Nanofluid lubrication and high pressure Raman studies of oxygen functionalized graphene nanosheets

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ABSTRACT

Ultralow friction coefficient in reduced graphene oxide (rGO) nanofluid was observed at high pressure lubrication conditions. High pressure Raman spectroscopic studies of graphene oxide (GO) and rGO in a hydrostatic pressure medium in diamond anvil cell (DAC) showed an increase in G-band linewidth in GO but this value was decreased in rGO at same pressure range due to the defect relaxation in sp^2 networks. Moreover, loss of recovery of G band linewidth in decompression cycles was clearly noticed in both the samples but it was significantly higher in GO due to the irreversible sp^3 into sp^2 planar phase.

Introduction

Two dimensional (2D) materials as additives in lubricants are particularly useful for the tribological applications [1–6]. Moreover, extremely small concentration of graphene oxide (GO) additives is proven to lubricate tribological contacts efficiently [5,6]. Enhancement of lubrication properties is largely defined by the unique structural, chemical and mechanical properties. They include effective dispersion stability in the lubricant due to the oxygen functional groups, large surface area, high mechanical strength and the effective inter-sheet shearing [5,7,8–13]. The ability of these materials for controlled functionlization is unique, and their dispersion is stable in a variety of lubricants that enhances their antifriction and antiwear properties [3–5,12]. Extremely small weight percentage of reduced graphene oxide (rGO) nanofluid effectively lubricates metallic contacts due to the adsorption of graphene oxide-like sheets (tribofilm) [3,5,13–15]. The mechanical strength of this sheet is high, therefore lubrication performance of sheet-like tribofilms is sustainable and durable.

However, antifriction and antiwear properties significantly degrade when there are excess oxygen functional groups in graphene [15,16]. Therefore, strictly controlling the concentration of oxygen functional groups is useful for improving the lubrication properties. Graphene is hydrophobic and dispersion in lube medium is challenging due to cohesive potential barrier [7]. Oxygen functionalization is a reliable method to reduce this barrier and introduce hydrophilic character in graphene [17–19]. At the same time, functionalization produces defects in graphene lattices and this is responsible for the deterioration of the lubrication properties [15,16,20–22]. Furthermore, ductility and mechanical strength reduce with oxygen functionalization and these are strongly associated to the defect and localized strain, originating from carbon-oxygen covalent coupling in various functional states [10,23–25]. Therefore, the issue of optimized loading of oxygen functional groups with graphene sheet is technically important for preserving the efficiency of inter-sheet shearability and protecting the mechanical strength of inter- and intra-layer of graphene sheets. The tribo-contact condition is equally important parameter for the performance of the lubricant additives adsorption in different regimes such as static and dynamic lubrication conditions [26,27]. High compressive strength and less shear resistance of the additive material is required to sustain a critical stress under boundary lubrication condition [27]. In this lubrication regime, the

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efficiency of most of the machine components deteriorates due to high frictional energy and finally devices fail mechanically due to the high stress of intimate contact during sliding. Therefore, analysis of ductility and strength of GO additives are important for the development of sustainable lubricant additives. Physical and chemical properties of GO/rGO at normal ambient conditions are well reported [7,17,18]. However, these properties in GO/rGO at high pressure are rarely explored [28–31]. Most of the material degrades at tribostressed condition, and therefore, high pressure sustainability of GO/rGO is a most relevant issue for tribological performance. X-ray diffraction (XRD) studies showed that unit-cell volume of GO was increased with pressure in the water medium due to the insertion of water molecules into the interlayer spacing [28]. The expanded volume was reversed back on decompression resulting in breathing of the structure upon pressure variation. Furthermore, Raman spectroscopy is one of the most effective methods for probing physical properties of graphene and graphite oxide at high pressure [29,30]. Ceppatelli et al. investigated the pressure induced insertion of certain gases between the GO layers and the stability of the GO structure at high pressure [31]. Lianqiang et al. showed reversible Raman bands upon decompression, indicating ductility of GO [30]. However, comparative physical properties versus amount of oxygen functional groups in GO/rGO are not yet studied at high pressure. This will be further useful for evaluating the tribological properties of these materials under high contact pressure where sustainable compressive strength is prime interest for several applications.

In this report, structural and chemical properties of chemically synthesized GO and rGO were investigated comprehensively. Pressure dependent ductility and strength of these materials were investigated by *micro*-Raman spectroscopy under hydrostatic compression and decompression. This is one of the most important aspects which could be related to the performance of additives in high pressure and boundary lubrication condition. An effective concentration of graphene additives was investigated for efficient antifriction and antiwear performance. A detailed and systematic comparative tribological study of these materials was carried out following the Stribeck relationship, which describes velocity dependent friction coefficient. Correlation of stress–strain and viscosity of graphene additives in lube medium was conducted by rheological test. To explain the friction and wear in GO and rGO nanofluid additives, a model based on the material properties and tribo-experimental results is proposed. Wear track was chemically analyzed for the tribofilm investigations.

Experimental methods

Synthesis of GO and rGO

The GO and rGO were prepared by a chemical method using graphite powder ($<20\,\mu$m, Sigma–Aldrich) as a precursor. The graphite powder was initially oxidized under a strong oxidizing environment using a mixture of H_2SO_4 (98%, Merck), $NaNO_3$ (98% Alfa Aesar), $KMnO_4$ (99%, Fisher Scientific). The oxidized product was rinsed with 30% H_2O_2 and 5% HCl solutions to remove the undigested content of the oxidizing reagents. This was followed by repetitive washing of brown colored graphite oxide with distilled water until the pH of decanted water was obtained as ~6. In the subsequent step, graphite oxide was exfoliated using an ultrasonic bath. The resultant aqueous dispersion of GO was centrifuged at 5000 rpm and it led to two distinct phases; upper phase containing highly dispersible fine components of GO and lower deposition constituting thick sheets of GO. The upper phase in centrifuge tubes was used for the chemical characterizations, tribological studies and preparation of rGO. The rGO was prepared by chemical reduction of GO in a convenient and scalable method. In a typical

experiment, 50 mL aqueous dispersion of GO ($5\,mg\,mL^{-1}$) was reduced in the presence of 2 mL hydrazine hydrate at $90\,°C$ overnight. During the reduction process, thoroughly dispersed brown-colored GO was gradually turned into black-colored segregated material. The developed product was collected via the membrane filtration under reduced pressure and then thoroughly washed several times with double-distilled water, until the pH of decanted water was found to be 7. The wet cake of rGO was dried in an oven at $110\,°C$ to obtain it in powder form.

Characterization techniques

Microstructure of GO and rGO samples were investigated by high resolution transmission electron microscope (HRTEM) (Titan cubed G2 60-300) in a transmission mode. The compositional structure was investigated by using high-angle annular dark-field–scanning TEM–energy-dispersive X-ray spectroscopy (HAADF–STEM–EDS). The detailed bonding structure was examined by using the electron energy loss spectroscopy (EELS) in HRTEM. EELS spectra were obtained with a GIF instrument attached to the transmission electron microscope operating at 80 keV and having an energy resolution of 0.3 eV. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology (resolution with probe Cs 0.07 nm). High resolution X-ray powder diffraction data were obtained by Rigaku-Smartlab diffractometer in a Bragg–Brentano configuration using CuKα X-rays of wavelength 0.15418 nm. Measurements of each sample were performed in the scattering 2θ range $5°–80°$ with a step size of $0.01°$. The wide range and high resolution XPS spectra of C 1s and O 1s of GO and rGO were recorded by Sigma probe-Thermo VG Scientific equipped with hemispherical analyser and microfocused monochromator X-ray source. The XPS was carried out using Al Kα radiation (E = 1486.6 eV) within energy resolution of 0.47 eV in ultra-high vacuum at 10^{-10} Torr. The functional groups present in these samples were analyzed by FTIR spectrometer (Bruker Optics), operating in transmission mode with a spectral resolution ~4 cm^{-1}.

High pressure Raman studies

In-situ high pressure Raman experiments were carried out using a compact, symmetric diamond anvil cell DAC. A few specks of sample GO/rGO were loaded into a 200 μm hole of a stainless steel gasket (preindented to a 70 μm thickness) in the DAC. 4:1 methanol–ethanol mixture as pressure transmitting medium and Ruby as pressure calibrant were loaded along with the sample. Ruby R1 fluorescence technique was used for pressure calibration. Raman spectra of the sample in DAC were measured using a 514.5 nm excitation line from an Ar-ion laser. The spectra were collected using a *micro*-Raman spectrometer (Renishaw, UK, model Invia) equipped with the charge coupled device (CCD) detector. A 20$\times$ long working distance objective was used to align the laser beam into a spot size about 1 μm on the sample. Raman spectra were also recorded in the decompression cycle. Moreover, Raman spectroscopy was also used for the chemical analysis of wear tracks.

Tribology tests

A ball-on-disc standard tribometer (CSM Instrument, Switzerland), operating in a linear reciprocating mode was used for the friction measurements. In the first set of experiments, concentration dependent effective tribological performance was optimized for the GO-10W40 and rGO-10W40 blends. For this purpose, a 100Cr6 spherical standard steel ball with a diameter of