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R.G. Abaszade[1], O.A. Kapush[2], S.A. Mamedova[1], A.M. Nabiev[3], S.Z. Melikova[4], S.I. Budzulyak[2]

Gadolinium Doping Influence on the Properties of Carbon Nanotubes

[1]*Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan, abaszada@gmail.com*
[2]*V.E. Lashkarev Institute of Semiconductor Physics NAS of Ukraine, Kyiv, Ukraine, savchuk-olja@ukr.net*
[3]*Baku State University, Baku, Azerbaijan, afig.nabiev@hotmail.com*
[4]*Institute of Radiation Problems, Azerbaijan National Academy of Sciences, Baku, Azerbaijan, sevinc.m@rambler.ru*

This article is devoted to the analysis of a carbon nanotube, a functionalized b-carboxyl group of a carbon nanotube and a gadolinium-doped carbon nanotube. Were analyzed the structure, purity, quality, and surface morphology, as well as the homogeneity (heterogeneity) of nanotubes. The analysis of a carbon nanotube were performed using a scanning electron microscope (SEM), energy dispersive analysis (EDX), X-ray diffraction analysis, Raman scattering, and IR luminescence. It was found that 10 % doping with gadolinium strongly affects the physical properties of carbon nanotubes functionalized by a carboxyl group.

Key words: carbon nanotube, functionalized carbon nanotube, gadolinium, Raman analysis, X-ray analysis, IR luminescent analysis.

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Introduction

Carbon nanotubes differ from other structures in their mechanical, electrical, magnetic, and optical properties [1, 2]. Carbon nanoribbons differ from carbon nanotubes is that nanoribbons have edges, whereas nanotubes have terminations only at their two ends [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 [5-8]. Doping carbon nanotubes with rare earth metals is one of the promising areas in nanotechnology. It was shown in [9] that gadolinium (Gd) and europium (Eu) catalyze the growth of single-walled carbon nanotubes using chemical vapor deposition. Characterization using transmission electron microscopy and Raman spectroscopy confirmed the presence of single-walled carbon nanotubes catalyzed by Gd and Eu with an average diameter of 2.05 nm.

This paper reports an investigation into rare earth metal doping effects on properties of carbon nanotubes. Experimental tools were SEM, EDX, X-ray, Raman scattering, FTIR.

I. Experimental details

Speciemen synthesis

Functionalization of carbon nanotubes. Carbon nanotubes were initially functionalized. Obtained by the arc discharge method, 0.5 g of high purity carbon nanotubes were mixed with 250 ml of 8 M sulfuric acid in a 500 mm beaker. In a magnetic mixer equipped with a heater, sulfuric acid was continuously mixed with carbon nanotubes [10]. The process was carried out at 50°C for 3 hours. The resulting compound (functionalized carbon nanotubes) was washed and filtered with distilled water until a neutral medium was removed, and dried in a vacuum dryer in a Petri dish.

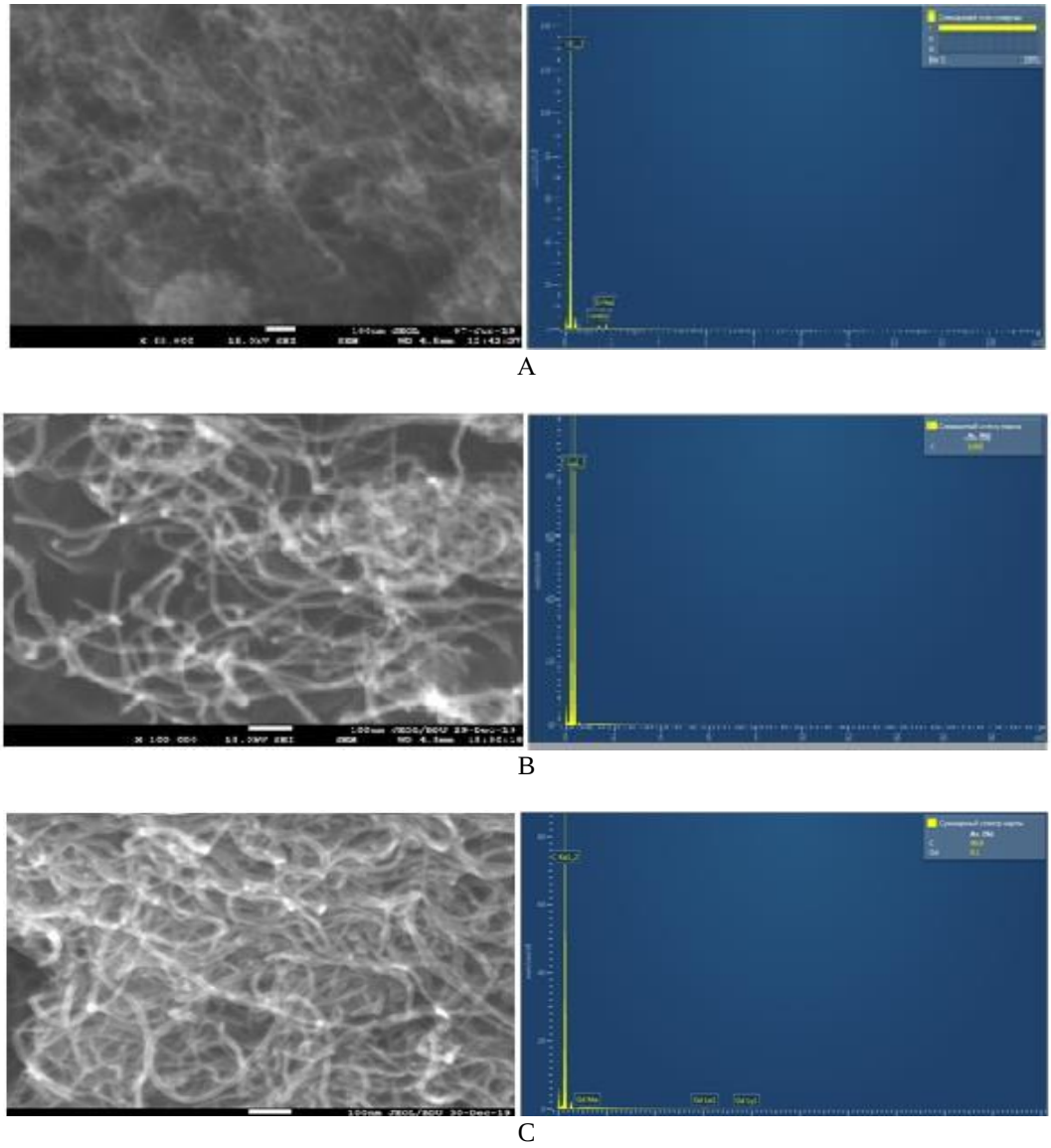

Fig. 1. SEM and EDX of a carbon nanotube (a), SEM and EDX of a functionalized b-carboxyl group of a carbon nanotube (b), and SEM and EDX of a gadolinium-doped carbon nanotube (c).

Doping with gadolinium process. 0.01 grams of Gd_2S_3 and 0.1 grams (1 - 10 %) of functionalized carbon nanotubes were mixed together in a Petri dish and placed in a 150 milliliter flask. 50 milliliters of distilled water were 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.

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

SEM and EDX spectroscopy. Twenty-four hours after functionalized carbon nanotubes and gadolinium-doped carbon nanotubes were obtained to study the structure, purity, quality, and surface morphology, as well as the homogeneity (heterogeneity) of nanotubes. Using a JOINT-JOB-7600F scanning electron microscope, SEM images and EDX spectra were analyzed. Images of carbon nanotubes were enlarged up to 100,000 times, and measurements were carried out at intervals of 1 - 100 μm.

From SEM images it is seen, that carbon nanotubes have a inner diameter of 16.8 nm and a outter diameter of 18.8 nm.

X-ray diffraction analysis. X-ray diffraction analysis of the spectra of carbon nanotubes, functionalized carbon nanotubes, and gadolinium-doped carbon nanotubes was carried out using a D2 Phaser (Bruker) diffractometer with CuKα rays (λ = 1.5406 Å) at 2θ = 0.50 - 800 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. The data of x-ray diffraction analysis of the samples are shown in Table 1.

Raman analysis. Based on the Raman analysis, the

properties of carbon nanotubes, functionalized 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. The results of the Raman analysis are shown in Table 2.

Luminescent analysis. Fourier-IR absorption spectra of CNT samples were obtained in the range of 4000 - 400 cm^{-1} on a Varian-640IR IR spectrometer. For this, 50 - 100 μm thick nanotubes were pressed. KBr powders (1:299 mg) were used as a binder.

Fig. 2a shows the Fourier-IR absorption spectrum of

Table 1

Data of x-ray diffraction analysis of the samples.

	Sample	I maximum	Intensity (cm^{-1})	II maximum	Intensity (cm^{-1})
1	Carbon nanotube	26.3^0	1550	42.5^0	480
2	Functionalized carbon Nanotube	26.5^0	1950	43.3^0	550
3	Gadolinium-doped carbon nanotube	26.7^0	1340	43^0	460

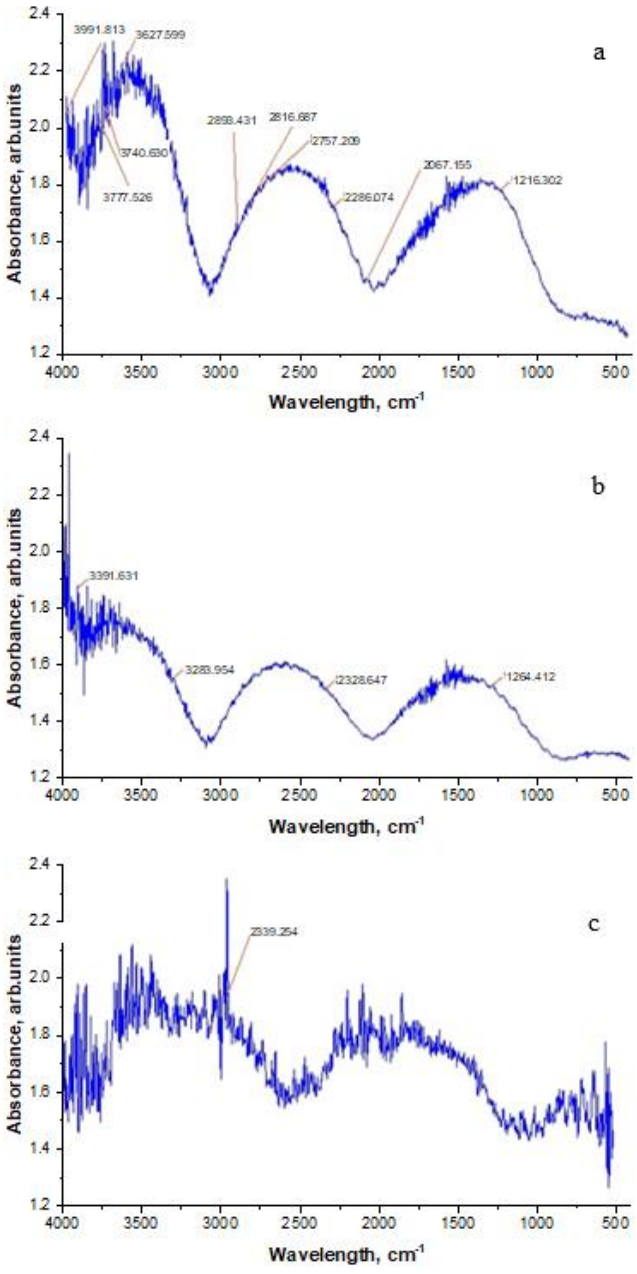

Fig. 2. IR spectrum of a carbon nanotube (a), a functionalized carbon nanotube (b), and a gadolinium-doped carbon nanotube (c).

Table 2

Results of the Raman analysis.

	Sample	D-peak (cm^{-1})	Intensity	G-peak (cm^{-1})	Intensity	2D-peak (cm^{-1})	Intensity
1	Carbon nanotube	1338	1075	1595	827	2676	565
2	Functionalized carbon Nanotube	1338	817	1595	703	2676	421
3	Gadolinium-doped carbon nanotube	1361	739	1614	610	2704	346

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 - 3700 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. The absorption band 3283 cm^{-1} observed in Fig. 2b is associated with valence vibrations of the same-phase and reverse-phase of C-H bonds. Observed in Fig. 2c, the absorption band of 926 cm^{-1} is associated with deformation vibrations of the sample doped with Gd.

Conclusions

Carbon nanotubes, functionalized carbon nanotubes, and 10 % gadolinium-doped carbon nanotubes were analysed by scanning electron microscope (SEM), energy dispersive analysis (EDX), X-ray diffraction analysis, Raman scattering, and IR luminescence. The energy-dispersed spectroscopy shows that nanotubes are homogeneously distributed. The results of Raman analysis are confirmed by those of SEM analysis. The analysis of Raman spectra revealed that the peaks observed in the dispersion spectra of carbon nanotubes doped with gadolinium shift to higher frequencies, and their intensities decreased accordingly. It has been seen that intensivity peaks of doped nanotubes exceed those of carbon nanotubes which is associated with the higher the defect concentration compared to carbon nanotubes the defect concentration in doped nanotubes compared to carbon nanotubes.

Abaszade R.G. – Ph.D, senior researcher, head of Innovation Research department;
Kapush O.A. - PhD degree in solid-state chemistry, Senior Researcher at of the Department of Surface Physics and semiconductor nanophotonics;
Mamedova S.A. – Ph.D;
Nabiyev A.M. – PhD student, researcher at the BSU and Innovation Research Department;
Melikova S.Z. – Ph.D, senior researcher;
Budzulyak S.I. – Ph.D, senior researcher.

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Р.Г. Абасзаде[1], О.А. Капуш[2], С.А. Мамедова[1], А.М. Набієв[3], С.З. Мелікова[4], С.І. Будзуляк[2]

Вплив легування гадолінієм на властивості вуглецевих нанотрубок

[1]*Інститут фізики, Азербайджанська національна академія наук, Баку, Азербайджан, abaszada@gmail.com*
[2]*Інститут фізики напівпровідників ім. В.Є. Лашкарева НАН України, Київ, Україна, savchuk-olja@ukr.net*
[3]*Бакинський державний університет, Баку, Азербайджан, afig.nabiev@hotmail.com*
[4]*Інститут радіаційних проблем, Азербайджанська національна академія наук, Баку, Азербайджан, sevinc.m@rambler.ru*

Стаття присвячена дослідженню властивостей вуглецевих нанотрубок, вуглецевих нанотрубок, функціоналізованих b-карбоксильною групою та вуглецевих нанотрубок, легованих гадолінієм. Вивчено структуру, чистоту, якість та морфологію поверхні, а також однорідність (гетерогенність) нанотрубок. Властивості вуглецевих нанотрубок вивчали за допомогою скануючої електронної мікроскопії (SEM), енергодисперсійного рентгенівського аналізу (EDX), рентгенівської дифракції, комбінаційного розсіювання світла (КРС) та ІЧ-люмінесценції. Було встановлено, що 10 % легування гадолінієм сильно впливає на фізичні властивості вуглецевих нанотрубок, функціоналізованих карбоксильною групою.

Ключові слова: вуглецеві нанотрубки, функціоналізовані вуглецеві нанотрубки, гадоліній, КРС, рентгенівський аналіз, ІЧ-люмінесцентний аналіз.