Low Dimensional Materials and Catalysts

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Electron holography probing interlayer charge redistributions in folded graphene membranes

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Graphene is a fascinating new material [1], and its peculiar properties hold promises for a great technological impact [2]. Around the Fermi energy, the band structure of graphene presents six conical points where the energy dispersion is perfectly linear in the momentum. For this reason, low energy excitations in graphene exhibit a charge conjugation between electrons and holes, and those carriers can be described as a 2D gas of effective massless Dirac fermions [3]. Unfortunately, upon stacking to form a Few-Graphenes-Crystal (FGC), the weak interlayer interaction could induce small valence charge redistribution in the crystal lattice, suppressing the linear dispersion in the band-structure [4].

In this contribution, we will show that the combination of electron holography and HREM based 3D reconstruction [5] can open interesting capabilities to a combined structural-electrical characterization of graphene membranes based on Transmission Electron Microscopy (TEM) interferometric techniques. More in detail, we will show that, in this framework, electron holography can be used to investigate the effects of the weak charge redistributions occurring upon interaction between stacked graphene layers

Figure 1-A shows the reconstructed phase map of an individual monolayer graphene folded over itself, as experimentally reconstructed following [5] and sketched in the cartoon of Fig. 1-B.: close to the border, where the two layers are curved, the two graphene membranes are stacked at a larger distance that in the internal part of the flake. Figure 2-A) reports an HREM image of a region close to previous one, showing large atomically clean areas and nanometric graphene islands on the surface, while the FFT, reported in the inset, shows the two stacked layers. Phase profile of Fig. 1-B, shows small charge redistribution, in correspondence to the regions where the two layers are separated and decoupled. Therefore, the larger distance between the folded graphene membrane is capable to induce a measurable phase change of 0.01-0.02 rad.

Electronic density and internal potential energy experienced by an electron can be computed using *ab-initio* approaches based on Density Functional Theory with high accuracy on single and multiple graphene layers, provided that the van der Waals bonding is suitably modelled according to recent studies in the literature (see [6] for a recent account). The computed phase-shift values reported in Fig. 2-B, show that for an interlayer distance larger than 0.5 nm the graphene layers start to decouple, resulting in a fully decoupled system for a distance of about 1 nm. Moreover, the computed values are in very good agreement with the ones measured by electron holography. Both these results strongly confirm the experimental results reported above, and at the same time show the capabilities of electron holography in measuring weak charge redistributions within stacked graphene systems, strengthening the perspectives of the application of the technique, as well as of the computational approach, to more complicated and interesting systems, like curved and functionalized graphene layers.

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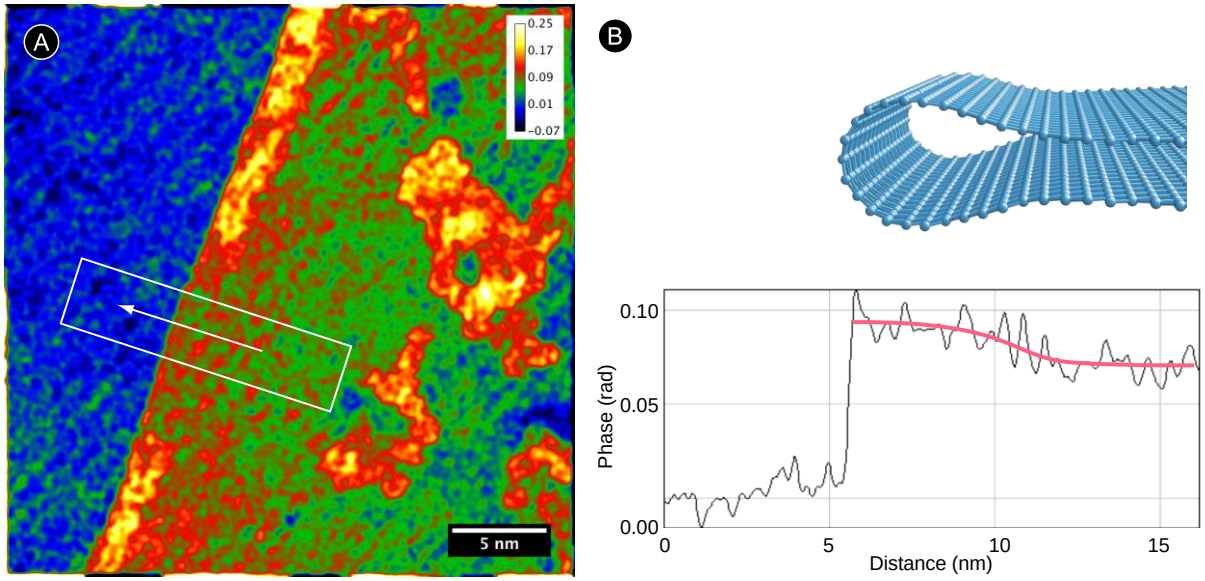

Figure 1. Holographic investigation of folded monolayer graphene. A) Reconstructed phase map obtained at 100kV of the folded border of a monolayer graphene crystal. B) Phase profile acquired over the region indicated by the white rectangle in A. Red line is guide for the eyes, highlighting the phase increasing from the internal to the curved region. A cartoon of the folded layer, as reconstructed following [5], is shown above the profile.

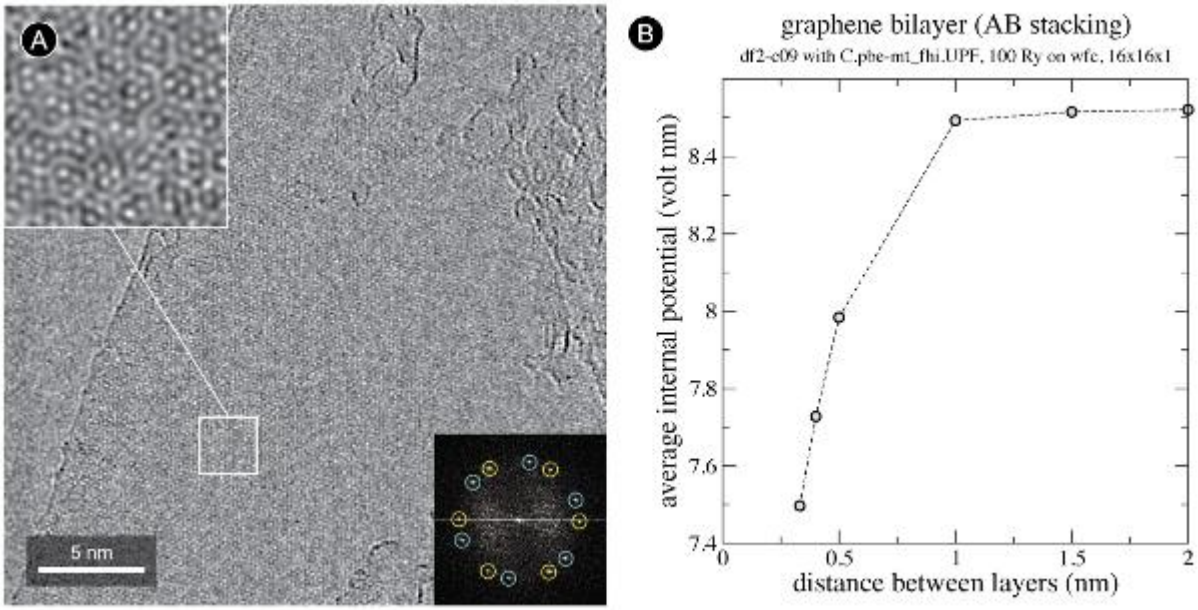

Figure 2. A) HREM image of a region close to where the hologram was acquired, showing large atomically clean areas and nanometric graphene islands on the surface. (inset) FFT of the image, showing reflections from the two stacked layers. B) Plot of the expected projected potential, resulting from DFT calculations, for two stacked graphene layers as a function of the interlayer distance.