Towards the control in 2D organization of covalent functionalization of graphene surfaces

Cristina Mattioli[1], Miguel Rubio-Roy[1], Olivier Couturaud[1], Maya Narayanan Nair[2],
Laurent Simon[2], Erik Dujardin[1], André Gourdon[1]

[1]Groupe NanoSciences, CEMES CNRS UPR 8011, BP 94347, 29 rue J. Marvig, 31055 TOULOUSE, France
[2]Equipe Molecule sur surface-spectroscopie champ proche, Institut de Sciences des Matériaux de Mulhouse, CNRS UMR 7361, 3 bis rue Alfred Werner, 68093 MULHOUSE, France

mattioli@cemes.fr

Graphene, a monolayer of carbon atoms packed in a two-dimensional honeycomb lattice, has lately become a very interesting material, being endowed with exceptional physical properties[1]. In particular, electronic properties constitute one of the most investigated aspects of graphene, which is considered a zero band gap semiconductor. Great efforts have been devoted to open a band gap into its energetic levels[2] and one of the followed routes is covalent chemical functionalization[3]. Some of the issues related to this strategy are that (1) pristine graphene shows a very low chemical reactivity; (2) if many ways have been proposed to functionalize the surfaces in a "random" fashion, controlled chemical functionalization (i.e. only at specific sites) has not yet been described.

In this context, our attention is focused in getting a control on the patterning of the eventually covalent functionalization of graphene in 2D. The chemistry we apply is that of Diels-Alder cycloaddition reactions[4], offering a better control on the reaction outcome, as for what it is concerned with the composition of the chemisorbed layer, compared to the strategies employing highly reactive radical species[5].

In a first step, we have carried out tests of functionalization of graphite and graphene devices by microwave-activated Diels-Alder reactions with maleimide derivatives. The Raman characterization of the samples has revealed the possibility of activating the reaction at the solid/liquid interphase on different substrates (graphite flakes, graphene on SiO_2).

In a second step, we have synthesised a series of oligo (phenylene-ethynylene) derivatives of different geometries, prone to self-assemble on graphene, characterised by the presence of functionalities potentially reactive with graphene by Diels-Alder reaction. Their self-assembling behaviour has been studied by STM at the liquid/HOPG interphase. In a next step, we will explore the possibility of achieving the controlled chemisorption of the molecules by STM local activation on epitaxial graphene in UHV.

References

[1] Geim, A., Novoselov, K ., *Nature Mater*., **2007**, *6,* 183-191
[2] a) Berger, C., Song, Z., Li, X., Wu, X., Brown, N., Naud, C., Mayou, D., Li, T., Hass, J., Marchenkov,A., N., Conrad, E. H., First, P. N., de Heer, W., A., *Science,* **2006**, *312*, 1191-1196; b) Han, M. Y., Oezyilmaz, B., Zhang, Y., Kim, P., *Phys. Rev. Lett.*, **2007,** *98*, 206805
[3] a) Balog R., Jørgensen, B, Nilsson, L., Andersen, M., Rienks, E., Bianchi, M., Fanetti, M., Lægsgaard, E., Baraldi, A., Lizzit, S., Sljivancanin, Z.,Besenbacher, F., Hammer, B., Pedersen, T. G., Hofmann, P., Hornekær, L., *Nature Mater*., **2010**, *9*, 315-319; b) Zhang , H., Bekyarova, E., Huang, J.-W., Zhao, Z., Bao, W., Wang, F., Haddon, R. C., Lau, C. N., *Nano Lett.*, **2011**, *11*, 10, 4047–4051
[4] Sarkar, S., Bekyarova, E., Niyogi, S., Haddon, R. C., *J. Am. Chem. Soc.*, **2011**, *133*, 3324–3327
[5] Hossain, M. Z., Walsh, M. A., Hersam, M. C., *J. Am. Chem. Soc.,* **2010**, *132*, 15399-15403