GRAPHITE NANOPATTERNING THROUGH INTERACTION WITH MACROMOLECULES

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The recent explosion of studies on graphene contributed to renew the interest in hybrid bio-organic/graphitic systems opening new perspectives towards applications in the field of single-molecule electronic devices and sensors. In the framework of a study on protein surface interaction, we previously investigated the adsorption of several globular proteins on HOPG. We observed the formation of surface nanopatterns that were tentatively assigned to the deposition of ordered molecular stripes on the HOPG surface [1].

With the aim of getting a more detailed understanding of the structural rearrangements occurring at the solution/HOPG interface we carried out a systematic investigation of the adsorption of quite different organic molecules, from water soluble macromolecular chains as synthetic polyelectrolytes down to single aminoacids and small aromatic molecules. The common point to all the experiments was the deposition of molecules from diluted aqueous solutions. A drop of solution was deposited on HOPG and after a proper adsorption time (typically 1 hour) samples were thoroughly rinsed and dried.

The interaction of the HOPG surface with an aqueous solution of the molecules results in the formation of quite extended and very regular nanopatterned domains consisting of parallel rows. Fig. 1a shows an AFM image of a HOPG sample after one hour interaction with a poly-styrenesulfonate (PSS) solution. Ordered domains are oriented according to a three-fold symmetry. The 'corduroy-like' texture of the pattern is magnified in fig. 1b. Quite remarkably, the row periodicity is found to be (6.2±0.2) nm, irrespectively of the investigated system. In regions where discontinuities in the uppermost patterned layer were present, a second patterned layer could be observed. The thickness of each patterned layer evaluated by AFM is (0.35±0.5) nm. Spectroscopic Ellipsometry (SE) data are consistent with the formation of a transparent Cauchy layer 0.7-0.8 nm thick, in good agreement with the AFM results.

The observation of the same pattern structure irrespectively of the investigated molecular systems, together with recent literature on liquid exfoliation of graphene in the presence of proper solutions [2,3], suggests to ascribe the nanopattern formation to a restructuring of the first graphite planes following the interaction with the molecular solution.

The interaction with the solution could weaken the graphite interplane interactions leading to weakly bound "graphene-like" layers which would undergo a rippling process. Experiments supporting the substrate origin of the nanopatterns will be discussed. The use of these nanopatterns as templates to guide the oriented deposition of supramolecular aggregates like amyloid fibrils will be presented.

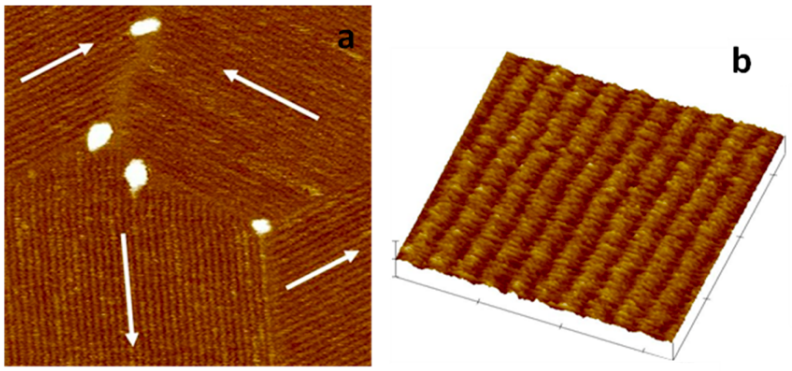

Figure 1: a) Height tapping mode AFM image of PSS on HOPG prepared by 1 hour adsorption from 10 nM solution. The arrows indicate the orientations of the coexisting ordered domains oriented according to the three-fold graphite symmetry. Image size: 300 nm x 300 nm; z scale: 2 nm; b) 3D rendering of a height tapping mode AFM image of the 6.2 nm patterned domain. Image size: 70 nm x 70 nm; z scale: 0.7 nm/div.

References

[1] T. Svaldo-Lanero et al., Soft Matter, 4 (2008), 965.
[2] M. Lotya et al. J. Am. Chem. Soc., 131 (2009) 3611.
[3] P. Laaksonen et al. Angew. Chem. Int. Ed., 49 (2010) 4946.