

## Exploring 2D nanomaterials as emergent solid tribology materials

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**1. Introduction**

Friction, wear, and lubrication can be covered with the word “tribology”, and this is inevitable in the mechanical system as well as our daily lives. Especially, friction and wear not only cause severe energy losses but also accelerate mechanical failures. Therefore, it is expected that we can save a lot of energy by reducing friction and wear, and thus, the necessity of the development of solid lubrication coating technology has been emerging.[1,2] The usage of the solid lubricants has been spanned over wide applications.

Two-dimensional (2D) materials have layered-structure, composing of thin atomic layers. They are expected to have superior tribological performance due to their weak van der Waals interlayer interaction and easy-shearing property, and these excellent performances render them proper candidates as solid lubrication coating materials. Especially, the principal lubrication mechanism of solid lubrication coating films using 2D materials is based on inducing the material transfer from an underlying coating film to a sliding interface. The transfer layer can play an essential role as protection layers to lowering the coefficient of friction (COF) and the wear by preventing the direct contact of a substrate with a counterpart material. There are various types of 2D materials such as graphene, transition metal dichalcogenides (TMD), hexagonal boron nitrides, and MXenes, having their own advantages under certain conditions, and all the materials are solution- processable. By taking advantages of the capabilities of various layered-structural designs, we can tailor the structures to control the tribological performance of the films for specific purposes.

While many attempts to improve the tribological properties have been focused on lowering the COF, there is still a lack of research for how we can enhance the coating durability. Since the wear of 2D material-based coating films is inevitable, for the real engineering scale applications, it is crucial to find out a proper strategy for prolonging the service lifetime of the coating film on any substrate or condition/environment. Recently, there have been some research emphasizing the importance of enhancing the durability of 2D material-based solid lubrication coating films. The main mechanism for achieving the long durability from previous research is to induce a material transfer onto the counterpart surface, making 2D material vs. 2D material contact, which implies that we can possibly prolong the durability by preventing direct contact between the counterpart surface and the substrate. It was reported that when the graphene coating film slides against  $\text{Si}_3\text{N}_4$  counterpart ball, the transfer layer wasn't formed whereas the transfer layer was observed when the solid graphene vs. solid graphene contact was made by sprinkling graphene flakes at the friction interface which resulted in the improved tribological properties. This implies that it is essential to develop a widely-usable transfer layer formation method so that we can realize the envisioned tribological performance of 2D materials in macroscale tribology applications at diverse environmental and load conditions.

In this study, we suggest a simple method to promote the material transfer from a graphene-based solid lubrication coating film, exhibiting the incredibly enhanced durability by simple sequential drop-casting of the graphene oxide on the pristine film. By thorough analysis of intrinsic tribological properties, we revealed that the graphene oxide has adhesive properties and utilized it as a gluing layer to promote the huge material transfer of pristine graphene, making a contact of solid transfer layer vs. solid coating film. The durability of this tailored stacking structure exhibits more than 100 times improved durable performance in comparison to that of the pristine graphene film only. To minimize the effect from the friction pairs, we utilized inert materials, that are silicon nitride ( $\text{Si}_3\text{N}_4$ ) ball and silicon oxide/silicon ( $\text{SiO}_2/\text{Si}$ ) substrate, which can provide possibilities to span over the selection of the materials for specific purposes. We expect that this can provide a new pathway of utilizing pristine graphene as solid lubricants for engineering scale applications, as well as a possibility of wide-range applications using various 2D materials by simply promoting transfer layer formation.

**2. Experimental procedure**

We utilized pristine graphene nanopowder (A-12) and ultra-highly concentrated single-layer graphene oxide aqueous solution purchased from Graphene Supermarket (United States). We dispersed the pristine graphene powder in ethanol solvent through bath sonication for 2 hours with a concentration of 15 mg/ml. We mixed the ethanol into the graphene oxide aqueous solution with a ratio of 1:1 for better deposition of the GO solution on the deposited PG film. To deposit each the PG and GO film onto the  $\text{SiO}_2/\text{Si}$  substrate ( $1.5 \times 1.5 \text{ cm}^2$ ), we utilized the drop-casting method. To fabricate the GO-on-PG heterostructure, we conducted the consequent drop-casting of GO dispersion on the PG film. First, we dropped the PG dispersion onto the substrate and dried it under ambient conditions. The PG film was further dried in the vacuum oven under  $80^\circ\text{C}$  and -1.0 bar (Gauge pressure) for 12 hours to completely evaporate the solvent. We conducted additional drop-casting of GO dispersion on the deposited PG film and dried it under ambient conditions which was followed by the drying in the vacuum oven at  $80^\circ\text{C}$  and -1.0 bar for 12 hours. For the

fabrication of the thinner GO-on-PG films, we controlled the amounts of the PG dispersion with the same amount of GO dispersion. Every tribological test was conducted with a ball-on-disk type of tribometer (TRB3, Anton Paar, Austria) under the ambient conditions (20-30°C, 40-60 R.H.%) with a normal load of 1 N, rotational reciprocating mode with a frequency of 20 Hz, a sliding radius of 3 mm, and a sliding speed 100 rpm (3.14 cm/s of linear speed) using Si3N4 ball of 6 mm diameter as a counterpart material. Every test was repeated at least 3 times for the reproducibility of the test results. For all the tribo-test results, all the outliers have been filtered by using a Fast Fourier transform (FFT) low-pass filter in Origin software.

### 3. Results and discussion

The surface topography, the cross-sectional image and the Raman spectra on the surface of the GO-on-PG film are shown in Figs. 3(a-c). In addition, to check whether the additional drop-casting affects the stacking status of the resulting film, energy-dispersive X-ray spectroscopy (EDS) was performed on the cross-section of the GO-on-PG film. The result shown in Figs. 3(d-f) show that the GO and the PG were well deposited separately showing clear boundaries, indicating the additional drop doesn't affect the whole structure of the film.

To explore the tribological properties of the GO-on-PG film, we conducted the tribo-test for the GO-on-PG coating film under ambient conditions. While the resulting COF was measured to be  $0.17 \pm 0.03$ , which is a similar value with that of the PG, the sliding distance was measured to be  $10.3 \pm 1.59$  km, exhibiting a remarkable enhancement of the film durability. For simple comparison of tribological performances of the PG, GO, GO-on-PG film and the substrate, we plotted the tribo-test results in Figs. 4(a) and 4(b), including the magnified tribo-test results from 0 to 400 m of the sliding distance, as shown in the inset of Fig. 4(a). These results show that, even with the simple additional drop-casting of the GO on the PG, the GO-on-PG film exhibits a remarkable enhancement, that is at least 100 times better durable performance in comparison to the PG film only, maintaining a similar COF to the PG film. For a better understanding of the transition of the transfer layer as well as the wear track, we investigated the transfer layer formation as well as the evolution of the wear track for four different samples tested at four different sliding distances, as shown in Fig. 6.

### 4. Conclusion

In conclusion, we suggest a new approach for utilizing pristine graphene(PG) as a superior solid tribology material in an macroscale applications by introducing a simple method for promoting transfer layer formation. This work provides a new pathway to utilize graphene-based solid lubrication coating films in real engineering applications by achieving huge material transfer supported by graphene oxide as a “bridging material”. We expect that this work can be extended as a basis to further developing new strategies of 2D materials as excellent solid lubrication coating films with a low COF as well as high durability which can be utilized in diverse real macroscale tribology applications.

#### Reference

- 1) R. Wang et al.: Review of two-dimensional nanomaterials in tribology: Recent developments, challenges and prospects, Adv. Colloid Interface Sci., 321 (2023) 103004.
- 2) A. Rosenkranz et al.: Perspectives of 2D MXene tribology, Adv. Mater., 35 (2023) 2207757.

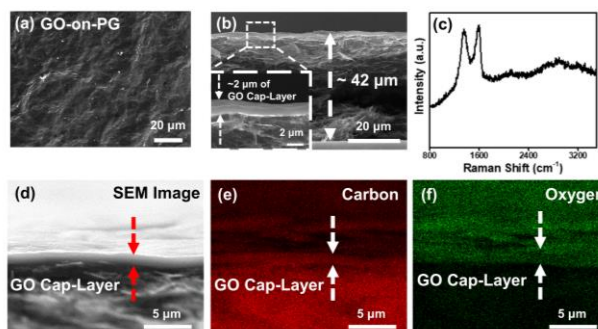


Fig. 1 Characterization results of a GO-on-PG film to show GO cap-layers for enhancing its durability

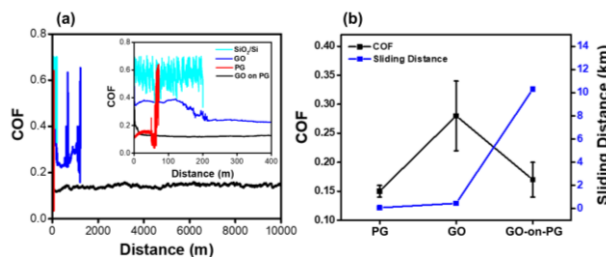


Fig. 2 (a) Tribo-test results for SiO<sub>2</sub>/Si substrate, PG film, GO film and GO-on-PG film. (b) Averaged COFs and sliding distances for each film

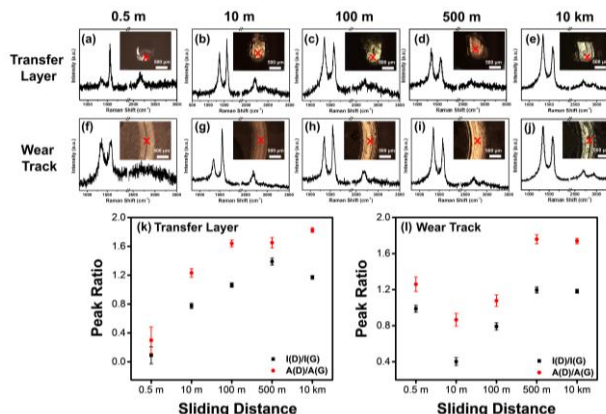


Fig. 3 Evolution of Raman spectra for the transfer layers and wear tracks after the tribo-tests and Graphs for the intensity and area ratios of G and D band peaks