Tribology International 122 (2018) 119–124

Contents lists available at ScienceDirect

Tribology International

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

Short Communication

Green laser irradiation-stimulated fullerene-like MoS_2 nanospheres for tribological applications

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ARTICLE INFO

Keywords:
Molybdenum disulfide
Fullerene-like
Laser irradiation
Tribological property

ABSTRACT

Tremendous mechanical energy loss on friction and serious mechanical failures caused by wear are attracting more and more researchers studying on friction and lubrication to ease the situation of energy shortage. We demonstrate a novel and green laser-assisted solution growth strategy for ideal fullerene-like MoS_2 nanospheres, in which both the morphology reshaping and bond reconstructing processes of MoS_2 nanoflakes are involved in the *one-step* laser irradiation under ambient conditions. Due to the spherical shape, solid structure, and improved chemical stability, such MoS_2 nanospheres as additives in paraffin liquid can effectively reduce the friction coefficient (~47% reduction) and enhance the extreme pressure property (>2.24 GPa).

1. Introduction

Reducing friction and wear in moving mechanical systems is widely recognized as one primary factor for energy saving and environmental protection due to nearly ubiquitous adverse impact of friction and wear on devices failure. Moreover, about 25% of the total energy loss in the world is due to friction or wear according to the statistical data from Oakridge National Laboratory (USA) [1,2]. Molybdenum disulfide (MoS_2), as one of typical layered transition-metal dichalcogenides, has been extensively investigated as catalysts, electrochemical electrodes, and solid lubricants [3–6]. Due to the easy interlayer sliding with low shear strengths facilitated by weak interlayer Van der Waals force, its application in mechanical tribology as solid lubricants or lubricant additives is highly desirable [7].

Since the discovery of inorganic-fullerene (IF) MoS_2 with few layer-closed structures, many studies have shown that spherical IF-MoS_2 as additive in lubricant oil usually exhibits superior lubricating properties than 2H-MoS_2 slice under variable operating conditions [8–13]. The friction and wear reductions are dependent on the microstructure, size, shape, and the concentration of nanoparticles added in lubricant. For MoS_2 flakes, due to the active dangling bonds at their edge sites, they can be easily oxidized to MoO_x, which weakens the lubricating effect [6,11]. Layer-closed IF-MoS_2 nanospheres without rim-edge surface have lower surface energy and better chemical stability under the high temperature, and allow the particles to roll rather than slide during friction [7,10,14,15]. Thus, much attention was focused on the synthesis and tribological properties of IF-MoS_2 nanoparticles. However, most reported synthesis strategies for IF-MoS_2 require harsh experimental conditions like high temperature (~900 °C) and expensive even toxic high-purity gas (H_2S/H_2), but still give low yields. Moreover, these particles are of low spherical degree, which seriously limits their application as lubricant additives [9,16]. Therefore, the growth of IF-MoS_2 nanospheres with stable tribological performance by tuning their microstructures via a green, fast, high-yield, and cost-effective method is still highly challenging.

Herein, we demonstrate a new and mild laser-assisted solution growth strategy for MoS_2 nanospheres with ideal fullerene-like structure and smooth surfaces, in which MoS_2 nanoflakes are chosen as new targets for laser irradiation in liquid. The reshaping of MoS_2 nanoflakes and bond reconstructing to fullerene-like structure are realized by a fast, green, and facile pulse laser irradiation method in water at ambient conditions, which can also effectively reduce the growth costs. Remarkably, due to the improved spherical shape, chemical stability, and weak intermolecular bonding of ideally fullerene-like structure, such

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https://doi.org/10.1016/j.triboint.2018.02.040
Received 24 November 2017; Received in revised form 4 February 2018; Accepted 24 February 2018
Available online 26 February 2018

MoS_2 nanospheres as paraffin liquid (PL) additives can effectively reduce the friction coefficient and enhance the extreme pressure property compared with the as-prepared MoS_2 nanoflakes.

2. Experimental section

2.1. Preparation of MoS_2 nanospheres

MoS_2 nanoflakes were synthesized by a hydrothermal method. Typically, 0.5 g sodium molybdate dehydrate (99.0% purity, Aladdin), 0.8 g thioacetamide (99.0% purity, Aladdin) and 0.2 g polyethylene glycol 5000 (Aladdin) were added into 50 ml deionized water. After being stirred for 30 min, the solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. The MoS_2 nanoflakes (Fig. 2a) were obtained after the autoclave cooled to room temperature. Then, the MoS_2 nanospheres were reshaped by one simple pulse laser irradiation of the above-prepared MoS_2 dispersions (Fig. 1). A KrF excimer laser (10 Hz, 25 ns, Coherent, CompexPro 205) was used as the light source. The laser beam was focused on the solution through a convex lens with a focal length of 150 mm. The laser irradiation on MoS_2 nanoflakes was performed for 15 min at an energy fluence of 300 mJ pulse^{-1} cm^{-1}. The dispersion was continuously stirred during laser irradiation to prevent sedimentation formation. After laser irradiation, the fullerene-like MoS_2 nanospheres (Fig. 2b) were collected by centrifugation and washed several times with the deionized water.

2.2. Characterization

The morphology of MoS_2 nanoparticles was observed with a scanning electron microscope (SEM, FEI Quanta 250 FEG). The X-ray diffraction pattern was obtained with an X-ray diffraction apparatus (XRD, D8-Advance, Bruker) operated at 40 kV and 40 mA using the Cu-Kα line ($\lambda = 0.154184$ nm) as the excitation source. Microstructural examination was characterized with a transmission electron microscope (TEM, JEM-2100F) under 200 kV acceleration voltages. Raman spectrometer equipped with a 532 nm laser (LabRAM HR Evolution, HORIBA) was used for recording the Raman scattering spectra of different samples.

2.3. Evaluation of the tribological properties

The tribological properties of MoS_2 nanoparticles as lubricating oil additives were first measured with a thrust-ring tester (MM-W1B, Shijin-Jinan) in terms of coefficient of friction (COF). Paraffin liquid (PL) with different mass concentrations were tested repeatedly. Detailed experimental conditions of thrust-ring test were set as follows: rotation speed at 1200 r min^{-1}, load of 392 N (corresponding to contact pressure of 3.14 MPa, Fig. S1), temperature at 75 °C and time of 60 min. The surface roughness (Ra) of thrust rings is ~20.4 nm. The lubrication regime is mixed lubrication (Fig. S1). During the friction test, thrust rings were fully immersed in the oil tank filled with lubricant, as shown in Fig. S1a. Their extreme pressure properties were tested by a load-climbing test with an Optimol SRV4 tribotester by the reciprocating ball-on-disk mode. 150 μL lubricant dropt to the disk by MicroPette Plus at the beginning of the test. The reciprocating mode was conducted by one linear oscillating steel ball (diameter 10 mm) pressed against a stationary columned disk (diameter 24 mm and thickness 8 mm) in the oil samples. Detailed experimental conditions of load-climbing test were set as follows: stroke of 2 mm, frequency of 50 Hz, temperature at 50 °C, load firstly kept at 100 N for 15 min, and then increased by 100 N every 2 min. The test was stopped when the COF increased abruptly over 0.5, which indicated that the lubrication had failed. All friction pairs are bearing steels (AISI 52100). The working picture of Optimol SRV4 tester is shown in Fig. S1b. The surface roughnesses (Ra) of steel ball and disk are ~18.5 nm and ~20.4 nm, respectively. The dynamic viscosity of PL is 2.43 ± 0.26 cP at 50 °C and 1.1 ± 0.22 cP at 120 °C. COF was recorded automatically with a computer controlled data acquisition card. After washing with petroleum ether and acetone, the morphologies of the wear scar area were evaluated by SEM.

3. Results and discussion

Pulsed laser irradiation in liquid can create extreme nonequilibrium conditions in nature such as ultrahigh temperature (10^4 K) and ultrahigh pressure (GPa) in nanoseconds, which can lead to the reshaping, phase transition, and even new phase that is different to the target material [17–21]. Due to the characteristics like high efficiency and non-pollution synthesis, it has become an important growth route for nanocomposites or nanostructures with special microstructure and composition [17]. In our experiment, the ideally fullerene-like MoS_2 nanospheres are grown by simply irradiating a water suspension with MoS_2 nanoflakes under ambient conditions (Fig. 1), rather than harsh conditions used in chemical vapor deposition [9], which can effectively reduce the sample growth costs. When the high-power laser beam irradiates the suspension, MoS_2 nanoflakes begin to bend or even melt and then change gradually to small quasi-spheres in order to release the high surface tension energy (Fig. S2), as the spherical structure has the smallest surface area among all surfaces enclosing a given volume. The fast and repeatedly heating-quenching process melts and solidifies the liquid MoS_2 droplet into ideal fullerene-like nanospheres gradually. Longer laser irradiation time produces, on one hand, more solid MoS_2 spheres evolved from the flakes, and, on the other hand, bigger aggregates conjugated from several small particles, as shown in Fig. 1. This is a typical laser induced surface energy releasing process, as we have demonstrated for typical oxide (ZnO, TiO_2, and Fe_3O_4) spheres and WS_2 spheres [22–24]. When fullerene-like MoS_2 nanospheres are introduced into PL as lubricant additives, excellent friction reduction, anti-wear, and extreme pressure properties can be expected as such MoS_2 spheres benefit from, on one hand, the ultrasmooth spherical shape changing more sliding friction into rolling friction under low load, and on the other hand, the easy exfoliation of defective nanospheres forming a tribofilm after deformation under high load, which is similar to the poorly crystallized IF-MoS_2 [6].

The morphology of as-synthesized MoS_2 nanoflakes by hydrothermal method and laser irradiation-induced MoS_2 nanospheres are elucidated through scanning electron microscope (SEM) and transmission electron microscope (TEM), as shown in Fig. 2a–c. Upon the simple laser irradiation, raw flake-like MoS_2 nanoparticles (Fig. 2a) are transformed into

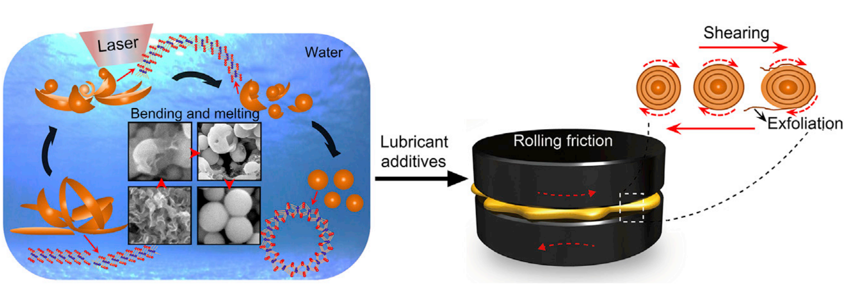

Fig. 1. Growth schematic of the fullerene-like MoS_2 nanospheres and the lubricating mechanism when used as lubricant additives. Under laser irradiation-induced instantaneous ultrahigh temperature and ultrahigh pressure, MoS_2 nanoflakes will bend and melt in water at ambient conditions. The following quenching process of surrounding water solidifies the liquid MoS_2 droplet into ideally fullerene-like nanospheres. Such ultrasmooth MoS_2 nanospheres as lubricant additives can effectively change silding friction into rolling friction under the shearing force of friction pairs. The insert grey images are the corresponding SEM images of MoS_2 nanoparticles with different laser irradiation time.

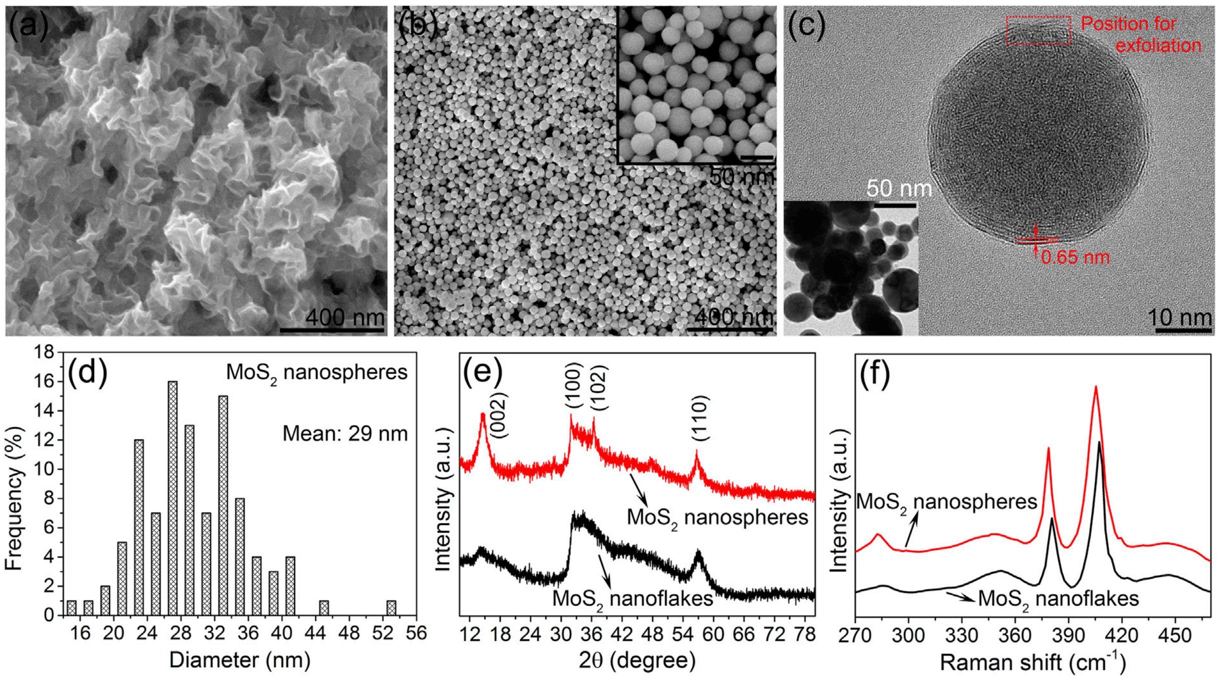

Fig. 2. Characterization of fullerene-like MoS_2 nanospheres. (a) SEM image of as-prepared MoS_2 nanoflakes by hydrothermal method. (b) SEM and (c) TEM images of ideally spherical MoS_2 nanoparticles induced by the simple laser irradiation method. (d) Size distribution of MoS_2 nanospheres. (e) XRD and (f) Raman spectra of raw MoS_2 nanoflakes and MoS_2 nanospheres.

ideally spherical nanoparticles (Fig. 2b). The mean diameter of the solid MoS_2 nanospheres is about 29 nm (Fig. 2d). The TEM observations reveal that the ultrasmooth MoS_2 nanospheres possess a nearly closed-cage structure due to the partial bonds closing at the edge of spheres, which indicates such more stable inorganic-fullerene structure is constructed due to the laser irradiation-induced ultrahigh temperature and pressure on the laser spot-material interface. The external layers with an interplanar distance of 0.65–0.68 nm between the (002) planes show a 5–10% dilation of interlayers spacing. The expansion is generally due to the presence of residual stresses in the curved layers [25]. Some edge dislocation can also be observed in the cage-closed structure as indicated in the red square in Fig. 2c, which can release the sphere internal mechanical strains. It also provides the exfoliation position for MoS_2 layers to form a tribofilm under high load when tribology test is performed.

Representative XRD patterns and Raman spectra of raw MoS_2 nanoflakes and MoS_2 nanospheres are displayed in Fig. 2e and f. Four characteristic diffraction peaks can be observed at 14.4°, 32.6°, 33.6°, and 58.3°, corresponding to the (002), (100), (101), and (110) planes of the hexagonal MoS_2 (JCPDS No. 37–1492), as shown in Fig. 2e. Compared with MoS_2 nanoflakes, MoS_2 nanospheres show better crystallization, especially along the *c* axis. Raman analyses excited by a 532 nm laser at room temperature (Fig. 2f) reveal a light displacement (blueshift) and widening of the peaks (in-plane E^1_{2g} and out-of-plane A_{1g}) in the ideally

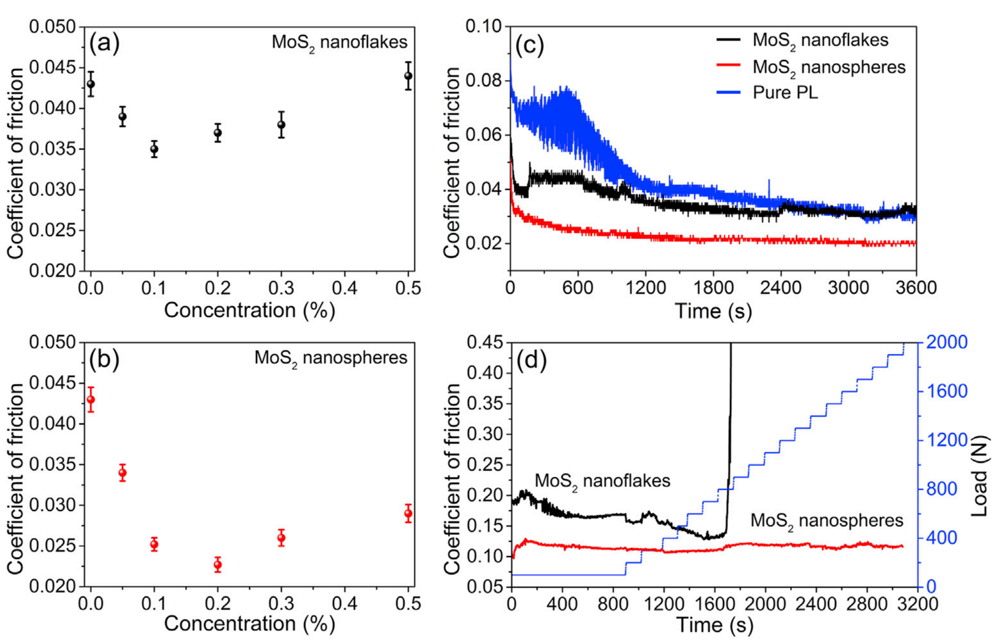

Fig. 3. Average COF of paraffin liquid with different mass percentage of (a) MoS_2 nanoflakes and (b) MoS_2 nanospheres measured by a thrust-ring tester. (c) Representative COF curves with time of pure paraffin liquid and oil samples with optimum concentration MoS_2 nanoflakes (0.1 wt%) and MoS_2 nanospheres (0.2 wt%). (d) Load-climbing tests by SRV4 tribotester of MoS_2 nanoflakes (0.1 wt%) and MoS_2 nanospheres (0.2 wt%).

spherical structure compared with flake-like structure. This blueshift can be attributed to residual strains in the cage-closed structure [25], which is consistent with the TEM observations.

MoS_2 nanoparticles were dispersed in PL with different mass concentrations to investigate their tribological properties as lubricant additives. Fig. 3a and b gives the average COF by thrust-ring test for 30 min. The friction reduction properties show a clear dependence on the mass percentage of MoS_2 nanoparticles. When the amounts of nanoparticles reach an optimal concentration, the biggest friction-reduction effect is acquired. The optimum concentrations are 0.1 wt% and 0.2 wt% for MoS_2 nanoflakes and MoS_2 nanospheres, respectively. The evolution of COF with time between the thrust-ring surfaces, lubricated by pure PL and PL with 0.1 wt% MoS_2 nanoflakes or 0.2 wt% MoS_2 nanospheres, is shown in Fig. 3c. According to the different states of lubrication, the whole experimental process can be divided into two parts: run-in period and relatively stationary period. In the run-in period, due to the severe

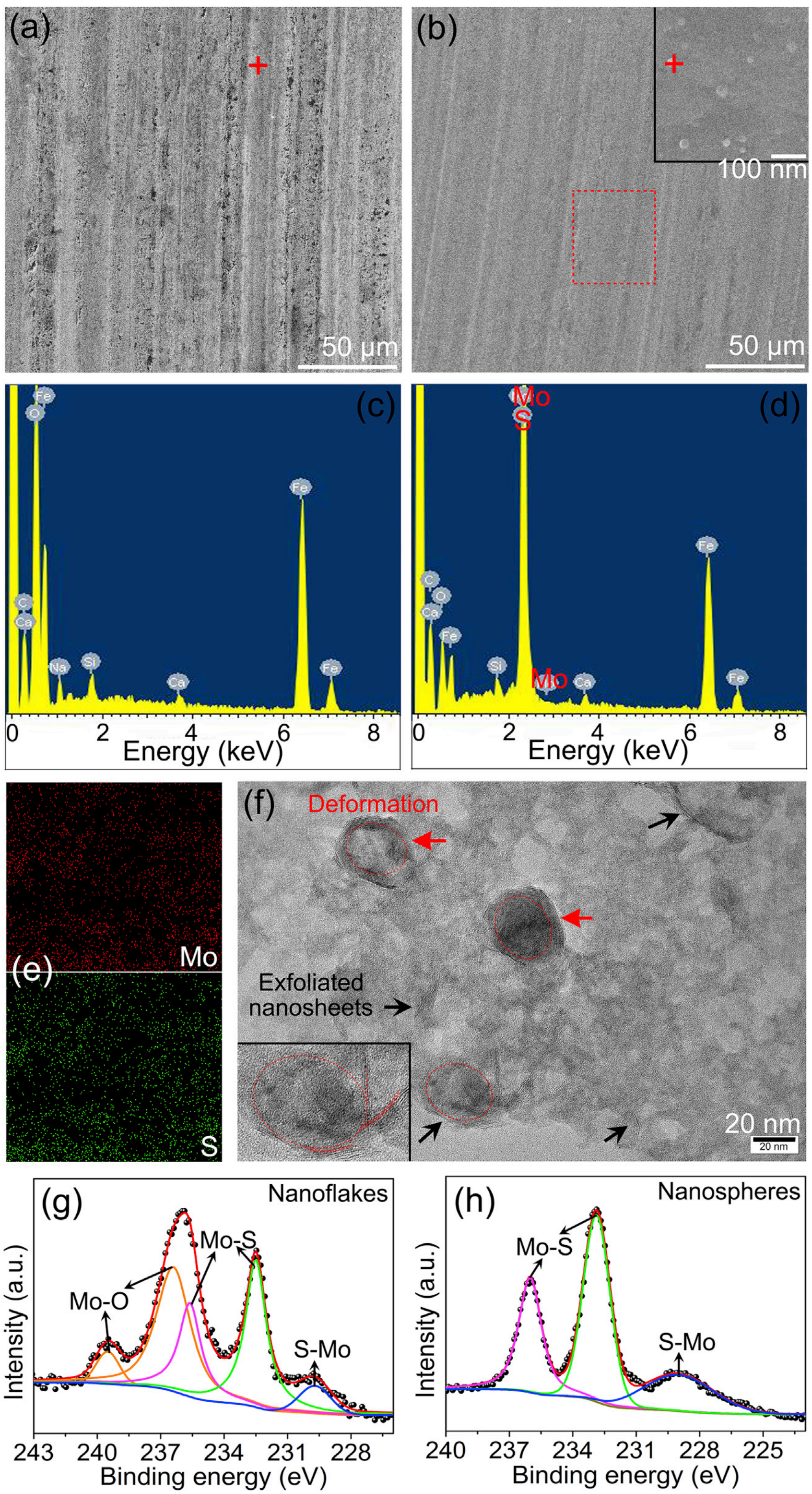

Fig. 4. SEM images of the wear metal surface lubricated by (a) pure PL and (b) PL containing 0.2 wt% MoS_2 nanospheres in the thrust-ring tests. Inset in b: Magnified image. (c) and (d) Corresponding EDS from the red cross area in a and b. (e) EDS mapping of the red dotted box in b. (f) The morphology and microstructure of fullerene-like MoS_2 nanospheres after the thrust-ring test. Their exfoliation of nanosheets and elastic deformation can be observed. XPS spectra of (g) MoS_2 nanoflakes and (h) MoS_2 nanospheres used as lubricant additives after thrust-ring test. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

wear, the COF is usually relatively high and unstable. Surprisingly, ideal cage-closed MoS_2 nanospheres as oil additives not only reduce the COF, but also significantly reduce the running-in time, which indicates nanospheres are easier to enter the space of the friction pairs to form the tribofilm, in comparison with the aggregates of MoS_2 nanoflakes. Then a stable COF around 0.02 is achieved and decreases about 47% compared with pure oil, which outperforms most of the previously reported MoS_2 nanoparticles as lubricant additives [1,26,27]. To investigate the extreme pressure properties of MoS_2 nanoparticles as lubricant additives, load-climbing tests are performed with the reciprocating ball-on-disk mode (Fig. 3d). The COF of PL containing 0.1 wt% MoS_2 nanoflakes rose abruptly when the load reached 800 N, indicating that the highest load with no seizure is 700 N, while the load-climbing test of the PL containing 0.2 wt% MoS_2 nanospheres did not stop until the load reached 1900 N, which is the highest load limit that can be provided by the tribotester. This means that the highest load with no seizure of the lubricant is no less than 1900 N (>2.24 GPa), as shown in Fig. S3.

In order to clarify the lubricating mechanism of such fullerene-like MoS_2 nanospheres as lubricant additives, the wear steel surface after thrust-ring tests were further analyzed with SEM and energy dispersive X-ray spectrometer (EDS). The cleaned wear steel surface after testing in pure PL is very uneven, while the wear furrows from the PL with 0.2 wt% MoS_2 nanospheres are small and light, as shown in Fig. 4a–b. For MoS_2 nanoflakes additives, the wear furrows on the surface were extremely nonuniform (left area and right area) (Fig. S4), which may be caused by the aggregation or oxidation of MoS_2 nanoflakes. The results confirm that such laser irradiation-induced ultrasmooth MoS_2 nanospheres as additives can also improve the anti-wear property of lubricating oil. Some nanospheres on the wear steel surface can be observed from the magnified SEM image in Fig. 4b (inset). Comparing the corresponding chemical compositions of the wear steel surfaces (Fig. 4c and d) with EDS, the obvious evidence of Mo and S element signals are observed, which indicates the formation of a tribofilm with MoS_2 nanospheres during the friction process.

Up to now, the exact mechanism of fullerene-like nanoparticles as additives to enhance the tribological properties is still not very clear. Several reasons may account for the enhanced tribological properties of such fullerene-like MoS_2 nanospheres as lubricant additives [25–29]. First, due to their perfectively spherical shape, solid structure, ultrasmooth surface, and small particle size (~29 nm), MoS_2 nanospheres can more easily enter the contact area than the sub-micron aggregates of nanoflakes (Table S1) and act as molecular bearings, which effectively change sliding friction into rolling friction under low-pressure friction [25–29], especially for surface-contact mode, e.g. the thrust-ring test (Fig. 4b and Fig. S5). Thus, the COFs of PL containing perfect MoS_2 nanospheres show more prominent reduction than that of raw nanoflakes in PL (Fig. 3). Second, when the friction test is performed under high contact pressure, e.g. the load-climbing tribology test, elastic deformation of fullerene-like MoS_2 nanospheres and exfoliation from external layers of the dislocation positions may happen easily (Fig. 4f and Fig. S5) [6,30]. Then, such MoS_2 layers are gradually transferred onto the contact steel surface to form a thicker tribofilm within PL, which can act as spacer to prevent the metal-to-metal direct contact and provide a reduced sliding friction between the friction pairs. This can be confirmed with the existence of Mo and S elements on the wear steel surface (Fig. 4d). Third, MoS_2 nanoflakes with many highly active rim and dangling bonds are easily oxidized into MoO_x (Fig. 4g and Fig. S6), which dramatically weakens the lubrication effect [26–29]. However, in this study, these MoS_2 nanoflakes were reconstructed to perfect MoS_2 nanospheres under ultrahigh temperature and pressure induced by high laser power. Due to the closed-cage structure with less dangling bonds, MoS_2 nanospheres possess high chemical stability (Fig. 4h) and exhibit stable COF with small fluctuations (Fig. 3c). In addition, nanoflakes with a high specific surface area easily aggregate in oil (Table S1), which usually results in serious wear and tear (Fig. S3a). As we all know, spherical particle has the smallest surface area among all surfaces enclosing a given volume, such perfect MoS_2 nanospheres with ultrasmooth surface as additives can effectively reduce the aggregation and give a relatively flat wear surfaces (Fig. 4b and Fig. S3b). Thus, the better tribological properties of perfect MoS_2 nanospheres may be attributed to their ideal spherical morphology and chemical stability.

4. Conclusion

In summary, comprehensively considering the lubricant mechanism of inorganic particles as oil additives, one ideally spherical fullerene-like MoS_2 lubricant is synthesized by a green and facile laser irradiation method under ambient conditions. The extreme non-equilibrium conditions created by the laser irradiation can reconstruct the MoS_2 nanoflakes into perfect solid nanospheres with layer-closed structure to release the high surface tension energy of nanoflakes. Moreover, such MoS_2 nanospheres as PL additives can effectively reduce the friction coefficients and enhance the extreme pressure properties. The excellent lubricity may be due to the rolling effect of fullerene-like MoS_2 nanospheres like molecular bearings and the forming of tribofilm among mechanical contacting faces. The improved anti-oxidation property is the result of the ideally spherical structure of MoS_2 nanospheres with ultrasmooth surface, less dangling bonds, and inactive edges. Thus our study is of great significance to advance studies on nanospheres as additives in engine oil for the usage period of fossil fuel to save mechanical energy and reduce mechanical failure caused by wear.

Acknowledgment

This work was supported by National Natural Science Foundation of China (51472110, 51671094, 51605247) and Natural Science Foundation of Shandong Provincial (ZR2016BM25). B.Q. Cao acknowledges the Taishan Scholar Professorship tenured at University of Jinan.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.triboint.2018.02.040.

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