# Formation of Nanostructures from Colloidal Solutions of Silicon Dioxide and Carbon Nanotubes

## D. A. Zhukalin*, A. V. Tuchin, D. L. Goloshchapov, and L. A. Bityutskaya

*Voronezh State University, Voronezh, 394006 Russia*
**e-mail: d.zhukalin@mail.ru*
Received July 17, 2014

**Abstract**—The formation of nanostructures from colloidal solutions of amorphous silicon dioxide ($SiO_2$) and carbon nanotubes (CNTs) in evaporating drops at room temperature has been studied. It is established that spherical aggregates with an average diameter of ~2 μm and rodlike nanostructures with diameters within 250−300 nm and lengths of ~4 μm are formed under these conditions. The mechanisms of covalent and van der Waals interaction between CNTs and $SiO_2$ are considered in the framework of a phenomenological model of the active center of a closed CNT.

Pure carbon nanotubes (CNTs) represent a polyfunctional quantum-dimensional material possessing a combination of unique physical properties [1]. Recent advances in the technology of carbon nanotubes with controlled parameters (symmetry, diameter, length) made it possible to pass on to a new stage of CNT applications—the development of nanocomposites with preset properties. These technologies include the creation of radiation-resistant materials capable of withstanding severe irradiation conditions (space, atomic power engineering) [2] and composites for nanoelectronics [3], sensorics, etc. [4]. A specific feature of these technologies is the emphasis on localization of the interaction between various components and CNTs on the nanoscale with allowance for their characteristic properties such as commensurability, symmetry, curvature, charged states, etc. Increasing role in this development belongs to quantum-chemical calculations, theoretical estimations, and numerical simulations [2, 4, 5]. This approach led the creation of new methods for the synthesis of nanocomposites based on CNTs with small diameters (0.8−1.3 nm for single-walled and 5−30 nm for multiwalled CNTs) [6].

For the creation of nanocomposites, it is very important to understand the local interaction of CNTs with oxygen and oxygen-containing phases [2, 4, 7]. In particular, Bolotov et al. [7] studied high-temperature vacuum annealing of $SnO_{2-x}$/CNT composites and observed the local formation of tin oxycarbide. In addition to using the external factors of CNT activation, it is important to take into account the internal reserve of nanotubes that is related to their dimensional properties, surface curvature, and structural defects [6, 8].

In the framework of this EC project (FP7-IRSES-295260 ECONANOSORB), we have synthesized nanostructures based on zelolite (clinoptylolite type) and CNTs with small diameters for the development of toxicant sensors [4]. The data of IR spectroscopy revealed a selective interaction between CNTs and the oxide anion sublattice of clinoptylolite, which was most clearly manifested by a nonlinear dependence of the intensity of Si−O oscillations on the CNT concentration. In the present work, we have studied the interaction of small-sized CNTs with a free amorphous nanodimensional form of silicon dioxide ($SiO_2$).

In order to provide commensurability of CNTs with the interacting component, the initial materials were amorphous $SiO_2$ (AEROSIL 300 grade) with an average particle size of 7 nm (*GOST* (State Standard) 14922-77) and an array of short (~0.5 μm) CNTs with a diameter of 20−35 nm synthesized by the electric-arc method. The interaction of amorphous $SiO_2$ with CNTs was studied in a homogeneous medium by the drop technique [9] upon mixing their colloidal solutions followed by evaporation of the dispersion medium (water). The drying drop was considered to be a nanoreactor with dynamic walls [10, 11].

The colloidal mixtures of initial components were treated by ultrasound for 15 min. The sizes of particles were determined by the dynamic light scattering (DLS) method on a Nicomp 380 ZLS instrument (United States). The morphology of obtained structures was studied by scanning electron microscopy (SEM) on a JSM-6390LV microscope (LEOL, Japan). Elemental analyses were performed on a Bruker AXS Microanalysis (Germany) instrument.

The DLS measurements showed that the initial suspension of amorphous $SiO_2$ contained particles belonging predominantly to three dimensional groups:
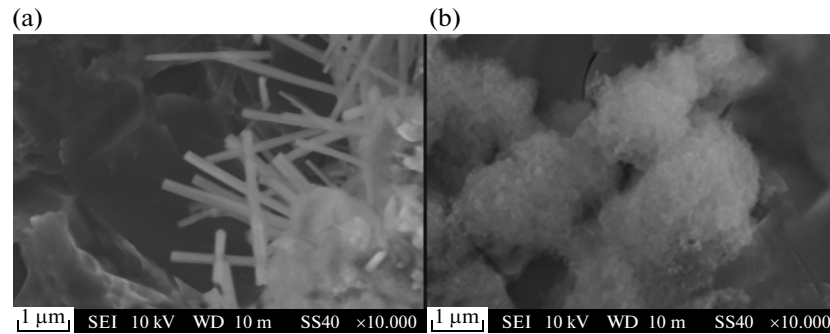
**Fig. 1.** SEM images of (a) rodlike and (b) spherical self-assembled SiO$_2$/CNT structures (magnification, ×10 000).

100−200, 2000−2500, and above 6000 nm. The addition of CNT suspension to the colloidal mixture of SiO$_2$ led to a change in the dimensions of particles in the main groups to 100−200, 500−700, and 600−1000 nm. Thus, the addition of CNTs leads to dispersion of coarse SiO$_2$ aggregates.

Upon drying of a drop of the SiO$_2$−CNT colloidal mixture, SEM measurements showed evidence of the formation of products of the two types: rodlike structures with diameters of 250−300 nm and lengths of ~4 μm (Fig. 1a) and spherical aggregates with diameters ~2 μm (Fig. 1b). These objects differ not only in their morphology, but also in the Si/O atomic ratio, which is 4 : 1 for the rodlike structures and 1 : 2 for the spherical aggregates. The results of elemental analysis are consistent with the formation of rodlike structures and spherical aggregates.

In order to explain the formation of observed structures as a result of the interaction of CNTs with amorphous SiO$_2$, we propose a phenomenological model of the active center appearing at the CNT body/cap interface. The model nanotube represents a closed armchair (5.5) single-walled CNT (SWCNT) with a length variable from 0.7 to 6.1 nm. The electron structure of CNTs and their interaction with SiO$_2$ was simulated by density functional theory in the LSDA/B3LYP approximation using a Gaussian09 program package.

It was established that effective charges at the CNT cap/body interface exhibit redistribution (see table) and rapidly converge to the values of $Q_{eff}$(cap) = −(0.041−0.037) au and $Q_{eff}$(body) = 0.035−0.038 au (au = atomic unit) for CNTs with lengths above 1.1 nm. Boundary pentagonal faces of the cap and hexagonal faces of the body are oriented perpendicularly to the CNT axis, which determines charge localization at the interface with a width of ≈3.7 Å (Fig. 2).

Numerical investigation [12] revealed selectivity of the interaction of radical groups −CH, −CH$_2$, and −CH$_3$ depending on the positions of carbon rings near the CNT cap/body interface. Let us consider peculiarities of the interaction of an amorphous SiO$_2$ fragment with CNT in the region of the charged cap/body interface. The results of our numerical simulations showed that there is an initial critical distance between carbon and silicon atoms, $r_{Si-C}^{cr} \approx 1.94$ Å, at which the formation of covalent Si−C and O−C bonds and C−Si−O−C bridges takes place. If the initial distance exceeds $r_{Si-C}^{cr}$, the calculated value is $r_{Si-C} \sim 2.54$ Å that is characteristic of van der Waals interactions. The formation of covalent bonds between silicon atoms and carbon atoms of the CNT cap is preferred to the formation of covalent Si−C bonds with carbon atoms of the CNR body.

In real experiments, a colloidal solution of CNTs comprises an array of nanotubes with various lengths, structures, and defect densities, representing an electrically active medium. Under dynamic conditions in a drying drop, including capillary flows and increasing concentrations of components, the distances between their particles are by no means constant. A close approach of a nanodimensional SiO$_2$ particle to the charged active center of a CNT leads to the local synthesis of a new oxycarbide phase, which can serve a nucleus for the subsequent structure formation involving the nanotube and surrounding nanocomponent. The formation of oxycarbide phases as a result of trans-
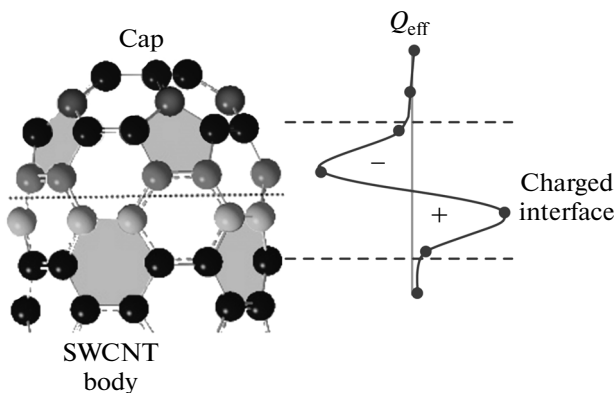


**Fig. 2.** Schematic diagram of the charged (5.5) SWCNT cap/body interface.

Charge redistribution in the (5.5) SWCNT cap/body interface

| Number of atoms in CNT | 60 | 70 | 80 | 90 | 100 | 150 | 200 | 250 |
|---|---|---|---|---|---|---|---|---|
| CNT length, nm | 0.67 | 0.80 | 0.92 | 1.04 | 1.16 | 1.77 | 2.39 | 3.00 |
| $Q_{\text{eff}}(\text{cap}) \times 10^{-2}$, a.u. | 0 | −2.6 | −2.9 | −3.8 | −3.7 | −4.0 | −3.9 | −4.1 |
| $Q_{\text{eff}}(\text{body}) \times 10^{-2}$, a.u. | 0 | 5.9 | 3.6 | 4.0 | 3.7 | 3.8 | 3.5 | 3.6 |

$Q_{\text{eff}}(\text{cap})$ and $Q_{\text{eff}}(\text{body})$ are the effective charges of carbon atoms in the CNT cap and body, respectively.

formation of the electron structure of $SnO_{2-x}$/CNT composite was convincingly demonstrated in [7].

Thus, our investigation of the interaction between colloidal solutions of CNTs and amorphous silicon dioxide in evaporating drops at room temperature showed that, at CNT lengths below 0.5 μm, spherical aggregates with an average diameter of ~2 μm and rod-like nanostructures with diameters within 250−300 nm and lengths of ~4 μm are formed under these conditions. The mechanisms of covalent and van der Waals interaction between CNTs and $SiO_2$ have been numerically studied in the framework of a phenomenological model of the active center existing at the CNT cap/body interface.

## REFERENCES

1. M. M. Shokrieh and R. Rafiee, Mech. Compos. Mater. **46** (2), 155 (2010).

2. L. S. Novikov, E. N. Voronina, and N. P. Chirskaya, Persp. Mater., No. 11, 12 (2013).

3. M. T. Byrne and Y. K. Gun'ko, Adv. Mater. **22** (15) (2010).

4. D. A. Zhukalin, A. V. Tuchin, D. G. Kulikov, A. A. Yatsenko, L. A. Bityutskaya, and A. N. Lukin, Kondens. Sredy Mezhfaz. Gran. **16**, 23 (2014).

5. K. Reich, E. Eidelman, M. L. Terranova, A. Ciorba, S. Orlanducci, V. Sessa, and M. Rossi, Adv. Sci. Lett. **3** (2), 110 (2010).

6. X. Miao, Y. Qi, X. Li, Y. Wang, X. Li, F. Tian, H. Li, F. Bian, J. Wang, and X. Li, Adv. Mater. Res. **652−645**, 15 (2013).

7. V. V. Bolotov, S. N. Nesov, P. M. Korusenko, and S. N. Povoroznyuk, Phys. Solid State **56** (9), 1899 (2014).

8. A. V. Tuchin, A. A. Ganin, D. A. Zhukalin, L. A. Bitytskaya, and E. N. Bormontov, Recent Adv. Biomed. Chem. Eng. Mater. Sci. **1**, 40 (2014).

9. Yu. Yu. Tarasevich and D. M. Pravoslavnova, Tech. Phys. **52** (2), 159 (2007).

10. B. Su, S. Wang, Y. Song, and L. Jiang, Nano Res. **4** (3), 266 2011).

11. R. Duggal, F. Hussain, and M. Pasquali, Adv. Mater. **18**, 29 (2006).

12. J. Wu and F. Hagelberg, Phys. Rev. B **81**, 155407 (2010).

*Translated by P. Pozdeev*