Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Facile Fabrication of Long-Chain Alkyl Functionalized Ultrafine Reduced Graphene Oxide Nanocomposites toward Enhanced Tribological Performance

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Synthesis of Graphene Oxide

Graphite oxide was synthesized from natural graphite power by a modified Hummers method. The specific preparation procedures are described as follows, 1g graphite and 1g $NaNO_3$ were added to ice-cooled solution of H_2SO_4 with magnetic stirring. After the graphite was well dispersed, 4g $KMnO_4$ was slowly added under the same condition. During this period, Temperature must be strictly controlled below 10 °C in order to avoid danger. Then, the reaction mixture was heated to 45 °C and kept the mixture at this temperature in oil bath for 2 h. After completion of the reaction, 50 mL of deionized water was gently added into the mixture. The mixture was maintained at 95 °C for 15 min. Then, the mixture was added into a beaker with 160 mL deionized water. After cooling to room temperature, 5 mL 30% H_2O_2 was added into the mixture under magnetic stirring. The mixture was filtered with 80 ml HCl (1mol/mL) for 2 times and centrifuged at high speed (10 000 r/min 20 min) with deionized water for 4 times until the pH is 7. Dialysis was done to remove some ions. After two weeks, the GO dispersion was obtained by mild ultrasonic. Finally, the product was dried at 60 °C.

Table S1. The recipe information of the finished oil.

Lubricating oil components		Weight fractions (wt%)
base stock (mineral oil)		96.0
additives package	polymeric friction modifier[a]	1.8
	ashless organic friction modifier (glycerol monooleate, GMO)	1.7
	antioxidants and silicon antifoamants	0.5

[a] preparation based on the procedures as described in US 9963655 B2, the detailed synthesis process was also presented as follows:

The polymeric friction modifier is a reaction product of maleinised polyisobutylene, PEG, glycerol and tall oil fatty acid, wherein the polyisobutylene of the maleinised polyisobutylene has an average molecular weight of around 950 amu, and an approximate saponification value of % mg KOH/g and the PEG has a hydroxyl value of 190 mgKOH/g. A suitable additive may be made by charging 110 g of maleinised polyisobutylene, 72 g of PEG, 5 g of glycerol and 25 g of tall oil fatty acid into a glass round bottomed flask equipped with a mechanical stirrer, isomantle heater and overhead condenser. The reaction takes place in the presence of 0.1 g of esterification catalyst terabutyl titanate at 200℃, with removal of water to a final acid value of 10 mg KOH/g.

Dispersion Stability of Finished Oil Added with RGO-*g*-OA (0.01 wt%) at a High-Temperature Environment

The thermal stability of octadecyl alcohol (OA) molecules onto GO was further evaluated using two sets of independent tests. On one hand, a certain amount of solid RGO-*g*-OA powder (~ 0.5 g) was put into an oven at 100 °C for 7 days, then washed with ethanol three times to remove the possible decoupling OA molecules and put again back into the oven at 60 °C for 4 hours to make it completely dry. The FT IR measurement of this sample was then performed, as shown in **Figure S1 (a)**. Clearly, except for other characteristic peaks of GO (including O-H, C=O, C=C, C-OH, C-O-C groups), the typical stretching vibration peaks of $-CH_2$ and $-CH_3$ (at 2927 and 2850 cm^{-1}) of long-chain alkyl groups, can be also observed in the FTIR spectrum of RGO-*g*-OA after the heat-treatment (100 °C for 7 days). Such a result demonstrates that the OA molecules are still covalently linked on the surface of GO nanosheets without any decoupling even after the long-term high-temperature treatment. On the other hand, the finished oil added with 0.01 wt% RGO-*g*-OA was put in an oven of 100 °C for 7 days and real-time recorded its dispersion state by taking photos. It can be seen from **Figure S1 (b)** that the color of the lube oil sample remains unchanged and no precipitations are found at the bottom of the bottle, revealing that RGO-*g*-OA has good thermal and dispersion stability in finished oil, which is consistent with the results of FTIR results. Therefore, these above results confirm that the elevated temperature won't cause the decoupling of the octadecyl alcohol chains from the graphene oxide, meanwhile the nano-additives can possesses a good dispersion stability in the lubricant oil.

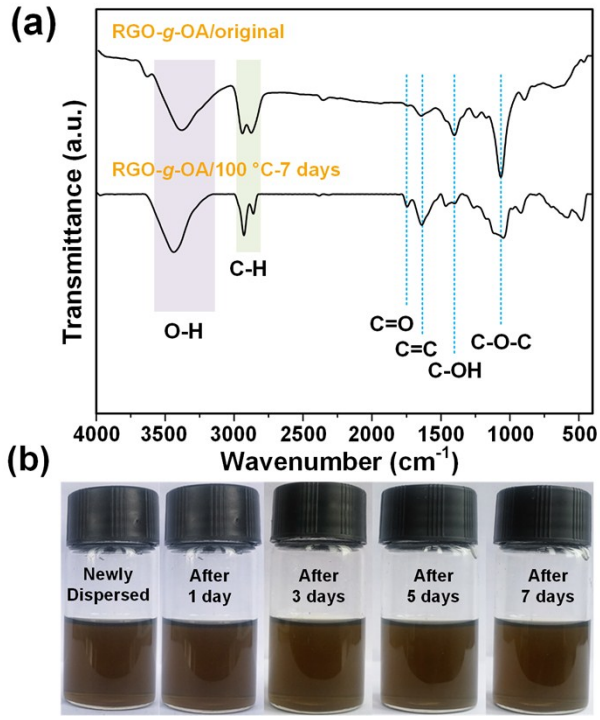

Figure S1. (a) FTIR comparison of RGO-*g*-OA between the original state and after heat-treatment (100 °C, 7 days); **(b)** Real-time digital images of the finished oil dispersed with 0.01 wt % of RGO-g-OA in the oven at 100 °C.

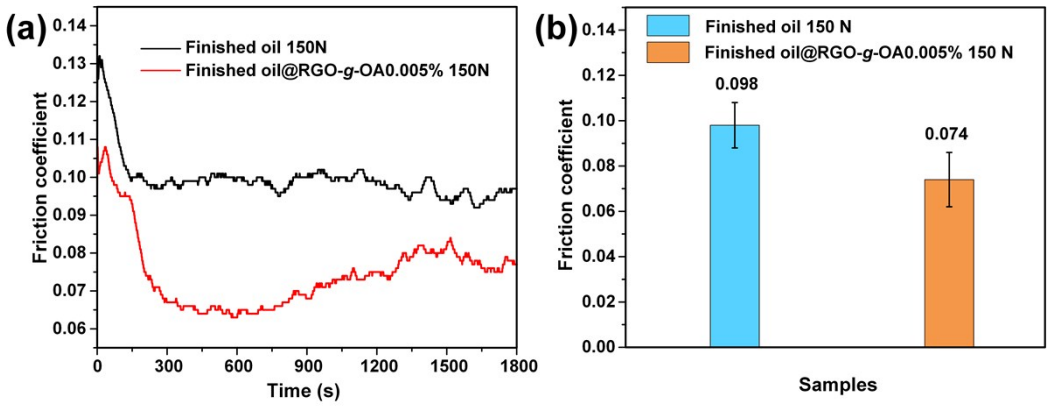

Figure S2. Typical friction coefficient **(a)** and average friction coefficient **(b)** of pristine finished oil and the corresponding counterpart filled with 0.005 wt% RGO-*g*-OA on the steel discs, the applied load is 150 N.

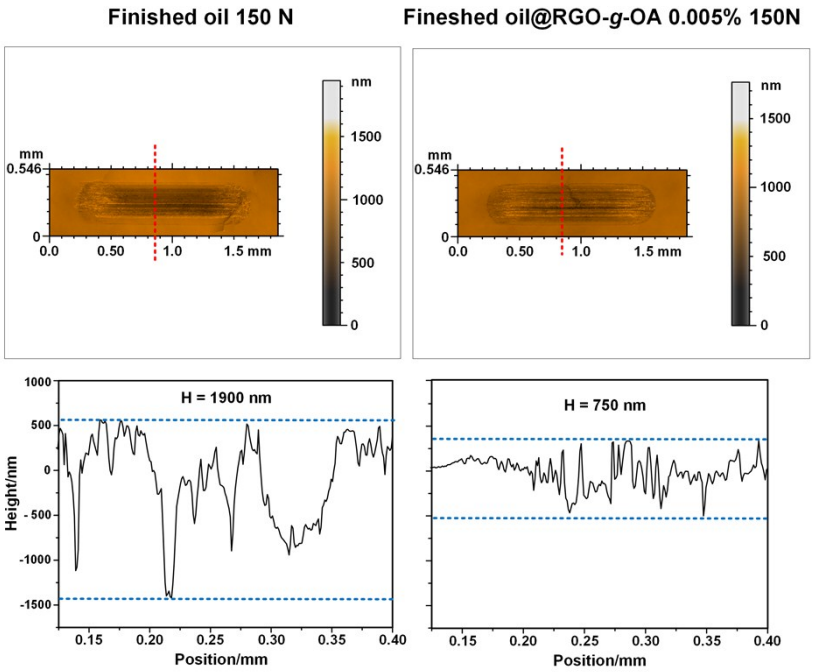

Figure S3. (a) Surface morphologies of the rubbed regions on the steel disks after the friction tests lubricated with the finished oil and finished oil filled with RGO-*g*-OA (0.005%), **(b)** the average cross-sectional height profiles of the dashed line areas labeled in (a), the applied load is 150 N.

Table S2. Wear volumes of the worn surfaces on the steel discs under the load of 150 N

Samples	Wear volume (μm^3)	Increment
Finished oil	56098	0%
Finished oil @RGO-*g*-OA 0.005%	45318	-19 %

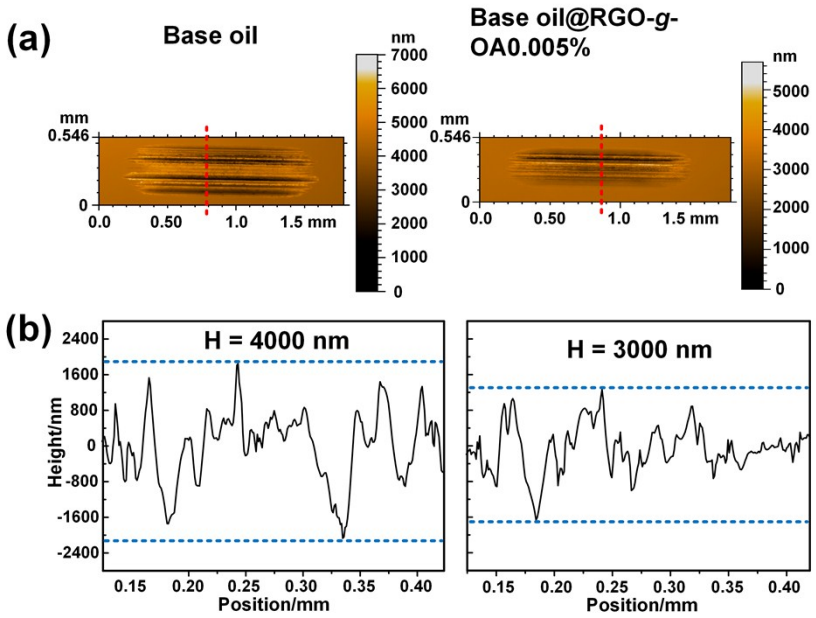

Figure S4. (a) Surface morphologies of the rubbed regions on the steel disks after the friction tests lubricated with the base oil and base oil filled with RGO-*g*-OA (0.005%), **(b)** the average cross-sectional height profiles of the dashed line areas labeled in (a), the applied load is 100 N.

Table S3. Wear volumes of the worn surfaces on the steel discs under the load of 100 N

Samples	Wear volume (μm^3)	Increment
Base oil	247383	0%
Base oil@RGO-*g*-OA 0.005%	191125	-23%

SEM, EDX, and Raman Spectra Measurements of Wear Scars

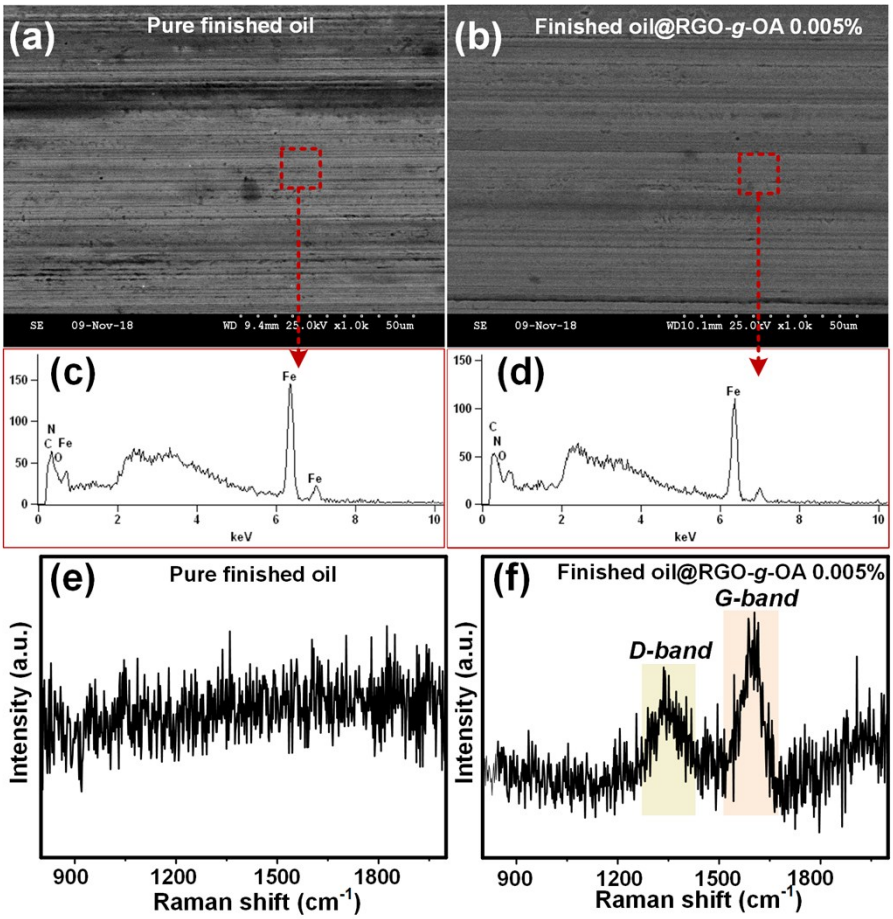

Figure S5. SEM images, energy dispersion X-ray analyses (EDX), and Raman spectra of the wear scars on the steel discs after the friction tests lubricated with the pristine finished oil **(a, c, e)** and finished oil filled with 0.005 wt% of RGO-*g*-OA **(b, d, f)**.

In order to identify deposition behavior of the lubricant (additives) onto the rubbing surfaces during the tribological testing process, the microstructure morphologies and chemical elements of wear scars on the worn surface have been systematically characterized by SEM and EDX, as shown in **Figure S5**. From **Figure S5 (a, b)**, it can be seen that the worn surface lubricated by pure finished oil shows a slightly serious wear with many apparent wear scratches and deeper grooves. In contrast, the worn surface treated with finished oil filled with RGO-*g*-OA (0.005 wt%) displays a relatively weaker wear, which only few wear scratches and shallow grooves. These results imply that the functionalized graphene additive of RGO-*g*-OA has significant anti-wear property, which is consistent with the wear volume results. Besides, **Figure S5 (c, d)** shows that both the two worn surfaces contain C, N, O, and Fe elements, suggesting the presence of lubricant oil on the rubbing surfaces. However, the results of EDX cannot conclude the deposition of the

lubricant additives (RGO-g-OA) on the worn surfaces.

To further confirm the presence of RGO-g-OA on the rubbed regions and tentatively illuminate the corresponding friction-reducing and anti-wear mechanism of the nano-additives, Raman spectra of the worn scars are measured, as indicated in **Figure S5 (e, f)**. Apparently, for the wear scar produced by the pure finished oil, no any peaks can be seen from the Raman spectrum. By contrast, the characteristic peaks of graphene-based nano-materials including D-band (1341cm^{-1}) and G-band (1612 cm^{-1}) can be clearly observed in the Raman spectrum of wear scar treated with finished oil dispersed with RGO-*g*-OA. Such distinct results confirm that the graphene-based additives (RGO-*g*-OA) indeed enter the worn surfaces, which display an excellent friction-reduction and anti-wear properties during the friction process.