

PROPERTIES OF CARBON NANOTUBES DOPED WITH GADOLINIUM

R. G. ABASZADE^{a,*}, O. A. KAPUSH^b, A. M. NABIEV^c

^a*Azerbaijan National Academy of Sciences of Physics Institute, Az-1143 Baku, J.Cavid ave. 131*

^b*Ukrainian National Academy of Sciences, Institute of Semiconductor Physics nm.V.E.Lashkarov, Nauky pros. 41, 02000, Kiev, Ukraine.*

^c*Baku State University, AZ 1143, Baku, Z. Xalilova str., 23*

An analysis of some properties of carbon nanotubes using X-ray diffraction analysis, Raman scattering, and IR luminescence is given. After doping with gadolinium the peak intensities in X-ray and Raman spectra drastically increase. It was found that 15% doping with gadolinium strongly affects the physical properties of carbon nanotubes functionalized by a carboxyl group.

(Received February 14, 2020; Accepted July 30, 2020)

Keywords: Carbon nanotube, Gadolinium, X-ray analysis, Raman analysis, IR luminescent analysis

1. Introduction

Carbon nanotubes differ from other structures in their mechanical, electrical, magnetic, and optical properties [1-3]. These nanostructured materials have attracted particular attention because of their simplicity, small physical size and the exciting new science they have introduced. Changes in nanotube compositions significantly influence their electronic structure and morphological properties [4]. The structure, specificity, and size of carbon nanotubes were studied in [5,6]. X-ray absorption of single-wall carbon nanotube through gadolinium (Gd) encapsulation has been studied in [7]. Single and double resonances in Raman scattering are introduced and six criteria for the observation and identification of double resonances stated [8]. The use of Raman spectroscopy to reveal the remarkable structure and the unusual electronic and phonon properties of single wall carbon nanotubes is reviewed comprehensively. The most common experimental techniques used to probe carbon nanotubes are summarized, followed by a review of the novel experimental findings for each of the features in the first order and second order Raman spectra for single wall carbon nanotubes is presented in [9]. Recent advances in Raman spectroscopy for characterizing graphene, graphite, and carbon nanotubes are reviewed comparatively, the first-order and the double-resonance (DR) second-order Raman scattering mechanisms in graphene, which give rise to the most prominent Raman features are discussed in [10]. Polarization analysis, surface enhanced Raman spectroscopy and complementary optical techniques are also discussed in terms of their advantages and limitations [11].

This paper reports an investigation into earth metal (gadolinium) doping effects on properties of carbon nanotubes. Experimental tools were X-ray, Raman scattering, IR luminescent analysis.

2. Experimental details

2.1. Specimen synthesis

2.1.1. Doping with gadolinium process

0.015 grams of Gd₂S₃ and 0.85 grams (1-15%) of functionalized carbon nanotubes were mixed together in a Petri dish and placed in a 150 milliliter flask. 50 milliliters of distilled water

* Corresponding author: r.abaszada@physics.science.az

was added to this solution. The mixture was stirred for 6 hours at 750°C in a magnetic stirrer equipped with a reflux condenser and a thermometer. The new compound was filtered, separated and dried in vacuum.

2.2. Characterisation

The structure and purity, quality, and surface morphology of carbon nanotubes and gadolinium-doped carbon nanotubes were analyzed by X-ray structural analysis, Raman spectroscopy and IR luminescent analysis.

2.2.1. X-ray diffraction analysis.

X-ray diffraction analysis of the spectra of carbon nanotubes and gadolinium – doped carbon nanotubes was carried out using a D2 Phaser (Bruker) diffractometer with CuK_α rays ($\lambda=1.5406 \text{ \AA}$) at $2\theta=0.5^\circ\div 80^\circ$ angles. Diffraction peaks, the intensity of which depends on the morphological characteristics of the samples, allows one to obtain data on the distance between the layers and walls of nanotubes.

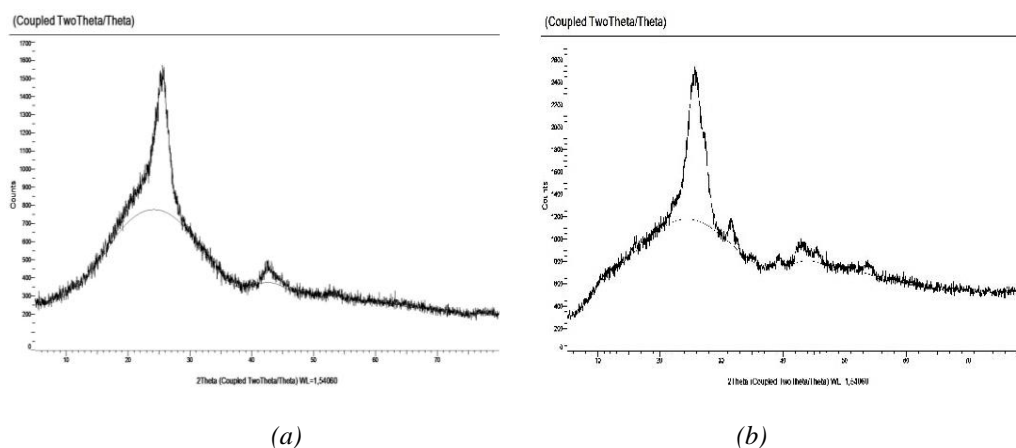


Fig. 1. X-ray spectrum of a carbon nanotube (a) and gadolinium-doped carbon nanotube (b).

X-ray curves of carbon nanoparticles are shown in Figure 1a. There are two maximum peaks, the first is a steep peak at the angular position $2\theta=26.3^\circ$, with the intensity $I=1550$, the second weaker peak at $2\theta=42.5^\circ$, and its the intensity is $I=480$. In Figure 1b, an X-ray curves of gadolinium-doped carbon nanotubes are given. There are two maximum peaks, the first sharp peak at the angle $2\theta=25.8^\circ$, with the intensity $I=2544$, and the second peak $2\theta=42.9^\circ$, and the intensity $I=1005$.

2.2.2. Raman analysis

Based on the Raman analysis, the properties of carbon nanotubes and carbon nanotubes doped with gadolinium were analyzed. As can be seen, in the scattering spectra a decrease in the intensities and a shift of the peaks at higher frequencies are observed. Changes in the peaks in the Raman spectrum are related to the concentration of defects.

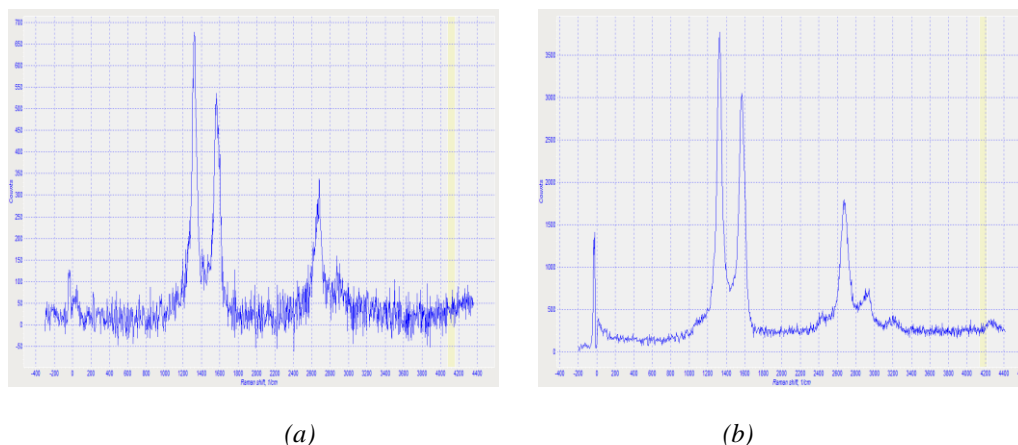


Fig. 2. Raman spectrum of a carbon nanotube (a) and gadolinium-doped carbon nanotube (b).

For semiconductor nanotubes, G band has an explicit doublet structure. Moreover, one of the peaks (G^+) is caused by vibrations of atoms along the axis of the nanotube (LO mode), the other, weaker in intensity and having a lower frequency, the peak G^- is associated with vibrations in the directions perpendicular to the axis (TO mode). The shift downward in frequency of the last peak is due to the presence of a small number of low-frequency phonon modes oscillating in perpendicular directions.

According to the Raman analysis in Figure 2a, the peak D is 1338 cm^{-1} , and the peak intensity is 1075, the peak G^- is 1517.5 cm^{-1} , the peak intensity is 258, the peak G^+ is 1595 cm^{-1} , the peak intensity is 827, the peak 2D is 2676 cm^{-1} and the peak intensity is 565.

The second important feature of the Raman spectra of carbon nanotubes is the presence in the low-frequency region of the so-called RBM-radial breathing mode, which is characteristic only of nanotubes and is associated with symmetric vibrations of carbon atoms in the radial direction. The RBM peak is 280.3 cm^{-1} and the peak intensity is 40.

The G^+ peak is identified with the TO mode, and the LO mode has a lower frequency, which is caused by the strong electron-phonon interaction. The presence of this region in the Raman spectrum indicates the presence of certain defects in nanotubes. These defects can be caused both by imperfections in the nanotube lattice and by the presence of impurities. The ratio of G and D bands helps to determine what is the intensity of various kinds of defects. For good samples, the D band is several orders of magnitude smaller than G.

According to the Raman analysis in Figure 2b, the RBM peak is 282.8 cm^{-1} , and the peak intensity is 196, and the peak D is 1325 cm^{-1} , and the peak intensity is 3773, the peak G^- is 1564 cm^{-1} , the peak intensity is 3053, the peak 2D is 2673 cm^{-1} and the peak intensity is 1790.

2.2.3. Luminescent analysis

Fourier-IR absorption spectra of carbon nanotubes samples were obtained in the range of $4000\div 400\text{ cm}^{-1}$ on a Varian-640IR IR spectrometer. For this, $50\div 100\text{ }\mu\text{m}$ thick nanotubes were pressed. KBr powders (1:299 mg) were used as a binder.

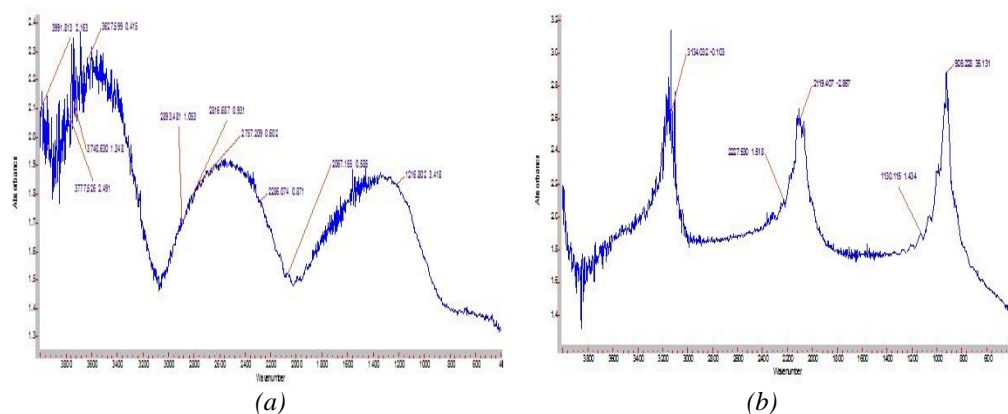


Fig. 3. IR spectrum of a carbon nanotube (a) and gadolinium-doped carbon nanotube (b).

Fig. 3a shows the Fourier-IR absorption spectrum of the initial nanotube. The low intensity of 1216 cm^{-1} observed in the spectrum is due to the defectiveness of the nanotube. The spectral position of this band is explained by the degree of opening of the phonon branch, which depends on the perfection of the sample structure, i.e., optical transitions in the 1216 cm^{-1} band occur in the wave vector $k > 0$. The bands observed in the region of $3500\div 3700\text{ cm}^{-1}$ are related to the Fermi resonance between C-H vibrations and overtones. When Gd is introduced into the sample, an increase in intensity is observed. Observed in Fig.3b, the absorption band of $926,23\text{ cm}^{-1}$ is associated with deformation vibrations of the sample doped with Gd.

5. Conclusions

Carbon nanotubes fabricated with the arc discharge method and 15% gadolinium-doped carbon nanotubes were analysed by X-ray diffraction analysis, Raman scattering, and IR luminescence. The analysis of Raman spectra revealed that the peaks observed in the dispersion spectra of carbon nanotubes doped with gadolinium shift to higher frequencies. The analysis of X-ray and Raman spectra showed that after doping with gadolinium the peak intensities substantially grow. The intensity peaks of doped nanotubes exceed those of carbon nanotubes which is associated with the higher defect concentration of carbon nanotubes. It has been revealed that carbon nanotubes doped with gadolinium drastically changes their properties.

References

- [1] M. J. O'Connell, CRC press, 360 (2018).
- [2] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, Annual Review of Materials Research **34**, 247 (2004).
- [3] R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, M. S. Dresselhaus Advances in Physics **60**(3), 413 (2011).
- [4] L. Vaccarini, Ch. Goze, L. Henrard, E. Hernandez, P. Bernier, A. Rubio, Carbon **38**, 1681 (2000).
- [5] X. Wang, X. Sun, D. Yu, B. Zou, Advanced Materials **15**(17), 1442 (2003).
- [6] M. R. Jiang, H. Zhou, X. H. Cheng, Journal of Materials Science **54**(14), 10235 (2019).
- [7] Alimin Narsito, I. Kartini, S. J. Santosa, IOP Conf. Ser.: Mater. Sci. Eng. **107**, 012051 (2016).
- [8] Ch. Thomsen, S. Reich, J. Maultzsch, Phil. Trans. R. Soc. Lond. A **362**, 2337 (2004).
- [9] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Physics Reports **409**, 47 (2005).
- [10] M. S. Dresselhaus, R. Saito, A. Jorio, Annu. Rev. Condens. Matter Phys. **1**, 89 (2010).

- [11] A. Jorio, M. A. Pimenta, A. G. Souza Filho, R. Saito, G. Dresselhaus, M. S. Dresselhaus, *New Journal of Physics* **5**, 139.1 (2003).