Synthesis of "Silica – Carbon Nanotubes" Composite and Investigation of its Properties

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Article info

Abstract

A new method for synthesis of CNT-SiO_2 composite was developed. Oligomethylhydridesiloxane (OMHS) was used as the SiO_2 precursor. The presence of active hydrogen in the composition of OMHS made it possible to obtain chemical interaction between the surface of carbon nanotubes and the deposited silica layer. The effect of the silica film on the CNT oxidizing ability was studied. It was found that the oxidation rate of the CNT-SiO_2 composite decreases approximately by an order of magnitude in comparison with as-prepared CNT. The morphology and structure of amorphous silica obtained after oxidation of the CNT-SiO_2 composite were studied. The thermal stability of the CNT-SiO_2 composite was also studied. The CNT-SiO_2 composite was found to be thermally stable up to temperatures of 1100-1200 ºC. An increase in the calcination temperature to 1300 ºC leads to segregation of the CNT-SiO_2 composite into individual components: CNT and SiO_2 particles.

1. Introduction

Carbon nanotubes (CNT) and carbon nanofibers (CNF) are some the most promising modern materials. They possess a wide range of unique properties: high strength and conductivity, corrosion resistance, compatibility with living tissues, etc. Therefore, the prospects for application of these materials in various areas are diverse [1-3]. In the last few years CNT and CNF are intensively studied for development of composite materials, in particular, based on polymer [4, 5] and metal matrices [6, 7]. Even wider application of carbon nanomaterials is impeded by their susceptibility to oxidation at moderate and high temperatures in the oxidative environments. It was reported [8] that it is possible to overcome this drawback by protecting carbon nanofibers prepared from polyacrylonitril by a ceramic matrix acting as a diffusion barrier between oxygen and the carbon surface. Experimental studies showed [9-16] that deposition of a thin SiO_2 film on the surface of carbon nanomaterials substantially slows down the carbon oxidation. The most widely used method for silica deposition on carbon nanomaterials includes tetraethoxysilane hydrolysis followed by the deposition of the obtained sol on the surface of carbon nanomaterials. Earlier sol-gel method was used for the SiO_2 deposition on the surface of various carbon materials (soot, activated carbon, Sibunit, carbon nanofibers (CNW) [17, 18].

In that study tetraethoxysilane (TEOS) was hydrolyzed in an acid environment (H_2O – HCl). To prepare the CNF-SiO_2 composite, the obtained sol was mixed with the carbon material, dried at room temperature and calcined at 300 ºC. However, the CNF-SiO_2 composite prepared by this procedure consisted of a SiO_2 matrix containing carbon nanowires.

The quality of a composite material depends on the type of interaction between the matrix and the filler. In the composites described above the interaction between carbon and silica is limited by the Van-der-Waals forces. Furthermore, the use of long TEOS hydrolysis lasting several days makes these methods not technological. So, attempts of improving the methods used for synthesis of "carbon material – SiO_2" composites are continued. For example, ethylsilicate was used as an alternative precursor for SiO_2 preparation on the surface of carbon nanotubes

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[19]. The use of a mixture of TEOS and methyl triethoxysilane in the presence of cetyltrimethylammonium bromide was also reported [20].

In this study we used oligomethylhydridesiloxane (OMHS) as the SiO_2 precursor for silica deposition on the CNT surface. A specific feature of the structure and composition of oligoorganohydridesiloxanes is the presence of Si-H bonds capable of reacting with various functional groups of solid surfaces. Such bonds interact with the surface functional groups forming a thin siloxane film on the surface [21]. Supposedly, the presence of the active hydrogen in OMHS can strengthen the interaction between the surface of the carbon nanotubes and the deposited silica layer that would have a positive effect on the properties of the obtained $CNT-SiO_2$ composites.

2. Experimental methods

OMHS used as the silica precursor has the following structure:

$$(CH_3)_3Si - O - \left[-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O - \right]_n - Si(CH_3)_3$$
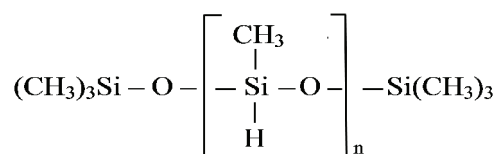
Here n varies from 4 to 80. The OMHS purity was 97 vol.%.

Carbon nanotubes were prepared by decomposition of a propane-butane mixture on the $31\%CoO$-$7\%MoO_3$-$24\%Fe_2O_3$-Al_2O_3 catalyst at 700 ºC [22]. Electron microscopy was used to determine their average dimensions. The external diameter of the nanotubes varied in the range of 10-25 nm with predominating size between 12 and 17 nm. Their internal diameter was in the range of 6-12 nm. The CNT length reached 10^4 nm. The fraction of the carbon nanotubes with these characteristics was about 95 wt.%.

To create acid sites on the CNT surface and remove residual catalyst used for the nanotube growth, the samples were treated in a mixture of acids. The as-synthesized CNT were covered with aqua regia, heated to the boiling temperature and mixed for 30 min. Then the liquid was decanted. The acid-treated carbon nanotubes were washed with distilled water and dried in a muffle furnace at 120 ºC for 30 min.

OMHS was deposited from an alcohol solution. CNT (5 g) was filled with 40 ml of 10 wt.% OMHS solution in ethanol. The solution was evaporated by heating on a magnetic mixer. The obtained OMHS-CNT composite was dried at 150 ºC for 1 h the CNT weight increased by 35-40% after the OMHS deposition. Then, the OMHS-CNT samples were heated in quartz flow reactor equipped with a McBain spring balance with the mass change sensitivity 1×10^{-4} g in an argon flow to 720 ºC and calcined at this temperature for 1 h. The use of the reactor with the spring balance allowed us to control changes of the sample weight during heating and calcination. The loading of the OMHS-CNT composite in the reactor was 2.5 g. The main weight loss took place during heating in the temperature range of 350-600 ºC after calcination at 720 ºC. The silica concentration in the $CNT-SiO_2$ composite was about 15 wt.%.

The CNT oxidation kinetics was studied in a quartz flow reactor with a McBain spring balance. First, the sample was heated to the desired temperature (600-750 ºC) in a 75 l/h argon flow. The oxidation of the $CNT-SiO_2$ composite was carried out in oxygen diluted with argon in the molar ratio O_2:Ar = 10:75. The purity of the used gases was 99.99 vol.% for Ar and 99.9 vol.% for O_2.

XRD studies of the samples were carried out using a Siemens D-500 diffractometer with monochromatized CuK_α irradiation.

High-resolution transmission electron microscopic (HRTEM) images were obtained using a JEOL JEM-2010 microscope with 0.14 nm lattice resolution. Local energy-dispersion X-ray microanalysis (EDX) was performed using a EDAX spectrometer equipped with a Si (Li) detector with energy resolution 130 eV.

Diffuse reflectance FTIR spectra were recorded using Shimadzu 8300 spectrometer equipped with an IFS-240 integrating sphere in the range of 400-4000 cm^{-1} with 4 cm^{-1} resolution. Each spectrum was averaged using 400 scans. The obtained spectra were converted from the reflectance scale to Kubelka-Munk function scale $F(R)=(1-R)^2/2R$, where R is the reflectance coefficient, and subjected to baseline correction. The obtained spectra are presented in wave number vs. F(R) coordinates. For presentation convenience, the spectrum intensity of the organosilicate precursor was decreased by a factor of 30 in the F(R) scale. Unfortunately, the signal/noise ratio at wave numbers above 2300 cm^{-1} was very high. So, the spectra in the high frequency range were not reliable and are not reported in the paper.

3. Results and Discussion

3.1. Genesis of the CNT-SiO₂ composite phase composition after OMHS deposition: FTIR study

Figure 1 presents an FTIR spectrum of CNT treated in aqua regia (Spectrum 1). The IR spectrum is characterized by the presence of weak absorption bands at wave numbers 956 and 1087 cm^{-1}, which

can be attributed to vibrations of graphite rings and stretching vibrations of C-O bonds, respectively. The other absorption bands observed in Spectrum 1 at 1271 and 1645 cm^{-1} are related to the presence of carboxylate groups on the CNT surface.
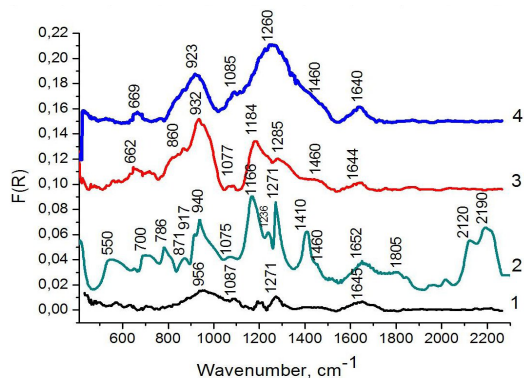

Fig.1. Diffuse reflectance FTIR spectra of CNT (1), OMHS (2), CNT after OMHS deposition (3) and CNT after OMHS deposition and calcination at 720 ºC (4).

The spectrum of pure OMHS was recorded before deposition on CNT. The amplitude of its spectrum shown in Fig. 1, spectrum 2 was decreased by a factor of 30. Simulation of the vibrational spectrum using Hyperchem software package showed that the band at 553 cm^{-1} belongs to bending O-Si-O vibrations. The band at 700 cm^{-1} is attributed to vibrations of the C-H bonds. The group of bands at 786, 871, 917 and 1805 cm^{-1} belongs to bending vibrations of the O-Si-H bonds. The absorption band at 940 cm^{-1} can be attributed to bending vibrations of Si-O-H hydroxyl groups. The vibration band at 1075 cm^{-1} belongs to stretching vibrations of C-O bands. The bands at 1166 and 1236 cm^{-1} are due to stretching vibrations of Si-O groups. The bands at 1271 and 1410 cm^{-1} belong to bending vibrations of CH$_3$ groups. The absorption band at 1645 cm^{-1} can be attributed either to bending vibration of molecular water or to stretching vibrations of carboxylate groups. Finally, the bands at 2120 and 2190 cm^{-1} belong to vibrations of Si-H bonds.

The absorption bands at 2120 and 2190 cm^{-1} corresponding to the vibrations of Si-H bonds are not observed in the spectrum of CNT after deposition of OMHS (Fig. 1, Spectrum 3). This means that Si-H bonds of siloxane react with acidic groups on the CNT surface, probably, according to Reaction (1)

$$C\text{-}OH + H\text{-}Si = C\text{-}O\,Si + H_2 \qquad (1)$$

In addition, the absorption band at 1166 cm^{-1} related to the formation of Si-O-Si siloxane network is shifted to higher frequency to 1184 cm^{-1}. This shift is an indicative of the 3D structure growth. After cal-

cination this band is shifted even further to 1260 cm^{-1} (Fig. 1, Spectrum 4). Consequently, the calcination of the CNT-SiO$_2$ composite at 720 ºC in inert atmosphere results in the formation of an amorphous silica film. Note that the frequency of the Si-O stretching vibrations observed at 1260 cm^{-1} for the sample heat-treated at 720 ºC is slightly higher than that typical for bulk silica. This difference can be related either to the specific properties of the structure (e.g. limited length of the Si-O-Si-O chains) or to high permittivity of the carbon support.

3.2. TEM study

A TEM image of CNT with deposited organosilicate after calcination at 720 ºC in inert atmosphere is shown in Fig. 2. One can see that calcination of organosilicate compounds deposited on CNT results in the formation of "CNT – amorphous SiO$_2$" composites.

The concentrations of components in the CNT-SiO$_2$ composite (C = 89, Si = 11 at.%) was determined by EDX (Fig. 3, inside the circle in Fig. 2). The presence of Cu is due to the use of a copper grid as a sample holder.

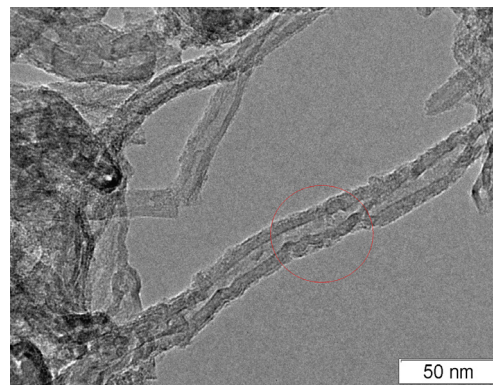So, calcination of organosilica compounds results in the formation of a "CNT – amorphous silica" composite.

Fig. 2. TEM micrograph of the CNT-SiO$_2$ composite.
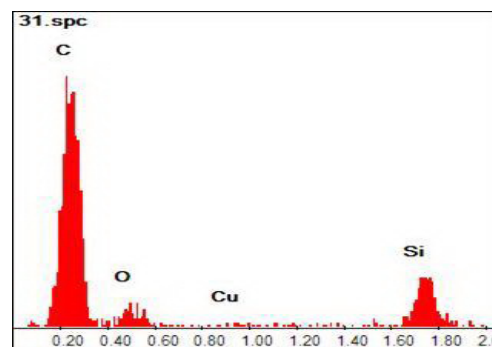

Fig.3. EDX spectrum of CNT-SiO$_2$ composite (inside the circle in Fig. 2).

3.4. Effect of silica film on the resistance of CNT-SiO₂ composite to oxidation by oxygen

Figure 4 presents kinetic curves of CNT oxidation by oxygen diluted with argon in the molar ratio $O_2:Ar = 10:75$ at different temperatures. One can see that as-prepared CNT are quickly oxidized under studied conditions. After oxidation their weight decreases by 97 wt.%. The remaining residue (3 wt.%) is ashy and consists of the catalyst used for the CNT growth. The CNT treatment in aqua regia leads to dissolution of the remaining CNT growth catalyst. This results in a decrease of the CNT oxidation rate. The kinetic oxidation curves of the as-prepared CNT (1) and CNT treated in aqua regia (2) at 600 ºC in oxygen diluted with argon in molar ratio $O_2:Ar = 10:75$ are shown in Fig. 5. The kinetic oxidation curve of the CNT-SiO₂ composite (3) is shown as well. One can see that the oxidations rate of the as-prepared CNT and the CNT-SiO₂ composite differ approximately by an order of magnitude.
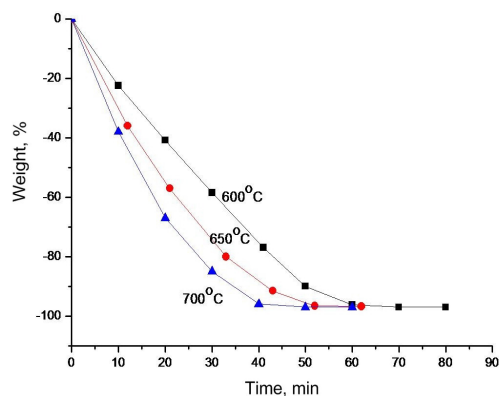
When the oxidation temperature of the CNT-SiO₂ composite is increased, the oxidation rate of the carbon nanotubes also grows. However, a significant difference in the oxidation rates of CNT and the CNT-SiO₂ composite is preserved at higher temperature as well (Fig. 6). This result indicates that a substantial fraction of the CNT surface in the composite is covered by a silica layer. This coverage effectively slows down the reaction of oxygen with the carbon surface.

Fig. 6. Oxidation kinetic curves of CNT-SiO₂ composite in oxygen diluted with argon in molar ratio $O_2:Ar = 10:75$ at different temperatures.

A TEM image of amorphous SiO₂ formed after combustion of CNT from the CNT-SiO₂ composite is shown in Fig. 7. One can see long channels in the structure of the formed silica (Fig. 7). These channels are due to the burning of CNT, which were covered with a silica film. So, the SiO₂ replicas are formed after the combustion of carbon nanotubes. The packing density of this SiO₂ is 0.06 g/cm³. Its specific surface area is 850 m²/g. Thus, an aerogel-like SiO₂ sample is formed after burning of carbon nanotubes from the CNT-SiO₂ composite.

Fig. 4. Oxidation kinetic curves of as-prepared CNT in oxygen diluted with argon in molar ratio $O_2:Ar = 10:75$ at different temperatures.
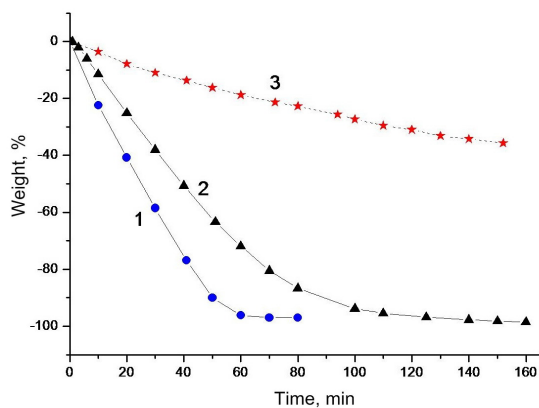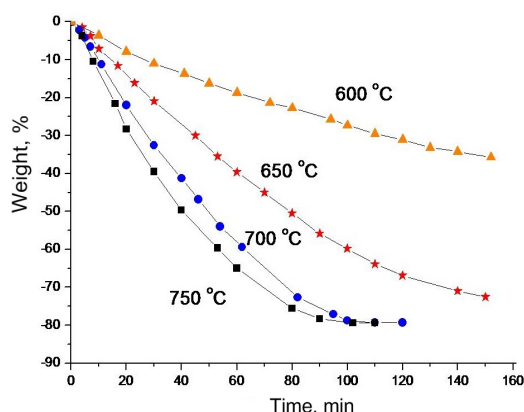

Fig. 5. Oxidation kinetic curves of as-prepared CNT (1), CNT after treatment in aqua regia (2) and CNT-SiO₂ (3) in oxygen diluted with argon in molar ratio $O_2:Ar = 10:75$ at 600 ºC.
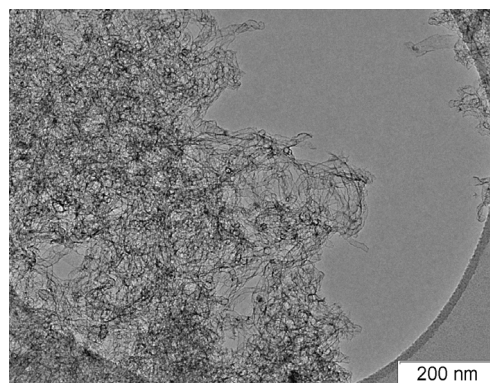

Fig. 7. Morphology of SiO₂ formed after burning of CNT from the CNT-SiO₂ composite.

3.5. Thermal stability of the CNT-SiO₂ composite

Samples of the CNT-SiO₂ composite sealed in quartz ampoules were heat-treated in inert atmosphere in a muffle furnace at 1100-1300 ºC. The calcination of the CNT-SiO₂ composite at 1100 ºC for 1 h did not result in any changes of the morphology or structure of the silica film. However, an increase of the calcination temperature to 1300 ºC led to partial sintering of the silica film with the formation of spherical particles of amorphous SiO₂. A TEM image of the CNT-SiO₂ composite after calcination at 1300 ºC for 1 h without access to the air is shown in Fig. 8. The sample consists of CNT and spherical SiO₂ particles with diameter about 60 nm.
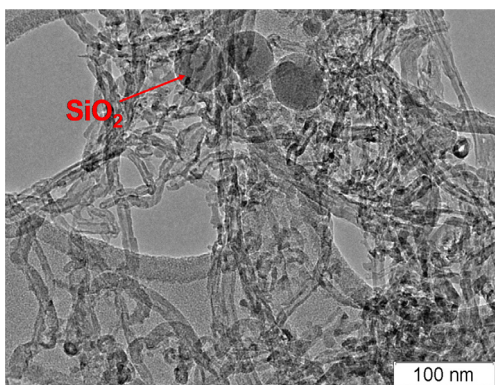

Fig.8. TEM micrograph of the CNT-SiO₂ composite after calcination without access to air at 1300 ºC for 1 h.

TEM studies showed that calcination of the CNT-SiO₂ composite at 1400 ºC results in further segregation of the composite components. Extended fibers consisting of SiO₂ and CNT can be observed in Fig. 9.
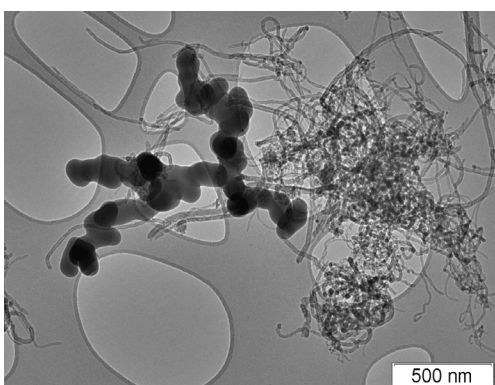

Fig. 9. TEM image of CNT-SiO₂ composite after calcination in argon flow at 1400 ºC for 1 h.

The EDX data demonstrate that the extended fibers are composed of SiO₂ (Fig. 10).

So, the CNT-SiO₂ composite is thermally stable until 1100-1200 ºC. An increase of the calcination temperature to 1300 ºC leads to segregation of the composite into its constituents – CNT and SiO₂.
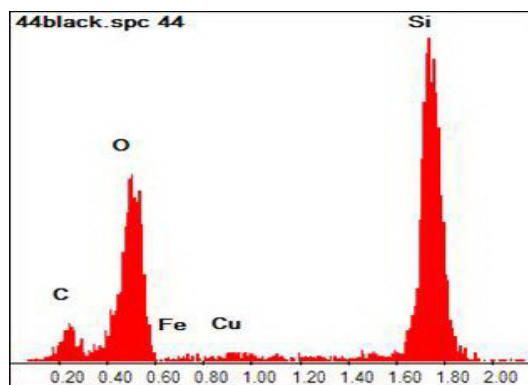

Fig. 10. EDX spectrum of CNT-SiO₂ composite (thick fibers shown in Fig. 9).

4. Conclusions

A method for synthesis of a CNT-SiO₂ composite using oligomethylhydridesiloxane (OMHS) as a SiO₂ precursor was developed. The presence of active hydrogen in OMHS allowed us to achieve chemical interaction between the surface of the carbon nanotubes and the deposited silica layer.

The effect of the silica film on the CNT resistance to oxidation in an oxygen-argon mixture was studied. It was found that the oxidation rate of the CNT-SiO₂ composite is lower approximately by an order of magnitude than that of as-prepared CNT without the SiO₂ coating.

The morphology and structure of amorphous silica formed after oxidation of the CNT-SiO₂ composite and carbon combustion was studied. The packing density of this SiO₂ is 0.06 g/cm³. Its specific surface area is 850 m²/g. These values suggest that the formed SiO₂ has aerogel-like porosity.

The thermal stability of the CNT-SiO₂ composite was studied in inert environment. The CNT-SiO₂ composite was found to be thermally stable until 1100-1200 ºC. An increase of the calcination temperature to 1300 ºC leads to segregation of the composite into its constituents – CNT and SiO₂.

Acknowledgements

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