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Effect of trapped water on the frictional behavior of graphene oxide layers sliding in water environment

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ABSTRACT

Two-dimensional materials have great potential for applications in the wide-reaching areas of sensing, drug delivery, and biomolecule nano-transportation. When considering graphene for possible applications, interactions with the surrounding environment should be always kept in mind, as they can cause wear and damage of the films and thus largely affect the overall performance of graphene-based devices. In this paper, we use Quartz Crystal Microbalance (QCM) to explore interactions of graphene oxide (GO) films with water at solid/liquid interface. We demonstrate that water trapped between GO layers during deposition from the water solution largely affects the response of the QCM in the liquid environment by unexpectedly increasing the resonant frequency of oscillations. Once the trapped water is released in the DI water environment or eliminated in case of graphene deposited from an ethanol solution, the resonant frequency decreases upon immersion as predicted from viscosity effect on the oscillations. The trapped water also increases friction against the QCM movement in the liquid environment, as indicated by 2–3 times larger mechanical resistance values. Our observations confirm the importance of GO composition and deposition procedures and propose a new method for releasing the trapped water from the structures and improving the tribological performance of the film in solid/liquid interface.

1. Introduction

The discovery of graphene, the two-dimensional form of carbon, attracted lots of attention to the new class of atomically thin films, which demonstrate specific structures and unique properties [1]. Transmission Electron Microscopy (TEM) confirmed that graphene can be used as a protective membrane to study the interactions of biological cells [2,3]. Graphene has seen applications as an electrochemical platform to sense explosive compounds [4] or biological species [5] and as an electrode material in batteries [6]. An important aspect of these potential applications is graphene immersed in a liquid. In this case, the surrounding liquid tends to largely impact the performance and reliability of graphene-based devices.

2D materials demonstrate their own unique way for interacting with water. Algara-Siller et al. showed that residual water molecules, locked between two graphene sheets, arrange into a new form of two-dimensional ice, 'square ice', at room temperature [7]. Ma et al. revealed that propagating thermal ripples in graphene lead to fast diffusion of water along the graphene plane [8]. It was also demonstrated that in contrast to classical interactions of water with solids, the retention force of water on chemically homogeneous graphene does not vary with the drop resting time [9]. Moreover, though the contact angle between the water and graphene is dependent on the substrate material [10], introducing graphene film on the rough surface prevents water penetration into surface defects and thus increases its mobility on the surface [11]. Despite the numerous efforts in understanding all the fundamental aspects of the material property and behavior, some basic questions on the tribology of water sliding on graphene and graphene oxide surface remain unexplored.

In the majority of the existing tribological studies, when graphene is deposited at the sliding interface, only the solid/solid contact is examined [12–15]. Meanwhile, quantitative estimation for liquid layers sliding on the graphene surface is limited to the available measurement techniques.

Previous studies demonstrated the unique sensitivity of Quartz Crystal Microbalance (QCM) to non-destructively reproduce in resonant frequency and amplitude feedback the smallest changes in contact mechanics and the surface morphology of QCM

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electrodes [16,17]. The physics of these interactions shows that when the adsorbed layers are not attached rigidly to the surface of electrodes, interfacial slip may occur as a result of extreme shear vibrations. Modulations in frequency and amplitude due to layers sliding on the QCM uncover new possibilities to evaluate tribological behavior at the sliding interface [18]. Even smallest changes in the morphology of QCM can be thus detected [19,20]. Previous studies have used QCM to study interactions of graphene with adsorbed monolayers of krypton [21].

In this paper, we suggest using QCM technique for evaluating the mechanical resistance of water sliding on graphene oxide film, and thus for understanding the friction of sliding liquid layers on graphene at the solid/liquid interface. Previous results have indicated the tendency of graphene to convert into graphene oxide in a water environment [22]; therefore, to avoid graphene chemistry changes during oscillation, initial samples were already oxidized.

2. Experimental procedure

In the QCM, a single crystal of quartz oscillates at an extremely sharp resonance frequency, on the order of several MHz, with very little internal energy dissipation. These oscillations are driven by applying the electrical potential difference to the metal electrodes deposited on the surface of the quartz.

When the adsorbed film is rigidly attached to the QCM electrodes, the change in frequency (δf_{film}) of QCM is negative and can be calculated by the following Eq. (1) [23]:

$$\delta f_{film} = -\frac{2f^2}{A\sqrt{\rho_q \mu_q}}\Delta m \tag{1}$$

where f is the fundamental frequency of the QCM, Δm is mass change, A is the surface area of QCM, $\rho_q = 2648$ kg/m^3 is the density of quartz, and $\mu_q = 2.947 \times 10^6$ kg × m/s^2 is the shear modulus of quartz.

When the QCM is oscillating in the viscous liquid environment, its frequency is also affected by the properties of the surrounding matter and slippage of the adsorbed layers on the QCM surface [24]:

$$\delta f_{film} = -f^{3/2}\sqrt{\frac{\rho_L \eta_L}{\pi \mu_q \rho_q}} \tag{2}$$

where ρ_L and η_L are the density and viscosity of the liquid, correspondingly.

By substituting the values into Eq. (2), the calculated change in resonant frequency when the QCM is immersed in water should be negative and approximately $\delta f = -(715 \pm 10)$ Hz.

The mechanical resistance measured in Ohms is the resistance to be added to the oscillator circuit to sustain stable QCM oscillations [25]. For the QCM immersed in liquid, the mechanical resistance is [26]:

$$\Delta R = (2fL_u)\sqrt{\frac{4\pi f \rho_L \eta_L}{\mu_q \rho_q}} \tag{3}$$

where L_u is inductance for the dry resonator. Mechanical resistance for a clean gold electrode QCM immersed in water should be around 400 Ω.

To investigate the effect of water on the level of interactions of graphene with liquid environment, 2.5-cm diameter QCMs with 1.3-cm diameter gold-plated electrodes were used. The resonant frequency for the monitors chosen was around 5 MHz. Graphene oxide layers were deposited from water containing (water GO) and ethanol (ethanol GO) containing solutions of 5 g/L concentration (purchased from Graphene Supermarket). One drop of the solution was drop-casted onto the gold surface of the QCM electrode, and the liquid was evaporated for 3 h in a dry nitrogen atmosphere. Heating of the samples was performed on a hot plate at 110 °C for 10 min. Based on the coverage area and considering the bulk density of the materials to be ~1 g/cm3, the estimated thickness of resulting graphene oxide film is ~300 nm. Therefore, the resulting graphene oxide films were rather thick and, based on the previous funding of the substrate effect on graphene/water interactions [10], the effect of the substrate on the friction measurements can be neglected.

Changes in QCM resonant frequency and mechanical resistance of oscillations were monitored using the SRS QCM 200 system. The specifically designed holder allows contact of the QCM with the liquid only at one side, while the second electrode and electric connections are kept isolated from water. When the samples were immersed in a liquid environment, resonant frequency and resistance were monitored after an initial 60 s equilibration period.

Scanning Electron Microscope (SEM) images of GO deposited from water and ethanol solution were collected with an FEI NOVA 200 system. Raman spectra of the resulting films were collected using Nicolet Almega XR Dispersive Raman spectrometer with green-light laser ($\lambda = 532$ nm). Additionally, the atomic concentration of oxygen in graphene oxide samples has been evaluated using PHI 5000 Versaprobe Scanning X-ray Photoelectron Spectroscopy (XPS). Changes in the water amount were estimated using a Nicolet 6700 Fourier Transformation Infrared spectrometer (FTIR) with 600–4000 cm^{-1} spectral range. The hydrophilicity/hydrophobicity of the surface after graphene oxide deposition was measured using the sessile water drop method of contact angle goniometers (Ramé-hart 250).

3. Results and discussion

To investigate the interactions of graphene with water, we prepared samples of graphene oxide from a water solution and from an ethanol solution. Fig. 1(a) and (b) highlight the original coverage of the graphene samples on the gold electrode surface. Raman analysis of the samples indicates the characteristic for graphene oxide D (at ~1300 cm^{-1}), G (at ~1560 cm^{-1}), and 2D (at ~2700 cm^{-1}) peaks [27,28]. In case of deposition from the ethanol solution, 2D peak is much higher. We attribute such differences to the fact that graphene oxide from water solution used in our experiments has higher degree of oxidation than the one from the ethanol solution. Moreover, SEM images indicate more flat nature of the as-deposited graphene oxide from ethanol, while the graphene oxide from water looks wavy and not conformally coating the surface. We further confirm oxygen content for both of the samples using XPS analysis (Fig. 1(c) and (d)). Results demonstrate higher content of oxygen in case of water solution.

Interestingly, the different methods of graphene oxide deposition resulted in completely different tendencies for resonant frequency changes (Fig. 1(e)). Graphene oxide deposited from an ethanol solution and immersed in water resulted in a negative frequency shift, as expected from Eq. (2); while graphene oxide deposited from a water solution exhibited an increase in the resulting resonant frequency of the sample immersed in water.

Fig. 2 demonstrates the typical behavior of resonant frequency (change in frequency relative to the value at time = 0) and mechanical resistance to sliding for two types of graphene oxide deposited. During initial sliding, graphene oxide from ethanol tends to adsorb small amounts of water (initial decrease in frequency and increase mechanical resistance to sliding) with partial delamination of graphene from the QCM surface afterwards