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Graphene as a protective coating and superior lubricant for electrical contacts

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Potential for graphene to be used as a lubricant for sliding electrical contacts has been evaluated. Graphene, being deposited as a sporadic flakes on the gold substrate sliding against titanium nitride ball shows not only significant improvement in tribological behavior by reducing both friction (by factor of 2–3) and wear (by 2 orders) but also, even more importantly, demonstrates stable and low electrical resistance at the sliding contacts undergoing thousands of sliding passes regardless of the test environment (i.e., both in humid and dry conditions).
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Production of low-friction, long-lasting, and highly conductive coatings is highly desired for many electromechanical applications but has been a great challenge for tribologists for a long time. In this case, the low contact resistance (CR) of the coating component becomes a necessary requirement for the successful candidate material.[1,2] Graphene's excellent mechanical[3–6] and electrical properties[7–9] over traditional materials and coatings make it very attractive for a wide range of electromechanical applications ranging in sizes from nano/macro-scales in nano and micro-electromechanical systems[10] to macroscale (electrical contacts, sliding/rolling, rotating and bearings, etc.). The majority of existing studies are directed towards careful investigation of the graphene electrical properties in the static contact with other materials at the nanoscale.[11–15] So far, no studies indicated graphene potential to be used for moving contacts at macroscale, when mechanical friction and wear affect the structure and electrical properties of materials. This is especially important if one considers using graphene as a lubricant in macroscale electrical connectors.

In previous studies, where sliding tests were performed at macroscales, much attention was directed toward the tribological performance of graphene at the sliding steel interfaces.[16–19] In that case, the remarkable friction and wear behaviors of graphene layers were attributed to their easy shear characters and corrosion protection of refined metals[20,21] due to graphene's impermeability to gas molecules.[22,23] Here, we report another remarkable aspect of graphene as a two dimensional tribomaterial providing excellent electrical conductivity along with superior wear/friction properties serving as an ideal lubricant material for rotating/sliding contacts. For this, we have chosen gold coating as it is the most commonly used material for electric contacts.[24,25] The counterface material was titanium nitride-coated steel balls to create high contact pressures and shear deformation during sliding. Results demonstrate that graphene was able not only to suppress the friction and wear regardless of the test environment (i.e., both in humid and dry conditions) but also to maintain low electrical contact resistance for extended period.

Tribological studies were performed in dry nitrogen (900 mbar) and humid air (30% relative humidity) environment at room temperature using a high vacuum tribometer (CSM instruments SA, Switzerland) with a ball on disk contact geometry. Flat sample was represented by 1 μm thick gold film deposited on quartz wafer (with 20 nm of titanium as an adhesion layer) using e-beam evaporator (the rms roughness of gold measured by the 3D profilometer was $R_q = 8$ nm). As a counterpart, the stainless steel ball (AISI 440C grade) of 16 mm diameter covered with 1-μm-thick titanium nitride layer was used (rms roughness $R_q = 130$ nm). The normal load during the tribotests was kept at 1 N (0.25 GPa Hertz contact pressure) and a series of wear tracks of 5–10 mm radius were generated in each flat. Sliding speed during the tests was 60 rpm (3–6 cm/s).

The electrical contact resistance measurements were conducted by measuring voltage drop across the gold/TiN contact being in series with 200 kΩ resistor, while the gold substrate is grounded and the TiN ball holder is insulated from other metallic parts of machine (Fig. 1(a)).

We used commercially available ethanol solution processed graphene (SPG) from Graphene Supermarket, Inc., as a graphene source.[26] The weight concentration of graphene was 1 mg/l containing mostly single layer graphene. Small SPG amount (2–3 drops or 0.1–0.15 ml of solution per 1 cm^2) was applied on the gold film in a colloidal liquid state. After evaporation of ethanol in dry nitrogen environment, formation of a discontinuous grayish deposit of graphene flakes on the gold surface has been confirmed by scanning electron microscope (SEM) (Fig. 1(b)). As it can be seen, the size of the deposited graphene flakes varies up to 2 μm in diameter, and the coverage of the deposited flakes (by the area) approaches 50% of the total surface area. Raman analysis of the gold surface performed with an Invia Confocal Raman Microscope using the green laser light ($\lambda = 514$ nm) confirms the presence of graphene flakes on the gold surface (Fig. 1(c)).[27] Characteristic Raman G ($\sim$1600 cm^{-1}) and 2D ($\sim$2700 cm^{-1}) peaks show that the deposition procedure has

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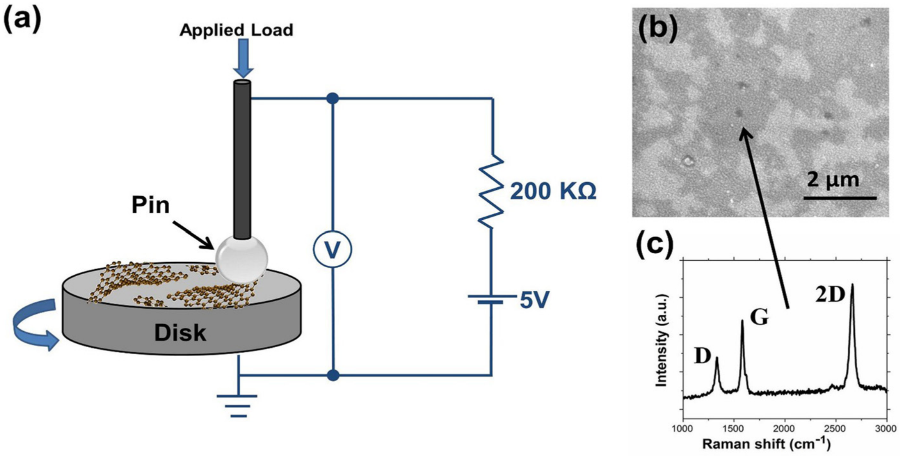

FIG. 1. Schematic of the experimental set-up (a). Fig. 1(b) shows SEM image of the discontinuous graphene layers (dark gray islands) covering gold sample (bright islands) with corresponding Raman signature (c) of few layer graphene on gold.

resulted in supply of few layers (2–3) of graphene. Partial oxidation of graphene during deposition process as well as non-planar deposition of the flakes results in the presence of defect peak D ($\sim 1350\,\mathrm{cm}^{-1}$).

To estimate the wear rate of the ball side after the tests, we calculated the wear volume

$$V = \left(\frac{\pi h}{6}\right)\left(\frac{3d^2}{4} + h^2\right), \tag{1}$$

where d is the wear scar diameter, r is the radius of the ball, and

$$h = r - \sqrt{r^2 - \frac{d^2}{4}}. \tag{2}$$

The wear rate was calculated as wear volume in mm^3 produced over applied load in N along the sliding distance in m.

Measuring the electrical CR along tribological tests for other materials have been used by researchers as an indirect technique of indicating the state of lubrication at the interface and the structural/chemical modifications of the protective coatings.[28,29]

Here, we measure the CR along with the coefficient of friction (COF) not only for indicating any modification of graphene layers at the sliding interface but also for revealing its potential to maintain high electrical conductivity of the macroscale contacts (Fig. 2). Results demonstrated unique ability of graphene to suppress the metal wear during mechanical sliding tests under high contact pressures. We believe that the macroscale lubrication properties of graphene, in the form of discontinuous flakes, originate from easy shearing mechanism occurring at the initial sliding regime and resulting in more uniform coverage of the wear track as observed in our previous publications.[18,19] Once the uniform protection layer along the wear track is formed, graphene minimizes the effect of surrounding environment and protects the surface underneath from tribo induced intensive wear debris formation while still maintaining excellent electrical conductivity of metal-metal contacts at the low levels due to its intrinsic electrical properties. For both humid and dry environment, bare Au/TiN contact sliding results in rapid increase of the contact resistance up to unstable 10^4–10^5 Ω values due to wear debris generation and gold layer removal from the wear track, which exposes insulating quartz substrate to the contact with TiN ball. Meanwhile, adding

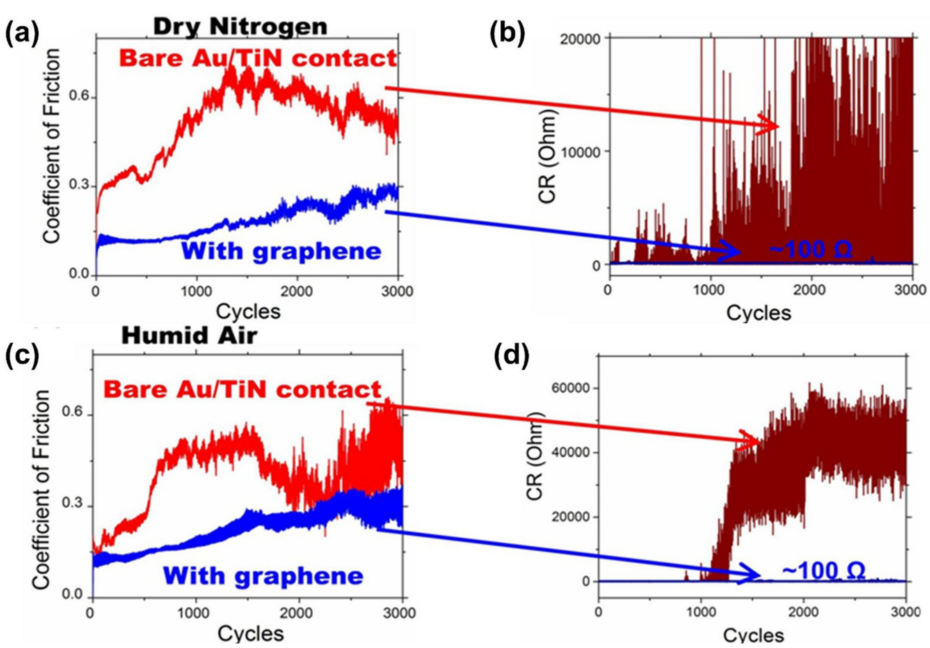

FIG. 2. COF with the corresponding CR evolution for bare gold/TiN contact and with graphene both in dry nitrogen (a) and (b) and in humid air (c) and (d) are presented. Graphene not only suppress the friction and wear but also maintains low contact resistance of the sliding interfaces.

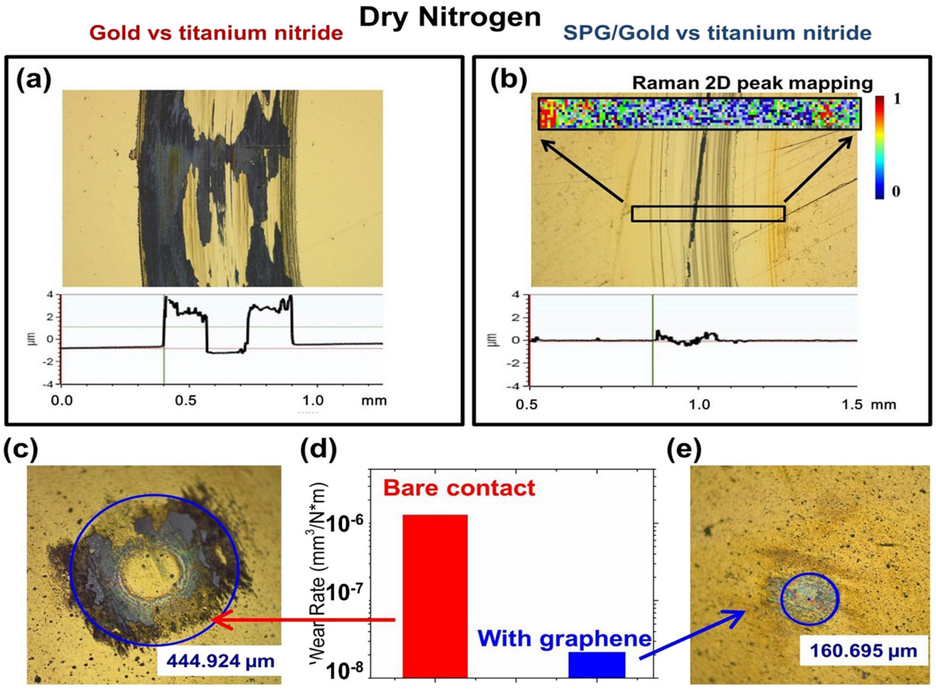

FIG. 3. Wear scar marks produced during tribo-test in dry nitrogen environment are presented. For bare gold/TiN contact, the flat side (a) undergoes high wear of gold down to quartz substrate and the ball side (c) demonstrates large wear scar with worn material accumulation. When graphene is provided to the contact interface, the wear for both the flat (b) and the ball (e) sides is dramatically reduced. (d) The wear rate comparison. The Raman mapping of 2D graphene peak is included in image (b) to demonstrate that graphene is still present in the wear scar even after 3000 cycles, thus providing low friction and low contact resistance.

graphene flakes not only suppresses the friction and wear of the contact interfaces (the COF for graphene/gold vs TiN stays at 0.15–0.3 value) but also results in stable low contact resistance at ∼100 Ω. Moreover, assuming the stable nature of the graphene induced CR during the sliding test, we believe that most of resistance is coming from the wire connections and the bulk materials resistance themselves, while the actual contact resistance is believed to be unaltered or even lower. The increase in the COF values is attributed to the fact that graphene flakes start to be pushed to the sides of the wear track, thus leaving behind the bare contact materials. However, the CR results demonstrate that even with the small amount of graphene left in the wear track after 3000 cycling period (as demonstrated by Raman mapping of graphene 2D peak on insets of Figures 3(b) and 4(b)), it is still possible to maintain high electrical conductivity at the contact interface. Moreover, there was no observable change in the contact resistance of the system over the entire period of testing, which is an essential requirement for the real electrical contacts.

Figs. 1 and 4 present the optical images of the wear produced both on the flat and ball side, as well as wear rate estimations based on the ball wear scar marks. More detailed study of the wear tracks produced on the flat side shows that for the bare Au/TiN contact sliding, high and sporadic friction results in wearing off thick gold layer (with worn gold

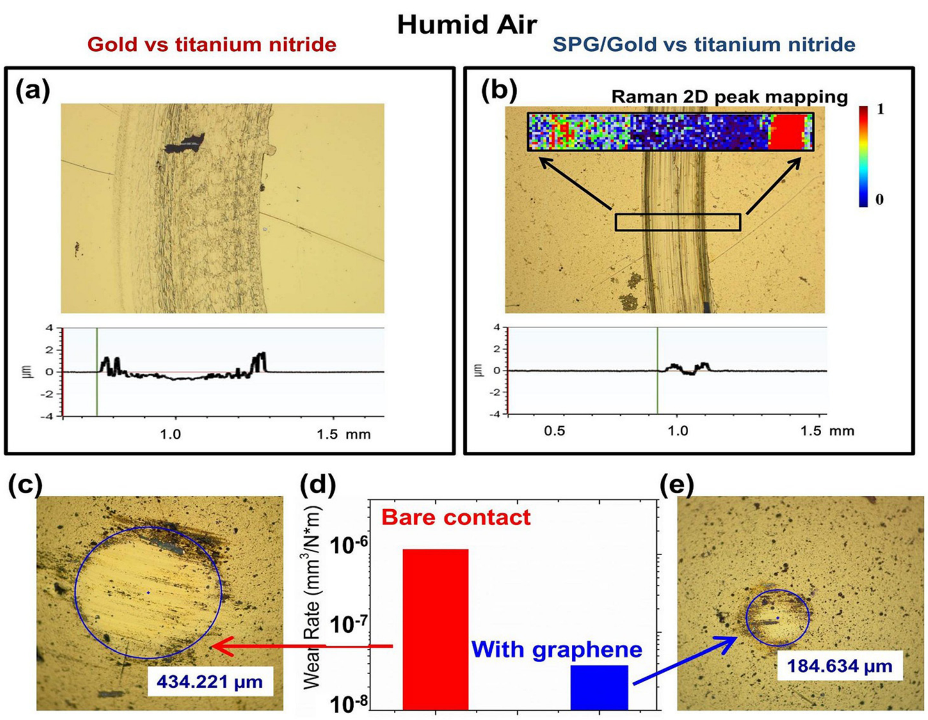

FIG. 4. Wear scar marks produced during tribo-test in humid air environment are presented. For gold/TiN contact, the flat side (a) undergoes high wear of gold down to quartz substrate and the ball side (c) demonstrates large wear scar again. When graphene is provided to the contact interface, the wear for both of the flat (b) and the ball (e) sides is dramatically reduced. (d) The wear rate comparison. The Raman mapping of 2D graphene peak is included in image (b) to demonstrate that graphene is almost completely pushed to the sides at this stage, which is also observed in the COF increase.

material accumulation both on the ball side and on the edges of the flat side wear track) and exposing bare quartz substrate to the sliding contact causing such a high CR value. For the cases where graphene was present on the surface, the resulting wear track is significantly smaller, and the Raman analysis reveals graphene's 2D signature (i.e., $\sim$2700 cm^{-1}) being present in the wear scar, thus indicating that graphene provides both friction protection and electrical conductivity stability.

In conclusion, the effect of graphene on friction and wear behavior of sliding Au/TiN substrates was demonstrated both in humid and dry environment. The results reveal that graphene as a two-dimensional material shears easily during mechanical sliding tests even under high contact pressures, while retaining excellent electrical conductivity of metal-metal contacts. More importantly, few-layer graphene shows low and stable friction and minimized wear for thousands of sliding passes without needs of being continuous or continuously replenished on the gold surface. These results open a new niche for graphene films to be used as a lubricant and wear resistant conducting coating for electrodes in a rotating/sliding contacts where the atomically thin nature of graphene coupled with superior mechanical and electrical performance makes it very unique and fitting for various applications.

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