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Effect of chemical treatment of multi-walled carbon nanotubes on the specific capacitance of supercapacitors

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Abstract

To date, the research on carbon nanomaterials has progressed rapidly. More than 400 papers were written in 2021 on the application of carbon nanomaterials in various fields. The high demand for the use of such materials has increased due to a sharp increase in the demand for semiconductor materials and materials for supercapacitor electrodes and other electrical devices. Despite the unique physical properties of carbon nanomaterials, there are limitations to their use. To solve this problem, various methods of modifying the surface, both through chemical interactions and physical adsorption, were proposed. One of these methods is chemical modification. The evaluation of effect of chemical treatment parameters on the properties of carbon nanomaterials is an urgent task due to the fact that the chemistry of the processes is poorly understood. In this work, the effect of concentrated sulfuric and nitric acids on the change of specific surface area, elemental composition, composition of functional groups, and also on the change of specific capacitance was considered. It is believed that both the porosity and the functional groups formed during oxidation contribute to the change in specific capacitance. The specific surface area of all samples decreased on average by a factor of 1.5–3 after the chemical treatment. Different oxygen and sulfur-containing functional groups are observed after the chemical treatment. The highest specific capacitance of the treated carbon nanofibers was 114 F/g.

Keywords

multi-walled carbon nanotubes
chemical treatment
functionalization
supercapacitors
cyclic voltammetry

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1. Introduction

The necessity of application of carbon nanomaterials (CNMs) is related to the possibility of obtaining them by means of decomposition of C_1–C_4 hydrocarbons over various catalysts. Thus, in [1] carbon nanofibers were produced from methane using Ni/Al_2O_3 catalyst in a fluidized bed reactor. Similarly, carbon nanotubes with different morphologies (single-walled and multi-walled carbon nanotubes (MWNTs)) can be produced by varying different catalysts and process parameters.

There are several types of surface modification of carbon nanomaterials: plasma treatment [2–4], electrochemical modification [5–7], chemical modification [8–10], etc.

2. Theory

Plasma treatment consists in the oxidation of CNMs in non-equilibrium plasma. The functionalization degree of these materials is low, e.g., up to 6.6 wt.%. Barrier discharge plasma is also used to oxidize CNMs while maintaining the morphology of the material [13]. These two high-energy methods do not require preheating, and the processing time takes no more than a few seconds. Microwave functionalization techniques can also be used [14] but the difficulty lies in the limitation of the materials (vertically oriented CNMs). The authors [15] used inductive coupled plasma for oxidation, but the degree of functionalization and product yield were extremely low and lead to the formation of ester and carboxylic groups.

Electrochemical methods of oxidation consist of passing electric current through dilute solutions of strong acids. In [16] surface modification methods using electric current of different strength were described. There was an increase in oxygen up to 5 at.%, but this method was not safe because of a rattlesnake mixture emission and the necessity of observance of certain safety rules.

It is also possible to modify the surface by grafting different polymers. Polyaniline [17] and polyacetylene [18] were among the first polymers used. Composites with these polymers can be employed in electrochemical current sources, sensors, etc. However, this technology has not found industrial application yet.

Chemical methods include a wider range of possibilities due to the large number of different oxidizing agents which can influence CNM morphology and functional group composition differently after processing. Chemical methods include alkaline activation [19] and acid etching. Alkaline activation has a number of limitations: only highly concentrated alkaline solutions are used. This treatment allows the pores to be reduced to a single size, most commonly, mesoporous.

The advantages of the acid method include the possibility of varying solution concentrations and using different acid solutions. As oxidizing reagents, oxygen-containing acids and their mixtures are most commonly used: HNO_3, H_2SO_4, $HClO_4$, $HNO_3 + H_2SO_4$, etc. [20].

In studies on the effect of mixtures of concentrated sulfuric and nitric acids in different ratios [19, 21], the authors claimed that applying a mixture of HNO_3:H_2SO_4 in a ratio of 3:1 to the surface of the carbon material led to the formation of sulfur-containing functional groups, mainly ($-SO_3H$). This is an interesting effect, as in the oxidation of tube-like compounds, polyaromatic hydrocarbons, such a mixture is used for nitration. For example, in [22] the effect of heating time of mixture on the formation of functional groups when treated with concentrated nitric acid was investigated.

Chemical modification of surface does not end with the oxygen-containing acid treatment. Another method of functionalization is the use of oxygen-free acids, e.g., HCl, HF and their mixtures with hydrogen peroxide [23]. In addition, solutions of acidic oxides are also used [24], etc. Also, various persulphates and hypochlorites have found their application in this area. There is a possibility of chemical modification by mixtures of hydrogen peroxide with different salts, such as the Fenton's reagent ($H_2O_2/FeSO_4$). Prolonged treatment with such a mixture leads to the formation of hydroxyl groups only [25].

Chemical methods of surface functionalization of CNMs are long processes (up to 24 h or more) carried out by heating the reaction mixture. After this functionalization, various functional oxygen-containing groups are observed: carboxylic, carbonyl, alcohol/phenolic [26].

In [27] the effect of chemical treatment on the specific capacity of nanofibrous carbon was investigated, and the data were obtained that the use of concentrated sulfuric acid was inexpedient, as the specific capacity of the material increased to 0.2 F/g. However, the treatment with nitric acid increased the specific capacitance to 10 F/g.

There are also many works which aim at secondary modification of the material. In [28] the synthesis of carboxyl carbon nanotubes with conducting amines was investigated, and material capacity of 200 F/g was obtained. This article is devoted to studying the effect of chemical treatment of multi-walled carbon nanotubes in nitric and sulfuric acids for their further use in supercapacitors.

3. Experimental

Commercial multi-walled carbon nanotubes labeled as L-MWNT-1020 and L-MWNT-4060 (hereinafter MWNT-1020, MWNT-4060) were chosen as the objects under study. The difference between MWNT-1020 and MWNT-4060 is that MWNT-1020 were purified from the catalyst by the manufacturer (it is seen from the TEM images). Also, the difference is in the diameter of the nanotubes. For MWNT-1020, the diameter of the nanotubes ranges within 10–20 nm, for MWNT-4060 – from 40 to 60 nm.

The experimental procedure was as follows: a sample of nanomaterial weighing 0.15 g was poured into 100 mL of concentrated acid, after which the reaction mixture was kept for 6 h, heated at 80 °C and stirred constantly. After that the samples were filtered off, washed several times with distilled water, dried and prepared for their further analysis.

The following acids were chosen as oxidizing agents: HNO_3 (concentrated, pure for analysis grade, GOST 111125-84 (mod.1), 64%), H_2SO_4 (concentrated, chemically pure grade, GOST 4204-77, 97%). Change of specific surface area was measured by low-temperature nitrogen adsorption using the BET method using a Quantachrome Nova 1000e, the adsorbate gas partial pressure range was 0.005–0.9995 P/P_0. The measurement error was no higher than 5%.

The composition of elements in the powdered samples was determined using scanning electron microscopy (SEM) (the beam energy was 10 keV). Instrumentation, S-3400N (Hitachi), was equipped with an energy dispersive X-ray analysis (EDX) unit from Oxford Instruments. The error of the device does not exceed 0.1%.

Qualitative composition of functional groups was measured by Fourier transform infrared spectroscopy (FTIR spectroscopy). Instrumentation: FT-IR spectrometer FT-801 (TU-4434-805-59962935-2019) with reflection attachment for examination of powdery samples PO-45N with angle of incidence of 45°, bottom sample position and a built-in visualization system.

Specific capacitance of the samples was measured by cyclic voltammetry at a sweep rate of 2–10 mV/s. Instrumenta-

tion: an IPC-compact potentiometer (Russia). A three-electrode circuit was used for the measurements: auxiliary electrode – Pt, reference electrode – Ag/AgCl (saturated KCl). The potentials in the work are given relative to the Ag/AgCl electrode. The carbon nanomaterials were deposited on the surface of the glassy carbon electrode. The specific capacitance of the studied carbon materials was determined by the formula [29, 30]:

$$C_{sp} = \frac{J}{V \cdot m}, \quad (1)$$

where C_{sp} is the specific capacitance, F/g; J is the sum of cathode and anode currents ($J = J_k + J_a$) at 500 mV, mA; m is the mass of material, g; V is the sweep rate, mV/s. Then the electrodes were dipped into 3.5 M sulfuric acid solution, and cyclic voltammetry curves were recorded by direct voltammetry when the electric potential varied from 0 to 1 V at the working electrode. The error of the sweep rate was 1.0% and the error of the potential setter was 0.03 mV.

A modified MWNT sample was used as the indicator electrode. The electrode was prepared in the following way: MWNT was mixed with 10–15% acetylene soot (Alfa Aesar, Russia); 0.01 g of the resulting composite was taken and mixed with 10% mineral oil (Russia) to obtain a paste-like material. The paste was uniformly applied to a graphite electrode ($S = 1$ cm²). Then the electrodes were immersed into 3.5 M sulfuric acid, and cyclic voltammetry curves were measured by direct voltammetry, with the electrical potential of the working electrode being varied from 0 to 1 V. The average sample mass was about 0.0015 g.

4. Results and discussions

The EDX and low-temperature nitrogen adsorption results are shown in Table 1. From the data presented in Table 1, it is clear that the acid treatment results in a low degree of functionalization (C:O ratio) for MWNT-1020. At the same time, the catalyst content after treatment was close to zero. This is due to the fact that MWNT-1020 were previously purified from the catalyst by the manufacturer. A reduction in specific surface area of 1.5–3 times was observed. This is caused by the oxidation of MWCNTs with the formation of CO/CO_2.

Table 1 The EDX and BET results.

Sample	Acid	Concentration of elements at.%					Specific surface area m²/g
		C	O	S	C:O	Oth.	
MWNT-1020	–	99.9	–	–	–	0.1	128
	H_2SO_4	96.6	2.8	0.2	35	0	48
	HNO_3	97	3	–	32	0	76
MWNT-4060	–	99.7	–	–	–	0.3	68
	H_2SO_4	91.4	6.9	1.4	13	0.1	46
	HNO_3	95.1	4.2	–	23	0.1	56

For MWNT-4060 the degree of functionalization of the obtained materials was much higher. There was a presence of sulfur in the composition of the material that may be due to the formation of some sulfur-containing functional groups. A decrease in specific surface area, similarly associated with the oxidation of carbon nanotubes, was also observed.

Figure 1a shows FTIR spectra of MWNT-1020 sample, representing the bands at 1125 cm^{-1} attributed to valence vibrations of the S=O bonds of sulfonic acids; this indirectly confirms the presence of sulfur detected by EDX spectroscopy. Valence vibrations of the C–O and C=O bonds at 1610, 1695, 1820 cm^{-1} were also observed. These vibrations refer to both carboxylic groups (1610, 1695 cm^{-1}) and anhydride groups (1820 cm^{-1}). The presence of carboxylic groups was confirmed by valence vibrations of O–H bonds in the carboxyls at 3231 cm^{-1}. For MWNT-4060 (Figure 1b) in the case of anhydride groups all is identical, but the vibrations of valence bonds at 1448 cm^{-1} related to sulfoxides were observed. Obtaining sulfur-containing groups will make it possible to use such materials not only as electrodes for supercapacitors, but also in a variety of sensors and membranes. Our data partially correlate with the data reported in [31].

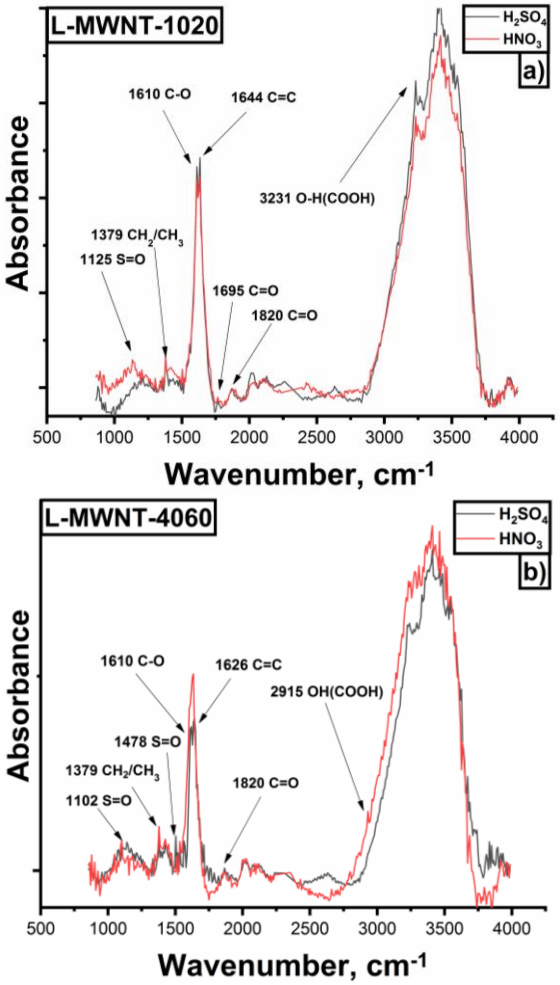

Figure 1 FTIR spectra of the treated samples: L-MWNT-1020 (a); L-MWNT-4060 (b).

For MWNT-1020 an increase in specific capacitance up to 114 F/g was observed. In spite of the fact that the degree of functionalization of the samples was much lower, the specific capacitance was much higher. This is most likely due to the formation of functional groups, which participate in the electron transfer at the oxygen atom C–O↔C=O [32]. Although the degree of functionalization was higher for the MWNT-4060 samples, in particular, for the sample treated in nitric acid, its specific capacity is lower than that of the original sample. This can be explained by the fact that the formed groups are mostly anhydride, or ester groups, which cannot participate in the redox processes. Figure 2a and 2b also show the cyclic voltammetry curves of the samples with the highest capacity at a sweep rate of 2mV/s.

Table 2 Cyclic voltammetry results.

Sample	Acid	Specific capacitance, F/g		
		10 mV/s	5 mV/s	2 mV/s
MWNT-1020	–	0.2	0.3	0.6
	H_2SO_4	36	49	67
	HNO_3	72	89	114
MWNT-4060	–	0.3	0.4	0.5
	H_2SO_4	32	49	96
	HNO_3	0.085	0.09	0.13

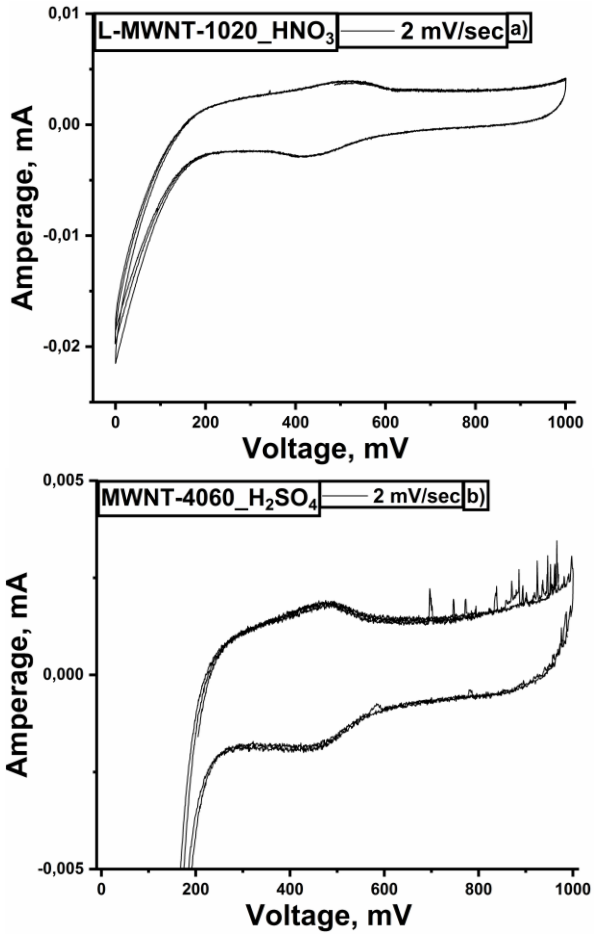

Figure 2 Cyclic voltammetry curves of the treated samples: L-MWNT-1020 (a); L-MWNT-4060 (b).

5. Conclusions

The study of the effect of different oxidizing agents on the functionalization and application of the obtained carbon nanomaterials is important. It should also be noted that there are practically no mathematical models describing the oxidation process of CNMs, which does not allow us to talk about the optimality of the various treatment parameters used. In the multi-walled carbon nanotubes, an increase in the quantity of the oxygen-containing groups was observed, especially in case of sulfuric acid treatment, where the formation of sulfur-containing groups occurred.

The electrical capacitance of the chemically treated CNTs reached 114 F/g. However, in spite of high oxygen content on the catalyst-free CNTs (MWNT-1020), after the treatment in nitric acid, the capacitance of the material decreases. The electrical properties of multi-walled carbon nanotubes as well as the influence of sulfur-containing groups on sensor properties will be investigated.

Even with a sufficiently high degree of functionalization, acidic treatment leads to bond destruction. In addition, the treatment in nitric acid could lead to a destruction of the conductive channels instead of functionalization (for MWNT-4060).

Supplementary materials

No supplementary materials are available.

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Conflict of interest

The authors declare no conflict of interest.

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