



Facile synthesis of molybdenum disulfide/nitrogen-doped graphene composites for enhanced electrocatalytic hydrogen evolution and electrochemical lithium storage



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ABSTRACT

A facile one-pot hydrothermal route with the mediation of ionic liquid (IL, [BMIM]BF₄) is presented to synthesize MoS₂/nitrogen-doped graphene (MoS₂/NG-IL) composites. It is found that as-prepared MoS₂/NG-IL composites exhibit that the de-layered MoS₂ sheets with more exposed edge sites and defects are well anchored on the N-doped graphene. Due to the synergism between de-layered MoS₂ and N-doped graphene, MoS₂/NG-IL composites exhibit better electrochemical performances for hydrogen evolution reaction (HER) and reversible lithium storage in comparison with MoS₂. Especially, when 1.0 mL of IL is added in hydrothermal solution, the obtained MoS₂/NG-IL10 displays very high electrocatalytic activity for HER with a low onset overpotential of 80 mV and a small Tafel slope of 48.0 mV/dec in 0.5 M H₂SO₄. As anode of lithium ion battery, MoS₂/NG-IL10 delivers a reversible capacity as high as 1169 mAh g⁻¹ at 100 mA g⁻¹ and enhanced rate capability of 782 mAh g⁻¹ at 1000 mA g⁻¹. After 800 cycles, a reversible capacity of about 800 mAh g⁻¹ at 500 mA g⁻¹ can be retained, indicating its excellent cyclic stability.

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1. Introduction

Recently, two-dimensional (2D) nanomaterials, such as graphene, have attracted a lot of attention due to their unique and exceptional physical, chemical and electronic properties [1,2]. It has been demonstrated that graphene, consisted of one-atom layer of graphite, exhibit high electrical and thermal conductivity, excellent charge mobility, large specific surface area and good flexibility, which make it be a favorite with various applications such as bio-sensors, field-effect transistors, electrochemical energy storage and conversion [3–9]. The great achievements of graphene have led to exploration of other 2D materials, such as 2D transition metal dichalcogenides (TMDs, e.g. MoS₂, WS₂, MoSe₂ and et al.) [2,10,11]. In particular, 2D MoS₂ nanosheets with single- and few-layers have been widely investigated and applied in versatile fields, including catalysis, electronics and optoelectronics, energy storage and conversion [11–18].

Nowadays, the rapid consumption of fossil fuels has brought about a series of serious environmental issues. Therefore, it is

strongly desired to find an alternative clean energy and develop an effective energy storage-conversion technology. As a clean and reproducible energy carrier, hydrogen (H₂) energy is thought as a promising candidate for replacing fossil fuels. Thus, cost-effective and sustainable hydrogen produced from electrochemical and photoelectrochemical water-splitting has received more and more attention. The hydrogen evolution reaction (HER, 2H⁺ + 2e⁻ → H₂) plays a great role in the water-splitting process [19]. On the other hand, rechargeable Li-ion batteries (LIBs) have been the current focus in energy storage and conversion due to their long cycle life, high energy density and environmental-friendliness [20]. 2D MoS₂ nanocrystals have been recently demonstrated to be a promising material for HER and LIBs. However, its poor conductivity and strong propensity towards restacking severely compromise its electrochemical performances [21]. In addition, it has been demonstrated that the HER active sites stem from the sulfur edges of MoS₂ layers, while their basal planes are inert [22]. Therefore, in order to improve electrochemical performances of 2D MoS₂ for HER and LIBs, the guiding principles have most often been to enhance its conductivity and increase its active edge sites over the inert basal plane sites.

One effective strategy to improve the conductivity of MoS₂ is to grow MoS₂ nanostructures on highly conductive matrices, such as

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graphene and carbon nanotubes [22–26]. Especially, graphene and its derivatives, such as N-doped graphene, can be used as an ideal scaffold for growing and anchoring of MoS₂ due to its outstanding properties [24,27,28]. Moreover, the well-matching layered structure between 2D MoS₂ and graphene not only increases the contact area for efficient charge transfer across the interface, but also exhibits better synergistic effects between two components, thereby greatly improving the electrochemical performances for HER and LIBs. In addition, N-doping of graphene can change the electron density in the graphene sheets, which provides an electrocatalytic surface [29–31]. Yang reported that the MoS₂/RGO hybrid fabricated via a solvent-evaporation-assisted intercalation method exhibited the excellent HER performances due to the combined effects of abundance of exposed active edge sites and excellent internal electrical conductivity [32]. Lin et al. designed a 3D honeycomb-like MoS₂ nanoarchitectures anchored on 3D graphene foam [33]. The obtained material delivered a high reversible capacity of 1172 mA h g⁻¹ at a current density of 200 mA g⁻¹ as LIB anode. Chen et al. designed and prepared the N-doped graphene/porous C₃N₄ nanosheets supporting few-layered MoS₂, which exhibited superior electrochemical performance for LIBs [34]. In addition, various strategies have also been proposed to enhance the electrocatalytic HER performances of MoS₂ by increasing the density and reactivity of active sites [35–40]. For example, Xie et al. prepared defect-rich MoS₂ nanosheets with additional active edge sites through a controllable defect modulation. Such defect-rich MoS₂ exhibited improved electrocatalytic activity with a small Tafel slope of 50 mV dec⁻¹ for HER [40].

Despite the electrochemical performances of HER and LIBs have been improved by increasing the conductivity and active sites of MoS₂ [22,41], certain pivotal issues are still unsolved for MoS₂/graphene composites. In particular, it remains a big challenge to stabilize the active centers of MoS₂. As mentioned-above, the active sites of MoS₂ centers on the sulfur edges of the catalyst surface [22]. However, these active sites are prone to turn into inactive sites since they are usually thermodynamically instable [42]. Thus, it's very essential to stabilize these active surface species to improve the HER performance of MoS₂. Room temperature ionic liquids (ILs) are attracting a lot of attention due to their unique chemical and physical properties, including negligible vapor pressure and excellent thermal stability [43–45]. Through electrostatic interactions, ILs are able to stabilize the edge sites of MoS₂ and induce a de-layered morphology of MoS₂ crystals, resulting in enhanced electrocatalytic activity for HER [46].

Herein, we report a facile one-pot hydrothermal method to synthesize MoS₂/nitrogen-doped graphene (MoS₂/NG-IL) composite with the mediation of an ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM]BF₄) and in the presence of graphene oxide sheets (GOS). Ammonium tetrathiomolybdate ((NH₄)₂MoS₄) was used as the molybdenum source. N₂H₄·H₂O and NH₃·H₂O acted as reductant and nitrogen source, respectively. The effects of IL on the microstructure and electrochemical performances of MoS₂/NG-IL composites for HER and LIB applications were investigated.

2. Experimental

2.1. Synthesis of MoS₂/NG-IL composites

GOS were prepared from the natural graphite power (Shanghai Colloid Chemical Plant, China) by the modified Hummers method, the details of which was described elsewhere [47,48]. MoS₂/NG-IL composites were prepared by hydrothermal reaction with the mediation of IL ([BMIM]BF₄) and in the presence of GOS. In a typical batch, a certain volume (0.2, 0.5, 1.0 or 2.0 mL) of IL was dissolved

into 20 mL deionized water. Then the IL solution was dropped into 20 mL suspension of GOS (3.0 mmol) under vigorous stirring. The mixture was stirred at room temperature for 12 h to allow [BMIM]⁺ well adsorbed on the GOS surface by electrostatic and π - π interaction. A solution of 1.5 mmol of (NH₄)₂MoS₄ in 20 mL deionized water was then added to the mixture. This was followed by the addition of 10 mL of hydrazine monohydrate (85%) as a reducing agent with continued stirring and NH₃·H₂O was dropped to adjust the pH value of 10.0. The reaction mixture was finally transferred to 100 mL Teflon-lined autoclave and heated at 240 °C for 24 h. The autoclave was cooled to room temperature naturally after the completion of reaction. The black precipitate was collected by centrifugation, washed with deionized water and ethanol, and dried in a vacuum oven at 80 °C for 12 h. Finally the MoS₂/NG-IL composite was obtained. Four composites, namely MoS₂/NG-IL02, MoS₂/NG-IL05, MoS₂/NG-IL10 and MoS₂/NG-IL20, were prepared with 0.2, 0.5, 1.0 and 2.0 mL IL in hydrothermal solution, respectively. In control experiment, the pristine MoS₂ was prepared by a similar synthetic route with neither IL nor GOS. MoS₂/NGO composite was prepared without IL. Without adding N₂H₄·H₂O and NH₃·H₂O, MoS₂/G-IL10 composite was also prepared by hydrothermal route with mediation of 1.0 ml of IL.

2.2. Characterizations

XRD patterns were recorded with a Thermo X'TRA X-ray diffractometer with Cu K α radiation ($\lambda = 0.154056$ nm). The morphologies of the samples were observed by using a SIRION-100 field emission SEM (FESEM). TEM and HTREM characterizations were performed on a JEOL JFL-2010 TEM operating at 200 kV, for which each sample was prepared by dispersing it in acetone and drop-casting onto a 200 mesh copper grid coated with holey carbon. X-ray photoelectron spectrum (XPS) analysis was performed on a PHI 5000 Versaprobe system using monochromatic Al K α radiation (1486.6 eV). All binding energies were referenced to the C 1s peak at 284.6 eV. Raman spectra were obtained using a 514 nm excitation laser with a Jobin Yvon Labor Raman HR-800 spectrometer under ambient conditions.

2.3. Electrocatalytic HER measurements

All electrochemical measurements were performed in a three-electrode system using saturated calomel electrode (SCE) as a reference electrode and a Pt slice as a counter electrode on electrochemical workstation (CHI660E). 4 mg of catalyst powder was firstly ultrasonically dispersed in 80 μ L of 5 wt% Nafion solution along with 1 mL of 4:1 v/v water/ethanol mixed solvent to form homogeneous ink. Then 5 μ L of the catalyst ink (containing 0.02 mg catalyst) was loaded onto a glass carbon electrode with 3 mm in diameter as a working electrode (loading ~ 0.285 mg cm⁻²). Linear sweep voltammetry polarization curves were obtained at the scan rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ by sweeping the potential from -0.60 to -0.15 V (vs. SCE). The current density was normalized by geometric area of the working electrode (0.07 cm²). The electrochemical impedance spectroscopy (EIS) measurements were carried out in the same configuration within the frequencies range of 10⁵–0.01 Hz with perturbation voltage amplitude of 5 mV. In all measurements, the saturated calomel electrode (SCE) was used as the reference. All potentials reported here in this work referenced to the reversible hydrogen electrode (RHE) by adding a value of 0.272 V.

2.4. Electrochemical lithium storage measurements

All the electrochemical measurements were performed using

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