Preparation, characterization, and tribological properties of silica-nanoparticle-reinforced B–N-co-doped reduced graphene oxide as a multifunctional additive for enhanced lubrication

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Abstract: Microwave-synthesized SiO2-reinforced B–N-co-doped reduced graphene oxide (SiO2–B–N–GO) nanocomposites were characterized by X-ray photon spectroscopy (XPS), X-ray diffraction (XRD), infrared (IR) spectroscopy, and transmission electron microscopy/energy dispersive X-ray (TEM/EDX) analysis. The tribological properties of the SiO2–B–N–GO prepared as anti-wear additives for enhanced lubrication were studied using a four-ball tester. The experiment results indicated that SiO2–B–N–GO exhibits excellent load-carrying, anti-wear, and anti-friction properties in a base oil, especially at the optimal concentration of additives at 0.15 wt%. The wear scar diameter decreased from 0.70 to 0.37 mm and the coefficient of friction was reduced from 0.092 to 0.070, which reductions are attributed to the formation of B–N and graphene layer tribofilms of several tens of nanometers in thickness that prevented direct contact between metals.

Keywords: SiO2–B–N–GO nanocomposites; material characterization; tribological properties

1 Introduction

Lubrication associated with nanotribology has aroused great public concern, and the lubricant industry must improve the performances of lubricants considering both efficiency and the environment [1–4]. Various lubricant-containing nanoparticles, such as metallic TiO2, CuO, SiO2 and graphene, are used to reduce the friction and wear between metals because a lubricating film composed of nanoparticles forms on the friction pair during sliding [2–4].

Graphene and graphene oxide have attracted much attention owing to their excellent electrical, thermal, and mechanical properties [5–9]. Graphene has long been shown to be an excellent solid lubricant with significant tribological properties due to its ability to undergo easy shear [7, 8]. Recent studies of graphene and graphene oxides have attempted to investigate the friction and wear behavior between metals with their use, but their application has not yet been fully studied in the field of lubrication [10, 11]. The addition of graphene has been shown to slow down the oxidation and corrosion on the surface of a friction pair [12]. Berman et al. [5] characterized the graphene tribological behavior by atomic force microscopy, and the results demonstrated that the friction coefficient decreases significantly and the surface morphology was improved under a load of 5 N. Moreover, intermittent graphene has been applied to ensure a reduction in the friction and wear between metals during an entire testing process [13]. The synergetic enhancement effect has been achieved using graphene-based composites, and the tribological properties of graphene have been improved, thereby allowing for the full utilization

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of graphene in tribological applications [14]. In another study of the tribological behavior of graphene-based composites, boron- and nitrogen-based additives were used. A boron nitride protective film was formed on the friction surface between the metals and showed excellent synergistic effects, thereby reducing the friction and wear [15]. In the field of tribology, silica nanoparticles have been widely studied as effective antifriction agents over recent years. Therefore, in order to study the significant reduction in friction and wear under high loads, SiO₂, B–N–GO, and SiO₂-reinforced B–N–GO nanoparticles are prepared and analyzed using X-ray photon spectroscopy (XPS), X-ray diffraction (XRD), infrared (IR) spectroscopy, and transmission electron microscopy/energy dispersive X-ray (TEM/EDX). The tribological behaviors of these prepared nanoparticles acting as multifunction additives in a base oil are then studied using a four-ball tester and the worn surfaces were observed by XPS. The wear and friction mechanisms of the nanoparticles used as anti-wear additives between the metal friction pairs are proposed.

2 Materials and methods

The materials used in these syntheses were graphite oxide flakes (1–2 mm, produced by NGS Naturgraphit GmbH), potassium permanganate (KMnO₄, ≥99.0%, produced by Fluka), boric acid (H₃BO₃, ≥98%, produced by Sigma-Aldrich), toluene (99% purity, produced by Sinopharm), tetraethylorthosilicate (TEOS, 99% purity, produced by Sinopharm), polyalphaolefin 100 (PAO as base oil, 99% purity, produced by ExxonMobil), and ethanol (99% purity, produced by Sinopharm).

2.1 Preparation of silica-nanoparticle-reinforced B–N-co-doped reduced graphene oxide (SiO₂–B–N–GO) lubricant

TEOS was added to a solution of ethanol and aqueous ammonia, and this was gently stirred for 3 h at 40 °C. Silica (SiO₂) nanoparticles were prepared by the Stöber method according to previous research [16], as shown in Fig. 1. B–N–GO was prepared by the microwave-assisted method [17]. Graphene oxide (GO, 250 mg) and SiO₂ were dispersed in ethanol (50 mL), followed by the addition of boric acid solution (1 mg/mL) and ammonium hydroxide (1 mg/mL), and this was stirred at 60 °C for 8 h to obtain B–N–GO and SiO₂–B–N–GO nanoparticles. The black-colored product was cooled to 25 °C and then dried at 85 °C, followed by microwave for 5 min at 800 W. The 1 mg/mL dispersions of nano-SiO₂, B–N–GO, and SiO₂–B–N–GO (450 mg) were well-dispersed in ethanol (96%, 50 mL) by sonication for 1 h at 55 °C.

2.2 Sample characterization

The morphologies of the prepared nanoparticles (SiO₂, B–N–GO, and SiO₂–B–N–GO) were observed through TEM with EDX analysis. XRD using Cu Kα1 radiation was employed to characterize the crystal structures of the samples. The molecular structures of SiO₂, B–N–GO, and SiO₂–B–N–GO were observed using Fourier transform infrared (FT-IR, Bruker VERTEX 80V) spectra in the range from 4,000 to 500 cm⁻¹. XPS (Sigma Probe, produced by Thermo VG Scientific) was used to characterize the synthesized SiO₂–B–N–GO.

2.3 Tribological characterization

Base oils containing the synthesized nanoparticles (SiO₂, B–N–GO, and SiO₂–B–N–GO) with various concentrations (0.00, 0.05, 0.10, 0.15, and 0.20 wt%) were prepared by magnetic stirring at 45–55 °C for 2 h and sonication for 60 min at 25 °C. Tribological tests were conducted using a four-ball tester according to ASTM D5183 and ASTM D4172. The balls are made of AISI 52100 alloy steel. In addition, the tribological properties of the base oil with the optimized concentrations...
0.15 wt%, of SiO₂, B–N–GO, and SiO₂–B–N–GO were evaluated using various loads (294, 392, 490, 588, 686, 784, and 881 N) in a 60-min test. Three replicate tests were carried out to calculate the mean values. The morphologies of the worn surfaces were observed by scanning microscopy electron (SEM), and the compositions of the films formed on the worn surfaces were analyzed by XPS.

2.4 Dispersion stability

The dispersion stabilities of the SiO₂, B–N–GO, and SiO₂–B–N–GO nanomaterials in the base oil were studied by the absorbance method. First, these prepared nanomaterials were ultrasonically dispersed in the base oil for 2 h, and the optimal concentration of these nanomaterials in the base oil was 0.15 wt% based on the results of the tribological tests. These solutions were then further diluted by 10 times. The absorbances of these solutions were evaluated at different time intervals using an UV-2600 ultraviolet-visible (UV-vis) spectrophotometer.

3 Results and discussion

3.1 Morphology and microstructure of B–N–GO, SiO₂, and SiO₂–B–N–GO

The TEM images of the synthesized B–N–GO, SiO₂, and SiO₂–B–N–GO samples are shown in Fig. 2. The flocculated morphology of the graphene oxide is observed in the TEM/HTEM images of B–N–GO (Fig. 2(a)), and the HRTEM images (Figs. 2(e) and 2(g)) illustrate the lattice fringes of the graphene sheets in B–N–GO.

![Fig. 2](image-url) Photographs of the PAO lubricant with nanoparticles and TEM/HTEM images, respectively. (a, e) B–N–GO, (b, f) SiO₂, and (c, g) SiO₂–B–N–GO with (d) the EDX spectrum.
and SiO$_2$–B–N–GO as 0.334 and 0.335 nm in the (002) plane. The SiO$_2$ particles are spherical (Figs. 2(b), 2(f), and 2(g)) with lattice spacings of 0.301 and 0.312 nm in the (302) planes of SiO$_2$ and SiO$_2$–B–N–GO, respectively. SiO$_2$ nanoparticles (30–50 nm) are dispersed on the graphene oxide in Fig. 2(c). The EDX spectrum of SiO$_2$–B–N–GO (Fig. 2(d)) shows C, Si, O, B, and N elements, and the semi-quantitative EDX results reveal the stoichiometric composition of SiO$_2$–B–N–GO. The peaks of the oxygen (~10.53% atomic weight) and silicon (~13.95% atomic weight) further confirm that the SiO$_2$ nanoparticles are distributed on the graphene oxide.

The XRD patterns of the synthesized SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO are shown in Fig. 3(a). The peak around 10.4° corresponds to the (001) planes of graphitic oxide in the XRD patterns of B–N–GO [18]. The XRD patterns of the SiO$_2$ nanoparticles show six distinct diffraction peaks at 28.7°, 30.9°, 33.1°, 37.8°, 41.2°, and 44.6° indexed with the (211), (202), (212), (203), (302), and (114) planes of SiO$_2$ (Joint Committee Powder Diffraction Standards (JCPDS) No. 47-1300), respectively, which has an face-centered cubic (fcc) structure. In the XRD patterns of SiO$_2$–B–N–GO, it is shown that the peaks are similar to the diffraction patterns of SiO$_2$ and B–N–GO, which reveals that the silica and graphene oxide phases are predominant in the SiO$_2$–B–N–GO sample. Figure 3(b) shows the IR spectra of the synthesized SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO samples. In the spectrum of B–N–GO, the absorption peak at 3,396 cm$^{-1}$ is broad and strong, which is due to –OH stretching vibrations, and the C=O stretching of –COOH groups from B–N–GO can be observed at 1,734 cm$^{-1}$. The absorption peaks at 1,127 cm$^{-1}$ and 1,438 cm$^{-1}$ result from the C–O–C and C–O vibrations, respectively. For SiO$_2$, the peaks at 1,596 cm$^{-1}$ and 1,445 cm$^{-1}$ are attributed to the stretching and bending vibrations of –OH, respectively, which are caused by water absorbing on the surface of the nanoparticles. The peak at 1,595 cm$^{-1}$ is the typical vibrational absorption peak of SiO$_2$. The SiO$_2$–B–N–GO nanocomposites had additional peaks at 1,445 cm$^{-1}$ (Si–O–Si) and 1,595 cm$^{-1}$ (Si–O–C), and there was no obvious absorption peak at 875 cm$^{-1}$ compared with B–N–GO. The intensity of the peak at 3,407 cm$^{-1}$ did not increase significantly. These results indicate that the SiO$_2$ was generated after the reaction of SiO$_2$–B–N–GO, and the processing did not consume the oxygen-containing functional groups.

The relative absorbances of the SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO nanomaterials in base oil over time are plotted in Fig. 4. The relative absorbances of the base oils containing SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO decrease over time. The deposition rates of the B–N–GO and SiO$_2$ in the solutions are much faster than that of SiO$_2$–B–N–GO. After 48 h, the relative absorbances of B–N–GO (~0.65) and SiO$_2$ (~0.64) are much lower than that of SiO$_2$–B–N–GO (~0.72). Thus, the dispersion stabilities of B–N–GO and SiO$_2$ are much lower than that of SiO$_2$–B–N–GO. Therefore, among these three nanomaterials, SiO$_2$–B–N–GO has the best dispersion.

![Fig. 3](https://mc03.manuscriptcentral.com/friction)
The chemical structures of the synthesized SiO$_2$–B–N–GO were further studied by XPS analysis, and boron, nitrogen, silicon, carbon, and oxygen elements were detected in the sample, as shown in Fig. 5. The atomic percentages of C, O, B, N, and Si are 87.78, 7.63, 1.86, 2.56, and 0.60, respectively. Additionally, the C1s spectra of SiO$_2$–B–N–GO can be deconvoluted into six components using peak fit software with binding energies of 292.1, 289.6, 286.2, 285.1, 284.7, and 283.8 eV, corresponding to O–C=O, C=O, N–sp$^3$C, N–sp$^2$C, sp$^2$C–sp$^2$C, and B–C bonds, respectively (Fig. 5(a)) [19]. As shown in Fig. 5(b), the spectra of B1s can be deconvoluted into three peaks at 193.2, 192.3, and 191.5 eV, corresponding to B–O, B–C, and B–CO$_2$ bonds, respectively [20]. The N 1s spectra were deconvoluted into three peaks at 401.5, 399.8, and 398.3 eV, corresponding to graphitic N, pyrrolic N, and pyridinic N, respectively, as show in Fig. 5(c). The Si 2p spectra show the presence of Si 2p (~103.6 eV), as shown in Fig. 5(d) [21].

### 3.2 Tribological properties

#### 3.2.1 Additive optimization

Figure 6(a) shows the variation of the maximum non-seizure load ($P_B$) for the base oil with an increasing additive concentration. It can be seen that all of the additives can improve the $P_B$ values of the base oil dramatically, and it is also illustrated that these nanomaterial additives play a large role in the load-carrying capacities of these materials. With the addition of 0.05 wt% SiO$_2$, the $P_B$ value of the base oil is enhanced by 43%. In addition, the $P_B$ value of the synthesized SiO$_2$–B–N–GO is the highest among all additives at the same concentration, which indicates that
the intensity of oil film formed by the SiO$_2$–B–N–GO nanoparticles on sliding surface is greater than that of SiO$_2$ and B–N–GO. Figure 6(b) shows the mean wear scar diameters (WSDs) at different concentrations of the synthesized SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO nanoparticles in the base oil under 392 N for 60 min. It is obvious that all WSD values are decreased with the addition of SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO nanoparticles to the base oil, and the anti-wear properties of the base oil are improved with each additive. When an additive concentration of only 0.05 wt% is used, the WSD value reduces from 0.700 to 0.688 mm (SiO$_2$), 0.682 mm (B–N–GO), and 0.680 mm (SiO$_2$–B–N–GO). The WSD of the balls first decreases with the additive concentration and then increases, and the lowest values of WSD were obtained by SiO$_2$ (0.46 mm), B–N–GO (0.39 mm), and SiO$_2$–B–N–GO (0.37 mm) at an optimized concentration of 0.15 wt%. When using SiO$_2$–B–N–GO, the WSD was reduced by about 47.1% compared to the original value of the base oil (0.70 mm).

Based on the maximum no-seizure load and WSD, a new performance indicator, the extreme pressure anti-wear coefficient, $\omega$, is proposed to analyze the tribological properties of lubricants using the following equation [22]:

$$\omega = 10 \log \left( \frac{P_B}{WSD} \right)$$

where $P_B$ is the maximum non-seizure load and WSD is the mean wear scar diameter. All of the tribological parameters are listed in Table 1.

As shown in Table 1, the values of $\omega$ for these nanomaterials are maximized at the optimized concentration of 0.15 wt%. These results indicate that these nanomaterials exhibit excellent load-carrying and anti-wear properties in the base oil, especially at the optimal concentration of 0.15 wt%.

### 3.2.2 Anti-wear properties

Figure 7(a) shows the average coefficient of friction (COF) values and the wear volumes of the balls lubricated by the base oil with and without the synthesized SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO nanoparticles under a load of 392 N for 60 min at 1,200 rpm. With the addition of all nano-additives, both the wear volumes and COF values are reduced significantly. When using

| Concentration (wt%) | SiO$_2$ | B–N–GO | SiO$_2$–B–N–GO |
|---------------------|--------|--------|-----------------|
|                     | $P_B$ (N) | WSD (mm) | $\omega$   | $P_B$ (N) | WSD (mm) | $\omega$   | $P_B$ (N) | WSD (mm) | $\omega$   |
| 0.00                | 274     | 0.7    | 2.59          | 274     | 0.7     | 2.59      | 274     | 0.7     | 2.59      |
| 0.05                | 392     | 0.69   | 2.75          | 490     | 0.68    | 2.86      | 534     | 0.68    | 2.90      |
| 0.10                | 490     | 0.54   | 2.96          | 515     | 0.5     | 3.01      | 613     | 0.45    | 3.13      |
| 0.15                | 517     | 0.46   | 3.05          | 585     | 0.41    | 3.15      | 686     | 0.37    | 3.27      |
| 0.20                | 538     | 0.50   | 3.03          | 618     | 0.48    | 3.11      | 734     | 0.42    | 3.24      |
| 0.25                | 585     | 0.55   | 3.03          | 686     | 0.51    | 3.13      | 824     | 0.46    | 3.25      |
SiO$_2$–B–N–GO, the wear volume and average COF are reduced by about 92.2% and 23.9%, respectively, compared to wear volume and average COF for the base oil, which are $92.8 \times 10^{-5}$ mm$^3$ and 0.092, respectively. The excellent anti-wear and anti-friction behaviors of the SiO$_2$–B–N–GO in the base oil is due to the formation of tribofilms (Fig. 10(b)) between metals. These tribofilms combine the synergistic effects provided by the nano-SiO$_2$ acting as nano-bearings and the flocculated structure of B–N–GO [23]. Figure 7(b) shows the various applied loads and WSDs of the synthesized nano-additives in the base oil at 0.15 wt% for 60 min. Under a 294 N load, the WSDs of the balls lubricated with SiO$_2$ (0.40 mm), B–N–GO (0.38 mm), and SiO$_2$–B–N–GO (0.35 mm) are much smaller than that of the base oil (0.67 mm), which implies that the additives play an anti-wear role in the metal-to-metal sliding process. The WSD value increases as the load increases, and this is mainly because the oil film thickness between the metals decreases or even breaks, resulting in direct metal contact [24]. The thin oil film cannot support a load beyond 686 N in the case of SiO$_2$ and B–N–GO additives in the base oil. However, SiO$_2$–B–N–GO can sustain this load and the WSD values are larger. The SiO$_2$-reinforced B–N–GO nanomaterial can further improve the load-carrying capacities of B–N–GO and SiO$_2$, which is attributed to the synergistic effect of the adsorbed B–N–GO on the sliding surfaces forming a protective tribochemical film [15] and the SiO$_2$ nanoparticles acting as nano-bearings between the metals [25]. Moreover, the maximum load-carrying capacities of SiO$_2$–B–N–GO providing enhanced lubrication was found to reach up to 882 N.

### 3.3 Surface characterization

Figure 8 shows the SEM morphologies of the worn surfaces with different lubrications. When lubricated with only the base oil, the WSD of the worn surface is very large (0.70 mm) and there is severe surface destruction, which results from the plastic deformation of the worn surface. However, a smoothening of the surfaces is observed with the addition of the synthesized nanomaterials, which is in agreement with the aforementioned order of the anti-wear properties. The WSD value is considerably reduced when lubrication...
with the SiO$_2$-reinforced B–N–GO is used, as shown in Fig. 8(d). Some adhesiveness structures can be seen on the wear tracks of the surfaces lubricated by B–N–GO and SiO$_2$-reinforced B–N–GO because the graphene sheets are adsorbed on the worn surface during sliding.

### 3.4 Tribochemistry

According to American Society for Testing Material (ASTM) D5183-05, Fig. 9 shows the XPS spectra of B 1s, C 1s, N 1s, O 1s, Si 2p, and Fe 2p for the sample lubricated with SiO$_2$–B–N–GO. Figure 9(a) shows the C 1s spectra, which is deconvoluted into three peaks at 287.9, 286.3, and 284.8 eV, corresponding to C=O, N–sp$^3$C, and sp$^3$C–sp$^3$C moieties, respectively [19]. The binding energies between B 1s (Fig. 9(b)) and N 1s (Fig. 9(c)) are indicated at 189.8 and 398.6 eV, respectively, which prove the existence of boron nitride among the tribopairs [26, 27]. Nevertheless, a prominent shift was not found in the peak of Si 2p, revealing that the SiO$_2$ nanoparticles were tribosintered onto the steel surface (Fig. 9(d)) [28]. The Fe on the surface has been oxidized to Fe$_2$O$_3$ under the testing conditions, which can be seen from the binding energies of 711.8 eV for Fe 2p and 530.6 eV for O 1s (Figs. 9(e) and 9(f)) [29]. Therefore, SiO$_2$–B–N–GO nanomaterials provide remarkable tribological benefits via the formation of in-situ protective tribofilms composed of boron nitride and graphene layers that are deposited on the steel-steel interfaces. The SiO$_2$ nanoparticles form a uniform layer and act as nano-bearings, which prevents the direct contact of the metals, thereby decreasing the friction and wear.

### 3.5 Proposed mechanism

The use of SiO$_2$, B–N–GO, and SiO$_2$–B–N–GO nanocomposites as multifunctional additives in a base oil has shown that they all possess excellent tribological properties based on the above tribological and surface characterization results. Compared with SiO$_2$ and B–N–GO, however, SiO$_2$–B–N–GO demonstrated better tribological properties. The reasons behind the enhanced tribological properties of SiO$_2$–B–N–GO can be summarized as follows. Initially, the nanomaterial evenly adheres between the friction pairs. During friction, SiO$_2$–B–N–GO reacts with the steel ball and forms a protective tribofilm of several tens of nanometers in thickness (Fig. 10(b)) to reduce the asperity-asperity adhesion under extreme conditions (Fig. 10(a)). The WSD value is therefore much smaller when SiO$_2$–B–N–GO is used, as shown in Fig. 8(d). Some adhesiveness structures can be seen on the wear tracks of the surfaces lubricated by B–N–GO and SiO$_2$-reinforced B–N–GO because the graphene sheets are adsorbed on the worn surface during sliding.
N–GO is used. The formation of this *in-situ* protective tribofilm is related to the sliding time, and as time progresses, the friction film forms more easily [30]. In addition, the SiO₂ nanoparticles deposited on the surface of B–N–GO further prevent agglomeration [30]. Spherical SiO₂ nanoparticles act as nano-bearings between the B–N–GO layers and friction pairs, thus decreasing both the friction and wear [25]. Therefore, the excellent tribological behaviors of SiO₂-reinforced B–N–GO result from the synergistic effects of the formation of an *in-situ* BN protective tribofilm of several tens of nanometers in thickness on the worn surface and the SiO₂ particles acting as nano-bearings during sliding.

### 4 Conclusions

SiO₂ nanoparticles (30–50 nm) were prepared using the Stöber method, B–N-co-doped GO (B–N–GO), and SiO₂-reinforced B–N–GO (SiO₂–B–N–GO) nanoparticles were successfully obtained by microwave-synthesis. These materials were characterized by TEM/EDX, XRD, IR spectroscopy, and XPS. The tribological behaviors of these materials were studied using a four-ball tester with the optimum concentration (0.15 wt%) of these nanoparticles in the base oil. The results indicated that SiO₂-reinforced B–N-doped GO exhibited a significant reduction in both the WSD (from 0.70 to 0.37 mm) and COF (from 0.092 to 0.070) values. These reductions are attributed to the *in-situ* formation of a tribofilm that is several tens of nanometers thick and consists of graphitic carbon, boron nitride, and tribosintered SiO₂ nanomaterials that prevent metal-metal contact.

The above results reveal that the prepared SiO₂–B–N–GO nanocomposites are potential candidates to be developed as effect anti-wear lubricant additives for enhanced lubrication under boundary lubricating conditions.

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