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Electronic properties of alkali–metal intercalated single walled carbon nanotubes

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Abstract

We present a comparative study of the electronic properties of sodium and lithium intercalated single walled carbon nanotubes in a bucky paper sample by electron energy loss spectroscopy and photoemission spectroscopy. We have found that at room temperature both sodium and lithium rapidly diffuse into the bulk of the sample while different magnitudes of charge transfer from Na and Li to the nanotube bundles have been observed. The maximum observed displacement of the Fermi level is almost the same for both alkali although Na and Li induce quite different changes in the carbon nanotube electronic structure. We interpret our results as a more covalent character of the Li–carbon nanotube interaction with respect to the ionic character of the Na–carbon nanotube interaction; the localization of the charge density along the Li–C bond is responsible for an intertube interaction within the carbon nanotube ropes.

Keywords: Carbon nanotubes; Intercalation; Electron energy loss spectroscopy; Electronic properties

Since their discovery [1] carbon nanotubes (CNTs) have generated considerable interest particularly for their peculiar physical properties and their possible applications ranging from nanodevices to hydrogen and energy storage [2–6]. Single walled carbon nanotubes (SWCNTs) are composed of a single graphene sheet rolled up into a cylinder whose diameter ranges in the 1–2 nm with length up to some 100 μm. In carbon nanotubes (CNTs) production system, multi-walled or single-walled carbon nanotubes are grown and organized in bundles or "ropes" consisting of several tubes, held together by van der Waals forces and arranged in a triangular lattice with an intertube spacing similar to graphite [7]. These ropes contain a variety of tube diameters and chiralities so that a real single crystal sample is not yet available [8,9]. The electronic properties of these one dimensional structures are determined by the chiral vector which lies along the circumference of the tube [10] so that both metallic and semiconducting CNTs, with a gap energy depending on the tube diameter and helicity, can be found, opening up possible applications in nanoelectronics.

It is thought that most of future applications of CNTs will depend on our ability in tailoring their properties by appropriate doping. One method to modify the electronic properties of CNTs is the addition of electron acceptors or donors [11,12]. The similarity of electronic structure of graphite and CNTs has suggested to engineer CNTs properties in a controlled way by alkali atoms as in a graphite intercalated compound (GIC) [13,14]. In a crystalline bundle the interstitial space and the internal cavity of nanotubes are good candidates for alkali–metal adsorption.

On the other hand it is also important to understand from a fundamental point of view the physical properties of these new one-dimensional materials. It is well known that the one-dimensional nature of these materials is also responsible of very sharp and intense singularities in the density of states. Recent angle-integrated photoemission measurements of the electronic states in SWCNTs have revealed direct observations of one-dimensional van Hove

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singularities (vHs) in good agreement with theoretical predictions [15].

Moreover, tight binding calculations [16] pointed out that in a "compositionally disordered" bundle the interaction between neighbouring tubes is weak and the entire rope behaves like a sum of many one dimensional weakly interacting tubes. Therefore measurements carried out on pristine SWCNTs bundles can be considered representative of a one-dimensional system.

In this paper we present two different set of measurements in which the electronic properties of SWCNTs have been investigated and the effects of the doping with alkali–metals, i.e., sodium and lithium have been compared.

The electronic properties of such systems have been characterized by high resolution electron energy loss spectroscopy and by photoemission spectroscopy.

Experiments were performed in an ultra-high-vacuum chamber with a base pressure of 1.5×10^{-10} Torr. The upper part of the system consists of an angle integrated hemispherical electron analyser, a non-monochromatic Al Kα ($h\nu = 1486.6$ eV, $\Delta E = 0.8$ eV) X-ray excitation source and a commercial He discharge lamp (He I: $h\nu = 21.22$ eV). Ultra violet photoemission spectra have been collected with an overall resolution $\Delta E = 0.2$ eV. Electron energy loss measurements at higher resolution were made with a VSW 50 hemispherical spectrometer mounted on a goniometer in the lower part of the chamber. The energy of the monochromatized electron gun could be varied from 0 to 300 eV, measurements were carried out for an incident electron energy of 100 eV and with an incident angle of 45° with respect to the sample normal; the energy resolution was set at 80 meV.

The sample was a commercial bucky-paper (by Carbon Solution) of highly purified SWCNTs obtained from laser vaporisation of graphite targets in presence of Ni catalyst. For its nature the bucky-paper is a mixture of SWCNTs of different diameters and chiralities, both metallic and semiconducting. Raman measurements carried out on our samples indicated that they have a narrow distribution of diameters which is centered around 1.2 nm. Before measurements the sample was heated to 1200 K for several hours in a pressure that never exceeded 5.0×10^{-8} Torr.

The alkali metals intercalation was carried out at room temperature by means of commercial SAES getter sources operating in ultra high vacuum chamber at a pressure always below 1.0×10^{-9} Torr.

The atomic concentrations have been evaluated by the ratio of alkali 1 s/C1s intensities taking into account the different photoionization cross sections. Due to the low photoionization cross section of the Li1s state, atomic concentration values lower than 3% have been evaluated taking into account the evaporation lengths.

The intercalation limit found at room temperature for the two alkali metals is quite different; the highest sodium concentration achieved in the sample is Na/C = 0.02 while the maximum lithium doping level is three times higher (Li/C = 0.06).

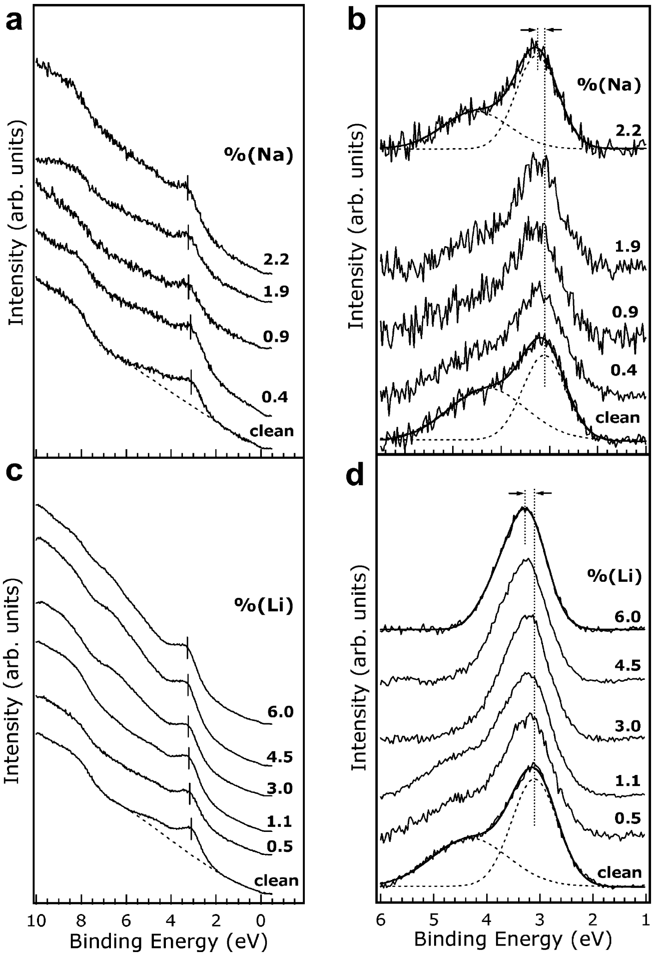

Fig. 1. (a)–(c): Valence band in the photoemission spectra measured on pristine SWCNTs and for increasing sodium and lithium concentration respectively. (b)–(d): the same spectra in the binding energy range (1–6) eV after a polynomial background subtraction. The peak intensities have been normalized to the same height and their energy position has been obtained by a Gaussian fitting procedure. Fitting results are shown as dotted line for curves relative to clean SWCNTs and maximum alkali doping level.

Fig. 1a reports the valence band in the photoemission spectra measured on pristine SWCNTs and for increasing sodium concentration. In Fig. 1b the same spectra in the binding energy range (1–6) eV are shown after a polynomial background subtraction. The peak intensities were normalized to the same height in order to optimize the comparison of different spectral line-shapes. The energy position of the main structure at about 3 eV and the shoulder at higher binding energy has been obtained by a Gaussian fitting procedure. Fitting results are shown as dotted line for curves relative to clean SWCNTs and maximum sodium doping level. The peak located for pristine carbon nanotubes at 3.10 eV is assigned to 2p-π states resulting from the sp^2 hybridization of the C atoms, while the shoulder at 4.30 eV has a dominant 2p-σ character.

Starting from the pristine SWCNTs the peaks exhibit a progressive shift toward higher binding energy (BE) as the Na intercalation increases. In a rigid-band picture the