Exploiting molecule-surface interaction to exfoliate few layers graphene in liquid

N. Haghighian[1], A. Penco[1], D. Convertino[2], A. Rossi[3], C. Coletti[2], F. Bisio[3], O. Cavalleri[1] and M. Canepa[1]*

[1] Dipartimento di Fisica, Università di Genova, Genova, Italy
[2] Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Pisa, Italy
[3] CNR-SPIN, Genova, Italy
[1*] Dipartimento di Fisica, Università di Genova, Genova, Italy email: haghighian@fisica.unige.it

Graphene has drawn a lot of attention in recent studies due to its desirable properties such as extremely high electron mobility, electric and thermal conductivity, optical transparency, and high mechanical strength. It consists of a single atomic layer of sp^2-bonded carbon atoms arranged in a honeycomb lattice. Graphite exfoliation from proper solvents is one of the methods to produce graphene. The overcoming of the van der Waals interactions between adjacent carbon layers likely leads to the exfoliation of the topmost stacked parallel layers from graphite, to produce high quality graphene. The exfoliation can be performed by different chemical methods in liquid phase. One of the simplest approach to disperse graphene sheets is ultrasonic treatment in organic solvent [1].

In this study, we investigated the liquid phase exfoliation of highly ordered pyrolytic graphite (HOPG) and a few layers of graphene (FLG) obtained by solid-state graphitization from SiC substrate, by exploiting the interaction of the carbon surface with aqueous solutions of Methionine and Dimethyl sulfoxide (DMSO), both with and without sonication-assisted techniques. Diluted Methionine and DMSO solutions (300ng/ml) were dropped onto freshly cleaved HOPG. After one hour incubation, samples were rinsed with Milli_Q water and dried under a nitrogen stream. Additional external forces for exfoliation were then introduced by employing sonication of graphite in these organic solvents. The surface exfoliation process has been followed by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

AFM analysis allowed us to monitor the morphological changes of the HOPG and FLG surfaces upon interaction with the organic solutions. A typical tapping mode amplitude AFM image of a sample dropped with Methionine is shown in Fig 1a. Ordered domains consisting of parallel rows with three-fold orientation can be observed on the surface. A few globular structures, preferentially located at the domain boundaries, are likely due to Methionine adsorption on HOPG surface [2,3]. Very similar results were observed for DMSO (Fig 1b) regarding both the formation of nanostructured domains and the incubation time needed for their formation. However, interaction with DMSO leads to a reduction of the amount of globular material and to an increase of the domain size. The ripple formation can be interpreted in terms of a weakening of the van der Waals interactions between the topmost graphite layers. Such a weakening could leads to a weakly bound graphene-like layer, undergoing a rippling process.
As shown in Fig (1b-c), typical domains with parallel rows were observed in samples exfoliated with sonication in Methionine, while ripples were never observed on samples sonicated in DMSO.

On the other hand, the same method was used to exfoliate the FLG on SiC samples. Structure properties of graphene grown on SiC are strongly affected by the substrate polytype and polarity. Growth of epitaxial graphene was observed on both (0001) or Si-face and (000-1) or C-face surfaces of SiC. Typically, the thickness control is relatively poor on C-face due to a significant thickness variation across the sample [4].

The exfoliation of the FLG from the C-face was analyzed by XPS and Raman spectroscopy. The increase of the Si_{2p} XPS signal of the SiC substrate and the increase of the substrate Raman signal upon sonication can be related to changes in the graphene layer number [5]. Raman spectroscopy allowed also to monitor the structural changes and defect formation following sonication.

The combined AFM and XPS analysis indicates that strong treatment (sonication in DMSO) results in the presence of defects and graphene flakes on the surface. On the other hand, mild treatment (dropping in Methionine and DMSO or sonication in Methionine) leads to the formation of highly ordered rippled domains that can be interpreted as a precursor step towards graphene exfoliation likely due to the presence of loosely bound rippled graphene layers.

References
[1]   M. Cai et al., Material Chemistry, 22 (2012) 24992-25002.
[2]   T.S. Lanero et al., Soft Matter, 4(2008) 965-965.
[3]   Z.Y. Xia et al., Advanced Functional Materials,10 (2013) 1002.
[4]   C. Berger et al., Physics Chemistry, 108 (2004) 19912.
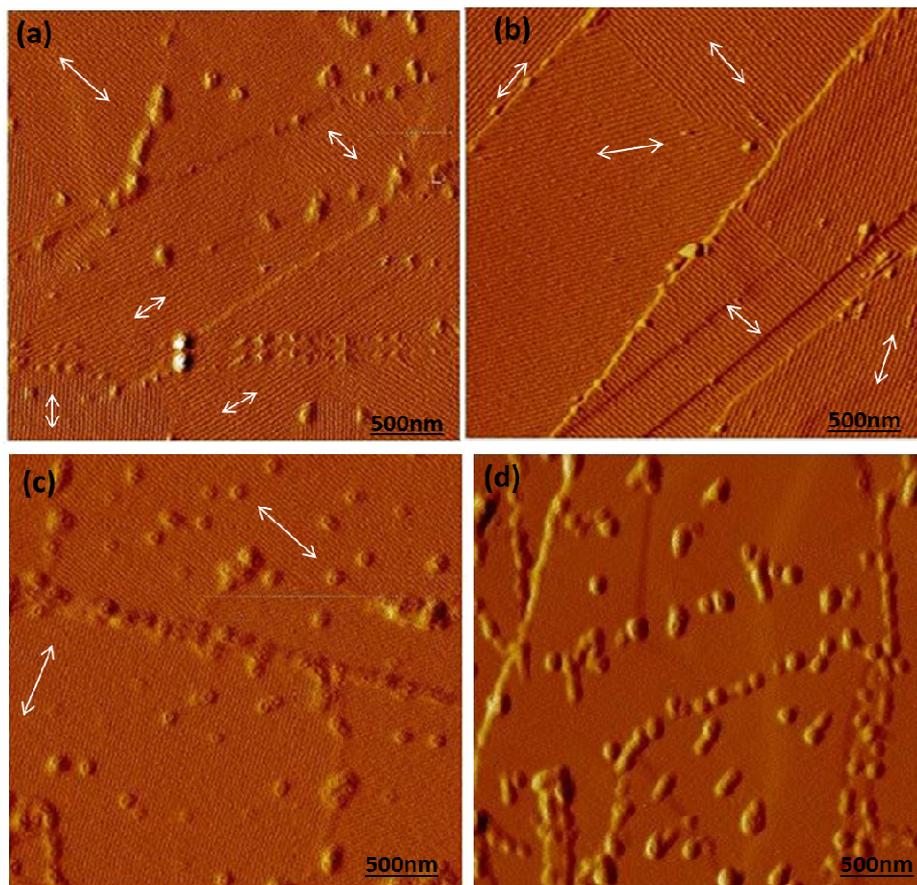[5]   S. Shivaraman et al., Electronic Materials, 38 (2009) 725-730.

Figure 1: AFM images of HOPG surface after treatment by: a) drop Meth, b) drop DMSO and c) sonication in Meth d) sonication in DMSO