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Solvent-free ionic molybdenum disulfide (MoS_2) nanofluids with self-healing lubricating behaviors

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ABSTRACT

Nanoscale ionic materials (NIMs) which have a core-corona-canopy structure are innovative materials that have drawn great attention. In our work, homogeneous and stable solvent-free ionic MoS_2 nanofluids, falling under the category of typical NIMs, were obtained by surface functionalizing and ionically tethering nanoscale graphite-like MoS_2 from hydrothermal synthesis. Rheological results and the fluidity of nanofluids showed the Newtonian liquid behaviors of the nanofluids, which is favorable for lubrication. Furthermore, nanotribological results reveal that the nanofluids show lower, more stable friction coefficients and self-healing lubricating behaviors under a certain limit of normal load. The nanofluids can protect the substrates from scratching and wear.

1. Introduction

MoS_2 is a kind of transition metal dichalcogenide compound with graphite-like layered structure and has been widely used as solid lubricants and lubrication additives, efficiently increasing the anti-wear ability and load-carrying capacity [1]. Nano-sized MoS_2 usually has better tribological properties and thus attracts more attention [2,3]. However, the results usually fail to reach a satisfactory dispersion in suspension systems. By surface modification, MoS_2 nanoparticles had better stability and solubility in organic solvents or lubricating oils. As reported, free-standing nanosheets of MoS_2 were obtained by a wet chemistry approach based on low-temperature decomposition in oleylamine. The protective coating of oleylamine stabilized the suspension and avoided aggregation [4].

Herein we report a kind of solvent-free ionic MoS_2 nanofluids, falling under the category of an innovative class of materials termed as nanoscale ionic materials (NIMs) [5–7]. Pioneered by Giannelis and his co-workers, NIMs are typically composed of inorganic nanoparticle cores, charged corona, and ionically tethered oligomeric canopy, resulting in homogeneous, one-phase fluids rather than two-phase dispersions of nanoparticles suspended in ionic liquids [6]. Based on our previous work [8], we present new evidences showing that the nanofluids have better nanotribological properties and self-healing lubricating behaviors.

2. Materials and methods

Synthesis of solvent-free ionic MoS_2 nanofluids: MoS_2 nanofluids were synthesized according to our previous paper [8]. Hydroxylamine hydrochloride ammonia ($NH_2OH \cdot HCl$, Sinopharm Chemical Reagent Co., Ltd.) was used to reduce sodium molybdate (Na_2MoO_4, Sinopharm Chemical Reagent Co., Ltd.), which was followed by sulfidation reaction with sodium sulfide (Na_2S, Sinopharm Chemical Reagent Co., Ltd.). The as-synthesized nanoscale MoS_2 suspension was sulphonated by 3-(trihydroxysilyl)-1-propane sulfonic acid (SIT, 30–35 wt% solution in H_2O, Fluorochem Ltd.) dropwise under vigorous stirring for 24 h at 70 °C. Free SIT and ionic impurities were removed by dialyzing in deionized water. The functionalized nanoparticles were passed through an ion-exchange column (732, Sinopharm Chemical Reagent Co., Ltd.) 4 times to ensure complete replacement of Na^+ ions by protons. Afterwards, oligomeric tertiary amine (ethomeen, $(C_{18}H_{37})N((CH_2CH_2O)_mH)$ $((CH_2CH_2O)_nH)$ (M_w=930 g mol^{-1}, Haishihua Inc.)) was ionically tethered to functionalized nanoscale MoS_2 as a canopy to balance the charge. Solvent-free ionic MoS_2 nanofluids were obtained after removal of extra solvent under vacuum at 50 °C for 4 days.

Characterization: A high resolution transmission electron microscope (HRTEM, JEM 2010F, JEOL, Japan) was used to analyze the structure of MoS_2 cores. An AVATAR 360 ESP FT-IR spectrometer was used to study the chemical structure of MoS_2 nanofluids. Rheological properties were measured using an ARES Rheometer (TA instruments) by dynamic strain frequency sweep at a strain of 1% and 25 °C. A cone of 1° and plate with 25 mm diameter measurement system was employed. Nanotribological properties were measured using an in-situ nanomechanical test

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system (Tribo Indenter, Hysitron Inc.) with a diamond tip of 60° and a radius of 1 μm under normal loads of 200 μN, 400 μN and 600 μN at 22 °C. Thin film of MoS_2 nanofluid (12.5 wt% MoS_2) was prepared by spin-coating technique on polished silicon substrates. The scratching experiments were conducted at a sliding speed of 1 μm s^{-1} for three cycles with a constant length of 5 μm. In-situ images of scratches were taken by scanning probe microscope (SPM) equipped with the tester. Scanning electron microscopy (SEM) images of silicon substrates after the scratching experiments and removal of coated films were obtained using Quanta 200 (FEI).

3. Results and discussion

Structures and rheological behaviors of MoS_2 nanofluids: The lamellar structure well-stacked with curving and parallel fringes of as-prepared nanoscale MoS_2 is shown in Fig. 1a. The lattice spacing distance is measured to be 0.31 nm corresponding to (004) planes, which can be interpreted as a layered structure with a half-monolayer stacking since twice of this value exactly fits the profile of (002) lattice plane [9]. The chemical structure of MoS_2 nanofluids as expected in Fig. 1b is verified by FTIR spectra shown in Fig. 1c. The presence of peaks at 2920, 2874 and 1180 cm^{-1}, corresponding to stretching vibrations of $-CH_2-$ and –C–O–C– groups, indicates the success of ionically tethering reaction.

The high graft density and uniform dispersion of inorganic cores ensure the fluidity of the nanofluids at room temperature. It is evident that the MoS_2 nanofluid with 28 wt% MoS_2 is a homogeneous amber-like fluid with no phase separation as shown in Fig. 2a. Further evidences of the uniform dispersion of MoS_2 nanofluids can be found from the HRTEM image and DLS result in our previous work [8]. The fluidity is attributed to ionic binding and organic canopy acting like a suspension agent of inorganic cores [5]. As shown in Fig. 2b, the higher loss modulus (G″) than the storage modulus (G′) throughout the measured frequency range indicates fluid-like behaviors. It is well acknowledged that frequency-independent complex viscosity speaks volumes for Newtonian liquid [5]. Fig. 2c presents the complex viscosity of the nanofluids with different core fractions. Nanofluids with core fraction of 28 wt% and 32 wt% display perfect Newtonian behaviors, while nanofluid with core fraction of 54 wt% shows shear thinning tendency. Similar behaviors have been reported by Rodriguez et al., who claimed tertiary amine-based silica nanofluids displayed Newtonian behaviors up to core volume fraction of about 19%. Above this concentration, shear thinning occurred [10]. It seems that all NIMs show non-Newtonian behaviors with strong shear thinning at high core fractions [5,10]. The critical concentration of tertiary amine-based silica nanofluids is much lower than that of our MoS_2 system. Since Newtonian liquid behavior is favorable for lubrication in terms of stability during friction and wear, the MoS_2 nanofluids are more suitable for lubricating applications. Besides, the rheological behaviors can be tailored by varying not only the core fraction, but also the core type and canopy structure, which contributes to controllability and diversity of flow behaviors.

Nanotribological properties of the MoS_2 nanofluids: For micro-dimension systems, such as microelectromechanical systems (MEMS) and magnetic storage systems, parameters like scratching resistance, wear and mechanical properties measured at the nano-/micro-scales are of significant importance and need to be well understood [11]. Likewise, we managed to study the nanotribological behaviors of the MoS_2 nanofluids using an in-situ nanomechanical test system. The values of friction coefficients under different applied normal loads are shown in Fig. 3. The three segments of each curve represent three tip scratching rounds in 15 s at a speed of 1 μm s^{-1}. As shown in Fig. 3a, silicon substrate coated with MoS_2 nanofluid shows significantly lower and more stable friction coefficient values under 200 μN compared with the bare substrate. The nanoscale friction coefficient values are found to be about 0.1, significantly lower in contrast with other materials, suggesting the potential application of the nanofluids for MEMS systems [11]. Under normal load up to 400 μN, friction coefficient values stay the same values with less fluctuation. The peculiar phenomenon during round 2 in Fig. 3b might be caused by tailing effect of the highly viscous property of the film. But this phenomenon decays rapidly and the friction coefficient values return to stable values in round 3. In our system, when the applied normal load reached 600 μN, the friction coefficient values increased to the same level as those of the bare substrate as shown in Fig. 3c, indicating that the film had been broken, and the friction coefficient values in round 2 and

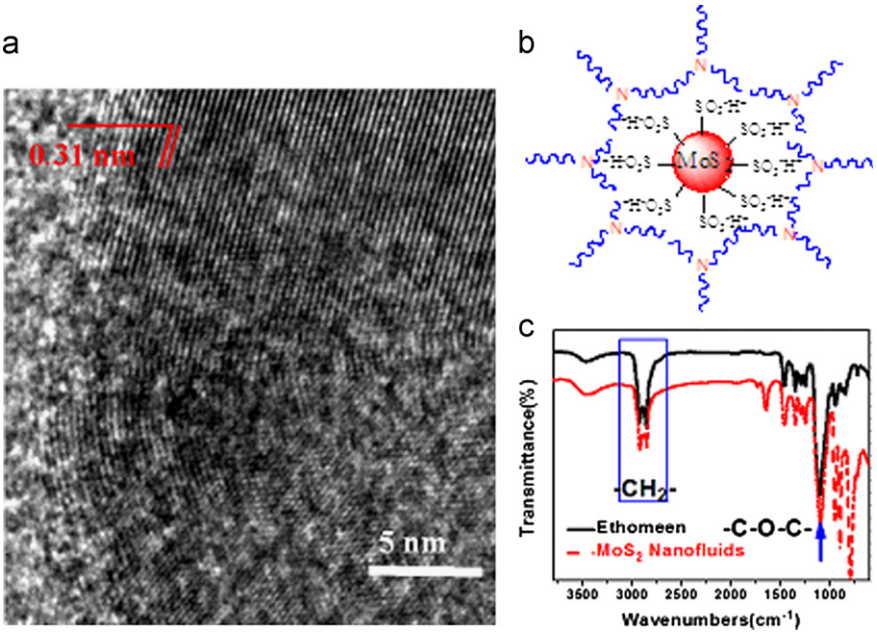

Fig. 1. (a) HRTEM image of the nanoscale MoS_2; (b) schematic of the structure and (c) FTIR spectra of the MoS_2 nanofluids.