Hierarchical assemblies of Cd$_{x}$Zn$_{1-x}$S complex architectures and their enhanced visible-light photocatalytic activities for H$_2$-production

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Abstract

The shape-controlled synthesis of hierarchically micro- and nanostructured materials has opened up new opportunities to improve their properties. In this work, Cd$_{x}$Zn$_{1-x}$S complex architectures, such as micro-flowers and microspheres, were prepared through a facile solvothermal method, by using diethylenetriamine (DETA) and water as solvent. Within the Zn content increase from 0.2 to 0.8 in the Cd$_{x}$Zn$_{1-x}$S solid solution, the morphology transformed progressively from microflowers agglomerates to microspheres. The photocatalytic H$_2$ evolution over the solid solutions was further investigated through the H$_2$ production rate evolution. It has attracted considerable attention$^1$. At 1.8 mmol g$^{-1}$ h$^{-1}$, the highest H$_2$ production even can reach under visible light irradiation (λ > 420 nm). The Cd$_{0.2}$Zn$_{0.8}$S microspheres exhibited the best photocatalytic activity with H$_2$ production rate of ca.1.8 mmol g$^{-1}$ h$^{-1}$, probably resulted from the needful surface area and surface defect. After loading 1 wt.% Pt on the surface of Cd$_{0.2}$Zn$_{0.8}$S, the rate of H$_2$ production even can reach 5 mmol g$^{-1}$ h$^{-1}$.

1. Introduction

Since the pioneering work by Fujishima and Honda, heterogeneous photocatalytic water splitting over inorganic semiconductor catalysts for H$_2$ evolution has attracted considerable attention$^1$. However, most of the developed photocatalyst with wide band gap can only absorb the ultraviolet light. To maximize the use of solar energy, visible light-responsive semiconductor photocatalysts should be developed$^{2–4}$. As an important semiconductor, cadmium sulfide (CdS) nanocrystals has the narrow band-gap (E$_g$ = 2.4 eV) and valence bands at relatively negative potentials, which make it suitable for hydrogen production under visible light in the presence of sacrifice agents$^{5–7}$. Nevertheless, the photocatalytic efficiency of CdS for water splitting is still limited, it is necessary to find suitable method for its structure modification. One strategy is to incorporate of ZnS into the structure of CdS for forming the series of Cd$_{x}$Zn$_{1-x}$S solid solution with adjustable band-gap$^{8,9}$, its conduction band and valence band can shift to more positive and negative position, leading to the increment of photocatalytic properties$^{10,11}$. It is well known that the applications for materials depend critically on their properties such as the crystal structure, size, shape, specific area and surface defect states. For improving the photocatalytic activity, it is very important to synthesize the nanocrystals with a specific size and morphology. To date, Cd$_{x}$Zn$_{1-x}$S compounds with different morphologies, including nanoparticles$^{12}$ and rod-like nanostructures$^{13,14}$, have been prepared and used as catalysts in photocatalytic systems. And it has been found that these photocatalysts have better photocatalytic H$_2$-production activities. Recently, some hierarchical micro- and nanostructured materials composed of nanosized building blocks such as nanoparticles or nanorods have been prepared and found to have new properties and exhibit potential applications in photocatalytic fields$^{15–17}$. For example, some semiconductors such as Fe$_2$O$_3$[18], ZnO[19], and TiO$_2$[20] with a hierarchical structure were successfully synthesized and exhibited well photocatalytic properties. However, there is no research on the photocatalytic water splitting for hydrogen production by using the complex hierarchical Cd$_{x}$Zn$_{1-x}$S micro- and nanostructure.

In the current study, a series of Cd$_{x}$Zn$_{1-x}$S solid solutions with hierarchical structures have been efficiently synthesized in a DETA aqueous solution through a one-step mix-solvothermal method. The photocatalytic performance was then evaluated through the H$_2$ evolution from aqueous solutions containing S$_2$O$_8^2−$/SO$_4^{2−}$ under visible light irradiation (λ > 420 nm). The Cd$_{0.2}$Zn$_{0.8}$S microspheres exhibited the best photocatalytic activity with H$_2$ production rate of ca.1.8 mmol g$^{-1}$ h$^{-1}$, probably resulted from the needful surface area and surface defect. After loading 1 wt.% Pt on the surface of Cd$_{0.2}$Zn$_{0.8}$S, the rate of H$_2$ production even can reach 5 mmol g$^{-1}$ h$^{-1}$.
2. Experimental

2.1. Cd$_{x}$Zn$_{1-x}$S nanocrystal syntheses

The chemicals used in this study were all analytical reagent grade and used without further purification. The Cd$_{x}$Zn$_{1-x}$S nanocrystals were prepared through a solvothermal route. First, a suitable amount of Cd(CH$_3$COOH)$_2$·2H$_2$O and Zn(CH$_3$COOH)$_2$·2H$_2$O (total amount of Cd$^{2+}$ and Zn$^{2+}$ = 10 mmol) and 20 mmol thiourea were dissolved in 24 mL deionized water. DETA (12 mL) was then added into the aqueous solution. The mixture was stirred to form a homogeneous solution and placed in an autoclave with an inner Teflon lining (the volume is 50 mL). Then the autoclaves were maintained at 180°C for 12 h and cooled to room temperature. Finally, the product was filtered, washed several times with distilled water and ethanol, and dried in a vacuum oven at 60°C for 12 h.

2.2. Characterization

The X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer (Germany) with Cu Kα radiation. The UV–Vis absorption spectra were obtained using a Shimadzu UV–Vis–NIR spectrophotometer (UV-3600, Japan). Photoluminescence (PL) spectra were recorded at room temperature on a fluorescence spectrophotometer (Hitachi F-7000, Japan) using Xenon lamps as the excitation source, all samples were excited using a wavelength of 300 nm. Scanning electron microscopy (SEM) was conducted using a LEO-438VP field emission microscope (Germany). Transmission electron microscopy (TEM) was performed using a JEM-2100 transmission electron microscope (Japan) using a 200 kV accelerating voltage. The Brunauer–Emmett–Teller (BET) surface area were measured by a nitrogen adsorption technique at 77 K using an ASAP2020M automated gas-sorption system (America).

2.3. Photocatalytic H$_2$ production on the Cd$_{x}$Zn$_{1-x}$S solid solution

The photocatalytic reaction was conducted in a closed glass circulation system. The Cd$_{x}$Zn$_{1-x}$S photocatalyst (0.1 g) was dispersed in a 100 mL aqueous solution containing 0.1 M Na$_2$S and 0.1 M Na$_2$SO$_3$, which served as sacrificial agents. Pt was in situ photodeposited from the H$_2$PtCl$_6$·6H$_2$O precursor to act as a co-catalyst for the promotion of H$_2$ evolution. The entire reaction process was irradiated using a 300 W Xe lamp (Trusttech PLS-300UV, China) with a cutoff filter (λ > 420 nm). The amount of H$_2$ evolved was determined using an online thermal conductivity detector (TCD) gas chromatograph with Ar as the carrier gas.

3. Results and discussion

3.1. Formation of Cd$_{x}$Zn$_{1-x}$S solid solutions

XRD was used to characterize the phase structure of the samples. From the Fig. 1, the patterns for CdS and ZnS match well with the standard spectra (JCPDS 41-1049 and 36-1450, respectively). And all of the samples exhibits a pure hexagonal wurtzite structure, with the prominent diffraction peaks corresponding to (100), (002), (101), (110), (103) and (112) planes. Due to the smaller Zn atomic radius than Cd atomic radius, the zinc atoms can form infinite solid solution. And it has been proved that the diffraction peaks of Cd$_{x}$Zn$_{1-x}$S solid solution can shift to lower angles as the value of $x$ in the Cd$_{x}$Zn$_{1-x}$S solid solution increases [12,13]. In our experimental, the diffraction peak also changes with different Cd and Zn composition, indicating

Table 1
The lattice constants and band gap of Cd$_{x}$Zn$_{1-x}$S solid solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CdS</th>
<th>Cd$<em>{0.2}$Zn$</em>{0.8}$S</th>
<th>Cd$<em>{0.4}$Zn$</em>{0.6}$S</th>
<th>Cd$<em>{0.6}$Zn$</em>{0.4}$S</th>
<th>Cd$<em>{0.8}$Zn$</em>{0.2}$S</th>
<th>ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice</td>
<td>a (Å)</td>
<td>4.1187</td>
<td>4.0916</td>
<td>4.0625</td>
<td>4.0525</td>
<td>4.0439</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>2.11</td>
<td>2.21</td>
<td>2.29</td>
<td>2.37</td>
<td>2.45</td>
<td>3.45</td>
</tr>
</tbody>
</table>
the successful synthesis of Cd\textsubscript{x}Zn\textsubscript{1−x}S solid solution. The lattice constants a and c for hexagonal phase of Cd\textsubscript{x}Zn\textsubscript{1−x}S solid solutions was calculated using the following equation:

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]

The calculated lattice constants a and c are listed in Table 1. The changes of lattice constants also demonstrate the formation of solid solutions.

The UV–Vis absorption spectra of the Cd\textsubscript{x}Zn\textsubscript{1−x}S solid solutions with different Cd concentrations are shown in Fig. 2. The absorption edge of ZnS is approximately 370 nm, but the other samples exhibit intense absorption bands with steep edges in the visible light region. In addition, the absorption edge of the Cd\textsubscript{x}Zn\textsubscript{1−x}S solid solution gradually red-shifts as the amount of Cd increase. This phenomenon can be attributed to a band transition rather than a transition from impurity levels, indicating the formation of the Cd\textsubscript{x}Zn\textsubscript{1−x}S solid solution. In view of the direct band gap nature of Cd\textsubscript{x}Zn\textsubscript{1−x}S, the relation between the absorption coefficient (α) and incident photon energy (hν) can be written as

\[
αhν = C(hν − Eg)^{1/2},
\]

where C is a constant and Eg is the direct band gap. Hence, the band gap value of Cd\textsubscript{x}Zn\textsubscript{1−x}S architectures can be obtained through extrapolating the linear part of the (hν)^2−(αhν) plot to (αhν)^2 = 0 (Inset Fig. 2). The specific band gap data can be shown in Table 1.

3.2. Cd\textsubscript{x}Zn\textsubscript{1−x}S alloy nanocrystal morphology

Since preparing the materials in nanoscale dimension is one of the significant methods to improve the photocatalytic activity, the morphology of Cd\textsubscript{x}Zn\textsubscript{1−x}S was investigated through SEM and TEM. Fig. 4 shows the SEM images of the synthesized Cd\textsubscript{x}Zn\textsubscript{1−x}S samples. The pure ZnS nanocrystals clearly consist of microspheres which were stacked by short nanorods. Under solvothermal conditions, the structures and morphologies of ZnS nanostructures have been studied in DETA or in an aqueous DETA solution [21]. With the increases of water and decreases of DETA, the morphologies of ZnS will transfer from nanosheets to microsphere. In our experimental, the volume of water and DETA is 2:1; the synthetic ZnS microspheres conformed to this rule. However, the morphologies of CdS were microflowers that assembled from short rods. CdS microflowers can also be produced in a mixed solution of DETA and deionized water via a facile solvothermal approach [22]. With decreasing the volume of DETA and water, the CdS microflowers would be formed. In our experimental, the morphologies of CdS may be associated with it. As the solid solution is formed, the
formed nanocrystals with different morphologies that depend on the Zn content of the solid solutions. The nanocrystals made of microflowers have a low Zn content (x = 0.2 or 0.4), but the microspheres would be found in the high Zn content (x = 0.2 or 0.4) samples. Similar Cd$_x$Zn$_{1-x}$S nanocrystals have been prepared by using (NH$_4$)$_2$S as sulfur source in a mixed solution of DETA and water [23]. The possible reason for the morphology change may be the difference of the M$^{2+}$ ion (M = Zn$^{2+}$ or Cd$^{2+}$) reactivity with S$^{2-}$, which follows the order, Cd$^{2+}$ > Zn$^{2+}$. More the detailed is needed further investigation. The morphologies of Cd$_x$Zn$_{1-x}$S solid solution was also characterized by TEM (shown in Fig. S1), the similar morphology change rule can be associated to the SEM results.

In order to further analyze the basic assembled units, the Cd$_{0.2}$Zn$_{0.8}$S sample was taken as an example to do HRTEM and selected-area electron diffraction (SAED) characterization. Fig. S2a shows the HRTEM images of the synthesized Cd$_x$Zn$_{1-x}$S samples, the clear lattice fringe indicates the products have high crystallization and single crystal properties. And the clear-cut 0.33 nm lattice spacing can be corresponding to the wurtzite (002) plane. Some structural deformations are also found in the HRTEM which can be due to the elemental default or asymmetric doping. The corresponding selected-area electron diffraction (SAED, Fig. S2b) pattern indicates that the typical Cd$_0.2$Zn$_{0.8}$S sample has a hexagonal single-crystal structure. These results show that Cd$_{0.2}$Zn$_{0.8}$S preferentially grew along the (001) direction.

3.3. Photocatalytic performance of the Cd$_x$Zn$_{1-x}$S solid solution

The photocatalytic performance of the Cd$_x$Zn$_{1-x}$S solid solution in H$_2$ production was investigated in a system consisting of 0.1 M Na$_2$SO$_3$/aqueous Na$_2$S$_2$O$_3$ solution. Fig. 5a shows that all the Cd$_x$Zn$_{1-x}$S photocatalysts exhibit high activities than that of ZnS and CdS, indicating that the formation and composition of the solid solution is significant for H$_2$ production. In particular, the Cd$_{0.2}$Zn$_{0.8}$S microsphere exhibits the best activity among the Cd$_x$Zn$_{1-x}$S solid solutions, with a H$_2$ production rate of ~1.8 mmol g$^{-1}$ h$^{-1}$, which is almost 30 times higher than that of CdS. Moreover, the rate of H$_2$ production for Cd$_x$Zn$_{1-x}$S decreases as the Cd concentration in the solid solution increases, suggesting the composition for solid solution has an important impact on the photocatalytic activities. In the same test conditions, the photocatalytic H$_2$-production activity of hierarchical Cd$_x$Zn$_{1-x}$S complex architectures is better than the reported nanoparticles [24–27].

During the photocatalytic water splitting process, co-catalysts like noble metals are often needed to promote the separation of photogenerated carriers and provide low activation potentials for H$_2$ evolution, thus serving as active sites for H$_2$ production. For the CdS and Cd$_x$Zn$_{1-x}$S solid solution photocatalyst, noble metal such as Pt, Pd and Rh were studied as co-catalysts to enhance the photocatalytic activity, and Pt has showed the most favorable effect on the improvement of CdS photocatalytic activity. When Pt is loaded into the Cd$_x$Zn$_{1-x}$S photocatalysts, the photocatalytic activity further increases. The rate of H$_2$ evolution over the Pt/Cd$_{0.2}$Zn$_{0.8}$S photocatalyst reaches as high as ~5 mmol g$^{-1}$ h$^{-1}$ (Fig. 5b), which is approximately 1.8 times higher than that over the Cd$_{0.2}$Zn$_{0.8}$S solid solution catalyst alone.

The Cd$_x$Zn$_{1-x}$S solid solution with a hexagonal wurtzite phase often has the best photocatalytic activity when the Zn content (1–x) is approximately 0.6–0.7, which may be attributed to the suitable band gap and negative shift of the conduction band. In the current results, the Cd$_{0.2}$Zn$_{0.8}$S solid solution gives a very high rate of H$_2$ production (~0.8 mmol g$^{-1}$ h$^{-1}$), most probably because of the aforementioned reason. However, the Cd$_{0.2}$Zn$_{0.8}$S solid solution exhibits the best photoactivity for H$_2$ production. Therefore, aside from the band-gap structure for the hierarchical Cd$_x$Zn$_{1-x}$S solid solution, other influence factors should be considered.

When photons with sufficient energy strike the semiconductor photocatalyst, they create pairs of electrons and holes, then the electron–hole pairs would be separated, transferred into the surface of catalyst and reacted with water, so the surface properties such as BET surface areas and surface defects have a great effect on the photocatalytic activities. In general, the bigger the specific area of semiconductor, the more of active sits with reactants, which is helpful for photocatalytic reaction. Conversely, it is unfavorable to the photocatalytic reaction. At the same time, the surface defects also have important influence on the catalytic activity. The suitable surface defects have a help to capture photogenerated electronic or hole, leading more electron or hole to migrate to the surface of the catalyst for photocatalytic reaction.

The synthetic hierarchical assemblies of Cd$_x$Zn$_{1-x}$S complex architectures have different morphology. In particular, the morphology changes from microflowers agglomerates to microspheres with the Cd content in the solid solution, which may generate changes of surface properties. Firstly, the BET of Cd$_x$Zn$_{1-x}$S solid solution has been changed. As shown in Table 2, the ZnS has a relatively high BET data (~40m$^2$/g), and the CdS exhibits low surface area, only 7 m$^2$/g. For the different constituent solid solution, the BET data will increase with the Cd content decrease, and the Cd$_{0.2}$Zn$_{0.8}$S microsphere especially has a higher BET results (~42 m$^2$/g). Apparently, the higher BET is in favor of providing more reaction site, causing the enhancement of photocatalytic activity. In addition, the change of Cd$_x$Zn$_{1-x}$S morphologies is also possible for
the difference of surface defect. From the PL spectrum (Fig. 3), it can be seen that the Cd_{0.2}Zn_{0.8}S has the strongest PL emission peak, implying there is more surface defect state as the electronic reservoir to improve the photocatalytic activity. In the reported literatures, through the modification of the surface defects of Cd_{0.2}Zn_{0.8}S nanocrystals, Cd_{0.2}Zn_{0.8}S also exhibits the highest rate of photocatalytic H_2-production [28]. Based on the above analysis, the Cd_{0.2}Zn_{0.8}S solid solution with the best photocactivity for H_2 production can be explained by Fig. 6. When the Cd_{0.2}Zn_{0.8}S photocatalyst absorbs the visible light, its suitable band position makes it have a stronger driver force for water reduction. Meanwhile, the specific morphology can absorb lots of water molecules. And the numbers of surface defect states play the role of electron pool to promote the separation of the charge carriers in photocatalysis, thus leading to the improvement of photocatalytic activity.

The stability of catalyst is also important in the photocatalytic process. A typical reaction time course of H_2 evolution over Cd_{0.2}Zn_{0.8}S photocatalyst was also shown in Fig. 7. The reaction system was evacuated after each run. By combination of SO_2^- and S^2- utilized as sacrificial agent, different reactions occurred for the photoexcited holes as follows:

\[
\text{Cd}_{0.2}\text{Zn}_{0.8}S \quad \text{h}^+ + e^- \\
2e^- + 2H_2O \rightarrow H_2 + 2OH^- \\
\text{SO}_2^- + 2OH^- + 2h^- \rightarrow \text{SO}_4^{2-} + 2H^+ \\
2S^2^- + 2h^- \rightarrow S_2^{2-} \\
S_2^{2-} + \text{SO}_2^- \rightarrow S_2\text{O}_6^{2-} + S^2- \\
\text{SO}_3^{2-} + 2h^- \rightarrow S_2\text{O}_6^{2-}
\]

Therefore, no significant decrease in the photocatalytic activity is observed, the hydrogen evolution rate still reached and 1.6 mmol g^{-1} h^{-1} in the fourth reaction run.

4. Conclusions

A series of hierarchical Cd_{x}Zn_{1-x}S micro- and nanostructure have been synthesized in a DETA and water solution using the solvothermal method. The morphology of the nanoflowers was characterized. Within the Zn content increase from 0.2 to 0.8 in the Cd_{x}Zn_{1-x}S solid solution, the morphology transformed progressively from microflowers agglomerates to microspheres. Furthermore, the photocatalytic performance of the Cd_{x}Zn_{1-x}S nanoflowers in H_2 evolution was investigated. The Cd_{0.2}Zn_{0.8}S solid solution composed of thin slices exhibited the best photocatalytic activity for H_2 evolution, with an initial rate of 1.8 mmol g^{-1} h^{-1}. This high activity may be due to the specific morphology which has a relatively high BET and surface defects, leading to a high number of reaction sites.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2013.07.013.

References