A novel sensitive calorimetric technique to study energy (heat) exchange at the nano-scale

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Every time a chemical reaction occurs, an energy exchange between reactants and environment occurs, which is defined as the enthalpy of the reaction. In the last decades, research has resulted in an increasing number of devices at the micro- or nano-scale. Sensors, catalyzers, and energy storage systems are more and more designed as nano-devices which represent the building blocks for commercial "macroscopic" objects. A general method for the direct evaluation of the energy balance of such systems is not available at present. Calorimetry is a powerful tool to investigate energy exchange, but it usually requires macroscopic sample quantities (10-100 mg). Here we report on the development of an original experimental setup able to detect temperature variations as low as 10 mK in a sample of ~10 ng using a sensitive gold film thermometer having physical dimensions of 5x5 mm^2 (Fig. 1). The technique has been utilized to measure the enthalpy release during the adsorption process of H_2 on a titanium decorated monolayer graphene (Ti-MLG). We chose the Ti-MLG system because of the previous extensive investigations on solid-state graphene-based devices for their application in the hydrogen storage field [1,2,3], which makes it a benchmark and a reference.

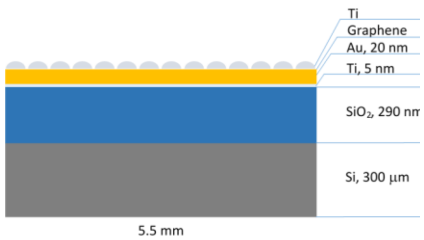

Fig.1. Scheme of the sensor.

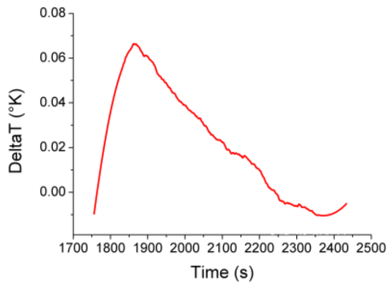

Fig.2. Temperature increase due to hydrogen adsorption.

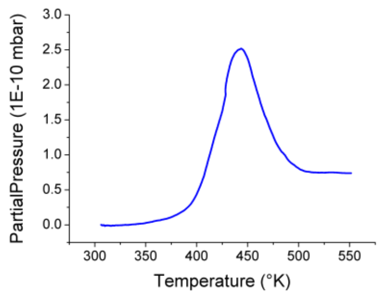

Fig.3. TDS spectrum during hydrogen desorption.

The MLG is grown by the CVD method on a copper foil and successively transferred on the thermometer, while the gold surface has been characterized by Scanning Tunnelling Microscopy before and after graphene transfer. Thermometric measurements are performed monitoring the resistance variation of the Au film with temperature. After a careful thermometer characterization and calibration, a thermal signal during hydrogen loading has been detected (Fig. 2). The sensitivity of this thermometer allowed to detect a hydrogen uptake of ~10^{-10} moles, corresponding to ~0.2 ng, with a temperature increase of ΔT=0.065 K and an enthalpy release of ~23 μJ. Each measurement has been cross-checked through Thermal Desorption Spectroscopy (Fig. 3), extracting the loaded hydrogen amount and the binding energy from the Redhead equation. Our experimental setup extends the application of calorimetry to nano-scale devices allowing, for the first time, the evaluation of the energy balance on nano-gram samples, very useful for the study of 2D materials. Moreover, this technique allows scalability towards even lower sample dimensions while the energy evaluation is non-destructive because the technique does not require desorption.

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