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Short Communication

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

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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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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 (λ = 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

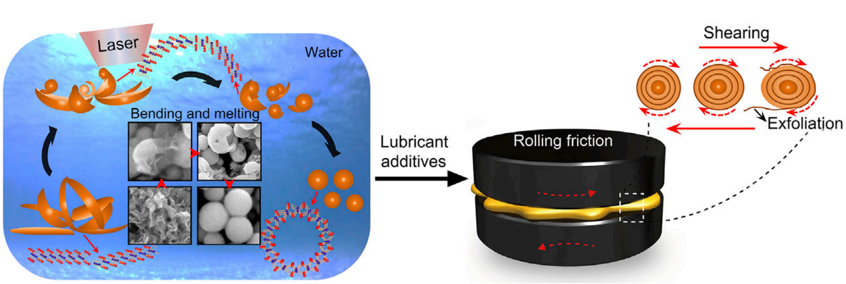

Fig. 1. Growth schematic of the fullerene-like MoS_2 nanospheres and the lubricating mechanism when used as lubricant additives. Under laser irradiation-induced instantaneous ultrahigh temperature and ultrahigh pressure, MoS_2 nanoflakes will bend and melt in water at ambient conditions. The following 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.