Structure and electrical conductivity of heat treated iodine-doped multi-walled carbon nanotubes

R Stolyarov\textsuperscript{1}, A Blohin\textsuperscript{1}, N Gorshkov\textsuperscript{2}, A Tkachev\textsuperscript{1}, B Kulnitskiy\textsuperscript{3}, T Pasko\textsuperscript{1}, A Sukhorukov\textsuperscript{1} and I Burmistrov\textsuperscript{2}

\textsuperscript{1}Department of Technology and methods of nanoproducts manufacturing, Tambov State Technical University, 106 Sovetskaya Street, Tambov 392000, Russia

\textsuperscript{2}Department of Chemistry and chemical technology of materials, Yuri Gagarin State Technical University of Saratov, 77 Politechnicheskaya Street, Saratov 410054, Russia

\textsuperscript{3}Department of structural research, Technological Institute for Superhard and Novel Carbon Materials, 7a Tsentralnaya Street, Troitsk 108840, Russia

E-mail: stolyarovra1985@gmail.com

Abstract. The present paper discusses the possibility of simultaneously using two methods for the modification of multi-walled carbon nanotubes - high-temperature annealing and halogen-assisted modification. The nanotube modification was carried out during the high-temperature annealing in the presence of iodine. A change in the structure and an increase in the electrical conductivity of the modified multi-walled carbon nanotubes was observed.

1. Introduction

The electrical properties of carbon nanotubes (CNTs) are largely related to the structural features of their structure [1]. It is generally accepted to distinguish nanotubes by the number of concentric graphene cylinders forming them: single- (SWCNTs), double- (DWCNTs), and multi-walled (MWCNTs). The main structural feature of single-walled nanotubes is chirality. MWCNTs differ from SWCNTs considerably by a wider variety of shapes and configurations. A variety of structures is manifested both in the longitudinal and in the transverse directions. The electric conductivity of cheaper MWCNTs is much lower compared to the SWCNTs, and in some cases, its values may differ by several orders of magnitude. This is primarily due to the presence of a much larger number of structural defects on the surface of the MWCNTs compared with the SWCNTs. In this regard, several researchers have tried to increase the electrical conductivity of the MWCNTs through various methods, in particular, through doping with silver [2,3], nitrogen [4,5], polyaniline [6,7], iodine [8,9], etc. The best result is achieved with iodine-modified MWCNTs and SWCNTs; their electrical conductivity increases by 60 % and 2000 % compared to the initial one [8,9]. On the other hand, it is possible to reduce the number of MWCNTs defects and increase their electrical conductivity using high-temperature annealing [10,11].

Thus, using both the high-temperature treatment and halogen-assisted modification, it is possible to significantly increase the electrical conductivity of the MWCNTs. Therefore, the goal of the present work was to increase their electrical conductivity by changing their structure and modifying with iodine.
2. Materials and methods

2.1. Multi-walled carbon nanotubes (MWCNTs)
Taunit-M carbon nanomaterial, representing MWCNTs with a diameter of 10-30 nm and a length of up to 2 μm (figure 1), was used in the present research. The material was synthesized via catalytic pyrolysis of natural gas at NanoTechCenter LLC (Tambov, Russia).

2.2. High temperature modification
The MWCNTs structure was modified by high-temperature treatment in the presence of iodine. The MWCNTs were placed in an isopropanol solution of chemically pure iodine. Then, the components were mechanically mixed and dried in a fume hood under normal conditions until complete evaporation of the isopropanol. After the dry mixture was distributed over the substrate, it was loaded into a sealed capacitive reactor equipped with a gas supply system. High-temperature modification of the MWCNTs with adsorbed iodine was carried out at a temperature of 620°C in argon for 2 h.

2.3. Characterization of MWCNTs
To characterize the MWCNTs structure, the following techniques were employed: high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and characteristic electron energy loss spectroscopy (EELS). Measurements of the electrical conductivity of the MWCNTs were performed using the method of impedance spectroscopy (IS).

The TEM studies of the material obtained were performed using a JEM-2010 high-resolution transmission electron microscope (JEOL, Japan) with energy dispersive spectroscopy (EDS) analyzer and a GIF Quantum attachment for EELS. The morphology and microstructure of the MWCNTs surface was studied using a Merlin scanning electron microscope (Carl Zeiss, Germany).

The electrical conductivity of the pristine and modified nanomaterials was measured using the IS on an Alpha AN impedance meter (NovoControl, Germany). Measurements were carried out for samples placed and pressed at a pressure of about 100 MPa between titanium electrodes with a diameter of 8 mm.

3. Results and discussion

3.1. Morphology and structure of the modified MWCNTs
The SEM and TEM images of the modified MWCNTs are presented in figure 2.
Figure 2. SEM (a) and TEM (b) images of the modified Taunit-M MWCNTs.

As a result of the iodine-assisted modification, the MWCNTs structure becomes deformed, and the outer layers are destroyed until a destructured carbon film is formed instead of them (figure 2b). Besides, during the modification, the compounds of single, closely spaced nanotubes are formed by means of the destructured outer layers (figure 2a). The mechanism of the nanotubes deformation during the thermal modification is schematically shown in figure 3.

Figure 3. Mechanism of the nanotube deformation during thermal modification.

Figures 2a and 2b clearly show the connections of individual nanotubes into a single monolith. Agglomerates of carbon nanotubes usually represent objects from a few to hundreds of micrometers. The MWCNTs are tangled in them and are linked to each other through simple contact. In thermally modified agglomerates, the individual nanotubes are firmly interconnected by the destructured outer layers and form a single electrically conductive structure. This morphology provides improved electrical conductivity within individual clusters and reduces the electrical resistance of bulk materials, as will be shown below.

The key role in increasing the electrical conductivity is played by changes in the MWCNTs morphology, which was indirectly shown during the elemental analysis (Table 1). The research data obtained showed almost complete absence of iodine in the modified MWCNTs (Table 1). As a result
of heat treatment, iodine is completely evaporated and removed by a stream of inert gas from the MWCNTs sample, and thus, cannot exert a direct influence on the charge transfer process.

Table 1. Elemental composition of the modified MWCNTs.

| Element | wt.% | at.% |
|---------|------|------|
| C       | 97.44| 99.50|
| O       | 0.10 | 0.03 |
| Co      | 1.24 | 0.26 |
| Fe      | 0.66 | 0.14 |
| I       | 0.56 | 0.05 |
| Sum     | 100.00| 100.00|

3.2. Electrical conductivity of the nanomodified MWCNTs

Figure 4 shows the dependence of the electrical conductivity on the frequency of the modified and the original (pristine) nanotubes.

The increase in the electrical conductivity of the modified nanotubes compared to the pristine ones can be explained by several known mechanisms: intercalation or adsorption of iodine [8] and oxygen [1,12], or changes in the MWCNTs structure [10]. The oxygen or iodine adsorption should cause an increase in the conductivity and strong p-doping of the MWCNTs. The increase in the conductivity due to the oxygen and iodine modification of the MWCNTs cannot exceed tens of percent [8,12]. Moreover, their high content in the samples was not recorded (Table 1). The obtained EELS spectra showed a small peak of oxygen in the region of 532 eV (figure 5), which indirectly confirms its low concentration and, consequently, the low contribution to the electrical conductivity changes.

Moreover, the linear form of the frequency dependences of the electrical conductivity is characterized by the absence of p-doping of the modified MWCNTs (figure 4), and they still possess electronic conductivity.

Thus, the TEM and SEM studies demonstrated that the nanotubes were linked to each other as a result of high-temperature modification in the presence of iodine. In this structure, mechanical conductive contacts are possible only between the individual agglomerates. As a result of the nanotubes connection, the contact resistance is significantly reduced and, consequently, the conductivity of the modified material increases by more than 3.5 times (figure 4).
4. Conclusion
An easily scalable technique for the thermal modification of MWCNTs in the presence of iodine was developed. The use of halogen-assisted high-temperature annealing made it possible to obtain a carbon nanomaterial superior in the electrical conductivity by 360%. The structure of the modified MWCNTs was studied. As a result of the iodine-assisted modification, the MWCNTs structure becomes deformed, and the outer layers are destroyed till the formation of a degraded carbon film instead. The MWCNTs cross-linked in the entire volume by means of this amorphous film could find wide practical application, for instance, as the main component of electrically conductive products based on polymers obtained through vacuum infusion.

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