Article

Wood-Powder-Template-Based Syntheses and Tribology of Copper Oxide Particles as Lubricating Oil Additives

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Abstract

Copper based particles were synthesized by a wood-powder-template-based process. Wood powders mixed with an aqueous copper salt solution were heated under N₂ gas flow, and then, the mixture of the charcoal powder and copper particles were heated in air to remove charcoal. Finally, oxidized wood-derived copper particles (OWCu) of less than 1 μm were synthesized. Wood powders acted as the template and limited the sizes of the copper particles. In addition, the tribological properties of OWCu in synthetic oil were investigated using a pin-on-plate reciprocating tribometer. Our results revealed that 0.5 mass% OWCu reduced both the friction coefficient (max 45%) and wear volume (max 39%) of SUJ2 lubricated by PAO4. The best reduction effect was obtained for OWCu synthesized at 400°C under N₂ gas flow, which had the smallest average particle size, where the coverage of the OWCu layer on the wear track was the largest. These facts suggest that the particle size reduction of OWCu can increase the coverage and improve the friction coefficient and wear volume reduction effects of the lubricant. Control of the wood-powder-template-based synthesized particles to the optimal size for the roughness of the sliding surface would help achieve better tribological performance.

Keywords

wood-powder-template, copper oxide particle, lubricant additives, boundary lubrication, PAO

1 Introduction

The minimization of friction energy loss is an urgent matter because carbon dioxide emissions causing global warming need to be reduced. In boundary lubrication, the application of metal nanoparticles as lubricant additives has been investigated to reduce the friction coefficient and wear. Metal nanoparticles are considered to enter the friction interfaces and adhere to the steel surface owing to their small size, and the formed elastic film separates the steel surfaces in contact, thus reducing friction and wear. These properties are suitable for lubricating additives. Numerous researchers have used metal nanoparticles of Cu [1-9] or Ni [10] or metal oxide nanoparticles of TiO₂ [11, 12] or ZrO₂ [13] as lubricant additives in various base oils such as mineral oil, vegetable oil, and synthetic oil. The friction and wear properties have been improved in many cases. Recently, metal nanoparticles were used with various nanomaterials by decorating the surface of nanomaterials, and it was found that the metal nanoparticles and nanomaterials showed synergetic

friction reducing effects [14, 15]. The friction reducing effect of the metal particles was caused by the film formation of an additive induced by the sintering of the metal nanoparticles under sliding and compression [13]. The wear volume was correlated to the diffusion coefficient of oxygen in the metal particles; lower diffusion coefficients lead to lower wear volume [16].

CuO is a metal oxide that has a low oxygen diffusion coefficient, and many studies have used it as a lubricant additive, whereby it improved friction and wear. Arc spray synthesized CuO nanoparticles with an average diameter of 5 nm mixed at 0.1 mass% in conventional engine oil improved both friction coefficient and wear [17]. In mineral oil, sodium oleate-capped CuO with an average diameter of 9 nm mixed at 2.0 mass% [18] and CuO with an average diameter of 50 nm mixed at 3.0 mass% [19] reduced friction coefficient. Furthermore, thermal plasma synthesized CuO with an average diameter of 40 nm mixed at 1.5 mass% improved both the friction coefficient and wear [20]. In vegetable oil, thermal

plasma synthesized CuO with a diameter of 20–150 nm mixed at 0.3 mass% improved both friction coefficient and wear [21, 22], and CuO prepared by an alcohothermal method with a diameter of approximately 10 nm mixed at 0.5 mass% did not improve tribological properties [23]. In synthetic oil of poly- α -olefin (PAO), chemically synthesized CuO capped by oleic acid with a diameter of 10–40 nm mixed at 2.0 mass% improved wear under extreme pressure [24] and the friction coefficient [25]; thermal plasma synthesized CuO with a diameter of less than 50 nm mixed at 2.0 mass% improved both friction coefficient and wear [26]; microwave synthesized CuO with an average diameter of 4.3 nm mixed at 0.1 mass% improved both friction coefficient and especially wear [27]; and commercially available CuO with an average diameter of 100 nm mixed at 1.0 mass% improved wear under rolling contact [28]. However, metal nanoparticle production is not cost effective enough for the use of the nanoparticles as lubricant additives despite the remarkable tribological properties.

Wood-powder-template-based synthesis of nanomaterials is a cost effective method [29–31]. Metal salt solution is impregnated to the wood powder before carbonization. In this process, metal particles act as catalysts for the crystallization of carbon. Typically, metal particles are eliminated after carbonization to obtain metal free nanocarbon materials. Conversely, metal particles can be produced by eliminating the carbon surrounding the metal particles. Carbon layers surrounded around metal particles prevent coarsening of metal particles [30]. Metal particles synthesized by wood-powder-template-based process can be suitable for mass production of low-cost metal particles to be used for tribological applications, although few researches to investigate the tribological properties of wood derived metal particles. In this study, we investigated a tribological properties of low-cost and environment-friendly synthesised metal particles using wood powder as a template of particle formation. We measured the friction characteristics of the synthesized OWCu particles in the synthetic lubricant oil of poly- α -olefin (PAO) using a pin-on-plate reciprocating tribometer. The effect of synthesis conditions of OWCu particles on the friction coefficient and wear volume were determined, and the effective features of the OWCu particles synthesized by wood-powder-template-based method were discussed.

2 Experiments

The synthesis processes for the metal particles are almost the same as that for charcoal combustion. Firstly, wood powders were mixed with an aqueous metal salt solution of copper nitrate and dried to adsorb Cu ions onto the wood powder

surface. Treated wood powders were heated under nitrogen flow of 0.4 L/min at 400, 600, and 800°C for 1 h. Next, they were heated in air at 600°C for 2 h to eliminate the amorphous carbon by oxidation, and then, oxidized wood-derived copper particles (OWCu) were obtained. The syntheses conditions of OWCu are listed in Table 1, in which three different heating temperature in nitrogen flow (OWCu400, OWCu600, and OWCu800) were used. The particle size of the synthesized OWCu was evaluated by SEM, and elemental analysis was conducted by energy dispersive X-ray spectrometry (EDS). The mass% of the elements included was determined by the peak area of the spectra.

Friction tests were conducted using a pin-on-plate reciprocating tribometer, as shown in Fig. 1. PAO4 was used as the base oil, and the synthesized copper oxide particles and PAO were mixed by ultrasonic vibration using a homogenizer with a concentration of 0.5–1.0 mass%. The conditions of the friction tests are shown in Table 2. An SUJ2 ball with a diameter of 10 mm and roughness of 0.1 μm and an SUJ2 substrate with a roughness of 0.5 μm were used as sliding materials. A normal load of 200 N and a maximum sliding velocity of 33.3 mm/s with a reciprocation length of 2.0 mm were applied. The friction force was measured by the load cell for 30,000 sliding cycles. Worn surfaces after the 30,000 cycles of sliding were observed by laser microscopy and SEM. Wear volume was measured for the wear track of the plate surface using a laser microscope. Wear volume was calculated by three-dimensional topography of the whole wear track. Elemental analyses of the worn surface were conducted by EDS at the central area of 100 μm on the wear track.

Fig. 1 Schematic diagram of the pin-on-plate reciprocating tribometer

Table 1 Conditions of wood-powder-based syntheses of copper oxide particles

Specimens		OWCu400	OWCu600	OWCu800
Impregnation of wood powder in metal salt solution	Concentration of Cu-nitrate solution	10wt% of Cu to wood		
Heating in nitrogen flow	N ₂ flow rate	0.4L/min		
	Temp	400°C	600°C	800°C
	time	1h		
Heating in air	Temp	600°C		
	time	2h		

3 Results and discussion

Figure 2 shows representative SEM images of the synthesized particles obtained at different heating temperatures—400°C (a, d), 600°C (b, e), and 800°C (c, f) in nitrogen flow at low (a-c) and high (d-f) magnification. In the low magnified images (a-c), the formation of agglomerated particles was observed under all synthesis conditions. In the high magnified images (d-f), the shape of the primary particles was polyhedral. It was observed that the size of the primary particles was increased by increasing heating temperature in nitrogen flow. Figure 3 shows the distributions of primary particle sizes (a-c) and average particles sizes (d) of OWCu400, OWCu600, and OWCu800 measured using the SEM images. The distribution of the particle sizes was broad, and the average particle size was higher for the particles heated under higher temperatures under nitrogen flow. The average sizes of the primary particles were 0.64 μm for OWCu400, 0.76 μm for OWCu600, and 1.32 μm for OWCu800. Figure 4 shows the results of elemental analysis of the synthesized particles by using EDS under SEM observations. For all specimens, carbon, oxygen, and copper were detected. In the case of OWCu400, the particles contained around 30 mass% of oxygen and around 10 mass% of carbon, and the rest of copper. The composition of OWCu600 was almost same as that of OWCu400. In the case of OWCu800, concentrations of carbon and oxygen were lower than that of the other specimens heated at less than 600°C. The

mass ratio of Cu/O for OWCu800 was 6.8, which is higher than that of stoichiometry CuO compound of 4.0. The high mass ratio Cu/O might be due to the reduction of CuO compound heated in relatively high temperature in nitrogen for OWCu800.

The synthesized OWCu particles were dispersed with PAO to investigate the tribological properties as lubricant additives. Figure 5 shows the friction coefficients of pure PAO, PAO dispersed with 0.5 mass% of OWCu400 (referred to as PAO-OWCu400), OWCu600 (referred to as PAO-OWCu600), and OWCu800 (referred to as PAO-OWCu800) with increasing reciprocation friction cycles before 30,000. The friction coefficient of pure PAO was high before approximately 2,000 cycles, after which it decreased to a stable level of approximately 0.22. In the case of PAO-OWCu400, the transition of the friction coefficient was almost the same before around 5,000 cycles, and it gradually decreased and became stable at approximately 0.12, which is a 45% reduction compared to that of pure PAO, at around 20,000 cycles. PAO-OWCu600 showed almost the same friction coefficient as OWCu400, but the reduction was slightly lower. PAO-OWCu800 showed no reduction effect. Figure 6 shows the optical microscopy images of the wear track on the plate after 30,000 cycles of reciprocating sliding (a-d) and wear volume measured by laser microscopy (e). After 30,000 cycles of sliding, an obvious wear track was observed for all conditions. Dark regions covered by deposits on the wear track were observed. For PAO alone and PAO-OWCu800, a little area was covered by deposits, but for PAO-

Table 2 Friction test conditions using pin-on-plate reciprocating tribometer

Materials	Ball	SUJ2, diameter: 10mm, Ra: 0.1 μm
	Plate	SUJ2, Ra: 0.5 μm
Friction conditions	Load	200 N
	Contact pressure	2.7 GPa
	Maximum sliding velocity	33.3 mm/s
	Reciprocation length	2.0 mm

Fig. 2 SEM images of the synthesized particles obtained at different heating temperatures—400°C (a, d), 600°C (b, e), and 800°C (c, f) under nitrogen flow with low (a-c) and high (d-f) magnification

Fig. 3 Distribution of primary particle size of synthesized OWCu particles of OWCu400 (a), OWCu600 (b), and OWCu800 (c) and the average particles size (d) measured by the SEM images

Fig. 4 Results of elemental analysis of the synthesized particles by using EDS under SEM observations

Fig. 5 Friction coefficients of the PAO base oil, PAO dispersed with the 0.5 mass% of OWCu400, OWCu600, and OWCu800 with increasing reciprocation friction cycles before 30,000

Fig. 6 The optical microscope images of the wear track on the plate after 30,000 cycles of reciprocating sliding (a-d) and wear volume measured by laser microscopy (e)

OWCu400 and PAO-OWCu600, a relatively large area was covered. A reduction in wear volume was observed for all the specimens with OWCu particles in PAO, as shown in Fig. 6(e). OWCu400 and OWCu600 showed a better wear reduction effect compared with OWCu800. The reduction effect of wear volume was 39% for OWCu400 compared with pure PAO. As for the surface of the counterpart ball, the wear diameter corresponded to the width of the wear track on the plate, and the features of the black deposits showed the same trend as the plate surface.

Figure 7 shows SEM images of the plate surfaces lubricated with PAO (a), PAO-OWCu400 (b), PAO-OWCu600 (c), and PAO-OWCu800 (d) observed on the wear track after 30,000 cycles of sliding. The vertical direction of the images corresponds to the sliding direction. A wear track was observed along the sliding direction. Figure 8 shows the elemental concentration of the wear track on plate surfaces lubricated by PAO (a), PAO-OWCu400 (b), PAO-OWCu600 (c), and PAO-OWCu800 (d) using EDS. Copper and oxygen were detected at the worn surfaces lubricated with OWCu containing PAO, which means OWCu particles in the lubricants adhered to the sliding surface. In the case of OWCu400, the largest copper concentration of 10.5 mass% was observed, which decreased as the temperature of the synthesis of OWCu particles under nitrogen flow increased; thus, the copper concentrations reduced for OWCu600 and OWCu800, which had larger average particle sizes. Concerning about the composition of Cu compound, the mass ratios of the Cu/O were slightly increased for the surface lubricated by OWCu400, OWCu600, and OWCu800 comparing to the as synthesized OWCu particles. It might be due to a reduction of Cu compounds occurred at the friction interface. The effect of the Cu reduction on the friction reduction of OWCu is considered to be not significant, because the increase of the Cu/O for OWCu400, which indicates lowest friction coefficient, was smaller than that for OWCu600.

The results show that the OWCu particles synthesized by the wood-powder-template-based method reduced the friction coefficient and wear volume. Especially OWCu400, which has the minimum average particle size, showed the best reducing effects of both friction and wear. The smaller particle size enables the OWCu particles to enter the sliding interface and separate the direct contact between the SUJ2 ball and plate which causes higher friction and wear. This effect was also supported by the fact that a higher concentration of OWCu containing black deposits was observed on the wear track lubricated by OWCu400. To investigate the relationship between the tribological properties and the quantities of the adhered OWCu particles on the sliding surface, the time evolution of wear and amount of OWCu particles adhered were evaluated. Five different friction tests were conducted under equal friction conditions with the exception of the number of friction cycles. Figure 9 shows the friction test results of PAO with 1.0 mass% OWCu400 with cycle numbers increasing from 250, 750, 5,000, 20,000, to 30,000. Notably, the OWCu concentration in PAO was different from friction tests shown in Figs. 5 and 6 (0.5 mass%). Figure 9(a) shows the dependency of the friction coefficient, wear volume (b), and Cu concentration on the wear track (c), and optical microscopy photographs of the wear track of the plate (d). As the transition of friction coefficients shown in Fig. 9(a), friction cycles were chosen at around the top and bottom of initial peak of the friction coefficient at 250 and 750 cycles, the decreasing region after the initial increase at 5,000 cycles, the last stage of decreasing region at 20,000 cycles, and getting stabilized at 30,000 cycles. Wear volume was drastically increased by increasing the number of friction cycles, and it got almost stable before 5,000 cycles, as shown in Fig. 9(b). Copper concentration on the plate surface was gradually increased with increasing cycles and became almost saturated to 9.3 mass% at 20,000 cycles when the friction coefficient became stable.

Fig. 7 SEM images of the plate surface lubricated by PAO (a) and PAO with OWCu400 (b), OWCu600 (c), and OWCu800 (d) observed on the wear track after the 30,000 cycles of sliding

Fig. 8 Elemental concentration measured on the plate surface after 30,000 sliding cycles lubricated by PAO (a), PAO+OWCu400 (b), PAO+OWCu600 (c), and PAO+OWCu800 (d) by using EDS

Oxygen concentration showed almost the same trend as copper concentration. Carbon concentration quickly increased till 5,000 cycles, after which it became stable. Because the carbon content in OWCu400 was relatively low at 12.4 mass%, the carbon content on the worn surface was mainly from the PAO lubricant. Photographs of the wear track in Fig. 9(d) correspond to the wear volume in Fig. 9(b). The width and length of the wear tracks also increased before 5,000 cycles. Black deposits were observed at the initial stages of friction cycles of 250, and the area covered by the black deposits increased when the number of friction cycles increased. Figure 10 shows the relationship between the coverage of black deposits on the wear track and the friction cycles (a) and Cu concentration (b). The coverage was measured by the area of the black deposits on the wear track from the images in Figs. 6(a-d) and 9(d). The coverage almost linearly increased with the friction cycles. At 30,000 friction cycles, the coverage of OWCu600 and OWCu800,

whose particle sizes are bigger than those of OWCu400, was less than that of OWCu400, as already shown, and the coverage of OWCu800 was about half of that of Cu400. In addition, the coverage was also dependent on the Cu concentration of the wear track, and the relationship between coverage and Cu concentration of Cu400 was the same as that for Cu600 and Cu800, as shown in Fig. 10(b), which means that the coverage depends on the Cu concentration on the wear track. Therefore, higher content of OWCu particles led to a higher coverage of the black deposit.

To further discuss the friction reducing mechanism, the dependency of the friction coefficients and the wear volumes per cycle on the coverage of black deposits are plotted in Fig. 11. The friction cycles before 250 cycles which is in the run-in period of the sliding were excepted from the plot. We found that the friction coefficient linearly decreased with increasing coverage. Wear volume per cycle also decreased with increasing

coverage. These results indicate that the friction coefficient is related to the coverage of the OWCu layer on the sliding surface. In addition, OWCu400 with the smaller particle sizes and which is likely to enter the friction interface showed the highest coverage. Therefore, the OWCu particles entering the friction interface could adhere to the worn surface under the contact pressure to form a friction reducing layer. The copper content on the wear track was relatively higher in this study compared with different friction conditions reported previously [23, 25]. The contact pressure was relatively high at 2.7 GPa in this study, which may have caused the higher content of copper on the wear track because of the sintering effect of the metal oxide under high contact pressure [16]. To confirm the friction reducing effect of OWCu deposits on the wear

track, a continuous lubricant changing test was conducted. Figure 12 shows the transition of the friction coefficient under continuously changing lubricants from PAO with 1.0 mass% OWCu400 and pure PAO at 30,000 cycles and then PAO with 1.0 mass% OWCu400 at 60,000 cycles. The friction coefficient stabilized at 30,000 cycles at 0.13 and gradually increased just after the lubricant was changed to pure PAO. The friction coefficient increased to 0.20 after additional 5,000 cycles, and it gradually decreased to 0.17 before 60,000 cycles. The friction coefficient then started to decrease after changing the lubricant to PAO with 1.0 mass% OWCu400, and it became 0.10 at 90,000 cycles. The gradual increase of the friction coefficient after stopping the supply of OWCu particles at 30,000 cycles can be explained by the reduction of the OWCu layer on the worn

Fig. 9 The dependency of the friction coefficient (a), wear volume (b), and elemental concentration on the wear track (c), and photos of wear tracks (d) of the plate sliding by PAO with 1.0 mass% OWCu400 in increasing friction cycles of 250, 750, 5,000, 20,000, and 30,000

Fig. 10 Relationship between the coverage of black deposits on the wear track and the friction cycles (a), and Cu concentration on the wear track (b)

Fig. 11 Dependency of the friction coefficients (a) and the wear volumes per cycle (b) on the coverage of OWCu deposits on the wear track

Fig. 12 Transition of the friction coefficient under continuous change of lubricant from PAO with OWCu400, PAO alone at 30,000 cycles, and PAO with OWCu400 at 60,000 cycles

surface without OWCu supply. This result also supports that the OWCu layer formed under the contact pressure reduces the friction coefficient.

The friction reducing mechanism of OWCu is not completely cleared, although the deposition of copper oxide on the steel surface is considered to contribute to lower friction. By the deposition to the sliding surface under boundary lubrication, copper oxide particles can contribute to reduce adhesive interaction with steel counter face compared to severe steel vs. steel contact. We found that one of the important factors to reduce friction coefficient and wear volume was to increase the coverage of OWCu on the worn surface. The smaller particle size seems to lead to higher coverage as OWCu400 with a particle size of 0.4–0.9 μm showed higher coverage than OWCu600 and OWCu800. In this study, the particle size of OWCu was larger than that of CuO particles which indicated friction and wear reducing properties in previous experimental studies [25]. The effective particle size of additives has been previously discussed, and it was revealed that the effective particle size of additives highly depends on the initial surface roughness of the sliding surface. Particles can effectively work when the particle size is compatible to the surface roughness [12]. In fact, OWCu400 with an average particle size of 0.64 μm , which is comparable to the initial sliding surface roughness of 0.5 μm , was effective to enhance friction coefficient in this study. The next step will be the precise control of the particle size by wood-powder synthesis to apply the particle for the surface of the lower roughness. Additionally, the effects of wood-based carbon content of OWCu particles on tribological properties and optimization of the composite particle structure will be studied in the future.

4 Conclusion

The tribological properties of the wood-templated-based synthesized OWCu particles in synthetic oil were investigated. It was revealed that 0.5 mass% wood-templated-based synthesized OWCu particles reduced both the friction coefficient (max 45%) and wear volume (max 39%) of SUJ2 lubricated by PAO4. The synthesized particles had sizes of 0.4–2.3 μm depending on the heating temperature used for synthesis under N_2 flow and the compositions of copper, oxygen, and carbon. The best effect was obtained for OWCu400, which had the smallest average particle

size. The coverage of the OWCu layer on the wear track was the highest. The reduction effects of friction and wear volume were correlated to the coverage of the OWCu layer. These results indicate that the optimum particle size for the roughness of the sliding surface can lead to an increase in the coverage, thus improving the reduction in the friction coefficient and the anti-wear effect of the lubricant.

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References

- [1] Zhou, J., Wu, Z., Zhang, Z., Liu, W. and Xue, Q., "Tribological Behavior and Lubricating Mechanism of Cu Nanoparticles in Oil," *Tribology Letters*, 8, 2000, 213–218.
- [2] Tarasov, S., Kolubaev, A., Belyaev, S., Lerner, M. and Tepper, F., "Study of Friction Reduction by Nanocopper Additives to Motor Oil," *Wear*, 252, 1–2, 2002, 63–69.
- [3] Yu, H. L., Xu, Y., Shi, P. J., Xu, B. S., Wang, X. L., Liu, Q. and Wang, H. M., "Characterization and Nano-Mechanical Properties of Tribofilms Using Cu Nanoparticles as Additives," *Surface and Coatings Technology*, 203, 1–2, 2008, 28–34.
- [4] Viesca, J. L., Hernández Battez, A., González, R., Chou, R. and Cabello, J. J., "Antiwear Properties of Carbon-Coated Copper Nanoparticles Used as an Additive to a Polyalphaolefin," *Tribology International*, 44, 7–8, 2011, 829–833.
- [5] Xiong, X., Kang, Y., Yang, G., Zhang, S., Yu, L. and Zhang, P., "Preparation and Evaluation of Tribological Properties of Cu Nanoparticles Surface Modified by Tetradecyl Hydroxamic Acid," *Tribology Letters*, 46, 3, 2012, 211–220.
- [6] Wang, X. L., Yin, Y. L., Zhang, G. N., Wang, W. Y. and Zhao, K. K., "Study on Antiwear and Repairing Performances about Mass of Nano-Copper Lubricating Additives to 45 Steel," *Physics Procedia*, 50, October 2012, 2013, 466–472.
- [7] Padgurskas, J., Rukuiza, R., Prosyčėvas, I. and Kreivaitis, R., "Tribological Properties of Lubricant Additives of Fe, Cu and Co Nanoparticles," *Tribology International*, 60, 2013, 224–232.

- [8] Li, Y., Liu, T. T., Zhang, Y., Zhang, P. and Zhang, S., "Study on the Tribological Behaviors of Copper Nanoparticles in Three Kinds of Commercially Available Lubricants," *Industrial Lubrication and Tribology*, 70, 3, 2018, 519–526.
- [9] Guzman Borda, F. L., Ribeiro de Oliveira, S. J., Seabra Monteiro Lazaro, L. M. and Kalab Leiróz, A. J., "Experimental Investigation of the Tribological Behavior of Lubricants with Additive Containing Copper Nanoparticles," *Tribology International*, 117, 2018, 52–58.
- [10] Chou, R., Battez, A. H., Cabello, J. J., Viesca, J. L., Osorio, A. and Sagastume, A., "Tribological Behavior of Polyalphaolefin with the Addition of Nickel Nanoparticles," *Tribology International*, 43, 12, 2010, 2327–2332.
- [11] Xue, Q., Liu, W. and Zhang, Z., "Friction and Wear Properties of a Surface-Modified TiO₂ Nanoparticle as an Additive in Liquid Paraffin," *Wear*, 213, 1–2, 1997, 29–32.
- [12] Peña-Parás, L., Gao, H., Maldonado-Cortés, D., Vellore, A., García-Pineda, P., Montemayor, O. E., Nava, K. L. and Martini, A., "Effects of Substrate Surface Roughness and Nano/Micro Particle Additive Size on Friction and Wear in Lubricated Sliding," *Tribology International*, 119, 2018, 88–98.
- [13] Khare, H. S., Lahouij, I., Jackson, A., Feng, G., Chen, Z., Cooper, G. D. and Carpick, R. W., "Nanoscale Generation of Robust Solid Films from Liquid-Dispersed Nanoparticles via in Situ Atomic Force Microscopy: Growth Kinetics and Nanomechanical Properties," *ACS Applied Materials and Interfaces*, 10, 46, 2018, 40335–40347.
- [14] Wang, Z., Ren, R., Song, H. and Jia, X., "Improved Tribological Properties of the Synthesized Copper/Carbon Nanotube Nanocomposites for Rapeseed Oil-Based Additives," *Applied Surface Science*, 428, 2018, 630–639.
- [15] Xu, Z., Lou, W., Zhao, G., Zheng, D., Hao, J. and Wang, X., "Cu Nanoparticles Decorated WS₂ Nanosheets as a Lubricant Additive for Enhanced Tribological Performance," *RSC Advances*, 9, 14, 2019, 7786–7794.
- [16] Kato, H. and Komai, K., "Tribofilm Formation and Mild Wear by Tribo-Sintering of Nanometer-Sized Oxide Particles on Rubbing Steel Surfaces," *Wear*, 262, 1–2, 2007, 36–41.
- [17] Wu, Y. Y., Tsui, W. C. and Liu, T. C., "Experimental Analysis of Tribological Properties of Lubricating Oils with Nanoparticle Additives," *Wear*, 262, 7–8, 2007, 819–825.
- [18] Ghaednia, H., Jackson, R. L. and Khodadadi, J. M., "Experimental Analysis of Stable CuO Nanoparticle Enhanced Lubricants," *Journal of Experimental Nanoscience*, 10, 1, 2015, 1–18.
- [19] Asrul, M., Zulkifli, N. W. M., Masjuki, H. H. and Kalam, M. A., "Tribological Properties and Lubricant Mechanism of Nanoparticle in Engine Oil," *Procedia Engineering*, 68, 2013, 320–325.
- [20] Jatti, V. S. and Singh, T. P., "Copper Oxide Nano-Particles as Friction-Reduction and Anti-Wear Additives in Lubricating Oil," *Journal of Mechanical Science and Technology*, 29, 2, 2015, 793–798.
- [21] Thottackkad, M. V., Perikinalil, R. K. and Kumarapillai, P. N., "Experimental Evaluation on the Tribological Properties of Coconut Oil by the Addition of CuO Nanoparticles," *International Journal of Precision Engineering and Manufacturing*, 13, 1, 2012, 111–116.
- [22] Koshy, C. P., Rajendrakumar, P. K. and Thottackkad, M. V., "Analysis of Tribological and Thermo-Physical Properties of Surfactant-Modified Vegetable Oil-Based CuO Nano-Lubricants at Elevated Temperatures - An Experimental Study," *Tribology Online*, 10, 5, 2015, 344–353.
- [23] Alves, S. M., Barros, B. S., Trajano, M. F., Ribeiro, K. S. B. and Moura, E., "Tribological Behavior of Vegetable Oil-Based Lubricants with Nanoparticles of Oxides in Boundary Lubrication Conditions," *Tribology International*, 65, 2013, 28–36.
- [24] Hernández Battez, A., González, R., Felgueroso, D., Fernández, J. E., del Rocio Fernández, M., García, M. A. and Peñuelas, I., "Wear Prevention Behaviour of Nanoparticle Suspension under Extreme Pressure Conditions," *Wear*, 263, 7–12, 2007, 1568–1574.
- [25] Hernández Battez, A., González, R., Viesca, J. L., Fernández, J. E., Díaz Fernández, J. M., Machado, A., Chou, R. and Riba, J., "CuO, ZrO₂ and ZnO Nanoparticles as Antiwear Additive in Oil Lubricants," *Wear*, 265, 3–4, 2008, 422–428.
- [26] Peña-Parás, L., Taha-Tijerina, J., Garza, L., Maldonado-Cortés, D., Michalczewski, R. and Lapray, C., "Effect of CuO and Al₂O₃ Nanoparticle Additives on the Tribological Behavior of Fully Formulated Oils," *Wear*, 332–333, 2015, 1256–1261.
- [27] Alves, S. M., Mello, V. S., Faria, E. A. and Camargo, A. P. P., "Nanolubricants Developed from Tiny CuO Nanoparticles," *Tribology International*, 100, 2016, 263–271.
- [28] Roy, S., Jazaa, Y. and Sundararajan, S., "Investigating the Micropitting and Wear Performance of Copper Oxide and Tungsten Carbide Nanofluids under Boundary Lubrication," *Wear*, 428–429, 2019, 55–63.
- [29] Sevilla, M., Sanchís, C., Valdés-Solís, T., Morallón, E. and Fuertes, A. B., "Direct Synthesis of Graphitic Carbon Nanostructures from Saccharides and Their Use as Electrocatalytic Supports," *Carbon*, 46, 6, 2008, 931–939.
- [30] Kodama, Y., Sato, K., Suzuki, K., Saito, Y., Suzuki, T. and Konno, T. J., "Electron Microscope Study of the Formation of Graphitic Nanostructures in Nickel-Loaded Wood Char," *Carbon*, 50, 10, 2012, 3486–3496.
- [31] Kinoshita, H. and Nishina, Y., "Investigations on Tribological Mechanisms of Graphene Oxide and Oxidized Wood-Derived Nanocarbons as Water-Based Lubricating Additives," *Tribology Online*, 11, 2, 2016, 235–241.