One-step hydrothermal synthesis of double core-shell oxygen-incorporated molybdenum disulfide and its tribological properties

1 | INTRODUCTION

Nowadays, with the rapid development of auto aftermarket, efficient lubrication technology plays a more and more important role in prolonging engine life and improving fuel economy [1]. However, traditional lubricant additives containing organophosphorus, sulphur and chlorine may cause subsequent pollution. Therefore, many studies have explored new lubricating additives to reduce environmental pollution. In recent years, with the development of nanotechnology, molybdenum disulfide (MoS2) nanomaterials have been widely used in various fields [2–8] such as enzyme-like applications [7] and photodegradation [9]. MoS2 has a typical sandwich-layered structure that makes it easy to slip and has good lubricating properties [10, 11]. Besides, there are tribological studies of MoS2 nanomaterials with various morphologies, such as flower and ball [12]. By introducing oxygen atoms into the MoS2, the interlayer spacing can be increased [13], and it is better to slide. There are few studies on oxygen-incorporated MoS2. So we used a hydrothermal method to prepare double core-shell oxygen-incorporated MoS2 (DB-O-MoS2) and studied its tribological properties by adding in engine oil (SN 5W-40 base oil) in this work.

2 | EXPERIMENTAL

2.1 | Materials

All chemical reagents used were commercially available in this work and were used without further purification: Sodium molybdate dihydrate (Na2MoO4·H2O), hydroxylamine hydrochloride (NH2OH·HCl), sulfocarbamide (CH4N2S), benzyl triethyl ammonium chloride (TEBAC), alcohol (C2H5OH), and hydrochloric acid.

2.2 | Materials synthesis

In the first place (Figure 1), different amounts of NH2OH-HCl and TEBAC were dispersed in H2O (20 ml), and this solution was noted as A. Next, 3 mmol CH4N2S was dispersed in 10 ml H2O and stirred for 30 min. Ten mL H2O (including 3 mmol CH4N2S) was added slowly into A. Following, 1 mmol Na2MoO4 were ultrasonically dispersed in H2O (25 ml) for 60 min, and this solution was noted as B. B was slowly dropped into A. The mixture was made to experience hydrothermal conditions in a Teflon-lined stainless-steel autoclave for 48 h at 200°C and restored at room temperature. In the end, the black product was separated by centrifugation and washed with 4–5 times with H2O and C2H5OH and finally dried in a drying cabinet at 60°C for 12 h.

Preparation and tribological properties of lubricating oil samples: The samples prepared were distributed into the SN 5W-40 base oil utilising 60 min ultrasonication. The tribological properties of the oil with samples were examined on an MRS-10A four-ball testing machine. The testing of tribological properties was conducted at a rotating speed of 1200 rpm and a load of 392 N for 3600 s. The experimental steel balls’ material conformed to the American ANSI standard E-52100 chromium alloy steel ball. Besides, the diameter of the steel ball was 12.7 mm, and the hardness of the ball was 61–66 HRC. The tribological behaviours of these samples were investigated under a rotational speed of 1200 rpm and a constant load of 392 ± 2 N at 75 ± 2°C for 3600 s. The average wear scar diameter (AWSD; ± 0.01 mm) of the three bottom balls decided the wear rate. Each experiment was repeated three times under the same conditions.

2.3 | Characterisation of the samples

The X-ray diffraction (XRD) patterns were operated by a D8 advance (Bruker-AXS) diffractometer with Cu Kα line (λ = 0.1546 nm). The microstructures of the sample were characterised by a scanning electron microscope (SEM; JEOL JXA-840A) at 20 kV equipped with an energy dispersive X-ray spectrometer (energy dispersive spectroscopy (EDS)) and transmission electron microscope (TEM; JEOL JEM-2100). Fourier transform infrared spectroscopy (FT-IR; D/max2500, Rigaku Company, Japan) was used to
determine the success of composite formation. N₂ adsorption-desorption curve and pore size analysis (BET) were measured by an American NOVA2000e type-specific surface area and porosity analyser. Thermal stability was analysed by thermogravimetry (TG) and derivative thermogravimetry (DTG) (TG-DTG; NETZSCH STA 449F3). The tribological properties were tested by an MRS-10A four-ball testing machine (Yihua Company, China).

3 RESULTS AND DISCUSSION

3.1 XRD analysis

The XRD patterns of DB-O-MoS₂ are shown in Figure 2(a) to investigate the structural information. The structure of DB-O-MoS₂ was confirmed by XRD as shown in Figure 2(a). Two labelled diffraction peaks, (101) and (110), could be indexed to those of the pure hexagonal phase of MoS₂, which were in good agreement with the values of the standard card (JCPDS No. 37-1492). From the diagram, the peaks at 2θ = 33.2 and 58.7 degrees were assigned to (101) and (110) crystal planes of 2H-MoS₂. For the (002), the peak at 10.4 degrees could be thought to divide into two peaks. In Figure 2(a), in the low angle diffraction region, there were two new characteristic peaks at 8.3 and 16.2 degrees. Detailed analysis with JADE 6 of these two peaks showed that the corresponding d spacings are 10.0 and 5.16 Å, respectively. The diploid relations between d spacing clearly showed the formation of a new layered structure with an enlarged interlayer spacing of 10.0 Å compared with that of 6.15 Å in 2H-MoS₂ (JCPDS card no. 73-1492). Combining the test conditions and literature reports, the reaction cannot be completely completed at a lower temperature, so the Mo-O bond in the precursor MoO₄²⁻ was retained, which lead to the incorporation of O element, that is, the prepared sample was oxygen-doped into MoS₂ [13].

3.2 Morphology analysis

According to the SEM images, Figures 3(a) and (b) show the pictures of DB-O-MoS₂. The morphologies of products were primarily investigated by SEM measurement. Figure 3(a) indicates that the sample is of ultrathin nanosheet morphology with uniform lateral size in the range of about 100 nm. The sample self-assembled the binuclear shells from nanosheets. Figure 3(b) shows that the obtained samples had a double core-shell structure of about 900 nm in size and we can see the outer and the inner shells. EDS analysis was performed for the elemental composition of oxygen-incorporated MoS₂. Figure 3(c) shows the EDS spectrum of oxygen-incorporated MoS₂, which
FIGURE 3  Scanning electron microscope (SEM) images, energy dispersive spectroscopic (EDS) spectrum and transmission electron microscope (TEM) image of DB-O-MoS2. (a) Double core-shell structure, (b) inner and outer shell structures, and (c) EDS spectrum, (d) TEM image

3.3 | FT-IR analysis

From the FT-IR spectra in Figure 4, for DB-O-MoS2, the characteristic Mo-O and Mo-S stretching vibration in MoS2 appeared at 956 and 524 cm\(^{-1}\). Mo-O stretching vibration appeared at 524 cm\(^{-1}\), which confirmed the insertion of oxygen atoms into the MoS2. The absorption peak owing to the O-H bending vibration, and epoxide groups were observed at 1622 cm\(^{-1}\). Due to $S = O$ asymmetric stretching vibration and symmetric stretching vibration, the absorption peaks were observed at 1120 and 1290 cm\(^{-1}\).

3.4 | TG-DTG analysis

The thermal gravimetric analysis of DB-O-MoS2 is shown in Figure 5. In Figure 5, the TG-TDG curves of DB-O-MoS2 underwent two stages of weight loss. The first stage was 50–200°C with a weight loss. The weight loss in this stage was mainly water, which was attributed to water volatilisation. The second stage was 200–500°C with a weight loss. The weight loss in the second stage was ascribed to the oxidation of DB-O-MoS2 [14].

3.5 | N\(_2\) absorption-desorption analysis

Figure 6 shows the N\(_2\) adsorption-desorption isotherms curves and pore size distributions of DB-O-MoS2. The N\(_2\)
adsorption-desorption isotherms curves of DB-O-MoS2 belonged to type IV, and their hysteresis loops were accorded with type H3, and it suggested the presence of mesoporous structures in DB-O-MoS2. The surface area of DB-O-MoS2 was 41.388 m²·g⁻¹. The surface area was relatively large, which was conducive to dispersion in lubricants.

3.6 Friction and wear properties analysis

All the samples were used as lubricating additives for SN 5W-40 base oil; Figure 7 shows the variations of friction coefficient in real time. The tribological properties were compared among the pure SN 5W-40 base oil and the base oil with samples of 0.02, 0.04, 0.06, 0.1, 0.3 and 0.5 wt% with a constant load at 392 N and a rotational speed of 1200 rpm for 3600 s. The friction coefficient of the pure SN 5W-40 base oil without any additives was quite unstable with the increasing times. With the addition of 0.3 wt% samples in the base oil SN 5W-40, the friction coefficient was reduced obviously. Moreover, the friction coefficient decreases with increasing concentration at 0.01–0.3 wt%. Obviously, with the addition of 0.3 wt% samples in the base oil SN 5W-40, the friction coefficient was minimal. Figure 7(c) shows the comparisons of the tribological properties among the pure base oil, the base oil with 0.3 wt% DB-O-MoS2 and the base oil with 0.3 wt% commercial MoS2. The results show that with the addition of 0.3 wt% DB-O-MoS2 in the base oil, the friction coefficient was reduced remarkably and stabilised. Therefore, 0.3 wt% of DB-O-MoS2 had better tribological properties than 0.3 wt% of commercial MoS2. As shown in Figure 8, the AWSD of the bottom steel ball lubricated by samples were smaller than that lubricated by pure SN 5W-40 base oil. When DB-O-MoS2 with the concentration of 0.1, 0.3 and 0.5 wt% was used in the SN 5W-40 base oil, the AWSD of the bottom steel decreased (Figures 8(a)–(d)). The smallest value occurred at the concentration of 0.30 wt% samples, and the average friction coefficient reached a low level at this point. Therefore, the SN 5W-40 base oil containing 0.3 wt% samples had better tribological properties.

The possible mechanism of DB-O-MoS2 in promoting the tribological properties of the SN 5W-40 is rolling, deformation, slip, and adsorption film. The biggest advantage is the ease of slip caused by the insertion of oxygen atoms. The binuclear shell structure enables each nanoparticle to play a more micro-axial role.

4 Conclusion

In this work, DB-O-MoS2 is successfully prepared by the authors through a simple one-step hydrothermal method. EDS analysis is performed for the elemental composition of oxygen-incorporated MoS2. The tribological performance effect of DB-O-MoS2 on the SN 5W-40 base oil has been investigated. The result of the experiment shows that the base oil with 0.3 wt% DB-O-MoS2 has excellent friction and wear properties.
The variations of friction coefficient of lubricant with times. (a) The concentration of the added sample is 0, 0.02, 0.04, 0.06, 0.08 and 0.1 wt%, (b) the concentration of the added sample is 0, 0.1, 0.3 and 0.5 wt%, (c) the concentration of the added 0.3 wt% sample and 0.3 wt% commercial MoS$_2$, respectively

**FIGURE 8** Average wear scar diameter images of the different concentration of the added sample. (a) No additives, (b) 0.1%, (c) 0.3%, and (d) 0.5%

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