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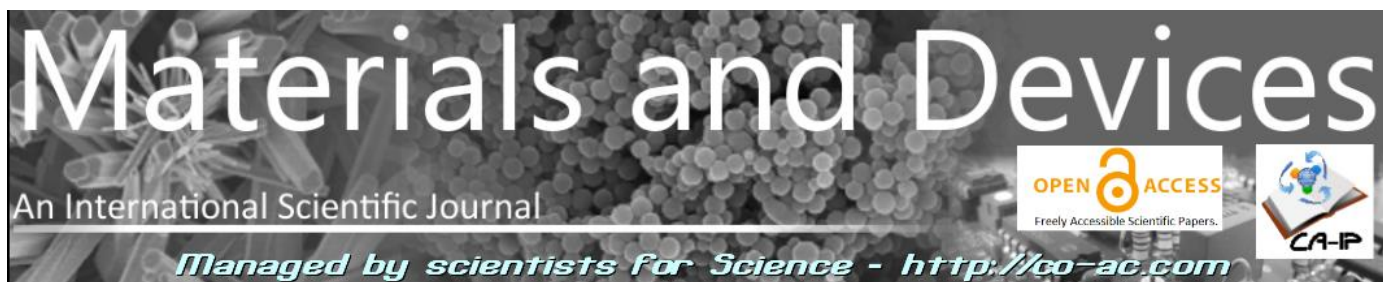
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Development of a homemade experimental setup for *in situ* coupling under vacuum of conductivity measurements, X-ray absorption and Raman Spectroscopies on bundles of single-walled carbon nanotubes intercalated with alkali metal

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Abstract : Here, we report the development of a homemade experimental setup to perform under vacuum an *in situ* study of the physical properties of bundles of single-walled carbon nanotubes intercalated with rubidium ions using electrical conductivity, X-ray absorption and Raman measurements. This set-up was successfully used at the SAMBA beamline at the Soleil synchrotron. The electrical resistance displays an important drop with the stoichiometry (intercalation time). The Raman radial breathing modes and the G-band of the nanotubes clearly indicate an important electron transfer. The G-band behaviour features a transition from semiconducting to metallic nanotubes, confirmed by the electrical resistance measurements as a function of the temperature after rubidium intercalation. This set-up can be used for the study of any type of extremely air sensitive materials.

Keywords : NANOTUBE, INTERCALATION, RUBIDIUM, X-RAY ABSORPTION, RAMAN, ELECTRICAL TRANSPORT

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Introduction

Carbon nanostructures have been recognized as very attractive systems for various applications as they combine many advantageous properties such as mechanical flexibility, chemical stability, robustness, lightweight... Single walled nanotubes (CNT) also display high carrier mobility, direct bandgap allowing to envisage applications in electronics and photonics.^[1-6] However, device fabrication requires i) control of the opto-electronic properties which is not straightforward as the CNT chirality cannot be perfectly controlled ii) easy processing (solubilization, diameter and/or chirality sorting) is also mandatory.

To overcome this two issues, many studies dealing with alkali metal intercalation into nanotubes^[7-16] and even graphene^[10,17-20] have been reported. Alkali metal intercalation (also called doping in the following) leads to a significant decrease of the resistivity^[5,12,21,22] together with an electronic density of states modification, evidenced by optical absorption.^[13,23] Furthermore, Raman spectroscopy reveals a charge transfer between alkali metal and CNTs.^[12,13] Combined *in situ* electrical resistance measurements with Raman studies evidenced strong correlations between changes in the resistance curve and the Raman spectrum as a function of the intercalation rate.^[12] Indeed, two distinct Raman responses have been identified in relation with two plateaus in the resistance curve and are assigned to two intrinsic doped states which could correspond to two different localizations of the doping ion within CNT bundles (as CNT self-organized into bundles thanks to van der Waals interactions, giving rise to a two-dimensional triangular lattice). However, structural information is still missing concerning the structural properties of intercalated CNTs, especially about the intercalation sites of the alkali metal ions. Several possible sites are available for guest species: the surface of the CNT bundle (surface site); in between two tubes at the surface of the bundle (the so-called groove site); the interstitial channel in between three tubes, the hollow cavity of the tube. Several attempts by x-ray and neutrons diffraction,^[11] x-ray absorption spectroscopy (EXAFS) and Transmission Electron Microscopy (TEM)^[15] have been led in order to derive the localization of the alkali metal ions within the bundles of nanotubes. The EXAFS study ruled out the interstitial site in between three tubes^[14] whereas diffraction^[11] and TEM investigations^[15] suggest only a partial filling of this site. Furthermore, most of the works look after the saturation stage, so that the intercalation process as a function of the stoichiometry was only poorly investigated and hence not really understood.

Thus, to go further in our understanding, our approach is to combine rubidium (Rb) *in situ* intercalation of CNT and their physical property investigations as a function of the stoichiometry by electrical resistance measurements, Raman and x-ray absorption experiments. To reach our objective, we developed an *ad-hoc* experimental set-up.

Experimental Methods

Raman data have been collected using a RXN1-785 Raman spectrometer from Kaiser Optical Systems Inc. (KOSI) equipped with a near-IR laser diode working at 785 nm as excitation light, and with a CCD detector for providing a fast and simultaneous full spectral collection of Raman data from 100 to 3450 cm^{-1} . The collection of Raman data is ensured using the patented HoloPlex transmission grating from KOSI, which provides a typical spectral resolution of 2 cm^{-1} . The excitation by the laser is provided through a single-mode optical fiber whereas the collection of the Raman signal measured in back-scattering geometry is ensured through a multi-mode fiber, both being connected to a laser probehead equipped with holographic Notch filters. The power of the laser beam at the sample position was measured in a separate experiment to be 10 mW. To achieve a 5 mm laser spot size at the sample position, a 50 \times Olympus long-working-distance objective (numerical aperture 0.45) was used to focus the incident beam on the sample located at about 15 mm. Typical collection times for a Raman spectrum are of a few seconds, and co-additions of a few spectra are sometimes required to improve the signal-to-noise (S/N) ratio. In the case of the nanotubes studied herein, the collection time was 50 s (ten spectra, each integrated over 5 s) whereas a good S/N ratio can be achieved for pure silicon in 5 s.

X-ray absorption spectroscopy measurements were performed at the Soleil Synchrotron (Saint-Aubin, France) on the Samba beamline. (<https://www.synchrotron-soleil.fr/en/beamlines/samba>). Samples were powder pressed into pellets, and run at 77 K in transmission mode Analyses at the Rb K-edge (15200 eV). The X-ray incident energy on the sample was tuned using a double-crystal Si (220) monochromator.

Home-made Experimental set-up

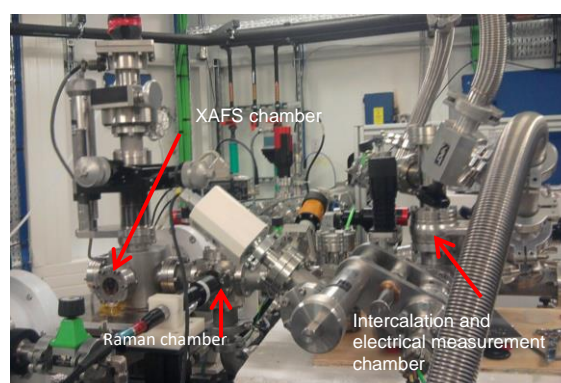


Figure 1: Homemade experimental setup. Three different chambers are used for respectively Rb intercalation and *in situ* electrical, Raman and XAS measurements

Our homemade setup (figure 1) has been developed to allow first *in situ* alkali metals intercalation of CNT bundles and second, combined experimental investigations by XAS and Raman spectroscopies together with electrical resistance measurements. Such a set-up is divided into three different chambers which can be isolated by gate-valves and which are devoted respectively to alkali metal intercalation, Raman measurements and XAS experiments. Therefore, a long transfer arm is used to move the sample under vacuum along the three chambers. Several important requirements have to be fulfilled. The first one concerns the atmosphere inside the set-up. Indeed, as alkali metals are extremely air sensitive, all measurements are performed under high vacuum (10^{-6} mb) to prevent oxidization. The second important point concerns the use of several electrical feedthroughs for the following tasks: i) measuring temperature via thermocouples ii) measuring the electrical resistance iii) heating the CNT sample and the rubidium by the Joule's effect. All the data are recorded on a computer thanks to a labview interface.

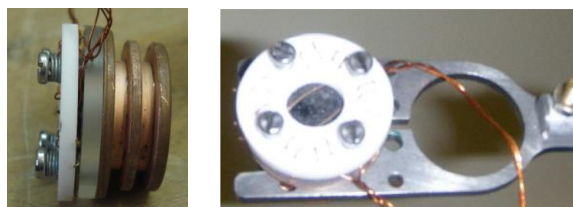


Figure 2a: Nanotubes sample in between copper sample holder and Macor disk. Left: side view; right: front view. Copper wires for electrical measurement using the four probe method are visible

The intercalation step requires first heating of the CNTs up to 200°C. The sample, deposited on a copper substrate (figure 2a), is put in contact with a cylinder heated by the Joule's effect (figure 2b) so that the sample temperature can reach 200°C. Then, the Rb metal, sealed in glass ampoule surrounding by conductive wire (figure 2c), is also heated.

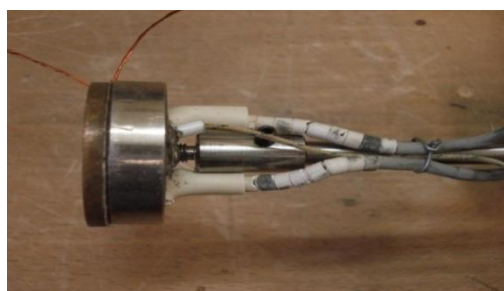


Figure 2b: Heating set-up for the sample

The ampoule is facing the vertical sample. A temperature of 180°C is necessary to trigger Rb sublimation. Temperatures are measured with K thermocouples. The temperature gradient of 20°C between the sample and the Rb is mandatory to

prevent Rb metal deposition onto the surface of the CNT pellet.

The electrical resistance measurement of the sample (a pellet of CNTs), which can be done everywhere in the set-up, is performed using the four-probe method. Four wires are stuck on the front side of the pellet thanks to a glass-ceramic MACOR disk (figure 2a). A Keithley source meter allows providing the current and measuring the voltage between wires. As soon as the rubidium sublimation temperature is reached, the electrical resistance starts to decrease, indicating the intercalation of alkali metal ions within bundles of nanotubes. Thus, we can follow the intercalation process almost continuously as a function of the stoichiometry (intercalation time). Once the electrical resistance has reached the chosen value, both the heating process of the rubidium ampoule and the nanotube sample are switched off.



Figure 2c: Rubidium metal sealed in a glass ampoule surrounding by a conductive wire

Then, the sample is moved into the second chamber to perform Raman measurements after the intercalation step (figure 1).

Finally, the sample is moved into the third chamber (figure 1) and the sample holder is transferred onto a cold finger in order to perform XAS measurements at low temperature (90 K) in order to minimize the Debye-Waller factor.

Results and discussion

Figure 3 displays the relative electrical resistance as a function of the intercalation time. The four doping steps correspond to the values at which Raman and EXAFS measurements have been performed. The plateau observed on the curve at the end of the doping process indicates that the saturation stage is reached.

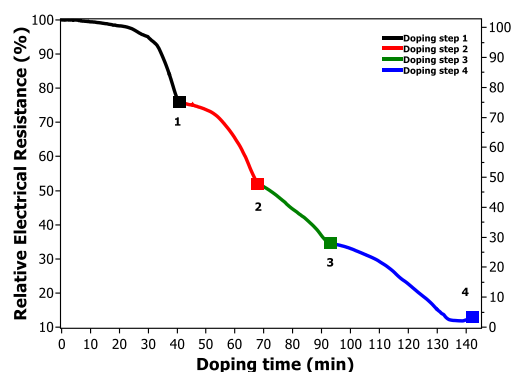


Figure 3: Relative electrical resistance as a function of the intercalation time

However, little is known about the different stoichiometries as the intercalation time is the only one measurable parameter. Thus, in order to get some insights on the stoichiometry, the following protocol was applied: the relative stoichiometry of the different intercalation steps is derived according to the white line intensities of the x-ray absorption spectra (fig. 4)

The absolute stoichiometry of the final interaction stage (saturation) is determined by x-ray photoemission spectroscopy. The Rb/C atoms ratio was then measured close to RbC_{10} . This value is consistent with other measurements of either graphite intercalated compounds^[24] or CNT.^[14,25] Thus, the other stoichiometries have been derived by looking at the relative intensity of the Rb K edge with respect to the saturation stage.

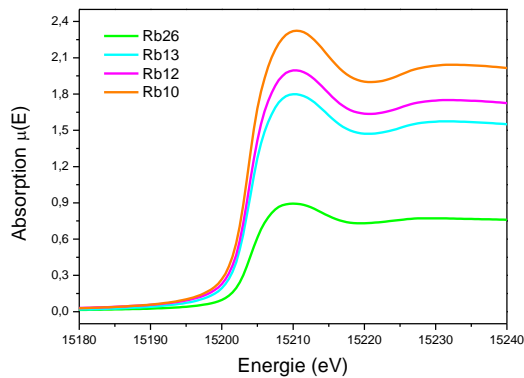


Figure 4: Absorption spectrum as a function of the stoichiometry

The comparison leads to the following intercalation rates: RbC_{26} , RbC_{13} , RbC_{12} and RbC_{10} . Figure 5 displays the EXAFS signals extracted from the absorption spectra of figure 4. The figure clearly exhibits a change in the structural properties from low doping rate (RbC_{26}) to high doping level (from RbC_{13} to RbC_{10}). More precisely, significant modifications are observed at 2.8 and 3.6 \AA^{-1} , evidencing different chemical environment around the Rb ion.

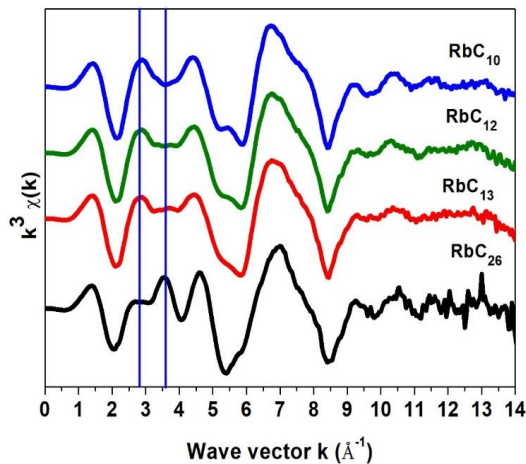


Figure 5: The EXAFS signal for the four doping steps

Figure 6 exhibits the Raman spectra of intercalated CNTs for the four doping steps. A typical Raman spectrum of carbon nanotubes displays mainly three regions of interest. The 100-300 cm^{-1} range displays the radial breathing modes (RBM) for which the frequency is directly related to the tube diameter via the following relationship: $\omega (\text{cm}^{-1}) = A/d(\text{nm})+B$. The second region is located around 1600 cm^{-1} and display the G-band (tangential modes) which gives information on the metallic or semiconducting character of the nanotubes. Finally, the second order 2D band around 2600 cm^{-1} can give some insights on the doping states.

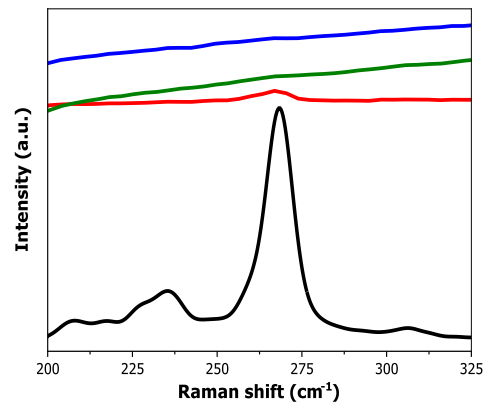


Figure 6.a: Nanotube RBM for different intercalation steps

Figure 6.a clearly shows the vanishing of the RBM intensity upon doping, consistent with an important charge transfer on CNT strongly modifying the resonance conditions. In addition, the G-band downshift observed after the first step of intercalation (figure 6.b) is the signature of an electron transfer into CNT.

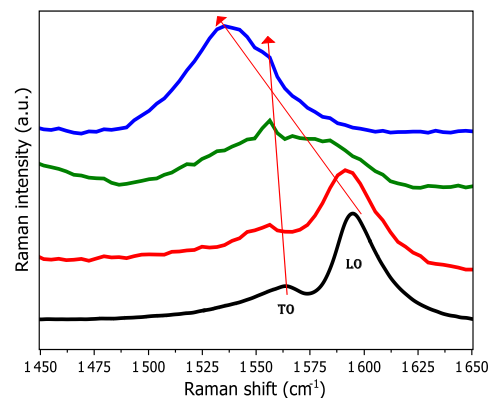


Figure 6.b: Nanotube Raman G-band for different intercalation steps

The G-band mode behaviors, respectively LO (longitudinal optical) and TO (transversal optical) are quite interesting. The downshift of the LO mode is much more important under doping than the TO one. Consequently, there is a crossing of both Raman modes, as shown on figure 5 and already observed for electrochemical doping of nanotubes. Such a behavior can be explained by a semiconducting-metallic phase transition of CNTs.

Indeed, the softening of the LO mode in metallic nanotubes is well explained by the Kohn anomaly and gives rise to a crossing between TO and LO modes. To the best of our knowledge, this is the first time that this phenomenon is observed for physical intercalation. This assumption is confirmed by the resistance measurements as a function of the sample temperature after each step of intercalation (figure 7). The electrical resistance for the first three steps of intercalation increases with the decrease of the temperature unlike the last intercalation step, for which the electrical resistance decreases, evidencing the metallic character of the sample.

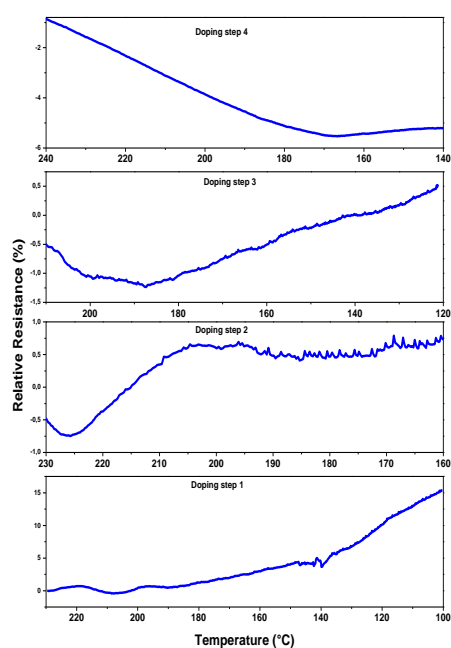


Figure 7: Relative electrical resistance after the four doping steps as a function of the sample temperature

Conclusion

We developed a home-made experimental set-up to perform *in situ* intercalation of bundles of single-walled carbon nanotubes with rubidium ions. We studied the physical properties under vacuum by combining electrical resistance, x-ray absorption and Raman measurements.

The electrical resistance measurements clearly show a transition from a semiconducting to metallic character of CNT. This result is confirmed by the Raman G-band shift upon intercalation. The structural properties investigated by EXAFS suggest different intercalation sites as a function of the doping rate. This home-made set-up allowed to correlate the structural and electronic properties upon rubidium intercalation. This set-up can be used for the study of any type of extremely air sensitive materials.

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