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MoS_2 hollow microspheres used as a green lubricating additive for liquid paraffin

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ABSTRACT

Molybdenum disulfide (MoS_2) hollow microspheres were prepared via a hydrothermal method, which were characterized by XRD, SEM, TEM and UV–vis spectroscopy. The tribological performances of liquid paraffin (LP) mixtures containing these hollow microspheres and the following photo-catalytic degradation behaviors of LP promoted by the worn MoS_2 powders were investigated. The results indicate that 0.50 wt% of MoS_2 hollow microspheres in LP can reduce the friction coefficient of the mixture remarkably, and the photo-catalytic degradation degree of LP also reaches a satisfactory level. MoS_2 serves as both lubricating additives and photo catalysts at the different life stages, and related mechanisms have been discussed, which suggests potential values in the design of novel and sustainable lubricating systems.

1. Introduction

Friction is a common physical phenomenon which reflects the tangential motion resistance between two contacting bodies under the relative motion (or relative motion trend) generated by the action of external force, while wear is the result of friction. Friction between materials consumes a lot of energy, and wear generated by friction is the main cause of mechanical failures. Effective controlling of friction, remarkable reducing of wear and great improving of lubrication are three important strategies to save energy and raw materials and to shorten maintenance time. Accordingly, lubricating oils and water-based lubricating systems are widely used for most of machine or mechanical system. Similarly, how to further enhance their lubricating performance is an important challenge in this field, in which many researchers have done a lot of research work during the past decades.

Being an old as well as young lubricating material, MoS_2 is one type of excellent solid lubricant and it has also been widely used as additives for lubricating oil and/or solid materials for many years [1–7]. To a great extent, the lubrication performance of MoS_2 as lubricating additive is closely related to or even considerably dependent on its morphology [8,9]. Nano-sized and micro-sized MoS_2 with different morphologies such as fullerene-like, tube-like, platelet-like, coral-like structures have been achieved via smart synthetic ways [10–13], and the existed studies indicates that they can promote the performances of lubricating systems when being used as additives [14–16], and related mechanisms, such as rolling, deformation, exfoliation, and chemical stability, have also been illustrated [8,17–19]. In addition, some nano-sized and micro-sized MoS_2 with special morphologies also have considerable photo-catalytic properties [20–23]. Considering the structure from a microscopic view, active atoms which are often located at rim-edge areas are difficult to exist in layer-closed structures (such as fullerene-like and hollow sphere-like structures) [10,24]. But slippage between S-Mo-S molecular layers can be found in some layer-opened structures (such as MoS_2 nano-platelets or nano-sheets), which will reduce the interlocking friction between the sliding surfaces as the “third bodies” [25,26]. Computer simulation results for the lubrication mechanism of layered 2H-MoS_2 have showed the active forces was the interlayer Coulombic repulsive interaction instead of the weak van der Waals gaps [27–29]. In addition, larger surface areas and active rim-edge atoms with dangling bonds in nano-platelets and nano-sheets can lead to higher catalytic activity without a doubt [25,30], which will strengthen its photo-catalytic properties [21,24,31]. Undoubtedly, MoS_2 with sphere-like morphology can serve as an additive for lubricating oils [8,14,32], while its layer-opened structure can result in better photo-catalytic properties [21,24], which can promote the photo-catalytic degradation of organic materials. In this work, MoS_2 hollow microspheres were prepared and used as lubricating additives for LP, and its photo-catalytic degradation effect on LP after four-ball friction tests were investigated.

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2. Experimental

2.1. Materials

Potassium thiocyanate (KSCN) was purchased from Sinopharm Chemical Reagent Co., Ltd, sodium molybdate (Na_2MoO_4) was provided by Shanghai Macklin Biochemical Co., Ltd, tetrabutyl ammonium bromide (Bu_4NBr) was bought from Shanghai Lingfeng chemical reagent Co., Ltd, LP, absolute alcohol, and other common chemicals were commercial available and they were used without further purification.

2.2. Techniques

X-ray diffraction (XRD) was recorded using a Rigaku K/max-γA X-ray diffractometer with a Cu Ka radiation (λ=1.5415 Å) at the scanning rate of 0.02° per second. Scanning electron microscopy (SEM) images were obtained on a FEI Inspect F50 instrument. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 transmission electron microscope. UV–Vis absorption spectra were carried on a UV-3600 Spectrometer, and the UV–vis diffuse reflectance spectra (DRS) were investigated by a UV-2600 Spectrometer. The tribological properties were tested by a MRS-10A four-ball testing machine. The steel balls were made from E52100 (ASTM) materials with hardness of 61–64 HRC and the roughness of Ra=0.02 μm. The tribological behaviors of these mixtures were investigated under a constant load of 280 ± 4 N and a rotational speed of 1450 rpm at 75 ± 2 °C. The wear rate was determined by the average wear scar diameter (AWSD) (± 0.01 mm) of the three bottom balls. Each tribological test was performed thrice under the same conditions.

2.3. Preparations of MoS_2 hollow microspheres

MoS_2 hollow microspheres were synthesized in the following ways: a mixture of 0.67g KSCN and 0.56g Na_2MoO_4 was dissolved in 65 mL deionized water under magnetic stirring, and 0.23g Bu_4NBr was dispersed in the above solution. Hydrochloric acid was added slowly into the above solution to adjust pH value (below 1.0). The resulting solution was transferred into a 100 mL Teflon-lined stainless autoclave and sealed tightly, and then it was heated to 240 °C and maintained for 24 h. After that, the autoclave was cooled to room temperature naturally. The obtained black precipitates were collected by centrifugation and then washed several times by deionized water and absolute ethanol; finally the products were dried in vacuum at 60 °C for 20 h.

2.4. Photo-catalytic tests

The worn MoS_2 powders were collected after frictional test by centrifugation and then washed several times by petroleum ether and deionized water; finally they were dried in vacuum at 60 °C for 10 h for photo-catalytic tests. The concentration of MoS_2 was set according to the values used in tribological tests. A certain amount of MoS_2 was added in 1.00g LP by ultrasonic dispersion for 40 min in dark, then 1.5g deionized water was added in the obtained mixtures respectively. All samples were placed in photochemical reaction instrument (JT-GHX-AC, Hangzhou, China) with continuous stirring and irradiation under high-pressure mercury lamp (HPLM) for 12 h. After MoS_2 was removed from the mixture, 10.00g dichloromethane was added in each solution, the mixture of LP and dichloromethane was separated from deionized water by a separating funnel. The concentration of LP in each mixture was determined by a UV Spectrometer with the background of dichloromethane. The test was repeated three times under the same conditions, and the final obtained data was the average value of all tests. To investigate the reusability of MoS_2, 0.50 wt% concentration of collected MoS_2 were reused to repeat photo-catalytic tests 4 times.

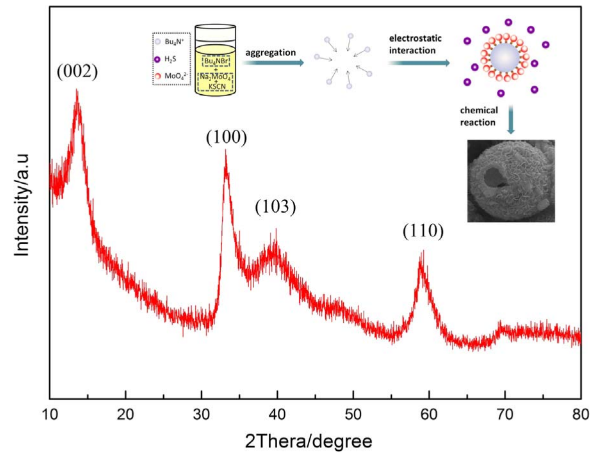

Fig. 1. X-ray diffraction patterns of as-prepared MoS_2. The inserted picture: schematic illustration of the formation process of hollow MoS_2 microspheres.

3. Results and discussion

3.1. Characterizations of MoS_2 hollow microspheres

The process in hydrothermal reaction can be illustrated as following reaction equations:

$$KSCN+2H_2O+HCl\rightarrow NH_3+H_2S+CO_2+NaCl$$

$$4NaMoO_4+9H_2S\rightarrow 4MoS_2+Na_2SO_4+6NaOH+6H_2O$$

The hydrothermal reaction process is showed in the inserted pictures of Fig. 1. Surface active agent Bu_4NBr works as a soft template, and Bu_4N^+ form small aggregates, and then many vesicles can be formed by increasing the aggregate size. After that, a large number of MoO_4^{2-} in solution is drawn to the surface of vesicles by electrostatic interaction. With the reaction temperature increasing, H_2S can be produced by the thermal decomposition of KSCN, which can react with MoO_4^{2-} attached on the surface of vesicles and result in MoS_2. The newly formed nano-sheets grow up gradually, stack, bend and eventually form hollow structures. XRD pattern of the MoS_2 presented in Fig. 1 shows four obvious diffraction peaks at 13.8°, 33.2°, 39.5° and 58.7°, corresponding to the (002), (100), (103), and (110) crystal planes of MoS_2. No other diffraction peaks corresponding to impurities phases are detected, which means a pure hexagonal phase has been generated.

The morphology and size of MoS_2 hollow samples were observed by SEM (Fig. 2a) and TEM (Fig. 2b), which show obvious hollow spherical structures with a diameter of 2.0 μm or so and a shell thickness of 200 nm or so. Plenty of curling nano-sheets can be found on the spherical surface. SEM images with lower magnification in the inserted picture at top right corner of Fig. 2a show uniform size of these microspheres.

3.2. tribological properties as LP additive

The obtained MoS_2 hollow microspheres were used as lubricating additives for LP, and the data in Table 1 show its good dispersion stability in the base oil (LP mixture containing 0.10 wt% of MoS2 hollow microspheres was centrifuged for 100 min at 2000 rpm and it was detected every 20 min by UV–vis spectrophotometry). Fig. 3a and b show the variation tendencies of average friction coefficients and AWSDs for LP mixtures containing different concentration of MoS_2 hollow microspheres. The average friction coefficient decreases very rapidly when their concentration is less than 0.02 wt%, corresponding to an average friction coefficient of 0.064. It almost reaches a stable value till the concentration increases to 0.20 wt%, while it is raised to