

Electronic Supplementary Information

Fast and non-invasive conductivity determination by the dielectric response of reduced graphene oxide: an Electrostatic Force Microscopy study

By *Cristina Gómez-Navarro**, *Francisco J. Guzmán-Vázquez*, *Julio Gómez-Herrero*, *Juan J. Saenz* and *G. M. Sacha*

Sample preparation

Graphite oxide was prepared by Hummer's method, diluted in water and treated with mild sonication to obtain single layers. This solution was then deposited on a SiO₂/Si substrate previously functionalized with APTS (Aminopropyltriethoxysilane). SiO₂/Si substrate had been decorated previously with a gold marker structure with a 10 μm periodicity by electron beam lithography.

EFM characterization

Measurements were done under a nitrogen atmosphere, with humidity <2% using a Nanotec Atomic Force Microscope using Pt covered tips with a nominal force constant of 2Nm⁻¹. Amplitude of oscillation was kept always under 7 nm in order to be in a low amplitude regime where the following expression applies:

$$\delta\omega(z, V) = \frac{\omega_0}{2k} \frac{\partial F(z, V)}{\partial z} = A(z)(V - \phi)^2$$

Parabola parameters from two frequency shift images

In the second mode of EFM described in the main text, for a faster characterization of the layers, we acquired frequency shift maps at two tip bias voltages (+9, -9V). The frequency shift on each feature of the substrate follows the equation above, which describes a parabola with curvature A and vertex Φ. These two parameters can be extracted given the acquired data at two bias voltages δω(± 9V) according to:

$$\phi = \frac{9\left(\sqrt{\frac{\delta\omega(-9)}{\delta\omega(+9)}} - 1\right)}{1 + \sqrt{\frac{\delta\omega(-9)}{\delta\omega(+9)}}}$$

$$A = \frac{\delta\omega(-9)}{(9 + \phi)^2}$$

Spherical tip model for our sample geometry

In order to ensure that the spherical tip model is a suitable approximation for our experimental geometrical configuration, we have performed a detailed previous analysis. Our study on the influence of the finite value of L reveals that the effects on the electrostatic forces involved in our set up differ when considering a spherical tip (F_{sp}) or a realistic macroscopic tip (F_{tip}); decreasing L induces a significant increasing of F_{tip} . This fact implies that the macroscopic shape (length and angle of the cone) of the tip is the element that is related to the interaction between the tip and the metallic plate. Focusing on the case where $L=300\text{nm}$, we found that the influence of the dielectric thickness almost compensates the difference between F_{sp} and F_{tip} implying that a spherical tip over a thin film with $L \rightarrow \infty$ is a good model for our particular case.

More in detail, we compare F for the macroscopic (F_{tip}) and spherical tip (F_{sp}) at $D=1\text{nm}$ as a function of h and ϵ_1 . Focusing on the limit where $L \rightarrow \infty$, we obtain that there is a huge difference between F_{tip} and F_{sp} , being F_{sp} the strongest interaction. In the case of the sphere (tip apex), the surface charge density is placed all around the tip, and the farthest side of the tip is at $z=2R_{tip}$. In the case of the macroscopic tip (cone included), the surface charge density is distributed between the tip apex and $z=L_{tip}$, which is a much larger distance than $z=R_{tip}$. Analyzing now the effect of smaller L values, we can see that the effect of the finite length of L affects in a different way F_{sp} and F_{tip} . Decreasing of L induces a significant increasing of F_{tip} . However, F_{sp} keeps constant as L decreases. This fact implies that the macroscopic shape (L and ϵ_1) of the tip is the element that is related to the interaction between the tip and the metallic plate. We also obtained that the influence of the SiO_2 thickness almost compensates the difference between F_{sp} and F_{tip} where $L=300\text{nm}$. This implies that a spherical tip over a thin film with $L \rightarrow \infty$ is a good model for the macroscopic

tip over a graphene flake and a SiO₂ thickness of 300nm on a highly doped Si substrate.

The details of this study can be found in J. Phys. Cond. Matt. 24, 155303, 2012