



Full Length Article

CO₂-assisted fabrication of novel heterostructures of h-MoO₃/1T-MoS₂ for enhanced photoelectrocatalytic performance



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ABSTRACT

Combining the peculiar properties of different ingredients in one ultimate material is an efficient route to achieve the desired functional materials. Compared to 2H-MoS₂, 1T-MoS₂ nanosheets display the perfect performance of hydrogen evolution reaction (HER) because of the excellent electronic conductivity. However, how to further realize HER in the visible and near-infrared (NIR) region is a great challenge. Herein, we develop an efficient method to locally pattern h-MoO₃ on the ultrathin metallic 1T-MoS₂ nanosheets and obtain the novel heterostructures of h-MoO₃/1T-MoS₂. The enhanced photoelectrochemical performance of the as-prepared heterostructures has been demonstrated. Our study indicates it is originated from the synergistic effect between h-MoO₃ and 1T-MoS₂, i.e., the strong optical absorption of h-MoO₃ in the visible and NIR region, the excellent electronic conductivity of 1T-MoS₂ and as well as the efficient separation of the photo-induced carriers from the heterostructures.

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1. Introduction

Successful exfoliation of graphene gave birth to a vast field of atomically thin materials, which further fueled vigorous investigation on more two dimensional (2D) materials [1–3]. These recently emerged 2D materials have presented excellent electronic, mechanical and optical properties that are different from their bulk counterparts [4–6]. Besides, the flexible 2D structure makes them be easily integrated into other systems or devices, or stacked layer by layer in a precisely chosen sequence to form heterostructures with desired functionalities [7–9]. Such heterostructures are distinct from the traditional 3D semiconductor heterostructures, as each layer acts simultaneously as the bulk material and the interface, thus leading to numerous exciting physical phenomena and extended range of functionalities [10–12].

As a promising alternative to noble metal catalysts for hydrogen evolution reaction, Molybdenum disulfide (MoS₂) is known to contain active edge sites and an inert crystal basal plane [13,14]. High catalytic activity can be achieved by either exposing more active sites [15–17] or transferring 2H-phase to 1T-MoS₂ [18–21]. With dense active sites and excellent electronic conductivity, 1T-MoS₂ nanosheets display dramatically enhanced performance of HER. However, single-component 1T-MoS₂ is still restricted by

its intrinsic features, such as weak light absorption in the visible and near-infrared (NIR) region [2,22]. Assembling 1T-MoS₂ with the second functional building block to form heterostructures should be a suitable route. It is known that the reduced MoO₃ and the amorphous MoO₃ treated with CO₂ display strong optical response in the visible and NIR region because of its localized surface plasmon resonance (LSPR) [23–25]. In addition, compared to thermodynamic stable phase of α-MoO₃ that has low carrier mobility, the open-structure of metastable h-MoO₃ not only exhibits unique photo-physical and photo-chemical properties, but also can facilitate intercalation as well as diffusion of ions [26,27]. How to successfully assemble 1T-MoS₂ with plasmonic h-MoO₃ is necessary, while is challenging.

Herein we demonstrate an efficient route based on supercritical CO₂-assisted phase engineering and recrystallization to fabricate h-MoO₃/1T-MoS₂ heterostructures. The as-prepared peculiar heterostructures can not only effectively minimize the recombination of photo-induced charge carriers, but also can display strong optical response in the visible and NIR region, thus the photoelectrochemical performance of this material can be greatly enhanced.

2. Experimental

2.1. Materials

Available MoS₂ powder was purchased from Sigma-Aldrich (Fluka, product number 69860) with the representative lateral par-

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ticle sizes in the range of 6–40 μm . MoO_3 powder was purchased from Alfa Aesar (product number 011837). Ethanol used in all experiments was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) without further purification. CO_2 with a purity of 99.99% was provided by the Zhengzhou Shuangyang Gas Co. and used as received. Aqueous solution was prepared with double-distilled water.

2.2. Preparation of *h*- MoO_3 /*1T*- MoS_2 heterostructures

MoS_2 powder (50 mg) and MoO_3 (50 mg) were added into a 100 ml flask. Ten milliliters mixture of aqueous solutions with controlled ethanol volume fractions of 50% for obtaining more nanosheets. The dispersion was ultrasonicated in the bath for 6 h, and then centrifuged at 6000 rpm for 25 min to remove aggregates. The supernatant (top three-quarters for the centrifuged dispersion) was collected by pipet and then quickly transferred into the supercritical CO_2 apparatus composed mainly of a stainless steel autoclave (50 ml) with a heating jacket and a temperature controller. The autoclave was heated to 313.2 K, and then CO_2 was charged into the desired pressure (16 MPa) under stirring. After a treatment time of 3 h, the gas was slowly released. Finally, the dispersion was collected.

2.3. Characterization

TEM (JEOL JEM-2100) and HRTEM (JEOL JEM-2100F) were used to study the morphologies of the nanomaterials. The XRD patterns were examined using Ultima IV instrument. The Raman measurements were carried out on a LabRAM HR Evolution with laser wavelength of 532 nm. XPS analysis was performed using ESCLAB 280. UV-vis-NIR spectra were measured to evaluate the light adsorption using Shimadzu UV-240/PC.

2.4. Photoelectrochemical (PEC) measurements

The photoelectrochemical performance of the electrodes was evaluated in a three-electrode configuration under front-side simulated AM1.5 illumination using an electrochemical workstation (CHI660D). The as-prepared sample (5 mg) dispersed in 3 ml ethanol was deposited on the fluorine-doped tin oxide (FTO, NGS glass). The electrolyte was a 0.1 M Na_2SO_4 solution. The reference electrode was Ag/AgCl in saturated KCl, and a Pt wire was used as the counter electrode. The photoresponse was measured under chopped irradiation from a 300 W Xe lamp (Osram) equipped with an ultraviolet filter (KG3 filter, 3 mm, Schott) with a Si diode to simulate AM1.5 illumination (100 mW cm^{-2}). The scan rate for the linear sweep voltammetry was 10 mV s^{-1} . Photocurrent stability tests were carried out by measuring the photocurrent produced under chopped light irradiation (light/dark cycles of 500 s) at a fixed electrode potential of 0 V versus RHE.

The PEC degradation experiment was performed in a 100 ml of three electrode quartz cell system with 300 W Xe lamp equipped with a UV cut-off filter (420 nm) on a CHI 660D Electrochemical Workstation, and the light intensity was kept as 150 mW cm^{-2} . The as-prepared sample (20 mg) dispersed in 3 ml ethanol was deposited on the fluorine-doped tin oxide (FTO, NGS glass). Cationic dye (RhB) was chosen as a model contaminant. The absorbance of RhB was measured at a wavelength of 554 nm, and cooled by flowing water to weaken the thermal influence. The initial concentration of RhB in the solution was 20 mg L^{-1} . 0.5 M Na_2SO_4 was used as electrolyte solution. PEC degradation experiment was carried out at a fixed electrode potential of 1 V versus RHE. Before irradiation, the system was kept in dark for 30 min to reach equilibrium of complete adsorption-deposition for the photoelectrode. Samples were

taken from the reactor every 20 min, and the concentration of RhB was determined by a UV-vis spectrophotometry.

3. Results and discussion

3.1. Characterization of the as-prepared heterostructures

The *h*- MoO_3 /*1T*- MoS_2 heterostructures are produced using an efficient SC CO_2 -assisted route (see the Experimental Section for details). High-resolution transmission electron microscopy (HRTEM) was utilized to assess the morphology and lattice arrangement of the MoO_3 / MoS_2 heterostructures. A typical HRTEM image is shown in Fig. 1a, and it shows the tunnel nanostructure of MoO_3 is vertical stacking on the plain nanosheets of MoS_2 . In the case of the MoS_2 nanosheets, the filtered micrograph and associated fast Fourier transfer (FFT) shown in Fig. 1b indicate the trigonal lattice areas (octahedral phase) of the *1T*- MoS_2 , rather than the honeycomb lattice area (trigonal prismatic phase) of the *2H*- MoS_2 [20]. As shown in Fig. 1c, the tunnel nanostructure is different from α - MoO_3 . To further investigate the unique structure, a typical selected area electron diffraction (SAED) is presented in Fig. 1d with clearly distinguishable diffraction spots, which indicates the molecular structure of *h*- MoO_3 [27,28]. In addition, more HRTEM images of the *h*- MoO_3 /*1T*- MoS_2 heterostructures can be observed from Fig. 1e–g, showing the nanocrystals of MoO_3 appear highly oriented within the aligned columns, which are locally pattern on the metallic MoS_2 nanosheets. The above-mentioned experimental results demonstrate that the as-prepared MoO_3 / MoS_2 nanosheets are highly heterogeneous in structure, predominantly consisting of *h*- MoO_3 and *1T*- MoS_2 .

The crystallographic phases of the as-prepared samples were evaluated using X-ray diffraction (XRD) to confirm the existence of the *h*- MoO_3 . According to Fig. 2a, the peaks of the initial bulk MoO_3 are perfectly matched to orthorhombic phase MoO_3 (JCPDS no. 05-0506) [29,30]. As the light blue square shows, it is found that the SC CO_2 treated samples exhibit a dominant crystal phase of hexagonal MoO_3 (JCPDS no. 21-0569), and two new diffraction peaks appear at $2\theta \sim 16.75^\circ$ and 19.45° , which are corresponding to the (110) and (200) planes of *h*- MoO_3 phase, respectively [26]. The disappearance of diffraction peak at 23.33° , which can be assigned to the (110) plane of α - MoO_3 , proves that the topotactic phase translation from stable α - MoO_3 phase to metastable *h*- MoO_3 phase. The result can be further confirmed by the Raman spectra. From Fig. S1, strong peaks located at ~ 280 , 659, 816 and 990 cm^{-1} of the initial bulk MoO_3 flakes are all in good agreement with orthorhombic α - MoO_3 [23,31,32]. After treatment with SC CO_2 , it is noteworthy that the additional peaks located at 690, 900, and 978 cm^{-1} all conform with hexagonal *h*- MoO_3 (Fig. 2b) [30,33]. Indeed, the disappearance of peaks located at 280, 659, 816 and 990 cm^{-1} also indicates the topotactic phase translation of the stable α - MoO_3 phase. For the initial *2H*- MoS_2 nanosheets (Fig. S2), the Raman spectra exhibits the peaks located at 283, 373, and 404 cm^{-1} , which are ascribed to the E_{1g} , E_{2g} and A_{1g} longitudinal acoustic phonon modes. After treatment with SC CO_2 , one new Raman peak can be observed at 218 cm^{-1} , which is assigned to the phonons mode of *1T* MoS_2 , indicating the *2H* to *1T* phase transition of pristine MoS_2 [19–21].

X-ray photoelectron spectroscopy (XPS) spectra can be used to further confirm the evolution of phase transition from the *2H*- MoS_2 to *1T*-phase, and verify the chemical composition and oxidation state of the as-prepared heterostructures as well. For the initial MoS_2 (Fig. 2c), Mo 3d spectrum consists of peaks at 229.4 and 232.6 eV corresponding to the $\text{Mo}^{4+} 3d_{5/2}$ and $\text{Mo}^{4+} 3d_{3/2}$ components, respectively. Following the treatment of SC CO_2 , the two new peaks located at 228.5 eV ($\text{Mo}^{4+} 3d_{5/2}$) and 231.6 eV ($\text{Mo}^{4+} 3d_{3/2}$) are assigned to metallic *1T*-phase MoS_2 [20,34]. In addition,

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