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Original Research Paper

One-step hydrothermal synthesis of few-layered and edge-abundant MoS_2/C nanocomposites with enhanced electrocatalytic performance for hydrogen evolution reaction

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ABSTRACT

MoS_2/C nanocomposite has been successfully synthesized by a one-step hydrothermal method with citrate ammonium as carbon source. The obtained samples are well characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, thermo gravimetric analyzer (TG) and X-ray photoelectron spectroscopy (XPS). Moreover, they are also evaluated as electrochemical catalysts in the hydrogen evolution reaction (HER). The results indicate that numerous ultrathin MoS_2 nanosheets which are characteristic of few layers (1–3 layers) and abundant exposed active edges and defects are well-dispersed in the amorphous carbon network to form MoS_2/C composite. As a consequence, the desirable microstructures endow the resultant MoS_2/C composite with significantly enhanced catalytic activity for HER such as more positive onset potential, larger current density as well as smaller Tafel slope of 64 mV dec^{-1} in comparison with the bare MoS_2.

1. Introduction

Depletion of fossil fuels and increased environmental concerns have prompted an urgent search for clean and sustainable alternative energy sources [1]. The electrochemical splitting of water via proton reduction in the hydrogen evolution reaction (HER) provides a feasible route toward this without dependence on consumable resources. Electrocatalyst always plays an indispensable role in reducing the overpotential of electrodes in HER, consequently promoting the reaction yield and thus the energy storage efficacy [2,3]. To date, the best known catalysts for HER are precious metals, such as platinum, ruthenium, and iridium, but the scarcity and high cost of these materials prohibit their wide-scale deployment [4]. It is desirable but rather challenging to develop a large-scale, environmentally friendly synthesis of inexpensive alternatives with high electrocatalytic activity to replace Pt-based catalysts.

Molybdenum sulfide (MoS_2) has a layered structure consisting of S–Mo–S arrangements connected to each sheet by van der Waals forces, which is a long-known catalyst for hydrodesulfurization [5,6]. Recent studies have shown that nanostructured MoS_2 is a promising electrocatalyst for HER, while the catalytic activity of its bulk counterpart is poor [7,8]. Theoretical calculations combined with experiments have revealed that the edge sites of MoS_2, especially the sulfur edge-terminated sites are identified as active sites for HER, on which the theoretical free energy of adsorption of hydrogen is similar to that of Pt, while the basal surfaces are catalytically inert [9,10]. Moreover, it has been demonstrated that the exchange current density of MoS_2 nanocrystals is proportional to the length of edge sites [9,10]. For this reason, great efforts have been unremittingly made to enlarge the edge sites of MoS_2 and various MoS_2 nanostructures with preferentially exposed edge sites such as doublegyroid MoS_2 [11], vertically aligned MoS_2 layers [12,13], porous films [14,15], ultrathin MoS_2 nanoplates [16,17], nanospheres [18,19], nanoflowers [20–23], highly divided or distorted MoS_2 [24,25], optimized and tailored MoS_2 nanosheets [26–30] as well as amorphous molybdenum sulfide and clusters [31,32] have been successfully prepared. However, the edge sites are highly energetic and unstable compared with basal plane. Therefore, the design and synthesis of nano-sized edge-terminated MoS_2 are quite difficult and still

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remain a critical issue for application of MoS_2 as a catalyst for HER [33,34].

Another pivotal inherent problem persecuting MoS_2 in HER is originated from its poor conductivity, especially the extremely low conductivity between two adjacent van der Waals bonded S–Mo–S layers, which greatly compromises the catalytic performance [35]. It is confirmed that the conductivity along two vertically stacked S–Mo–S interlayers is about 2 orders of magnitude lower than that of the intralayers [36]. In addition, the stacking of MoS_2 layers would severely decrease the amount of exposed active sites [37]. Fortunately, layered features along with the weak interlayer interaction has provided the potential capability of exfoliation of bulk MoS_2 into graphene-like single-layered (SL-) or few-layered (FL-) nanosheets through mechanical or chemical techniques [38]. Apparently, reduction of the layers is favorable to decreasing the interlayered resistance and improving the hopping efficiency of electrons between MoS_2 layers [35]. To the present, graphene-like MoS_2 nanosheets has gradually become a very competitive alternative electrocatalyst in HER [17,39–41]. Another approach toward improving the electrical contact is to couple MoS_2 with other conductive materials such as carbon nanotubes, pyrolyzed carbon as well as graphene to fabricate engineered composites [12,17,20,42–48]. It has been demonstrated that incorporation of these conductive materials can effectively promote electron transport from the active sites to the electrodes, accelerate the kinetics of electrode reaction and thus enhance the HER catalytic activity [12,17,20].

Herein, we present a one-step hydrothermal approach to synthesize MoS_2/C nanocomposite with citrate ammonium as carbon source and appraise them as an electrocatalyst for HER activity. The samples are characterized by XRD, SEM, EDX, TEM/HRTEM, Raman, TG and XPS techniques. The experimental results indicate that the as-prepared MoS_2/C composite is composed of numerous few-layered and edge-abundant ultrathin MoS_2 nanosheets dispersed in amorphous carbon. As a result, the as-prepared MoS_2/C nanocomposite demonstrates prominently enhanced electrocatalytic performance for hydrogen evolution reaction compared with the bare MoS_2.

2. Experimental Method

2.1. One-step hydrothermal synthesis of MoS_2/C nanocomposite

In a typical synthetic procedure, 1.5 mmol of ammonium citrate were dissolved into 50 mL deionized water to form a solution. Then 1.5 mmol of ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ were dissolved to the above solution with constant stirring. After that, 10 ml of hydrazine hydrate solution was dropwise added into the above solution under vigorous stirring. Afterwards, the solution was transferred into the 100 mL Teflon-lined stainless steel autoclave, which was heated and maintained at 240 °C for 24 h. After cooling naturally, the black solid product was collected by centrifugation and washed several times with deionized water and ethanol, and dried in the vacuum oven at 80 °C for 12 h. In control experiment, the bare MoS_2 sample was also prepared by a similar synthetic route without ammonium citrate in hydrothermal solution.

2.2. Characterizations

XRD patterns were recorded with a Thermo X'TRA X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm). The morphologies of the samples were observed by using a SIRION-100 field emission SEM (FESEM). The elemental composition of the samples was analyzed by energy dispersive X-ray spectroscopy (EDX, GENENIS-4000) and thermogravimetric analysis (TG), which was carried out with a NETZSCH STA 409 PC apparatus at a heating rate of 10 °C min^{-1} in flowing air. TEM and HRTEM 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. Raman spectra were recorded with 514 nm Ar ion laser at 6 mW for 50 s employing a Jobin Yvon LabRam HR spectrometer. X-ray photoelectron spectra (XPS) were processed on a Perkin-Elmer PHI5000c XPS, using C1s (B.E. 284.6 eV) as a reference.

2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system at an electrochemical station (CHI660D). Typically, 4 mg of catalyst and 80 μL Nafion solution (5 wt%) were dispersed in 1 mL water–ethanol solution with volume ratio of 4:1 by sonicating for 1 h to form a homogeneous ink. Then 5 μL of the dispersion (containing 20 μg of catalyst) was loaded onto a glassy carbon electrode with 5 mm diameter (loading ca. 0.102 mg cm^{-2}). Linear sweep voltammetry with scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4 (purged with pure N_2) using saturated calomel as the reference electrode, a Pt wire as the counter electrode, and the glassy carbon electrode with various samples as the working electrode. All the potentials were calibrated to a reversible hydrogen electrode (RHE). Number of active sites was estimated according to the methods reported previously [16]. AC impedance measurements were carried out in the same configuration at η = 200 mV from 10^6 to 0.01 Hz with an AC voltage of 5 mV.

3. Results and discussion

3.1. Microstructure and morphology of MoS_2/C composite

The crystalline structure and crystallinity of the as-prepared materials are inspected by X-ray diffraction (XRD) and the results are plotted in Fig. 1. Fig. 1 shows that the pattern of the bare MoS_2 agrees well with a hexagonal structure (JCPDS 37-1492) which belongs to the space group $P6_3/mmc$. The peaks at 2θ = 13.9°, 33.7°, 57.6° and 69.2° are attributed to the (002), (100), (110) and (201) planes, respectively. The appearance of the (002) peak signifies a stacked layered structure though the weak diffraction peaks are indicative of the low crystallinity of the bare MoS_2. In sharp contrast to that of the bare MoS_2, the (002) plane peak of the MoS_2/C composite become extremely weak and obscure, indicating that the stacking of MoS_2 layers

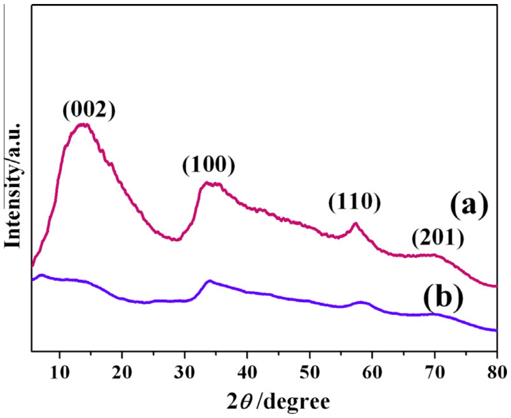

Fig. 1. XRD patterns of the as-prepared (a) bare MoS_2 and (b) MoS_2/C composite.