FACILE PREPARATION AND CHARACTERIZATION OF LAYERED MoS_2 NANOSHEETS

X. WU[a], X. YAN[a, b, *], Y. DAI[a], D. SHA[a], J. LIU[a], H. ZOU[a], J. WANG[a]
[a]*School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China*
[b]*Institute for Advanced Materials, Jiangsu University, Zhenjiang 212013, Jiangsu, China*

Free-standing two-dimensional (2D) nanomaterials, such as graphene, boron nitride (BN), and molybdenum disulfide (MoS_2) with atomic thickness, have attracted extensive attentions because of their unique properties. In recent years, the study of atomically thick 2D nanosheets has mainly focused on the layered materials with weak van der Waals forces between the layers. Here, MoS_2 nanosheets have been successfully prepared by a facile, efficient, and scalable method using combined low-energy ball milling and sonication. The obtained products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM) and Raman spectroscopy. The influences of milling speed on the exfoliation of MoS_2 nanosheets were carefully investigated.

(Received January 21, 2015; Accepted March 12, 2015)

Keywords: MoS_2, 2D nanosheet, Preparation, Raman

1. Introduction

Transition metal dichalcogenides MX_2 (M = Mo, W, Nb and Ta, X = S, Se), which possess a layered structure, striking properties and promising applications, have attracted great attentions [1]. MoS_2 is one of the layered transition metal dichalcogenides. Monolayer MoS_2, compared to its bulk form, is a semiconductor with a direct band gap of 1.8 eV, and has a high fluorescence yield [2]. These unique properties make them promising candidates for wide applications in catalysis [3], energy storage [4], electronics [5,6], solid lubrication [7,8], hydrogen storage [9], and Li batteries [10]. The layered MoS_2 is constructed by unit S-Mo-S atoms, which has a covalent bond between metal and chalcogen, and weak van der Waals forces among the layers. Therefore, single or few-layer nanosheets of these materials can be obtained by using adhesive tapes for micromechanical cleavage, which was applied as the first method for mechanical fragmentation of layered materials into individual 2D nanosheets and has been used to prepare MoS_2 nanosheets [11]. Although this method provides high quality 2D nanosheets, the extremely low yield is a critical problem. Therefore, much effort has been devoted to prepare MoS_2 nanosheets with high yields and unique properties.

[*] Corresponding author: xhyan@mail.ujs.edu.cn

Recently, Zeng et al. have demonstrated a controllable lithium intercalation process via incorporation of layered bulk materials, such as MoS_2, WS_2, TiS_2, TaS_2, ZrS_2, and graphite, as the cathode in an electrochemical set-up [12]. However, the complicated electrochemical process is time consuming, extremely sensitive to the environment and incompatible with most solvents. Hence, it is desirable to develop an effective and facile approach for the preparation of MoS_2 nanosheets on a large scale in order to broaden their practical applications.

Herein, we demonstrate a simple and effective method to fabricate high-yield, single-layer 2D nanomaterials using a combined low-energy ball milling and sonication method. Also, the influences of the milling speed on the exfoliation of MoS_2 nanosheets were studied. The approach produced high yield MoS_2 nanosheets, which opens up possibilities for potential scalable applications.

2. Experimental details

2.1 Preparation of MoS_2 nanosheets samples

For preparing 2D MoS_2 nanosheets, 3.0 g MoS_2 raw powders and 200 ml 0.05 wt.% SDBS–water were loaded in a sealed polyethylene bottle with 90 g agate balls and then ball milled. The rotation speed of the planetary mill was set at 200 rpm. Some of the milled samples were taken out after milling for 12 h, followed by centrifugation at 5000 rpm for 20 minutes. After that, an additional 3 h of sonication of MoS_2 supernatants was applied.

2.2 Characterization methods

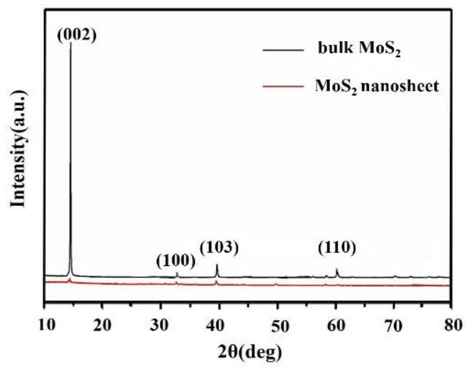
The X-ray diffraction (XRD) patterns were obtained using a D8 advance (Bruker-AXS) diffractometer with the 2θ range from 10 to 80°. The morphologies and structures of the samples were characterized by transmission electron microscopy (TEM) with a Japan JEM-100CX II transmission electron microscope and Atomic Force Microscope (AFM, MicroNano D3000). SERS spectra were investigated by Raman laser spectrometer (DXR) at the excitation line of 632.8 nm.

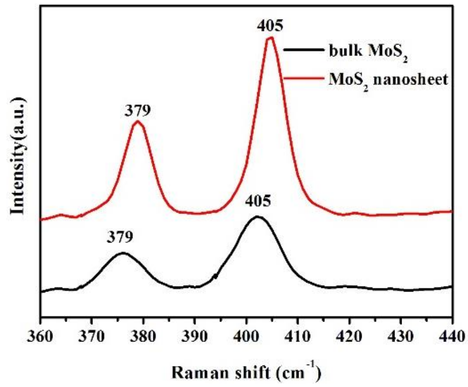
3. Results and discussion

3.1 Structure and morphology characterization

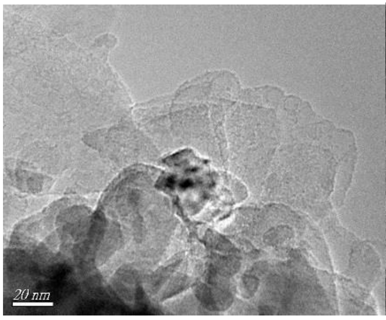
MoS_2 nanosheets were obtained by a combined low-energy ball milling and sonication method. The crystalline structure of initial bulk MoS_2 powders and the obtained MoS_2 nanosheets were confirmed by XRD, as shown in Fig. 1a. In the XRD patterns, the (002) reflection of the MoS_2 nanosheets is significantly weaker than that of the bulk MoS_2 powders. The weak peak can be caused by both a reduction in crystallite size and an increase in lattice strain [13]. Fig. 1b displays the Raman spectra of initial bulk MoS_2 powders and MoS_2 nanosheets excited by 632.8 nm line. The Raman spectra of both the initial bulk powders and the thin nanosheets of MoS_2 show two peaks at 379 and 405 cm^{-1}. The intense Raman peaks of the MoS_2 nanosheets offer strong evidence that the MoS_2 nanosheets are successfully prepared and of high quality.

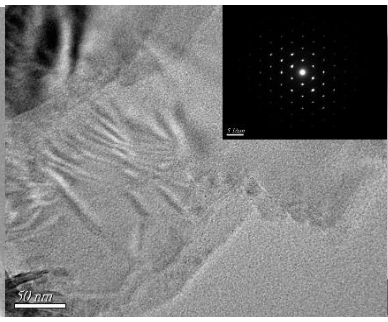
The structure and morphology of MoS_2 nanosheets were studied by TEM (Fig. 1c and d). As shown in Fig. 1c, the MoS_2 nanosheets were transparent to the electron beam due to their ultrathin thickness. The inset in Fig. 1d shows the SAED pattern of MoS_2 nanosheets. The pattern reveals a typical six-fold symmetry of MoS_2 nanosheets with high crystallinity, few defects, and an intrinsic structure. A typical photograph of MoS_2 suspension is shown in Fig. 1e. In our work, we also found that the dispersion of MoS_2 nanosheets is stable over periods of hundreds of hours.





(a) (b)



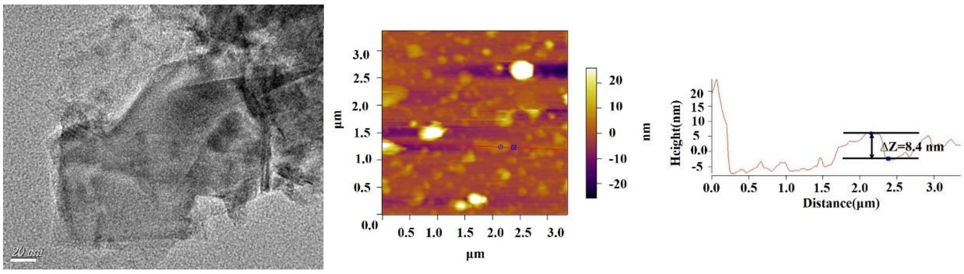


(c) (d) (e)

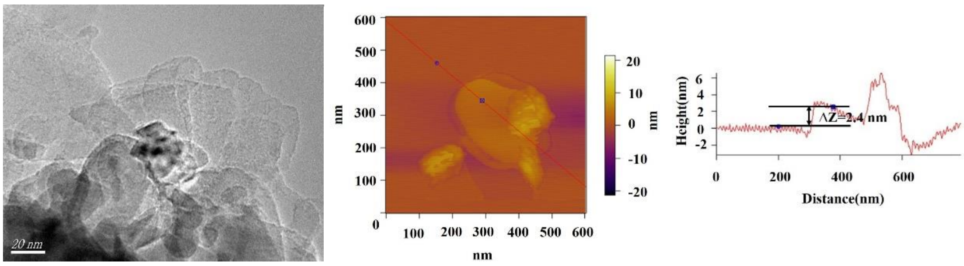
Fig. 1 XRD(a),Raman(b),TEM(c,d) and dispersion images(e)of the as-prepared MoS_2 nanosheets

3.2 Influences of the milling speed

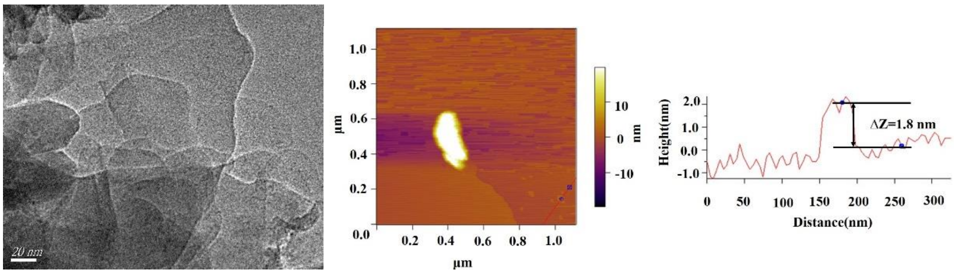
In order to study the influences of the milling speed on the exfoliation of MoS_2 nanosheets, a series of experiments have been performed. The milling speed was set at 100 rpm, 200 rpm and 250 rpm, respectively. Fig. 2 shows TEM and AFM images of the exfoliated MoS_2 nanosheets. It can be seen from the TEM and AFM images (Fig. 2a) that the nanosheets corresponding to the products of the milling speed at 100 rpm are poorly exfoliated and stacked together. An enlargement area was characterized using AFM and the red line was marked. The height of the selected two points on the red line was 8.4 nm. The selected nanosheet possesses about 14 layers from the previous theoretical and experimental results that the monolayer thickness is 0.6 nm for S-Mo-S structures [14]. MoS_2 nanosheets were sharply thinning at the milling speed of 200 rpm and the thickness reached to 2.4 nm, which indicated that the number of layers was reduced to four (Fig. 2b). The milling speed was further increased to 250 rpm, and the height of the selected two points of AFM images (Fig. 2c) was measured to be 1.8 nm. It can be seen that nanosheets thickness decreases with the increasing milling speed. The thickness of the nanosheets varies little when the milling speed reaches to 250 rpm. What’s more, from the TEM images (Fig. 2b and 2c), it can be seen that we have already successfully prepared monolayer and few-layered MoS_2 nanosheets though the monolayer MoS_2 nanosheet didn’t appear yet in the selected area of AFM images.



(a)



(b)



(c)

Fig. 2. TEM and AFM images of MoS_2 nanosheets obtained at different milling speed: a) 100 rpm, b) 200 rpm and c) 250 rpm

SERS spectra of MoS_2 nanosheets prepared at different milling speed are shown in Fig. 3. It displays the Raman spectra of MoS_2 nanosheets excited by 632.8 nm line in air ambient environment. As shown in Fig.3, the peaks of the MoS_2 nanosheets is nearly consisten. The characteristic peaks of the MoS_2 nanosheets obtained at the milling speed of 200 rpm is relatively strong, which may result from its relatively uniform layers and size.

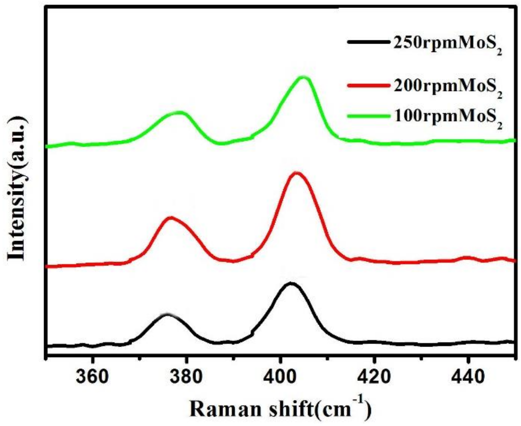


Fig. 3. Raman characterization of MoS_2 nanosheets obtained at different milling speed: (a) 100 rpm, b) 200 rpm and c) 250 rpm

4. Conclusions

In summary, 2D MoS_2 nanosheets have been obtained successfully via a combined low-energy ball milling and sonication method. The influences of the milling speed on layers of the MoS_2 nanosheets were discussed. When the milling speed is 250 rpm, the MoS_2 nanosheets have already been deeply exploited. This efficient and simple method can be applied as a general method for the production of 2D nanosheets especially transition metal dichalcogenides. This proposed approach will have great potential prospects for development of large scale 2D materials-based devices.

Acknowledgements

This work is supported by the Six Talents Peak Project in Jiangsu Province (2011-ZBZZ045), the Jiangsu Province Ordinary University Graduate Student Innovation Project (SJLX_0462) and the Student Research Training Program of Jiangsu University (13A388, Y13A159, 201410299009Z).

Reference

[1] J. Xu, H. Tang, G. Tang, C. Li, Chalcogenide Lett. **11**, 265 (2014).
[2] Y Yao, Z Lin, Z Li, X Song, K Moon, C Wong, J. Mater. Chem. **22**, 13494 (2012).
[3] R. R. Chianelli, M. H. Siadati, M. P. D. Rosa, G. Berhault, J. P. Wilcoxon, R. Bearden, B. L. Abrams, Catal. Rev. Sci. Eng. **48**, 1 (2006).
[4] J.W. Seo, Y.W. Jun, S.W. Park, H. Nah, T. Moon, B. Park, J.G. Kim, Y.J. Kim, J. Cheon, Angew. Chem. **119**, 8984 (2007).
[5] A. Ayari, E. Cobas, O. Ogundadegbe, M.S. Fuhrer, J. Appl. Phys. **101**, 014507 (2007).
[6] H. Li, Z.Y. Yin, Q.Y. He, H. Li, X. Huang, G. Lu, D.W.H. Fam, A. I. Y. Tok, Q. Zhang, H. Zhang, Small **8**, 63 (2012).

[7] J.A. Oflivy, Wear **160**, 171 (1993).
[8] R.L. Fusaro, ASLE Trans. **25**, 141 (1982).
[9] Z.Z. Wu, B.Z. Fang, A. Bonakdarpour, A.K. Sun, D.P. Wilkinson, D.Z. Wang, Appl. Catal. B: Environ. **125**, 59 (2012).
[10] J. Rourel, R. Brec, Rev. Mater. Sci. A **16**, 137 (1986).
[11] B. Radisavljevic, M. B. Whitwick, A. Kis, ACS Nano **5**, 9934 (2011).
[12] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, H. Zhang, Angew. Chem. Int. Ed. **50**, 11093 (2011).
[13] O.M. Lemine, Superlattice. Microst. **45**, 576 (2009).
[14] J. Zhao, Z.C. Zhang, S.S. Yang, H.L. Zheng, Y.B. Li. J. Alloys Compd. **559**, 87 (2013).