

available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue of Photocatalysis for Solar Fuels)

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

ARTICLE INFO

Article history:

Received 27 September 2017

Accepted 21 October 2017

Published 5 March 2018

Keywords:

Coprecipitation

Cocatalyst

Phosphide

Photocatalysis

Hydrogen production

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.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

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

This work was supported by the National First-rate Discipline Construction Project of Ningxia (Chemical Engineering and Technology), the Major Innovation Projects for Building First-class Universities in China's Western Region (ZKZD2017003), the University Research Project of Ningxia (NGY2015027), the National Natural Science Foundation of China (21263018), and the Project of Science and Technology of Personnel of Study Abroad (Ningxia (2014) 486).

DOI: 10.1016/S1872-2067(17)62931-0 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 3, March 2018

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].

Download English Version:

<https://daneshyari.com/en/article/6505725>

Download Persian Version:

<https://daneshyari.com/article/6505725>

[Daneshyari.com](https://daneshyari.com)