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Ionic-liquid mediated synthesis of molybdenum disulfide/graphene composites: An enhanced electrochemical hydrogen evolution catalyst

Jianbo Ye, Zheting Yu, Weixiang Chen, Qiannan Chen, Lin Ma*

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

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ABSTRACT

The ionic liquid (IL, [BMIM]BF_4) is employed to mediate the preparation of molybdenum disulfide/graphene composites by hydrothermal route in the presence of graphene oxide sheets. The effects of ionic liquid on the microstructure and hydrogen evolution reaction performances of molybdenum disulfide/graphene are investigated. The molybdenum disulfide/graphene composite (MoS_2/G-IL10) prepared with 1.0 mL of ionic liquid displays numerous de-layered molybdenum disulfide sheets with short slab length and discontinuous crystal fringes on the surface of grapheme. Due to the rich exposed edge sites, as well as the synergetic effect of de-layered molybdenum disulfide and graphene sheets, the MoS_2/graphene composite prepared by IL-mediated hydrothermal method shows excellent electrocatalytic performance for hydrogen evolution reaction with a small Tafel slope of 52 mV/dec in acidic medium.

Introduction

The combustion of fossil fuels has caused an adverse climate change, greatly influencing our daily life and environment. In order to solve the contradiction between energy consumption and environment issues, hydrogen is praised highly as a promising energy carrier to replace the fossil fuels. A renewable and scalable method to produce hydrogen is the splitting of water. Recently, the production of H_2 through photocatalytic and electrocatalytic water splitting has received much attention [1,2]. One key step in water splitting is the hydrogen evolution reaction (HER). Pt-group materials are the most effective HER electrocatalysts, but their high cost and rareness on the earth limit their practical application for the large-scale production of hydrogen. Recently, nanostructured MoS_2 and MoO_2 have drawn great attention as noble-free electrocatalysts for HER owing to their good electrocatalytic property and large reserves [3,4]. However, issues such as poor conductivity and limited catalytic active sites have hindered MoS_2 as a competitive electrocatalysts to replace noble metal platinum and Pt-based catalysts, which are well known for their superior catalytic ability towards HER in acidic medium [5,6]. Therefore, both enhancing the conductivity and increasing the number of active sites are believed as essential to improve the electrocatalytic performance of MoS_2 catalyst for HER.

One efficient route to improve the conductivity of electrocatalyst is to use graphene as a substrate to grow MoS_2. Graphene, composed of single-layer sp^2-hybridized carbon atoms, has attracted great interest due to its exceptional physical and chemical properties, such as excellent electronic

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* *Corresponding author*. Tel.: +86 571 87952477; fax: +86 571 87951895.
E-mail address: weixiangchen@zju.edu.cn (W. Chen).

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conductivity, high charge mobility, inherent mechanical flexibility and large surface area [7,8]. Through the incorporation of graphene with MoS_2, numbers of MoS_2/graphene composite catalysts with enhanced electrocatalytic HER efficiency have been demonstrated [7,9–13]. For example, Dai et al. developed a selective solvothermal synthesis of MoS_2 nanoparticles on graphene sheets and superior electrocatalytic activity in HER has been observed for such composites [9]. Zhang et al. reported the synthesis of three-dimensional (3D) MoS_2/rGO hydrogel with enhanced HER activity by hydrothermal route together with freeze-drying process [11]. Hu et al. also prepared MoS_2/RGO (reduced graphene oxides) composites by a similar solvothermal route using dimethyl-formamide as solvent, which exhibited better HER performance [12]. Zhou et al. designed and prepared the hierarchical MoS_2–rGO nanosheets with enhanced HER performance [13]. For these MoS_2/graphene composites prepared by solvothermal or hydrothermal route, graphene can not only be used as ideal platform for the selective growth of MoS_2 crystals with small layers, but also greatly increase the conductance of the composites. Such MoS_2/graphene nanocomposites exhibited an excellent electrocatalytic activity with a low HER overpotential. Due to the synergetic effect between the MoS_2 and graphene, MoS_2/graphene can also serve as an electron collector and a source of active adsorption sites for enhanced photocatalytic activity. Xiang et al. reported a new hybrid of TiO_2/MoS_2/graphene prepared by a two-step hydrothermal process and demonstrated that MoS_2/graphene was used as cocatalyst to enhance photocatalytical H_2 production activity of TiO_2 nanoparticles [14].

Another drawback of MoS_2 catalyst is the limited catalytic active sites. To realize the potential of MoS_2 based catalyst, it is urgent to increase the number of active sites. As we all know, a MoS_2 layer is a sandwiched layer structure, which is composed of Mo layer situated between two S layers. HER activity of MoS_2 mainly stems from the edges of MoS_2, which contains uncoordinated S or Mo atoms, while the basal planes terminated by sulfur atoms are catalytically inactive [15,16]. Thus, it is rational to increase the number of uncoordinated S or Mo atoms along edge sites. Recently, Cui et al. reported a synthesis process to grow MoS_2 thin films with vertically aligned layers, thereby maximally exposing the edges on the film surface [17]. Guo et al. reported the oxygen-incorporated MoS_2 ultrathin sheets grown on graphene by SDS-assisted hydrothermal route. It was found that oxygen-incorporation increased the exposed edges of MoS_2 sheets, resulting in enhanced HER activity [10]. However, to large-scale synthesis MoS_2 with a high concentration of active sites through a cost-effective method remains a big challenge.

Due to that the uncoordinated species of MoS_2 possess high energies and are thermodynamically unfavorable, the edges of MoS_2 are apt to relax to low-energy and catalytically inactive surface species [18]. To overcome this problem, the ionic liquids (ILs) have been employed as the synthesis medium of MoS_2. ILs are the organic or partially inorganic molten salts at room-temperature with melting points generally below 100 °C. They are receiving more and more attention because of their low vapor pressure, wide electrochemical stability, high ionic conductivity and excellent stability [19,20]. For a long time, ILs have been investigated for applications in catalysis and energy storage [21–24]. When ionic liquids (ILs) are introduced to synthesis MoS_2 crystal, ILs are able to passivate thermodynamically disfavored crystal facets through electrostatic interactions. Recently, nanometer-size crystal layers of MoS_2 have been synthesized by thermal decomposition of $(NH_4)_2MoS_4$ in various ILs [25]. The MoS_2 fabricated by using 1-alkyl-3-methylimidazolium triflate ionic liquid displayed a de-layered morphology with very high number of stable active edge sites, thereby exhibited great electrocatalytic activity for HER [25]. Despite of this, Tafel slopes for such IL-synthesized MoS_2-based catalysts are still very high (up to 205–323 mV/dec), which is due to the poor conductivity of MoS_2. Many works have demonstrated that to synthesize MoS_2 with the incorporation of graphene is an effective method to improve the HER electrocatalytic activity of MoS_2-based composites with both low overpotential and small Tafel slopes [7,9,26,27].

In this study, we prepared MoS_2/graphene composites by hydrothermal reacting Na_2MoO_4 with L-cysteine in the presence of graphene oxide sheets and with the mediation of IL (1-butyl-3-methylimidazolium tetrafluoroborate, ($[BMIM]BF_4$)). In comparison with other preparing methods mentioned above, this work employed the positively-charged imidazolium IL to mediate hydrothermal reaction. IL can easily modify the surface of graphene oxide sheets to reduce the charge incompatibility between graphene oxide sheets and anionic MoO_4^{2-}, which facilitates well-growth of MoS_2 layers on graphene. Moreover, IL can reduce the surface energy of MoS_2 edges, resulting in the formation of the de-layered MoS_2 with more exposed active edge sites. The results of characterizations demonstrate that the MoS_2/graphene composites prepared in this work display numerous upwrapped MoS_2 sheets with more exposed edges, which are well dispersed and anchored on the graphene surface. The as-prepared composites exhibit enhanced HER performances. In particular, the MoS_2/G-IL10 composite prepared with 1.0 mL of IL showed excellent hydrogen evolution reaction activity and durability in acidic medium, which was superior to other samples.

Experimental

Synthesis of MoS_2/G-IL composites

Graphene oxide sheets (GOS) were prepared from natural graphite power (Shanghai Colloid Chemical Plant, China) by the modified Hummers method [28], the details of which was described elsewhere [29]. MoS_2/G-IL composites were prepared by IL-mediated hydrothermal route in the presence of GOS. In a typical batch, a certain volume (0.2, 1.0 or 5.0 mL) of IL ($[BMIM]BF_4$) was diluted by 20 mL of deionized water and 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. Then a solution of 1.5 mmol Na_2MoO_4 and 7.5 mmol L-cys in 20 mL deionized water was added to the mixture. The resulting mixture was transferred to 100 mL Teflon-lined autoclave and adjusted the volume of the mixture to about 80 mL, being heated at 240 °C for 24 h. The autoclave was cooled to room temperature naturally after the hydrothermal reaction. The black

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