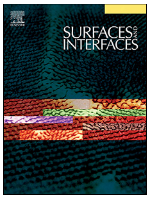
Surfaces and Interfaces 12 (2018) 41–49

Contents lists available at ScienceDirect

Surfaces and Interfaces

journal homepage: www.elsevier.com/locate/surfin



Controllable solution-fabrication of triphasic 2H@1T-MoS_2/graphene heterostructure with assistance of supercritical CO_2[☆]

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ARTICLE INFO

Keywords:
Two-dimensional
Heterostructure
Graphene
1T-MoS_2
Photo- response
Hydrogen evolution reaction

ABSTRACT

Successful assembling fabrication of two-dimensional (2D) materials is regarded as a positive strategy to explore the mechanical, electronic, and optical properties of 2D materials and it can further broaden their application as well. Herein we demonstrate the convenient fabrication of a triphasic 2H@1T-MoS_2/graphene heterostructure by stacking lateral 2H-/1T-molybdenum disulfide (MoS_2) heterostructures on graphene with the assistance of supercritical carbon dioxide (SC CO_2). More importantly, during the stacking process of heterostructure, it can be found out that graphene plays an important role on the transfer of 2H-MoS_2 to 1T-MoS_2, and the latter is advantageous in electrochemical and photoelecrochemical evolution of hydrogen. Therefore, the controllable fabrication of triphasic 2H@1T-MoS_2/graphene heterostructure with different ratios of 2H-/1T-MoS_2 can be achieved. Further the application of the as-fricated triphasic heterostructure in hydrogen evolution reaction has been demonstrated in this study.

1. Introduction

Beyond research on graphene-like two dimensional (2D) nanomaterials, creation of vertically stacked van der Waals heterostructures has attracted considerable attention due to their unique physical, chemical, structural properties and potential applications in electronic and optoelectronic devices [1–6]. Building Van der Waals heterostructures including vertical (stacking layer-by-layer) and in-plane heterojunctions, have brought about unprecedented opportunities for device engineering [7–13]. Graphene with extremely high carrier mobility is a highly promising building blocks for future nanoelectronics, but there is no bandgap in it [14,15]. Semiconducting transition metal dichalcogenide (TMD) have been proposed as active and efficient catalysts for hydrogen evolution reaction (HER) [16], but the poor electrical conductivity restricts their application [17]. Coupling graphene and TMD in one material system can be used for band-structure engineered applications such as electronics [18], photonics, and photocatalysis [19–23].

As a typical transition metal dichalcogenide and direct bandgap material, molybdenum disulfide (MoS_2) shows great application potentials in electrical and optoelectronic devices [24–27]. Layered MoS_2 mainly exists in two phases: 2H and 1T. Usually, metallic 1T-MoS_2 polymorph can be used as efficient hydrogen evolution reaction (HER) catalysts, its high-yield fabrication is very important. In terms of the atomic structure, these two phases can be transformed into each other by shifting one of the S layers in the $\langle 2100\rangle$ direction by $a/\sqrt{3}$ [28]. The electron doping approaches, such as electron irradiation and lithium intercalation, have been used to transfer 2H-MoS_2 to 1T-MoS_2 [29–31]. In our previous study, it can be found that the coherent atomic lateral 2H and 1T heterojunctions of MoS_2 nanosheets can be successfully fabricated with the assistance of supercritical carbon dioxide (SC CO_2) processing. The mechanism for the formation of 2H@1T-MoS_2 nanosheets can be proposed via two stages. First, SC CO_2 exfoliates the MoS_2 materials due to its high diffusion and low viscosity, and single and few layer MoS_2 and nanosheets can be obtained. After that, the existing CO_2 in the interlayers of MoS_2 nanosheets can partially convert some 2H-MoS_2 into 1T phases to form the 2H@1T-MoS_2 heterostructure owing to the preferential interaction between CO_2 and 1T-MoS_2 [28].

In our previous work, we have successfully synthesized 2H@1T-MoS_2/graphene heterostructure [32]. However, the effect of different ethanol/water ratios on the triphasic 2H@1T-MoS_2/graphene heterostructure is failed to be investigated. Herein, we designed a controllable solution experimental system to fabricate MoS_2/graphene heterostructure as well as 2H-and 1T-lateral heterojunctions. Here, we can synergistically regulate and control the exfoliation yield of MoS_2 and graphene through tuning the ethanol/water ratios on the emulsions system. Surprisingly, we found the introduction of different content of graphene plays an important effect. One hand, its Fermi level is higher

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[☆] The authors declare no competing financial interest.

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https://doi.org/10.1016/j.surfin.2018.04.009
Received 4 December 2017; Received in revised form 7 March 2018; Accepted 29 April 2018

than the valence band maximum (VBM) of 2H-MoS_2 [33], so the heterostructure with suitable band alignment and high electronic conductivity can be acquired. On the other hand, it has a decesive effect on the transfer of 1T-MoS_2 from 2H-phase [34]. Our study indicates that the amount of exfoliated graphene in the solution system is positive for the achievement of 1T-MoS_2. Therefore, we not only use a controllable solution method to fabricate the triphasic 2H@1T-MoS_2/graphene heterostructure, but also can effectively control the component of lateral heterostructure of 2H- and 1T-MoS_2, which can be demonstrated to have a significant effect on the photocatalytic HER performance.

2. Experiment

2.1. Materials

Commercially available MoS_2 powder was purchased from Sigma-Aldrich (Fluka, product number 69,860). Graphite powder was purchased from ACROS ORGANICS (USA, CAS:7782-42-5). Polyvinylpyrrolidone was purchased from STREM CHEMICALS (Fluka, Product Number: 07–1815). Ethanol in all experiments was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification. CO_2 with purity of 99.99% was provided by the Zhengzhou Shuangyang Gas Co. and used as received. Aqueous solution was prepared with deionized water.

2.2. Exfoliation process and preparation of heterostructures

In a typical process, 200 mg PVP were added into ethanol/water mixtures (10 mL) at respective 7:3, 5:5 and 3:7 ethanol/water ratios. After PVP were completely dissolved, graphite powder (200 mg), MoS_2 powder (200 mg) were added to these solutions. The mixture was sonicated in an ice bath continuously for 2 h. These dispersions were quickly added 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 CO_2 was subsequently charged into the autoclave to the desired pressure (16 MPa) under stirring. After a reaction time of 3 h under SC CO_2, the gas was slowly released. Finally, the as-obtained dispersion was sonicated for additional 3 h, and then the dispersion was centrifuged at 3000 rpm for 45 min to remove aggregates. The supernatant was taken out by a pipet. As-obtainedmixing dispersion of graphene flakes and MoS_2 nanosheets was centrifuged at 20,000 rpm for 20 min to obtain the precipitate, washed for three times with ethanol to remove PVP, and re-dispersed a respective 7:3, 5:5 and 3:7 ethanol/water ratio mixtures (10 mL), then sonicated for 2 h to form a homogeneous solution. These dispersions were quickly added into the supercritical CO_2 apparatus, and the autoclave was heated to 433.2 K and then CO_2 was charged into the autoclave to the desired pressure under stirring. After a reaction time of 6 h, the gas was slowly released. Finally, the dispersion was collected before further characterization.

2.3. Photoelectrochemical measurements

The PEC measurements were taken using an electrochemical workstation (CHI660D) with a typical three-electrode cell. The as-prepared sample was used as the working electrode, and a Ag/AgCl electrode and Pt or graphite were used as reference and counter electrodes, respectively. Na_2SO_4 (0.5 mol L^{-1})was used as the electrolyte. The working electrodes were prepared by dropping the suspension onto the surface of a clean FTO glass substrate. The light ON − OFF switches were set as 500 s or 200 s when measuring the i − t curves of the absolute values under visible light. The bias for the measurement was set at −0.6 V.

2.4. Photocatalytic measurements

The catalyst (5 mg) was dispersed in water (80 mL) and triethanolamine (15%v/v; 12 mL) as a sacrificial agent in a quartz vessel. The 0.15 mM Eosin Y was used as the sensitizer. The vessel was irradiated under 300 W Xe lamp with constant stirring of the mixture. The amount of produced hydrogen gas was measured using gas chromatography.

3. Results and discussion

3.1. Fabrication and characterization of triphasic 2H@1T-MoS_2/graphene heterostructure

We use a facile and tunable method to construct 2H@1T-MoS_2/graphene heterostructure as depicted in Fig. 1. The images of low-magnification transmission electron microscope (TEM) shown in Fig. 1a and Fig. S3 confirm that single-layer and few-layer MoS_2 and graphene nanosheets were successfully obtained. In addition, we can clearly observe that MoS_2 nanosheets are stacking on the graphene, indicating the generation of freestanding MoS_2/graphene heterostructure (Fig. S2). The selected area electron diffraction (SAED) pattern (Fig. 1b) indicates the typical hexagonal symmetry of obtained MoS_2 and graphene nanosheets are intact, confirming that their outstanding crysallinity is not damaged during the exfoliation process [35]. In the other hand, the SAED pattern confirms both MoS_2 and the underlying graphene layer preferred orientation relationship. The blue dashed line in Fig. 1b indicates that the single-layer MoS_2 and the freestanding graphene substrate exhibit the same orientation, verifying epitaxial growth of MoS_2 on the graphene membrane [36,37].

In this assembling system, we also discover that the coherent atomic lateral 2H and 1T hetero-junctions of MoS_2 nanosheets can also be fabricated. To further detail the atomic arrangement, the high-resolution TEM analysis was performed on SC CO_2- treated exfoliated MoS_2 and graphene sheets. As is shown in Fig. 1c, the 2D atomic lateral heterostructures with 1T-(upper square) and 2H-(underside square) phases could be clearly visualized. Honeycomb lattice intensity variation with minor contrast between two adjacent sites is a signature of the 2H-MoS_2 single layer, whereas the hexagonal lattice is a signature of the 1T structure [38]. Here, we successfully fabricate freestanding MoS_2/graphene heterostructure as well as 2H-and 1T- lateral heterojunctions in-plane MoS_2. In order to unambiguously verify that a majority of exfoliated sheets are monolayers, we conducted high angle annular dark field scanning transmission electron microscopy (HAADF STEM) imaging. Since the HAADF STEM image intensity relies on the atomic number, it also delivers direct information about the arrangement of Mo and S atoms in the MoS_2 nanosheets. Fig. 1d indicates a region of the monolayer MoS_2 where the atomic structure is resolved and Mo and S atoms can be clearly distinguished. The atomic-resolution HAADF STEM image from the edge of a MoS_2 film shows zigzag edges with Mo atom termination [39–41]. The corresponding elemental mapping images (Fig. 1f-h) clearly reveal that C element is nearly homogeneous distributed over the detection area, while Mo and S element are localized on it, indicating the generation of MoS_2/grapheme stacking heterostructures.

In the recent years, our group developed a controllable SC CO_2 exfoliation process for preparation of high-yield, single-layer MoS_2 and graphene nanosheets. Wang et al. reported that effect of ethanol/water ratios on the exfoliation yield of MoS_2, and the highest concentration was calculated to be approximately 0.139 mg/mL, which is higher than those reported [42]. Xu et al. concluded that the concentration of graphene dispersions is strongly dependent on the volume fraction of ethanol in PVP − water solution, and the yield has been increased to 1.93 mg/mL accordingly [43]. Here, we can synergistically regulate and control the exfoliation yield of MoS_2 and graphene through tuning the ethanol/water ratios on the emulsions system. We investigate three ethanol/water ratio, which is 7:3, 5:5 and 3:7, respectively. As is shown