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SELF-ORGANIZATION OF FULLERENE C60/70 MOLECULES IN SOLUTIONS AND IN THE VOLUME OF DRYING DROP

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САМООРГАНИЗАЦИЯ МОЛЕКУЛ ФУЛЛЕРЕНА C_{60/70} В РАСТВОРАХ И В ОБЪЕМЕ ВЫСЫХАЮЩЕЙ КАПЛИ

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C_{60/70} ФУЛЛЕРЕНИ МОЛЕКУЛАЛАРИНИНГ ЭРИТМАЛАРДА ВА БУГЛАНАЁТГАН ТОМЧИЛАР ҲАЖМИДА ЎЗ-ЎЗИДАН ТАШКИЛЛАНИШИ

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Abstract. *The results of experiments on the self-organization of fullerene C_{60/70} molecules both inside a xylene solution and in the volume of a drying drop of C_{60/70} solution on a flat substrate surface are presented. The studies of C_{60/70} solution using transmission electron microscopy and UV-Vis absorption spectroscopy methods revealed the possibility of synthesis of porous fractal quasispherical clusters with a diameter of ~300÷800 nm at concentration of C_{60/70} in xylene ~2.6·10⁻⁴ mol·L⁻¹. It has been shown by scanning electron microscopy method that large nanoclusters and nanostructured coatings based on them are formed in the volume of an evaporating droplet of a colloidal solution of fullerene C_{60/70} sessile on the surface of a flat glass substrate.*

Keywords: fullerene C_{60/70}, colloidal solution, self-organization, nanostructure, fractal, semiconductor nanocoating, glass substrate.

Аннотация. *Представлены результаты экспериментов по самоорганизации молекул фуллерена C_{60/70} как внутри раствора фуллерена в ксилоле, так и в объеме высыхающей капли раствора на плоской поверхности подложки. В ксилольном растворе C_{60/70} методами просвечивающей электронной микроскопии и абсорбционной (УФ-видимой) спектроскопии была выявлена возможность синтеза пористых фрактальных квазисферических нанокластеров диаметром ~300÷800 нм при концентрации C_{60/70} ~2.6·10⁻⁴ моль·л⁻¹. Методом сканирующей электронной микроскопии показано формирование крупных нанокластеров и наноструктурированных покрытий на их основе в объеме испаряющейся капли коллоидного раствора фуллерена C_{60/70}, лежащей на поверхности плоской стеклянной подложки.*

Ключевые слова: фуллерен C_{60/70}, коллоидный раствор, самоорганизация, наноструктура, фрактал, полупроводниковое нанопокрывание, стеклянная подложка.

Аннотация. *C_{60/70} фуллерени молекулаларининг ҳам ксилолдаги эритмасида, ҳам силлиқ таглик сиртида эритманинг буғланаётган томчиси ҳажмида ўз-ўзидан ташкилланиши бўйича тажрибалар натижалари келтирилган. C_{60/70} фуллеренининг ксилолдаги эритмасида ёритувчи электрон микроскопия ва ютилиши спектроскопияси методлари*

орқали $C_{60/70}$ нинг $\sim 2,6 \cdot 10^{-4}$ моль·л⁻¹ концентрациясида $\sim 300\div 800$ нм диаметрли говак фрактал квазисферик нанокластерлари синтезланиши имконияти аниқланди. Ясси шиша таглик сиртида ётган $C_{60/70}$ фуллерени коллоид эритмасининг бузланаётган томчиси ҳажмида катта ўлчамли нанокластерлар ва улар асосида наноструктурали қопламаларнинг ҳосил бўлиши сканерловчи электрон микроскопия методи орқали аниқланди.

Таянч сўзлар: фуллерен $C_{60/70}$, коллоид эритма, ўз-ўзидан ташкилланиши, наноструктура, фрактал, яримўтказгичли нанокатлам, шиша таглик.

Introduction. The self-organization of fullerenes nanoparticles and their derivatives in single- and multi-component solvents and in their drying drops, and the features of fullerene clusters' growth and size stabilization are tasks of practical interest in modern physics of condensed matter [1-2]. Study of fullerene molecules' self-organization has great scientific importance in view of the unique ability of clusters to change the physico-chemical properties of solutions [3]. These changes depend on the forms and the sizes of the formed clusters. By this time, there are many publications devoted to the gradual transition of fullerenes from a molecular to a colloidal state in a liquid medium [4-6], but this issue still requires additional research.

The aims of the present work are to study the properties of cluster growth and the formation of a fullerene $C_{60/70}$ (mixture of C_{70} – 95 mass percent and C_{60} – 5 mass percent) in xylene solution and in the volume of a drying drop of $C_{60/70}$ solution on a flat substrate surface. The physical features and regularities that characterize the processes of self-organization of $C_{60/70}$ particles in the solvent medium and in a volume of a drying drop will be determined.

Note that our previous work was devoted to the study of the syntheses of fullerene C_{60} nanoclusters in two-component solvents (xylene/tetrahydrofuran) and in the volume of evaporating drop of solution on a substrate [7].

Samples and techniques. In the experiments crystalline powders of fullerene $C_{60/70}$, containing 95 mass percent of fullerene C_{70} (D_{5h} symmetry) and 5 mass percent of fullerene C_{60} (I_h symmetry) from SES Research (USA) were studied. Xylene of the special purity grade (>99.5%) was used as a solvent from Sigma-Aldrich (USA). The initial $C_{60/70}$ working solutions with a given concentration was prepared in a dark room by a non-equilibrium method, namely by constantly mixing the solution in a hermetically sealed glass flask on the programmable laboratory magnetic stirrer (MS-11H, WIGO, Poland) in a vibration mode with a frequency of ~ 4.0 Hz for 4 hours at room temperature ($T=24\pm 1^\circ\text{C}$). Before measurements, the solution was filtered using a ~ 0.22 μm PTFE filter to remove dust and particulate matter.

Absorption spectra of the ground state fullerene $C_{60/70}$ solutions in xylene were recorded by Shimadzu UV-2700 UV-Vis recording spectrometer (Shimadzu, Japan) in the spectral range 190-1100 nm with resolution ≤ 0.1 nm.

Dimensional characteristics and structural properties of synthesized clusters of $C_{60/70}$ in solution have been studied by using transmission electron microscopy LEO-912 AB (ZEISS, Germany) with resolution of ~ 0.2 nm. For preparing transmission electron microscopy (TEM) samples one drop (~ 20 μl) of the solution ($\sim 2.6 \cdot 10^{-4}$ mol·L⁻¹) was transferred onto TEM grid (copper grid with thin formvar film, 3.05 mm, 300 mesh) and then was ultra-rapidly frozen in fully automated Vitrification Robot FP 5350/62 with cooling rate of $\sim 10^3$ °C/s.

Morphology of the synthesized clusters of $C_{60/70}$ in a volume of a drying drop of $C_{60/70}$ molecular solution on a flat substrate surface was studied via field emission scanning electron microscope (Hitachi S-4800, Japan).

Results and discussion. Fig. 1 shows the changes in the electronic absorption spectra of the $C_{60/70}$ solutions in xylene at different stages after their preparation. The spectrum of the freshly prepared solution (Fig. 1(a)) contains three pronounced absorption bands with maxima at $\lambda_{\text{max}1} = 335.7$ nm (common absorption band for C_{60} and C_{70}), $\lambda_{\text{max}2} = 391.8$ nm and $\lambda_{\text{max}3} = 538.1$ nm (typical only for C_{70}). Together with the above-mentioned peaks, very weak absorption bands at

$\lambda_{\max 4} = 472.0$ nm (attributed to C_{70}) and at $\lambda_{\max 5} = 582.3$ nm (attributed to C_{60}) were observed. We should note that the absorption band at $\lambda_{\max 1} = 335.7$ nm is observed at relatively low concentrations of fullerene in xylene and is related to the monomolecular characteristics of C_{60} and C_{70} in solution. It should be noted that the exact value of the molar absorptivity of fullerene in xylene is $\sim 50.4 \cdot 10^3 \text{ mol}^{-1} \cdot \text{cm}^{-1}$ at a maximum of $\lambda_{\max 1} = 335.7$ nm. The absorption band $\lambda_{\max 1}$ is commonly used to identify the extinction coefficients of fullerene mixtures in different solutions, for precise definition of their monomolecular concentration in solvents, and for identification of the critical concentrations at which processes of dimerization and self-organization of fullerene molecules in solution start.

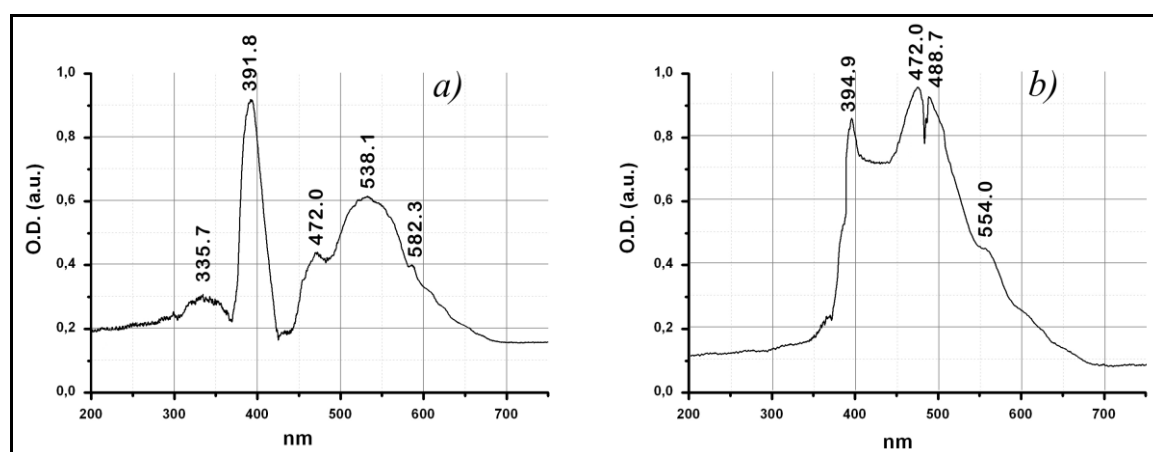


Figure 1. Optical absorption spectra of $C_{60/70}$ in xylene: (a) freshly prepared solution, (b) 40 days after preparation. The fullerene concentration in the solution is $\sim 2.6 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

The storage $C_{60/70}$ solution was provided in isothermal conditions ($T=24 \pm 1^\circ\text{C}$) in dark. After long-term storage (40 days), the UV/VIS spectra of a solution undergoes essential changes (Fig. 1(b)) as follow: (i) The absorption band at $\lambda_{\max 1} = 335.7$ nm disappears, which indicates a dramatic decrease in the monomolecular components of fullerene C_{70} and C_{60} . This effect is caused by self-organization of fullerene molecules to clusters; (ii) The absorption band at $\lambda_{\max 2} = 391.8$ nm is significantly reduced and red shifted (~ 3.1 nm), which is accompanied by an increase in longer wave bands (~ 472.0 , ~ 538.1 , ~ 582.3 nm) and a giant blue shift of the last two absorption bands (~ 538.1 and ~ 582.3 nm) by ~ 50.6 nm and ~ 28.3 nm, respectively. The results show that the absorption spectrum of the $C_{60/70}$ solution after storage for 40 days are practically indistinguishable,

which allows us to conclude that the synthesized $C_{60/70}$ fullerene clusters in solution reach stability.

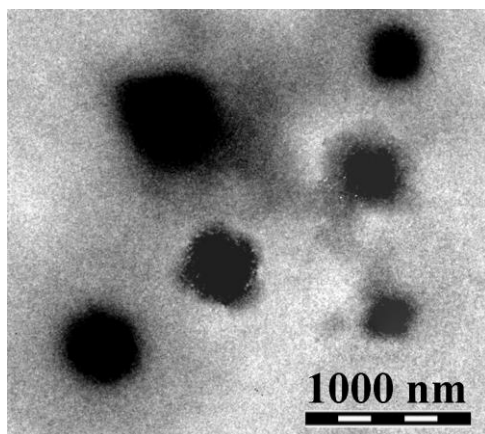


Figure 2. TEM image of ball-shaped clusters formed by fullerene $C_{60/70}$ molecules in xylene.

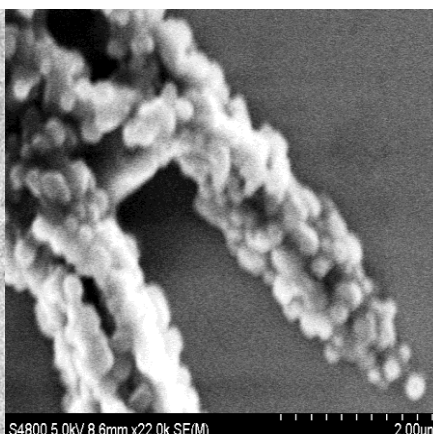


Figure 3. SEM image of $C_{60/70}$ clusters synthesized by thermal evaporation of xylene from the volume of single drop of

shown in Fig. 2, which revealed very clearly quasi-spherical shapes of C_{60/70} fullerene clusters. These spheres are poly-dispersive and have a tendency to be aggregated with each other. In a solution occur self-organization of fullerene molecules and synthesis of porous fractal clusters of quasispherical shape with the diameters ranging from ~300÷800 nm.

Fig. 3 shows a scanning electron microscopy (SEM) image of large clusters of C_{60/70} fullerene synthesized by transferring only one drop of a C_{60/70} molecular solution in xylene to the surface of a glass substrate at a temperature of ~28°C. It can be seen, that in an open dissipative system, which is an evaporating drop of C_{60/70} solution, due to the processes of thermal evaporation of the solvent, large volumetric clusters of fullerenes with a fan-shaped ($\leq 5 \mu\text{m}$) were synthesized on the surface of a glass substrate. Note that a drop of C_{60/70} solution, which locates on the surface of an optical glass substrate, is actually a microreactor. The process of self-assembly of fullerene C_{60/70} molecules in a droplet involves some time-limited evolution of the system from a certain initial state to a certain final state when droplets with particles have mobility. When droplets with particles (molecules and discrete clusters of fullerene C_{60/70}) lose mobility, they form the ensemble of new micro- and nanostructures based on particles with final morphology.

Figure 4 shows an SEM-image of a fully organic nanocoating with the dimensions $5 \times 5 \mu\text{m}^2$ and a thickness of ~800 nm obtained by transferring to the smooth surface of the optical glass only 3 (three) drops (with a total volume of $V \approx 60 \mu\text{l}$) of a colloidal fullerene C_{60/70} solution in xylene. The picture in Fig. 4 was obtained immediately after complete thermal evaporation of xylene from the volume of transferred drops of the colloidal fullerene solution. Note that, at a fixed concentration of C_{60/70} in a droplet of the working solution, an increase in the substrate temperature (up to ~30°C) led to a more accelerated nucleation and growth of crystalline nanoclusters, as well as the ordering of nanoclusters in the form of a porous nanocoating.

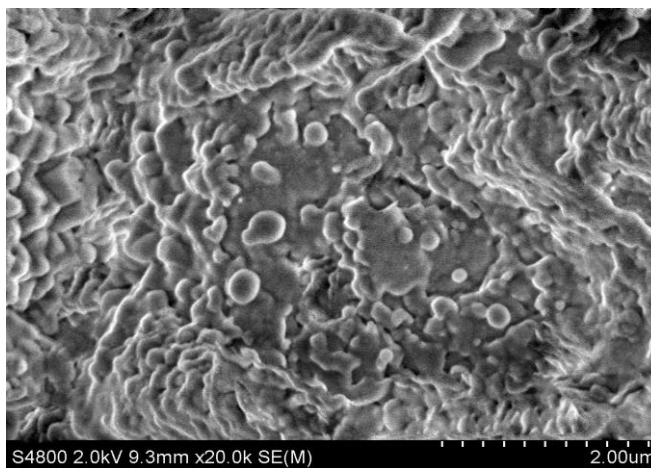


Figure 4. SEM-image of nanostructured coating consists of C_{60/70} clusters synthesized by thermal evaporation of xylene from the volume of drying drop of fullerene solution. The substrate temperature was ~30°C. The initial fullerene concentration in the solution is $\sim 2.6 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

Conclusions. Self-assembled nanostructured clusters of fullerene C_{60/70} of fractal type formed in organic solvent (xylene) were studied by high-resolution electron microscopy and UV-Vis absorption spectroscopy methods. The physical mechanisms and regularities that characterize the processes of self-organization of fullerene C_{60/70} molecules in the initial molecular solution are established.

By the absorption spectroscopy methods it has been established that if a colloidal solution (with initial concentration $\sim 2.6 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) of fullerene C_{60/70} is stored for a 40 days, then the structure of the synthesized nanosized clusters C_{60/70} remains stable. It was found that porous fractal clusters of a quasi-spherical shape with a diameter of up to ~800 nm are synthesized in this solution.

The thin nanostructured semiconductor coating which consist of only one layer of C_{60/70} fractal clusters densely arranged to each other with the dimensions $5 \times 5 \mu\text{m}^2$ and a thickness of ~800 nm were obtained.

The fundamental scientific results obtained in studying the self-organization of $C_{60/70}$ fullerene molecules in xylene, as well as the drying drop method for the synthesis of fully organic nano- and microclusters and semiconductor nanostructured coatings from $C_{60/70}$ molecules, proposed in the work can be practically used in the preparation of various thin nanocomposite materials based on various carbon molecules.

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