Two-dimensional molecular crystals of phosphonic acids on graphene


Federal University of Minas Gerais, Belo Horizonte, Minas Gerais, 30123-970, Brazil
bernardo@fisica.ufmg.br

Much attention has been drawn to graphene in the past years due to its remarkable properties and it is expected that this material will play a major role in nanotechnology and industrial applications [1]. In order to fulfill such great potential, some basic issues concerning graphene’s electronic properties such as control of bandgap and doping levels are in need. In this work, we report synthesis and characterization of two-dimensional (2D) molecular crystals from long and linear phosphonic acids atop graphene (see Fig. 1). These crystals deposited on graphene provide an easy way to determine the flake orientation and induce a well-defined shift in the Fermi-level.

Scanning Probe Microscopy (SPM), Raman Spectroscopy and ab initio calculations were employed to characterize the self-assembled monolayers of two phosphonic acids OPA (octadecylphosphonic acid) and TPA (tetradecylphosphonic acid) atop graphene [2]. Atomic Force Microscopy (AFM) measurements easily detect the period of the 2D crystal after deposition on graphene flake (see Fig. 1). Our calculations show a significant difference in the formation energy of OPA or TPA monolayers when different orientations of the molecule with respect to substrate are considered, clearly showing that the monolayer most stable configuration is along the graphene zigzag direction. Thus, a simple AFM measurement, with no need of atomic resolution, is all it takes to determine the graphene crystallographic orientation.

In addition, Raman spectroscopy measurements, before and after monolayer deposition, confirm the results of our ab initio calculations regarding the doping effect of the OPA/TPA monolayer, where both show a hole doping of graphene with carrier concentration of about $10^{13}$ cm$^{-2}$. The 2D crystal formation on graphene flakes on top of Si/SiO$_2$ is easily achieved via spread coating with ethanolic solution [3,4] making this a fast and practical method to discover flake orientation and achieve chemical doping of graphene.

References

Figure 1. AFM characterization of 2D phosphonic acid crystals atop graphene single and multilayers. (a) Schematic representation of both phosphonic acids employed in this work: the octadecylphosphonic acid (OPA), which is 2.5 nm long, and the tetradecylphosphonic acid (TPA), which is 2.1 nm long. (b) AFM-topography image of 2D OPA crystals (green-yellow) partially covering a multilayer graphene (blue-purple). (c) Fast Fourier transform of the previous image, showing well-defined periodicity and angle between OPA crystals. (d) AFM-topography and (e) AFM-phase images of 2D TPA crystals partially covering a graphene monolayer. (f) Fast Fourier transform of the image in (e) evidencing the regular periodicity of the TPA crystals. Some periodic features are also seen in certain purple regions of image (b). These are simply color rendering artifacts, caused by the natural corrugation of the sample. Therefore, such periodic (purple) regions are, indeed, also OPA-covered regions and not the bare graphene, which shows no periodicity.