Experimental Report

Proposal: **7-04-126** **Council:** 10/2012

Title: Neutron spectroscopy on chemicallysynthesized metal-decorated graphene

This proposal is a new proposal

Researh Area: Materials

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Samples: Li-graphene
Ni-graphene

Instrument	Req. Days	All. Days	From	To
IN4	7	6	25/03/2013	31/03/2013

Abstract:

The study of the hydrogen interaction, atomic and molecular, is of great importance to evaluate the relevance of carbon nanostructures as hydrogen-storage device for future applications. In particular many recent theoretical works suggest that graphene could meet the stringent restrictions imposed by US-DOE, when decorated with alkali, alkali earth or transition metals ions. Recently, we managed to produce gram-scale bulk defective graphene by chemical methods and to decorate it with Lithium and Nickel atoms. We already performed some preliminary neutron scattering experiments but a clear comprehension of hydrogen uptake mechanism and the interaction between the hydrogen molecules and the modified graphene planes is still missing. The aim of the proposed experiment is to get a deeper insight into the dynamical properties of Li- and Ni-decorated graphene and investigate their interaction with hydrogen. For this purpose we require 7 days on the thermal-neutron Time-of-Flight IN4 spectrometer and 6 days on the hot-neutron two-axis Lagrange spectrometer at the ILL.

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Date: 25/03/2013 – 31/03/2013

The interest in the graphene-hydrogen interaction is very broad and embraces a lot of theoretical and technological issues, from the interstellar chemistry to spintronics and hydrogen storage, just to cite few examples.
Up to now, the difficulties in producing big quantities of samples limited the studies to theoretical investigations. However the progressive development of chemical methods that allow to synthesize graphene in gram scale has opened the door to more practical investigations and in the same time has allowed the detection of hydrogen using experimental techniques which are usually reserved to bulk systems.
Hydrogen can interact with graphene through physisorption or chemisorption. If the physisorption requires too low working temperature for concrete applications, chemisorbed hydrogen can be stored very efficiently but the reversibility of the process constitutes the bottleneck for designing an effective storage material.
Thermal exfoliated graphite oxide, a defective graphene produced by chemical methods, may be a potential very good candidate for hydrogen storage applications, especially when it is further decorated with metals [1]. Alkali, alkali earth or transition metals could enhance the hydrogen absorption capabilities in graphene, promoting and supporting more favourable mechanisms, as Kubas-binding interaction or spillover [2].
In this experiment, we measured highly defective graphene samples chemically decorated with Li and Ni atoms, with the stoichiometry of LiC3 and NiC80 respectively, both in the pristine form and after hydrogenation. The hydrogenation was got by thermal treatment under hydrogen pressure. IN4c allows to probe dynamical processes in a wide energy region, from 0 up to 150meV, with a resolution of 8% at the elastic line. Concerning the effect of hydrogen, in the presence of molecular hydrogen, we expect to extract information about the local potential, as well as about the interaction induced by the metal from the frequency of para-ortho transition, usually occurring at 14.7meV. The acquisition of high resolution data in the Anti-Stokes side will allow us to probe the high energy region (100-150meV), where are usually located the C-H bending modes, then witnessing chemisorbed hydrogen at the graphene surface. Similarly we expect to evidence the dynamical effects induced by the decorating metals in the carbon lattice, in comparison with the already measured density of states for as-prepared graphene [3].
About 500 mg of samples were put in a flat Al-cell. Sample handing was done in an Argon glove box, to prevent any possible oxygen moisture contamination and consequent oxidation. All the measurements were performed in a standard orange cryostat. Data are presented in the form of Generalized Density of States (GDOS), that can be obtained from ToF data as discussed in [4]. We used the configuration HR at 320K using 2.4 Å as incident wavelength and the 1.11 Å and 1.5 Å wavelengths at low temperature (10K).

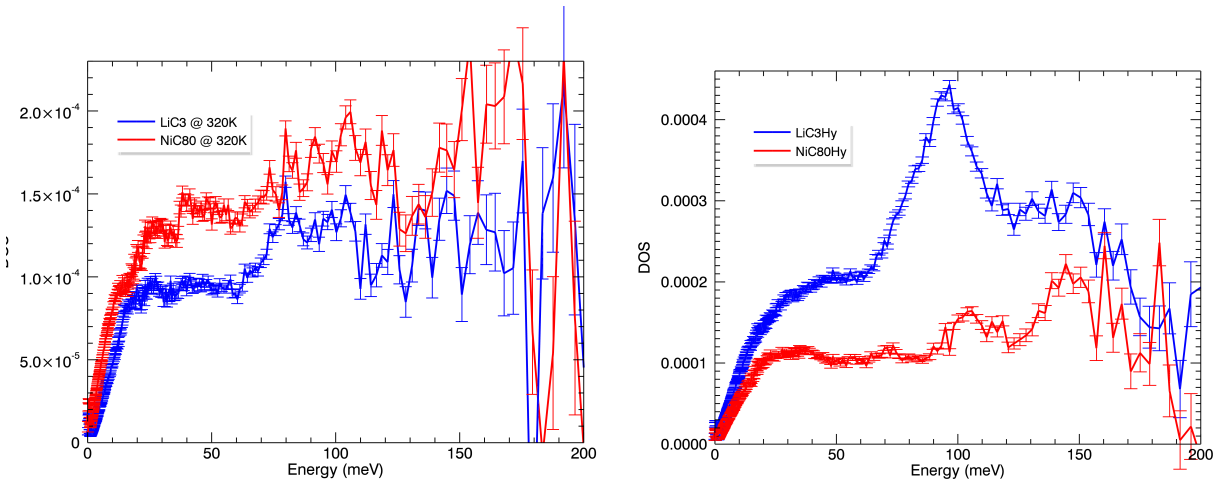

Figure 1 and Figure 2: GDOS collected at 320K (λ=2.4Å) of the as-prepared samples (left) and after hydrogenation (right).

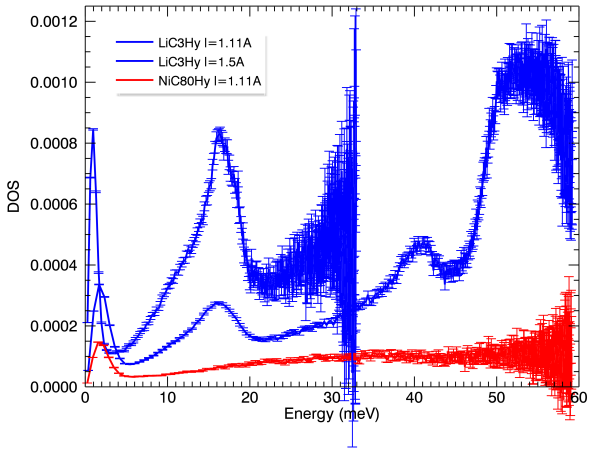

Figure 2: GDOS collected at 10K (λ=1.11Å, 1.5 Å) of hydrogenated samples. The strong peaks at 17meV,40 meV, 57meV are not ascribable to hydrogen, since they are present in the as-prepared Li-graphene samples as well. They are likely due to the Lithia decoration of the carbon backbone, however a more detailed study, involving atomistic simulations is required to determine their origin.

The effect of the hydrogenation seems not to induce the trapping of molecular hydrogen (we didn't evidence any intense peak at low energy at low temperature, neither any thermal evolution of the density of states, in both of the samples). On the contrary, we observed the rising of high-energy peaks, which are likely ascribable to the formation of Li-H (bands at 100meV) in LiC3Hy and in-plane C-H (bands at 150meV) in NiC80Hy. Nevertheless, atomistic simulations are required to better clarify the hydrogen interaction with metal decorated graphene, as well as the effects of the decoration of its dynamical properties

References:
[1] Gaboardi M. , J.Mat.Chem. A (2013)
[2] Ming Liu X. et al, NanoLett (2012)
[3] Pontiroli et al., J. Phys. Chem. C (2014)
[4] Bousige et al. PRB (2010)