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Rolling friction performance and functional conversion from lubrication to photocatalysis of hollow spherical nano-MoS_2/nano-TiO_2

K.H. Hu [a,*], Y. Xu [a,b], E.Z. Hu [a], J.H. Guo [a], X.G. Hu [b]

[a] Department of Chemical and Materials Engineering, Hefei University, Hefei 230601, China
[b] Institute of Tribology, Hefei University of Technology, Hefei 230009, China

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ABSTRACT

The rolling friction performance of hollow spherical nano-MoS_2/nano-TiO_2 (HSMT), as well as the conversion from lubricant to photocatalyst, was studied. By combining the strengths of nano-MoS_2 and nano-TiO_2, HSMT could not only effectively roll with the rolling friction pair but also form a lubricating film to reduce friction and wear. The increase in HSMT photocatalytic activity was ascribed to three reasons. First was the exfoliation of nano-MoS_2 into nanosheets. Second was the synergistic catalysis between nanosheets and nano-TiO_2. Third was the good lubrication of nano-MoS_2, which protected nano-TiO_2 against acute friction and loss of crystal structure. The findings provide a possible approach for designing a novel green lubricant that may be re-used as a photocatalyst after lubricating service life.

1. Introduction

Molybdenum disulfide (MoS_2) has extensive application in lubrication and catalysis [1]. MoS_2 is a well-known solid lubricant used specifically in high-vacuum and high-temperature environments, wherein liquid lubricants cannot function because of volatilization and decomposition. MoS_2 is usually used as a lubricating additive in lubricating oil and grease [2,3], polymers [4,5], and coatings [6,7] to reduce friction and wear. For catalysis, MoS_2 is one of the most important hydrodesulfurization catalysts and has been widely used in the industry to remove S from crude oil [1]. Moreover, some studies reported that MoS_2 also has potential application in photocatalysis [8,9]. Thus, improvement in the lubricating and catalytic performances of MoS_2 has received much research attention [10–19].

Three main approaches can be used to improve the performances of MoS_2. First, the size of MoS_2 particles can be reduced to nanoscale. Recent studies confirmed that nanosized MoS_2 (nano-MoS_2) may be synthesized via chemical and physical methods and present better lubricating and catalytic performances than bulk microsized MoS_2 in most cases [9–11]. Second, the morphology of MoS_2 particles must be controlled. MoS_2 usually contains a hexagonal crystal structure and exists in laminar shape. The layered MoS_2 contains strong interlayer covalent bonds separated by a weak Van der Waals gap that is generally regarded as an important reason for its catalysis and lubrication. Daage and Chianelli proposed a “rim-edge site” model to explain the catalytic activity of laminar MoS_2 [20]. The surface of MoS_2 with laminar shape comprises three sites, namely, basal plane, edge, and rim. Catalytic activity is related to both edge and rim sites. Lubrication is mainly due to the easy sliding between MoS_2 layers under friction shearing [21,22]. If laminar MoS_2 is transformed into layer-closed structures, such as sphere and tube, the rim and edge sites will disappear and the layers will be unable to slide. The absence of rim-edge sites remarkably reduces the catalytic activity of layer-closed structures [23]. However, the sliding inability does not weaken the lubrication of layer-closed MoS_2. The formation of sphere-like and tube-like structures is beneficial to improve lubrication in most cases [11–15,24]. This phenomenon may be explained by several new lubricating mechanisms of layer-closed MoS_2, involving rolling, deformation, exfoliation, and shifting of exfoliated nanosheets [25–27]. The last approach exerts synergistic effects between MoS_2 particles and other materials. For example, layered MoS_2 may present synergistic lubrication and catalysis with TiO_2 [8,16,17,19,28].

A previous study reported the synthesis and tribology of hollow sphere nano-MoS_2/nano-TiO_2 (HSMT) composite in rapeseed oil [15]. The synthesized HSMT showed better lubricating performance than both commercial micro-MoS_2 and single spherical nano-MoS_2 during four-ball sliding friction in rapeseed oil. The present work investigated the four-ball rolling friction behavior of HSMT. The lubricating mechanism and exfoliation behavior of HSMT were also characterized. Moreover, the relation between

* Corresponding author.
E-mail addresses: hukunhong@gmail.com, hukunhong@163.com (K.H. Hu).

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rubbing exfoliation and photocatalysis was explored. The MoS_2 nanosheets/TiO_2 exfoliated from HSMT contained good photocatalytic activity for removal of organic pollutants. This finding provides a possible approach for designing a novel green lubricant that may be re-used as a photocatalyst to degrade organic pollutants after lubricating service life.

2. Experimental

2.1. Materials

Anatase nano-TiO_2 (TiO_2 content, > 92 wt%) was provided by Laiyang Zixilai Environmental Protection Technology Co., Ltd., China (detailed information can be found on http://en.zixilai.com/products_detail/&productId=37.html). Spherical MoS_2 nanoparticles (s-MoS_2) and HSMT were prepared according to previously described methods [11,15]. HSMT was characterized by high-resolution transmission electron microscopy (HRTEM; JEOL model 2010) with energy dispersive spectrometry (EDS) and X-ray powder diffraction (XRD; Rigaku D/Max-γB X-ray powder diffractometer) with Cu K_α radiation. The characterization results in Fig. 1a and b are similar to these in a previous study [15]. Elemental distribution of S from MoS_2 and Ti from TiO_2 in Fig. 1c showed that the sphere was mainly composed of MoS_2, and the MoS_2 content inside the sphere was lower than that in the shell. A negligible amount of Ti was also observed in the sphere, and low-content TiO_2 was almost distributed homogeneously in the whole sphere, including the shell and the inside. Characterization confirmed that nano-TiO_2 and MoS_2 were both not the core of the sphere. Although the inside of the sphere possibly contained a small quantity of MoS_2 and TiO_2, which did not exert a visible effect on elemental distribution, the MoS_2 sphere should at least be mostly hollow. An element S analyzer (Huayuan Company, Hebei, China) was used to determine the weight percent of S and the composition of HMST. The result showed that HMST contained 50.8% TiO_2 and 49.2% MoS_2. Steel balls (ϕ12.7 mm, ASTM E52100 bearing steel, 61–63 HRC in hardness) used as rolling friction pairs were purchased from SINOPEC Research Institute of Petroleum Processing.

2.2. Powder rolling friction test

Three styles of solid samples, namely, nano-TiO_2, s-MoS_2, and HSMT, were used as powder lubricants. Powder rolling friction tests were conducted on an MRS-10D four-ball tribometer (Shunmao Test Instrument Co., Ltd., China) equipped with a rolling friction pair. The schematic of four-ball rolling friction and characterization of wear scar is shown in Fig. 2. A rotation velocity of 0.077m/s of the upper steel ball and a constant load of 500N were applied in rolling friction tests. The dosages of powder lubricant were 1.0 and 0.6g. The upper steel balls rubbed for 10, 60, and 120min were characterized by 3D laser scanning microscopy (Keyence model VK-X100) and energy dispersive spectrometry (EDS) on a Hitachi model SU8010 scanning electron microscope. The powders after and before friction were characterized by XRD (Rigaku D/Max-γB X-ray diffractometer with Cu Kα radiation) and X-ray photoelectron spectroscopy (XPS; Thermo model ESCALAB250). HMST after friction was characterized using HRTEM (JEOL model JEM-2100F HRTEM) coupled with EDS.

2.3. Photocatalytic test

Photocatalytic activity was evaluated in a Bilon model BL-GHX-V photoreactor. Catalysts of 25 mg were added to 50 mL of 80 mg/L methyl orange (MO) solution. The obtained suspension was placed in the photoreactor and stirred for 30 min to complete adsorption balance. Subsequently, the suspension was exposed under light from a metal halide lamp of 1000 W at the middle of the photoreactor. About 2 mL of suspension was sucked after the reaction using an injector and clarified by centrifugation at 5000 rpm for 5 min. The ultraviolet–visible spectra of MO solution were recorded on a Meipuda model UV6300PC spectrophotometer.

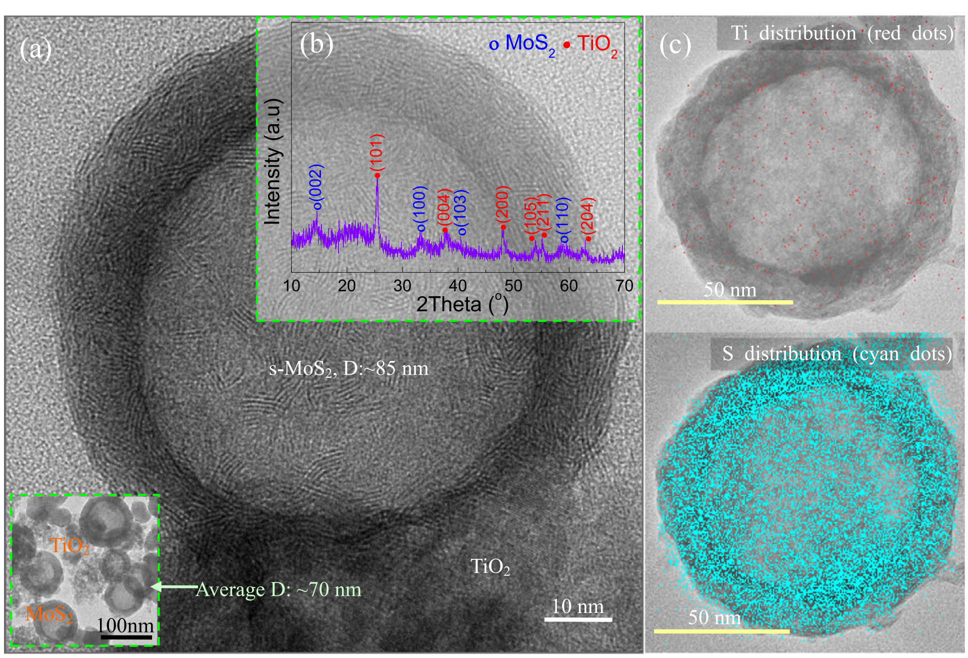

Fig. 1. Characterization results of (a) high-resolution transmission electron microscopy, (b) powder X-ray diffraction of hollow sphere nano-MoS_2/nano-TiO_2 (HSMT), and (c) elemental distribution of S (cyan dots) and Ti (red dots) via energy dispersive spectroscopy (EDS). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)