

Hydrogen adsorption on doped-carbon and novel boron nanotubes

María J. López, Iván Cabria, and Julio A. Alonso

Dpto. de Física Teórica, Universidad de Valladolid, 47011 Valladolid, Spain

maria@lab2.fam.cie.uva.es

In the development of fuel cell vehicles, hydrogen storage is the biggest remaining research problem. The U.S. Department of Energy has established for the year 2010 a hydrogen storage target of 6 % of the storage system weight for onboard automotive applications. Several technologies based on physical and chemical storage of hydrogen are being developed simultaneously. One of the promising technologies to store hydrogen is based on the adsorption of molecular hydrogen on low-weight materials with a large specific surface area such as carbon nanotubes (CNTs). This has prompted the search of suitable materials for hydrogen storage among different light-weight nanostructures. In this presentation we investigate, using the density functional formalism (DFT), the hydrogen storage capacity of two materials: i) Li-doped CNTs and ii) the recently discovered boron nanotubes.

The actual consensus of the scientific community is that the hydrogen storage capacity of pure CNTs is small (<1 wt%) at room temperature and moderate pressures. The small storage capacity of CNTs can be understood from the small binding energies, 80-90 meV/molecule, involved in the molecular physisorption of hydrogen on CNTs [1]. Thermodynamic analyses, based on the Van't Hoff equation, have shown that a binding energy of about 300-400 eV/molecule would be required for viable adsorption/desorption at room temperature and normal pressures [2]. Notice that the dissociative chemisorption of hydrogen is not a suitable mechanism since high energy barriers are involved. We have performed DFT calculations of the adsorption of molecular hydrogen on Li-doped CNTs and Li-doped graphene layers. The result of our investigation is that the physisorption of a hydrogen molecule near a Li atom on the surface of a doped carbon nanotube is a factor of two more intense than the physisorption on the pure nanotube, and the same occurs for planar graphene layers [3]. This is due to charge transfer from the Li impurity to the surface, which increases the charge density of the graphitic surface around the impurity (See Fig. 1). This leads to the optimistic expectation that Li doping may enhance the capacity of carbon nanotubes to store hydrogen, as some experiments have reported [4].

Other low-weight nanostructures that could be good candidates for hydrogen storage are boron nanotubes (BNTs). BNTs were first predicted by ab initio calculations [5] and had been recently synthesized [6]. We have first elucidated the geometric and electronic structures of BNTs and boron sheets [7]. These two novel boron structures present buckled surfaces with alternating up and down rows of B atoms, with a large buckling height of about 0.8 Å. The buckled structures are about 0.20 eV/atom more stable than the corresponding flat ones. However, the helicity of some BNTs does not allow for the formation of alternating up and down B rows in the surface and, therefore, those nanotubes have flat surfaces. The buckled and flat nanostructures have different geometric and bonding characteristics (see Fig.2), but both are metallic. Molecular hydrogen physisorption energies are about 30-60 meV/molecule on boron sheets and nanotubes [8], actually lower than in CNTs. Chemisorption binding energies on BNTs are about 2.4-2.9 eV/H atom, similar to the ones obtained in CNTs. However, the energy barrier from molecular physisorption to dissociative chemisorption of hydrogen is about 1.0 eV per molecule. Therefore the calculations predict physisorption as the leading adsorption mechanism of hydrogen at moderate temperatures and pressures. The expected hydrogen adsorption capacity of these novel B materials is even smaller than that of CNTs.

References:

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Figures:

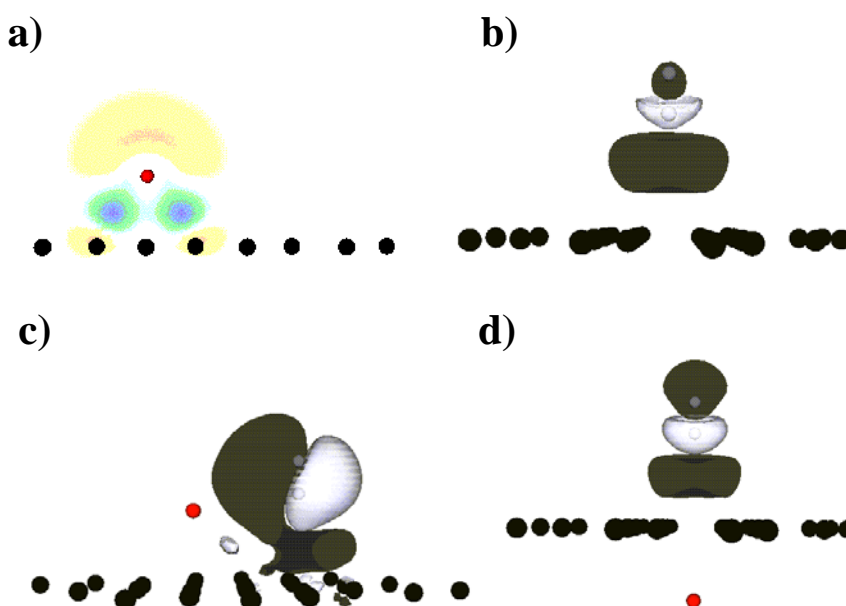


Fig. 1: a) Charge density redistribution for the adsorption of Li on graphene. Red, yellow, green, and blue contours correspond to $\Delta\rho = -3, -1, +1, \text{ and } +3 \times 10^{-3} \text{ e/a.u.}^3$, respectively. b)-d) Surfaces of constant charge density difference for the adsorption of H₂ on b) a clean graphene layer and c) and d) on a graphene doped by a Li impurity (red dot). Dark and light isosurfaces correspond to $+2 \text{ and } -2 \times 10^{-4} \text{ e/a.u.}^3$, respectively.

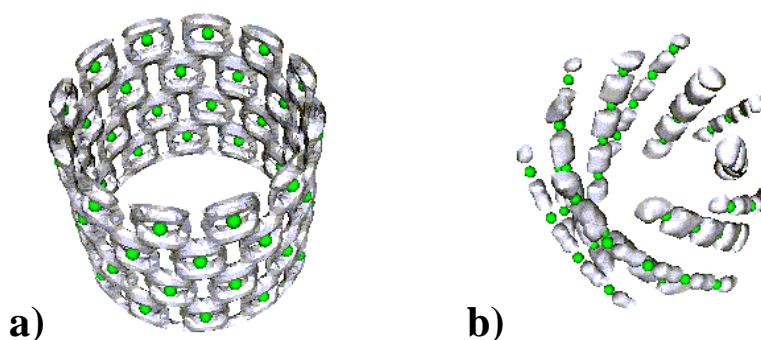


Fig. 2: Isosurfaces of the charge density of two structures of the (4,4) BNT. a) Metastable flat tube and b) buckled tube. $\rho = 0.8e^{-\text{\AA}^{-3}}$. The green dots represent the boron atoms.