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STUDYING OF STRUCTURAL CHANGES OF GRAPHENE LAYERS OF CARBON NANOTUBES FUNCTIONALIZED BY RAMAN SPECTROSCOPY

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The effect of oxidizing treatment conditions (concentrated nitric acid, hydrogen peroxide vapor) and direct fluorination on the structural integrity of graphene layers of carbon nanotubes (CNTs) was studied using Raman spectroscopy-based method. Changes in the functionalization of the CNTs defect indices estimated by the intensity of the characteristic peaks: D (1320–1350 cm^{-1}), G (1550–1580 cm^{-1}), 2D (~2660 cm^{-1}), D+G (~2900 cm^{-1}), and 2G (~3200 cm^{-1}) in Raman spectra and their ratios were elucidated. It was established that ordering of the CNTs graphene layers can be observed at the initial stage of various oxidation and fluorination methods. This can be apparently relate to the predominance of the processes of residual amorphous phase removal. Then, the defectiveness indicators begin to grow, thereby indicating the destructive changes in nanotubes during the functionalization. With each chemical treatment method, it is possible to minimize the destruction of the CNTs surface by selecting the process conditions. The CNTs oxidized in hydrogen peroxide vapor are characterized by the most ordered structure of the graphene layers.

Key words: *functionalization, oxidation, direct fluorination, carbon nanotubes, Raman spectroscopy.*

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ИССЛЕДОВАНИЕ ИЗМЕНЕНИЯ СТУКТУРЫ ГРАФЕНОВЫХ СЛОЕВ УГЛЕРОДНЫХ НАНОТРУБОК ПРИ ФУНКЦИОНАЛИЗАЦИИ МЕТОДОМ СПЕКТРОСКОПИИ КОМБИНАЦИОННОГО РАССЕЯНИЯ

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Методом спектроскопии комбинационного рассеяния исследовано влияние условий окислительной обработки (концентрированной азотной кислотой, парами перекиси водорода) и прямого фторирования на структурную целостность графеновых слоев углеродных нанотрубок (УНТ). Изучено изменение при функционализации показателей дефектности УНТ, оцениваемых по интенсивности характерных пиков D (1320–1350 см$^{-1}$), G (1550–1580 см$^{-1}$), 2D (~2660 см$^{-1}$), D+G (~2900 см$^{-1}$) и 2G (~3200 см$^{-1}$) на спектрах комбинационного рассеяния и их соотношениям. Установлено, что при различных способах окисления и при фторировании на начальном этапе наблюдается упорядочение структуры графеновых слоев УНТ, связанное, по-видимому, с преобладанием процессов удаления остаточной аморфной фазы. Затем показатели дефектности начинают расти, что свидетельствует о деструктивных изменениях нанотрубок при функционализации. При каждом способе химической обработки возможна минимизация *разрушения поверхности УНТ путем подбора условий процесса. Наиболее упорядоченной структурой графеновых слоев характеризуются УНТ, окисленные в парах перекиси водорода.*

Ключевые слова: *функционализация, окисление, прямое фторирование, углеродные нанотрубки, спетроскопия комбинационного рассеняния.*

Introduction

Numerous sources report that carbon nanotubes (CNTs) have prospects for wide applications in the composition of electrically conductive, heat-conducting and reinforced polymer composites, due to a combination of their unique physical and chemical properties [1–3]. To improve the compatibility of CNTs with polymer matrices and reduce their aggregation, functionalization methods are often used [4], among which fluorination and oxidation in various systems are one of the most effective [5–6]. CNTs graphene layers undergo changes during the formation of functional groups [7]. This phenomenon should be considered even when using functionalized CNTs in systems with liquid crystals [8–11], since the destruction of CNTs surface layers may change the character of their interactions with the matrix and influence on the nematic phase properties.

Raman spectroscopy appears to be the most informative of modern methods for studying the structure defectiveness of graphene layers of various carbon materials. In Raman spectra of multilayered CNTs, the following characteristic peaks can be observed: G (1500–1600 cm^{-1}) – due to the vibrations of carbon atoms in the graphene layer plane, and D (1250–1450 cm^{-1}) – due to the presence of carbon atoms in the sp^3 hybridization state [12]. The i_D/i_G ratio is used to estimate the degree of defectiveness of the CNTs surface. The additional information on the structure of CNTs graphene layers can be obtained with the peaks D' (1600–1630 cm^{-1}), 2D (~2700 cm^{-1}) and D+G (~2900 cm^{-1}) also identified in Raman spectra [13].

A number of works devoted to studying the effect of certain types of functionalization on the shape of Raman spectra, as well as the position and intensities of their characteristic lines, are known [14–15]. However, there are practically no systematic data on changes in Raman spectra of CNTs under various conditions of covalent functionalization.

In this regard, the present paper aims at investigating the structural integrity of graphene layers of multiwalled CNTs based on Raman spectroscopy under various oxidation and fluoridation conditions.

Experimental

«Taunit-M» multiwalled CNTs (with external and internal diameters of 8–15 nm and 4–8 nm, respectively, and a length of 2 μm) produced at NanoTechCenter Ltd. (Tambov, Russia) were used herein (Fig. 1).

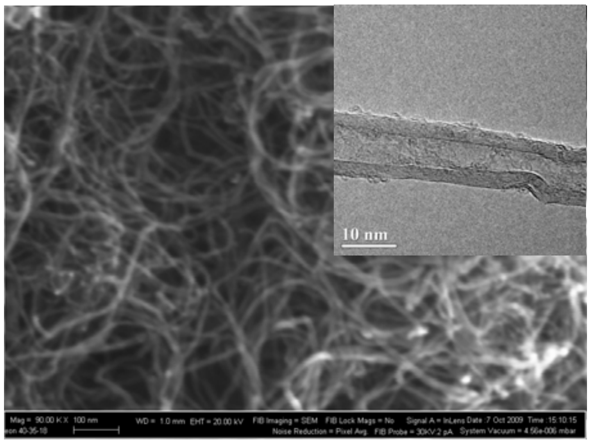


Fig. 1. SEM and TEM images of the «Taunit-M» CNTs

They were functionalized using several methods – oxidation with concentrated nitric acid, oxidation in hydrogen peroxide vapor, and fluorination.

The CNTs oxidation using concentrated HNO_3 (65 %, chemically pure) was carried out by treating at 100 °C in a flask with a reflux condenser. 50 mL of nitric acid were taken per 1 g of initial CNTs. The process time varied from 0.5 to 6.5 hrs. At the end of the treatment, the CNTs were separated from excess nitric acid were washed on a filter with distilled water to get a neutral pH of the filtrate. The resulting paste was dried in an argon flow at a temperature of 70–80 °C.

The CNTs oxidation in 37-% hydrogen peroxide (pure) vapor was performed at 140 °C for 0.5 to 30 hrs. A laboratory setup was used, the characteristics of which are presented elsewhere [16].

The CNTs fluorination was conducted in a steel reactor at fluorine gas pressures of 0.7–1.0 atm and temperatures of 100–250 °C. Fluorine was introduced into the reactor preheated. The duration of the process was 9 min –2 hrs.

Raman spectra of the initial and functionalized CNTs samples excited by monochromatic radiation with a wavelength of 532 nm were recorded on a Raman spectrometer with a DXR Raman confocal microscope (Termo Scientific) on a Raman amorphous alumina substrate.

The exposure time was 2 s, number of exposures – 5, and number of exposures for the background – 512. A grid of 900 lines/mm was used. The aperture of the "slit-type" spectrograph was 50 µm. The «Omnic 9» software was employed for analyzing spectra.

Results and Discussion

The Raman spectra of the multiwalled CNTs have a number of characteristic features. In the first-order scattering spectra (1000–1700 cm^{-1}), two peaks at about 1340 and 1600 cm^{-1} are fixed (Fig. 2, *a*). The former – D – indicates the formation of diamond-like sp^3-bonds when topological defects in the graphene layers take place, and the presence of amorphous carbon particles. The latter is divided into two smaller peaks – G (~1560–1590 cm^{-1}) and D' (~ 1600–1630 cm^{-1}). The presence of the G peak stands for the availability of regular graphene layers consisting of carbon atoms in sp^2-hybridization state.

The D' band indicates the presence of structural defects in the materials, it appears due to violations of the selection rules for the wave vector, which lead to activation of phonons from the interior points of the Brillouin zone in the Raman spectra [17]. Because of this peak separation, it seemed to us to be worthwhile to estimate their area (i), not height.

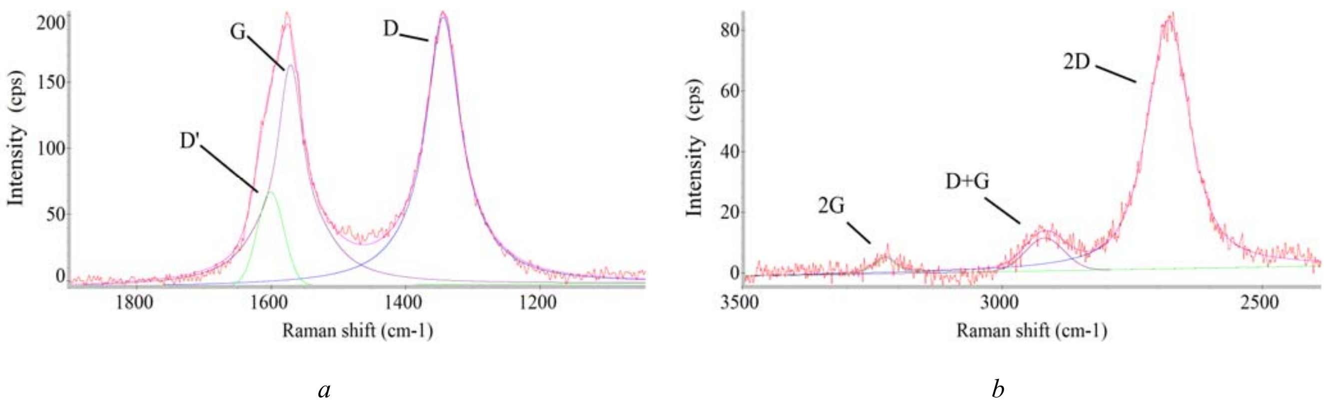


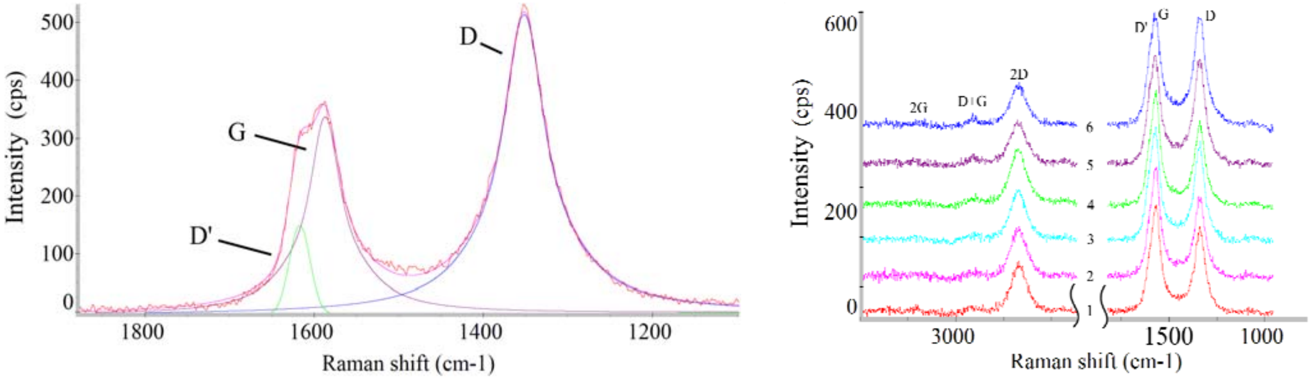
Fig. 2. The Raman spectra of the first (*a*) and second (*b*) order recorded for the initial CNTs

The second-order scattering spectra (2400–3200 cm^{-1}) shown in Fig. 2, *b* also allows us to judge on the structural integrity of the CNTs. The 2D peak (~2700 cm^{-1}) is an overtone of the D peak. According to [18], the D+G (~ 2900 cm^{-1}) peak characterizes the presence of C-H bonds existing on the surface of CNTs obtained by the CVD method, due to incomplete conversion of the hydrocarbon raw material. The 2G peak (~3200 cm^{-1}) is an overtone of the G peak. The D+G and 2G intensities are usually very weak, and thus, these peaks hardly stand out from the noise.

The defectiveness of the CNT surface, the degree of which is indirectly estimated from the ratio of the peak intensities i_D / i_G in the Raman spectra, in this case is due to a combination of two factors: 1) violation of the symmetry of the surface CNTs graphene layers because of the presence of carbon atoms in the sp^3-hybridization state (e.g., in the composition of alkyl groups); and 2) availability of the amorphous carbon layer on the side surfaces of the CNTs (it can be distinguished in the TEM image – Fig. 1).

During the oxidation and fluorination, the amorphous phase can be removed, since it is the most reactive. In this case, the i_D / i_G ratio value should decrease. If the functional groups are formed only as a result of the chemical transformation of the alkyl groups initially present on the surface, then significant changes in the degree of defectiveness should not be expected. The increase in the i_D/i_G value will mean the destructive effect of the oxidizer on the surface layers of the CNTs, as a result of which new defects take place.

In the course of the CNTs oxidation using concentrated nitric acid, the D' peak becomes more distinct starting from a certain moment (Fig. 3, *a*). The presence of this peak is associated with the destruction of the graphene layers. However, when treating the CNTs with hydrogen peroxide vapor, on the contrary, the G peak becomes more acute and distinct (Fig. 3, *b*), thereby indicating the ordering of the CNTs side walls and the decrease in the number of defects in them.



a *b*

Fig. 3. Changes in the Raman spectra during the CNTs oxidation:
a – first-order spectra of the CNTs oxidized with concentrated nitric acid for 6.5 hrs; *b* – spectra of the initial CNTs (1) and oxidized in hydrogen peroxide vapor at 1400 ºC for 2 (2), 5 (3), 10 (4), 20 (5), and 30 (6) hrs

The changes in the characteristics of the Raman spectra when the CNTs are treated with concentrated nitric acid and hydrogen peroxide vapor can be estimated on the basis of the data presented in Table 1. It shows that the dependence of the i_D/i_G CNTs defect index on the oxidation duration in both reagent systems passes through the minimum at τ equal to 0.5 and 20 h for the liquid-phase and gas-phase oxidation, respectively.

Thus, irrespective of the reagent nature, the processes of removal of the residual amorphous phase from the surface and ordering of the graphene layers prevail at the initial stage of the CNTs oxidation. Moreover, the rate of the liquid-phase process is much higher than that of the CVD process, which is the reason for the earlier initiation of destructive changes in the CNTs surface.

It is noteworthy that the indicator of the CNTs graphene layer ordering can be the i_{2D}/i_G value, which is inversely related to the i_{2D}/i_G defect index. It can also be noted that as the orderliness of the graphene layers decreases, there is a tendency shifting the position of the characteristic peaks in the Raman spectra to the region of higher wave numbers.

Table 1. **Raman spectroscopy data for the CNTs - initial and oxidized under different conditions**

Functionalization type	Duration (τ), hrs	Peak osition , см$^{-1}$					i_D/i_G	i_{2D}/i_G
		D	G	2D	D+G	2G		
Initial	-	1343	1577	2676	2912	3218	1.011	0.570
Oxidation with concentrated nitric acid (liquid-phase)	0.5	1343	1577	2677	2904	3218	0.941	0.659
	2.5	1343	1580	2679	2923	3218	1.340	0.422
	3.5	1346	1581	2688	2926	3217	1.350	0.377
	6.5	1349	1585	2697	2944	3222	1.577	0.240
Oxidation with hydrogen peroxide vapor (gas-phase – CVD)	2	1341	1573	2674	2900	3218	1.007	0.490
	10	1339	1569	2672	2900	3217	0.897	0.620
	20	1334	1569	2669	2900	3211	0.809	0.737
	30	1336	1570	2667	2909	3204	0.850	0.677

During the direct fluorination of the CNTs, despite the different nature of the functional groups formed on their surfaces, the changes in the Raman spectra are of the same qualitative nature (Fig. 4). With soft processing modes, the 2D peak intensity increases. The G peak becomes acute and pronounced. As the temperature, pressure, and duration of fluorination increase, the manifestation of the D' band becomes more pronounced.

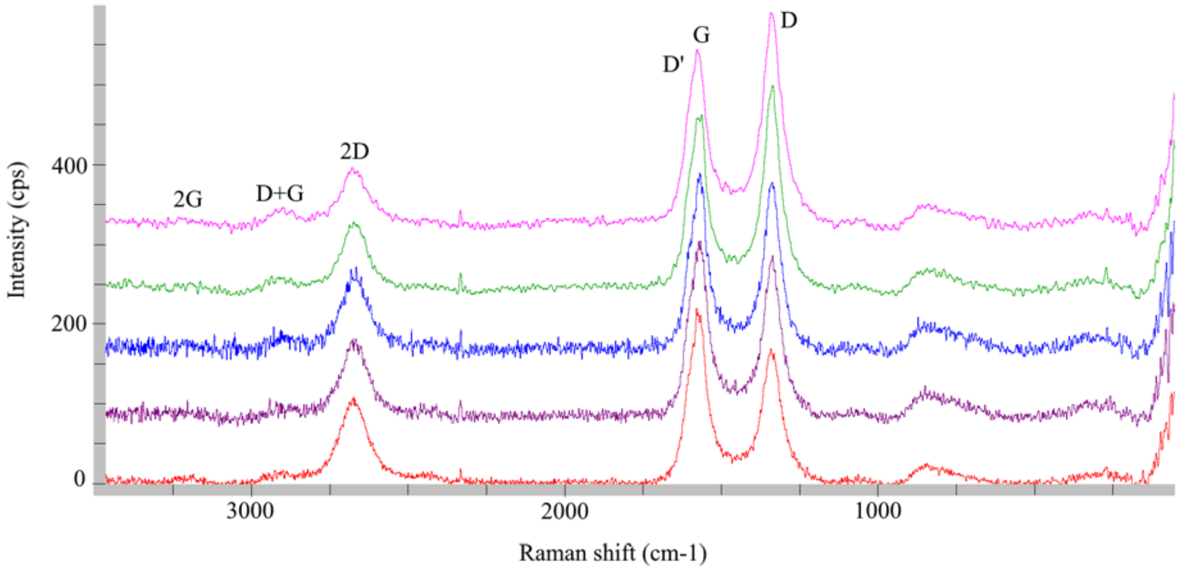


Fig. 4. Raman spectra of the CNTs treated with gaseous fluorine under various conditions: (F-1) t = 100 °C; p = 0.8–0.9 atm; τ = 9 min; (F-2)) t = 150 °C; p = 0.8–0.9 atm; τ = 10 min; (F-3) t = 150 °C; p = 0.8–0.9 atm; τ = 2 hrs; (F-4) t = 150 °C; p = 0.9–1.0 atm; τ = 2 hrs; (F-5)) t = 250 °C; p = 0.9–1.0 atm; τ = 2 hrs

The analysis of the Raman spectra of the CNTs subjected to the direct fluorination is presented in Table 2. In this case, the decrease in i_D/i_G and increase in i_{2D}/i_G during the short-term treatment under the most sparing conditions can also be observed. The positions of the D, G, 2D, D+G and 2G peaks correlate with the changes in the defectiveness (i_D/i_G) and ordering (i_{2D}/i_G) values, just as it was observed in the case of the CNTs oxidation.

Table 2. **Raman spectroscopy data for the CNTs fluorinated under various conditions**

Fluorine gas CNTs treatment conditions (see captions for Fig. 4)	Peak position, cm^{-1}					i_D/i_G	i_{2D}/i_G
	D	G	2D	D+G	2G		
F-1	1335	1568	2669	2890	3207	0.953	0.544
F-2	1333	1564	2663	2887	3202	0.895	0.696
F-3	1337	1570	2664	2917	3186	1.060	0.563
F-4	1338	1568	2667	2922	3190	1.166	0.427
F-5	1339	1568	2667	2926	3195	1.226	0.386

The comparison of the aggressiveness of various reagents with respect to the CNTs structure shows that for the preparation of functionalized CNTs with the best indices of the orderliness of graphene layers, it is necessary to use hydrogen peroxide vapor. However, according to [16], the content of oxygen-containing functional groups formed does not exceed 0.82 at. %, which may not be sufficient for efficient CNTs distribution in polar matrices.

Concentrated nitric acid and fluorine gas approximately equally cause the destruction of the CNTs surface. Among the reagent systems studied herein, the most pronounced damages to the CNTs surface are caused by nitric acid during prolonged treatment. Moreover, the degree of functionalization of the CNTs oxidized with the carboxyl groups proves to be maximal [19].

These data given above show that the use of Raman spectroscopy for assessing the structural integrity of graphene layers allows for finding compromise chemical treatment conditions for the CNTs, thereby making it possible to obtain their functionalized forms with the required composition of functional groups while maintaining acceptable defectiveness index values.

Conclusions

With different methods of the CNTs chemical treatment, a similar pattern is observed in the variation of the ordering (i_{2D}/i_G) and defectiveness (i_D/i_G) indices of the graphene layers estimated using Raman spectroscopy. At the initial stage or under the mildest oxidation and fluorination conditions, the residual amorphous phase is removed from the CNTs surface, but noticeable destructive changes can further occur. By selecting the conditions for functionalization conditions, it is possible to minimize the CNTs graphene layers.

Continuous oxidation with concentrated nitric acid causes noticeable damages to the nanotube side walls Processing in hydrogen peroxide vapor allows for obtaining the CNTs functionalized forms characterized by the highest index value of the graphene layer orderliness.

Further perspectives of the present study are related to the investigation of the effect of the structural integrity of functionalized CNTs on the tribological, mechanical, and electrically conductive properties of nanocomposites based on a variety of matrices.

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