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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 СТРУКТУРЫ 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 cm–1), G (1550–1580 cm–1), 2D (~2660 cm–1), D+G (~2900 cm–1) и 2G (~3200 cm–1) на спектрах комбинационного рассеяния и их соотношениями. 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
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 sp³ hybridization state [12]. The iD/iG 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 HNO₃ (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 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.
Studying of structural changes of grapheme layers by Raman spectroscopy

The 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 sp³-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 sp²-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](image)

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 iD / iG 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 sp³-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 iD / iG 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 iD/iG 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.

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 º С 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 $\tau$ 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

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

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**

<table>
<thead>
<tr>
<th>Fluorine gas CNTs treatment conditions (see captions for Fig. 4)</th>
<th>Peak position, cm(^{-1})</th>
<th>( i_D/i_G )</th>
<th>( i_{2D}/i_G )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>G</td>
<td>2D</td>
</tr>
<tr>
<td>F-1</td>
<td>1335</td>
<td>1568</td>
<td>2669</td>
</tr>
<tr>
<td>F-2</td>
<td>1333</td>
<td>1564</td>
<td>2663</td>
</tr>
<tr>
<td>F-3</td>
<td>1337</td>
<td>1570</td>
<td>2664</td>
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<tr>
<td>F-4</td>
<td>1338</td>
<td>1568</td>
<td>2667</td>
</tr>
<tr>
<td>F-5</td>
<td>1339</td>
<td>1568</td>
<td>2667</td>
</tr>
</tbody>
</table>

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 (i2D/iG) and defectiveness (iD/iG) 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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References


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