

## Features of oxidative functionalization of multiwalled carbon nanotubes

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**Abstract:** The paper studies the oxidation laws of multiwalled carbon nanotubes (MWCNTs) of various types, which differ in geometric parameters (diameter, length, specific surface), using nitric acid. In different experiments, the duration of oxidation, the concentration of nitric acid, and the consumption of HNO<sub>3</sub> per 1 g of MWCNTs were varied. The qualitative composition of the formed oxygen-containing functional groups and the changes occurring with the graphene layers of nanotubes were established by the methods of IR and Raman spectroscopy, and transmission electron microscopy. The total oxygen content in the samples was determined by energy dispersive analysis. The degree of MWCNTs functionalization with acidic functional groups was determined by Boehm titration. An X-ray structural analysis of the obtained samples was carried out and their specific surface area was estimated.

It was determined that the most serious changes in the functionalization degree occurred during the first 1–3 hours of oxidation. During this time interval, the achieved values of the functionalization degree were determined mainly by the shape of the MWCNTs graphene layers. At 7–10 hours of treatment, regardless of the initial parameters, MWCNTs have the functionalization degree in the range of 0.5–0.7 mmol·g<sup>-1</sup>. At the initial stage of oxidation, the amorphous phase is removed. Using dilute solutions of nitric acid does not allow obtaining oxidized nanotubes with the high functionalization degree. It is expedient to reduce the consumption of 65 % HNO<sub>3</sub> to 40 mL per 1 g of MWCNTs.

**Keywords:** multiwalled carbon nanotubes; oxidative functionalization; carboxyl groups; destruction; IR spectra; Raman spectra; X-ray diffraction patterns; interplanar distances.

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## Особенности окислительной функционализации углеродных нанотрубок

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**Аннотация:** Проведено комплексное исследование закономерностей окисления азотной кислотой многослойных углеродных нанотрубок (МУНТ) разных типов, отличающихся по геометрическим параметрам (диаметр, длина, удельная поверхность). В разных экспериментах варьировались продолжительность окисления, концентрация азотной кислоты и расход HNO<sub>3</sub> на 1 г МУНТ. Методами ИК- и рамановской спектроскопии и просвечивающей электронной микроскопии установлены качественный состав формирующихся кислородсодержащих функциональных групп и изменения, происходящие с графеновыми слоями нанотрубок. Общее содержание кислорода в образцах определялось методом энергодисперсионного анализа. Степень функционализации МУНТ

функциональными группами кислотного характера определена титрованием по Бозму. Осуществлялся рентгеноструктурный анализ полученных образцов, и проводилась оценка их удельной поверхности.

Определено, что наиболее серьезные изменения в степени функционализации происходят в течение первых 1–3 часов окисления. В этот промежуток времени достигаемые значения степени функционализации определяются, главным образом, формой графеновых слоев МУНТ. При 7–10-часовой обработке независимо от исходных параметров МУНТ имеют степень функционализации в интервале 0,5–0,7 ммоль/г. На начальном этапе окисления происходит удаление аморфной фазы. Использование разбавленных растворов азотной кислоты не позволяет получить окисленные нанотрубки с высокой степенью функционализации. Целесообразным является снижение расхода 65%-й  $\text{HNO}_3$  до 40 мл на 1 г МУНТ.

**Ключевые слова:** многослойные углеродные нанотрубки; окислительная функционализация; карбоксильные группы; деструкция; ИК-спектры; рамановские спектры; рентгеновские дифрактограммы; межплоскостные расстояния.

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## 1. Introduction

Multiwalled carbon nanotubes (MWCNTs) are widely used in various fields of science and technology due to their outstanding mechanical, electrical and chemical properties. They are more commonly used as components of composite materials [1]. However, due to high specific surface area and hydrophobicity, MWCNTs tend to agglomerate in polymer matrices. Therefore, the effect of their application may be lower than expected. Improving the compatibility of MWCNTs with modifiable materials requires chemical functionalization of the initially inert and hydrophobic nanotubes surface by forming various functional groups thereon [2].

Oxidation often appears to be the first and sometimes the only step in the chemical treatment of the MWCNTs. The following substances have been used as oxidizing agents: potassium permanganate [3], hydrogen peroxide [4], potassium dichromate [5], perchloric acid [6], hypochlorites [7], persulfates [8], etc. Nitric acid [4, 9–11] and its mixture (1 : 3) with sulfuric acid [10, 11] are the most frequently used substances among them. In the latter case, the oxidation is more efficient, though it is accompanied by more significant destructive changes in MWCNTs [12]. Besides, it has been reported that sulfonation, resulting in the formation of sulfur-containing functional groups, takes place together with oxidation processes when using the mixture of nitric and sulfuric acids [13].

The most commonly used oxidizing agent is nitric acid. At the same time, information on the effect of this treatment on the characteristics of the nanotubes surface is rather scattered.

In [14], it is shown that oxidation in nitric acid leads to the formation of oxygen-containing

functional groups on the MWCNTs surface, among which carboxyl groups can more easily be quantitatively determined [15]. These groups are attached primarily to the initial structural defects and then to the end fragments of the MWCNTs. Besides, the oxidative treatment may cause washing out of metal-oxide catalyst particles, opening of ends, truncation of some nanotubes, and fragmentation of sidewalls [16]. When performing prolonged treatment in concentrated nitric acid, MWCNTs are subjected to pronounced destructive changes [4]. On the other hand, when using diluted nitric acid solutions, the degree of the MWCNTs functionalization is quite small [9].

The presence of carboxyl groups improves dispersibility of MWCNTs in polar solvents and polymer matrices [2] and makes it possible to achieve other advantageous effects; however, it may adversely affect the conductive properties [11]. The COOH groups generally act as sites for adsorption of transition metal ions and nanoparticles [17]. Due to these adsorption effects, the oxidized MWCNTs can extract dissolved hazardous substances from aqueous media [18]. Furthermore, the carboxyl surface groups can participate in various chemical reactions, thereby making it possible to obtain esterified, thiolated, aminated, amidated, and other forms of functionalized nanotubes [19].

The growing demand for the functionalized MWCNTs sharply raises the problem of their industrial production. At present, MWCNTs are synthesized in sufficient quantities at laboratory and industrial levels using different techniques (e.g., chemical vapor deposition (CVD) [20]), but their functionalization is usually carried out under laboratory conditions.

Scaling of functionalization processes requires a detailed study of their laws and determination of the

conditions for chemical treatment of various types of nanotubes, when the required number of functional groups is formed on the surface, but the destructive changes are insignificant.

This paper studies the features of changes in the functionalization degree and surface structure of carbon nanotubes of various morphological types, differing in geometric parameters and shape of graphene layers, upon oxidation with nitric acid.

## 2. Materials and methods

### 2.1. Initial materials and their functionalization

“Taunit” ( $d = 20 \div 50$  nm, length  $l \geq 2$   $\mu\text{m}$ , and specific surface area  $\geq 160$   $\text{m}^2 \cdot \text{g}^{-1}$ ), “Taunit-M” ( $d = 10 \div 30$  nm, length  $l \geq 2$   $\mu\text{m}$ , and specific surface area  $\geq 270$   $\text{m}^2 \cdot \text{g}^{-1}$ ) and “Taunit-MD” ( $d = 30 \div 80$  nm, length  $l \geq 20$   $\mu\text{m}$ , and specific surface area  $\geq 200$   $\text{m}^2 \cdot \text{g}^{-1}$ ) MWCNTs produced by “NanoTechCenter” Ltd. (Tambov, Russia) were used herein. MWCNTs of the first type are characterized by the conical shape of graphene layers as shown by transmission electron microscopy (TEM) (Fig. 1a), while the second and third types are cylindrical (Fig. 1b and c).

These MWCNTs were oxidized with a 10–65 % nitric acid solution under reflux at 110 °C for 0.5–10 h (1 g of MWCNTs in 50 mL of the acid).

### 2.2. Material characterization methods

Functional groups at the MWCNTs surface were qualitatively identified by infrared (IR) spectroscopy using a Thermo Nicolet NEXUS 870 FTIR Spectrometer in transmission mode in potassium bromide pellets. The MWCNTs structure was analyzed by Raman spectroscopy using a DXR (Thermo Scientific) Raman Microscope (wavelength of the irradiating laser – 532 nm). Carboxyl groups were quantitatively determined by

the potentiometric acid-base reverse titration method described in [15].

Elemental composition of MWCNTs was estimated by energy-dispersive spectra analysis. The nanotubes microstructure was investigated by TEM using a JEM 2100 F/Cs microscope (JEOL) and then analyzed using a built-in JED 2300 X-ray instrument.

The specific surface area of MWCNTs was determined by the BET method by nitrogen adsorption at 77 K on a Nova1200 analyzer (Quantachrome Autosorb iQ).

X-ray structural analysis of the samples was carried out on a Diffrey-401 instrument. The values of the interplanar distances were calculated in accordance with the Wulff-Bragg condition.

## 3. Results and Discussion

After oxidation of MWCNTs with nitric acid, the IR spectra (Fig. 2) show peaks characteristic of O—H ( $3749$   $\text{cm}^{-1}$ ), C=O ( $1711$   $\text{cm}^{-1}$ ) bonds, and other hydrated oxygen-containing groups (a group of peaks at  $950$ – $1250$   $\text{cm}^{-1}$  [21]).

The energy dispersive spectra of “Taunit” MWCNTs with a conical graphene layer are shown in Fig. 3. The presence of oxygen in the composition of the initial “Taunit” MWCNTs with a conical shape of graphene layers is explained by their higher reactivity and possibility of oxidation immediately after CVD synthesis. When this conical MWCNTs are treated with nitric acid, the oxygen content increases to ~ 8 wt. % only at the initial stage of the process, and then remains practically unchanged.

There is no oxygen in the samples of the initial cylindrical “Taunit-M” and “Taunit-MD” MWCNTs. In samples of thin cylindrical “Taunit-M” MWCNTs, oxygen is detected after 2 hours of oxidation and its concentration increases in the entire time range reaching ~14 wt. % upon 10-hour treatment with nitric acid (Fig. 4).

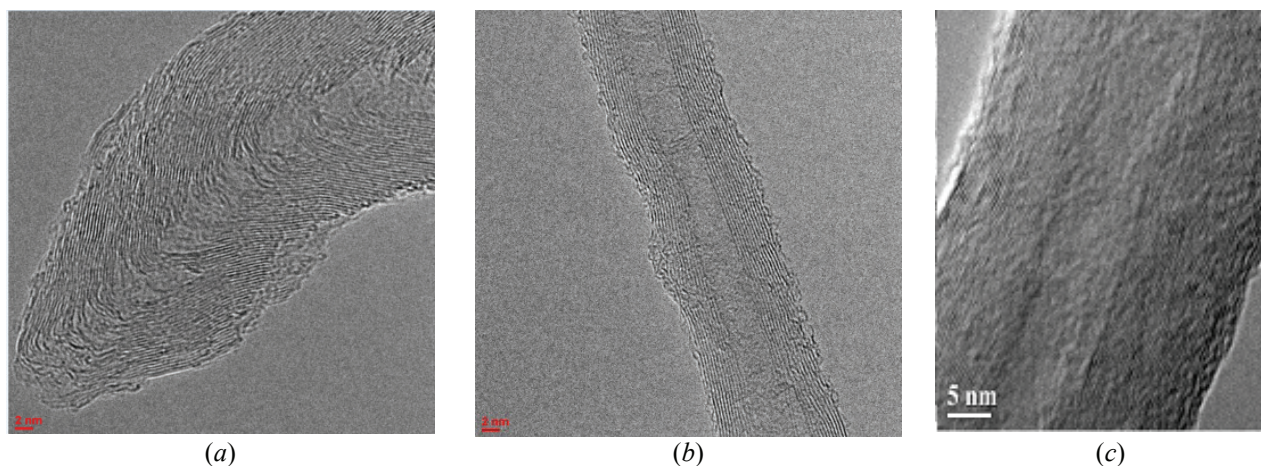


Fig. 1. TEM-images of the MWCNTs: “Taunit” (a), “Taunit-M” (b) and “Taunit-MD” (c)

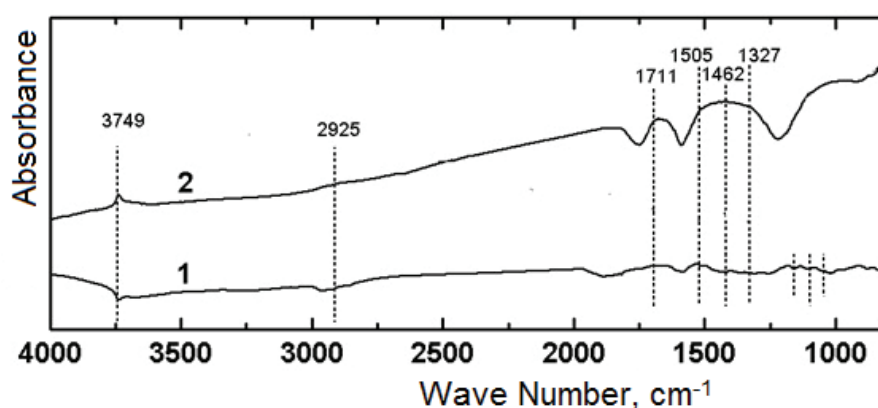


Fig. 2. Typical IR spectra of the initial (1) and oxidized with nitric acid (2) MWCNTs

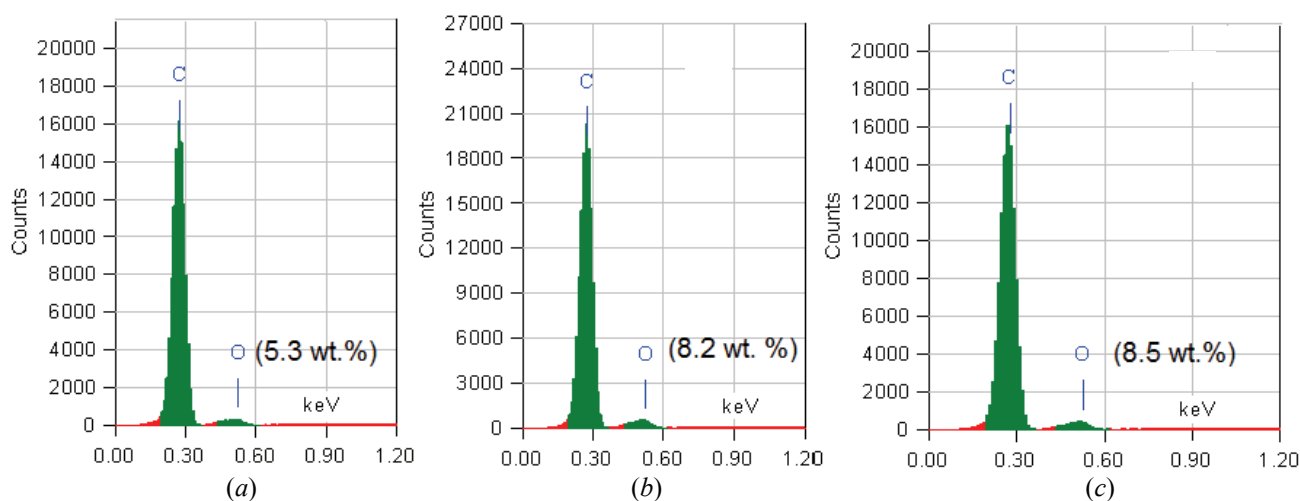


Fig. 3. Energy dispersive spectra of the initial (a) and oxidized with nitric acid for 2 (b) and 8 (c) hours "Taunit" MWCNTs

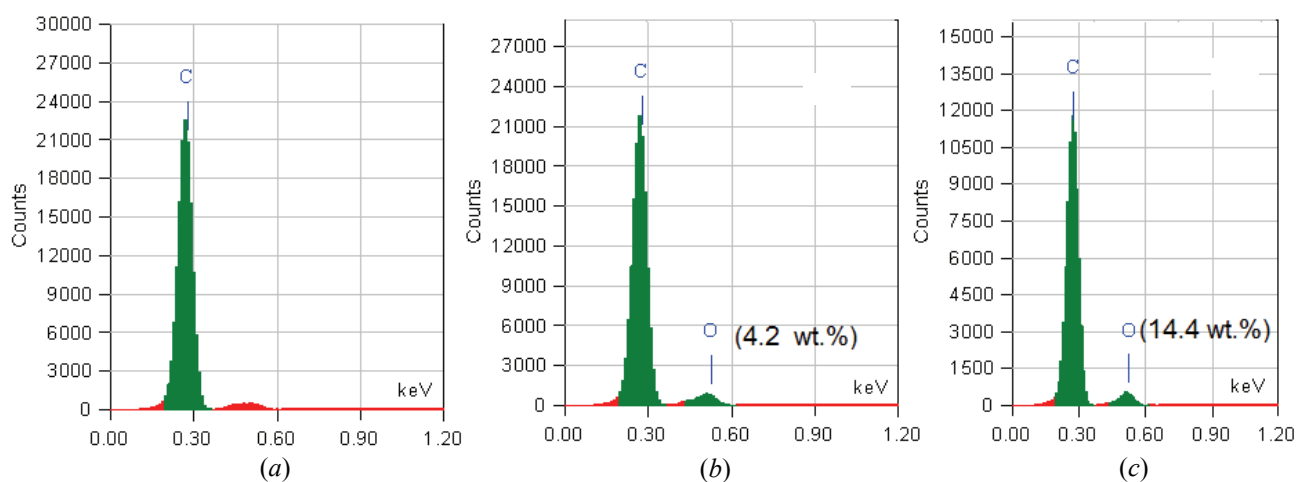
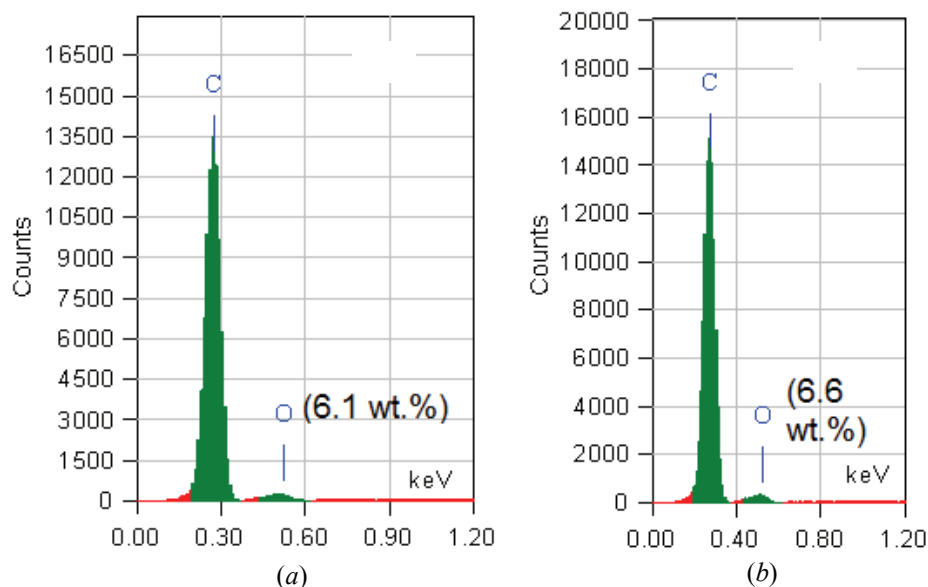
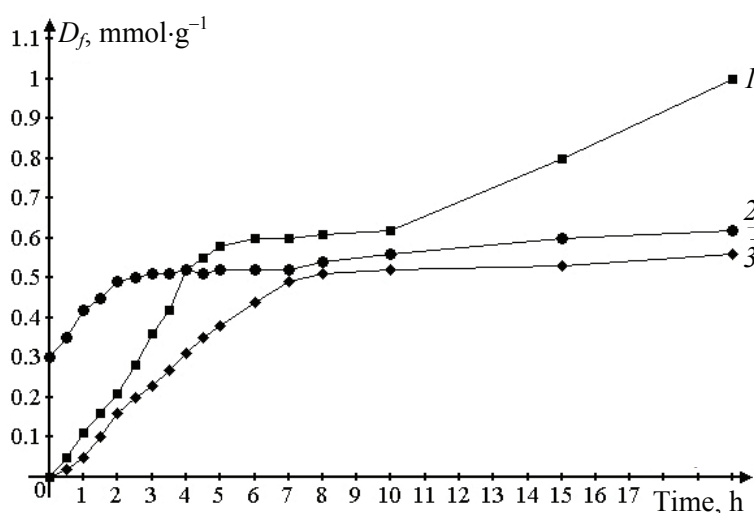


Fig. 4. Energy dispersive spectra of the initial (a) and oxidized with nitric acid for 2 (b) and 10 (c) hours "Taunit-M" MWCNTs





**Fig. 5.** Energy dispersive spectra of “Taunit-MD” MWCNTs after 8 (a) and 10 (b) hours of oxidation in nitric acid



**Fig. 6.** Dependency of the functionalization degree of “Taunit-M” (1), “Taunit” (2) and “Taunit-MD” (3) MWCNTs by carboxyl groups on the duration of oxidation with concentrated nitric acid

Mass fraction of O in samples of cylindrical “Taunit-MD” MWCNTs with a large diameter begins to increase much later and is contained in an amount of about 6 wt. % in samples subjected to oxidation for 8–10 hours (Fig. 5).

Thus, the total content of oxygen atoms at the beginning of MWCNTs oxidation is primarily determined by the shape of the graphene layers. So, conical “Taunit” MWCNTs, having the smallest specific surface area ( $S_{\text{BET}}$ ), contain the most oxygen at the initial stage of oxidation. Large diameter “Taunit-MD” MWCNTs with practically defect-free surface are the least reactive.

The titrimetric analysis data (Fig. 6) qualitatively correlate with the regularities discussed above.

In the first hours of oxidation, “Taunit” MWCNTs are characterized by the highest value of the functionalization degree by carboxyl groups ( $D_f$ ), which is due to the greater reactivity of the conical layers and the presence of oxygen-containing groups in the initial material. However, then the difference becomes less significant. After 7–10 hours of oxidation, all MWCNTs, regardless of type, have the functionalization degree equal to 0.5–0.7 mmol·g<sup>−1</sup>. Moreover, for “Taunit” and “Taunit-MD” MWCNTs, these values of  $D_f$  are retained during further oxidation, while for “Taunit-M” MWCNTs, the degree of functionalization begins to increase again, which is accompanied by destruction of the nanotubes structure according to TEM data (Fig. 7).

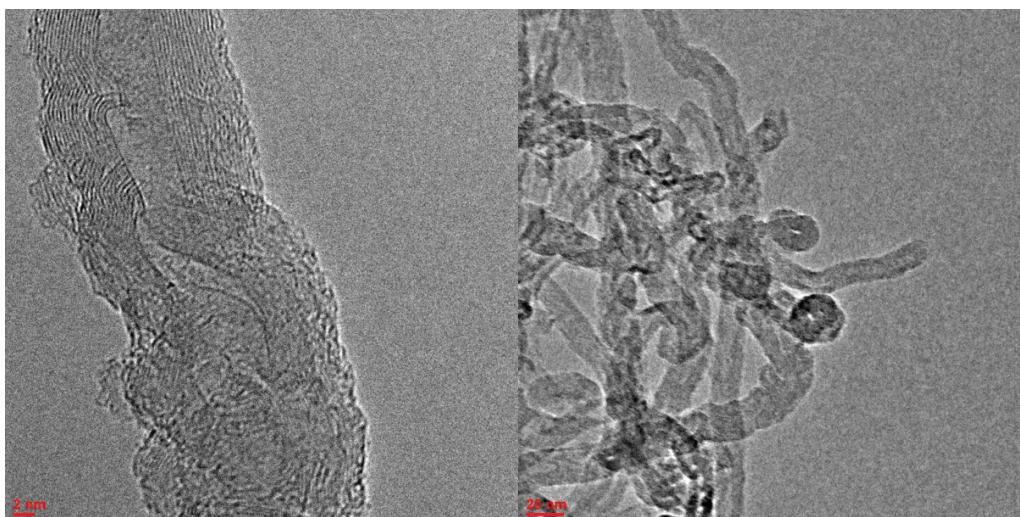


Fig. 7. TEM-images of “Taunit-M” MWCNTs after 10-hour oxidation with nitric acid

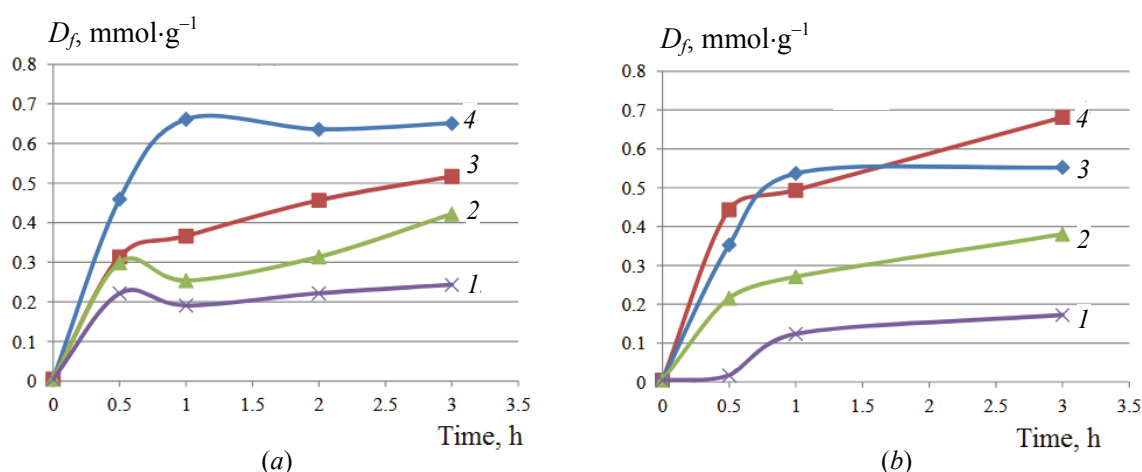


Fig. 8. Change in the functionalization degree of “Taunit-M” MWCNTs by carboxyl groups during oxidation with 10 (1); 30 (2); 50 (3) and 65 (4) % nitric acid at  $m_{\text{MWCNTs}}(\text{g}) : V_{\text{NAS}}(\text{mL})$  equal to 1 : 50 (a) and 1 : 40 (b)

Thus, the long-term treatment of MWCNTs with nitric acid is inappropriate, and the most significant changes in the functionalization degree occur at the beginning of the process.

For “Taunit-M” MWCNTs, we analyzed the change in the functionalization degree in the first 3 hours of oxidation with nitric acid of various concentrations and at ratios of the MWCNTs mass ( $m_{\text{MWCNTs}}$ ) to the volume of  $\text{HNO}_3$  solution ( $V_{\text{NAS}}$ ) equal to 1 : 50, 1 : 40 and 1 : 20 (Fig. 8).

The achieved  $D_f$  values are determined by both the concentration of nitric acid and its consumption. The time dependency of the functionalization degree is sometimes observed as early as an hour after the start of oxidation. Moreover, if 65 % acid is selected as a reagent, then even with a decrease in its consumption per unit mass of MWCNTs, after 3 hours, the same functionalization degree is achieved as at a higher consumption.

However, the use of dilute  $\text{HNO}_3$  solutions is justified only when it is necessary to obtain a product with the low functionalization degree.

Using the approaches outlined in [22], the Raman spectra of MWCNTs oxidized under various conditions were analyzed (Table 1).

Considering that  $D/G$  for initial MWCNTs was 1.050, it can be noted that there is no dramatic increase in the defect degree during oxidation for up to 3 hours. On the contrary, in some cases, due to the removal of the amorphous phase from the nanotubes surface, a decrease in  $D/G$  occurs. Attention is drawn to the fact that MWCNTs with the same functionalization degree can have different defect index. This is explained by the fact that titrimetrically determined acidic groups can have different localization and are located in side wall defects, ends of nanotubes, and on particles of the surface amorphous phase.

**Table 1.** The results of processing the Raman spectra of “Taunit-M” MWCNTs oxidized with nitric acid under various conditions

HNO <sub>3</sub> concentration, wt. %	$m_{\text{MWCNTs}}(\text{g}) : V_{\text{NAS}}(\text{mL})$	D/G ratio of MWCNTs for duration of oxidation		
		0.5 h	1 h	3 h
65	1 : 50	0.907	0.844	1.108
	1 : 40	1.010	1.011	1.054
	1 : 20	1.009	–	0.942
50	1 : 50	1.010	0.985	0.959
	1 : 40	0.992	1.044	0.953
30	1 : 50	0.920	0.982	1.042
	1 : 40	1.048	1.041	1.042
10	1 : 50	1.004	0.909	1.023
	1 : 40	1.093	0.995	0.924
	1 : 20	0.965	–	1.060

**Table 2.** X-ray structural analysis data and changes in the specific surface area of “Taunit-M” MWCNTs oxidized with nitric acid at  $m_{\text{MWCNTs}}(\text{g}) : V_{\text{NAS}}(\text{mL}) = 1 : 50$ 

HNO <sub>3</sub> concentration, wt. %	Duration of oxidation, h	2 $\theta$	$d$ , Å	Peak width (002)	$S_{\text{BET}}$ , m <sup>2</sup> ·g <sup>-1</sup>
High-purity graphite		39.34	3.403	0.98	–
Purified MWCNTs		37.55	3.559	3.93	360
65	0.5	36.78	3.630	4.11	275
	1	38.05	3.514	4.20	252
	2	38.48	3.476	4.18	259
	3	36.88	3.621	4.23	263
45	0.5	37.15	3.596	4.38	296
	1	37.05	3.605	4.26	355
	2	37.00	3.610	4.45	281
	3	37.09	3.601	4.41	306
30	0.5	37.15	3.596	4.12	412
	1	37.05	3.605	3.98	150
	2	37.09	3.601	4.46	286
	3	36.88	3.621	4.24	279
10	0.5	36.93	3.616	4.15	192
	1	37.11	3.600	4.26	173
	2	38.39	3.484	4.05	245
	3	37.26	3.586	4.44	212

Obviously, the formation of new defects, removal of unstructured carbon and leveling of layers, the formation of functional groups and their transformations during oxidation of MWCNTs with nitric acid proceed in parallel.

Additionally, an assessment of the X-ray diffraction patterns of the MWCNTs samples and their specific surface was carried out (Tables 2 and 3). For comparison, Table 2 shows the crystallographic parameters for high-purity graphite and unoxidized

MWCNTs purified from the metal oxide catalyst impurities.

MWCNTs (initial and oxidized) are characterized by higher interplanar distances ( $d$ ) than in high-purity graphite, which is associated with the curvature of their surface. At the initial stage of oxidation, a decrease in the value of  $2\theta$ , an increase in  $d$ , and an increase in the width of the corresponding peak are observed. This is due to the opening of the nanotube ends while removing the metal oxide catalyst impurities. The change in interplanar distances during chemical processing correlates with the data of Raman spectroscopy: when using 65 and 10 % acid, the interlayer distance decreases to a minimum for samples oxidized for 2 hours, and the  $D/G$  value is also the minimum. When a more dilute acid (30 and 45 %) is used, no significant changes are observed in the X-ray diffraction patterns of the oxidized samples. Variations in the peak width (002) can be attributed to the unstructured carbon content.

It can also be noted that during oxidation of MWCNTs with 65 % nitric acid at the initial stage (up to 1 h), corresponding to the removal of amorphous carbon, there is a direct relationship between the change in the angle  $2\theta$  and the defect index  $D/G$ . When the duration increases, this dependence is reversed. Interplanar distances and  $2\theta$  values vary opposite to each other. A symbatic relationship between the change in the defect index and the peak width (002) is also observed upon oxidation of

MWCNTs with 45 % nitric acid. When using diluted nitric acid (10 and 30 %), such a relationship between the indicators of oxidized MWCNTs samples ceases to be observed.

It was found that, regardless of the processing conditions, the specific surface area of oxidized MWCNTs is lower than that of the initial ones. This is largely due to the removal of amorphous carbon.  $S_{\text{BET}}$  is minimized for 1 hour treatment in 65 % acid when samples have the lowest defect index. An even lower specific surface area of materials obtained at low acid concentrations is apparently due to the irreversible agglomeration of the material upon heating.

The data analysis given in Table 3 shows that at a lower consumption of the oxidizing reagent per unit mass of MWCNTs at the initial stage of the process, as in the previous case, the interplanar distances decrease. However, the relationship between the peak width (002) and the  $D/G$  index is different here. Besides, in this case, the specific surface area of the materials does not decrease so significantly.

Upon oxidation of MWCNTs with 65 and 30 % acids, a monotonic decrease in  $S_{\text{BET}}$  is observed in the studied time interval. In other cases, the change in specific surface area is non-monotonic. However, all samples oxidized at  $m_{\text{MWCNTs}}(\text{g}) : V_{\text{NAS}}(\text{mL}) = 1 : 40$  are characterized by lower  $S_{\text{BET}}$  values than the initial MWCNTs and samples oxidized at a higher nitric acid consumption.

**Table 3.** Data on X-ray structural analysis and changes in the specific surface area of “Taunit-M” MWCNTs oxidized with nitric acid at  $m_{\text{MWCNTs}}(\text{g}) : V_{\text{NAS}}(\text{mL}) = 1 : 40$

HNO <sub>3</sub> concentration, wt. %	Duration of oxidation, h	$2\theta$	$d$ , Å	Peak width (002)	$S_{\text{BET}}$ , m <sup>2</sup> ·g <sup>-1</sup>
65	0.5	38.39	3.484	4.30	324
	1	38.39	3.484	4.32	271
	3	37.86	3.531	4.08	258
50	0.5	38.01	3.517	4.20	252
	1	38.28	3.493	3.51	295
	3	38.38	3.485	4.13	261
30	0.5	38.00	3.518	4.45	294
	1	37.92	3.526	4.23	278
	3	38.32	3.490	4.09	226
10	0.5	37.96	3.522	4.28	260
	1	38.27	3.495	4.10	298
	3	37.92	3.526	4.39	353



#### 4. Conclusions

As a result of a comprehensive study, it was found that the formation rate of oxygen-containing groups on the MWCNTs surface at the initial stage of oxidation is primarily due to the structure of the graphene layers of nanotubes. However, in a certain time interval, the functionalization degree by COOH groups has similar values for MWCNTs of various morphological types. The most significant changes in the functionalization degree are observed in the first 1–3 hours of the process, and then the  $D_f$  dependency reaches a plateau. The resumption of growth in the functionalization degree for thin cylindrical MWCNTs during prolonged oxidation is due to destructive changes. A decrease in the defect index of MWCNTs at the initial stage of oxidation with nitric acid is accompanied by a decrease in interplanar distances. It should be noted that prolonged oxidation of MWCNTs, as well as a decrease in the concentration of nitric acid, is inappropriate. However, a decrease in the consumption of the oxidizing agent from the generally accepted 50 to 40 mL per 1 g of MWCNTs makes it possible to achieve a number of positive effects upon reaching the same functionalization degree as at a high acid consumption.

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#### 7. Conflict of interests

The authors declare no conflict of interest.

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