Synthesis and tribological properties of MoS_2 composite nanoparticles with different morphologies

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Molybdenum disulphide composite particles made of both hollow nanospheres and nanoplatelets were synthesised in a single process using a chemical method that was optimised by adjusting the relative proportions of Na_2S and thioacetamide (TAA) precursors. The composite nanoparticles were characterised using powder X-ray diffraction, transmission electron microscopy and thermal analysis; four-ball tribological tests were used to assess their lubricating effect when used as additives in liquid paraffin dispersions. The results showed that composite nanoparticles of appropriate shape distribution could only be synthesised with a high dosage of TAA: too high concentrations of Na_2S were shown to destroy the template chain of TAA and disturbed the formation of nanospheres. The MoS_2 composite particles exhibited a better lubricating effect as compared to composite particles produced by mechanical mixing of separately produced nanospheres and nanoplatelets, confirming that the chemical method can lead to a better synergistic lubrication between two kinds of MoS_2 nanoparticles.

Keywords: MoS_2, Lubrication, Tribology, Nanoparticles, Morphology

Introduction

Considerable attention has been paid to molybdenum disulfide (MoS_2) nanoparticles and coatings because of their excellent tribological properties.[1–3] At present, some routes were reported to synthesise MoS_2 nanoparticles (nano-MoS_2) and coatings, such as sputtering,[4,5] hydrothermal synthesis,[6,7] electroless coating[8] and a chemical bath deposition method.[9] The synthesis of nano-MoS_2 might lead to some novel MoS_2 structures such as inorganic fullerene particles, nanorods and hollow nanospheres.[10–12]

In a previous article, a simple method was designed to prepare molybdenum disulfide in different shapes including nanospheres and nanoslices (nanoplatelets).[13] A study investigated the tribological properties of the two MoS_2 structures in liquid paraffin.[14] It was found in the literature that the morphology of MoS_2 had an influence on the tribological properties of MoS_2. However, the synergistic lubrication was not investigated between the two MoS_2 structures.

The synergistic lubrication of different lubricants has been well known such as MoS_2–graphite–Sb (SbS_4) materials[15] and nanostructured WC–Co based composite coatings.[16] However, there are few studies on the synergistic lubrication of congener lubricants only with different morphologies and sizes. Hu[17] reported that MoS_2 with different sizes had a synergistic lubrication effect.

Recently the combined lubrication of MoS_2 particles with two different morphologies produced by mechanical mixing was investigated: a synergistic effect was observed, which was ascribed to the cooperation of their different lubrication mechanisms.[18] The mechanical mixture of MoS_2 nanospheres and nanoplatelets could improve the wear resistance and friction reduction of the basal oil better than each of them singly did.

The purpose of the present work was to explore the possibilities of using a chemical method to replace the mechanical mixing in the preparation of MoS_2 composite nanoparticles with both nanospheres and nanoplatelets. The chemical method generally shows advantages over the mechanical one in mixing different ingredients of a composite. It was possible to obtain a better synergistic lubrication between nanospheres and nanoplatelets by the chemical synthesis than by the mechanical mixing. The work provided an understanding of the synergistic lubrication from different morphologies and the formation mechanism of nanospheres. The present synthesis method caused no inconvenience in the preparation of MoS_2 composite nanoparticles, which will be possibly applied in a large scale production.

Experimental

Synthesis of MoS_2 composite nanoparticles

All chemical reagents used in this work were of analytical grade including sodium molybdate (Na_2MoO_4),

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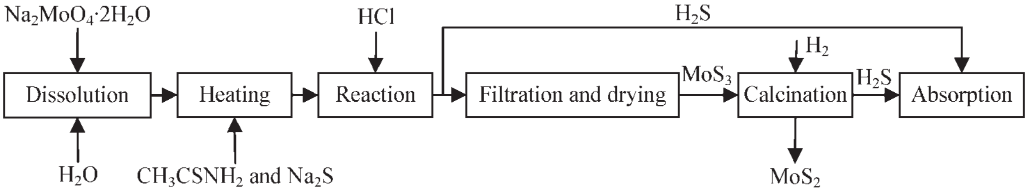


1 Preparation process flow of MoS_2 composite nanoparticles

thioacetamide (CH_3CSNH_2, TAA), ethyl alcohol, sodium sulphide (Na_2S), hydrochloric acid and $CuSO_4$. A typical preparation process was described as follows: 2·5 mmol $Na_2MoO_4.2H_2O$ and 15·0 mmol sulphides (a mixture of Na_2S and TAA with a molar proportion varying from 3 : 1 to 1 : 4) were dissolved in 100 mL deionised water. The obtained solution was heated to 82°C. Ethyl alcohol of 10 mL and 11·0 mL 12M HCl were then dumped into the reaction system and the reaction began. The resultant precipitation was washed by deionised water and dried at 105°C. The dried precipitation was calcined in a tube furnace at 780°C for 50 min in pure hydrogen (99·999%) and the desired MoS_2 samples were obtained. The preparation process flow was described in Fig. 1.

Characterisation of materials

Powder X-ray diffraction (XRD) was performed on a MAC model MXPAHF diffractometer with Cu K_α radiation. Micrographs were obtained using a Hitachi model H-800 transmission electron microscope (TEM) or a JEOL model JEM-2010 high resolution transmission electron microscope (HRTEM). Thermal analysis was performed on a Shimazu model DTG-60H thermal analyser.

Tribological tests

The liquid paraffin (LP) samples with 1·5 wt-%MoS_2 composite nanoparticles were prepared using ultrasonic dispersion for 10 min. The tribological behaviours of the obtained LP/MoS_2 samples were investigated on an MQ-800 four-ball tribometer at 15°C at a rotating speed of 1450 rev min^{-1} and a constant load of 300 N. The steel balls (Φ12·7 mm) used were fabricated according to the national standard GB/T308-2002 of China with a roughness of 0·032 μm. The average wear scar diameter (AWSD, ±0·01 mm) of the three bottom balls was measured to assess their antiwear effect.

Results and discussion

Synthesis of MoS_2 composite nanoparticles

The synthesis reactions of MoS_2 nanospheres and nanoplatelets, already proposed in Ref. 13, were adapted to the simultaneous production of the two different shapes and are resumed below:

(i) formation of H_2S from TAA

$$CH_3CSNH_2+2H_2O+HCl=CH_3COOH+NH_4Cl+H_2S \quad (1)$$

(ii) formation of H_2S from Na_2S

$$Na_2S+2HCl=2NaCl+H_2S \quad (2)$$

(iii) formation of precursor MoS_3 (MoS_3 nanospheres from TAA and bulk particles from Na_2S)

$$3H_2S+Na_2MoO_4+2HCl=MoS_3+4H_2O+2NaCl \quad (3)$$

(iv) formation of MoS_2 (nanospheres from MoS_3 nanospheres and nanoplatelets from bulk MoS_3)

$$MoS_3+H_2 \xrightarrow{\text{Heating}} MoS_2+H_2S \quad (4)$$

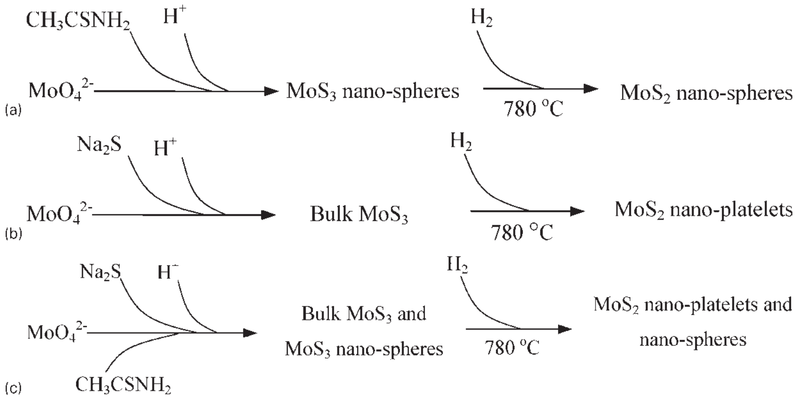
According to these reactions mentioned above, the preparation of MoS_2 nanospheres and nanoplatelet includes two steps: preparation of noncrystalline MoS_3 and transformation of MoS_3 into MoS_2 after calcining in H_2. The two steps were described in Fig. 2*a* and *b*. A main difference between preparing the two kinds of MoS_2 was the sulphur sources provided by TAA and sodium sulphide respectively. It was possible to prepare nanoMoS_2 lubricants with different morphologies by adjust the proportion of the two sulphides with a chemical technique. Therefore, it was easy to design a chemical process to obtain MoS_2 with both nanospheres and nanoplatelets, as shown in Fig. 2*c*. However, there was possibly the mutual disturbing between the formation processes of nanospheres and nanoplatelets, which need to be clarified by TEM images.

Reaction (5) describes the formation of H_2S from the mixture of TAA and Na_2S, in which the molar ratio of TAA and Na_2S is x/y

$$xCH_3CSNH_2+2xH_2O+yNa_2S+(x+2y)HCl$$
$$=2yNaCl+xCH_3COOH+xNH_4Cl+(x+y)H_2S \quad (5)$$

The calcination reaction of MoS_3 was studied using a thermal analyser and the results are provided in Fig. 3, including thermogravimetric analysis and differential thermal analysis. As shown in the figure, the initial decomposition temperature of MoS_3 was ~376°C and the peak temperature was ~400°C. When the temperature was >483°C, the decomposition of MoS_3 was finished. Therefore, the calcination temperature used should at least be higher than ~483°C. When the temperature reached 780°C, MoS_2 could attain a good crystalline state,[12] which was confirmed by the following XRD result. Therefore, a 780°C temperature was used in this work.

Figure 4 shows the XRD pattern of the calcined product of MoS_3 at 780°C from the mixed sulphides (molar ration of TAA and Na_2S is 4 : 1). The four main diffraction peaks were all indexed to these of nano-MoS_2 reported in a previous study,[12] including (002), (100), (103) and (110) lines. This indicates that possible new phases were not formed except for nano-MoS_2. Moreover, the gas products included H_2S which was detected by a $CuSO_4$ solution. The findings confirm that



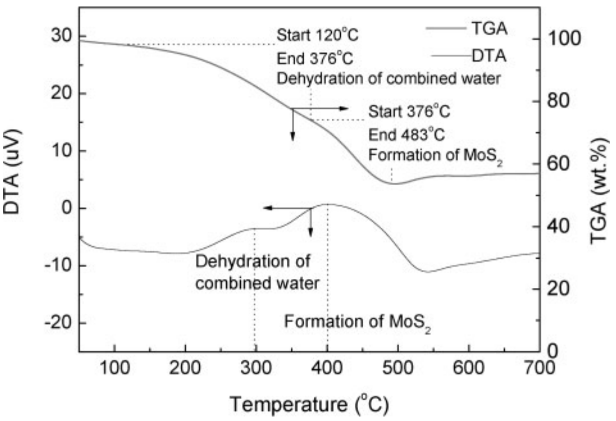
2 Schematic of formation of nano-MoS_2: *a* nanospheres; *b* nanoplatelets; *c* MoS_2 composite nanoparticles with both nanospheres and nanoplatelets

the nano-MoS_2 was successfully prepared according to reaction (6)

$$MoS_3 + H_2 \xrightarrow{\text{Heating}} MoS_2\,(\text{composite nanoparticles}) + H_2S \quad (6)$$

The literature reported that the average thickness of the nanoplatelets varied from 5 to 10 nm, while their lengths varied from 10 to 40 nm.[13] With the very small thickness, MoS_2 nanoplatelet could be clearly observed only using an HRTEM, as shown in Fig. 5*a* and *b*. The MoS_2 nanoplatelets occurred in two manners on the copper net used in the TEM characterisation: parallel or vertical to the copper net. However, the MoS_2 nanospheres with relative large sizes can be clearly characterised using a common TEM (Fig. 5*c*).

Figure 6 provides TEM images of MoS_2 prepared from the different proportion of Na_2S and TAA. As shown in the figure, the proportion of Na_2S and TAA had a remarkable effect on the morphology of MoS_2. When high molar proportions were used, such as 3 : 1 and 2 : 1 (Na_2S/TAA), the nanospheres were not found and the products mainly included nanoplatelets (Fig. 6*a* and *b*). This indicates that the formation of nanospheres was disturbed by the high concentration Na_2S, which would be discussed in the next section. When the Na_2S/TAA molar ratio was decreased to 3 : 4, hollow nanospheres were still not observed in the particles (Fig. 6*c*), and only loose, unaggregated solid nanoparticles were produced. The disturbance effect was weakened in the particles prepared using the 1 : 2 proportion, and some deformed nanospheres could be observed (Fig. 6*d*). Although the proportion attained 1 : 3, it was still difficult to form very intact nanospheres according to Fig. 6*e*, in which the surface of a nanosphere was slightly broken. The intact nanospheres were only observed in the MoS_2 composite nanoparticles from the 4 : 1 proportion of TAA and Na_2S (Fig. 6*f*). These mentioned above indicates that the MoS_2 composite with both nanospheres and nanoplatelets could only be synthesised with high concentration TAA and low concentration Na_2S.

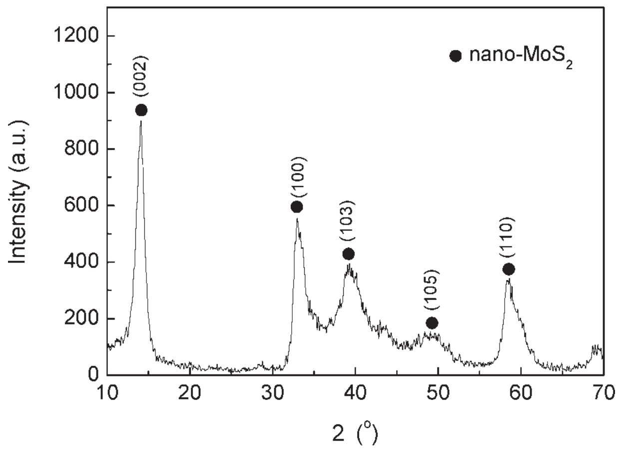


3 Thermal analysis of preparation process of MoS_2 composite nanoparticles from MoS_3

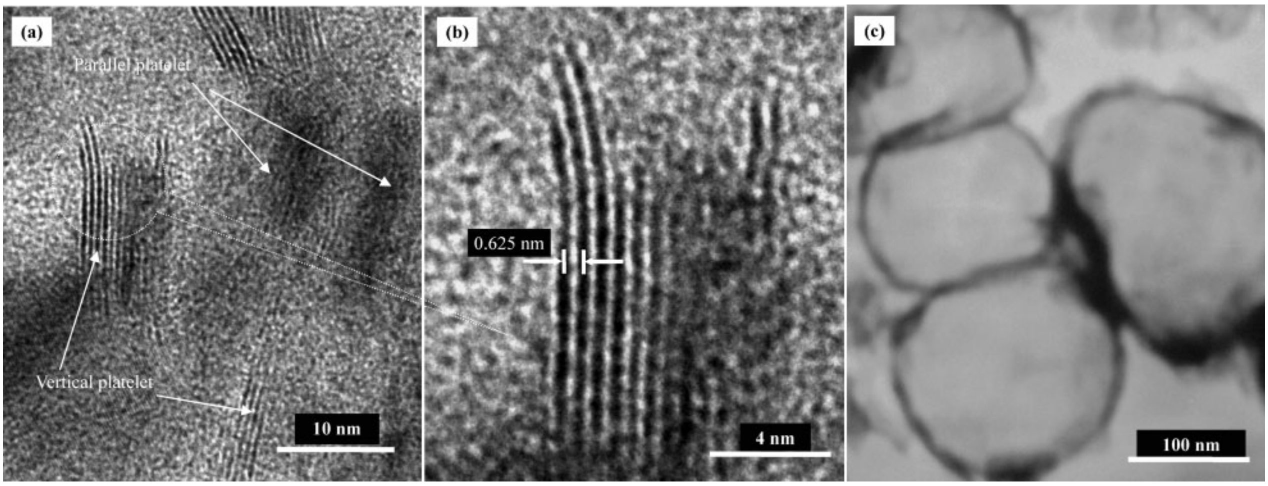
Effect of Na_2S on formation of nanospheres

Na_2S reacted with hydrochloric acid quickly, leading to lots of H_2S gas. The reaction between H_2S and Na_2MoO_4, therefore, was very quick. However, the reaction between TAA and Na_2MoO_4 was relative slow. Na_2MoO_4 in the reaction system was mostly consumed by Na_2S. Therefore, it is very difficult to obtain the nanospheres with low concentration TAA. When the content of TAA used was increased to a proper proportion (4 : 1), the reaction also became quick between TAA and Na_2MoO_4. Consequently, the reaction between Na_2S and Na_2MoO_4 was slowed down. Therefore, the Na_2MoO_4 used reacted with both TAA and Na_2S simultaneously and the disturbing from Na_2S became weakened enough to form nanospheres.

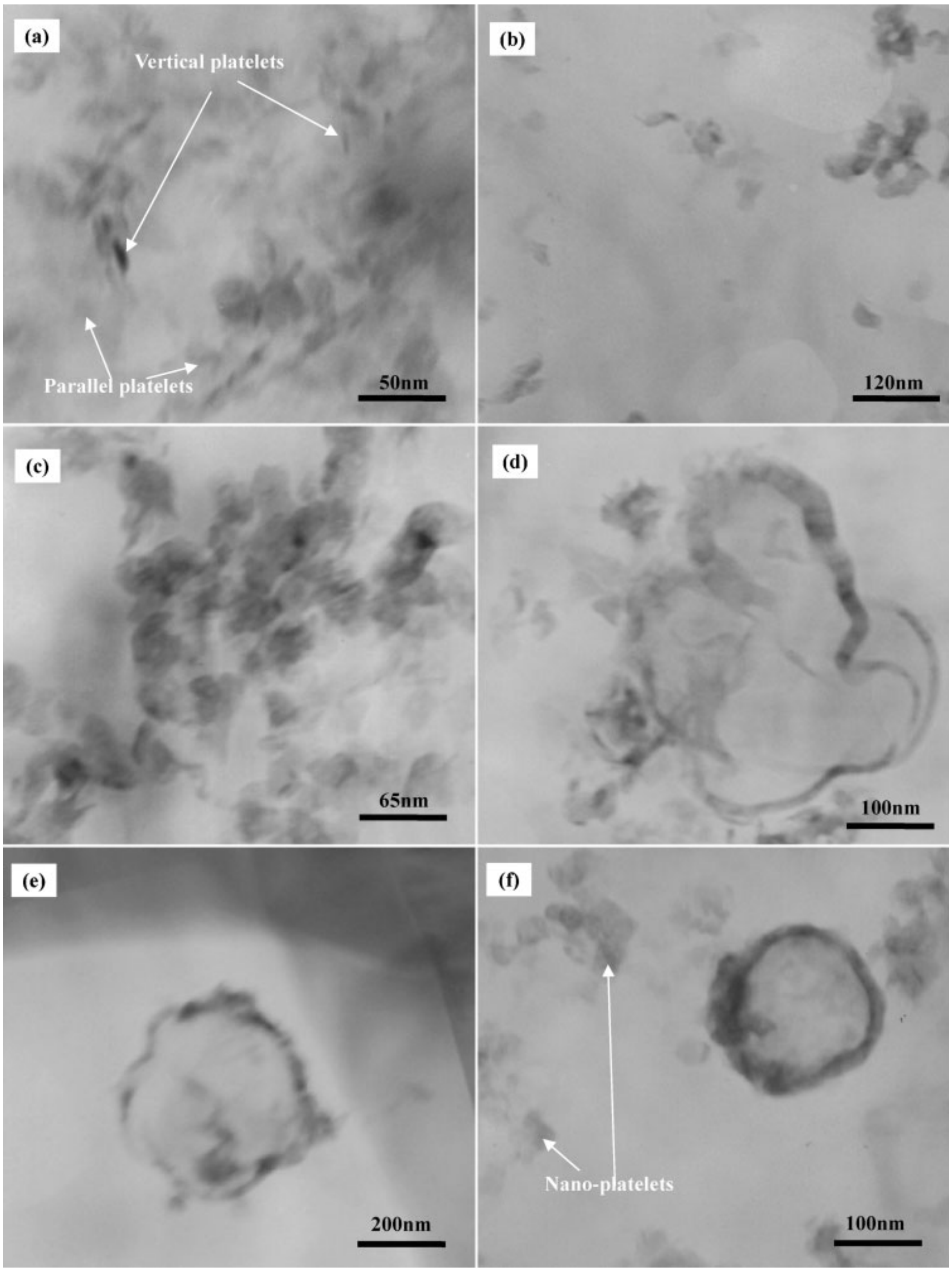
Figure 7 shows TEM images of degradated nanospheres, either loosen and dispersed into single nanoparticles (Fig. 7*a*), or broken (Fig. 7*b* and *d*) or strongly



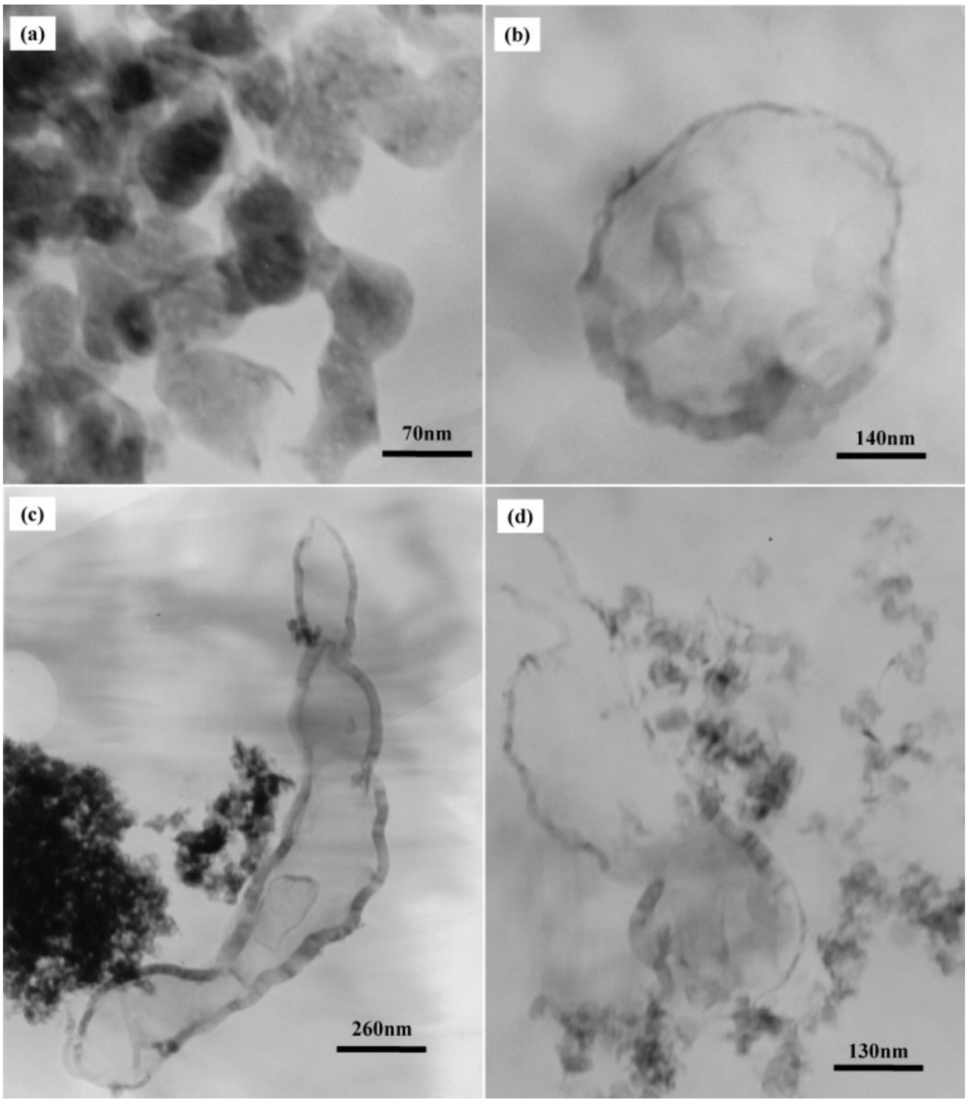
4 X-ray diffraction pattern of calcined product of MoS_3 from mixed sulphides at 780°C (molar ration of TAA and Na_2S is 4 : 1)



5 Micrographs of MoS_2: *a* image (HRTEM) of nanoplatelets; *b* magnified part of *a*, *c* TEM image of nanospheres



6 Image (TEM) of MoS_2 prepared from different molar proportions of Na_2S and TAA: *a* 3 : 1; *b* 2 : 1; *c* 3 : 4; *d* 1 : 2; *e* 1 : 3; *f* 1 : 4

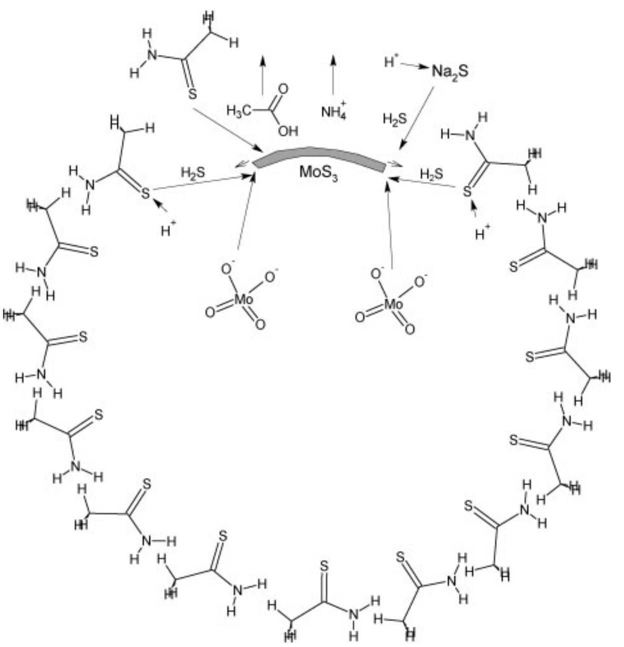


7 Images (TEM) of destroyed and deformed MoS_2 nanospheres: *a* forming solid nanoparticles; *b* being slightly broken; *c* deformed nanosphere; *d* broken nanosphere

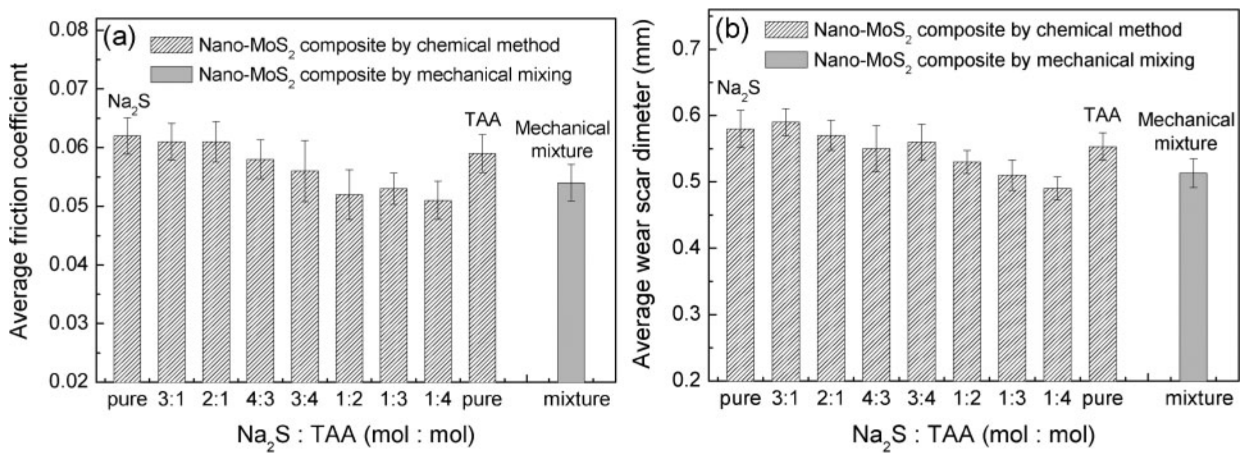
deformed (Fig. 7*c*). Thioacetamide acted as both a reactant and a template in the growth process of hollow nanospheres.[13] The template resulted from the close chain-like structure of TAA by hydrogen bond, as shown in Fig. 8. The chain of TAA molecules by hydrogen bond was relatively weak and could easily be disturbed by the resultant H_2S from Na_2S (Fig. 8). The molecular chain of TAA template was completely broken with high concentration Na_2S and the nanospheres could not form (Fig. 7*a*). If the chain of TAA template was partly destroyed, the formation of nanospheres was seriously disturbed leading to deformed and incomplete balls (Fig. 7*c* and *d*). If the chain was slightly broken, the formation of nanospheres was weakly disturbed, and the morphology became approximately spherical (Fig. 7*b*). The intact nanospheres occurred until the disturbing was negligible.

Tribological properties of MoS_2 composite nanoparticles

Figure 9*a* is the variation of the average friction coefficient with the decreasing proportion of Na_2S and TAA. The LP sample with 1·5 wt-%MoS_2 nanospheres from pure TAA presented better friction reducing



8 Schematic of template of TAA and disturbing from Na_2S



9 Variation of *a* average friction coefficient and *b* AWSD of nano-MoS_2 composite in LP with decreasing proportion of Na_2S and TAA

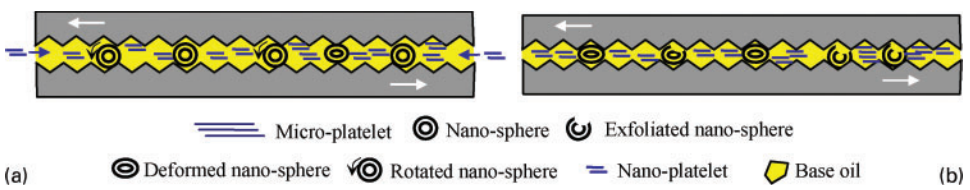
properties than that with 1·5 wt-% nanoplatelets from pure Na_2S. The friction coefficient of LP decreased with the increasing contents of TAA in the total sulphides (Na_2S and TAA). When the proportion of Na_2S and TAA was up to 1 : 4, the LP sample presented the lowest friction coefficient (0·051). Figure 9*b* shows the variation of the AWSD with the increasing contents of TAA in the total sulphides. The variation of AWSD was approximately correlated to the change in friction coefficients. The steel balls lubricated by LP with MoS_2 from Na_2S and TAA of 1 : 4 also presented the lowest AWSD (0·49 mm).

The smallest AWSD and the lowest friction coefficient was observed in the LP sample with 60 wt-% nanospheres and 40 wt-% nanoplatelets mixed by the mechanical method (Fig. 9). The mechanical mixture presented a friction coefficient of 0·054 and an AWSD of 0·51 mm. This indicates that the obtained MoS_2 composite nanoparticles presented better tribological properties by the chemical method than by the mechanical mixing. The chemical method can mix the nanospheres and nanoplatelets better than the mechanical one. Therefore, the MoS_2 composite nanoparticles by chemical method showed better tribological properties.

The lubrication mechanism of layered bulk 2H–MoS_2 is associated with the shearing and sliding of weak van der Waals gaps between molecular layers. MoS_2 nanoplatelets with the layered 2H structure should also present a shearing and sliding lubrication mechanism. However, the lubrication mechanism of spherical nano-MoS_2 is ascribed to its chemical inertness, rolling friction, deformation and exfoliation delivery of MoS_2 sheets to the contact area.[3,19–21] The synergistic lubrication between two different MoS_2 structures resulted from the cooperation of their different lubrication mechanisms.[18] The good tribological properties of the obtained composite MoS_2 additive were ascribed to the synergistic lubrication between nanospheres and nanoplatelets. The chemical method could lead to a better synergistic lubrication between two kinds of MoS_2 nanoparticles.

The thickness of oil film and the distance between the friction pairs significantly affected the lubricating efficiency, which has been clarified by the Stribeck curves of LP with MoS_2 addtives.[14] The boundary lubrication occurred from 800 to 1200 rev min^{-1}, while the mixed lubrication from 1200 to 1500 rev min^{-1} and the hydrodynamic lubrication after 1500 rev min^{-1} when lubricated by LP with nano-MoS_2. The oil film thickness h between the friction pairs (the interface space) was close to the surface roughness R of the friction pairs in the mixed lubrication region.[22,23]

The balls used in this work have a roughness of 0·032 μm (G20, GB/T308-2002 of China). The rotation speed (1450 rev min^{-1}) used in this work fell in the end of the mixed lubrication, and the oil film thickness should be slightly larger than 0·032 μm (32 nm). Therefore, the MoS_2 nanoplatelets with sizes varied from 5 to 40 nm easily penetrated into the interface of the friction pairs functioning as lubrication. The nanospheres with relatively large sizes ($\sim$150 nm in Fig. 6*f*) were difficult to penetrate into the interface of the friction pairs. The MoS_2 nanospheres in the contact region mainly came from its previous adsorption on the surface of steel balls. When the contact region area on the steel balls was increased because of abrasion, nanospheres were taken to the contact surface again. The nanospheres functioned as a separation body between the friction pairs and the thickness of the oil film was slightly magnified. The beginning lubrication was provided by the deformation and rolling of the nanospheres. The mixed nanoplatelets were then easier to penetrate into the contact region (Fig. 10*a*). When the nanospheres were worn by the deformation and exfoliation, the size of the nanospheres became close to the thickness of the oil film. Then it occurred that the



10 Schematic of synergistic lubrication between two kinds of MoS_2 particles: *a* initial stage; *b* stable stage

cooperation between the shearing–sliding of 2H structure and the deformation–exfoliation of nanospheres. Because the thickness of the lubrication oil film was very small, the rolling of nanospheres became restricted (Fig. 10*b*).

Conclusion

In order to improve the synergistic lubrication between two kinds of MoS_2 with different morphologies, a chemical method in this paper is designed to synthesise MoS_2 composite nanoparticles as a substitute for the mechanical mixture. The chemical synthesis mechanism is ascribed to the effect of sulphur sources (sulphides) on the morphology of MoS_2: TAA can produce MoS_2 nanospheres after reacting with Na_2MoO_4 while Na_2S leads to MoS_2 nanoplatelets. The high content Na_2S used may destroy the template chain of TAA molecules by hydrogen bond and restricts the formation of nanospheres. The MoS_2 composite nanoparticles with both nanospheres and nanoplatelets can only be synthesised with a high TAA dosage (1 : 4 molar proportion of Na_2S and TAA). The chemical method can mix the nanospheres and nanoplatelets better than the mechanical one does. Therefore, the two kinds of MoS_2 nanoparticles have better synergistic lubrication properties in the composite nanoparticles prepared by the chemical method than that by the mechanical mixing.

Acknowledgements

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