

Frictional behavior of oxide graphene nanosheets as water-base lubricant additive

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Abstract Oxide graphene (GO) nanosheets were prepared by modified Hummers and Offeman methods. The products were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FTIR), and thermogravimetric analysis (TGA). The tribological properties of GO nanosheets as water-base lubricant additive were investigated using a UMT-2 ball-plate tribotester. By the addition of GO nanosheets in pure water, the antiwear ability was improved and the friction coefficient was decreased. The water with GO nanosheets showed better tribological properties than the water with oxide multiwall carbon nanotubes (CNTs-COOH). It is concluded that the formation of a thin physical tribofilms on the substrate can explain the good friction and wear properties of GO nanosheets.

1 Introduction

Recently, water-based lubricants are widely used for numerous areas such as hydraulic fluid, cutting fluid, metal-forming operations, and the oil extraction industry. Compared with conventional oil and grease lubricants, water-based lubricants consisting of less than 5% additives may offer many merits, such as high thermal conductivity, saving oil resources, low working temperature, etc. Therefore, it is a new, necessary, and promising domain to develop a high-performance lubricating additive in water [1, 2].

Lamellar compounds such as graphite and metal dichalcogenides (MoS_2 , WS_2) are widely used as solid lubricants or as additives to liquid lubricants [3–6]. These

materials are characterized by weak interatomic interactions between their layers (Van der Waals forces), allowing easy, low-strength shearing [7]. Unfortunately, those lamellar compounds (MoS_2 , WS_2) tend to stick to the mating metal pieces through the reactive dangling bonds on the prismatic edges (0110), which leads to their rapid annihilation through burnishing and oxidation. Recently, due to high load-bearing capacity, low surface energy, high chemical stability, weak intermolecular, and strong intramolecular bonding, nanocarbon materials have also received much attention in the field of tribology. For example, the tribological properties of fullerene particles, as an additive to liquid lubricants, were studied by a few groups [8, 9]. The results indicated that the presence of fullerene was able to increase the load-carrying ability and decrease the friction coefficient and wear. Tu et al. have found the graphite nanosheets as an additive in oil at proper concentration show better tribological properties than pure paraffin oil. The load-carrying capacity and antiwear ability of the lubricating oil was improved [10]. Hao and coworkers adopted polyacrylamide-modified CNTs as water-based lubricant additive, which can be dispersed in liquid paraffin. Friction tests indicate that CNTs have excellent load-carrying capacity, good extreme pressure, antiwear, and friction-reducing properties [11].

As a rising nanostructure attracting rapidly increasing research effort, the graphene sheet, a two-dimensional monolayer of carbon atoms [12], seems to be the only known material that can rival carbon nanotubes (CNTs) in tensile modulus and strength [13, 14]. A CNT, which can be considered as a rolled-up graphene sheet, is strong only along its length direction. Comparably, a single-layered graphene sheet is strong along all its plane directions and enjoys a larger surface-to-volume ratio [15], lower raw material cost as well as easier industrialization [16]. These merits guaran-

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tee a bright future for dispersed graphene sheets as a promising reinforcement of nanocomposites [17].

Based on above discussion, we have synthesized the GO nanosheets as water-base lubricant additive via low cost chemical synthesis routes. The results showed that these GO nanosheets can improve the antiwear and reduced frictional properties of water under proper conditions. Their antiwear and reduced friction mechanisms are also discussed and in situ solid film deposition mechanism was proposed. To our knowledge, this is the first report on GO nanosheets as a water-based lubricant additive.

2 Experimental methods

2.1 Preparation of GO nanosheets

GO nanosheets were prepared from purified natural graphite by the method reported by Hummers and Offeman [18, 19]. Simply, 10 g of graphite powder was added to 230 mL of cooled (0°C) concentrated H₂SO₄. 30 g of KMnO₄ was added gradually with stirring and cooling, so that the temperature of the mixture was maintained below 20°C. The mixture was then stirred at 35°C for 30 min. 460 mL of distilled water was slowly added to cause an increase in temperature to 98°C and the mixture was maintained at that temperature for 15 min. The reaction was terminated by adding 1.4 L of distilled water followed by 10 mL of 30% H₂O₂ solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulfate could not be detected with BaCl₂, then the suspension was dried in a vacuum oven at 60°C for 24 h to obtain GO nanosheets.

2.2 Tribological properties of GO nanosheets as additive

The as-prepared GO nanosheets were distributed into pure water via 30 min ultrasonication, leading to the desired samples with different content of GO nanosheets. By similar treatment, comparative pure water and others with CNTs-COOH (purity > 95 wt%, 20–30 nm outer diameters, 10–30 μm length, and 1.23 wt% COOH content) were purchased from Chendu Organic Chemicals Co. Ltd., Chinese Academy of Science) were also prepared.

The friction and antiwear properties of the water with GO nanosheets were examined on a UMT-2 ball-plate machine, in comparison to the pure water and the water with CNTs-COOH. The friction and wear tests were conducted at a rotating speed of 120 rpm and under a constant load of 10 N, for the test duration of 10 min. A dependence of the wear scar diameter (WSD) on friction time was also measured, the operation procedure of which was given as follows: measured WSD after rubbing for given time, then went on friction for another given time, and repeated the operation. The balls (diameter in 12.7 mm) used in the tests

were made of GCr15 bearing steel (AISI 52100) with a hardness of 61 HRC. Before each test, the steel balls were cleaned in petroleum ether and dried. The balls after testing were cleaned using an ultrasonic bath in ligroin and then in distilled water for 10 min, respectively. Wear behavior was evaluated by the resultant WSD of the 45# steel disk after friction. The WSD value was obtained from images taken by a Leica DM 2500M optical microscope equipped with DFC 420 CCD digital camera, taking the mean average of the readings at five positions.

2.3 Characterization

The general morphology of the products was examined by SEM on a JEOL JSM 6700F instrument operated at 20 kV. TEM measurements were conducted on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. FTIR was used to characterize the changes in a chemical structure of the GO nanosheets after each surface treatment step. TGA was performed on a Boyuan DTU-2C thermogravimetric analyzer from 20 to 800°C at a heating rate of 5°C/min in air flow.

3 Results and discussions

The as-prepared GO nanosheets and CNTs-COOH were dispersed in water to a nominal concentration of 0.5 mg mL⁻¹ with the aid of bath ultrasonication, and the dispersions were then allowed to settle for several weeks. Figure 1 shows digital pictures of all of the dispersions immediately after sonication (a) and 5 weeks after sonication (b). It is well known that artificial graphite is extremely hydrophobic naturally. After oxidation, the obtained GO nanosheets become partially hydrophilic and are well dispersed in water. In contrast to black graphite, GO nanosheets exhibit a slight golden color due to the loss of electronic conjugation brought about by the oxidation. On one hand, carboxyl, hydroxyl and epoxy groups are introduced onto the edge sites and basal planes of GO nanosheets, which makes GO nanosheets partially hydrophilic that guarantees the stable existence in aqueous medium (as shown in the digital photo of colloid suspension of GO nanosheets, Fig. 1a). However, CNTs-COOH in water displayed only short-term stability and precipitated completely in a matter of hours to a few days (Fig. 1b). By contrast, the as-prepared GO dispersions in water were seen to exhibit long-term stability comparable to that observed for the dispersions of CNTs-COOH in water.

The graphite oxide powders were exfoliated via ultrasonic vibration to produce GO nanosheets. The morphology and structure of the GO nanosheets were observed by SEM and TEM analysis in Fig. 2. SEM observation

Fig. 1 Digital pictures of GO nanosheets and CNTs-COOH of the dispersions immediately after sonication (a) and 5 weeks after sonication (b)

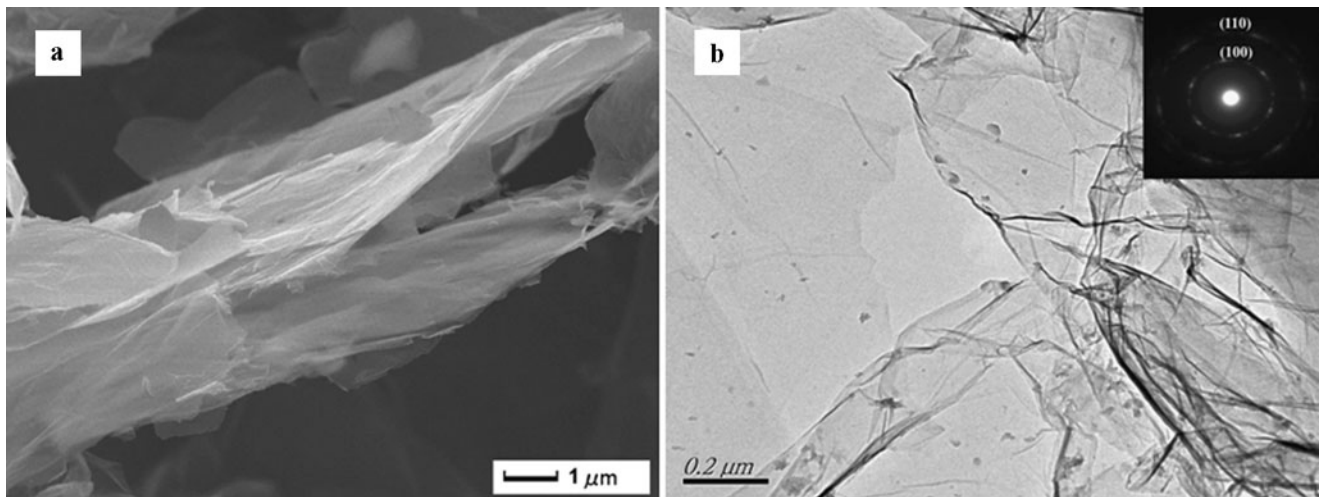
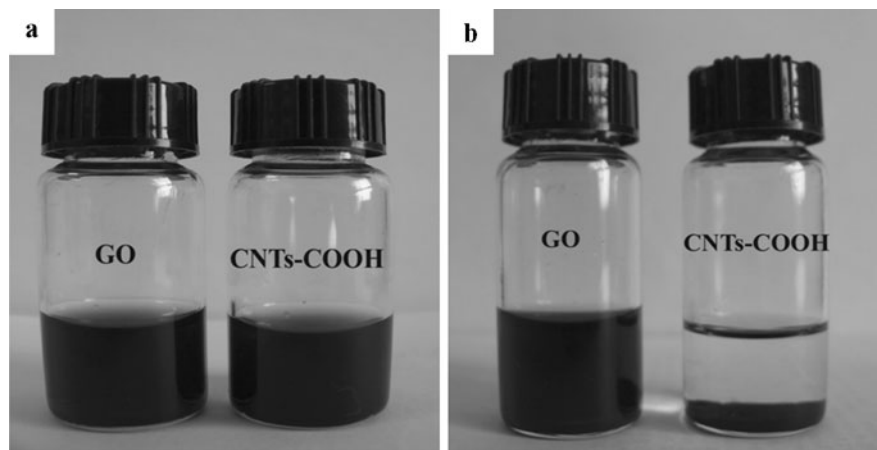


Fig. 2 (a) SEM image of GO nanosheets. (b) TEM image of GO nanosheets and the corresponding SAED pattern

of the resulting products (Fig. 2a) shows that the GO nanosheets in the products are highly transparent with folding at the edges, suggesting a very small thickness. Because of their high specific area, the GO nanosheets aggregated and formed a stacked graphitic structure when their dispersions were dried. In contrast to GO restacks seen by SEM, the typically flat GO deposited on TEM grid shows a clean GO nanosheets having a smooth finish and plenty of wrinkles owing to the thin structure of the sheets. The long wrinkles were observed in greater quantities on larger GO nanosheets. The corresponding selected area electron diffraction (SAED) pattern (inset in Fig. 2b) of GO nanosheets shows only diffraction rings and the diffraction dots are unresolved, unambiguously indicating that the GO nanosheets are amorphous.

Figure 3a shows the typical FTIR spectrum obtained for GO nanosheets. The most characteristic features are the broad, intense band at 3430 cm^{-1} (O–H stretching vibrations) and the bands at 1726 cm^{-1} (C=O stretching vibrations from carbonyl and carboxylic groups), 1588 cm^{-1}

(skeletal vibrations from unoxidized graphitic domains), 1226 cm^{-1} (C–OH stretching vibrations), and 1103 cm^{-1} (C–O stretching vibrations). Figure 3b shows the TGA of GO nanosheets. In agreement with previous reports in the literature for GO nano sheets [20], the main mass loss (51%) takes place around $20\text{--}300^\circ\text{C}$ and is ascribed to the decomposition of labile oxygen functional groups present in the material. There is also a mass loss below 100°C attributed to the removal of adsorbed water and a slower, steady mass loss (49%) over the whole temperature range between 400 and 600°C , which can be assigned to the removal of more stable oxygen functionalities.

Figure 4a showed the effect of content of GO nanosheets or CNTs-COOH on the friction coefficient at room temperature under a load of 10 N. It was seen that the addition of GO nanosheets or CNTs-COOH could reduce the friction coefficient of the water, and the friction coefficient went down with the lower content (below 0.1 wt%) of GO nanosheets or CNTs-COOH. The reason is that the GO nanosheets and CNTs-COOH were composed of many laminated graphite

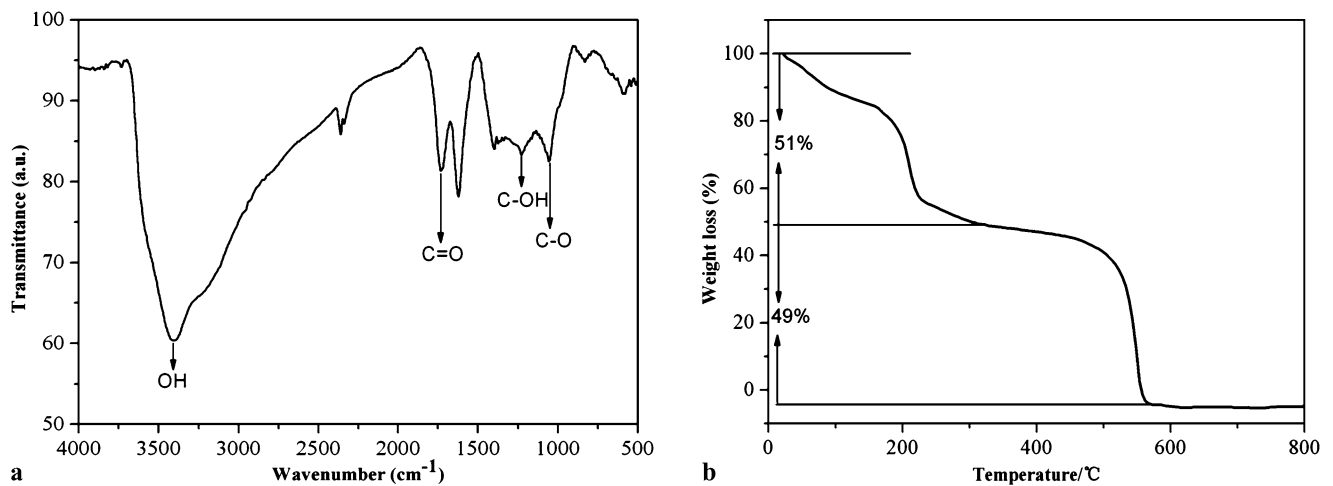


Fig. 3 FTIR (a) and TGA (b) of GO nanosheets

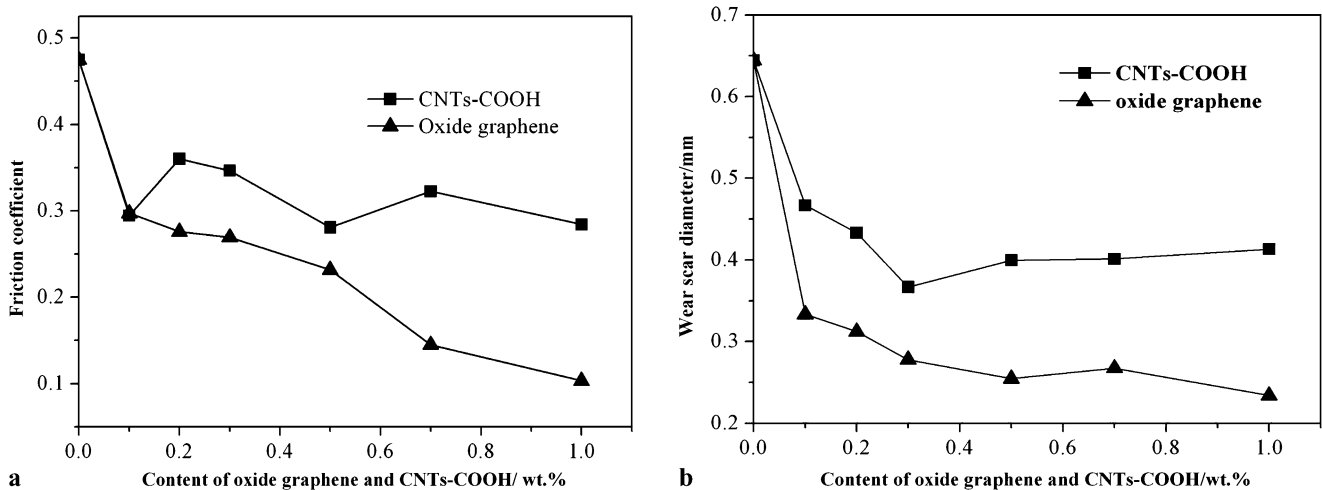


Fig. 4 Friction coefficient (a) and WSD (b) as a function of GO nanosheets or CNTs-COOH concentration (10 N, 3.142 m/s, 10 min)

planes, and endowed it with self-lubricating characteristics. For the content of GO nanosheets between 0 and 1.0 wt%, the friction coefficient went down with an increasing content of GO nanosheets. However, for content of CNTs-COOH between 0 and 0.1 wt%, the friction coefficient decreased with an increasing content of CNTs-COOH. Above 0.1 wt%, the friction coefficient increased with the content of CNTs-COOH going up. It was seen that as the content of CNTs-COOH further increased in water, the CNTs-COOH were easily aggregated during the wear process, resulting in the increase of the friction coefficient. Figure 4b shows the relationship between the concentration of the GO nanosheets or CNTs-COOH in pure water and the WSD. As a comparison, the results of pure water are also given. Seen from the curves, the GO nanosheets or CNTs-COOH can obviously improve the antiwear properties of pure water. First, with the concentration of the GO nanosheets increasing, the WSD dropped strikingly from 0.64 mm for the base stock

alone to 0.23 mm, when 1.0% of the GO nanosheets were added into pure water the best antiwear properties were obtained. The reason may be due to a film of GO nanosheets on the rubbed surface. When the concentration increases, the WSD becomes a little higher, perhaps abrasive wear occurs. As a result, both GO nanosheets and CNTs-COOH had high the friction-reduction and antiwear ability, while the friction-reduction and antiwear ability of GO nanosheets was better than CNTs-COOH with the same content.

Variations of friction coefficient and WSD with applied load for the water filled with GO nanosheets or CNTs-COOH are shown in Fig. 5. It can be seen that the friction coefficient of water/GO nanosheets or water/CNTs-COOH decreased with the increase of an applied load. The friction coefficient of water/CNTs-COOH is higher than that of water/GO nanosheets. For instance, the friction coefficient of water/GO nanosheets at 60 N was 0.127, which is about 67% lower than that of water/CNTs-COOH (0.188). This

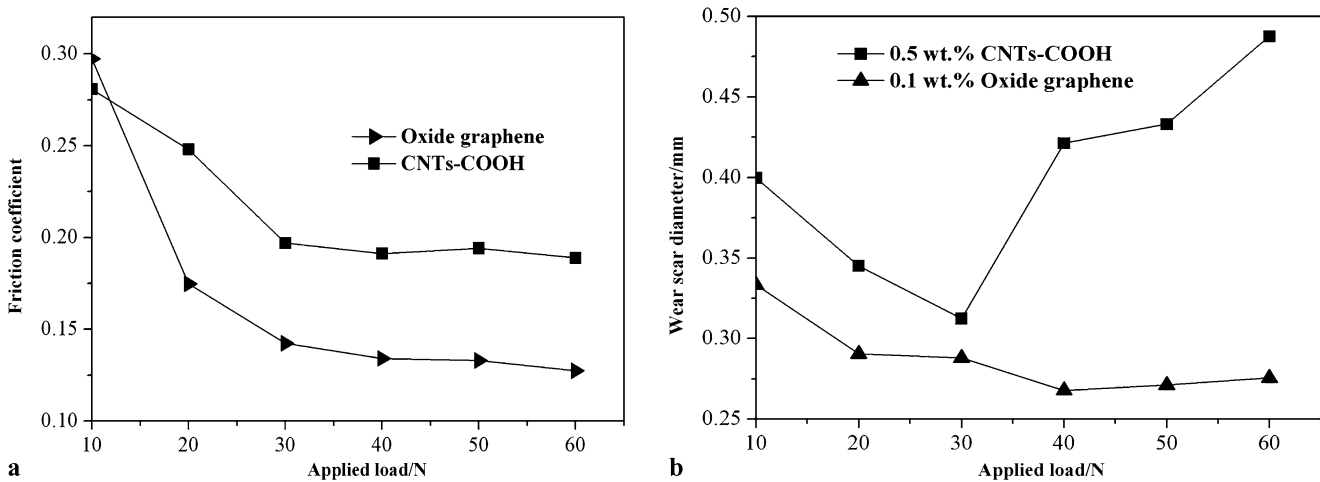


Fig. 5 Variations of friction coefficient (**a**) and WSD (**b**) with applied load. (3.142 m/s, 10 min)

indicated that GO nanosheets were more effective for improving the friction property of the water under higher applied load. Moreover, the WSD decreases more remarkably with increasing applied load. With increasing applied load further, however, the WSD increases. It can be seen that the optimum applied load for water/CNTs-COOH is both 30 N, which shows the smallest WSD. However, the WSD for water/GO nanosheets decreased with increasing the applied load, while the value was greatly lower than that of water/CNTs-COOH under the whole load range. When the load was 60 N, the water/CNTs-COOH was rapidly worn off, while the water/GO nanosheets still maintained excellent friction property. The relative low friction coefficient and WSD of these water/GO nanosheets is desirable in many practical applications. The friction-reduction ability of GO nanosheets as lubricant additive could be explained by better dispersion and superior property than CNTs-COOH.

It could be deduced that CNTs-COOH presented poor dispersion in water, the large CNTs-COOH bundles were easily formed in water, resulting in the friction coefficient increasing, while GO nanosheets were two-dimensional nanosheets and could be easily dispersed in water. Therefore, two mating wear surfaces were filled with the dispersed GO nanosheets during the wear process, and then GO nanosheets on wear surface could serve as spacers, preventing rough contact between the two mating wear surfaces. In addition, the two-dimensional sheet shape of GO nanosheets could provide very easy shear and more easily a slider between the two mating wear surfaces, so the friction coefficient of water with GO nanosheets decreased greater than with CNTs-COOH.

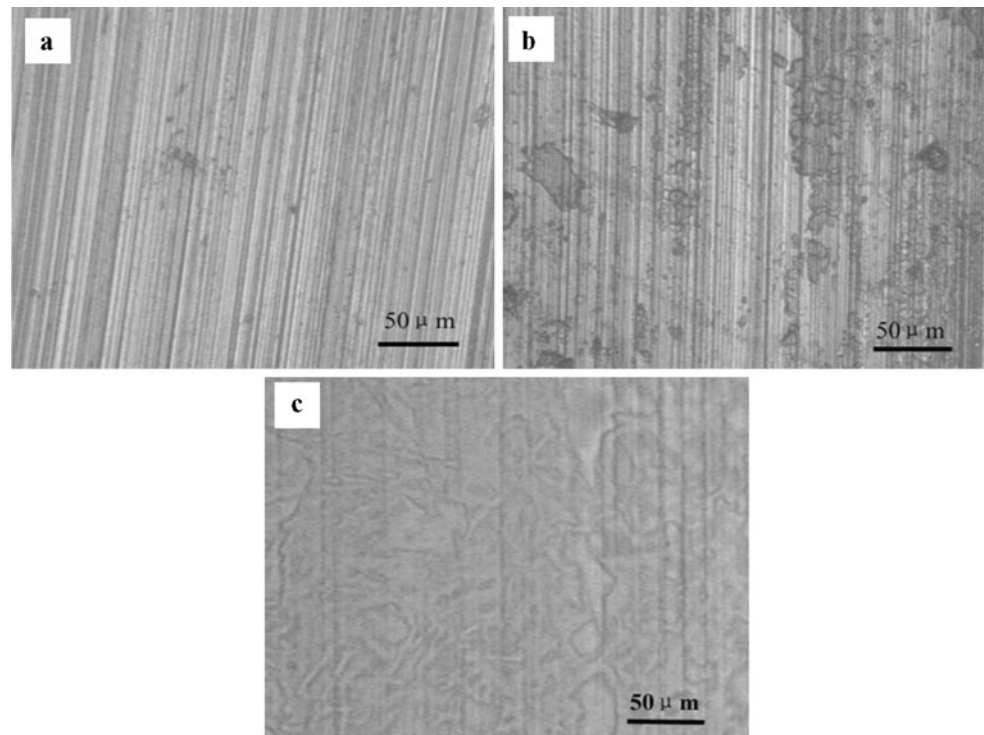
Figure 6 presents optical micrographs (OM) images of the rubbed surface lubricated with pure water and water added 0.1 wt% CNTs-COOH and GO nanosheets. The worn surface lubricated with pure water presented in Fig. 6(a) is evidently rough with many thick, deep furrows and many

pits or spalls because of contact fatigue and adhesive fatigue. In Fig. 6(b), the worn surface lubricated with pure water added 0.1 wt% CNTs-COOH smoother than that lubricated with pure water. The furrows are shallower and exhibits one smooth microgroove formed by small hard CNTs-COOH. As presented in Fig. 6(c), the rubbing surface lubricated with pure water added 0.1 wt% GO nanosheets is smoother. Thus, the mechanism of the reducing friction and antiwear of nanoparticles dispersed in pure water can be confirmed by the results of OM. In this work, it has been shown that under a certain condition of GO nanosheets, the good antiwear ability has been obtained, and at the same time, a very low friction coefficient is reached. It can be explained as follows: Firstly, the GO nanosheets enter the contact with the water and roll between the two rubbing surfaces. Secondly, during the sliding, because of the high contact pressure creating stressed zones of traction/compression, a thin physical tribofilm is formed on the metal substrate, as shown in Fig. 6. The physical tribofilms could not only bore the load of the steel ball, but also prevent from direct contact of two mating metal surfaces. Therefore, the antiwear ability of the water with GO nanosheets was improved, and the friction coefficient was decreased significantly and remained constant.

4 Conclusions

GO nanosheets well dispersed in water were prepared by modified Hummers and Offeman methods. The water with addition of GO nanosheets showed the best friction and wear properties, in comparison with the pure water and the water with CNTs-COOH. From the characterization performed after friction tests, it indicated that the GO nanosheets entered the contact with the water and slid between the two rubbing surfaces, and furthermore, a thin physical tribofilms formed

Fig. 6 Optical micrographs of the transfer films formed on the counterpart ball surface (10 N, 0.431 m s^{-1} , 10 min): (a) pure water; (b) water with 0.5 wt% of CNTs-COOH; (c) water with 0.1 wt% of GO nanosheets



on the rubbing surface, which could not only bear the load of the steel ball but also prevent them from direct contact. A combination of both effects can explain the good friction and wear properties of GO nanosheets.

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