

## Investigation of Physicochemical and Electrochemical Properties of Single-Walled Carbon Nanotubes Modified with Nitrogen

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### Abstract

Composites of the type “nitrogen-containing carbon coating – single-walled carbon nanotubes” were obtained by the treatment of single-walled carbon nanotubes (SWCNT) in a gaseous 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixture at temperatures 600–750 °C. Single-walled carbon nanotubes etched in aqua regia (SWCNT<sub>et</sub>) and doped with nitrogen (N-SWCNT) were studied by XPS, electron microscopy and IR spectroscopy. Various oxygen-containing functional groups were found to reside on the surface of initial SWCNT<sub>et</sub>. Upon treatment of SWCNT<sub>et</sub> in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>, polymerization and condensation of hydrocarbons resulted in the formation of a thin nitrogen-containing carbon coating. Specific capacitance per a weight of initial and nitrogen-doped carbon nanotubes in an aqueous electrolyte with 1 M H<sub>2</sub>SO<sub>4</sub> was measured. Specific capacitance of carbon electrodes was found to change symbately with the content of nitrogen-containing functional groups on the SWCNT surface.

### 1. Introduction

Electrochemical supercapacitors (SC) form a relatively new and rapidly developing class of systems for accumulation of electrical energy, which ensure fast charging and high energy storage capacity in the electrical double layer on the electrode surface. In this connection, electrodes with highly developed surface are among the most essential components of such supercapacitors. Therewith, the properties of electrodes play the key role in creating high specific capacitance of supercapacitors with respect to the stored energy as well as the attainable current density and supercapacitor discharge. An additional accumulation of electric charges, i.e. pseudocapacitance or redox capacity, is provided by faradaic processes occurring on the surface of supercapacitor electrodes. Conducting nitrogen-containing polymers [1] are employed in electrochemical supercapacitors. However, electrodes with deposited electroactive polymers do not provide high stability. In distinction to electrochemical batteries, the charging-discharging rate

of supercapacitors is commonly not limited by the rate of redox electrochemical processes. As a result, supercapacitors are able to ensure very high charging-discharging rates and more than a million recharge cycles [2]. However, the attained specific energy density in supercapacitors still remains by an order of magnitude lower as compared to advanced lithium-ion cells. So it is important to increase the stored energy density with retaining the number of supercapacitor recharge cycles and high specific power.

Among promising materials for the development of electrodes are carbon nanotubes, especially the single-walled ones (SWCNT), which have ideally a specific surface area up to 1300 m<sup>2</sup>/g, high electron conductivity along the tube, and good stability in various media. In addition, specific capacitance of SWCNTs can be enhanced by modification of the carbon surface with different heteroatoms [3]. It was found [4, 5] that substitution of carbon atoms by heteroatoms strongly affects the electronic properties of CNTs. For example, intercalation of nitrogen atoms into the carbon structure improves

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the conductivity of CNTs. Nitrogen-doped CNTs are synthesized by a catalytic method on metal catalysts. It was noted [6] that the use of spiral N-CNTs increases specific capacitance of supercapacitors in comparison with undoped CNTs. It is known [7] that the formation of carbon from olefins and acetylenic hydrocarbons on the carbon surface proceeds by the consecutive mechanism via polymerization and condensation of compact monomers.

This paper demonstrates the possibility to obtain a carbon coating modified with nitrogen atoms by carbonization of the SWCNT surface in the ammonia-hydrocarbon mixture. The effect of such modification on electrochemical properties of the produced carbon electrodes was studied.

## 2. Experimental

The study was carried out using single-walled carbon nanotubes (OCSiAl Ltd., Novosibirsk) with a specific surface area of 950 m<sup>2</sup>/g. The initial carbon nanotubes are 1–2 nm in diameter, they are aggregated into bundles and contain up to 25 wt.% iron, which is related to their production technology. Thus, for our experiments the initial carbon nanotubes were treated with aqua regia, which was prepared from a mixture of concentrated nitric and hydrochloric acids taken in a weight ratio HNO<sub>3</sub> : HCl = 1 : 3. After such a treatment, the content of metallic iron in the SWCNT<sub>et</sub> sample decreased to 10 wt.%; however, a complete removal of iron did not occur since the remaining iron particles had a carbon coating.

The synthesized SWCNT<sub>et</sub> samples were doped with nitrogen atoms in a gaseous 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixture at a temperature of 600, 650, 700 and 750 °C.

Argon (99.99 vol.%) and hydrogen (99.9 vol.%) were employed in the study. The 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixture was prepared using individual gases: ethylene (99.9 vol.%), acetylene (99.8 vol.%), and ammonia (99.9 vol.%).

Changes in the SWCNT<sub>et</sub> weight upon treatment in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> were studied directly in the experiment that was performed in a flow quartz reactor with a quartz balance by a technique described in [8]. Weight sensitivity of the technique was 1×10<sup>-4</sup> g. The initial SWCNT<sub>et</sub> loading was varied over the range of 0.1–0.5 g. At the beginning of the experiment, a sample was heated in flowing argon to a specified temperature. After that, the argon flow was stopped, and the 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixture was fed.

SWCNT<sub>et</sub> and N-SWCNT samples were examined by transmission electron microscopy (TEM) on a JEM-2010 (JEOL, Japan) microscope with the line resolution of 1.4 Å.

Specific surface area of the synthesized SWCNT<sub>et</sub> and N-SWCNT samples was measured using thermal desorption of argon.

Diffuse reflectance IR spectra were taken on a Shimadzu 8400 S spectrometer equipped with a DRS-8000 attachment (an integrating sphere) in a range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Each spectrum was recorded after averaging over 200 scans.

### 2.1. XPS study of samples

X-ray photoelectron spectroscopy (XPS) was used to study the initial SWCNT<sub>et</sub> sample and the N-SWCNT samples treated in a mixture of ammonia and ethylene at 600 and 700 °C. The samples were mounted in a spectrometer using a double-sided carbon Scotch tape. XPS spectra of the samples were recorded on a ES 300 KRATOS instrument. The Kα line of aluminum with a photon energy of 1486.6 eV was used as the primary radiation. The X-ray power was 170 W. Calibration was made against the positions of Au4f<sub>7/2</sub> and Cu2p<sub>3/2</sub> lines taken equal to 84.0 and 932.7 eV for bulk gold and copper, respectively. Internal calibration of the spectra was not performed due to high conductivity of the samples, which prevented their static charging. To determine the qualitative chemical composition and the presence of impurities, survey spectra were taken over the binding energy range of 0–1200 eV at a 1 eV step. The qualitative chemical composition and the state of individual elements were determined from the main photoelectron spectra of elements recorded with a binding energy step of 0.1 eV. When recording the spectra, a residual gas pressure in the chamber did not exceed 10<sup>-7</sup> Torr. The main background gases were CO, CO<sub>2</sub> and H<sub>2</sub>.

The concentration ratio of individual components in a sample was found from the area of the corresponding XPS lines of elements using empirical atomic sensitivity factors (ASF) after recording narrow regions of the corresponding atomic levels [9].

### 2.2. A technique for studying the electrochemical properties

The electrochemical properties of SWCNT<sub>et</sub> and N-SWCNT samples were studied using a symmet-

ric two-electrode cell of a supercapacitor, which was described in detail elsewhere [10].

The SC electrodes with a weight of 10 mg were prepared from SWCNT<sub>et</sub> or N-SWCNT after drying in a rarefied atmosphere at 105 °C for an hour. After that, several drops of an aqueous H<sub>2</sub>SO<sub>4</sub> (1 M) solution were added to the obtained powder, and the resulting suspension was placed in the SC cell and slowly compressed using special current-collecting graphite cylinders with springs.

The SC cell was connected to a PARSTAT 4000 measuring-feeding device, the data array from which was automatically transferred to a computer via a USB port.

Electrode characteristics were measured by cyclic voltammetry on a PARSTAT 4000 measuring-feeding device in a range from -1 to 1 V at different potential scanning rates: 10, 20, 40, and 80 mV/s. The data array from the PARSTAT 4000 device was automatically transferred to a computer via a USB port. The capacitance of the cell (C<sub>0</sub>) was calculated [11] from the area limited by cyclic voltammetry curves using the formula

$$C_0 = \frac{\int IdU}{mv\Delta U} \quad (1)$$

where *m* is the electrode weight, g; *v* is the potential scanning rate, V/s;  $\Delta U$  is the potential variation range, V; and  $\int I(U)dU$  is the area limited by cyclic voltammetry curves, [A×V].

### 3. Results and Discussion

Figure 1 displays an IR reflectance spectrum of SWCNT<sub>et</sub>. It is seen that the external surface of SWCNT<sub>et</sub> gives the absorption bands corresponding to stretching vibrations of OH groups (3350 cm<sup>-1</sup>) and CH stretching vibrations of CH<sub>2</sub> and CH<sub>3</sub> groups (2863, 2917 and 2959 cm<sup>-1</sup>). The spectrum contains also the bands of carboxylate structures at 1540, 1580 and 1390 cm<sup>-1</sup>, carbonyl groups at 1712 cm<sup>-1</sup>, and the bands below 1350 cm<sup>-1</sup> that were assigned to vibrations of the carbon framework.

Thus, a considerable amount of oxygen-containing functional groups reside on the SWCNT<sub>et</sub> surface, which may be related to the method of sample preparation. The SWCNT<sub>et</sub> surface was modified with nitrogen atoms by treating in the 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixture at 600 and 700 °C.

Investigation of changes in the SWCNT<sub>et</sub> weight upon treatment in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> directly during the experiment in the flow quartz reactor with a quartz balance revealed that at

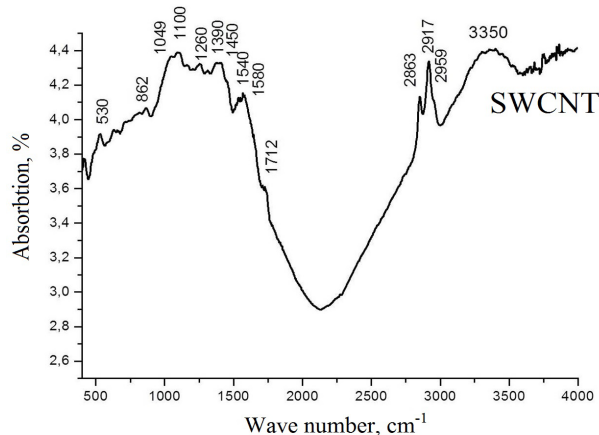


Fig. 1. IR reflectance spectra of SWCNTs treated in aqua regia (SWCNT<sub>et</sub>).

600 °C the SWCNT<sub>et</sub> weight decreased by 6.2 wt.% for the first 20 min. After 20 min of the reaction, the weight of the sample increased by 2 wt.%. The decrease in the SWCNT<sub>et</sub> weight can be attributed to the reduction of oxygen-containing functional groups and hydrogenation of the most reactive carbon species.

As the treatment temperature was raised to 700 °C, a decrease in the sample weight in the course of experiment was not observed, because under such conditions the formation rate of the nitrogen-containing carbon coating on the SWCNT surface substantially increased. Within an hour after SWCNT<sub>et</sub> treatment in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>, the weight of the sample increased by 3.4 wt.% as compared to the initial weight of the loaded sample.

Figure 2 displays an electron microscopy image of the SWCNT<sub>et</sub> bundle after treatment in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> at 700 °C. One can see that the surface of carbon nanotubes after treatment in the reaction mixture is covered with a thin layer of amorphous carbon.

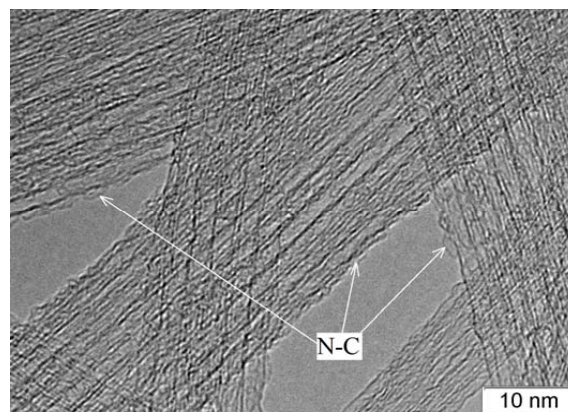


Fig. 2. TEM image of the SWCNT<sub>et</sub> bundle after treatment in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> at 700 °C.



An XPS study of SWCNT<sub>et</sub> and modified N-SWCNT samples started from the precision recording of C1s, O1s and N1s lines for the synthesized carbon materials.

The qualitative analysis of the surface composition of carbon materials detected by XPS is presented in Table 1.

**Table 1**

Content of elements on the surface of initial SWCNT<sub>et</sub> and samples treated in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> (N-SWCNT) according to XPS

Sample	C	N	O
Initial SWCNT <sub>et</sub>	95.9%	-	4.1%
SWCNT <sub>600 °C</sub>	97.2%	0.1%	2.7%
SWCNT <sub>700 °C</sub>	97.2%	0.5%	2.3%

Thus, the XPS study revealed the presence of a considerable oxygen amount on the surface of SWCNT<sub>et</sub> samples, which is consistent with the IR spectroscopy data reported above. On the surface of the SWCNT<sub>et</sub> sample, which was then treated in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> at 600 °C, a 0.1 at.% content of nitrogen was detected, while the oxygen content decreased from 4.1 to 2.7 at.%. When the treatment temperature was raised to 700 °C, the nitrogen content in SWCNT reached 0.5 at.%.

Figure 3 displays the N1s spectral lines with the normalized intensity that were deconvoluted into individual components.

The spectrum was deconvoluted into five components with the binding energies of N1s peaks in the region of 398.5, 400.1, 401.2, 402.5–402.9 and 404.2–404.7 eV. According to the literature data, peaks with Eb(N1s) = 398.5, 400.1 and 401.2 eV can be assigned to nitrogen residing at pyridinic, pyrrolic and graphitic (quaternary nitrogen) posi-

tions in the carbon matrix [11, 12]. N1s peaks with the binding energy close to 403 eV are commonly attributed to the oxidized nitrogen species, for example, in the composition of pyridine oxide. A tail in the region of 405 eV can be related to the presence of nitrite- or nitrosyl-like NO<sub>x</sub> species on the surface. Thus, the SWCNT<sub>700</sub> sample contains different nitrogen species incorporated into the carbon film structure.

### 3.1. Investigation of electrochemical properties of the synthesized samples

Electrode characteristics (specific capacitance) of carbon nanotubes and nitrogen-doped carbon nanotubes were measured in an aqueous 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Voltammetric curves for the initial SWCNT<sub>et</sub> sample are displayed on Fig. 4.

Specific capacitance values of electrodes calculated from voltammetric curves at different scanning rates for SWCNT<sub>et</sub> are listed in Table 2.

According to Table 2, specific capacitance decreases with increasing the scanning rate.

Similar voltammetric curves were measured for N-SWCNT samples treated in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> at 600–750 °C.

The experimentally obtained specific capacitance values for the initial SWCNT<sub>et</sub> and nitrogen-doped carbon nanotubes are listed in Table 3.

**Table 2**

Specific capacitance of SWCNT<sub>et</sub> estimated at different scanning rates

Scanning rate, mV/s	Specific capacitance of SWCNT <sub>et</sub>
10	72
20	69
40	68
80	66

**Table 3**

Effect of treatment temperature on specific surface area and specific capacitance of initial and nitrogen-doped SWCNTs

Sample	Treatment temperature, °C	Surface area, m <sup>2</sup> /g	Specific capacitance*, F/g
SWCNT <sub>et</sub>		950	72
N-SWCNT <sub>600</sub>	600	970	93
N-SWCNT <sub>650</sub>	650	840	113
N-SWCNT <sub>700</sub>	700	640	85
N-SWCNT <sub>750</sub>	750	480	59

\* – specific capacitance calculated from voltammetric curves at a scanning rate of 10 mV/s

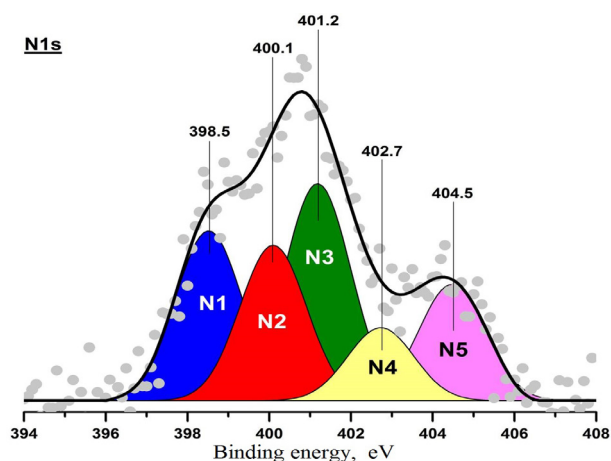


Fig. 3. Deconvolution of the N1s spectrum of carbon nanotubes treated in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> at 700 °C.

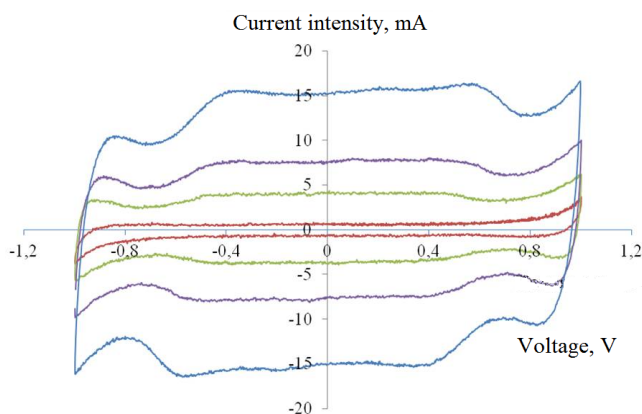


Fig. 4. Voltammetric curves of a symmetrical cell with electrodes based on SWCNT<sub>et</sub>.

One can see that doping of SWCNTs with nitrogen at 600 °C increased specific capacitance by 20% in comparison with initial SWCNT<sub>et</sub> samples, and elevation of the treatment temperature to 650 °C allowed us to obtain specific capacitance of the N-SWCNT<sub>650</sub> sample equal to 113 F/g. However, a further increase in the treatment temperature decreased the specific capacitance due to a considerable decrease in specific surface area of the tested samples.

The results obtained in our study agree with the data reported in Refs. [4, 6], which showed that nitrogen doping of the surface of multiwalled carbon nanotubes produces a 2-4-fold increase in specific capacitance as compared to the initial undoped CNTs. Thus, according to [4], the capacitance of pristine CNTs measured in the 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte was 20 F/g, and pseudocapacitance of N-CNTs, 50–60 F/g. However, specific capacitance obtained in our study was several fold higher than the literature values. This is certainly related to the fact that the most essential characteristic of a nanomaterial, which determines the possibility of its efficient use in the energy storage systems based on supercapacitors, is its specific surface area. In our case, specific surface area of SWCNTs was 960–480 m<sup>2</sup>/g, whereas specific capacitance of multiwalled carbon nanotubes was 172–272 m<sup>2</sup>/g. Specific energy density (E) was estimated for the synthesized N-SWCNT<sub>700</sub> electrodes using the equation  $E = 1/2 CU^2$ , where C is the specific capacitance and U is the operating voltage. The energy density for N-SWCNT<sub>700</sub> was equal to 16 W·h/kg. Note that in the known commercial supercapacitors created with the use of activated carbon, the energy density is 4–5 W·h/kg [14, 15]. Taking into account that the weight of electrodes in commercial supercapacitors constitutes approx-

imately 30% of the capacitor weight, energy density for the electrodes made of N-SWCNT<sub>700</sub> is comparable with that for the known commercial supercapacitors.

#### 4. Conclusions

A method for chemical modification of the SWCNT surface with nitrogen atoms has been developed. The “nitrogen-containing carbon coating – SWCNTs” composites were synthesized by treatment of carbon nanotubes in the 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixture at 600–750 °C. Raising the treatment temperature of SWCNT<sub>et</sub> in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> from 600 to 750 °C was shown to increase both the amount of deposited carbon and the content of nitrogen.

Specific capacitance of carbon nanotubes in electrolyte with 1 M H<sub>2</sub>SO<sub>4</sub> was measured. It was found that specific capacitance of nitrogen-doped carbon nanotubes increases with raising the treatment temperature in 40%NH<sub>3</sub>-1%C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> to 650 °C, which is related to the increased contribution of faradaic processes responsible for pseudocapacitance of the system. A further increase in the treatment temperature decreases the specific capacitance due to decreasing the specific surface area of N-SWCNT samples.

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