TEMPLATE-FREE SYNTHESIS OF $MoSe_2$ HOLLOW NANOSPHERES WITH EXCELLENT TRIBOLOGICAL PROPERTIES

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Novel $MoSe_2$ hollow nanospheres with diameter ~50 nm, consisted of 3~ layered structure $MoSe_2$ nanosheets, were successfully synthesized by a facile one-step hydrothermal method using selenium powders and ammonium molyb date as raw materials. The as-prepared products were characterized using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM); UMT-2 tribotester was used to assess their lubricating effect when used as additives in base oil dispersions. And the topography of worn scars was measured using a BRUKER Contour GT non-contact 3D optical profile testing instrument. Tribological performance showed that the obtained $MoSe_2$ hollow nanospheres possessed anti-wear and friction-reducing properties as a lubrication additive compared with pure base oil, which will deform and exfoliateand enter into the interface with base oil, then form tribofilmon rubbing surface, enhancing the tribological properties.

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1. Introduction

Molybdenum selenide ($MoSe_2$), as a typical layered transition metal selenide [1–4], in recent years, has garnered a respectable interest for its unusual combination properties and extensive applications in catalysis[5-6], photoluminescence devices [7-8], lithium ion batteries [4], lubricants [9–11], field-effect transistors[12] and so forth. Therefore, it is extraordinarily important to synthesise $MoSe_2$ with well-controlled dimensionality, size, morphology, and crystal structure for industrial and high technology applications [2,13–16].

To date, several methods, such as hydrothermal and solvothermal method [17, 18], chemical vapor deposition (CVD) [19-21], solid-state reactions [22,23], mechanical exfoliation [24,25], liquid exfoliation [26], and soon have been employed to synthesise $MoSe_2$nanomaterials. Compared with the other methods, hydrothermal or solvothermal methods can not only induce the formation of well crystallized products with mild synthetic conditions and simple manipulation, but can also control the phase, shape and size of the resultant products simply through adjusting the synthesis conditions such as composition of the solution, pH, temperature, duration, etc.

Hollow nanospheres materials have been regarded as fascinating nanomaterials in the field of batteries [27,28], photocatalysis [29,30], supercapacitor electrodes[31], biosensing [32], gas-sensing[33],and so on. However, $MoSe_2$ hollow nanospheres have rarely been reported,

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therefore, it is still a great challenge to develop a facile and effective process to fabricate $MoSe_2$ hollow nanospheres. In addition, it was found that $MoSe_2$ has an excellent tribological property, especially coatings [34-35]. However, to the best of our knowledge, little work focused on the tribological properties of $MoSe_2$ as lubrication additive.

In this work, the $MoSe_2$ hollow nanospheres were successfully prepared by hydrothermal reaction $(NH_4)_2MoO_4 \cdot 2H_2O$ and Se powder in mixture of hydrazine hydrate and water at high temperature. The tribological properties of$MoSe_2$ hollow nanospheres as additives in the 100SN base oil were also investigated. This study provides a simple and novel route for the hydrothermal preparation of$MoSe_2$ and will be useful for $MoSe_2$ practical application in the future.

2. Experimental

2.1. Synthesis of $MoSe_2$hollow nanospheres:

All chemical reagents were of analytic purity and applied directly without further purification. First, ammonium molybdate $(NH_4)_2MoO_4 \cdot 2H_2O$ (0.507 g), hydrazine hydrate $(N_2H_4 \cdot H_2O)$ (10 mL), Se powder (0.316 g) were dissolved in 60 ml deionized water under constant stirring. The pH value of the mixture was adjusted to 12 by addition of NaOH solution. The final solution was transferred into a 100 ml Teflon-lined stainless steel autoclave, which was sealed and treated at 200°C for 48 h and cooled down to room temperature naturally. The resulting suspension were washed several times with distilled water and absolute ethanol, and dried in air at 70°C for 12 h.

2.2. Characterisation of $MoSe_2$ samples:

The phase and crystallinity of the as-synthesized products were characterized by X-ray diffraction with aD8 advance (Bruker-AXS) diffractometer employing CuKα radiation operated at 40Kv and 20mA, data analysis with Jade software. The composition was characterised by energy-dispersive spectroscopy (EDS). The morphologies and structures of the samples were investigated by scanning electron microscopy (SEM, JEOL JSM-7001F) equipped with single crystal W cathode, and transmission electron microscope (TEM, JEOL JEM-2100)equipped with LaB_6cathode using an accelerating voltage of200 kV. The samples for the SEM and EDS studies were prepared by placing the $MoSe_2$ powders on to a copper disk with conducting resin followed by metal spraying. The samples for the TEM studies were prepared by dispersing the powdersin ethanol through ultra-sonication and drop casting the dispersion onto a carbon coated copper grid.

2.3. Tribological properties of $MoSe_2$ hollow nanospheres as a lubrication additive:

The as-prepared $MoSe_2$ hollow nanospheres were distributed into the 100SN base oil via 60 min ultra-sonication without any active reagent. The friction and anti wear properties of the oil with $MoSe_2$ samples were examined on a UMT-2 ball-on-disc friction and wear tester at ambient conditions. The testing of the friction reduction and wear resistance was conducted at a rotating speed of 300 rpm and a load of 5–30 N for 200 m. The material of the upper sample was a 440C stainless-steel ball with a diameter of 10 mm, a hardness of 62 HRC and the counterpart is a 45 steel disc of Ø30 mm × 5 mm in size. The friction coefficient was recorded automatically. Morphologies of wear scars were examined using a BRUKER Contour GT non-contact 3D optical profile testing instrument.

3. Results and discussions

The crystallinity, structure, and phase purity of the prepared samples were confirmed by XRD and EDS. Fig. 1a shows the XRD pattern of the $MoSe_2$ sample fabricated by the hydrothermal reaction $(NH_4)_2MoO_4 \cdot 2H_2O$ and Se powder in mixture of hydrazine hydrate and distilled water at 200 ^oC for 48 h. All peaks in the XRD pattern can be readily indexed to the hexagonal ($P6_3$/mmc space group) $MoSe_2$ phase, with lattice constants a=3.288Å, c=12.930Å, which are in good agreement with the reported values (JCPDScardno.87-2419). No characteristic peaks from other impurities are observed in the XRD pattern, indicating the high purity of the $MoSe_2$ samples. The XRD peaks are a little broad and this suggests that the as-prepared products are somewhat amorphous during the hydrothermal process. Energy-dispersive X-ray spectrometer (EDS) result as shown in Fig. 1b reveals that the sample consisted of element Mo and Se, no another element is observed. Furthermore, the quantification of the peaks shows that the atom ratio between Mo and Se is about 1:2.22, which is close to the stoichiometric $MoSe_2$.

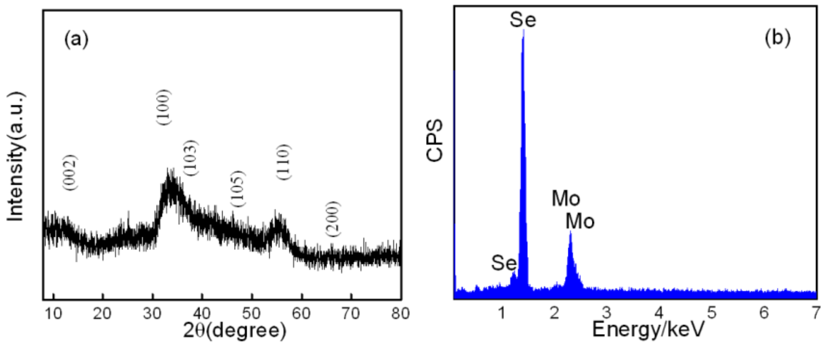

Fig. 1.(a) XRD pattern and (b)EDS of the as-prepared $MoSe_2$.

The morphology of the obtained $MoSe_2$ products was investigated by SEM (Fig. 2a and 2b) TEM (Fig. 2c) and HRTEM (Fig. 2d). Fig. 2a displayed the low magnification SEM images of $MoSe_2$ nanomaterials architecture, and these nanomaterials composed of many aggregated particles. An enlarged SEM image apparently showed that the obtained samples mainly comprised of nanospheres, as shown in Fig. 2b. Further insight into the morphology and microstructure of $MoSe_2$ nanomaterials was gained by TEM. As shown in Fig. 2c, the low-magnification TEM imaged shows that the as-synthesized $MoSe_2$nanomaterials assembled of many uniform hollow nanospheres with an average size of ~50nm,the results are consistent with the above SEM observation. The high- magnification TEM image, as shown in Fig. 2d, indicatesthat$MoSe_2$hollow nanospheres mainly consisted of 3~ layers stacking of the monatomic sheets, the interlayer separation between the $MoSe_2$ layers is about0.67 nm.

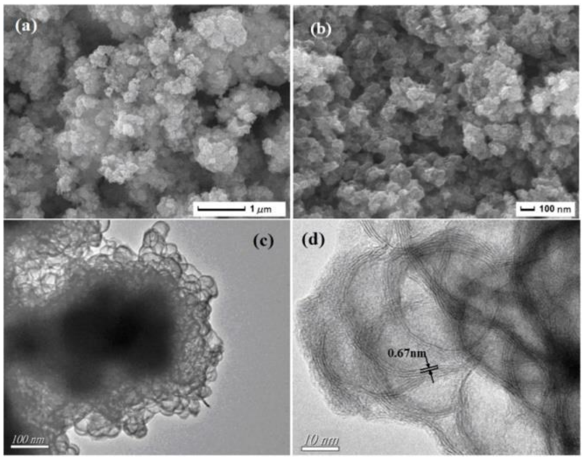

Fig. 2. FESEM (a,b), TEM(c) and HRTEM (d) image of the $MoSe_2$ nanospheres.

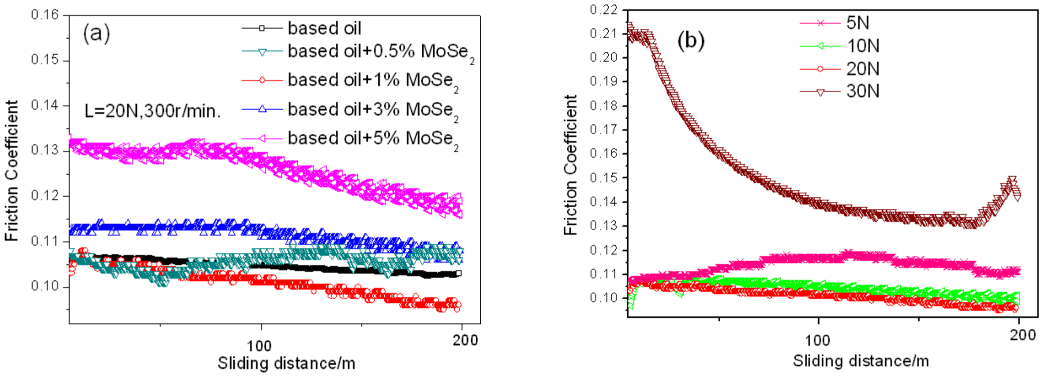

Fig. 3. Friction coefficients vs. sliding distance curves for base oil containing different concentrations $MoSe_2$ (a) and base oil mixed with 1.0 wt% $MoSe_2$ additive under different loads (b).

In order to investigate the evolutions of the friction coefficients with the different concentrations of$MoSe_2$, the tribological performance of the oil with different contents of $MoSe_2$ were tested under a condition of 20 N, 300r/min and 200m, respectively, as provided in Fig. 3a. It can be found that the base oil with 1wt% $MoSe_2$ gives a lower and more stable friction coefficient than others. This is not the case with the 0.5 %, 3% and 5% content of $MoSe_2$ additive. With regards to the 0.5wt % content of $MoSe_2$, the friction coefficient is decreases firstly, and then it progressively increases. With regards to the 3wt % content of $MoSe_2$, at the beginning of the test and up to 100m, the friction coefficient is fairly stable at ~0.113, then it progressively decreases along the sliding distance. The oil formulated with 5wt % $MoSe_2$ shows different distance dependence to that of with other content of $MoSe_2$, and with somewhat higher and unstable friction coefficient. When the concentration of synthesized $MoSe_2$ is 1wt%, the best friction coefficient-reducing property is obtained. The excellent tribological performance can be attributed to their hollow spheroidal and extremely thin laminated structure. Moreover, the nanoparticles can easily enter into the interface with base oil and deposit a continuous protective film, so the performance of friction coefficient is more stable than others, however, too much higher concentration of the nanoparticles exhibited extensive agglomeration, could not enter the contact area easily [36–37], also could destroy the stability of the colloid system of the base oil [38]. Therefore, the optimum concentration of the synthesized $MoSe_2$ as an additive in base oil is suggested to be 1wt%.

Fig. 3b show the variations of friction coefficient of 1 wt% $MoSe_2$hollow nanospheres as an additive of lubricant under different loads, respectively. It can be seen that there is a tendency that the friction coefficient of$MoSe_2$decreases firstly and then increases as the load increases, also, the curves of 5N and 30N have higher noise than the curves of 10N and 20N. We can get the optimal load for friction performance at 10N and 20 N. In a certain pressure range, $MoSe_2$ hollow nanospheres is crushed and delaminated easily at the contact zone and form a tribofilm, which can decrease shearing stress and give a low friction coefficient. When the applied load is 5 N, $MoSe_2$ cannot be compacted on the worn surface to mend wear scar, so the protective film was not formed. On the contrary, if the applied load is too high, the protective film at the contact zonewill be destructed, finally leading to high noise and friction coefficient.

In order to investigate the wear resistance property of $MoSe_2$ hollow nanospheres as lubricant oil additives, the wear scars of plate after rubbing were tested by a BRUKER Contour GT non-contact 3D optical profile testing instrument. Fig. 4 illustrates wear scars of the base oil and oil with 1wt % $MoSe_2$at 300 r/min under 20 N loads. It can be clear seen that the wear scar for base oil is composed of wide grooves and irregular pits along the sliding direction (Fig 4a), and the grinding crack caused by the base oil with 1wt% $MoSe_2$ hollow nanospheres (Fig 4b) is shallower and smoother than that caused by the base oil (Fig 4a). From the images we can see that the depth and width of the wear scar for base oil with 1wt% $MoSe_2$ hollow nanospheres are about 30μm and 110μmrespectively, while those for pure base oil are about 60μm and 180 μm. This proves that the base oil with 1wt% $MoSe_2$ hollow nanospheres represented better anti-wear capability than base oil.

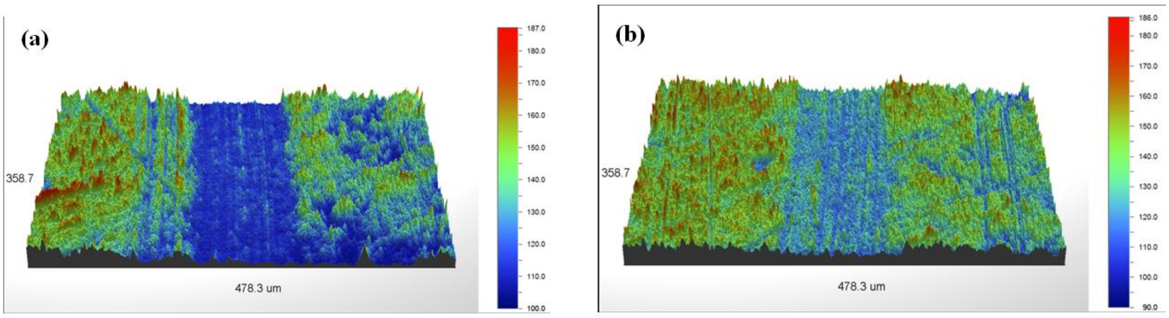

Fig.4. Non-contact 3D optical profile testing instrument images of the wear scars of (a) the base oil, (b) the base oil with 1w.t.%$MoSe_2$ at 300 r/min under 20 N loads for 200m

From the above results, $MoSe_2$ hollow nanospheres as lubrication additive could improve tribological properties of the base oil. The tribological mechanism between the rubbing surfaces in base oil with $MoSe_2$ hollow nanospheres is vividly proposed in Fig. 5. It is believed that the suitable content of $MoSe_2$ hollow nanospheres could enter in the gap between the friction surfaces effectively, which is responsible for the friction coefficient improvement. Studies have shown that the exfoliated molecular sheets from hollow nanospheres transfer onto the rough surface and form a tribofilm, which is the main mechanism for improving the tribological behavior of hollow nanospheres, while the rolling friction here also plays some role. In this experiment, $MoSe_2$ hollow nanospheres having a rolling antifriction temporarily at the initial stage, with the prolong of sliding time and the change of normal load, hollow nanospheres gradually deformed and began exfoliated, then the exfoliated $MoSe_2$nanosheetis adsorbed on the surface of the friction pair to form a layer of tribofilm, which can decrease shearing stress, and result in a decrease of the friction coefficient.

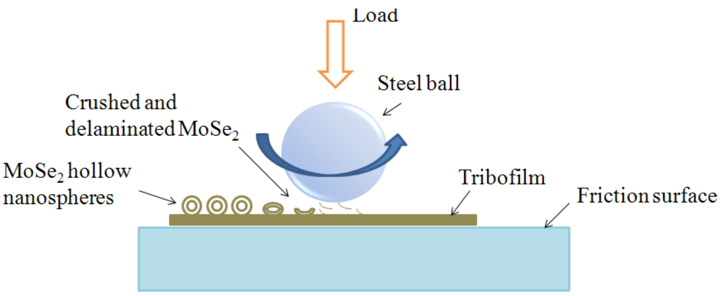

Fig. 5.Mechanism model of friction reduction and wear resistance between friction surfaces in the base oil with $MoSe_2$ hollow nanospheres

4. Conclusions

The novel $MoSe_2$ hollow nanospheres have successfully synthesized by a facile and effective hydrothermal method. The results indicated that the $MoSe_2$hollow nanospheres with diameter~50 nm, and consisted of 3~ layered structure $MoSe_2$nanosheets. The tribological measurements showed that the optimum concentration (1.0 wt%)$MoSe_2$hollow nanospheres by mixing with base oil has excellent friction reduction and wear resistance properties. Furthermore, the experiment results suggested that $MoSe_2$hollow nanospheres crushed and delaminated and formed a tribofilm on the worn surface, which could improve the tribological properties. So, $MoSe_2$ hollow nanospheres reveal a potential application in lubrication.

Acknowledgments

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