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Large-scale synthesis of noble-metal-free phosphide/CdS composite photocatalysts for enhanced H₂ evolution under visible light irradiation

Baojun Ma ^{*}, Ruisheng Zhang, Keying Lin, Hongxia Liu, Xiaoyan Wang, Wanyi Liu, Haijuan Zhan*State Key Laboratory of High-Efficiency Coal Utilization and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, Ningxia, China*

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ABSTRACT

Photocatalytic H₂ evolution under visible light irradiation is an ideal process for solving energy shortage. The low cost of photocatalysts and high efficiency of hydrogen evolution are the two key factors to realize the industrialization of the process. The substitution of a noble-metal cocatalyst with a non-noble-metal catalyst can significantly reduce the cost of the photocatalyst. The large-scale synthesis and assembly of semiconductors and non-noble-metal cocatalysts to form photocatalysts through a simple method can further decrease the cost of photocatalysis. Here, we report a large-scale and low-cost coprecipitation method to form phosphide/CdS photocatalysts to realize photocatalytic H₂ evolution. CoP and MoP cocatalysts significantly enhanced the photocatalytic production of hydrogen. The optimal H₂ production rates on CoP/CdS and MoP/CdS were 140 and 78 μmol/h, which were 7.0 and 4.0 times higher than those obtained with bare CdS, respectively, and 2.0 times and 1.1 times higher than those obtained with 1.0% Pt/CdS, respectively. This work provides a practical method for the large-scale preparation of low-cost photocatalysts.

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1. Introduction

The global energy crisis and the combustion of fossil fuels have created environmental pollution problems, which have attracted much attention [1–3]. In recent decades, mankind has urgently searched for environmentally friendly and renewable energy sources and energy storage solutions. The photocatalytic evolution of hydrogen on semiconductor photocatalysts has been extensively considered as a promising strategy for converting solar energy into chemical energy storage [4–10].

To realize the industrialization of photocatalytic hydrogen evolution, the problems associated with the cost of the photocatalysts and the efficiency of hydrogen evolution must be resolved. To obtain highly efficient hydrogen evolution, noble-metal cocatalysts are usually used [11–15]. The substitution of noble-metal cocatalysts with non-noble metal cocatalyst, such as metal oxides [16–18], metal sulfides [19,20], metal nitrides [21], and metal phosphides [22–25] can greatly reduce the cost of the photocatalyst. The preparation of semiconductors and the assembly of semiconductors with cocatalyst are other fac-

^{*} Corresponding author. Tel: +86-18795112365; E-mail: bjma@nxu.edu.cn

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tors that can affect the cost of photocatalysis. Large-scale synthesis and assembly of semiconductors and non-noble-metal cocatalyst to form photocatalysts by a simple method can further decrease the cost.

Cadmium sulfide (CdS) is a famous semiconductor that has been widely used in water splitting for H₂ evolution under visible light irradiation [26–28]. The synthesis of CdS is mainly performed through a solvent thermal method [29], chemical bath deposition method [30], or a hydrothermal method [31]. Although these methods have been used to successfully synthesize CdS semiconductor materials, the synthesis cost is relatively high and the process is cumbersome.

To further reduce the overall cost of photocatalysis, the assembly of cocatalysts and semiconductors to form photocatalysts has become another important process. In the past, the assembly of cocatalysts/semiconductors has been mainly performed by photodeposition [32], microwave irradiation synthesis [33], sol-method [34,35], impregnation vulcanization [36], and a two-step hydrothermal method [37]. Although these methods can be used to successfully synthesize composite photocatalysts, the photocatalyst production cost is still high and not beneficial for the industrialization of photocatalytic H₂ production. Therefore, the development of a simple synthesis process at a large scale and low cost is very crucial.

Here, we report a large-scale and low-cost coprecipitation method to form CdS, CoP/CdS, and MoP/CdS photocatalysts and realize effective photocatalytic H₂ evolution. The phosphide and CdS combined closely, and the hydrogen evolution rate on the phosphide/CdS catalysts was higher than that on Pt/CdS. This work provides a practical way to prepare noble-metal-free photocatalysts at a low cost.

2. Experimental

2.1. Materials

All materials were of analytical grade and used without further purification. Co(NO₃)₂·6H₂O, NaH₂PO₂·H₂O, NaCl, H₂PtCl₆·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, polyethylene glycol (PEG), and urea were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Na₂S, anhydrous ethanol, phosphoric acid, and lactic acid were obtained from Yantai Shuangshuang Chemical Co., Ltd.

2.2. Synthesis of CoP, MoP, CoP/CdS and MoP/CdS

The synthesis of CoP was performed in two steps. The first step was the synthesis of the CoP precursor by adding 2.18 g of Co(NO₃)₂·6H₂O, 1.35 g of urea, 1 g of NaCl, and 1.2 g of the surfactant PEG to 70 mL of deionized water under stirring at 70 °C for 30 min. The above solution was transferred into a 100 mL Teflon-lined autoclave and heated at 160 °C for 48 h. After cooling to room temperature, the produced material was then washed several times with deionized water and ethanol and dried in an oven at 80 °C for 6 h and then ground in an agate mortar. The second step was the phosphating process. The precursor and sodium hypophosphite were mixed at a mass

ratio of 1:4 and then placed in a tube furnace at 300 °C for 2 h under a nitrogen atmosphere. The sample was then passivated using a mixed gas of 99% N₂ and 1% O₂ for 12 h at room temperature to form a stable material.

MoP was prepared from the molybdenum precursor by temperature programmed reduction (TPR). Phosphoric acid and ammonium molybdate were mixed at a molar ratio of 1:1 of phosphorous and molybdenum atoms, evaporated to dryness at 85 °C, and then ground in an agate mortar. The material was calcined in a muffle furnace at 500 °C for 4 h, then cooled to room temperature. The obtained material was then reduced at 700 °C for 4 h under a H₂ atmosphere at a flow rate of 80 mL/min. After cooling to room temperature, the as-synthesized MoP was kept in the passivation gas (N₂/O₂ = 99/1) for 12 h at room temperature to form a stable material.

Both CoP/CdS and MoP/CdS were prepared by a coprecipitation method. For example, 2%CoP/CdS was prepared by dispersing CoP (0.04 g) in 100 mL Cd(NO₃)₂·4H₂O (0.14 mol/L). Then, 120 mL Na₂S solution (0.14 mol/L) was added dropwise under vigorous agitation and then allowed to stand for 12 h. Finally, the deposit was filtered and washed with distilled water and ethanol several times and then dried at 80 °C for 12 h in a vacuum drying oven. Other CoP/CdS or MoP/CdS catalysts with different amounts of CoP or MoP were prepared using the same method as that for 2%CoP/CdS by changing the initial amount of CoP or MoP in the dispersion.

2.3. Characterization

The crystal phases of the phosphide/CdS samples were analyzed on an X-ray diffractometer (D/MAX 2500, Rigaku, Japan) with Cu-K_α radiation at a voltage of 4 kV at room temperature. The morphologies of the samples were characterized using scanning electron microscopy (SEM; JSM7500F). High-resolution transmission electron microscopy (HRTEM) and TEM images were taken on a transmission electron microscope (F20/G20). The UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) was performed on a spectrometer (U-4100) calibrated with BaSO₄ as a baseline.

2.4. Photocatalytic activity testing

The photocatalytic hydrogen evolution experiments were performed in a closed system for evacuation and gas circulation in a quartz cell. A 300W Xe lamp (Perfect, China) with a 420 nm filter (1 to 420 nm) was used to simulate the visible light source. In a typical photocatalytic experiment, 0.1 g of CoP/CdS photocatalyst was dispersed in an aqueous solution (200 mL) containing 20 mL lactic acid. Before irradiation, the reaction system was evacuated to vacuum. The hydrogen was analyzed by a gas chromatograph equipped with a 5 Å molecular sieve column, a TCD detector, and Ar as the carrier gas. The cell was maintained at room temperature by using a circulating water system. For the analysis of the photocatalytic activity of the noble-metal-catalyst-loaded photocatalyst, an in situ photoprecipitation method was used for loading 1.0% Pt on CdS, as reported in the literature [38].

3. Results and discussion

3.1. Material characterization

A systematic illustration of the preparation of the phosphide/CdS catalysts is shown in Scheme 1. First, the phosphides CoP and MoP were prepared by phosphating their precursors containing P in a N_2 and H_2 atmosphere, respectively. Then, a Na_2S solution was directly added to the solution of $Cd(NO_3)_2 \cdot 4H_2O$ containing phosphide to precipitate the phosphide/CdS. This coprecipitation method for the preparation of the phosphide/CdS catalysts was simple and suitable for large scale production.

Fig. 1(a) shows the XRD patterns of the CoP/CdS composite photocatalysts loaded with different amounts of CoP cocatalyst. The XRD patterns of CdS matched with that of the standard card PDF #89-0440. The diffraction peaks at diffraction angles (2θ) of 26.4° , 43.9° , and 51.9° corresponded to the (111), (220), and (311) planes of CdS, respectively. The XRD patterns of pure CoP matched with that of the standard card PDF #65-2593. The characteristic peaks at $2\theta = 31.6^\circ$, 36.3° , 48.1° , and 56.7° corresponded to the (011), (111), (211), and (013) planes of CoP,

respectively. After the CoP was loaded, the characteristic diffraction peak positions of CdS did not change significantly, indicating that the loading of CoP does not affect the crystal form of CdS. The characteristic diffraction peaks of CoP were not observed when the loading amount of CoP was less than 5% owing to the small amount of CoP. When the loading amount of CoP was 20%, the characteristic peaks of CoP were observed at 36.3° and 48.1° , demonstrating that the CoP/CdS composite was formed. Fig. 1(b) shows the XRD patterns of MoP/CdS loaded with different amounts of MoP cocatalyst. The XRD spectrum of CdS matched with that of the standard card PDF #42-1411. The XRD patterns of MoP matched with that of the standard card PDF #65-6487. The XRD of MoP displayed seven characteristic diffraction peaks at $2\theta = 27.9^\circ$, 32.0° , 43.0° , 57.1° , 57.7° , 64.7° , and 67.6° , corresponding to the (001), (100), (101), (002), (111), (102), and (201) crystal planes of MoP, respectively. After MoP was loaded on CdS, the characteristic peaks of MoP gradually appeared at 32.0° and 43.0° , indicating that the MoP/CdS materials were formed (the loading amount of CoP was 5% and 20%).

The SEM images used to investigate the morphology and crystallinity of the cocatalyst are shown in Fig. 2. As shown in

Scheme 1. The systematical illustration of the large-scale coprecipitation method to form phosphide/CdS.

Fig. 1. XRD patterns of phosphide/CdS with different loading amounts of CoP (a) and MoP (b).

Fig. 2(a), CoP had a rod-like structure with rod length of 2.3–3 μm and a diameter of 60–100 nm. Fig. 2(b) shows that MoP was formed as a sludge with different particles agglomerated together. Fig. 2(c) shows that the CdS particles agglomerated together with the smallest particle size of 10 nm.

The morphology and microstructure of the cocatalysts and composite photocatalysts were further investigated by TEM and HRTEM, as shown in Fig. 3. Fig. 3(a) shows that the particle size of CdS was approximately 10–80 nm. Fig. 3(b) shows that the CoP rods had a length of 2.3–3 μm and a diameter of 60–100 nm. Fig. 3(c) shows the irregular shape of MoP with a particle size of 20–200 nm and extensive agglomeration. Fig. 3(d) shows the CdS particles were loaded on the surface of the CoP rod with some degree of CdS agglomeration. Fig. 3(e) shows the images of MoP/CdS, which were similar to the CdS image (Fig. 3(a)) because of the small amount of MoP (2%). Fig. 3(f) shows the HRTEM of 2%CoP/CdS. It was evident that CoP and CdS were tightly combined. The lattice fringes of CoP with interplanar distances of 0.28 nm were indexed to the (011) planes of CoP, whereas the lattice fringes of CdS with interplanar distances of 0.17 nm were indexed to the (311) planes of CdS. Fig. 3(g) shows the HRTEM of 2%MoP/CdS. The MoP and CdS were tightly combined. The lattice fringes of MoP with interplanar distances of 0.31 nm were indexed to the (001) planes of MoP, whereas the lattice fringes of CdS with interplanar distances of 0.33 nm were indexed to the (111) planes of

CdS, respectively. The TEM images (Fig. 3(e) and (d)) and HRTEM images (Fig. 3(f) and (g)) indicated that the cocatalysts closely combined with the semiconductors photocatalysts. This demonstrated that compact composite photocatalysts were formed by our simple coprecipitation method.

Fig. 4 shows the UV-Vis DRS spectra of CoP/CdS and MoP/CdS photocatalysts. As shown in Fig. 4(a), the cocatalyst CoP had an effect on the CdS light absorption properties. As the amount of CoP increased, the absorption edge of CdS slightly shifted towards a higher wavelength, and the CoP/CdS showed a markedly enhanced light absorption in the visible region owing to the strong absorption of CoP. The light absorption of MoP/CdS was similar to that of CoP/CdS. Furthermore, the light absorption in the visible region was enhanced after the loading of MoP on CdS, as shown in Fig. 4(b).

3.2. Photocatalytic hydrogen evolution

Fig. 5 shows the effect of the amount of phosphide cocatalysts on the photocatalytic activity under visible light. The CoP cocatalyst significantly enhanced the CoP/CdS photocatalytic H_2 production activity, whereas the CoP alone displayed no activity, as shown in Fig. 5(a). At the optimal CoP loading of 2%, the photocatalytic H_2 evolution rate of CoP/CdS was 140 $\mu\text{mol/h}$, which was 7.0 times higher than that of CdS alone. The bare MoP also displayed no activity, whereas the introduction

Fig. 2. The SEM images of CoP (a), MoP (b) and CdS (c).

Fig. 3. The TEM images of the samples of CdS (a), CoP (b), MoP (c), 2%CoP/CdS (d) and 2%MoP/CdS (e), and HRTEM images of 2%CoP/CdS (f) and 2%MoP/CdS (g).

Fig. 4. UV-vis diffuse reflectance spectra of phosphide/CdS with different loading amounts of CoP (a) and MoP (b).

Fig. 5. Photocatalytic H₂ evolution on phosphide/CdS with different loading amounts of CoP (a) and MoP (b).

of MoP significantly improved the activity of CdS (Fig. 5(b)). The optimal loading amount of MoP was 2%, which showed the highest H₂ evolution rate of 78 μmol/h, 4.0 times higher than that of CdS alone. As demonstrated in Fig. 5, the low-cost non-noble-metal phosphide compounds CoP and MoP were efficient cocatalysts for the photocatalytic H₂ evolution.

Fig. 6 shows the comparison of the photocatalytic activities of the phosphide/CdS, CdS, and Pt/CdS catalysts. Pt was selected as a typical noble metal. It has been reported that 1%Pt/CdS shows the highest activity [38]. Therefore, the activity of 1%Pt/CdS was chosen and compared with that of the phosphides/CdS. The activities of 2%CoP/CdS and 2%MoP/CdS were 2.0 and 1.1 times higher than those of 1%Pt/CdS, respectively. This demonstrated that the phosphides CoP and MoP were excellent low-cost non-noble-metal cocatalysts that can replace noble metals as cocatalysts for the photocatalytic evolution of H₂. The stabilities of the CoP/CdS and MoP/CdS catalysts were also investigated; the two photocatalysts had similar stabilities. The photocatalytic activity of the composite photocatalyst did not significantly decrease in the first 18 h, which indicated that the phosphide/CdS composite photocatalysts were an effective and stable hydrogen evolution photocatalyst. As the exposure to light was increased, the photocatalytic decomposition of hydrogen production began to decrease. After an irradiation time of 33 h, the photocatalytic

activity for the production of hydrogen was reduced to half of that in the first 3 h.

The mechanism of the photocatalytic evolution hydrogen on the phosphide/CdS catalysts is shown in Scheme 2. The CoP or MoP phosphides closely combined with the CdS semiconductor. Under visible light irradiation, the CdS was photoexcited and electron-hole pairs were generated in CdS. The photocatalytic oxidation reaction (lactic acid oxidation) occurred on the surface of the CdS semiconductor. The photoexcited electrons transferred to the phosphide owing to the close combination of

Fig. 6. Comparison of photocatalytic activities of phosphides/CdS with CdS and Pt/CdS.

Scheme 2. Photocatalytic H₂ production mechanism of phosphides/CdS Composites.

the phosphide and CdS. At the surface of the phosphide, the photocatalytic reduction reaction (H₂ evolution) occurred. Here, the phosphide played the role of a cocatalyst for the photocatalytic H₂ evolution. The phosphide cocatalyst contained photocatalytic active sites [39,40] and improved the charge separation and transition in CdS. Thus, the photocatalytic activity of CdS was significantly enhanced by the loading of the phosphides.

4. Conclusions

A simple coprecipitation method was used for the preparation of phosphide/CdS composite photocatalysts without the use of noble metals to form composite photocatalysts for H₂ evolution. The CoP and MoP phosphides were demonstrated to be efficient non-noble-metal cocatalysts for photocatalytic H₂ evolution. The optimum hydrogen evolution rates of CoP/CdS and MoP/CdS were 140 and 78 μmol/h, respectively, which were 7.0 and 4.0 times higher than those of bare CdS, respectively. The properties of the CoP and MoP cocatalysts were superior to those of a Pt-based noble metal catalyst. The hydrogen evolution of CoP/CdS and MoP/CdS was approximately 2.0 and 1.1 times higher than that of Pt/CdS, respectively. The HRTEM images of CoP/CdS and MoP/CdS showed the phosphide cocatalyst combined closely with the CdS semiconductor, which demonstrated the effectiveness of the coprecipitation method for the preparation of the cocatalyst/semiconductor

composite photocatalysts. The close combination of the phosphide with CdS facilitated the transfer of the photoexcited electrons from CdS to the phosphide, which significantly improved the photocatalytic activity of the catalysts for the production of hydrogen. This work provides a practical way for large-scale preparation of low-cost photocatalysts and paves the way for industrialization of photocatalytic evolution of H₂.

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Graphical Abstract

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Large-scale synthesis of noble-metal-free phosphide/CdS composite photocatalysts for enhanced H₂ evolution under visible light irradiation

Baojun Ma *, Ruisheng Zhang, Keying Lin, Hongxia Liu, Xiaoyan Wang, Wanyi Liu, Haijuan Zhan
Ningxia University

The phosphides/CdS Composites can be synthesized by this coprecipitation method, and it is simple and suitable for large scale production. CoP and MoP can replace Pt as cocatalysts for photocatalytic H₂ evolution reactions.

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大规模合成非贵金属磷化物/CdS复合光催化剂高效可见光催化产氢

马保军*, 张瑞生, 林克英, 刘红霞, 王晓燕, 刘万毅, 詹海娟

宁夏大学化学化工学院省部共建煤炭高效利用与绿色化工国家重点实验室, 宁夏银川750021

摘要: 目前, 在可见光照射下光催化产氢是一条解决能源短缺的理想途径。该途径实现工业化的两个关键因素是得到低成本的光催化剂和高的产氢效率。非贵金属助催化剂代替贵金属可大大降低光催化剂的成本。通过简单的方法大规模合成并组装半导体和非贵金属助催化剂以形成复合光催化剂可进一步降低成本。

本文采用大规模和低成本的共沉淀法合成了磷化物/CdS光催化剂, 实现了光催化产氢。当负载CoP和MoP助催化剂后, 光催化产氢活性得到大幅度提高。其中CoP/CdS和MoP/CdS的最佳产氢量分别为140和78 $\mu\text{mol/h}$, 并分别为CdS的7.0倍和4.0倍, 分别为Pt/CdS的2.0倍和1.1倍。这说明磷化物CoP和MoP是具有优良催化活性的低成本非贵金属助催化剂, 可以代替贵金属助催化剂应用在光催化产 H_2 中。

在制备磷化物/CdS时, 先将两种磷化物反应原料分别在水热反应釜和马弗炉中煅烧合成前驱体, 再分别在管式炉氮气和氢气氛围中进行磷化得到磷化物MoP和CoP。然后, 将得到的MoP和CoP分别溶解在 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 溶液中, 在搅拌状态下逐滴加入 Na_2S 溶液形成沉淀, 即可得到复合物磷化物/CdS。

CoP/CdS和MoP/CdS的HRTEM观察显示, 磷化物助催化剂与CdS半导体紧密结合, 证明了共沉淀法制备助催化剂/半导体复合光催化剂的有效性。磷化物与CdS的紧密结合促进了光激发电子从CdS向磷化物转移, 从而大大提高了光催化产氢活性。这项工作为低成本大规模制备光催化剂和光催化产 H_2 实现工业化提供了一条可行性思路。

关键词: 共沉淀; 助催化剂; 磷化物; 光催化; 产氢

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*通讯联系人. 电话: 18795112365; 电子信箱: bjma@nxu.edu.cn

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