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Constructing 2D layered hybrid CdS nanosheets/MoS_2 heterojunctions for enhanced visible-light photocatalytic H_2 generation

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ABSTRACT

In this work, a 2D hybrid CdS nanosheets(NSs)/MoS_2 layered heterojunctions were successfully synthesized by a two-step hydrothermal method and subsequent ultrasonic treatment. The results showed that the loading ultrathin MoS_2 NSs as co-catalysts could significantly boost the photocatalytic H_2-evolution activity of CdS NSs. It is demonstrated that the optimized 2D CdS NSs/MoS_2 (1.0 wt%) layered heterojunctions could achieve the highest photocatalytic H_2-evolution activity of 1.75 mmol g^{-1} h^{-1} from an aqueous solution containing sulfide and sulfite under visible light, which is 2.03 times as high as that of the pristine CdS NSs. It is believed that the deposition of ultrathin MoS_2 NSs and intimate 2D–2D coupling interfaces are mainly responsible for the excellent H_2-evolution performance of 2D CdS NSs/MoS_2 layered heterojunctions, owing to the effectively promoted separation and transportation of charge carriers and the enhanced following surface H_2-evolution kinetics. Interestingly, the lactic acid and formic acid have also been demonstrated to be better sacrificial reagents than the Na_2S/Na_2SO_3, for the photocatalytic H_2 evolution over the 2D CdS NSs/MoS_2 layered heterojunctions. It is hoped that the strategy of 2D–2D interfacical coupling based on CdS NSs can become a general strategy to improve the H_2-evolution activity over various kinds of conventional semiconductor NSs.

1. Introduction

As one of the most ultra-clean, promising, powerful and environmentally friendly alternative energy carriers to the traditional fossil fuels, hydrogen has been identified as a wide range of attention by global scientists over the past 3 decades [1,2]. Among various low-cost H_2-genertaion technologies, photocatalytic H_2 production has proven to be a potentially ideal, regenerative, eco-friendly and inexhaustible approach to simultaneously solve both serious crisis of fossil energy and energy-related environmental pollution [3–5]. Since Fujishima and Honda firstly reported the groundbreaking work about the photoelectrochemical water decomposition over a Pt-attached rutile TiO_2 cell under UV light in the early 1970s [6], numerous semiconductors have been successfully utilized in the photocatalytic water splitting in the past decades [4,7]. As well known, the *n*-CdS semiconductor with suitable band gap ($E_g \approx 2.40$ eV) and conduction band level (−0.9 V vs. NHE, pH = 7) has proven to be one of the most promising materials for visible-light hydrogen evolution from aqueous Na_2S–Na_2SO_3 or lactic acid solutions [8]. Unfortunately, the ultrafast recombination of photo-generated charge carriers and the strong self-oxidation of CdS driven by photo-excited holes lead to the low photocatalytic activity and stability of CdS photocatalysts, thus significantly restricting their practical applications in photocatalytic H_2 evolution. Therefore, a wide variety of modification strategies such as tuning dimensionality [9–16], tailoring porous textures [17–19], constructing heterojunctions with other organic/inorganic semiconductors [20–25], fabricating Z-scheme systems [26–30], loading suitable co-catalysts [31,32], coupling with nano carbon materials [8,33–36], and their integration and optimization [37], have been widely employed to determine the photocatlytic H_2 evolution over CdS. Among them, loading appropriate co-catalysts on CdS appears to be more promising in improving the photocatalytic H_2-evolution activity, because the suitable co-catalysts on CdS can act as effective H_2-evoluton active sites, thus simultaneously achieving the promoted charge separation, the accelerated sluggish H_2-evolution kinetics, and the decreased activation energy for H_2 evolution [38]. So far, various co-catalysts such as Pt [19], MoS_2 [39–42], MoP, [43] WS_2 [44,45], WC [46], FeP_x [47,48], CoP_x [49–51], Co_3O_4 [52,53], $Co(OH)_2$ [54,55], Ni [56–62], NiO [63,64], Ni_2P [65,66], NiS [16,32],

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$Ni(OH)_2$ [31], molecular nickel complex [13], amorphous Ni(II) [67], Cu_xS [68,69], Cu_3P [70], PdS [14,71], and Ag_2S [72] have been widely employed to enhance photocatalytic H_2 generation over CdS.

MoS_2, as a promising earth-abundant 2D layered H_2-evolution electrocatalyst, has attracted considerable research interest in the communities of both electrocatalytic and photocatalytic H_2 evolution [73–79], since its excellent electrocatalytic H_2-evolution activity and active edge defect sites were theoretically and experimentally revealed [80,81]. In 2008, Zong et al. first demonstrated that loading MoS_2 (0.2 wt%) co-catalysts onto CdS particles could achieve a 36-fold enhancement in H_2-evolution activity [40]. More interestingly, it was also found that the H_2-evolution activity of 0.2 wt% MoS_2/CdS was even higher than that of 0.2 wt% Pt/CdS under the same reaction conditions [40]. Further research demonstrated that the junctions formed between MoS_2 and CdS played an important role in enhancing the photocatalytic activity of MoS_2/CdS catalysts [39]. Following these works, the hybrids of MoS_2/CdS based on different physical dimensions, such as 0D/0D [82], 0D/1D [83], 0D/2D [84–86], and 1D/2D [87] have been widely constructed and applied in the photocatalytic H_2 evolution. For example, Chen et al. demonstrated that the nanohybrids of 0D wurtzite CdS nanocrystals and single-layer MoS_2 NSs with lateral size of 4–10 nm exhibited significantly enhanced photocatalytic H_2 evolution activity, which was 12 times higher that of pure CdS [84]. Chang et al. found that the photocatalytic H_2-evolution activity of MoS_2/CdS dramatically increased with decreasing the layer number of MoS_2 [85]. Surprisingly, the single-layer MoS_2/CdS sample could achieve an apparent quantum efficiency (AQE) of 30.2% for H_2 generation in Na_2S–Na_2SO_3 solutions (420 nm). More recently, He et al. demonstrated that CdS nanowires decorated with ultrathin MoS_2 NSs could exhibit an excellent H_2 evolution rate of 1914 μ mol h^{-1} (20 mg catalyst) under visible light ($\lambda \geq 400$ nm) and an AQE of 46.9% (420 nm) [87]. However, so far, little work has focused on fabricating the 2D–2D hybrids of CdS NSs/MoS_2 and applying them in the photocatalytic H_2 evolution. It is believed that one of the main challenges is how to obtain the ultrathin 2D NSs of non-layered inorganic CdS materials.

Recently, Xu et al. reported the synthesis of ultrathin CdS nanosheets through a simple and cost-effective L-cysteine-assisted solution-phase ultrasonic exfoliation method of the lamellar inorganic–organic hybrid CdS-DETA precursors [14]. These well-dispersed CdS ultrathin NSs in aqueous solution show excellent activity for photocatalytic H_2 evolution under visible light irradiation. This work paves a way for fabricating 2D CdS nanosheet-based photocatalysts for various applications. Recently, as a successful example, 2D hybrid nanostructure of RGO/CdS NSs have been demonstrated to exhibit ~2.5 times higher activity for degradation of Methylene Blue dye under visible light, as compared to that of pure CdS NSs samples [88]. In this regard, it is naturally expected that the 2D hybrid layered heterojunctions between CdS NSs and MoS_2 NSs can be designed and fabricated and further applied in the photocatalytic H_2 evolution. In the present study, the 2D Hybrid CdS NSs/MoS_2 layered heterojunctions were successfully synthesized by a two-step hydrothermal method and subsequent ultrasonic treatment (as shown in Fig. 1). The results demonstrated that the activity of the CdS NSs for hydrogen evolution was significantly enhanced in the presence of the ultrathin MoS_2 NSs as co-catalysts under visible light irradiation from an aqueous solution containing sulfide and sulfite. A possible enhancement mechanism for the improved photocatalytic activity of 2D Hybrid CdS NSs/MoS_2 layered heterojunctions was also proposed.

2. Experimental section

2.1. Materials

All materials were of analytical grade and used without any further purification, including cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), sulfur powder, diethylenetriamine (DETA), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), and thiacetamide (C_2H_5NS).

2.2. Synthesis mthods

2.2.1. Synthesis of CdS nanosheets

The CdS NSs were synthesized by a solvothermal method. 0.3206 g of sulfur powder and 0.3654 g of $CdCl_2 \cdot 2.5H_2O$ were dissolved in 60 mL DETA and stirred for 1 h. Then, the mixture was transferred and sealed in a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 80 °C for 48 h. After that, it was cooled to room temperature, and a pale yellow product was collected by centrifugation. The product was washed several times with ethanol and distilled water, respectively. Finally, it was dried at 60 °C in a vacuum drying oven.

2.2.2. Synthesis of thin layered MoS_2

0.2351 g of sodium molybdate and 0.4 g of thiacetamide were dissolved in 30 mL of distilled water and kept stirring for 1 h. Then, the mixture was transferred and sealed in a 100 mL Teflon-lined stainless-steel autoclave and heated at 210 °C for 24 h before cooling to room temperature. The black power was collected by centrifugation. Afterwards it was washed by distilled water and ethanol before being heating at 60 °C for 10 h.

2.2.3. Synthesis of CdS-MoS_2 composites

To fabricate the CdS-MoS_2 hybrid, a sample process was followed as above, 5 mg of MoS_2 powders were firstly dispersed in

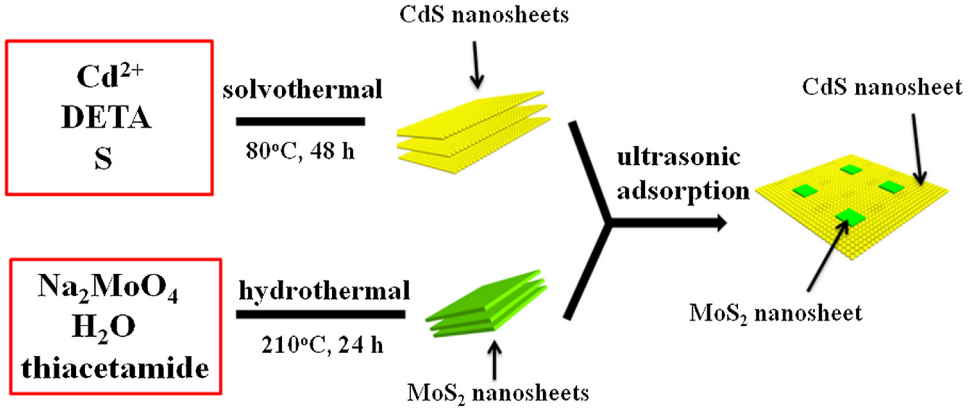

Fig. 1. Schematic illustration of the fabrication of the 2D Hybrid CdS NSs/MoS_2 layered heterojunctions.

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