



# Photocatalytic hydrogen production in a noble-metal-free system catalyzed by in situ grown molybdenum sulfide catalyst



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## ABSTRACT

The establishment of cost-effective photocatalytic system based on earth-abundant materials is crucial for the practical utilizations of solar energy. To achieve this goal, it is highly desirable to employ photosensitizers and catalysts that are both derived from earth-abundant materials. Herein, we report an efficient noble-metal-free system by integrating the above two components. We found that functional  $\text{MoS}_x$  nanoparticles can be obtained with an in situ photoreduction manner during photocatalytic reactions in the presence of inexpensive organic sensitizers. The thus-obtained  $\text{MoS}_x$  catalysts demonstrated quite high efficiency for catalyzing  $\text{H}_2$  evolution under visible light. The factors influencing the performance of the photocatalytic system was investigated and a two-step reaction mechanism was proposed. The concept of in situ formation of hydrogen evolution catalyst paves the way for investigating biomimetic molybdenum sulfide catalysts for photocatalytic  $\text{H}_2$  production in systems without the presence of noble metals.

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## 1. Introduction

Conversion of solar energy to hydrogen via photocatalytic water splitting offers an attractive solution toward energy and environmental problems [1–5]. To facilitate the liberation of hydrogen from water, the employment of catalysts that can offer low activation energy for  $\text{H}_2$  evolution is crucial. In this regard, platinum group metals have been traditionally used and showed unrivalled activity for catalyzing hydrogen evolution reaction (HER) [6]. However, large-scale hydrogen production with platinum group metals will be severely baffled by some inevitable challenges such as scarcity and high cost, which has inspired tremendous endeavor of finding alternative non-precious metal catalysts [7,8].

In biological systems, enzymes such as hydrogenases and nitrogenases catalyze hydrogen evolution and the responsible active sites are composed of earth-abundant elements such as Fe, Ni, Mo, and sulfur atoms [9,10]. Inspired by nature, much effort has been devoted to the development of functional materials that can mimic the active sites of these enzymes for  $\text{H}_2$  production [7,11]. In this regard, the investigation of biomimetic molybdenum sulfide ( $\text{MoS}_x$ ), an inorganic analogue of nitrogenase, as a heterogeneous electrocatalyst for catalyzing HER has attracted renewed interest [6,11–21]. The work on electrochemical hydrogen evolution on bulk  $\text{MoS}_2$  was pioneered by Tributsch and co-workers in

the 1970s [22]. In recent years, different  $\text{MoS}_x$  materials such as  $\text{MoS}_2$ ,  $\text{MoS}_3$ , and  $\text{Mo}_3\text{S}_4$  particles or nanosheets in the amorphous or crystalline form were reported to show high efficiency for catalyzing HER in electrochemical and photocatalytic reactions, and  $\text{MoS}_x$ -based materials have been supposed to be a potential alternative for noble metals in catalyzing  $\text{H}_2$  production [20]. Despite the aforementioned progresses, most of the efforts have been devoted to the electrochemical hydrogen production with  $\text{MoS}_x$  electrodes or photocatalytic hydrogen production in a heterogeneous system where semiconductors are used as the light absorber [12,13,20]. While much less attention has been paid to hydrogen production in a system sensitized with organic dyes that typically resembles the artificial photosynthesis process. Moreover, even though numerous systems have shown activity for  $\text{H}_2$  production, most of them are based upon photosensitizers consisting of noble metals such as Ru, Ir, Pt, and Rh [23–25]. From a practical standpoint, the development of a noble-metal-free system for hydrogen production is still a great challenge to be met and thus is highly significant and important research topic [26–29].

Herein, we report that functional molybdenum sulfide nanoparticles can be obtained with an in situ approach during photocatalytic reactions. The thus-obtained molybdenum sulfide catalysts demonstrated quite high efficiency for catalyzing  $\text{H}_2$  evolution in a noble-metal-free system under visible light. To our knowledge, this is the first successful example of employing molybdenum sulfide catalyst for catalyzing  $\text{H}_2$  production in a noble-metal-free system sensitized by organic dye, which could shed light on the design of “green” and economical chemistry cycles.

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## 2. Materials and methods

### 2.1. Catalysts preparation and chemicals

Triethanolamine (TEOA, Sigma–Aldrich), Erythrosin B (EB, Sigma–Aldrich),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (Sigma–Aldrich), and  $(\text{NH}_4)_2\text{S}$  solution (21%, Fluka) were of reagent quality and used as received.  $(\text{NH}_4)_2\text{MoS}_4$  was synthesized from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  and  $(\text{NH}_4)_2\text{S}$  solution according to a reported procedure [30]. In a typical synthesis, 1.5 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  was added to 20 ml of  $(\text{NH}_4)_2\text{S}$  solution at ambient temperature under stirring conditions. The mixture was then heated at 353 K to obtain a deep red solution. The solution was stirred for 2 h and then transferred to a refrigerator with duration of 12 h. The precipitated red crystals were thoroughly washed with ethanol, dried, and stored under nitrogen. All solutions in the experiments were prepared with deionized ultrapure water (18 M cm) that was obtained by an Elga water purification system.

### 2.2. Characterizations

The UV–visible absorption spectra of the samples were obtained on an UV visible spectrophotometer (UV-2200, Shimadzu). X-ray photoelectron spectroscopy (XPS) was recorded with an X-ray photoelectron spectrometer (Thermo Escalab 250, a monochromatic Al K $\alpha$  X-ray source). The morphologies of  $\text{MoS}_x$  catalysts were characterized with transmission electron microscopy (TEM, Philips Tecnai F20). X-ray diffraction (XRD) patterns of  $\text{MoS}_x$  catalysts were collected using an X-ray diffractometer (Rigaku Miniflex). Fluorescence spectra were measured using a Jobin–Yvon Horiba Fluorolog in steady-state mode using a xenon lamp as the excitation source.

### 2.3. Photocatalytic reactions

Photocatalytic hydrogen evolution reaction was performed in a TEOA/photosensitizer/ $\text{MoS}_x$  three-component system. Typically, Erythrosin B (2 mM) and  $(\text{NH}_4)_2\text{MoS}_4$  (1 mM) were added to a quartz reaction cell containing 100 mL of 10 vol% TEOA aqueous solution under vigorous stirring. The reaction cell was then connected to a closed gas circulation and evacuation system. The solution was thoroughly degassed and irradiated by a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV). The Xe lamp was equipped with an optical cut-off filter ( $\lambda > 420$  nm) to eliminate ultraviolet light, and the reactor was equipped with a water filter to remove infrared light. The amount of  $\text{H}_2$  produced was analyzed using an on-line gas chromatography (GC-2014, Shimadzu) with a thermal conductivity detector (TCD). The temperature of the reaction solution was controlled by a flow of cooling water with thermo-controller. The pH value of the TEOA solution was adjusted to different values using concentrated  $\text{HNO}_3$  prior reaction.

## 3. Results and discussion

Photocatalytic hydrogen evolution reaction was performed in a three-component system containing Erythrosin B (EB) as the photosensitizer (PS), triethanolamine (10 vol%) as the sacrificial electron donor, and  $(\text{NH}_4)_2\text{MoS}_4$  as the precursor for molybdenum sulfide catalyst. Upon visible light irradiation ( $\lambda > 420$  nm), vigorous gas bubbles were observed, and the gas was confirmed to be  $\text{H}_2$  using on-line gas chromatography. Control experiments showed that the absence of any of the three components led to negligible  $\text{H}_2$  production.

The original reaction solution is bright red color and remains unchanged when kept in dark condition. After irradiating the solution with visible light ( $\lambda > 420$  nm), the color of the solution changed from bright red to dark brown within 10 min. UV–Vis analysis

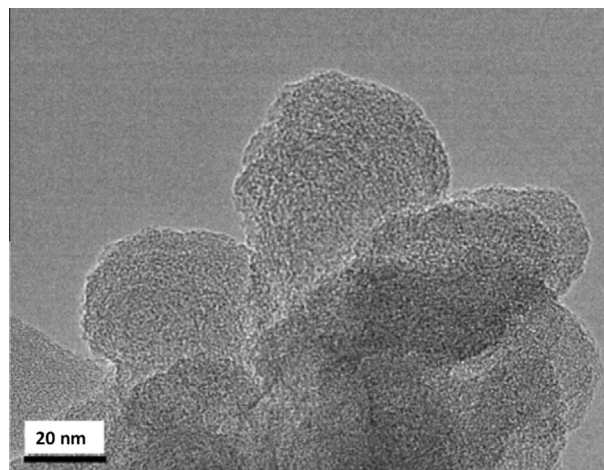


Fig. 1. TEM image of molybdenum sulfide nanoparticles.

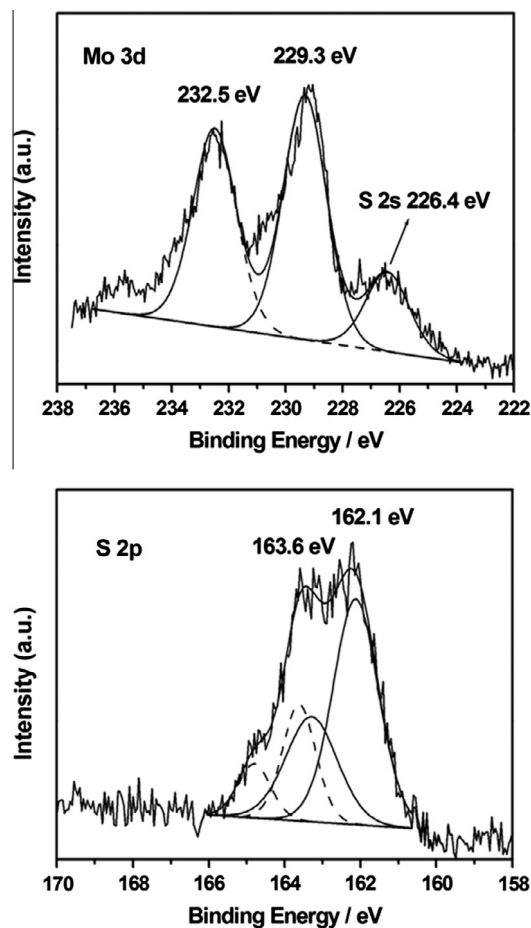


Fig. 2. High-resolution XPS spectra of Mo 3d and S2p measured on molybdenum sulfide nanoparticles.

indicated the absence of  $(\text{NH}_4)_2\text{MoS}_4$  after the reaction (Detailed UV–Vis results will be discussed later). However, when EB was added to the reaction solution after the cessation of the reaction, efficient hydrogen production was still observed (Fig. S1). This is quite different from common three-component homogeneous system, where the addition of both PS and catalyst are necessary to restart hydrogen evolution after their decomposition [26,27]. Therefore, it is reasonable to suppose that some active species

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