Large-Area Atomically Thin MoS₂ Nanosheets Prepared Using Electrochemical Exfoliation

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ABSTRACT Molybdenum disulfide (MoS₂) is an extremely intriguing material because of its unique electrical and optical properties. The preparation of large-area and high-quality MoS₂ nanosheets is an important step in a wide range of applications. This study demonstrates that monolayer and few-layer MoS₂ nanosheets can be obtained from electrochemical exfoliation of bulk MoS₂ crystals. The lateral size of the exfoliated MoS₂ nanosheets is in the 5—50 μm range, which is much larger than that of chemically or liquid-phase exfoliated MoS₂ nanosheets. The MoS₂ nanosheets undergo low levels of oxidation during electrochemical exfoliation. In addition, microscopic and spectroscopic characterizations indicate that the exfoliated MoS₂ nanosheets are of high quality and have an intrinsic structure. A back-gate field-effect transistor was fabricated using an exfoliated monolayer MoS₂ nanosheet. The on/off current ratio is over 10⁶, and the field-effect mobility is approximately 1.2 cm² V⁻¹ s⁻¹; these values are comparable to the results for micromechanically exfoliated MoS₂ nanosheets. The electrochemical exfoliation method is simple and scalable, and it can be applied to exfoliate other transition metal dichalcogenides.

KEYWORDS: electrochemical exfoliation · MoS₂ nanosheets · field-effect transistor · layered material · solution process

Two-dimensional (2D) materials have attracted great attention in the past decade.¹⁻³ Graphene is by far the best-known 2D material because of its outstanding physical,⁴ optical,⁵ and mechanical properties,⁶ although its zero band gap limits its application in low-power electronics and digital circuits.⁶ Recently, considerable interest has focused on transition metal dichalcogenides, especially molybdenum disulfide (MoS₂), because they are atomically thin and possess a large band gap.⁸ Structurally analogous to graphene, layered MoS₂ comprises planes wherein the S—Mo—S atoms are covalently bonded and the neighboring planes attach to each other through van der Waals forces. Like graphite, bulk MoS₂ crystals can be easily exfoliated along these planes because of the weak interlayer interactions.⁹

MoS₂ exhibits unique properties and has great potential in electronic, optoelectronic, and energy-harvesting applications.¹⁰⁻¹⁶ The electronic properties of MoS₂ are strongly dependent on the number of layers.¹⁷ Multilayer MoS₂ is an indirect-band gap semiconductor, with a gap of around 1.2 eV.¹⁸ On the other hand, when the number of layers decreases to one, the monolayer MoS₂ turns into a direct-band gap semiconductor with a gap of around 1.8 eV.¹⁹ Monolayer MoS₂ field-effect transistors (FETs) with a hafnium-oxide gate dielectric demonstrated typical mobilities that are over 200 cm² V⁻¹ s⁻¹ and on/off current ratios as high as 10⁸ at room temperature.¹⁰ Monolayer MoS₂ is suitable for applications in flexible transistors and sensors, which is because it possesses mechanical strength 30 times higher than that of steel.²⁰⁻²² A great enhancement of photoluminescence (PL) has been detected in monolayer MoS₂, and it is related to quantum-confinement effects resulting from the indirect-to-direct band gap transition.¹⁹,²³ In one study, a photodetector fabricated using monolayer MoS₂ showed an ultrahigh photoreponsivity of 880 A W⁻¹, which is 10⁵ times better than that of a graphene photodetector (6.1 mA W⁻¹).¹³,²⁴ In addition,
MoS\textsubscript{2} and its nanocomposites are considered attractive electrode materials for applications in Li-ion batteries because of their excellent charge-storage capacity and cycling performance.\textsuperscript{14,25,26}

Large-area, atomically thin MoS\textsubscript{2} nanosheets must be prepared for such applications. Micromechanically exfoliated MoS\textsubscript{2} nanosheets with high-quality and high crystallinity have been used in fundamental studies.\textsuperscript{10,13,19,22,27,28} However, this method is very inefficient, and the experimental results are not repeatable because of the random thickness and size of the exfoliated MoS\textsubscript{2} nanosheets. Thin-layer MoS\textsubscript{2} has been synthesized using chemical vapor deposition.\textsuperscript{29,30}

In this study, we demonstrate that atomically thin MoS\textsubscript{2} nanosheets can be prepared by electrochemical exfoliation of the bulk MoS\textsubscript{2} crystal. The exfoliated MoS\textsubscript{2} nanosheets have lateral sizes that are as large as 50 \textmu m. In addition, they exhibit a low degree of oxidation, high quality, and an intrinsic structure. A back-gate FET fabricated on exfoliated monolayer MoS\textsubscript{2} exhibits a high on/off current ratio and good field-effect mobility. The excellent properties of the MoS\textsubscript{2} nanosheets obtained by this method are comparable to those of mechanically exfoliated MoS\textsubscript{2} nanosheets.

RESULTS AND DISCUSSION

Figure 1a shows a schematic illustration of the experimental setup for the electrochemical exfoliation of bulk MoS\textsubscript{2} crystals. A bulk MoS\textsubscript{2} crystal, a Pt wire, and a 0.5 M Na\textsubscript{2}SO\textsubscript{4} solution were used as a working electrode, a counter electrode, and an electrolyte, respectively. A DC bias was applied between MoS\textsubscript{2} and the Pt wire for the electrochemical exfoliation. A low positive bias of +2 V was initially applied to the working electrode for 10 min to wet the bulk MoS\textsubscript{2} crystal. The bias was then increased to +10 V for 0.5–2 h to exfoliate the crystal. As a result, many MoS\textsubscript{2} flakes dissociated from the bulk crystal and became suspended in the solution (Figure 1b and c). A summary of the electrolytes and exfoliation conditions tested in this work, together with the key results are listed in Table S1 (Supporting Information). The exfoliated MoS\textsubscript{2} flakes were collected using vacuum filtration and then redispersed in \textit{N}-methyl-2-pyrrolidone (NMP) to obtain a uniformly distributed MoS\textsubscript{2}-nanosheet solution (Figure 1d).\textsuperscript{24} The concentration of obtained MoS\textsubscript{2}-nanosheet dispersions has a range of 0.007–0.014 mg mL\textsuperscript{–1} and the yield of MoS\textsubscript{2} nanosheets is about 5–9\% (Figure S1, Supporting Information).

The mechanism of electrochemical exfoliation of bulk MoS\textsubscript{2} crystals is described in Figure 1e. First, by applying a positive bias to the working electrode, the oxidation of water produces \textit{HOH} and \textit{HO} radicals assembled around the bulk MoS\textsubscript{2} crystal. The \textit{HOH} and \textit{HO} radicals and/or SO\textsubscript{4}\textsuperscript{2–} anions insert themselves between the MoS\textsubscript{2} layers and weaken the van der Waals interactions between the layers. Second, oxidation of the radicals and/or anions leads to a release of O\textsubscript{2} and/or SO\textsubscript{2}, which causes the MoS\textsubscript{2} interlayers to greatly expand.\textsuperscript{28} Finally, MoS\textsubscript{2} flakes are detached from the bulk MoS\textsubscript{2} crystal by the erupting gas and are then suspended in the solution. The surface of the bulk MoS\textsubscript{2} crystal should be oxidized during electrochemical exfoliation, and this is directly related to the quality and degree of oxidation of the exfoliated MoS\textsubscript{2} nanosheets. By optimizing the experimental conditions, we obtained a bulk MoS\textsubscript{2} crystal with a barely oxidized surface (see Experimental Section and Figure S2, Supporting Information).

Figure 2a shows a transmission electron microscopy (TEM) image of a thin MoS\textsubscript{2} nanosheet with a lateral size of about 10 \textmu m. The high-resolution TEM (HRTEM) image in Figure 2b shows a folded edge of a monolayer MoS\textsubscript{2} nanosheet. Figure 2c reveals that the hexagonal lattice structure of the MoS\textsubscript{2} nanosheet was not damaged during the electrochemical exfoliation process. The white blur on the surface of the MoS\textsubscript{2} nanosheet is probably residues.\textsuperscript{35} The electron diffraction pattern collected from the exfoliated MoS\textsubscript{2} nanosheets in Figure 2d shows the hexagonal symmetry characteristic of 2H-MoS\textsubscript{2}.\textsuperscript{39} The HRTEM results indicate that the thin MoS\textsubscript{2} nanosheets obtained in this study exhibit few defects, high crystallinity, and an intrinsic structure.

Figure 3a shows an optical microscope image of a typical electrochemically exfoliated MoS\textsubscript{2} nanosheet.
deposited on a SiO2/Si substrate by dip coating. The lateral size of the MoS2 nanosheet is about 25 μm. More optical microscope images of the exfoliated MoS2 nanosheets are shown in Figure S3a (Supporting Information). The electrochemically exfoliated nanosheets exhibit lateral sizes in the range of 5–50 μm, which is much larger than that of chemically and liquid-phase exfoliated MoS2 nanosheets.32–36 On the basis of their optical contrasts, we found that the exfoliated MoS2 nanosheets had different number of layers in one sheet,40 which is attributed to non-uniform distribution of surface resistance inducing the current damage.

The Raman frequencies of in-plane E12g and out-of-plane A1g modes can be used as reliable and convenient features to identify the number of layers in atomically thin MoS2 nanosheets.28,41 The obtained monolayer and few-layer MoS2 nanosheets were characterized using Raman spectroscopy (Figure S4a, Supporting Information). The 514.5 nm laser line was excited using a power of <1 mW to avoid any heating effects. All of the spectra show two peaks around 384 (E12g mode) and 407 cm−1 (A1g mode); the two modes exhibit a well-defined dependence on the number of layers. The frequency of the E12g mode decreases while that of the A1g mode increases with increasing number
of layers. These results are consistent with mechanically exfoliated MoS$_2$, which indicates that the obtained MoS$_2$ nanosheets are of high quality.

To better understand the uniformity of the layer thickness, we constructed a spatial map depicting the difference between the Raman frequencies of the E$_{12g}$ and A$_{1g}$ modes of the MoS$_2$ nanosheet presented in Figure 3b. The map reveals that the majority of the MoS$_2$ nanosheet is bilayer (pink region), but parts of it are monolayer (purple region) and in bulk form (white region). This result is consistent with the optical microscope image. Atomic force microscopy (AFM) was used to evaluate the topographies of the exfoliated MoS$_2$ nanosheets (Figures 3c and S5, Supporting Information). We can clearly see folds and aggregations in the AFM images, which were generated during the deposition and drying processes, and these features lead to exfoliated MoS$_2$ nanosheets with rough surfaces. To understand the distribution of the thickness, 100 MoS$_2$ nanosheets deposited on SiO$_2$/Si substrate were randomly selected. About 7% of these MoS$_2$ nanosheets are monolayer and more than 70% of them comprised 2–5 layers (Figure S6, Supporting Information).

In addition to Raman characteristics, we also investigated the PL properties of the exfoliated MoS$_2$ nanosheets. The PL spectra were investigated using 514.5 nm laser excitation at room temperature and normalized using the intensity of A$_{1g}$ Raman peaks for direct comparison. Figure 4a shows the PL spectra of a monolayer MoS$_2$ nanosheet before and after thermal annealing. The PL spectrum of the as-prepared monolayer MoS$_2$ nanosheet contains two peaks located at 669 and 622 nm, which correspond to the A1 and B1 direct excitonic transitions at 1.85 and 1.99 eV, respectively. For the nanosheet that was annealed at 200 °C in a N$_2$ environment for 2 h, the PL intensity is higher by a factor of 10. This is because the residual solvent absorbed by the MoS$_2$ nanosheet surface evaporated. We also investigated the PL spectra of exfoliated MoS$_2$ nanosheets with different numbers of layers (Figure S4b, Supporting Information). The strongest PL signal appears in the spectrum for monolayer MoS$_2$, while the emission intensity significantly decreases as the number of layers increases. The different PL properties of the monolayer and few-layer MoS$_2$ nanosheets agree with the fact that monolayer MoS$_2$ has a direct band gap structure and few-layer MoS$_2$ has an indirect one.

The surface chemical properties of an as-prepared MoS$_2$ nanosheet were studied using X-ray photoelectron spectroscopy (XPS) (Figure 4b). The Mo 3d spectrum shows two strong peaks at 229.5 and 232.6 eV.
corresponding to Mo$^{4+}$ 3d$_{5/2}$ and Mo$^{4+}$ 3d$_{3/2}$, respectively.\cite{32,43} Additionally, the spectrum shows four weak peaks at 231.1 and 234.2 eV corresponding to Mo$^{5+}$ 3d$_{5/2}$ and Mo$^{5+}$ 3d$_{3/2}$, respectively; at 232.8 and 235.9 eV corresponding to Mo$^{6+}$ 3d$_{5/2}$ and Mo$^{6+}$ 3d$_{3/2}$, respectively.\cite{44} In the S 2p spectrum, two peaks are observed at 162.3 and 163.5 eV corresponding to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively. These results are consistent with the reported values for MoS$_2$ single crystals, indicating that the obtained MoS$_2$ nanosheets are the 2H phase.\cite{33} This is in contrast to the chemically exfoliated MoS$_2$ nanosheets that lose their pristine semiconducting properties because their structure changes from 2H to 1T phase as a result of Li intercalation. The Mo$^{5+}$ and Mo$^{6+}$ are thought to be generated by the oxidation of MoS$_2$ during electrochemical exfoliation; the total amount of them is approximately 15.6 at.%, which indicates that the exfoliated MoS$_2$ nanosheets have a low degree of oxidation. The Mo$^{6+}$ can be reduced to Mo$^{5+}$ by thermal annealing in N$_2$ (Figure S7 and Table S2, Supporting Information).\cite{45}

A dispersion of MoS$_2$ nanosheets in NMP with a concentration of about 0.011 mg mL$^{-1}$ was characterized using UV–visible absorption spectroscopy (Figure 5a). The spectrum shows two excitonic peaks at 676 nm (1.83 eV) and 613 nm (2.02 eV), which are related to A1 and B1 via direct transition with energy separation, suggesting the existence of high-quality semiconducting MoS$_2$ nanosheets.\cite{33,46} A MoS$_2$ thin film can be fabricated using the solution by applying vacuum filtration. Figure 5b shows the scanning electron microscopy (SEM) image of the surface of a MoS$_2$ thin film. It can be seen that the large MoS$_2$ nanosheets form a smooth plane and many small flakes reside on it.

We analyzed the X-ray diffraction (XRD) (Figure 5c) and Raman spectroscopy (Figure 5d) results of the MoS$_2$ thin film. An initial bulk MoS$_2$ crystal before electrochemical exfoliation was also measured for comparisons. In the XRD patterns, the (002) reflection of the MoS$_2$ thin film is significantly smaller than that of the bulk MoS$_2$ crystal, which indicates that a large number of the MoS$_2$ nanosheets prepared were highly exfoliated.\cite{47} The Raman spectra of both the thin film and bulk crystal of MoS$_2$ show two peaks at 382 and 407 cm$^{-1}$. The intense Raman peaks of the MoS$_2$ thin film offer strong evidence that the exfoliated MoS$_2$ nanosheets are of high quality.

To evaluate the electrical properties of the exfoliated MoS$_2$ nanosheets, back-gate FETs were fabricated by depositing Au/Ti electrodes via electron-beam evaporation onto the top of the MoS$_2$ nanosheets on SiO$_2$/Si substrates. Figure 6a and b show, respectively, an optical microscope image of a monolayer MoS$_2$ nanosheet and an SEM image of a transistor device.
fabricated on it. The lateral size of the monolayer MoS2 nanosheet is as large as 50 μm. The channel region of the MoS2 FET was measured using AFM and the Raman spatial map to determine the thickness and uniformity of the MoS2 nanosheet (Figure S8, Supporting Information). The height profile shows that the thickness is approximately 0.7 nm, which is consistent with previous theoretical and experimental values.9,10,48 Additionally, it shows that the monolayer MoS2 is almost homogeneous, even on the 20-μm scale, with the exception of a few thick spots. A three-dimensional (3D) schematic of the monolayer MoS2 device structure is shown in Figure 6c.

Figure 6d displays the output characteristics (drain current $I_{ds}$ vs drain voltage $V_{ds}$) at different gate voltages ($V_{gs}$) for the monolayer MoS2 transistor. The $I_{ds}$ vs $V_{gs}$ curves show linear characteristics and clear current saturation at low and high drain voltage, respectively. The transfer characteristics (drain current $I_{ds}$ vs gate voltage $V_{gs}$) of this device are shown in Figure 6e. The field-effect mobility ($\mu$) was estimated in the saturation regime using the following equation:

$$I_{ds} = \frac{W}{2L} C_{ox} \mu (V_{gs} - V_{th})^2$$

where $L$ is the channel length, $W$ is the channel width, $C_{ox}$ is the gate capacitance, and $V_{th}$ is the threshold voltage. For $V_{ds} = 20$ V, the calculated field-effect mobility of the monolayer MoS2 transistor is around 1.2 cm² V⁻¹ s⁻¹, and the on/off current ratio is higher than 10⁶. The small spots in Figure S8b (Supporting Information) may represent thick flakes or wrinkles in monolayer MoS2 nanosheet.49,50 These flakes or wrinkles would have degraded the performance of the device owing to the chemisorption of oxygen and water at the flakes’ edges and the introduction of interlayer resistance.51,52 Even so, the calculated field-effect mobility is much higher than that for the previously mentioned liquid-phase exfoliated MoS2 nanosheets (0.01 cm² V⁻¹ s⁻¹),34 and it is also comparable to previously reported data collected from mechanically exfoliated monolayer MoS2 devices (0.1–10 cm² V⁻¹ s⁻¹).10,53–55 Note that the FET shows typical n-type field-effect behavior; this is very different from the chemically exfoliated MoS2 nanosheets that show p-type behavior as a doping effect of the residual Li.32 Our MoS2 nanosheets were directly detached from the bulk MoS2 crystal through the insertion of electrolyte ions, as well as production and eruption of gases. As a result, these MoS2 nanosheets retain their intrinsic properties and structures.

**CONCLUSION**

We have demonstrated that monolayer and few-layer MoS2 nanosheets can be prepared by electrochemically exfoliating the bulk MoS2 crystal in an ionic...
solution. The lateral size of the exfoliated MoS2 nanosheets can reach 50 μm, which is much larger than that of mechanically, chemically, and liquid-phase exfoliated MoS2 nanosheets. The n-type FET based on the exfoliated monolayer MoS2 exhibits an on/off current ratio of over $10^6$ and a field-effect mobility of around 1.2 cm² V⁻¹ s⁻¹. This electrical performance analysis, when combined with TEM, Raman, PL and XPS measurements, confirms that the exfoliated MoS2 nanosheets exhibit high quality, an intrinsic structure, and a low degree of oxidation. This work provides a simple, efficient and scalable approach to preparing large-area atomically thin MoS2 nanosheets, which are promising for a wide range of applications.

EXPERIMENTAL SECTION

Electrochemical Exfoliation of MoS2. Natural, single-crystalline bulk MoS2 (SPI Supplies, 429MM-AB) was used as the working electrode and source for the electrochemical exfoliation. The bulk MoS2 crystal was clamped to a Pt clip and the MoS2 crystal alone was immersed in the ionic solution. A grounded Pt wire was used as the counter electrode and was placed 2 cm away from, and parallel to, the bulk MoS2 crystal. The 0.5 M Na₂SO₃ solution was prepared by mixing 4.0 g of sodium hydroxide (Duksan) and 5.2 g of sulfuric acid (95%, Samchun) dilute solutions, then adding DI water to obtain 100 mL of the combined solution.

The electrochemical exfoliation process was carried out by applying a positive bias on the working electrode. The intensity of the electrochemical reaction could be estimated by the amount of gas bubbles produced on the MoS2 bulk surface. After the electrochemical-exfoliation efficiency was optimized, the bulk MoS2 crystal developed a barely oxidized surface when the Pt clip was 0.5 cm above the liquid level. In the exfoliation process, electrolysis of water released O₂ and H₂, which led to a drawdown of the liquid level. This caused the current passing through two electrodes to decrease with increasing time. To eliminate the effect of current variation on experimental results, we used a tube to connect the experimental setup (shown in Figure 1a) with a big beaker that also contained the 0.5 M Na₂SO₃ solution. The beaker was big enough to allow us to ignore the lower liquid-level drawdown because of water electrolysis. As a result, the current remained stable during the exfoliation process.

The exfoliated MoS2 flakes were collected using porous membranes (0.2 μm, JGWP, Millipore) and washed with DI water using vacuum filtration. After drying, the collected MoS2 flakes were redispersed in an NMP solution, using low-power sonication in a water-bath for 1 h and centrifugation at 1500 rpm for 30 min to remove the unwanted thick MoS2 flakes. The top half of the solution was used for further characterization and film fabrication.

Characterizations. The MoS2 nanosheets prepared using electrochemical exfoliation were deposited by dip coating onto a 300 nm SiO₂/Si substrate for optical microscopy, Raman, PL, XPS, and AFM studies. Raman and PL spectra were measured using a multipurpose spectrometer (LabRAM HR800, Horiba Jobin Yvon) with laser excitation at 514.5 nm. The PL spectra were normalized using the intensity of A1g Raman peaks. Raman spatial mappings were measured using a combined Raman and FTIR microscope system (LabRAM ARAMIS IR², Horiba Jobin Yvon) with laser excitation at 523 nm. The Raman and PL analyses were performed in ambient conditions, the power of the laser lines was below 1 mW, the laser spot-size was approximately 1 μm, and the Si peak at 520.7 cm⁻¹ was used as a reference for wavenumber calibration. The XPS measurements were performed using an Uvica PHI X-ray spectrometer with Al Kα X-ray radiation (1486.6 eV). The binding energies were calibrated with C 1s at 284.5 eV. The AFM images were obtained using a microscope (XE-100, PSIA) in noncontact mode. The atomic structure of the MoS2 nanosheets was characterized using a TEM ( Tecnai G2 F30 ST, FEI) with an accelerating voltage of 300 eV. The SEM images were taken using a field-emission SEM (FE-SEM; S-4800, Hitachi) coupled with energy-dispersive X-ray spectroscopy (EDS). Absorption spectra were collected for a MoS2 thin film in a Varian Cary 50 UV–visible spectrophotometer. XRD patterns were recorded on an X-ray diffractometer (D/Max-2500, Rigaku) using Cu Kα radiation. The electrical measurements were carried out at room temperature in ambient conditions using a probe station (CPX-VP, Lakeshore).

Fabrication of MoS2 Thin Films. The MoS2 nanosheets dispersed in the NMP solution were first vacuum-filtered through a porous membrane (0.02 μm, Anodisc, Whatman or 0.2 μm, JGWP, Millipore). They were then washed with isopropyl alcohol and DI water. After that, the film was peeled off and dried in an air oven at 80 °C for 2 h to evaporate the residual moisture.

Fabrication of MoS2 Field-Effect Transistors. The exfoliated MoS2 nanosheets were deposited onto a 300 nm SiO₂/Si substrate using the dip-coating method. They were then dried at room temperature for 1 h. After that, the MoS2 nanosheets were carefully washed with DI water and dried again. The Au/Ti electrical contacts on MoS2 were fabricated using photolithography and electron-beam evaporation of Ti (10 nm) and Au (50 nm), followed by annealing at 150 °C in a vacuum oven for 2 h.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: XPS, SEM, EDS, optical microscopy, Raman, PL and AFM analyses of the electrochemically exfoliated MoS2 nanosheets. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


