

Alteration of the Conductivity of Carbon Nanotubes' Percolation Networks by Functionalization

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A study on the dependence of the electric conductivity of carbon nanotube (CNT) percolation networks on the type and degree of functionalization has been carried out. The influence of the most commonly used $-\text{COOH}$, $-\text{OH}$ and $-\text{CONH}_2$ groups has been studied. A non-linear dependence of the conductivity on the number of functional groups has been detected. A small number of functional groups can improve conductivity, while a large number reduces it. We assume the existence of competing processes that increase conductivity (creation of impurity levels, changes in CNT geometry) and increase resistance (appearance of defects and scattering centers). The data can be used for manipulating the conductive properties of CNTs as well as selecting the optimal degree of functionalization while developing composites, nanodevices and heating surfaces.

Keywords: carbon nanotubes, electrical conductivity, functionalization, percolation network.

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The conductivity of carbon nanotubes (CNTs) ranges from semiconductor to metallic. The conductivity type of CNT is determined by its geometry and the number of defects. Before use CNTs are often functionalized, i.e. radicals $-\text{OH}$, $-\text{COOH}$, $-\text{CO}$ are covalently attached by chemical means. Most often, the radical is attached during a reaction involving oxidizing agents (HNO_3 , H_2O_2 , KMnO_4) [1]. This procedure simultaneously changes the conductivity, thermal conductivity and sorption capacity of CNTs, as well as adhesion to the polymer, which shall be taken into account when creating composites. Currently, there are no detailed studies of the influence of the number of functional groups on the properties of CNTs, and in similar studies [2–5] it is customary to simply state the fact of a change in the electrical properties. The influence of adsorbed metal atoms was studied, but they do not form a covalent bond with the CNT.

In this paper CNTs of the brands „Taunit“, „Taunit-M“ and Taunit-MD [6] were studied, their characteristics are given in the Table. For their functionalization the reactions well known in the literature were used: attachment of groups $-\text{COOH}$ [7] (by heating CNTs in solution KMnO_4 at a temperature $T = T = 64^\circ\text{C}$, the degree of functionalization was determined by the mass ratio of CNTs and KMnO_4 , the ratio varied from 0.2 to 12), $-\text{OH}$ groups [8] (by heating in 30% hydrogen peroxide at $T = 100^\circ\text{C}$, the degree of functionalization was determined by the reaction time, from 20 to 180 min), heating of $\text{CNT}-\text{COOH}$ in ammonia vapor at $T = 250^\circ\text{C}$ for twelve hours to obtain $\text{CNT}-\text{CONH}_2$ [1]. The number of functional groups grafted during the reaction was measured with Seven Compact conductivity meter (Mettler Toledo, Switzerland) using the conductometric titration method. The electrophysical properties of the resulting CNTs were measured using

Novocontrol Consert 80 dielectric spectrometer; the measurement accuracy is no less than 2% at a frequency of 100 Hz.

The data obtained suppose that the qualitative view of conductivity vs. degree of functionalization is similar for different types of functional groups and multilayer CNTs. The dependence can be divided into several sections, marked in the insert in Figure 1.

Section A — CNTs cleaning of contaminants (amorphous carbon, catalyst metal nanoparticles) [9]. Removal of the amorphous phase shall increase conductivity, since the amorphous carbon between CNTs plays the role of an insulator, and removal of the iron-nickel catalyst shall reduce

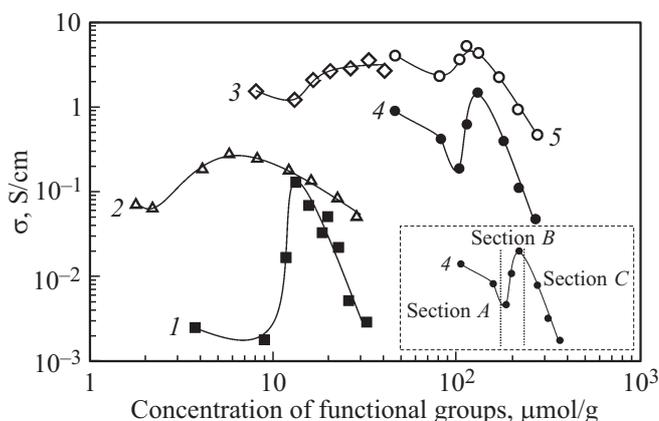


Figure 1. Sample electrical conductivity vs. degree and type of functionalization for Taunit-M-COOH (1), Taunit-COOH (2), Taunit-MD-OH (3), Taunit-MD-COOH (4), Taunit-MD-CONH₂ (5). The letters A, B, C in the insert indicate various sections of dependence (4), the interpretation of which is given in the text.

Characteristics of carbon nanotubes, according to the manufacturer data

Characteristics	Taunit	Taunit-M	aunit-MD
Outer diameter, nm	20–50	10–30	8–30
Inner diameter, nm	10–20	5–15	515
Length, μm	2	≥ 2	≥ 20
Admixtures, %	≤ 10	≤ 5	≤ 5
Specific surface, m^2/g	≥ 160	≥ 270	≥ 270
Bulk density, g/cm^3	0.3–0.6	0.025–0.06	0.025–0.06
Price per 1 g, rub.	~ 50	175	175

conductivity, since free charge carriers are removed from the percolation network. Cleaning involves calcination in air, which also increases the number of defects in CNTs.

Section *B* — increase in conductivity with number increasing of functional groups. The geometry of CNT changes [10], and this always leads to a change in the interatomic distances and band structure. Mesomeric and inductive effects generated by the difference in the affinity of atoms of the functional group and nanotubes for electrons can have an effect similar to the effect of donor and acceptor impurities in semiconductors.

Section *C* — drop in conductivity with number increasing of functional groups. Functionalization was carried out using oxidative reactions, so the number of defects increases. Defects scatter charge carriers and destroy the ballistic conductivity of electrons and phonons. The insertion of functional group opens the covalent bond in the carbon skeleton, which leads to the creation of an additional defect. An ideal defect-free CNT has ballistic conductivity [11], the electrons in it move without scattering, their free path exceeds the CNT length, and the CNT resistance does not depend on its length. As the number of defects increases, the conductivity mechanism becomes quasi-ballistic — the conductivity decreases, but the dependence on the tube length does not appear. A further increase in the number of defects initiates a transition to a diffuse conduction mechanism. An excessive number of functional groups can interfere with the electrical contact of CNTs with each other — radicals $-\text{OH}$, $-\text{H}$, $-\text{O}$ are not part of the conjugated polyaromatic system of CNT and play the role of insulator. The region is absent for the CNT dependences $-\text{OH}$, since with a long time of functionalization with hydrogen peroxide, saturation occurs, and the number of functional groups does not increase.

The type of functional group greatly influences the result. Nitrogen is a good electron donor, so the highest conductivity appears when groups — CONH_2 are inserted. This is clearly visible when comparing the dependences of $\text{CNT}-\text{COOH}$ and $\text{CNT}-\text{CONH}_2$. The second type of groups is obtained by the method of secondary functionalization (the reaction of substituting one group for another), which means that at any given time the number of $-\text{COOH}$ groups is equal to the number of $-\text{CONH}_2$ groups. Taunit and Taunit-M are approximately by an order of magnitude shorter than

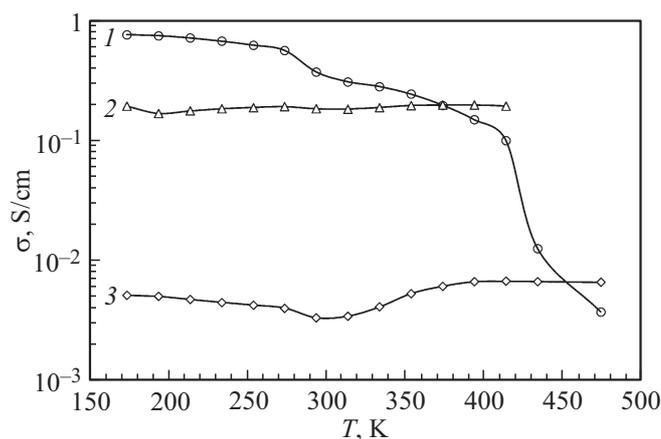


Figure 2. Electrical conductivity of CNTs „Taunit-M“ vs. temperature: $\text{CNT}-\text{CONH}_2$ (1), $\text{CNT}-\text{OH}$ (2), clean CNT (3).

Taunit-MD. This explains the lower conductivity of their percolation network. Note that the intervals of concentration values of functional groups along the horizontal axis in Figure 1 are not random — when trying to increase the number of functional groups, active destruction of CNTs occurs, and when trying to attach them, their detection is less difficult.

The mechanism of covalent functionalization influence is not completely clear. The paper [10] describes the functional groups influence on the geometry of CNTs. At low concentrations of functional groups, the cross section of CNTs can vary from round to polygonal. Surface curvature influences the degree of overlap of delocalized aromatic bonds located in adjacent hexagons of carbon atoms that make up the CNT surface. The lower the curvature of the CNT surface area is, the lower the probability is of scattering of an electron moving at a small angle to the tube axis. Similar effects associated with bending of the carbon skeleton are known for conducting polymers. The assumption is confirmed by the dependence of the CNT band gap on the radius of curvature of the tube [3].

The effect of functionalization on the temperature dependence of conductivity is clearly represented (Figure 2). Since we are considering percolation network of CNTs, in which only one third of the tubes have metallic conductivity, and all the remaining tubes are semiconductors [12] through

which electric current practically does not flow, then, accordingly, for clean tubes a weak dependence is observed conductivity depending on temperature, similar to metal.

In the case of CNT–OH the conductivity of the sample is higher than that of pure CNTs. The type of dependence, despite the high conductivity, is similar to the dependence for semiconductors. Due to the attachment of –OH groups, the number of tubes with metallic conductivity increased, and for the remaining semiconductor tubes the attachment of –OH groups contributed to decrease in the band gap due to the formation of additional levels in the electronic structure.

For CNT–CONH₂ the dependence has a pronounced metallic nature. Abrupt decrease in conductivity after 413 K is due to the fact that functional groups detach from the tube upon overheating, leaving behind defects in the CNT structure. The subsidence of the graph in the region of 273–353 K should also be associated with the presence of residual water in the sample, which begins to evaporate with temperature increasing. The dependence of conductivity on current frequency is absent in the frequency range of 10⁻² to 10⁶ Hz for all studied samples.

The mechanisms determining changes in the CNT conductivity upon covalent functionalization require further study. It is necessary to measure the electrophysical properties of single CNT.

We suppose the existence of competing processes that increase conductivity (creation of impurity levels, changes in CNT geometry) and increase resistance (appearance of defects and scattering centers). The data obtained can be used to control the conductive properties of CNTs, as well as to select the optimal degree of functionalization when developing composites and nanodevices.

The technology of covalent functionalization of CNTs makes it possible to obtain CNTs with given concentration of functional groups, which can be varied within wide limits, and this helps to vary the conductivity of CNTs from a dielectric [4,5] to a metal [3]. The authors hope that this article will increase interest in the proposed problem and, perhaps, provide researchers with material for making theoretical models describing charge and heat transfer in percolation CNT systems. To maximize the CNT conductivity the amidation of CNT–COOH is recommended.

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Conflict of interest

The authors declare that they have no conflict of interest.

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