Experimental Report

18/02/2014

Proposal:	**6-06-449**	**Council:**	10/2012

Title: High energy neutron powder diffraction on graphene and metal-decorated graphene

This proposal is a new proposal

Researh Area: Materials

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Samples: Chemically synthesized graphene(exfoliated graphite oxide) and metal decorated graphene (LiC3 and NiC80)

Instrument	Req. Days	All. Days	From	To
D4	4	3	21/02/2013	24/02/2013

Abstract:

Graphene is a very promising material and appears particularly suitable for developing efficient hydrogen storage systems, if it is “decorated” with proper metal ions. Recently, we managed to produce gram-scale bulk defective graphene by chemical methods and to decorate it with Lithium and Nickel atoms. Although a structural characterization of chemically synthesized graphene is missing, the investigation of the defects as well as of the decorating metal local environment is a fundamental prerequisite in order to develop an efficient graphene-based gas storage device. Hence we propose to investigate the morphology of these systems at the nanoscale, by means of high energy neutron diffraction and atomic pair distribution function (PDF) data analysis using the D4 diffractometer at the ILL.

Experimental report: 6-06_449
Date: 21/02/2013 – 24/02/2013
Instrument: D4c

"High energy neutron powder diffraction on graphene and metal-decorated graphene"

Aim of the experiment

Graphene is a very promising material for different technological applications and it seems to be particularly suitable for developing efficient hydrogen storage devices, especially when it is decorated with proper metal ions, which could induce either enhanced physisorption, spillover mechanism or Kubas binding interactions.

We synthesized gram-scale graphene samples, through the thermal exfoliation of graphite oxide. This is a well-known and established process that provides bulk quantities of defective graphene. Even if thermal exfoliated graphite oxide (TEGO) has been proven to be constituted by single and few carbon layers structures, a direct extended study of the morphology and defects' characterization is still missing. In addition, we used the as-prepared graphene samples (TEGO) as precursor to prepare by chemical methods graphenes decorated with Lithium and Nickel atoms.

The aim of the performed experiment was to provide a structural characterization of chemically synthesized graphene and metal-decorated graphene samples, as well.

We expect that the morphology of defects and the localization of the metal ions in the carbon backbone will profit by the pair distribution function (PDF) analysis which the high Q values probed by D4c made possible.

Experimental details

Around 300mg of samples were put in a 7mm cylindrical Vanadium cell.

The wavelength used was 0.5Å (refined value λ=0.4989 Å), which provides a good compromise between high neutron flux and high Q_{max} = 23.5 Å^{-1}, very useful for space Fourier transforms and analysis in the direct space.

Our study was focused on three graphene samples: as-prepared graphene, Ni-decorated graphene and Li-decorated graphene, with the stoichiometry of NiC_{80} and LiC_3, respectively. Graphite powder was measured as reference too.

Measurements were performed at 20K, to reduce thermal vibrations and point out static disorder. Stability tests, background, empty cryostat and empty cell runs were performed as well.

Data were then regrouped, corrected from backgrounds and inelastic contributions. The graphene density and number density were taken into account in the data reduction and treatment.

Preliminary results

The structure factor S(Q) of graphene (big plot, in blue), in comparison with the S(Q) of graphite (inset, in red), is reported in figure 1. Graphene data show some strong similarities with the graphite one, especially regarding the low angle reflections. (002) reflection is present also in graphene data and it is located at 1.79Å^{-1}, instead of 1.86Å^{-1} as in the graphite data.

This denotes the averaged presence of graphene multilayers, in which the interlayer distance is increased with respect to the one of graphite (3.4 Å). From the width of the peak and taking into account the instrumental broadening, it has been possible to estimate the dimensions of the coherence domains L_c, along the c direction. We found the value of $L_c \sim 35$ Å. Important small angle intensity emerges in graphene data, demonstrating the large (nano-micro) scale nature of the graphene flakes. Small angle dedicated studies are currently in progress.

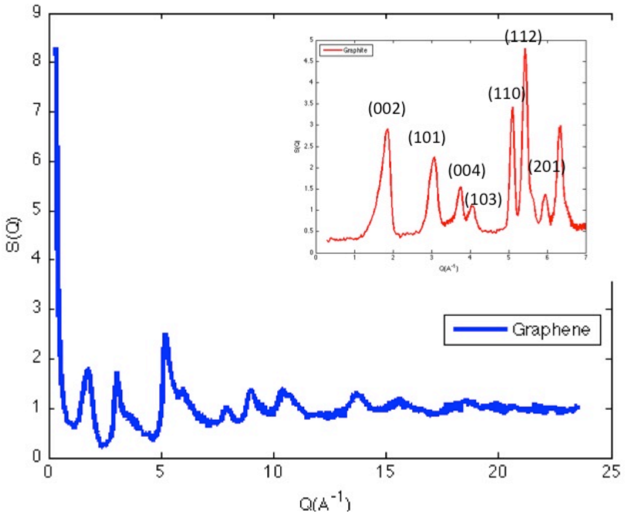

Figure 1: S(Q) of graphene (thermal exfoliated graphite oxide). A zoom up to 6Å^{-1} of the S(Q) for a graphite powder sample is reported in the inset on the right top of the figure

In addition, by simply Fourier transform of the total scattering structure factor, it has been possible to directly calculate the G(r) or reduced pair distribution function (PDF). This gives access to the atom-atom distances r (Å) in direct space. The G(r) of as-prepared graphene, Ni-decorated and Li-graphene are reported in figure 2 (a simple shift along the y-axis has been applied to the decorated graphene data, in order to make the plot clearer). No important differences can be evidenced. The stoichiometric quantities of metal introduced by the chemical decoration are probably too scarce to be easily identified and only the carbon fingerprint appears in the G(r).

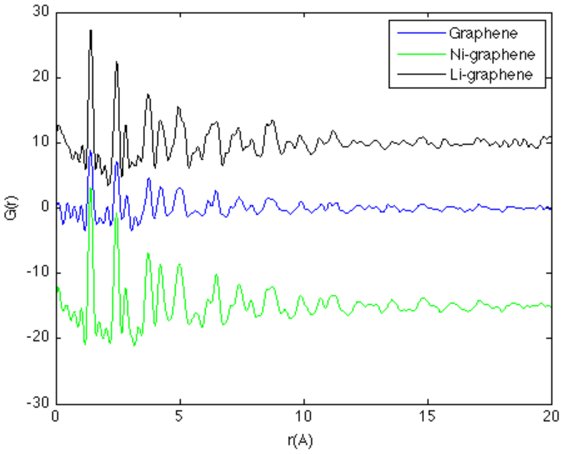

Figure 2: G(r) of as-prepared and metal decorated graphenes. Arbitrary scale along the y-axis.

The comparison between the experimental PDF data and the one rising from an atomistic model of graphene has to be done in order to complete the microstructural investigation of thermal exfoliated graphite oxide and eventually evidence the effects due to the metal decoration. Ultimately a more precise knowledge of the morphology could help in better understanding the interaction with hydrogen and its mechanism.