

# Synthesis of water-soluble Cu nanoparticles and evaluation of their tribological properties and thermal conductivity as a water-based additive

Junhua ZHAO, Guangbin YANG\*, Chunli ZHANG, Yujuan ZHANG, Shengmao ZHANG, Pingyu ZHANG\*

Engineering Research Center for Nanomaterials, Henan University, Kaifeng 475004, China

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**Abstract:** Efficient and sustainable use of water-based lubricants is essential for energy efficiency. Therefore, the use of water-lubricated mechanical systems instead of conventional oil lubricants is extremely attractive from the viewpoint of resource conservation. In this study, water-soluble Cu nanoparticles of size approximately 3 nm were prepared at room temperature (around 25 °C) via *in-situ* surface modification. The tribological behavior of the as-synthesized Cu nanoparticles as an additive in distilled water was evaluated using a universal micro-tribotester. The results show that the as-synthesized Cu nanoparticles, as a water-based lubricant additive, can significantly improve the tribological properties of distilled water. In particular, the lowest friction coefficient of 0.06 was obtained via lubrication with a concentration of 0.6 wt% of Cu nanoparticles in distilled water, which is a reduction of 80.6% compared with that obtained via lubrication with distilled water alone. It is considered that some Cu nanoparticles entered the contact area of the friction pairs to form a complex lubricating film and prevent direct contact of the friction pairs. Furthermore, some Cu nanoparticles in the solution accelerate the heat transfer process, which also results in good tribological properties.

**Keywords:** Cu nanoparticles; water-soluble; lubricant additive; tribological properties

## 1 Introduction

Oil depletion, energy crisis, and increasingly serious environmental pollution are major global problems and must be urgently solved. To satisfy the special requirements of mechanical equipment and environmental protection, many countries are vigorously developing water-based lubricants. Over the past few decades, water-based lubricants have been studied and widely used in many areas, such as metal processing, chemical mechanical planarization, drilling equipment, and other industrial fields. Gao et al. prepared TiO<sub>2</sub> nanoparticles using oleic acid as a modifier. The carrying capacity of water was significantly increased when the mass fraction of TiO<sub>2</sub> nanoparticles was very small [1]. Wang et al. prepared oleylamine-modified

Ni-Al LDH (NiAl-LDH/OAm) nanoplatelets as water-based lubricant additives, which exhibited good tribological properties [2]. Currently, water-based lubrication is a popular research topic. More importantly, water is a cheap, pollution-free, eco-friendly, and safe lubricant [3]. However, water-based lubricants still have some shortcomings, such as poor corrosion resistance, insufficient lubrication performance, and short life, which have limited the development of water-based lubricants to some extent. Therefore, research and development of high-performance water-soluble additives is the key to improve the overall performance of water-based lubricants, further expanding their scope of application. Friction reduction, anti-wear, and extreme pressure agents are the core features of water-based lubricant additives. They are very

\* Corresponding authors: Guangbin YANG, E-mail: yang0378@vip.henu.edu.cn; Pingyu ZHANG, pingyu@henu.edu.cn

important to ensure good tribological performance of a water-based lubricant. Currently, mainly animal oils and plant oils, fatty acids and their salts and esters are used as friction reduction and anti-wear agents for lubricating oil and emulsified water-based lubricants; their application in water-based lubricants is limited owing to poor solubility and other reasons [4].

Nanoparticles have attracted attention in many applications and are a popular research topic currently, owing to their special properties. Previous test results indicated that the reported nanoparticles, when used as lubricant additives, have a small required dose and can significantly improve the tribological properties of base oils, such as friction reduction, anti-wear, self-healing ability, and extreme pressure properties [5–8]. In the past, many reports on nanoparticles as lubricating additives have focused on oil-based lubricating additives, and the research on nanoparticles as water-based lubricating additives is scant. Furthermore, most nanoparticles that have been reported as additives in water-based lubricants are oil-soluble nanoparticles (the oil-soluble nanoparticles are first dissolved in mineral oil; thereafter, the nanoparticles are transferred to water using a certain amount of surfactant, but the tribological properties are poor because of its poor solubility) or oil-soluble nanoparticles surface-modified using complex methods to obtain water-soluble nanoadditives (cannot be used universally because of its complex composition) [9–11]. However, complex nanoparticles, when used as water-based lubricant additives, have many shortcomings such as a complex composition, relatively poor stability, and easy precipitation.

The growth of nanoparticles strongly depends on the structure of the surface-capping ligands. Therefore, it is crucial to choose an appropriate modifier for the preparation of nanoparticles. Only the modifier can be chemically adsorbed on the surface of the nanometer cores and form a dense molecular layer. The modified nanoparticles can be stable owing to the strong interaction between the functional groups of the modifying agent. This strong interaction is helpful to effectively inhibit the agglomeration of the nanoparticles, and to enable the nanoparticles to have an affinity for the solvent dithiocarbamates and dithiophosphates have attracted considerable attention owing to their bidentate nature, and it is anticipated

that they will exhibit stronger affinity toward the metal surface than simple alkanethiols and hence smaller particle cores. Nanoparticles with smaller particle diameters can more easily enter the frictional contact area and form a lubricant film to improve tribological performance. Zhou et al. reported a series of works on the preparation and tribological properties of Cu nanoparticles with *O,O'*-dialkyldithiophosphate (DDP) as the capping agent [12, 13]. The obtained DDP-modified Cu nanoparticles could be well dispersed in some organic solvents and had good anti-oxidation stability in air. It was supposed that the hydrophobic groups on the surface of the DDP-Cu nanoparticles contributed to the improvement of the dispersive behavior. *N, N'*-dialkyldithiocarbamate (DDC) was used as a capping ligand to synthesize gold and silver nanoparticles. The as-synthesized DDC-modified Au, Ag, and Cu nanoparticles were highly stable under ambient conditions owing to the excellent capping effect of the bidentate DDC [14–16]. In our previous work, it was observed that Cu nanoparticles capped with dithiocarbamates and dialkyldithiophosphates exhibited excellent anti-wear and friction-reducing properties in base oils [12, 13, 17] because Cu nanoparticles have a small particle size, high surface area and activity, low melting point, and low shear strength. In this study, as a water-based lubricant additive, copper nanoparticles were synthesized via *in-situ* surface modification, and the prepared water-soluble bis (2-hydroxyethyl) dithiocarbamic acid (HDA) was used as a capping ligand, wherein the two polar groups of hydroxyethyl improve the dispersive capability of Cu nanoparticles in distilled water, and the dithiocarbamate ligand strongly prefers to form a chelating bond with the Cu atom. The as-prepared Cu nanoparticles of size approximately 3 nm showed good dispersibility and stability in distilled water and could significantly improve the tribological properties of distilled water.

## 2 Experimental

### 2.1 Chemicals

Polyvinylpyrrolidone (PVP, average molecular weight: 1300000) was purchased from Sigma–Aldrich. Anhydrous ethanol was supplied by Anhui Ante

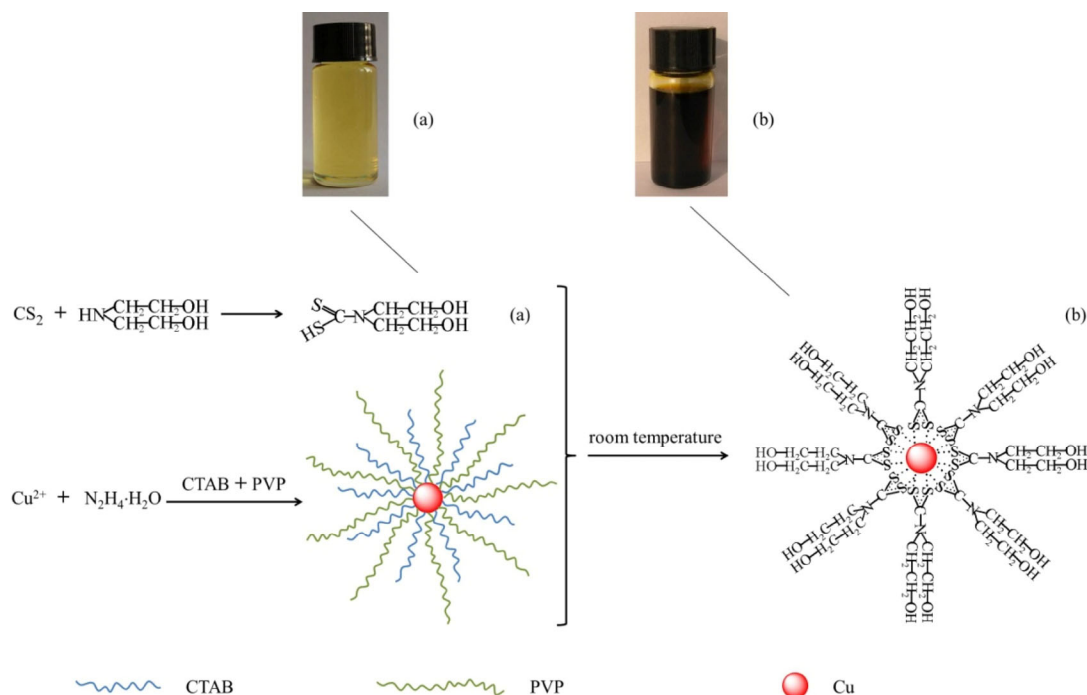
Foodstuffs Company Limited (Anhui, China). The other analytical-grade reagents were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China) and used as received. Distilled water was used as the experimental water.

## 2.2 Preparation of bis (2-hydroxyethyl) dithiocarbamic acid and water-soluble Cu nanoparticles

The detailed preparation of HDA is described as follows. Briefly, 4 mL of diethanolamine and 20 mL of absolute ethanol were mixed in a 150 mL three-neck flask under magnetic stirring in an ice bath. Subsequently, a mixture of 20 mL of carbon disulfide and 20 mL of absolute ethanol was added drop-wise to the three-neck flask, maintaining the reaction system temperature below 10 °C. After completion of the drop-wise addition, the solution was stirred for 1 h at 25 °C. A yellow transparent solution was obtained. Finally, the absolute ethanol and unreacted material were removed via rotary evaporation, thus obtaining a light yellow transparent viscous liquid as a modifier for synthesizing Cu nanoparticles. The synthetic route and optical image of HDA are shown in Fig. 1.

The preparation of water-soluble Cu nanoparticles

is described as follows. First, 2 mmol of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (4 mL, 0.5 M) was dissolved in 20 mL of distilled water in a 100 mL single-neck flask. Subsequently, 2 mmol of cetyltrimethyl ammonium bromide was added to the  $\text{Cu}(\text{NO}_3)_2$  solution under magnetic stirring for 20 min until it was fully dissolved. Thereafter, 0.44 g of PVP was added to the single-neck flask under magnetic stirring for 10 min until it was fully dissolved. Subsequently, 2 mL of hydrazine hydrate (content of 80%) was measured with a pipette and added to the single-neck flask at once, and the solution quickly became light brown. After maintaining the reaction under magnetic stirring for 10 min, 10 mmol of HDA dissolved in 20 mL of absolute ethanol was poured into the single-neck flask at once. The reaction system rapidly turned dark brown. The bottle stopper was closed and the reaction was allowed to proceed for 1 h. A reddish-brown liquid of water-soluble Cu nanoparticles was obtained. All the reactions were carried out at room temperature (around 25 °C). The reaction pathway, schematic structure, and optical image of water-soluble Cu nanoparticles are illustrated in Fig. 1. It can be observed that the as-prepared water-soluble Cu nanoparticles were in the form of a



**Fig. 1** Schematic illustration for the reaction pathway and corresponding optical pictures of products (a) HDA modifier and (b) water-soluble Cu nanoparticles.

reddish-brown uniform liquid without precipitation and they showed excellent dispersibility in distilled water.

### 2.3 Characterization of water-soluble Cu nanoparticles

The crystalline phase of the water-soluble Cu nanoparticles was examined using X-ray diffraction (XRD, D8-Advance, Bruker, Germany) with Cu-K $\alpha$  radiation ( $\lambda = 1.54$  nm) operating at 40 kV and 40 mA. Their morphology and chemical structure were examined using a transmission electron microscope (TEM, JEOL JEM-2100) and a Fourier-transform infrared spectrometer (FT-IR, Avatar 360 Fourier Transform Infrared), respectively. Ultraviolet–visible light (UV–vis) absorption spectra and chemical states were obtained using UV–vis absorption spectrometry and X-ray photoelectron spectroscopy (XPS), respectively. The thermal stability was evaluated using a thermogravimetric analyzer (TGA).

### 2.4 Tribological properties and thermal conductivity of water-soluble Cu nanoparticles

The tribological properties of water-soluble Cu nanoparticles, as a water-based lubricant additive, were investigated using a universal micro-tribotester (UMT-2, CETR) in a reciprocating ball-on-plate mode. The upper counterpart was a GCr15 stainless steel ball of diameter 4 mm and the lower plate was a silicon wafer. The roughness of the ball was 25 nm and the roughness of the silicon wafer was 0.5 nm. Further detailed information on the ball, silicon wafer, and lubricants is given in Table 1. The balls and silicon wafer were ultrasonically cleaned three times with anhydrous ethanol before use. The reciprocating stroke length was 5 mm, and the test duration was 30 min. The loads ranged from 1.0 to 4.0 N (when the loads were 1 N, 2 N, 3 N, and 4 N, the maximum Hertz contact pressures were 823 MPa, 1,037 MPa, 1,187 MPa, and 1,307 MPa, respectively) under a frequency of 2.0 Hz (corresponding to the average sliding velocity 0.02 m·s<sup>-1</sup>). The friction coefficient between the friction surfaces lubricated by aqueous solutions of Cu nanoparticles with different concentrations from 0.1 wt% to 2.0 wt% was recorded automatically. Upon completion of the friction and wear tests, a three-dimensional (3D)

**Table 1** The detail information of ball, plate and lubricants.

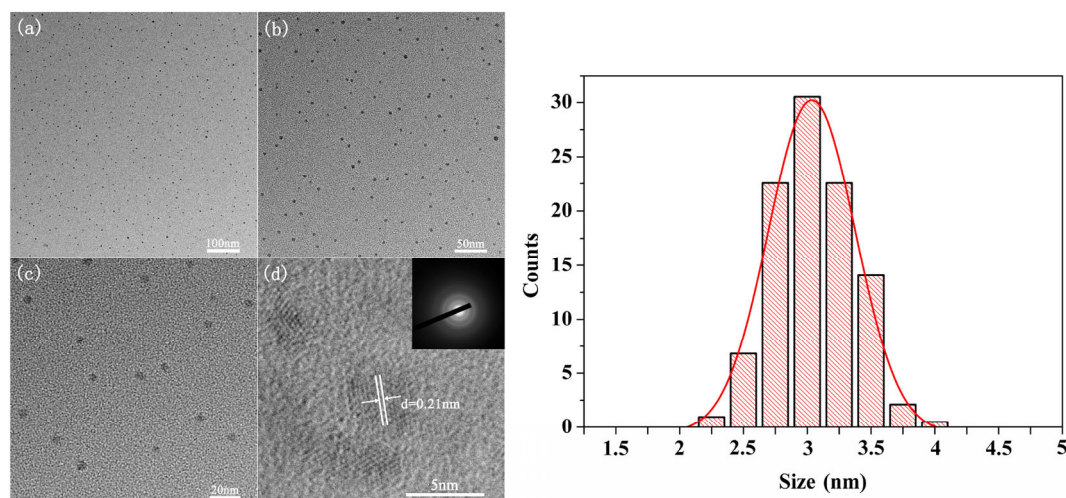
Material	Steel ball	Silicon wafer	0.6 wt% Cu
Size	$\phi = 4$ mm	$\phi = 100 \pm 0.5$ mm $d = 450 \pm 20$ $\mu$ m	/
Roughness	25 nm	0.5 nm	/
Hardness	800 HV	1161 HV	/
Elastic Modulus	208 GPa	187 GPa	/
Poisson's ratio	0.3	0.278	/
Viscosity	/	/	$2.2 \times 10^{-3}$ Pa·S

surface profiler (Contour GTK-1, Bruker) was used to evaluate the surface morphology, width, and depth of the track. XPS was employed to confirm the elemental composition and chemical states of some typical elements on the worn surfaces of the silicon wafer. After the friction test, the silicon wafer was washed several times with distilled water in an ultrasonic bath and dried in atmosphere prior to the XPS analysis. The coefficient of thermal conductivity of the aqueous solution of water-soluble Cu nanoparticles was evaluated using a thermal conductivity instrument (TC 3000E, 22 °C, 1.5 V, 6.5 s, atmospheric environment).

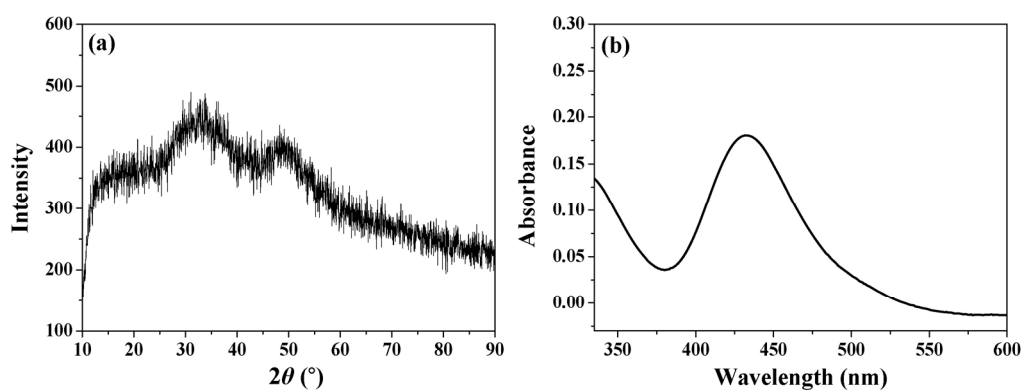
## 3 Results and discussion

### 3.1 Structural characterization of water-soluble Cu nanoparticles

The morphology and size of the as-prepared Cu nanoparticles were observed using high-resolution TEM (HRTEM). Figure 2 shows the HRTEM images, selected-area electron diffraction pattern (SADP), and size distribution of the water-soluble Cu nanoparticles. It can be observed that the Cu nanoparticles have a uniform spherical shape and narrow size distribution. The average particle diameter of Cu nanoparticles was approximately 3 nm with no sign of obvious aggregation. The lattice spacing was approximately 0.21 nm, and the corresponding SADP is shown in Fig. 2(d), which is consistent with the XRD result in Fig. 3(a). Two large protrusions were present at 2 $\theta$  angles of 26°–55° in the XRD pattern of the water-soluble Cu nanoparticles, indicating that the as-synthesized Cu nanoparticles have a small grain size, polycrystalline structure, and poor crystallinity [18, 19],



**Fig. 2** HRTEM images, SAED pattern and size distribution of as-prepared water-soluble Cu nanoparticles.



**Fig. 3** XRD pattern and UV-vis absorption spectrum of water-soluble Cu nanoparticles.

possibly owing to a relatively high content of the organic modifying layer [17, 20]. Figure 3(b) shows the UV-vis absorption spectrum of the water-soluble Cu nanoparticles. A large protrusion can be observed in the range 400–500 nm, which is attributed to the very small sizes of the as-prepared Cu nanoparticles, resulting in the shift of the absorption peak toward short wavelengths in the UV-vis absorption spectrum [21–22]. Dithiocarbamate-based bidentate ligands provide better passivation during the particle growth, resulting in a smaller core size of the obtained Cu nanoparticles [14].

To further demonstrate the formation of Cu nanoparticles, the sample was characterized using XPS. Figure 4 shows the XPS spectra of Cu2p, O1s, S2p, and N1s. The characteristic peak of Cu2p<sub>1/2</sub> can be observed at 952.1 eV and that of Cu2p<sub>3/2</sub> can be observed at 932.3 eV. Notably, the satellite peak of

Cu<sup>2+</sup> is absent, which indicates that Cu is present as metallic Cu or/and in the Cu<sup>+</sup> oxidation state [23–25]. However, Cu<sup>+</sup> is unstable [26], and the peak related to O1s located at 530.3 eV, which corresponds to cuprous oxide, is not observed in the spectrum. Moreover, the apparent O1s peak at approximately 531.3 eV corresponds to the hydroxyl groups of dithiocarbamic acid [27]. Thus, we can infer that the prepared particles are metallic copper nanoparticles. Furthermore, the peaks of N1s and S2p are also detected in the water-soluble Cu nanoparticles derived from the modifier HDA, indicating that HDA is well capped on the surface of the copper nanoparticles.

FT-IR was performed to explore the interaction between the modifier and Cu nanoparticles. Figure 5(a) shows the FT-IR spectra of HDA and the water-soluble Cu nanoparticles in the range 400–4,000 cm<sup>-1</sup>. For pure HDA, as expected, the hydroxyl functionality produces

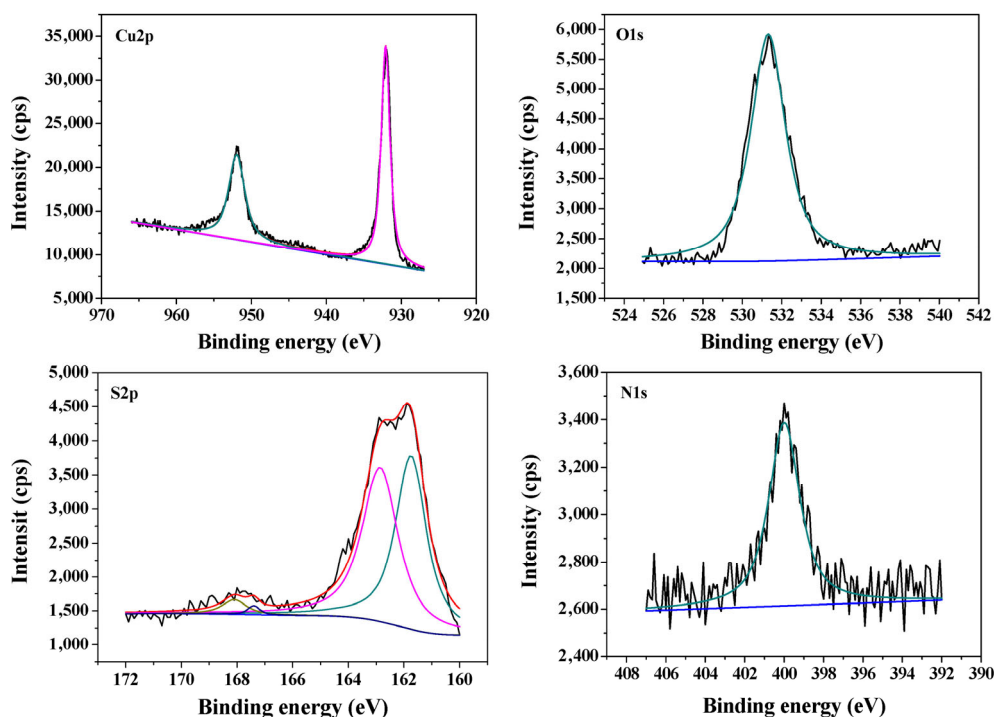


Fig. 4 XPS spectra of Cu2p, O1s, S2p and N1s for water-soluble Cu nanoparticles.

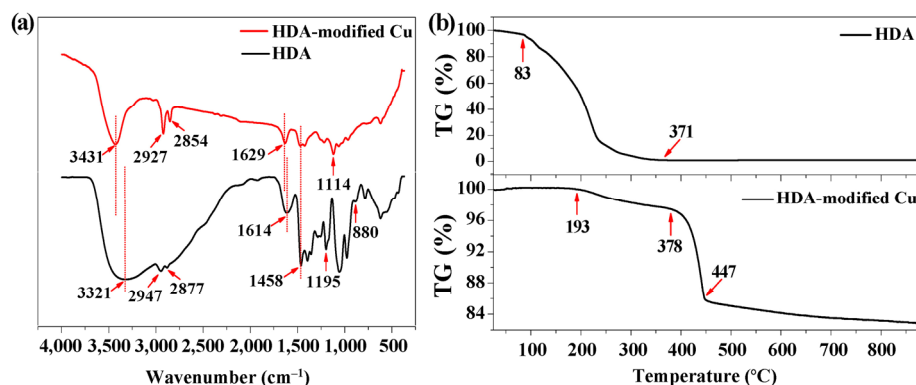


Fig. 5 (a) FT-IR spectra and (b) TGA curves of HDA and water-soluble Cu nanoparticles.

a broad band at  $3,321\text{ cm}^{-1}$  [28], and the absorption peak at  $1,614\text{ cm}^{-1}$  is attributed to the O–H bending vibration. The absorption peaks at  $2,877$  and  $2,947\text{ cm}^{-1}$  are attributed to the symmetric and asymmetric stretching vibrations of C–H, respectively. The FT-IR spectrum of the water-soluble Cu nanoparticles also showed the absorption bands of  $-\text{CH}_2$  ( $2,854$  and  $2,927\text{ cm}^{-1}$ ) and O–H stretching and bending vibrations, but the absorption bands of O–H shifted to higher wave numbers (shifted to  $3,431$  and  $1,629\text{ cm}^{-1}$ ), as the surface modifier HDA was bound to the Cu nanoparticles [29]. Moreover, the strong absorption peak at  $1,458\text{ cm}^{-1}$  is associated with the partial double-bond

character of the C–N bond owing to a significant contribution of the resonance form in HDA [30]. Further, the characteristic absorption band of C–N in HDA, located between the absorption peaks of C–N ( $1,251$ – $1,351\text{ cm}^{-1}$ ) and C=N ( $1,641$ – $1,691\text{ cm}^{-1}$ ), is retained in the water-soluble Cu nanoparticles. Moreover, the absorption peaks in the pure HDA spectrum at  $1,195$  and  $880\text{ cm}^{-1}$  are assigned to the vibration of C=S and C–S bonds, respectively. These are absent in the spectrum obtained from the water-soluble Cu nanoparticles, which presented a new absorption peak at  $1,114\text{ cm}^{-1}$ , which is lower than the peak attributed to the vibrations of C=S but higher

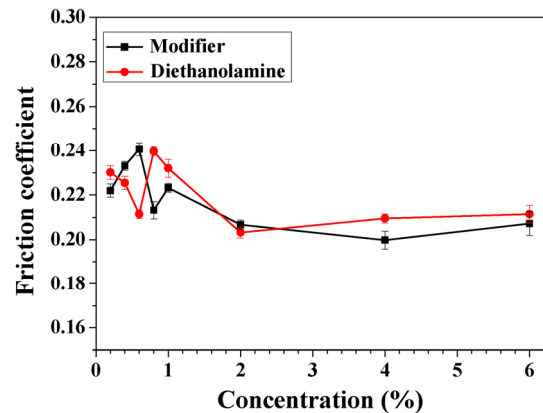
than the peak attributed to the vibrations of C–S. This suggests that the HDA ligand strongly prefers a coordination mode with Cu nanoparticles, which formed two equivalent carbon-sulfur bonds in the water-soluble Cu nanoparticles [31]. Based on the FT-IR data, it was confirmed that HDA was successfully introduced to the surface of Cu nanoparticles, and water-soluble copper nanoparticles were obtained. The HDA ligand can not only effectively bind with Cu nanoparticles via chemical bonds, but also offer polar groups to enable Cu nanoparticles to achieve appreciable water solubility.

Figure 5(b) illustrates the TGA curve of HDA and the as-prepared water-soluble Cu nanoparticles in the temperature range 25–875 °C. It can be observed that the weight loss of HDA is 100% within 83–371 °C and the weight loss at 83 °C is due to the moisture content. The weight loss of the as-prepared Cu nanoparticles is approximately 20% in the temperature range 25–875 °C. The relatively slow weight loss in the range 193–378 °C is related to the evaporation of a small amount of HDA, which was physically adsorbed on the surface of the Cu nanoparticles. The drastic weight loss in the range 378–447 °C corresponds to the decomposition of HDA, which was chemically adsorbed on the surface of the Cu nanoparticles, and the slight weight loss above 447 °C may be attributed to the elimination of decomposed residuals.

### 3.2 Tribological properties and thermal conductivity of water-soluble Cu nanoparticles in distilled water

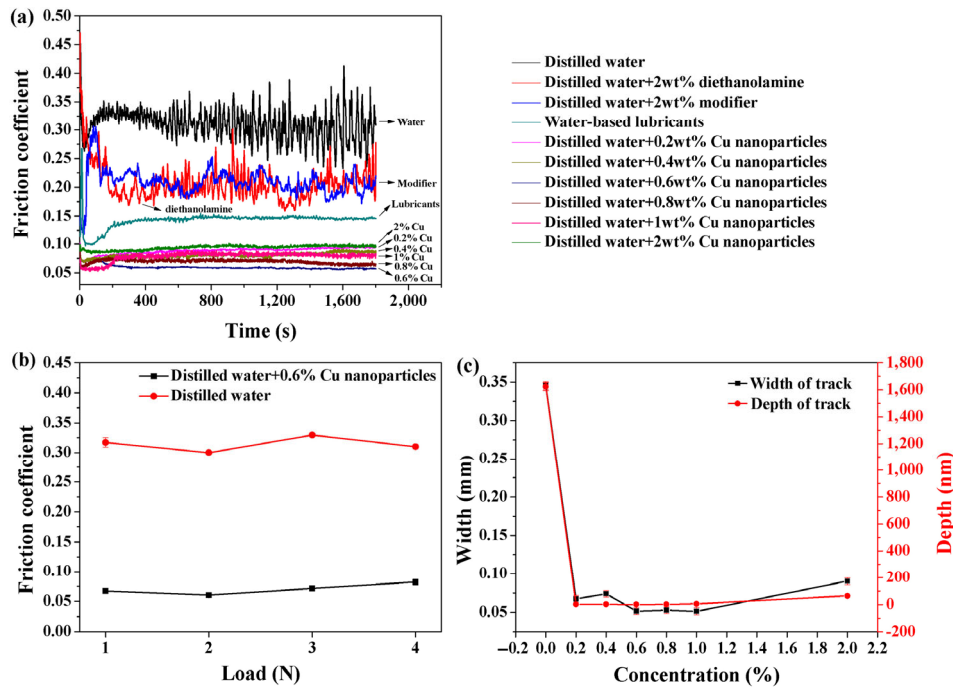
As the raw material for the synthetic modifier is diethanolamine, which is a good lubricant, the tribological properties of diethanolamine and the as-prepared HDA modifier are evaluated as shown in Fig. 6. It can be observed that the friction coefficients of the HDA modifier and diethanolamine show no obvious change with the increase in concentration. Further, they fluctuate around 0.22. The concentration of 2 wt% was selected for both the HDA modifier and diethanolamine in the following test.

Figure 7(a) illustrates the relationship between the friction coefficient and sliding time for the water-soluble Cu nanoparticles with different concentrations in contrast to the HDA modifier, diethanolamine, and



**Fig. 6** Variations of the friction coefficient of the steel–silicon sliding pairs with concentration under the load of 2.0 N lubricated by distilled water containing modifier and diethanolamine (speed: 0.02 m/s, time: 30 min).

water-based lubricants (commercially available). From the chart, it can be observed that the friction coefficients of the steel–silicon sliding pairs via lubrication with distilled water, distilled water containing 2.0 wt% HDA modifier, and distilled water containing 2.0 wt% diethanolamine are higher and fluctuate more widely than that via lubrication with distilled water containing the water-soluble Cu nanoparticles at an applied load of 2.0 N. Although the introduction of the HDA modifier and diethanolamine to distilled water can reduce the friction coefficient to some extent, water-soluble Cu nanoparticles used as an additive are advantageous over the HDA modifier and diethanolamine in terms of tribological properties. After the addition of the water-soluble Cu nanoparticles to distilled water, the curves of the friction coefficient remained relatively low and stable in the test concentration range 0.2–2.0 wt%. In particular, the lowest friction coefficient of 0.06 was obtained via lubrication with a concentration of 0.6 wt% in distilled water, which showed a reduction of 80.6% and 57.1% as compared with that obtained via lubrication with distilled water alone (0.31) and commercially available water-based lubricants (0.14), respectively. Furthermore, it can be observed that the as-prepared Cu nanoparticles effectively improve the friction-reducing ability of distilled water in the test load range 1.0–4.0 N (Fig. 7(b)). The counterpart materials were changed to further test the tribological properties of the as-prepared water-soluble Cu nanoparticles. For example, the ball-on-disk sliding pairs were assembled using an



**Fig. 7** The results of the tribological tests (a) variations of the friction coefficient with sliding time at different concentration of water-soluble Cu nanoparticles in contrast to modifier and diethanolamine, and water-based lubricants, (b) friction coefficient as a function of applied load, and (c) the depth and width of wear tracks (speed: 0.02 m/s, time: 30 min).

$\text{Si}_3\text{N}_4$  ball of diameter 4 mm and a 304 stainless-steel disk (Table S1 in the Electronic Supplementary Material (ESM)). The as-prepared Cu nanoparticles, as a water-based lubricant additive, also showed excellent tribological properties on different friction surfaces (see Fig. S1 in the ESM). This indicates that Cu nanoparticles used as a water-based lubricant additive have a wide range of applications. Further, they have excellent friction-reducing properties, which can be attributed to the low melting point, small size, and low shearing strength of copper nanoparticles [32]. It is believed that the friction-reducing performance depends on the shearing strength, and a low shearing strength leads to a low friction coefficient [33, 34]. The as-prepared Cu nanoparticles were deposited on the surface of the friction pairs, which resulted in a stable and low friction coefficient.

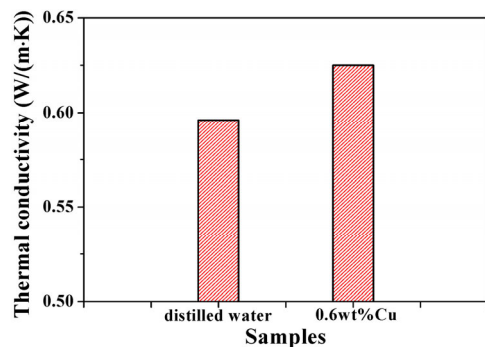
The size of the wear track (see Fig. 7(c)) after each friction test was measured to evaluate the anti-wear property using the 3D optical profiler. It can be observed that the wear depth and wear width were significantly reduced when the water-soluble Cu nanoparticles were added to the distilled water, even at a low dosage of 0.2 wt%. Further, the minimum wear

depth of 0.676 nm and wear width of 0.051 mm were recorded at an additive concentration of 0.6 wt%, which were much smaller than the corresponding wear depth (1.824  $\mu\text{m}$ ) and wear width (0.346 mm) obtained via lubrication with distilled water alone, indicating a reduction of 99.9% and 85.3%, respectively. Notably, the depth and width of the wear tracks changed very slightly with the increase in the additive concentration from 0.2 to 2.0 wt%. The reason may be that a complete and dense lubricating film can be formed on the surfaces of friction pairs at a low additive concentration (e.g., 0.2 wt%). It is beneficial to prevent the direct contact of rough peaks on the surfaces of friction pairs and significantly reduce wear [35].

Furthermore, copper is an excellent conductor of heat, and hence, the as-prepared Cu nanoparticles, used as an additive in distilled water, are effective for improving the heat dissipation ability of the frictional contact area and avoiding local overheating [36–39], which is beneficial to improve the tribological properties. The cooling capacity is an important function of water-based lubricants, and the main factor that affects the cooling capacity of the lubricant is its thermal conductivity. The thermal conductivity of the water-



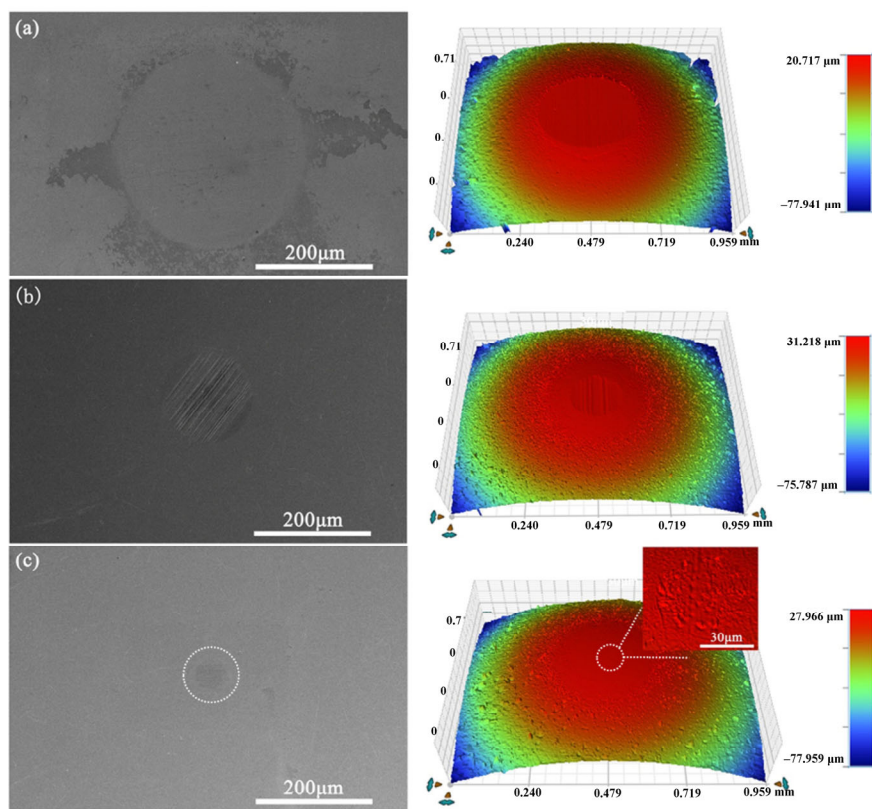
soluble Cu nanoparticles with a concentration of 0.6 wt% was 0.625 W/mK, which increased by 5% compared with that of distilled water (0.596 W/(m·K)) (see Fig. 8). The addition of even a small quantity (i.e., 0.6 wt%) of the as-prepared Cu nanoparticles to distilled water demonstrated a significant improvement in the thermal conductivity. The increased thermal conductivity of the distilled water is an indication of the ability of the water-based lubricants to cool faster at the rubbing surfaces.



**Fig. 8** The thermal conductivity of distilled water and distilled water containing 0.6 wt% as-prepared Cu nanoparticles.

### 3.3 Analyses of worn surfaces

To investigate the friction reduction and anti-wear mechanisms, the morphologies of the worn surfaces were observed using the 3D surface profiler and SEM. Figure 9 shows the SEM morphologies of the wear scar on steel balls lubricated with distilled water, a commercially available water-based lubricant, and distilled water containing 0.6 wt% water-soluble Cu nanoparticles (speed: 0.02 m/s, load: 2 N, time: 30 min). It can be observed that the wear scar of the steel ball lubricated with distilled water is large (Fig. 9(a)) with a diameter of 0.35 mm, and the wear scar lubricated with a commercially available water-based lubricant is rough with a diameter of 0.18 mm. Moreover, there are many wide and deep furrows along the sliding direction (Fig. 9(b)), possibly owing to the erosion by water-based lubricants during the sliding process. In contrast, the wear scar on the steel ball lubricated with distilled water containing 0.6 wt% water-soluble Cu nanoparticles is small and smooth (Fig. 9(c)) with a diameter of 0.05 mm. The sizes of the wear scar

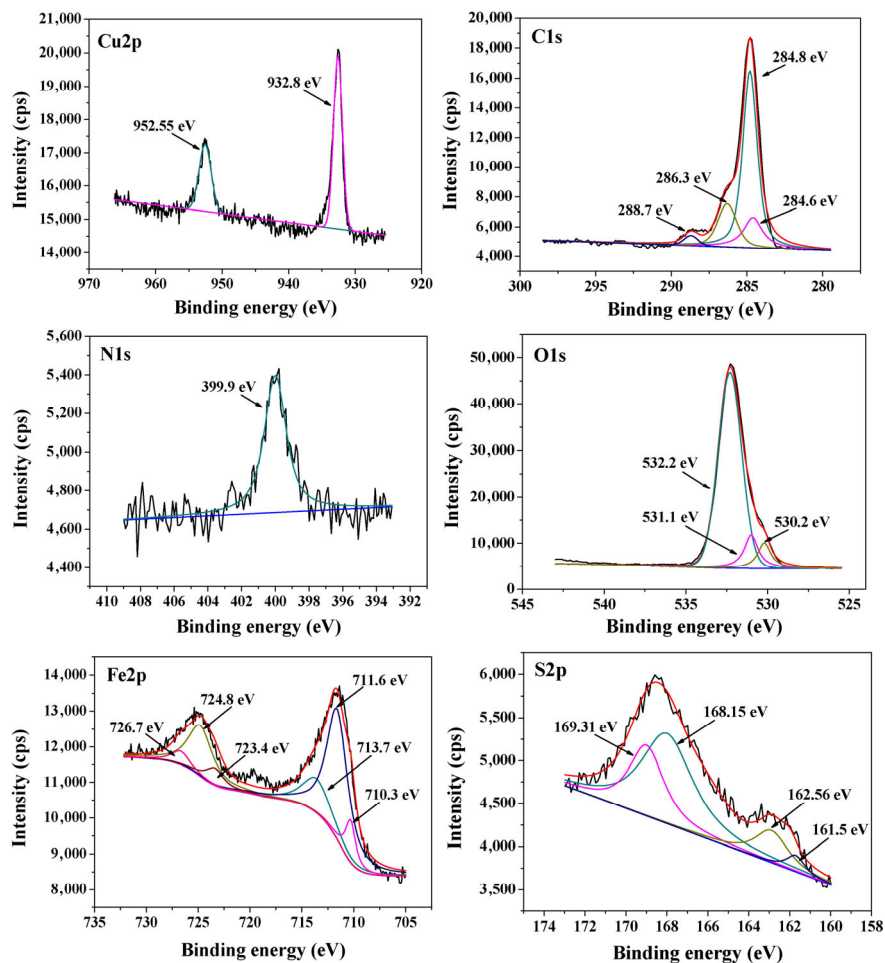


**Fig. 9** SEM micrographs and 3D profile of the worn steel surface lubricated by (a) distilled water, (b) commercial products water-based lubricants, and (c) distilled water containing 0.6% water-soluble Cu nanoparticles (the insert is the enlarge figure of wear scar).

could be reduced by 85% and 71% compared with that obtained by using pure distilled water and commercially available water-based lubricant, respectively, which is consistent with the good anti-wear ability of the water-soluble Cu nanoparticles. The 3D profiles of the worn steel surfaces lubricated with distilled water, a commercially available water-based lubricant, and distilled water containing 0.6 wt% water-soluble Cu nanoparticles are shown in Fig. 9. It can be observed that the wear scars obtained via lubrication with distilled water and a commercially available water-based lubricant are larger than the one obtained via lubrication with distilled water containing 0.6 wt% water-soluble Cu nanoparticles. The wear volumes are  $9.99 \times 10^4 \mu\text{m}^3$ ,  $1.93 \times 10^4 \mu\text{m}^3$ , and  $7.30 \mu\text{m}^3$ , respectively, for the wear scars obtained via lubrication with distilled water, a commercially available water-based lubricant, and distilled water containing 0.6 wt%

water-soluble Cu nanoparticles. This corresponds well with the above results, indicating that the water-soluble Cu nanoparticles used as an additive can significantly improve the tribological properties of distilled water.

Figure 10 shows the XPS spectra of Cu2p, C1s, N1s, O1s, Fe2p, and S2p on the silicon wafer surface lubricated with distilled water containing 0.6 wt% water-soluble Cu nanoparticles at a load of 10 N for 5 h (the wear tracks are too small to be detected for the shorter sliding time of 30 min and smaller load of 2 N). The peak in the spectrum of Cu2p at 932.8 eV is attributed to Cu2p<sub>3/2</sub> and the peak at 952.5 eV is attributed to Cu2p<sub>1/2</sub>; further, satellite peaks, which are caused by charge-transfer processes, are not detected [40]. Thus, we can conclude that metallic Cu was deposited on the rubbing surfaces to form the boundary film, thereby impeding the direct contact of rough peaks on the surfaces of friction pairs, resulting in



**Fig. 10** XPS spectra of silicon wafer surfaces lubricated with distilled water containing 0.6% water-soluble Cu nanoparticles (load: 10 N; time: 5 h).

improved tribological properties of distilled water.

C1s peaks at 284.8 eV, 286.3 eV, and 288.7 eV correspond to C–C, C–O, and C–N bonds in organic matter, respectively. Further, the N1s peak at 399.9 eV is assigned to an organic N-containing compound, indicating that the HDA modifier of the Cu nanoparticles was also chemically or/and physically adsorbed on the surface of the friction pairs. Furthermore, Fe2p3/2 peaks and Fe2p1/2 peaks (corresponding to the satellite peaks at 719 eV) correspond to Fe<sup>3+</sup>. It can be observed that the satellite peaks of Fe<sup>3+</sup> are relatively strong, and hence, the friction surface contains more Fe<sup>3+</sup> and may contain a small amount of Fe<sup>2+</sup>. The former, in combination with the Fe2p peak at a binding energy of 711.6 eV and O1s peak at 530.2 eV, is attributed to the formation of Fe<sub>2</sub>O<sub>3</sub>. The Fe2p peak at 713.7 eV, O1s peak at 532.2 eV, and S2p peak at 168.15 eV can be assigned to Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The Fe2p peak at 710.3 eV, in combination with the S2p peak at 161.5 eV, is attributed to FeS. Complex chemical reactions occurred between the additives and counterparts in the frictional contact area under a high temperature and pressure during the rubbing process. The modifier of the Cu nanoparticles decomposed on the surface of the steel ball. Some decomposed products were directly adsorbed on the contact surface of the counterparts, and others reacted with the other materials. The decomposed modifier underwent a complex tribochemical reaction with the steel ball to form Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and FeS on the friction surface of the steel ball, which were finally transferred to the surface of the silicon wafer, as the hardness of silicon wafer is much greater than that of the steel ball. Moreover, the O1s peak at 531.1 eV corresponds to the hydroxyl groups of organic compounds. For comparison, a stainless-steel disk was selected as the lower counterpart to detect the composition of the lubricating film. It can be observed that the composition of the lubricating film on the wear track of the steel disk (see Fig. S2 in the ESM) is similar to that of the silicon wafer (see Fig. 10), except that there is a Fe<sup>0</sup> peak (Fe2p3/2: 706.7 and Fe2p1/2: 719.8) in the Fe2p spectrum. These XPS results reveal that the modifier of Cu nanoparticles underwent a complex tribochemical reaction on the friction pairs during the test and generated a lubricating film on the rubbing surface, which effectively improved the

tribological properties of distilled water.

From the above XPS results of the worn surface of the silicon wafer, we can infer that a boundary film mainly composed of Cu, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeS, and an organic N-containing compound was formed via lubrication with distilled water containing water-soluble Cu nanoparticles. The resulting lubricating film was physically and chemically adsorbed on the surface of the friction pairs, which could effectively prevent the direct contact of the rubbing surfaces, thereby improving the tribological properties. Furthermore, the following empirical formula was used to calculate the thickness of the lubricating film [41, 42].

$$\lambda = \frac{h_{\min}}{R'q},$$

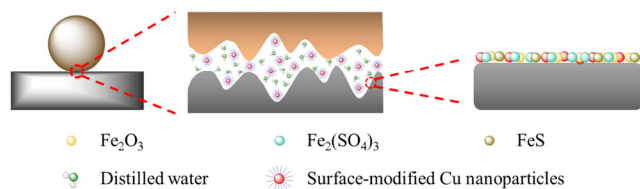
$$h_{\min} = 1.92 \times R' \left( \frac{V\eta_0}{R'E'} \right)^{0.67} \times (\partial E')^{0.53} \times \left( \frac{P}{R'^2 E'} \right)^{-0.067}, \quad (1)$$

$$\eta_0 = V_t \rho_t,$$

$$R'q = \sqrt{R'^2 q_1 + R'^2 q_2}$$

In Eq. (1),  $\lambda$  is the film thickness ratio, and it is often used as the criterion to determine the lubrication state. If  $\lambda$  is not greater than 0.8, the lubrication regime is boundary lubrication. If  $\lambda$  is between 0.8 and 3, the lubrication state is mixed lubrication. When  $\lambda$  is greater than 3, the lubrication state is hydrodynamic lubrication.  $h_{\min}$  is the thickness of the lubricating film, and  $R'q$  is the comprehensive surface roughness.  $R'q_1$  and  $R'q_2$  are the root mean square roughness values of the two surfaces.  $R'$  is the mixing radius; if the contact is a point contact,  $R'$  is the ball radius.  $V$  and  $\eta_0$  are the sliding speed and kinematic viscosity, respectively.  $\partial$  is the viscosity–pressure coefficient.  $E'$  and  $P$  are the mixed elastic modulus and load, respectively. The lubricating film thickness ( $h_{\min}$ ) is calculated to be  $3.69 \times 10^{-10}$  m using the empirical formula, when the concentration of water-soluble Cu nanoparticles is 0.6 wt%. The value of  $\lambda$  is 0.04, indicating that the lubrication regime is boundary lubrication when the concentration of water-soluble Cu nanoparticles is 0.6 wt%.

According to the above results, the lubrication model of the water-soluble Cu nanoparticles used as an additive in distilled water is schematically illustrated in Fig. 11.



**Fig. 11** The lubrication model of as-synthesized water-soluble Cu nanoparticles as additive in distilled water.

First, the water-soluble Cu nanoparticles are uniformly dispersed in distilled water and they enter the friction zone during the friction process, becoming adsorbed on the surface of the friction pairs. The copper nucleus is deposited on the surface of the friction pairs and the surface modifier undergoes a physical adsorption or/and chemical reaction on the frictional surface at the local high temperature and high pressure, forming a lubricating film containing Cu,  $\text{Fe}_2(\text{SO}_4)_3$ , FeS, and N-containing organic matter on the surface of the friction pairs, demonstrating friction-reducing and anti-wear mechanisms in the friction process. Furthermore, the Cu nanoparticles in the distilled water can accelerate the heat transfer process, reducing the local high temperature, thereby reducing friction and wear.

## 4 Conclusions

Water-soluble Cu nanoparticles were prepared using *in-situ* surface modification. The as-prepared water-soluble Cu nanoparticles had a diameter of 3 nm. They were readily soluble in water and could significantly improve the tribological properties of distilled water. Compared with lubrication using pure water alone, the friction coefficient, wear scar diameter, and wear rate could be reduced by 80.6%, 85%, and 99.9% via lubrication with 0.6 wt% water-soluble Cu nanoparticles, respectively. This is because water-soluble Cu nanoparticles used as an additive in distilled water underwent a tribochemical reaction during the friction process to form a boundary lubrication film consisting of Cu,  $\text{Fe}_2(\text{SO}_4)_3$ , FeS, and an organic N-containing compound on the surface of the friction pairs, which significantly improved the tribological properties of distilled water. Furthermore, the as-prepared Cu nanoparticles in distilled water also improved the heat transfer process and reduced the

local temperature of the friction pairs, thereby reducing the friction and wear of the friction pairs.

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**Pingyu ZHANG.** He is a professor and director of the Engineering Research Center for Nanomaterials in Henan University. He received his Ph.D. degree from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences in

2000. His current research interests cover nanoparticle lubricant additives, high performance lubricants and functional materials, and the tribology of materials. He has published over 100 journal papers and gained a number of ministerial and provincial-level science and technology awards.



**Guangbin YANG.** He received his Ph.D. degree in condensed matter physics in 2011 from Henan University. Now he is an associate professor at Henan University. His

research areas cover the nanotribology, the lubricants and nano-additives. He has published more than 50 journal papers and possesses 2 ministerial and provincial-level science and technology awards.



**Junhua ZHAO.** She received her bachelor degree in inorganic non-metal material engineering in 2015 from North China University of Water Resources and Electric Power, Zhengzhou, China. After then, she

is a master graduate student in the Engineering Research Center for Nanomaterials, Henan University, Kaifeng, China. Her research interests are focused on preparation and tribological properties investigation of water-based lubricating additives.