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Tribological Properties of Tungsten Disulfide Nanoparticles Surface-Capped by Oleylamine and Maleic Anhydride Dodecyl Ester as Additive in Diisooctylsebacate

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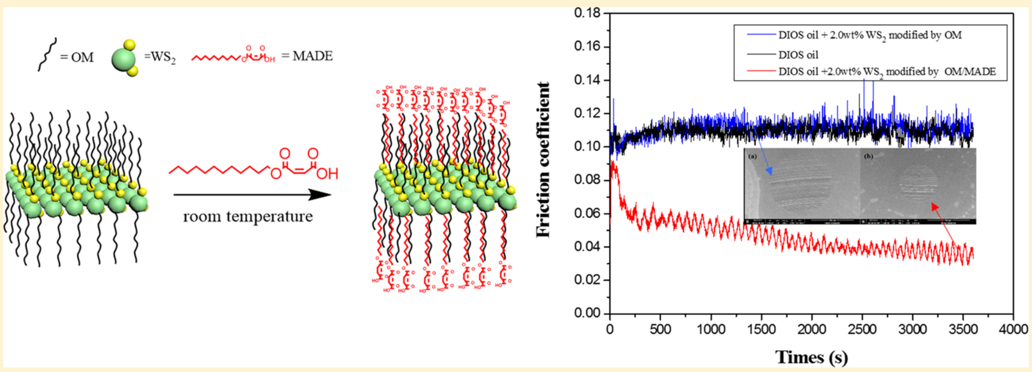
Supporting Information



ABSTRACT: Oleylamine (OM) and maleic anhydride dodecyl ester (MADE, synthesized at our laboratory) were adopted as the surface modifiers to prepare OM/MADE-capped tungsten disulfide (WS_2) nanoparticles. An X-ray diffractometer and a transmission electron microscope were performed to analyze the microstructure and phase ingredients of the OM/MADE-capped WS_2 nanoparticles. Moreover, a four-ball friction and wear tester and a reciprocating tribometer were employed to evaluate the tribological properties of the surface-capped WS_2 nanoparticles as the lubricant additive in diisooctylsebacate (DIOS) from room temperature to 150 °C. The morphology of the worn steel surfaces and wear scars and their chemical states were investigated with a scanning electron microscope, three-dimensional profilometry, and an X-ray photoelectron spectroscope. Results show that OM-capped WS_2 nanoparticles nearly have no effect on the tribological properties of the DIOS base oil. The OM/MADE-capped WS_2 nanoparticles added in the same base stock at a concentration of 2.0% (mass fraction), however, exhibit good dispersibility and result in greatly improved tribological properties. The reason lies in that, after surface-capping by MADE containing polar group and OM containing coordination group, the OM/MADE-capped WS_2 particulates added in the base oil are well adsorbed on the sliding surfaces of the steel−steel contact to afford a chemisorption film with a low shear force. At the same time, OM/MADE-capped WS_2 nanoparticles as the additive in DIOS base oil take part in tribochemical reactions to form tribofilm composed of WO_3 and iron oxides on sliding surfaces, which also contributes to reducing the friction and wear of the steel sliding contact.

1. INTRODUCTION

Conventional lubricants on the market consist of base stock and a variety of multifunctional additives, and their tribological properties are closely related to the compatibility between the base oil and additives. As a category of frequently used lubricating base stocks, synthetic ester oils are worth special attention, because synthetic esters often possess better viscosity−temperature characteristics, fluidity at lowered temperature, antioxidation ability, biodegradability, and renewability than mineral oils and poly-α-olefin (PAO).[1,2] However, conventional antiwear additives applied in mineral oils are usually unsuitable for low viscous synthetic ester oils.[3−6]

To deal with the above-mentioned issue, some scientists paid special attention to multifunctional additives applicable to synthetic ester base oils. For example, Waara et al.[3] prepared a variety of extreme pressure and antiwear additives as well as Cu passivators, and they found that the antiwear additives and Cu passivators have little or no contribution to the friction-reducing and antiwear abilities of synthetic polyol ester base oil and mineral base oil. They also reported that traditional

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antiwear additives and EP additives often exhibit poor tribological properties in synthetic ester base oil. Minami et al.[5] said that conventional antiwear additives do not work at all in polar esters. Jiménez et al.[6] reported that some synthetic lubricants increase the wear of aluminum, and traditional antiwear additives with good lubricating performance in mineral oils can hardly improve the tribological properties of low viscous esters.

In terms of a variety of multifunctional additives used in lubricating oils, nanoadditives are of particular significance, because they exhibit lower dosage as well as better tribological properties than conventional lubricant additives widely used in mineral oil.[7−15] However, the nanoadditives are usually unsuitable for synthetic ester oils. For example, we previously found that WS_2 nanoparticles modified by oleylamine (denoted as OM), obtained by a solution-phase route at 300 °C, exhibit excellent lubricating properties in PAO base oil.[9] However, OM-capped WS_2 nanoparticles as the lubricant additive in synthetic ester oil diisooctylsebacate (denoted as DIOS) worsen the friction-reducing ability. Therefore, it is imperative to manipulate the surface chemical properties of nanoadditives like OM-capped WS_2 nanoparticles in order to improve their compatibility with synthetic ester oil and effectively enhance the tribological properties.

Here we focus on tuning the surface chemistry of nanoadditives, hoping to develop novel nanoadditives applicable to synthetic ester base oils over a wide range of temperature.[16] This article reports the synthesis of amphiphilic maleic anhydride dodecyl ester (denoted as MADE) with a simple and efficient method.[17] It also deals with tuning surface properties of OM-capped WS_2 nanoparticles by the as-synthesized amphiphilic MADE surfactant,[9,18] and the tribological properties of the OM/MADE-capped WS_2 nanoparticles added in DIOS from room temperature to 150 °C.

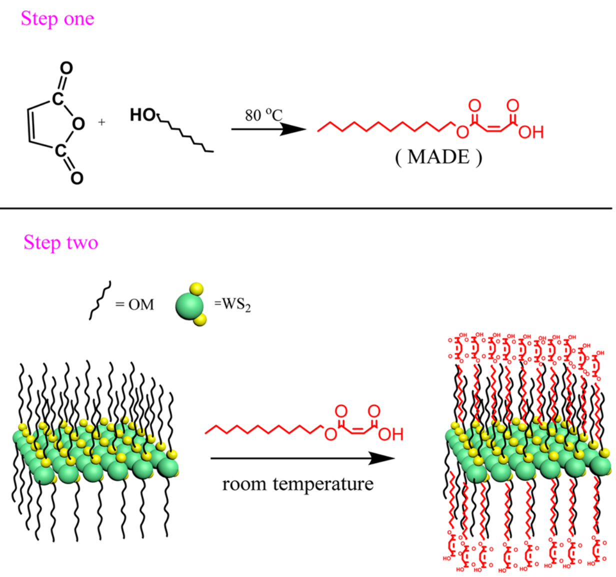
2. EXPERIMENTAL SECTION

2.1. Synthesis of Maleic Anhydride Dodecyl Ester Surfactant. The powders of tungsten hexachloride (WCl_6, 99.99%) and sulfur (S, 99.98%) as well as analytical reagents OM (90%), 1-octadecene (90%), maleic anhydride, dodecanol, ethanol, methanol, chloroform, hexane, and heptane were all commercially obtained.

Monoalkylmaleic anhydride dodecyl ester surfactant was synthesized with maleic anhydride and dodecanol as the starting materials.[17] Briefly, a proper amount of maleic anhydride (0.20 mol) and dodecanol (0.20 mol) were placed into a three-necked flask and stirred for 60 min under 80 °C. Then 100 mL of heptane was added into the flask under an additional 15 min of stirring at 80 °C. Upon completion of heating, the reaction solution was held at ambient conditions for 180 min, followed by cooling at 15 °C for 120 min under continuous stirring to allow the formation of a precipitate. The as-obtained precipitate was collected by filtration and purified with heptane (100 mL) to provide a white bright crystal, the target product maleic anhydride dodecyl ester in a yield of 91.6%.

2.2. Preparation of Ultrathin WS_2 Nanoparticles Capped by Oleylamine and Maleic Anhydride Dodecyl Ester. Ultrathin WS_2 nanoparticles capped by oleylamine and maleic anhydride dodecyl ester (denoted as OM/MADE-capped WS_2) were synthesized by a surface modification method. Scheme 1 schematically shows the route to synthesizing the target ultrathin WS_2 nanoparticles, and it covers two stages of reactions. The first step involves the preparation of OM-capped WS_2 nanoparticles according to the route reported in our previous research.[9] In brief, 20 mL of OM, 10 mL of 1-octadecene, and 1 mmol of WCl_6 was sequentially placed in a three-necked flask (50 mL). The flask was vibrated ultrasonically for 30 min to achieve the complete dissolution of WCl_6. Then it was heated to 140 °C and kept there for 30 min to allow the removal of H_2O and O_2 with the assistance of strong magnetic stirring under protection in argon atmosphere. Upon completion of H_2O and O_2 removal, the flask was heated to 300 °C in 15 min and held there for an additional 30 min under Ar protection. Then an injection pump was performed to inject 5 mL of OM with 2 mmol of dissolved sulfur powder into the flask within 10 min. At the end of injection, the flask was held at 300 °C for 60 min to generate WS_2 nanoparticles. When the reaction was completed, the mixture in the flask was cooled to ambient temperature, fully cleaned with water-free ethanol under ultrasonic vibration, and centrifuged to eliminate residual organics, thereby yielding OM-capped WS_2 nanoparticles.

Scheme 1. Schematic Diagram Showing the Synthesis of OM/MADE-Capped WS_2 Nanoparticles



The second step covers the preparation of OM/MADE-capped WS_2 nanoparticles. Namely, 2.000 g of the OM-capped WS_2 nanoparticles was dispersed in 20 mL of chloroform with a flask while 2.000 g of MADE was added under 1 h of magnetic stirring at ambient condition. The chloroform in the flask was slowly evaporated by rotation under vacuum. The as-evaporated reaction mixture was then fully cleaned with water-free ethanol under ultrasonic vibration and centrifuged to eliminate residual organics under ultrasonic vibration, thereby affording desired OM/MADE-capped WS_2 nanoparticles.

2.3. Characterization of Maleic Anhydride Dodecyl Ester Surfactant. A proper amount of maleic anhydride dodecyl ester solution was coated on KBr crystal and dried in air. The chemical structure of the as-dried MADE was analyzed with an AVATAR 360 Fourier transform infrared spectrometer (FTIR; Themlo Nicolet, USA) and an AVANCE 400 nuclear magnetic resonance spectroscope (^{1}H NMR, 400 MHz, dimethyl sulfoxide; Bruker, Germany).

2.4. Characterization of Ultrathin WS_2 Nanoparticles Capped by Oleylamine and Maleic Anhydride Dodecyl

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Ester. An X'Pert Pro diffractometer (XRD; Cu Kα radiation, λ = 0.154 18 nm) was performed under a voltage of 40 kV and a current of 40 mA to identify the phase ingredients of OM/MADE-capped WS_2 nanoparticles. A JEM-2010 microscope (Jeol Corp., Japan) was employed under an accelerating voltage of 200 kV to analyze the microstructure of the surface-capped WS_2 nanoparticles. A small amount of the surface-capped WS_2 nanoparticles was dispersed in water-free ethanol, and then a drop of the resultant dispersion was spread on a copper grid with carbon film and fully dried under ambient conditions to acquire the specimens used for transmission electron microscopy (TEM) observation.

2.5. Examination of Thermal Stability and Dispersibility as Well as Tribological Properties of OM/MADE-Capped WS_2 Nanoparticles. The dispersion stability of the OM/MADE-capped WS_2 nanoparticles in DIOS base oil was estimated from the absorbance of the dilute solution. The absorbance of the dilute solution was measured with a Cary 60 UV−vis (ultraviolet−visible light) spectrophotometer (Agilent Technologies, USA) at different centrifugal rotational speeds (1000−8000 rev/min, time 10 min) and different centrifugation times (centrifugal rotational speed 5000 rev/min).

In the meantime, the as-prepared OM/MADE-capped WS_2 nanoparticles were dispersed in DIOS base oil and stored at room temperature for 6 months. Upon completion of storage, the pictures of the as-stored dispersion were taken with a digital camera, and the dispersibility and stability of the dispersion was then estimated accordingly.

Thermogravimetric analysis (TGA) in N_2 flow was conducted with a TGA/SDTA851e thermal analyzer (scanning rate 10 °C/min) to estimate the thermal stability of the OM/MADE-capped WS_2 nanoparticles. Also, a proper amount of the OM/MADE-capped WS_2 nanoparticles was ultrasonically dispersed in DIOS for 10 min to obtain a solution with an optimal concentration of 2.0% (mass fraction; determined according to the results of friction and wear tests). The resultant solution was further diluted with DIOS base oil to a concentration of 0.2%.

A four-ball friction and wear tester (SHIJIN Group Corp.; Jinan, China) was performed to evaluate the tribological properties of OM/MADE-capped WS_2 nanoparticles as the lubricant additive in DIOS. The sliding pair was assembled with SAE-52100 steel balls (diameter 12.7 mm, hardness HRC 61-64, Poisson ratio 0.30, elastic modulus 208 GPa) produced by Shanghai Bearing Factory (Shanghai, China). The sliding tests were run at a rotary speed of 1200 rev/min, a load of 92−592 N, and a duration of 60 min from ambient temperature to 150 °C. The Hertzian pressure of the sliding pair in relation to the applied load is listed in Table S1. An optical microscope was employed to determine the wear scar diameter (WSD) of the three lower balls at an accuracy of 0.01 mm. A computer attachment of the four-ball test rig was performed to record the friction coefficient. Three repeat sliding tests were run under each preselected condition, and the WSD and friction coefficient were measured at a relative deviation of ±5.0% and ±0.004, respectively. Upon completion of the sliding tests, the WSD of the three lower steel balls was averaged and reported here. Table 1 lists the physicochemical properties of DIOS. The organic moieties of the base stock are stable after being heated at 150 °C for 180 min (see the differential scanning calorimetry (DSC) curve of DIOS in Figure S1).

A Nova Nano SEM 450 scanning electron microscope (SEM; FEI, USA) was performed to observe the morphology of the worn steel surfaces, and a Contour GT-I three-dimensional (3D) optical profiler (Bruker, Germany) was employed to determine the wear volume. An AXIS ULTRA X-ray photoelectron spectroscope (XPS; Kratos, U.K.) was conducted to analyze the chemical states of the major elements on worn steel surfaces. Before XPS analysis was commenced, the steel balls were ultrasonically cleaned with acetone and completely dried at ambient conditions.

Table 1. Physicochemical Properties of DIOS Ester Oil

item	value
density at 25 °C	0.912 g/cm
kinematic viscosity at 40 °C	11.5 mm^2/s
kinematic viscosity at 100 °C	3.1 mm^2/s
viscosity index	≥120
acid number	≤0.1 mg of KOH/g
pour point	≤ −60 °C
flash point (open)	≥215 °C

An MFT-R4000 reciprocal friction and wear test rig (Huahui Instrument Technology Co., Ltd., Lanzhou, China; contact mode, ball-on-disk) was employed to measure the Stribeck curves of DIOS and DIOS with 2.0% (mass fraction) of OM/MADE-capped WS_2. The lubricating performance of various lubricants was described, and their actual working conditions were simulated in relation to the Stribeck curves. According to the Stribeck curves, a total of four lubrication regions, i.e., boundary lubrication, mixed lubrication, elastohydrodynamic lubrication, and hydrodynamic lubrication, are differentiated.[19] The ball-on-disk sliding pair was assembled with an SAE-52100 steel ball with a diameter of 4 mm (Poisson ratio 0.3, elastic modulus 208 GPa) and ASTM 304 stainless steel disk with a size of 20 mm × 20 mm (Poisson ratio 0.285, elastic modulus 204 GPa). Prior to reciprocal sliding against the disk, the lower steel ball was completely immersed in the to-be-tested lubricant that was placed in the oil box. The Stribeck curves were measured at a stroke of 10 mm, temperatures of 20, 75, and 150 °C, and a duration of 220 min under preset normal load and frequency. A computer connected to the ball-on-disk test rig was employed to record friction coefficients. Three repeat sliding tests were run at each preselected sliding condition, where the friction coefficients were measured with a relative deviation of ±0.004 and then averaged to calculate the Stribeck curves.

3. RESULTS AND DISCUSSION

3.1. Tribological Properties of WS_2 Nanoparticles Modified by OM as Additive in PAO Oil and DIOS Oil. As shown in Figure 1, OM-capped WS_2 nanoparticles, obtained by a solution-phase route at 300 °C, exhibit excellent lubricating properties in PAO6 base oil (Figure 1a).[9] However, OM-capped WS_2 nanoparticles as the lubricant additive in DIOS lead to increased friction coefficients (Figure 1b). This might be related to the polarity of DIOS. Namely, the OM-capped WS_2 nanoparticles exhibit weak polarity attributed to OM, which makes it feasible for the additives rather than the nonpolar PAO6 base oil to be readily adsorbed on the sliding surfaces of the steel balls to reduce friction and wear.[20] Differing from nonpolar PAO6, DIOS containing polar group −COO− (Figure S2) can be more easily adsorbed on the sliding surfaces of the steel balls than the OM-capped WS_2 nanoparticles. As a result, the tribological function of the lubricant additive is retarded, and an increased friction

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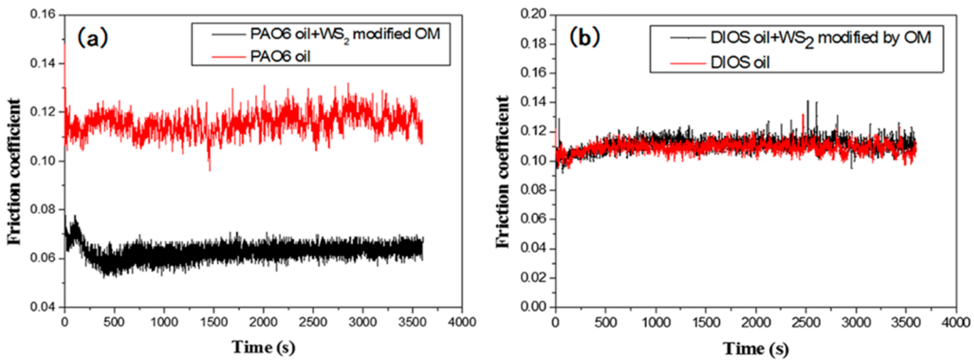

Figure 1. Friction coefficient of the steel−steel sliding pair lubricated by (a) PAO6/OM-capped WS_2 and (b) DIOS/OM-capped WS_2 (four-ball tester; load 392 N, speed 1200 rev/min, time 60 min, temperature 75 °C; additive concentration 2.0%).

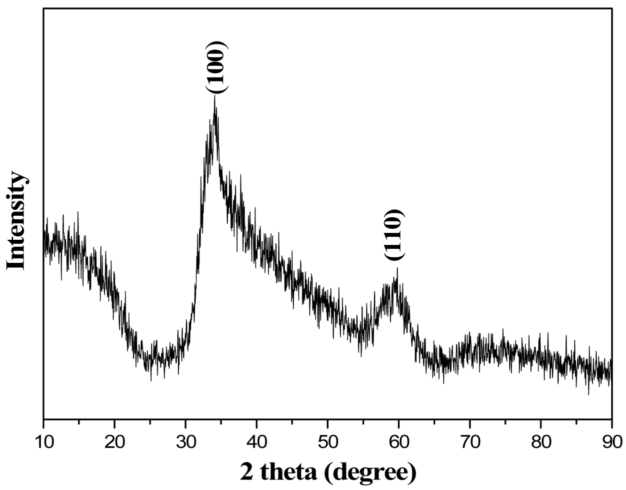

Figure 2. XRD pattern of OM/MADE-capped WS_2 nanoparticles.

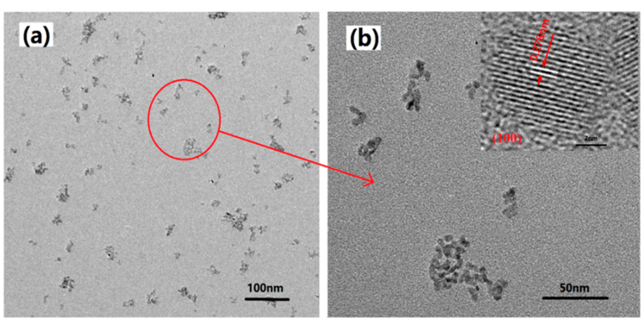

Figure 3. TEM (a) and HRTEM (b) images of OM/MADE-capped WS_2 nanoparticles.

coefficient even larger than that under the lubrication of DIOS base oil alone is obtained when OM-capped WS_2 nanoparticles are introduced in DIOS base oil.[3,6,21] For this reason, we select amphiphilic MADE surfactant to tune the surface properties of OM-capped WS_2 nanoparticles.

3.2. FTIR and ^{1}H NMR Characterizations of Maleic Anhydride Dodecyl Ester. The chemical structure of maleic anhydride dodecyl ester was confirmed by FTIR. As shown in Figure S3, no absorption peak emerges at 1776 cm^{-1}, which is due to the decomposition of anhydride. The absorption peak at 1725 cm^{-1} is assigned to −COOH. The absorption band at 1172 cm^{-1} corresponds to the C−O−C group of ester generated through the chemical reaction between maleic anhydride and dodecanol. Moreover, the absorption bands at 2940 and 2850 cm^{-1} correspond to the alkyl chain of monoalkyl maleate.[22] The ^{1}H NMR spectrum of maleic anhydride dodecyl ester is shown in Figure S4.

3.3. TEM, XRD, and FTIR Analyses of OM/MADE-Capped WS_2 Nanoparticles. The XRD pattern of OM/MADE-capped WS_2 nanoparticles is shown in Figure 2. The (100) and (110) peaks in Figure 2 could be indexed to the 2H (hexagonal) WS_2 (JCPDS Card No. 08-0237) with no discernible impurity but poor crystallization.[18,23,24] The absence of the (002) peak at 2θ = 14.32 indicates that the WS_2 layers are not well-stacked. Based on the Bragg equation, the *d*-spacing of the (100) peak is calculated to be 0.274 nm, and it is similar to that described in JCPDS Card No. 08-0237. Also, the XRD pattern of OM/MADE-capped WS_2 nanoparticles shows sign of obvious broadening, which corresponds to their nanoscale dimension. This could be because the OM/MADE-capped WS_2 nanoparticles are surface-passivated by solvent molecules, thereby exhibiting retarded crystallographic ordering.[25]

The TEM and HRTEM images of OM/MADE-capped WS_2 nanoparticles are shown in Figure 3. OM/MADE-capped WS_2 nanoparticles have an average size of 6−8 nm. Also, as evidenced by the parallel fringes with a (100) spacing of 0.276 nm, WS_2 in the surface-capped nanoparticles belongs to the 2H poly type of platelets (referring to a lattice spacing of 0.273 nm specified in JCPDS Card No. 08-0237),[23,24] which is consistent with corresponding XRD data. Figure S5 shows the selected area electron diffraction (SAED) pattern of OM/MADE-capped WS_2 nanoparticles. Based on the *hkl* Miller indices, the two strong diffraction rings are assigned to the (100) and (110) lattice planes, which well conforms to relevant XRD data.

Figure S6 shows the FTIR spectrum of OM/MADE-capped WS_2 nanoparticles. The absorption bands at 1725 and 1167 cm^{-1} correspond to maleic anhydride dodecyl ester, which indicates that maleic anhydride dodecyl ester has been successfully coated on the surface of OM-capped WS_2 nanoparticles.

3.4. Dispersivity and Thermal Stability of WS_2 Nanoparticles Modified by OM/MADE. The dispersion stability of OM/MADE-capped WS_2 nanoparticles in DIOS was evaluated by UV−vis spectroscopy. Figure S7 shows the relative absorbance of the additive in base oil under different centrifugal rotational speeds (1000−8000 rev/min; time 10 min), while Figure S8 shows the relative absorbance of the additive in DIOS under different centrifugation times (centrifugal rotational speed 5000 rev/min). It can be seen that the relative absorbance of OM/MADE-capped WS_2

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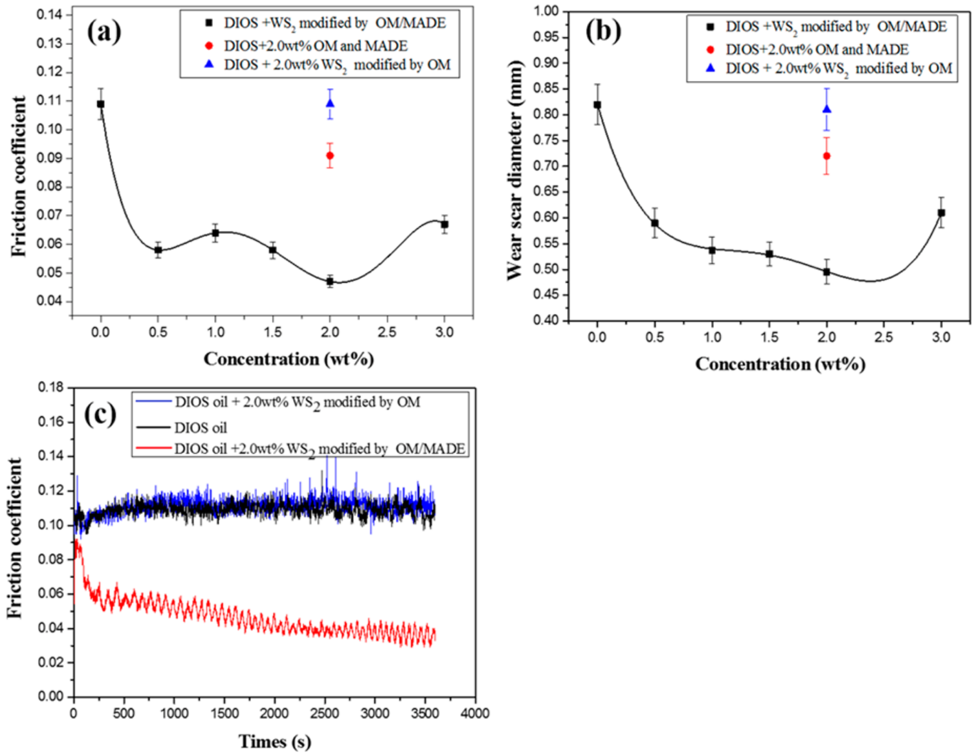

Figure 4. Friction coefficient (a) and WSD (b) vs OM/MADE-WS_2 nanoparticles concentration in DIOS as well as friction curves (c) of DIOS, DIOS with 2.0% of OM-capped WS_2, and DIOS with 2.0% of OM/MADE-capped WS_2 (conditions the same as those in Figure 1).

Table 2. Friction Coefficient, Wear Scar Diameter, and Wear Volume at Various Temperatures

	friction coefficient			wear scar diameter (mm)			wear volume ($\times 10^7$ μm^3)		
oil	20 °C	75 °C	150 °C	20 °C	75 °C	150 °C	20 °C	75 °C	150 °C
DIOS oil	0.113	0.108	0.097	0.780	0.813	1.312	1.52	0.611	4.66
DIOS + OM/MADE-WS_2	0.057	0.047	0.082	0.670	0.479	1.140	0.492	0.101	2.24

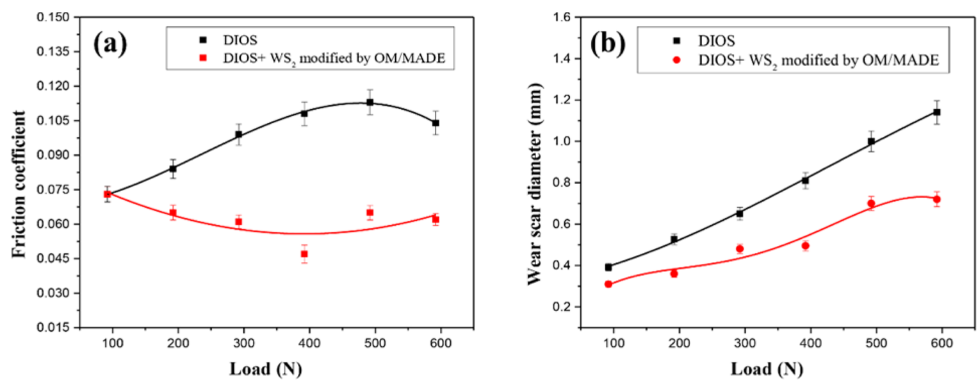

Figure 5. Friction coefficient and WSD vs load curves (conditions the same as those in Figure 1 except for load).

nanoparticles in DIOS reduces marginally with the increase of centrifugal rotational speed. After a long period of centrifugation time (60 min), the relative absorbance of the as-synthesized WS_2 nanoparticles in DIOS maintains at a high level of 97%. This means that OM/MADE-capped WS_2 nanoparticles exhibit good dispersion stability in DIOS.

Figure S9 shows the pictures of the dispersion of as-prepared OM/MADE-capped WS_2 in DIOS and of the same dispersion after 6 months of storage at ambient conditions. The dispersions look black, and no sediment occurs after the long-term storage. This indicates that OM/MADE-capped WS_2 nanoparticles exhibit good dispersion stability in DIOS oil, which is significant for their application as the lubricant additive in synthetic ester.

Figure S10 shows the TGA and DTG curves of OM/MADE-capped WS_2 nanoparticles. The as-prepared product undergoes the initial maximum thermal decomposition at 172.7 °C, which means that it could be used as the lubricant additive in DIOS base oil up to a temperature of about 170 °C. Also, the OM/MADE-capped WS_2 nanoparticles undergo complete thermal decomposition around 473.6 °C and leave about 15.66% (mass fraction) of residue. Such a residue, mainly WS_2, could be

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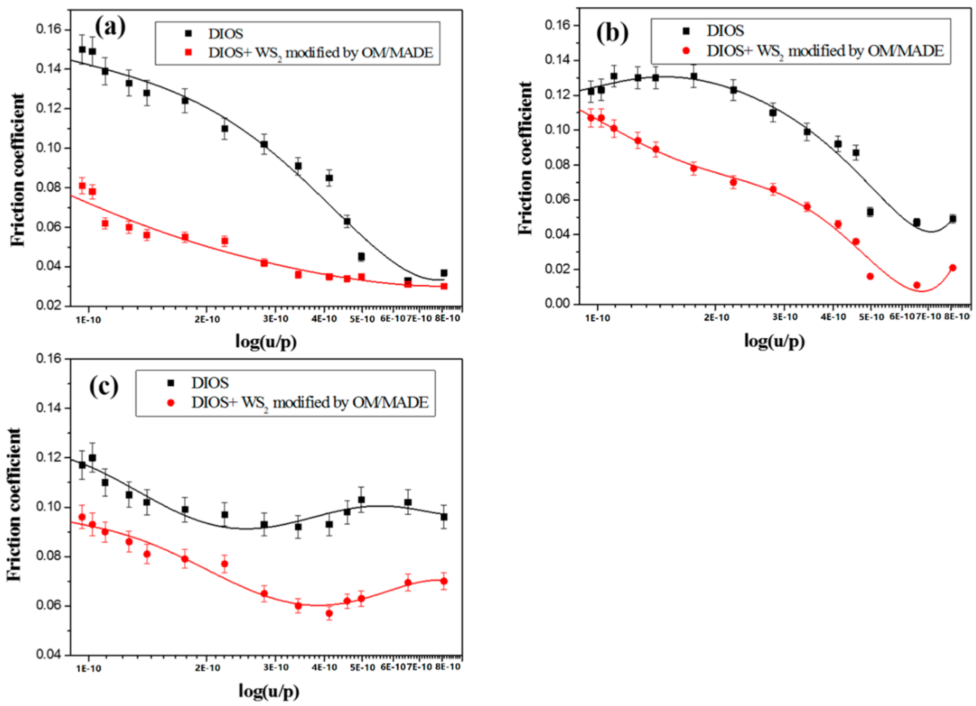

Figure 6. Stribeck curves of DIOS oil and DIOS oil with 2.0% of OM/MADE-capped WS_2 nanoparticles at room temperature (a), 75 °C (b), and 150 °C (c).

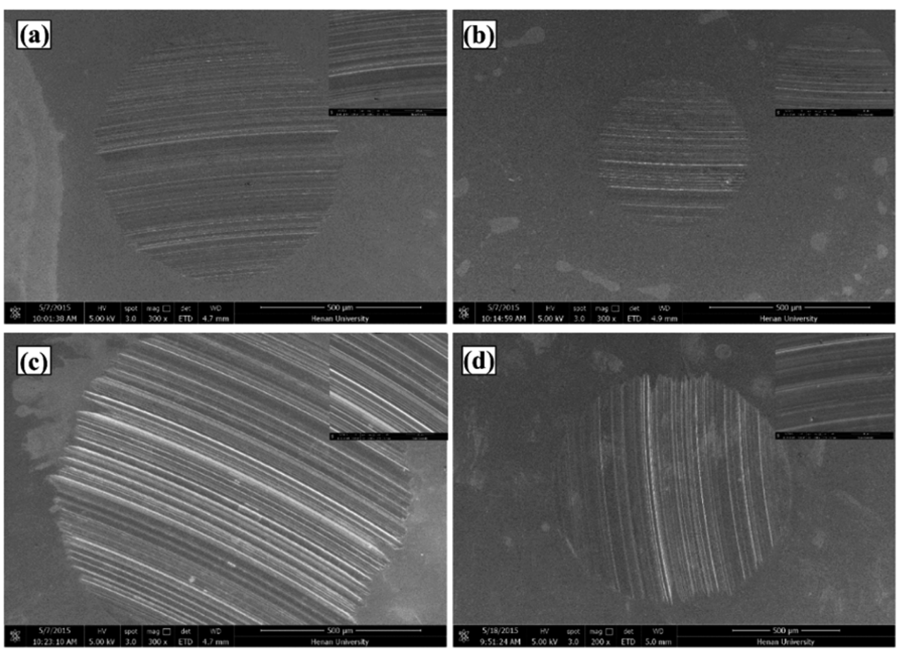

Figure 7. SEM images of worn surfaces of steel ball lubricated by DIOS oil (a, 75 °C; c, 150 °C) and DIOS oil with 2.0% of OM/MADE-capped WS_2 nanoparticles (b, 75 °C; d, 150 °C) under different temperatures (DIOS oil was tested at 75 °C).

favorable for decreasing the friction and wear of the steel sliding contact under elevated temperature.

3.5. Tribological Properties of OM/MADE-Capped WS_2 Nanoparticles as Additive in DIOS Oil. The variations in the friction coefficients and WSD with the dosage of OM/MADE-capped WS_2 in DIOS are shown in Figure 4a,b. As seen in Figure 4a,b, OM/MADE-capped WS_2 as the additive in DIOS can effectively reduce the friction coefficient and WSD of the steel−steel pair. Namely, when 2.0% of OM/MADE-capped WS_2 nanoparticles were added into DIOS, the best antiwear performance and friction-reducing ability were obtained: the wear scar diameter and the friction coefficient were reduced by 39.6 and 56.9%, respectively. Nevertheless, when OM/MADE-capped WS_2 nanoparticles were added in DIOS oil with a concentration above 2.0%, both the friction coefficient and wear scar diameter tend to increase slightly with the increase in the additive concentration.

We could infer that, when the lubricant additive was added into the base oil at a too low concentration, it was unable to form a tribofilm to well cover the sliding steel surface. As a

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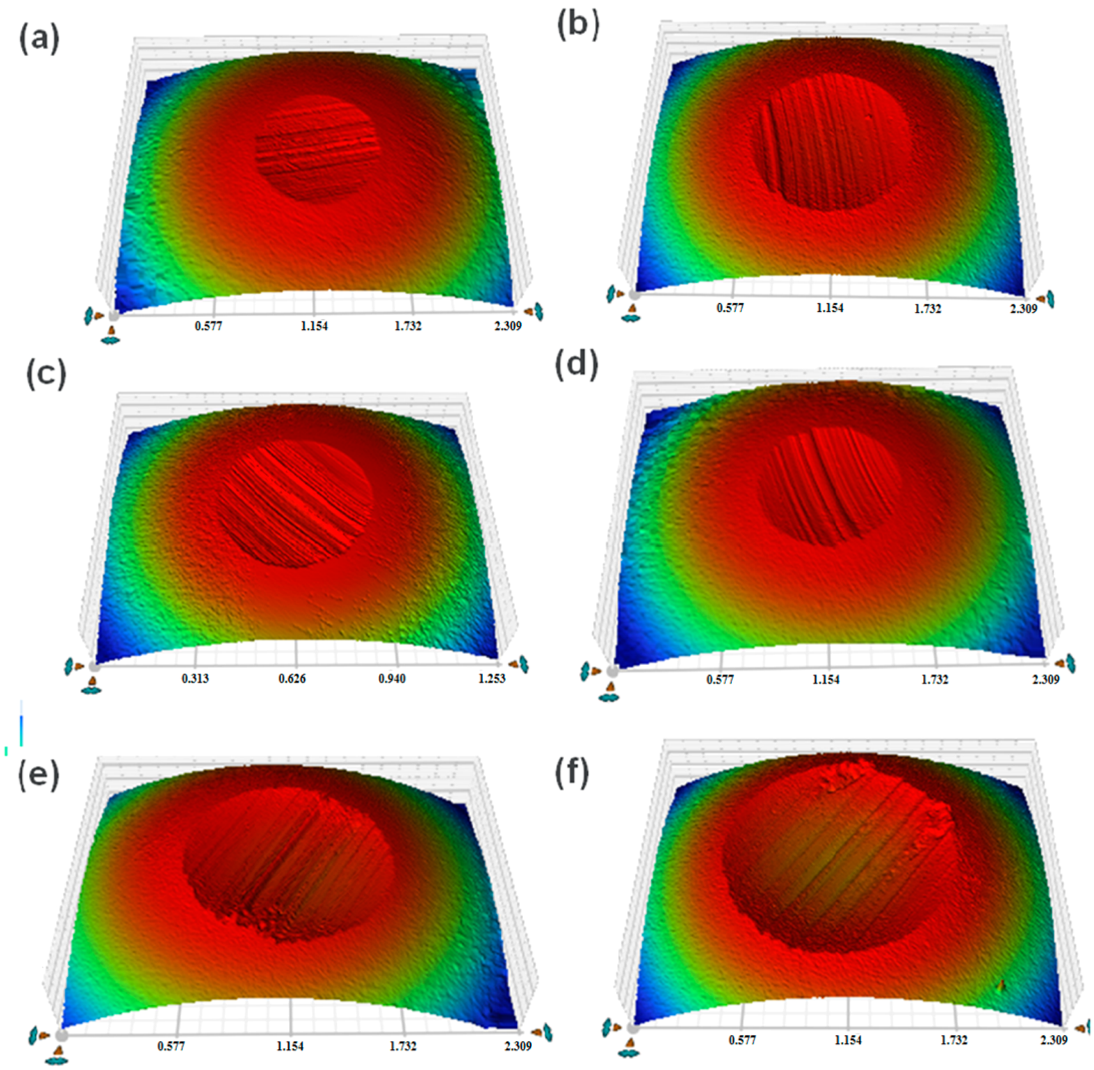

Figure 8. Three-dimensional morphologies of wear scars lubricated by DIOS base oil and DIOS−2.0% OM/MADE-capped WS_2 nanoparticles (four-ball tester; load 392 N, speed 1200 rev/min, time 60 min): (a) lubricated by DIOS−2.0% lubricant additive at room temperature; (b) lubricated by DIOS at room temperature; (c) lubricated by DIOS−2.0% lubricant additive at 75 °C; (d) lubricated by DIOS at 75 °C; (e) lubricated by DIOS−2.0% lubricant additive at 150 °C; (f) lubricated by DIOS oil at 150 °C.

result, a relatively high friction coefficient was obtained, due to local direct contact of the sliding surfaces. As the surface-capped WS_2 nanoparticles were added into the base stock at a too high concentration, they could form large aggregates. As a result, the interasperity valleys of the sliding surfaces cannot be well filled by the lubricant, and the friction coefficient tends to rise owing to enhanced scratching and shearing.[9,25,26]

Moreover, OM/MADE-capped WS_2 nanoparticles as the additive in DIOS base oil are advantageous over OM-capped WS_2 nanoparticles. Namely, when 2.0% of OM-capped WS_2 was added in DIOS, the friction coefficient remained nearly unchanged, but the WSD rose as compared with that under the lubrication of DIOS alone. Also, a friction coefficient of 0.091 and a WSD of 0.720 mm were achieved under the lubrication of DIOS with 2.0% OM and MADE, and both the friction coefficient and wear scar diameter were larger than those under the lubrication of DIOS containing 2% of OM/MADE-capped WS_2 nanoparticles. Figure 4c shows the friction curves of DIOS and DIOS with OM-capped WS_2 or OM/MADE-capped WS_2. Under the lubrication of DIOS with 2.0% of OM/MADE-capped WS_2 nanoparticles, the friction coefficient reduces gradually and eventually stabilizes at about 0.036 while OM-capped WS_2 nanoparticles nearly have no friction-reducing ability. Therefore, we suggest that the concentration of OM/MADE-capped WS_2 in DIOS be maintained at 2.0% so that the best friction-reducing and antiwear abilities are achieved.

Table 2 shows the variation of friction coefficient, wear scar diameter, and wear volume with temperature under the lubrication of DIOS oil containing 2.0% of OM/MADE-capped WS_2 nanoparticles (conditions the same as those in Figure 1 except for temperature (from ambient temperature to 150 °C)).

It is seen that OM/MADE-capped WS_2 nanoparticles are able to improve the friction-reducing and antiwear abilities of DIOS base oil in a broad range of temperature. Namely, the friction coefficients under the lubrication of DIOS−2% OM/MADE-capped WS_2 nanoparticles at room temperature and 150 °C are 0.057 and 0.082, and they are lower than those under the lubrication of DIOS alone. Similarly, the WSDs of the steel balls lubricated by DIOS with 2.0% of OM/MADE-capped WS_2 nanoparticles at room temperature and 150 °C are 0.670 and 1.140 mm, and they are also smaller than those of the

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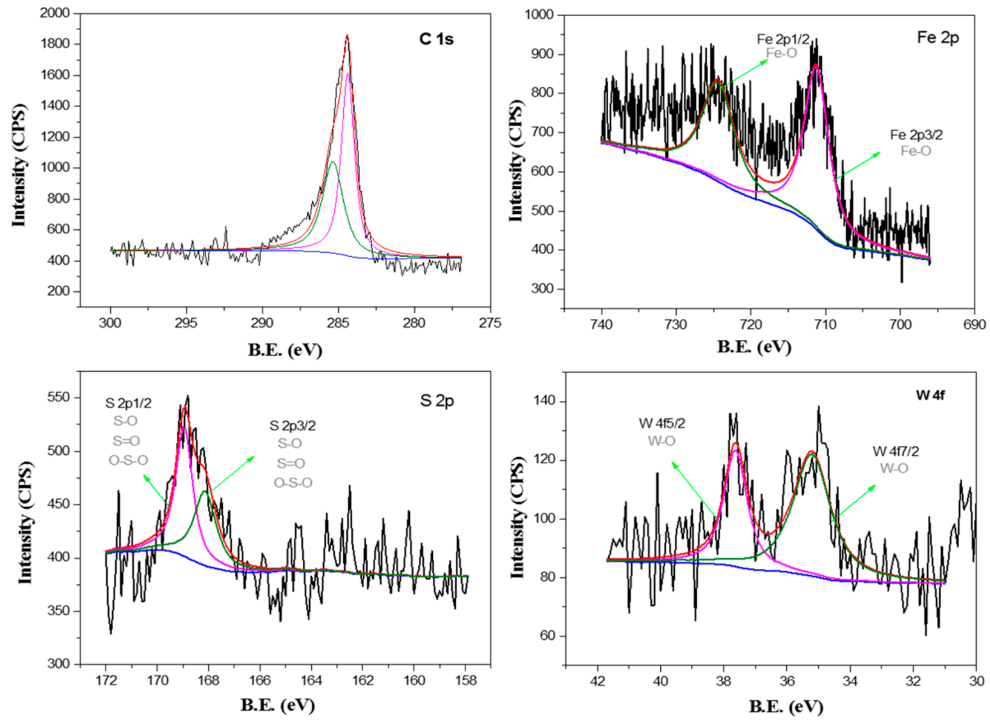

Figure 9. XPS spectra of C 1s, W 4f, S 2p, and Fe 2p of worn steel ball surfaces lubricated by DIOS containing OM/MADE-capped WS_2 nanoparticles (conditions the same as those in Figure 8 except for temperature (150 °C); B.E. is the abbreviation of binding energy).

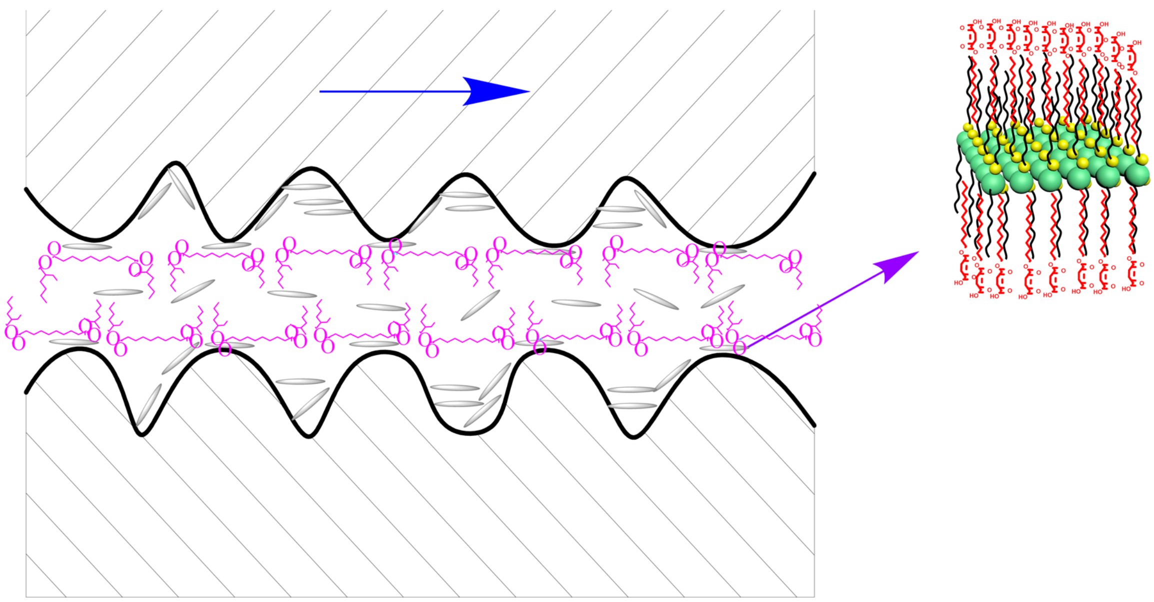

Figure 10. Tribological model of OM/MADE-capped WS_2 nanoparticles in DIOS.

steel sliding pair lubricated by DIOS alone. Therefore, we can draw the conclusion that the OM/MADE-capped WS_2 nanoparticles as the lubricant additive contribute to effectively improving the friction-reducing and antiwear abilities of DIOS ester oil from ambient temperature to 150 °C.

Figure 5 shows the WSD and friction coefficient vs load curves under the lubrication of DIOS and DIOS with 2.0% of OM/MADE-capped WS_2 nanoparticles (conditions the same as those in Figure 1). The lubricant additive added in the DIOS base stock contributes to reducing the friction and wear of the sliding steel pair at various loads. The lowest friction coefficient emerged at 392 N, while the WSD increases continuously with increasing load. This could be because the surface-capped WS_2 nanoparticles form a stable suspension in DIOS; and the suspension was readily transferred onto the contact zone of the sliding steel pair and deposited thereon, thereby forming a surface protective and lubricious layer to reduce friction and wear.[9,20]

Figure 6 shows the Stribeck curves measured at ambient temperature and elevated temperatures. Under the lubrication of DIOS with 2.0% of OM/MADE-capped WS_2 nanoparticles, the sliding steel pair can enter elastohydrodynamic lubrication region under elevated temperature (except for 150 °C) earlier than under the lubrication of DIOS base oil. In the meantime,

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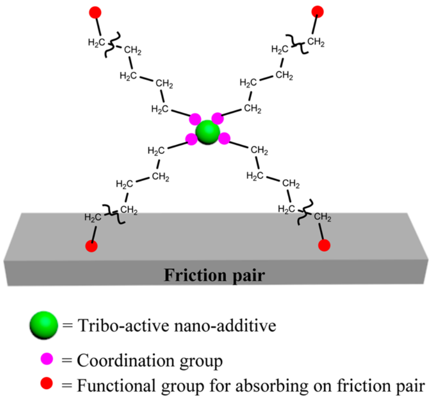
Scheme 2. Strategy for Designing Nanoadditive Suitable for Synthetic Ester Oil



DIOS with 2.0% of surface-capped WS_2 provides Stribeck curves that always stay below those of DIOS base oil. This implies that, under the tested high temperatures, the surface-capped WS_2 additive can improve the friction-reducing ability of the DIOS base oil in various lubrication regions.

The SEM morphologies of the wear scar of steel balls lubricated by DIOS oil and DIOS oil containing 2.0% of OM/MADE-capped WS_2 nanoparticles at various temperatures are shown in Figure 7 (four-ball machine; conditions the same as those in Figure 1 except for temperature). The worn steel surfaces lubricated by DIOS containing 2.0% of the lubricant additive are smoother and show fewer signs of scratching as compared with those lubricated by the base oil alone (Figure 7b,d), which is consistent with the good antiwear ability of OM/MADE-capped WS_2 in a broad temperature range.

The planar and 3D images of the worn surfaces of steel are shown in Figure 8. The wear scar of the sliding steel pair under the lubrication of DIOS with 2.0% of OM/MADE-capped WS_2 is always smaller than that under the lubrication of DIOS alone in the whole temperature range. This is consistent with the good ability of OM/MADE-capped WS_2 in improving the tribological properties of DIOS base stock from ambient condition to 150 °C.

The XPS analysis of the worn surfaces of the upper steel ball lubricated by DIOS with 2.0% of OM/MADE-capped WS_2 was conducted in order to obtain further information about the tribochemical reactions. As seen in Figure 9 (four-ball tester; load 392 N, speed 1200 rev/min, time 60 min, temperature 150 °C), the tribofilm shows a weak XPS signal of S 2p, and it also covers W $4f_{7/2}$ and W $4f_{5/2}$ signals (corresponding to WO_3) as well as Fe 2p signals (assigned to iron oxides). This confirms that, as compared with the DIOS base oil, the OM/MADE-capped WS_2 nanoparticles could be preferentially adsorbed on sliding steel surfaces, thanks to the polar groups of the modifiers, thereby forming a surface protective and lubricious layer via tribochemical reactions and reducing the friction and wear of the steel—steel sliding pair.[20] WS_2 nanoparticles with multilayered structure and weak van der Waals forces can easily slip under a small shear force. This is why OM/MADE-capped WS_2 nanoparticles as the additive can well improve the tribological properties of DIOS even after WS_2 was partially oxidized into WO_3 during the sliding process. The surface-capped WS_2 nanoparticles exhibit better lubricating properties than WO_3. Even so, WO_3 is also employed as a lubricant material.[27−29] Therefore, OM/MADE-capped WS_2 nanoparticles, in association with WO_3 and other metallic oxides generated through tribochemical reactions, contribute to decreasing the friction and wear of the steel sliding pair.[9]

Figure 10 schematically shows the lubricating model of OM/MADE-capped WS_2 nanoparticles as the additive of DIOS base oil. The OM/MADE-capped WS_2 nanoparticles have micellar structure and contain many carboxyl groups on the surfaces, which makes it feasible for them to be adsorbed readily on sliding steel surface as compared with base oil.[16] That is, lamellar WS_2 nanoparticles can be deposited on the sliding surface of steel, thereby forming a surface protective and lubricious layer to improve the lubricating behavior of the base stock.[30,31] In the meantime, OM/MADE-capped WS_2 can take part in tribochemical reactions during the friction process and form a tribochemical reaction film consisting of WO_3 and iron oxides. The surface protective and lubricious layer and the tribochemical reaction film jointly contribute to reducing the friction and wear of the steel sliding couple.

3.6. Strategy for Designing Nanoadditives for Synthetic Ester Oil. Viewing that OM-capped WS_2 nanoparticles as the additive nearly have no influence on the lubricating performance of DIOS while OM/MADE-capped WS_2 nanoparticles result in greatly improved friction-reducing and antiwear abilities, we can infer that the surface properties of nanoadditive have a decisive influence on their tribological properties. This further enlightens us to establish a strategy for the design of nanoadditive suitable for synthetic ester oil (Scheme 2). Namely, three aspects, i.e., nanoadditive with triboactivity, surface modifier with coordination group, and surface modifier with polar functional groups, should be considered in terms of the development of high-performance nanoadditives suitable for synthetic ester oil. First, the desired nanoadditive should be tribologically active to participate in tribochemical reactions during the friction process, thereby contributing to reduced friction and wear. Second, the surface modifier should contain a coordination group that helps to bind the modifier on the surface of the nanoadditive as well as an alkyl group to improve the dispersion stability of the nanoadditive in base oil. Third, the surface modifier should contain a functional group at the alkyl terminal in order to promote its adsorption on sliding metallic surface, thereby contributing to reduced friction and wear. With the assistance of the triboactivity as well as the coordination group and functional group of the surface modifiers (OM and MADE), OM/MADE-capped WS_2 nanoparticles are able to form physicochemically adsorbed film and/or tribochemical reaction film on the sliding steel surfaces, thereby effectively improving the tribological properties of synthetic ester base oil.

4. CONCLUSIONS

Surface-capping with OM and MADE contributes to greatly improving the dispersion stability of WS_2 nanoparticles in synthetic ester base oil and increasing their compatibility with the base oil as well. As-prepared OM/MADE-capped WS_2 nanoparticles as the additive of DIOS base oil possess excellent friction-reducing and antiwear abilities from ambient temperature to 150 °C. The reason lies in that OM/MADE-capped WS_2 nanoparticles are liable to be deposited on sliding steel surfaces to form a surface protective and lubricious layer. In the meantime, they are able to take part in tribochemical reactions, thereby forming a tribochemical reaction film consisting of metal oxides (e.g., WO_3 and iron oxides) on rubbed steel surfaces. It is just the joint function between the surface protective and lubricious layer and the tribochemical reaction

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film that is responsible for reduced friction and wear of the steel−steel sliding contact.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b04074.

Table listing Hertzian pressure of the sliding steel pair in relation to applied load; figures showing DSC curve of DIOS, structural formulas of PAO6 and DIOS, FTIR spectra of maleic anhydride, of maleic anhydride dodecyl ester, and OM/MADE-capped WS_2 nanoparticles, ^{1}H NMR spectrum of maleic anhydride dodecyl ester, electron diffraction pattern of OM/MADE-capped WS_2 nanoparticles, dispersion stabilities of the base oil containing OM/MADE-capped WS_2 nanoparticles under different centrifugal rotational speeds and centrifugation times, photographs of dispersion of as-prepared OM/MADE-capped WS_2 nanoparticles in DIOS base stock and the same dispersion after 6 months, and TGA and DTG curves of OM/MADE-capped WS_2 nanoparticles (PDF)

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Notes

The authors declare no competing financial interest.

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