

Facile synthesis of MoS₂ nanosheets–carbon nanofibers composite as catalysts for hydrogen evolution reaction

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MoS₂ nanosheets (NS) were directly grown on carbon nanofiber (CF) and employed as electrocatalyst for hydrogen evolution reaction (HER). The structural, surface morphology and chemical composition of the nanocomposites were characterized by field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy. XRD and TEM-EDS measurements showed that the molybdenum oxide precursor was successfully transferred into MoS₂ nanosheets. It was confirmed from FE-SEM and TEM images that NS was uniformly distribution on surface of the CF. The HR-TEM images disclosed that the NS was formed perpendicular to surface of CF fibers via the MoS₂ layers growth parallel to CF surface which act as interface. The HER current density was about 12 mA cm⁻² at catalyst loading of only 60 μg cm⁻² at -0.384 V (vs. RHE).

Key words: Molybdenum disulfide, Nanocomposite, Electrocatalyst, Hydrogen evolution.

Introduction

Hydrogen is considered as a major energy carrier for the future carbon - neutral energy production [1,2]. The most abundant source of hydrogen is water as it is available everywhere and carbon-free. Hydrogen is produced from water (water splitting) via two half-cell reactions which results in both hydrogen and oxygen. The HER ($2H^+ + 2e^- \rightarrow H_2$) requires catalysts to minimize the overvoltage necessary to drive it and to achieve high energetic efficiency. Precious metals such as platinum, ruthenium or iridium are best-known catalysts for HER but the high cost and scarcity prevent them from large scale application. Therefore, development of new catalysts which are inexpensive, high active, scalable and stable are still remained of interests.

Metal dichalcogenides, especially molybdenum disulfide (MoS₂), have been showing high activity and stability for HER [1, 3-7] but the preparation methods are complicated with usage of toxic solvents, sulfurization with H₂ and/ or H₂S gases which may

affect the range of application. There are two strategies to prepare high active MoS₂-based catalysts for HER which involve into the increment of sulfur edge sites of catalysts or improvement of the contact layer between the active sites and electrode [3, 5, 6]. From this view point, MoS₂ have been synthesized on many other types of carbon-based materials such as mesoporous carbon, carbon nanotubes or reduced graphene oxide [4-6].

Herein we report a facile method for preparation of MoS₂ nanosheets uniformly grown onto surface of carbon nano fibers. The physical characterization disclosed that the NS was formed perpendicular to surface of CF fibers via the MoS₂ layers growth parallel to CF surface which act as interface.

Experimental

Molybdic acid (HMo), sublimed sulfur powder, hydrogen peroxide 31% solution, iso-propanol and methanol were supplied by Wako while carbon nanofiber and Nafion 5% solution were purchased from Sigma-Aldrich. All the chemicals were reagent grade and used without further purification.

In a typical experiment, 1g of HMo was immersed into 30 ml of H₂O₂ 31% solution and shaken until

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completely dissolved to achieve a transparent yellow solution. Then the yellow solution and isopropanol were mixed with 1:1 volume ratio to obtain the precursor solution. 0.2 g of carbon nanofiber was dispersed into 16 ml of precursor solution via sonification for 5 min following with evaporation till dryness at 60 °C in an electric oven. The dry MoO₃-CF was loaded into an alumina boat and placed in the middle of an alumina tube. Sulfur powder was also loaded into another alumina boat and placed outside the heating zone beforehand. Its place was chosen so that when the sample reached 650 °C, the temperature of the sulfur-containing boat was about 250 °C. The alumina tube was heated to 700 °C at a rate of 20 °C/min and then maintained at 700 °C for 1 hr before cooling naturally. The alumina tube was flushed with nitrogen at a flow rate of 50 mL/min during the experiment.

The phase structure of the as-prepared samples was investigated using a Bruker D8 advance diffractometer with Cu K α radiation ($\lambda = 0.154$ nm). The morphological features of the prepared samples were examined using a field emission scanning electron microscope (Hitachi S-4800 FE-SEM System, Japan) operated at an accelerating voltage of 15 kV. High resolution transmission electron microscopy (HR-TEM) was carried out using a JEOL JEM-2100F TEM (JEOL Ltd., Tokyo, Japan) at an acceleration voltage of 200 kV in the bright field image mode. Samples for TEM imaging were prepared by drop casting the dispersions on a carbon-coated copper grid, followed by drying under vacuum for 24 hours at 50 °C. Energy dispersive X-ray (EDX) spectroscopy and elements mapping of the composite samples were obtained using an EDX spectrometer (EDX, Oxford Inca X-max 80) by TEM with an acceleration voltage of 200 kV. The Raman scattering spectra were recorded at room temperature using a HORIBA Xplora Plus micro-Raman spectrometer. The measurements were performed with a laser excitation line of 532 nm focused through a 20 \times lens. The system was calibrated with a SiO₂ wafer with a peak at 520 ± 0.5 cm⁻¹. The laser power measured at the sample surface was about 2 mW in all measurements to avoid thermal decomposition of the sample. The exposure time was 1 s and accumulation was 16 times.

To study electrochemical properties, 4.0 mg of the prepared catalyst was dispersed into 1 ml of methanol containing 40 μ l of 0.5% (w/w) Nafion. Subsequently, an amount of catalyst dispersion was pipetted onto glassy carbon electrode (GCE, 3 mm in diameter) embedded in TEFLON tube and dried in air at 80 °C for 2hrs. The electrochemical study was performed in a 3 electrodes set up in 0.5M H₂SO₄ solution saturated with hydrogen gas using HSV-100 potentiostat (Hokuto Denko).

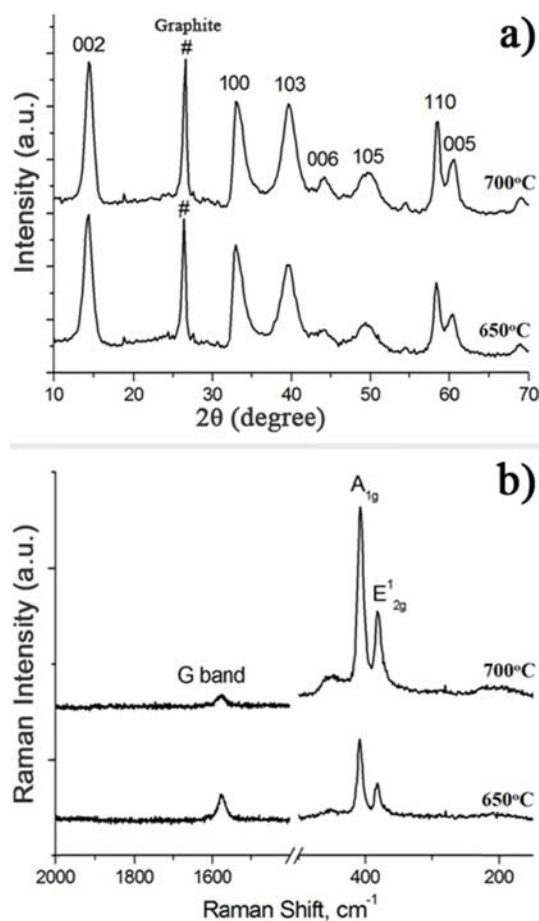


Fig. 1. XRD patterns (a) and Raman spectra (b) of MoS₂ nanosheet-carbon nanofiber composite prepared at 650 °C and 700 °C, respectively.

Results and Discussion

Fig. 1(a) showed XRD patterns of MoS₂ NS–CF composite prepared at 650 and 700 °C. Except for the peak at $2\theta \sim 26.6^\circ$ illustrating the existence of graphite structure, all the other reflections can be indexed to JCPDS 01-070-9263 of hexagonal MoS₂ (2H-MoS₂). These results prove that the molybdenum oxide precursor was successfully sulfurized to form molybdenum MoS₂ by usage of sulfur vapor directly generated from sulfur powder. In addition, the peak intensities of [002] plane (edge side) and [100] plane (basal side) are nearly equal which express that the form MoS₂ NS have no clearly orientation.

Raman spectra of those samples are also depicted in Fig. 1(b). MoS₂ NS-CF composite is characterized with three main peaks located at 1578, 408 and 381 cm⁻¹. The first mentioned peak is the well-known G band of graphite structure while other features of carbon nanotubes or graphene weren't detected. The two other peaks are assigned to out-of-plane (A_{1g}) and in-plane (E_{12g}) vibrations of MoS₂. The ratio of these two peaks is usually employed to evaluate the thickness and

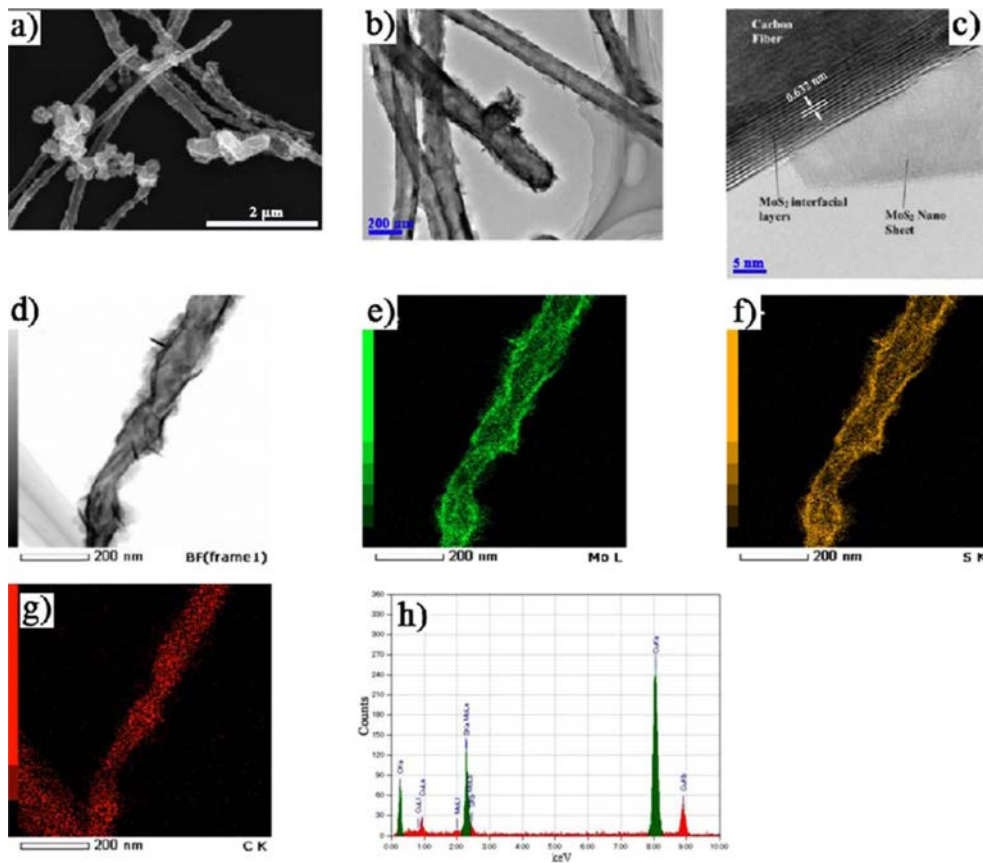


Fig. 2. (a) SEM image, (b) TEM, (c) HR-TEM, (d - h) TEM-EDS of NS-CF composite.

orientation of MoS₂ NS [7-12]. The very thin MoS₂ thin sheets with the basal plane exposed to laser beam (composed of less than 10 layers) are often reported to have this value being about 1 while the bulk ones have this value of about 1.5. In controversy, the value of higher than 3 was reported for the NS with the edge side exposed to laser beam [7, 13]. The peak intensities ratio is observed being slightly higher than 3 in this study, suggesting that the MoS₂ NS growth direction is perpendicular to the CF surface.

Fig. 2 illustrated the FE-SEM image (a), TEM (b), HR-TEM (c), TEM-EDS (f-h) of NS-CF composite. The FE-SEM and TEM images showed that the MoS₂ NS were uniformly grown on the carbon fiber surface and most of the nanosheets are perpendicular to the fiber surface which is in agreement with the Raman measurement. To date, most of the studies related to MoS₂ NS synthesis have been reporting the formation of the NS with the basal plane parallel to the substrate [11, 14, 15]. In order to look further inside the formation of the vertical alignment NS, HR-TEM was performed to examine the interface between CF and NS. It is very interesting to find out that the NS do not directly attach to the CF but through interfacial layers which is MoS₂ layers growth parallel to the CF surface (Fig. 2(c)). Thus, it may suggest the formation mechanism

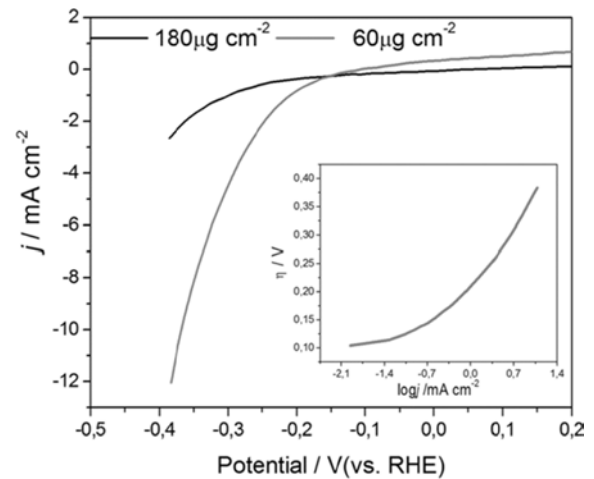


Fig. 3. LSV potential curves of composite prepared at 700 °C at different weight loading and Tafel plot (small inset).

of the NS and interfacial layers as follows: At the beginning of the sulfurization process, S vapor will react with the MoO₃ top layers to form MoS₂; then S atom will diffuse through the MoS₂ layers to reach MoO₃ layers beneath. Due to the differences in crystal structures between MoS₂ and MoO₃, stress will be

arising which is the driving force for the exfoliation of MoS₂ layers to form NS.

The TEM image of composite and its EDS mapping results are depicted in Fig. 2(d-g) respectively. The mapping results suggest that the carbon fiber is covered by the MoS₂ nano sheets and none of graphene nano sheet was detected. The energy dispersion graph discloses the absence of oxygen, proving that the entire of oxide precursor was successfully converted into MoS₂ which is in agreement with XRD data.

The electrochemical properties of the catalyst toward HER was performed and depicted in Fig. 3 (linear sweep voltammetry and Tafel plot). The catalyst exhibited relatively low current density toward HER as comparison with the other studied. The Tafel slope of about 56mV/decade calculated from the LSV polarization curve indicated that a larger surface coverage of adsorbed hydrogen and a rate determining recombination. This Tafel slope value is also higher than those reported for MoS₂-carbon composite, which is 41 mV/decade [5, 6] and similar to those observed from MoS₂ crystals, which is about 55-60 mV/decade [3]. The resemblance of slope values of the composite and crystals suggest that the NS act as the active component toward HER while the MoS₂ interlayer role as a barrier which separate the CF and NS, resulting in high overvoltage and low current density in HER.

Conclusions

MoS₂ NS-CF nanocomposite was successfully prepared by a simple thermal evaporation method. The physical characterization methods suggested that the NS and CF were connected via a thin MoS₂ layer which is grown parallel to the CF surface. This special structure may be the origin of the low current density toward HER.

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