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PEG-mediated hydrothermal synthesis of hierarchical microspheres of MoS_2 nanosheets and their potential for lubrication application

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ABSTRACT

Lamellar-structured nanomaterials are gaining large interest for tribological applications owing to their remarkable mechanical and low shearing properties. Herein, polyethylene glycol (PEG)-mediated hierarchical microspheres of MoS_2 nanosheets are synthesized by a facile and single-step hydrothermal reduction of ammonium molybdate in the presence of thiourea. The PEG functions as a soft templating material and provides hierarchical microspheres of MoS_2 nanosheets. Detailed chemical and microstructural features of hierarchical microspheres of MoS_2 nanosheets are probed by FTIR, XPS, Raman, XRD, TGA, FESEM, and HRTEM analyses. Each nanosheet of MoS_2 microspheres is composed of limited number (10–20) of atomic-thick lamellae as deduced from HRTEM images. The MoS_2 microspheres, as additive provide significantly improved lubrication properties for steel tribo-pair by reducing the friction (~21%) and the wear (42%) compared to that of fully formulated 10W40 lubricant. The elemental mapping of worn surfaces revealed the deposition of MoS_2 nanosheets on the contact-interfaces. The improved lubrication properties are attributed to collective effect of deposition of delaminated MoS_2 lamellae on the contact interfaces, low shearing and high mechanical strength of MoS_2 nanosheets.

Introduction

Molybdenum disulfide (MoS_2) nanosheets, inorganic analogous to graphene, exhibit remarkable electronic, optical and mechanical properties, which are attributed to the quantum confinement, low dimension, bonding structure, layering patterns and surface defects [1–3]. Inspired by the recent advances of graphene research, nanostructural MoS_2 has attracted increasing interest for wide range of applications such as transistors, lubrication, catalysis, energy storage, sensors, optoelectronic devices etc [3–9]. The bulkier-form of MoS_2 is often referred as an excellent solid lubricant and provides remarkable lubricious properties even under severe environments such as extreme pressure, high temperature, and vacuum [10,11]. The MoS_2 possesses hexagonal close packed layered structure, where Mo atoms are covalently linked to upper and lower layers of S atoms in trigonal prismatic fashion, and resultant S–Mo–S layers are held together by the weak van der Waals interaction. These layers under the sliding stress provide low resistance to shear. The interlayer van der Waals coupling and low-frequency phonon modes monitor the in-plane shearing and out-of-plane breathing force constants of MoS_2 and offer excellent lubrication properties [12]. Over the last two decades, several studies have been done revealing tribological properties of 2H-MoS_2, IF-MoS_2 (inorganic fullerene-like) nanoparticles, nanotubes, nanosheets etc. [7,8,13–20]. The IF-MoS_2 nanoparticles, as additive to lubricant and thin film, showed remarkable tribo-performance and this was attributed to their high resistivity towards oxidation and rolling mechanism under the tribo-stress. The curved hexagonal planes in the IF-MoS_2 nanoparticles enhance their stability in humid environment and thus help to preserve the lamellar structure. The 2H-MoS_2 nanosheets interact with iron oxide of steel tribo-bodies and forms the tribo-chemical thin film *via* S–O, Mo–O and Fe–S linkages. The friction and wear reductions in the presence of 2H-MoS_2 nanosheets were attributed to their deposition on the tribo-interfaces [18]. The stable dispersion of MoS_2 nanosheets provide superior extreme-pressure property under boundary lubrication regime. They can enter into the contact area of tribo-interfaces and act like a protective film to prevent direct contact and seizure between them [20].

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The size and shape of MoS_2 nanoparticles significantly control their fundamental properties. In this context, various methodologies have been developed for synthesis of MoS_2 nanoparticles, nanosheets, nanotubes, nanospheres etc., including, scotch tape-assisted micro-mechanical exfoliation, solvent-processed exfoliation, intercalation-assisted exfoliation, sono-chemical synthesis, gas-phase reduction of MoO_3, wet-chemistry based approaches, hydrothermal and electrochemical synthesis [9,21–28,3]. The solvent-processed exfoliation of MoS_2 approach is promising for preparation, functionalization and hybridization of MoS_2 nanosheets. However, this method generally gives dispersion of low concentration. Currently, hydrothermal methods are gaining large interest for mass-scale preparation of MoS_2 owing to their simplicity and low energy consumption. The temperature, reaction precursors, surfactants and templating materials play important roles to control the size and shape of MoS_2 nanomaterials [15,26,27,29,30]. Recently, Luo et al. have demonstrated the synthesis of hierarchical MoS_2 microspheres composed of few-layered nanosheets using the polystyrene template [26]. However, the high temperature (800 °C) annealing was required under the inert atmosphere to decompose the polystyrene templating material.

The polyethylene glycol (PEG) has been widely used as a stabilizer, complexing agent and morphology controller for synthesis of various metal oxide and metal nanomaterials [31–33]. The PEG can be selectively adsorbed onto different crystal facets of atomic clusters and thus controls the growing rate. Herein, PEG 200 (average molecular weight: 200) was used as a structure-directing agent for the preparation of regular hierarchical microspheres of MoS_2 nanosheets, without using any solid template. The structural and chemical features of MoS_2 microspheres are examined by XRD, HRTEM, Raman, FTIR and XPS analyses. These microspheres having thin sheets of atomic-thick lamellae of MoS_2 are found to be wear-preventive and friction-reducing additive for the commercial lubricant and mineral lube base oils. A plausible mechanism is discussed to understand the role of MoS_2 lamellae in reducing the friction and wear.

Experimental

Synthesis of hierarchical microspheres of MoS_2 nanosheets

The hierarchical microspheres of MoS_2 nanosheets were prepared by following a hydrothermal reduction route. In a typical procedure, 1.21 g sodium molybdate ($Na_2Mo_4{\cdot}2H_2O$) was dissolved in 30 mL distilled water and then thoroughly mixed with 10 mL PEG 200 (average mol. wt. ~200). After 10 min of stirring, 1.56 g thiourea [$(NH_2)_2CS$] was gradually added to the sodium molybdate solution and reaction mixture was further stirred for 20 min. The reaction mixture was then transferred into a teflon-lined stainless steel autoclave. The autoclave was tightly sealed and kept in the oven at 230 °C for hydrothermal reduction of sodium molybdate in the presence of thiourea. After 24 h, the autoclave was removed from the oven and then allowed to cool down at room temperature. The developed black colour material suspended in the water was then separated by centrifuging at 5000 rpm for 40 min. The collected wet cake of MoS_2 was repetitively washed with distilled water until the neutral pH of decanted water was attained. Ethanol was used for the final washing.

Chemical and structural characterizations

Fourier transform infrared (FTIR) transmittance spectrum of MoS_2 microspheres was recorded using a Thermo Scientific Nicolet 8700 research spectrometer. The X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., ESCA 3400) measurement of MoS_2 microspheres was carried out using an Mg Kα line as the X-ray source. The peak-fitting of the Mo 3d and S 2p spectra were carried out by using a Gaussian–Lorentzian function after considering a Shirley background correction. X-ray diffraction (XRD) pattern of MoS_2 microspheres was collected using a Bruker D8 Advanced diffractometer at 40 kV and 40 mA using Cu Kα radiation (λ = 0.15418 nm). Field emission scanning electron microscopic (FESEM) images of MoS_2 microspheres were collected using an FEI Quanta 200 F microscope. Elemental mapping of MoS_2 microspheres was carried out using the Energy Dispersive Spectrometer (EDS) coupled with FESEM. High resolution transmission electron microscopic (HRTEM) images of MoS_2 microspheres were captured using a JEOL 300KV JEM 3010 microscope. A TEM grid was prepared by drop-casting of ethanolic dispersion of MoS_2 microspheres on the 200 mesh Cu grid. The Raman spectrum of MoS_2 microspheres was recorded using a Renishaw micro-Raman spectrometer (Model INVIA) equipped with an Ar-ion laser (λ = 514.5 nm).

Lubrication properties of MoS_2 microspheres

The lubrication properties in terms of the coefficient of friction and the wear were probed using a ball-on-disc standard tribometer (CSM Instruments, Switzerland) operating in a reciprocating mode. The 100Cr6 steel ball (ϕ = 6 mm) was used as a sliding material against the lubricated 316LN steel disc. A sliding ball is mounted in a holder which is connected through a lever coupled with friction force transducer. A little quantity of lubricant (~200 μL) was applied between the steel ball and the disc ensuring that lubricant is always present between the sliding interfaces. The 10W40 fully formulated commercial lubricant and N-150 mineral lube base oils were used as references throughout this study. All tribo-experiments were conducted at applied normal load of 2 N and linear speed of 3 cm s^{-1} for sliding distance of 100 m. Each tribo-test was repeated for minimum two times to ensure the repeatability of the results. Furthermore, the error bars of friction and wear results are provided to understand the repeatability of results. The wear rate is calculated using wear track depth and width, which were measured by two-dimensional wear profiling of worn tracks using a Dektak 6M – stylus profiler fixing 5 mg contact load at scanning speed of 10 μm/s. The stylus is mechanically coupled to the core of an LVDT sensor. Furthermore, the changes in morphological and elemental features on the worn tracks after the lubrication tests were examined by using FESEM (FEI Quanta 200 F) coupled with EDS.

Results and discussion

As shown in Fig. 1a, the synthesized material exhibits the microspheres of MoS_2 with sizes of 1–5 μm. These microspheres are composed of thin sheets of atomic-thick lamellae of MoS_2. The high-resolution TEM images (Fig. 1$b_{ii–iii}$) explicitly illustrate that each MoS_2 nanosheet is constituted by 10–20 molecular thick lamellae. The interlayer spacing between the MoS_2 lamellae is estimated to be ~0.63 nm and is very close to the characteristic interlayer distance (0.616 nm) for (0 0 2) plane of MoS_2. These hierarchical microspheres of MoS_2 nanosheets were prepared by hydrothermal reduction of sodium molybdate. The H_2S, generated by hydrolysis of thiourea in the closed reaction vessel at high temperature and pressure, reduces the Mo(VI) into Mo(IV) and forms the MoS_2. The PEG can be selectively adsorbed onto different crystal facets of MoS_2 *via* weak coordination linkage and that control the growth rate and direction of different facets [33,34]. Under hydrothermal condition, MoS_2 seeds grow with continuous feeding of MoS_2 nucleate and eventually develop the MoS_2 nanosheets. Simultaneously, excess units of PEG forms the

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