Current Applied Physics 14 (2014) 264–268

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

# Controlled exfoliation of molybdenum disulfide for developing thin film humidity sensor

Shao-Lin Zhang [a], Hyang-Hee Choi [b], Hong-Yan Yue [c], Woo-Chul Yang [a,*]

[a] Department of Physics, Dongguk University, Seoul 100-715, Republic of Korea
[b] Institute of Nanoscience and Nanotechnology, Yonsei University, Seoul 120-749, Republic of Korea
[c] School of Material Science and Engineering, Harbin University of Science and Technology, Harbin 150-040, China

ARTICLE INFO

*Article history:*
Received 15 August 2013
Received in revised form
7 November 2013
Accepted 21 November 2013
Available online 2 December 2013

*Keywords:*
Molybdenum disulfide
Liquid exfoliation
Ultrasonic power
Dynamic light scattering
Humidity sensor

ABSTRACT

We report a facile, size-controllable exfoliation process using an ultrasound-assisted liquid method to fabricate few-layer molybdenum disulfide ($MoS_2$) nanosheets. The morphology, structure and size distribution of the nanosheets processed with different ultrasonic powers were examined by atomic force microscopy, Raman spectroscopy and dynamic light scattering. It was revealed that the size of nanosheets reduces and final yield increases with elevating ultrasonic power. Bulk and exfoliated $MoS_2$ based thin film sensors are fabricated by a simple drop casting method on alumina substrates. Our sensors exhibit excellent sensitivity with very quick response and recovery speed to humidity gas. Comparative studies are carried out to draw up the size or ultrasonic power dependent sensing behavior.



## 1. Introduction

Over the last few years, two-dimensional (2D) nanomaterials, such as graphene, tungsten disulfide ($WS_2$), and molybdenum disulfide ($MoS_2$), have become the hottest research issue, because they exhibit unusual electronic, optical, thermal, and mechanical properties, which are introduced by the quantum size effect associated with their ultra-thin structure [1–4]. These exceptional physical properties enable them to be the crucial elements for a range of applications, such as monolithic graphene circuits [5], high-performance $MoS_2$-based FET devices [6], and photo-transistors [7]. Two-dimensional (2D) nanomaterials also possess inherently high surface-to-volume ratio, which make them be a dominant candidate for gas sensor applications [8,9]. The 2D nature of these materials allows a total exposure of all their atoms, and the electron transport through these exposed surface atoms is highly sensitive to the absorbed molecular species. Moreover, the intrinsic low electric noise, due to the quality of their crystal lattice and 2D nature, tends to screen charge fluctuations more than that of other nanomaterials [10]. These distinct characteristics of 2D nanomaterials strongly suggest their potential for chemical catalyst and gas sensor utilization [11]. A recent study showed that a graphene-based gas sensor exhibited an excellent sensing property that a detection limit down to the single-molecule level was achieved [12].

As the analog of graphene, $MoS_2$ with semiconducting character, together with lower background carrier densities, is thus expected to display a comparative or preferable sensing performance. Several previous researches have demonstrated the promising sensing properties of mono- and multi-layer $MoS_2$ nanosheets toward various gases at room temperature. F. Perkins et al. fabricated single monolayer $MoS_2$ by the mechanical cleavage method, and their sensor exhibited highly selective reactivity to triethylamine among a range of analytes [13]. In another group, Hai Li et al. developed mono- and multi-layer $MoS_2$ film based field-effect transistors using a similar exfoliation method. Their $MoS_2$ nanosheets have successfully been used for sensing NO gas at room temperature, with rapid and dramatic response [14]. These results fully proved that $MoS_2$ nanosheets have potential for gas detection. Unfortunately, the fabrication methods used in these previous studies involve manual mechanical exfoliation, which is unsuited to mass production, and decreases the reproducibility of the electronic device. Moreover, the complicated and expensive e-beam lithography process utilized in these experiments also hinders their practical application. A facile method to efficiently exfoliate $MoS_2$, and economical process to fabricate sensor devices with high reliability are urgently required.

* Corresponding author. Tel.: +82 2 2290 1397; fax: +82 2 2260 8713.
*E-mail address:* wyang@dongguk.edu (W.-C. Yang).

1567-1739/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cap.2013.11.031

Bulk $MoS_2$ consists of hexagonal layers of molybdenum (Mo) sandwiched between two layers of sulfide (S) atoms. The bonding within these trilayer sheets is covalent, while the adjacent sheets are stacked via weak van der Waals interaction. The weak interlayer bonding allows the bulk $MoS_2$ to be exfoliated by proper external force. Up to now, besides the first adopted mechanical cleavage method [6,15], several methods have been developed to exfoliate $MoS_2$ bulk material, including chemical ion intercalation [16], and ultrasound-assistant liquid exfoliation [17,18]. Compared to the time-consuming and tough environment required for the ion intercalation method, the ultrasound-assistant liquid method possesses advantages, such as low-cost, ease of process, and potential for scale-up.

In this study, utilizing the ultrasound-assistant exfoliation method, we fabricated $MoS_2$ nanosheets in large scale in a solvent mixture with low boiling point. The effects of ultrasonic power on the size distribution and total yield of the final production were systematically examined. The successfully prepared $MoS_2$ nanosheets were fabricated into thin film sensors by a facile drop casting method. The thin film sensors were tested to moisture gases with relative humidity (RH) from 0 to 60%. It was found $MoS_2$ nanosheets based sensors exhibited excellent sensing performance towards humidity gas with very quick response and recovery. Moreover, the nanosheets fabricated with higher ultrasonic power exhibited better sensing properties than those with lower ultrasonic power. The size-dependent sensing performance of $MoS_2$ nanosheets based thin film sensors was carefully investigated. A reasonable sensing mechanism was proposed.

## 2. Experimental details

### 2.1. Ultrasonic power dependent exfoliation of $MoS_2$

All chemical regents were of analytical grade and were obtained commercially. Typically, $MoS_2$ powder (300 mg, 2 um, Aldrich–Sigma) was dispersed in 100 ml of a mixture of chloroform and acetonitrile with the ratio of 65:35. Then the dispersion was ultrasonically treated in iced water for 1 h using a horn probe sonic tip (Sonic VCX 750). Pulsed ultrasonic irradiation was performed for 20 s on and 10 s off to avoid damage to the ultrasonic processor, and reduce solvent heating and resultant degradation of the $MoS_2$ nanosheets. Various ultrasonic powers ranging from 350 W to 550 W were adopted to explore the ultrasonic power dependent effect on the final production. After ultrasonic treatment, the dark green dispersion was centrifuged at 3000 rpm for 30 min and the supernatant was collected. This process was repeated one time more to completely remove the un-exfoliated powder and aggregates. For the characterization of exfoliated $MoS_2$, a drop of solution containing the produced $MoS_2$ nanomaterial was placed on a $Si/SiO_2$ substrate, and then dried in air before it was observed by atomic force microscopy (AFM, Bruker Nano N8 NEOS) and Raman spectroscopy (HORIBA HR800). In order to examine the size evolution of $MoS_2$ nanosheets exfoliated with different ultrasonic power, as-prepared $MoS_2$ nanosheets were also investigated by dynamic light scattering (DLS). The DLS measurements were carried out by Malvern Zetasizer Nano ZS using a 633 nm HeNe laser. Samples were tested in quartz cuvettes having a 10 mm path length. The DLS apparatus was operated in backscatter mode at an angle of 173°. Before the measurement, the samples were equilibrated to 25 °C for 120 s. Values for solvent viscosity at 25 °C, as provided by the solvent suppliers, were entered into the software. An automatic measurement duration setting was used with automatic measurement positioning and automatic attenuation.

### 2.2. Fabrication and measurement of $MoS_2$ nanosheets based thin film sensor

Alumina substrates (4 mm × 4 mm) with interdigital Pt electrodes were pre-prepared and used as the sensor substrate. The alumina substrate were placed on a hot-plate with a temperature of about 60 °C. $MoS_2$ nanosheets solutions were then drop-cast onto the sensor substrates with micro-pipettes. The thickness of $MoS_2$ thin films was about 1 um which was controlled by the volume of solution in the micro-pipettes. After coating, the alumina substrates were heated at 80 °C for 1 h to eliminate the remaining solvent, and then sintered at 400 °C in Ar gas for 1 h to improve the adhesion and contact. The sensing performance of the $MoS_2$ nanosheets based thin film sensor towards humidity was tested. A source of humidity gas was created by a bubbling system with water bath. The humidity gas was then mixed with synthetic dry air with a mixing system equipped with mass flow controllers and mass flow meters. The desired humidity concentration was accurately tuned by the flow ratio of the humidity gas and dry air. The total flow was constantly set to 1000 sccm. A commercial humidity sensor was used to validate the actual relative humidity. The sensitivity is defined as follows:

$$S = \frac{R_H}{R_D}, \tag{1}$$

where, $R_D$ and $R_H$ represent the resistance of the sensor upon exposure to a dry air and a humidity gas, respectively. The response and recovery time are defined as the time taken by the sensor to achieve 90% of the total resistance change in the respective cases of adsorption and desorption.

## 3. Results and discussion

### 3.1. Characterization of exfoliated $MoS_2$ nanosheets

There are two main parameters affecting the quality of final production in ultrasound-assistant liquid exfoliation. These are solvent type and ultrasonic dosing. Hitherto, most of the former researches have focused on the selection of solvents to improve the dispersion of $MoS_2$ in solution, while very few studies have been carried out on the effect of ultrasonic dosing. It is believed that the parameters of the ultrasonic process also play a key role in the exfoliation process. Herein, we demonstrate the ultrasonic power dependent morphology evolution of $MoS_2$ nanosheets. Fig. 1(a) and (b) shows the typical AFM images of $MoS_2$ nanosheets obtained by ultrasonic power of 350 W and 550 W, respectively. It was found that the average size of nanosheets decreased as the ultrasonic dosing increased. The quantitative characterization made from the profile line in Figs. (a′) and (b′) further confirm this tendency. The average size of nanosheets obtained by 350 W ultrasonic treatment was about 200 nm, which is almost 2 times compared to that obtained by 550 W process. On the other hand, the thickness of both exfoliated $MoS_2$ nanosheets are similar ranging from 6 nm to 12 nm. Given that the thickness of a $MoS_2$ monolayer is about 0.9–1.2 nm [10], it suggests that the obtained $MoS_2$ existed as few-layer nanomaterials. This was also evidenced by the Raman spectroscopy, as shown in Fig. 1(c). A typical few-layer $MoS_2$ nanosheet gave bands at 386.54 and 407.69 $cm^{-1}$, which are associated with the in-plane vibrational ($E^1_{2g}$), and out-of-plane vibrational ($A_{1g}$) modes, respectively. Compared to the corresponding bulk sample, a slight red-shift of the $E^1_{2g}$ band and blue-shift of the $A_{1g}$ band in few-layer $MoS_2$ nanosheets were observed, which is consistent with previous reports [14,19].