

Research Article

Effect of PdS on Photocatalytic Hydrogen Evolution of Nanostructured CdS under Visible Light Irradiation

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To investigate the effect of PdS as a cocatalyst for photocatalytic hydrogen evolution, nanostructured PdS/CdS were prepared by an in situ coprecipitation and hydrothermal method, respectively. The as-prepared photocatalysts were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), UV-visible absorption spectra, and photoluminescence spectra (PL). With PdS highly dispersed in the CdS nanostructures, the photoactivity was evaluated by hydrogen evolution from aqueous solution containing Na₂S/Na₂SO₃ as sacrificial reagents under visible light irradiation. When the concentration of PdS was 1% by weight, PdS/CdS, prepared by the in situ coprecipitation, showed the highest photocatalytic activity, while that prepared by hydrothermal method showed the most stability for hydrogen evolution. The effect of highly dispersed PdS on the photoactivity was discussed.

1. Introduction

Hydrogen, as a kind of renewable energy, has attracted more and more attention due to the depletion of fossil fuels and the pollution caused by continuously increasing energy demands [1–3]. Photocatalytic water-splitting hydrogen evolution using semiconducting photocatalysts is one of the most ideal ways to make full use of solar energy to produce hydrogen [4]. Up to now, a lot of semiconducting photocatalysts have been reported to produce hydrogen, such as TiO₂ [5], CdS [6], and ZnS [7]. Among them, CdS has been widely studied because of its excellent light absorption property in the visible region [8].

CdS alone demonstrates low photoactivity and bad stability for hydrogen evolution under visible light because, in its photocatalytic process, the phenomenon of photocorrosion is prone to occur [9]. Many efforts have been made to overcome the problem of photocorrosion, such as photosensitizing CdS with photosensitizers [4, 10], combining CdS with another semiconductor [11], and exploiting alternative preparation approaches to control the size and shape of CdS [12].

Loading a cocatalyst onto CdS is also a good method to improve its photoactivity and stability. A suitable cocatalyst cannot only promote the separation of photoexcited electrons and holes and suppress their recombination, but also decrease the activation potentials for H₂ evolution [13]. Transition metals and their oxides (sulfides) have been widely used as cocatalysts including Pd [14–16], Pt [17, 18], NiO [19], RuO₂ [20], and MoS₂ [21]. Therefore, it is highly desirable to find suitable cocatalysts to improve the photoactivity and stability of CdS. Recently, Yan et al. reported that CdS loaded with Pt-PdS bicomponent cocatalyst achieved the highest quantum yield of about 93% in the presence of sacrificial reagents under visible light irradiation [22]. Therefore, it would be of great interest to investigate the effect of the cocatalyst on the photocatalytic performance of CdS.

In this paper, nanostructured PdS/CdS photocatalysts were synthesized by in situ coprecipitation and hydrothermal method, respectively. The effect of PdS on the photoactivity and stability of CdS was investigated for hydrogen evolution under visible light from water containing Na₂S and Na₂SO₃ as sacrificial reagents.

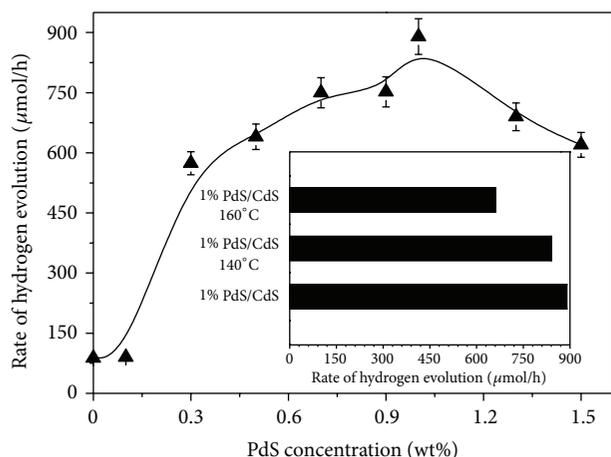


FIGURE 1: Rate of hydrogen evolution on PdS/CdS samples loaded with different amounts of PdS under visible light; (insert) rate of hydrogen evolution on PdS/CdS samples loaded with 1 wt% amount of PdS prepared by different hydrothermal temperatures and in situ coprecipitation.

2. Experiments

2.1. Synthesis of PdS/CdS. All of the chemicals were of analytical grade and used without further purification. Deionized water was used in the sample synthesis.

The nanostructured CdS particles were synthesized as follows: an aqueous solution of 0.14 M Na_2S was added slowly to 0.14 M $\text{Cd}(\text{OAc})_2$ solution under vigorous stirring at room temperature. The yellow mixture was stirred for 12 h and kept for additional 12 h. The resulting yellow solid was collected by filtration and washed with deionized water several times. The wet solid was suspended in deionized water and transferred into a 100 mL stainless Teflon-lined autoclave. The autoclave was sealed and heated at 200°C for 24 h and then cooled down to room temperature naturally. The yellow solid was filtered and washed with water and ethanol subsequently, followed by drying at 80°C for 24 h.

The loading of PdS on CdS producing PdS/CdS was realized by the following two methods. For the in situ coprecipitation, a PdCl_2 aqueous solution was added dropwise under stirring at room temperature to a suspension of CdS nanoparticles (0.2 g, as prepared above) dispersed in Na_2S aqueous solution just before the photocatalytic reaction. For the hydrothermal method, the mixture obtained by the in situ coprecipitation was stirred for 12 h. The resulting precipitates were centrifuged and washed with deionized water several times. The precipitates were suspended in deionized water, transferred into a 100 mL stainless Teflon-lined autoclave, and heated at a certain temperature for 6 h.

2.2. Characterization. The X-ray diffraction (XRD) patterns of catalysts were obtained from a Panalytical X'pert Pro X-ray diffractometer equipped with $\text{Cu K}\alpha$ irradiation with the scanning step of 0.05°/s; the operation voltage and current were 45 kV and 40 mA, respectively. UV-visible absorption spectra were measured by a HITACHI UV4100 instrument,

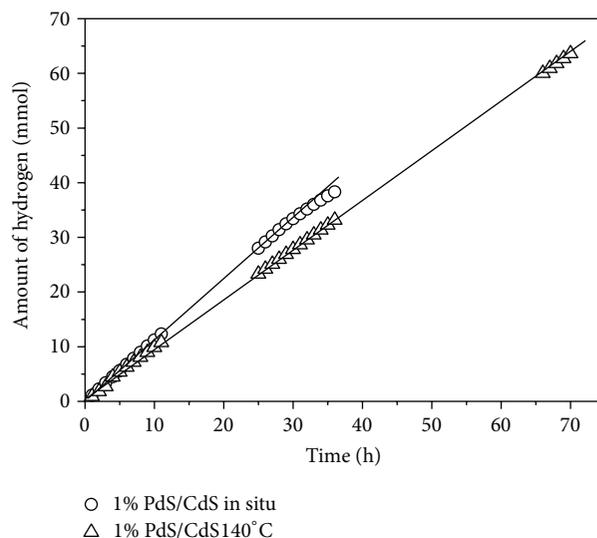


FIGURE 2: Time courses of hydrogen evolution on PdS/CdS samples loaded with 1 wt% PdS prepared by different methods.

with the scanning range from 300 to 800 nm. The photoluminescence spectra (PL) were measured at room temperature using a PTI QM-4 fluorescence spectrophotometer. The crystallite morphologic micrograph was observed on a high resolution transmission electron microscopy (HRTEM) JEOL JEM-3010 instrument and a field emission scanning electron microscopy (SEM) JSM-6700F (Japan).

2.3. Evaluation of Photocatalytic Activity. Photocatalytic reaction was carried out in a side-irradiation Pyrex cell. The effective irradiation area for the cell is 12.56 cm^2 . The powder of photocatalyst (0.2 g) was dispersed by a magnetic stirrer in an aqueous solution (200 mL) consisting of Na_2S (0.5 M) and Na_2SO_3 (0.5 M) as electron donors in the cell. The photocatalysts were irradiated with visible light through a cutoff filter ($\lambda > 430 \text{ nm}$, $T = 65\%$) from a 300 W Xe lamp. The amount of H_2 gas was determined by an online thermal conductivity detector (TCD) gas chromatograph (NaX zeolite column, nitrogen as a carrier gas).

3. Results and Discussion

Figure 1 shows the rate of hydrogen evolution on PdS/CdS photocatalysts loaded with different amounts of PdS prepared by the in situ coprecipitation under visible light, together with those prepared by the hydrothermal method (insert in Figure 1). As the amount of PdS increases from 0 to 1%, the hydrogen evolution rate on PdS/CdS increases markedly from $\sim 88.1 \mu\text{mol/h}$ to $\sim 890.3 \mu\text{mol/h}$, about 10 times higher. However, when the amount of PdS increases to 1.3%, the photocatalytic activity decreases slightly. The surplus PdS can work as an optical filter to shield incident light and hence suppress further enhancement of photocatalytic activity for hydrogen evolution. For comparing, the insert in Figure 1 shows the rate of hydrogen evolution on the PdS/CdS photocatalyst loaded with 1 wt% PdS prepared by hydrothermal

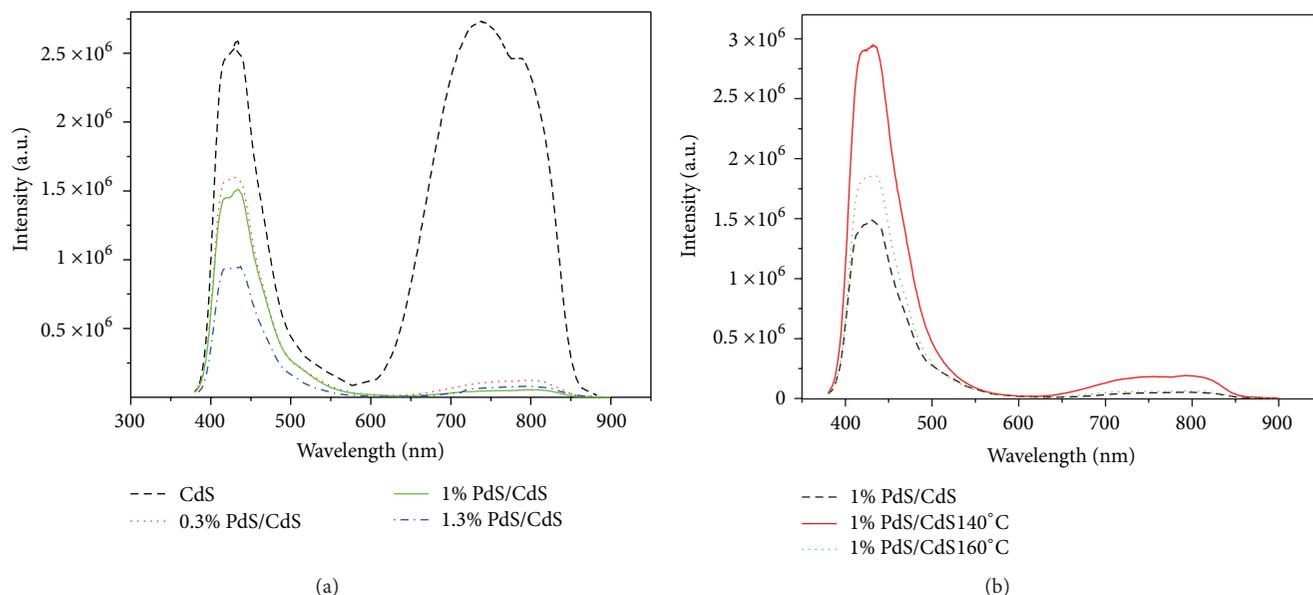


FIGURE 3: (a) Photoluminescence spectra of PdS/CdS samples loaded with different amounts of PdS. (b) Photoluminescence spectra of PdS/CdS samples loaded with 1wt% PdS prepared by different methods.

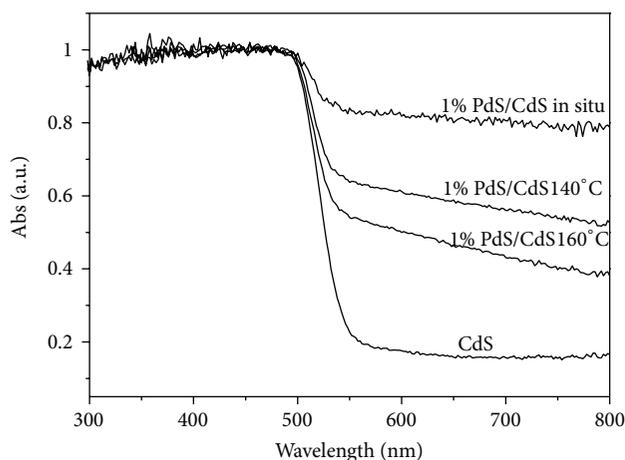


FIGURE 4: UV-visible absorption spectra of CdS and PdS/CdS samples.

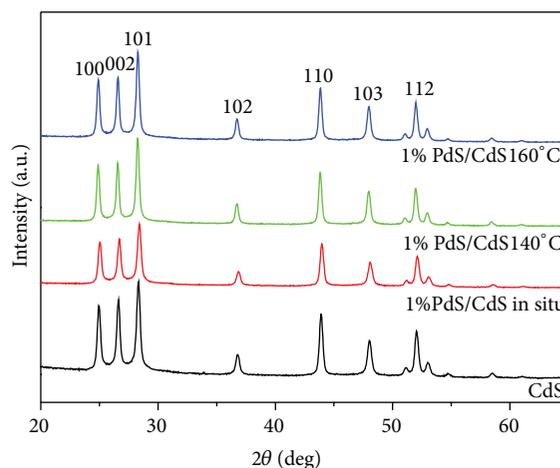


FIGURE 5: XRD patterns of PdS/CdS samples.

method. It appears that the photocatalytic activity also decreases slightly. But the photocatalytic stability improves, as shown in Figure 2 which shows the hydrogen evolution on PdS/CdS photocatalysts loaded with 1% PdS prepared by different methods as long as $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ is present. PdS/CdS photocatalysts prepared by the in situ coprecipitation can act stably for less than 40 hours. It is noted that PdS/CdS photocatalysts prepared by hydrothermal method can exhibit significantly improved stability, showing steady hydrogen production more than 70 hours. The observation suggests that the dispersion of Pd in nanostructured CdS can improve the photoactivity, but the stable photocatalytic activity for hydrogen evolution can be influenced by the synthesis method.

To analyze the reason, Figure 3 shows the photoluminescence spectra of PdS/CdS photocatalysts. The photoluminescence spectroscopy can give information about the photoexcited energy/electron transfer and recombination process, and it has been widely used to investigate the photophysical and photochemical properties of photocatalysts [23]. As shown in Figure 3(a), the pure CdS exhibits broad fluorescence peak related to Stoke's shifts ~ 435 nm and ~ 750 nm [4]. The band at ~ 432 nm is due to intrinsic emission, whereas that at 750 nm originates from transition of electrons rapped at surface state to the valance band of CdS. This fact suggests that nanostructured CdS has defects. By loading PdS, the fluorescence intensities are quenched, which reveals that the recombination of photoelectrons and holes is efficiently suppressed resulting in the improved photoactivity.

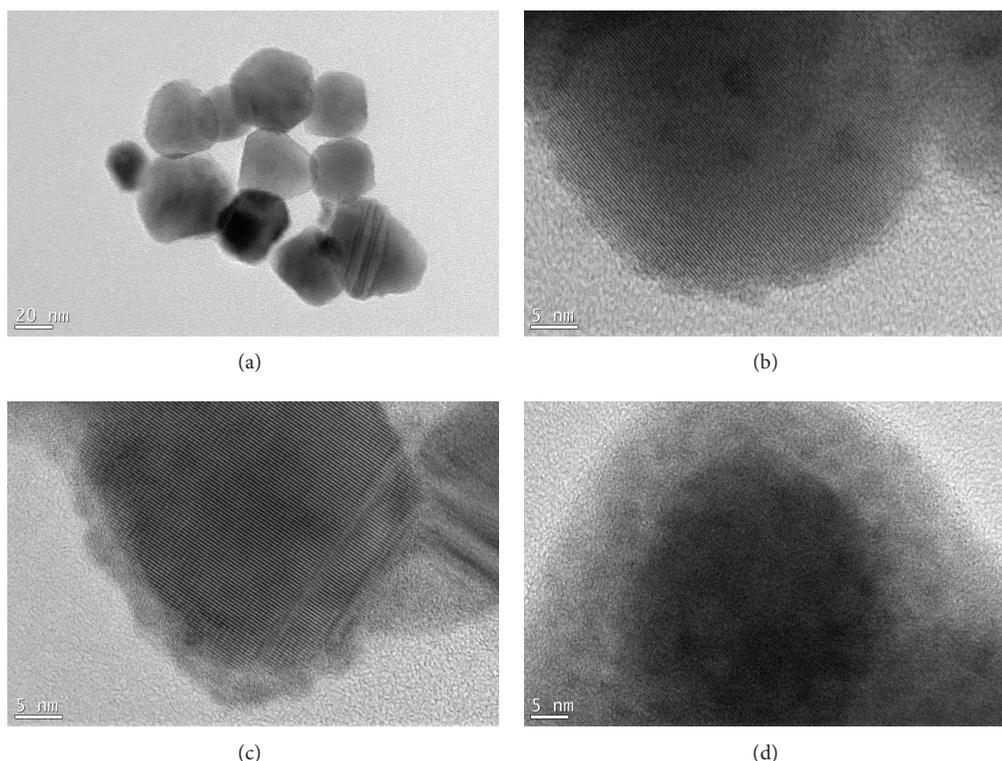


FIGURE 6: TEM image of (a and b) CdS, (c) PdS/CdS prepared by in situ coprecipitation, and (d) PdS/CdS prepared by hydrothermal method at 160°C.

However, the fluorescence intensities of PdS/CdS prepared by hydrothermal method are slightly enhanced as shown in Figure 3(b). This fact might be beneficial for the stability of photocatalysts. Then it can be concluded that the weaker the fluorescence intensity of the photocatalyst is, the higher the photoactivity is.

The UV-visible absorption spectra for PdS/CdS are shown in Figure 4. The pure CdS has an absorption edged at about 550 nm, with energy gap estimated to be 2.3 eV. The spectra of PdS/CdS show an enhanced absorption in visible light region. Such an enhancement can be assigned to the existence of PdS phase. It was reported that PdS could not absorb visible light [4]. Therefore, the fact suggests that the PdS phase can enhance the absorption of CdS phase. From Figure 4, it can be seen that the enhancement of the absorption in visible light region is different which is dependent on the preparation condition. It suggests that the higher the visible adsorption is, the higher the photoactivity is.

The XRD patterns of various samples displayed in Figure 5 can be readily indexed as the (100), (002), (101), (110), (103), and (112) planes of the hexagonal phase of the wurtzite CdS structure, which are well matched with the standard values (JCPDS Card No. 02-0549) according to the main diffraction peaks at 24.9°, 26.6°, 28.4°, 43.7°, 48.1°, and 52.0°. It is worth noting that there are no characteristic peaks associated with PdS in these XRD patterns, which may be

due to the low concentration of PdS and its relatively low crystallinity for the PdS/CdS samples prepared by the in situ coprecipitation and due to the high dispersion of PdS particles in the nanostructured CdS and the low concentration of PdS for the PdS/CdS samples prepared by hydrothermal method. By the way the diffraction peak would not shift when Pd²⁺ was doped into the lattice of CdS, considering that an ionic radius of Pd²⁺ (0.88 Å) is lower than that of Cd²⁺ (0.97 Å). The fact indicates that no significant lattice deformation occurred with different treatments of PdS/CdS samples.

Morphology of the as-prepared photocatalysts is shown in Figure 6. From Figure 6(a), it can be seen that the nanostructured CdS is mainly composed of nanospheres. As shown in Figure 6(b), for the higher magnification of CdS, these nanospheres are well crystallized. When PdS is loaded, there appears spherical nanoparticles on the surface of CdS which disperse more uniformly by comparing Figures 6(b) and 6(c). PdS by itself displays no photoactivity for H₂ production, but PdS can act as a cocatalyst together with CdS. Then it suggests that PdS exists on the surface of CdS which can enhance the photoactivity of CdS. However, there appears a nanoparticle layer for PdS/CdS prepared by hydrothermal method as shown in Figure 6(d). This indicates that the loading of PdS can improve the photoactivity of CdS, but the nanoparticle layer may decrease the

photoactivity in spite of the increase in the stability of CdS.

4. Conclusion

Nanostructured PdS/CdS photocatalysts were synthesized by an in situ coprecipitation and a hydrothermal method, respectively. With a concentration of PdS approximately 1.0%, PdS/CdS photocatalysts synthesized by the in situ coprecipitation displayed the highest photocatalytic activity for hydrogen evolution under visible light irradiation from an aqueous solution containing sulfide and sulfite. However, PdS/CdS photocatalysts synthesized by the hydrothermal method showed the highest stability for hydrogen evolution. This study indicates that it is an effective method for preparing a stable, efficient photocatalyst by using a suitable cocatalyst.

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