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Oxygen-driven surface segregation of lithium from single-wall carbon nanotubes

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ABSTRACT

We have investigated the effects of oxygen exposure on lithium-intercalated single-wall carbon nanotube bundles at room temperature, and the evolution of surface configuration versus temperature. X-ray and ultraviolet photoelectron spectroscopy measurements show a remarkable increase of surface lithium concentration, associated to modifications suffered by both core-level O 1 s line shape and valence band spectra. These results have been attributed to the occurrence of lithium surface segregation induced by interaction with oxygen species. Moreover, lithium oxide and peroxide related features are observed indicating that lithium oxidation takes place at the nanotube bundle surface.

The extreme sensitivity of both electronic and transport properties of Carbon Nanotubes (CNTs) upon gas exposure, together with their peculiar structure offering large surface areas, make the study of gas adsorption on CNTs an attractive topic for gas sensing applications [1]. It has been found that the electrical resistance of semiconducting nanotubes undergoes dramatic changes at room temperature upon exposures to NO_2, NH_3 [2], or O_2 [3], while the removal of gas molecules (especially oxygen) from the sample induces a decrease of metallic tubes resistance [4]. Electronic and transport properties of Single-Wall Carbon Nanotubes (SWCNTs) have proved to be sensitive especially to NO_2 and O_2, due to the charge transfer and charge fluctuations [5]. Furthermore, a Scanning Tunneling Spectroscopy (STS) investigation has evidenced that small amounts of oxygen doping tune the local density of states of semiconducting nanotubes, which assume metallic character [3].

It is well known that chemical procedures are required to remove metal catalytic particles, which have been used during the growth process of SWCNTs. However, even after these purification procedures there are some impurities left within the sample, that can be detected only by chemical sensitive techniques and that can strongly modify the gas–SWCNT interaction. Recent experimental photoemission spectroscopy studies have accurately monitored the relation between gas–SWCNT interaction and contaminants in SWCNT samples [6–8]. It has been found that oxygen adsorption is promoted only when residual sodium particles are still trapped into the bundles, as their removal cannot be achieved through mild annealing procedures. SWCNT mats subject to long-lasting annealing at 1300 K are instead insensitive to oxygen exposures for pressure not higher than 10^{-4} Pa, and temperatures ranging from 150 K to 300 K. These findings are consistent with the results of some recent experimental and theoretical works [9–11], showing that the adsorption of oxygen on SWCNTs has the characteristics of physisorption, and that oxygen desorbs completely at $T<100$ K.

In this paper we report on a photoemission study concerning the effects of molecular oxygen exposure on Li-intercalated SWCNT bundles. Experiments have been carried out in a ultra-high vacuum chamber at a base pressure of nearly $3 \cdot 10^{-8}$ Pa. The apparatus is equipped with a non-monochromatic X-ray source (Al Kα – hν = 1486.6 eV), a commercial He discharge lamp (He I – hν = 21.22 eV) and an angle-integrated hemispherical electron analyzer. X-ray and Ultraviolet Photoemission Spectroscopy (XPS, UPS) measurements have been performed at normal emission geometry, and with energy resolution set at 0.8 eV and 0.2 eV, respectively. The sample, a self-standing SWCNT bucky-paper by Carbon Solutions, Inc. (average nanotube diameter (1.4 ± 0.1) nm) was heated to 1200 K at a pressure below $5.0 \cdot 10^{-6}$ Pa. Lithium intercalation was carried out at room temperature by means of a commercial SAES getter source, at a total pressure in the chamber never exceeding $1.0 \cdot 10^{-7}$ Pa. Lithium evaporations cycles have been performed until reaching the intercalation limit. The saturation of atomic alkali concentration has been evaluated from the ratio between the Li 1 s and C 1 s core edge intensities and taking into account the different photo-ionization cross sections. O_2 was dosed at room temperature by backfilling the chamber.

We have investigated the behavior of the O 1 s and Li 1 s core level line shape and of the valence band spectra upon oxygen exposures and thermal treatments. XPS spectra reported in Figs. 1 and 2 have been Shirley-type background subtracted. The O 1 s spectrum of the clean sample (bottom curve in Fig. 1(a)) is characterized by a small amount of oxygen (the atomic concentration value is 1%), which cannot be removed even after several annealing cycles at 1200 K. Since oxygen does not adsorb on a perfectly pure SWCNT sample [6], this effect is likely induced by the presence of some residual impurities, which do not completely desorb at our annealing temperature.

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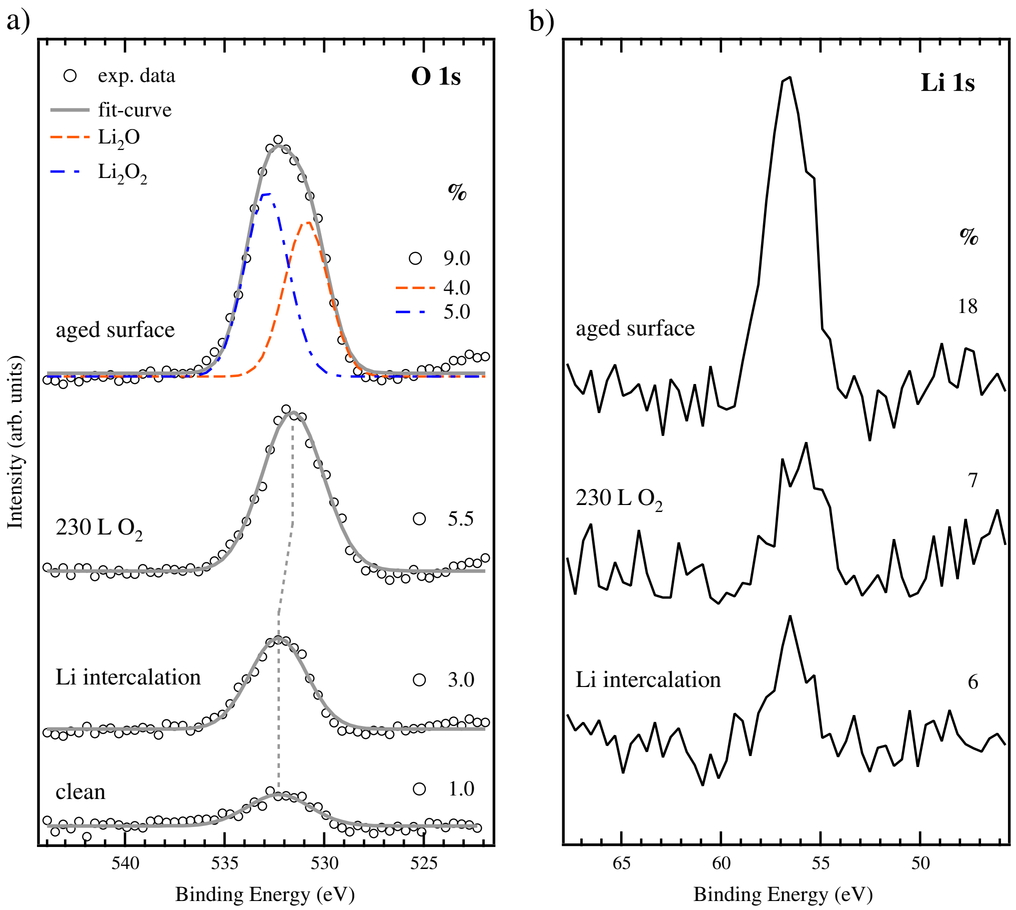

Fig. 1. (a) O 1 s and (b) Li 1 s core level spectra (excitation source: Al Kα – hν = 1486.6 eV). Solid lines in the panel (a) are the Gaussian fitting results of O 1 s curves; the total and partial atomic concentrations are reported next to each curve.

At the Li intercalation limit, the lithium and oxygen atomic concentration are 6% and 3%, respectively. After exposing the sample to 230 L ($1\ L = 1.0 \cdot 10^{-6}$ Torr s) of oxygen, the O 1 s peak shifts toward lower binding energy and the oxygen atomic concentration grows up to 5.5%, while lithium concentration is quite unchanged. Surprisingly, the Li 1 s spectrum recorded some hours after dosing shows a remarkable enhancement of Li 1 s line signal (Fig. 1(b)): the estimated lithium concentration value is 18%, three times larger with respect to the one evaluated just before dosing oxygen. This effect is accompanied also by a raise of oxygen concentration up to 9% and by a broadening of the O 1 s line shape. The intensity of peaks changes over a long time scale, and about 10 h occurred to reach the saturation condition, this being the focus of our work. We have monitored the aging while keeping the sample in the best high vacuum environment we can achieve, so the amount of residual oxygen cannot be further reduced.

We have carried out a Gaussian fitting procedure on the O 1 s spectra, finding that soon after the oxygen exposure there is only one component located at 532 eV, as expected for oxidized carbon [12]. Since oxygen has no chemical interaction with the tubes in highly pure SWCNTs, the occurrence of oxygen chemisorption indicates a change of the sample reactivity due to lithium atoms intercalated among the tubes. This is consistent with former results [13], pointing out that the Li-nanotubes interaction has a covalent character and induces strong modifications of SWCNTs electronic properties. The best-fit curve of the aged surface spectrum is characterized instead by two distinct peaks at 531 eV and 533 eV. According to previous photoemission results [14,15], we attribute these two features to lithium oxide (Li_2O) and peroxide (Li_2O_2) species, respectively. We believe that initially oxygen is linked to nanotubes because of the modified chemical environment determined by lithium intercalation, but it is still not forming Li oxides: the 532 eV peak of O 1 s spectrum corresponds indeed to an oxidized SWCNT sample, and only after aging it splits in the two Li oxides-related components.

We interpret the dramatic increase of surface lithium concentration as a consequence of alkali atoms de-intercalation from the bulk, induced by the high surface concentration of electronegative oxygen atoms. This hypothesis is consistent with the outcome of a study concerning potassium and cesium doped SWCNT bundles, analyzed by Transmission Electron Microscopy (TEM) [16]. The authors show in fact that, due to alkali atoms de-intercalation, structural damages caused by the alkali presence are partially restored after exposing the doped sample to air.

Regarding our experiments, the oxygen-induced increase of surface lithium concentration determines in turn an enhanced reactivity of the sample to oxygen. Residual oxygen present in the vacuum chamber can therefore chemisorb in some hours on the sample, resulting in the detected growth of oxygen concentration. It is likely that, in the Li-rich sample, oxygen atoms bind to lithium atoms leading to the formation of oxygen–lithium compounds on the surface.

The spectra reported in Fig. 2(a) account for the temperature effects on the O 1 s line shape. The concentration of both components has been evaluated with respect to the C 1 s spectrum area and is reported next to each curve. Annealing at 420 K leads to an increase of the lithium oxide component at expenses of lithium peroxide, which can be attributed to the temperature induced decomposition of Li_2O_2. We notice that lithium peroxide is the less stable compound, since it is decomposed just after a mild heating at 570 K, which does not affect lithium oxide component. Lithium and oxygen concentrations are strongly suppressed upon heating at 720 K: they are reduced in fact to