Investigation of Tribological Properties of Oleic Acid-modified RGO-based Engine Oil Nano Fluid

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Abstract

In this study, reduced graphene oxide was synthesized using hydrothermal method. After reducing the graphene oxide, oleic acid was added to the reduced graphene oxide solution in order to increase the solubility and dispersion of RGO in oil. Final, RGO/GO was mixed with engine oil. Structural and morphological properties of GO, RGO and OL-RGO were studied by TEM, FTIR, PL, XRD analysis. Investigation the friction force for rotating the pin-on-disk shows that the lowest friction force is related to the addition of graphene oxide at a concentration of 0.01 mg / ml.

Key Words: Reduced Graphene Oxide, Oleic Acid, Engine Oil, Tribological Properties, Nano Fluid.

DOI Number: 10.14704/nq.2020.18.6.NQ20182 **NeuroQuantology 2020; 18(6):49-54**

Introduction

Today, in addition to *lubrication* and reducing the wear of engine components, motor oils have functions such as sealing the distance between components, washing and cleaning the parts of soot and the compounds from oil and sediment degradation, protecting the surfaces from rusting and chemical corrosion, buffering, suspending the waste material and preventing their deposition on components [1]. But since liquid lubricants are not optimally able to provide all of the above requirements, motor oil additives are used to achieve most of the above properties or to improve them [2]. In the meantime, using the nano-additives to increase engine efficiency, by providing the above properties as well as saving in fuel consumption, has received in the past years a lot of attention.

These nano-additives improve and enhance the properties of the base liquid lubricant using several functional mechanisms including the conversion of sliding friction to rolling friction, very high heat transfer capability, repairing of friction surfaces, and shielding film formation on friction surfaces [3].

The nano-particles have attracted the attention of researchers because of their very small size and large specific surface area. Using the nano-particles as an additive in lubricating oils is rapidly increasing. For example, the results show that using the dispersed PbS [4], Zinc borate [5, 6] and SiO_2 [7] nano-particles in the oil exhibits very good friction and anti-wear properties.

The results also show that adding the carbon nano-materials to basic lubricants such as carbon nano-tubes [8, 9], *fullerene* [10] and graphite nano-plates [11] improve the anti-wear properties of the lubricants and significantly reduce the friction coefficient. The small size of the nano-particles allows them to quickly and easily enter surfaces. The very good chemical stability of the nano-particles reduces their dangerous emissions and they are less toxic than organic additives.

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Relevant conflicts of interest/financial disclosures: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Received: 08 May 2020 **Accepted:** 30 May 2020

Among the nano-additives, graphene and graphene oxide are very popular because they have the desirable properties in terms of lubrication. For example, they have high thermal stability and good conductivity [12-15]. The results show that graphene and reduced graphene oxide have high potential for using as the additive in lubricants and can improve the tribological properties of oils. The results show that graphene oxide nano-plates have a positive role in reducing the friction and improving their anti- wear properties. Reducing the friction coefficient and wear volume was reported to be 36.4% and 37.5%. Pure graphene cannot be dissolved and dispersed in most solvents. This problem can be overcome by chemical and physical corrections. Oleic acid (CH_3 $(CH_2)7CH=CH$ $(CH_2)7COOH$) is a surfactant which contains the hydrophilic hydroxyl and alkyl that is important to increase the solubility and dispersion of nano-particles in oils. Therefore, in the study, we decided to use the oleic acid - modified reduced graphene oxide as a nano-additive in oil [16].

Construction Method

Synthesis of Oleic Acid - Modified Reduced Graphene Oxide

A solution of graphene oxide purchased from Borhan Nano Scale Company at the concentration of 1mg / ml was irradiated by mechanical sound waves in ultrasound bath for 30 minutes (Figure 1). After adding a small amount of zinc chloride, the solution was placed in the water / ice bath and stirred well. The solution was then heated in an autoclave at 160°C for 10 hours. After cooling the autoclave, it is observed that a black mass is formed in a transparent solution that is actually the reduced graphene oxide. After reducing the graphene oxide, oleic acid was added to the reduced graphene oxide solution at concentrations of 0.01 mg / ml, 0.005 mg / ml and the solution was heated at 80°C for 3 hours. The material obtained was mixed with the small amounts of deionized water and stirred by a 400 watt ultrasonic probe for 15 minutes, in order to blend well. The color of the final solution is milky white that is shown in Figure 1. Some solutions was dried at 60 ° C and used for TEM, FTIR, PL, XRD tests.

Mixing the Engine Oil with Oleic Acid - Modified GO, RGO and RGO

5 cc of 0.01 mg/ml graphene oxide was mixed with 95 cc of engine oil and stirred for 40 minutes. The sample was called GO5 (0.01). 5 cc of reduced graphene oxide at concentrations of 0.01 mg / ml, 0.005 mg / ml were mixed with 95 cc of engine oil and stirred for 40 minutes. These samples were called RGO5 (0.01) and RGO5 (0.005). 10 cc of reduced graphene oxide at concentrations of 0.01 mg / ml, 0.005 mg / ml was mixed with 90 cc of engine oil and stirred for 40 minutes. These samples were called RGO10 (0.01) and RGO10 (0.005). 10 cc of oleic acid - modified reduced graphene oxide at the concentrations of 0.01 mg / ml, 0.005 mg / ml was mixed with 90 cc of engine oil and stirred for 40 minutes. These samples were called OL-RGO10 (0.01) and OL-RGO10 (0.005). Finally, the anti-wear and friction properties of the above samples were investigated using the wear testing machine in a fluid environment (pin-on-disk).

Figure 1. Graphene Oxide Colloid, Reduced Graphene Oxide and Oleic Acid - Modified RGO

Results and Discussion

Investigating the Structural and Morphological Properties

X-ray diffraction patterns for graphene oxide and reduced graphene oxide and reduced graphene oxide with oleic acid is shown in Figure 2 (a, b and c). The diffraction peak for graphene oxide is about 2θ=10° which is related to a 0.88 nm interlayer distance that is similar to other articles [17]. The image of the diffraction pattern showed a larger interlayer distance for graphene oxide than graphite powder layers, due to the placement of oxygen - containing functional groups between the layers [18]. XRD analysis also confirmed the reduction of graphene oxide. As can be seen in Figure 1(b), the diffraction peak of graphene oxide shifts to 2θ=23.8°, that is related to an interlayer distance of 0.37 nm.

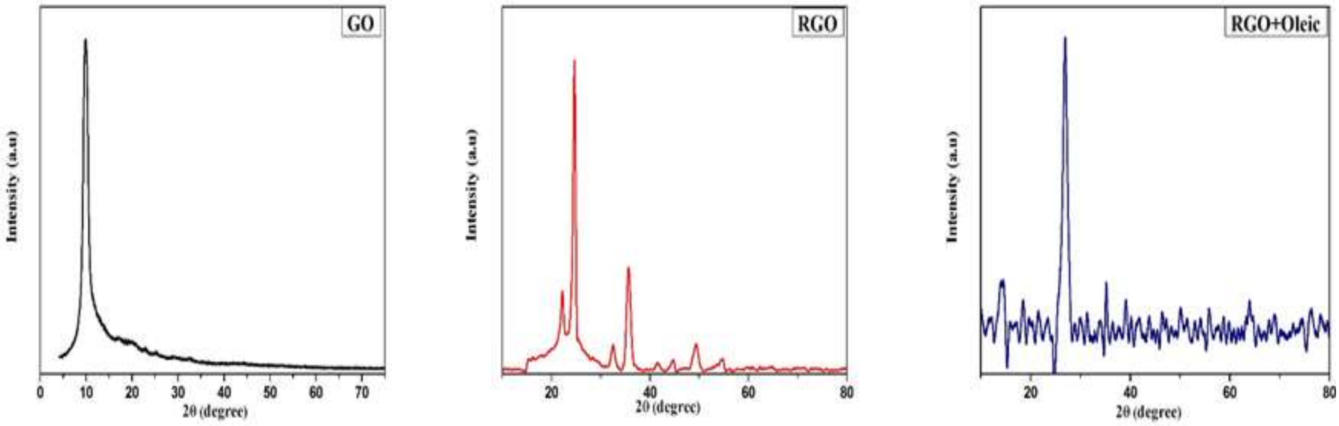

Figure 2. X-ray Diffraction Image for the Samples of Graphene Oxide (GO), Reduced Graphene Oxide (RGO) and Oleic Acid - Modified Reduced Graphene Oxide (RGO + Oleic)

This indicates that when graphene oxide is reduced to reduced graphene oxide, the interlayer distance is reduced due to the removal of oxygen - containing functional groups, which reduces the reduced graphene oxide plates again. A very high peak is also seen at 2θ=25°, that this peak is also seen in the diffraction image of reduced graphene oxide with oleic acid.

The transmission electron microscope image for the samples of graphene oxide, reduced graphene oxide and oleic acid - modified reduced graphene oxide is shown in Figure 3. TEM image of the graphene oxide sample shows the presence of monolayer graphene oxide plates. After the reduction and formation process of RGO, the layers appear to be interconnected and wrinkled. The sheets of Graphene oxide and reduced graphene oxide are in micrometer size [19]. Compared to the reduced graphene oxide, oleic acid - modified RGO has a smoother surface, which may be due to changes in the type of functional groups such as OH and COOH that is caused by surface modification using oleic acid and is consistent with FTIR spectrum.

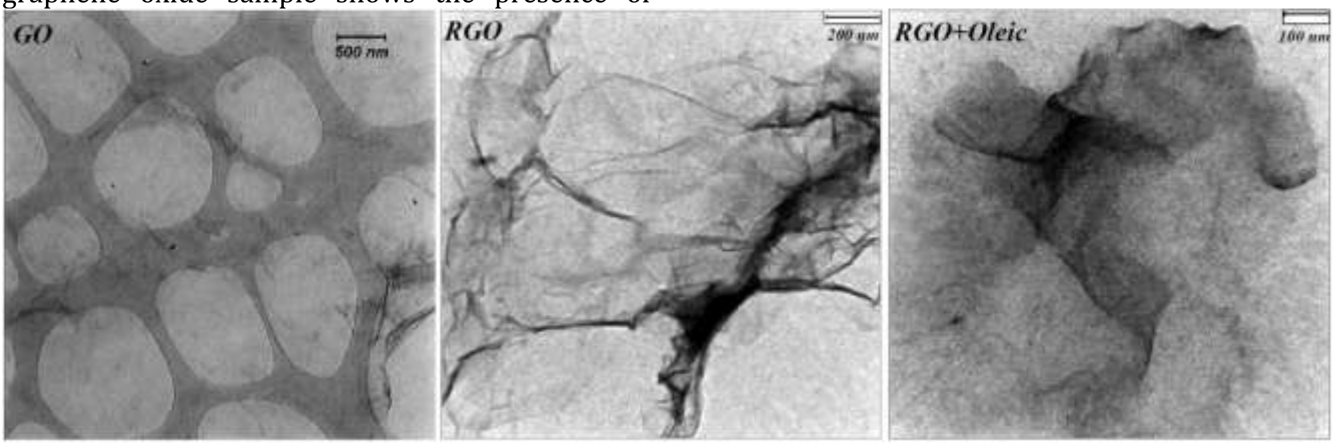

Figure 3. Transmission Electron Microscope Image for the Samples of Graphene Oxide (GO), Reduced Graphene Oxide (RGO) and Oleic Acid - Modified Reduced Graphene Oxide (RGO + Oleic)

Investigating the Chemical and Optical Properties

FTIR Analysis

Figure 4 shows the FTIR spectrum of graphene oxide (GO), reduced graphene oxide (rGO) and reduced graphene oxide with oleic acid (RGO-OA). Graphene oxide spectrum, as shown in the Figure, has a peak at 1066 Cm^{-1} that is attributed to the C-O bonds. The peak at 1288 Cm^{-1} is confirmed as the C-O-C bending and the C-OH bond is also observed at 1587 Cm^{-1}. A broad peak at 3448 Cm^{-1} is the O-H bond of the C-OH groups that represents water in the material. RGO peaks show the reduction of oxygen-containing groups in GO. According to the Figure, these peaks were confirmed by removing and reducing the intensity of the peaks.

The peaks of 1066 Cm^{-1}, 1288 Cm^{-1}, 1724 Cm^{-1} and 3448 Cm^{-1} disappeared and reduced dramatically, indicating the elimination of oxygen-containing groups in GO. These observations of the rGO spectrum confirmed that most of the oxygen-containing functional groups in GO were eliminated. The peaks at 1600 Cm^{-1} in rGO show strong bonds, indicating the improvement of the sp^2 lattice [20].

According to the diagram of reduced graphene oxide with oleic acid, the peaks at 2924 Cm^{-1} and 2853 Cm^{-1} show the CH_2 and CH_3 groups, indicating the existence of long alkyl chains in the reduced graphene oxide with oleic acid. The peak at 1709 Cm^{-1} corresponds to the C = O groups. The peaks below 1500 Cm^{-1} represent the C-H groups [21].

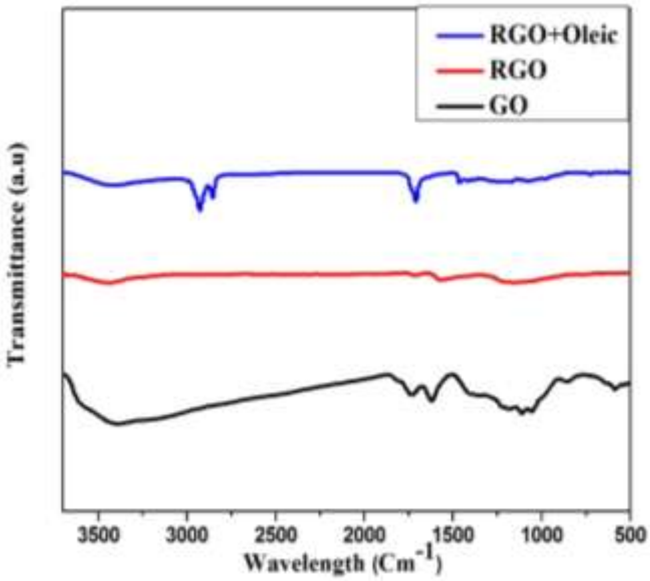

Figure 4. Infrared Spectroscopy Diagram for the Samples of Graphene Oxide (GO), Reduced Graphene Oxide (RGO) and Oleic Acid - Modified Reduced Graphene Oxide (RGO + Oleic).

PL Analysis

Photoluminescence studies were conducted to investigate the optical properties of graphene oxide (GO), reduced graphene oxide (rGO) and reduced graphene oxide with oleic acid (RGO-OA). Figure 5 (a, b and c) shows the results of the PL emission spectrum. A *luminescence* peak is seen by a high-intensity peak between 650 - 700 nm, with a maximum value at 680 nm.

Infrared spectroscopy in this sample confirms the existence of several oxygen functional groups, that is shown in Figure 3, confirming the existence of GO. The PL intensity at the excitation wavelength is approximately $\lambda ex = 343$ nm that in rGO is much lower than graphene oxide (GO), and this peak disappears in the diagram of reduced graphene oxide with oleic acid [22].

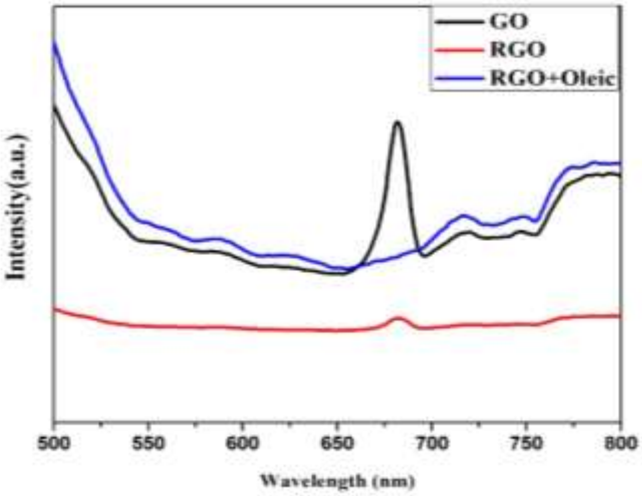

Figure 5. PL Spectra for the Samples of Graphene Oxide (GO), Reduced Graphene Oxide (RGO) and Oleic Acid - Modified Reduced Graphene Oxide (RGO + Oleic)

Investigating the Tribological Properties

The changes in friction force in terms of distance traveled for one sample of pure engine oil (oil), one sample of engine oil + grapheme oxide [GO5 (0.01)], four samples of engine oil + reduced oxygen oxide (RGO5 (0.01), RGO10 (0.01), RGO10 (0.005), RGO5 (0.005)) and two samples of engine oil + oleic acid - modified reduced graphene oxide (OL-RGO10 (0.01), OL-RGO10 (0.005) were examined using the wear testing machine in a fluid environment (pin-on-disk). The rotation speed of the machine of 300 rpm and the applied vertical force of about 100 N and the distance traveled of 1500 m at approximately 3500 seconds were chosen. The results are plotted in Figures 6 - 8. The value of friction force for rotating the pin-on-disk in the presence of pure engine oil, engine oil in the presence of graphene oxide, reduced graphene oxide, and oleic acid-modified RGO at the intervals of 0.3 m, 500 m, 1000 m, 1500 m are reported in Table 1. Comparison of the Figures shows that the lowest friction force is related to the addition of graphene oxide at a concentration of 0.01 mg / ml and 5 vol%, and this reduction remains unchanged at a distance of 1500 m. Therefore, pure graphene oxide exhibit better anti-wear properties than reduced graphene oxide and oleic acid - modified RGO. Adding the graphene oxide to the engine oil creates a *shielding* layer on the surface that improves its anti-wear performance. By reducing the graphene oxide, the functional groups at the surface are reduced and thus its anti-wear properties are reduced compared to the graphene oxide.

Table 1. The Values of Friction Force for Rotating the Pin-On-Disk in the Presence of Pure Engine Oil, Engine Oil in the Presence of Graphene Oxide [GO5 (0.01)], Reduced Graphene Oxide (RGO) at the Different Concentrations and Volume Ratios, and Oleic Acid - Modified RGO (OL-RGO) at the Different Concentrations for the Distances of 0.3 m, 500 m, 1000 m, 1500 m.

Distance (m)	Pure Oil	GO 5(0.01)	RGO 5(0.005)	RGO 5(0.01)	RGO 10(0.005)	RGO 10(0.01)	OL-RGO 10(0.005)	OL-RGO 10(0.01)
0.3	0.15	0.13	0.17	0.14	0.14	0.16	0.13	0.15
500	0.13	0.11	0.12	0.12	0.11	0.13	0.11	0.13
1000	0.16	0.11	0.11	0.13	0.15	0.16	0.13	0.13
1500	0.15	0.11	0.14	0.13	0.15	0.15	0.12	0.12

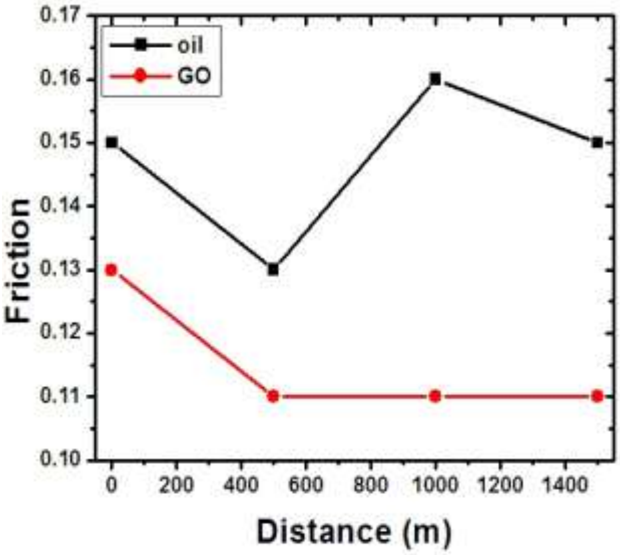

Figure 6. The Changes in Friction Force in Terms of Distance Traveled for Rotating the Pin-On-Disk in the Presence of Pure Engine Oil and Engine Oil + Graphene Oxide [GO5 (0.01)].

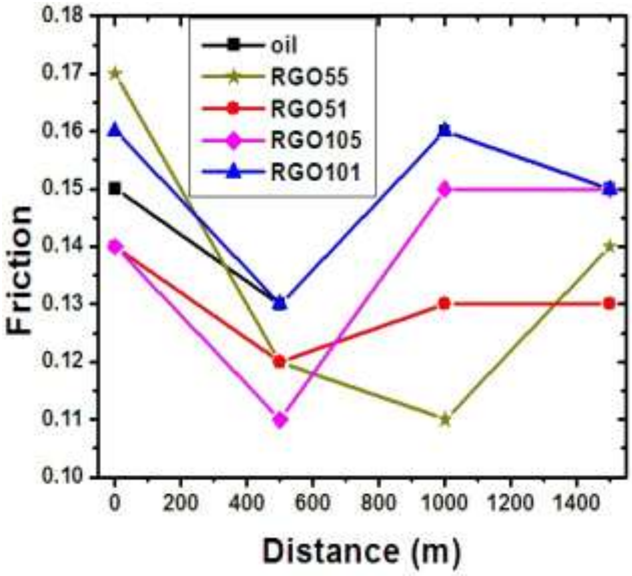

Figure 7. The Changes in Friction Force in Terms of Distance Traveled for Rotating the Pin-On-Disk in the Presence of Pure Engine Oil and Engine Oil + Reduced Graphene Oxide (RGO) at the Different Concentrations and Volume Ratios

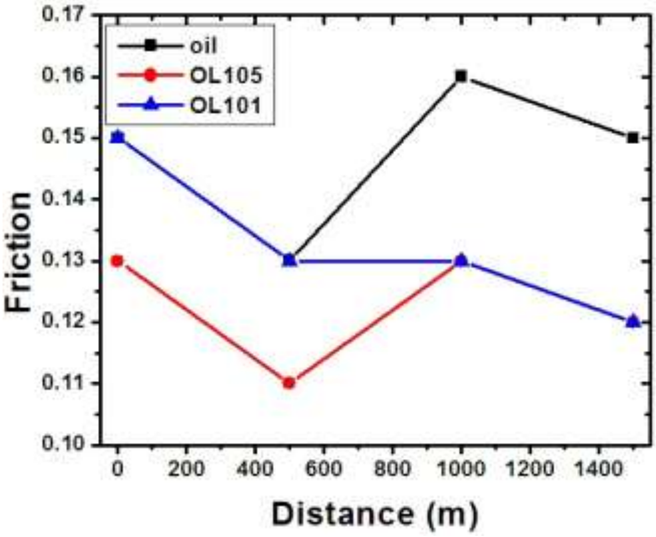

Figure 8. The Changes in Friction Force in Terms of Distance Traveled for Rotating the Pin-On-Disk in the Presence of Pure Engine Oil and Engine Oil + Oleic Acid-Modified RGO (OL-RGO) at the Different Concentrations

Conclusion

In this paper, reduced graphene oxide and OL-modified RGO were synthesized and characterized by TEM, FTIR, PL, XRD tests. XRD analysis confirmed the reduction of graphene oxide. RGO peaks in FTIR spectrum also show the reduction of oxygen-containing groups in GO. The PL intensity at the excitation wavelength in RGO is much lower than graphene oxide (GO), and this peak disappears in the diagram of reduced graphene oxide with oleic acid. The effect of adding GO, RGO and RGO-OL on the tribological properties of engine oil studied. Investigation the friction force for rotating the pin-on-disk shows that the lowest friction force is related to the addition of graphene oxide at a concentration of 0.01 mg / ml. Adding the graphene oxide to the engine oil creates a *shielding* layer on the surface that improves its anti-wear performance. By reducing the graphene oxide, the functional groups at the surface are reduced and thus its anti-wear properties are reduced compared to the graphene oxide.

References

Eswaraiah V, Sankaranarayanan V, Ramaprabhu S. Graphene-Based Engine Oil Nanofluids for Tribological Applications, ACS Appl. Mater. Interfaces 2011; 3: 4221–4227.

Zhang W, Zhou M, Zhu H, Tian Y, Wang K, Wei J, Ji F, Li X, Li Z, Zhang P, Wu D. Tribological properties of oleic acid-modified graphene as lubricant oil additives", J. Phys. D: Appl. Phys., 2011; 44: 205303 (4pp).

Xie H, Jiang B, Dai J, Peng C, Li C, Li Q, Pan F. Tribological Behaviors of Graphene and Graphene Oxide as Water-Based Lubricant Additives for Magnesium Alloy/Steel Contacts", Materials 2018; 11: 206.

Chen S, Liu W. Preparation and Characterization of Surface-Coated ZnS Nanoparticles" Langmuir 1999; 15(23): 8100-8104.

Dong JX, Hu ZS. A study of the anti-wear and friction-reducing properties of the lubricant additive, nanometer zinc borate. Tribol. Int., 1998; 31: 219–223.

Motevalizadeh L, Shohany BG, Abrishami ME. Effects of Mn doping on electrical properties of ZnO thin films. Modern Physics Letters B 2016; 30(04): 1650024.

Peng DX, Chen CH, Kang Y, Chang YP, Chang SY. Size effects of SiO_2 nanoparticles as oil additives on tribology of lubricant. Industrial Lubrication and Tribology 2010; 62(2): 111-120.

Chen CS, Chen XH, Liu TG, Yang D, Zhang G, Yi GJ. Chemical modification of carbon nanotubes and tribological properties as lubricant additive. Acta Chim Sinica 2004; 62(14): 1367–72

Chen CS, Chen XH, Liu TG, Yang D, Zhang G, Yi GJ. Chemical modification of carbon nanotubes and tribological properties aslubricant additive. Acta Chim Sinica 2004; 62(14): 1367–72.

Shohany BGh, Roknabadi MR, Kompany A. Computational study of edge configuration and the diameter effects on the electrical transport of graphdiyne nanotubes. Physica E 2016; 84: 146–151.

Konya Z, Vesselenyi I, Niesz K, Kukovecz A, Demortier A, Fonseca A. Large scale production of short functionalized carbon nanotubes. Chem Phys Lett 2002; 360: 429–35.

Lei H, Guan W, Luo J. Tribological behavior of fullerene–styrene sulfonic acid copolymer as water-based lubricant additive. Wear 2002; 252(3): 345–350.

Huang HD, Tu JP, Gan LP, Li CZ. An investigation on tribological properties of graphite nanosheets as oil additive. Wear 2006; 261: 140-144.

Nair RR, Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, Peres NM, Geim AK. Fine structure constant defines visual transparency of graphene. Science 2008; 6(320): 1308

Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene" Science 2008; 321(5887): 385-8.

Bolotina KI, Sikesb KJ, Jianga Z, Klimac dM, Fudenberga G, Honec J, Kima P, Stormera HL. Ultrahigh electron mobility in suspended graphene. Solid State Communications 2008; 146: 351–355.

Filleter T, McChesney JL, Bostwick A, Rotenberg E, Emtsev KV, Seyller Th, Horn K, Bennewitz R. Friction and Dissipation in Epitaxial Graphene Films. Phys. Rev. Lett., 2009; 102: 086102.

Li ZW, Zhu YF. Surface modification of SiO_2 nanoparticles with oleic acid. Appl. Surf. Sci., 2003; 211(4): 315-320

Allahbakhsh A, Sharaf F, Mazinani S, Kalaee MR. Synthesis and Characterization of Graphene Oxide in Suspension and Powder forms by Chemical Exfoliation Method. International Journal of Nano Dimension 2014; 5(15): 11-20.

Lerf A, Buchsteiner A, Pieper J, Schöttl S, Dekany I, Szabo T, Boehm HP. Hydration behavior and dynamics of water molecules in graphite oxide. Journal of Physics and Chemistry of Solids 2006; 67(5-6): 1106-1110.

Wang G, Wang B, Park J, Yang J, Shen X, Yao J. Synthesis of enhanced hydrophilic and hydrophobic graphene oxide nanosheets by a solvothermal method. Carbon 2009; 47(1): 68-72.

Darrudi H, Adelifard M. Inuence of Deposition Temperature as a Reducing Agent on Synthesis of Reduced Graphene Oxide (RGO) Nanosheets. Iranian Journal of Materials Science and Engineering 2018.

Zhang W, Zhou M, Zhu H, Tian Y, Wang K, Wei J, Wu D. Tribological properties of oleic acid-modified graphene as lubricant oil additives. Journal of Physics D: Applied Physics 2011; 44(20): 205303.

Rea I, Casalino M, Terracciano M, Sansone L, Polili J, Destefano L. Photoluminescence enhancement of graphene oxide emission by infiltration in an aperiodic porous silicon multilayer. Optics Express 2016; 24(21): 24413.