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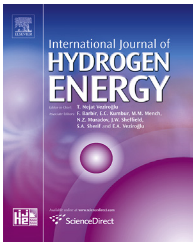

A bifunctional catalyst for hydrogen evolution reaction: The interactive influences between CdS and MoS_2 on photoelectrochemical activity

Jing Ji, Liangliang Guo, Qian Li, Feng Wang*, Zhilin Li, Jingjun Liu, Yi Jia

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

Bifunctional leaf-like CdS/MoS_2 hybrids were successfully prepared by electrodeposition. The interactive influences between MoS_2 and CdS on the photoelectrocatalytic activity for catalyst of CdS/MoS_2 were characterized by analyzing the current density (J)–potential (V) curves of cathodic and anodic polarization. On the one hand, the CdS/MoS_2 hybrid showed the improved photoelectrochemical performance which was attributed to the visible light absorption enhanced by MoS_2 and the formation of p–n junction between CdS and MoS_2. On the other hand, the CdS/MoS_2 hybrid exhibited superior electrocatalytic activity in the hydrogen evolution reaction (HER) relative to the MoS_2 catalyst. A Tafel slope of ~42 mV/decade was measured for CdS/MoS_2 hybrid in the HER, which exceeded by far the activity of previous MoS_2 catalysts and resulted from the abundance of catalytic edge sites on the MoS_2 nanoparticles. The Tafel slope of~42 mV/decade suggested the Volmer_Heyrovsky mechanism for the CdS/MoS_2-catalyzed HER, with electrochemical desorption of hydrogen as the rate-limiting step.

Introduction

Photocatalytic production of H_2 from water splitting has received considerable attention as a solar energy driven pathway to hydrogen [1–8]. Development of efficient and low-cost photocatalysts for H_2 production from water splitting using solar energy is indispensable for the utilization of the main part of the solar spectrum, which is of great importance for the practical application of the semiconductor photocatalytic system.

Studies on semiconductor-type photocatalysts have indicated that metal chalcogenides are promising as catalysts for photocatalytic water reduction due to their unique properties, such as high extinction coefficient of light absorption, tunable bandgap, and carrier multiplication effect, etc. Among the numerous types of semiconductor systems studied, CdS has been most frequently investigated for its efficient absorption of visible light and sufficient conduction band potential for reduction of H^+ to H_2 [9–14]. Moreover, CdS is less expensive and easily prepared. However, CdS alone exhibits very low photocatalytic activities under visible light.

To achieve high photocatalytic activity, co-catalysts loaded on the surface of CdS is a promising method [15–22]. An appropriate co-catalyst can accommodate the photogenerated charge carriers, suppress charge recombination,

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* Corresponding author.
E-mail addresses: jijing@mail.buct.edu.cn (J. Ji), wangf@mail.buct.edu.cn (F. Wang).

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and provide designated redox reaction sites to avoid back reactions. The efficient photocatalytic cocatalysts usually contain noble metals [23–29], and some nonnoble metals [5,30–36]. Among these cocatalysts, MoS_2 is highlighted, as MoS_2 and CdS share the same hexagonal crystalline structure, which ensures that a high-quality, intimate heterojunction can be obtained. Moreover, molybdenum disulfide, composed of Mo atoms sandwiched between two layers of hexagonally close packed sulfur atoms, can effectively catalyze the electrochemical activities for the hydrogen evolution, even without the assistance of noble metal co-catalysts [37–42]. Previous studies on HER have shown that the HER activity of MoS_2 stemmed from the sulfur edges of MoS_2 plates [37,38]. Therefore, the cocatalyst of CdS/MoS_2 is not only an efficient photocatalyst, in which the p–n junction formed between the MoS_2 and CdS could promote the separation of photoexcited electrons and holes, and decrease the activation potentials for H_2 evolution, thus greatly enhancing the photocatalytic activity of CdS for H_2 evolution [5,34], also a more effective electrochemical catalyst for HER in comparison with that of the solitary MoS_2. Although the effectiveness of the advantages of the cocatalyst of MoS_2 in improving electrochemical hydrogen evolution has been extensively demonstrated in several highly active catalysts, such as MoS_2/graphene, MoS_2/carbon nanosphere [43–49], the utilization of the MoS_2/CdS nanohybrid as a catalyst for electrochemical catalytic H_2 evolution has not been adequately addressed. In addition, MoS_2, as a cocatalyst in enhancing the electrochemical H_2 evolution, should have been further demonstrated although its activity on CdS under light irradiation has been reported [5].

Up to the present, many researchers mainly focus their attention on either CdS-based photocatalysts or active MoS_2-based electrocatalysts, where different morphology and crystal CdS or MoS_2 are synthesized; and the influence of the cocatalyst on the photoactivity of CdS or of the improved electronic contact between the active sites and the underlying electrode on the electroactivity of MoS_2 is investigated. The interactive influences of the CdS/MoS_2 cocatalyst on photoelectrochemical activity are seldom studied to the scope of our knowledge.

In the present study, a flowerlike CdS/MoS_2 heterostructure was prepared by electrodeposition. In this investigation, a thin nanoplatelet structure of MoS_2 was fabricated not only to create a large percentage of edge sites, but also to increase the contact area with the flower-like CdS sheet, which will facilitate the charge transfer at the MoS_2/CdS interface. To investigate the interactive influences of MoS_2 and CdS on the production of hydrogen, the electrochemical experiments on HER for catalysts of CdS, MoS_2 and CdS/MoS_2 are conducted under the light irradiation, while the bias potential is applied. Herein, MoS_2 not only acts as a catalytic center but also as a photocenter for absorbing solar light to generate charge carriers. This work indicates that effectively integrated structure and the suitable band position of CdS/MoS_2 nanohybrid lead to a highly photoelectrochemical activity. Under the condition of anodic polarization, or reverse bias potential, the CdS/MoS_2 junction catalyst exhibits much better photocatalytic activity toward HER as compared with that of solitary MoS_2 and CdS due to the n-type characteristics of semiconductors. In the case of cathodic polarization, or forward bias potential, CdS/MoS_2 hybrid exhibits superior electrocatalytic activity in the hydrogen evolution reaction (HER) relative to MoS_2 catalysts, with low overpotential and small Tafel slopes, although photogenerated electrons have little influence on the HER for the CdS/MoS_2.

Experimental section

Materials

Cadmium chloride was obtained from Kermel (Tianjing, China). Na_2S, HCl, $Na_2S_2O_3$ and KCl was purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium tetrathiomolybdate was obtained from J&K. Indium tin oxide (ITO) coated glass was purchased from China South Glass. Deionized water (Resistivity >18.4 MΩ/cm) was produced using a pure water system (TTL-6B). All chemical reagents were used without further purification.

Preparation of CdS, MoS_2 and MoS_2/CdS thin films

A simple electrochemical process was preferred to prepare CdS and MoS_2 thin film on the ITO substrate. For the preparation of CdS thin films, the galvanostatic electrochemical deposition was carried out in 200 ml of the electrolyte under the current density of −0.7 mA using three-electrode system in which platinum plate, ITO glass and saturated calomel electrode were used as the counter, working and reference electrodes, respectively. The ITO electrode were initially washed by acetone, ethanol and deionized water respectively in a water-bath sonicator for 10 min. An aqueous solution, composed of 10 mM $CdCl_2$ and 2 mM $Na_2S_2O_3$, was prepared and maintained at 70 °C for 30 min with vigorous stirring to obtain transparent solution, followed by electrodeposition for 30 min. During the electrodeposition, HCl was used to adjust the electrolyte, and the pH value of the electrolyte prepared is at ~1.6. The as prepared CdS film was cooled down to room temperature, washed with deionized water several times, and then dried in a vacuum oven at 80 °C. For preparation of MoS_2 film, an aqueous solution, composed of 2 mM $(NH_4)_2MoS_4$, 2 mM Na_2S and 0.1 M KCl, was ultrosoniced for 10 min to obtain red transparent solution, followed by electrodeposition for 10 min. For preparation of CdS/MoS_2 film, the as prepared CdS/ITO was immersed in the aqueous solution of 2 mM$(NH_4)_2MoS_4$, 2 mM Na_2S and 0.1 M KCl for 30 s, followed by electrodeposition for minutes, ranging from 2 to 15 min, then the film was rinsed by deionized water. The as prepared sample was annealed at 400 °C for 1hr under the protection of argon atmosphere to obtain the CdS/MoS_2 electrode.

Characterization

The morphology and structure were carried out on a SEM (JEOL-6701F) and a high-resolution transmission electron microscopy (HRTEM, JEOL-3010) which was operated at 200 kV. The scanning current is 10 μA, and the accelerating voltage is 5 kV. X-ray diffraction (XRD) patterns, obtained on a Rigaku D/max-2500B2+/PCX system operating at 40 kV and 20 mA using