Research Article

Carbon Nanotube Supported Amorphous MoS₂ via Microwave Heating Synthesis for Enhanced Performance of Hydrogen Evolution Reaction

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Amorphous molybdenum disulfide (MoS₂) is a promising electrochemical catalyst for hydrogen evolution reaction (HER) due to more active sites exposed on the surface compared to its crystalline counterpart. In this study, a novel fast three-minute one-pot method is proposed to prepare the single-wall carbon nanotube- (SWCNT-) supported amorphous MoS₂ via a microwave heating process. Compared to traditional hydro- or solvent thermal methods to prepare MoS₂ which usually consume more than 10 hours, it is more promising for fast production. An overpotential at 10 mA/cm² of amorphous MoS₂@SWCNT is 178 mV, which is 99 mV and 22 mV lower than crystalline MoS₂@SWCNT and pure amorphous MoS₂, respectively. After running 1000 cycles of polarization, ~2% increase in overpotential is observed, indicating its good stability. The enhanced performance results from the beneficial combination of the SWCNT substrate and the amorphous microstructures. The introduction of SWCNT increases catalyst conductivity and prevents MoS₂ aggregation. The amorphous microstructures of MoS₂ prepared by a microwave heating method lead to more Mo edges or active sites exposed.

1. Introduction

Due to its light weight, hydrogen delivers many merits as an energy carrier, such as high specific energy density and high energy conversion efficiency. Moreover, it is regarded as a clean and environment-friendly energy source due to the fact that water is the only by-product. As an electrochemical process, hydrogen evolution reaction (HER) can split water for producing the clean hydrogen to alleviate the fossil fuel shortage crisis. To be an advanced catalyst for HER, electrochemical performance of reduced overpotential and the low Tafel slope are highly required. Many materials have been studied as the efficient catalyst for HER [1]. Among them, noble metals, such as platinum (Pt), are considered as the most effective catalyst for HER due to their excellent catalytic activity [2, 3]. However, such noble metals suffer from scarcity in earth and high cost [4]. It is essential to develop highly active

HER catalysts based on materials that are more abundant and lower-cost.

Materials based on transition metals (TMs, such as Mn, Mo, Fe, Co, and Ni) have been investigated for electrocatalysts, including pure metals, alloys, carbides, nitrides, chalcogenides, phosphides, oxides, hydroxides, and/or their composites [5–12]. Among them, the transition metal chalcogenides, such as MoS₂, CoS, and Ni₂S₃, have been proven to be effective catalysts for HER [13]. MoS₂ is a typical transition metal dichalcogenide (TMD) material which is composed of earth-abundant elements, possessing a layered structure with weak van der Waals force interaction among each S-Mo-S layer [14, 15]. It is a competitive catalyst with high electrochemical activity. Based on a previous study, the HER performance of MoS₂ is restricted by the exposure of active sites, poor electrical conductivity, and insufficient contact to the catalyst [16]. Jaramillo et al. pointed out that the HER

activity of MoS_2 resulted from the metallic molybdenum edge sites, while the basal planes were catalytically inert [17]. Hence, increasing impurities and active sites in the crystal structure play crucial roles in enhancing HER performance. Several strategies have been proposed to improve the number of active edge sites, including synthesizing 1T phase MoS_2 [18], amorphous molybdenum sulfides [19], and exfoliated MoS_2 ultrathin nanosheets [20].

To increase electric conductivity and avoid aggregation of catalysts, conducting supports such as reduced graphene oxide [21], carbon nanotube (CNT) [22], carbon fiber [23], and carbon cloth [24] are usually introduced as current collectors and structure stabilizers. Many researches have been conducted on MoS_2 - and CNT-composited material [25–27]. Wang et al. prepared novel composite thin films by vacuum filtration of mixed exfoliated MoS_2 and CNT dispersion through a nitrocellulose membrane [28]. However, this method suffers from insufficient contacting between CNT and MoS_2 . A traditional hydro- or solvent thermal method is time-consuming, which takes hours to prepare composited catalysts [4, 26]. In this study, high HER performance of single-wall carbon-nanotube- (SWCNT-) supported amorphous MoS_2 (A- MoS_2 @SWCNT) has been synthesized through a novel one-pot method by three-minute microwave heating in an acid digestion vessel. The as-prepared catalyst exhibits a low overpotential of 178 mV at 10 mA/cm^2 and a low Tafel slope of 49 mV/dec with good durability. Compared to the traditional hydro- or solvent thermal methods, the microwave heating method is beneficial to fast synthesis with rich active sites introduced.

2. Experimental Section

2.1. Pretreatment of SWCNT. 2 g single-wall carbon nanotube solution (TUBALL, 0.2% water solution) was mixed with 10 ml nitric acid (HNO_3 , Sigma-Aldrich) and 10 ml H_2O . After stirring for 10 minutes, the mixture was transferred to a Microwave Acid Digestion Vessel (Parr 4782) and put into a microwave machine. After heating at 375 watts for 3 minutes, the vessel was cooled down to room temperature naturally or by flushing with cold water. Then, SWCNTs were filtrated and washed for several times and redispersed into 20 ml water by sonication.

2.2. Synthesizing A- MoS_2 @SWCNT. 177 mg ammonium molybdate tetrahydrate $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich) and 300 mg thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, Sigma-Aldrich) were dissolved in the prepared 20 ml SWCNT solution. Then, the solution was transferred to a Microwave Acid Digestion Vessel in a microwave machine. After heating at 375 watts for 3 minutes, the vessel was cooled down to room temperature naturally or by flushing with cold water. Then, A- MoS_2 @SWCNT was collected by vacuum filtration and washing with water for several times and redispersed into water by sonication. The final powder of A- MoS_2 @SWCNT was collected by freeze-drying in a lyophilizer. As the total mass of added SWCNT was 4 mg in each pot, the final product is 100 mg. Therefore, the composition of CNTs was 4 wt % in the product.

2.3. Synthesizing 2H- MoS_2 @SWCNT. As-gained A- MoS_2 @SWCNT was transferred to a tube furnace filled with Ar gas and heated at 500°C for 2 hours with the ramping rate of 2°C/min . The powder of 2H- MoS_2 @SWCNT was collected after cooling down to room temperature with the cooling rate of 3°C/min .

2.4. Synthesizing A- MoS_2 . The preparation of A- MoS_2 was similar to that of A- MoS_2 @SWCNT except that no SWCNT was added.

2.5. Material Characterization. Transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), selected area electron diffraction (SAED), and energy-dispersive spectroscopy mapping (EDS mapping) images were obtained using Thermo Scientific Talos F200X. A Rigaku Miniflex-II diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV and 15 mA was used to perform X-ray diffraction (XRD). Thermogravimetric Analysis (TGA) was conducted by using TA Instruments Q500. Raman spectra were collected using a Renishaw 2000 Raman microscope with a wavelength of 532 nm green laser excitation.

2.6. Electrochemical Measurements. All the tests were conducted in a typical three-electrode electrochemical workstation (CHI 760C). A typical working electrode preparation procedure is as follows: 5 mg of catalyst was dispersed in 1 ml 1:1 water-ethanol mixed solvent with $15 \mu\text{l}$ of NAFION solution (5%) added in. Then, the solution was ultrasonicated for 30 min to prepare a homogeneous ink. A rotating disk glassy carbon electrode was polished using an alumina suspension ($0.05 \mu\text{m}$, Allied High Tech Products) for 30 min, and it was cleaned with DI water. $5 \mu\text{l}$ of catalyst ink was drop-casted on the glassy carbon electrode with a 5 mm diameter (area = 0.196 cm^2) resulting in a catalyst mass loading around 0.128 mg/cm^2 . The catalyst ink-incorporated electrode was dried in air before the electrochemical measurements. All electrochemical measurements for the HER were performed under a typical three-electrode cell setup: electrocatalyst-incorporated rotating disk glassy carbon electrode as the working electrode, Ag/AgCl (4 M KCl) as the reference electrode, and a graphite rod as the counter electrode. An acid solution of 0.5 M H_2SO_4 was used as the electrolyte. The three-electrode potentials were converted into the reversible hydrogen electrode (RHE) potential utilizing the Nernst equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.205$. The rotational speed of the rotating disk glassy carbon electrode was maintained at 1600 rpm for all measurements. Linear sweep voltammetric (LSV) polarization curves were tested at a scan rate of 5 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out from 10^5 Hz to 0.1 Hz at an applied potential of -0.1 V vs. RHE and 5 mV of AC amplitude after catalytic activation. Electrocatalytic activities were analyzed with iR compensation. A long-term cycling was tested for 1000-cycle polarization from 0 to -0.25 V vs. E_{RHE} at a higher scan rate of 20 mV/s.

Potential Hazards. Overheating or overloading may cause excessive temperature and pressure inside the

FIGURE 1: Schematic illustration of the preparation of the A-MoS₂@SWCNT catalyst.

acid digestion vessel, which may cause explosion or other risks. It is dangerous to use organic liquids or volatile liquids as a solvent in the acid digestion vessel. The size and volume of a microwave machine may affect the heating efficiency of the vessel, and the temperature may not be linear to heating time or power. Hence, it is better to reproduce the experiment in a milder condition. Do not unclothe the lid before the vessel cools down to room temperature.

3. Results and Discussion

The nanocomposited A-MoS₂@SWCNT synthesis process is illustrated in Figure 1. SWCNT, ammonium molybdate tetrahydrate, and thioacetamide were mixed in water to form a homogeneous solution as shown in step 1. The mixture was microwaved at 375 W for 3 min (step 2), followed by washing and drying (step 3). The A-MoS₂@SWCNT black powder was collected successfully for further characterization.

XRD was used to detect the phase purity and crystallinity. The XRD patterns of A-MoS₂@SWCNT and 2H-MoS₂@SWCNT are shown in Figure 2(a). No sharp peak was observed in the pattern of A-MoS₂@SWCNT, indicating its amorphous feature by a microwave heating method with low reactive temperature and short reaction time. After annealing in argon gas at 500°C, the XRD pattern shows sharp peaks corresponding to the 2H-MoS₂ crystal phase (PDF no. 37-1492). The phase identity of the as-synthesized A-MoS₂@SWCNT and 2H-MoS₂@SWCNT was further confirmed by Raman spectroscopy (Figure 2(b)). The characteristic MoS₂ peaks at 379 and 402 cm⁻¹ are expected for E_{2g}¹ and A_{1g}¹, which relate to the in-plane opposite vibration of the Mo atom to the other two S atoms and the out-of-plane vibration of S atoms along opposite directions, respectively [29]. A broad peak of A-MoS₂@SWCNT around 543 cm⁻¹ is ascribed to the feature of the amorphous MoS₂ phase [30].

Figure 3 shows the TGA curve of the A-MoS₂@SWCNT in air at temperature from 30°C to 800°C with a scan rate of

10°C min⁻¹. A mass loss of 5.53% is observed when the temperature rises to 250°C, which is in regard to the loss of water molecule. At the range of 250°C to 380°C, the mass loss is 9.12%. It is attributed to the deintercalation of NH₄⁺ and the desorption of H₂S. From 380°C to 500°C, there is a sharp mass decrease (15.62%) relating to the oxidation of MoS₂ and the combustion of the carbon nanotube. Figure S1a depicts the XRD patterns of the annealed A-MoS₂@SWCNT in air at 400°C and 500°C for 3 hours. All peaks can be indexed as MoO₃ (PDF no. 35-0609), which is consistent with TGA results. Figure S1b-e is the digital images of A-MoS₂@SWCNT raw powder, annealed in air at 300°C, 400°C, and 500°C, respectively. The pictures show that the black powder turns to gray at 400°C and finally becomes white at 500°C, indicating the gradient oxidation of MoS₂ from 380°C to 500°C. The reaction can be expressed as

The mass loss beyond 640°C is ascribed to the sublimation of MoO₃ [31].

Figure 4 shows TEM images of the A-MoS₂@SWCNT. The uniform nanotube can be observed in Figure 4(a). There is no aggregation of MoS₂ nanoparticles, indicating that MoS₂ is well grown on the SWCNT surface. Figure 4(b) exhibits the rough surface of the nanotubes due to the cover of MoS₂, while pure SWCNT shows a smooth surface from the TEM image (Figure S2a). The good quality of SWCNT is confirmed by the HR-TEM image in Figure S2b which shows the diameter of tubes around 1.6 nm and the high G/D band ratio in Raman spectra (Figure S2c). Figure S3 shows that the synthesized MoS₂ nanoparticles aggregate to form a cluster with no SWCNTs added. The hydroxyl groups (-OH) on the pretreated SWCNTs can be combined with Mo ions, and then, Mo ions react with H₂S molecules decomposed from thioacetamide to form well-dispersed MoS₂. The

FIGURE 2: (a) XRD patterns and (b) Raman spectra for A-MoS₂@SWCNT and 2H-MoS₂@SWCNT.

FIGURE 3: TGA curve of A-MoS₂@SWCNT at the temperature range from 30 to 800°C.

SWCNT substrate can prevent the aggregation of MoS₂ and increase the contacting area of MoS₂ with electrolyte solution. Hence, there are more active sites of A-MoS₂@SWCNT exposed compared to the MoS₂ cluster. Figure 4(c) shows the HR-TEM image for a string of A-MoS₂@SWCNT. No MoS₂ crystal lattice can be observed, and the broad halo rings in its SAED pattern (inserted in Figure 4(c)) are manifested, which confirms the amorphous feature of MoS₂. In contrast, 2H-MoS₂@SWCNT shows a clear lattice on the edge of the nanotubes as shown in Figure S4, indicating the crystal nature of 2H-MoS₂. To get a general view over the elemental distribution, the EDS mapping was conducted. Figure 4(d) shows a uniform distribution of Mo, S, and C elements, indicating the well-covered MoS₂ on the surface of SWCNTs.

HER performance measurements on the glassy carbon electrode were carried out using a three-electrode configuration with a 0.5 M sulfuric acid electrolyte. Figure 5 shows the electrochemical performance of A-MoS₂@SWCNT, A-MoS₂ without SWCNT, and 2H-MoS₂@SWCNT. Pt/C and pure

SWCNT were also tested for comparison. Figure 5(a) exhibits the polarization curve for different catalysts. The A-MoS₂@SWCNT presents a good performance with onset potential around 95 mV and overpotential of 178 mV at 10 mA/cm². Pure A-MoS₂ shows lower electrocatalytic activity with onset potential around 110 mV and higher overpotential of 200 mV. The higher performance of A-MoS₂@SWCNT comes from more active sites exposed from the MoS₂ due to the introduction of SWCNT rather than SWCNT itself, which is confirmed by the poor performance of pure SWCNT. Even though the performance of A-MoS₂@SWCNT is still inferior to the Pt/C catalyst, which has the lowest overpotential of 69 mV, the performance is comparable to recent published works related to HER performance of MoS₂ as shown in Table S1 [32–41]. After annealing at 500°C in argon, 2H-MoS₂@SWCNT exhibits an overpotential of 277 mV, which is caused by the decrease in active sites as the basal plane being inert to HER reaction. After crystallization, less Mo edge sites of the 2H phase are exposed to the electrolyte.

FIGURE 4: TEM images of A-MoS₂@SWCNT at (a) overall view and (b) magnified image and (c) HR-TEM (inset SAED image) and (d) EDS mapping of A-MoS₂@SWCNT.

To further analyze HER activity, the Tafel slope of all the catalysts was calculated and plotted in Figure 5(b). The Tafel slope is a parameter to value HER performance. It is obtained by fitting the polarization curve with Tafel equation $\eta = a + b \times \log |J|$, where η is the potential, J the current density, and b the value of the Tafel slope [19]. A smaller Tafel slope value further indicates a higher catalytic activity [42]. The A-MoS₂@SWCNT shows a low Tafel slope of 49 mV/decade after iR correction, which is close to the Pt/C catalyst (30 mV/decade). The A-MoS₂ cluster shows a slightly higher Tafel slope of 55 mV/decade, which is caused by the aggregation of A-MoS₂. The higher Tafel slope of 2H-MoS₂@SWCNT (104 mV/dec) results from the inactive crystal plane. The Tafel slope of SWCNT is 583 mV/dec (Figure S5), indicating that the electrochemical performance of pure SWCNT can be ignored. This outcome of the Tafel slope is competitive to the previously published electrochemical performance. For instances, Xie et al. reported a defect-rich ultrathin MoS₂ nanosheets with a Tafel slope of 50 mV/dec [43], Ye et al. showed phosphorous-doped MoS_{2(1-x)P_x} with the Tafel slope of 57 mV/dec [44], and Luo et al. designed a two-dimensional (2D) MoS₂-confined Co(OH)₂ nanoparticle electrocatalyst with the Tafel slope of 53 mV/dec [45]. Table S1 shows the comparison of recent publications, indicating the top performance of this work [32–41].

The electrochemical active surface areas (ECSAs) of A-MoS₂@SWCNT have been studied by measuring cyclic voltammetry (CV) curves at the voltage range between 0.1 V and 0.3 V (vs. RHE) as shown in Figure 5(c). The testing voltage range is in the non-Faradic region without charge-transfer reaction on the electrode surface [46]. By linear fitting, the

slope of A-MoS₂@SWCNT is 6.53 mF/cm². The larger slope, which means the larger active surface area, results in enhanced catalytic performance [42]. The ECSAs of A-MoS₂, 2H-MoS₂@SWCNT, and pure SWCNT were tested in the same conditions and plotted in Figure 5(d). The ECSA of A-MoS₂@SWCNT (6.53 mF/cm²) is larger than that of A-MoS₂ (4.17 mF/cm²), which can be ascribed to the uniform covering of MoS₂ on the SWCNT surface with more Mo edges exposed. 2H-MoS₂@SWCNT exhibits a lower slope (2.49 mF/cm²) compared to A-MoS₂@SWCNT, which can be attributed to the fewer exposed molybdenum edges in the crystal phase. The pure SWCNT shows the slope of 0.25 mF/cm², indicating the trivial influence by physically introducing the SWCNT substrate. The relating CV curves of A-MoS₂, 2H-MoS₂@SWCNT, and pure CNT at different scan rates are shown in Figure S6.

In order to study the electrode kinetics, charge-transfer resistance (R_{ct}) is analyzed by the impedance spectra of catalysts as shown in Figure 5(e). A-MoS₂@SWCNT shows a relatively low R_{ct} which is 25 Ω . 2H-MoS₂@SWCNT and A-MoS₂ exhibit larger R_{ct} of 28 and 42 Ω , respectively. The introduction of SWCNT can sharply decrease R_{ct} , due to the higher electrical conductivity of SWCNTs. Therefore, by using 4 wt% SWCNT substrate, the HER performance of A-MoS₂@SWCNT can be greatly enhanced. Stability is an important character to evaluate the catalyst performance. The HER stability of A-MoS₂@SWCNT was obtained by a continuous polarization curve test in 0.5 M H₂SO₄ for 1000 cycles as shown in Figure 5(f). The initial performance was gained as shown in Figure 5(f) (black line). After 1000 cycles, the performance shows a slight decrease. For example, the overpotential changes from 178 mV to 180 mV at 10 mA/

FIGURE 5: Electrochemical performance: (a) HER polarization curve comparison; (b) Tafel slopes derived from (a); (c) cyclic voltammograms of the A-MoS₂@SWCNT electrode at different scan rates; (d) the double-layer capacitance value comparison; (e) Nyquist plots in the frequency range of 0.1 Hz to 100 kHz at -0.1 V vs. RHE; (f) stability before and after 1000 cycles.

cm². It demonstrates a good cyclic stability performance of microwave heating-synthesized A-MoS₂@SWCNT.

4. Conclusion

The A-MoS₂@SWCNT electrochemical catalyst has been successfully prepared through a superfast microwave heating method with the condition of 375 W for 3 min in an acid digestion vessel. The homogeneous A-MoS₂@SWCNT with abundant active sites is obtained due to the introduction of SWCNT as the substrate. The as-synthesized catalyst shows an outstanding HER activity with a low overpotential of 178 mV at 10 mA/cm² and a Tafel slope of 49 mV/dec with good durability. The enhanced catalytic activity is ascribed to the SWCNT substrate, and the amorphous microstructures with high intrinsic activity resulted from the exposure of the Mo edge. This new approach has a promising potential for commercial fast production as well as other nanomaterial preparations.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Authors' Contributions

D.D. and H.L. conceived ideas and supervised the project. W.T., J.J., and J.Y. carried out the experiments. G.C. and W.B. contributed to figures and data analysis. H.W. and M.Z. contributed to the interpretation of the results. W.T. and G.C. took the lead in writing the first draft of the manuscript. All authors provided critical feedback and helped with the research and manuscript. H.L. and D.D. are the corresponding authors (e-mails: hliao@nmsu.edu and dong.ding@inl.gov, respectively).

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Supplementary Materials

The supporting information is available free of charge at <https://spj.sciencemag.org/journals/energymatadv/2020/8140964/>. XRD patterns of A-MoS₂@SWCNT annealed in air at 400°C and 500°C. Digital photographs of A-MoS₂@SWCNT, annealed in air at 300°C, 400°C, and 500°C. TEM images for A-MoS₂. TEM and HR-TEM images of 500°C annealed crystalline 2H-MoS₂@SWCNT. TEM and HR-TEM images and Raman spectra of SWCNT. Tafel slope of SWCNT. Cyclic voltammetry curves of the A-MoS₂, 2H-MoS₂@SWCNT, and SWCNT electrodes at different scan rates. (Supplementary Materials)

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