Ultrasound-Assisted Alkaline Solution Reflux for As-Exfoliated MoS$_2$ Nanosheets

Pei-Rong Wu, Zan Liu, and Zhi-Lin Cheng*

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

ABSTRACT: A facile approach was developed to produce MoS$_2$ nanosheets by ultrasound-assisted reflux exfoliation, which was highly efficient for large-scale production and sustainable for environment. The interlayer force of bulk MoS$_2$ was first exhausted in employing LiOH/NaOH solution by reflux and thereafter quickly exfoliated by ultrasound. The lateral size of the as-prepared MoS$_2$ nanosheets with about 2–9 layers became smaller. Definitely, the average friction coefficient and wear scar diameter of 0.08 wt % MoS$_2$-based oil decreased by about 21.87 and 38.09% relative to the base oil, which displayed better antifriction and antwear performances.

1. INTRODUCTION

MoS$_2$ has attracted the attention of many researchers, owing to the interlayer van der Waals force and intralayer covalent bond, which showed excellent properties in the field of catalyst, battery, sensor, transistor, hydrogen storage, supercapacitor, and so on. More importantly, MoS$_2$ also exhibited excellent lubrication performance due to the interlayer van der Waals force. At present, the bulk MoS$_2$ has been widely used as an antiwear additive in solid greases, but it cannot be used in liquid lubricants due to its unstable dispersion. The specific surface area of the bulk MoS$_2$ is increased through nanotechnology to obtain MoS$_2$ nanosheets and enhance the stable dispersion in liquid lubricants. Definitely, various MoS$_2$ nanomaterials have proven to exhibit preferable friction-reducing performance. This finding showed that the structure of MoS$_2$ nanomaterials obviously affected the friction-reducing properties. Yi et al. synthesized three morphologies of MoS$_2$ nanomaterials, including flower-like, microspheres, and nanosheets, by hydrothermal and solvothermal methods. The as-synthesized MoS$_2$ in liquid paraffin improved the tribological properties. MoS$_2$ nanosheets exhibited excellent tribological performances compared to flower-like MoS$_2$ and MoS$_2$ microspheres under the same testing conditions. As far as the antifriction and antwear in oil are concerned, the quality of nanosheets required is much lower than for other purposes. Conversely, too thin or too large, both are improper to be used in oil.

Up to now, many highly efficient exfoliating methods have been exploited to prepare MoS$_2$ nanosheets. Krishnamoorthy et al. successfully prepared MoS$_2$ nanosheets with few layers using 1-methyl-2-pyrrolidinone (NMP) as an exfoliated solvent and via a ball milling method. Varrla et al. demonstrated that the bulk MoS$_2$ in the aqueous surfactant solution was massively sheared and exfoliated to MoS$_2$ nanosheets with a mean thickness of 4.6 nm using a kitchen blender. Bang et al. provided an easy liquid-phase exfoliation method with NMP and NaOH to improve the yield of single-layered MoS$_2$ nanosheets and the thickness of the as-prepared MoS$_2$ nanosheets varied from 1 to 9 nm. Additionally, the Li-intercalated exfoliation has been successfully achieved in many types of nanosheets. Therefore, Liu et al. obtained ultrathin and high-yield MoS$_2$ nanosheets with a uniform thickness of 4.68 nm through the hydrothermal exfoliation route using Li$^+$ and ethylene glycol. However, the expensive Li source and hazardous organic solvent still hindered the scalable production. Meanwhile, the superimposing of MoS$_2$ nanosheets usually took place after cleaning the organic solvent. Recently, we successfully exfoliated BN to few layers via the hydrothermal intercalation and exfoliation method with NaOH/KOH solutions. Due to this idea, the exfoliation of bulk MoS$_2$ in mixed alkaline solution became a feasible method.

In this paper, we provided an efficacious exfoliation method based on the well-established ultrasound-assisted reflux method to prepare MoS$_2$ nanosheets. The as-exfoliated MoS$_2$ nanosheets were detected through a series of characterization methods. Then the friction and wear performances of MoS$_2$ nanosheets in oil were tested through a four-ball friction machine.

2. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of MoS$_2$ and four kinds of as-exfoliated MoS$_2$. In Figure 1a, all of the MoS$_2$ samples show four feature peaks at 14.4, 32.7, 39.5, and 58.3°, ascribing to the (002), (100), (103), and (110) planes of MoS$_2$ (JCPDS No. 37-1492), respectively. Every peak is attributed to the lattice of representative MoS$_2$ and there is no additional peak from MoO$_3$. It proves that this MoS$_2$ is a single phase and polycrystalline structure. In particular, all lattice planes of
four kinds of as-exfoliated MoS$_2$ show weaker peak intensities than bulk MoS$_2$. The possible reason is that the as-exfoliated MoS$_2$ has fewer layers than bulk MoS$_2$. In Figure 1b, the bulk MoS$_2$ has larger lateral size and thickness. Obviously, four kinds of as-exfoliated MoS$_2$ exhibit a smaller size and more transparent nanosheets (Figure 1c−f). More importantly, after the processes using a single alkali solution (Figure 1c,d) and a single reflux method using alkaline solution (Figure 1e), the bulk MoS$_2$ is exfoliated into multilayer. In comparison to these as-exfoliated MoS$_2$ samples, the thickness of MoS$_2$−Li$^+$/Na$^+$ is thinnest. This result proves that the ultrasound after the reflux process using mixed alkali solutions accounts for the deep exfoliation of the bulk MoS$_2$ into fewer layers.23

This indicates that bulk MoS$_2$ exfoliated by both Li$^+$ and Na$^+$ under the ultrasound-assisted alkaline solution reflux route plays an important role in the exfoliation process. In addition, the percentage of the size for MoS$_2$−Li$^+$/Na$^+$ is calculated (Figure 2d) according to the TEM image of MoS$_2$−Li$^+$/Na$^+$ in 10 μm (Figure 2c). The percentage of the nanoscale size (<1 μm) is as high as 78.29% and the vast majority size is below 2.0 μm.

The thickness and size of MoS$_2$−Na$^+$, MoS$_2$−Li$^+$, and MoS$_2$−Li$^+$/Na$^+$ are verified by atomic force microscopy (AFM) (Figure 3a−c). In Figure 3a,b, MoS$_2$−Na$^+$ and MoS$_2$−Li$^+$ have about 2.70−5.33 and 2.54−6.15 nm of the height and the number of the corresponding layers is about 4−9 layers and 4−10 layers. MoS$_2$−Li$^+$/Na$^+$ (Figure 3c) has a larger irregular-shaped size, the height is about 1.00−5.48 nm, which is lower than 25 cm$^{-1}$ of the bulk MoS$_2$. This suggests that the number of layers for MoS$_2$−Li$^+$/Na$^+$ decreases after exfoliation.26,27

In Figure 2b, two peaks at about 630 nm (1.97 eV) (B) and 680 nm (1.82 eV) (A) are shown in the UV−vis spectra of MoS$_2$−Li$^+$/Na$^+$ dispersions. The two peaks are assigned to the exciton transitions of MoS$_2$ at the first Brillouin zone.28 After exfoliation, the peak of MoS$_2$−Li$^+$/Na$^+$ is consistent with the bulk MoS$_2$. However, MoS$_2$−Li$^+$/Na$^+$ shows more pronounced peaks than MoS$_2$, indicating that the ultrasound-assisted alkaline solution reflux route plays an important role in the exfoliation process. In addition, the percentage of the size for MoS$_2$−Li$^+$/Na$^+$ is calculated (Figure 2d) according to the TEM image of MoS$_2$−Li$^+$/Na$^+$ in 10 μm (Figure 2c). The percentage of the nanoscale size (<1 μm) is as high as 78.29% and the vast majority size is below 2.0 μm.
and the number of corresponding layers is about 2–9 layers. The as-exfoliated MoS$_2$–Li$^+$/Na$^+$ is further examined by high-resolution transmission electron microscopy (HRTEM) (Figure 3d). The thickness of MoS$_2$–Li$^+$/Na$^+$ with 0.62 nm of interlayer basal spacing is up to about 2–4 layers due to more easily exfoliated edges of nanosheets, which corresponds to the (002) plane of MoS$_2$. The corresponding selected area electron diffraction pattern (Figure 3e) of MoS$_2$–Li$^+$/Na$^+$ reveals polylattice diffraction rings, showing the retention of polycrystalline MoS$_2$–Li$^+$/Na$^+$ during exfoliation.

Figure 3 displays the tribology data of 150 SN base oil and the base oil with 0.08 wt % MoS$_2$–Li$^+$/Na$^+$ inspecting for 6 h. In Figure 4a, the friction coefficient (COF) of MoS$_2$–Li$^+$/Na$^+$ is less than that of base oil throughout the test time. Compared to the base oil, the average COF and average wear scar diameter (AWSD) of MoS$_2$–Li$^+$/Na$^+$ are decreased by about 21.87 and 38.09%, respectively. The result indicates that the bulk MoS$_2$ slides with difficulty into the contact surface of the steel ball with the flow of the base oil to reduce the COF and WSD due to MoS$_2$ with a large size, a thick thickness and poor dispersibility in base oil. Owing to the MoS$_2$–AC-S with fewer layers and smaller size, it is easy to infiltrate into the contact surfaces of counterpart to become a tribofilm. Surprisingly, the COF of MoS$_2$–Li$^+$/Na$^+$ in base oil is unsatisfied in testing time. Figure 4c,d show three-dimensional (3D) profiles of wear surfaces of balls tested by base oil and the base oil with 0.08 wt % MoS$_2$–Li$^+$/Na$^+$. The contact areas of testing balls are severely damaged to a different degree after 6 h. Compared with the two kinds of wear mark, the damaged surface of the steel ball after MoS$_2$–Li$^+$/Na$^+$ as additives is decreased owing to preferably becoming the tribofilm on the wear surface, when the MoS$_2$–Li$^+$/Na$^+$ nanosheets in base oil contacted the steel balls. For further demonstration of the tribofilm, the wear surfaces of balls are determined by Raman spectroscopy. The appearance of two characteristic peaks of MoS$_2$ on the contact surfaces examined by MoS$_2$–Li$^+$/Na$^+$. The friction value decreasing mechanism is deduced that MoS$_2$ nanosheets in base oil can smoothly slip into the contact surface to prevent the wear of steel ball.32,33

3. CONCLUSIONS

In summary, the MoS$_2$ nanosheets with about 2–9 layers were successfully prepared by an ultrasound-assisted reflux exfoliation method. The ultrasound processing played an important role in the union exfoliation. MoS$_2$–Li$^+$/Na$^+$ as lubrication additives were added into 150 SN base oil to evaluate their lubrication properties. COF and WSD of 0.08 wt % MoS$_2$–Li$^+$/Na$^+$ nanosheets in base oil decreased by 21.87 and 38.09% compared to the base oil, revealing better tribological properties.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. Two-dimensional MoS$_2$ nanosheets were obtained by the exfoliation method combining the reflux and ultrasound process. In particular, 0.73 g of LiOH and 1.22 g of NaOH were dispersed in 180 mL of deionized water, then 1.02 g of bulk MoS$_2$ (Sinopharm Chemical Reagent Co., Ltd) was added into the above solution and stirred at room temperature for 2 h. Next, the suspension was transferred to a 250 mL three-necked flask with a stirrer and refluxed at 100 °C for 3 h, denoted as MoS$_2$–R. Then, the three-necked flask with MoS$_2$ nanosheets was placed in an ultrasonic bath for 2 h, and the cold water was continuously added into the ultrasonic bath to control the water temperature during the ultrasonic process. Next, the solution was allowed to stand for 30 min and the precipitate was removed. Finally, the upper liquid was cleaned by deionized water and anhydrous ethanol at least three times, dried at 60 °C for 24 h, denoted MoS$_2$–Li$^+$/Na$^+$. In addition, the MoS$_2$–Li$^+$ sample was obtained in the absence of NaOH and the MoS$_2$–Na$^+$ sample was obtained in the absence of LiOH in the same reflux and ultrasound exfoliation method. The exfoliation illustration of MoS$_2$ nanosheets is proposed in Figure S.

4.2. Tribological Properties Testing. MoS$_2$–Li$^+$/Na$^+$ nanosheets were added into 150 SN base oil through the
An ultrasound method to obtain MoS$_2$−Li$^+$/Na$^+$-based oils. The testing of tribological properties was executed in an MMW-1 four-ball machine (Jinan Chenda Ltd. Co., in China). The rotating speed, stably applied load, and testing time of the test parameters were set to 1200 rpm, 100 N, and 6 h, respectively. The wear scar of the steel ball was cleaned with ethanol to remove the base oil and then detected through the Raman spectrometer and 3D laser scanning microscope.

4.3. Characterization. XRD analysis was performed by Powder X-ray diffraction (Bruker AXS, German). The SEM images were obtained by an S-4800 II Field emission scanning electron microscope (Hitachi, Japan). The TEM images were obtained by a Tecnai 12 transmission electron microscope (Philips, Netherlands). The Raman spectra were recorded by an InVia Raman spectrometer (Renishaw, Britain). The UV−vis spectra were recorded on a Cary 5000 spectrophotometer (Varian). HRTEM images were obtained by a Tecnai G2 F30 S-TWIN field emission transmission electron microscope (FEI). The AFM images were obtained on a nanoscope (Digital Instruments). The wear scar micrographs were recorded by an LSM 700 3D Laser Scanning Microscope (CARL ZEISS, German).

Figure 4. (a) COFs and (b) the AWDSs of base oil and the base oil with 0.08 wt % MoS$_2$−Li$^+$/Na$^+$. The Raman spectra and 3D laser scanning micrographs (inset) of the wear steel ball examined by (c) base oil and (d) the base oil with 0.08 wt % MoS$_2$−Li$^+$/Na$^+$.

Figure 5. Exfoliation illustration of MoS$_2$ nanosheets.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was funded by the Talent Introduction Fund of Yangzhou University (2012), the Zhenjiang High Technology Research Institute of Yangzhou University (2017), the Innovative Talent Program of Green Yang Golden Phoenix (yzlyjfk2015CX073), the Yangzhou Social Development Project (YZ2016072). The authors also acknowledge the project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (PPZY2015B112). The data of this paper originated from the Test Center of Yangzhou University.

**REFERENCES**

1. Wang, X. W.; Wu, P. Y. Aqueous phase exfoliation of two-dimensional materials assisted by thermoresponsive polymeric ionic liquid and their applications in stimuli-responsive hydrogels and highly thermally conductive films. *ACS Appl. Mater. Interfaces* **2018**, *10*, 2504−2514.

2. Yu, H.; Zhu, H. L.; Dargusch, M.; Huang, Y. L. A reliable and highly efficient exfoliation method for water-dispersible MoS$_2$ nanosheet. *J. Colloid Interface Sci.* **2018**, *514*, 642−647.

3. Chen, L.; Ji, L. F.; Zhao, J.; Zhang, X.; Yang, F. C.; Liu, J. T. Facile exfoliation of molybdenum disulfide nanosheets as highly efficient electrocatalyst for detection of m-nitrophenol. *J. Electroanal. Chem.* **2017**, *801*, 300−305.

4. Voiry, D.; Salehi, M.; Silva, R.; Fujita, T.; Chen, M. W.; Asefa, T.; Shenoy, V. B.; Eda, G.; Chhowalla, M. Conducting MoS$_2$...
nanosheets as catalysts for hydrogen evolution reaction. *Nano Lett.* 2013, 13, 6222–6227.

(5) Cui, Z.; Chu, H.; Gao, S. P.; Pei, Y.; Ji, J.; Ge, Y. C.; Dong, P.; Ajaney, P. M.; Shen, J. F.; Ye, M. X. Large-scale controlled synthesis of porous two-dimensional nanosheets for hydrogen evolution reaction through a chemical pathway. *Nanoscale* 2018, 10, 6168–6176.

(6) Bang, G. S.; Nam, K. W.; Kim, J. Y.; Shin, J.; Choi, J. W.; Choi, S. Y. Effective liquid-phase exfoliation and sodium ion battery application of MoS 2 nanosheets. *ACS Appl. Mater. Interfaces* 2014, 6, 7084–7089.

(7) Guo, B. J.; Peng, Y.; Chen, X. F.; Li, B.; Yu, K. Preparation of yolk-shell MoS 2 nanosheets covered with carbon shell for excellent lithium-ion battery anodes. *Appl. Surf. Sci.* 2017, 434, 1021–1029.

(8) Gan, X.; Zhao, H. M.; Dong, K. Y.; Lei, D. Y.; Zhang, Y. B.; Qian, X. Covalent functionalization of MoS 2 nanosheets synthesized by liquid phase exfoliation to construct electrochemical sensors for Cd (II) detection. *Talanta.* 2018, 182, 38–48.

(9) Bhattacharjee, S.; Ganapathi, K. L.; Mohan, S.; Bhat, N. A sub-thermionic MoS 2 FET with tunable transport. *Appl. Phys. Lett.* 2017, 111, 163501–163505.

(10) Cao, J. M.; Zhou, J.; Zhang, Y. F.; Liu, X. W. Theoretical study of H 2 adsorbed on monolayer MoS 2 doped with N, S, P. *Microelectron. Eng.* 2018, 190, 63–67.

(11) Gao, Y. P.; Huang, K. J.; Wu, X. T.; Hou, Z. Q.; Liu, Y. Y. MoS 2 nanosheets assembling three-dimensional nanosystems for enhanced-performance supercapacitor. *J. Alloys Compd.* 2018, 741, 174–181.

(12) Wu, P. R.; Li, W.; Liu, Z.; Cheng, Z. L. Preparation and tribological properties of oleic acid-decorated MoS 2 nanosheets with good oil dispersion. *J. Dispersion Sci. Technol.* 2018, 39, 1742–1751.

(13) Wu, P. R.; Feng, Y. M.; Ge, T.; Kong, Y. C.; Ma, Z. S.; Liu, Z.; Cheng, Z. L. An investigation on tribological properties of the chemically capped zinc borate(ZB)/MoS 2 nanocomposites in oil. *J. Ind. Eng. Chem.* 2018, 63, 157–167.

(14) Hu, E. Z.; Xu, Y.; Hu, K. H.; Hu, X. G. Tribological properties of 3 types of MoS 2 additives in different base greases. *Lubr. Sci.* 2017, 29, 1–15.

(15) Tang, G. G.; Zhang, J.; Liu, C. C.; Zhang, D.; Wang, Y. Q.; Tang, H. Z.; Li, C. S. Synthesis and tribological properties of flower-like MoS 2 microspheres. *Ceram. Int.* 2014, 40, 11575–11580.

(16) Zhao, J.; He, Y. Y.; Wang, Y. F.; Wang, W.; Yan, L.; Luo, J. B. An investigation on the tribological properties of multilayer graphene and MoS 2 nanosheets as additives used in hydraulic applications. *Tribol. Int.* 2016, 97, 14–20.

(17) Chen, Z.; Liu, X. W.; Liu, Y. H.; Gunsel, S.; Luo, J. B. Ultrathin MoS 2 nanosheets with superior extreme pressure property as boundary lubricants. *Sci. Rep.* 2015, 5, No. 12869.

(18) Yi, M. R.; Zhang, C. H. The synthesis of MoS 2 particles with different morphologies for tribological applications. *Tribol. Int.* 2017, 116, 285–294.

(19) Krishnamoorthy, K.; Pazhamalai, P.; Veerasubramani, G. K.; Kim, S. J. Mechanically delaminated few layered MoS 2 nanosheets based high performance wire type solid-state symmetric super-capacitors. *J. Power Sources* 2016, 321, 112–119.

(20) Varrla, E.; Backes, C.; Paton, K. R.; Harvey, A.; Gholamvand, Z.; McCauley, J.; Coleman, J. N. Large-scale production of size-controlled MoS 2 nanosheets by shear exfoliation. *Chem. Mater.* 2015, 27, 1129–1139.

(21) Bang, G. S.; Nam, K. W.; Kim, J. Y.; Shin, J.; Choi, J. W.; Choi, S. Y. Effective liquid-phase exfoliation and sodium ion battery application of MoS 2 nanosheets. *ACS Appl. Mater. Interfaces* 2014, 6, 7084–7089.

(22) Liu, Y. D.; Ren, L.; Qi, X.; Yang, L. W.; Hao, G. L.; Li, J.; Wei, X. L.; Zhong, J. X. Preparation, characterization and photo-electrochemical property of ultrathin MoS 2 nanosheets via hydrothermal intercalation and exfoliation route. *J. Alloys Compd.* 2013, 571, 37–42.

(23) Ma, Z. S.; Ding, H. L.; Liu, Z.; Cheng, Z. L. Preparation and tribological properties of hydrothermally exfoliated ultrathin hexagonal boron nitride nanosheets (BNNSs) in mixed NaOH KOH solution. *J. Alloys Compd.* 2019, 784, 807–815.

(24) Zhang, Y. F.; Zuo, L. Z.; Huang, Y. P.; Zhang, L. S.; Cai, F. L.; Fan, W.; Liu, T. X. In-situ growth of few-layered MoS 2 nanosheets on highly porous carbon aerogel as advanced electrocatalysts for hydrogen evolution reaction. ACS Sustainable Chem. Eng. 2015, 3, 3140–3148.

(25) Wang, D. Z.; Zhang, X. Y.; Bao, S. Y.; Zhang, Z. T.; Fei, H.; Wu, Z. Z. Phase-engineering of multiphase 1T/2H MoS 2 catalyst for highly efficient hydrogen evolution. *J. Mater. Chem. A* 2017, 5, 2681–2688.

(26) Wu, S. Y.; Huang, H.; Shang, M. X.; Du, C. C.; Wu, Y.; Song, W. B. High visible light sensitive MoS 2 ultrathin nanosheets for photoelectrochemical bioinspiring. *Biosens. Bioelectron.* 2016, 92, 646–653.

(27) Liu, R. N.; Liao, B. X.; Guo, X. D.; Hu, D. B.; Hu, H.; Du, L. J.; Yu, H.; Zhang, G. Y.; Yang, X. X.; Dai, Q. Study of graphene plasmons in graphene-MoS 2 heterostructures for optoelectronic integrated devices. *Nanoscale* 2017, 9, 208–215.

(28) Hai, X.; Chang, K.; Pang, H.; Li, M.; Li, P.; Liu, H. M.; Shi, L.; Ye, J. H. Engineering the edges of MoS 2 ( WS 2) crystals for direct exfoliation into monolayers in polar micromolecular solvents. *J. Am. Chem. Soc.* 2016, 138, 14962–14969.

(29) Wu, J. Z.; Dai, J.; Shao, Y. B.; Cao, M. Q.; Wu, X. H. Carbon dot-assisted hydrothermal synthesis of flower-like MoS 2 nanospheres constructed by few-layered multiphase MoS 2 nanosheets for supercapacitors. *Rsc Adv.* 2016, 6, 77999–78007.

(30) Wu, P. R.; Cheng, Z. L.; Kong, Y. C.; Ma, Z. S.; Liu, Z. Templated synthesis of plate-like MoS 2 nanosheets assisted with HNTs and their tribological performance in oil. *J. Nanopart. Res.* 2018, 20, No. 138.

(31) Yang, C. Z.; Hou, X.; Li, Z. W.; Li, X. H.; Yu, L. G.; Zhang, Z. J. Preparation of surface-modified lanthanum fluoride-graphene oxide nanohybrids and evaluation of their tribological properties as lubricant additive in liquid paraffin. *Appl. Surf. Sci.* 2016, 388, 497–502.

(32) Wu, P. R.; Liu, Z.; Cheng, Z. L. Growth of MoS 2 nanotubes templated by halloysite nanotubes for the reduction of friction in oil. *ACS Omega* 2018, 3, 15002–15008.

(33) Zhang, L.; He, Y.; Feng, S. W.; Zhang, L.; Zhan, Y. Q.; Wang, Y. J. Preparation and tribological properties of novel boehmite/graphene oxide nano-hybrid. *Ceram. Int.* 2016, 42, 6178–6186.