Controllable synthesis of different morphologies of CuO nanostructures for tribological evaluation as water-based lubricant additives

Junhua ZHAO, Guangbin YANG*, Yujuan ZHANG, Shengmao ZHANG, Chunli ZHANG, Chuanping GAO, Pingyu ZHANG*

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

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Abstract: In this study, water soluble CuO nanostructures having nanobelt, nanorod, or spindle morphologies were synthesized using aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NaOH by adjusting the type of surface modifier and reaction temperature. The effect of morphologies of these various CuO nanostructures as water-based lubricant additives on tribological properties was evaluated on a UMT-2 micro-friction tester, and the mechanisms underlying these properties are discussed. The three different morphologies of CuO nanostructures exhibited excellent friction-reducing and anti-wear properties. Tribological mechanisms differed in the initial stage of frictional interactions, but in the stable stage, a tribochemical reaction film and adsorbed lubricious film on the rubbing surfaces played important roles in hindering direct contact between friction pairs, leading to improved tribological properties.

Keywords: CuO nanostructures; morphology; water-based lubricant additive; tribological properties

1 Introduction

As the society is progressing, people are increasingly demanding environmental protection and resource conservation. Protecting the environment has become an important global concern, particularly in relation to conserving resources. Water-based lubricants are environmentally friendly, inexpensive, safe, and easy to clean, and possess excellent cooling properties. Consequently, they find application in many fields, including metal cutting, mechanical processing, and as drilling fluids [1–4]. However, water-based lubricants experience limitations to their wider practical application [5] due to their intrinsic limitations, including insufficient lubricity, poor rust resistance, and short service life. Therefore, it is necessary to develop high performance water-soluble additives with friction-reducing, anti-wear, and thermal conductivity to expand

the application range of water-based lubricants.

Many nanomaterials are beneficial for improving tribological properties of water-based lubricants [6–8]. Graphene and graphene oxide [9–11], carbon dots [12], hard carbon spheres [13], carbon nanotubes [14], ionic liquids [15], sulfides [16–18], oxides [2, 7, 19], and metal nanocopper [20, 21] have been designed and synthesized to improve the performance of water. Furthermore, a number of lubrication mechanisms have been proposed to explain the improvement of tribological performance, including: (a) formation of physical or/and chemical tribofilms. Such protective films prevent direct contact between friction surfaces, leading to promising tribological properties; (b) generation of a rolling effect, whereby nano-additives rolled between frictional surfaces result in decreased friction and wear; (c) mending effect, whereby nano-additives infill the defects of friction surfaces, thus improving

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

their wear resistance; (d) polishing effect, whereby nano-additives polish the rough surface and decrease frictional forces.

The molecular structure of nanoparticles has a significant influence on tribological behaviors. The morphology of nanoparticles also exerts an effect on reducing friction, but has a trivial influence on anti-wear properties. Onion- and flake-shaped nanoparticles exhibited superior tribological properties compared to other morphologies (nanotube and granular) [6]. Recently, Dong et al. [22] demonstrated that smooth flaky MoS_2 exhibited better lubrication than spherical MoS_2 nanoparticles. This was because it was easier to shear for flaky MoS_2 and subsequently transfer the sheared nanoparticle to the metal surfaces, where they acted as a lubricant. Israelachvili et al. [23, 24] demonstrated that ZnS nanorods exhibited superior micro-tribological behavior compared to nanowires and spherical nanoparticles. It is pertinent to note the geometrical shape of ZnS nanorods, which tend to roll, and possibly slide, in confined layers. The influence of morphology on tribological properties needs further study.

Cupric oxide (CuO) has attracted significant attention in a wide range of applications due to its unique physical and chemical properties. It has been widely used as a coloring agent, antifouling coating, and has a non-negligible influence in many fields, including as sensors, electrochemistry, semiconductor optics, electronics, and solar cell film [25–28]. Nanoparticles of CuO can also kill microorganisms [29–31] and therefore have potential applications in biology [32, 33]. Researchers have also studied the tribological properties of CuO nanoparticles. Peña-Parás et al. [34] selected CuO and Al_2O_3 nanoparticles as additives to a fully-formulated oil and PAO8 based oil. CuO nanoparticles showed positive effects on the tribological properties for both oils due to nanoparticle triboentering onto the surfaces. However, Al_2O_3 nanoparticles acted as an abrasive and exerted a detrimental effect on both oils. In addition, Alves et al. [35] highlight that the tribological behavior of CuO and ZnO nanoparticles is pertinent to base oil. Mineral oil can achieve the best performance following the introduction of ZnO nanoparticles, while synthetic oil, combined with CuO nanoparticles, produced excellent tribological properties.

In contrast, the addition of CuO and ZnO nanoparticles to sunflower and soybean oils resulted in weak tribological performance. However, the introduction of CuO nanoparticles to coconut oil was beneficial to improving friction-reducing and anti-wear properties [36]. Chimeno-Trinchet et al. [37] prepared spherical and prolate CuO nanoparticles modified with silane as additives in base oil 68. The addition of 0.1% CuO nanoprolates reduced both the friction coefficient and wear volume, compared to the base oil, owing to the mending effect of CuO nanoprolates between the contacting bodies. However, CuO nanospheres did not improve lubricity. Spherical CuO nanoparticles, with a diameter of 50–300 nm, were inferior to MoS_2 nanosheets. Thus, the tribological properties of the friction pairs significantly depend on size, morphology and composition of nanomaterials, and type of base oil.

As a stable oxide of copper, CuO with different morphologies have been synthesized, including nanoneedle, nanowire, nanosheet, nanorod, nanobelt, nanotube, nanowhisker, and nanoparticle [38–44]. It also has good thermal conductivity and excellent stability in air. Yang et al. [45] used a double coating of CuO nanoparticles with sodium oleate and ethyl acetate to prepare water-soluble CuO nanoparticles, using a homogeneous precipitation method. They found that CuO nanoparticles in distilled water had friction-reducing and anti-wear properties. In addition, Minakov et al. [46] used CuO nanoparticles, modified with xanthan gum polymers, as nano-fluid additives and demonstrated a significant increase in the heat transfer coefficient and the coefficient was proportional to the concentration of CuO additive. Previous studies have demonstrated that nanomaterials with good thermal conductivity can accelerate heat transfer and reduce localized high temperatures of frictional surfaces [18, 21].

In this paper, CuO nanostructures with different morphologies (nanobelts, nanorods, and spindle shapes) were synthesized, using polyvinyl pyrrolidone (PVP) as dispersant and polyethylene glycol (PEG) as guiding agent, by *in-situ* surface modification. The tribological properties of CuO with three different morphologies were compared and their tribological mechanisms are discussed.

2 Experimental

2.1 Chemicals

Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and PEG-400 were acquired from Tianjin Kemiou Chemical Reagent Co., Ltd. PVP-300000 was produced by Sigma-Aldrich. Sodium hydroxide and ammonia were obtained from Luoyang Haohua Chemical Reagent Co., Ltd. Commercial water-based lubricants were provided by Henan Xindaxin Materials Co., Ltd. All the chemical reagents used in our research are of analytical grade and used without further purification. The experiments were carried out in distilled water.

2.2 Material synthesis

2.2.1 Synthesis of nanostructured CuO with nanobelt morphology

In a typical synthesis experiment, 0.22 g of PVP and 0.234 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 10 mL of distilled water agitated with a magnetic stirrer. After the mixture was heated to 90 °C, 2 mL of NaOH (1 M) was added and stirred for another 60 min. The color of the solution changed from blue to dark brown and CuO nanobelts were obtained.

2.2.2 Synthesis of nanostructured CuO with nanorod and spindle shapes

CuO nanostructures were synthesized by *in situ* surface modification. First, 0.22 g of PVP, 5 mL of PEG, and 1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 5 mL of distilled water in a round-bottom flask and the solution was agitated with a magnetic stirrer. 2 mL NaOH solution (1 M) was added to the resultant mixture at a range of specific temperatures, and stirred for a range of durations, until the color of the solution turned dark brown. CuO nanomaterials with nanorod or spindle shapes were obtained through adjustments of the reaction time and temperature.

In each instance, the final CuO nanostructures were obtained by centrifugation and repeated washing, and were subsequently dried at 80 °C.

2.3 Characterization

The crystallography and composition of the as-prepared CuO nanostructures were characterized by D8-Advance

X-ray power diffraction (XRD). The morphologies of the nanomaterials were surveyed by transmission electron microscopy (TEM, JEM-2010). The thermal stability analysis was conducted by a thermogravimetric analyzer (TGA, Mettler Toledo) in a nitrogen atmosphere. Finally, the surface chemistry structures of the CuO nanostructures were measured by a Vertex 70 Fourier transform infrared (FTIR) spectrometer.

2.4 Tribological properties evaluation

The tribological properties of the nanobelt, nanorod, and spindle shaped CuO nanostructures as lubricant additives were evaluated on a UMT-2 tribotester in a ball-on-plate mode, at a sliding speed of 20 mm/s, and a test duration of 30 min. Si_3N_4 balls ($\phi 4$) and 304 stainless steel plate were selected as counterparts in reciprocating sliding with a stroke of 5 mm. The test concentration of CuO nanostructures ranged from 0.1 wt% to 2.0 wt% in distilled water and the plot of friction coefficient with time was automatically recorded by the tribotester.

The thermal conductivity of CuO nanomaterials as additives to distilled water was tested on a TC 3000E thermal conductivity meter at a test temperature of 22 °C, a test voltage of 3 V, and an acquisition time of 6.5 s.

A Contour GT-K white light interferometer was employed to determine the morphology, depth, and width of wear scar and wear track. An AXIS ULTRA X-ray photoelectron spectroscope (XPS) was used to examine the chemical composition of the protective film formed on the rubbing surface.

3 Results and discussion

3.1 Controllable synthesis of CuO nanostructures

CuO nanobelts were synthesized using an aqueous solution of NaOH and $\text{Cu}(\text{NO}_3)_2$ in the presence of PVP. TEM images of CuO nanobelts demonstrated that they were uniformly dispersed without obvious agglomeration (Fig. 1). The width and length of the CuO nanobelts were approximately 7 nm and 25–130 nm, respectively. CuO nanobelts were obtained upon the decomposition of the copper hydroxide,

Fig. 1 TEM images of as-prepared CuO nanobelts with different magnification: (a) 10,000 $\times$, (b) 30,000 $\times$, (c) 50,000 $\times$, and (d) 80,000 $\times$.

which was an intermediate product formed during the experimental process under alkaline conditions, as previously reported [44].

The volume of distilled water was reduced by half, 5 mL of PEG was added to the water, and other reactants were the same as those for preparing CuO nanobelts. By changing reaction temperature and duration, CuO nanorods and spindle CuO nanostructures were obtained. When the reaction temperature remained at 90 °C, the final product was CuO nanorods. At this temperature, the reaction solution blackened rapidly after adding NaOH because CuO nanostructures can be rapidly formed at high temperature. With increasing reaction time, the diameter of CuO nanostructures increased (see Fig. S1 in the Electronic Supplementary Material (ESM)). Nanorods produced after 3 h reaction time were uniform in size, well dispersed, and with a length and diameter of about 20–30 nm and 6 nm, respectively (Fig. 2).

When the reaction temperature was 50 °C, the nanostructures produced were all spindle shaped. Spindle CuO nanostructures produced at 50 °C and a reaction time of 8 h were about 60 nm in the widest part and 230 nm in length (Fig. 3). The spindle CuO nanostructures were composed of slender nanorods and were well dispersed and distributed (Fig. S2 in the

Fig. 2 TEM images of CuO nanorods prepared at 90 °C for 3 h with different magnification: (a) 40,000 $\times$ and (b) 80,000 $\times$.

Fig. 3 TEM images with different magnification of the as-prepared spindle shape CuO nanostructure obtained by reaction temperature of 50 °C and reaction time of 8 h: (a) 10,000 $\times$, (b) 15,000 $\times$, (c) 40,000 $\times$, and (d) 100,000 $\times$.

ESM). It is inferred that spindle CuO nanostructures were formed by self-assembly of CuO nanorods. With increasing reaction time, the morphology of spindle CuO nanostructures became more regular and their size gradually increased.

Reaction time, reaction temperature, and PEG concentration played significant roles in controlling the morphology of CuO nanostructures. The process of formation of CuO nanostructures with different morphologies is presented in Fig. 4. The intermediate $\text{Cu}(\text{OH})_2$ was formed by adding NaOH to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Nanobelts of CuO were synthesized by thermal decomposition of $\text{Cu}(\text{OH})_2$ with PVP as the dispersant and coating agent in the reaction

Fig. 4 Schematic diagram of the formation process of CuO nanostructures.

solution. Following the interaction of PVP and PEG, CuO rapidly nucleated to form CuO nanorods at a high temperature of 90 °C. Conversely, CuO slowly nucleated to form slender nanorods, which ultimately assembled into spindle CuO nanostructures. In this reaction process, PEG acted as a molecular guiding agent to align the nanorods in parallel, thereby achieving the same crystallization orientation. Moreover, hydrophilic groups in PEG result in a uniform dispersal of CuO nanostructures in water.

3.2 Structural analysis of CuO nanostructures

Major peaks in XRD patterns for the CuO nanostructures with different morphologies were located at 2θ values of 25° to 90° (Fig. 5), which correspond to the typical diffraction characteristics of monoclinic phase CuO [47]. This XRD pattern was consistent with Joint Committee on Powder Diffraction Standards (JCPDS) card no. 45-0937, and no other peaks corresponding to impurities obtained, indicating the presence of pure monoclinic CuO. Among the XRD patterns of CuO nanostructures with three different morphologies, the (002) peak strength of spindle CuO nanostructures was the highest because of the

Fig. 5 Representative XRD patterns of the CuO nanostructures with different morphologies.

clear crystal orientation. The XRD peak broadening of CuO nanorods was the most prevalent due to the small sizes of the CuO nanorods prepared in this study.

The FTIR spectra of the CuO nanostructures with different morphologies and using the raw materials of PVP and PEG were recorded for 400–4,000 cm^{-1} (Fig. 6). The characteristic peaks positioned at 516 and 608 cm^{-1} can be ascribed to the stretching vibrations of Cu–O bonds [48, 49]. In the FTIR spectra of CuO nanobelts, the broad absorption peak at $\sim 3,434$ cm^{-1} was due to H–O–H vibrations of hydroxyl groups in water molecules, indicating that there were some adsorbed water molecules on the surface of CuO nanobelts [47]. The absorption peaks of 2,923 and 2,862 cm^{-1} in the spectra of the CuO nanobelts correspond to the asymmetric and symmetrical stretching vibration of C–H. Finally, the peak at 1,636 cm^{-1} may be attributed to the stretching vibration of C=O resulting from PVP capped on the surface of CuO nanobelts. The CuO nanorods and spindle CuO nanostructures were also analyzed by FTIR spectroscopy. The absorption peaks positioned at around 3,434 cm^{-1} in CuO nanorods and spindle CuO nanostructure can be assigned to the stretching vibration of OH groups originating from PEG or water. The existence of peaks at about 1,636 cm^{-1} was assigned to the ketone

Fig. 6 FTIR spectra of CuO nanostructures with different morphologies.

group of PVP adsorbed on the CuO surface. The peaks of 2,923 and 2,862 cm^{-1} in the spectra show $-\text{CH}_2$ and $-\text{CH}_3$ stretching band. The stretching vibration bands for the three morphologies of CuO were clearly observed at 1,441 cm^{-1} (CH_2) and 1,281 cm^{-1} (C–N), indicating a successful coating of PVP on the surface of the CuO nanostructures. Furthermore, the peak at 1,103 cm^{-1} was due to the C–O stretching vibration [50], indicating PEG also coated the surface of CuO nanorods and spindles.

Thermogravimetric analysis curves of CuO nanobelts, nanorods, and spindles are presented in Fig. 7. The three CuO nanostructures started weight loss at around 100 °C because of the small amount of moisture associated with them. The largest and most pronounced weight loss occurred at about 280 °C, and this was ascribed to the decomposition of PVP coated on the surface of all three nanostructures of CuO. In contrast to the TGA curve of CuO nanobelt, CuO nanorods and spindle nanostructures exhibited another relative slow weight loss at near 350 °C, which was due to the decomposition of PEG on the surface of CuO. No significant additional weight loss was observed from 500 to 800 °C, indicating PVP and PEG had been almost completely decomposed. It can therefore be concluded that the surface of CuO nanobelts were coated only with PVP as a modifier, and the weight fraction was approximately 17.1%. CuO nanorods and spindle were coated with two modifiers, PVP and PEG,

Fig. 7 TGA curves of CuO nanostructures with different morphologies under N_2 atmosphere at a heating rate of 10 °C/min.

and their total weight fractions were about 21.0% and 17.1%, respectively. PVP and PEG were coated on the surface of hydrophilic CuO nanostructures [51, 52] by physical adsorption and this further improved the water solubility of CuO nanostructures.

3.3 Tribological properties of CuO nanostructures

Figure 8 illustrates the test results of the friction coefficient for distilled water, water-based lubricants, PEG, and the three different morphologies of CuO nanostructures in distilled water. The friction coefficient (about 0.57) did not change significantly as the concentration of PEG in water increased to a maximum of 2 wt% (Fig. 8(a)). When CuO nanostructures with different morphologies were added to water, the friction coefficient initially decreased and then increased with increased concentration. The friction coefficient was the lowest (0.168, 0.169, and 0.199 for nanobelts, nanorods, and spindles, respectively) when the concentration of CuO nanostructures was 0.8 wt%. Compared with the friction coefficient of distilled water (0.576), the friction coefficients were reduced by 70.9%, 70.7%, and 65.4%, for nanobelts, nanorods, and spindles, respectively. Similarly, the friction coefficients were reduced by 52.2%, 51.8%, and 43.2%, compared to the friction coefficient of commercial water-based lubricants (0.351; Fig 8(b)), respectively, showing good friction-reducing performance. When the concentration of CuO nanostructures in water exceeded 0.8 wt%, the friction coefficient increased, indicating that the optimal concentration (0.8 wt%) at which the friction coefficient is the minimum, under the given experimental conditions [36]. At lower concentrations, a homogenous and continuous lubricating film was not formed on the rubbing surface during the test. At the optimum concentration (0.80 wt%), the nanoadditives filled the valleys within asperities, and formed a fine lubricating film which prevented the friction pairs from direct contact, leading to a reduced friction coefficient. Above the optimum concentration, random aggregation occurred on the surface of the friction pairs, which was higher than the thickness of the water film in the contact region and this caused abrasive wear, resulting in an increased friction coefficient [10, 36, 53–55]. Variations of friction coefficient with sliding time are presented in Fig. 8(b). The friction

Fig. 8 The results of the friction test. (a) Friction coefficient as a function of concentration, (b) variations of friction coefficient with sliding time, and (c) relationship between friction coefficient and applied load.

coefficient did not exhibit an obvious change after the addition of 0.8 wt% PEG to distilled water and the friction coefficient remained at about 0.57, equivalent to the friction coefficient of water (0.576) (Fig. 8(b)). The friction coefficient of the water-based lubricant was significantly lower than that of distilled water. When 0.8 wt% of the three morphologically different CuO nanostructures in aqueous solutions were used as lubricants, the friction coefficient was significantly reduced, and the curve of friction coefficient *versus*

time was relatively stable, compared with commercial lubricants and water. Running-in time was the shortest during lubrication with 0.8 wt% CuO nanobelts. Nanobelts were able to easily enter between the rubbing surfaces and formed a protective film. Furthermore, it was easily sheared and transferred to the counterpart [22, 56, 57], thereby enhancing the reduction of the friction coefficient. During lubrication with 0.8 wt% CuO nanorods, the friction coefficient was the smallest during the running-in period, which may be due to the rolling effect of nanorods [58, 59]. It required a relatively long time (about 200 s) for the spindle CuO nanostructures to attain a stable friction coefficient. It is speculated that the spindle CuO nanostructures were destroyed during the friction test and were dispersed to form slender nanorods. As wear increased, the CuO nanostructures with different morphologies formed a protective film and effectively reduced the friction coefficient. Figure 8(c) depicts the relationship between the friction coefficient and applied load for the 0.8 wt% aqueous solution of the three different CuO nanostructures compared with distilled water. The friction coefficients were relatively stable and much lower than those under distilled water lubrication with the increase of applied load, within the test range, thereby demonstrating excellent lubricity.

3.4 Worn surface analysis

The 3 dimensional (3D) morphologies and 2D profiles of wear scar and wear track were tested on a white light interferometer. Figure 9 exhibits the 3D morphologies of wear scar and corresponding wear track of surfaces lubricated with aqueous solution of 0.8 wt% CuO nanostructures with different morphologies, compared to distilled water and commercial water-based lubricants. The 2D profiles of the wear scars and matched wear tracks are presented in Fig. 10. The wear scar and the wear tracks of surfaces lubricated with distilled water were very large and wide, and the furrows were very deep on the worn surface (Figs. 9(a) and 10). The wear scar arising on surfaces lubricated with a water-based lubricant was slightly smaller, compared with that lubricated with distilled water, but many furrows along the direction of friction were apparent (Figs. 9(b) and 10). When 0.8 wt% aqueous solutions of CuO nanostructures with different

Fig. 9 The 3D morphologies of the worn surface on Si_3N_4 ball (left) and 304 stainless steel plate (right) lubricated by (a) distilled water, (b) commercial water-based lubricants, (c) 0.8 wt% CuO nanobelts, (d) 0.8 wt% CuO nanorods, and (e) 0.8 wt% spindle CuO nanostructures (speed: 0.02 m/s, load: 2.0 N, time: 30 min).

morphologies were used as lubricants, the size of wear scars were significantly reduced, and the surface roughness of wear scars were relatively small and smooth. The volumes of the wear scars lubricated by CuO nanobelts, nanorods, and spindle nanostructures were 3,458.2, 4,444.5, and 8,702.6 μm^3 , respectively, a reduction of 89.1%, 86.0%, and 72.6%, compared with distilled water lubrication (31,795.7 μm^3), respectively. Compared with the volume of wear scar during lubrication with a commercial water-based lubricant,

the volume of the wear scars lubricated by CuO nanobelts, nanorods, and spindle nanostructures were reduced by 84.9%, 80.6%, and 62.0%, respectively. Thus, the CuO nanostructures with different morphologies exhibited significantly better, and excellent, anti-wear properties than distilled water and water-based lubricants. Moreover, CuO nanobelts exhibited the most remarkable anti-wear property. The width of wear tracks lubricated by 0.8 wt% CuO nanorods and spindles were similar to those lubricated by a

Fig. 10 The cross-section profiles of (a) wear scar on Si_3N_4 ball and (b) wear track on 304 stainless steel plate.

water-based lubricant. However, the width of the wear tracks was significantly narrower than those of distilled water. The width of wear tracks lubricated by 0.8 wt% CuO nanobelts was the narrowest, and its wear rate was $22.2 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$, 16.5% lower than that of wear tracks arising during lubrication with water ($26.5 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$), and 3.5% smaller compared with a commercial water-based lubricant. A possible explanation for the reduction in wear is the formation of a protective film, which separated direct contact between asperities, thereby reducing wear.

To analyze the tribological mechanisms of CuO nanostructures with different morphologies as lubricant additives in distilled water, surface analysis by XPS was

performed on the rubbing surface of 304 stainless steel plates. Figure 11 presents the XPS spectra of C 1s, O 1s, N 1s, Cu 2p, and Fe 2p of wear tracks on stainless steel plates lubricated by aqueous solution of 0.8 wt% CuO nanobelts. The peaks of 284.6, 284.8, 288.6, and 289.0 eV in C 1s were assigned to C–H, –C, C–N, and C=O in PVP, respectively, while peaks of 530.2, 531.1, 532.0, and 533.0 eV in O 1s correspond to Fe_2O_3 , Cu_2O , O–H, and C=O, respectively. The hydroxyl group was derived from the surface of CuO since CuO is a hydrophilic oxide. The peaks of 932.7 and 952.5 eV in Cu 2p and O 1s at 531.1 eV were attributed to the formation of Cu_2O . Combining the peaks of 710.8 and 724.0 eV in Fe 2p and the peaks of O 1s at 530.2 eV, it is

Fig. 11 XPS spectra of wear track on 304 stainless steel plate lubricated by aqueous solution of 0.8 wt% CuO nanobelts (speed: 0.02 m/s, load: 2.0 N, time: 30 min).

concluded that Fe_2O_3 was formed during the friction test. The peak at 399.9 eV in N1s is due to nitrogen-containing organic compounds. Therefore, when 0.8 wt% CuO nanobelts in aqueous solution was used as the lubricant, a protective film composed of Cu_2O , Fe_2O_3 , and organic nitrogen compounds was formed on the surface of the wear track, which played an important role in reducing friction and increasing anti-wear.

Figure 12 shows the XPS spectra of C 1s, O 1s, N 1s, Cu 2p, and Fe 2p on the wear track of surfaces lubricated by 0.8 wt% CuO nanorods in aqueous solution. The peaks at 284.6, 284.8, 286.5, 288.6, and 289 eV in C 1s correspond to C–H, C–C, C–O, C–N, and C=O in organic modifiers, respectively. In particular, the C–N and C=O bonds were derived from the modifier PVP, while the C–O bond originated from PEG. The peaks of 531.7 and 533.0 eV in O 1s were assigned to C–O and C=O bonds, respectively. The peaks at 932.7 and 952.5 eV in Cu 2p correspond to Cu 2p_{3/2} and Cu 2p_{1/2}, corresponding to Cu_2O , where the oxygen corresponds to the peak of 531.1 eV in O 1s. It is noteworthy that there was no satellite peak (941 eV) of divalent copper in Cu 2p [60, 61]. Instead of CuO, Cu_2O was generated here because CuO decomposed under high temperature and high pressure to produce Cu_2O and O_2 . In Fe 2p,

the peaks at 707.0 and 720.1 eV correspond to 2p_{3/2} and 2p_{1/2} of zero-valent iron, which originated from 304 stainless steel. The combination of 710.9 eV (2p_{3/2}) peak in Fe 2p and 530.2 eV peak in O 1s demonstrated that Fe_2O_3 had been formed, indicating the occurrence of a tribological chemical reaction between oxygen and the metal friction pairs during the friction test. In addition, the peak of O 1s at 532.2 eV was ascribed to the O–H bond from PEG, while the peak of N 1s at 399.9 eV was designated as nitrogen-containing organic compound, indicating that the PVP on the surface of CuO was decomposed and adsorbed on the surface of the friction pairs during rubbing.

The XPS spectra of wear tracks on steel plates lubricated by an aqueous solution of 0.8 wt% spindle CuO nanostructures (Fig. S3 in the ESM) were consistent with those on the surface of wear tracks lubricated by an aqueous solution of 0.8 wt% CuO nanorods. When an aqueous solution of 0.8 wt% spindle CuO nanostructures was used as the lubricant, the friction coefficient required a longer time to stabilize than that of CuO nanorods and nanobelts (Fig. 8), which is ascribed to the self-assembly of nanorods of CuO by CuO spindles. During the friction test the spindle structure was destroyed and dispersed into slender CuO nanorods because of the high temperature

Fig. 12 XPS spectra of wear track on 304 stainless steel plate lubricated by aqueous solution of 0.8 wt% CuO nanorods (speed: 0.02 m/s, load: 2.0 N, time: 30 min).

and high pressure. Subsequently, the mechanism of amelioration of friction was similar to that of CuO nanorods.

Based on the experimental wear data and the friction surface analysis discussed above, models of the mechanisms of lubrication by CuO nanostructures with different morphologies were proposed (Fig. 13). At the beginning of sliding, the extremely small thickness of CuO nanobelts allowed them to enter the sliding contact area easily (Fig. 13(a)). When one roughness peak of one surface was approaching a peak on the second surface, CuO nanobelts were absorbed on the contact surface and were not pushed away [57, 62]. When the two opposite peaks on the ball and plate surfaces touched, they were prevented from direct contact because of the thin layer of CuO nanobelts between them [62]. Although they may be deformed owing to the imposition of a load, wear of the two surfaces was minimized under the protection of the thin CuO nanobelts. After the two roughness peaks separate, the nanobelts may adhere to the peaks or return to the lubricant. As the reciprocating sliding continued, a protective film was formed across the rubbing surfaces and some tribochemical reactions may take place under high contact pressure during sliding. Finally, a complex adsorbed film and/or

tribochemical reaction film on the friction surfaces was formed which were sufficiently smooth to result in low friction and wear [22, 57].

The anti-wear and friction-reducing properties of CuO nanorods could be attributed to their rolling effect [58, 59]. During the running-in stage, the friction coefficient was effectively reduced because the roller like nanorods facilitate a rolling effect between the contact surfaces [59] (Fig. 13(b)). Under the repeated action of pressure and frictional heat, CuO nanorods can be entrapped and then deposited onto contact interfaces. As the sliding continues, a CuO protective film is formed on the rubbing surface. Furthermore, the CuO nanorods can participate in tribochemical reactions and generate tribochemical reaction films on the rubbing surfaces, thereby preventing direct contact between asperities on the Si_3N_4 ball and the 304 stainless steel plate, and improved the tribological properties [59]. When spindle CuO nanostructures entered the interface between the friction pairs, they decomposed into CuO nanorods under the action of friction and shear [6] (Fig. 13(c)). Subsequently, the tribological mechanisms were similar to those of CuO nanorods. Finally, CuO nanomaterials can significantly increase the thermal conductivity of distilled water (Fig. S4 in the ESM), which accelerates heat dissipation

Fig. 13 The schematic of lubrication mechanisms under aqueous solution lubrication of (a) CuO nanobelts, (b) CuO nanorods, and (c) spindle CuO nanostructures.

and avoids local overheating of friction pairs, further contributing to the improvement of tribological properties.

4 Conclusions

In summary, three CuO nanostructures with different morphologies (nanobelt, nanorod, and spindle shaped) were synthesized in aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NaOH by adjusting the type of surface modifier present, reaction time, and reaction temperature. The tribological test results demonstrated that the morphology of CuO nanostructures exerted a great influence on their friction-reducing and anti-wear properties. The CuO nanostructures, as water-based lubricant additives, all significantly enhanced the tribological performance of distilled water. In particular, CuO nanobelts exhibited excellent anti-wear effects and were more effective than the other two nanostructures. This was attributed to the formation of a protective film on the surface of the friction pairs. CuO nanorods exhibited a lower friction coefficient than the remaining two at the running-in stage because the nanorods demonstrated a rolling effect between the friction pairs and reduced the friction coefficient. As duration of frictional interaction increased, the surface of friction pairs lubricated with a CuO nanorod aqueous solution formed the same uniform and complete protective film as surfaces lubricated with nanobelts, achieving almost the same friction coefficient. The spindle CuO nanostructures with large particle size were assembled from slender rods. They decomposed into slender rods during the frictional interaction. Subsequently, the mechanism underpinning the reduction in friction was similar to that of nanorods. It is concluded that a complex protective film was formed and prevented the direct contact between asperities of the friction pairs, thereby enhancing the anti-wear and friction-reducing capacities of water.

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Reference

- [1] Yang Y, Zhang C, Dai Y, Luo J. Tribological properties of titanium alloys under lubrication of SEE oil and aqueous solutions. *Tribol Int* **109**: 40–47 (2017)
- [2] Wu H, Zhao J, Xia W, Cheng X, He A, Yun JH, Wang L, Huang H, Jiao S, Huang L. et al. Analysis of TiO_2 nano-additive water-based lubricants in hot rolling of microalloyed steel. *J Manuf Process* **27**: 26–36 (2017)
- [3] Saffari H, Soltani R, Alaei M, Soleymani M. Tribological properties of water-based drilling fluids with borate nanoparticles as lubricant additives. *J Petrol Sci Eng.* **171**: 253–259 (2018)
- [4] Chen Q, Wang X, Wang Z, Liu Y, You T. Preparation of water-soluble nanographite and its application in water-based cutting fluid. *Nanoscale Res Lett* **8**: 52 (2013)
- [5] Tomala A, Karpinska A, Werner W, Olver A, Störi H. Tribological properties of additives for water-based lubricants. *Wear* **269**: 804–810 (2010)
- [6] Dai W, Kheiraddin B, Gao H, Liang H. Roles of nanoparticles in oil lubrication. *Tribol Int* **102**: 88–98 (2016)

- [7] Wu H, Zhao J, Xia W, Cheng X, He A, Yun J H, Wang L, Huang H, Jiao S, Huang L. A study of the tribological behaviour of TiO₂ nano-additive water-based lubricants. *Tribol Int* **109**: 398–408 (2017)
- [8] Ali M K A, Hou, Mai L, Chen B, Turkson R F, Cai Q. Reducing frictional power losses and improving the scuffing resistance in automotive engines using hybrid nanomaterials as nano-lubricant additives. *Wear* **364**: 270–281 (2016)
- [9] Xie H, Dang S, Jiang B, Xiang L, Zhou S, Sheng H, Yang T, Pan F. Tribological performances of SiO₂/graphene combinations as water-based lubricant additives for magnesium alloy rolling. *Appl Surf Sci* **475**: 847–856 (2019)
- [10] Guo P, Chen L, Wang J, Geng Z, Lu Z, Zhang G. Enhanced tribological performance of aminated nano-silica modified graphene oxide as water-based lubricant additive. *ACS Appl Nano Mater* **1**: 6444–6453 (2018)
- [11] Fan K, Liu J, Wang X, Liu Y, Lai W, Gao S, Qin J, Liu X. Towards enhanced tribological performance as water-based lubricant additive: Selective fluorination of graphene oxide at mild temperature. *J Colloid Interf Sci* **531**: 138–147 (2018)
- [12] Tang W, Wang B, Li J, Li Y, Zhang Y, Quan H, Huang Z. Facile pyrolysis synthesis of ionic liquid capped carbon dots and subsequent application as the water-based lubricant additives. *J Mater Sci* **54**: 1171–1183 (2018)
- [13] Cheng G, Dong L, Kamboj L, Khosla T, Wang X, Zhang Z, Guo L, Pesika N, Ding J. Hydrothermal synthesis of monodisperse hard carbon spheres and their water-based lubrication. *Tribol Lett* **65**: 141 (2017)
- [14] Wang B, Tang W, Liu X, Huang Z. Synthesis of ionic liquid decorated multi-walled carbon nanotubes as the favorable water-based lubricant additives. *Appl Phys A* **123**: 680 (2017)
- [15] Wang Y, Yu Q, Cai M, Zhou F, Liu W. Halide-free PN ionic liquids surfactants as additives for enhancing tribological performance of water-based liquid. *Tribol Int* **128**: 190–196 (2018)
- [16] Wang Y, Du Y, Deng J, Wang Z. Friction reduction of water based lubricant with highly dispersed functional MoS₂ nanosheets. *Colloid Surface A* **562**: 321–328 (2019)
- [17] Liu L, Liu Z, Huang P, Wu Z, Jiang S. Protein-induced ultrathin molybdenum disulfide (MoS₂) flakes for a water-based lubricating system. *RSC Adv* **6**: 113315–113321 (2016)
- [18] Zhao J, Yang G, Zhang Y, Zhang S, Zhang P. A simple preparation of HDA-CuS nanoparticles and their tribological properties as a water-based lubrication additive. *Tribol Lett* **67**: 88 (2019)
- [19] Bao Y, Sun J, Kong L. Effects of nano-SiO₂ as water-based lubricant additive on surface qualities of strips after hot rolling. *Tribol Int* **114**: 257–263 (2017)
- [20] Zhang C, Zhang S, Song S, Yang G, Yu L, Wu Z, Li X, Zhang P. Preparation and tribological properties of surface-capped copper nanoparticle as a water-based lubricant additive. *Tribol Lett* **54**: 25–33 (2014)
- [21] Zhao J, Yang G, Zhang C, Zhang Y, Zhang S, Zhang P. Synthesis of water-soluble Cu nanoparticles and evaluation of their tribological properties and thermal conductivity as a water-based additive. *Friction* **7**: 246–259 (2019)
- [22] Dong C, Yuan C, Wang L, Liu W, Bai X, Yan X. Tribological properties of water-lubricated rubber materials after modification by MoS₂ nanoparticles. *Sci Rep* **6**: 35023 (2016)
- [23] Akbulut M, Belman N, Golan Y, Israelachvili J. Frictional properties of confined nanorods. *Adv Mater* **18**: 2589–2592 (2006)
- [24] Min Y, Akbulut M, Prud'homme RK, Golan Y, Israelachvili J. Frictional properties of surfactant-coated rod-shaped nanoparticles in dry and humid dodecane. *J Phys Chem B* **112**: 14395–14401 (2008)
- [25] Zoolfakar A S, Rani R A, Morfa AJ, O'Mullane A P, Kalantar-Zadeh K. Nanostructured copper oxide semiconductors: a perspective on materials, synthesis methods and applications. *J Mater Chem C* **2**: 5247–5270 (2014)
- [26] Kumar SK, Suresh S, Murugesan S, Raj S P. CuO thin films made of nanofibers for solar selective absorber applications. *Sol Energy* **94**: 299–304 (2013)
- [27] El-Trass A, ElShamy H, El-Mehasseb I, El-Kemary M. CuO nanoparticles: synthesis, characterization, optical properties and interaction with amino acids. *Appl Surf Sci* **258**: 2997–3001 (2012)
- [28] Klinbumrung A, Thongtem T, Thongtem S. Characterization and gas sensing properties of CuO synthesized by DC directly applying voltage. *Appl Surf Sci* **313**: 640–646 (2014)
- [29] Booshehri A Y, Wang R, Xu R. Simple method of deposition of CuO nanoparticles on a cellulose paper and its antibacterial activity. *Chem Eng J* **262**: 999–1008 (2015)
- [30] Pelgrift RY, Friedman AJ. Nanotechnology as a therapeutic tool to combat microbial resistance. *Adv Drug Deliver Rev* **65**: 1803–1815 (2013)
- [31] Padil VVT, Černík M. Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application. *Int J Nanomed* **8**: 889–898 (2013)
- [32] Abboud Y, Saffaj T, Chagraoui A, El Bouari A, Brouzi K, Tanane O, Ihssane B. Biosynthesis, characterization and antimicrobial activity of copper oxide nanoparticles (CONPs) produced using brown alga extract (*Bifurcaria bifurcata*). *Appl Nanosci* **4**: 571–576 (2014)

- [33] Wongrakpanich A, Mudunkotuwa I A, Geary S M, Morris A S, Mapuskar K A, Spitz D R, Grassian V H, Salem A K. Size-dependent cytotoxicity of copper oxide nanoparticles in lung epithelial cells. *Environ Sci-Nano* **3**: 365–374 (2016)
- [34] Peña-Parás L, Taha-Tijerina J, Garza L, Maldonado-Cortés D, Michalczewski R, Lapray C. Effect of CuO and Al₂O₃ nanoparticle additives on the tribological behavior of fully formulated oils. *Wear* **332–333**: 1256–1261 (2015)
- [35] Alves S, Barros B, Trajano M, Ribeiro K, Moura E. Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions. *Tribol Int* **65**: 28–36 (2013)
- [36] Thottackkad M V, Perikinalil R K, Kumarapillai P N. Experimental evaluation on the tribological properties of coconut oil by the addition of CuO nanoparticles. *Int J Precis Eng Manuf* **13**: 111–116 (2012)
- [37] Chimeno-Trinchet C, Fernandez-Gonzalez A, Garcia Calzon J A, Diaz-Garcia M E, Badia Laino R. Alkyl-capped copper oxide nanospheres and nanoplates for sustainability: water treatment and improved lubricating performance. *Sci Technol Adv Mater* **20**: 657–672 (2019)
- [38] Qi J Q, Tian H Y, Li L T, Chan H L W. Fabrication of CuO nanoparticle interlinked microsphere cages by solution method. *Nanoscale Res Lett* **2**: 107–111 (2007)
- [39] Son D I, You C H, Kim T W. Structural, optical, and electronic properties of colloidal CuO nanoparticles formed by using a colloid-thermal synthesis process. *Appl Surf Sci* **255**: 8794–8797 (2009)
- [40] Chen L-J, Li G-S, Li L-P. CuO nanocrystals in thermal decomposition of ammonium perchlorate. *J Therm Anal Calorim* **91**: 581–587 (2008)
- [41] Xiao H-M, Zhu L-P, Liu X-M, Fu S-Y. Anomalous ferromagnetic behavior of CuO nanorods synthesized via hydrothermal method. *Solid State Comm* **141**: 431–435 (2007)
- [42] Wang X, Xi G, Xiong S, Liu Y, Xi B, Yu W, Qian Y. Solution-phase synthesis of single-crystal CuO nanoribbons and nanorings. *Cryst Growth Des* **7**: 930–934 (2007)
- [43] Zhang X, Guo Y-G, Liu W-M, Hao J-C. CuO three-dimensional flowerlike nanostructures: Controlled synthesis and characterization. *J Appl Phys* **103**: 1025–1030. (2008)
- [44] Shrestha K M, Sorensen C M, Klabunde K J. Synthesis of CuO nanorods, reduction of CuO into Cu nanorods, and diffuse reflectance measurements of CuO and Cu nanomaterials in the near infrared region. *J Phys Chem C* **114**: 14368–14376 (2010)
- [45] Yang P, Zhao X, Liu Y, Lai X. Preparation and tribological properties of dual-coated CuO nanoparticles as water based lubricant additives. *J Nanosci Nanotechnol* **16**: 9683–9689 (2016)
- [46] Minakov A V, Rudyak V Y, Guzei D, Lobasov A S. Measurement of the heat transfer coefficient of a nanofluid based on water and copper oxide particles in a cylindrical channel. *High Temp* **53**: 246–253 (2015)
- [47] Jagadeesan M S, Movlaee K, Krishnakumar T, Leonardi S G, Neri G. One-step microwave-assisted synthesis and characterization of novel CuO nanodisks for non-enzymatic glucose sensing. *J Electroanal Chem* **835**: 161–168 (2019)
- [48] Konar S, Sen S, Pathak A. Morphological Effects of CuO Nanostructures on Fibrillation of Human Serum Albumin. *J Phys Chem B* **121**: 11437–11448 (2017)
- [49] Javed R, Ahmed M, ul Haq I, Nisa S, Zia M. PVP and PEG doped CuO nanoparticles are more biologically active: Antibacterial, antioxidant, antidiabetic and cytotoxic perspective. *Mater Sci Eng C* **79**: 108–115 (2017)
- [50] Teodorescu M, Bercea M, Morariu S. Biomaterials of PVA and PVP in medical and pharmaceutical applications: *Perspectives and challenges*. *Biotechnol Adv* **37**: 109–131 (2019)
- [51] Dey K K, Kumar P, Yadav R R, Dhar A, Srivastava A K. CuO nanoellipsoids for superior physicochemical response of biodegradable PVA. *RSC Adv* **4**: 10123–10132 (2014)
- [52] Chang F-M, Cheng S-L, Hong S-J, Sheng Y-J, Tsao H-K. Superhydrophilicity to superhydrophobicity transition of CuO nanowire films. *Appl Phys Lett* **96**: 114101 (2010)
- [53] Wu H, Zhao J, Cheng X, Xia W, He A, Yun J-H, Huang S, Wang L, Huang H, Jiao S, Jiang Z. Friction and wear characteristics of TiO₂ nano-additive water-based lubricant on ferritic stainless steel. *Tribol Int* **117**: 24–38 (2018)
- [54] Ali M K A, Hou X, Abdelkareem M A A. Anti-wear properties evaluation of frictional sliding interfaces in automobile engines lubricated by copper/graphene nanolubricants. *Friction* **8**: 905–916 (2020)
- [55] Liu L, Liu Z Q, Huang P. Novel POSS based nanohybrids for improving tribological properties of liquid paraffin. *RSC Adv* **6**: 94876–94883 (2016)
- [56] Su F, Chen G, Huang P. Lubricating performances of graphene oxide and onion-like carbon as water-based lubricant additives for smooth and sand-blasted steel discs. *Friction* **8**: 47–57 (2020)
- [57] Liu L, Zhou M, Jin L, Li L, Mo Y, Su G, Li X, Zhu H, Tian Y. Recent advances in friction and lubrication of graphene and other 2D materials: Mechanisms and applications. *Friction* **7**: 199–216 (2019)
- [58] Gusain R, Khatri OP. Ultrasound assisted shape regulation of CuO nanorods in ionic liquids and their use as energy efficient lubricant additives. *J Mater Chem A* **1**: 5612–5619 (2013)
- [59] Kumar N, Bhaumik S, Sen A, Shukla A P, Pathak S D. One-pot synthesis and first-principles elasticity analysis of

polymorphic MnO₂ nanorods for tribological assessment as friction modifiers. *RSC Adv* **7**: 34138–34148 (2017)

- [60] Paschoalino M, Guedes N, Jardim W, Mielczarski E, Mielczarski J, Bowen P, Kiwi J. Inactivation of *E. coli* mediated by high surface area CuO accelerated by light irradiation > 360 nm. *J Photoch Photobio A* **199**: 105–111 (2008)

- [61] Hernández Battez A, Viesca JL, González R, Blanco D, Asedegbega E, Osorio A. Friction reduction properties of a CuO nanolubricant used as lubricant for a NiCrBSi coating. *Wear* **268**: 325–328 (2010)

- [62] Chen Z, Liu X, Liu Y, Günsel S, Luo J. Ultrathin MoS₂ nanosheets with superior extreme pressure property as boundary lubricants. *Sci Rep* **5**: 12869 (2015)

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 60 journal papers and possesses 3 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. Then, she was a master graduate student in the

Engineering Research Center for Nanomaterials, Henan University, Kaifeng, China. She obtained her master's degree in materials science in 2018. Her research interests focus on preparation and tribological properties investigation of water-based lubricating additives.