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**Abstract:** In the present work, Black Phosphorus Quantum Dots (BPQDs) were synthesized via sonication-assisted liquid-phase exfoliation. The average size of the BPQDs was  $3.3 \pm 0.85$  nm. The BPQDs exhibited excellent dispersion stability in ultrapure water. Macroscale superlubricity was realized with the unmodified BPQDs on rough Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interfaces. A minimum coefficient of friction (COF) of 0.0022 was achieved at the concentration of 0.015 wt%. In addition, the glycerol was introduced to promote the stability of the superlubricity state. The COF of the BPQDs-Glycerol aqueous solution (BG<sub>aq</sub>) was 83.75% lower than that of the Glycerol aqueous solution (G<sub>aq</sub>). Based on the above analysis, the lubrication model was presented. The hydrogen-bonded network and silica gel layer were formed on the friction interface, which played a major role in the realization of macroscale superlubricity. In addition, the adsorption water layer could also prevent the worn surfaces from making contact with each other. Moreover, the synergistic effect between BPQDs and glycerol could significantly decrease the COF and maintain the superlubricity state. The findings theoretically support the realization of macroscale superlubricity with unmodified BPQDs as a water-based lubrication additive.

Keywords: macroscale superlubricity; Black Phosphorus Quantum Dots; lubrication; glycerol; friction

# 1. Introduction

Superlubricity, which is an ideal state (coefficient of friction (COF) < 0.01), was described in 1990 by Hirano and Shinjo [1]. Previous research indicates that superlubricity can be classified into two groups based on the lubrication materials. First, solid superlubricity describes a state in which the COF is lower than 0.01 between two sliding interfaces. Solid lubricants with incommensurate structures or weak interlayer interactions, such as diamond-like carbon film [2],  $MoS_2$  [3], carbon nitride film [4,5] and graphite [6], were used. Although superlubricity can be achieved via solid lubricants, the process needs to be carried out under special conditions with relatively perfect materials. In comparison, the liquid superlubricity described by the second group indicates a state of superlubricity that can be obtained via liquid lubricants. This superlubricity can be achieved easily, continuously and steadily on a macroscopic scale under the proper atmospheric conditions.

Until now, superlubricity could be realized by various liquid lubricant systems, such as hydrophilic polymer brushes [7], ionic liquid [8,9], polyhydroxy aqueous solutions [10–13], acid-based solutions [14–16] and two-dimensional (2D) nano-additives, after a period of running-in. Compared with other liquid lubricant systems, the introduction of 2D nano-additives efficiently enhances the contact pressure of the lubricants. Therefore, 2D nano-additives such as graphene oxide [17], MXene [18], double hydroxide nanosheets [19] and black phosphorus [20,21] show great potential for liquid superlubricity. Among



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). these 2D nano-additives, black phosphorus (BP) has inspired a great deal of curiosity from researchers in the lubricant field owing to its excellent tribological performance and extreme pressure and anti-wear property. Wang et al. [22] showed that macroscale superlubricity can be obtained with BP-OH modified by NaOH. It was revealed that the addition of BP-OH can result in macroscale superlubricity under different conditions, even on the roughest friction surface. Ren et al. [23] reported that stable superlubricity could be achieved with oxidized black phosphorus nanosheets. Macroscale superlubricity could also be achieved with aqueous ethylene glycol via the introduction of BPQDs under high contact pressure (336 MPa) [24]. Wu et al. [25,26] reported on the superlubricity of degraded black phosphorus, demonstrating that the degradation of black phosphorus significantly favors lubrication. However, there is scant research on the use of unmodified BPQDs as a water-based lubrication additive to realize macroscale superlubricity.

In the present study, macroscale superlubricity could be realized by unmodified BPQDs on a rough silicon nitride  $(Si_3N_4)/silicon dioxide (SiO_2)$  surface. This is the first work to show that unmodified BPQDs can be used as a water-based lubrication additive to achieve macroscale superlubricity. However, macroscale superlubricity with BPQDs could not be maintained for a longer period. To solve the issue of the unstable macroscale superlubricity behavior of BPQD aqueous solution ( $B_{aq}$ ), glycerol was introduced into ultrapure water. Macroscale superlubricity remained steady for more than 1 h when the glycerol was introduced. In addition, the systematic tribological performance of  $B_{aq}$  and BPQDs-glycerol aqueous solution ( $BG_{aq}$ ) were also tested. The chemical composition of a worn surface was examined by X-ray photoelectron spectroscopy (XPS). The morphology of the worn surface was characterized via scanning electron microscopy (SEM) and via optical microscope. The superlubricity mechanisms were proposed and analyzed in detail.

#### 2. Materials and Methods

#### 2.1. Preparation of BPQDs, B<sub>aq</sub> and BG<sub>aq</sub>

The black phosphorus powder was fabricated via the high-energy ball milling method from red phosphorus (RP, > 99.9%) which has already been reported by our group [27,28]. The BPQDs were prepared from bulk BP by sonication-assisted liquid-phase exfoliation. Figure 1a illustrates the synthesis process of the BPQDs. 100 mg of BP powder was added into 80 mL of N-methyl pyrrolidone ( $\geq$  99.5%) for 6 h probe sonication. During the process of probe sonication, an ice bath was used to maintain the temperature below 0 °C. Subsequently, the processed solution was centrifuged, then the supernatant was gathered and centrifuged, and the precipitate was BPQDs. Subsequently, the precipitate was washed with ethanol (AR) and ultrapure water (1.0 mL, 18.2 MΩ) through centrifugation for 2~3 times. After the BPQDs fabrication, four concentrations of the B<sub>aq</sub> were prepared by complete dispersion of BPQDs (400, 200, 150, 100 µg) in ultrapure water via sonication at 25 °C for 30 min. In addition, the glycerol (AR) was introduced. The glycerol aqueous (G<sub>aq</sub>) was obtained by mixing glycerol and ultrapure water with the ratio 1:5. Then, the BPQDs were dispersed in the G<sub>aq</sub> via sonication for 30 min, which was named BG<sub>aq</sub>.

#### 2.2. Characterization of BPQDs

The crystal structures of BPQDs were observed via X-ray diffraction (XRD, Bruker D8) in the 2 $\theta$  range of 5–90°. The XRD instrument with Cu K $\alpha$  radiation using 40 kV and 40 mA and scan rate of 5° min<sup>-1</sup> was used. The chemical composition of BPQDs was determined by Raman spectroscopy (HORIBA Evolution JYT6400, HORIBA Scientific, France). The morphology of BPQDs was evaluated via transmission electron microscopy (TEM, FEI Talos F200S, Thermo Fisher Scientific Inc., US) operated at 200 kV acceleration voltage. The thickness of the BPQDs was characterized via atomic force microscopy (AFM, Bruker Dimension Icon, Germany). The stability of the B<sub>aq</sub> was evaluated via Zeta meter (Malvern Zetasizer Nano ZS90, Malvern Panalytical, UK).



**Figure 1.** (a) Schematic diagram of the synthesis process of the  $B_{aq}$  (b) TEM of BPQDs and (c) HRTEM image of the BPQDs, (d) Statistical analysis of the size of 120 BPQDs based on the TME image, (e) XRD spectrum of BP power, (f) Raman spectrum of BPQDs, (g) AFM image of BPQDs, (h) Height profiles along the white line in (g), (i) Thickness histogram of BPQDs based on the AFM image, (j) Zeta potential of  $B_{aq}$ .

#### 2.3. Tribological Tests

The universal microtribotester (UMT-5, Bruker, Germany) was used to evaluate the tribological performance. The Si<sub>3</sub>N<sub>4</sub> ball ( $\Phi$  = 10 mm or  $\Phi$  = 4 mm,  $R_a \approx 54$  nm) and SiO<sub>2</sub> plate (15 × 15 × 5 mm,  $R_a \approx 0.674 \mu$ m) were used as friction pair. During the tribological tests, the different volumes (100 µL, 50 µL and 20 µL) of the lubricant were introduced. A load of 0.5–3.5 N (401–890 MPa) was applied. The sliding speeds in this work were in the range 31.4–157 mm·s<sup>-1</sup>. Three independent tribological tests were carried out. The tribological tests were done at room temperature.

## 2.4. Characterization of the Worn Surfaces

400 Position (nm)

After the tribological tests, the morphologies of the worn surfaces were characterized via the 3D white-light interferometer (Bruker, Contour GT-K, Germany) and SEM (Gemini 300, Zeiss, Germany) and optical microscope (GX51, Olympus Corporation, Japan). The wear volume was measured via the 3D white-light interferometer, and the wear rate was calculated as [29].

$$W_B = \frac{V}{P \cdot S} \tag{1}$$

where  $W_B$  is the wear rate, V is the wear volume of ball and plate, P is the normal load and S is the sliding distance. Further, the chemical properties of the worn surface were analyzed via XPS (PHI-5000 VersaProbe III, ThermoFischer, US). The Al-K $\alpha$  radiation (1486.6 eV) was used as the excitation source. The XPS spectra were calibrated by the C 1s peak. The XPS instrument used 14.6 kV and 13.5 mA.

# 3. Results and Discussion

The crystal structure, chemical properties and morphologies of BPQDs were characterized via XRD, Raman, TEM and AFM (Figure 1b–i). The TEM image revealed that the BPQDs have a relatively spherical shape (Figure 1b,c). A lattice fringe of 0.21 was observed, which can be attributed to the BPQDs [30]. The average diameter of BPQDs was about  $3.3 \pm 0.85$  nm, as shown in the diameter distribution histogram (Figure 1d). In addition, the XRD spectrum exhibited characteristic peaks at  $16.5^{\circ}$ ,  $26.45^{\circ}$  and  $35.0^{\circ}$ , corresponding to the orthorhombic BP (JCPSD No. 21-1272). The characteristic peaks on the Raman spectrum located at 366.2, 431.5 and 459.4 cm<sup>-1</sup> were attributed to  $A_g^1$ ,  $B_{2g}$  and  $A_g^2$  [31]. The AFM images of the BPQDs, as shown in Figure 1g–i, revealed the average thickness of the BPQDs was  $3.18 \pm 0.144$  nm. As mentioned above, the results revealed that the BPQDs were synthesized successfully via sonication-assisted liquid-phase exfoliation.

Dispersity plays a key role in the realization of the excellent lubrication performance. To evaluate the stability of the  $B_{aq}$ , the Zeta potential was measured by Zeta meter. A higher absolute value (35 mV) of Zeta potential was obtained, which indicated that the  $B_{aq}$  is a stable suspension (Figure 1j) [32,33]. Furthermore, the dispersity of the  $B_{aq}$  was also evaluated via optical images (Figure 2). A series of the dispersions with different concentrations were obtained via sonication, the colors of dispersion became darker as the concentration increased, as shown in Figure 2a. When the dispersion settled for 7 days, no evident separation and sediment appeared (Figure 2b) and the color of the dispersion changed only slightly. This indicates that the stability of the  $B_{aq}$  was excellent, which is consistent with the value of Zeta potential.



Figure 2. The optical image of the B<sub>aq</sub> with varied concentration (a) 0 h and (b) after 7 days.

The tribological tests were carried out at the  $Si_3N_4/SiO_2$  interface under different conditions. Firstly, the  $B_{aq}$  lubricant and  $Si_3N_4$  balls with a diameter of 10 mm were used in this tribological test. Before the tribological test, the 100 µL lubricant was introduced into the friction surface. The COF curve under the lubrication condition of ultrapure water and  $B_{aq}$  (0.015 wt%) is shown in Figure 3a. Unless otherwise stated, the load of 3 N and the sliding speed of 62.8 mm·s<sup>-1</sup> was used in tribological tests. Under the lubrication condition of ultrapure water, the COF decreased from 0.45 to 0.28 at first, then suddenly increased to about 0.5 and fluctuated in the range of 0.45–0.65. The high COF value for ultrapure water can be attributed to the evaporation of free water molecules and the lack of formation of an effective lubrication film [34]. By contrast, the COF dramatically decreased when the  $B_{aq}$  was introduced. After about 3100 s of a running-in period, the COF entered the region of superlubricity (approximately 0.0022). Furthermore, the superlubricity performance of  $B_{aq}$  was also evaluated under different concentrations, loads and sliding speeds. Obviously, macroscale superlubricity was achieved for all the tests (Figure 3b–d). The average COF decreased firstly then increased with the increasing of concentration and load (Figure 3b,c),

reaching the minimum value of 0.0022 under the concentration of 0.015 wt% and the load of 3 N. It was revealed that the BPQDs could trigger macroscale superlubricity. The trend in COF curve variation under the lubrication of  $B_{aq}$  suggested the possible formation of the lubrication films during the running-in period, making it easy to realize macroscale superlubricity. However, the macroscale superlubricity with  $B_{aq}$  could not be maintained for a longer period; the macroscale superlubricity period was about 1100 s (Figure 3a). In the end, the COF curve sharply increased to 0.6. This suggests that the lubrication film was possibly broken in this case.



**Figure 3.** (a) The COF curves under the lubrication condition of ultrapure water (UW) and  $B_{aq}$  (3 N, 62.8 mm·s<sup>-1</sup>); the average COF value of the  $B_{aq}$  under different concentrations (b), loads (c) and sliding speeds (d).

In order to solve the issue of unstable superlubricity under the lubrication condition of Baq, glycerol was introduced into the ultrapure water. As a contrast, the tribological test under the lubrication condition of  $G_{aq}$  was carried out. After the introduction of glycerol to the ultrapure water, the COF gradually reduced from 0.28 to 0.032 and then fluctuated in a range of 0.03–0.045 (Figure 4a). It was revealed that the lubrication films were unable achieve macroscale superlubricity. When the BPQDs were added into the  $G_{aq}$ , the COF gradually decreased to 0.01 and then entered the superlubricity state (COF < 0.01). In addition, the superlubricity performance of BG<sub>aq</sub> was evaluated under different lubricant volumes (Figure 4b). The running-in time reduced from 1320 s to 380 s when the lubricant volume decreased from 100  $\mu$ L to 20  $\mu$ L. The running-in time is dependent on the evaporation of the free water molecules; the larger the initial volume of lubricant, the longer the running-in time. By contrast, the average COF was increased from 0.0026 to 0.007 with the decrease in lubricant volume. In the subsequent section, the 20  $\mu$ L volume of the lubricant was selected for a more elaborate discussion. Furthermore, macroscale superlubricity remained steady for more than 1 h under the lubrication condition of BG<sub>ad</sub>. The tribological tests of different conditions were conducted, and the  $\Phi$  4 mm ball was used in the following section. Macroscale superlubricity can be observed for all conditions with the  $BG_{aq}$  after the running-in period, as shown in Figure 4c–h. With the increase of the concentration from 0.01 to 0.04 wt%, the COF firstly decreased from 0.0076 to 0.0065, and then increased to 0.008, under the lubrication condition of BG<sub>aq</sub>. The minimum COF

(~0.0065) was achieved under the concentration of 0.015 wt% (Figure 4c,d). The average COF was 83.75% less than that of  $G_{aq}$ . Furthermore, the minimum COF value was achieved at a load of 0.5 N (~0.004). Notably, the COF first decreased then increased, and the running-in time reduced from 500 to 300 s with the increase of sliding speed from 62.8 to 157 mm·s<sup>-1</sup> (Figure 4g,h). The reduction of the running-in time revealed that the high sliding speed favors the formation of effective lubrication film. Stability is important when evaluating the quality of a lubricant. In order to investigate the stability of BG<sub>aq</sub>, the optical image and superlubricity performance were evaluated after one week. After one week, no significant difference in color, and no distinct sediment could be observed. Furthermore, the macroscale superlubricity also could be obtained with BG<sub>aq</sub> after a week, and the average COF value increased slightly, as shown in Figure 4i. The results revealed that the BG<sub>aq</sub> has better stability and dispersity.



**Figure 4.** (a) The COF curves under the lubrication conditions of  $G_{aq}$  and  $BG_{aq}$  as lubricant (3 N, 62.8 mm·s<sup>-1</sup>); (b) The COF curves under the different volumes of  $BG_{aq}$ ; the COF curve and the average COF value under the lubrication condition of the  $BG_{aq}$  with different concentrations (**c**,**d**), loads (**e**,**f**) and sliding speeds (**g**,**h**); (**i**) Variations of COF of  $BG_{aq}$  after one week.

After the tribological tests, the morphology of the worn surface was characterized via optical microscope, SEM and 3D white-light interferometer. The worn surface on the Si<sub>3</sub>N<sub>4</sub> balls and SiO<sub>2</sub> plate under the lubrication condition of ultrapure water and B<sub>aq</sub> are shown in Figure 5, respectively. When the ultrapure water was utilized, the wear scar on the Si<sub>3</sub>N<sub>4</sub> ball lubricated with ultrapure water was extremely rough. The diameter of the wear scar was 803.8  $\mu$ m, and there were deep furrows on the worn surface, which indicated that the wear mechanism was mainly abrasive wear. In comparison, the furrows were shallow and the worn surface became smooth after the introduction of BPQDs in ultrapure water. In addition, the diameter of the wear scar under the lubrication condition of B<sub>aq</sub> was 463.9  $\mu$ m, which was 42.3 % less than that of the ultrapure water. Furthermore, the wear volume was measured via 3D white-light interferometer (Table 1) and the wear rate was calculated (Figure 5g). The wear rates of SiO<sub>2</sub> plate and Si<sub>3</sub>N<sub>4</sub> ball lubricated by ultrapure water were 7.9323 × 10<sup>-8</sup> and 6.05298 × 10<sup>-9</sup> mm<sup>3</sup>/(N·m), respectively. By comparison, the wear rates of SiO<sub>2</sub> plate and the Si<sub>3</sub>N<sub>4</sub> ball lubricated by B<sub>aq</sub> were decreased by 78.3 % and

87.2 %. The results revealed that the water molecules will remain on the worn surface due to the excellent water retention property of BPQDs. Therefore, starved lubrication or boundary lubrication would occur. Even though the wear rate under the lubrication of B<sub>aq</sub> was less than that of ultrapure water, severe wear had also occurred during the tests. Similarly, when the glycerol was introduced into ultrapure water, shallow furrows and wear debris appeared (Figure 6b). By contrast, the wear debris disappeared and the worn surface became smoothly lubricated by  $BG_{aq}$ . The diameter of the wear scar on the Si<sub>3</sub>N<sub>4</sub> ball under the lubrication condition of ultrapure water, G<sub>aq</sub> and BG<sub>aq</sub> were 574.4, 280.9 and 264.4  $\mu$ m (Figure 6a–c), respectively. The diameter of the wear scar under the lubrication condition of BG<sub>ag</sub> was 54.3 % less than that of ultrapure water. Similarly, the width of the worn track on the SiO<sub>2</sub> plate was obviously decreased (Figure 6d-i) after the introduction of glycerol and BPQDs. The worn track had a depth of  $5.85 \,\mu\text{m}$  and a width of 0.645 mm under the lubrication condition of ultrapure water. The width of worn track under the lubrication condition of BG<sub>aq</sub> was 0.395 mm, which was 38.8% less than that of ultrapure water. However, the width of the worn track was increased slightly under the lubrication condition of  $BG_{aq}$ , compared with  $G_{aq}$  (0.21 mm). The depth of worn surface on the SiO<sub>2</sub> plate under the lubrication conditions of  $G_{aq}$  and  $BG_{aq}$  were 0.685 and 0.355  $\mu$ m, respectively. Furthermore, the wear volume was measured via 3D profilometer (Table 2), and the wear rates were calculated (Figure 6j). The wear rates of the  $SiO_2$  plate and  $Si_3N_4$ ball lubricated by  $G_{aq}$  were  $1.41543 \times 10^{-8}$  and  $3.38337 \times 10^{-10}$  mm<sup>3</sup>/(N·m), respectively. By comparison, the wear rates of plate and ball under the lubrication condition of BG<sub>ag</sub> were  $9.46568 \times 10^{-9}$  and  $2.57577 \times 10^{-10}$  mm<sup>3</sup>/(N·m), which were 33.1 % and 23.9 % lower than that of  $G_{ad}$ . It was revealed that serious wear occurred under the lubrication condition of  $G_{aq}$ . In addition, the wear rates of ball and plate were calculated after lubrication by  $BG_{aq}$  under different conditions (Figure 7). The wear rate of the SiO<sub>2</sub> plate decreased with the increase of the concentration, when the  $BG_{aq}$  was used as lubricant. The wear rate of the  $Si_3N_4$  ball increased with the concentration. The wear rate of the  $SiO_2$  plate decreased with the increase in normal load, and the wear rate of the Si<sub>3</sub>N<sub>4</sub> ball first decreased and then increased with the increase of load. In addition, with the increase of sliding speed, the wear rate of the SiO<sub>2</sub> ball first decreased then increased.



**Figure 5.** The optical image of the wear scar on the  $Si_3N_4$  ball lubricated with (**a**) ultrapure water and (**b**)  $B_{aq}$ ; the morphology of the worn surface on the  $SiO_2$  plate under the lubrication condition of ultrapure water (**c**,**e**) and  $BG_{aq}$  (**d**,**f**); the wear rate of  $SiO_2$  plate and  $Si_3N_4$  ball ( $\Phi$  10 mm) (**g**).

Condition		Average COFs	Wear Volume /um <sup>3</sup>	
			$Si_3N_4$ Ball	SiO <sub>2</sub> Plate
Ultrapure Water	$3 \text{ N}$ , 62.8 mm $\cdot \text{s}^{-1}$	/	$4.1054 imes10^6$	$5.3800  imes 10^7$
B <sub>aq</sub> with different concentration	0.01 wt%	0.0071	$1.0514  imes 10^6$	$2.2980  imes 10^7$
	0.015 wt%	0.0024	$5.2355  imes 10^5$	$1.1660  imes 10^7$
	0.002 wt%	0.0034	$7.7463  imes 10^5$	$1.6740\times 10^7$
	0.004 wt%	0.0062	$5.8154 imes10^5$	$1.4960  imes 10^7$
B <sub>aq</sub> with different load	2.0 N	0.007	$3.8851  imes 10^5$	$1.0490  imes 10^7$
	2.5 N	0.0038	$4.5477  imes 10^5$	$1.3730  imes 10^7$
	3.5 N	0.0049	$1.2518 imes10^6$	$1.5720  imes 10^7$
B <sub>aq</sub> with different sliding speed	$31.4 \text{ mm} \cdot \text{s}^{-1}$	0.0072	$7.5252 \times 10^5$	$3.0560  imes 10^7$
	$94.2 \text{ mm} \cdot \text{s}^{-1}$	0.0038	$1.4740  imes 10^6$	$1.3180  imes 10^7$
	$125.6 \text{ mm} \cdot \text{s}^{-1}$	0.0027	$1.1428  imes 10^6$	$1.4230  imes 10^7$

Table 1. The average COFs and wear volumes under the lubrication condition of ultrapure water and  $B_{aq}$ .

Table 2. The average COFs and wear volumes under the lubrication condition of  $G_{aq}$  and  $BG_{aq}$ .

Condition		Average COFs —	Wear Volume /um <sup>3</sup>	
			Si <sub>3</sub> N <sub>4</sub> Ball	SiO <sub>2</sub> Plate
G <sub>aq</sub>	$3N, 62.8 \text{ mm} \cdot \text{s}^{-1}$	/	$1.5298 \times 10^5$	$6.40  imes 10^6$
BG <sub>aq</sub> with different concentration	0.01 wt%	0.0076	$1.2580 \times 10^5$	$4.96  imes 10^6$
	0.015 wt%	0.0065	$1.1647  imes 10^5$	$4.28 imes10^6$
	0.02 wt%	0.0077	$1.5081 \times 10^5$	$3.82  imes 10^6$
	0.04 wt%	0.008	$2.0608  imes 10^5$	$2.14 imes10^6$
BG <sub>aq</sub> with different load	0.5 N	0.004	$1.0700 \times 10^5$	$4.00  imes 10^6$
	1.0 N	0.0065	$3.7734 \times 10^4$	$5.80  imes 10^6$
	1.5 N	0.0074	$4.6759\times 10^4$	$5.37 \times 10^{6}$
	2.0 N	0.0083	$7.1887  imes 10^4$	$4.31  imes 10^6$
	2.5 N	0.0063	$1.0485  imes 10^5$	$4.24 imes10^6$
	3.5 N	0.0088	$1.6510 \times 10^5$	$4.52  imes 10^6$
BG <sub>aq</sub> with different sliding speed	$94.2 \text{ mm} \cdot \text{s}^{-1}$	0.0055	$1.4154  imes 10^5$	$5.99  imes 10^6$
	$125.6 \text{ mm} \cdot \text{s}^{-1}$	0.0083	$1.5761 \times 10^5$	$1.52  imes 10^7$
	$157.0 \text{ mm} \cdot \text{s}^{-1}$	0.0095	$2.3144  imes 10^5$	$3.93  imes 10^6$

**(a)** 

(**d**)

Height (µm)

(g)

2.740

5.481

4 6 Lateral (mm)

200 µn

574.4 μm



์ พ. 30

Wear rate (×10<sup>-9</sup> r 00 r 70 r

UW

 $G_{aq}$ 

BG<sub>aq</sub>

**Figure 6.** The optical microscope image under the lubrication condition of ultrapure water (Note: UW is ultrapure water) (**a**),  $G_{aq}$  (**b**) and  $BG_{aq}$  (**c**); the 3D micrographs and two-dimensional profiles of worn surface of SiO<sub>2</sub> plate under the lubrication condition of ultrapure water (**d**),  $G_{aq}$  (**e**) and  $BG_{aq}$  (**f**); the optical microscope image of the worn track lubricated by ultrapure water (**g**),  $G_{aq}$  (**h**) and  $BG_{aq}$  (**i**) using the  $\Phi$  4 mm ball; (**j**) the wear rate of SiO<sub>2</sub> plate and Si<sub>3</sub>N<sub>4</sub> ball ( $\Phi$  4 mm) after the tribological tests.



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**Figure 7.** The wear rates of BG<sub>aq</sub> under different conditions; (**a**) concentration, (**b**) loads, (**c**) sliding speeds. (Note: UW is ultrapure water).

To further clarify the lubrication mechanism, the chemical composition of the  $SiO_2$  plate-worn surface was analyzed via XPS. The full-scan XPS spectra of the worn surfaces lubricated by  $B_{aq}$  and  $BG_{aq}$  are shown in Figure 8a,f. The C 1s, O 1s, P 2p and Si 2p both could be detected. The chemical composition of the worn surface on the  $SiO_2$  plate after the tribological test (unclean) with the  $B_{aq}$  and  $BG_{aq}$  are shown in Figure 8. The C 1s three

peaks under the lubrication condition of  $B_{aq}$  (BG<sub>aq</sub>) are located at 283.4 (283.2), 284.8 (284.6) and 286.9 (286.5) eV, corresponding to C–Si [17], C–H/C=H [27] and C–O bond [17], respectively. The O 1s peak at 531.2 eV is attributed to P-OH [28] for the worn surface lubricated by the B<sub>aq</sub>. For the worn surface lubricated by BG<sub>aq</sub>, the positions of O 1s peak is located at 530.9 eV, corresponding to the P=O bond [26]. For the worn surface under the lubrication condition of B<sub>aq</sub>, the Si 2p shows the peak at 101.9 eV, assigned as the Si–O, which is indicative of polymerized siloxane [22,35]. In comparison, the double peaks on the Si 2p at 101.5 and 100.2 eV are assigned to Si–O and Si–OH [17]. For the spectrum of P 2p on the worn surface lubricated by B<sub>aq</sub>, the double peaks at 131.6 and 132.5 eV are identified as P–O–P and O–P=O [23]. For the worn surface lubricated by BG<sub>aq</sub>, the peak located at 131.6 eV is attributed to bridging (P–O–P) phosphorus-oxygen bond.



**Figure 8.** XPS spectra of the worn surface on the SiO<sub>2</sub> plate under the lubrication condition of  $B_{aq}$  (**a–e**) and  $BG_{aq}$  (**f–j**).

Some research reported that the bonds of P=O and P–OH are favorable to combining with free water molecules [23,25]. In the present work, the bonds of P–OH and P=O were detected on the worn surface of the SiO<sub>2</sub> plate under the lubrication condition of  $B_{aq}$ and  $BG_{aq}$ , respectively. Therefore, the free water layers could have been formed on the worn surface during the tribological test. Furthermore, the greater number of combined water molecules could have caused the massive P–OH bonds to be released, due to the bond breakage of P–O–P. The water layers also could form via hydrogen bonds of the P=O···HOH and P–OH···OH<sub>2</sub>. The adsorption and retention of free water molecules for BPQDs play a significant role in achieving and sustaining a superlubricity state. In addition, the P=O bonds have a greater inclination to immediately form two hydrogen bonds, allowing the hydrogen-bonded network to be formed via the hydrogen-bond interactions [24]. For the system of ceramics materials, the colloidal silicon oxide film was formed by tribochemical reactions during the running-in period as follows [18,36,37].

$$\begin{split} Si_3N_4 + 6H_2O &\rightarrow 3SiO_2 + 4NH_3\\ SiO_2 + H_2O &= Si(OH)_4 \end{split}$$

In addition, the hydrolysis reaction could take place due to the thermal activation during the tribological tests. The hydrolysis reaction was conducted as follows [22,38].

$$\equiv$$
 Si-O-Si  $\equiv$  + H<sub>2</sub>O  $\rightarrow$   $\equiv$  Si-OH  $\cdots$  OH-Si

The Si-O bond on the XPS spectrum revealed the formation of a silica gel layer on the surface of the  $SiO_2$  plate. In addition, the existence of Si-OH/Si-O bonds on the worn surface lubricated by  $BG_{aq}$  demonstrated the formation of silica layers on the worn

surface [26]. Beyond that, the existence of the Si-OH bonds allows for the absorption of free water molecules, which is favored for the formation of the water layer on the worn surface. The minimum lubrication film thickness ( $h_{min}$ ) under the lubrication condition of BG<sub>aq</sub> was calculated by the Hamrock–Dowson theory [39,40].

$$h_{\min} = 2.56 \frac{\alpha^{0.53} R^{0.464} u^{0.67} \eta_0^{0.67}}{E'^{0.073} W^{0.067}} (1 - 0.61 e^{-0.73k})$$
(2)

where *R* is the equivalent radius of the ball,  $\alpha$  is the pressure-viscosity coefficient of the BG<sub>aq</sub> (about  $4 \times 10^{-9}$  Pa<sup>-1</sup>) [41] and *u* is the sliding speed of the Si<sub>3</sub>N<sub>4</sub> ball and SiO<sub>2</sub> plate (62.8 mm/s). The applied load *W* is 3 N.  $\eta_0$  is the dynamic lubricant viscosity. *E'* is the effective modulus of elasticity of the friction pair, which can calculated as follows:

$$\frac{1}{E'} = \frac{1}{2} \left[ \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \right]$$
(3)

where  $v_1$  and  $v_2$  are the Poisson's ratio of the Si<sub>3</sub>N<sub>4</sub> ball ( $v_1 = 0.26$ ) and SiO<sub>2</sub> plate ( $v_2 = 0.17$ ), respectively.  $E_1$  and  $E_2$  are the elasticity modulus of the ball ( $E_1 = 310$  GPa) and plate ( $E_2 = 77.8$  GPa). The *R* is the equivalent radius of the ball, which can be calculated as follows:

$$R = \frac{E'' d^3}{6W} \tag{4}$$

where *d* is the diameter of the worn scar of the ball, and the E'' is the effective elastic modulus of the friction pair, which can be calculated by the following:

$$\frac{1}{E''} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \tag{5}$$

In the end, the calculation of  $h_c$  is about 34.4 nm with a load of 3 N and a sliding speed of 62.8 mm/s. Then the  $\lambda$  can be calculated by the ratio of the theoretical minimum film thickness ( $h_{min}$ ) to the roughness as follows:

$$\lambda = \frac{h_{\min}}{\sqrt{\sigma_1^2 + \sigma_2^2}} \tag{6}$$

where  $\sigma_1$  and  $\sigma_2$  are the roughness of the Si<sub>3</sub>N<sub>4</sub> ball and SiO<sub>2</sub> plate. Thus, the  $\lambda < 1$  in this present study, which indicated that the superlubricity state corresponds to boundary lubrication.

Nevertheless, a superlubricity state is difficult to sustain under the lubrication condition of  $B_{aq}$  (Figure 3a). To solve this issue, glycerol was selected to promote the stability of the superlubricity state. The reason that glycerol can promote the stability of the friction is that the water molecules can be aggregated on the worn surface due to the degradation of glycerol. In addition, it can adsorb molecular water from humid air [42]. To exclude the influence of the glycerol on superlubricity, the tribological performance of  $G_{aq}$  was evaluated, and the result indicated that the macroscale superlubricity could not be achieved on the Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> interface. However, the synergistic effect between BPQDs and glycerol could effectively decrease the COF and maintain the superlubricity state.

As mentioned above, the lubrication mechanisms were proposed, and the schematic diagram is shown in Figure 9. During the tribological tests, the boundary lubrication occurred in the contact zone. The colloidal silicon oxide film was formed due to the tribochemical reaction, and the silica gel layer was formed due to the hydrolysis reaction. The colloidal silicon oxide film can promote boundary lubrication [37]. Additionally, the hydrogen-bonded network was formed during the tribological reaction via the hydrogen-bond interactions (Figure 9b,d). On the one hand, the hydroxyl group can be attached to the surface of the silica gel layer via the hydrogen bond interactions, which can form the

hydrogen-bonded network. On the other hand, the existence of the P=O bonds are favor the formation of two hydrogen bonds, which can be attached to the surface of BPQDs, thereby forming the hydrogen-bonded network. Moreover, the adsorption water layers were formed via the combination of P=O/P–OH and free water molecules. Meanwhile, the Si–OH group on the worn surface facilitated the formation of the free water layer. The existence of the hydrogen-bonded network and adsorption water layer played a major role in the reduction of the average COF. Furthermore, the hydrogen-bonded network and adsorption water layer could prevent the worn surfaces from contacting one another. In addition, the synergistic effect between BPQDs and glycerol could maintain a low and stable COF.



**Figure 9.** Schematic illustration of the lubrication model with BPQD additives in glycerol aqueous solution. (**a**,**b**) the Macroscopic schematic diagram, (**c**) formation of silica gel layer and colloidal silicon oxide film, (**d**) the formation of hydrogen-bonded network and the synergistic effect between BPQDs and glycerol.

#### 4. Conclusions

BPQDs were successfully prepared via sonication-assisted liquid-phase exfoliation. The average particle size of the BPQDs was  $3.3 \pm 0.85$  nm. The BPQDs exhibited excellent dispersion stability in ultrapure water. Macroscale superlubricity could be realized with the unmodified BPQDs on the roughest interfaces. The minimum COF of 0.0022 was achieved at the concentration of 0.015 wt% (3 N, 62.8 mm·s<sup>-1</sup>). The wear rates of the SiO<sub>2</sub> plate and Si<sub>3</sub>N<sub>4</sub> ball were 78.3 % and 87.2 % lower than that of ultrapure water. Furthermore, glycerol was introduced into the ultrapure water to promote the stability of the superlubricity state. Similarly, the macroscale superlubricity could be obtained with the BG<sub>aq</sub>, and the superlubricity remained steady for more than 1 h. The wear rates of plate and ball under the lubrication condition of BG<sub>aq</sub> were 9.46568 × 10<sup>-9</sup> and 2.57577 × 10<sup>-10</sup> mm<sup>3</sup>/(N·m), which were 33.1% and 23.9% lower than that of G<sub>aq</sub>. In addition, the macroscale superlubricity state could still be achieved after one week, and the average COF value increased slightly. Ultimately, the macroscale superlubricity mechanisms were proposed. During the tribological tests, the colloidal silicon oxide film and the silica gel layer were formed due to the tribochemical reaction and hydrolysis reaction. The hydrogen-bonded network

was formed via hydrogen-bond interactions. The silica gel layer and hydrogen-bonded network play major roles in realizing macroscale superlubricity. Additionally, the adsorption water layers could also reduce the COF during the tribological tests. The synergistic effect between BPQDs and glycerol can effectively decrease the COF and maintain the superlubricity state.

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## Nomenclature

- $\Phi$  The diameter of the Si<sub>3</sub>N<sub>4</sub> ball
- Ra The roughness of the friction pairs
- W<sub>B</sub> Wear rate
- V Wear volume
- P Normal load
- S Sliding distance of the Si<sub>3</sub>N<sub>4</sub> ball
- $h_{\min}$  The minimum lubrication film thickness
- $\alpha$  Pressure-viscosity coefficient
- *R* Equivalent radius of the Si<sub>3</sub>N<sub>4</sub> ball
- u Sliding speed of the Si<sub>3</sub>N<sub>4</sub> ball and SiO<sub>2</sub> plate
- $\eta_0$  Dynamic lubricant viscosity
- *E'* Effective modulus of elasticity of the friction pair
- W Applied load
- $v_i$  Poisson's ratio of the friction pair
- $E_i$  Elasticity modulus of the friction pair
- *E'* Effective elastic modulus of the friction pair
- *d* Diameter of the worn scar of the ball
- $\lambda$  The ratio of the theoretical minimum film thickness to the roughness
- $\sigma$  The roughness of the friction pair after the tests

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