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 materials. 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 used. In order to remove catalyst particles and obtain the bulk scale purity, acid treatments have often been reported e.g. nitric acid reflux. 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 transfer. 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. Br).

To follow this behavior in greater detail, spectroscopic studies, such as resonance Raman response and optical absorption spectroscopy (OAS), have been carried out. 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) and the SWCNT produced via the laser ablation technique. 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 (λ = 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 features, 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 2nm.

In Figure 1a the RBM spectra of the CVD-S1 sample before (solid line), after acid treatment (dashed line) and
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 ~8 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 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 E\(_{11}\)s and E\(_{22}\)s 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 E\(_{11}\) tubes for the modified sample decreases while the other transition is preserved (Figure 3). The calculation of the areas under the E\(_{11}\)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.
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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