Synthesis of silicon carbide at room temperature from colloidal suspensions of silicon dioxide and carbon nanotubes

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Abstract. Experimental and theoretical approaches were used for the investigation of mechanisms and conditions of self-organized nanostructures formation in the drying drop of the mixture of colloidal suspensions of nanoscale amorphous silicon dioxide and carbon nanotubes. The formation of rodlike structures with diameter 250-300nm and length ~4µm was revealed. The diffraction analysis of the obtained nanostructures showed the formation of the silicon carbide phase at room temperature.

1. Introduction
The use of carbon nanotubes (CNT) is commonly assumed while producing composite and hybrid nanomaterials as well as elements of nanoelectronics, sensing, energetic, microsystems technology [1–10]. There is a great interest to Si/CNT composites as nanomaterials for structural stable anodes of lithium-ion batteries with the high energy density [11–13]. The synthesis of Si/CNT composites often includes a high-temperature anneal [6, 13]. Bolotov et al. [1] showed that during high-temperature treatment of the composite SnO$_2$-multi-walled CNT in vacuum, there was a transformation of its electronic structure along with local synthesis of tin oxycarbide. In addition to external high-energy CNT activation methods, it is important to consider the internal reserve of nanotubes themselves related to their qualities, surface curvature and defects [5]. The uniqueness of carbon nanotubes is based on the dependence of the reactivity of carbon atoms on their topological positions: the increasing curvature is the reason of the decreasing activation energy of chemical reactions [14–16]. Caps of carbon nanotubes have the greatest curvature, which allows to consider caps as active centers. Defects of the hexagonal structure define the local charge redistribution near caps [5, 16]. The charged active center is the core of the interaction between carbon nanotubes and second nanocomponent of the similar size. Zhukalin et al. [5] using this approach investigated the formation of nanostructures from colloidal suspensions of nanoscale amorphous silicon dioxide particles and carbon nanotubes. The indirect methods indicated the formation of the silicon oxycarbide phase from the drying drop at the room temperature. In the present work we carried out a further investigation of mechanisms and conditions of aggregation and synthesis of self-organized structures in the nanosystem SiO$_2$-CNT using the methods of numerical and natural experiments.

2. Methodology
The investigation of the interaction of amorphous silicon dioxide (aerosil brand 300, the average size of particles 7nm) (figure 1a) with the array of short carbon nanotubes (average diameter and length are 20–40 nm and ~500 nm respectively) in homogeneous environment was conducted by mixing
colloidal solutions of SiO$_2$ and CNTs using the drop method [17–19], with the subsequent evaporation of a dispersion medium – water. A drying drop is viewed as nanoreactor with dynamic walls and internal parameters, such as, the concentration of components, pressure, temperature [20–21].

Colloidal suspensions of initial components were dispersed by the ultrasound disperser for 15 minutes at 60 W. The morphology of obtained structures was investigated on the scanning electron microscope JSM-6390LV (JEOL, Japan). The elemental analysis was conducted with the help of the analytical console Bruker AXS Microanalysis GmbH (Germany). The investigation of powder-like samples of pure aerosil and nanostructures SiO$_2$/CNT was controlled on IR-spectrometer VERTEX-70 (Germany) by the method of interrupted full internal reflection in the range from 600–4000 cm$^{-1}$. The transmission electron microscopy (TEM) was performed on Carl Zeiss Libra 120. The analysis was performed on PANalytical EMPYREAN with the use the Cu K$_\alpha$ radiation. Measurements were made in the reflection mode ($\theta/2\theta$ scan with a step 0.013°/2θ). The measure range 2θ was 5–60 °.

Numerical simulations of the interaction of carbon atoms of the charged interface of the capped armchair SWCNT (5, 5) with atoms of different electronegativity (H, O, F) were carried out using hybrid DFT (density functional theory) method of Becke [22] and Lee, Yang, Parr [23] (B3LYP) and 6-31G basis set [24] with the help of the Gaussian09 program package [25] in the Supercomputing center of Voronezh State University.

3. Results and discussions

During the interaction of certain concentrations of amorphous SiO$_2$ and CNTs in the drying drop at room temperature 2 kinds of self-organized structures: rodlike and spherical was revealed (figure 1b). These structures differ not only by the shape, but also by the ratio of atomic concentrations of Si:O:C – 3.5:1:1.5 for rodlike structures, and 1.9:3.9:1 for spherical structures. It is known that the absorption band in the IR spectra in the region 1100 (SiO$_2$) – 980 – (SiO) – 943 cm$^{-1}$ (Si) are linked to stretching vibrations of the bridging oxygen Si–O–Si (stretching mode Si–O–Si) and widely used for the determination of the composition of SiO$_x$ layers. A displacement of the oscillation mode to lower frequencies indicates the increase of the silicon concentration in rodlike structures SiO$_2$/CNT. On the basis of IR spectroscopic studies and elemental analysis, we can conclude that composite SiO$_2$/CNT rodlike structures have a high content of the silicon.

![Figure 1](image-url)

**Figure 1.** The electron microscopy of initial silicon dioxide (a) and nanostructures obtained after the dry drop (b).
The XRay diffraction analysis of obtained nanostructures revealed the formation of the silicon carbide phase with a polytype 4H-SiC (figure 2). Lattice parameters are $a=b=3.081 \text{ Å}$, $c=10.060 \text{ Å}$. The formation of oxycarbide phases during the high temperature treatment of amorphous SnO$_{2-x}$ with multi-walled CNTs, was convincingly shown by Bolotov et al. [1]. The synthesis of silicon carbide commonly occurs at 2200–2500°C. Reasons of the formation of silicon carbide at the room temperature are not obvious and relate to complex dynamical processes in the drying drop and features of the CNT structure.

A capped armchair single walled carbon nanotube (SWCNT) (5, 5) was taken as a model object. Capes of SWCNT (5, 5) are two halves of the fullerene C$_{60}$ dissected perpendicular to the five-fold axe [26, 27]. The boundary ring of carbon atoms of the cap is formed by sides of pentagons. The boundary ring of carbon atoms of the SWCNT’s body is formed by sides of hexagons. That results in the shift of the electron density from the body of SWCNT to near lying ring of atom of the cap. Hence the charged interface forms.

The calculated potential curves are presented in figure 3. The energies of covalent bonds of hydrogen and fluoride with the atoms of carbon from negatively charged ring of the cap were 3 and 1.5 times higher than with positively charged ring of the tube’s body. Therefore, negatively charged ring of the cap can be viewed as local activity center with increased reactivity.

![Figure 2. TEM image (a) and diffraction pattern of the nanostructure of SiO$_2$/CNT (b).](image)

![Figure 3. Potential curves of interaction of hydrogen atoms (solid lines), fluorine (dash lines) and oxygen (dot-dash lines) with negatively-charged ring of carbon atoms of the cap and positively charged ring of SWCNT’s body (5, 5). Full energy of non-interacting nanotube and H, F, O was set as a zero point.](image)
The strong interaction with the oxygen was observed (figure 3). Binding energies of the oxygen with carbon atom of negatively and positively charged ring are 2.629 and 2.502 eV which exceeds the binding energy H-C and F-C by more than two times. The structure of the amorphous silicon dioxide is tetrahedral [28]. All silicon atoms are surrounded by four oxygen atoms. Base elements of the surface of the amorphous silicon dioxide are two tetrahedrons with the common oxygen atom. In that case the strong interaction of CNT with the nanoscale silicon dioxide is quite realistic. We conducted simulation of local interaction between nanofragment of SiO$_2$ and carbon nanotube. If the initial distance is greater than $r_{\text{Si-C}}^\text{cr}$, then the calculated value is $r_{\text{Si-C}}^\text{cr}$~2.54 Å, which is characteristic of Vander-Waals interactions. The formation of covalent bonds Si-C and O-C, as well as bridges C-Si-O-C was revealed by the geometry optimization if the initial distance is less than $r_{\text{Si-C}}^\text{cr}$. Hence, when the silicon dioxide and CNT are enough close each other the formation of silicon carbide is going on. This condition is fulfilled during the dry drop due to the rise of pressure, active flow and increase of concentration of CNT and silicon dioxide.

4. Conclusion

The interaction of nanoscale amorphous silicon dioxide and carbon nanotubes in the drying drop of colloidal suspension with the certain concentration of components leads to the formation of self-organized rodlike structures with diameter 250-300nm and length ~4µm. The elemental analysis and IR- spectroscopy showed the high content of the silicon in rodlike structures. The diffraction analysis of the obtained nanostuctures revealed the formation of the phase of silicon carbide at the room temperature. Theoretical analysis confirmed that the mechanism of formation of such structures is due to the curvature effects and presence of charged active centre near caps of CNTs, which increases their reactivity. Complex dynamical processes in the drying drop and high reactivity of short CNT with high concentration of chemically active atoms are the basis for the development of energy-saving technologies of synthesis of functional composite nanomaterials and high-temperature phases.

Acknowledgments

This work was supported by the project FP7-IRSES-295260 “ECONANOSORB” under Marie Curie Actions of the 7th Framework Program of European Union, by RFBR, research projects N 14-02-31315 mol_a.

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