Experimental report

05/02/2018

Proposal: **7-05-474**

Council: 10/2016

Title: Inelastic neutron scattering of hydrogen interaction with Pt and Ni decorated graphene

Research area: Materials

This proposal is a continuation of 7-05-454

Main proposer: **Daniele PONTIROLI**

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Samples: Graphene
Pt:C100
Ni:C100

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	0		
IN4	5	3	17/02/2017	20/02/2017

Abstract:

We propose to investigate different transition-metal decorated graphene samples, either with nichel or platinum nanoparticles, by means of inelastic neutron scattering under H2 atmosphere, in order to clarify the hydrogenation process and to possibly highlight the presence of spillover effect. In fact, this kind of investigation is uniquely able to reveal the molecular or atomic state of the hydrogen in these systems: molecular H2 presence is revealed at low temperature via the detection of the para- to ortho-H2 rotational transition peak at 15 meV, while atomic H chemically bound to graphene is probed through the typical C-H bending modes in the energy range 80-200 meV.

Report on the experiment #7-05-474
Main proposer: D. Pontiroli from Physics Department, Parma University, Italy
Experimental Team: D. Pontiroli, C. Cavallari, G. Magnani, C. Milanese, M. Riccò
Local Contact: S. Rols
Instruments: IN4C with in-situ hydrogenation apparatus, orange cryostat and cryo-furnace

This was the continuation experiment of the experiment #7-05-454. Here we investigated different transition-metal decorated graphene samples, respectively with Nickel and Platinum nanoparticles, and pristine graphene sample, by means of inelastic neutron scattering under H_2 atmosphere. The aim of experiment was to clarify the hydrogenation process in these systems and to possibly highlight the presence of “H spillover effect”, a phenomenon which is still debated, although recently new evidences were provided in literature [1,2].

Graphene was produced by the thermal exfoliation of graphite oxide (TEGO) [3], while Pt and Ni decorated TEGO were prepared following a reaction route, previously described in Report #07-05-454.

Particular care was used to avoid the oxygen and moisture contamination of the samples. Aluminum thick cans were filled with the sample in an Ar glovebox equipped with a special device which permitted to mount the can to the stick directly in glovebox. Inside the stick, a stainless-steel capillary connected to a “Hiden Isoschema IMI” manometric analyzer injected a controlled amount of hydrogen gas in the sample space.

We measured the in-situ inelastic spectrum of the three samples, Pt-TEGO, Ni-TEGO and TEGO (the sample mass was approximately 280 mg for Pt-TEGO and Ni-TEGO, and approximately 340 mg for pristine TEGO) using the IN4C spectrometer in presence of H_2 atmosphere at the temperature of 40 K, respectively:

1) after the H_2 injection, which was performed at 77 K;

2) after a thermal treatment performed in the cryo-furnace at 450 K in static conditions overnight;

3) after a sample treatment at 450 K in dynamic vacuum for several hours.

The hydrogen injection was performed in the SET mode, namely letting stabilize the system at a chosen pressure (200 mbar) at 77 K. The measuring temperature was chosen to maximize the ortho-to-para signal and, at the same time, to avoid the condensation of free hydrogen gas possibly remaining in the sample chamber. The measurements were performed at the wavelength of 1.1 Å, an optimized value to cover the energy range from 0 to 50 meV.

In case of Pt- TEGO, Figure 1 shows the differential signal at 40 K, obtained subtracting the $S(Q_0,\omega)$ of the as prepared sample, with Q_0 = 1.75 $Å^{-1}$, with, respectively, the $S(Q_0,\omega)$ just after the hydrogen dose (on the left) and after the thermal treatment at 423 K (on the right). The effects of the high-temperature treatment are the following:

1) A very large increase of the elastic intensity;
2) A clear decrease of the para-to-ortho transition at 14.7 meV.

The increase of the elastic intensity originates from the transformation of neutron scattering by hydrogen from coherent to incoherent. This can be rationalized considering the cracking of the molecular H_2 into two atomic H, as the elastic intensity for molecular hydrogen in the para state is purely coherent. The reduced number of the para state is also observed by the reduced intensity of the inelastic line. The ratio between the variation of the elastic and inelastic intensity excludes that this observation could originate from a system out of equilibrium. In addition, no clear increase of the ortho-to-para transition (at -14.7 meV) is observed.

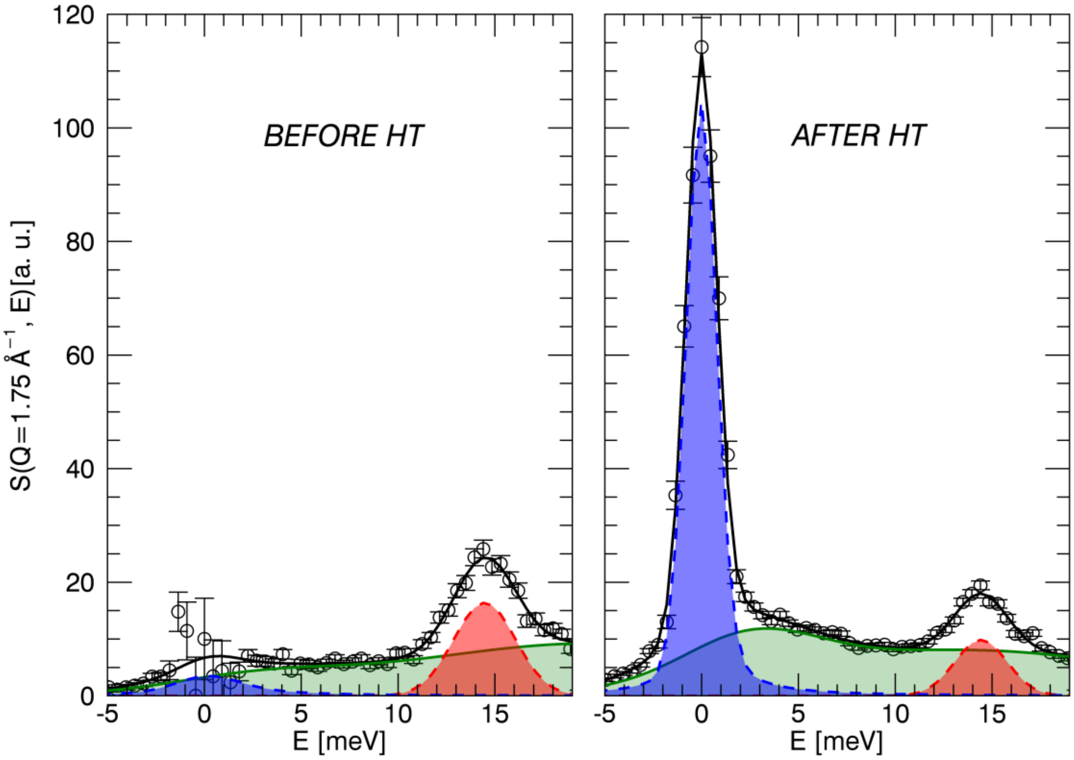

Figure 1: Left) Difference of the neutron signal at 40 K between the Pt-TEGO just after the hydrogenation (200 mg, SET mode) and the as-prepared Pt-TEGO. **Right)** Difference of the neutron signal at 40 K between the thermal annealed hydrogenated Pt-TEGO at 450 K and the as-prepared Pt-TEGO.

Similar behavior was observed also in Ni-TEGO and pristine TEGO, even if the effect is much smaller and a correct interpretation of data still requires further analysis, which is in progress.

The observed behavior strongly suggests that a mechanism of H spillover should be present in these systems and it was also confirmed by parallel H_2 isotherm absorption measurements performed on these systems in collaboration with Prof. K. F. Aguey-Zinsou of the MERlin lab at the University of New South Wales (Australia).

References:

[1] C. S. Tsao et al., Chem. Phys. Lett. 2 (2011), 2322.

[2] Y. Liu et al., Carbon 50 (2012), 4953.

[3] M. Riccò et al., Nanolett. 11 (2011), 4919.