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Preparation and Tribological Behavior of Nitrogen-Doped Carbon Nanotube/Ag Nanocomposites as Lubricant Additives

Shaokun Jia [1,2], Jiahuan Zhao [1], Guangzhen Hao [1], Jifeng Feng [1], Chuanbo Zhang [1], Zhihui Wang [1], Zhengfeng Jia [1,*] and Yungang Bai [3]

[1] School of Materials Science and Engineering, Liaocheng University, Liaocheng 252059, China; h15864371243@163.com (G.H.)
[2] School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China
[3] Shandong Qichanxintu Composite Material Co., Ltd., Liaocheng 252059, China
* Correspondence: jiazhfeng@lcu.edu.cn

Abstract: In this study, nitrogen-doped carbon nanotube/Ag nanocomposites (denoted as N-C/Ag) have been synthesized in a urea solution using a hydrothermal method. The carbon nanotubes, $AgNO_3$ solution, urea and poly-dopamine (PDA) served as carbon, silver, nitrogen and carbon sources, respectively. The results show that the diameter of the carbon tubes was about 30 nm, and the Ag nanoparticles, with a diameter of ca. 10 nm, dispersed on the carbon tube surface. The Ag particle size decreased with a lower degree of crystallinity at a high temperature in the presence of urea. The friction and wear behavior of the oil acid (OA) modified N-C/Ag (OAN-C/Ag) as an additive in liquid paraffin (LP) were studied using a four-ball friction and wear tester. The results have shown that the coefficients of friction (COFs) and wear scar diameters (WSDs) of steel balls lubricated with LP-OAN-C/Ag decreased by 27.3% and 25.3%, respectively, relative to pure LP. Tribofilms containing Ag, carbon and nitride were formed on the worn steel ball surfaces. Details, the carbon, Fe_2O_3, azides and nitride, Ag and alloy and other compounds on the wear scars may improve tribological properties. The synergistic effect of carbon, Ag and urea plays a critical role during sliding.

Keywords: N-doped carbon nanotube/Ag nanocomposites; polydopamine; hydrothermal; wear; friction

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1. Introduction

In recent years, nanomaterials have been widely studied in many fields [1–4]. Carbon nanomaterials, including fullerenes, carbon nanotubes (CNTs) and graphene, possess excellent mechanical properties, thermal properties and corrosion resistance [5]. In common with graphene, CNTs are characterized by a special sp^2-hybridized structure, which has been the subject of considerable attention in interfacial science and tribology. However, CNTs exhibit shortcomings, notably aggregation and poor dispersion in matrices, which have limited the range of applications. Functionalization and modification of CNTs and associated composites can improve dispersion in base oil [6,7]. Hao et al. [6] synthesized a brushlike polystyrene with a method of reversible addition–fragmentation chain transfer, which was modified on the surfaces of hydroxylated CNTs. The results showed that the dispersity of the CNT-polystyrene in base oil was outstandingly enhanced. The tribological properties of the LP containing CNT–polystyrene were better than those of pure LP, which were attributed to the synergistic effect of CNT and polystyrene and the improved dispersibility in base oil. Jesús ACC et al. [7] investigated the tribological properties of single-walled and muti-walled carbon nanotubes being treated with carboxylic acid and strong acid, respectively, as additives of oil or water. The results showed that coefficients of friction and mass losses of twin-disk pairs lubricated with oil or water containing additives were smaller than those lubricated with pure oil or water, respectively. The carbon

tribofilms were formed on the worn surfaces of disks with lubricants of oil or water containing carbon tubes and played an important role in reducing friction and wear resistance. Diana-Luciana C et al. [1] synthesized single-wall CNTs at a temperature of 850 °C and a pressure of 6 atm. The tribological properties of the CNTs as additives of mineral oil for different pairs were executed. The results show that mineral oil containing CNTs possesses a smaller coefficient of friction than pure base oil and oil with zinc dialkyldithiophosphates, respectively. The synergistic effect of CNTs and zinc dialkyldithiophosphates occurred due to the modification of zinc dialkyldithiophosphates on the surfaces of CNTs.

Furthermore, methods to improve the tribological properties of CNTs and composites containing CNTs have been reported in much of the literature. Chen et al. [8] investigated the tribological properties of a CNTs/ZnS hybrid in epoxy coatings and found that the hybrid can enhance friction reduction and anti-wear capability. Researchers have proposed that the micro-fluid characteristics of CNTs and synergistic effects in composites can endow lubricant coatings with excellent tribological properties. Ramaprabhu [9] synthesized Fe-carbon tube composites at 800 °C in a nitrogen atmosphere with the precursors of ferric chloride hexahydrate and melamine, respectively. The composites were directly added to different base oils (gearbox oil, vegetable oil and engine oil, respectively) to evaluate their tribological properties. The results showed that the engine oil containing the additives possessed better tribological properties than the other two base oils containing Fe-carbon tube composites, which might be attributed to the formation of stable tribofilms during rotation in engine oil containing additives. The Fe-carbon tube composites impeded the formation of iron oxides and residues on the worn surfaces and entered into the furrow to form tribofilms. Saeed Zeinali Heris [3] compared the physical and chemical properties of titanium dioxide nanoparticles (TiO_2) and muli-walled carbon nanotubes (MW-CNT) as additives to oil. To obtain stable lubricants, TiO_2 and MW-CNT were modified with oleic acid and triton 100, respectively. The depths of wear pins under the lubrication of base oil containing TiO_2 and MW-CNT (0.1 wt.%) were about 40 and 30 μm, respectively, which is about one-fourth of the depth of pure base oil.

A number of papers have revealed that the use of elements (such as S, P and N) as doped additives can result in enhanced tribological properties due to the formation of tribo-chemical films and/or strong absorption of the additives on worn surfaces [10,11]. Pyrolysis and hydrothermal reactions are common procedures in doping nitrogen and/or sulphur on carbon [10,12]. Sun et al. [10] investigated the tribological properties of nitrogen hybridized carbon quantum dots and MoS_2 as additives of the lubricant glycerol. Nitrogen hybridized carbon quantum dots were synthesized via the solvothermal method using polydopamine as the carbon and nitrogen source. A chemical reaction between the nitrogen hybridized carbon quantum dots and the metal disks was executed during rotation because of the nitrogen and oxygen on the carbon quantum dots. On the other hand, the atoms of sulfur in MoS_2 reacted with metal surfaces during sliding to protect the worn surfaces from severe wear. Liu et al. [11] synthesized nitrogen/sulfur-doped porous carbon nanospheres at high temperatures using melamine and thiourea as a nitrogen source and sulfur source, respectively. The excellent tribological properties of the 500 SN-containing composites were attributed to the protective tribofilms being formed between the N/S-doped carbon nanosphere and substrates. In detail, the tribofilm containing iron oxides, iron sulfide and carbonitride played an important role in anti-wear and reduced friction.

Soft metals (such as silver and copper) attract much attention because of their excellent embeddability and deposition ability during running to form tribofilms. Song [13] synthesized Cu/PDA/CNTs composites using $NaH_2PO_2 \cdot H_2O$ as a reducing agent at 80 °C. The results showed that the Cu/PDA/CNTs markedly reduced the coefficients of friction and wear track widths, which were attributed to the tribofilms and self-lubricating properties of the composites. However, fabricating CNT composites in an eco-friendly manner remains a challenge. Jia et al. [14] synthesized silver/polydopamine (Ag/PDA) composites in a facile environment using Ag+ and dopamine as the Ag source and reductant, respectively. The results show that the COFs and WSDs of steel balls lubricated with poly-alpha-olefin

(PAO) containing oleic acid-modified Ag/PDA nanocomposites were lower than those lubricated with pure PAO. A tribofilm containing iron oxides, silver oxides and PDA was formed during rotation, which protected the steel balls from violent wear. Our team [15] also synthesized hexagonal boron nitride/copper nanocomposites through the method of ultrasonic exfoliation and in situ reduction. Steel balls lubricated with LP containing the OA-modified BN/Cu nanocomposites possess lower COF and WSD than pure LP. On the one hand, the tribofilm containing BN, oxides of boron, metal and carbon was formed on the worn surfaces to avoid violent wear. On the other hand, increasing the reduction time can enlarge the interplanar spaces and decrease the thickness of BN, which might decrease the van der Waals forces between the layers and provide good friction reductions. Waralorn Limbut et al. [2] synthesized a phosphor-doped carbon nanotube composited with silver nanoparticles using $Na_4P_2O_7$ and $AgNO_3$ as the phosphor source and silver source, respectively. N,N-dimethylformamide and $NaBH_4$ were used as a solvent and a reducing agent, respectively. Synthesizing composites in a facile way is still a challenge.

In this study, carbon nanotube/Ag nanocomposites have been synthesized with dopamine (DA) as a reducing agent at room temperature. The N-doped C/Ag was obtained using a hydrothermal method using urea as the nitrogen source. The OA-modified N-CNT/Ag were dispersed in paraffin in order to investigate their friction and wear properties. A possible wear mechanism has also been studied.

2. Experimental Procedures

2.1. Materials and Preparation

$AgNO_3$, DA hydrochloride, urea, hydroxylated multi-walled carbon nanotubes (HO-MW-CNTs) and other agents were purchased from Aladdin Biochemical Technology Company (Shanghai, China) and used as supplied. LP, with a viscosity of 17.2 mm^2/s (25 °C), was employed as the base oil, and AISI-52100 steel balls (Ø 12.7 mm) were used in testing.

The $AgNO_3$ solution and Tris-buffer solution (pH = 8.5) were prepared following procedures reported previously [14]. A sample (8 g) of urea powder and 0.04 g CNTs were added to a 25 mL Tris-buffer solution and stirred for 30 min. Then, 4 mL $AgNO_3$ solution and 0.4 g DA were added to the above solution and stirred for 24 h at room temperature. The solution was transferred to the hydrothermal reactor at a temperature of 140 °C for 12 h to generate the target product (denoted as N_8-$C_{0.04}/Ag_4$). The composite product was modified with OA (denoted as OAN_8-$C_{0.04}/Ag_4$) as described previously [15]. Tests to investigate tribological behavior were conducted using an MRS-10A four-ball tester (392 N, 1450 rpm, 30 min).

2.2. Characterization

The microstructure of the synthesized N-C/Ag was evaluated using a high-resolution transmission electron microscope (JEM-2100, HRTEM), a field-emission scanning electron microscope (SIGMA 500/VP, FE-SEM) equipped with energy-dispersive X-ray analysis (SEM-EDXA, Kevex Sigma, St. Louis, MO, USA), a Horiba LabRam HR evolution spectrometer (with 532-nm laser) and a Bruker D8 Advanced X-ray Diffractometer. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB Xi+ X-ray photoelectron spectrometer to determine chemical bonding and surface structure. The FT-IR spectra were obtained using a Bruck IFs66v spectrometer.

3. Results and Discussion

3.1. Characterization

The FE-SEM and EDXA analyses of the N-C/Ag have shown that the tubes, with diameters of ca. 50 nm, were covered with a cracked coating (Figure 1a) that must represent the PDA/Ag composite. The EDXA measurements have demonstrated the presence of C, Ag, O and N, confirming the inclusion of silver on the carbon tubes (Figure 1b). The TEM analysis has established that the diameter of the carbon tubes was ca. 30 nm, and the Ag nanoparticles exhibited a diameter of ca. 10 nm dispersed on the carbon tube

surface (Figure 1c). The high-resolution images of the composites illustrate the interlayer spacing (0.63 nm) of the carbon nanotubes and the lattice spacing (0.218 nm) of the (111) Ag plane [16]. Elemental mapping of the composites has revealed the presence of Ag, N and O covering the tubes, confirming that the PDA/Ag composites form the observed rough coating.

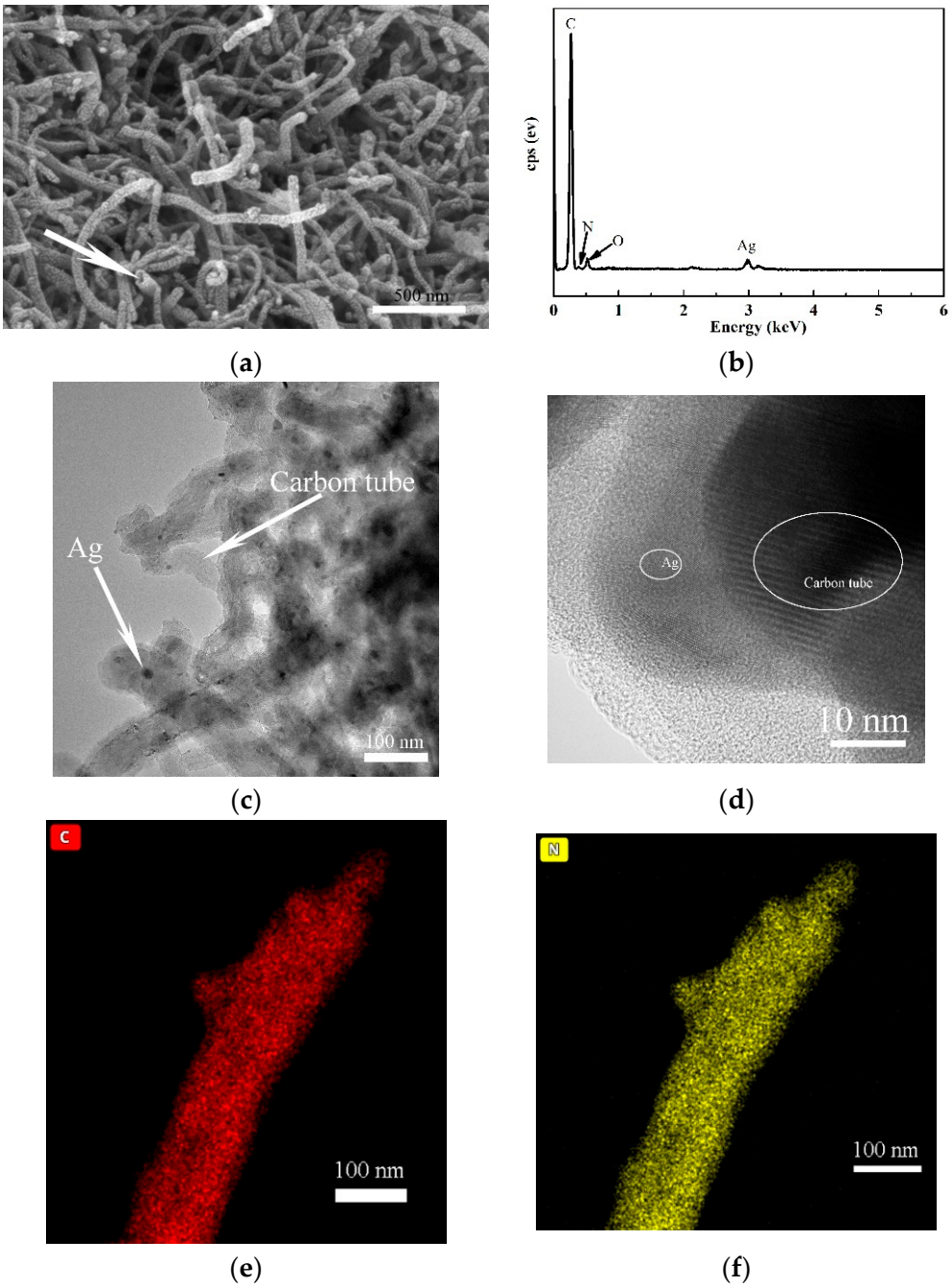
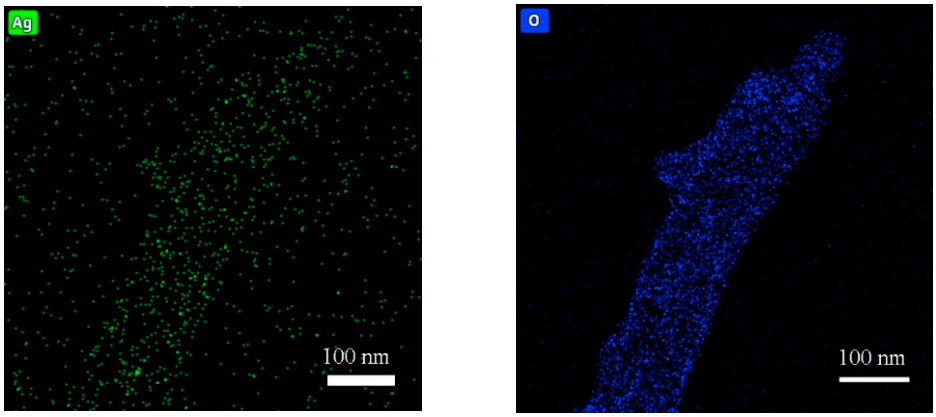


Figure 1. *Cont.*



(**g**) (**h**)

Figure 1. FE-SEM (**a**) and EDXA spectra (**b**), TEM (**c**,**d**) and corresponding elemental mapping (**e**–**h**) of the N-C/Ag.

The FT-IR spectrum of the OA-modified N-C/Ag is presented in Figure 2. The broad peak stretching from 3150 to 3350 cm^{-1} can be attributed to the asymmetry stretching vibration of aromatic −OH and $-NH_2$ due to OA, poly-dopamine and hydroxylated carbon nanotubes [14,17]. The peaks at ca. 2893 cm^{-1} and 2827 cm^{-1} are ascribed to the $-CH_3$ and $-CH_2$ groups, respectively. The peak at ca. 2255 cm^{-1} may be due to the cumulene bond of PDA [14]. The broad peak from 1694 to 1280 cm^{-1} is assigned to C=O and C=C [14,17], and the broad peak from 1167 to 1160 cm^{-1} is attributed to PDA quinoid groups [18].

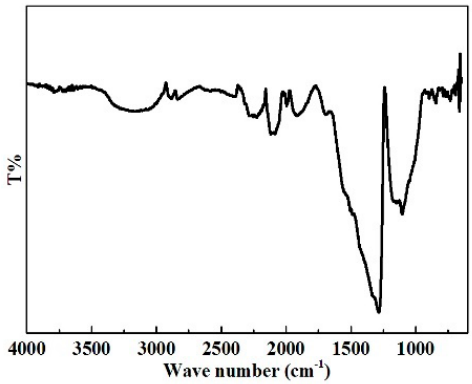


Figure 2. FT-IR spectrum of the N-C/Ag modified with OA.

3.2. Friction and Wear Behaviors

The WSD–concentration and COF–concentration curves for steel balls lubricated with LP-OAN_8-$C_{0.04}$/Ag_4 at different temperatures are presented in Figure 3a,b. The steel balls lubricated with LP-OAN_8-$C_{0.04}$/Ag_4 exhibited lower COFs and WSDs than those recorded using pure LP. Increasing the reaction temperature to 140 °C, the LP-OAN_8-$C_{0.04}$/Ag_4 decreased the COFs and WSDs from 0.195 and 0.745 mm for LP to 0.131 and 0.55 mm, respectively. A further increase to 160 °C resulted in equivalent WSDs to those achieved with the samples synthesized at room temperature (RT). In contrast, the COFs of lubricants containing additives synthesized at 160 °C with concentrations greater than 0.2 wt.% are smaller than those obtained for the room temperature sample. Accordingly, the hydrothermal reaction temperature was fixed at 140 °C for subsequent tests. The effects of varying the amounts of urea on the WSD–concentration and COF–concentration curves are shown in Figure 3c,d. It is clear that the balls lubricated with LP-OAN_8-$C_{0.04}$/Ag_4 exhibited lower WSDs than those recorded for other samples. The COFs of the balls lubricated with LP-OAN-$C_{0.04}$/Ag_4 with different amounts of urea are smaller than those obtained with

pure LP. However, there are no obvious differences in COFs of the balls lubricated using samples with different amounts of urea. The amount of urea used was fixed at 8 g. The WSD–concentration and COF–concentration curves for LP-N_8-C/Ag_4 with different amounts of carbon nanotubes were determined and are shown in Figure 4e,f. At a concentration less than 0.5 wt.%, the WSDs of the balls lubricated with LP-OAN_8-C/Ag_4 containing nanotubes are lower than those without nanotubes. The steel ball WSDs for lubrication using LP-N_8-C/Ag_4s (0.2 wt.%) with 0.04 g and 0.08 g carbon tubes were ca. 0.56 mm, which is lower than those for LP-N_8-C/Ag_4 without carbon tubes (0.61 mm) and pure LP (0.75 mm). In the case of the COF–concentration curves for LP-N_8-C/Ag_4 with different amounts of carbon tubes, the steel ball COFs were much smaller than those measured for the other lubricants. At a concentration of 0.2 wt.%, the average COF associated with lubrication using LP containing N_8-$C_{0.08}$/Ag_4 was 0.125, lower than those of LP containing N_8-C_0/Ag_4 (0.135) and N_8-$C_{0.04}$/Ag_4 (0.155). The amount of carbon nanotubes was then fixed at 0.08 g.

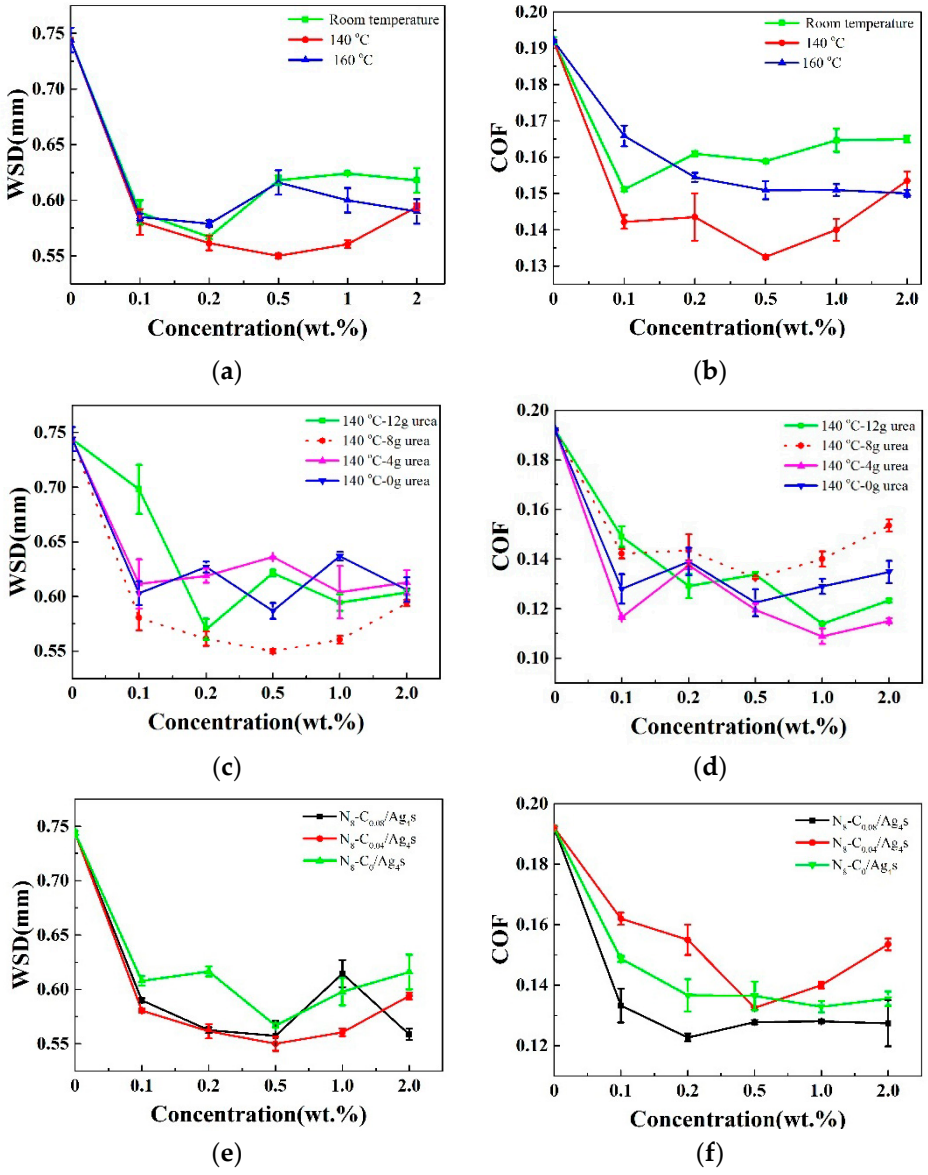


Figure 3. WSD–concentration and COF–concentration curves of LP-OAN_8-$C_{0.04}$/Ag_4 for different synthesis temperatures (**a**,**b**), different amounts of urea (**c**,**d**) at 140 °C and different amounts of CNTs (**e**,**f**).

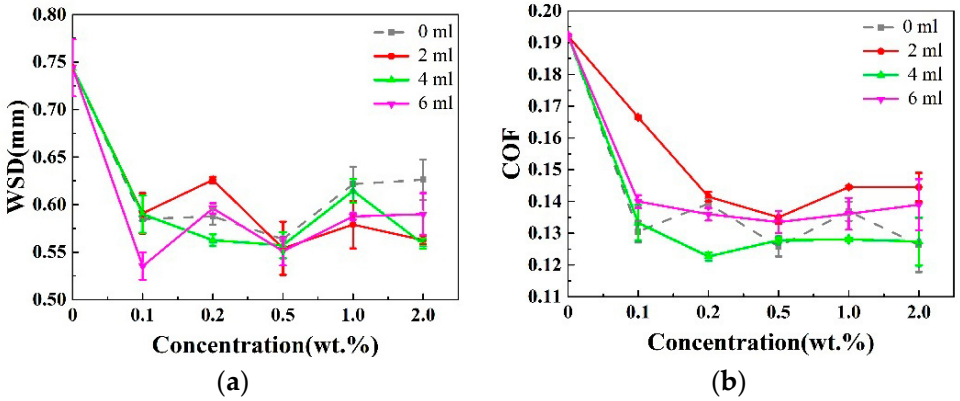


Figure 4. WSD–concentration (**a**) and COF–concentration (**b**) curves of LP-OAN$_8$-C$_{0.08}$/Ag with different volumes of $AgNO_3$ solution at 140 °C.

The effect of varying $AgNO_3$ solution volume on the WSD–concentration and COF–concentration curves for LP-OAN$_8$-C$_{0.08}$/Ag at 140 °C is presented in Figure 4. It can be seen that the WSDs of the steel balls with the three lubricants are lower than those with LP. For instance, at a concentration of 0.5 wt.%, the WSDs associated with the three lubricants are ca 0.56 mm, which is approximately three-quarters of the WSD with LP lubrication. The three WSD–concentration curves overlap with an increase in additive concentration. The COF–concentration curves reveal that the LP-OAN$_8$-C$_{0.08}$/Ag$_4$ possesses better friction-reducing capability than the other samples. At a concentration of 0.2 wt.%, the COF of steel balls lubricated with LP-OAN$_8$-C$_{0.08}$/Ag$_4$ is ca. 0.122, which is lower than those obtained with LP-OAN$_8$-C$_{0.08}$/Ag$_2$ (0.142) and LP-OAN$_8$-C$_{0.08}$/Ag$_6$ (0.138). The volume of the $AgNO_3$ solution was fixed at 4 mL. Use of LP-OAN$_8$-C$_{0.08}$/Ag$_4$ resulted in smaller COFs and WSDs than the samples without an $AgNO_3$ solution at almost all concentrations. At a concentration of 0.2 wt.%, the COFs and WSDs of steel balls lubricated with LP-OAN$_8$-C$_{0.08}$/Ag$_0$ are 0.14 and 0.58 mm, respectively, which are larger than those obtained with LP containing OAN$_8$-C$_{0.08}$/Ag$_4$ (0.12 and 0.55 mm, respectively).

3.3. Discussion

Taking an overview of the results generated, tribological properties can be enhanced through the combined use of a suitable temperature and the amount of carbon nanotubes, $AgNO_3$ solution and urea. This suggests a synergistic effect involving these process variables. In order to account for this effect, an additional investigation has been conducted.

Optical images of worn surfaces lubricated with LP and LP-OAN$_8$-C$_{0.08}$/Ag$_4$ are shown in Figure 5a,b, respectively. It is immediately evident that the worn surfaces lubricated with LP-OAN-C/Ag are smaller and smoother than those with LP. The element maps and EDXA spectrum of the worn surface lubricated with LP-OAN$_8$-C$_{0.08}$/Ag$_4$ show the presence of Fe, C, Ag, O and N, suggesting the formation of a tribofilm containing these elements during rotation. The urea-treated C/Ag nanoparticles generated a tribofilm containing a high percentage of C, O and N (Table 1).

Table 1. Percentage elemental content of the worn surfaces with lubrication using LP containing C$_{0.08}$/Ag$_4$ with/without urea.

	Fe (at.%)	C (at.%)	O (at.%)	N (at.%)	Ag (at.%)
N$_8$-C$_{0.08}$/Ag$_4$	72.26	22.23	4.12	1.05	0.34
N$_0$-C$_{0.08}$/Ag$_4$	86.68	11.15	1.21	0.19	0.77

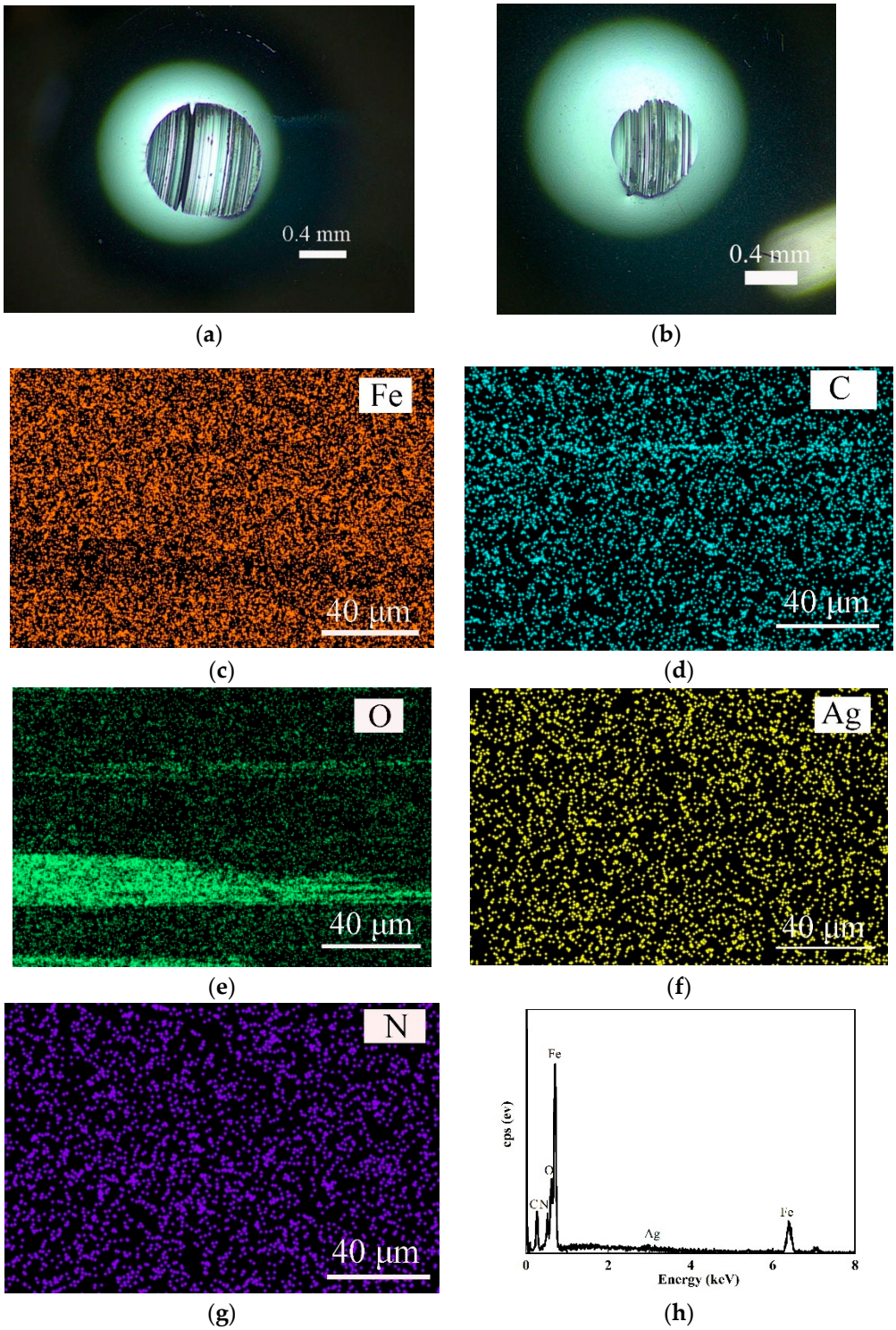
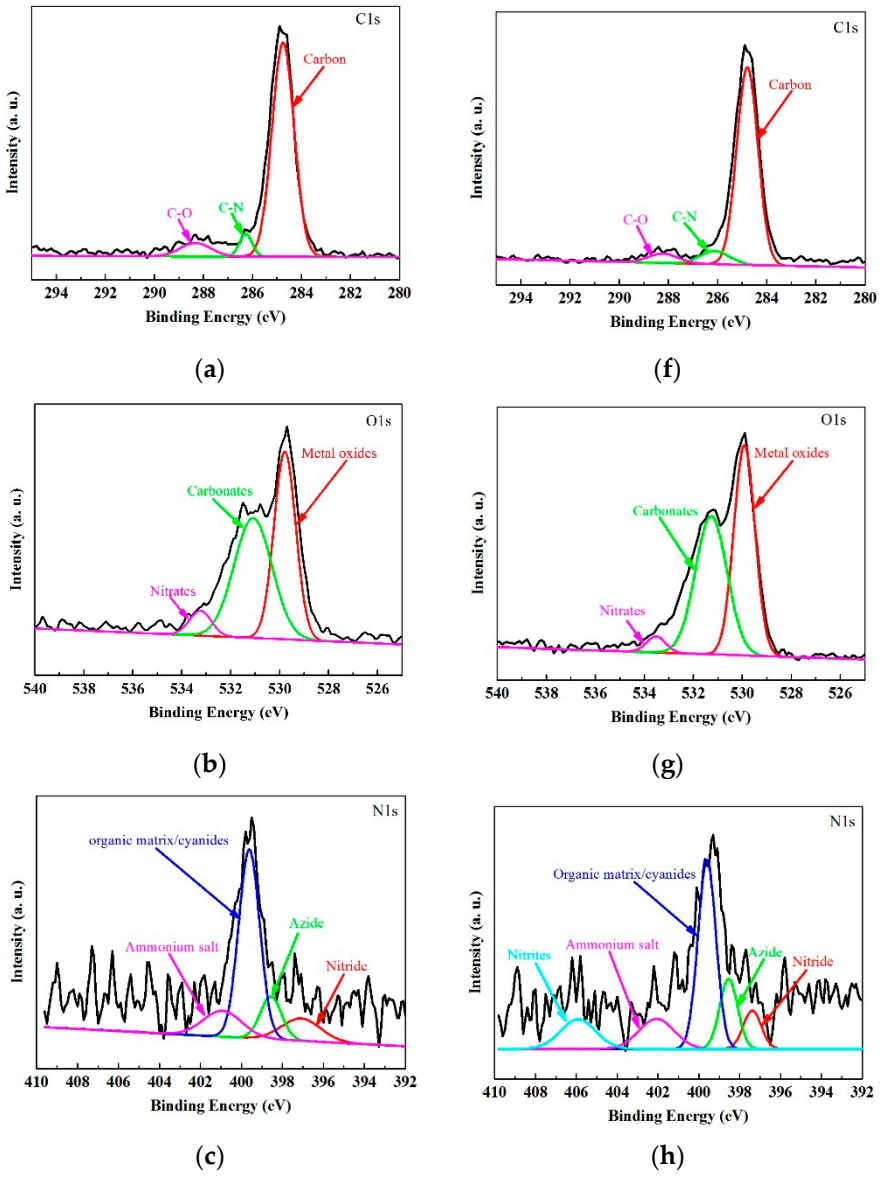


Figure 5. Optical images of worn surfaces lubricated with LP (**a**) and LP-OAN_8-$C_{0\cdot08}$/Ag_4 (**b**). Elemental maps and EDXA spectrum of the worn surfaces lubricated with LP-OAN_8-$C_{0.08}$/Ag_4 (**c**–**h**).

The results of the XPS analysis of the worn steel ball surfaces are presented in Figure 6 for lubrication using LP-OAC/Ag with and without urea. The C1s signal was fitted to three peaks with binding energies of 284.75 eV, 286.14 eV and 288.18 eV, which are attributed to carbon, C-N and C-O, respectively [15,19,20]. The O1s signal was deconvoluted into three peaks at 529.92 eV, 531.27 eV and 533.54 eV, which are assigned to metal oxides, carbonates and nitrates, respectively [19]. Oxidation of Fe, C and N during rotation may

have resulted in the formation of Fe_2O_3, carbonates and nitrates. The N1s signal was deconvoluted into five peaks at 397.36 eV, 398.49 eV, 399.60 eV, 402.12 eV and 405.92 eV, which are attributed to nitride, azide, organic matrix/cyanides, ammonium salt and nitrites, respectively. Nitrogen may have reacted with the available metal, nitrogen, oxygen and other elements to generate these surface species [15,20]. Comparing the N1s signal for the worn surfaces using lubricants containing additives with/without urea, the peaks due to nitrites and ammonium salt were less intense with the inclusion of urea. This suggests that the nitride associated with the tribofilm improved the tribological properties of the steel balls lubricated with LP-OAN-C/Ag [21,22]. The Fe2p peak at 710.92 eV is assigned to Fe_2O_3 [15,19]. The weak Ag3d signal was deconvoluted into three peaks at 367.53 eV, 368.13 eV and 368.72 eV, which are attributed to oxides, Ag and alloys, respectively [20,23]. The results indicate that a tribofilm containing C, O, N, Fe and Ag was formed on the worn surfaces of the steel balls. The presence of carbon, Fe_2O_3, azides and nitride, Ag and alloy and other compounds associated with the wear scars may improve tribological properties.



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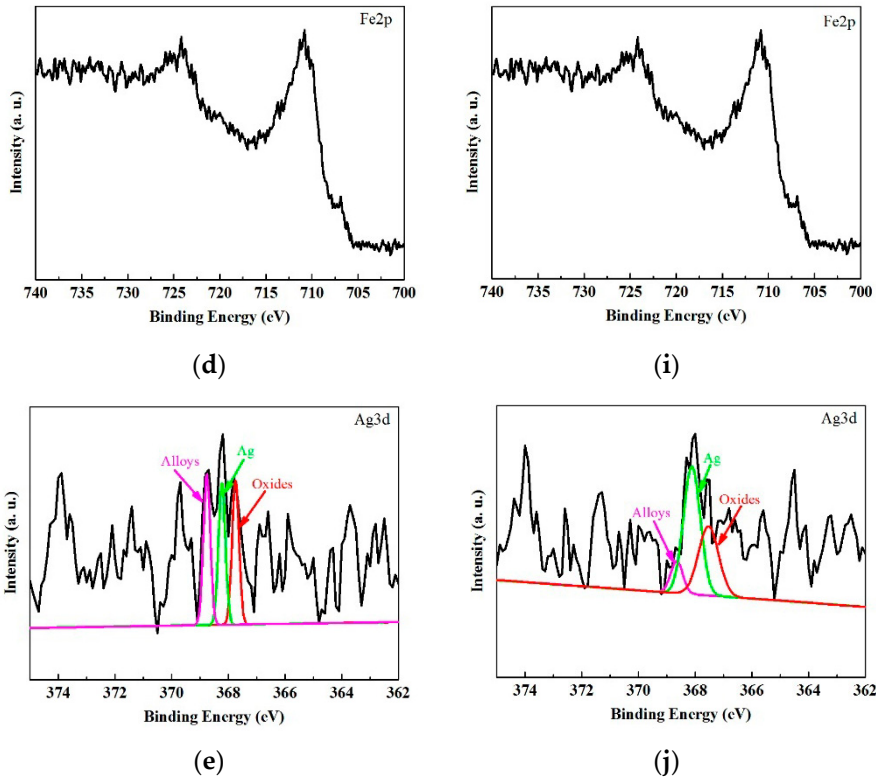
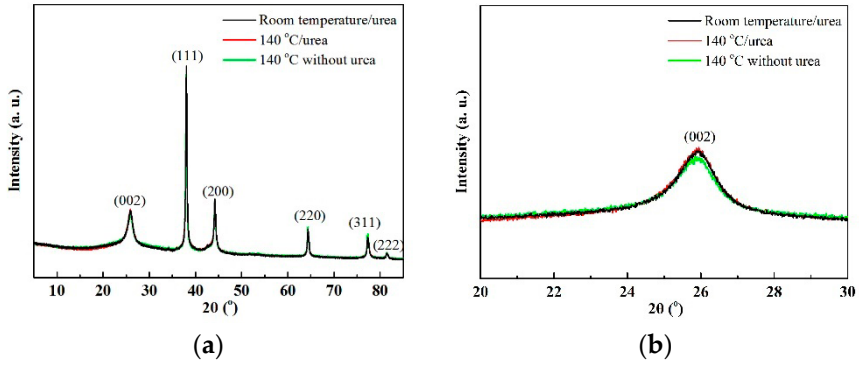


Figure 6. XPS analysis of the worn surfaces lubricated with LP-OAN$_8$-C$_{0.08}$/Ag$_4$ (**a**–**e**) and LP-OAN$_0$-C$_{0.08}$/Ag$_4$ (**f**–**j**).

In order to establish the relationship between temperature/urea and tribological properties, XRD analysis was conducted for samples with different temperatures and amounts of urea, and the results are presented in Figure 7. The peaks with 2θ values of 26.10°, 38.27°, 44.20°, 64.48°, 77.31° and 81.48° are assigned to (002), (111), (200), (220), (311) and (222) crystalline planes, respectively [8,14]. The (002) peak for carbon nanotubes was stable with increasing reaction temperature and/or added urea. The intensity of the (111) and (200) peaks for Ag was reduced and shifted to lower 2θ values as the reaction temperature was increased from ambient to 140 °C, and the peak intensities were further reduced with the addition of urea at high temperature. This indicates that Ag particle size decreased with a lower degree of crystallinity at high temperatures in the presence of urea [15]. Previous reports have suggested that "soft" Ag nanoparticles are deposited on worn surfaces [24]. Our results suggest that a smaller Ag particle size and reduced crystallinity may be beneficial to friction reduction and anti-wear properties.



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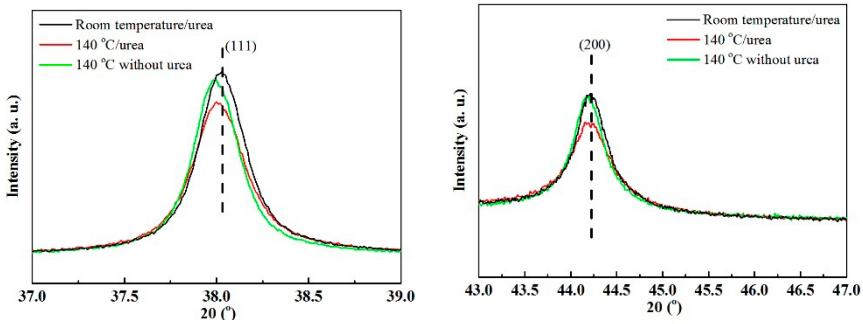
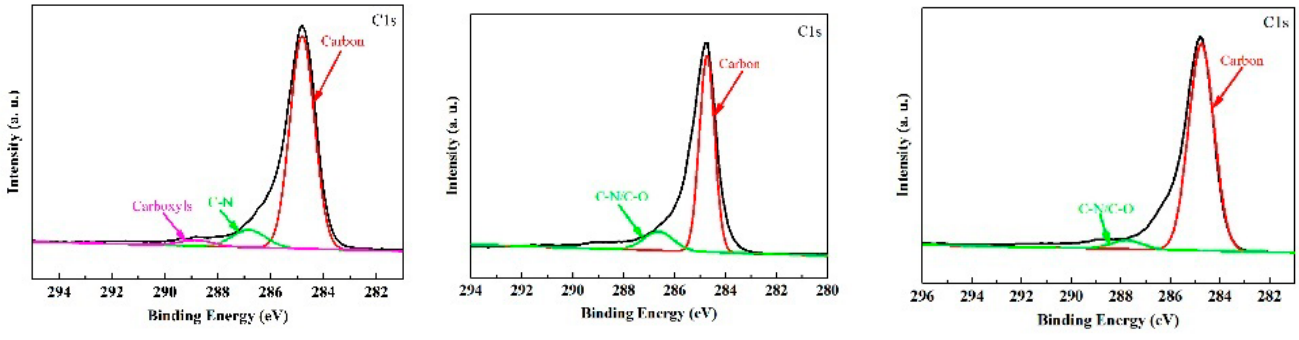


(**c**) (**d**)

Figure 7. XRD patterns of samples with different reaction temperatures and urea inclusion (**a**) and magnified peaks at different 2θ values (**b**–**d**).

Structural analysis of the composites was also conducted to establish the tribological mechanism. The XPS spectra with/without urea at room temperature and 140 °C are presented in Figure 8. The C1s signals for the three samples were deconvoluted into peaks ascribed to C-C at 284.71 eV, C=N/C=O at 286.68 eV and carboxyl at 289.08 eV [14,25]. The carboxyl peak intensity was reduced with increasing reaction temperature, which may be attributed to a thermal-induced polymerization of dopamine [26]. The O1s peaks were deconvoluted into Ag-O (529.92 eV), C-O (531.26 eV) and nitrates (533.13 eV) [14,25]. The nitrogen component in PDA/urea may interact with the CNT and Ag nanoparticles to generate nitrates. The N1s peaks were deconvoluted into four peaks at 397.97 eV, 400.17 eV, 401.59 eV and 402.82 eV, attributed to nitride, organic matrix, ammonium salt and azide species, respectively [25,27]. An increase in reaction temperature from ambient to 140 °C resulted in the formation of nitrides (C_xN_y), as shown in Figure 8c,j,k [25]. Moreover, cyanide and nitride formation can be linked to the inclusion of urea during hydrothermal treatment. The Ag3d signal was deconvoluted into two peaks at 367.71 eV and 368.56 eV, which are ascribed to silver oxides and Ag metal, respectively [14]. Raman analysis was also conducted, and the results are presented in Figure 9. The intensity ratios (I_D/I_G) of the composites with urea at room temperature, without urea at 140 °C and with urea at 140 °C were 0.798, 0.905 and 0.957, respectively. The increased values of I_D/I_G may suggest that new carbon and/or N-disrupted carbon were formed as a result of the solvothermal method of doping [2]. Formation of C_xN_y at high temperature and pressure can improve the tribological properties of the carbon nanotube/Ag nanocomposites, where urea promotes the formation of cyanides and nitrides.



(**a**) (**e**) (**i**)

Figure 8. *Cont.*

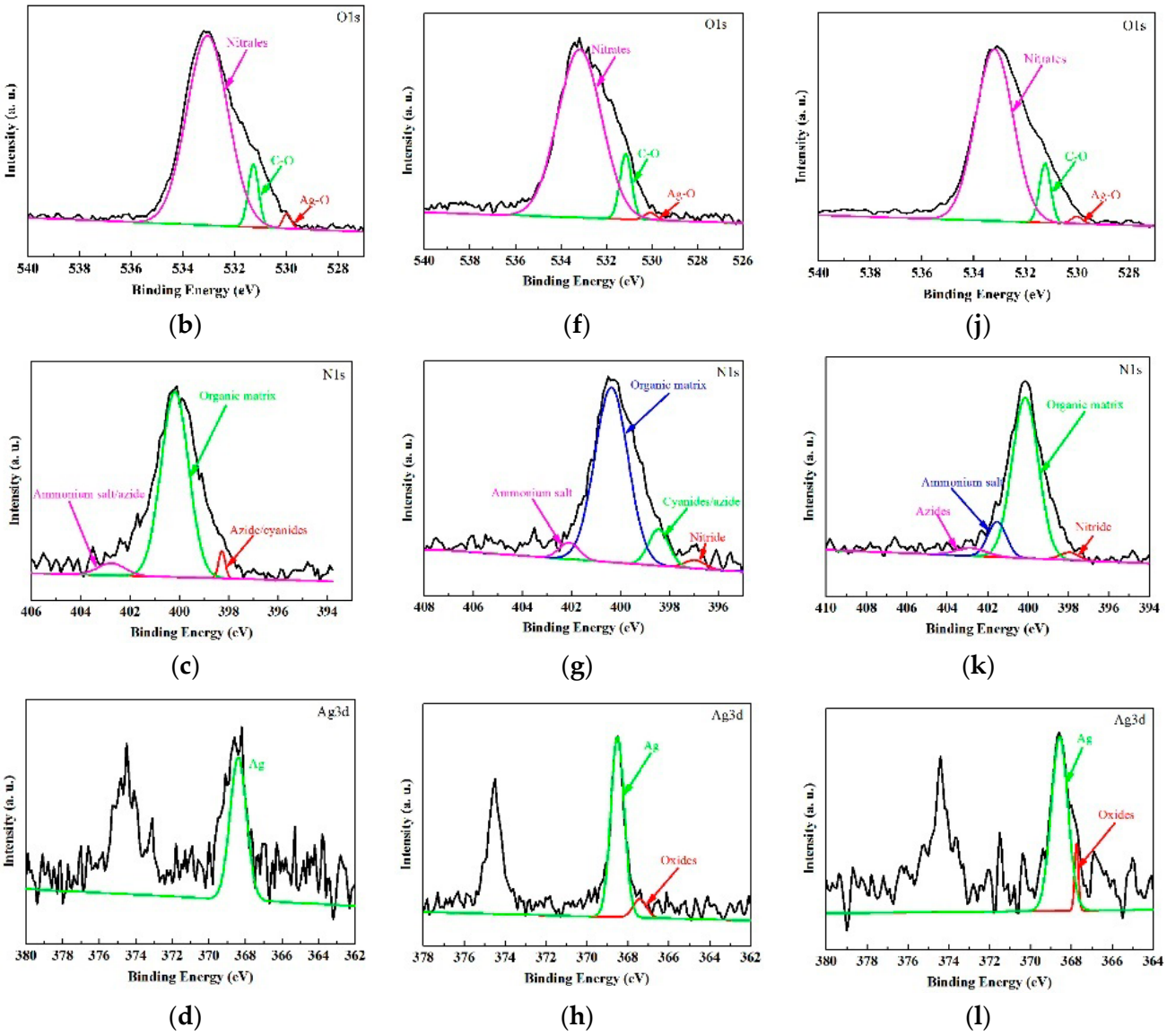


Figure 8. XPS spectra of samples with urea at room temperature (**a**–**d**), with urea at 140 °C (**e**–**h**) and without urea at 140 °C (**i**–**l**).

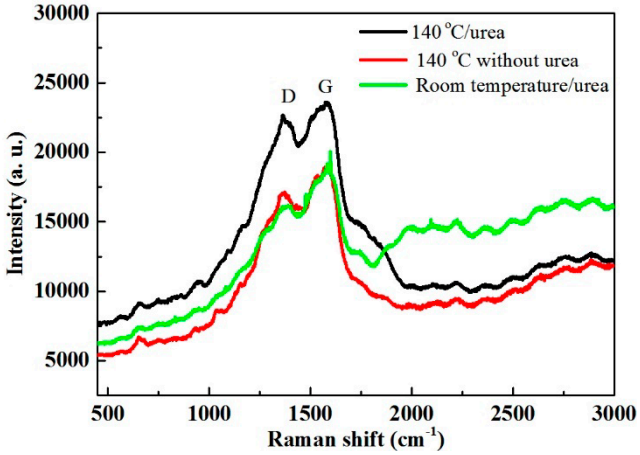


Figure 9. Raman spectra of samples with urea at room temperature, with urea at 140 °C and without urea at 140 °C.

4. Conclusions

Carbon nanotube/Ag nanocomposites have been synthesized in a urea solution using a hydrothermal method. The analysis reveals that the diameter of the carbon tubes was about 30 nm, and Ag nanoparticles with a diameter of ca. 10 nm covered the carbon tube surface. The XRD analysis shows that the (002) peak for carbon nanotubes was stable, and the intensity of the (111) and (200) peaks for Ag was reduced and shifted to lower 2θ values as the temperature was increased with the addition of urea, which means that the Ag particle size decreased with a lower degree of crystallinity at a high temperature in the presence of urea. Steel balls under the lubrication of LP-OAN$_8$-C$_{0.04}$/Ag$_4$ exhibited lower COFs and WSDs than those recorded using pure LP. Increasing the reaction temperature from room temperature to 140 °C, the LP-OAN$_8$-C$_{0.04}$/Ag$_4$ decreased the WSDs from 0.745 mm for LP to 0.55 mm. It is obvious that the steel balls under the lubrication of LP-OAN$_8$-C$_{0.04}$/Ag$_4$ exhibited lower WSDs than those recorded for other samples. The COFs of the balls lubricated with LP-OAN-C$_{0.04}$/Ag$_4$ with different amounts of urea are also smaller than those obtained with pure LP.

A synergism has been established between the preparation variables relating to the quantity of carbon nanotubes, the volume of a $AgNO_3$ solution and urea at a reaction temperature of 140 °C. A tribofilm containing Ag, carbon, nitride and other compounds was formed on the worn surfaces during sliding. Ag particle size decreased with a lower degree of crystallinity at a high temperature in the presence of urea; the smaller Ag particle size and reduced crystallinity may be beneficial for friction reduction and anti-wear properties. At a high temperature, the nitrogen component in PDA/urea may interact with the CNT and Ag nanoparticles to generate nitrates. The nitride (C_xN_y), organic matrix, ammonium salt and azide species were formed at high temperature. Moreover, urea promoted the formation of N-doped carbon and/or carbon, which contributes to the improvement in tribological properties.

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