

Surfactant-assisted hydrothermal synthesis and tribological properties of flower-like MoS₂ nanostructures

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Flower-like molybdenum disulfide (MoS₂) nanostructures with high purity were successfully synthesised via a facile surfactant-assisted hydrothermal route. The structure and morphology of the as-prepared products were characterised by X-ray powder diffraction, energy dispersive spectroscopy, scanning electron microscopy and transmission electron microscopy. The influence of the surfactant and the pH value of the initial mixture on the formation of the MoS₂ nanostructures was investigated. A possible evolutionary process of the flower-like MoS₂ nanostructures is proposed to explain the formation of various MoS₂ nanostructures on the basis of the experimental results. In addition, the tribological properties of the as-prepared MoS₂ powders as additives in HVI500 base oil were investigated on an UMT-2 multispecimen tribo-tester. The topography of worn scars was obtained using a common SEM. It is found that the addition of MoS₂ nanoflowers can improve the tribological properties of the base oil.

1. Introduction: In recent years, interest in the synthesis and application of transition metal dichalcogenides MS₂ (M: Mo, W) nanomaterial has steadily grown because of their unique structure and superior properties [1]. As we know, transition metal dichalcogenides have a sandwich interlayer structure formed by the stacking of the S–M–S layers, which are loosely bound to each other only by van der Waals forces and are easily cleaved [2]. Moreover, MS₂ exhibits unique physical, optical and electrical properties correlated with their layer structure. In addition, their electronic structure is such that band-edge excitation corresponds largely to a metal centred d–d transition. Owing to these features, laminar MS₂ materials have numerous applications such as solid lubricants, catalysis, electrocatalysis, high-density batteries and efficient solar energy cells [3–6].

Molybdenum disulfide (MoS₂), a typical layered compound, has been used for decades in specialised applications as a solid lubricant or an additive for lubricating oils and greases. As a lubricant, MoS₂ nanomaterials exhibit low friction coefficients and have a long lifetime in dry air, inert or vacuum environments [7]. To date, MoS₂ nanomaterials have attracted considerable attention and have been synthesised by a great diversity of methods, for instance, gas-phase reactions, laser ablation, sonochemical process, hydrothermal synthesis and thermal decomposition [8–11]. A large number of MoS₂ nanoparticles with different morphologies such as nanowires, nanotubes, nanorods, nanosheets and nanoflowers have been prepared by the above-mentioned methods. Previous studies have shown that nanosized MoS₂ such as nanorods and nanosheets usually have better tribological properties, either in friction reduction or wear resistance than bulk MoS₂ [12]. However, MoS₂ flower-like self-assembled nanostructures and their application in the tribological field have rarely been reported. In this work, the authors developed a mild and facile hydrothermal method to prepare MoS₂ nanoflowers by using cetyltrimethylammonium bromide (CTAB) as a surfactant. The products were characterised by X-ray powder diffraction (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A possible formation mechanism is discussed on the basis of the results of the controlled experiments. In addition, we have also investigated the tribological properties of MoS₂ nanoflowers as a lubrication additive in HVI500 base oil. The superior antiwear and friction-reducing properties indicate MoS₂

nanoflowers are a good lubrication additive, and the fundamental data presented will be useful for its further industrial application in the future.

2. Experimental

2.1. Synthesis of MoS₂ nanoflowers: All chemical reagents (analytical purity) were purchased from SCRC Chemical Co. and used directly without further purification. The experimental procedure was designed as follows: 0.88 g of Na₂MoO₄, 0.725 g NH₂OH·HCl and 1.40 g of CH₄N₂S were dissolved in 50 ml deionised water, and then 0.18 g of CTAB was added into the solution under constant stirring. The pH value of the mixture was adjusted to 6 by the addition of 2 mol/l HCl. The mixture was then transferred into a 100 ml Teflon-lined stainless-steel autoclave and sealed, and the autoclave was placed in a pre-heated oven at 180°C for 24 h and naturally cooled down to room temperature. Black precipitates were collected by centrifugation, washed with distilled water and absolute ethanol several times, and finally dried in a vacuum at 60°C for 10 h.

2.2. Preparation and tribological properties of lubricating oil samples: The as-prepared MoS₂ samples, modified by the dispersing agent sorbitan monooleate (Span-80), were distributed into the HVI500 base oil via 60 min ultrasonication. The friction and antiwear properties of the oil with MoS₂ nanoflowers were examined on a UMT-2 ball-on-plate friction and wear tester. The testing of the friction reduction and wear resistance was conducted at a rotating speed of 50–300 rpm and a load of 6–30 N for 1 h. The dependence of the wear scar diameter on friction time was measured under the constant load of 10 N. 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 was a 45 steel disc of Ø40 mm × 3 mm in size.

2.3. Characterisation of MoS₂ samples: The X-ray diffraction patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu K α radiation ($\lambda = 0.1546$ nm). The morphologies and structures of the samples were characterised by a SEM (JEOL JXA-840A) and a TEM with a Japan JEM-100CX II TEM. The topography of the worn scars was obtained using an

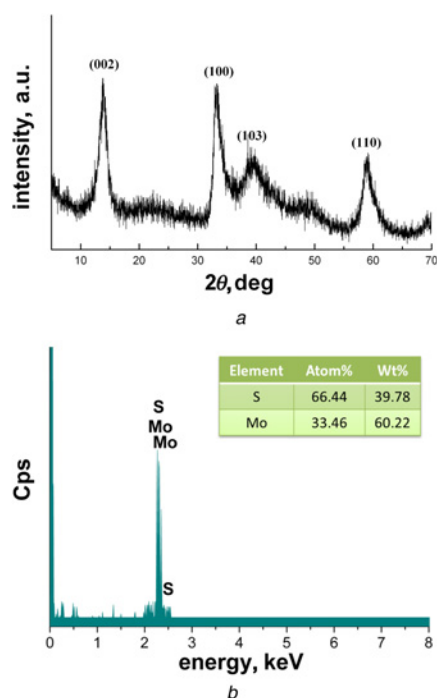


Figure 1 XRD pattern and EDS result of the as-prepared MoS₂ nanoflowers
 a XRD pattern
 b EDS result

electronic beam-based microscope (SEM, HITACHI S-3400N). All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Characterisation of MoS₂ nanoflowers: The structure and phase purity of the as-prepared MoS₂ were confirmed by XRD, as shown in Fig. 1a. All labelled diffraction peaks can be indexed to those of the pure hexagonal phase of MoS₂ with lattice constants $a = 3.161$, $c = 12.84$ Å, which are in good agreement with the values of standard card (JCPDS No. 37-1492). No characteristic peaks were detected from other impurities, indicating that the sample was of high purity. Moreover, the XRD patterns reveal

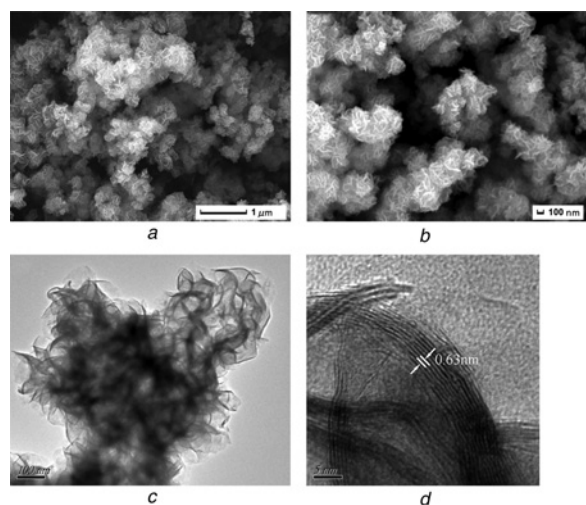


Figure 2 SEM, TEM and HRTEM images of the as-prepared MoS₂ nanoflowers
 a and b SEM
 c TEM
 d HRTEM images of the as-prepared MoS₂ nanoflowers

wide and weak diffraction peaks, which is evidence of the formation of small nanoparticles of the as-prepared MoS₂. The shift of the (002) peak in the XRD pattern, which is usually regarded as a key mechanism for the strain relief of the folded structure [13], was observed in the experiment. The EDS result (Fig. 1b) demonstrates that the MoS₂ nanoflowers consist of only elements Mo and S, and no other elements was observed. Furthermore, the quantification of the peaks shows that the atom ratio of Mo:S is about 1.98:1, which matches well with the stoichiometric MoS₂; hence the as-prepared product is a hexagonal MoS₂.

The morphologies of the MoS₂ products were primarily investigated by SEM measurement. Figs. 2a and b show that the obtained samples have a flower-like structure of ~200–500 nm in size. Fig. 2b clearly reveals the structure of the MoS₂ nanoflowers, and it is obvious that many irregular nanosheets might aggregate together and assemble into nanoflowers with the help of a surfactant. Fig. 2c is a TEM image of MoS₂ nanoflowers; the results are consistent with the above SEM observation and further indicated that the as-prepared MoS₂ nanoflowers might be built up with a sheet-like structure. More details for the MoS₂ structure are illustrated by high-resolution transmission electron microscopy (HRTEM) studies in Fig. 2d, which indicates the layer structures of the products overlap each other. As a mean value the distance between the lattice fringes is 0.63 nm, which is coincidental with the theoretical spacing for (002) planes of the hexagonal MoS₂ structure.

3.2. Formation mechanism: Crystal growth mechanisms in a hydrothermal process are so complicated that the research of the crystallisation mechanism remains a challenge [14]. Oriented aggregation, self-assembly, Ostwald ripening etc. were adopted to account for the process of crystal growth [15]. Recently, many novel techniques have been developed for the synthesis of MoS₂ self-assembled structures, and a number of studies have focused on the formation mechanism of these flower-like MoS₂ nanostructures. Ma *et al.* [16] reported flower-like MoS₂ microspheres assembled by nanosheets synthesised via a hydrothermal route, and found that the intermediate product H₄SiMo₁₂O₄₀ could serve as a self-sacrificial template for the initial nucleation and the formation of flower-like MoS₂ microspheres. Wei *et al.* [17] employed the hydrothermal method to synthesise MoS₂ flower-like morphology with a mean diameter of about 1 μm; however, the growth mechanism has not been discussed at length. In our previous study [18], time-dependant shape evolution of MoS₂ nanoflowers was conducted under standard synthesis conditions, and we found that by the oxidation–reduction reaction many MoS₂ nanoparticles assembled together and spontaneously aggregated into petal-like nanosheets. Under optimal conditions, well-defined MoS₂ nanoflowers were formed from several MoS₂ nanosheets, through a self-assembly and Ostwald ripening process, with the help of the surfactant.

However, the various influences on the morphologies evolution of the flower-like MoS₂ nanostructure have not been investigated in more detail. The surfactant plays a vital role during the hydrothermal process and further research has indicated that the initial concentration of CTAB has a great influence on the evolution of MoS₂ morphologies. Fig. 3 shows SEM images of the as-prepared MoS₂ obtained from various amounts of CTAB. When no CTAB was added and other reaction conditions were kept constant, many block-like and a few sheet-like products were obtained (Fig. 3a). Increasing the CTAB amount to 0.10 g, the percentage of MoS₂ flower-like structures obviously increased compared with that obtained in the absence of CTAB (Fig. 3b). With a further increase of CTAB up to 0.15 g, uniform MoS₂ nanoflowers were obtained (Fig. 2). However, once the CTAB amount reached 0.3 g, the obtained products were mainly larger size flower-like structures and few aggregates (Fig. 3c). It can thus be concluded that, in this study, an appropriate concentration of CTAB is crucial for the formation of well-defined MoS₂ nanoflowers.

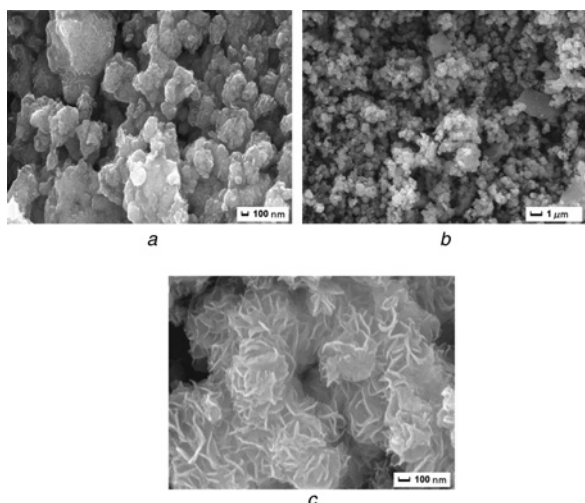


Figure 3 SEM and TEM images of products obtained with a various amounts of CTAB

a 0 g
b 0.10 g
c 0.3 g

It is well known that CTAB has turned out to be very effective in the shape-controlled synthesis of nanomaterials as a typical cationic surfactant. Surfactant CTAB can influence crystal habit by a selective adsorption process that leads to preferential growth inhibition for distinct crystal faces under well-controlled conditions. If such processes take place within a multistep growth mechanism, complex crystal morphologies can be produced [19]. The preferential adsorption of CTAB must play an important role in the growth of the flower-like MoS_2 nanostructure with uniform size and morphology. CTAB was adsorbed on the certain face of the newly formed MoS_2 nanoparticles during the initial growth stage, which inhibited the aggregates of the MoS_2 nanoparticles [20]. The as-prepared MoS_2 samples, obtained in the presence of CTAB, had a better dispersion and its agglomeration significantly decreased. When the concentration of CTAB went beyond a critical value (e.g. 0.15 g), the intercalating and intertwining among these high molecules caused a higher surface free energy and serious aggregation of the MoS_2 particles [21, 22], which resulted in the formation of larger size flower-like structures and few aggregates (Fig. 3c).

In addition, it was also found that the pH value of the initial solution plays another important role in the formation of the final

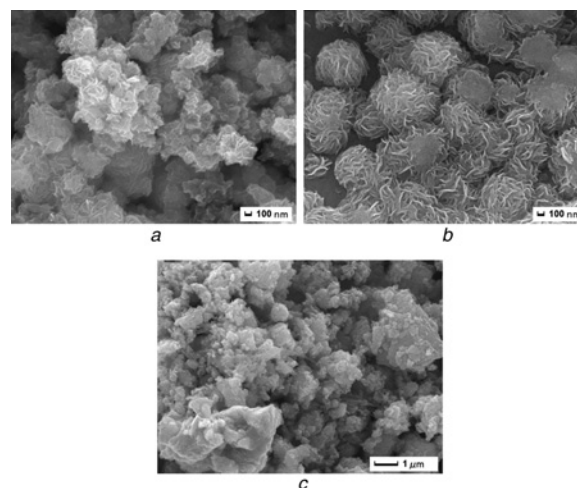


Figure 4 SEM images of products obtained at various pH values

a 2
b 8
c 12

products besides the influence of the surfactant (CTAB). Fig. 4 shows the SEM images of as-prepared MoS_2 obtained at various pH values of the initial mixture. When the pH value of the solution is adjusted to 2 and the other conditions are kept constant, the morphologies of the products varied greatly. The obtained products were mainly composed of a large amount of nanoflowers and their aggregations (Fig. 4a). Under standard synthesis conditions, many uniform MoS_2 nanoflowers were obtained (Fig. 2). If the pH value was further increased up to 8 by the addition of NaOH (2 mol/l), flower-like spherical structures with a diameter of about $1\ \mu\text{m}$ were formed (Fig. 4b). When the pH value of the solution reached 12, the morphologies of the as-prepared MoS_2 were similar to the previous experimental results obtained under stronger acidic conditions (Fig. 4a). The aggregation of the MoS_2 particles was serious and the dispersion property was very poor (Fig. 4c). $\text{NH}_2\text{OH}\cdot\text{HCl}$ was adopted as a common reductant, which has a better reduction ability under acidic and weak alkaline conditions. In the present system, if the pH value is acidic (e.g. 2), the chemical reaction rate in the formation of the MoS_2 nuclei is rapid because of the strong reducing ability of the $\text{NH}_2\text{OH}\cdot\text{HCl}$ in acidic conditions. Then a large amount of MoS_2 nuclei were produced in a relatively short period of time, which resulted in the formation of a large amount of nanoflowers and their aggregations (Fig. 4a). When

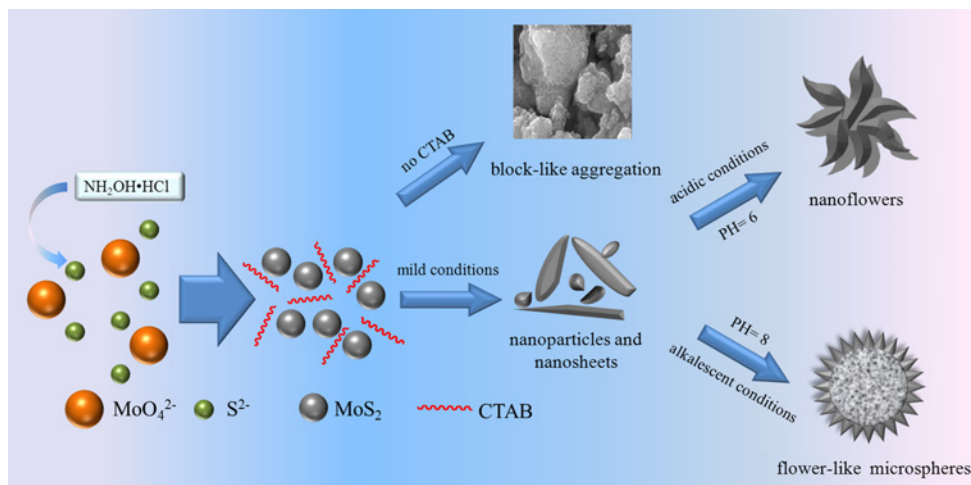


Figure 5 Schematic illustration of different MoS_2 nanostructures

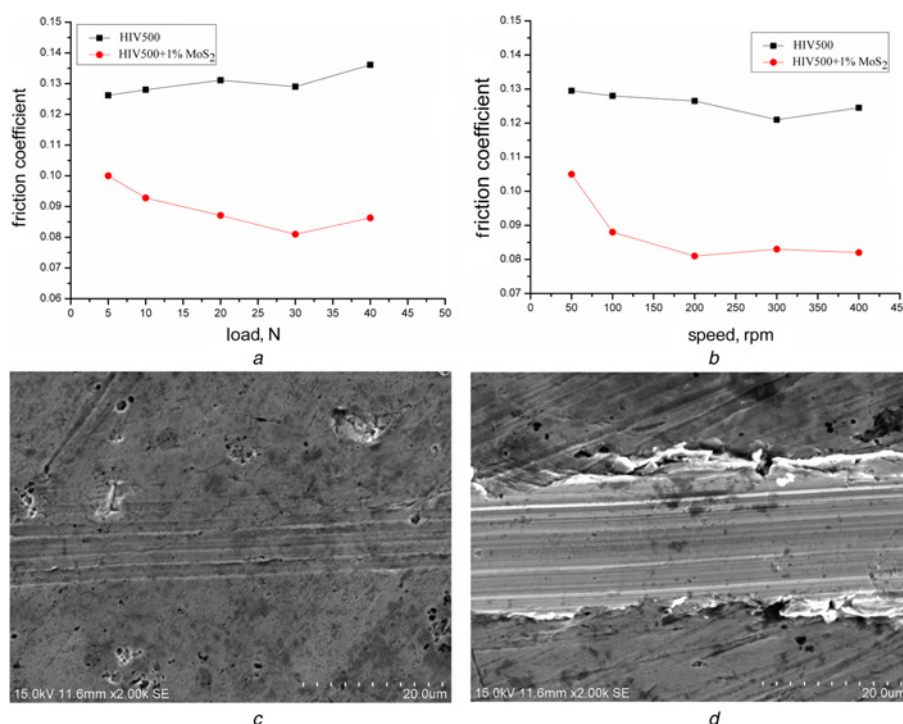


Figure 6 Variations of friction coefficient of lubricant with increasing load
 a Under diverse speeds
 b Wear scar of plate
 c HVI500 base oil 1.0 wt.% MoS₂ nanoflowers
 d HVI500 base oil

the pH values were strong alkaline (e.g. 12), the reducing ability of NH₂OH•HCl was inhibited. Tian *et al.* [23] have confirmed that the redox reaction and the sulphured reaction had not reacted completely in the synthesis process of MoS₂ by NH₂OH•HCl as a reductant when the solution of pH value was above 8 (pH > 8). Moreover, MoO₄²⁻ or H₂MoO₄ can be transformed into MoO₃ particles in the solution. In this study, a large amount of MoS₂ nanoparticles along with a small quantity of MoS₂ aggregations were obtained, in which certain aggregations were found to be composed of interconnected nanoflowers that were constructed from nanoplates.

Therefore based on the above experimental results, a possible evolutionary process of the flower-like MoS₂ nanostructures dependent on experimental conditions is schematically illustrated in Fig. 5.

3.3. Friction and wear properties of MoS₂ nanoflowers: It is well known that the tribological properties of the MoS₂ nanoflowers are directly concerned with its dispersion stability in the basic oil. Fig. 6a shows the comparisons of the tribological properties among the pure base oil and the base oil with 1.0 wt.% MoS₂ nanoflowers with an increasing load at 50 rpm for 1 h. The friction coefficient of the pure base oil without any additives was increased with the increasing load. With the addition of 1.0 wt.% MoS₂ nanoflowers in the base oil, the friction coefficient was reduced remarkably and stabilised at a higher load. Fig. 6b provides curves of friction coefficient against rotational speed under 10 N loads for 1 h. The experimental results show that MoS₂ nanoflowers are able to improve the friction reduction of the base oil at different rotating speeds. Therefore the base oil containing the additive MoS₂ nanoflowers has better tribological properties.

To further study the wear resistance tribological properties of the MoS₂ nanoflowers, the topography of the worn scar lubricated by the MoS₂ nanoflowers was investigated using a SEM. The wear scar of the steel disc is shown in Fig. 6c (the base oil containing MoS₂ nanoflowers) and Fig. 6d (the base oil) after rubbing with 20 N load and 200 rpm rotating speed for 1 h. It can be easily observed

from the SEM images that the rubbed surface lubricated by the base oil had lots of wide and deep furrows whereas the surface lubricated with MoS₂ nanoflowers only presented slender furrows. This confirms that the base oil containing MoS₂ nanoflowers had a better wear resistance.

4. Conclusions: The authors have developed a facile cationic surfactant-assisted hydrothermal method for the synthesis of flower-like MoS₂ nanostructures with a mean diameter of about 1–2 μm under well-controlled conditions. The experimental results show that the as-prepared MoS₂ nanoflowers had good crystallinity with a well-stacked layered structure and consisted of many irregular MoS₂ nanosheets. It was found that the surfactant CTAB and pH value of the initial mixture played a crucial function in the final morphology of MoS₂ nanoflowers. On the basis of the results from the controlled experiments, we put forward a possible growth mechanism for the formation of MoS₂ nanoflowers. Moreover, preliminary tribological tests showed that the MoS₂ nanoflowers were able to improve the tribological properties of the base oil as a lubricant additive.

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