Peapod synthesis on substrates

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[2] JARA Fundamentals of Future Information Technologies
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We present how carbon nanotubes can be grown and filled with fullerene molecules directly on a substrate. The resulting peapods are very clean and thus suitable for the fabrication of electronic devices. Since oxidation of the nanotubes is a crucial step during the peapod synthesis, we investigate the effects in more detail using high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. Two different oxidation methods, heating in air and acid treatment, are compared.

Carbon nanotubes (CNTs) filled with fullerene molecules, so-called "peapods", recently have generated a lot of interest as systems for electronic applications. The C_{60} fullerenes inside the tubes modulate the local density of states due to hybridization of the molecular orbitals with the conduction band and $Gd@C_{82}$ fullerenes inside a semiconducting tube can change the band gap. These effects allow one to build ambipolar CNT field effect transistors and to tune the gate-dependent conductance of single electron transistors. Filling with fullerenes can change mechanical properties of CNTs, e.g., softening the vibrational modes, which is interesting for the fabrication of nano-electro-mechanical devices.

For electronic applications it is desirable to use CNTs synthesized by chemical vapor deposition (CVD). This method yields CNTs which can be several micrometers long and grown on predefined sites on the substrate. Therefore, they do not cluster to ropes like CNTs dispersed on a substrate from solution. Carbon nanotubes grown with CVD have to be filled directly on the substrate in order to keep these advantages for the resulting peapods.

The carbon nanotubes grown by CVD are closed and have to be opened before they can be filled. This is usually done using oxidation either by heating in air or by acid treatment. For CNTs grown on substrate only the former method had been studied [1, 2]. We investigated the influence of both methods on the creation of defects [3]. By doing so, we gained information on how chemical reactions affect single tubes compared to powder samples.

The carbon nanotubes were grown with CVD directly on TEM substrates (DuraSiN^{TM}, Protochips Inc.). Oxidation by annealing in air was done at 450 °C for 20 min, oxidation by acid treatment was carried out in 5 molar HNO_3 at 100 °C for 3 h. The defects and filling of individual CNTs were studied with high-resolution transmission electron microscopy (HRTEM) using aberration correction.

After oxidation the tubes are filled with amorphous carbon (see Fig.1). Both methods damage the caps of the CNTs as well as the sidewalls. Annealing the tube in air seems to have the same effect for individual tubes as for "bulk" samples. The inner walls are opened along with the outer walls, as expected (Fig.1a). In contrast, the acid treatment has a stronger impact on single tubes than on tubes in powder samples. We could show that the tubes can be dissolved from inside (Fig.1b). Thus, the carbon residue inside the CNTs may consist of remnants from destroyed inner walls.

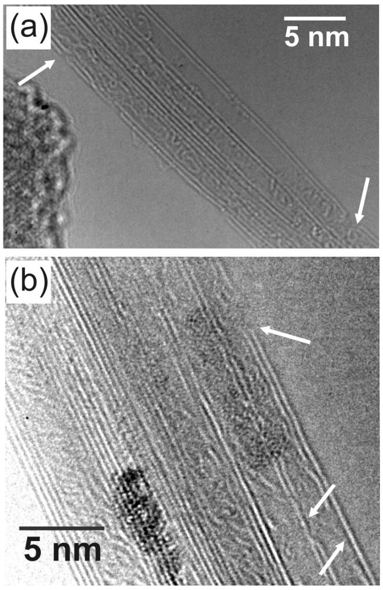

FIG. 1: Oxidation of CVD carbon nanotubes leads to amorphous carbon residue inside the tubes. Arrows indicate defects on the sidewalls. Atoms appear bright in this case due to the negative spherical aberration imaging used for optimized phase contrast. (a) Heating in air usually affects inner walls along with the outer walls. (b) Acid treatment can dissolve walls from inside-out (bottom arrows).

This residue inside the tube can be removed at least for CNTs oxidized by heating in air. High temperature annealing at 900 °C and with a pressure $p \leq 1 \cdot 10^{-6}$

mbar seems to remove the plug, since afterwards the nanotubes can be filled with fullerenes as shown in Fig.2. Filling was carried out under UHV conditions ($p \leq 1 \cdot 10^{-7}$ mbar). A thin film of C_{60} was evaporated onto the TEM substrate with the opened nanotubes. Afterwards the sample was held at 400°C $\leq T \leq 450^\circ$C for 24 h. During this step, the fullerenes are free to move along the nanotube walls until they can enter through a defect. Finally, the substrate was heated above 700°C for 24 h in order to clean the sample from excess fullerenes. Indeed, we obtain very clean peapods after this procedure suitable for transport devices.

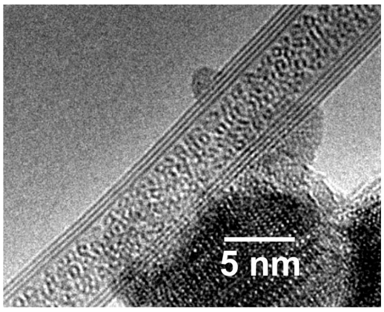

FIG. 2: Peapods can be synthesized after an additional step for removing the plugs of amorphous carbon. Atoms appear dark in this case for the benefit of enhanced contrast.

High resolution TEM imaging can cause defects on nanotubes as well as on fullerenes and even completely destroy them. Therefore it is desirable to find a different method for characterization of the nanotube structure and chemical modifications, in particular the filling with fullerenes. Raman spectroscopy is a versatile tool to determine the effects of functionalization, for example creation of defects or changes in the electronic structure. In order to correlate the changes of Raman modes with particular defects, we use the complementary information about the atomic structure gained by HRTEM. As a first step towards detecting the degree of filling for a single CNT, we investigated the change of Raman modes during the oxidation process on "bulk" samples [4]. We focused on the shift of the D*-mode at a Raman shift of ~ 2600 cm^{-1}, which is an overtone of the defect mode D at ~ 1300 cm^{-1} and sensitive to changes of the electronic structure.

The D*-mode shows an up-shift for all methods investigated (Fig.3). However, we observed different behavior of the shift depending on the oxidation method. For heating in air, the shift of the D*-mode is strongest and about twice as large as the shift of the D-mode, as expected (Fig.3a). For the acid treated sample shown in Fig.3b, the D*-mode shows an up-shift of 5.3 cm^{-1} after 4 hours, while the D-mode shifts by 4.1 cm^{-1}. Thus, the shift of the D*-mode is smaller than expected from the shift of the D-mode and may be related to changes of the electronic structure. However, the origin remains unclear as treatment with HNO_3 causes p-doping of the CNTs, which should result in a shift to larger wave numbers [5]. During subsequent heating, the peaks shift further until they reach the limit $\Delta\omega^* \approx 2\Delta\omega$ (not shown here). This indicates that the effect of the acid treatment can be at least partially reversed.

Additional information was gained from the changes of the peak intensities. In case of thermal oxidation changes in the D/G ratio, usually used to characterize the purity of a sample, are rather caused by defects than by increase of amorphous carbon. In contrast, the increase of the D/G ratio could be traced back to the shielding effect, i.e. amorphous carbon around the tubes leads to a decrease in the intensity of the G-mode and the D*-mode.

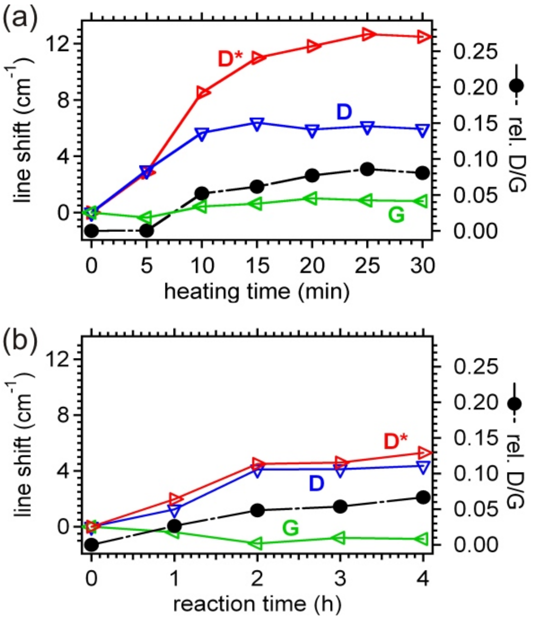

FIG. 3: Relative shifts of the D-mode (blue), G mode (green), D mode (red) and the D/G ratio (black) for heating in air (a) and for acid treatment (b).*

Our future plans are to investigate the influence of the other steps during the peapod synthesis on the Raman spectrum before comparing the results on bulk samples to confocal Raman measurements on individual carbon nanotubes.

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