

## Self-assembly and Self-organization Processes of Carbon Nanotubes in the Colloidal Systems

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The features and patterns of self-organization processes in the diffusion-limited conditions (method of drops) of carbon-containing compounds and carbon nanotubes have been studied. The results of the research influence of the substrate temperature and solvent on the formation of nanoscale fractal structures in sediments of colloidal solutions are provided.

**Keywords:** Self-organization, The carbon-containing colloidal solution, Multi-walled carbon nanotubes, Fractal structures, Benzene ring.

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### 1. INTRODUCTION

Transition in nanorange is accompanied by a display of the new dimensional of physicochemical effects and phenomena, in particular, self-organization and self-assembly [1]. There is no alternative in terms of their implementation for new generations of both electronics and nanostructured materials. An important role in the processes of self-organization and self-assembly are played by the substrate temperature and solvent composition of colloidal system, whose role at fractals formation under the diffusion-limited conditions (method from the drop – wedge dehydration) has not been studied enough with the use of standard measurement techniques [2, 3], that have a significant effect on the processes themselves. Previously in a colloidal solution of carbon nanotubes, methods of atomic-force microscopy (AFM), confocal microscopy (CM) and fluorescence microscopy allowed to find out the variety and development of structural formations of the dendrite type in the form of fractals [3]. Application of Raman scattering of light (RSL), FT-IR analysis, low-voltage SEM and fluorescence microscopy and energy-dispersive analysis allowed establishing that the sedimentation of CNTs has a central-axis structure which is made up of a pinning ring, areas of stagnation and formation of fractals [4]. Also, that made it possible to develop a qualitative physical model of fractals formation in those colloidal solutions that considers compensation of Rayleigh-Benard streams and surface capillary Marangoni streams proposed in [5], and also to add data concerning volume convection. Of interests are investigations of structures formed from single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs). However, their application involves great difficulties due to natural aggregation, which is characteristic for such nano-dimensional systems [6].

The present work considers, with nano instrumental techniques, including CM with the help of AFM coordinate scanning heated up to 160 °C, with AFM, SEM, UV-spectrophotometry, FT-IR analysis, RSL effect of the substance temperature and the solvent composition on the self-organization processes and the rearrangements of structure after evaporation of drop (SAED) of colloidal solutions with CNTs.

### 2. TECHNIQUES AND INVESTIGATION RESULTS

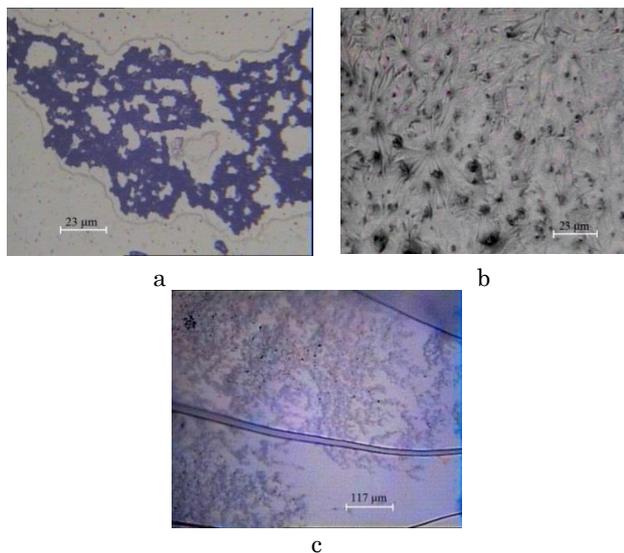
Research of MWCNTs synthesized by catalytic pyrolysis method of ethanol (95 % purity nickel nanocatalyst installation Domna) – MWCNTs I, and also obtained by the CCVD method (purity 90 %, nanocatalyst cobalt oxide, Nanocyl Belgium) MWCNTs II has revealed that the diameter of the all MWCNTs was the same  $d = 10 \div 20$  nm, however, the CCVD characterized tube has the length ( $L$ ) of up to 10  $\mu\text{m}$ , whereas  $L$  of MWCNTs I was up to 500 nm. An aspect ratio  $L/d$  for MWCNTs I and II reached  $\sim 25 \div 50$  and  $\sim 10^3$ , respectively.

SAED of both types of MWCNTs have been examined with the drop method (3  $\mu\text{l}$ ) on the coverslip, silicon single crystal and cleavage of mica depending on the concentration of CS with different solvents. Additionally, as a colloidal solution of silica –  $\text{SiO}_2$  was also used.

MWCNTs underwent purification and chemical oxidation, during which the following procedures were subsequently conducted: mixing in an USB of MWCNTs with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in ratio of 3 : 1, cooling, and addition of deionized water, filtration, washing and drying, in accordance with [7]. Mechanochemical treatment causes the dimension reductions, functionalization, prevented from agglomeration of MWCNTs. Analysis of CM images of SAED in CS of various composition with MWCNTs has revealed: benzene rings (BR), piecewise linear structures (PLS), fractal structure (FS), BR of particles, clusters.

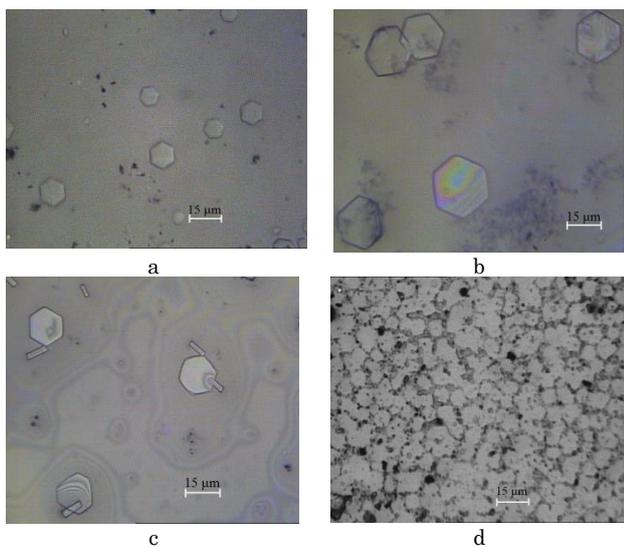
The most typical CM images (Fig. 1) are demonstrated diversity of structural forms. These results have been selected solvents, from mixture of acids, toluene, pyridine, DMFA were used. For example, the formation of FS in SAED of MWCNTs in toluene (Fig. 1a, b) occurred only at thermo activation, starting at the temperature from 313 K. It is characteristic that the length of FS branches with further heating did not changed, but they became less in thickness (Compare Fig. 1a and b). However, even at 343 K FS were destroyed, individual fragments of MWCNTs became larger in size, and the space between them was filled

with a heavily corrugated surface (Fig. 1b). In SAED of CS with MWCNTs, in distinction to [4], the central-axis symmetry was not explicitly occurred. Nevertheless, at drop evaporation the formation of the pinning ring, the stagnation region, and also the central region were always observed. Structuration, including fractal formation, took place mainly near the pinning ring, as is seen from Fig. 1a. However, when heating, the corrugation structure appeared over the whole surface of the evaporated droplet (Fig. 1b).

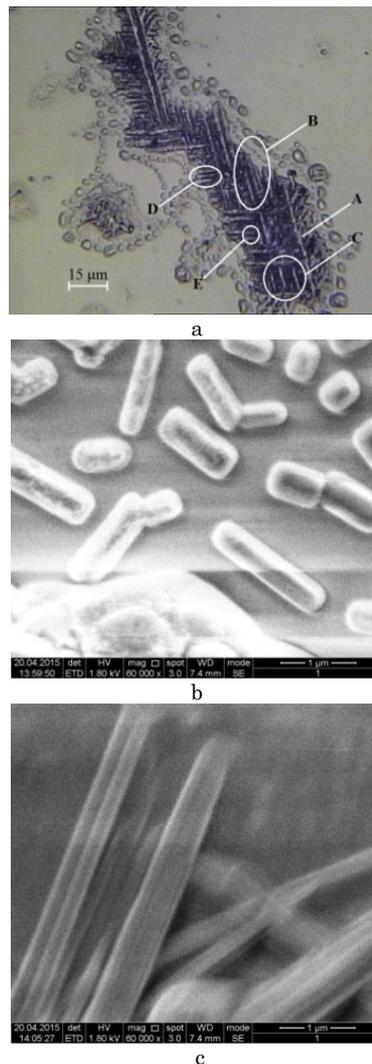


**Fig 1** – Temperature effect on the FS formation in the CS of toluene + MWCNTs: a – 313, b – 343 Kuc – CS SiO<sub>2</sub> + MWCNTs

Fractal structure was also found in composition (Fig. 1c) that presented MWCNTs in CS of SiO<sub>2</sub> with a ratio of 1 : 1 with an addition of H<sub>2</sub>O. SAED represented a crystallized film with a thickness of not more than 5 μm where MWCNTs were uniformly distributed throughout by volume. As seen from shown in Fig. 1c, in CM images of several fragments such sectors separated by cracks, within them FSs were formed through all thickness of the SiO<sub>2</sub> film. Thus, if the previously



**Fig 2** – Structuration of CS of MWCNTs + H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>: a – 4 % USD 5 min; 0.4 % with USD, b – 5 min; and also c – 55 min; d – C5H5N 1 : 1, USD 50 min



**Fig 3** – Structuration of CS of MWCNTs + H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> with 0.4 % and USD 55 min according to: a – RM, b and c – SEM

FSs formed, generally only on the substance surface [3], including the formation of 3D structures [4], here FS became abundant and distributed throughout thickness film of the silica (Fig. 1).

When MWCNTs treated with USD by the mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, in SAED the formation of either regular «benzene rings» BR (Fig. 2a) or deformed BR was found, which is illustrated in Fig. 4b. It is seen that, there are also areas in which FSs are observed. When the concentration of acids was reduced by an order of magnitude at a constant time of USD treatment (5 min), BRs became sharper and larger practically by two times (Compare Fig. 2a and b). When the time of USD treatment increased at a constant concentration, both the increase in size of BR (up to 50 %) and, beginning with 10 min of USD, the appearance of a piecewise linear structures (PLS) (Fig. 2c) was observed. This inference is in accord with the conclusions about the fracture of MWCNTs at an ultrasonic cavitation [6].

Besides that, for SAED of CS (MWCNTs + mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) with a concentration of 4 % at USD for 40 min, regions with practically mutually-

perpendicular PLSs were found (Fig. 3a). It can be assumed that the regions with similar structurization from MWCNTs are clustered congregations of rectangular structural elements (Fig. 2c). In this case, as seen from the figure, equal size elements multiples of 1/2 became ordered in parallel. This fact, as already noted, is in line with conclusions [6] about fracture of initial MWCNTs at cavitation in USD. Determined from Fig. 3a PLS from MWCNTs noted with arrows take on values:  $A \sim 48$ ,  $B \sim 24$ ,  $C \sim 12$ ,  $D \sim 6$ ,  $E \sim 3$ , really, multiples of 1/2. At AFM measurement, the part of wall of BR or PLS was up to  $7 \mu\text{m}$  in height and made up of ordered entities of about  $1 \mu\text{m}$  in length. According to SEM results, the minimal PLSs diameter reached  $250 \text{ nm}$  (Fig. 3b). These were constructed from the individual MWCNTs (Fig. 3c) combined into bundles.

In SAED of CS from pyridine, BRs from MWCNTs were also found. The formation of BR was reached after 50 min of USD treatment when the initial size of MWCNTs was dramatically reduced. In this case, BRs were constructed on the dramatically different basis, namely, made up of individual micro and nanoparticles, which is shown in Fig. 2d. As a result, in distinction from BRs in Fig. 2a-c, only hexagonal shape characteristic of BR repeated. The size of such BR was significantly dependent on the substrate material. For example, the structure in Fig. 2d was obtained at the mica substrate. Similar structures were observed at a glass substrate, whereas the sizes of structures at the single silicon were greater roughly by two times.

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## 3. DISCUSSION OF RESULTS

Discussing the results of SAED of CS with MWCNTs described in the second part, pay close attention to their considerable distinction in terms of sample dissection for studying and diversity of the observed structures, among which highlighted were BR, PLS and FS. Besides qualitative selection of solvents for CS of MWCNTs, it was established that the length of the side ( $a$ ) that forms BR is a linear function of the USD time ( $t_{\text{USD}}$ ):  $a \sim kt_{\text{USD}}$ . In doing so, the rate of growth of  $a$ , as well as the length of the component  $L$  of PLS –  $k = da, L/dt_{\text{USD}}$  increases with MWCNTs concentration in CS. At the same time, the length of the branch of FS at such variations of concentration and time of USD reduces.

Implementation of BR, PLS, and FS in SAED of CS is determined by quantities  $\sigma$  and  $\eta$ , including, with consideration for  $\sigma(T)$  and  $\eta(T)$  from the condition of minimum free energy in such a system with an external energy source at the expense of the drop evaporation.

## 4. CONCLUSION

After evaporation of a droplet colloidal solution (on the basis of  $\text{H}_2\text{SO}_4 + \text{HNO}_3$ , pyridine, toluene, dimethylformamide, or silica) of purified and functionalized multi-walled carbon nanotubes as a result of self-assembly and/or self-organization structures appear as benzene rings, piecewise linear structures, or fractals.