

Supporting information to: "Reversible changes in the electronic structure of carbon nanotube-hybrids upon NO₂ exposure at ambient conditions"

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The main article explains how the presence of molecules of nickel acetyl acetonate inside single-walled carbon nanotubes increases the interaction between the tube and the surrounding NO₂. Analyzing the N_{1s} in XPS can reveal important information to understand the reaction pathway of gas molecules that adsorb onto the nanotubes.

N_{1s} in XPS

The N_{1s} line (here recorded with a photon excitation energy of 525 eV) provides information about the sensitivity of the structures and the molecular adsorption scenario. Fig. S1 corresponds to metallicity sorted pristine SWCNTs exposed to NO_2 . The spectra show that there is a clear intensity difference for both types of materials during NO_2 exposition. However, this does not imply that the molecular reaction pathways are necessarily different. On the other hand, Fig. 2 compares the spectra corresponding to the semiconducting and metallic hosts filled with molecules (top spectra) against the ones with nanocluster filling inside the corresponding host (bottom spectra) using 80L of exposure to NO_2 in all four cases. The deconvolution of these high resolution signals using Voigtian functions suggest the presence of at least five components. The previous work on metallicity mixed[?] and metallicity sorted SWCNTs did not show any component located below 400 eV binding energy (consistent with Fig. S 1). This suggests that these new environments are generated by the presence of the filling inside of the SWCNTs. According to the NIST database,[?] these smaller binding energy values in XPS are clearly associated to complex molecules that have Ni, C and O in their stoichiometry. This is very consistent with the observations on the C_{1s} line and it opens interesting questions that should be in the scope of future theoretical work. In addition to the lineshape, the intensity of the signals could provide more

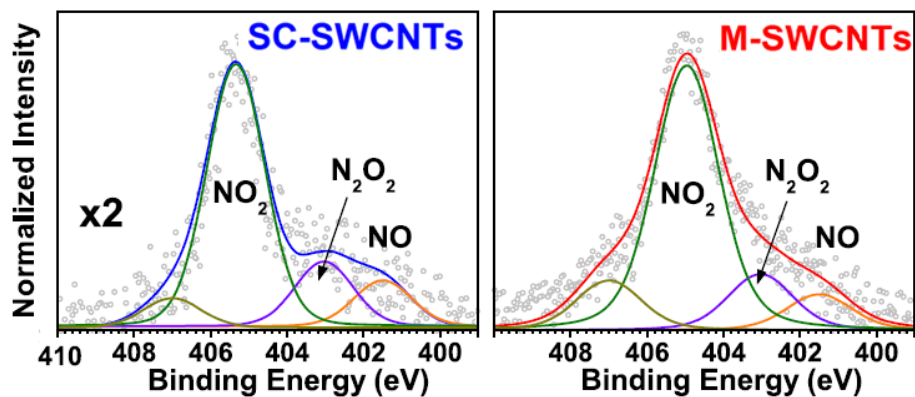


Figure 1: N_{1s} line recorded from pristine SC and M nanotubes exposed to 80L of NO_2 .

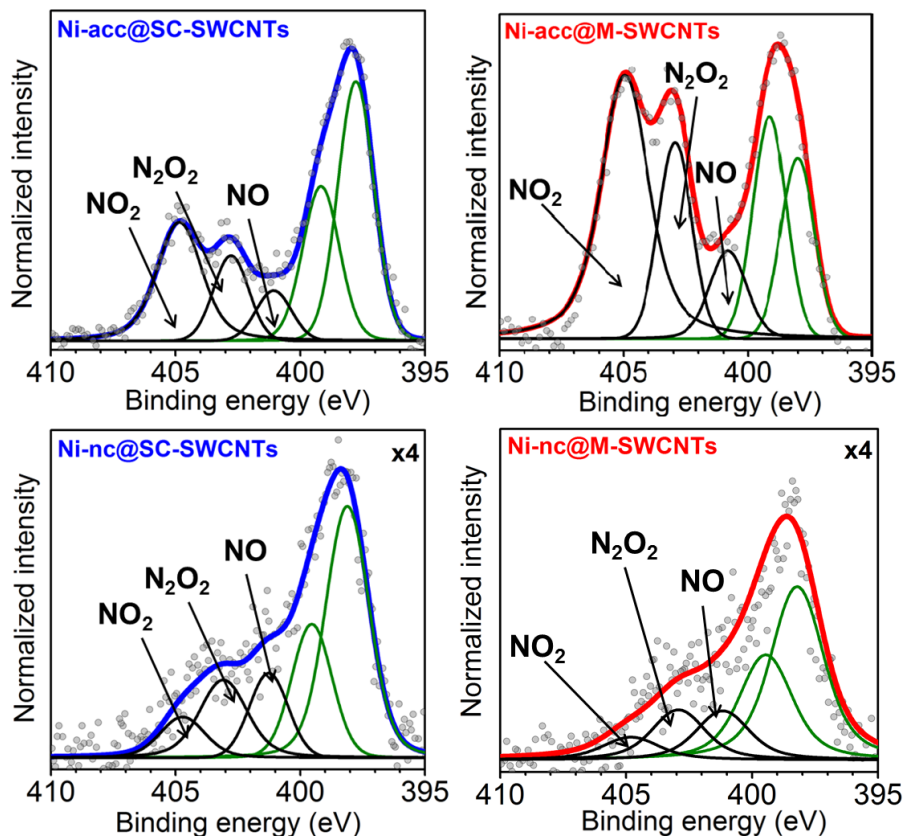


Figure 2: **Left:** N_{1s} line for the semiconducting nanotubes dosed with 80L of NO_2 filled with Ni-acc molecules (top) and with metal clusters (bottom). **Right:** equivalent case for metallic SWCNTs. The spectra have been plotted normalized but the intensities of the Ni-acc filled systems are ~ 4 times larger compared to the Ni-nc filled systems.

information. The plots in Fig. S2 were normalized for illustrative purposes but the original intensities of the Ni-nc filled systems are 4 times smaller than those corresponding to the Ni-acc filled ones. These results hint that the role of the encapsulated molecules of Ni-acc is in both cases much stronger in the reactivity of the system as a whole in presence of NO_2 than that of the encapsulated nanoclusters.

For the purpose of sensing it might be better to have a more reactive system but it is also important that its interaction with the surrounding gas is governed by physisorption rather than chemisorption for recovery purposes.

It is worth trying to understand in detail the higher binding energy components against the work on metallicity mixed and metallicity sorted SWCNTs, and observe that the hosts

(both, metallic and semiconducting) behave to certain extent like the pure carbon tubes regarding the adsorption mechanism on them excluding the interaction with Ni-acc. At first glance the intensity ratio of the higher to the lower binding energy components is much larger for the molecular filled tubes of both metallicities, and even larger for the case of the metallic hosts. For empty clean tubes that are metallicity sorted,[?] preferential physisorption of NO₂ has been reported given its inability to dissociate rapidly due to a much smaller number of defects and almost nonexistent metallic impurities in the clean separated samples. The case of the filled tubes could also be explained to some extent using the work Huffman et al. interpreting that the injected NO₂ could dissociate in the following manners $2(\text{NO}_2)\text{NO}_3+\text{NO}$ and $2(\text{NO}_2 + \text{NO})2\text{NO}_3 + \text{N}_2$. Based on this, the results in Fig.S 2 where the intensity in the cluster filled material is much lower, serves as clear hint that the nanocluster-filled tubes induce more dissociation NO₂ very fast but combining this with the small variations on the C1s, as shown in the main manuscript, induce us to think that this must be linked to a physisorption process. For molecular filling, chemisorption and physisorption can be seen to a certain extent but it is not totally clear yet what happens regarding the reaction pathway with the cluster filling since both the C1s and N1s give hints of a complex molecular interaction.