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Solvothermal fabrication of MoS₂ anchored on ZnIn₂S₄ microspheres with boosted photocatalytic hydrogen evolution activity

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ABSTRACT

The MoS₂/ZnIn₂S₄ composites with MoS₂ anchored on the surface of ZnIn₂S₄ microspheres were fabricated by a facile solvothermal method. To clarify the crystal phases, morphologies, chemical compositions, optical properties, and special surface areas of the obtained photocatalysts, the corresponding characterization measurements were performed. The photocatalytic H₂ evolution activities of MoS₂/ZnIn₂S₄ composites were evaluated and compared with using lactic acid as sacrificial reagents. The results showed that integrating MoS₂ with ZnIn₂S₄ could remarkably boost the photocatalytic H₂ evolution performance and the maximum H₂ evolution rate of 201 μmol h⁻¹ was achieved over 1 wt% MoS₂ loading on the ZnIn₂S₄, corresponding to the apparent quantum efficiency (AQE) about 3.08% at 420 nm monochromatic light. The photoelectrochemical tests and photoluminescence spectra (PL) verified that the efficient charge transfer and separation were achieved over MoS₂/ZnIn₂S₄ composite in contrast with single ZnIn₂S₄, which would significantly benefit the enhancement of photocatalytic H₂ activity. This work provides a desired strategy to design and synthesize the visible-light-response photocatalysts with MoS₂ as cocatalysts to enhance the photocatalytic activity.

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Introduction

With the increasing of global energy demand and the climatic variation associated with burning fossil fuels, exploring a clean and sustainable energy resource has become an urgent task for humanity. Hydrogen energy is regarded as an ideal energy carrier to substitute fossil fuels in view of its overwhelming superiority. Photocatalytic splitting water for H₂ evolution over semiconductors is an attractive and economic strategy to produce hydrogen energy [1–4]. So far, the researchers have explored and developed a good great deal of photocatalysts to apply into photocatalytic reactions [5–21].

Among these photocatalysts, ternary chalcogenide ZnIn₂S₄, a layered structure with band gap energy about 2.0–2.4 eV, has been paid more attention in recent years owing to its excellent visible-light-response, considerable photostability and low toxicity [22–25]. However, the bare ZnIn₂S₄ usually undergoes the rapid recombination of photogenerated charge carriers and the large kinetic barrier for photocatalytic H₂ evolution reaction due to deficiency of active sites, which leads to the low photocatalytic activity. To promote the photocatalytic H₂ evolution activity of ZnIn₂S₄, a large number of efforts have been made to restrain the recombination of charge carriers and increase the charge carriers separation efficiency, such as loading noble metal platinum (Pt) as cocatalysts or

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incorporation with other semiconductors [26–33]. In this case, loading cocatalysts are always considered to be indispensable for acquiring high photocatalytic H_2 evolution activity because they can more effectively trap the photoexcited electrons derived from the semiconductor and lower the reactive overpotential in the hydrogen evolution reaction (HER). Although deposition precious metal Pt on the surface of $ZnIn_2S_4$ as cocatalysts could apparently enhance the photocatalytic H_2 evolution activity, this method would inevitably increase cost in the practical application. Considering the cost and scarcity of noble metal Pt, it is imperative to seek the low-cost, earth-abundant, low-toxic and high-efficient materials to replace Pt as cocatalysts for enhancing photocatalytic H_2 evolution activity [34–36].

Recently, the layered structure MoS_2 has attracted intense attentions in the photocatalytic H_2 evolution field. Density functional theory calculations deduce that the free energy of atomic hydrogen bonding to MoS_2 is close to that of Pt, which approaches to zero [37]. Furthermore, the excellent photocatalytic H_2 evolution activity of MoS_2 is ascribed to the active edge defect sites [38]. In other words, MoS_2 could be used as effective cocatalysts substitution for Pt [39–55]. For instance, Ye's group has integrated the exfoliated monolayers MoS_2 with commercialized CdS, which exhibits the dramatically enhanced photocatalytic H_2 evolution activities [39]. Zhao et al. have synthesized the $MoS_2/Cd_{0.5}Zn_{0.5}S$ composites by a two-step hydrothermal route. The maximum H_2 evolution rate of $12.30 \text{ mmol h}^{-1} \text{ g}^{-1}$ is achieved [40]. Yu et al. have adopted the *in-situ* transformation method to synthesize amorphous $MoS_2/g-C_3N_4$ hybrids with remarkably enhanced photocatalytic H_2 evolution activity [41]. The systems of MoS_2 combining with $ZnIn_2S_4$ have also been considerably reported in recent years. Meng's group has loaded MoS_2 on the surface of $ZnIn_2S_4$ by *in-situ* photo-assisted deposition method. The H_2 evolution rate of $8.047 \text{ mmol h}^{-1} \text{ g}^{-1}$ is obtained, obviously higher than that of single $ZnIn_2S_4$ [42]. Huang et al. have prepared $MoS_2/ZnIn_2S_4$ composites with a two-step hydrothermal method, and the maximum photocatalytic H_2 evolution rate is achieved at 0.5 wt% MoS_2 loading [43]. Li's group has obtained $MoS_2/ZnIn_2S_4$ composites through calcining $(NH_4)_2MoS_4$ and $ZnIn_2S_4$ blender under H_2S flow at high temperatures. The photocatalytic H_2 production activity is significantly improved by loading MoS_2 [44]. Tian et al. has constructed the hierarchical $MoS_2/ZnIn_2S_4$ composite by growing two dimensional (2D) ultra-thin $ZnIn_2S_4$ nanosheets on the MoS_2 slices, which markedly promote the photocatalytic H_2 evolution performance [45]. Although these reports are about using MoS_2 as cocatalysts for $ZnIn_2S_4$, exploring and developing the new avenues to anchor MoS_2 on the surface of $ZnIn_2S_4$ are still deserved to challenge.

Herein, we report the fabrication of MoS_2 anchoring the surface of $ZnIn_2S_4$ microspheres by a facile solvothermal procedure, which is different from previous reports on the formation of $MoS_2/ZnIn_2S_4$ composites. Significantly enhanced photocatalytic H_2 evolution activity is realized by introducing a little amount of MoS_2 as cocatalysts. Moreover, the influence of loading contents of MoS_2 on photocatalytic H_2 evolution activity is investigated and compared in detail. The tentative mechanism of improved photocatalytic activity is also proposed. We hope that this work may provide a new

insight to construct of non-noble metal photocatalysts for H_2 generation.

Experimental

Material preparation

All chemicals are analytical grade reagents and are purchased from Sinopharm Chemical Reagent Co., China, without further purification. Deionized water is used for all experiments. $ZnIn_2S_4$ microspheres precursor were prepared according to our previous report [23]. Typically, 1.0 mmol $Zn(NO_3)_2 \cdot 6H_2O$ and 2.0 mmol $In(NO_3)_3 \cdot 4.5H_2O$ were dissolved in 70 mL deionized water, and then the pH value of solution was adjusted to 1.0 by adding 1 mol L^{-1} hydrochloric acid. Next, 10 mmol thiourea (TAA) was added into the above solution with stirring. After stirring for 30 min at ambient temperature, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at $160^\circ C$ for 12 h in an electric oven. After the autoclave was cooled down to room temperature, the light yellow products were collected by centrifugation, washed respectively three times using deionized water and ethanol, and dried at $60^\circ C$ for 12 h.

$MoS_2/ZnIn_2S_4$ Composites were fabricated by a solvothermal method. A typical procedure as follows: 0.2 g as-obtained $ZnIn_2S_4$ microspheres were dispersed into 25 mL N-N'-dimethyl formamide (DMF) and H_2O mixed solvents (volume ratio 2:1) by ultrasound treatment for 30 min. Then 0.0022 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 0.0041 g thiourea were respectively added into the above suspension. After stirring another 30 min, the suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at $200^\circ C$ for 24 h. The resultant products with theoretical mass ratio of 1 wt% MoS_2 were collected and washed with deionized water and ethanol for several times, and dried at $60^\circ C$ for 12 h. For optimizing the loading amount of MoS_2 , a series of $MoS_2/ZnIn_2S_4$ composites with MoS_2 theoretical mass ratios (0.5 wt%–20 wt%) were prepared by varying the adding amounts of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and thiourea. The pristine MoS_2 sample was prepared by the same procedure except for adding $ZnIn_2S_4$ precursor. For comparison, the 1 wt% Pt loaded $ZnIn_2S_4$ sample via light-assistance reduction method was as reference.

Material characterization

The crystal phases were detected by powder X-ray diffraction (XRD) with a Shimadzu XRD-7000 diffractometer with $CuK\alpha$ irradiation at a setting of 40 kV and 30 mA. The morphology and energy dispersive X-ray spectrometer (EDS) were obtained on a JSM-7100F field emission scanning electronic microscope (FESEM) and a JEOL JEM 2100F high-resolution transmission electronic microscope (HRTEM). The X-ray photoelectron spectra (XPS) were carried out on a VG Multilab 2000 with Al $K\alpha$ source operating at 300 W. Raman spectra were measured using a Jobin Yvon LabRAM HR800 spectrometer. The UV–vis diffuse reflectance absorption spectra (UV-DRS) were recorded by a Purkinje General TU-1901 spectrophotometer using $BaSO_4$ as reference. The Brunauer-Emmett-Teller (BET)

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