Exfoliated MoS$_2$ nanosheets as efficient catalysts for electrochemical hydrogen evolution

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**Abstract**

An efficient electrocatalyst for hydrogen evolution has been developed based on liquid exfoliation of bulk MoS$_2$ via a direct dispersion and ultrasonication method. Transmission electron microscopy and atomic force microscopy measurements show that the exfoliated MoS$_2$ consists of two-dimensional nanosheets. The exfoliated MoS$_2$ nanosheets modified glass carbon electrode (E-MoS$_2$/GCE) with various loadings is fabricated via a drop-casting method. The electrocatalytic activity of E-MoS$_2$/GCE toward hydrogen evolution reaction is examined using linear sweep voltammetry. It is shown that the E-MoS$_2$/GCE with an electrode loading of 48 $\mu$g cm$^{-2}$ exhibits a high catalytic activity for hydrogen evolution with a low overpotential ($\sim 0.12$ V) and a high current density (1.26 mA cm$^{-2}$ at $\eta = 150$ mV).

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1. Introduction

Hydrogen has been proposed as future energy carrier that could be used to power up electronic devices, vehicles, and homes [1–3]. The most desirable source of hydrogen is water as it is abundant and contains no carbon [2]. The hydrogen production from water splitting needs an advanced catalyst to reduce the overpotential ($\eta$) and consequently increase the efficiency [4]. The most effective hydrogen evolution reaction (HER) electrocatalysts are Pt-group metals. However, large-scale applications of Pt catalysts are limited due to their high cost and low abundance [5–7]. Although Ni-based catalysts show high activity for the HER in alkaline electrolytes; unfortunately, it often degrades in acidic solutions [8–10]. Therefore, the challenge in finding alternative catalysts which are based on preferably cheap, non-toxic, stable and abundant materials still remains.

MoS$_2$ has usually been investigated as a catalyst for hydrodesulfurization [11]. Recent studies have shown that nanstructured MoS$_2$ is a promising electrocatalyst for HER, even though bulk MoS$_2$ material is a poor HER catalyst [12–14]. Both computational and experimental results confirmed that the HER activity of MoS$_2$ stemmed from S-atoms on the so-called Mo-edge (1 0 1 0) [15,16,18]. Thus, developing nanized MoS$_2$ with more exposed edges is considered as an efficient strategy to create excellent electrocatalysts for HER. However, previous procedures for synthesizing nanoparticulate MoS$_2$ catalysts have typically involved high-temperature treatment [15,18], ultra-high vacuum conditions [16,17], or sulfidation using H$_2$S gas [15–18], which are sophisticated, costly, and/or energy intensive. Therefore, development of a simple, large-scale and environmental-friendly synthesis method for an inexpensive catalyst with high HER activity is a crucial step toward a sustainable ‘hydrogen economy’.

Recent studies have shown that exfoliated MoS$_2$ exhibits an enhanced catalytic activity [19–23]. Bulk MoS$_2$ powder can be exfoliated into single layer platelets using the chemical exfoliation based on a lithiation process [24]. The exfoliated MoS$_2$ has significantly higher activity for hydrodesulfurization [19], as well as nitrogen and metal removal [20] as compared to the MoS$_2$ derived from molybdenum naphthenate. Del Valle et al. [21] also reported a 3.5-fold increase in thiophene hydrodesulfurization activity of exfoliated MoS$_2$ compared to crystalline MoS$_2$. It was suggested that the increase in catalytic activity was due to the increase in catalytically active edge sites generated by exfoliation. Simple ultrasonication can also be used to exfoliate bulk MoS$_2$ [25,26]. Wang et al. [23] successfully obtained ultrasmall MoS$_2$ nanoparticles (with diameters of $\sim 1.47$ nm) from bulk MoS$_2$ powder, using a long time ultrasonication method. Self-assembly of these ultrasmall nanoparticles onto an Au electrode surface via the formation of the Au–S bond, can significantly enhanced the catalytic property of the Au electrode for HER. In this work, we fabricate two-dimensional MoS$_2$ nanosheets from commercial MoS$_2$ powder via a direct dispersion and ultrasonication method. The resulting two-dimensional MoS$_2$ nanosheets can be directly deposited onto GCE substrate via a drop-casting method. Our studies show that the

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two-dimensional MoS2 nanosheets possess an excellent electrocatalytic activity for HER with a low overpotential (~0.12 V) and a high current density (1.26 mA cm$^{-2}$, at $\eta = 150$ mV).

2. Experimental

2.1. Reagents

Commercially available MoS2 powder was purchased from Alfa Aesar. Dimethylformamide (DMF, ≥99.5%), $\text{H}_2\text{SO}_4$ (95–98%), and ethanol were supplied from Shanghai Chemical Reagent Company. Nafion solution (5%) was purchased from Sigma–Aldrich. All of the reagents were of analytical grade and used without further purification.

2.2. Preparation of exfoliated MoS2 nanosheets

According to the literature [25], DMF was chosen as the exfoliation solvent for MoS2 since it was reported to be efficient and easily obtainable. The exfoliated MoS2 nanosheets were obtained via direct dispersion and ultrasonication. A common sonicator (SK250HP) was used in this study with an output power of 250 W. Bulk MoS2 powder was added to DMF (15 ml in a 20 ml vial), with an initial concentration of 10 mg ml$^{-1}$. The vial was then sonicated for 5 h. After sonication, the resultant dispersion was allowed to settle for 72 h. The top 1/2 of the dispersion was then decanted into glass vials, and subsequently centrifuged at 1500 rpm for 45 min to remove any unexfoliated material. The top 1/4 of the dispersion was decanted by pipette and retained for use.

2.3. Characterization of exfoliated MoS2 nanosheets

Transmission electron microscopy (TEM) images were recorded on a JEOI 2100 TEM operating at 200 kV. The specimens for TEM observations were prepared by dropping the dispersions on the copper grids with subsequent drying in air. Atomic force microscopy (AFM) measurements were carried out using a JPK Nanowizard®3 BioScience AFM. Silicon cantilevers from Budget Sensors were used for AC mode (non-contact mode) operation. X-ray diffraction (XRD) patterns were recorded with a Bruker GADDS X-ray diffractometer using Cu Kα radiation under a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectroscopy (XPS) analyses were made with a VG ESCALAB 220i-XL device. All XPS spectra were corrected using C1s line at 284.6 eV. Curve fitting and background subtraction were accomplished using XPS PEAK 41 software.

2.4. Fabrication of E-MoS2/GCEs

After being successively polished with 1.0, 0.3 and 0.05 $\mu$m alumina powder, glass carbon electrodes were ultrasonicated in a 1:1 ethanol/water mixture for 15 min to remove any traces of alumina. E-MoS2/GCEs were fabricated by a drop-casting method. The concentration of exfoliated MoS2 nanosheets in DMF was 0.34 mg ml$^{-1}$, which was gravimetrically determined by weighing the solid residue after evaporation of the suspension for a 10 ml aliquot. A drop (10 μl) of the suspension was added on the surface of glass carbon electrodes and allowed to dry in air. More suspension drops can be added consecutively on the surface of glass carbon electrodes after the solvent from the previous drop(s) has been fully evaporated. Electrodes with E-MoS2 loadings of 12 μg cm$^{-2}$, 24 μg cm$^{-2}$, 36 μg cm$^{-2}$, 48 μg cm$^{-2}$ and 60 μg cm$^{-2}$ were prepared by drop casting 1, 2, 3, 4 and 5 drops, respectively. As a reference, bulk MoS2 modified glass carbon electrode (B-MoS2/GCE) was also prepared for comparison. 6.8 mg of MoS2 powder was dispersed in 5 ml of a solution composed of 4:1 (v/v) distilled water and ethanol containing 0.5% (w/w) Nafion by sonication for 30 min to form a homogeneous slurry. Then 10 μL of the slurry was pipetted on the surface of a GCE with a bulk MoS2 loading of 48 μg cm$^{-2}$.

2.5. Electrochemical studies

All electrochemical studies were performed using a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a standard three-electrode setup. A platinum wire was used as the counter electrode and the modified glass carbon electrode was used as the working electrode. A saturated calomel electrode was used as the reference electrode for all the electrochemical tests and the potential was calibrated to the reversible hydrogen electrode (RHE) at the end. The electrocatalytic activity of exfoliated MoS2 nanosheets toward HER was examined using linear sweep voltammetry (LSV) with a scan rate of 2 mV s$^{-1}$ at room temperature in nitrogen purged electrolyte. For Tafel analysis, polarization curves were measured in nitrogen purged 0.5 M H$_2$SO$_4$ solution. Counter electrode, reference electrode and working electrode were placed in the same compartment cell with magnetic stirring. AC impedance measurements were carried out in 0.5 M H$_2$SO$_4$ solution in the frequency range 10$^{-2}$ to 10$^{6}$Hz with an AC voltage of 5 mV.

3. Results and discussion

3.1. Morphology of exfoliated MoS2 nanosheets

The resultant dispersion of exfoliated MoS2 nanosheets in DMF is dark green. Photograph of a typical dispersion, which is stable over periods of hundreds of hours, is shown in the inset of Fig. 1A. The morphology of exfoliated MoS2 nanosheets was confirmed by TEM and AFM. Fig. 1 shows the TEM images of the typical two-dimensional MoS2 nanosheets. The individual layer edges can be observed near the periphery of these MoS2 flakes (red arrows in Fig. 1E and F). The lateral size of these two-dimensional nanosheets was several micrometers. Besides, some smaller fragments with lateral size of a few tens of nanometers were found to be adsorbed on the large sheets (red circles in Fig. 1E). The electron diffraction pattern (i.e., the inset in Fig. 1F) indicated that the hexagonal lattice of the MoS2 nanosheets was not damaged during the exfoliation process [25–28]. Fig. 2A shows the AFM image of the exfoliated MoS2 nanosheets. The two-dimensional nanosheets are several micrometers wide, while smaller fragments are observed on the surface of the big flakes, which are consistent with the TEM data. The height profile of AFM image reveals that the thickness of the exfoliated MoS2 nanosheets varies from ~1 to 10 nm (Fig. 2B). Given that the thickness of an exfoliated MoS2 monolayer is ~1 nm [25–28], this suggests that the obtained MoS2 nanosheets contain ~1 to 10 layers. The XRD patterns of the exfoliated MoS2 nanosheets and bulk MoS2 powder are shown in Fig. 3. As compared with the bulk MoS2 sample, the very weak signal of the (0 0 2) reflection for the as-prepared MoS2 sample is implicative of a highly exfoliated nature [29,30]. The XPS survey spectra of the exfoliated MoS2 are dominated by the characteristic Mo and S peaks in addition to some smaller peaks of C and O from adventitious impurities (Fig. S1(A), Supporting Information). The binding energies of Mo 3d$_{5/2}$ and S 2p$_{3/2}$ are 228.8 eV and 162.6 eV, respectively, indicating a +4 oxidation state of Mo and the presence of $\text{S}^{2-}$ ligand (Fig. S1(B) and (C), Supporting Information). From high-resolution Pt 4f spectra, we did not see the presence of Pt, proving that Pt contamination was not observed on the working electrode (Fig. S1(D), Supporting Information).
SEM measurements were carried out to characterize the particle size of bulk MoS$_2$. The initial particle size of the MoS$_2$ powder ranges from several micrometers to about forty micrometers (Fig. 4A). After sonication for 30 min in an ethanol/water mixed solution, the final size of these particles seems to be diminished, varying from several micrometers to about twenty micrometers (Fig. 4B).

3.2. **Optimization and catalytic properties of E-MoS$_2$/GCEs**

The dependence of HER activity on the loading of exfoliated MoS$_2$ nanosheets is shown in Fig. 5. LSV of E-MoS$_2$/GCEs with various loadings was measured in nitrogen purged 0.5 M H$_2$SO$_4$ solution. From the LSV polarization curves shown in Fig. 5A, we can conclude that the optimal loading of exfoliated MoS$_2$ nanosheets is 48 µg cm$^{-2}$. In general, higher loading (e.g., 60 µg cm$^{-2}$) will lead to a lower catalytic activity. This is clearly illustrated in Fig. 5B, which shows the loading-dependent current densities at overpotential of $\eta = 150$ and 200 mV respectively. The current densities at the optimal loading (i.e., 48 µg cm$^{-2}$) are 1.26 and 6.36 mA cm$^{-2}$ at $\eta = 150$ and 200 mV, respectively. The catalytic activity of MoS$_2$ nanosheets for HER is related to the amount of the active sites.

The higher catalyst loading contains more active sites indicating a higher HER activity. However, on the other hand, higher catalyst loading may result in an increase of its resistance and a decrease of the efficiency of electron and proton transfer, thus leading to an inferior HER activity. Therefore, an optimal loading (48 µg cm$^{-2}$) is used here.

The dependence of HER activity on the pH value has also been studied. LSV for E-MoS$_2$/GCE with an electrode loading of 48 µg cm$^{-2}$ was measured at different pH values. Fig. 6A shows the LSV polarization curves performed at pH = 0, 1, 2 and 3 respectively. It can be seen that the apparent current densities decrease noticeably with the increase of pH values, and reduce to almost zero at pH = 3. This is further illustrated in Fig. 6B, which plots the pH-dependent current densities at $\eta = 150$ and 200 mV respectively. At pH = 0, the current densities at overpotentials of 150 and 200 mV are 1.64 and 7.78 mA cm$^{-2}$, respectively. And at pH = 3, the current densities at 150 and 200 mV overpotential are being reduced to 0.15 and 0.23 mA cm$^{-2}$, respectively. As the protons participate the HER reaction catalyzed by MoS$_2$ nanosheets, thus the lower pH values the MoS$_2$ nanosheets exhibit the higher HER activity.

Catalytic activity for HER of Pt, bulk MoS$_2$ powder and exfoliated MoS$_2$ nanosheets was studied comparatively. LSV polarization
curves of Pt, B-MoS2/GCE and E-MoS2/GCE with the GCE loadings of 48 μg cm⁻², are shown in Fig. 7A which is within a cathodic potential window. It can be seen that the Pt exhibits high HER catalytic performance (with a near zero overpotential), which is consistent with the reported values [10,13,15]. The bulk MoS2 powder exhibits litter HER activity. However, the exfoliated MoS2 nanosheets show a low overpotential of −0.12 V for HER reaction, with high current densities of 1.26 and 6.36 mA cm⁻² at overpotentials of 150 and 200 mV, respectively. The improved electrocatalysis exhibited by the E-MoS2/GCE suggests a smaller activation energy for HER. During the drop-casting process, the exfoliated MoS2 nanosheets appear to randomly restack on the surface of glass carbon electrodes. The disordered stacking of the exfoliated MoS2 nanosheets may permit more efficient electron transfer between the catalytic edge sites and underlying electrode than the bulk MoS2. To further confirm this hypothesis, we performed impedance measurements at an overpotential of η = 0.12 V (Fig. S2, Supporting Information). The exfoliated MoS2 exhibits a much lower Faradaic impedance (or charge-transfer impedance of ~1.6 kΩ) than the bulk MoS2 (Faradaic impedance of ~14 kΩ). The resulting fast electron transfer between the exfoliated MoS2 catalyst and electrode greatly facilitates the kinetics for HER.

In order to evaluate the performance of the HER catalyst, a comparison of the exfoliated MoS2 nanosheets with other typical molybdenum sulfide based HER catalysts reported previously is shown in Table 1. It can be observed that the current density of exfoliated MoS2 nanosheets (at η = 150 mV) is larger than most of those molybdenum sulfide based catalysts [16,18,31,32], but still smaller than those of the MoS2/reduced graphene oxide hybrid [10] and MoS2/mesoporous carbon nanospheres hybrid [33]. Thus, catalytic activity, in terms of the observed current densities, is high for exfoliated MoS2 nanosheets. There are two kinds of molybdenum sulfide based HER catalysts in Table 1. One kind of molybdenum sulfide is grown on carbon materials [10,33,37] or promoted by other elements [38], while another kind is pure molybdenum sulfide [16,18,31,32]. Due to the excellent conductive properties of carbon materials, the hybrid catalysts show an improved electronic contact between the active sites and the underlying electrode, thus exhibiting an enhanced HER activity [10,33]. Among the pure molybdenum sulfide HER catalysts, however, the catalytic activity of exfoliated MoS2 nanosheets is relatively high.
Fig. 5. (A) LSV polarization curves for E-MoS2/GCEs with different loadings in nitrogen purged 0.5 M H2SO4 solution. Scan rate: 2 mV s⁻¹. (B) Current densities for E-MoS2/GCEs with various loadings at overpotentials of 150 and 200 mV respectively.

Fig. 6. (A) LSV polarization curves for E-MoS2/GCE at different pH values. Scan rate: 2 mV s⁻¹. (B) Current densities for E-MoS2/GCE at different pH values at overpotentials of 150 and 200 mV respectively.

3.3. The mechanism of HER at the E-MoS2/GCEs

Tafel slope is an inherent property of the electrocatalyst materials that is determined by the rate-limiting step of the HER. The Tafel plots for both Pt and the exfoliated MoS2 nanosheets are shown in Fig. 7B. The linear portions of the Tafel plots are fitted to the Tafel equation (i.e., $\eta = b \log(j) + a$, where $\eta$ is the overpotential, $j$ is the current density and $b$ is the Tafel slope), yielding Tafel slopes of $\sim 30$ and $\sim 70$ mV dec⁻¹ for Pt and exfoliated MoS2 nanosheets, respectively. Three possible reaction steps have been suggested for the HER in acidic solutions [34]:

$$\text{H}_2\text{O} + \varepsilon \rightarrow \text{H}_2 + \text{O}_2$$

A fast discharge reaction (1) followed by a rate-limiting combination reaction (2) leads to a Tafel slope of $\sim 30$ mV dec⁻¹. When (1) is fast and followed by a slow electrochemical desorption

Table 1
Catalyst loadings, Tafel slopes and current densities at given overpotentials for various molybdenum sulfide based HER catalysts.

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Catalyst loading (μg cm⁻²)</th>
<th>$c_{MoS2}$ (M)</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>$j_{100\text{mV}}$ (mA cm⁻²)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS2/Au (111)</td>
<td>-</td>
<td>0.5</td>
<td>55–60</td>
<td>0.2</td>
<td>[16]</td>
</tr>
<tr>
<td>MoS2/carbon paper</td>
<td>4</td>
<td>0.5</td>
<td>120</td>
<td>0.1</td>
<td>[18]</td>
</tr>
<tr>
<td>MoS2/MCNs/GCE</td>
<td>7</td>
<td>0.5</td>
<td>41</td>
<td>7</td>
<td>[33]</td>
</tr>
<tr>
<td>MoS2/RGO/GCE</td>
<td>190</td>
<td>1.0</td>
<td>40</td>
<td>30</td>
<td>[31]</td>
</tr>
<tr>
<td>MoS2/GCE</td>
<td>285</td>
<td>1.0</td>
<td>41</td>
<td>9</td>
<td>[10]</td>
</tr>
<tr>
<td>MoS2/3D Ni foam</td>
<td>5010</td>
<td>0.5</td>
<td>42.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Fe-MoS2/GCE</td>
<td>30.4</td>
<td>1.0</td>
<td>39</td>
<td>1.55</td>
<td>[38]</td>
</tr>
<tr>
<td>E-MoS2/GCE</td>
<td>48</td>
<td>0.5</td>
<td>70</td>
<td>1.26</td>
<td>This work</td>
</tr>
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</table>

<table>
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<tr>
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<th>$^{a}$</th>
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</thead>
</table>
| $^a$ Concentration of H2SO4 aqueous solution.  
$^b$ Some of these values are estimations on the basis of polarization curves.  
$^c$ Estimated values on the basis of the description of electrode preparations.  
$^d$ A current density of 0.3 mA cm⁻² is observed which is not due to HER but oxygen reduction. HER occurs at $\eta = 200$ mV.  
$^e$ Mesoporous carbon nanospheres.  
$^f$ Reduced graphene oxide.  
$^g$ Graphene.
reaction (3), a Tafel slope of \( \sim 40 \text{ mV dec}^{-1} \) is obtained. If (1) is rate-limiting or the surface coverage is close to one, the Tafel slope is \( \sim 120 \text{ mV dec}^{-1} \). Therefore, the HER on a Pt surface is followed by a combination of reactions (1) and (2). Unfortunately, the reaction mechanism on molybdenum sulﬁde catalysts remains indeﬁnite since its ﬁrst HER study more than 40 years ago [35]. In this work, the Tafel slope for the exfoliated MoS2 nanosheets is similar to that (60 mV dec\(^{-1}\)) of MoS2 nanoplatelets grown on Au (1 1 1) [16]. According to Thomas [36], a large Tafel slope (60 mV dec\(^{-1}\)) can be obtained when the chemisorption of hydrogen from aqueous solution requires an activation energy. Therefore, the mechanism is a fast discharge reaction (1) followed by either a rate-determining combination (2) or a rate-determining electrochemical desorption reaction (3). The two possible mechanisms cannot be distinguished from the Tafel analysis alone.

4. Conclusions

In summary, we have demonstrated that the exfoliated MoS2 nanosheets, which are produced from bulk MoS2 crystals via a direct dispersion and ultrasonication method, can be directly deposited onto the surface of GCE and exhibit high electrocatalytic activity for hydrogen evolution reaction. The increased catalytic activity of exfoliated MoS2 was attributed to an improved conductivity compared to the bulk MoS2 particles. Therefore, this study provides a new approach for a cheap and effective HER catalyst, which can be easily prepared and is promising for large-scale production.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2013.07.094.

References


