MRS Communications (2020), *10*, 317–323

doi:10.1557/mrc.2020.26

MRS Communications

Research Letter

Convenient synthesis of inorganic fullerene-like WS_2 self-lubricating films and their tribological behaviors

Shikai Liu, **Kunlun Jia**, **Yingxin Chen**, and **Sankui Xu**, School of Materials Science and Engineering, Henan University of Technology, Zhengzhou 450001, Henan, P. R. China
Feng Li, Key Laboratory of Surface and Interface Science and Technology, Zhengzhou University of Light Industry, Zhengzhou 450002, Henan, P. R. China; American Advanced Nanotechnology, Houston, TX 77459, USA
Address all correspondence to Shikai Liu at **shikai_liu@haut.edu.cn** and Sankui Xu at **sankui_xu@haut.edu.cn**

(Received 29 February 2020; accepted 25 March 2020)

Abstract

In the present work, an efficient route has been further explored to achieve the batch synthesis of inorganic fullerene (IF)-WS_2 nanoparticles, and the self-lubricating film is conveniently prepared by coating these nanoparticles on the surface of metal substrates. The as-synthesized IF-WS_2 nanoparticles have a closed hollow structure with an average particle size of about 50 nm and are evenly distributed in the self-lubricating film. Further friction tests show that the film has excellent friction properties, with its lowest friction coefficient of approximately 0.008, which can be mainly attributed to the unique hollow cage structure and a smaller particle size of the IF-WS_2 nanoparticles.

Introduction

Friction and wear of the surfaces in many mechanical working environments seriously affect the power loss and mechanical durability. The development of efficient lubricants that possess lower friction coefficients is an effective way to improve the lubrication performance of mechanical surfaces. In recent decades, inorganic fullerenes (IFs) have good prospects in the field of lubrication due to their unique hollow-cage structure and excellent physical and chemical properties.[1–3] As early as 1992, it was recognized that layered metal dihalides (such as MoS_2 and WS_2) can form IF-like structures.[4,5] At that time, it was known that these layered solids had good lubrication performance. The researchers then demonstrated that IF-WS_2 or IF-MoS_2 nanoparticles have significantly better lubrication performance than that of the corresponding layered structure.[6–8] With the development of modern industrial technology, great attention have been attracted to solve the lubrication problems under special working conditions (e.g. vacuum or strong radiation and corrosion).[9,10] A large number of studies show that IF-MS_2 (M = W, Mo) has a good potential to solve these problems,[11–15] but there are still many problems in a large-scale application.

Self-lubricating films are often used as an alternative lubricant when these lubricating oils (greases) cannot be used. It has been found that introducing WS_2 or MoS_2 nanoparticles into the workpiece surface to form self-lubricating films can reduce friction very well. However, to make these lubricating films, either the synthesis method and process are complex and difficult to control, or special conditions and equipment are needed.[16–19] Recently, lubricating films were obtained with good friction properties by electrodeposition. It is shown that the introduction of nanoparticles into metal electrodeposition can change the surface roughness and the wettability.[20,21] However, it is not effective in the low-cost, simple, and efficient preparation of IF-MS_2 self-lubricating films, which need further investigations.

In this work, the batch synthesis of IF-WS_2 nanoparticles is further studied based on our previous study,[22] and a uniform IF-WS_2 self-lubricating film is prepared on the surface of 45# steel by a simple deposition method. The tribological characteristics of the lubricating film are also systematically studied. The possible lubrication mechanism is also proposed.

Experimental

Preparation of IF-WS_2 nanoparticles

IF-WS_2 nanoparticles were successfully synthesized by the enlarged "Thermal Sulfurized Method",[22] which yields several hundred gram quantities and can well meet the requirements of production in batches. The basic preparation process is shown in Supplementary Fig. S1. Firstly, WO_3 nanoparticles were prepared by an ultrasonic-assisted chemical precipitation method. Then, the composite powders of WO_3 and sulfur (S) were obtained by mixing them with S powder in a molar ratio of 1:3 and ball milling with anhydrous ethanol as the grinding medium. Finally, the composite powders were placed in a vacuum furnace and reacted in hydrogen atmosphere of 60 kPa at 550 °C for 1 h to obtain IF-WS_2 nanoparticles.

Preparation of IF-WS_2 self-lubricating films

A total of 0.1 g of as-synthesized IF-WS_2 nanoparticles were uniformly dispersed into 8 mL of absolute ethanol aqueous solution (V_{C2H6O}: V_{H2O} = 3:1). After ultrasonic vibration for

10 min, 1 mL of 5 wt% polyvinyl alcohol solution was added dropwise, and the suspension was prepared by ultrasonic dispersion for another 5 min. And then, IF-WS_2 was coated on the surface of the test piece (45# steel) of the friction testing machine by a spin coating method and dried at 110 °C for 3 h to obtain IF-WS_2 dry lubricating film.

For comparison, 2H-WS_2 lubricating film was prepared by the same method. The selected 2H-WS_2 was purchased from Hunan Changsha Lianheng Technology Co., Ltd., and the average particle size was about 0.5 μm after ball milling.

Characterization

The phase composition of as-synthesized IF-WS_2 nanoparticles was determined using x-ray diffraction (XRD, BRUKER D8 ADVANCE) over the range of $2\theta = 10–90°$ with a scanning speed of 0.02 °/s. The morphology and elemental composition of the samples were obtained by field emission scanning electron microscopy (FE-SEM, JSM-6700F) equipped with x-ray energy dispersion spectrometer (EDS). Transmission electron microscopy (TEM, H-800) and high-resolution electron microscopy (HRTEM, JEM-3010) were used to study the morphology, structure, and average particle size of IF-WS_2 nanoparticles. The surface of the friction test pieces was characterized by an optical microscope.

Friction tests

All the friction experiments were performed in the laboratory atmosphere by using a screen display terminal face friction and a wear tester (MMU-10G, Jinan Shijin Group Co., Ltd, China). The friction test principle of the lubricating film is shown in Supplementary Fig. S2(a). The shape and main size of the upper test piece are shown in Supplementary Figs. S2 (b) and S2(c), respectively. In this study, the test load and speed are two main experimental parameters. During the test,

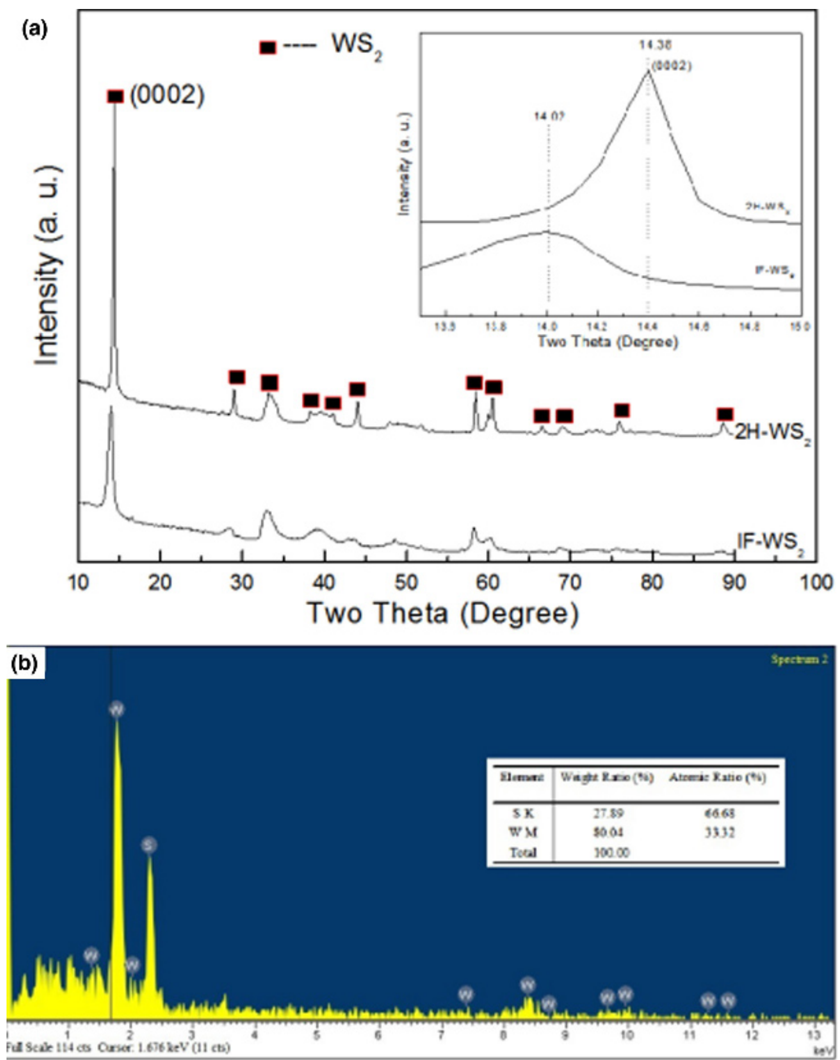

Figure 1. (a) XRD patterns of as-prepared IF-WS_2 nanoparticles and commercial 2H-WS_2 after ball milling and (b) EDS pattern of as-synthesized IF-WS_2 nanoparticles.

we should install the lubricating film test piece, then turn on the tester, add the test force to the preset value, and then slowly increase the speed to the set value. In all tribological tests, IF-WS_2 and 2H-WS_2 were compared under the same conditions.

The friction coefficient was measured at the speed of 300 and 600 r/min, and the test load is between 150 and 1200 N. The friction load used in this study can be converted into the pressure value used in common tribological tests. The specific comparison data is shown in Supplementary Table S1.

During the test, the friction data were transmitted to the microcomputer data acquisition and analysis system of the tester in real time through the tension sensor and converted into the friction coefficient. After the test, the average friction coefficient (μ_{avg}) was given by the data analysis system. Since the fourth digit after the decimal point is not scientifically valid, only the first three digits are taken as the friction coefficient data.

The extreme pressure value of the lubricating film is determined according to the principle and method of the extreme pressure value of ordinary lubricating oil. In this study, the research of extreme pressure value is carried out at the speed of 300 r/min, and the test load is gradually increased. If there is no dry wear of friction pair within 30 s, it means that the extreme pressure value is larger than the current test force. The test load should be continued to increase until dry wear occurs and finally get the extreme pressure value of the lubricating film.

The wear resistance test was carried out under the condition that the test load was lower than the extreme pressure value. Different lubricating films were tested under the same test load, speed, and test time. At the end of the test, the wear condition of the friction pairs was analyzed with the zoom microscope (EMZ-5TR, MEI JI, Japan) to evaluate the wear resistance of the lubricants.

Results and discussion

Morphology and structure of IF-WS_2

The phase composition and morphology of as-prepared IF-WS_2 nanoparticles and the IF-WS_2 self-lubricating films were investigated. Figure 1(a) shows the XRD patterns of IF-WS_2 prepared in batch and commercial 2H-WS_2 after ball milling. As shown in Fig. 1(a), pure WS_2 is the only product for the commercial 2H-WS_2 after ball milling and can be well indexed to the hexagonal WS_2 (JCPDS card No. 08-0237). Compared with 2H-WS_2, no other discernible diffraction peaks were observed in the XRD spectra of IF-WS_2 nanoparticles, which indicated that WO_3 and S had completely reacted to form WS_2 under the current reaction conditions. And the diffraction intensity of the diffraction peak is obviously lower and the diffraction peak is significantly wider, which are the typical characteristics of nanomaterials. The grain size of as-prepared IF-WS_2 nanoparticles calculated by Debye–Scherrer formula is about 30 nm. The (0002) diffraction peak of IF-WS_2 moves to a lower angle [inset of Fig. 1(a)] than that of 2H-WS_2, indicating the lattice expansion. According to the

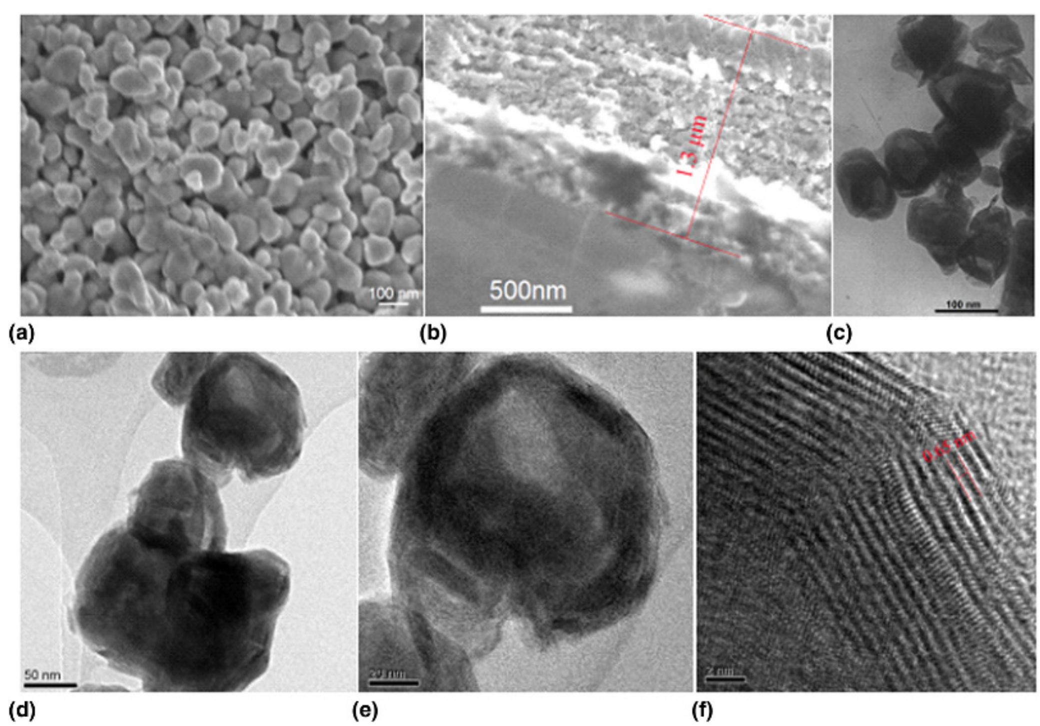

Figure 2. FE-SEM image of as-prepared IF-WS_2 self-lubricating film: (a) surface image, (b) cross-section image; TEM (c and d) and typical HRTEM and (e and f) images of as-synthesized IF-WS_2 nanoparticles.

existing literature,[4,14] these characteristics provide direct evidence for the formation of fullerene like structure (IF).

Figure 1(b) shows the EDS spectrum of IF-WS_2 nanoparticles. The test was performed on FE-SEM (JSM-6700F). Through the analysis of the computer software system, there are only two elements W and S in the product, and their atomic number ratio is about 1:2, which is consistent with the theoretical stoichiometric ratio of WS_2. Thus, the XRD analysis result is further confirmed, that is, the product is pure WS_2.

Figure 2(a) shows the surface FESEM image of as-prepared IF-WS_2 self-lubricating film, and the cross-section image is shown in Fig. 2(b). It can be found that IF-WS_2 nanoparticles in the lubrication film are evenly distributed, and there is no direct coalescence between particles, which provides a guarantee for its good dry lubrication performance. According to Fig. 2(b), the thickness of the lubricating film is about 1.3 µm. Figures 2(c) and 2(d) show TEM images of IF-WS_2 nanoparticles synthesized under the current conditions. It is shown that the morphology of IF-WS_2 is mostly spherical, and these nanoparticles are likely to have a closed hollow structure. The average particle size is about 50 nm. For the formation of IF-like structure, the more direct evidence comes from the HRTEM image of the prepared product [as shown in Figs. 2 (e) and 2(f)]. All nanoparticles possess a closed hollow structure [Figs. 2(d) and 2(e)], and the interlayer spacing is about 0.65 nm [Fig. 3(f)].

The shift of (0002) peak in the XRD pattern and the results of TEM and HRTEM tests confirmed the formation of IF nanostructures. Furthermore, the TEM analysis shows that the nanoparticles are hollow but not perfectly closed. Combined with the XRD test results, it is fully indicated that the nanoparticles are far from perfectly crystalline. Since the literature reported that the less crystalline are the IF nanoparticles, the better is their tribological performance,[23] we are confident that the as-prepared IF-WS_2 self-lubricating film has excellent lubricating properties.

Tribological properties of IF-WS_2 self-lubricating films

The measured average friction coefficients (μ_{avg}) of IF-WS_2 films and 2H-WS_2 films at the rotational speeds of 300 and 600 r/min are shown in Supplementary Tables S2 and S3, respectively. Changes in friction coefficients for each of IF-WS_2 film and 2H-WS_2 film as a function of different test loads from 150 to 1200 N are shown in Fig. 3(a). It should be noted that the friction test time at each speed and load is 50 min, and the number of revolutions of the friction test pieces are sufficient.

As shown in Fig. 3(a), the friction coefficients of IF-WS_2 films obtained under the same conditions are significantly lower than that of 2H-WS_2 films. The friction coefficients of IF-WS_2 films and 2H-WS_2 films both increase with the test speed (from 300 to 600 r/min), while that of 2H-WS_2 films increased more significantly. When the test load is 150 N under 300 r/min, the average friction coefficient value of the IF-WS_2 films is only 0.008 (Supplementary Table S2), which shows the superfine lubricate characteristics. Moreover, with the increase of test loads, the friction coefficients of the IF-WS_2 films are relatively stable without sudden changes, showing good tribological properties. With the increase of rotational speed (600 r/min), the friction coefficients of IF-WS_2 films increased, but the range is small, while the situations of 2H-WS_2 films are significantly different.

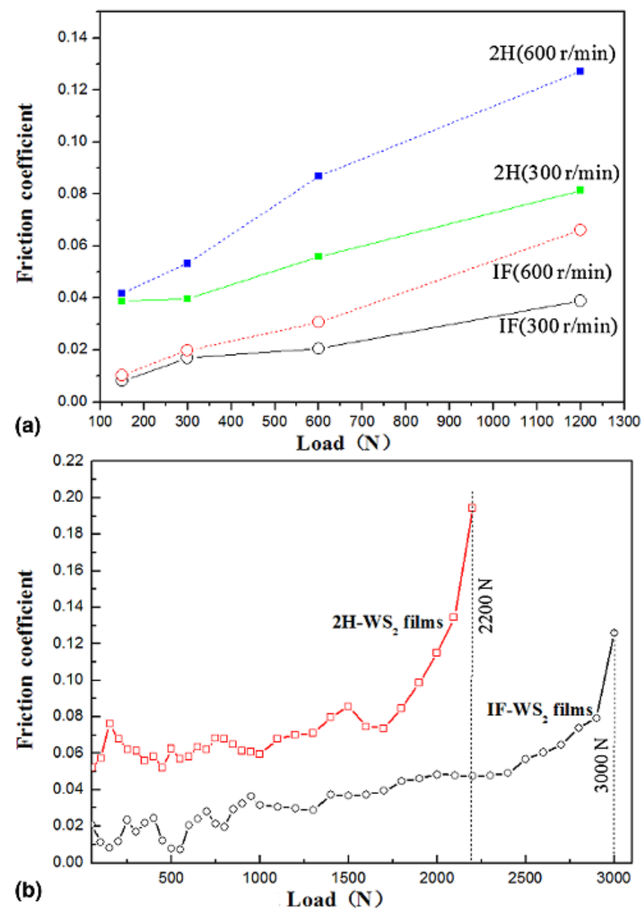

Figure 3. (a) Changes in friction coefficients for each of IF-WS_2 film and 2H-WS_2 film as a function of different test loads from 150 to 1200 N . (b) The relationship between friction coefficients and test loads of IF-WS_2 film and 2H-WS_2 film at the rotating speed of 300 r/min.

The friction coefficients of IF-WS_2 films are lower significantly than that of 2H-WS_2 films, which indicate its superiority as a dry lubricant, especially under lower test loads. The advantages of IF-WS_2 films as a dry lubricant can be mainly due to its unique structure and smaller particle size. And the IF-WS_2 nanoparticles are not easy to be destroyed under low load, so its advantages can be brought into full play.

According to the test method of extreme pressure performance, the as-prepared IF-WS_2 film and 2H-WS_2 film were investigated. Figure 3(b) shows the change curve of friction coefficients of IF-WS_2 and 2H-WS_2 lubricating films with the increase of test loads at the speed of 300 r/min. For both of the two films, the sudden increase of friction coefficient indicates that the friction service life has been obtained.[16] The test force corresponding to the end of each curve is the extreme pressure value of the dry lubricating films. It can be seen that the extreme pressure value of IF-WS_2 film is about 3000 N, and that of IF-WS_2 film is no more than 2200 N. Because in the process of testing, the time of staying at each test loads is not long enough, the measured friction coefficients are not completely credible, but it can fully reflect the general relationship between the friction coefficients and the test loads under such test conditions, that is, the trend relationship between the friction coefficient and the test load is credible. Consistent with the results in Fig. 3(a), the friction coefficient of IF-WS_2 film is lower than that of 2H-WS_2 film under all test conditions.

In order to study the wear resistance of as-prepared IF-WS_2 lubricating films, the wear trace morphology of the lower friction pieces (corresponding tests in Supplementary Table S3) was analyzed under the conditions of higher speed (600 r/min) and higher test loads (600 and 1200 N), respectively, and compared with that of 2H-WS_2 under the same conditions. The main test results are shown in Fig. 4. Figures 4(a) and 4(c) are the wear marks of IF-WS_2 friction pairs under the test loads of 600 and 1200 N, respectively. As shown in Fig. 4(a), there are a small number of thin and shallow regular "ploughs" in the abrasion marks of the friction test surface. There are some discontinuous small flakes in these "ploughs", but the whole friction surface is relatively flat, and no serious abrasion marks are found. It can be seen from Fig. 4(c) that the friction surface is relatively flat, and the "ploughs" are thin and shallow and evenly distributed. But the discontinuous small flakes on the friction test surface in Fig. 4(c) are more obvious than that in Fig. 4(a). The wear marks of 2H-WS_2 friction pairs under 600 and 1200 N test loads are shown in Figs. 4(b) and 4(d), respectively. As shown in Fig. 4(b), the friction surface is not smooth, with some large granular protrusions, obvious wear marks with some deep and irregular "furrows". In Fig. 4(d), it can be clearly observed that serious wear occurs on the friction surface, and the "furrows" are deep and wide. In addition, some materials with strong metallic luster were observed at the bottom of "furrows", which indicated that there was a certain phenomenon of "grinding" between friction pairs under the current test conditions.

Lubrication mechanism

It is obvious that the as-prepared self-lubricating film has excellent lubrication performance which is superior or, it is safe to say, not inferior, to those reported before.[11,16,20] In situ observation is very useful for the study of lubrication mechanism, and some progress has been made.[24,25] On the basis of previous studies, combined with our experimental results, the possible lubrication mechanism can be attributed to the following points:

(1) The size of IF-WS_2 nanoparticles in the lubricating film is small. As an average particle size of nanoparticles only 50 nm, IF-WS_2 is easy to enter and reside in the rough pits or

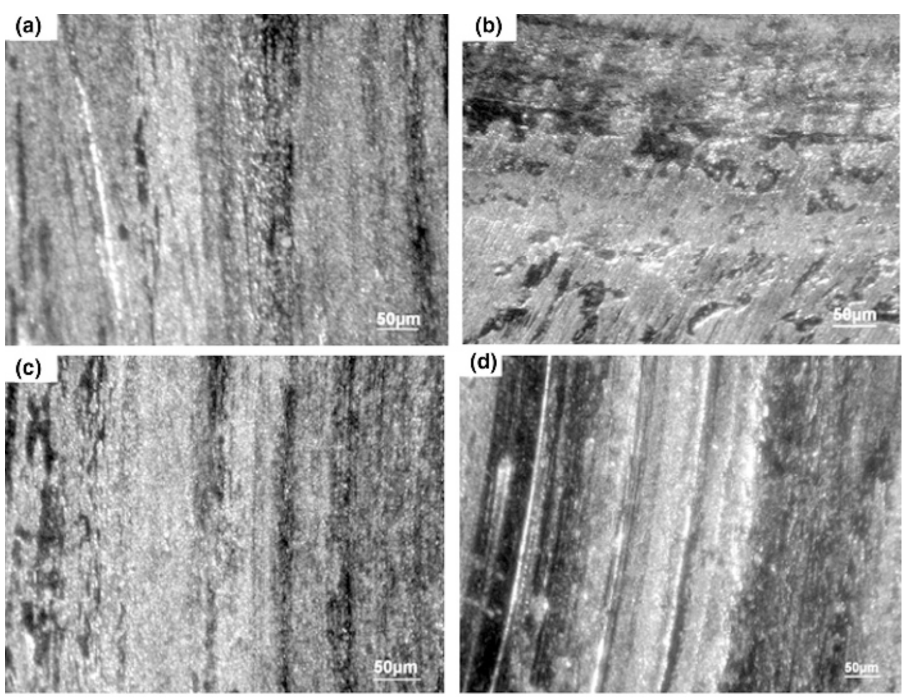

Figure 4. Micrographs of wear marks of friction pairs at the rotating speed of 600 r/min under different test loads: (a) IF (600 N), (b) 2H (600 N), (c) IF (1200 N), and (d) 2H (1200 N).

wear marks on the two surfaces of the friction pair, thus filling the surface grooves, avoiding direct friction between the rough surfaces of the friction pair, and increasing the friction contact area between the friction pairs, so as to improve the friction performance.

(2) The IF-WS_2 nanoparticles have a closed hollow spherical-like structure. The closed hollow structure of IF-WS_2 makes it more flexible, easier to roll, and different from 2H-WS_2. The surface of IF-WS_2 is basically free of unsaturated suspensions and has good chemical inertia, which reduces the adhesion between nanoparticles and the surface of friction pairs. Unfortunately, in the process of friction, under the condition of high temperature and high loads, this structure of IF-WS_2 may be seriously damaged, so that its excellent lubrication characteristics can be damaged.

(3) IF-WS_2 is easy to form stable lubrication (transfer) film. Because the dry lubricant is easy to form the energy accumulation in the friction process, especially under the condition of high loads, the structure of IF-WS_2 may be destroyed and thus become the common nano-WS_2 which is easy to form the WS_2 film. The formed film can be firmly adsorbed on the two surfaces of the friction pairs. In the process of friction, when the WS_2 lubricating film formed by WS_2 is worn off, they can quickly reabsorb on the two surfaces of the friction pairs to continue to play a lubricating role because of the high surface energy of nanoparticles.

Given the important research results that we got, it is necessary to clearly describe the main advantages of the present work. *Firstly,* the synthesis method of IF-WS_2 nanoparticles has not been reported, which has significant advantages compared with our previous work. To our best knowledge, there are few reports on the synthesis of IF-MX_2 nanoparticles in our present route. The main difference from our previous work is that in the current work, WO_3 nanoparticles and S are directly mixed by special ball milling, instead of being placed in toxic and harmful carbon disulfide (CS_2) and carbon tetrachloride (CCl_4) solutions containing S. This is not only able to ensure the adequate output, but also economical, environmentally friendly, and easy to operate. *Secondly*, the preparation of IF-WS_2 self-lubricating film is facile and the processes are easy to control. In this work, the preparation of self-lubricating film is simple and expensive or complex equipments are not required. What's more, the base material of self-lubricating film is not limited to metal and also can be replaced by ceramics or glass. The shape of the base is basically unlimited. *And the third*, the current work is of great significance to promote the practical application of IF-MX_2 self-lubricating film. At present, IF-WS_2 nanoparticles are easy to be prepared in batches. The present method can be suitable for exploring other IF-MX_2 nanoparticles, which will provide an important material guarantee for the practical application of IF-MX_2 self-lubricating films.The controllable preparation of nanocomposite self-lubricating film can be further realized by adding other components in the method, so as to obtain better lubrication performance.

Conclusion

We used a simple, efficient, and convenient route to fabricate IF-WS_2 nanoparticles possessing a closed-hollow uniform spherical-like structure with an average particle size of about 50 nm. A facile procedure based on simple deposition was adopted to prepare IF-WS_2 self-lubricating film and its tribological characteristics were further evaluated in air. Results indicated that when compared to its respective 2H-WS_2 films, the self-lubricating films exhibited excellent lubricating behaviors. It was believed to be due to as-prepared IF-WS_2 nanoparticles' unique hollow cage structure, surface inertia, as well as its smaller average particle size and the easy formation of stable lubricating film. The present approach provides a convenient and low-cost route to prepare IF-WS_2 self-lubricating films, which can also be applied to the synthesis of self-lubricating films on other substrates with other IFs. The present self-lubricating films show great potential to improve the durability compared with the current ultra-low friction films and may be suitable for a wide range of applications.

Supplementary material

The supplementary material for this article can be found at https://doi.org/10.1557/mrc.2020.26.

Acknowledgments

This work was supported by the Key Scientific and Technological Project of Henan Province (No. 122102210078) and the Plan for Scientific Innovation Talent of Henan University of Technology (No. 11CXRC16). The authors thank Mr. Xinxin Liu and Mrs. Chunxia Cheng, former graduate students of our research group, who helped with the experiments and also thank Mrs. L.P. Guo of the Henan University of Technology for her editing of English.

References

1. L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, and R. Tenne: Hollow nanoparticles of WS_2 as potential solid-state lubricants. *Nature* **387**, 791 (1997).
2. L. Cizaire, B. Vacher, T.L. Mogne, J.M. Martin, L. Rapoport, A. Margolin, and R. Tenne: Mechanisms of ultra-low friction by hollow inorganic fullerene-like MoS_2 nanoparticles. *Surf. Coat. Technol.* **160**, 282 (2002).
3. R. Tenne and A.N. Enyashin: Inorganic fullerene-like nanoparticles and, inorganic nanotubes. *Inorganics* **2**, 649 (2014).
4. R. Tenne, L. Margulis, M. Genut, and G. Hodes: Polyhedral and cylindrical structures of tungsten disulphide. *Nature* **360**, 444 (1992).
5. R. Tenne, R. Rosentsveig, and A. Zak: Inorganic nanotubes and fullerene-like nanoparticles: synthesis, mechanical properties, and applications. *Phys. Status Solidi A* **210**, 2253 (2013).
6. L. Rapoport, V. Leshchinsky, M. Lvovsky, O. Nepomnyashchy, Y. Volovik, and R. Tenne: Friction and wear of powdered composites impregnated with WS_2 inorganic fullerene-like nanoparticles. *Wear* **252**, 518 (2002).
7. L. Rapoport, N. Fleischer, and R. Tenne: Applications of WS_2, (MoS_2) inorganic nanotubes and fullerene-like nanoparticles for solid lubrication and for structural nanocomposites. *J. Mater. Chem.* **15**, 1782 (2005).
8. R. Rosentsveig, A. Margolin, A. Gorodnev, R. Popovitz-Biro, Y. Feldman, L. Rapoport, Y. Novema, G. Naveh, and R. Tenne: Synthesis of fullerene-

like MoS_2 nanoparticles and their tribological behavior. *J. Mater. Chem*. **19**, 4368 (2009).
9. D. Berman, A. Erdemir, and A.V. Sumant: Graphene: a new emerging lubricant. *Mater. Today* **17**, 31 (2014).
10. H.-X. Wu, L.-G. Qin, G.-N. Dong, M. Hua, S.-C. Yang, and J.-F. Zhang: An investigation on the lubrication mechanism of MoS_2 nano sheet in point contact: the manner of particle entering the contact area. *Tribol. Int*. **107**, 48 (2017).
11. M. Chhowalla and G.A.J. Amaratunga: Thin films of fullerene-like MoS_2 nanoparticles with ultra-low friction and wear. *Nature* **407**, 164 (2000).
12. L. Rapoport, O. Nepomnyashchy, I. Lapsker, A. Verdyan, A. Moshkovich, Y. Feldman, and R. Tenne: Behavior of fullerene-like WS_2, nanoparticles under severe contact conditions. *Wear* **259**, 703 (2005).
13. L. Rapopor, O. Nepomnyashchy, I. Lapsker, A. Verdyan, Y. Soifer, R. Popovitz-Biro, and R. Tenne: Friction and wear of fullerene- like WS_2 under severe contact conditions: friction of ceramic materials. *Tribol. Lett*. **19**, 143 (2005).
14. L. Rapoport, N. Fleischer, and R. Tenne: Fullerene-like WS_2 nanoparticles: superior lubricants for harsh conditions. *Adv. Mater*. **15**, 651 (2010).
15. D. Haba, T. Griesser, U. Müller, and A.J. Brunner: Comparative investigation of different silane surface functionalizations of fullerene-like WS_2. *J. Mater. Sci*. **50**, 5125 (2015).
16. S. Watanabe, J. Noshiro, and S. Miyake: Tribological characteristics of WS_2/MoS_2 solid lubricating multilayer films. *Surf. Coat. Technol*. **183**, 347 (2003).
17. A. Katz, M. Redlich, L. Rapoport, H.D. Wagner, and R. Tenne: Self- lubricating coatings containing fullerene-like WS_2 nanoparticles for orthodontic wires and other possible medical applications. *Tribol. Lett*. **21**, 135 (2006).
18. B. Višić, L.S. Panchakarla, and R. Tenne: Inorganic nanotubes and fullerene-like nanoparticles at the crossroads between solid-state chemistry and nanotechnology. *J. Am. Chem. Soc*. **139**, 12865 (2017).
19. O. Elianov, S. Garusi, R. Rosentsveig, and S.R. Cohen: Deposition of metal coatings containing fullerene-like MoS_2 nanoparticles with reduced friction and wear. *Surf. Coat. Technol*. **353**, 116 (2018).
20. Y. He, W.-T. Sun, S.-C. Wang, P.A.S. Reed, and F.C. Walsh: An electrodeposited Ni-P-WS_2 coating with combined super-hydrophobicity and self-lubricating properties. *Electrochim. Acta* **245**, 872 (2017).
21. G.-C. Zhao, Y.-P. Xue, Y.-F. Huang, Y. Ye, F.C. Walsh, J. Chen, and S.-C. Wang: One-step electrodeposition of a self-cleaning and corrosion resistant Ni/WS_2 superhydrophobic surface. *RSC Adv*. **6**, 59104 (2016).
22. H.-B. Yang, S.-K. Liu, J.-X. Li, M.-H. Li, G. Peng, and G.-T. Zou: Synthesis of inorganic fullerene-like WS_2 nanoparticles and their lubricating performance. *Nanotechnology*. **17**, 1512 (2006).
23. J. Tannous, F. Dassenoy, A. Bruhács, and W. Tremel: Synthesis and tribological performance of novel $Mo_xW_{1-x}S_2$ ($0 \le x \le 1$) inorganic fullerenes. *Tribol. Lett*. **37**, 83 (2010).
24. I. Lahouij, F. Dassenoy, L. de Knoop, J.-M. Martin, and B. Vacher: In situ TEM observation of the behavior of an individual fullerene-like MoS_2 nanoparticle in a dynamic contact. *Tribol. Lett*. **42**, 133 (2011).
25. I.Z. Jenei and F. Dassenoy: Friction coefficient measured on a single WS_2 nanoparticle: an in situ transmission electron microscope experiment. *Tribol. Lett*. **65**, 86 (2017).