

Diameter selective charge transfer in p- and n-doped single wall carbon nanotubes synthesized by the HiPCO method

A. Kukovecz,^{*a} T. Pichler,^{ab} R. Pfeiffer^a and H. Kuzmany^a

^a Universität Wien, Institut für Materialphysik, Strudlhofgasse 4, A-1090 Vienna, Austria.

E-mail: akos@ap.univie.ac.at; Fax: +43 1 4277 51375; Tel: +43 1 4277 51369

^b Institut für Festkörper- und Werkstofforschung, Dresden, Germany. E-mail: pichler@ap.univie.ac.at;

Fax: +49 351 4659 537; Tel: +49 351 4659 519

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The unusually broad diameter distribution of single wall carbon nanotubes (SWCNTs) in a HiPCO derived sample made it possible to observe for the first time a selective loss of Raman resonances corresponding to large diameter tubes upon both p- (FeCl₃) and n-type (K) doping.

A major focus of contemporary research on single wall carbon nanotubes¹ (SWCNTs) is exploiting their unique features in real-world applications. SWCNTs are tested as composite additives, field emission devices, microelectronics components and templates for novel nanomaterials. Although the properties of the tubes are mainly governed by their helicity, it is expected that their range of applications could be extended by post-synthetic treatments. Covalent functionalization² changes the bond structure of the nanotube and introduces defects. The reversible fine tuning of the SWCNT's electronic properties was found to be possible by creating charge transfer compounds analogous to graphite intercalation compounds (GICs).³ Prepared by introducing electron donor or acceptor molecules⁴ (referred to as n- and p-type doping, respectively) into the hollows of the SWCNT lattice, the electrical properties can be modified without generating defects in the SWCNT bond network. Albeit manipulating only a chosen fraction of SWCNTs is certainly a crucial point in application development, the issue of selectivity was not addressed in such intercalation studies up till now. We have recently reported⁵ on the unusually broad diameter (*d*) distribution of SWCNTs synthesized by the HiPCO (high pressure decomposition of CO) process,⁶ and realized that combining this feature with different dopant molecule sizes could offer a method for shifting the work function of certain tubes while leaving others intact. Resonant Raman spectroscopy is an excellent tool for such observations, because (i) it possesses a well-developed theory⁷ for assigning different peaks in the radial breathing mode (RBM) part of the Raman spectrum to nanotubes with different diameters, and (ii) changes in the relative peak intensities mirror the changes in the work function due to the resonance effect. In this communication, we present proofs of diameter selective SWCNT doping for the first time.

Doping of standard HiPCO buckypapers (quasi Gaussian diameter distribution centred at 1.0 nm with a width of 0.2 nm) was performed *in situ* as follows. The dopant (99.99% anhydrous FeCl₃ for p-doping and 99.95% K for n-doping) was placed into a quartz tube in Ar atmosphere and mounted on the sample chamber *via* a valve. The system was kept in a dynamic vacuum better than 5×10^{-5} Pa for 24 hours. Then the sample and the dopant were heated to 573 K and sublimation temperature, respectively. Several hours were required to reach the final doping stage, marked "max. doped" in the figures. The highest achievable intercalation level was higher for n-type than for p-type doping. Raman spectra were taken at 80 K with excitation lines of an Ar⁺/Kr⁺ laser in 180° back-scattering geometry, using a Dilor xy spectrometer and a CCD detector.

In Fig. 1 we show the evolution of the normalized Raman RBM at 676 nm excitation upon n- (left side) and p-type (right side) doping, respectively. Both dopants reduce the absolute intensity of the spectrum in general, and superimposed on this

trend we see the selective reduction of certain peaks. At an intermediate K intercalation level the 180 cm⁻¹ peak and the 315 cm⁻¹ shoulder (corresponding to *d* ~ 1.4 and *d* ~ 0.75 nm tubes, respectively) are already wiped out, and the 200 cm⁻¹ and 298 cm⁻¹ peaks (*d* ~ 1.25 nm and *d* ~ 0.82) have lost 75% of their absolute intensity, while peaks between 220 and 270 cm⁻¹ are rather intact. These peaks gradually diminish as the doping continues. The peak experiencing the smallest overall intensity reduction is the one corresponding to the radial breathing modes of some thin tubes (*d* ~ 0.9 nm) and was chosen as a basis for normalization. When doping with FeCl₃ the peaks at 180, 230 and 315 cm⁻¹ are gently reduced while others remain unchanged.

Spectra collected at the same doping levels using 514 nm excitation are presented in Fig. 2. Once again, we observe the disappearance/pronounced reduction of the lowest and highest frequency (184 and 310 cm⁻¹) peaks upon K/FeCl₃ intercalation, respectively. Peaks belonging to SWCNTs of intermediate diameters are smoothly and gradually reduced to baseline when K doping, but suffer only small intensity changes from FeCl₃. Fig. 2 offers an excellent opportunity to observe the selective preservation of peaks in the middle of the RBM region (200–260 cm⁻¹). It is important to emphasize that the observed trends are the same for red and green lasers, even though the former probes thin (*d* ~ 1.0 nm) semiconducting and thicker (*d* ~ 1.4 nm) metallic SWCNTs while the latter induces optically allowed transitions in thicker semiconducting and thinner metallic tubes. Thus, the selective reduction of peak intensities appears to be a primarily diameter selective process which is apparently not directly linked to the electronic conductivity of the SWCNTs.

From the point of view of Raman spectroscopy n- and p-type doping are rather similar. Electron donors⁸ transfer electrons to the conduction band of the SWCNTs while electron acceptors

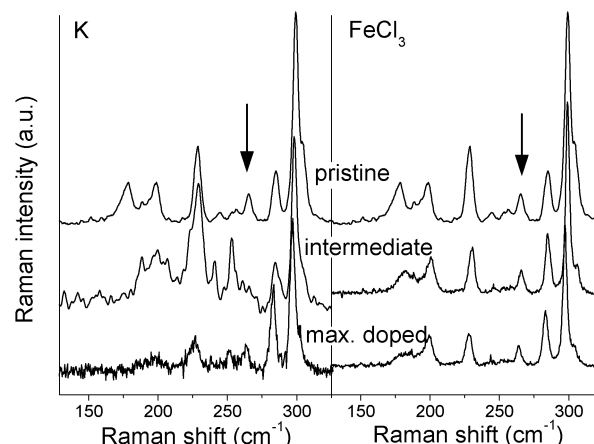


Fig. 1 Raman radial breathing mode as a function of dopant concentration, measured using 676 nm laser excitation. All spectra are normalized to the intensity of the 265 cm⁻¹ peak indicated by an arrow. Peaks at lower wavenumbers correspond to larger diameter SWCNTs which are selectively intercalated while bundles of thinner tubes are not.

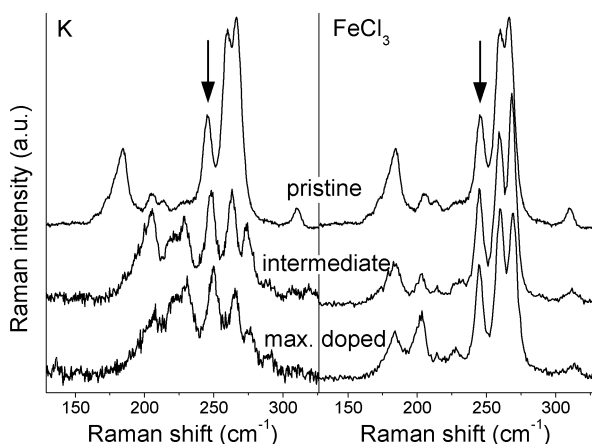


Fig. 2 Raman radial breathing mode as a function of dopant concentration, measured using 514 nm laser excitation. All spectra are normalized to the intensity of the 246 cm^{-1} peak indicated by an arrow.

empty the uppermost states of the valance band. Either way, the one dimensional spikes known as van Hove singularities in the total density of states are filled with electrons or holes to a certain extent, the Fermi level is shifted, and the first few optical transitions between the singularities become forbidden.⁹ This results in a loss of Raman resonance which manifests as a decrease in the intensity of the corresponding peak in the spectrum.¹⁰ However, this simple picture does not explain the observed complexity of the spectral changes as a function of dopant and doping time.

The experimental data can be interpreted as evidence for a diameter selective doping process: the intertube channels in SWCNT bundles consisting of wider tubes are proportionally broader than those of thinner tubes, therefore, the diffusion speed of a given dopant can be larger in them and thus, a larger degree of intercalation can be reached during the period of observation. This is why the RBM peaks are reduced from left to right with doping time in both figures showing K doping. Moreover, wider intertube channels can be entered by larger dopant molecules. It is known that below 600 K iron(III) chloride vapour consists of mainly Fe_2Cl_6 molecules of D_{2h} symmetry.¹¹ Modelling Fe_2Cl_6 by a cylinder and K^+ by a sphere it can be derived that the effective radius of the former is nearly two times larger than that of the latter. Therefore, it seems reasonable to assume that Fe_2Cl_6 can only enter the bundles of the SWCNTs with the largest diameter, resulting in a selective loss of peak intensity in the left end of the RBM spectra.

It should be mentioned that the intertube channels of the SWCNTs abundant in a typical HiPCO sample are not necessarily wide enough even for potassium. The possibility of lattice expansion upon intercalation is well-known from the chemistry of GICs,³ and has been suggested to occur in doped nanotubes as well by *e.g.* Rao *et al.*⁴ Grigorian *et al.*¹² utilized XRD and Raman data to show experimentally that the tubes in a SWCNT rope can be opened and closed 'zipperlike' upon polyiodide intercalation. Taking $r_{\text{K}} = 138$ pm and $r_{\text{Fe}_2\text{Cl}_6} = 362$ pm as the effective van der Waals radius of K^+ spheres and Fe_2Cl_6 cylinders, respectively and assuming an ideal close packed triangular lattice of identical SWCNTs, the lattice expansion needed to fit a dopant molecule into the nanotube bundle can be calculated easily. Results of such calculations for SWCNTs thought to be present in a HiPCO sample are given in Table 1. The required expansion is quite reasonable for K doping, but quickly reaches unrealistically high figures for Fe_2Cl_6 doping. It seems logical to assume that the diameter selective intercalation phenomenon originates from differences in the lattice expansion work needed by various 'SWCNT diameter-dopant diameter' pairs. The unexpected loss of intensity at the right end (very thin tubes) of the RBM may originate from the inversely proportional diameter dependance of the van der Waals forces keeping the tubes together.¹³

Table 1 Calculated isotropic expansion of the triangular SWCNT lattice necessary to accommodate a dopant molecule

$d_{\text{SWCNT}}/\text{nm}$	Required lattice expansion (%)	
	For K	For Fe_2Cl_6
1.4	0.4	22.6
1.2	2.1	27.3
1.0	4.4	33.4
0.8	7.5	41.6

Because of the smaller number of carbon atoms available for secondary bonding and the larger pyramidization angle, bundles of the thinnest SWCNTs are probably more easily pushed apart by a potential dopant species than those of thicker ones. This inverse effect is thought to compete with the primary dopant size dependance, the overall result being a complex dopability vs. SWCNT diameter curve which probably has a minimum between $d \sim 0.9$ and $d \sim 1.2$ nm.

We believe that this study has raised an important issue concerning the intercalation compounds of SWCNTs, which was previously overlooked because of the lack of nanotube samples possessing a broad enough diameter distribution centred at a sufficiently small value such as the now available HiPCO tubes. More studies are required to (i) quantify the non-selective doping caused by dopants adsorbed on the outer surface of bundles, (ii) to extend the model to SWCNT bundles consisting of tubes of different diameters and (iii) to examine the limits of energetic feasibility of tube-tube separation by dopant molecules.

On the basis of the present findings we suggest that by using HiPCO SWCNTs and systematically varying the size and electrostatic potential of dopants a full map of 'tube diameter-dopant molecule-Fermi level shift' triplets could be obtained. This could be a real asset for carbon nanotube technology, since it would open the road for *selectively* modifying the electronic properties of SWCNTs using the *existing* synthesis techniques without any special purification process.

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