

## ADSORPTION OF NEUTRAL AND CHARGED NITROGEN DIOXIDE MOLECULES ON CARBON NANOTUBES: THE SELECTIVE REMOVAL OF THE METALLIC TUBES.

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After more than 15 years of intense research on carbon nanotubes, CNTs, since its discovery, most of the production techniques yield bundles of CNTs of mixed radii and chiralities. However, samples of CNTs of well defined characteristics, specific radius and either metallic or semiconducting character, are required for many applications and also for basic research. Therefore, the selective production and the separation and sorting of CNTs become key issues for further scientific and technological developments based on CNTs.

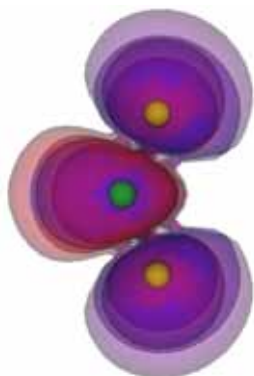
Recently, a new experimental technique has been introduced which leads to the selective removal of the metallic, mCNTs, from the semiconducting, sCNTs, single wall carbon nanotubes in the presence of nitronium ions ( $\text{NO}_2^+$ ) [1]. To investigate the mechanism through which the nitronium ions selectively attack the metallic CNTs, leaving intact the semiconducting ones, we have performed Density Functional (DFT) calculations of the adsorption of nitronium ions and neutral nitrogen dioxide ( $\text{NO}_2$ ) molecules on both metallic and semiconducting nanotubes. The calculations show that the nitronium ions bind to both, metallic and semiconducting tubes through a charge transfer mechanism. One electron is transferred from the tube to the LUMO of the nitronium ion that becomes the HOMO of a neutral  $\text{NO}_2$  molecule (see Fig. 1) adsorbed onto a charged nanotube. The bonding in the semiconducting tubes is due almost exclusively to the charge transfer and very little further electronic density redistribution takes place, as can be seen in Fig.2 (left panel). However, in the case of metallic tubes, there is a substantial redistribution of the electronic density after the electron has been transferred to the nitronium ion (see Fig.2, right panel). This redistribution leads to a stronger adsorption of the nitronium ions in the mCNTs (2.1 eV) than in the sCNTs (1.4 eV). Moreover, the geometric structure of the sCNTs remains almost unaffected upon adsorption whereas the structure of the mCNTs relaxes outwards the tube in the vicinity of the adsorbed molecule. The adsorption of more than one nitronium ions is also analyzed.

On the other hand, the binding mechanism of neutral nitrogen dioxide molecules,  $\text{NO}_2$ , to CNTs is completely different.  $\text{NO}_2$  molecules bind to the tubes through weak Van der Waals forces. A small charge transfer of about 0.2 e from the tube to the molecule also contributes to the molecular adsorption. The structure of both metallic and semiconducting tubes remains unaffected upon adsorption of these neutral molecules. The changes in the electronic structure of the tubes and a possible sensor effect are discussed.

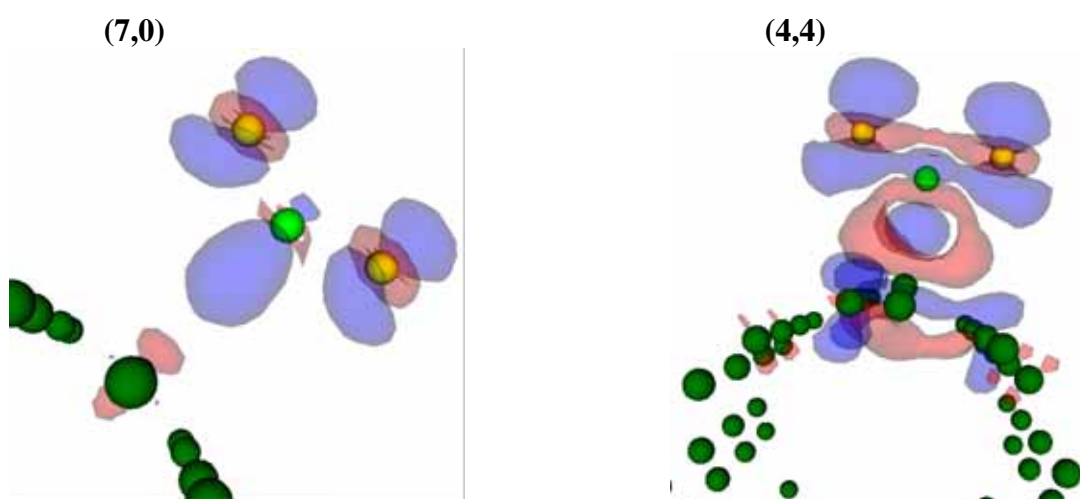
From our results it becomes apparent that although the neutral  $\text{NO}_2$  molecules can be adsorbed on CNTs through weak interactions, these molecules are not able to modify or destroy the nanotube structure. However, the relatively strong adsorption of nitronium ions on mCNTs (stronger than on sCNTs) together with the structural changes taking place in those tubes upon adsorption of the nitronium ions provide the basis to understand the selective removal of the metallic tubes found in the experiments.

**References:**

[1] K.H. An, et al., J. Am. Chem. Soc., **127** (2005) 5196.

**Figures:**

**Fig. 1.-** Highest occupied molecular orbital, HOMO, of the free neutral NO<sub>2</sub> molecule.



**Fig. 2.-** Electronic density redistribution upon adsorption of a nitronium ion on a semiconducting (left) and a metallic (right) Carbon nanotube. Blue areas correspond to an increase of the electronic density and the red areas correspond to a reduction of the electronic density.