

New Advances of Superlubricity

Jianbin Luo

State Key Laboratory of Tribology, Tsinghua University, Beijing, China
Corresponding author: luojb@tsinghua.edu.cn

1. Introduction

Superlubricity has developed very fast in recent years as a new and an important area in tribology. Many new phenomena, new materials, and new mechanism both in liquid and solid superlubricity have been obtained. In the liquid area, a new system of superlubricity liquids with new mechanism has been found, which exhibits very good properties of superlubricity under the higher pressure. In solid area, more materials in superlubricity have been observed both by experiment and the molecular dynamics simulation (MDS), such as grapheme to grapheme surfaces, highly oriented pyrolytic graphite (HOPG) to grapheme etc. Mechanism for different tribo-systems has been discussed.

2. Liquid Superlubricity

2.1 Superlubricity of mixture of acid and polyhydroxy alcohol

The acid solution has been found having superlubricity properties between glass plate and Si₃N₄ ball in our group in 2010^[1-3]. The superlubricity was achieved after a running-in process^[4]. Li et al.^[5] found superlubricity is related to hydrogen ions and proposed that the existence of hydrogen bond network among H₃PO₄, H₂PO₄⁻ and H₂O is in favor of getting superlubricity. Based on such assumption, most acid solutions mixed with polyhydroxy alcohol have been found to realize the superlubricity, as shown in Figure 1.

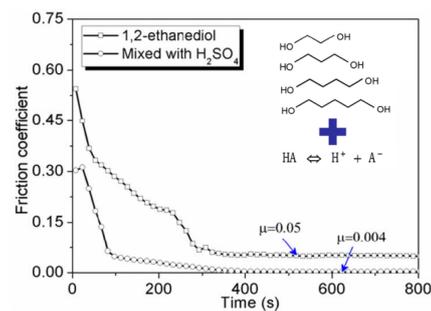


Figure 1. The friction coefficient with time ^[5]

2.2 Superlubricity mechanism of the mixture of acid and polyhydroxy alcohol

In order to understand the superlubricity mechanism the mixture of acid and polyhydroxy alcohol, based on the film thickness measured, variation of the lubrication regime has been investigated in the running-in process. Experiments indicate that mixed lubrication is changed into thin film lubrication in the superlubricity state in the running-in period^[6]. The acid solution in the running-in process plays the key role on achieving superlubricity. A superlubricity mechanism was proposed as shown in the inset of Figure 2^[7]. The superlubricity is attributed to the ability of the acid to (i) provide favorable conditions for thin film lubrication, and (ii) generate a repulsive double-layer force through the adsorption of hydrogen ions on the friction surfaces.

2.3 Superlubricity of PAO oils with running-in by acid

There is a question of whether superlubricity can be achieved using oil-based lubricants. A novel approach was approached, that the superlubricity of silicone oil can be achieved between tribo-surfaces (Si₃N₄/glass) by running-in with an acid solution^[8]. As shown in Figure 3, the friction coefficient of silicone oil (100) after the running-in with acid can be reduced to about

0.004, which is only one-thirtieth of its original value ($\mu=0.13$).

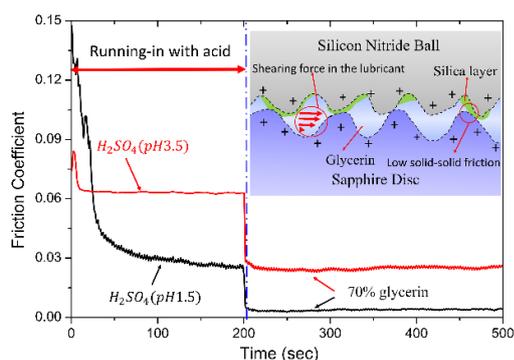


Figure 2. Friction coefficient of the glycerin solution (70%) after the running-in process with sulfuric acid. The inset shows the schematic illustration of the superlubricity model [7].

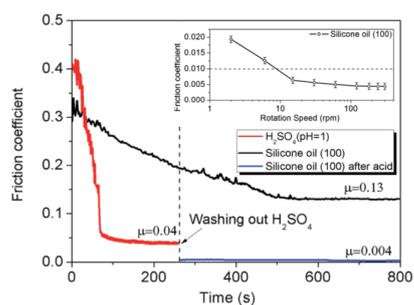


Figure 3. Friction coefficient of silicone oil and that after running-in process with H_2SO_4 [8].

3. Solid Superlubricity

3.1 2D Material as based lubricants

Recently, Ge X. et al. [9] in our group achieved a macroscale superlubricity state through the synergy effect of graphene-oxide nanoflakes (GONFs) prepared via a modified Hummers method and ethanediol (EDO) at a Si_3N_4/SiO_2 tribopair. GONFs were 0.8 nm thick, had an interlayer spacing of 0.45 nm, and had an oxygen content of 30%–40%, as depicted in Figure 4 (a–e). The results for the friction and wear of GONFs-EDO are depicted in Figure 4. (f–g). The COF of GONFs-EDO decreased to less than 0.01 after the wearing-in period of 600 s; and then to 0.0037 remaining stable for 2 h. Furthermore, the wear results show that the wear volume of the ball under lubrication with GONFs-EDO ($5.1 \times 10^4 \mu m^3$) was only 5% of that of the ball under lubrication with EDO ($1.3 \times 10^6 \mu m^3$). These results indicate the excellent superlubricity and anti-wear performances of GONFs-EDO. GONFs were adsorbed on the surfaces of the tribopair (Figure 4h), preventing direct contact between asperities. The super-low shear stresses between the GONFs interfaces contributed to the superlubricity and super-low wear, as depicted in Figure 4 (i). Moreover, the formation of the GONFs-

EDO hydrated network and the partial-slip boundary condition at the GONFs-EDO interface contributed to the super-low shear stresses of the liquid layer, leading to superlubricity, as depicted in Figure 4 (j).

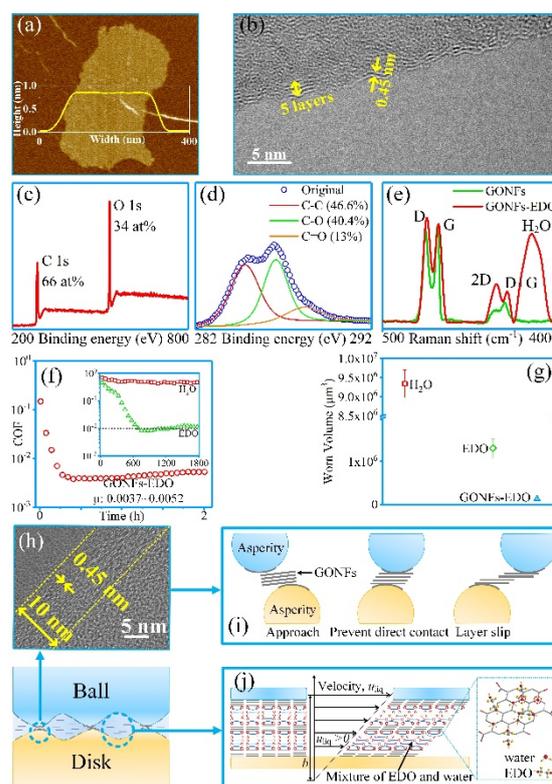


Figure 4. Characterization of GONFs: (a) atomic force microscopy image; (b) high-resolution transmission electron microscopy (HRTEM) image; (c, d) XPS spectra; (e) Raman spectra. (f, g) Friction and wear testing results for GONFs-EDO. (h) HRTEM image of the cross-sectional area of the worn surface. (i, j) Proposed superlubricity and anti-wear mechanism of GONFs-EDO. [9]

3.2 Superlubricity of graphene-coated microsphere

More solids have been found in superlubricity state in recent years [10–12]. In our group, a direct measurement of sliding friction between graphene and graphene, and between graphene and hexagonal boron nitride (h-BN) under high contact pressure has been achieved by employing a graphene-coated microsphere (GMS) probe prepared by a metal-catalyst-free chemical vapor deposition method, as shown in Figure 5 [12]. The exceptionally low and robust friction coefficient of 0.003 is accomplished. Moreover, the superlubricity has been achieved under the asperity contact pressure up to 1 GPa and is insensitive to relative humidity up to 51% RH. This ultralow friction is attributed to the sustainable overall incommensurability due to the multi-asperity contact covered with randomly oriented graphene nanograins. This realization of microscale superlubricity can be extended to the sliding between varieties of two-dimensional (2D) layers.

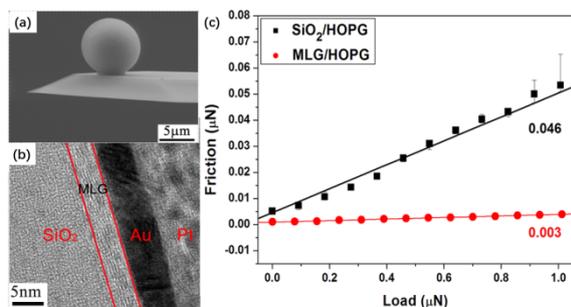


Figure 5. (a) SEM side view of the graphene-coated microsphere probe. (b) Pt and Au films are deposited as the protective film during TEM sample preparation of focused ion beam process. (c) Friction force as a function of the applied normal load for SiO₂ microsphere sliding against HOPG and MLG-coated SiO₂ microsphere against HOPG respectively [12].

In 2018, Y. Liu et al. in our group propose an approach of thermally assisted mechanical exfoliation and transfer to fabricate various 2D flake-wrapped atomic force microscopy (AFM) tips and to directly measure the interlayer friction between 2D flakes in single-crystalline contact. A superlow friction coefficient about 1×10^{-4} between different 2D flakes and layered bulk materials is achieved as shown in Figure 6. The rotation angle dependence of superlubricity is observed for friction between graphite layers, whereas it is not observed between graphite and h-BN because of the incommensurate contact of the mismatched lattices.

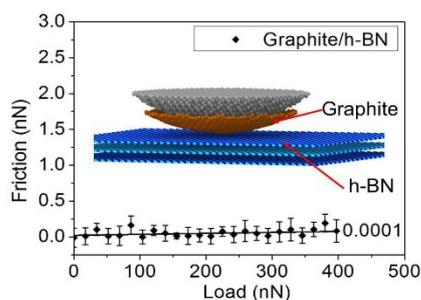


Figure 6. Friction coefficient between graphite and h-BN [13]

4. Conclusions

The recent researches on superlubricity in our group have been reviewed. Several kinds of lubricants, including liquids and solids, have been found having superlubricity properties at macro- or micro-scale. These superlubricity phenomenon exhibited different dependences on sliding velocity, contact pressure and environment, due to diverse tribological mechanism. At present, there does not exist the uniformed mechanism for different kinds of superlubricity, nor a relationship between superlubricity at macro- or micro-scale. The application for superlubricity on the practical engineering is just the beginning. More efforts need to be carried out in the field of

superlubricity.

Acknowledgment

The work is financially supported by NSFC (51527901, 51335005).

References

- [1] J. B. Luo, Z. Z. Ma, J. J. Li, C.H. Zhang, Progress in Superlubricity of Liquid Lubricants, *Keynote Speech on Advance Forum on Tribology 2010, Morioka, Iwate University*, November 7-8, 2010.
- [2] Z. Z. Ma, C. H. Zhang, J. B. Luo JB, Superlubricity of a Mixed Aqueous Solution, *Chinese Physics Letters*, 28(5) (2011) 056201.
- [3] J. J. Li, C. H. Zhang, J. B. Luo, Superlubricity behavior with phosphoric acid-water network induced by rubbing, *Langmuir*, 27 (2011) 9413–9417.
- [4] J. J. Li, C. H. Zhang, L. Sun, X. Lu, J. B. Luo, Tribochemistry and superlubricity induced by hydrogen ions, *Langmuir*. 28 (2012) 15816–15823.
- [5] J. J. Li, C. H. Zhang, J. B. Luo, Superlubricity achieved with mixtures of polyhydroxy alcohols and acids. *Langmuir*. 29 (2013) 5239–5245.
- [6] M. M. Deng, C. H. Zhang, J. J. Li, L. R. Ma, J. B. Luo, Hydrodynamic effect on the superlubricity of phosphoric acid between ceramic and sapphire, *Friction*, 2 (2014) 173–181.
- [7] M. M. Deng, J. J. Li, C. H. Zhang, J. Ren, N. Zhou, J. B. Luo, Investigation of running-in process in water-based lubrication aimed at achieving super-low friction, *Tribol. Int.*, 102 (2016) 257–264.
- [8] J. J. Li, C. H. Zhang, M. M. Deng, J. B. Luo, Superlubricity of silicone oil achieved between two surfaces by running-in with acid solution, *RSC Adv.* 5 (2015) 30861–30868.
- [9] X. Ge, J. Li, R. Luo, C. Zhang, J. Luo, Macroscale superlubricity enabled by synergy effect of graphene-oxide nanoflakes and ethanediol. *ACS Appl. Mater. Interfaces*, 10 (2018), 40863–40870.
- [10] M. Dienwiebel, G.S. Verhoeven, N. Pradeep, J.W.M. Frenken, J.A. Heimberg, H.W. Zandbergen, Superlubricity of graphite, *Phys. Rev. Lett.*, 92 (2004) 126101–1.
- [11] A. Erdemir, G. Ramirez, O. L. Eryilmaz, B. Narayanan, Y. F. Liao, G. Kamath, S. Sankaranarayanan, Carbon-based tribofilms from lubricating oils, *Nature*, 536 (2016) 67-71
- [12] S. W. Liu, H. P. Wang, T. B. Ma, G. Yu, C. H. Zhang, D. H. Geng, Y. Z. Hu, H. Wang, J. B. Luo, Robust Superlubricity under High Contact Pressure Enabled by Graphene-coated

Microsphere, Nature Commu. (2017),
DOI:10.1038.

- [13] Y. Liu, et al. “Interlayer Friction and Superlubricity in Single Crystalline Contact Enabled by Two-dimensional Flake-Wrapped Atomic Force Microscope Tips”. *ACS Nano* 12, (2018), 7638-7646.