

Studies of Multiwall Carbon Nanotubes using Raman Spectroscopy and Atomic Force Microscopy

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Abstract. Preliminary results of Raman scattering measurements of multiwall carbon nanotubes (MWNT) are presented. The nanotubes have been carefully dissolved, separated and then characterized by AFM. The micro-Raman spectra are taken with 514,5nm wavelength excitations in the range 4K - 400K. Basically the spectra are quite similar to the well known single wall carbon nanotube spectra, but the low frequency band is absent. The major Raman bands, 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 cm^{-1} . Metallic and semiconducting type of conductivity is distinguished through analysis of the G (LO) mode at \sim 1600 cm^{-1} . A new feature in these spectra exists at \sim 843 cm^{-1} . Low energy radial breathing mode absence has been explained.

Introduction

The rapid development of carbon nanotubes research shows that atomic force microscopy (AFM) is an excellent tool for single nanotube characterization and treatment and that Raman spectroscopy is 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 the Raman spectra of relatively simple single wall carbon nanotubes [1] stimulated further Raman studies of more complicated multiwall carbon nanotubes. The combination of Raman spectroscopy and AFM for characterization of MWNT gives a new wider approach to the structure and quality of characterization..

Sample Preparation and Experimental Procedure

The nanotubes were grown by the catalytic (Ni:Ce) method and were purified. The functionalization of the MWNT was performed as follows. First, a small amount of nanotubes in powder form were immersed in appropriate solvent. A few different solvents were tested, but dichloromethane gave the best results. For preliminary separation of the nanotubes a solution of MWNT was used and exposed to ultrasonic agitation for a few hours. The spin-coating method to place completely separated nanotubes on an appropriate surface was also used. Three surfaces were tested: HOPG (Highly Oriented Pyrolytic Graphite), Si and SiO_2 , and finally SiO_2 was chosen. It was noticed that interaction between SiO_2 and MWNT is very significant, probably due to strong van der Waal's forces. The adhesion of nanotubes is astonishingly strong which is an important factor in the procedure of nanotube separation. The spin-coating method is quite simple. We put the drop of the solution with nanotubes onto fast rotating SiO_2 surface (2500rpm), what cause that nanotubes are uniform spread on the surface. This 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 the Raman spectra was recorded using DILOR 800 XY spectrometer. The Raman experiments were performed in ambient conditions and in helium for low temperature

measurements, in backscattering configuration. For laser excitation 514.5 nm (2.41eV) line from an Ar⁺ was used and AFM experiments were performed in ambient condition. For sample scanning silicon tips were used.

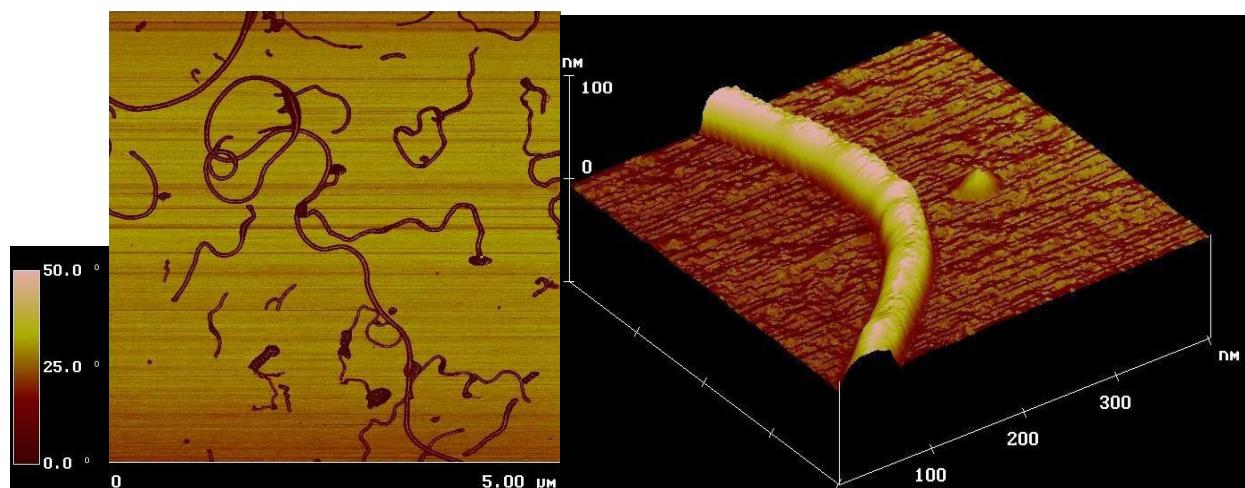


Fig. 1 Left part: AFM scan image (phase mode) of separated multiwall carbon nanotubes on SiO₂ surface; right part: 3D view (topography mode) on one of these nanotubes. Nanotubes are from catalytic (Ni:Ce) method. There is Si (001) layer under the SiO₂ 250 nm layer.

Results and discussion

Interpretation of Raman spectra of SWNT has been provided by Rao et al. [2] and Dersselhaus et al. [3]. Recently multiwalled nanotubes have been studied extensively by Raman scattering [5, 6, 7] and compared with SWNT. All the Raman spectra shown in this paper were taken on samples containing randomly oriented MWCNT with two different concentrations of nanotubes on the SiO₂ surface. One sample had a nanotube concentration of approximately a few hundreds per 1 μm circle (diameter of the laser spot) and second, with a few thousands nanotubes per 1 μm spot. The Raman spectra are presented at Fig. 2. The difference between the samples can be seen by considering the peaks from Si (303 cm⁻¹, 521 cm⁻¹, 963 cm⁻¹). It was noticed that carbon nanotubes are good light absorbers, so the sample of high MWCNT concentration (Fig. 2a) has Si modes of lower intensity.

Raman studies of multiwalled nanotubes with large diameter distribution showed quite strong similarities to the SWNT modes [4]. The Raman spectra show three dominating features. In 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 other 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 absent. The position and intensity of Raman peaks are in good agreement with theoretical calculations for single walled nanotubes, showing that the vibration structure of MWCNT is similar to single walled nanotubes [4].

The tangential G-band (at ~1580 cm⁻¹), which derived from the graphite-like in-plane mode, (Fig. 2) is here split into two distinct peaks: G1 (1577 cm⁻¹) and G2 (1610 cm⁻¹). This was also reported in 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 the possibility of distinguishing between semiconducting or metallic nanotubes. It is believed that these nanotubes are associated with semiconducting type of conductivity. In the purified sample the G band is narrower than with the unpurified, which shows that these samples were well purified.

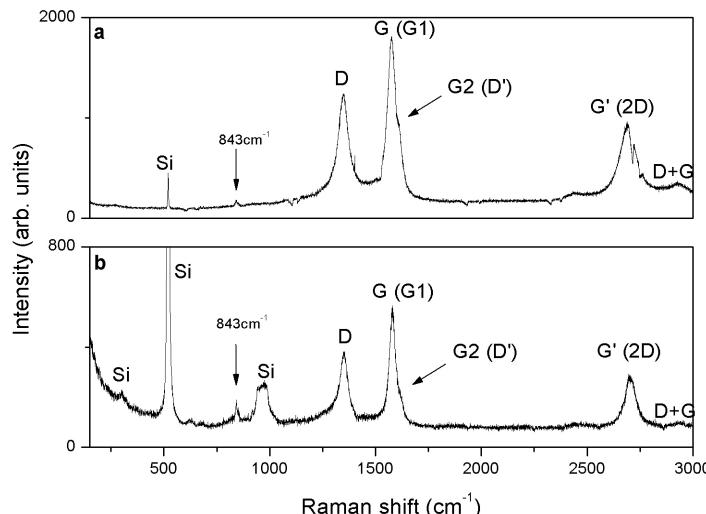


Fig. 2 Raman spectra of a bundle of multiwalled carbon nanotubes with high concentration (a) and low concentration (b).

The disorder-induced D-band and its second-order harmonic, the G'-band were observed in all 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 the same intensity for the D-band was observed. Intensity variation of the G'-band was also seen. AFM was used (Fig. 1) to check if the nanotubes were of good quality, i.e. what is the arrangement of nanotubes on the surface; if the nanotubes were bent or straight. The arrangement of nanotubes can cause some structural changes e.g. strain deformation, and these changes can be detected with Raman spectroscopy. In addition AFM can detect for impurities on the sample, i.e. small amount of soot, amorphous carbon and catalyst residue.

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 the semiconducting type of nanotubes. That confirms the conclusion drawn from the G-band. This feature was not observed in other studies of Raman spectroscopy of multiwall nanotubes.

Radial breathing mode peaks were not found in any of the spectra. The explanation of this behaviour can be made in two ways. First, when the nanotubes consists of too many walls (>20) and secondly the inner wall diameter is too big ($>2\text{ nm}$) [5], consequently the low energy peaks are too weak to be observed. From AFM studies the estimated outer diameter of nanotubes was between 18nm and 40nm. Unfortunately from AFM nothing can be said about the internal diameter. Only from Raman spectra can it be estimated that internal diameters exceed 2 nm.

To reduce noise low temperature Raman spectroscopy (Fig. 3) was performed but radial breathing mode was still not visible. Besides there were no significant changes in the spectra in the temperature range 4K - 400K. Only some insignificant shift of the major Raman peaks can be observed as well as an anharmonic broadening of the peaks.

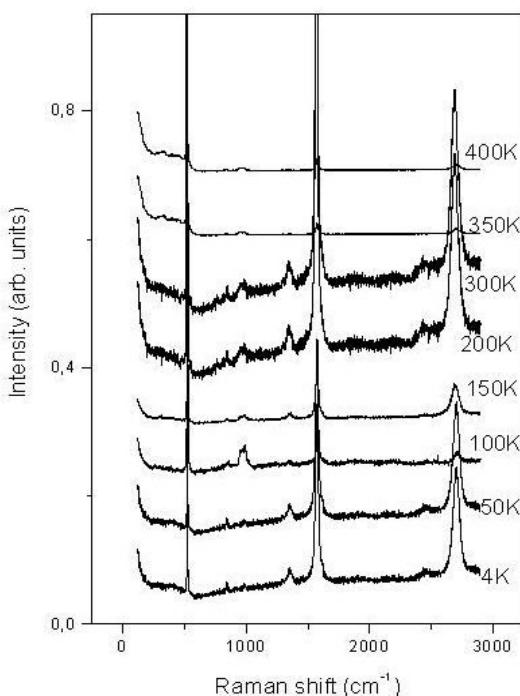


Fig. 3 Temperature dependence of Raman spectra of a bundle multiwalled carbon nanotubes.

Conclusion

Raman spectroscopy and AFM are excellent methods for characterization of the electronic and structural properties of multiwalled carbon nanotubes. The Raman experiments were performed on bunches of nanotubes and are in good agreement with results given in existing literature. There is also a new feature in Raman spectra at 843 cm^{-1} , which was not observed in other Raman spectra studies but it was theoretically calculated. A method of functionalization of nanotubes was developed which probably allows work on a single nanotube. By optimizing functionalization parameters it is believed that it is possible to obtain such good separation of nanotubes that work could be done on a single nanotube.

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