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Hydrogen storage measurements in oxidised and metal decorated single-wall carbon nanohorns

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Hydrogen storage is one of the main challenges toward its generic use as energy carrier. The currently available approaches for on-board storage of H2 as compressed gas or cryogenic liquid have plentiful inherent limitations and do not fulfil the application requirements. Intense efforts have been thus devoted to the development of new storage systems, with particular emphasis on solid-state storage of H2, based on either the formation of chemical bonds, or H2 physisorption on high surface area adsorbents. In this context, the potential use of carbon-based materials as hydrogen stores has been explored extensively. Carbon nanotubes, fullerene, and graphene are the mostly studied materials, however the H2 storage capacity and overall performance of these materials is resulting from weak van der Walls interactions between H2 molecules and the surface of the carbonaceous matrix, thus the amount of H2 that can be stored at room temperature is very low.

Nevertheless, carbon related research remains vivid and progresses fast, leading to novel structures such as nanohorns which have shown interesting hydrogen storage properties. Single-walled carbon nanohorns (SWNHs) consist of graphitic structures with an average size of 2-3 nm, formed out of a single-walled graphene sheet. They exhibit a cone-shape tip and aggregate to form flowerlike structures with sizes of about 80-100 nm. These nanostructures are characterized by very large surface areas approaching 1500 m2/g and are therefore attractive candidates for gas and liquid storage. Moreover, no metal catalyst is required for their synthesis thus enabling low-cost, large-scale production of high-purity samples.

Several studies have shown that the interaction of hydrogen with SWNHs is far stronger than in the case of carbon nanotubes, suggesting that they are quite appealing candidates for hydrogen storage. More specifically, there have been reported H2 adsorption isotherms suggesting a higher adsorbate density than that of the liquid at 20 K, with values approaching those of solid H2 near its triple point (T=13.83 K). This remarkable solid-like behavior was attributed to strong quantum effects, as also confirmed later by detailed quantum simulations. Furthermore there are literature data on isosteric heats of adsorption for H2 on SWNHs nearly 3 times as large as those on SWNTs, corresponding to

H2 binding energies as high as 100-120 meV. This increase in H2 binding energy was attributed to strong solid-fluid interactions at the conical tips. Weaker H2 adsorption was also observed away from the SWNH tips, with an interaction very similar to what has been found for SWNTs. In addition, thermal cycling from 10 to 290 K and back to 10 K recovers a

spectrum close to that measured after the initial low-temperature loading, indicating that most H2 remains firmly attached to these carbon nanostructures.

Our group has studied the effects of confining molecular hydrogen within SWNHs. High-resolution quasielastic and inelastic neutron spectroscopies have been used to characterize the confinement effects and to study its temperature dependence. The results have shown that hydrogen interacts far more strongly with the SWNHs than it does with carbon nanotubes, suggesting that nanohorns and related nanostructures may offer significantly better prospects as lightweight media for hydrogen storage applications. We have recently started looking into the possibility of investigating more directly different enhancements of this confinement such as thermal/chemical oxidation, metal decoration etc. (which have shown in other cases to enhance hydrogen sorption at room temperature) in an attempt to tailor appropriately the functionality/activity of the carbon surface and thus improve the hydrogen storage performance of pristine SWNHs.

For the accurate characterisation of the hydrogen storage properties of the developed materials it will be necessary to perform a systematic series of H2 adsorption/desorption measurements (volumetric but also gravimetric) at different temperatures (77 K, 150 and 298 K) and pressures (1-120 bar). The HYSORB facility of NCSR "Demokritos" is the best suited facility with advanced, state-of-the-art instrumentation for these challenging measurements.

Therefore, the proposed experiment will focus more specifically on the investigation of at least four (4) samples of modified SWNHs according to the following plan:

(a) pretreatment (outgassing) of appropriate amounts of all samples by heating under high vacuum for several hours prior to each measurement (ca. 24 hours)
(b) N2 adsorption/desorption measurements at 77K for the determination of the pore properties (specific surface area, pore size/volume etc.) of all samples
(c) low pressure (up to 1 bar) volumetric H2 sorption measurements at 77 K and 298 K
(d) high pressure (up to 120 bar) volumetric H2 sorption measurements at 77 K and 298 K
(e) high pressure (up to 120 bar) gravimetric H2 sorption measurements at 77 K and 298 K
(f) thermal desorption spectroscopy measurements from 20 - 200 K.

It is estimated that the above set of measurements will require approximately 28 days (4 weeks).