Experimental report

15/09/2016

Proposal:	**7-05-454**	**Council:**	4/2015
Title:	Inelastic neutron scattering of hydrogen interaction with Pt and Ni decorated graphene		
Research area:	Materials		

This proposal is a new proposal

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Samples:
Ni:C80
Pt:C100

Instrument	Requested days	Allocated days	From	To
IN4	5	4	16/06/2016	23/06/2016

Abstract:

We propose to investigate different transition-metal decorated graphene samples, either with nichel or platinum nanoparticles, by means of inelastic neutron scattering under H_2 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 H_2 presence is revealed at low temperature via the detection of the para- to ortho-H_2 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 #7-05-454
Main proposer: D. Pontiroli from Physics Department, Parma University, Italy
Experimental Team: D. Pontiroli, G. Magnani, A. Girella, C. Cavallari, M. Gaboardi, C. Milanese, M. Riccò
Local Contact: S. Rols
Instruments: IN4C with in-situ hydrogenation apparatus and orange cryostat

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During this experiment we probed the ability of some selected transition-metal (Platinum and Nickel) nanoparticle decorated graphene compounds to absorb hydrogen at low temperature, through the catalytic splitting of the hydrogen molecules by metallic cluster and the subsequent diffusion of hydrogen atoms on the graphene planes. Bulk graphene samples were produced by the thermal exfoliation of graphite oxide (TEGO). Recently, we proved that, simply by exposing TEGO to molecular hydrogen at moderate conditions (1 bar H2, 800°C), a significant amount of hydrogen can be chemically absorbed (H-TEGO), thanks to the reactivity of the in-plane defects (C vacancies and edges) produced during the exfoliation process. Moreover, the atomic hydrogen bound to TEGO turn out to be mobile already at low temperatures, as shown by 1H NMR investigation and DFT calculations [1,2]. These findings suggest that TEGO-based systems can be promising systems to absorb hydrogen already at low temperature via the so called “H spillover” process. Although this phenomenon is still strongly debated, recently some new evidences were given in literature [3].

We prepared Pt and Ni-nanoparticles decorated TEGO (Pt-TEGO and Ni-TEGO) by a new synthesis method exploiting metal-carbonyl clusters, which allowed us to obtain a very high dispersion of the metal on the carbon plane: typical dimension of clusters is 2-5 nm and also single Pt/Ni atoms are visible with TEM/STEM microscopy [4]. Particular care was used to avoid the oxygen and moisture contamination of the samples. Aluminium 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. Initial calibrations allowed us to precisely measure the volume of the sample space and of the capillary.

We have the measured the *in-situ* inelastic spectrum of Pt-TEGO and Ni-TEGO (the sample mass was approximately 350 mg for each sample) using the IN4C spectrometer in presence of H2 atmosphere (up to 2 bar) and as a function of temperature (in the range 10-320 K), in order to study the interaction of molecular hydrogen with the metal nanoparticles and the possible diffusion of atomic hydrogen on the graphene plane. Three different incident wavelengths (0.74 Å, 1.1 Å and 2.4 Å HR) were used to cover the [0, 100 meV] frequency range. In particular, we followed the following steps:

1) Measurement of the inelastic spectrum of the bare sample at 5 K as a reference.
2) Cooling of the sample at 77 K, when the H2 physisorption is sizeable, thanks to the high porosity of the system (ssa ~ 500 m2/g, measured with BET protocol) and injection of a known dose of H2.
3) Sealing of the sample space, then cooling down to 5 K and measurement of the inelastic spectrum.
4) Heating up to 320 K and annealing at this temperature for ~6 hours.
5) Cooling down at 5 K and measurement of the inelastic spectrum.

Pt-TEGO (atomic dispersion):

The sample underwent two hydrogen doses, the first corresponding to approximately to the 0.02 wt% H2 and the latter corresponding to approximately to the 0.1 wt% H2.

In Figure 1 the differential signal obtained subtracting the S(W) of the as-prepared sample collected at 5 K, with neutrons wavelength of 1.7 Å, to respectively the S(W) just after the hydrogen dose (red curve) and after the thermal treatment at 320 K, is shown. Although the difference of signal is low, it is possible to notice that hydrogenation causes both an increasing of the elastic signal and the onset of a broad band in the inelastic region, especially around 15 meV, where the para-to-ortho H2 rotational transition peak is expected to grow. However, after the thermal treatment, surprisingly the inelastic signal resulted suppressed, while the elastic contribution clearly became more intense.

These two features seem to suggest that a fraction of hydrogen, which was initially weakly interacting with the sample, thus preserving its molecular state, was then converted to atomic and somewhat got strongly bound to the backbone. This H2 molecular splitting is likely induced on the surface of Pt nanoparticles, but at this stage it was not clear if H atoms were located on the metal cluster or managed to diffuse on the graphene surface.

In order to understand if this process is able to sustain the hydrogen spillover, we performed a further hydrogenation of the sample at the same conditions, injecting approximately 0.1 wt % H2 in the sample.

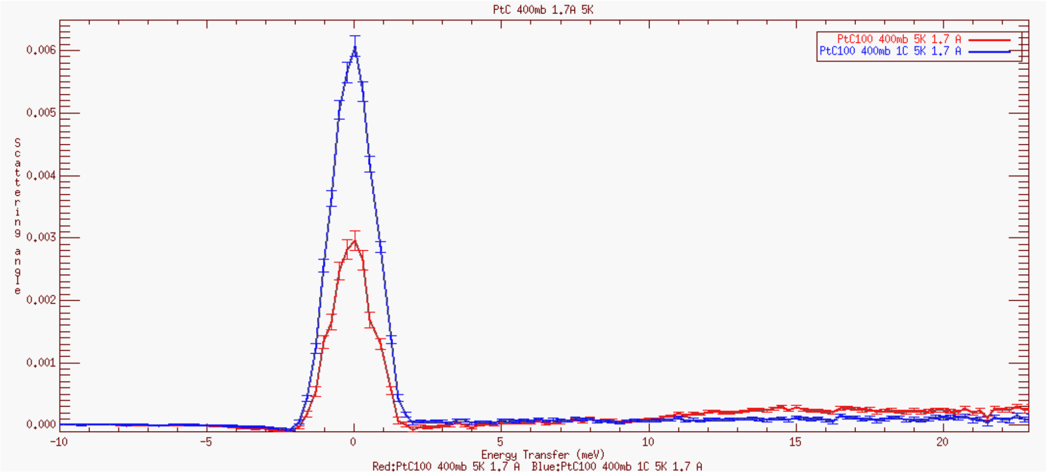

Figure 1: Difference of the neutron signal at 5 K between the hydrogenated and the as-prepared Pt-TEGO, respectively just after the hydrogenation (red curve) and after 6 h thermal annealing at 320 K (blue curve). The neutron wavelength was 1.7 Å and the hydrogen amount was approximately 0.02 wt %.

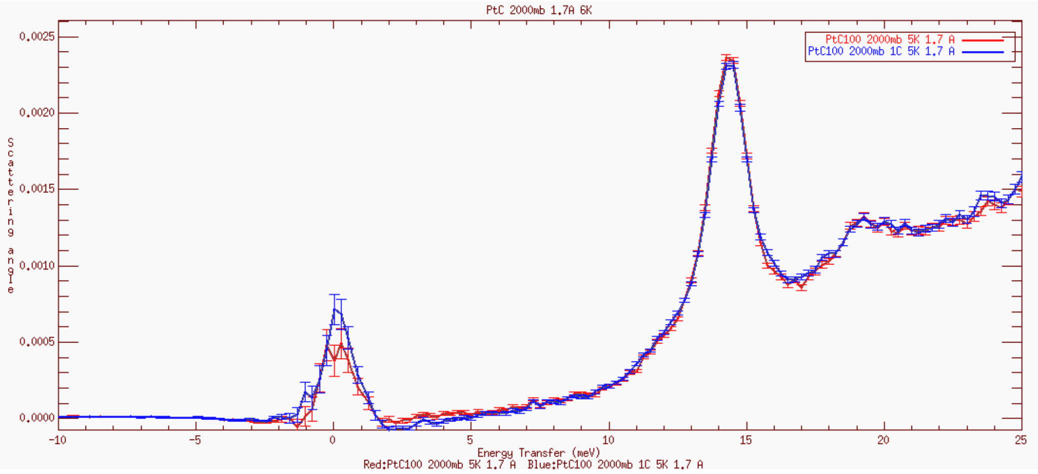

Figure 2: Difference of the neutron signal at 5 K between the hydrogenated and the as-prepared Pt-TEGO, respectively just after the hydrogenation (red curve) and after 6 h thermal annealing at 320 K (blue curve). The neutron wavelength was 1.7 Å and the hydrogen amount was approximately 0.1 wt %.

In Figure 2 a comparison of the differential signal similar as before is displayed. Thanks to the larger amount of hydrogen physisorbed by the sample, the para-to-ortho H2 rotational transition peak is now much more intense and centred around 14.7 meV, as expected. However, in this case the differences of the two measurements, before and after the thermal annealing at 320 K are

strongly reduced, suggesting that the molecular-to-atomic hydrogen conversion by the sample was no longer effective. This fact seems to suggest that, although the Pt nanoparticles are active to split the hydrogen molecule, probably the diffusion of H atoms to the carbon backbone is somewhat hampered and the splitting process quickly stops, as soon as the Pt clusters get saturated. The presence of a further inelastic peak at ~20 and ~30 meV is compatible with the onset of Pt-H riding modes [5], confirming the interaction of hydrogen with Pt-nanoparticles.
Measurements collected at different neutron wavelength allowed to probe the frequency range up to 100 meV, were no clear features of C-H bonds were detected (not shown).

Ni-TEGO (atomic dispersion):

The sample underwent only one hydrogen dose, corresponding to approximately to the 0.1 wt% H2.
In Figure 1 the differential signal obtained subtracting the S(W) of the as-prepared sample collected at 5 K, with neutrons wavelength of 1.7 Å, to respectively the S(W) just after the hydrogen dose (red curve) and after the thermal treatment at 320 K, is shown.
Similar to Pt-TEGO, also in this case the hydrogen physisorbed by the sample gives rise to a strong para-to-ortho H2 rotational transition peak centred around 14.7 meV, although with a slightly different broadening. The lack of the evolution of the signal after the thermal annealing does not allow to evidence any clear molecular-to-atomic hydrogen conversion induced by Ni clusters at these conditions.

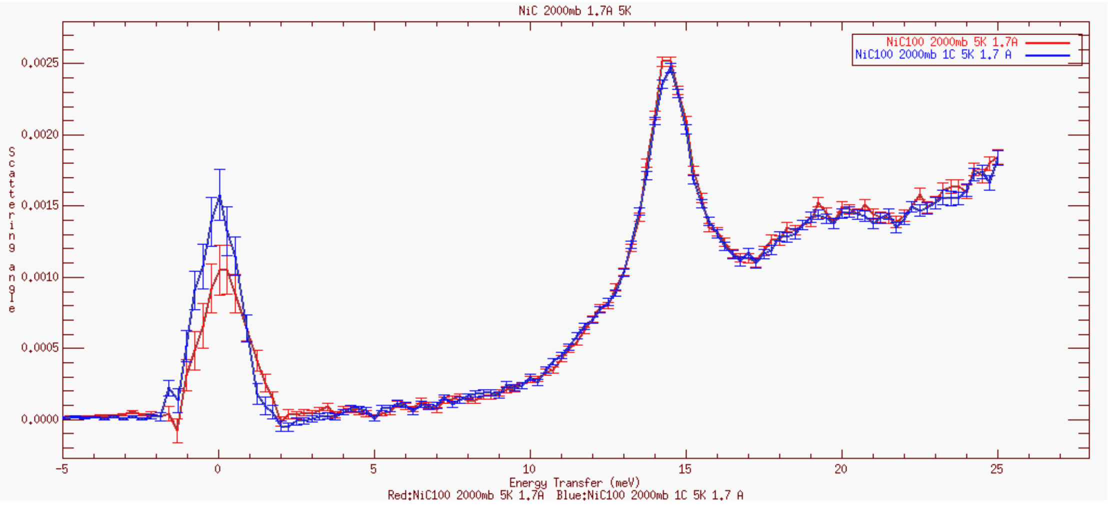

Figure 3: Difference of the neutron signal at 5 K between the hydrogenated and the as-prepared Ni-TEGO, respectively just after the hydrogenation (red curve) and after 6 h thermal annealing at 320 K (blue curve). The neutron wavelength was 1.7 Å and the hydrogen amount was approximately 0.1 wt %.

Further measurements are however required in order to evidence possible catalytic effects by Ni nanoparticles at different temperature/pressure conditions.

References:

[1] D. Pontiroli, S. Sanna et al., J Phys. Chem. C 118 (2014), 7110.
[2] C. Cavallari, D. Pontiroli et al., Phys. Chem. Chem. Phys. 18 (2016), 24820.
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[5] P. C. H. Mitchell et al., J. Phys. Chem. B 107 (28) (2003), 6838.