Tribology Properties of Graphene-coated Silica Particles

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Abstract. Recent years, graphene shows enormous potential in reducing friction force and wear, due to its unique characteristics. In this study, friction tests show that graphene-coated silica particles which were prepared by plasma enhanced chemical vapor deposition can reduce friction and wear on fused silica substrate. The existing of graphene-coated silica particles convert sliding friction into rolling friction, resulting in a significant decrease in friction coefficient from 0.2 to 0.03. Residual graphene films at the scratches are observed. The mechanism of low friction coefficient and wear is proposed through analysis of scratches. The low friction coefficient and wear are contributed to the combined lubrication effect of graphene debris and graphene-coated silica microparticles.

Introduction

Graphene, a two-dimensional (2D) material with distinct structure and unique properties, has shown enormous potential applications in wide fields, including supercapacitors [1], biosensor [2], thermal interface materials [3] and photodetectors [4]. Especially, its extraordinary physical properties, such as high strength, ultrathin film thickness, low shear strength and lamellar structure [4-7], make it be a potential candidate for solid lubricants that reduce the adhesion and friction forces. Therefore, many researchers focus on graphene's tribological performance from microscale to macroscale. At the microscale, there is a consensus that graphene can achieve superlubricity under incommensurate sliding contact. For example, Feng et al. [8] reported a study of the sliding behavior of graphene nanoflakes on a graphene surface by using scanning tunneling microscopy and frictional force microscope. They found that, once the sliding motion was initiated, the graphene nanoflakes showed facile translational and rotational motions between commensurate initial and final states. Ma et al. [9] tested the sliding friction between graphene and highly oriented pyrolytic graphite (HOPG) and accomplished the low and robust friction coefficient of 0.003 by using commercial atomic force microscopy with homemade graphene-coated microsphere tip. At the macroscale, there are few literatures focus on tribological behavior of graphene. But its unique quality, keeping good friction and wear performance regardless of dry or humid environment [10], worth further investigation and widely application. Berman et al.'s research [11-13] found graphene drastically reduce the friction coefficient from 1 to 0.3 of steel under low load conditions (2-5 N), whatever single-layer or multilayer. But, there was a major issue, when the graphene was worn out, the friction coefficient rapidly increased. As the development of graphene growth method, chemical vapor deposition (CVD) method is a desirable way to achieve low-cost and large-scale preparation of graphene. Kim et al. [14] tested the tribology properties of graphene films which were grown on Cu and Ni metal catalysts by chemical vapor deposition and transferred onto the SiO_2/Si substrate. The graphene films effectively reduced the friction forces. And Ni-grown graphene on SiO_2 exhibited better friction-reduce behaviors with the friction coefficient about 0.12. Even though CVD grown graphene films have shown great antifriction and wear resistance properties. The transfer process is complicated and may introduce organic contaminants and the surface cracks. Our previous work [15] introduces a transfer-free growth method-plasma enhanced chemical vapor deposition (PECVD).

In this article, we used PECVD method to directly grow multilayer graphene films (MLG) on quartz substrates and investigated the tribological properties of this graphene films. And then, the graphene-coated silica microparticles (GSMPs), prepared by PECVD, were applied to reduce the friction force by spreading GSMPs-containing ethanol on the graphene-coated quartz substrate surface and then evaporating ethanol. Finally, the tribological tests indicated that the GSMPs show excellent friction reduction and anti-wear performance.

Experimental details

Materials and deposition of PECVD graphene coatings. The tribopair used in the experiments were 4 mm-diameter quartz ball (Zhenke Quartz Products Co. Ltd., China) with the mean roughness Rq = 0.6 nm and quartz plate (12×12×2 mm^3, Zhenke Quartz Products Co. Ltd., China) with the mean roughness Rq = 0.5 nm measured by the 3D surface profiler (NewView 5022, ZYGO, USA). The silica microparticles were bought from Fuhong Mineral Products Co. Ltd. (Hunyuan, China). And its mean diameter was 500 nm.

Multilayer graphene coatings on the quartz plates and silica particles surface were prepared by PECVD. First, the sample was put in a sliding tube furnace (BTF-1200C-Ⅱ-SL, AnHui BEQ Equipment Tech., China), and then heated to setting temperature with H_2 flow of 20 sccm. After the temperature reaches 900 ℃, a gas mixture of CH_4 and H_2 was flowed over the sample surface with rates of 16 and 20 sccm with the assistance of plasma (250 W) to catalyze the growth of graphene. After growth for 30 min, the sample was rapidly cooled to room temperature with H_2 flow of 20 sccm. The graphene coatings were characterized by Raman spectroscopy (Renishaw plc, UK, laser wavelength: 532 nm), field emission scanning electron microscopy (FE-SEM, QUANTA FEG250, FEI, USA) and transmission electron microscopy (TEM, FEI Tecnai F20, USA).

Graphene-coated silica particles film. After the growth of graphene, the particles were suspended in ethanol. The weight concentration of particles was 1 g/L. And then, particle-containing ethanol suspension was spread on the graphene-coated quartz plates and evaporated in the air.

Friction test and scratch characterization. Tribology tests were performed in air at room temperature using a reciprocating type of homemade tribometer under the ball-on-plate contact configuration. The tribometer was designed and manufactured by State Key Laboratory of Tribology, Tsinghua university, and the details of this tribometer could be found in their previous work [16]. During the friction tests, the applied normal load was set to 30 mN. The sliding length was 2 mm and the sliding speed was 0.4 mm/s.

After friction tests, the analyses of scratch were characterized by Raman spectroscopy, Optical microscope (Leica DM2500 M, Germany) and 3D surface profiler.

Results and discussion

Characterizations. Figure 1 shows the characterization of graphene-coated quartz plate (GQP) and GSMPs. Fig. 1 (a), (b) show the optical images of original quartz plate and silica microparticles. And Fig. 1 (c), (d) is the optical images of GQP and GSMPs after the growth of graphene. As shown in Fig.1 (e), (f), it is the cross-sectional TEM images of MLG on the quartz plate and silica microparticle, respectively. The thickness of graphene films was about 3 nm representing around 9 layers graphene. Fig. 1 (g) shows the SEM image of GSMPs film on GQP. As shown in Fig.1(h), it can be observed there exist a D peak at 1350 cm^{-1}, a G peak at 1580 cm^{-1} and a weak 2D peak at 2700 cm^{-1}. The D peak reflects structural disorder and effects of graphene. The G peak is the result of first-order scattering of the E_{2g} mode observed for sp^2 carbon domains, and the 2D peak is the most prominent feature of highquality graphene [17]. Moreover, the ratio of the relative intensity between 2D and G peak reflects the number graphene layers. In this Raman spectrum, the ratio indicated a MLG structure.

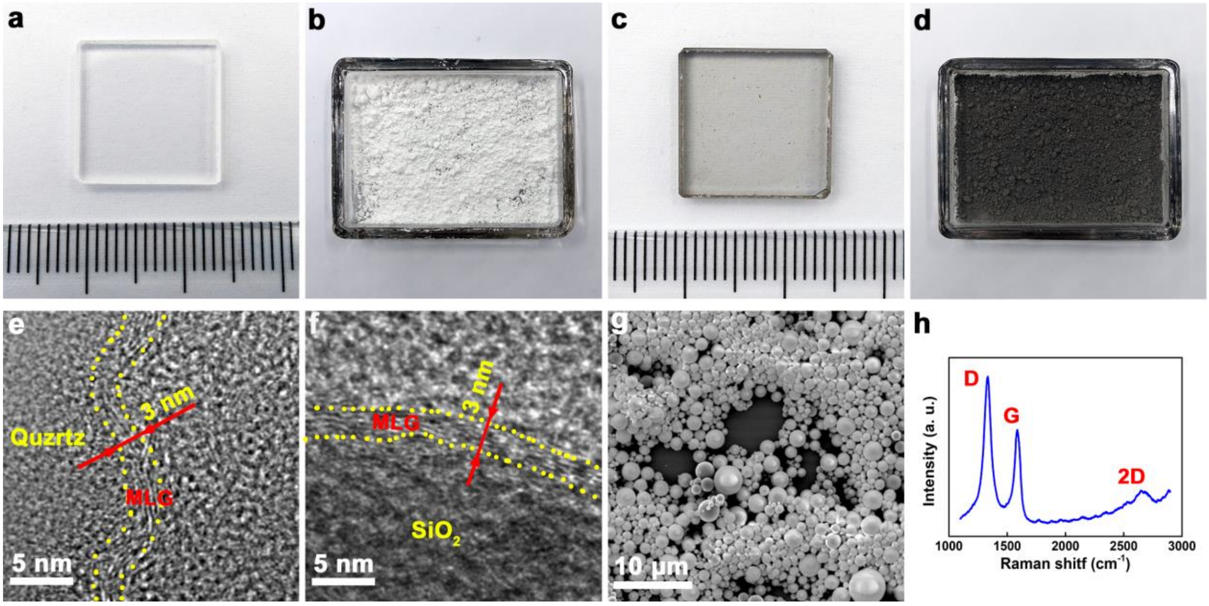

Fig. 1 Characterization of GQP and GSMPs. Optical images of (a) original quartz plate and (b) silica microparticles. Optical images of (b) GQP and (d) GSMPs. Cross-sectional TEM images of MLG on (e) quartz plate and (f) silica microparticle. (g) SEM image of GSMPs films on GQP. (h) Raman spectrum of MLG.

Friction behavior of GSMPs. Fig. 2 shows the friction coefficient (COF) of quartz ball against bare quartz plate, quartz ball against GQP, and quartz ball against GSMPs film on GQP, respectively, obtained by homemade tribometer in air at room temperature at macroscale. It can be seen that the COF of quartz against bare quartz was about 0.3 and slowly increased. And the COF of quartz ball against GQP was significantly lower than bare quartz and reached to 0.12. This result demonstrated that multilayer graphene films, prepared by PECVD, can reduce friction force effectively at macroscale. After we introduce silica particles, the COF was decreased to 0.05, as the yellow line shown in Fig. 2. In contrast, after growing graphene on the particles surface, the COF was further decreased to 0.03. This clearly confirmed the friction-reducing effect of GSMPs.

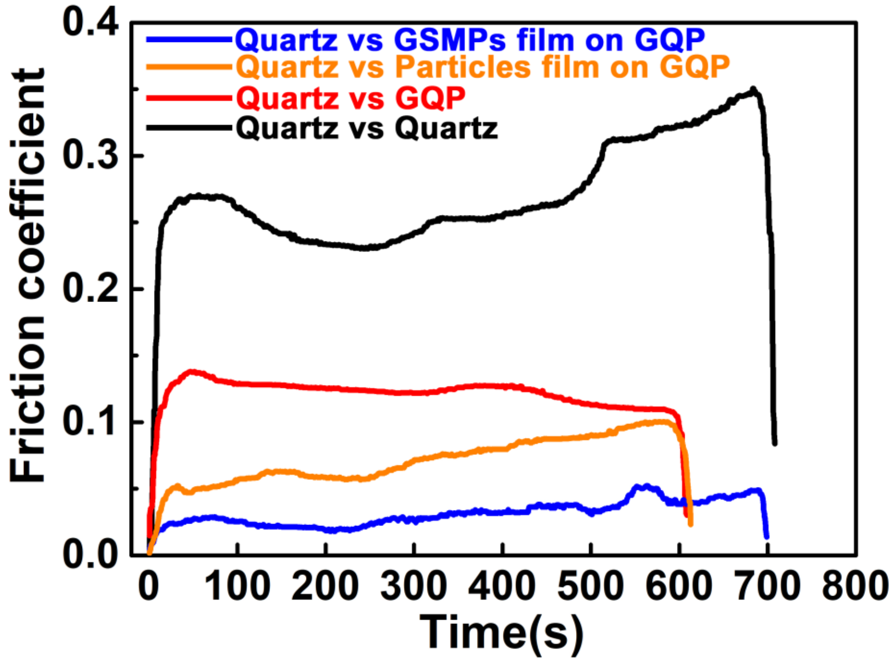

Fig. 2 Coefficients of friction for quartz ball against quartz plate, quartz ball and GQP, and quartz against GSMPs film on GQP.

Wear behavior of GSMP. In the following, we will show the excellent anti-wear property of GSMPs, by comparing the graphene films wear degree between quartz ball against GQP and quartz ball against GSMPs film on GQP. Fig. 3 shows the optical images, 3D surface morphologies and Raman spectra of the wear tracks produced on the GSP without and with GSMPs after friction tests. During friction test, the MLG on quartz plate got worn out and damaged. So, the surface morphology of wear tracks reflects the wear degree of MLG. It was found that the depth and width of the wear tracks without GSMPs (Fig.3 (a), (e)) was 10 nm and 75 µm, respectively. In comparison, the width of wear tracks with GSMPs (Fig.3 (b)) was 250 µm. Though the wear tracks become wider, it was found that, as Fig.3 (b), (f) shown, the wear tracks were much shallower in the cases where GSMPs were spread to the GQP surface. Moreover, Raman spectra of the wear tracks after the tribotests without and with GSMPs were also presented on Fig.3 (c), (d). As Fig.3 (c) shown, although there existed D, G and 2D peaks, the Raman spectra signal was quite weak, suggesting that the MLG grown on the quartz plate were badly worn out. By contrast, for the case of adding GSMPs to the sliding surface, the Raman spectra signal shown on Fig.3 (d) was similar to the original spectra shown on Fig.1 (h), except for fewer reduction of 2D peak, indicating less wear of MLG. It could be reasonably concluded that the GSMPs were able to enhance the wear life of graphene films, indicating the remarkable anti-wear properties of GSMPs.

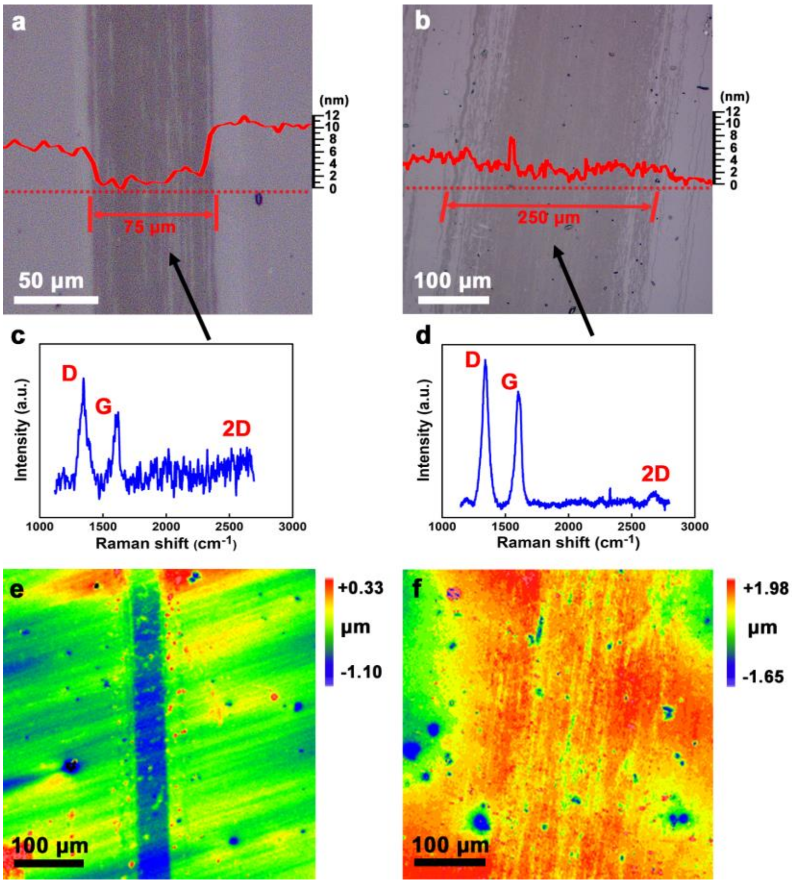

Fig.3 Analyses of wear tracks. Optical images of wear tracks on quartz plate (a) without GSMPs and (b) with GSMPs. Raman spectrums of wear tracks on quartz plate (c)without GSMPs and (b) with GSMPs. 3D surface morphologies of wear tracks on quartz plate (e)without GSMPs and (f) with GSMPs.

In a word, due to adding GSMPs to the sliding surface, the sliding friction converted into rolling friction. Meanwhile, the exfoliated graphene flakes participated in the testing process as low shear and lamellar lubricant additive. The co-effect of these two aspects greatly reduced the friction force between tribopairs. Furthermore, the wider wear track, resulting in the bigger sliding contact areas, reduced the contact stress and improves the wear resistance.

Conclusion

In summary, we develop a new lubrication system by introducing graphene-coated silica microparticles into the sliding contact area. A series of experiments were conducted to test the wear and friction behavior of this system in air at room temperature at macroscale. Due to the co-effect of GSMP and graphene, the friction COF decreased from 0.3 to 0.03, and the wear life of graphene films on the sliding contact area improved significantly. So, the results show that this lubrication system exhibits excellent friction-reduce and anti-wear properties.

Acknowledgments

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References

[1] Q. Wu, Y. X. Xu, Z. Y. Yao, A. Liu and G. Q. Shi, Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films, Acs Nano. 4 (2010) 1963-1970.
[2] N. Mohanty and V. Berry, Graphene-Based Single-Bacterium Resolution Biodevice and DNA Transistor: Interfacing Graphene Derivatives with Nanoscale an Microscale Biocomponents, Nano Lett. 8 (2008) 4469-4476.
[3] A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calio, D. Teweldebrhan, F. Mao and C. N. Lau, Superior Thermal Conductivity of Single-Layer Graphene, Nano Lett. 8 (2008) 902-907.
[4] F. N. Xia, T. Mueller, Y. M. Lin, A. Valdes-Garcia and P. Avouris, Superior Thermal Conductivity of Single-Layer Graphene, Nat. Nanotechnol. 4 (2009) 839-843.
[5] C. Lee, X. D. Wei, J. W. Kysar and J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, Science. 321 (2008) 385-388.
[6] S. Stankovich1, D. A. Dikinl, G. H. B. Dommett1, K. M. Kohlhaas1, E. J. Zimneyl, E. A. Stach, R. D. Piner1, S. T. Nguyen and R. S. Ruoff, Graphene-based composite materials, Nature. 442 (2006) 282-286.
[7] W. T. Gu, W. Zhang, X.M. Li, H. W. Zhu, J. Q. Wei, Z. Li, Q. K. Shu, C. Wang, K. L. Wang, W. C. Shen, F. Y. Kang and D. H. Wu, Graphene sheets from worm-like exfoliated graphite, J. Mater. Chem. 19 (2009) 3367-3369.
[8] X. F. Feng, S. K. Kwon, J. Y. Park and M. Salmeron, Superlubric Sliding of Graphene Nanoflakes on Graphene, Acs Nano. 7 (2013) 1718-1724.
[9] S. W. Liu, H. P. Wang, Q. Xu, T. B. Ma, G. Yu, C. H. Zhang, D. Z. Geng, Z. W. Yu, S. G. Zhang, W. Z. Wang, Y. Z. Hu, H. Wang and J. B. Luo, Robust microscale superlubricity under high contact pressure enabled by graphene-coated microsphere, Nat. Commun. 8 (2017) 14029.
[10] D. Berman, A Erdemir and A. V. Sumant, Graphene: a new emerging lubricant, Mater. Today. 17 (2014) 31-42.
[11] D. Berman, A Erdemir and A. V. Sumant, Reduced wear and friction enabled by graphene layers on sliding steel surfaces in dry nitrogen, Carbon. 59 (2013) 167-175.
[12] D. Berman, A Erdemir and A. V. Sumant, Few layer graphene to reduce wear and friction on sliding steel surfaces, Carbon. 54 (2013) 454-459.
[13] D. Berman, S. A. Deshmukh, S. K. R. S. Sankaranarayanan, A. Erdemir and A. V. Sumant, Extraordinary Macroscale Wear Resistance of One Atom Thick Graphene Layer, Adv. Funct. Mater. 24 (2015) 6640-6646.
[14] K. S. Kim, H. J. Lee, C. G. Lee, S. K. Lee, H. Jang, J. H. Ahn, J. H. Kim and H. J. Lee, Chemical Vapor Deposition-Grown Graphene: The Thinnest Solid Lubricant, Acs Nano. 5 (2011) 5107-5114.
[15] L. C. Guo, Z. Y. Zhang, H. Y. Sun, D. Dai, J. F. Cui, M. Z. Li, Y. Xu, M. S. Xu, Y. F. Du, N. Jiang, F. Huang and C. T. Lin, Direct formation of wafer-scale single-layer graphene films on the rough surface substrate by PECVD, Carbon. 129 (2018) 456-461.
[16] H. Y. Xu, C. H. Zhang and P. Wu, Design and testing of micro-tribometer with macro applied load, Sci. China Tech. Sci. 59 (2016) 1666-1672.
[17] J. Y. Chen, Y. G. Wen, Y. L. Guo, B. Wu, L. P. Huang, Y. Z. Xue, D. C. Geng, D. Wang, G. Yu and Y. Q. Liu, Oxygen-Aided Synthesis of Polycrystalline Graphene on Silicon Dioxide Substrates, J. Am. Chem. Soc. 133 (2011) 17547-17551.