure solves the two major obstacles of core@shell heterostructure: (i) poor photocatalytic activity of the single component in the core–shell heterostructure, especially the wide-bandgap protective shell,\(^17,49\) and (ii) inferior lattice and band structure matching between the two semiconductors of the core–shell heterostructure.\(^11,12\) Compared with the randomly distributed and \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) interface mediated heterostructure, this CdS sensitized \( \text{Zn}_{1-x}\text{Cd}_x\text{S}@\text{ZnS} \) core@shell heterostructure can take full advantage of excellent stability of ZnS, high photocatalytic activity of CdS, and tunable parameters of \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \). Moreover, the porous ZnS shell could dramatically improve the transport of reactants.\(^17,28\)

4. CONCLUSION

In summary, various novel ternary heterostructures were fabricated using ZnS, CdS, and \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) with different features as the composed semiconductors. Both the morphology and semiconductor configuration were facilely modulated via a one-pot hydrothermal method using the different solvents with different molecular structures as precursors. The photocatalytic activity was found to depend on the morphology, especially the semiconductor configuration, and the rational designed CdS sensitized porous \( \text{Zn}_{1-x}\text{Cd}_x\text{S}@\text{ZnS} \) core@shell heterostructure, which completely utilize the features of these semiconductors, showing the optimal photocatalytic activity of 100.2 mmol/h/g and best photocatalytic stability. This excellent \( \text{H}_2 \)-production rate is 143- and 911-times higher than those of CdS prepared using DETA and DIW as solvents, respectively, and it is also considerably better than other CdS-based heterostructures.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b11388.
Additional XRD, UV–vis, SEM, TEM, EDX, ICP, and XPS results; absorption/desorption isotherms; Nyquist plots; PL spectra (PDF)

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**Notes**
The authors declare no competing financial interest.

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