

Studies of multiwall carbon nanotubes using Raman spectroscopy and atomic force microscopy

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Abstract. We present preliminary results of Raman scattering measurements of multiwall carbon nanotubes (MWCNT). The nanotubes have been carefully dissolved, separated and then characterized by AFM. The micro-Raman spectra of the objects are taken with 514,5nm wavelength excitations and in the temperature range 4K - 400K. Basically the spectra are quite similar to the well known single wall carbon nanotube spectra, with the exception of the absence of low frequency band. The major Raman bands, that are observed in single wall nanotubes are found in the spectra. In particular the disorder effects are visible due to the pronounced D band at $\sim 1350\text{ cm}^{-1}$. Metallic and semiconducting type of conductivity is distinguished through an analysis of the G (LO) mode at $\sim 1600\text{ cm}^{-1}$. We noticed new feature in these spectra at $\sim 843\text{ cm}^{-1}$. Low energy radial breathing mode absence has been also explained.

Introduction

The rapid progress of interest in carbon nanotubes research shows that atomic force microscope (AFM) is also an excellent tools for single nanotube characterization and treatment. At the same time it has been shown that Raman spectroscopy is also a sensitive method of carbon nanotube characterization. Due to the specific combination of strong van Hove singularities of the phonon density of states and Raman resonance effects it is possible to measure Raman scattering spectra of a small bundle of carbon nanotubes or even of a single nanotube. Recent progress in understanding of the Raman spectra of relatively simple single wall carbon nanotubes [1] stimulate the further Raman studies of more complicated multiwall carbon nanotubes. The combination of these two methods (Raman spectroscopy and AFM) of characterization of MWNT gives a new wider approach to the structure and quality characterization carbon nanotubes.

Experiment and sample preparation

The nanotubes have been grown by catalytic (Ni:Ce) method and have been purified. The functionalization of the MWNT was performed as follows. First, a small amount of nanotubes (powder form) has been immersed in solvent. We have tested four different kinds of solvents (chloroform, dichloromethane, toluene, isopropanol, 1,2-dichloroethane), but dichloromethane gave the best results. For preliminary separation of nanotubes we used solution (MWNT with solvent), which was exposed to ultrasonic agitation for a few hours. We have also used spin-coating method to place completely separated nanotubes on an appropriate surface. We tested simultaneously three surfaces: HOPG (Highly Oriented Pyrolytic Graphite), Si and SiO₂, and finally we have chosen the latter one. We noticed here that interaction between SiO₂ and MWNT is very significant, likely due to strong van der Waals forces. Adhesion of nanotubes is astonishingly strong which is an important factor of the procedure of nanotubes separation. The idea of spin-coating method is quite simple. A drop of the falls onto fast rotating surface (2500rpm) and is homogenously splashed on the surface. The procedure gives an additional contribution to the separation of nanotubes.. The nanotubes were characterized with AFM (Fig. 1) in tapping mode (Nanoscope IIIa, Digital Instruments) and Raman

spectra was recorded using DILOR 800 XY spectrometer. The Raman experiments were performed in ambient conditions and in helium condition for low temperature measurements, in backscattering configuration. For laser excitation we used 514.5 nm (2.41eV) line from an Ar⁺. AFM experiments were performed in ambient condition. For sample scanning we used silicon tips.

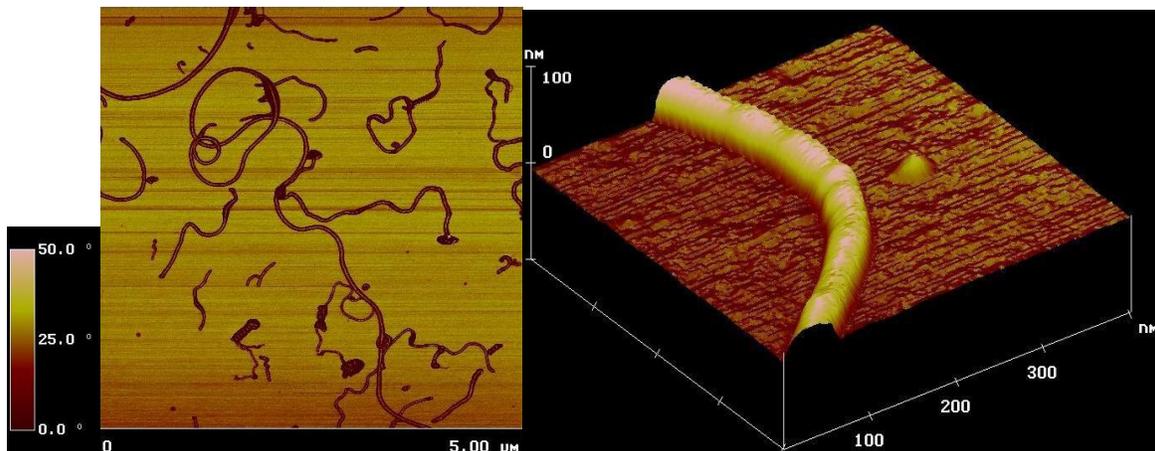


Fig. 1 Left part: AFM scan image (phase mode) of separated multiwall carbon nanotubes on SiO₂ surface; right part: 3D view (topography mode) on one of these nanotubes. Nanotubes are from catalytic (Ni:Ce) method. There is Si (001) layer under the SiO₂ 250 nm layer.

Results and discussion

Interpretation of Raman spectra of SWNT has been provided by Rao et al. [2] and Dersselhaus et al. [3]. Recently less known multiwalled nanotubes have been studied extensively by Raman scattering [5, 6, 7]. The results have been compared with SWNT.

All the Raman spectra shown in this paper were taken on the sample that contained randomly oriented MWCNT with different concentration of nanotubes on the SiO₂ surface. Two different concentrations of nanotubes have been examined, one with nanotube concentration of approximately a few hundreds per 1 μ m circle (diameter of the laser spot) and second, with the concentration of few thousands nanotubes per 1 μ m spot. The Raman spectra are presented at Fig. 2. The difference between concentration can be seen considering the peaks which come from Si (303cm⁻¹, 521 cm⁻¹, 963 cm⁻¹). We noticed that carbon nanotubes are good light absorbent, so the sample with high concentration of nanotubes (Fig. 2a) have Si modes with lower intensity.

Raman studies of multiwalled nanotubes with large diameter distribution showed quite strong similarities to the well known SWNT modes [4]. In our Raman spectra three dominating features are seen. At Fig. 2: two sharp Raman peaks, namely G(graphite)-, D(disorder)-band are seen. Their second-order harmonic (the G' band), explicitly appears at ~1580 cm⁻¹, ~1360 cm⁻¹ and ~2700 cm⁻¹, respectively. In addition, a small feature called G2 or D' near 1610 cm⁻¹ and others distinguishable features like G+D band (~2930 cm⁻¹) and a small peak at ~ 843 cm⁻¹, were observed. One important feature, a low energy radial breathing mode at 248/d_t cm⁻¹, where d_t is tube diameter usually observed in SWNT Raman spectra is not seen in our spectra.

Position and intensity of our Raman peaks are in good agreement with theoretical calculations for single walled nanotubes, which shows that the vibration structure of multiwalled is quite similar to the single walled nanotubes [4].

The tangential G-band (at ~1580 cm⁻¹), which derived from the graphite-like in-plane mode, here (Fig. 2) is split into several modes where these two are the most distinct: G1 (1577 cm⁻¹) and G2 (1610 cm⁻¹). This result was also observed in the other papers [2,8]. These bands are related to the lattice vibration of all carbon materials with sp² bonds. The shape of the G Raman peak gives

possibility to distinguish between semiconducting or metallic nanotubes. Here, we think, the nanotubes are associated with semiconducting type of conductivity. In purified sample G band is narrower than in not purified, so the spectra shows that our samples were well purified.

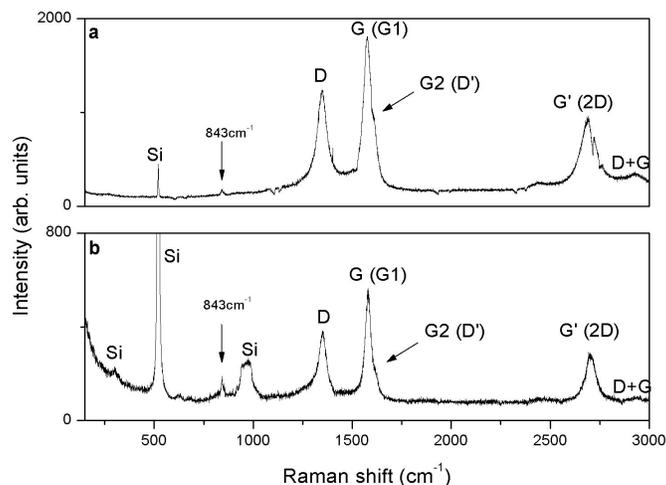


Fig. 2 Raman spectra of a bundle of multiwalled carbon nanotubes with high concentration (a) and low concentration (b).

The disorder-induced D-band and its second-order harmonic, the G'-band were observed in all our spectra. These two features both appear in the Raman spectra of semiconducting and metallic carbon nanotubes. In the purified sample, the D-band is weaker [5], but it can be also connected with intrinsic impurities (defects) of nanotubes. It means that these carbon nanotubes are not the same quality, because in all spectra we observed the same intensity for the D-band. We also observed intensity variation of the G'-band. AFM has been used here (Fig. 1) to check the sample if the nanotubes are good quality, i.e. what is the arrangement of nanotubes on the surface; if the nanotubes have bends or are they straight. The arrangement of nanotubes can cause some structural changes e.g. strain deformation, and these changes can be detected with Raman spectroscopy. Additionally with AFM we can detect some impurities on the sample, i.e. small amount of soot, amorphous carbon and catalyst leftovers.

There is the interesting small feature at 843 cm^{-1} , which is associated with armchair ($n=8$ to 11) single walled nanotubes [2]. All armchair nanotubes with this chirality are assigned as a semiconducting type of nanotubes. That confirms the conclusion drawn from the G-band. This feature was not observed in other studies concerning Raman spectroscopy of multiwall nanotubes.

In all our spectra we didn't find radial breathing mode peaks. The explanation of this behavior can be made in two ways. First, when the nanotubes can consist of too many walls (>20) and second the inner wall diameter is too big ($>2\text{ nm}$) [5], and consequently the low energy peaks are too weak to be observed. From AFM studies we estimate outer diameter of nanotubes between 18 nm and 40 nm . Unfortunately from AFM we can say nothing about internal diameter. Only from Raman spectra we can estimate that internal tubes are bigger than 2 nm in diameter.

To reduce noise we performed low temperature Raman spectroscopy (Fig. 3) but radial breathing mode was still not visible. Besides there was not significant changes in spectra in temperature range $4\text{ K} - 400\text{ K}$. Only some insignificant shift of the major Raman peaks can be observed as well as an anharmonic broadening of the peaks.

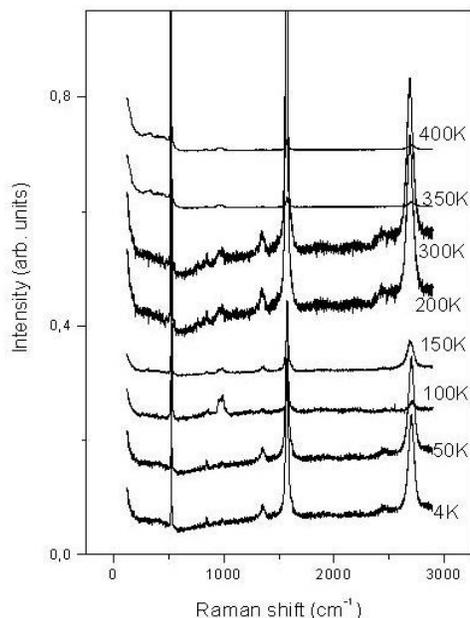


Fig. 3 Temperature dependence of Raman spectra of a bundle multiwalled carbon nanotubes.

Conclusion

Raman spectroscopy and AFM are excellent method of characterization of electronic and structural properties of multiwalled carbon nanotubes. Our Raman experiments have been performed on bundles of nanotubes and are in good agreement with existing literature results. There is also new feature in Raman spectra at 843 cm^{-1} , which was not observed in other Raman spectra studies but it was theoretically calculated. We developed a method of functionalization of nanotubes which probably allows to work also on a single nanotubes. By optymalization of functionalization parameters we think it is possible to obtain such good separation of nanotubes that we could work only on one of them.

Reference

- [1] Raman spectroscopy on isolated single wall carbon nanotubes M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, R. Saito, *Carbon* **40**, 2043-2061, (2002).
- [2] A.M. Rao, E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, G. Dresselhaus, M. S Dresselhaus, *Science* **275**, 187 (1997)
- [3] M.S. Dresselhaus, G. Dresselhaus, A. Jorio, et al., *Carbon* **40**, (2002) 2043-2061
- [4] P.C. Eklund, J.M. Holden, R.A. Jishi, *Carbon* **33**, (1995) 959
- [5] J.M. Benoit, J.P. Buisson, O. Chauvet, C. Godon, S. Lefrant, *Phys. Rev. B* **66**, 073417 (2002)
- [6] H. Jantoljak, J.P. Salvetat, L. Forro, C. Thomsen, *Appl. Phys. A: Mater. Sci. Process.* **67**, 113 (1998)
- [7] H. Kataura, Y. Achiba, X. Zhao, and J. Robertson et al., *Amorphous and Nanostructured Carbon*, edited by J. Robertson et al., Mater. Res. Soc. Symp. Proc. No. 593 (Materials Research Society, Warrendale, 2000), p.113
- [8] G. S. Duesberg, I. Loa, M. Burghard, K. Syassen, and S. Roth *Phys. Rev. Let.* **85**, 25 (2000)