One-pot reduction and diazonium functionalization of graphene oxide

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The expectations around graphene come from huge potentialities for various applications (RF transistor, (bio)sensors...). Graphene high specific surface, mechanical resistance and conductivity make it specifically attractive for energy related applications [1]. Its interfacing with various compounds has been shown to make it more processable, to tune its electrical/optical properties and to create functional materials [2].

In this presentation, the fabrication of graphene using the chemical exfoliation route consisting on the oxidation of graphite followed by its reduction will be presented. A wide range of reduction techniques have been described in the literature and the laboratory uses mainly chemical reducing agent (hydrazine, Fe and SnCl₂ – [3]). The oxidation/reduction confirmation and extent are assessed thanks to XRD, XPS, TGA characterization. In turn the exfoliation degree can be identified by specific surface area determination as well as by microscopic analyses (SEM, TEM). The rGO obtained displays a large surface area (Fig. 1) and its degree of exfoliation is important.

These graphene derivatives have all been modified by diazonium functionalization– aiming at passivating the graphene surface with carboxylic acid functions and decreasing its hydrophobicity. Diazonium chemistry on chemically exfoliated graphene is more often performed on rGO as this reaction is known to proceed in presence of a reducing agent which is the role played by rGO in the reaction. However rGO is more complicated to disperse than GO. The idea presented here is to functionalize GO by diazonium chemistry in presence of Fe to reduce GO into rGO and initiate the diazonium grafting at the same time. Based on XPS, TGA and BET results, the interest of such "one-pot reduction functionalization" will be highlighted.

The use of such chemistry to introduce molecular entities chosen to target the formation of a graphene framework will also be presented. These specific compounds have been chosen as to possess two anchoring sites. The idea is to develop a graphene matrix held together by these molecular pillars. Different pillar lengths and number of equivalents have been tested. The characterization of these matrices will be discussed.

References

[1] S. Yang, R. E. Bachman, X. Feng and K. Müllen, Acc. Chem. Res., 46 (2013) 116.

[2] T. Kuila, S. Bose, A. K. Mishra, P. Khanra, N. H. Kim and J. H. Lee, Prog. Mat. Sci., **57** (2012) 1061.

[3] N. A. Kumar, S. Gambarelli, F. Duclairoir, G. Bidan and L. Dubois, J. Mater. Chem. A, 1 (2013) 2789.



Fig. 1: SEM (left) and TEM (right) images of rGO