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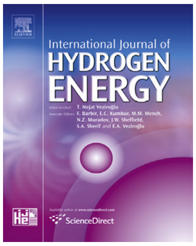

In-situ photochemical fabrication of transition metal-promoted amorphous molybdenum sulfide catalysts for enhanced photosensitized hydrogen evolution

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ABSTRACT

Amorphous molybdenum sulfide catalysts (MoS_x) can efficiently catalyze the H_2 evolution reaction (HER); however, their catalytic activities are still limited that need to be improved. Herein, transition metal-promoted MoS_x H_2 evolution catalysts were facilely fabricated through an in-situ photochemical reduction with inexpensive organic dye as photosensitizers. Under visible light ($\lambda \geq 420$ nm), the promotional effect of transition metals on the H_2 evolution over MoS_x follows the order of Co > Fe ≈ Ni > unpromoted > Cu > Zn in Erythrosin B-triethanolamine (ErB-TEOA) system. The most active Co-promoted MoS_x (Co-MoS_x) catalyst is amorphous and composed of inter-connected nanoparticles with diameters of 30–50 nm. The Co-MoS_x catalyst contains both CoMoS phase and Co oxides/hydroxides. At the optimal reaction conditions, the Co-MoS_x catalyst with Co:Mo ratio of 4:6 exhibits enhanced H_2 evolution activity by 2 times as compared to unpromoted MoS_x and turnover numbers (TONs) of 30 and 60 based on ErB and catalyst used, respectively. The Co-MoS_x catalyst also shows a long-term stability without noticeable activity degradation. The formation pathways of Co-MoS_x catalyst and the photocatalytic mechanism for enhanced H_2 evolution performance were studied and a two-step reaction mechanism involved an oxidative quenching pathway of dye was proposed. This study demonstrates that in-situ concurrent photochemical fabrication with transition metal modification of amorphous MoS_x catalyst is an effective strategy for development of MoS_x-based HER catalysts with enhanced performances.

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Introduction

Hydrogen evolution *via* photocatalytic water splitting has being extensively pursed as an attractive solution to resolve issues associated with global warming and environmental problems [1–5]. To increase the efficiency of photocatalytic H_2 evolution reaction (HER), a catalyst that is stable and active is required [6–9]. Among many different HER catalysts, the most effective one is platinum (Pt) that exhibits the highest efficiency in the HER [6], but its scarcity and high cost significantly limit its use for large-scale applications [7]. Thus, development of noble-metal-based alternatives has attracted growing attention and remains a great challenge.

Recently, molybdenum sulfides-based materials, as common hydrodesulfurization (HDS) catalysts, have regained research interests due to the findings of they can be potential alternatives of noble metals for efficiently catalyzing the electrochemical and photochemical HER [10–43]. For electrocatalytic HER, great progresses have been made in design and preparation of catalyst, identification of active sites, and structure-related performance modifications as well as catalytic mechanism by integrating experimental and theoretical studies [10–24]. In the case of photocatalysis studies, several photocatalytic H_2 evolution systems have been developed and showed enhanced performances for photocatalytic HER, where crystalline MoS_2, amorphous MoS_x ($2 < x < 3$), or their composites with conductive supports such as graphene and carbon nanotubes as HER catalysts and either semiconductor or dye as photosensitizer [25–43]. For example, Li et al. [25,26] has shown that loading MoS_2 as cocatalyst on CdS nanoparticles leads to a comparable H_2 evolution activity to Pt loaded CdS. Yu et al. [28] has reported a synergistic effect of MoS_2/graphene cocatalyst for efficient H_2 evolution over TiO_2 nanoparticles. Following above pioneer works of employing MoS_2 as HER catalyst in semiconductor photocatalytic systems, extensive efforts has also been devoted to construct dye sensitized H_2 evolution systems with or without an electron transfer mediator and were reported to show high efficiency for catalyzing HER [44–50]. In this context, Min et al. [45] have demonstrated the utilization of MoS_2/graphene nanohybrid as a catalyst for visible light photocatalytic H_2 evolution by using Eosin Y as a photosensitizer. Zong et al. have developed an efficient photosensitized system by simply integrating Erythrosin B as a light absorber and in-situ generated MoS_x as an HER catalyst [47]. The main advantages of this system are that it excluded the use of electron transfer mediator and simplified the preparation of MoS_x catalyst, making this system more promising for large-scale and on-demand H_2 production. Following this work, in-situ generation of MoS_x on metal-free g-C_3N_4 as efficient HER catalyst was also demonstrated in ErB photosensitization system [50]. Although above-mentioned progresses have demonstrated the effectiveness of MoS_x catalyst, most of the efforts have only been paid to seek the more efficient combinations of semiconductor or dye with MoS_x catalyst [46,48,49], and much less endeavors has been attempted to improve the intrinsic catalytic activity of MoS_x for photocatalysis.

Inspired by past successes in MoS_2 thermocatalysis for HDS processes, several strategies have also been attempted, including the control of microstructure [16–18], exposed edge sites [19,21,22], and modification with transition metal ions [52–54], to improve the intrinsic activity of MoS_x for HER. Among them, doping with transition metal ions is shown to be more efficient. It has been well-established that adding small amounts of transition metal dopants including Fe, Co, and Ni to MoS_2 can significantly increase its activity for electrocatalytic HER [52]. Studies of DFT calculations showed that these dopants can efficiently modify the hydrogen bonding energy (ΔG_H) at the S-edges of MoS_2, *i.e.*, from 0.18 eV for MoS_2 to 0.10 eV for Co doped MoS_2 [52,55,56], thus increasing the number of active sites in nanostructured MoS_2 catalysts by activating the S-edges. Transition-metal Ni, Co, and Fe have also been used to improve the activity of amorphous molybdenum sulfide (MoS_x) catalysts [52]. Co ions doping was also proven to be most successful, yielding changes in the catalyst morphology that increased the active surface area and catalyst loading and resulting in highly-active HER electrodes. Although the effectiveness of the promotional effects of transition metals in improving catalytic activity of both crystalline and amorphous MoS_2 have been demonstrated for electrocatalytic HER, there are only few reports to elucidate their effects on photocatalytic HER [57]. Moreover, there are few researches studying the preparation and HER performances of amorphous MoS_x in dye sensitized systems [47,50], but the in-situ photochemical fabrication along with transition metal modification of amorphous MoS_x catalyst for preparing high-active MoS_x-based HER catalysts have not been adequately addressed.

Herein, we report that amorphous transition metal (Co, Ni, Fe, Cu, Zn)-promoted MoS_x catalysts can be facilely fabricated with an in-situ photochemical reduction method with molecular complex as precursor and inexpensive organic dyes as photosensitizers. The in-situ generated promoted catalysts then can serve as efficient catalysts for catalyzing H_2 evolution and the Co-promoted MoS_x (Co-MoS_x) was identified as a most active and stable HER catalyst. In addition, the parameters influencing the performance of the photocatalytic system were optimized and the formation pathway of catalyst and photocatalytic mechanism was also studied using UV–vis absorption and photoluminescence measurements. This work indicates that the in-situ formation of amorphous MoS_x and its modification by transition metals can be accomplished through a simple one-step photochemical reduction, which would be promising strategy for development of highly-active noble-metal-free HER catalysts for large-scale H_2 production.

Experimental

Chemicals and instruments

All reagents including triethanolamine (TEOA), Erythrosin B (ErB), Eosin Y (EY), Rose Bengal (RB), fluorescein sodium (FS), rhodamine B (RhB), $(NH_4)_6Mo_7O_{24}$, $(NH_4)_2S$ solution (21%), $Ni(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $CuSO_4\cdot 5H_2O$, and $FeSO_4\cdot 7H_2O$ were of analytical grade and used without further purification. $(NH_4)_2MoS_4$ was synthesized from $(NH_4)_6Mo_7O_{24}$ and $(NH_4)_2S$ solution (21%) according to a reported procedure [47]. All solutions in the experiments were

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