

Hydrothermal synthesis and tribological properties of MoSe₂ nanoflowers

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Molybdenum selenide (MoSe₂) nanoflowers have been favourably synthesised by a mild hydrothermal route using sodium molybdate and selenium powder at low temperatures. The gained crystallographic products were analysed by powder X-ray powder diffraction (XRD), energy-dispersive spectroscopy, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy. The XRD pattern of the product can be easily indexed to hexagonal MoSe₂. SEM and transmission electron microscopy graphics of the products reveal that the MoSe₂ nanoflowers with diameters of about 100 nm consist of nanosheets. The tribological behaviours of MoSe₂ as oil additives were evaluated on a ball-on-disc tribometer. Under the given experimental conditions, the oil containing MoSe₂ gave lower friction coefficients than that of the base oil. A smooth tribofilm formed on worn surfaces is believed to be responsible for the good lubricating effects of MoSe₂ as additives.

1. Introduction: Molybdenum selenide (MoSe₂) is a member of transition metal dichalcogenides with a general expression of MX₂, where M stands for a transition metal, such as Mo, W, Nb or Ti; X is S or Se [1–6]. MX₂ nanomaterials exhibits outstanding properties [7–15], such as optical, electronic, magnetic, thermoelectric, electrocatalytic and optoelectronic properties, and have received considerable attention from scientific researchers.

Recent studies have shown that these nanomaterials have far-reaching applications, such as lubricant additives [16], field-effect transistors [17, 18], photoluminescence devices [19, 20], lithium-ion batteries [21], phototransistors [22], integrated circuits [23] and catalysis [24, 25] and so on [26, 27].

To date, several methods, including the hydrothermal method [28, 29], thermal reduction [30], solid-state reactions [31–33], chemical vapour deposition [34, 35], mechanical exfoliation [36], liquid exfoliation [37] and so on, have been adopted to synthesise MoSe₂. However, MoSe₂ hierarchical self-assembled nanostructures have rarely been reported; so, it is a necessary task to progress a mild and practical method to synthesise MoSe₂ nanomaterials. Moreover, it was discovered that MoSe₂ has remarkable tribological performance, particularly as coatings [38, 39]. However, as far as we know, few studies paid attention to the tribological behaviours of MoSe₂ as a lubrication additive.

In the work reported in this Letter, MoSe₂ nanoflowers were successfully prepared by hydrothermal reaction of Na₂MoO₄ and Se powder in a mixture of hydrazine hydrate and water at 200°C. The tribological behaviours of MoSe₂ nanoflowers as lubricating oil additives were also studied. The excellent anti-wear and friction reducing performance manifests MoSe₂ nanoflowers as an excellent lubrication additive, and the basic data supplied will be beneficial in further engineering applications in the future.

2. Experimental

2.1. Synthesis of MoSe₂ nanoflowers: Selenium powder and Na₂MoO₄·2H₂O were bought from the Sinopharm (Shanghai) Chemical Reagent Co. Ltd. All other chemicals were of analytical grade reagents and were used first hand without further purification. In a typical synthesis, 0.483 g of Na₂MoO₄·2H₂O, 0.316 g Se powder was dissolved in a mixture of 10 ml of hydrazine hydrate (N₂H₄·H₂O) and 60 ml of deionised water under constant stirring and stirred into a red solution, and then the pH value of the solution was adjusted to about 12 by the

addition of an NaOH solution. After violent stirring, the resulting mixture was transferred to a 100 ml Teflon-lined stainless autoclave, sealed tightly and maintained at 200°C for 48 h, then cooled down to room temperature naturally. The suspension was then repeatedly filtered and washed with distilled water and absolute ethanol. Finally, the as-prepared powder was dried in air at 70°C for 12 h, and black MoSe₂ was obtained.

2.2. Characterisation of MoSe₂: The structure and phase of the as-prepared samples were recorded using X-ray diffraction (XRD) with a diffractometer employing Cu-Kα radiation operated at 40 kV and 20 mA, and data analysis was conducted with Jade software. The morphologies of the as-prepared product were characterised using a scanning electron microscope (SEM, JEOL, JSM-7001F), and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100). The composition was characterised by energy-dispersive spectroscopy (EDS).

2.3. Tribological behaviours of MoSe₂ samples as a lubrication additive: The as-prepared MoSe₂ samples were dispersed ultrasonically in a base oil without any active reagent. The tribological properties of the oil with MoSe₂ samples were investigated using a UMT-2 ball-on-disc tribometer at ambient conditions. The testing of the anti-wear and friction reducing performance was carried out at 200 rpm under a 10–50 N applied load for 800 s. Balls of 10 mm diameter used in the tests were made of 440C stainless steel with a hardness of 62 HRC. The discs were of 45 steel disc (Ø 30 × 5 mm). The friction coefficient was recorded automatically by a computer and the wear scars widths (WSW) of the discs were measured with a metallographic microscope. The morphologies of the worn surface were analysed under a scanning electron microscope (SEM, JSM-5600LV).

3. Results and discussions

3.1. Characterisation of MoSe₂ nanoflowers: The crystal structure and phase purity of the obtained products were analysed through XRD and EDS. Fig. 1a reveals the XRD pattern of the MoSe₂ sample prepared by the hydrothermal reaction of Na₂MoO₄·2H₂O and Se powder in a mixture of hydrazine hydrate and distilled water at 200°C for 48 h. All major observed diffraction peaks can be indexed to the hexagonal MoSe₂ phase, with lattice constants $a = 3.288 \text{ \AA}$ and $c = 12.930 \text{ \AA}$, which coincide with standard

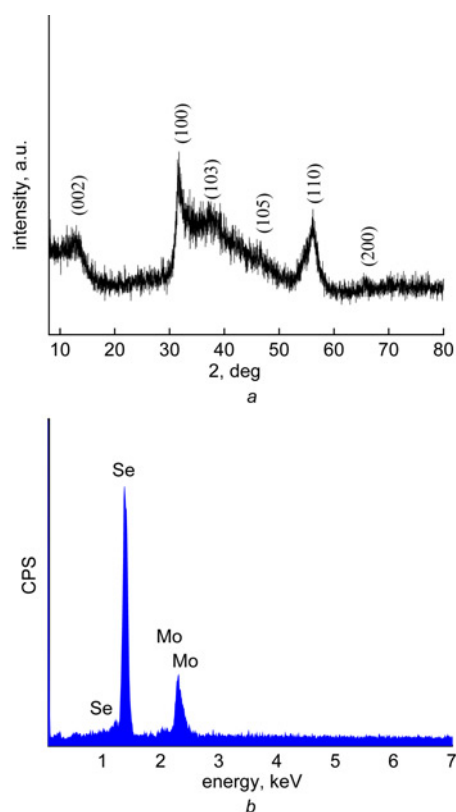


Figure 1 XRD pattern (Fig. 1a) and EDS (Fig. 1b) of as-obtained MoSe₂

values (JCPDS No. 87-2419). No characteristic diffraction peaks from other impurities are detected in the XRD pattern, manifesting the high purity of the MoSe₂ samples. The XRD peaks are somewhat broad and this implies that the as-synthesised samples were slightly amorphous during the hydrothermal process. The EDS result as given in Fig. 1b shows that the product is composed of elements Mo and Se, and no other element is detected. Besides, the quantification of the peaks reveals that the atomic ratio between Mo and Se is approximately 1:2.08, which gives extremely approximate MoSe₂ stoichiometry.

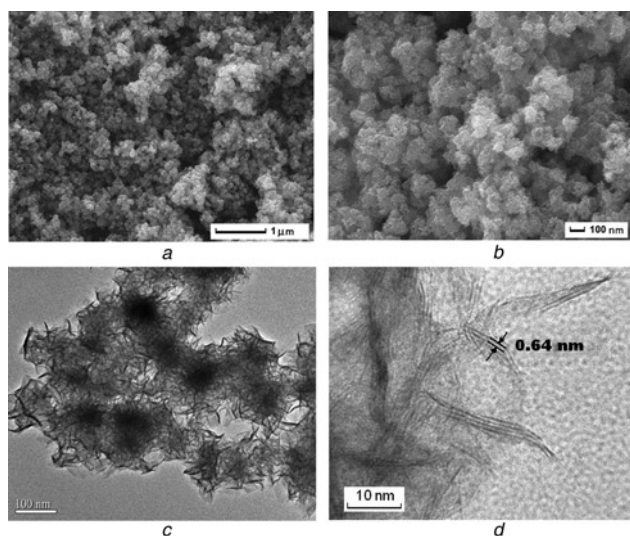


Figure 2 SEM (Figs. 2a and b), TEM (Fig. 2c) and HRTEM (Fig. 2d) images of MoSe₂ nanoflowers

The morphology and structure of the prepared MoSe₂ products were examined with a SEM (Figs. 2a and b), TEM (Fig. 2c) and HRTEM (Fig. 2d). It can be observed from Fig. 2a that the sample consisted of many agminated particles. Fig. 2b the field emission scanning electron microscope image displays a distinct view of the morphology. It shows that the prepared products were mostly composed of nanoflowers with an average size of ~100 nm. Further understanding the morphology and structure of MoSe₂ nanoflowers was obtained by transmission electron microscopy. As in Fig. 2c, the TEM image reveals that the as-prepared MoSe₂ nanoflowers were assembled by many irregular nanosheets, the results are in agreement with the above SEM observation and further demonstrated that the as-obtained MoSe₂ nanoflowers may be assembled from a sheet-like structure. The HRTEM observation Fig. 2d, shows that the MoSe₂ nanosheets mostly consisted of approximately four-tier stacking of monatomic layers and overlap each other, the interlayer separation between the MoSe₂ layers being about 0.64 nm.

3.2. Tribological properties of MoSe₂: Fig. 3a shows the change of the friction coefficient of the lubricant with different contents of MoSe₂ with the 15 N load and 200 rpm rotating speed. It can be seen that the friction coefficient is sensitive to the concentration of the MoSe₂ nanoflowers additive. The friction coefficient is clearly reduced by adding synthesised MoSe₂, compared with pure oil, the base oil containing synthesised MoSe₂ having a comparatively lower friction coefficient. When the concentration of the synthesised MoSe₂ is 1 wt%, the lowest friction coefficient is acquired.

Fig. 3b shows the wear scar width of the disc of the lubricant with different contents of MoSe₂ with the 15 N load and 200 rpm rotating speed. It can be observed that the wear scar width of the pure oil is 0.243 mm, while that of the base oil with 1 wt% synthesised MoSe₂ is 0.232 mm. However, the wear scar widths of the oil with 2 and 4 wt% synthesised MoSe₂ are slightly increased, which is consistent with the friction coefficient result in Fig. 3. The possible explanation could be that a very high concentration

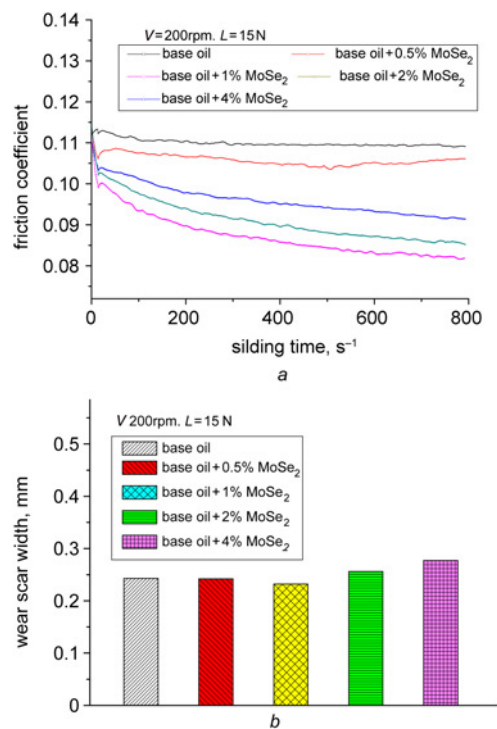


Figure 3 Effect of additive concentration of MoSe₂ on friction coefficient (Fig. 3a) and wear scar width (Fig. 3b)

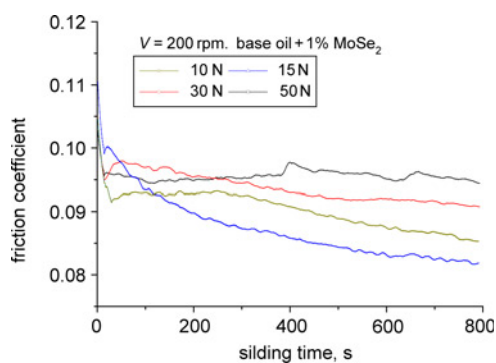


Figure 4 Effect of load on friction coefficient under the lubrication of base oil containing 1.0 wt% MoSe₂ additive

of MoSe₂ could undermine the stability of the colloidal system of the oil [40]. Hence, a suitable concentration of the prepared MoSe₂ as an additive in base oil should advisably be 1 wt%.

Fig. 4 shows the friction coefficients of the base oil containing 1% synthesised MoSe₂ at diverse applied loads. It is clear that after an evident running-in stage, the friction coefficients of the base oil containing 1% synthesised MoSe₂ became stable and almost unchanged close to 0.081–0.094 with increasing applied load; the friction coefficients continuously reduce with the sliding time at the load 15 N.

The morphologies of the worn surfaces lubricated with the base oil and the base oil containing 1 wt% MoSe₂ at 15 N are displayed in Fig. 5. It can be seen from Fig. 5a that the worn surface lubricated with the base oil has obviously rough furrows. In Fig. 5b, however, the worn surface lubricated with base oil containing 1.0 wt%

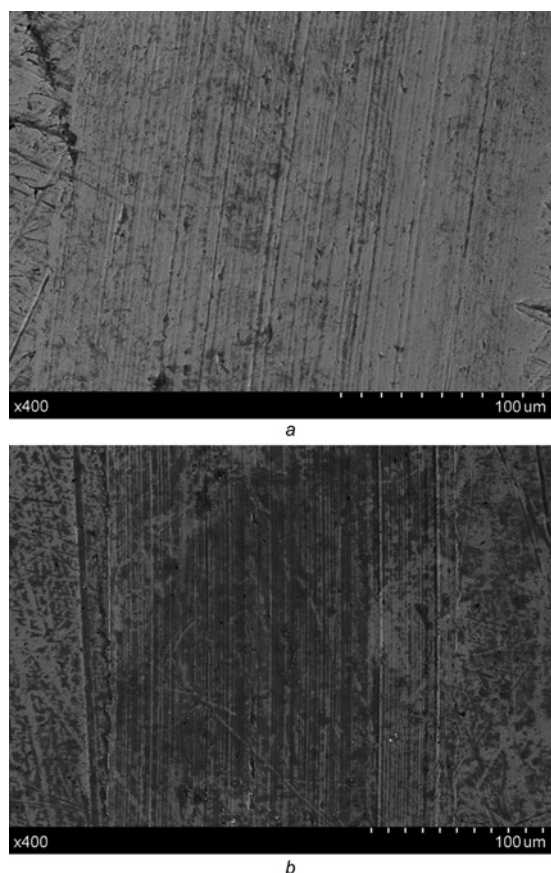


Figure 5 SEM images of worn surface lubricated with pure base oil (Fig. 5a) and base oil containing 1 wt% MoSe₂ (Fig. 5b)

MoSe₂ is more smooth and shows shallow furrows, in the mean-time, suggesting that a protective tribofilm was produced on the worn surfaces.

The above results demonstrate that MoSe₂ nanoflowers as a lubrication additive could enhance the tribological performances of the base oil. This may be due to the fact that the layered MoSe₂ nanosheet is related to the shearing of the weak van der Waals bonds between the molecular layers [33]. When MoSe₂ was dispersed in base oil, an MoSe₂ nanosheet was gathered and formed a layer of tribofilm on the friction pair's surface, which can reduce shearing stress, and lead to a reduction of the friction coefficient.

4. Conclusion: In summary, novel MoSe₂ nanoflowers with a mean diameter of about 100 nm have been successfully synthesised via hydrothermal reaction. The experimental results reveal that the as-synthesised MoSe₂ nanoflowers consisted of many layered MoSe₂ nanosheets. Furthermore, preliminary tribological tests indicated that the optimum concentration (1.0 wt%) of MoSe₂ suspended in base oil exhibits excellent tribological properties. Tribological experiments suggested that the smooth tribofilm formed on the worn surface could be beneficial in reducing friction.

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