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Remarkable positive effect of $Cd(OH)_2$ on CdS semiconductor for visible-light photocatalytic H_2 production

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ABSTRACT

In the past decade, photocatalytic H_2 production over CdS semiconductor has garnered considerable interest due to its visible-light response, suitable band structure, and controllable morphologies. To pursue higher photocatalytic efficiency and more feasibility for practical industrial applications, $Cd(OH)_2$ nanoparticle decorated CdS rod composites were designed and successfully fabricated in this study by a facile one-step hydrothermal method in strong alkali NaOH solution. The synthesis process followed a "mother liquor circulation" criteria since no NaOH was lost during the whole preparation course, which could greatly save costs and be conducive to the realization of large-scale production. When the content of $Cd(OH)_2$ was 17.6 mol% in the obtained composite, the photocatalytic H_2 production rate reached the highest (579.0 μmol h^{-1}) with the help of 0.6 wt% platinum (Pt), which was more than 386 and 15 times higher than that of Pt/$Cd(OH)_2$ and Pt/CdS, respectively. It was evidenced that such surprising and prominent enhancement of photoactivity was mainly attributed to the presence of Cd^0 as an electron transport intermediary, which was produced by in-situ photoreduction of $Cd(OH)_2$ interfacial layer between CdS and Pt. This work could not only highlight the significant roles of $Cd(OH)_2$ on invigorating the photoactivity of CdS for H_2 production, but also open an avenue of using the concept of mother liquor circulation in the photocatalyst synthesis process to satisfy the industrial manufacture requirement.

1. Introduction

In modern times, excessive use of fossil fuels by human beings has caused both energy shortages and resource waste, accompanied by serious environmental pollution. One of effective ways to solve these problems is replacing fossil fuels with green, pollution-free hydrogen (H_2) energy [1,2]. However, the H_2-production technologies used in current industries still directly or indirectly rely on non-renewable resources, which are neither environmentally friendly nor economical. In 1972, as a milestone, the discovery of photocatalytic water splitting technology over TiO_2 electrode offered a new way to produce valuable H_2 energy via renewable solar energy over semiconductor materials [3]. Since then, efficient photocatalyst systems have been extensively explored [4–8].

The advancement of a high-efficiency photocatalyst requires two important aspects: light harvesting ability and charge separation efficiency [9,10]. In the solar radiation that can be received by the earth, visible light accounts for about 43% of the total energy, while ultraviolet (UV) light only accounts for 4%. Therefore, visible-light-driven semiconductor photocatalysts attracts much more interest than traditional UV-light-driven ones in recent years [11–14]. Especially, cadmium sulfide (CdS) with a narrow bandgap of 2.4 eV and a negative enough conductive band (CB) edge potential is an attractive native candidate for visible-light-driven photocatalytic H_2 production [15–17]. However, every one has its weak side. The quick recombination of photogenerated charge carriers in the bulk and on the surface of CdS material usually exists and largely prohibits its wide applications. To solve this intrinsic problem, many approaches have been proposed to enhance the charge separation efficiency and photocatalytic activity of CdS, including controlling the morphology [18–23], deposition of noble or non-noble metal cocatalysts [24–32], construction of heterogeneous semiconductors [33–36], and so on.

On the one hand, the photocatalytic H_2 production efficiency of CdS could be directly affected by its geometrical morphology and surface structure. Particularly, one-dimensional (1D) materials including nanorods [37], nanowires [18], nanotubes [38] and nanobelts [39,40] provide a shorter bulk-to-surface diffusion distance than irregular particles for the photogenerated charge carriers, and thus suppress the electron-hole recombination in the bulk. On the other hand, deposition of cocatalysts could enhance the separation efficiency of

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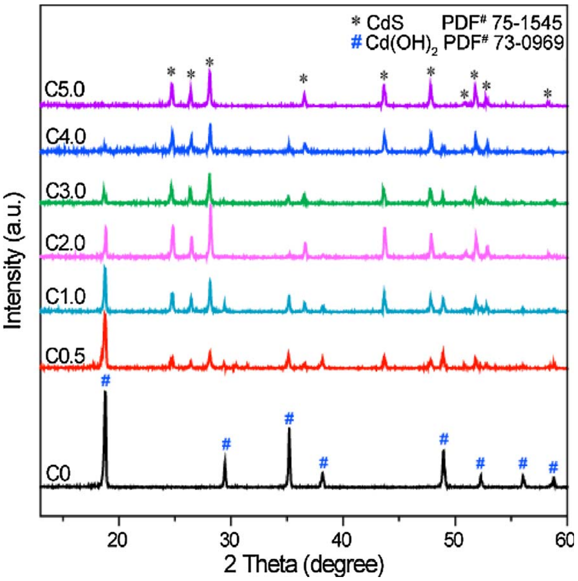

Fig. 1. XRD patterns of the Cx (x = 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0) samples.

photogenerated electrons and holes on the surface. Considering the high price and scarce resource of noble metals, non-noble metal based materials such as Cd [41,42], Ni [43], NiO [44], $Ni(OH)_2$ [45], $Cu(OH)_2$ [46] were more frequently utilized as cocatalysts in recent years [47]. For example, Wang et al. prepared Cd/CdS photocatalyst through a photochemical method using $CdSO_4$ and $Na_2S_2O_3 \cdot 5H_2O$ as precursors [41]. Superior photoactivity for H_2 production of Cd/CdS composite was observed than that of pure CdS. Shang et al. prepared Cd nanosheet by a low-temperature, low-cost polyol reduction method and then deposited CdS nanoparticles onto it through a oxidation-sulfurization process [42]. The Cd nanosheet reduced the aggregation of CdS nanoparticles, enhanced light absorbance, accelerated charge transfer, and consequently promoted the photocatalytic H_2 production efficiency of CdS. In addition, Yu's group successively prepared $Ni(OH)_2$-TiO_2 [48], $Cu(OH)_2$-TiO_2 [46] and $Ni(OH)_2$-CdS [45] composite photocatalysts, and verified the apparent promotion effect of these cocatalysts for photocatalytic H_2 production. Because the potentials of Ni^{2+}/Ni (−0.23 V) and Cu^{2+}/Cu (−0.224 V) in relation to the normal hydrogen electrode (NHE) are less negative than the CB levels of TiO_2 (−0.26 V vs. NHE) and CdS (−0.7 V vs. NHE), these transition metal hydroxides could accept electrons from the CB of semiconductor and be reduced to be metal atoms or clusters, which acted as a electron trapping center to promote the separation and transfer efficiency of charge carriers. From the thermaldynamic point of view, the potential of Cd^{2+}/Cd (−0.403 vs. NHE) makes Cd-$Cd(OH)_2$ possess similar properties as Ni-$Ni(OH)_2$ and Cu-$Cu(OH)_2$ couples [49]. However, few researches reported on the effect of $Cd(OH)_2$ cocatalyst on the photocatalytic H_2-production performance of CdS [50].

Based on the previous works, we designed and successfully prepared $Cd(OH)_2$ nanoparticles decorated CdS rods photocatalyst through a facile one-step hydrothermal method in a strong alkali solution. Typically, 2 mmol of CdO was dissolved in a mixed aqueous solution of NaOH (16 M, 13 mL) and Na_2S (1 M, 2 mL). The mixture was stirred for 2 h at room temperature and then transferred into a Teflon-lined autoclave and held at 200 °C for 12 h. After that, the Teflon-lined autoclave was rapidly cooled to room temperature. The precipitates from the mixture were collected by centrifugation and then rinsed with water and ethanol for several times. The final product was dried in an oven at 80 °C overnight. In order to control the $Cd(OH)_2$ content and investigate its effect on the photocatalytic H_2-production activity of the prepared $Cd(OH)_2$-CdS composite photocatalyst, the concentration of Na_2S aqueous solution was varied from 0 to 5.0 M. The resulting samples were labeled as Cx, where x = 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0, respectively. It is pleasantly surprised to find that, with the help of a small quantity of Pt (0.6 wt%) as cocatalyst, a suitable amount of $Cd(OH)_2$ nanoparticles could tremendously enhance the photocatalytic H_2 production performance of Pt/CdS rods by 15 times. Series of characterizations were carried out to investigate the effects of $Cd(OH)_2$ on the physicochemical properties of CdS, and the enhancement mechanism was also deeply explored and proposed. It is anticipated that our work could inspire ongoing interest in exploring novel trasition metal based cocatalysts to further enhance the photocatalytic performance of sulfide semiconductors and lower the cost of photocatalysis technology.

2. Results and discussion

2.1. Phase structure and chemical composition

Powder X-ray diffraction (XRD) patterns were recorded for the Cx (x = 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0) powders to confirm their crystallographic phase. The results are shown in Fig. 1. Typically, for the C0 sample, all diffraction peaks can be readily indexed to pure $Cd(OH)_2$ (PDF 73-0969). With increasing x value, the co-existence of two crystalline phases (i.e. CdS (PDF 77-2306) and $Cd(OH)_2$ (PDF 73-0969)) can be observed for the Cx (x = 0.5, 1.0, 2.0, 3.0, and 4.0) samples. When x = 5.0, all diffraction peaks are indexed to CdS, indicating the phase purity of CdS. The XRD result demonstrated that $Cd(OH)_2$-CdS composite materials could be abtained using CdO and Na_2S as precursors under strong alkali condition. Furthermore, Material Analysis Using Diffraction (MAUD) was employed to calculate the phase composition of these samples [51], and the result was presented in Table 1. With increasing x value from 0 to 5.0, the CdS content gradually increased from 0 to 100% at the expense of the decreasing $Cd(OH)_2$ content. When x = 1.0, the calculated $Cd(OH)_2$ content in the composite was 12.3 mol%.

Table 1
Effects of Na_2S concentration on photoactivity and physicochemical properties of the Cx (x = 0, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0) samples.

Samples	Calculated $Cd(OH)_2$ content (mol%)[a]	Detected $Cd(OH)_2$ content (mol%)[b]	S_{BET} ($m^2 g^{-1}$)[c]	H_2 production rate ($\mu mol\ h^{-1}$)	QE(%)[d]
C0	100	100	13.0	1.5	0
C0.5	80.4	68.1	23.9	85.0	2.5
C1.0	12.3	17.6	19.8	579.0	16.3
C2.0	9.8	11.3	15.4	510.0	14.2
C3.0	6.6	8.1	12.0	162.5	4.5
C4.0	4.0	4.0	8.6	68.5	2.0
C5.0	0	0	4.9	37.5	1.0

[a] The calculated $Cd(OH)_2$ contents in the samples were obtained using a method of MAUD.

[b] The detected $Cd(OH)_2$ contents in the samples were converted from the measured mass fractions of O atoms in the composites by CHNS/O elemental analyzer.

[c] S_{BET} refers to the Brunauer-Emmett-Teller (BET) specific surface area.

[d] QE refers to the apparent quantum efficiency.

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