

Effect of ionic and covalent defects on the properties of transparent carbon nanotube films

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Abstract. Transparent conducting films are rapidly emerging as one of the most promising applications of carbon nanotubes. In these less-than-perfect materials, understanding the types of defects and their effect on the transport and optical properties plays a significant role. In this contribution, we present examples of these effects, both beneficial and adverse.

1. Introduction

Carbon nanotubes can be insulating or conducting depending on their diameter and electronic structure, and certainly contain many defects [1]. Defect types vary on a wide scale. Structural defects can be geometric deviations from the perfect hexagonal structure including pentagons and/or heptagons (Stone-Wales defects)[2, 3] or heteroatoms built into the carbon framework (mostly boron or nitrogen) [4]. Electronic defects can stem from free radical-like sites resulting from broken bonds, charged or neutral, and atoms other than carbon (hydrogen or organic functional groups) covalently attached to these sites [5]. Finally, double C-C bonds can be attacked by mostly organic reagents, resulting in sidewall functionalization [6]. Unfortunately, the literature does not distinguish clearly between these processes. Often, all or most of them are simply summarized as "doping", creating a significant controversy as to what the exact features and consequences are.

In this paper, we concentrate on three types: electronic charge transfer, and covalent functionalization involving defects and sidewalls, respectively. We compare the change in physical properties caused by these treatments, concentrating on the electrical conductivity and the visible transmission, because of the potential application of these structures as transparent conducting layers.

All experiments described in this paper have been conducted on single-walled nanotube (SWNT) samples varying in composition and diameter distribution. Multiwalled nanotubes have certain advantages over single-walled samples, but it is much more difficult to describe both their physical properties and their chemistry based on simple models. In what follows, we usually neglect the interaction between tubes and as we will see, we can even test the validity of such an approximation in the case of single-walled nanotubes.

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2. Optical and electrical characterization of carbon nanotube networks

The two main parameters determining the quality of a transparent conducting layer are obviously the optical transmittance in the range of interest (in most cases, the visible region) and the dc conductivity. As in the case of nanotubes the thickness of the layers cannot be defined unambiguously in most cases, the electrical quantity used for comparison is the sheet resistance $R_{\square} = \rho/d$, which is independent of the thickness d (ρ is the resistivity of the sample).

The transmission is usually wavelength-dependent and the knowledge of the optical spectra is a strong prerequisite for determining the feasibility of a given nanotube type for a given application. Knowing the spectrum in a wider frequency range, especially extending the measurements towards lower frequencies, yields important additional information.

Carbon nanotubes, depending on their geometry, can be either metallic or semiconducting. The semiconducting tubes show well-defined interband transitions in the near infrared and visible region [7], but for metallic tubes, the most significant absorption is that of free carriers in the far infrared [8, 9]. The spectra at terahertz frequencies are also indicative of the dc conductivity: the value extrapolated to zero frequency is a good estimate of the intrinsic value of a nanotube, while transport measurements can be influenced by intertube barriers. In the midinfrared region, vibrational signatures of defects or sidegroups can be easily identified, because the infrared modes of the nanotubes themselves are extremely weak [10].

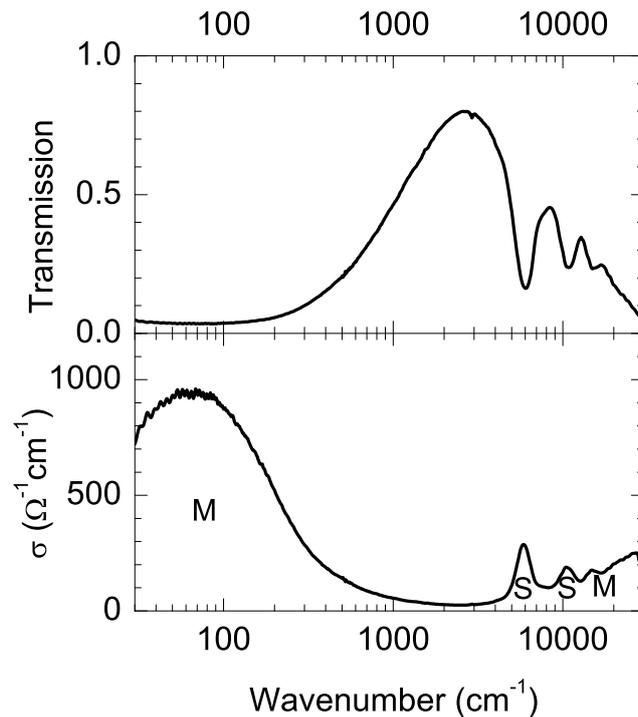


Figure 1. Wide-range transmission (upper panel) and optical conductivity (lower panel) spectra of a laser-deposited nanotube sample [9]. Note the logarithmic frequency scale, which emphasizes the terahertz region. The optical conductivity at low frequencies can be compared to the dc conductivity of a nanotube sheet.

Wide-range transmission can be best measured on freestanding samples [11], because in this case no substrate absorption has to be considered and the measured transmission can be converted to optical functions *via* a straightforward Kramers-Kronig transformation [12]. (For specific applications appropriate substrates can then be used in order to improve other properties, *e.g.* mechanical stability.) In Fig. 1 we depict the transmission and the calculated optical conductivity of a laser-deposited carbon nanotube film from the far infrared through the ultraviolet. In this specific case, the extrapolated intrinsic dc conductivity is $\approx 800 \Omega^{-1} \text{cm}^{-1}$, close to the value of $700 \Omega^{-1} \text{cm}^{-1}$ determined from sheet resistance measurements [9]. The agreement is not always this good, but it shows that in high-quality samples the contacts do not

necessarily have a large influence on the transport properties, and that studying the change in low-frequency spectra after modification can be at least as informative as a direct conductivity measurement.

Figure 1 also shows the contributions from several types of nanotubes in our inhomogeneous sample: the peaks marked M originate in metallic tubes and those marked S in semiconducting tubes. Thus, the dc conductivity is mainly determined by the metallic content and the transmission by the semiconducting content. Changing the composition can have a profound effect on both transport and optical properties and can significantly improve the parameters. Such treatment is now possible [13] and offers the perspective of significant improvement in the near future.

3. Effect of modification on transparent conducting behavior

3.1. Doping by nitric acid: electronic charge transfer and defect functionalization

Aggressive treatment by oxidizing acids during the workup of carbon nanotubes is a common example of both defect functionalization and modification of the overall electronic structure. Nanotubes are refluxed in boiling concentrated nitric acid, with the primary purpose to dissolve the metal catalyst used in the course of production, but an important side effect is the oxidation of the nanotubes themselves.

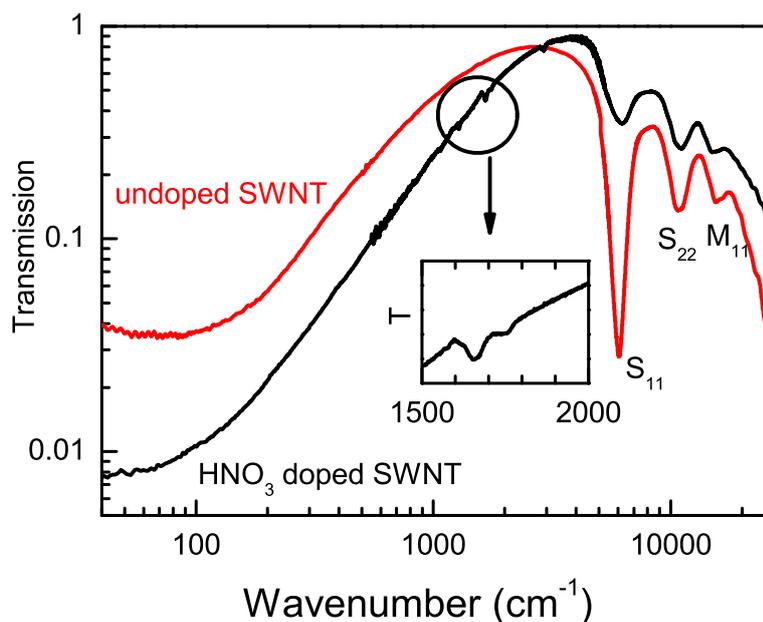


Figure 2. The effect of doping on the transmission of a laser-deposited nanotube sample [9]. Note the logarithmic scale in both frequency and transmission. The overall transmission decreases at low frequency (indicating increasing dc conductivity), and increases in the near infrared/visible region. The labels S_{11} , S_{22} and M_{11} correspond to the transitions illustrated in Fig. 3 for semiconducting and metallic species, respectively. The inset shows the vibrational signatures of carboxylic groups attached to the defect sites and tube ends as a result of acid doping.

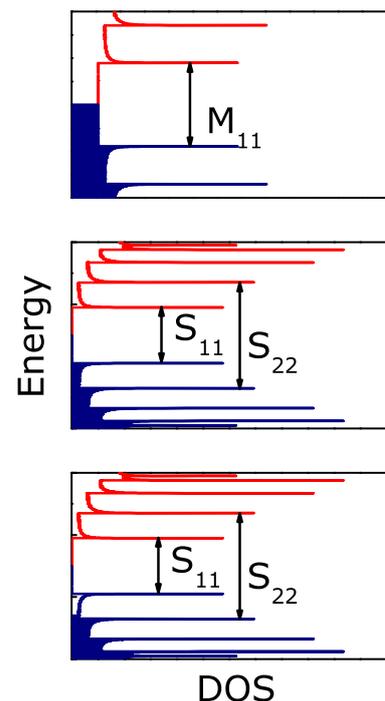
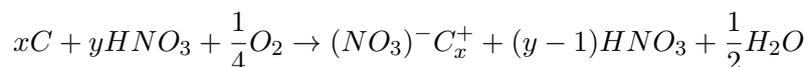


Figure 3. Density of states for various nanotubes. Top: metallic, undoped; middle: semiconducting, undoped; bottom: semiconducting, hole-doped.

Oxidation can happen in two ways, either analogous to the intercalation of graphite [14, 15, 16]:



where the positive charge will delocalize over the collective π -electron system of the nanotubes. A "chemical" oxidation at the tube ends and defects is also possible, where these sites are converted to carboxylic groups [17, 18]. Because both reactions occur at the same time, acid-treated nanotubes offer a good model system for both electronic charge transfer and defect functionalization.

In Fig. 2 we compare the spectra of an acid-treated nanotube film ("HNO₃ doped") with the same film after annealing to remove the doping ("undoped"). Three effects of doping are evident from the figure. First, the decrease in transmission which translates to increase in the optical and consequently dc conductivity. (Independent transport measurements support this observation [19].) Second, the decrease in the intensity of the interband transitions of the semiconducting tubes, caused by the decrease in the number of charge carriers in the initial states of the transitions as electrons are removed from the system by doping. Further explanation is provided in Fig. 3: here the density of states of typical metallic and semiconducting nanotubes is shown. Upon removing electrons from a semiconducting nanotube (bottom panel), the electronic structure develops a Fermi level and becomes analogous to the metallic tube structure in the top panel. Hole doping also empties the initial state of the S₁₁ (and, as doping proceeds further, eventually S₂₂ etc...) transition, thereby reducing the intensity of the corresponding spectral feature.

Both effects described above improve the quality of the material as a transparent conductor. The third effect is emphasized in the inset of Fig. 2: defect functionalization by carboxylic groups results in the vibrational peaks around 1700 cm⁻¹. This functionalization can play an important role in improving the solubility of the material, but it is apparent that, concerning optical properties, the electronic charge transfer is the primary process and cannot be neglected. Under mild conditions, when undoped nanotubes are subjected to nitric acid vapor at room temperature, the electronic doping can even be achieved without defect functionalization [20].

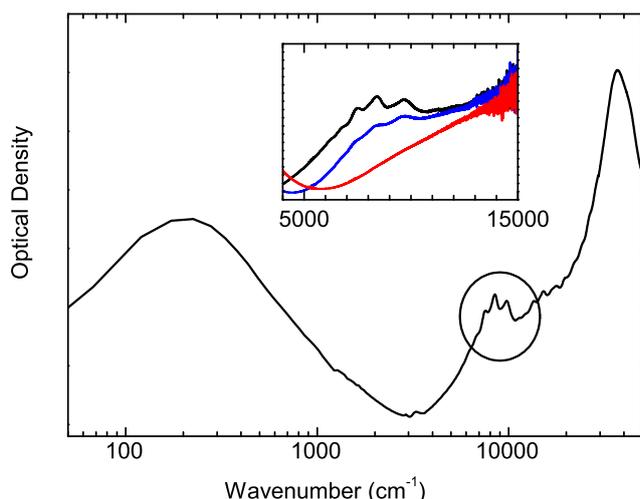


Figure 4. The development of the optical density with time during treatment of a CoMoCat nanotube network with nitric acid vapor at room temperature. The inset shows three (baseline-corrected) spectra in the circled region, from top to bottom: before treatment, at an intermediate position and after saturation. It is apparent that the spectral features corresponding to tubes with a lower transition energy disappear first. For the complete series, see the movie in the Supplementary information.

Figure 4 shows the evolution of the spectrum during such a mild acid treatment in the region of the first interband transition of semiconducting tubes. The sample used here is a CoMoCat tube ensemble [21], consisting of relatively few types of nanotubes [22], so that in the NIR spectrum the individual peaks are well resolved. In the inset of the figure, we enlarged the region

corresponding to the first interband transition of semiconducting tubes and present the evolution of the spectra with time when the sample was exposed to nitric acid vapor. Within a few minutes, the interband transitions completely disappear and an increase in absorption appears at the low-frequency end. The latter corresponds to the free-carrier absorption generated by the holes on doping (Fig. 3). The supplementary information includes a movie of the time dependence: it proves that the disappearance of the individual peaks is not uniform but happens in the order of energy, i.e. the depletion of the semiconducting energy levels occurs first for tubes with lower transition energy S_{11} . (Since this energy scales inversely with tube diameter this means that larger diameter tubes are doped sooner.)

3.2. Sidewall functionalization

Intensive sidewall functionalization converts sp^2 carbon atoms into sp^3 ones [23], thereby reducing both the conductivity and the optical absorption. Figure 5 compares a HiPco nanotube sample before functionalization and after converting 23% of the carbon atoms converted by addition of dichlorocarbene. In contrast to doping, in this case both the free-carrier absorption and the interband transitions lose intensity, consequently the transmission increases in the terahertz region and the sample becomes insulating. While such a change can be desirable e.g. in nanoelectronics, it is clearly not a step towards better transparent conductors.

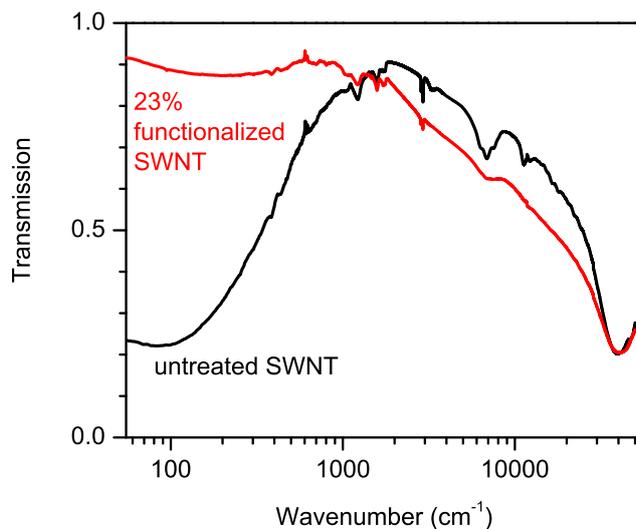


Figure 5. Change in transmission of an arc-produced nanotube sample on heavy sidewall functionalization with dichlorocarbene [23]. All features corresponding to the collective π -electron system are strongly attenuated.

4. Conclusions

We have compared several controlled ways of introducing defects into carbon nanotubes with respect to their applications as transparent conducting layers. We found that defect functionalization has little effect on both optical and transport properties, because it involves only a few per cent of carbon atoms. Sidewall functionalization, on the other hand, influences the electrical properties towards lower conductivity. Doping by electrons or holes, analogous to intercalated graphite, causes an increase in conductivity and at the same time an increase in transparency, the ideal combination for applications as transparent conductors. Our spectroscopic data, together with transport measurements, prove that the changes in conductivity of nanotube networks are intrinsic, and not just a result of improving the contact between nanotubes.

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