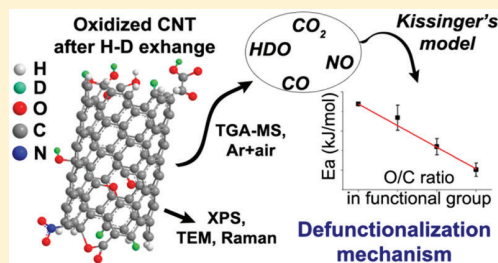


Mechanism of Thermal Defunctionalization of Oxidized Carbon Nanotubes

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Supporting Information

ABSTRACT: The mechanism of thermal defunctionalization of multiwalled carbon nanotubes (CNTs) oxidized by nitric acid was studied. X-ray photoelectron spectroscopy and thermal analysis under different heating rates combined with mass spectrometry of evolved gases (TGA–MS) were used to reveal the transformations on the CNT surface. Hydrogen–deuterium exchange and mathematical handling of TGA–MS curves were carried out to evaluate the impact of a small amount of residual oxygen on CNT defunctionalization. Water, CO, CO₂, and NO/CH₂O mass curves recorded during TGA–MS study were curve fitted. The resultant peaks were attributed to the different stages of CNT defunctionalization. Deuterium exchanged CNTs allowed one to reveal the mechanism of water release during heating. Kissinger's model was applied to estimate the activation energy of the decomposition of different functional groups on the surface of CNTs.



1. INTRODUCTION

Unique properties of multiwall carbon nanotubes (CNTs) make them attractive for applications in different fields of science and technology.¹ High strength, rigid structure, and high thermal and electroconductivity enable their use in polymer materials,² and as supports for metal-based catalysts.³

Modification of the CNT surface with oxygen-containing functional groups is a popular way of improving their distribution into polymer matrixes for new hybrid materials' design as well as metal or oxide nanoparticles on the CNT surface,⁴ which is required for preparation of new catalysts. Depending on the nature of the oxidizing agent, the oxidation of CNTs can be carried out both in gas and in liquid phases. The most often used liquid-phase oxidants are nitric acid,⁵ the mixture of nitric and sulfuric acids,⁶ hydrogen peroxide,⁷ and potassium permanganate.⁸ Ozone,⁹ nitric acid vapor,¹⁰ carbon dioxide,¹¹ and plasma jet¹² are usually used for gas-phase oxidation of CNTs.

Because oxidized CNTs by themselves or as a component of a composite or catalyst can be used in high temperature applications, their thermal transformations are of great importance. The most sensitive in this case are surface functional groups. Decomposition process is accompanied by the formation of water, CO₂, or CO.⁸ Moreover, it is a stepwise process and its parameters (decomposition rates and temperature ranges) are affected by the nature and close environment of the functional groups.¹³ A lot of researches have been devoted to the defunctionalization of CNTs, graphite, and other carbon materials.^{13–22} However, the majority of them lack the detailed mechanism of CNT defunctionalization. At the same time, along with the decomposition of functional

groups, other transformations may occur on the surface of CNTs during heating. These transformations change the composition and content of functional groups.

XPS and TPD are the most widely used techniques for characterizing functionalized CNTs.^{15,17,18,20} Despite the significant number of publications in this field, the mechanism of the defunctionalization is still being debated. Application of XPS and TPD in such studies is often limited to the degree of surface oxidation.^{23–25} To reveal the mechanism of CNT defunctionalization, this work focuses on the comprehensive study of the processes on the surface of nitric acid-oxidized CNTs during heating using XPS, Raman spectroscopy, and thermal analysis combined with mass spectrometry of evolved gases (TGA–MS). The majority of previous studies of thermal behavior of oxidized CNTs focused only on the decomposition temperatures of different functional groups^{13,15,18,25} or quantitative analysis of oxygen content and its chemical state on the CNT surface.²⁰ This Article presents new and comprehensive insight into the mechanism of the defunctionalization of CNTs using interdisciplinary approach: both from organic and from physical chemistry points of view. We have tried to consider all possible processes on the surface of CNTs during heating including the reactions of functional groups with each other. Moreover, activation energies of the decomposition of functional groups, prevailing on the surface of CNTs, and correlation of the activation energy with the structure of the functional group were studied. We also revealed two stages of

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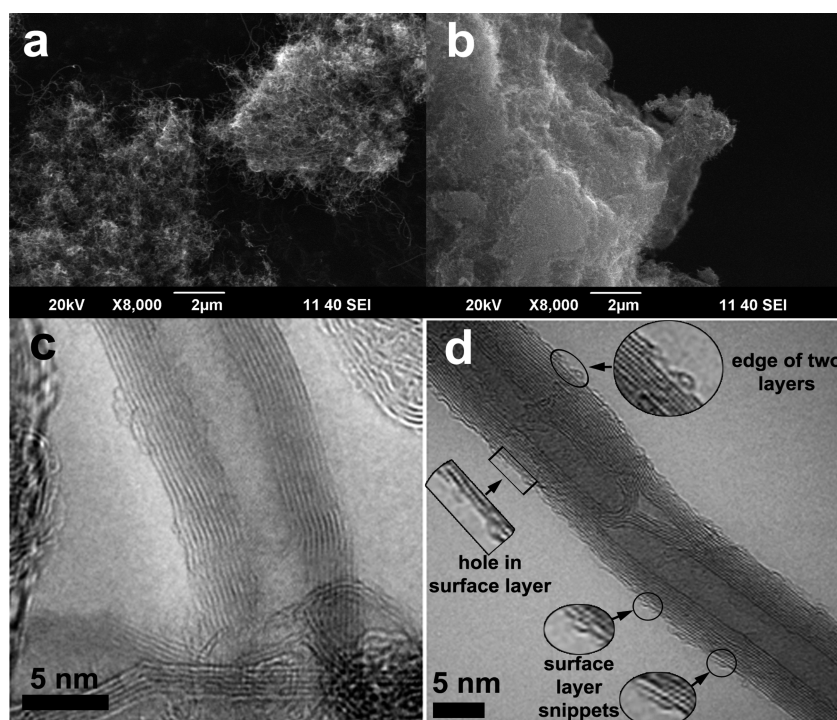


Figure 1. SEM (a,b) and TEM (c,d) images of pristine (a,c) and oxidized (b,d) CNTs.

the air oxidation of CNTs: burning of defects on the surface and burning of bulk CNTs. The detailed investigation of the water release mechanism was significantly assisted by hydrogen–deuterium exchange. The results of this work may be useful in predicting and simulating the behavior of CNT-containing materials during heating in both oxidizing and inert atmosphere.

2. EXPERIMENTAL SECTION

2.1. CNT Synthesis, Functionalization, and Isotopic Exchange. Multiwalled CNTs with the outer diameter of 10–30 nm were synthesized by catalytic chemical vapor deposition method using hexane as a carbon precursor in the presence of Co–Mo/MgO catalyst.²⁶ For this purpose, the catalyst, obtained by the combustion method from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$, citric acid, and glycine, was placed inside a quartz tubular reactor. The reactor then was heated to 750 °C in N_2 flow. After that, N_2 flow was switched to bubble through hexane for 5 h. The obtained material was cooled in N_2 flow up to 400 °C and then cooled to room temperature in air atmosphere to remove amorphous impurities. The resultant powder was refluxed in concentrated HCl for 3 h to dissolve growth catalyst. Finally, material was filtered and washed in deionized water until neutral pH and dried at 130 °C for 12 h.

The material obtained was refluxed in concentrated HNO_3 solution (Chimmed, Russia, 99.99%) under vigorous stirring for 12 h, then filtered and washed with distilled water to neutral pH according to the technique described earlier.²⁷ Finally, it was dried at 130 °C and named as “CNTox”. For the hydrogen–deuterium exchange, CNTox was ultrasonicated in D_2O for 6 h and then dried in a rotary evaporator under vacuum.

2.2. Annealing of Oxidized CNTs. CNTox was annealed in the thermal analyzer in argon atmosphere at 160, 370, 530, and 840 °C for 2 h. The heating rate was 10 °C/min. Obtained

samples were denoted as CNT1, CNT2, CNT3, and CNT4, respectively.

2.3. Characterization. The morphology of the catalysts was studied using scanning electron microscopy (SEM, JEOL JSM-6390LA) and transmission electron microscopy (TEM, JEOL 2100F). Temperature ranges of the decomposition of oxygen groups on the surface of CNTox were determined by thermal gravimetric analysis (TGA) in argon atmosphere using Netzsch STA 449 Jupiter instrument coupled with Netzsch QMS Aeolos 403 mass spectrometer for evolved gas analysis. Different heating rates of 2, 10, 20, 40, and 50 °C/min were used. To minimize the influence of residual oxygen, the argon flow was reduced to 8 mL/min and two heating cycles were used. At each cycle, CNT sample was heated from room temperature to 1200 °C. TGA mass loss and the mass spectrum of evolved gases were continuously recorded during heating. The m/z curves were extracted from the recorded mass spectra. TGA mass loss and m/z curves for the first and second heating cycles were subtracted from each other. Before the subtraction, the intensity of the m/z curve in each temperature point was corrected to the mass of the sample determined by TGA. Subtracted m/z curves were deconvoluted into Gaussian and bi-Gaussian²⁸ components using OriginLab software.

XPS was used to determine the surface composition and content of functional groups. Spectra were recorded on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with a monochromatic Al $K\alpha$ source ($h\nu = 1486.6$ eV, 150 W). The pass energy of the analyzer was 160 eV for the survey spectra and 20 eV for the high-resolution ones. Raman spectra were registered using a LabRam HR800 UV (Horiba Jobin Yvon, Japan) microscope-spectrometer using 5 mW argon laser excitation (514.5 nm) and 50× Olympus lens. For each sample, the spectrum was collected in 3–5 points.

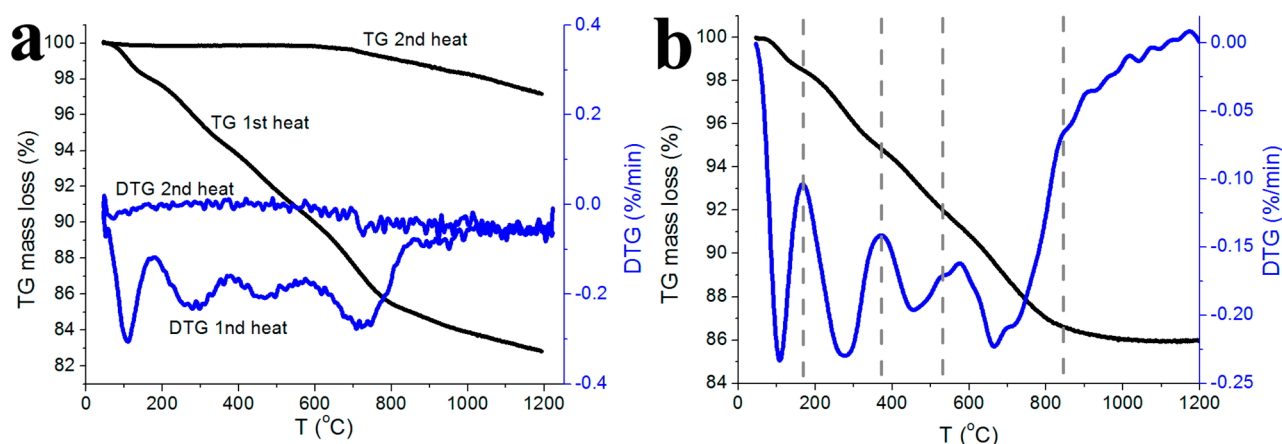


Figure 2. Illustration of TGA data optimization using TG and DTG curves of two consecutive heating cycles: (a) TGA and DTG curves of CNTox recorded during two heating cycles (argon flow, 10 °C/min); and (b) subtracted and smoothed TGA and DTG curves.

3. RESULTS AND DISCUSSION

3.1. Electron Microscopy Results. Pristine and oxidized CNTs were studied by SEM and TEM to reveal the changes in their morphology and structure after oxidation (Figure 1). It is clearly seen that nitric acid treatment led to the compaction of CNTs due to the hydrogen bonds of functional groups and overall surface polarity in oxidized CNTs (Figure 1a,b). TEM images show the defect formation during the oxidation (Figure 1c,d), which is typical for nitric acid treatment.²⁷

3.2. TGA, Raman, and XPS Analysis. TGA allowed tracing of mass loss of oxidized CNTs that resulted from the decomposition of functional groups on their surface during heating. Figure 2a shows TGA and differential TGA (DTG) curves of CNTox recorded during two consecutive heating cycles. To eliminate the effect of possible oxidation of CNTs by the residual oxygen, TGA and DTG curves for the second cycle were subtracted from the corresponding curves for the first cycle. The subtracted mass loss curve (Figure 2b) can be divided into four temperature ranges; each of them corresponds to the decomposition of various functional groups according to the literature (Table 1). The highest mass loss is observed in the temperature ranges of 160–370 and 530–840 °C.

Table 1. Identification of Mass Losses in TGA Curve of CNTox

temp range (°C)	mass loss (wt %)	decomposed groups ¹³
up to 160	1.5	water desorption
160–370	3.7	carboxyls
370–530	2.8	lactones, anhydrides
530–840	5.4	anhydrides, lactones, phenols, carbonyls, quinones, ethers

To trace the structural changes on the CNTox surface at different stages of decomposition of functional groups, four annealing temperatures (160, 370, 530, and 840 °C) were chosen on the basis of TGA results.

Structural changes in CNTox after annealing were studied by Raman spectroscopy. The ratio of the intensities of D and G bands (I_D/I_G) in Raman spectra characterizes the defectiveness of sp^2 carbon material.²⁹ Table 2 shows the I_D/I_G ratio in Raman spectra of oxidized and annealed CNTs. This ratio is slightly reduced after annealing at 370 °C as compared to the sample annealed at 160 °C. Similar dependence was observed

Table 2. I_D/I_G Ratio in Raman Spectra, and O and N Content, Measured by XPS, in Oxidized and Annealed (10 °C/min Heating Rate) CNTs

sample	annealing temp (°C)	I_D/I_G	O _{XPS} (at. %)	N _{XPS} (at. %)
CNTox		1.26 ± 0.06	8.6	0.5
CNT1	160	1.35 ± 0.03	7.2	0.4
CNT2	370	1.25 ± 0.02	5.2	0.2
CNT3	530	1.28 ± 0.05	3.0	0.2
CNT4	840	1.58 ± 0.06	1.3	0.0

in ref 30 after annealing of CNTs in air, and the authors attributed this effect to the combustion of highly unstructured carbon impurities as well as defective CNTs at temperatures below 400 °C. Annealing at 840 °C dramatically increased the I_D/I_G ratio. This is apparently a result of CNT oxidation by the residual oxygen in argon flow and analyzer chamber, which led to the CNT destruction and increased the number of defects. The reason for the increase in I_D/I_G ratio between CNTox and CNT1 is not yet clear.

Annealed samples were studied by XPS to trace the oxygen content on the CNT surface (see survey spectra in Figure S-1.1). The decrease of total oxygen content with the annealing temperature is clearly seen in Table 2. According to XPS data, the fastest loss of oxygen was observed in the temperature range of 370–530 °C, whereas the maximum weight loss in TGA was seen between 530 and 840 °C (Table 1). This contradiction may be explained by the different thermal treatment of the sample during TGA and before XPS study. In contrast to TGA, where the sample was gradually heated, before XPS analysis it was annealed at a fixed temperature. Isothermal annealing could cause the decomposition of oxygen-containing groups at lower temperatures than in the case of nonisothermal conditions of TGA. The presence of a noticeable amount of oxygen on the surface of CNTs after high-temperature annealing at 840 °C may indicate a partial oxidation of the sample by the residual oxygen in argon flow or analyzer chamber. Air exposure during sample transfer to XPS instrument may be another reason for the relatively high oxygen content on the surface of CNT4.

C 1s and O 1s XPS spectra of the studied samples were deconvoluted into components to evaluate oxygen–carbon bonding (Figure S-1.2). Figure 3 and Table S-1 show the results of the deconvolution. The intensity of the C 1s

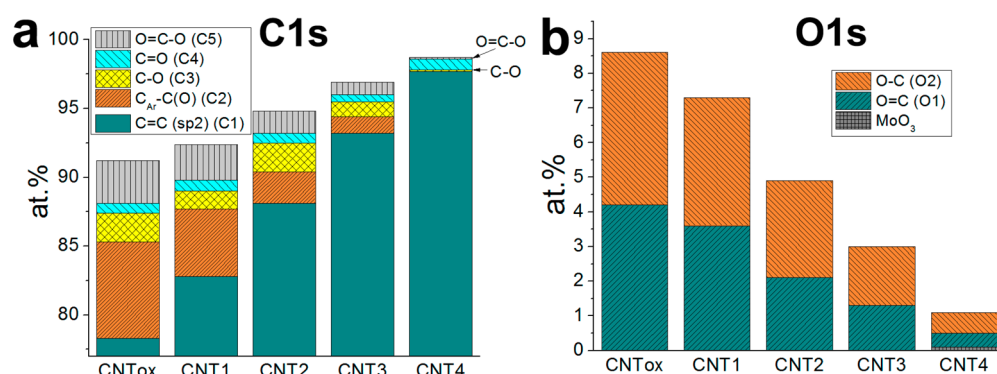


Figure 3. Results of the deconvolution of C 1s (a) and O 1s (b) XPS spectra of studied samples.

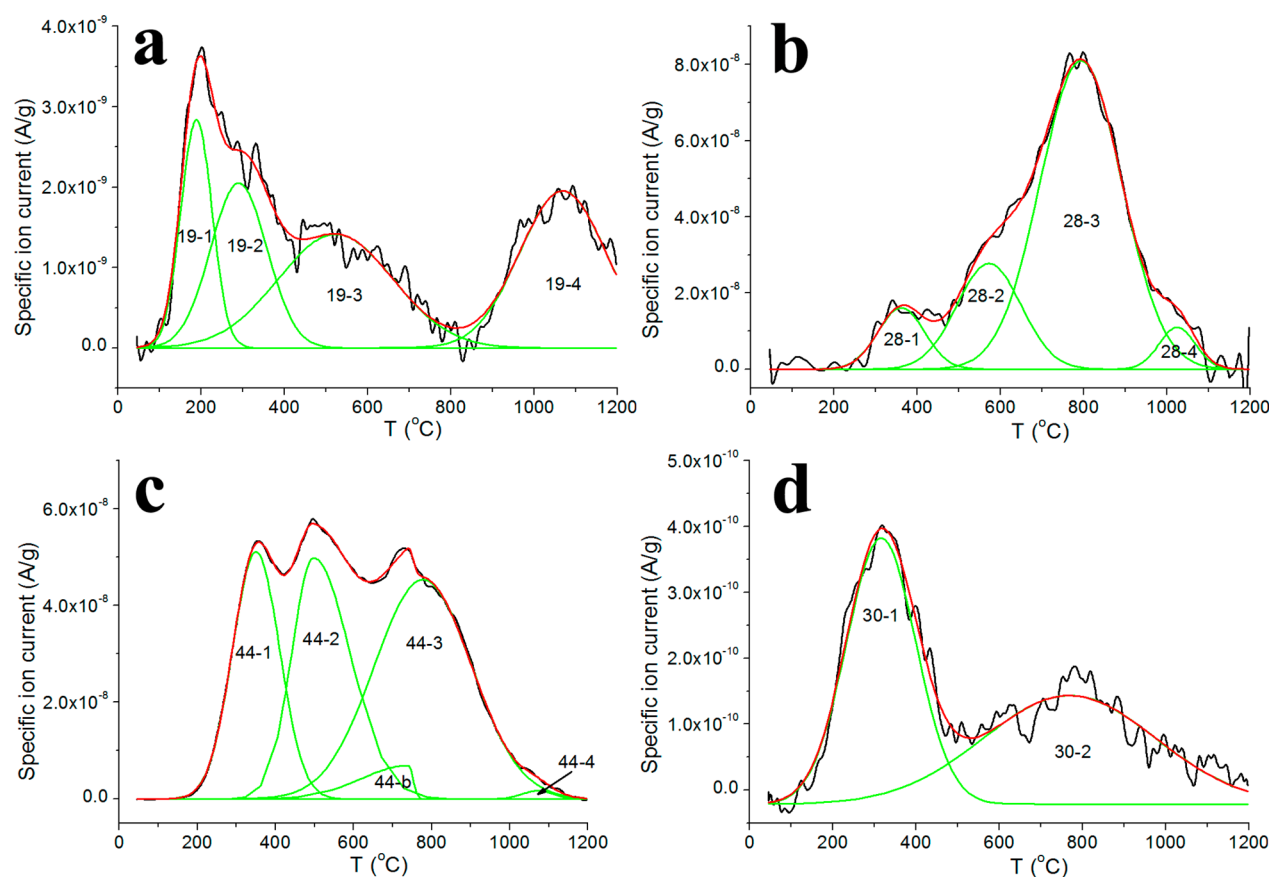


Figure 4. TGA-MS results for CNTox (heating rate $-40\text{ }^{\circ}\text{C/min}$) after data processing of MS signals of two consecutive heating cycles. The subtracted curves of m/z : (a) 19 (HDO); (b) 28 (CO); (c) 44 (CO_2); and (d) 30. Attribution of m/z 30 will be discussed further.

component at 285.0 eV decreased during annealing. Although this component is sometimes assigned to the sp^3 -carbon,⁹ Raman spectroscopy demonstrated that in our case the defectiveness of carbon structure, which correlates with the presence of sp^3 -hybridized carbon atoms, did not change significantly up to $530\text{ }^{\circ}\text{C}$ and then considerably increased after annealing at $840\text{ }^{\circ}\text{C}$. The authors of the work³¹ studied aromatic polyesters and found that the C 1s binding energy of aromatic carbon atoms with the oxygen bonded carbon atoms in their close environment ($\text{C}_{\text{Ar}}-\text{C}(\text{O})$) was shifted from the typical values for sp^2 -hybridized carbon atoms toward higher binding energy, but still remained lower than the binding energy typical for C–O bonds. It was also shown that the binding energy of aromatic carbon atoms bonded with $-\text{C}(\text{O})\text{N}$ group shifted approximately 0.5 eV toward higher values.³²

The intensity of the component at 285.0 eV in our case correlates with the total amount of functional groups on the surface of CNTs (Figure 3, Table S-1), which confirms the suggestion about $\text{C}_{\text{Ar}}-\text{C}(\text{O})$ contribution to C 1s XPS spectrum. To make further discussion easier, the chemical states of carbon and oxygen atoms identified by XPS were designated as C1–C5 for carbon and O1–O2 for oxygen atoms (Figure 3, Figure S-1.3).

Deconvolution of XPS spectra suggests the presence C3, C5, and quaternary aromatic carbons $\text{C}_{\text{Ar}}-\text{C}(\text{O})\text{OR}$ (where $\text{R} = -\text{H}, -\text{C}(\text{O})-\text{C}_{\text{Ar}}, \text{C}_{\text{Ar}}$) (C2) groups on the surface of studied materials. The intensities of C3 and, especially, C4 components in C 1s XPS spectra are difficult to extract in a reliable way because these low intensity components overlap with the high intensity asymmetric component from sp^2 -hybridized carbon

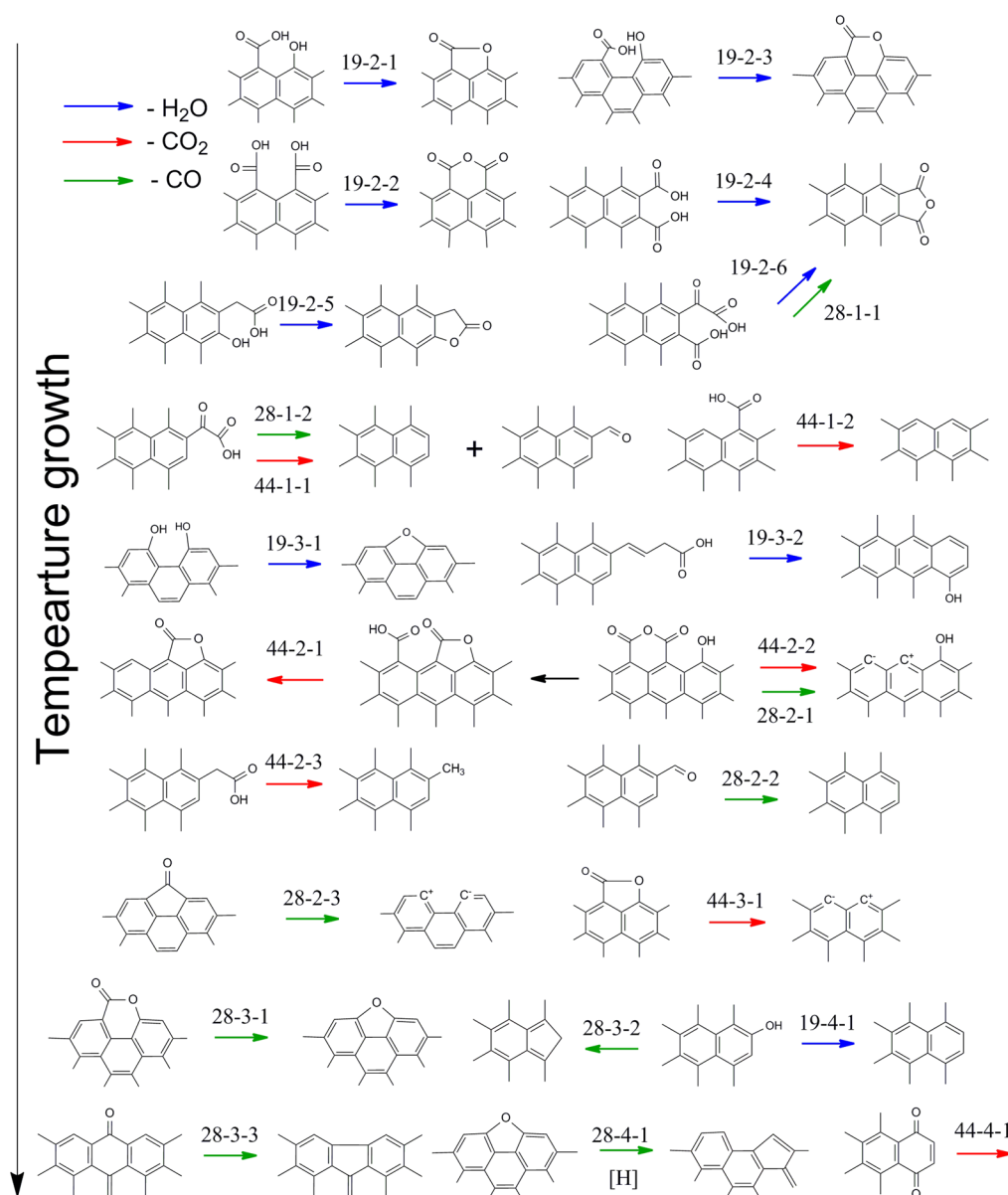


Figure 5. Proposed mechanism of the CNT defunctionalization.

atoms (Figure S-1.2a). Therefore, we will focus further discussion of the XPS results for annealed samples on the components in O 1s spectra and C5 component in C 1s spectra.

The MS analysis of the gases evolved during TGA experiment was carried out to more accurately identify the decomposition of functional groups on the surface of CNTox. First, to minimize the effect of residual oxygen in argon flow and analyzer chamber, we subtracted m/z curves for the second heating cycle from those for the first cycle. The subtracted 44, 28, and 32 m/z curves for the heating rates of 10 and 40 °C/min are shown in the Figure S-2. Consumption of oxygen in the range of 400–700 °C is clearly seen in Figure S-2a, which testifies the oxidation during the first heating cycle. This process can be attributed to both CO oxidation to CO₂ and, more likely, to burning of defect sites on the CNT surface. Increase in heating rate to 40 °C/min almost completely eliminated this process (Figure S-2b). This heating rate was chosen for further study. We also assumed that the oxidation by

the residual oxygen did not noticeably affect CO profiles in this case. For the detailed study of evolved gases, the following subtracted m/z curves were plotted and curve fitted: 19 (HDO), 28 (CO), 30, and 44 (CO₂) (Figure 4). Hydrogen–deuterium exchanged CNTs allowed one to analyze the water signal (m/z 19) originated only from the processes on the CNT surface, whereas the presence of the residual water in argon flow and chamber significantly affected the signal for m/z 18, making it difficult to analyze; this is clearly seen in Figure S-3.

Because the desorption temperatures of the functional groups on the surface of CNT depend on the heating rate we will focus on the discussion of sequence of desorption processes on the CNT surface rather than on their exact temperatures. The m/z signals recorded at a heating rate of 10 °C/min were also curve fitted (see Figure S-4). All peak temperatures and temperature ranges of the processes for both heating rates are summarized in Table S-5.

3.3. Discussion of the Defunctionalization Mechanism. Rigid binding of functional groups is typical for the surface of CNTs. As a result, these groups have a limited degree of freedom associated with bond angles and bond lengths, as well as the rotation of the carboxyl groups along the carbon–carbon bond. This increases the probability of their interaction with each other. Figure 5 demonstrates the supposed mechanism of transformations on the CNT surface during defunctionalization. All processes in this scheme are denoted according to the peak labels in the curve fitting of the m/z curves in Figure 4.

Because the oxygen-containing groups on the surface of CNTs promote the adsorption of water through the formation of hydrogen bonds, the first step in the defunctionalization of the CNT surface corresponds to the release of all adsorbed water (Figure 4a, peak 19-1). Immediately after the beginning of water desorption, dehydration of “unblocked” functional groups starts to form lactones, pyrones, and anhydrides (peak 19-2).⁸ According to XPS data, the surface of CNTox contains predominantly carboxyl and hydroxyl or, more likely, phenol groups. Thus, lactones, pyrones, and anhydrides are the most possible functionalities formed during the dehydration stage. It is worth noting that the structure of these groups depends on the localization of initial functionalities relative to CNT surface. For example, armchair edge promotes 1,2-pyrones (Figure 5, 19-2-3) but the zigzag one leads to unsaturated γ -lactones (Figure 5, 19-2-1). In some cases, like phenylacetic acids, armchair edge may also promote the formation of unsaturated γ -lactones (19-2-5). Some highly oxidized fragments such as keto acids may also form anhydrides and release CO or directly decompose yielding CO and CO₂ (Figure 5, 19-2-6, 28-1-1, 28-1-2, 44-1-1).

As CNTs had been oxidized by nitric acid, the residual nitrogen-containing groups could also be removed from the CNT surface during heating. According to XPS data, nitrogen was released in two stages: before 370 °C and at 530–840 °C (Table 2). Indeed, the curve of m/z 30, which can be attributed to both NO and CH₂O fragments, demonstrates two peaks. In ref 20, NO release was also detected during heating of CNTs oxidized by nitric acid, but the authors did not identify this process. Release of NO or/and CH₂O corresponding to peak 30-1 in Figure 4d may be attributed to the decomposition of the rest of the organic nitrates or residual nitric acid in CNTox. Benzyl nitrates are known to decompose into the mixture of aromatics, NO, NO₂, and CH₂O at ~150–200 °C.^{33,34} At the same time, NO₂ was not observed in the mass spectra of evolved gases. It is not a surprise because NO₂ is difficult to detect by mass spectrometry.^{35,36} Moreover, the signal of m/z 46 may also originate from the ¹²C¹⁶O¹⁸O compound.³⁶ It was shown that nitrobenzene layers deposited on Si-surface evolve NO even at 200 °C.³⁷ NO release from nitrocompounds should lead to hydroxyl formation. As a result, the increase in the intensity of C3 component and the decrease in the intensities of O2 component relative to O1 component are observed in XPS spectra of CNT2 as compared to CNT1 (Figure 3, Table S-1). The increase in C3 intensity in the C 1s spectrum of oxidized CNTs after annealing at 300 °C was also detected in ref 20. Nitrogen content in CNTs was almost negligible (Table 2), and hence it was impossible to detect the nitrogen bonding by XPS.

The first peak in the m/z curve of CO₂ (Figure 4c, 44-1) corresponds to the destruction of different carboxylic acids.^{13,18,38} Along with separate carboxyls (Figure 5, 44-1-2)

various types of keto or hydroxy acids (Figure 5, 44-1-1) or other carboxyls with acceptor in α - and β -positions (for example, salicylic acid fragments³⁹) may also contribute to CO₂ signal. It is important that during the reaction, 44-1-1 benzaldehyde fragments may be generated.⁴⁰ Interestingly, the temperature range for the processes 19-2, 28-1, 44-1, and 30-1 is almost the same, indicating the similarity in the nature of the reacting groups. At this stage of the defunctionalization, the majority of the acidic groups are removed from the surface of oxidized CNTs, which was also confirmed by titration methods.⁴¹

The peak of the third process of water release (19-3) is very broad (Figure 4a). To explain this fact, we analyzed the m/z signal of HDO at the heating rate of 10 °C/min (Figure S-4a and Table S-5). In the case of slower heating rate, the oxidation process may involve hydrogen atoms, which are localized at defect sites of the CNT surface. According to the m/z curve of O₂ (Figure S-2a), oxygen uptake is observed as an asymmetric peak in the temperature range of ~400–700 °C. This process may be attributed to both water (HDO) and CO₂ formation due to the burning of highly defective sites in CNT structure, which were generated during the nitric acid oxidation. Partial oxidation of CO is also possible at these temperatures. To separate the impact of these processes on the curves of m/z 19 and 44, we added the asymmetric peaks 19-b (only in Figure S-4a) and 44-b to the fitting of these curves. Thus, in the case of the heating rate of 40 °C/min, the broadening of peak 19-3 may result from the burning of defects. This process is impossible to separate in peak 19-3, as it was done for a heating rate of 10 °C/min, due to its low intensity. Nevertheless, peak 19-3 apparently corresponds to the dehydration of phenols (Figure 5, 19-3-1) and to self-acylation of unsaturated carboxylic acids such as phenylisocrotonic acid fragment (Figure 5, 19-3-2). The acylation is an important reaction because the phenol groups are formed. This increases the intensity of C3 component in XPS spectrum of CNT2 as compared to CNT1 (Figure 3a, Table S-1). In ref 20, the authors were unable to deconvolute water signal into components and assigned it to both anhydride and ether formation. In our work, the hydrogen–deuterium exchange allowed us to distinguish more than one water release process.

Peaks 28-2 and 44-2 are usually attributed to the decomposition of carboxylic anhydrides.^{13,16,18} In the present study, peak 44-2 was fitted by an asymmetric function. The asymmetry of the anhydride decomposition can be explained by the complexity of the mechanism of this process. We suggest the two-stage mechanism. At lower temperatures, anhydrides may acylate nearby localized hydroxyl groups and form lactones and carboxylic groups. The latter then decompose releasing CO₂ (Figure 5, 44-2-1). At higher temperatures, the direct decomposition of anhydrides is accompanied by both CO and CO₂ mass signals (Figure 4b,c; Figure 5, 44-2-2, 28-2-1). In this temperature range (~600 °C), fragments of phenylacetic acid produce CO₂ too (Figure 5, 44-2-3).⁴⁰ Benzaldehyde and benzophenone fragments may be an additional source of CO (Figure 5, 28-2-2, 28-2-3).⁴² However, XPS results for CNT3 show a uniform decrease in the intensity of both O1 and O2 components in the O 1s spectrum and a strong decrease in the intensity of C3 component in the C 1s spectrum (Figure 3, Table S-1). Zhou et al. suggested peroxide decomposition at 520 °C.¹⁸ As a result of this reaction, both O2 and C3 components are expected to decrease. Peroxides may be formed either during the nitric acid treatment or at the active

sites originated from the decomposition of some functional groups.⁴³ The possibility of process 28-3 in the case of isothermal annealing at 530 °C cannot be excluded.

Further thermal treatment of oxidized CNTs led to CO₂ and CO release (peaks 44-3 and 28-3 in Figure 4b,c). Most likely, CO₂ desorption relates to the decomposition of lactone groups.^{13,18} It was proposed that lactones located on different sites release CO₂ before 900 K (627 °C).¹⁷ At the same time, it is well-known that pure lactones are stable until 500–600 °C and completely decompose only at ~900–1000 °C.⁴⁴ Peak 28-3 corresponds to the destruction of pyrones,^{45,46} phenols,⁴⁷ and semiquinones¹³ (Figure 5, 28-3-1, 28-3-2, 28-3-3, respectively). High-temperature water peak 19-4 in Figure 4a is apparently due to the phenol decomposition by different mechanism (Figure 5, 19-4-1) where no carbon loss is observed.⁴⁷ XPS data show the total disappearance of C3 and C5 components in the case of CNT4 (Figure 3a, Table S-1), which is in agreement with the decomposition of predominantly lactones, pyrones, and phenols.

In the curve of m/z 30, the broad peak is observed at 600–1000 °C (Figure 4d). It apparently corresponds to different nitroaromatic compounds, the decomposition of which may yield NO and CO through the phenol formation as an intermediate.⁴⁸ Attribution of this peak to CH₂O is unlikely due to its instability at such high temperature toward decomposition to CO.⁴² High-temperature CO peak 28-4 in Figure 4b presumably arises from ethers decomposition due to the high thermal stability of this type of functional groups. Although cyclic saturated ethers release CO at 500–600 °C,⁴⁹ aromatic ones are converted into phenols at extremely high temperatures.⁵⁰ The obtained phenols release CO (Figure 4, 28-4-1). Ethers were formed either during acid treatment or decomposition/dehydration of other groups (Figure 5, 19-3-1 and 28-3-1). CO₂ peak 44-4 is significantly weaker than peak 28-4. It can be attributed to the decomposition of benzoquinones (Figure 5, 44-4-1; this process is accompanied by char formation⁴⁵). The disproportionation or oxidation of CO cannot be ruled out either.

Some reactions, which involve functional groups, may lead to the surface reconstruction. For example, processes 28-3-2 and 28-4-1 result in the formation of surface defects: cyclopentadienyl fragments or aromatic 5-fold rings with the distorted bond angles in sp^2 sites. Because phenol and ether groups are a significant part of CNT surface functionalities, these processes can increase the I_D/I_G ratio in Raman spectra after high temperature annealing (Table 2, CNT4).

On the basis of the proposed mechanism, it can be suggested that the desorption temperature of functional groups predominantly depends on the O/C ratio in this groups. Functionalities decompose in the following sequence: carboxylic acids (2O/1C), anhydrides (1.5O/1C), lactones/phenols/pyrones (1O/1C), and ethers (0.5O/1C).

3.4. Air Oxidation of Functionalized CNTs. The oxygen consumption during the first and second heating cycles of TGA–MS can be used to study the oxidation of CNTox. Figure 6 shows MS curves of m/z 32 during two heating cycles and the difference between them. Burning of oxidized CNTs may be clearly divided into two stages. During the first stage, irreversible burning of defect sites and snippets, which were formed during nitric acid treatment of CNTs, is observed. During the second stage, the bulk of CNTs burns. It is interesting that these stages are well-separated in temperature. These results clarify the oxidation behavior of functionalized

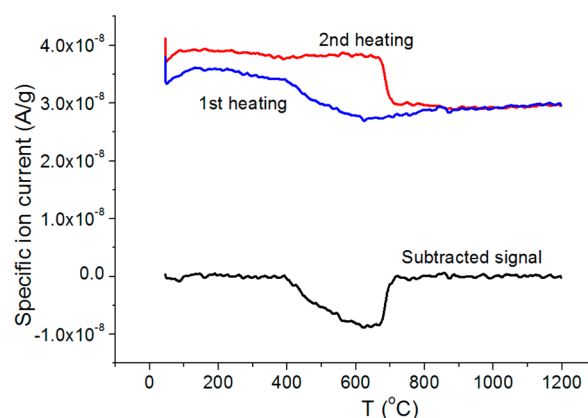


Figure 6. Oxygen mass signal (m/z 16) from two heating cycles (10 °C/min) of TGA–MS study of CNTox. The subtracted signal of two cycles is also shown.

CNTs, which is important for their high temperature applications.

3.5. Kinetics Study of the Decomposition of Functional Groups. Thermal analysis at different heating rates provides the way of calculation of activation energies of decomposed substances as well as other kinetic parameters such as reaction order and frequency factor. There are a number of models in the literature,^{51–55} but among them Kissinger's method is the most commonly used due to its simplicity and convenience. It allows calculating the effective activation energy of decomposition processes. This model suggests that at the maximum of the DTG curve, the conversion of the compound is the same for the different heating rates.⁵³ The main equation of this method is

$$\ln(\varphi/T_m^2) = -E_a/RT_m + \ln(AR/E_a)$$

where φ is the heating rate, T_m is the temperature of the DTG peak, E_a is the activation energy, A is the frequency factor, and R is the gas constant. Activation energy can be calculated from $\ln(\varphi/T_m^2)$ versus $1/T_m$ plot (slope = $-E_a/R$). In our case, DTG curves of the defunctionalization of CNTox contain four main peaks. Each of them includes numerous processes of decomposition of various groups. Therefore, it was impossible to attribute E_a determined from DTG data to the decomposition of particular groups because the signals of CO, CO₂, water, and NO/CH₂O release were overlapped in DTG curves. Thus, we used T_m values in m/z curves of CO and CO₂ to determine the activation energies of decomposition of functional groups. For example, Figure 7a shows the shift of the peak position in the curve of m/z 44 with the heating rate. This peak is responsible for the decomposition of predominantly carboxylic groups. The corresponding Kissinger's plot is shown in Figure 7b. It is worth noting that such method gives only the approximation of the effective activation energy. Calculated activation energies of the decomposition of different groups on the surface of oxidized CNTs are presented in Table 3.

It was impossible to calculate E_a for lactones, quinines, and nitrocompounds due to uncertainty in the position, low intensity, and large width of peaks, respectively. Interestingly, E_a for keto and hydroxy acids calculated from m/z curves of CO is lower than that for carboxylic groups calculated from m/z curves of CO₂ despite the same temperature range of their decomposition. This is apparently due to the lower stability and higher lability of carboxyl groups with the acceptor in α -

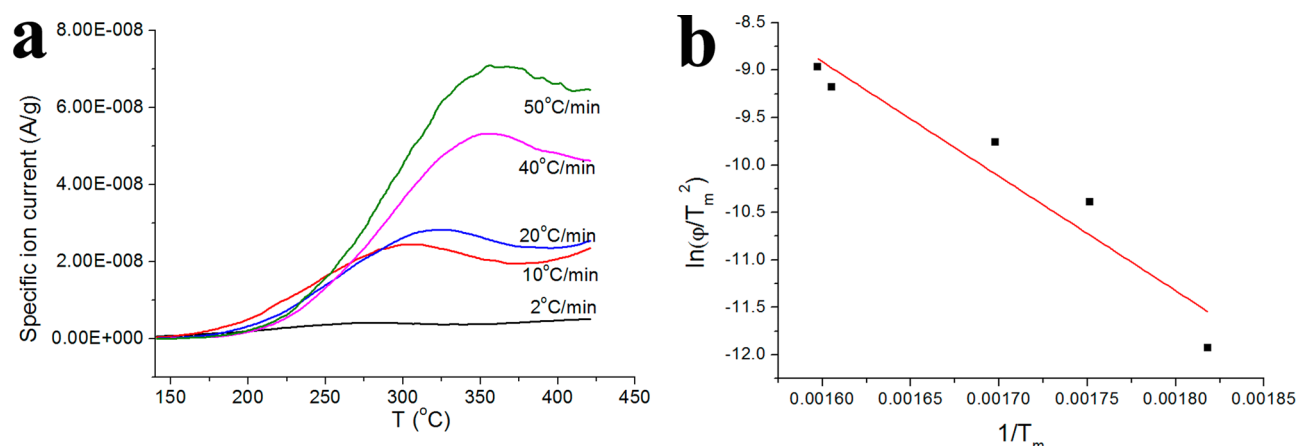


Figure 7. TGA–MS curves of m/z 44 (CO_2) in the temperature range of decomposition of carboxylic groups recorded at different heating rates (a) and the corresponding Kissinger's plot (b). Despite the fact that any peak of CO_2 release can be attributed to the simultaneous decomposition of different groups, the approximation was assumed that each peak predominantly resulted from the decomposition of a particular type of functional groups (such as carboxylic acids, anhydrides, and lactones in the case of CO_2). The decomposition of other groups was supposed to insignificantly affect the peak position.

Table 3. Calculated Activation Energies for the Decomposition of Different Functional Groups on the Surface of CNTox

functional group:	keto and hydroxy acids	carboxyls	anhydrides	phenols, pyrones	ethers
E_a (kJ/mol):	74 ± 22	101 ± 17	160 ± 21	234 ± 32	269 ± 2

position. Comparable E_a values (~ 92 kJ/mol) were found for decarboxylation of acetoacetic acid.⁵⁶ E_a of anhydrides (160 ± 21 kJ/mol) is close to that of thermal decomposition of 1,8-naphthalic anhydride (196 kJ/mol, peak 1) calculated in ref 57. Lower E_a in the case of functional groups on the CNT surface can be explained by their rigid binding to the carbon surface and the presence of other acceptor groups nearby. In ref 57, the decrease in activation energy of anhydride was demonstrated after grafting of this substance on silica surface (70 kJ/mol, peak 1). Rigid binding of functional groups to the carbon surface and the presence of other acceptor groups nearby can explain the lower temperatures of decomposition of the functionalities as compared to appropriate organic compounds (for example, benzoic acid and naphthalic anhydrides destruct at slightly higher temperatures^{40,58}). We used the same model to estimate the activation energy of water desorption (peak 19-1). The obtained value of 24 ± 2 kJ/mol was about 2 times lower than that of acetone desorption from highly oriented pyrolytic graphite, which was also measured using Kissinger's model.⁵⁹

In the previous subsection, we emphasized the correlation between the decomposition sequence of different functional groups and O/C ratio in their structure. Estimated values of activation energies confirm this statement. Figure 8 shows the linear correlation between E_a and the O/C ratio. We could not include the keto/hydroxy acid value in this plot because it was impossible to correctly determine the O/C ratio for such fragments due to the complex mechanism of their decomposition. Thus, we can assume that the decomposition of each functional group is well-separated from other groups in terms of activation energy, which depends on the O/C ratio. It should be noted that the obtained values of E_a may vary depending on the structure of carbon matrix (for example, in case of CNTs they depend on their diameter).²¹

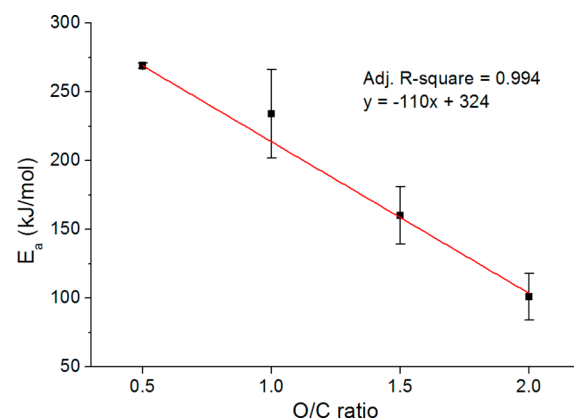


Figure 8. Plot of the activation energy of the decomposition of functional groups on the CNT surface versus O/C atomic ratio in these groups.

4. CONCLUSIONS

Thermal decomposition of oxygen-containing functional groups on the surface of oxidized CNTs was studied. The XPS oxygen content on the CNT surface after isothermal decomposition does not comply with the mass loss determined by TG-DTA under nonisothermal decomposition. The difference is explained by the decomposition of functional groups at higher temperature at nonisothermal conditions. Increase in heating rate minimizes air oxidation of CNTs during TGA study. At the same time, a lower heating rate simplifies the separation of the oxidation processes on the CNT surface in slightly oxidizing environment: at 10 °C/min heating rate, defect sites resulting from the acid treatment burn at 400–700 °C, while bulk CNTs burn at >700 °C. This result may be useful for the practical high-temperature applications of oxidized CNTs.

H₂O, CO, CO₂, and NO/CH₂O were detected in evolved gases during TGA–MS study of CNTox. Hydrogen–deuterium exchange provided the precise determination of surface processes that involved water release: complex dehydration, burning of defect sites, and phenol decomposition. Detailed mechanism of defunctionalization was proposed on the basis of the *m/z* curves registered to aforementioned compounds and literature data. Temperature ranges of decomposition of different functional groups on the CNT surface are strongly influenced by the heating rate and cannot be tabulated. Only the sequence of surface transformations can be determined from TG–MS study, and this sequence correlates with the O/C atomic ratio in decomposed functional groups.

Kissinger's model was applied for the calculation of the effective activation energies of the decomposition of functional groups on the CNT surface. *E_a* increases from keto/hydroxy acids to carboxyls, anhydrides, phenols, and ethers. The obtained value for keto/hydroxy acids demonstrates higher lability of these groups on the CNT surface as compared to regular carboxylic acids. Rigid binding of functional groups to the surface of CNTs and the presence of neighboring acceptor sites decrease *E_a* of the decomposition as compared to the compounds with a similar structure.

The results of this work may be useful in predicting and simulating the transformations on the surface of oxidized CNT during heating in both oxidizing and inert atmosphere, which is very important for materials or composites totally or partially consisting of CNTs. Further study of activation energies of the decomposition of different functional groups seems to be important and interesting to reveal the *E_a* dependence from the structure of the carbon matrix.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05178.

XPS results for oxidized and annealed CNTs; mass signals of O₂, CO₂, and CO at different Ar flows in thermoanalyzer (these figures illustrate the minimization of oxygen effect in the mass-spectrometry analysis of the evolved gases); water mass curve (*m/z* 18) for 40 °C/min heating rate; curve fitting of MS signals detected at a heating rate of 10 °C/min; and temperature ranges for the decomposition processes (PDF)

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Notes

The authors declare no competing financial interest.

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