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Tribological Properties of Polydopamine-Modified Ag as Lubricant Oil Additives

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Abstract: Nanoparticles agglomerate easily because of their high surface energy, which seriously reduces their tribological properties as lubricant additives. In this work, the core-shell nanoparticles Ag@polydopamine (PDA) were successfully prepared by the self-oxidation of dopamine hydrochloride on the surface of Ag nanoparticles and the dispersion of Ag nanoparticles in PAO6 was improved to promote anti-wear behaviors. The tribological properties of Ag@PDA nanocomposites as additives in poly alpha olefin (PAO) oil were studied under different concentrations, pressure and speed conditions by UMT-5 tribometer. It was demonstrated that the strong electrostatic repulsion of the PDA structure made the Ag nanoparticles better dispersed in PAO oil, thus playing a better lubricating role. When the concentration of the modified nanoparticles was 0.25 wt%, the friction coefficient of the lubricating oil decreased by 18.67% and no obvious wear was observed on the friction pair surface. When the Ag@PDA content was higher than 0.25 wt%, the tribological performance of the lubricating oil was weakened, which may be due to excessive Ag@PDA acting as an abrasive on the friction surface, thereby increasing friction and wear. The friction coefficient of the lubricating oil containing Ag@PDA decreased with the increase in load, but hardly changed with the increase in frequency.

Keywords: Ag; polydopamine; core-shell; additives; dispersion

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1. Introduction

Mechanical friction and wear problems are usually improved by the use of lubricating oil [1], which forms a thin film between the opposite sides to withstand the load and avoid direct solid contact [2]. However, under extreme working conditions, the base oil may have problems such as poor temperature resistance, low viscosity retention rate and a limited effect on reducing the friction coefficient. Recently, nanoparticles have received research attention [3]. The addition of nanoparticle additives to lubricating oil plays an important role in improving lubrication performance and reducing friction and wear [4,5]. This is mainly determined by the mechanism of the nanoparticle additives [6–8]: (1) nanoparticles use their spherical characteristics to convert sliding friction into rolling friction between contact surfaces in the process of friction; (2) they lubricate the contact surface by filling in the surface valleys while polishing the contact surface; (3) they form a protective film between the friction pairs to compensate the mass loss (mending effect) and prevent direct mechanical contact. Ali et al. [9] prepared a hybrid nano-lubricant according to the formula of 0.05 wt% Al_2O_3 + 0.05 wt% TiO_2 + 1.9 wt% oleic acid and 98 wt% engine oil (5W-30). Compared with commercial lubricant, the friction power loss and wear rate of the simulated piston ring assembly were 40–51% and 17%, respectively. Ádám et al. [10] used an oil mixture with 0.4 wt% yttrium-stabilized zirconia (YSZ) nanoparticles to reduce the ball disk wear diameter by 30% and the wear volume by 90% at the same coefficient of friction.

Battez et al. [11], by dispersing CuO, ZnO, ZrO_2 nanoparticles into PAO6, found that all nanoparticle suspensions exhibited reductions in friction and wear compared to the base oil.

Although nanoparticles are friendly to environment [12] and display certain tribological advantages as additives to lubricants [13], there are still some concerns to be resolved. Metal nanoparticles containing metal elements, resulting in high density and poor dispersion in base oil, eventually lead to serious agglomeration and increase friction, which limit their application. At present, researchers mainly rely on two strategies to prevent the agglomeration of metal nanoparticles: one is to add the blend of dispersant and nanoparticles to the base oil, and the other is to modify the surface of metal nanoparticles with organic chemicals [14]. If the first strategy is adopted, in most cases, multiple dispersants need to be used simultaneously, so determining the appropriate dispersant formula is the difficulty for the implementation of this method [15]. Relatively speaking, it would be easier to find a suitable organic substance to absorb on the surface of metal nanoparticles to form an organic layer which can sterically stabilize the metal nanoparticles.

It is reliably proven that introducing polar groups, such as a carboxyl group, to the surface of metal nanoparticles can effectively improve the dispersion of metal nanoparticles and retard agglomeration [16,17]. Huang et al. [18] prepared pure calcium borate nanoparticles (PCBN) modified with lauric acid (CBLA) containing -COOH, which have good dispersion in organic solvents. Dopamine, a derivative of 3,4-dihydroxyphenylalanine (DOPA) in mussel adhesion protein, can spontaneously oxidize and polymerize in alkaline solution at room temperature to form poly(dopamine) (PDA). PDA has strong adhesion, providing good adsorption on the surface of arbitrary materials, including the low energy surface. Specifically, the formed PDA adsorption layer has abundant functional groups on the surface, such as catechol, amine and imine, especially the polar hydroxyl group [19–21], which can be coated on the surface of metal nanoparticles to improve its dispersion. Chen et al. [22] successfully synthesized the Cu-doped PDA nanocomposites (PDA@Cu) by a one-pot synthesis method. The oil with PDA@Cu stored at room temperature for one week still had great dispersibility; the coefficient of friction and the wear depth were reduced by 45 and 97%, respectively. Dong et al. [23] wrapped TiO_2 nanoparticles on the PDA layer, and then dispersed the obtained TiO_2/PDA directly in Gr, which showed high dispersion. All in all, using PDA to prevent the agglomeration of metal nanoparticles is an effective means with simple operation and easy realization.

Ag provides good embeddability, stable thermochemistry properties and low shear strength, and has received great attention in lubrication [24–26]. In this work, by the self-polymerization of dopamine in alkaline solution, a layer of PDA film was coated on the surface of Ag nanoparticles, and the well-dispersed Ag@PDA core-shell nanoparticles were successfully prepared. A variety of measures (Fourier Transform Infrared Spectrometer, Scanning Electron Microscope, tribology test, etc.) were used to analyze and compare the differences in the Ag nanoparticles before and after modification. The results show that the dispersion stability of Ag nanoparticles coated with polydopamine was significantly improved, resulting in the improvement of tribological properties. As a successful example of the modification of lubricating additives, it improved the use limitation of nanoparticles, by reducing its ease in agglomerating, and could be extended to the modification of other additives.

2. Materials and Methods

The Ag nanoparticles were purchased from Beijing Zhongke Keyou Technology Co., Ltd. (Beijing, China). The Ag nanoparticles were 80–150 nm in size with a spherical crystallographic structure and gray color and 99.9% pure. Dopamine hydrochloride (DA) was supplied by Shanghai Richjoint Chemical Reagent Co., Ltd. (Shanghai, China) and tris (hydroxymethyl) aminomethane buffer (Tris-HCl, 99%) was bought from Damao Chemical Reagent Factory (Tianjin, China). In addition, anhydrous ethanol was obtained from Aladdin Chemical (Shanghai, China) Co., Ltd. The base oil, polyalphaolefin 6 (PAO6) was

obtained from Shandong Yousuo Chemical Technology Co., Ltd. (Heze, China). Borated polyisobutylene succinimide (T154B) was purchased from Jinzhou Xinxing Petroleum Additive Co., Ltd. (Jinzhou, China) and used without further purification.

A schematic diagram of the preparation process is presented in Figure 1. A measure of 1 g of Ag nanoparticles was weighed and dispersed ultrasonically in 25 mL Tris-HCl buffer solution with pH = 8.5. Subsequently, 0.1 g dopamine hydrochloride was added to the previous solution, which was stirred magnetically for 1 h at 70 °C to maintain a homogeneous state. Polydopamine uniformly attached to the surface of Ag to form a dense PDA film. Next, the modified nanoparticles were separated from the solution by centrifugation, and washed repeatedly to absorb excess dopamine with anhydrous ethanol until the filtrate became transparent. Then, the sample was transferred to a vacuum oven and dried for 1 h at 90 °C. Finally, a large number of dry modified nanoparticles were obtained. In addition, we adjusted the thickness of the PDA shell by changing the reaction time and the amount of dopamine hydrochloride, and investigated the influence of nanoparticles with different shell thicknesses on the tribological properties of lubricating oil (Figures S2 and S3).

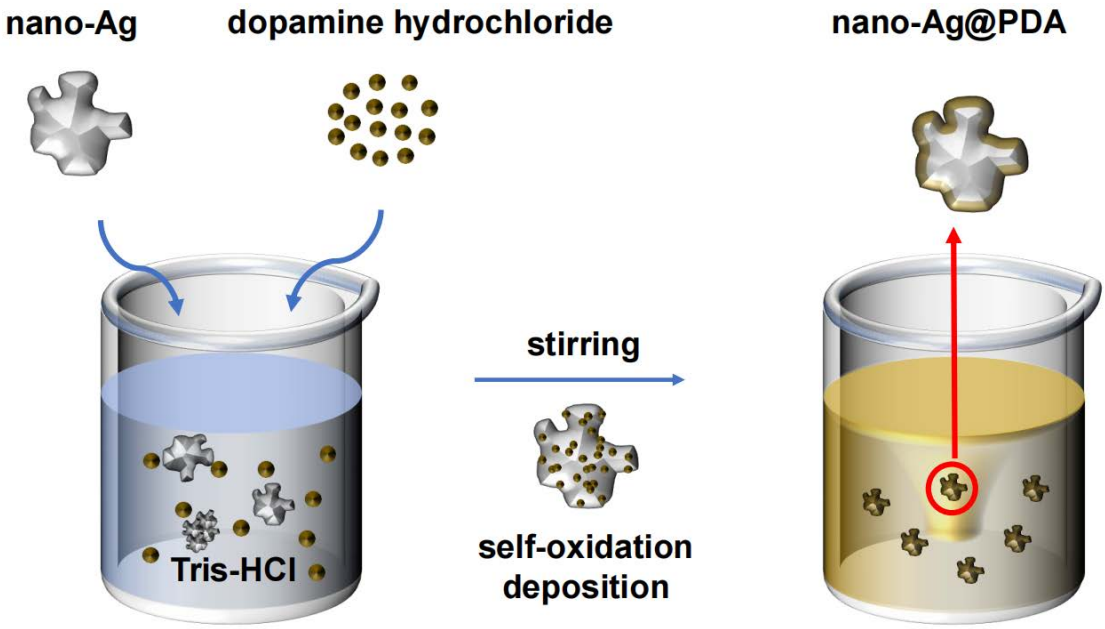

Figure 1. Schematic representation of the synthesis of Ag@PDA.

In order to confirm that the surface of Ag was successfully coated with PDA film, a variety of measurements were used for analysis. The changes in the surface functional groups of nanoparticles before and after modification were investigated by Fourier transform infrared (FTIR, Nicolet NEXUS 670, Thermo Nicolet Corporation, Madison, Wisconsin, USA). Samples were prepared for transmission mode analysis using a KBr window and scanned between 400 and 4000 cm^{-1}. Furthermore, the morphology and microstructure were observed by scanning electron microscopy (SEM, HITACHI SU8220, Hitachi Manufacturing Co., Ltd, Tokyo, Japan and FEI Quanta 200 FEG, FEI Company, Eindhoven, The Netherlands) and transmission electron microscopy (TEM, JEOL JEM-2100PLUS, JEOL Ltd., Tokyo, Japan), respectively. Before testing, 5 mg samples were added to anhydrous ethanol and dispersed by ultrasound for 2 h.

To determine the effect of the polydopamine layer on Ag@PDA, a Zeta potentiometer (Malvern, Spectris China, Shanghai, China) was used to measure the nanoparticle size distribution and Zeta potential of samples. Prior to the testing, the oil sample with the dispersed Ag/Ag@PDA was sonicated for 2 h to obtain the nanofluid lubricant. The friction and wear experiments were carried out at room temperature and ambient humidity, using a ball-on-plate tribometer (UMT-Tribolab, Bruker, Billerica, MA, USA). The tests were

performed under conditions of 15 N load and 5 Hz frequency at least 3 times to obtain averages. The stable coefficients of friction for the samples were obtained on the basis of the data in the time range of 1700–1800 s friction time. The ball with a diameter 5.99 mm consisted of 304 stainless steel and the disc with a sliding contact radius of 5 mm was composed of epoxy resin and isophorone diamine in a mass ratio of 5/1.2. The surface roughness (Ra) of the epoxy resin disc was around 80 nm. In addition, a disc with a sliding contact radius of 2 mm composed of stainless steel (AISI 40300, Wuxi Zhongdian Construction Special Steel Materials Co., Ltd, Wuxi, China) was also used whose Ra was around 5 nm. After tribo-tests, the friction pairs comprising the ball and the disc were ultrasonically cleaned in ethanol and dried in air. The friction coefficient was recorded automatically by a strain sensor, the wear scar diameter of the ball and the wear scar width of the disc were measured by SEM (FEI Quanta 200 FEG, FEI Company, Eindhoven, Netherlands) and optical microscope (VHX-6000, KEYENCE Co., Ltd, Osaka, Japan). Then, the wear scar profile and the wear scar depth were measured by the 3D surface topography (ZYGO NexView, AMETEK, San Diego, CA, USA). Eventually, after the friction and wear experiments, the chemical composition of the worn surfaces of the steel ball was identified via X-ray photoelectron spectroscopy characterization (XPS, Thermo Scientific K-Alpha, Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussion

3.1. Synthesis of Ag@PDA

The FTIR spectra of PDA and the nanoparticles after modification are illustrated in Figure 2. The diffraction peaks of the nanoparticles after modification appeared near 1260 and 1510 cm^{-1} and were attributed to the C–N or phenolic C–O group's stretching vibration and the N-H bending vibration of PDA. The absorption peak at 1630 cm^{-1} was correlated to the stretching vibration of C=N [20,23]. In addition, the absorption peak appeared at 3450 cm^{-1}; it mainly corresponded to the stretching vibrations of -OH and $-NH_2$ of PDA [27,28]. The appearance of the characteristic peaks of these functional groups belonging to PDA indicated that PDA was introduced onto the surface of Ag.

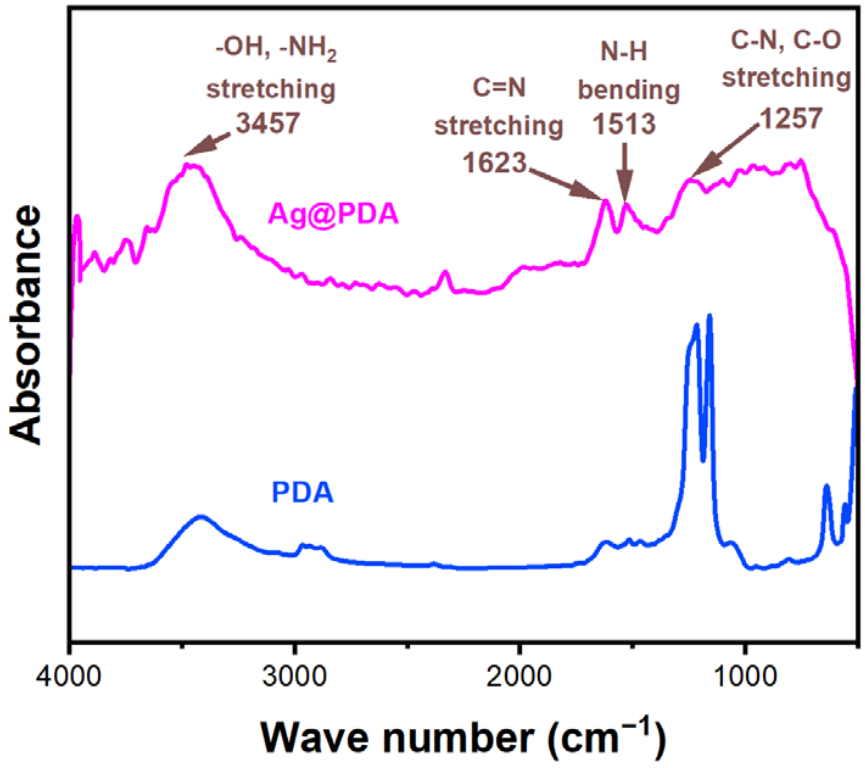

Figure 2. FTIR spectrum of Ag@PDA.

In order to further confirm that the Ag nanoparticles were coated with PDA, the surface morphology, composition and structure of the two kinds of nanoparticles were analyzed. As shown in Figure 3, a large number of Ag nanoparticles were agglomerated, and only the Ag element was detected by EDS. After modification, the agglomeration phenomenon of the modified Ag nanoparticles was obviously reduced. In addition, elemental analysis exhibited that nitrogen existed on the surface of the modified nanoparticles, indicating the existence of PDA. As shown in Figure 4, the unmodified Ag nanoparticles were seriously agglomerated, and the cluster size was much larger than that of the modified nanoparticles. For the modified nanoparticles, an obvious core-shell structure was observed, and the thickness of the shell was approximately equal to 10 nm (as shown in Figure S1). The above results further proved that the Ag@PDA core-shell nanoparticles were successfully synthesized.

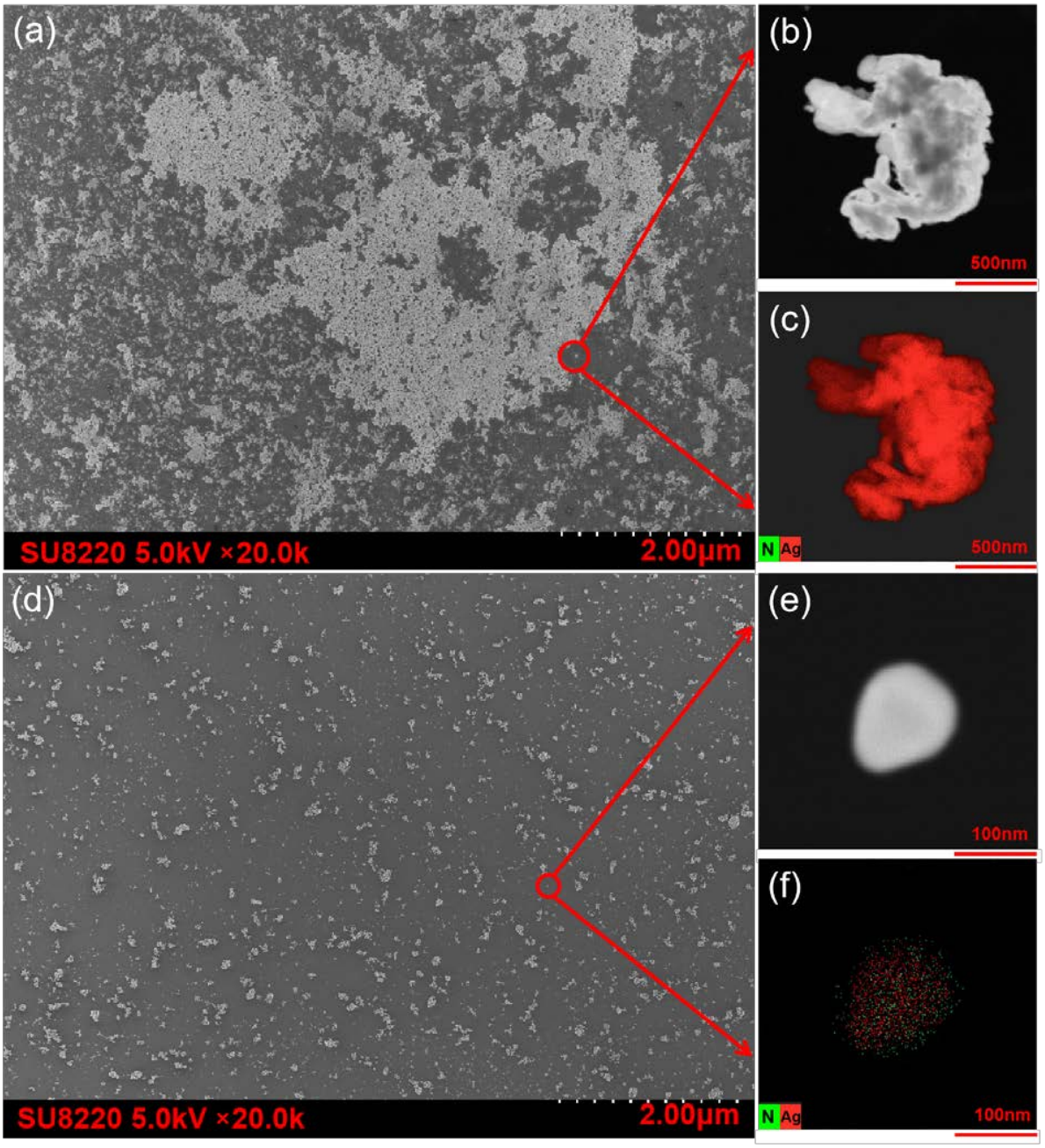

Figure 3. (**a**) SEM micrograph of unmodified Ag; (**b**,**c**) TEM-EDS maps of unmodified Ag; (**d**) SEM micrograph of modified Ag; (**e**,**f**) TEM-EDS maps of modified Ag.

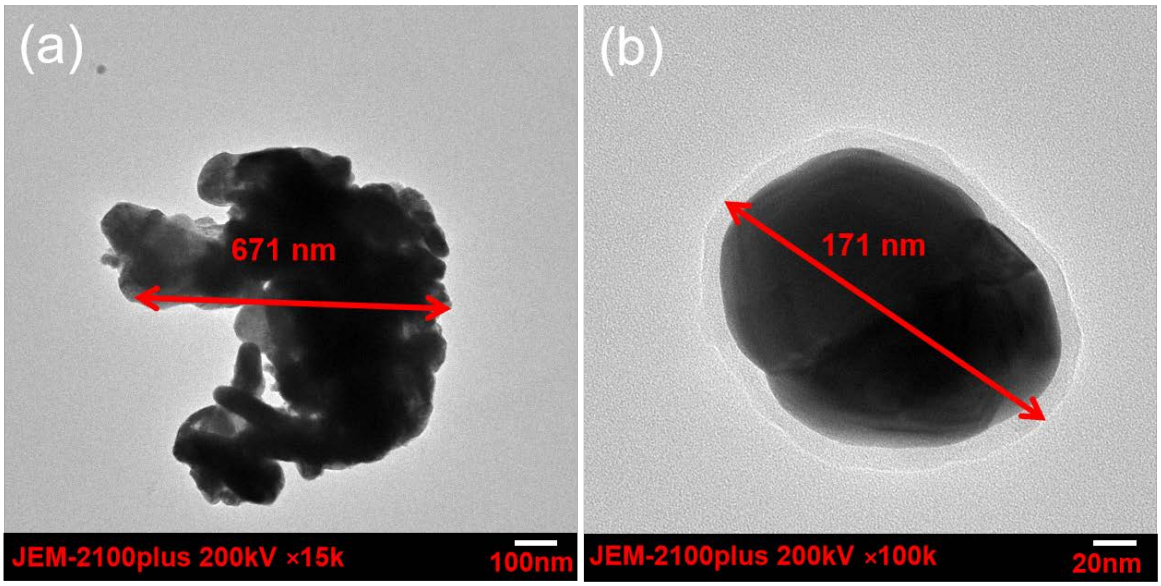

Figure 4. TEM micrographs of Ag (**a**) unmodified; (**b**) modified.

3.2. Dispersibility

In order to observe the dispersion of nanoparticles in the PAO more intuitively before and after modification, the still-standing observation method was employed to investigate the suspension stability of the Ag and Ag@PDA additives in the PAO base oil under ultrasonic treatment with the assistance of T154B (50 wt% of nanoparticles) at room temperature (as shown in Figure 5). No obvious difference was observed between the two dispersions just prepared. However, it can be clearly observed that the unmodified Ag had begun to form sediment at 3 days, and basically completely settled after standing for 14 days, which was credited to the strong Van der Waals interaction between nanoparticles. By comparison, the Ag@PDA suspension just began to precipitate after 14 days (only a small amount of sediment was observed at the bottom of the bottle; no precipitates of agglomerates were observed at the bottom or on the wall of the bottle), and the suspension became stable after 20 days, suggesting that the surface modification enhanced the suspension capacity of nano-additives in PAO. The surface of the modified nanocomposites has a large number of negatively charged catechol groups and amine groups which improve the dispersion of nanoparticles using electrostatic interaction [29].

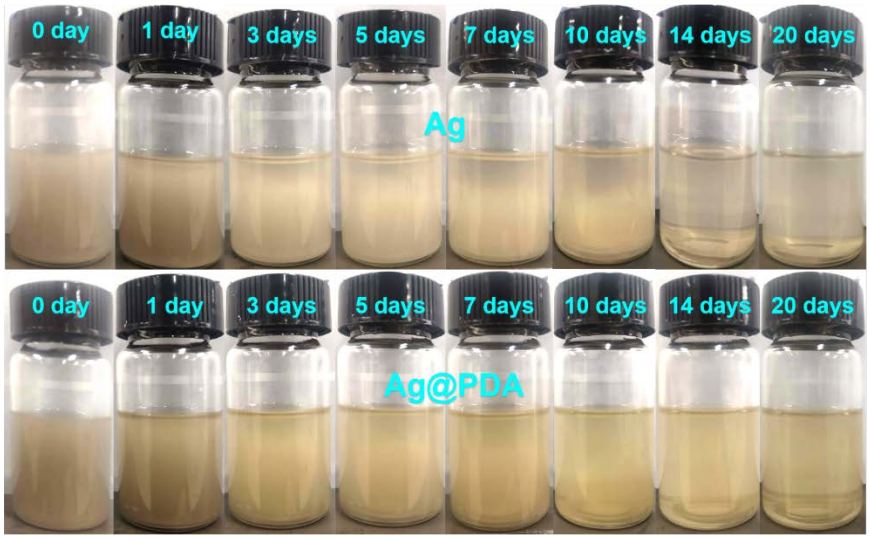

Figure 5. Dispersion state of nanoparticles in oil phase when standing for different times.

The Zeta potential test can be used to evaluate the dispersion stability of nano-additives in the base liquid. The nanoparticle Zeta potential distribution of Ag before modification and that of Ag modified with dopamine hydrochloride are shown in Figure 6a. The peak for pure Ag was located at −26.8 mV, while for modified Ag, it was located at −32.6 mV. For the samples under the same conditions, the larger the Zeta potential (absolute value), the better the stability of the nano suspension system [30]. The change of the potential indicated that the electronegativity of the nanoparticles became stronger and the nanoparticles had stronger stability in the oil phase. Figure 6b demonstrates the particle size distribution of the samples unmodified/modified. The comparison shows that after modification, the average particle size (Z-average) reduced from 628 nm to 164 nm which was in accordance with the data from the TEM, and the nanoparticles' polydispersity indexes (PDI) were 0.612 and 0.185, respectively. A PDI close to 0 indicates that the sample is monodisperse [31], which indicates that the size distribution of Ag@PDA is relatively concentrated. These results demonstrate convincingly that polydopamine is effective in improving the dispersion of Ag nanoparticles.

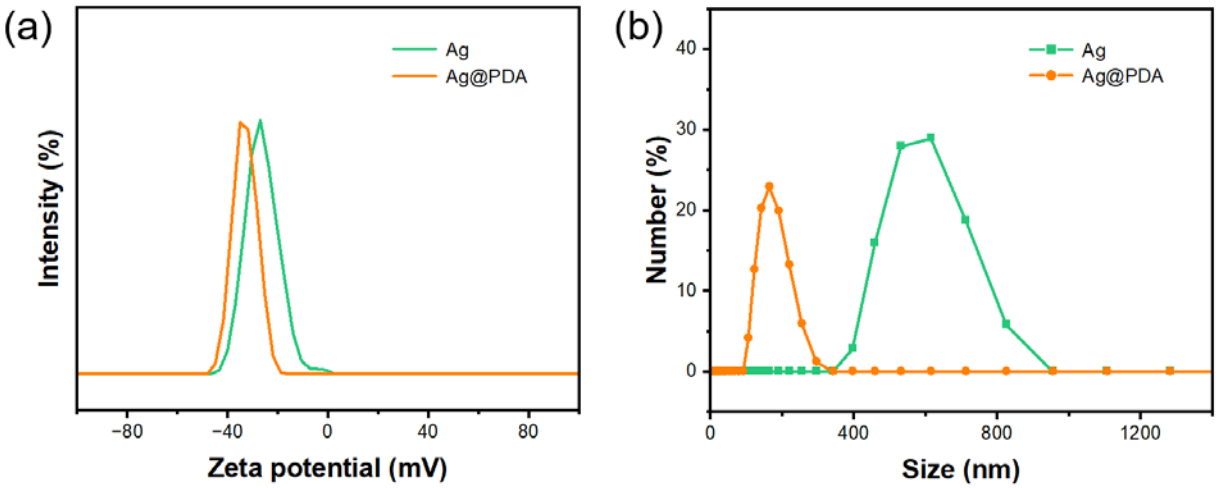

Figure 6. (**a**) Zeta potential of samples unmodified/modified; (**b**) particle size distribution of samples unmodified/modified.

3.3. Tribology Performances

3.3.1. Different Kinds of Additives

Figure 7 shows the coefficients of friction (COF) of different samples. In the whole test process, the friction coefficient of PAO6 changed little, and at the end of the test, the friction coefficient was about 0.075. For the sample added with unmodified Ag, the friction coefficient rapidly increased to 0.11 after about 200 s, then suddenly decreased after a period of stability (about 800 s), and finally stabilized at about 0.080. After adding unmodified nanoparticles, the lubrication performance was not improved, which may be related to the adsorption and agglomeration between nanoparticles caused by their high surface energy [32] and these clusters became abrasive particles between friction pairs, thus increasing friction. For the samples with modified Ag nanoparticles added, the friction coefficient decreased by 18.67% compared with PAO, and was relatively stable in the whole test process. During friction, Ag@PDA, with a smaller particle size, entered the friction contact area with the base oil, and then entered the pits on the friction pair surface to make the friction surface flat, thus resulting in the reduction of the friction coefficient. On the other hand, Ag is soft and has oxidation resistance [33], easily forming a softer and more compliant layer during friction, and reducing shear force to reduce friction [34].

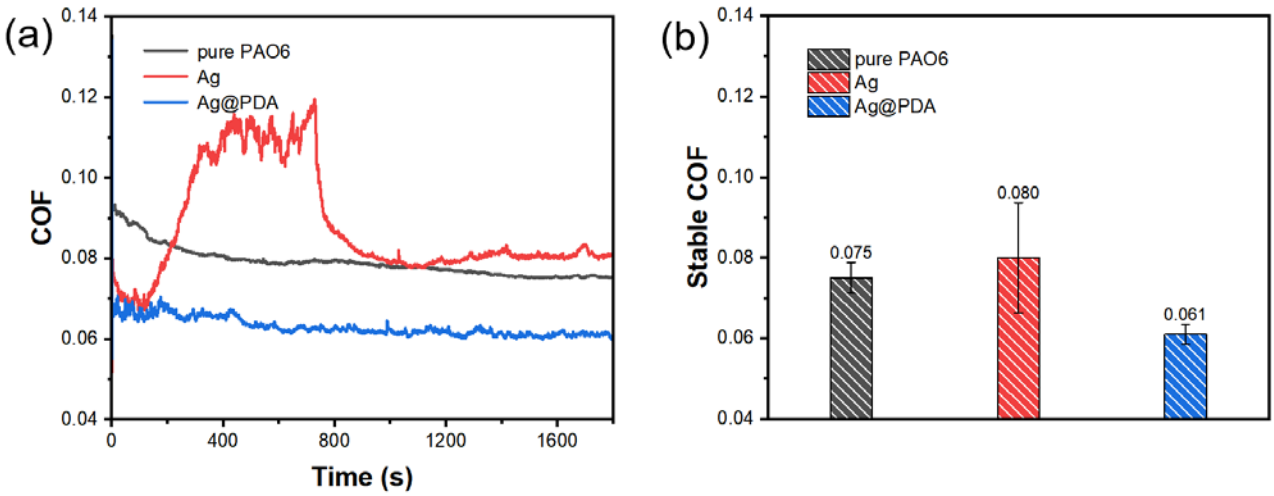

Figure 7. (**a**) Coefficients of friction for samples with different additives under test conditions and (**b**) stable coefficients of friction for samples with different additives under test conditions.

Figure 8 shows the optical images of the wear scar of the steel balls and resin matrix after the tribological test. The wear interfaces of the three groups were significantly different. For PAO6, the diameter of the wear scars on the steel ball surface and the width of the wear scar on the resin were about 500, 412 μm, respectively, and obvious grooves due to sliding were observed. After adding unmodified Ag nanoparticles, the diameter of wear scar on the surface of steel ball was about 510 μm, and the width of the wear scar was 451 μm. Both the area and width of the wear scar were larger than those of the PAO6 group; at the same time, a rough surface and severe wear were observed on the friction area of the resin matrix. This states clearly that the wear of the friction surface was worse when the unmodified Ag was added. As for the oil with 0.25 wt% Ag@PDA, no obvious wear was observed on the steel ball and resin matrix surface, and the wear contact surface maintained excellent surface morphology, which was quite different from the friction surface state of the other two groups. These results may be due to the possibility that the PDA surface modification could reduce the formation of Ag clusters, and small Ag nanoparticles could enter and repair the wear area of the friction pairs [35].

3.3.2. Different Concentrations of Ag@PDA

It should be noted from Figure 9 that the friction coefficient decreased at first and then increased with the increase in additive concentration. When the addition amount was less than 0.50 wt%, the friction coefficient changed slightly, but the stable friction coefficient decreased continuously, reaching the minimum when the addition amount was 0.25 wt%. When the addition amount was greater than 0.50 wt%, the friction coefficient fluctuated violently, and the stable friction coefficient increased continuously. It should be mentioned that adding a handful of nano-additives can effectively improve the friction performance of base oil; however, excess nanoparticles might accumulate at the interface of the contact pairs, probably blocking the oil film, thus increasing wear [36]. Examples in the literature show that the concentration of nanoadditives significantly affects the tribological properties of liquid lubrication. Zeng et al. [37] reported that adding 1.0 wt% boron nitride nanoparticles in PAO6 oil led to the super-lubricity state under the Si_3N_4/DLC contact. Zhang et al. [38] found that oleic acid-modified graphene with concentrations of 0.02–0.06 wt% in oil showed superior wear and friction performances.

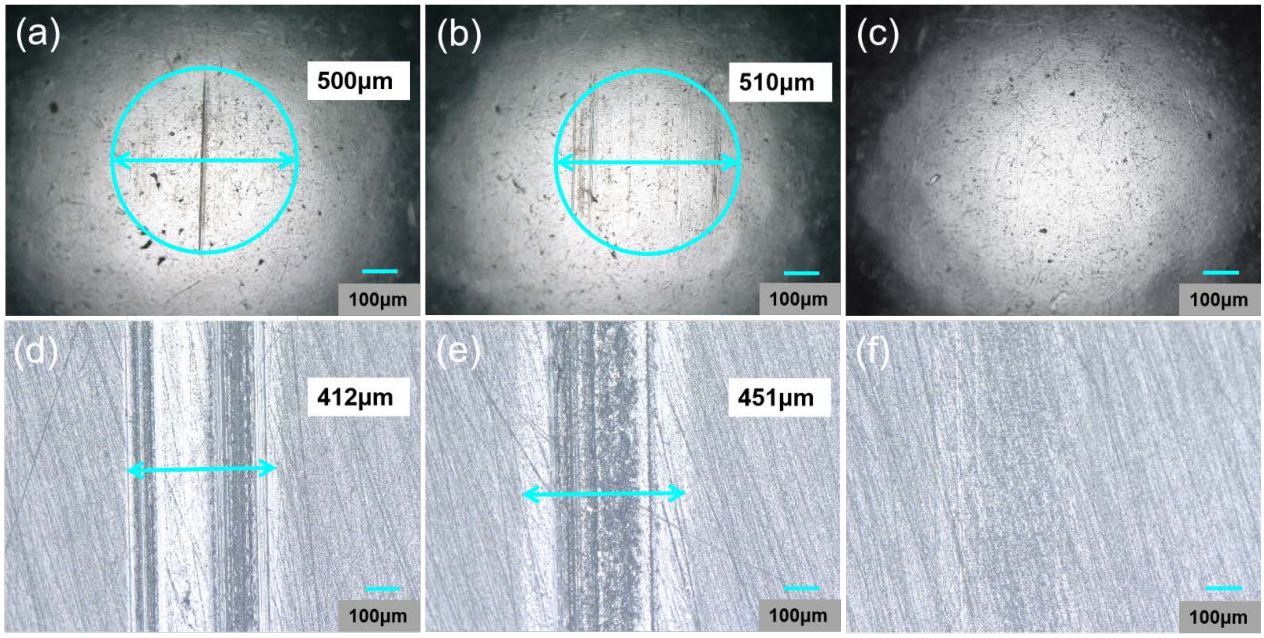

Figure 8. Optical images of wear scar diameter of steel balls (**a**) pure PAO6; (**b**) oil with 0.25 wt% Ag; (**c**) oil with 0.25 wt% Ag@PDA and wear scar width of resin matrix (**d**) pure PAO6; (**e**) oil with 0.25 wt% Ag; (**f**) oil with 0.25 wt% Ag@PDA.

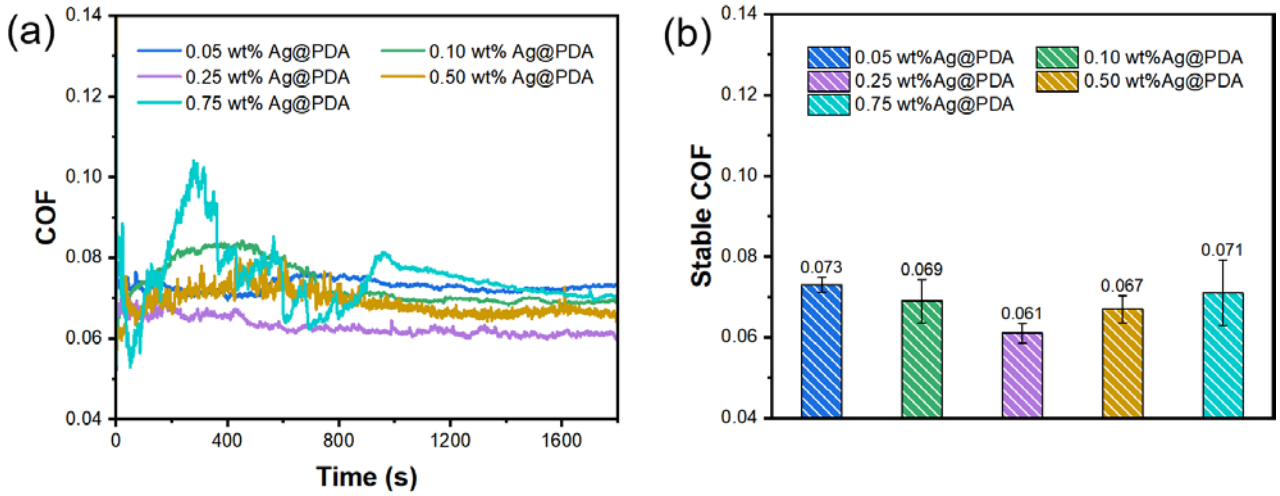

Figure 9. (**a**) Coefficients of friction for samples with different concentrations of Ag@PDA additives under test conditions and (**b**) stable coefficients of friction for samples with different concentrations of Ag@PDA additives under test conditions.

3.3.3. Different Applied Loads

Figure 10 shows the COFs versus applied loads for PAO6 with 0.25 wt% Ag and 0.25 wt% Ag@PDA. Compared with the two groups of samples containing unmodified Ag and modified Ag additives, the unmodified Ag additive fluctuated and lacked stability, which was related to the agglomeration of nanoparticles. In the meantime, with the increase in applied loads, the stable friction coefficient of the base oil added with Ag decreased first and then increased. However, the stable friction coefficient of the base oil added with Ag@PDA displayed a downward trend. When the load was 15 N, the friction coefficient reduced by 23.75% comparing with unmodified Ag. This indicated that Ag@PDA had better load-bearing capacity than unmodified Ag.

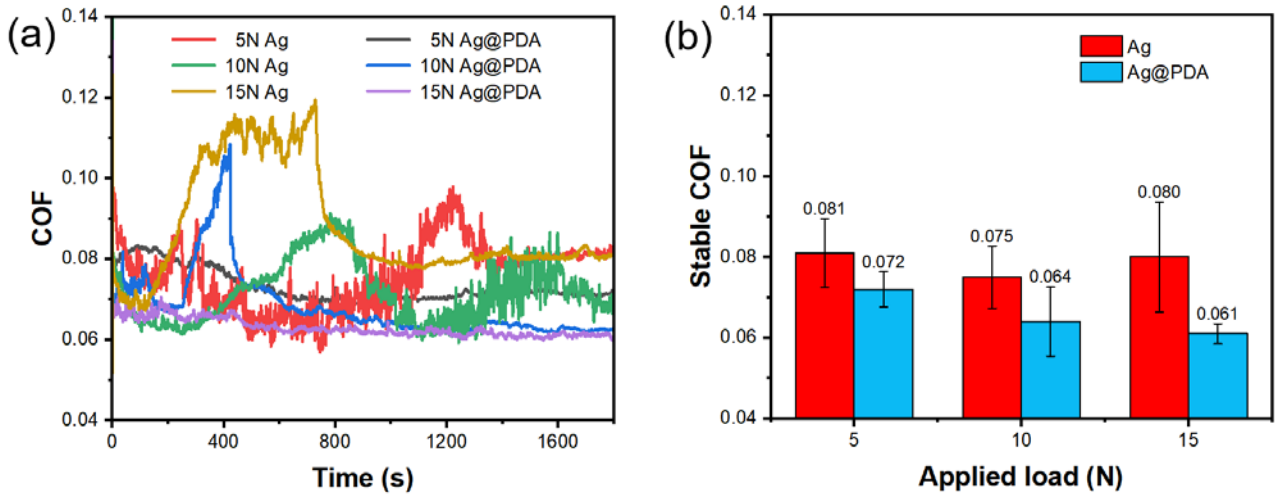

Figure 10. (**a**) Coefficients of friction for samples with different applied loads under test conditions and (**b**) stable coefficients of friction for samples with different applied loads under test conditions.

3.3.4. Different Frequencies

Figure 11 shows that with the sliding friction, the stable friction coefficient of unmodified nanoparticles increased continuously, and the stability was terrible. As a comparison, the friction coefficient of the modified Ag nanoparticles changed little with the frequency, and reached the minimum value (0.61) when the frequency was 5 Hz. In general, the modified Ag nanoparticles showed better tribological properties as lubricating oil additives, and the stable friction coefficient of Ag@PDA was lower than that of unmodified Ag nanoparticles at every test frequency, which was related to the better dispersion of Ag@PDA than Ag.

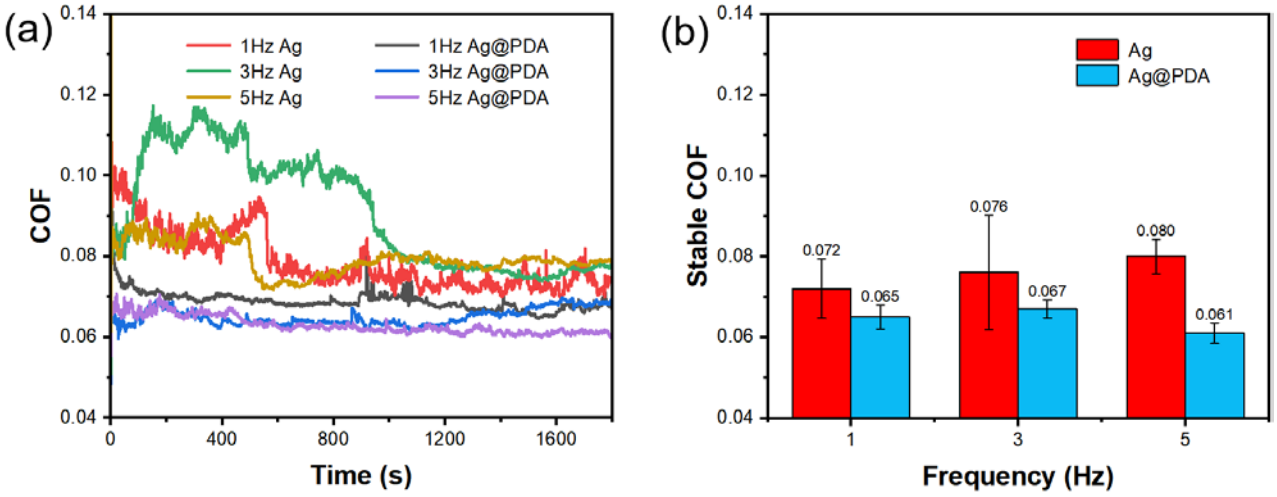

Figure 11. (**a**) Coefficients of friction for samples with different frequencies under test conditions and (**b**) stable coefficients of friction for samples with different frequencies under test conditions.

3.3.5. Different Friction Pairs

Figure 12 shows the coefficients of friction for different samples when 304 steel was used as the friction matrix. Compared with the data in Figure 7, the stable friction coefficient of all samples rubbed on the steel matrix was higher than that of the epoxy resin matrix, but the overall change was small and the stability was better. The stable friction coefficient only reduced from 0.114 to 0.101 after adding modified Ag nanoparticles, which reduced it by 11.40%. It was shown that when epoxy resin was used as matrix, the oil with modified Ag nanoparticles had better tribological properties, which may be due to the reason that

compared with polymers, it is difficult to form transfer films on hard metals and usually they cannot exhibit self-lubricating properties.

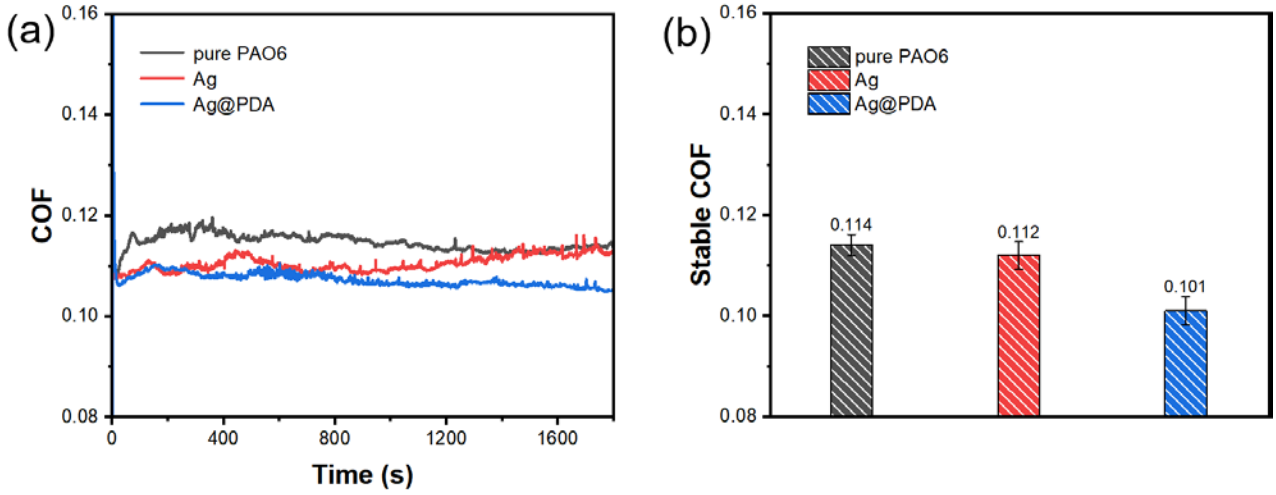

Figure 12. (**a**) Coefficients of friction for samples with 304 steel matrix and (**b**) stable coefficients of friction for samples with 304 steel matrix.

Figure 13 presents the SEM micrographs of steel balls and 3D morphologies of different worn surfaces of 304 steel matrix. It can be clearly seen that the wear scar diameter of the sample with PAO oil was the largest (192 μm), and those of the samples with Ag and Ag@PDA decreased by 5.73 and 19.27% (as shown in Table 1), respectively. For PAO6 oil, the width and depth of the wear scars on the steel substrate surface were larger, and the wear condition was slightly improved after adding Ag nanoparticles. When PAO containing modified nano-additives was added to the friction interface, the friction surface was smoother, the width and depth of the wear scars were the smallest, and, compared with PAO, the friction surface was reduced by 19.65 and 35.90%, respectively. These results show that the modified Ag additives could effectively improve the tribological properties of the lubricating oil.

Table 1. Wear scar widths using 304 steel matrix.

Samples	Wear Scar Width (μm)	Wear Scar Depth (μm)
Pure PAO6	173	0.078
0.25 wt% Ag + PAO6	149	0.058
0.25 wt% Ag@PDA + PAO6	139	0.050

3.3.6. XPS Analysis of Wear Surface

The surface chemistry and chemical states of the steel ball surface after friction with the different matrixes were measured by XPS, as shown in Figure 14. The XPS results show that the wear mark surface using 304 steel matrix only contained C, O and N elements, while the wear mark surface using epoxy resin matrix also contained Ag element. The elemental compositions expressed in atomic percentage (at%) were: C—78.08%, O—18.10%, N—3.61% and Ag—0.21%. Depending on the material structure, the C, O and N elements mainly came from PDA, and Ag element was related to Ag. There were five peaks in the C 1s spectrum, consisting of C-C (284.8 eV), C-O (285.6 eV), C-N (286.5 eV), C=O (287.1 eV) and O-C=O (288.8 eV) [30,39,40]. In the N 1s spectrum, there existed -NH_2 (397.9 eV), -NH- (399.3 eV) and -N= (401.6 eV), which were totally in line with the theoretical values [23,41]. As well, the Ag 3d spectra appeared at 367.6 eV and 373.7 eV, consistent with their respective binding energies [42,43]. This corresponded to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks, respectively, indicating that all Ag species existed in the form of Ag (0) rather than in the Ag^+ with Ag oxide combination state [44,45]. Therefore, it can be concluded that during the friction

process, the modified Ag nanoparticles were transferred onto the steel ball to form a film with low shear stress and good lubricity when the matrix was EP resin. There was no Ag element found on the steel ball surface using the steel matrix, which revealed that it was difficult for Ag nanoparticles to form a transfer film on the dual pairs under the experimental conditions, resulting in the poor tribological properties of the lubricating oil.

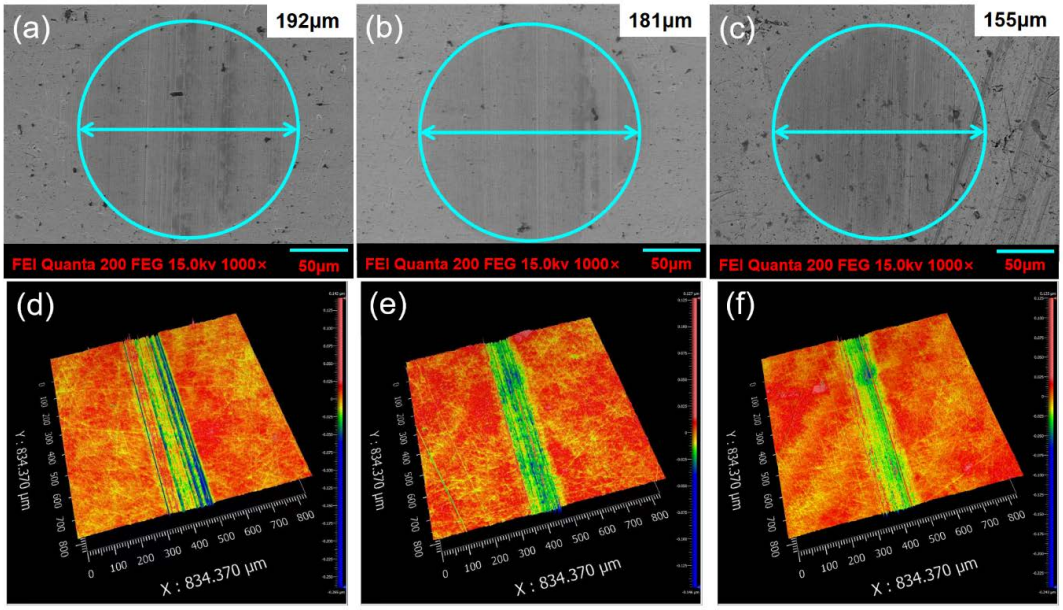

Figure 13. SEM micrographs of steel balls and 3D morphologies of different worn surfaces of 304 steel matrix using: (**a**,**d**) pure PAO6; (**b**,**e**) PAO6 with 0.25 wt% Ag; (**c**,**f**) PAO6 with 0.25 wt% Ag@PDA.

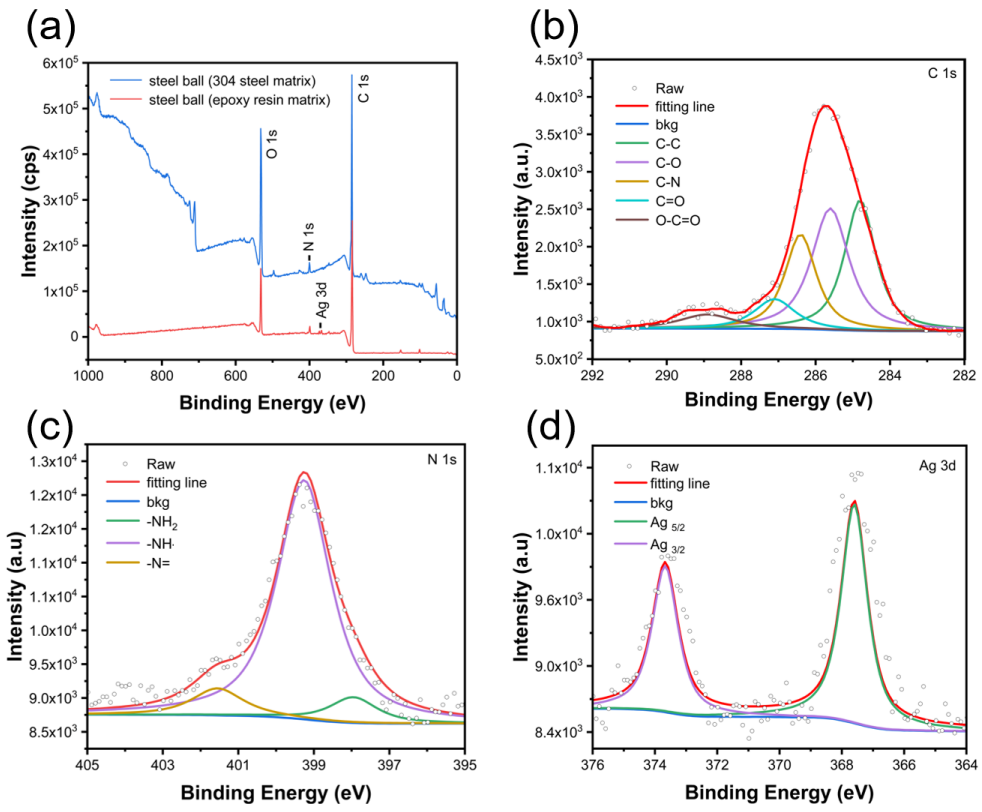

Figure 14. XPS spectra of steel ball surface after friction with (**a**) Ag@PDA 304 steel and Ag@PDA epoxy resin; high-resolution XPS spectra in the core level (**b**) C 1s, (**c**) N 1s and (**d**) Ag 3d regions for Ag@PDA epoxy resin.

4. Conclusions

In this work, Ag@PDA nanocomposites with a core-shell structure were successfully prepared and characterized. The effects of surface modification, additive concentration, test load, test frequency and friction pair type on the tribological behaviors of PAO6 oil with nanoadditives were studied. The modified Ag nanoparticles remained stably dispersed in PAO6 containing T154B for 14 days. Meanwhile, when the concentration of Ag@PDA was 0.25 wt%, the friction coefficient of PAO6 decreased from 0.075 to 0.061 and no obvious wear scar was observed on the friction surface, showing excellent tribological performance. When the additive concentration increased, abundant nanoparticles concentrated on the interface of the friction pair to block the oil film, and made the contact surface rough, resulting in some areas of the friction pair being in direct contact, thus intensifying the wear. The friction coefficient of the lubricating oil with Ag@PDA decreased with the increase in load, but hardly changed with the increase in frequency. The XPS analysis demonstrated that the low friction and wear of the friction interface were diminished by the synergism of Ag and PDA. The method applied in this work is expected to be extended to the modification of other additives for enhancing the dispersibility of nanoparticles.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/lubricants10120343/s1, Figure S1: TEM micrographs of modified Ag; Figure S2: TEM micrographs of modified Ag with different shell thicknesses; Figure S3: coefficients of friction for samples with different shell thicknesses.

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