

Investigation of effects produced by chemical functionalization in single-walled and multi-walled carbon nanotubes using Raman spectroscopy

SHAHIR HUSSAIN¹, KHURSHED A. SHAH^{2*}, S. S. ISLAM¹

¹Nano-Sensor Research Laboratory, Dept. of Applied Sciences & Humanities, Faculty of Engineering and Technology, Jamia Millia Islamia (Central University), New Delhi-110025, India

²Department of Physics, Govt. Degree College for Women Anantnag Kashmir, (J&K), India-192101

Single-wall carbon nanotubes (SWNTs) as well as multi-wall carbon nanotubes (MWNTs) were characterized by Raman spectroscopy to observe the changes in their physical and structural properties on functionalization. When SWNTs or MWNTs are chemically treated, the defects are created. The analysis of radial breathing mode (RBM) showed that the diameter of the single wall carbon nanotubes changed after functionalization. In the carboxylated sample, the intensity of the disordered band (D-mode) increased more than in the pristine samples. The increase in the D-band intensity in SWNTs after functionalization can be attributed to carbon atoms excited from sp^2 to sp^3 hybridization. A higher intensity ratio in D-and G-mode (I_D/I_G) was observed after functionalization with carboxylic group (COOH). The intensity ratio I_D/I_G increased on acid treatment which was evident from the Raman spectra and their analysis. In case of MWNTs, the intensity of D band became equal to the intensity of G band, which was due to the huge number of defects that had been introduced in the sidewalls. Moreover, it was found in this study that the MWNTs can be much easier chemically functionalized than SWNTs under the same physical conditions.

Keywords: *carbon nanotubes characterization; intensity ratio; chemical functionalization; Raman spectroscopy*

© Wrocław University of Technology.

1. Introduction

Since their discovery in 1991 by Iijima and co-workers [1] carbon nanotubes (CNTs) due to their unusual electronic, electrical [2] and adsorptive properties as well as their good chemical stability, have attracted the attention of researchers worldwide. They are expected to have numerous potential applications, for example, high-strength composites [3] sensors [4] actuators [5] gas storage media [6] field emitters [7] tips for scanning probe microscopy [8] and nanoelectronic devices [9]. CNTs produced by different methods contain some catalyst particles, amorphous and other carbon materials, and it is difficult to disperse CNTs in solvents, which is the reason of their poor processability. To overcome this limitation, several strategies have been developed by functionalization. Initial

studies indicated that chemical functionalization of the open ends and the walls of CNTs would play a vital role in tailoring their properties and applications [10]. Functionalization process decreases van der Waals forces between CNTs leading to their de-bundling, and aids binding to other materials [11]. As a model for functionalization [12] the carboxylic groups (COOH) were found on the sidewall or open end of a tube after oxidation of carbon nanotubes by strong acids [13]. The leading approaches to functionalization include covalent chemistry of conjugated double bonds within the CNTs, $\pi - \pi$ stacking, covalent interactions at nanotube ends, sidewalls and defects as well as wrapping of polymers [13–15].

An oxidation method is the oldest and the simplest method that does not require any special equipment and is still widely used for CNT purification and functionalization [16–19]. Liu et al. reported that 3:1 concentrated H_2SO_4/HNO_3

*E-mail: drkhursheda@gmail.com

mixture could be used to cut the long CNT ropes into short, open-ended pipes and thus produce many carboxylic groups (COOH) at the open ends [20]. Strong acid treatments of CNTs have been introduced traditionally for purification, chemical oxidation [21] modification of lengths and functionalization of the tube ends or sides. Due to the chemical oxidation, the ends and walls of the nanotubes are covered with oxygen containing the groups such as carboxylate groups or ether groups [22–26].

In the present paper, we have systematically investigated the comparative effect of chemical treatment on the structure of CNTs by means of Raman spectroscopy at room temperature. We have carried out the oxidation of SWNTs as well as MWNTs by two methods (a) ultrasonication and (b) refluxing in an oxidizing medium. The experimental conditions of ultrasonication and acid refluxing were the same for both SWNT and MWNT samples.

2. Experimental section

SWNTs (purity 90 %, ash 1.5 %, length 30 μm and diameter $< 1 - 2$ nm) and MWNTs (purity 95 %, length 1 – 2 μm and diameter < 10 nm) were procured from NTP, China. 15 mg CNT of both types, SWNTs as well as MWNTs were added to a solution containing HNO_3 : H_2SO_4 at a ratio of 1:3 in separate containers. A multi-frequency ultrasonicator was used to disperse the CNTs in the acid solution. The sonication was conducted at a frequency of 40 kHz for 10 min. After dispersion, the solution was transferred to an acid refluxing flask and refluxing was carried out for 10 h, using a rotary evaporator. After acid treatment the solution was quenched in ice-cold water, and the samples were diluted. After base neutralization of the acid solution, the CNTs were extracted on a polycarbonate membrane with 0.2 μm pore size using a vacuum filtration assembly. The resulting CNTs were dried in an oven at 70 $^\circ\text{C}$ for 12 h. The pristine (raw) and functionalized samples were studied by Raman scattering measurements with a Raman spectrometer (Lab Ram HR 800, JY). The samples were excited with a laser at a excitation wavelength of 488 nm.

3. Results and discussions

One of the most popular techniques for the analysis of carbon nanotubes is Raman spectroscopy. It is a non-destructive measurement, which is made at ambient conditions. In particular, resonance Raman spectroscopy can select those nanotubes in a nanotube sample which are resonant with the excitation laser energy. Thus we can observe the properties of a nanotube by resonance Raman spectroscopy even for a bundle of nanotubes. However, a specific nanotube with a definite diameter/or chirality cannot be produced or selected at will. Raman spectroscopy is very informative and important for characterizing functionalized carbon nanotubes (F-CNTs). The most important is that it indicates the evidence of covalent functionalization by the analysis of D-mode. It has the greatest significance among all available techniques applied to characterization of functionalized carbon nanotubes.

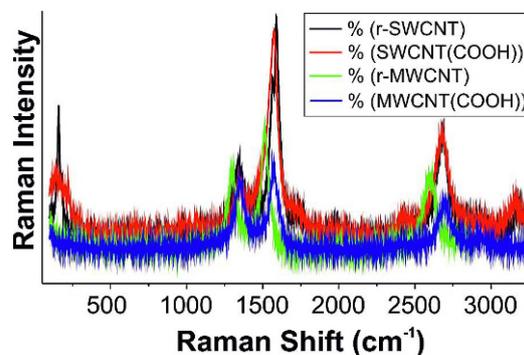


Figure 1. Raman spectra of pristine and functionalized single-wall and multi wall-carbon nanotubes for laser excitation line 488 nm.

Raman spectra are usually divided into three first order bands called modes, the radial breathing mode (RBM), the disorder mode (D-mode), and the tangential mode (G mode). We have focused on three main features of CNT Raman scattering: the radial breathing mode (RBM) ($\sim 100 - 300$ cm^{-1}), the Raman active D band (~ 1300 cm^{-1}), G band (~ 1592 cm^{-1}) [27–29]. Fig. 1 shows the comparative Raman spectra of pristine and functionalized single-wall and multi-wall carbon nanotubes.

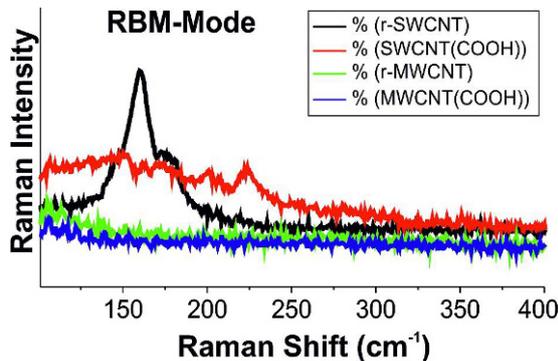


Figure 2. RBM-mode Raman spectra of pristine and functionalized SWNTs and MWNTs for laser excitation line 488 nm.

In all the spectra, the RBM, the D-mode and the G-mode can be observed. The RBM gives the information about diameter distribution in the sample, the D-mode appears due to disruption of sp^2 network of SWNTs. However, the occurrence of D-band in Raman spectra can also be related to the presence of defects such as vacancies, 5 – 7 pairs, or dopants. The tangential G-mode is characteristic of sp^2 carbon in the hexagonal graphene network. The RBM spectra of single and multi-wall nanotubes in pre and post functionalization are shown in Fig. 2.

It is seen from Fig. 2 that the Raman intensity of the RBM spectra decreases for SWNTs after oxidation. On the other hand, the RBM in MWNTs is usually too weak to be observable because of the large diameter of the outer tubes for typical MWNTs. Fig. 3 shows the RBM spectra of SWNTs in pre and post functionalization states. Consider the peaks at 138, 143, 160, 172 and 199 cm^{-1} in the RBM spectra of pristine SWNTs (Fig. 3a), which represent the major peaks in the tube diameter distribution of the SWNTs. Using the relation:

$$\omega_{RBM} = A/d_t + B \quad (1)$$

where A and B are determined experimentally ($A = 234 \text{ cm}^{-1}$, and $B = 10 \text{ cm}^{-1}$ for SWNT bundle) [30], the corresponding diameters d_t are 1.828, 1.759, 1.570, 1.444, 1.238 nm respectively. Similarly, considering the peaks at 131, 150, 160, 200, 223 cm^{-1} in the RBM spectra of functionalized SWNTs (Fig. 3b) and using the re-

lation 1, the corresponding tube diameters are 1.933, 1.671, 1.560, 1.231, 1.098 nm respectively. It is clear that the diameter of the carbon nanotubes after functionalization changes. The spectra of pristine and functionalized SWNTs are shown in Fig. 4a and 4b, respectively. The D mode at 1350 cm^{-1} has been known in graphite for over a few decades and this is induced by disorder and not by Γ point phonon. In carbon nanotubes the D mode is observed at somewhat smaller wavenumber than in graphite and shifts at a rate between 38 and 65 cm^{-1}/eV with laser excitation energy. In our spectra, Fig. 4a, the D-mode is observed at 1339 cm^{-1} which is lower than the D-mode wavenumber from graphite. The intensity of D-mode peak increases in SWNTs after functionalization, Fig. 4b. The Raman spectra indicate that the acid treatment leads to a high level of defects on the tube walls. This results in the relative intensity of the D mode which can be attributed to the increased number of structural defects and to the sp^3 hybridization of carbon for chemically induced disruption of the hexagonal carbon order in the nanotube after chemical functionalization.

In MWNTs (COOH) (Fig. 5b) the D-mode at (1000 – 1400 cm^{-1}) caused by sp^3 defects is almost equal to G-mode (1594 cm^{-1}) peak intensity [31]. The intensity ratio of D-mode to G-mode was compared for the pristine and functionalized MWNTs. In SWNTs spectra shown in Fig. 4 the intensity ratio I_D/I_G increases from 0.083 for pristine to 0.118 for the COOH functionalized. In MWNTs shown in Fig. 5, the intensity ratio I_D/I_G increases from 0.541 for pristine to 0.974 for the COOH functionalized.

This shows that the intensity ratio of functionalized MWNTs is greater than in the pristine MWNTs. This is due to oxygenated functional groups introduced onto the sidewalls and the end walls of the tubes. Furthermore, the difference in the ratio I_D/I_G for MWNTs is higher than for SWNTs. This shows that more oxygenated functional groups are introduced onto the sidewalls of MWNTs than on the sidewalls of SWNTs. The attached chemical functional groups can perform as either an electron acceptor or a donor and it makes possible to transfer charge with nanotubes.

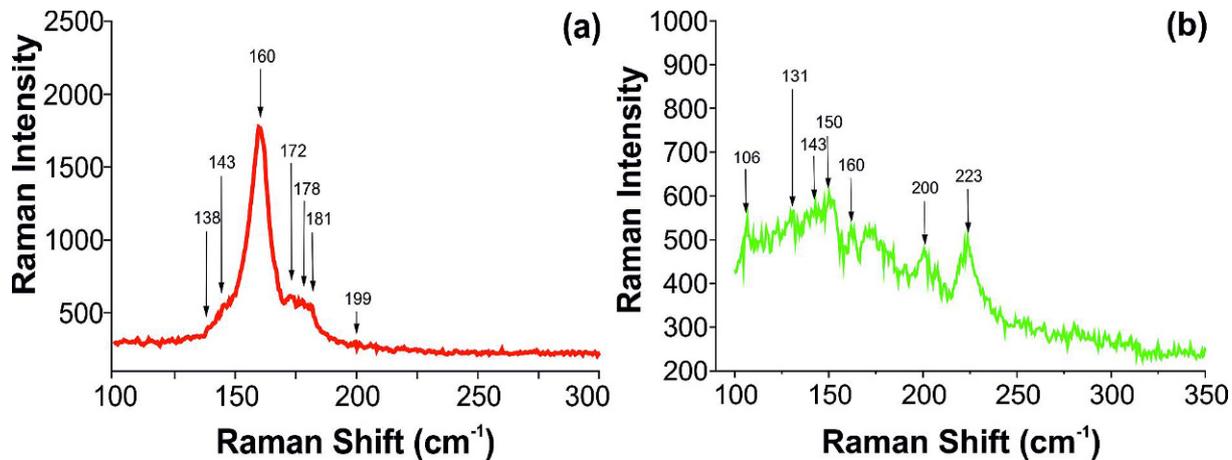


Figure 3. RBM Raman spectra of pristine (a) and SWNTs (COOH) (b) for laser excitation line 488 nm.

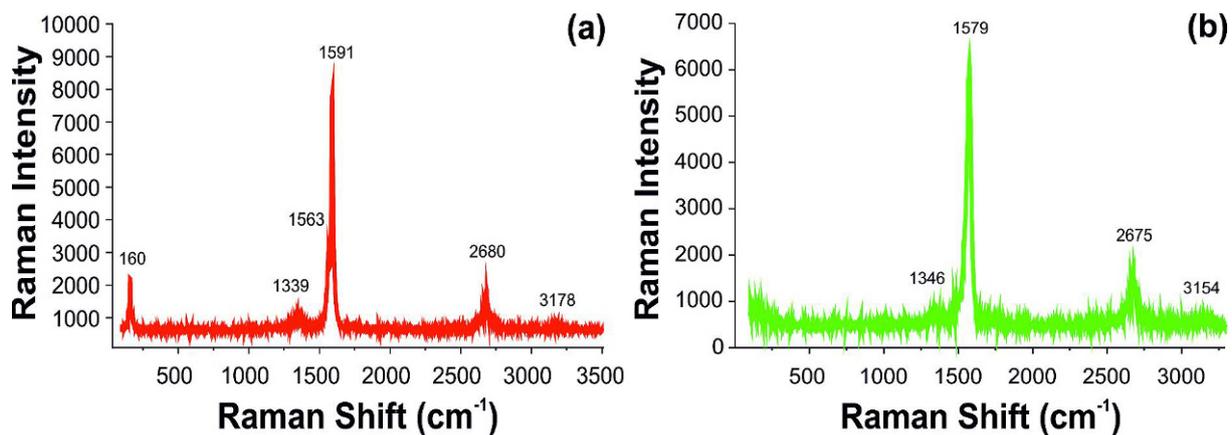


Figure 4. Raman spectra of pristine (a) and SWNTs (COOH) (b) for laser excitation line 488 nm.

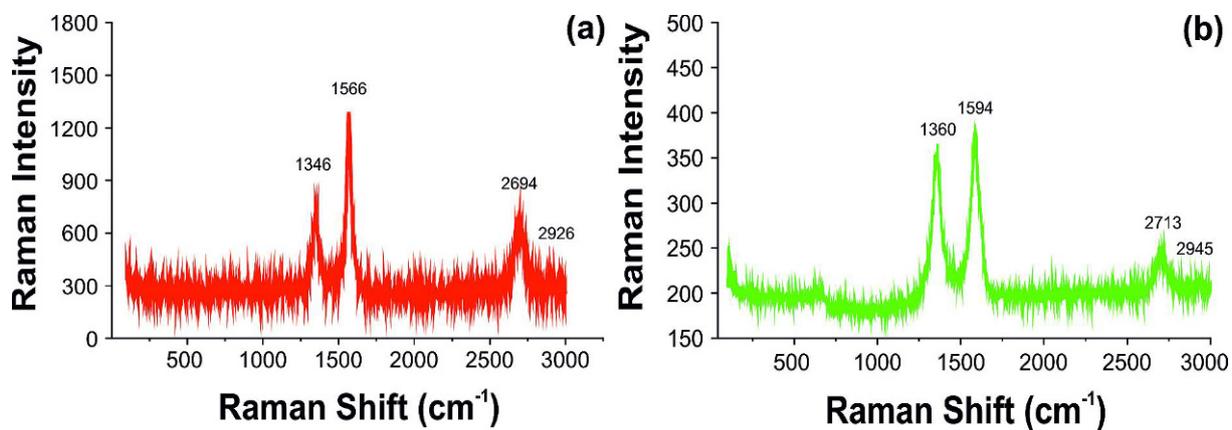


Figure 5. Raman spectra of pristine (a) and MWNTs (COOH) (b) for laser excitation line 488 nm.

The increase in the D-band intensity may be attributed to the sp^3 carbons present in the CNTs after functionalization. In pristine MWNTs, the peak at $\sim 1566\text{ cm}^{-1}$ in the G band region, related to metallic tubes, is clearly observed in Fig. 5. But this peak is no longer observed in the spectrum of the tubes after functionalization due to the loss of metallic tubes. Our result is in agreement with the published reports [30, 31].

4. Conclusions

Pristine CNTs were functionalized by carboxyl group (COOH) through chemical route and characterized by Raman spectroscopic analysis. The vibrational modes like RBM, D-and G-mode were observed in pristine as well as functionalized samples. The analysis of RBM spectra showed that the diameter of SWNTs changed after chemical functionalization. It was observed that the ratio of I_D/I_G of functionalized CNTs is greater than in the pristine CNTs. The shift of D- and G-mode confirmed the attachment of the functional group to the sidewalls of the tubes and charge transfer from the functional group. It was observed that there were more defects in the MWNTs compared to the SWNTs. The increase in the D-band intensity after functionalization can be attributed to the carbon atoms excited from sp^2 to sp^3 hybridization. The results of this study show that the diameter of SWNTs changes after acid treatment and the multi-wall carbon nanotubes can be easier functionalized than the single-wall carbon nanotubes under the same chemical and physical conditions.

References

- [1] IJIMA S., *Nature*, 354 (1991), 56.
- [2] EBBESEN T.W., LEZEC H. J., HIURA H., BENNETT J. W., GHAEMI H. F., THIO T., *Nature*, 382 (1996), 54.
- [3] CALVERT P., *Nature*, 399 (1999), 210.
- [4] KONG J. et al., *Science*, 287 (2000), 622.
- [5] BAUGHMAN R. H. et al., *Science*, 284 (1999), 1340.
- [6] DILLON A.C., JONES K. M., BEKKEDAHL T. A., KIANG C. H., BETHUNE D. S., HEBEN M. J., *Nature*, 386 (1997), 377.
- [7] DE HEER W. A., CHATELAIN A., UGARTE D., *Science*, 270 (1995), 1179.
- [8] WONG S. S., JOSELEVICH E., WOOLLEY A. T., CHEUNG C. L., LIEBER C. M., *Nature*, 394 (1998), 52.
- [9] SAITO S., *Science*, 278 (1997), 77.
- [10] AUSMAN K. D., PINER R., LOURIE O., RUOFF R. S., KOROBV M., *J. Phys. Chem. B*, 104 (2000), 8911.
- [11] NIYOGI S., HAMON M.A., *Acc. Chem. Res*, 35 (2002), 1105.
- [12] PENG H., ALEMANY L.B., MARGRAVE J. L., KHABASHESKU V. N., *J. Am. Chem. Soc.*, 125 (2003), 15174.
- [13] HIRSCH A., *Angew. Chem. Int. Ed.*, 41, (2002), 1853.
- [14] BAHR J.L., TOUR J. M., *J. Mater. Chem.* 12 (2002), 1952.
- [15] GEORGAKILAS V., KORDATOS K., PRATO M., GULDI D. M., HOLZINGER M., HIRSCH A., *J. Am. Chem. Soc.*, 124 (2002), 760.
- [16] EBBESEN T. W., AJAYAN P.M., HIURA H., TANIGAKI K., *Nature*, 367 (1994), 519.
- [17] KNELLER J. M., SOTO R. J., SURBER S. E., PIETRA T., *J. Am. Chem. Soc.*, 122 (2000), 10591.
- [18] DUJARDIN E., EBBESEN T.W., KRISHNAN A., TREACY M. M. J., *Adv. Mater.*, 10 (1998), 61.
- [19] RINZLER A. et al., *J. Applied. Phys. A*, 67 (1998), 29.
- [20] LIU J., RINZLER A. G., DAI H. J., HAFNER J. H., BRADLEY R. K., BOUL P. J., *Science*, 280 (1998), 1253.
- [21] ZHANG J. et al., *J. Phys. Chem B.*, 107 (2003), 3712.
- [22] TSANG S. C., HARRIS P. J. F., GREEN M. L. H., *Nature*, 362 (1993), 520.
- [23] AJAYAN P. M., EBBESEN T. W., ICHIHASHI T., IJIMA S., TANIGAKI K., HIURA H., *Nature*, 362 (1993), 522.
- [24] KUZNETSOVA A., MAWHINNEY D. B., NAUMENKO V., YATES JR. J.T., LIU J., SMALLEY R. E., *Chem. Phys. Lett.* 321 (2000), 292.
- [25] KUZNETSOVA A. et al., *J. Am. Chem. Soc.*, 123 (2001), 10699.
- [26] LI Q. W., YAN H., YE Y. C., ZHANG J., LIU, Z. F., *J. Phys. Chem. B*, 106 (2002), 11085.
- [27] JORIO A. et al., *Phys Rev. Lett.*, 86 (2001), 1118.
- [28] RAO A. M., RICHTER E., BANDOW S., *Science*, 275 (1997), 187.
- [29] BACHILO S.M., STRANO M. S., KITTRELL C., HAUGE R. H., SMALLEY R. E., WEISMAN R. B., *Science*, 298 (2002), 2361.
- [30] ISLAM S. S., SHAH, K. A., *IEICE Electronic Exp. (Japan)* 1 (2006), 5.
- [31] TITUS E., ALI N., CABRAL G., GRACIO J., BABU P. R., JACKSON M. J., *J. Mater. Eng. and Performance*, 15 (2006), 182.

Received 2012-01-15
Accepted 2013-02-27