Direct measurement of the enthalpy released during Hydrogen adsorption on Ti-decorated graphene

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Since its discovery in 2004 [1], research on graphene has achieved remarkable results. In the last years, a huge research effort has been devoted to engineering carbon-based nanomaterials able to adsorb hydrogen molecules with high storage capacity and easy release of them. Monolayer graphene (MLG) represents an appealing material, owing to its favourable physical-chemical properties and its high specific surface area, which makes it ideal for functionalization. Thus, metal-functionalized MLG [2-6] has been widely investigated both theoretically end experimentally. One of the most promising, and investigated [4,5,6], metals is titanium which has been predicted to allow a gravimetric hydrogen storage density of 7.8 wt%, well above DOE prescriptions. The choice of Ti in the present investigation is mainly due to the wide research on the Ti-MLG system, which makes it a benchmark and a reference. The purpose of this work is to provide a new experimental tool to directly measure the heat released during the hydrogen loading of functionalized graphene.

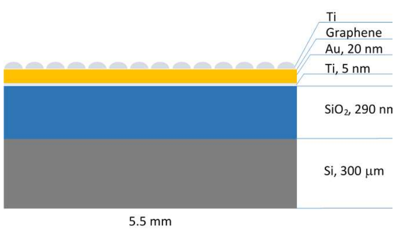

Fig.1. Scheme of the sensor.

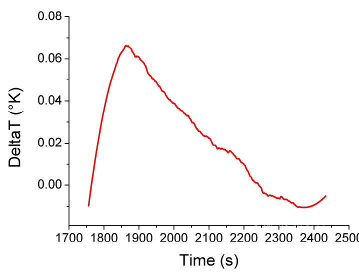

Fig.2. Temperature increase due to hydrogen adsorption.

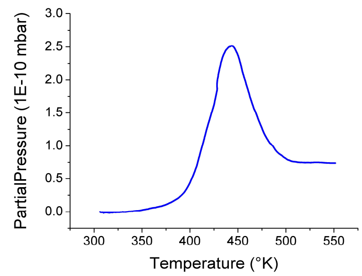

Fig.3. TDS spectrum during hydrogen desorption.

For this purpose, a sensitive gold film thermometer has been realised. The gold film deposited on a Si wafer acts as temperature probe and sample holder for MLG (Fig. 1), with dimensions ~5x5 mm^2. Thermometric measurements are performed monitoring its resistance variation with temperature. The MLG is grown by CVD method on a copper foil and successively transferred on the thermometer. Samples' quality has been checked with Raman spectroscopy. Gold surface has been characterized by Scanning Tunnelling Microscopy before and after graphene transfer. After a careful thermometer characterization and calibration, a thermal signal during hydrogen loading has been detected (Fig. 2). These results represent the first direct measurements of Enthalpy (H_r) released during hydrogen loading process in functionalized graphene. In two successive experiments, temperature increases of $\Delta T = 0.065$ K and $\Delta T = 0.25$ K have been measured, corresponding to $H_r = (23.2 \pm 4.7)$ µJ and $H_r = (58 \pm 12)$ µJ. Each measurement has been cross-checked through Thermal Desorption Spectroscopy (TDS), extracting the loaded hydrogen amount and the binding energy using the Redhead equation. TDS spectra (Fig. 3) gave an average binding energy $E_b = (1.32 \pm 0.07)$ eV/molecule and a desorbed hydrogen amount of $N = (9.77 \pm 0.10) \times 10^{13}$ molecules, which corresponds to $H_r = (20.6 \pm 1.3)$ µJ for the first experiment. Similarly, we obtain $E_b = (1.24 \pm 0.09)$ eV/molecule and $N = (2.57 \pm 0.03) \times 10^{14}$ molecules, which correspond to $H_r = (51.0 \pm 4.3)$ µJ, for the second exposure. Results are in good agreement with thermometric measurements. This represents the first direct measurement of heat release in metal-decorated graphene during hydrogen adsorption.

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