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Synthesis of MoS_2 quantum dots cocatalysts and their efficient photocatalytic performance for hydrogen evolution

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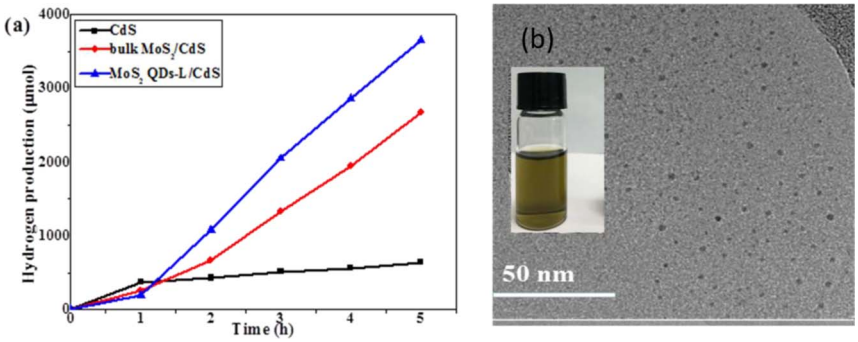
GRAPHICAL ABSTRACT

Exploiting noble-metal free cocatalysts is of great importance for water splitting via solar energy. Molybdenum disulfide (MoS_2) has been identified as a promising non-precious-metal cocatalyst to replace Pt. Here, two facile synthetic routes including a hydrothermal process and a liquid exfoliation strategy were adopted and screened for finely controlled synthesis of MoS_2 QDs cocatalyst and their application in the visible-light photocatalytic hydrogen production. It was confirmed that the MoS_2 QDs-L (L is the abbr'eviation of liquid exfoliation method) as cocatalyst can remarkably enhance the photocatalytic hydrogen activity of CdS under visible-light irradiation. Notably, with lactic acid as a sacrificial agent, the MoS_2 QDs-L/CdS photocatalyst achieved an optimal hydrogen production activity with a rate of 1032.1 μmol h^{-1}, which was 2.7 times more effective than that of the corresponding bulk MoS_2/CdS (383.5 μmol h^{-1}) and 15.4 times more effective than that of the bare commercial CdS (66.9 μmol h^{-1}). In the meantime, the MoS_2 QDs-L/CdS exhibited a good stability of in the cyclic runs for the photocatalytic hydrogen production. Impressively, it was found that a higher electrocatalytic activity of MoS_2 QDs-L/CdS is directly consistent with a higher photocatalytic activity of MoS_2 QDs-L/CdS during the hydrogen production. These findings will open opportunities for developing low-cost, high efficiency and stable photocatalyst that will find potential applications both in environmental protection and in renewable energy areas.



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ABSTRACT

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1. Introduction

Semiconductor-based visible-light photocatalytic hydrogen production from water splitting has attracted increasing attention because of their potential to resolve the global energy and environmental issues [1,2]. Until now, a rich variety of semiconductor materials have been explored as photocatalysts for hydrogen production [3,4]. However, the low photocatalytic efficiency over single photocatalyst due to the narrow solar spectral response and rapid recombination of photo-induced electron-hole pairs is still a barrier for practical application [5–7]. An attractive way to solve the above-mentioned problem is to load optimum amount of cocatalyst on the host semiconductor to form heterostructure [8]. The existence of cocatalyst not only can effectively separate the photoinduced electron-hole pairs but also provide more proton reduction sites, and thereby contributing to the improvement of photocatalytic efficiency [9–12]. In particular, noble metals are extensively used as cocatalysts for their good efficiencies, such as Pt, Pd, Au, Ru, and so on [13–16]. However, the high cost and natural scarcity of these metals prevent their widespread use. Much attention is therefore now being paid on exploiting the noble-metal free alterative cocatalysts.

As a typical layered transition metal sulfide, molybdenum disulfide (MoS_2), with sandwich structure of three stacked atomic layers (S-Mo-S), has been proved to be an excellent cocatalyst towards hydrogen production [17–25]. For example, Han et al. fabricated one-dimensional (1D) CdS@MoS_2 core-shell nanowires and got the hydrogen production activity with a rate of 493.1 μmol h^{-1} [19]. Wang and coworkers used a hydrothermal exfoliation method to controllable synthesize TiO_2@MoS_2 reaching a high H_2 evolution rate [23]. Yin and his group fabricated a unique MoS_2/CdS nanohybrid system which showed the H_2 evolution rate of 49.8 mmol $g^{-1}h^{-1}$ [25]. However, it should be noted that the utilization of bulk MoS_2 as a cocatalyst has two inherent shortcomings: few active sites and the poor intrinsic electron conductivity [26–30]. Most fascinating current work on photocatalysis has proved that nanostructured MoS_2 cocatalyst, such as nanoparticles [26], nanowires [27], nano flowers [28], and quantum dot (QDs) [30] can generate more active sites and improve electron conductivity, and thus manifest superior performance to the bulk MoS_2. Especially, MoS_2 QDs has been explored as the most favorable candidate with great enthusiasm in recent years. There appears to be a great demand to develop an effective and low-cost strategy to produce fine MoS_2 QDs in order to further facilitate the development of hydrogen production.

At present, the common routes for the synthesis of MoS_2 QDs include electrochemical synthesis [31], ultrasonic exfoliation and solvothermal treatment [32], electro-Fenton treatment [33], hydrothermal synthesis [34] and liquid exfoliation strategy [35]. Among those methods, both hydrothermal synthesis and liquid exfoliation have the advantages of easy operation, mild synthetic conditions, economic and environmental feasibility and so on [36]. Thus, the development of hydrothermal synthesis and liquid exfoliation preparation of MoS_2 QDs is very attractive. Herein, both hydrothermal strategy and liquid exfoliation process were adopted and screened for finely controlled synthesis of MoS_2 QDs cocatalysts and for their application in the visible-light photocatalytic hydrogen production. It was shown that the as-prepared MoS_2 QDs-L as cocatalyst can remarkably enhance the photocatalytic hydrogen activity of CdS under visible-light irradiation. This research is critical to investigate and develop novel visible-light responsive photocatalysts with low-cost, high efficiency and good stability.

2. Experimental

2.1. Materials

Sodium dihydrate sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), dibenzyl disulfide ($C_{14}H_{14}S_2$), commercial molybdenum sulfide (bulk MoS_2), N-methylpyrrolidone (NMP), N-hexane (C_6H_{14}), anhydrous ethanol (C_2H_5OH), trichloromethane ($CHCl_3$), ammonium sulfite monohydrate ($(NH_4)_2SO_3{\cdot}H_2O$, 92%), lactic acid ($C_3H_6O_3$) were purchased from China Pharmaceutical Chemical Reagent Co., Ltd. (Shanghai, China). Cadmium sulfide (CdS, 98%) was purchased from Naiji Chemical Co., Ltd. (Shanghai, China). Nafion solution (5 wt%) was purchased from Alfa Aesar Chemical Co., Ltd. (Shanghai, China). All reagents were used as received without further treatment.

2.2. Synthesis of MoS_2 QDs by a hydrothermal method

In a typical synthesis for MoS_2 QDs: 0.2 g sodium dihydromyldimolate ($Na_2MoO_4{\cdot}2H_2O$) and 0.19 g dibenzyl disulfide ($C_{14}H_{14}S_2$) was separately ultrasonically dispersed in 15 mL of

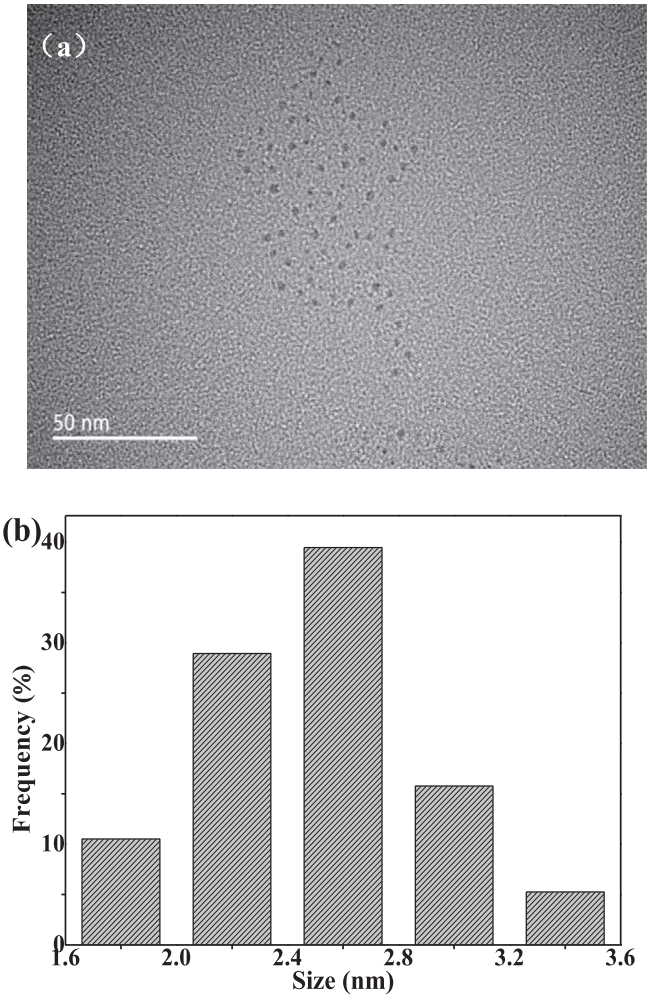

Fig. 1. (a) TEM image of MoS_2 QDs-H, and (b) the corresponding particle size distribution of MoS_2 QDs-H.