

Reversible electron charge transfer in single-wall carbon nanotubes

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Single-wall carbon nanotubes (SWCNT) have proved to be very special materials due to their unique electronic properties. Over the last years many scientists have dedicated their research to the study of these materials as an electronic system. Amphoteric doping effects (n-type and p-type), which can be reversed, became a very popular way of manipulating the optic and electronic properties of carbon nanotubes. In the particular case of SWCNT, the most common and widely used procedure, which changes their properties, is acid treatment applied as a purification procedure. The effect of the addition of this kind of the dopant has been widely studied but not fully understood so far. Here, we present a study, of two kinds of SWCNT, produced within different techniques: (i) chemical vapors deposition and (ii) laser ablation. The main difference between the two types is the diameter distribution of the obtained materials, which is broad in the first technique and narrow in the second. After the acid treatment it is possible to observe a diameter sensitive doping effect on both samples. Resonance Raman spectroscopy, optical absorption spectroscopy (OAS) in UV/Vis/NIR and the Fourier transform middle-infrared (FTIR) spectroscopy have been applied for the characterization of the samples.

Keywords: SWCNT, doping, Raman.

INTRODUCTION

Carbon nanotubes (CNT) have been investigated very intensely over the last years. Single-wall carbon nanotubes (SWCNT), in particular, are currently the aim of research investigations due to their multiple interesting properties. The SWCNT can be synthesized by different routes with arc discharge, laser ablation and chemical vapor deposition as the most widely used¹. In order to remove catalyst particles and obtain the bulk scale purity, acid treatments have often been reported e.g. nitric acid reflux²⁻⁴. However, this is a procedure which leads to the formation of functionalized products in which the electronic properties are modified so that the molecules can penetrate the graphite layer, generating defects and charge transfer⁵. By the introduction of host molecules into the SWCNT, the so-called doping, it is possible to modify their electronic properties without generating defects in the SWCNT bond network. Considering the type of host molecule the doping can be classified into two types: (i) n-doping, for the electron donor molecules (e.g. K) or (ii) p-doping, for the electron acceptor (e.g. Br₂)⁵.

To follow this behavior in greater detail, spectroscopic studies, such as resonance Raman response and optical absorption spectroscopy (OAS), have been carried out.⁶⁻⁹ Many efforts have been made to understand these modifications. Nevertheless, the full understanding of this field still remains a challenge.

The importance of this study comes from the fact that carbon nanotubes are now being widely considered for medical applications and the acid purified samples are often used for further bio-functionalization. Therefore, a better understanding of the influence of the purification procedure on the SWCNT properties is still a necessity. Here, we present a study on the concentrated acid treated SWCNT which leads to a shortening of the C-C bonds in the carbon nanotube structure and to a Fermi level shift which is reflected in drastic changes in the radial breathing mode region and in the response of the carbon

nanotubes, respectively. These findings are observed for the selected tube diameters.

EXPERIMENTAL

In the current work two different samples of SWCNT were studied: the SWCNT produced by the CVD process (CVD-S1)¹⁰, and the SWCNT produced via the laser ablation technique^{11,12}. The main difference between the two samples is the diameter distribution, which is broad in the CVD sample (0,82 – 1,87 nm), and narrow in the laser ablation produced sample (LA-S2 (1,22 ± 0,16 nm)). As a first purification step the samples were annealed in air at 300°C. Afterwards, the annealed samples were refluxed for 24h in acid solution of *aqua regia* composed of a mixture of HNO₃:HCl:H₂O with the ratio of 1:3:12. Finally, the samples were filtered with a microfiltration system and washed with distilled water and acetone. In order to remove any functional groups formed on the nanotube surface an annealing procedure in high vacuum (10⁻⁵ mbar) at 800°C was performed. The Renishaw In Via Raman microscope spectrometer ($\lambda = 785$ nm) and a Jasco-570 UV/Vis/NIR spectrophotometer were used for the spectroscopy analysis.

RESULTS AND DISCUSSION

In our study, the dopant (HCl and HNO₃) molecules are electron acceptors and charge transfer from the SWCNT to the acceptor molecule is expected. Therefore, a shortening of the C-C bond which leads to upshifts in Raman modes e.g. in RBM features¹, can occur. RBM is composed of many features corresponding to the atomic vibration of the C atoms in the radial direction as if the tube was breathing. RBM is carbon nanotube diameter sensitive and is very useful for the characterization of nanotube diameters up to 2nm¹³.

In Figure 1a the RBM spectra of the CVD-S1 sample before (solid line), after acid treatment (dashed line) and

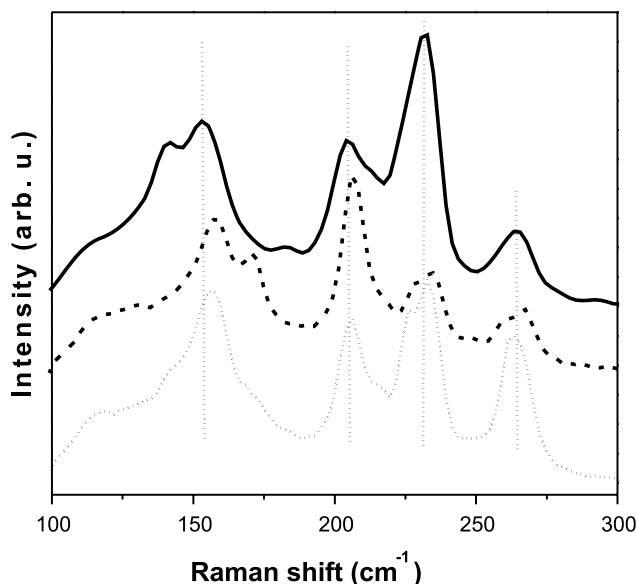


Figure 1. RBM feature in the Raman spectrum of the CVD-S1 pristine (solid line), acid treated (dashed line) and annealed (dotted line) samples. Upon acid treatment a shift is observed in the peaks. This shift is more evident for the low wave number region and less pronounced for the high wave number region.

the acid treated sample after the annealing (dotted line) are presented. This sample exhibits a very wide diameter distribution from 0.82 nm to 1.87 nm. Here, one can observe two effects for the acid treated specimen: (i) a decrease in the intensity of all the components in general, (ii) an upshift of the RBM modes of the acid treated sample, in respect of the pristine one. One can also notice that the shift value is not the same for all the peaks. The strongest shift, of up to 17 cm^{-1} , occurs for the lower wave number region corresponding to the tube diameters of 1.62 up to 1.87 nm. The shift gradually dropped to $\sim 8\text{ cm}^{-1}$ at 182 cm^{-1} , corresponding to the tubes' diameter at around 1.36 nm, and to only ca. 2 cm^{-1} for the remaining RBM components at 204 cm^{-1} (tubes with diameter smaller than 1.21 nm). Hence, the shift is directly proportional to the tubes diameter. In the case of the acid treated CVD-S1 sample after annealing, the RBM position was almost fully reversed to its initial position, although a slight downshift of the position only in the lowest wave-number region was observed (see the dotted line in Figure 1). The intensity of the components of RBM modes increased significantly but the total intensity of the starting material was not reached. These facts can be explained by two different effects. The doping process is diameter selective, which was reported by Kukovec et al, in the case of K and FeCl_3 doped HiPCO SWCNT¹⁴, and the second effect of the acid treatment – exohedral functionalization. The defects on the nanotube walls become an active site for chemical reactions and the formation of $-\text{COOH}/-\text{OH}$ groups can occur. These functional groups also interact with the carbon walls, which could result in the stronger upshift of the RBM components corresponding to the wider tubes.

In order to confirm these data the same experiments were performed on the sample produced via laser ablation. Figure 2 presents the RBM modes of the acid treated sample LA-S2 (dashed line) with respect to the pristine

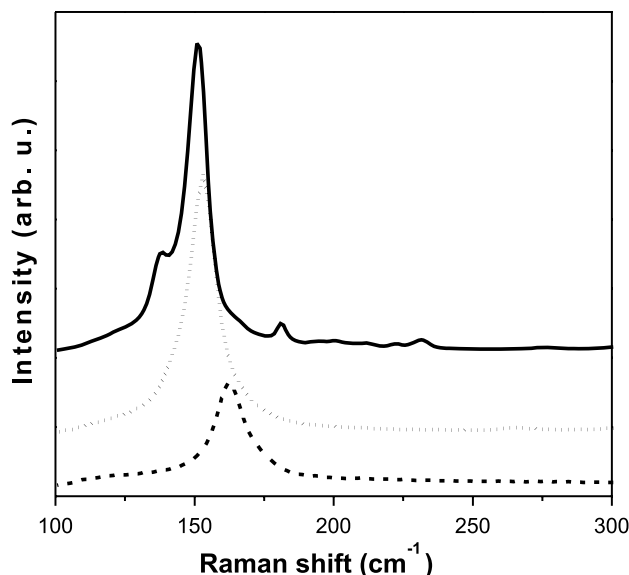


Figure 2. RBM feature of the Raman spectrum of the LA-S2 pristine (solid line), acid treated (dashed line) and annealed (dotted line) samples. A strong shift is observed however the initial pristine position of the peak is almost recovered after the annealing step

sample (solid line) and the acid treated sample after the annealing (dotted line) with the diameter distribution from 1 nm to 1.63 nm. Here, one can observe similar effects to those described above. The intensity of all the peaks strongly decreases after acid treatment, but after annealing the RBM components shift back almost completely to the initial positions detected for the pristine sample. Once more, the wider diameter tubes exhibited stronger upshifts, while the smaller ones are much less affected by acid treatment.

The D and G regions of Raman response were also the analyzed samples and their G/D intensity ratios were calculated as a measure of the relative sample quality (data not shown here). As expected, the annealed samples were the ones that show a higher G/D ratio, and therefore higher quality. This can be explained by a reduction of amorphous carbon content, which increased the purity of the sample and by the decrease in the number of defects in the nanotube walls during the annealing process.

In order to investigate the optical properties of these samples, an optical absorption study was performed. Because of the fact that laser ablated material has narrower diameter distribution than the CVD material, and therefore, the van Hove singularities are much better pronounced, only the LA-S2 sample was analyzed. Figure 3 indicates that the optical response of the modified sample (dashed line) with respect to the reference sample (solid line) is strongly influenced upon the interaction with the foreign molecules. The sample presents the E₁₁s and E₂₂s peaks, related to the transitions between the densities of states (DOS) singularities in semi-conducting tubes. However, the first transition between vHS of the semiconducting E₁₁^s tubes for the modified sample decreases while the other transition is preserved (Figure 3). The calculation of the areas under the E₁₁^s peaks shows that its intensity in the acid treated sample decreases by a factor of four with respect to the pristine sample. In addition, the intensity of the remaining peaks dropped.

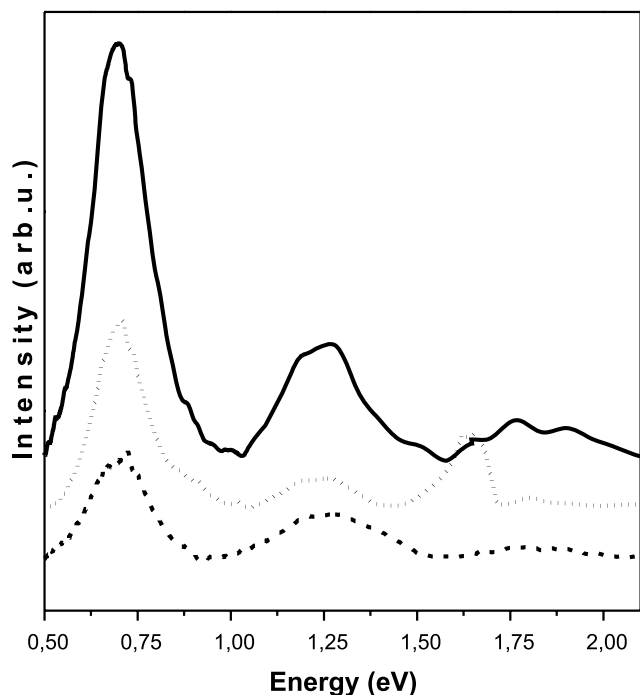


Figure 3. (a) OAS spectra on the pristine (solid line), acid treated (dashed line) and annealed (dotted line) SWCNT of the LA-S2 sample. The spectra are presented after baseline subtraction and normalization. In order to promote better interpretation the spectra were also vertically translated.

However, this transition could be recovered during the high temperature annealing at 600°C for 1h ($2.5 \cdot 10^{-3}$ mbar) of the sample (dotted line of Figure 3). A supporting experiment of *in situ* annealing of the LA-S2 sample in Raman microscope was performed. The shift of ca. 10 cm^{-1} in the RBM modes of the acid treated sample was fully recovered (data not shown here).

The decrease in the intensity of the optical absorption spectra in both samples can be assigned to the fact that the introduction of dopant molecules, such as HNO_3 , provokes oxidation^{15,16} or 1,3-cycloaddition¹⁷, by the attachment of carboxylic groups (-COOH) formed in the graphite layer. Modifications in the SWCNT structure can be explained by the H-bonding promoted by -COOH groups as suggested by Kukovec *et al*¹⁵. One of the main sources of the reactivity of SWCNT is the curvature given by the non-planar geometry of sp^2 carbon atoms. When the oxidation occurs a certain number of carbon atoms are forced to change into an sp^3 state, leading to structural modifications^{5,15-19}. During the thermal treatment (decarboxylation) a fraction of these atoms changes back to the sp^2 state, recovering the pristine properties. This is the reason why the optical and vibronic response of the annealed samples is similar to the pristine one.

To confirm the presence of the functional groups on the SWCNT surface the measurements via infrared spectroscopy were also performed (data not shown here). As it can be expected from the previous reports⁵ only the sample after the acid treatment, shows the presence of functional groups, once they are introduced by the dopant molecules.

CONCLUSIONS

Concluding, the study of the influence of acid treatment on the optical and vibronic properties of SWCNT with two different diameter distributions and produced via different techniques (CVD and laser ablation routes) was presented. The data presented clearly showed that the diameter sensitive effect was observed. For wider carbon nanotubes stronger upshifts of RBM components were detected. In addition, the concentrated acid treatment led to the modifications in the Fermi level and changed strongly the features of the OAS spectra of the samples. The high temperature annealing reversed these effects and the RBM modes and the optical response of SWCNT returned to their initial state. The relative purity of the sample with respect to the pristine tubes did not change consistently for both batches of the tubes. However, after the annealing step in high vacuum the number of defects strongly decreased and the relative purity increased significantly.

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