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SELF-AGGREGATION OF C_{60} PARTICLES IN A VOLUME OF EVAPORATING DROPLETS ON A FLAT SURFACE

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Abstract

The experimental results on the self-aggregation of fullerene C_{60} particles in a microvolume of drying droplets of a colloidal solution of fullerene on a solid substrate are presented. Using methods of scanning electron microscopy and atomic force microscopy, it was shown that in the volume of an evaporating droplet of a solution of fullerene C_{60} in xylene, deposited on the surface of a flat silicon substrate at room temperature, nanostructured and porous mC_{60} aggregates of quasispherical and elongated spherical shapes with geometrical sizes in average diameter up to $D \approx 4000$ nm are synthesized. It is established that an increase in the fullerene concentration in the initial drop of the same solution leads to an increase in the average size of the resulting fullerene aggregates. The basic physical features and regularities characterizing the processes of self-aggregation of fullerene particles in a volume of drying drop were determined.

Keywords: Fullerene C_{60} , Self-aggregation, Solvent, Sessile droplet, Evaporation, SEM.

PACS: 61.46.Bc, 81.05.Tp.

1 Introduction

Currently one of the most important conceptual issues in modern physics is the development of relatively inexpensive highly efficient selective methods for the synthesis of new nanosized particles and nanomaterials with new physicochemical properties, as well as the determination of the basic physical laws of the processes that take place. Therefore, recently, researchers' interest in the processes that occur during drying of droplets of nanoparticle solutions on a flat substrate has increased significantly [1, 2, 3, 4]. The layer obtained by this method is an excellent candidate for use the inexpensive manufacture of ultrathin film materials in modern opto- and microelectronics such as optical devices [5, 6], data storage media [7, 8], and highly sensitive sensors [9, 10].

Unlike other famed allotropic forms of carbon, C_{60} fullerene is highly soluble in the vast majority of low-polarity organic solvents (for example, benzene, toluene, tetralin, and others), but practically insoluble in polar solvents (for example, alcohols, water,

and others) [11, 12, 13]. In addition, an aqueous dispersion of fullerene C_{60} (so-called aqu/n C_{60}) can be obtained relatively easily by slowly evaporating the organic component of the solvent with the gradual addition in small quantities of distilled water into the C_{60} solution [14, 15, 16], as well as by popular method based on the functionalization of fullerene molecules such as the formation of fullerenol [17, 18]. The aqueous dispersions of C_{60} retain their structural stability for 3-4 months [19] and find the most important practical application in medicine as powerful antiviral [20, 21, 22] and anti-allergic drugs [23, 24], drugs for the fight against cancer [25, 26], as well as in substances that stimulate the immune system [27, 28], as a powerful antioxidant [29, 30], to protect the brain from alcohol [31, 32], to stimulate hair growth [33, 34], to protect the body from radiation and ultraviolet radiation [35, 36, 37], to slow down aging [38, 39] and others.

It should be noted that nanostructured materials based on fullerenes obtained by thermal evaporation of solvent from a volume of fullerene solution droplets will be expected to play a crucial role in the newest bio-chemical technologies, medicine, solar energy and other spheres of human life in the near future. However, the physical foundations and mechanisms of self-aggregation processes during the drying of droplets of nanoparticle solutions on a flat horizontal substrate are still not fully understood which complicates the transition to selective control of the processes of synthesis and production of nanomaterials.

The purpose of this work is an experimental study self-aggregation of fullerene C_{60} particles in the volume of an evaporating sessile drop of its solution, as well as to obtain nano- and micro-sized structures of fullerene C_{60} on the flat surface of a silicon substrate.

2 Experimental section

To prepare the initial solutions of fullerene (from which the studied "drop" was hereinafter taken), we used xylene (99.9 % purity, Sigma-Aldrich, USA) as the solvent of dry crystalline C_{60} powder (>99.8% pure, SES Research, USA). The C_{60} solubility at the room temperature in xylene is ~ 8.7 mg/ml. The initial fullerene working solutions of C_{60} with a given concentrations was prepared by a non-equilibrium method, namely by constantly mixing the solution in a hermetically sealed glass flask on the programmable laboratory magnetic stirrer of the brand MS-11H, WIGO (Poland) in a vibration mode with a frequency of ~ 2.5 Hz for 3 hours at room temperature ($\sim 25 \pm 1^\circ\text{C}$). Before each series of experiments, the surface of the used silicon substrate was accurately cleaned with plasma using a PDC-002 plasma cleaner device (Harrick Plasma Inc., USA). The nano- and micro-sized m C_{60} structures (where m is the number of C_{60} molecules in the aggregate) synthesized were characterized by scanning electron microscope (SEM; Hitachi S-4800, Japan), atomic force microscope (AFM; NT-MDT Solver Next, Russia), and optical binocular microscope (Motic B1-220A, Germany). The C_{60} colloidal solutions used were characterized on a Shimadzu UV-2700 spectrometer (Shimadzu, Japan).

3 Results and Analysis

Figure 1 shows the electronic absorption spectra of freshly prepared solutions of fullerene C_{60} in xylene at lower onset concentrations of C_{60} in the visible spectral region. The electronic spectrum of the C_{60} solution had four characteristic absorption peaks with positions at ~ 407 , ~ 540 , ~ 598 and ~ 625 nm. It is seen that with an increase in the concentration of C_{60} in a fresh solution, the amplitudes of the optical absorption bands in both the short-wave and long-wave parts of the spectrum increase unevenly and dependence deviates from the Bouger-Lambert-Beer law. This evidence indicates that the solution of C_{60} in xylene, which we used in the experiments on drying the droplets, is colloidal, i.e. the chemical composition and physical properties of the fullerene solution are different throughout the volume.

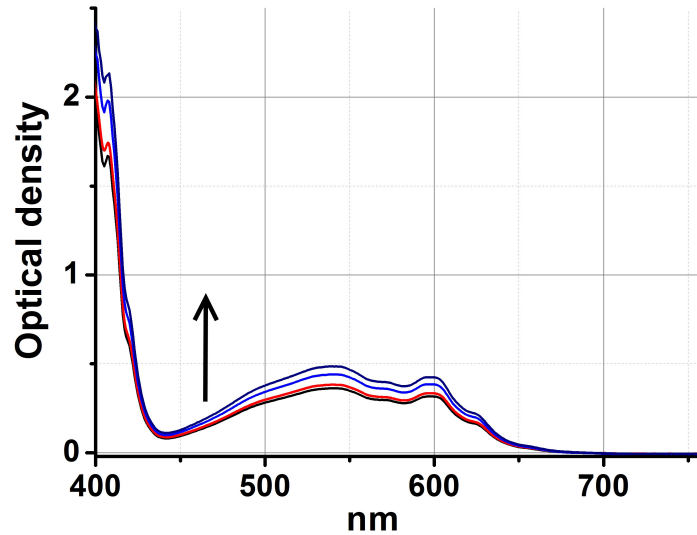


Figure 1: Electronic absorption spectra of freshly prepared solutions of fullerene C_{60} in a xylene at various initial fullerene concentrations in the direction of the arrow: ~ 0.16 , ~ 0.20 , ~ 0.24 and ~ 0.32 mg/ml .

Next, we experimentally investigated the features of the evaporation of droplets of C_{60} solutions (initial fullerene concentration ~ 0.24 mg/ml) installed on the surface of a horizontally mounted flat silicon substrate. Figure 2 shows the evolution of the formation of a concentric rings (in the sequence a-b-c-d) consisting of mC_{60} nanoaggregates on the surface of the substrate during the thermal evaporation of xylene from an isolated drop at room temperature. In this case, the base of the C_{60} droplet remains constant, the "pinning" of the contact line is implemented, and the edge angle of the droplet gradually decreases to 0 degrees. In the experiment, after the thermal evaporation of xylene from the droplet was completed, three characteristic ring-shaped structures were found on the surface of the substrate. The formation of the ring can only be explained by the self-assembly of colloidal fullerene particles during the evaporation of a solution drop and the formation of mC_{60} aggregates in

three different size ranges. In this case, due to the influence of the known Rayleigh-Benard and Marangoni effects, strong capillary flows appear both in the volume and in the surface layers of the evaporating drop of the C_{60} solution. The latter transfers particles from the volume to the periphery and simultaneously initiates the mutual approach of colloidal particles of C_{60} and the synthesis of large nano- and microaggregates mC_{60} on the substrate surface.

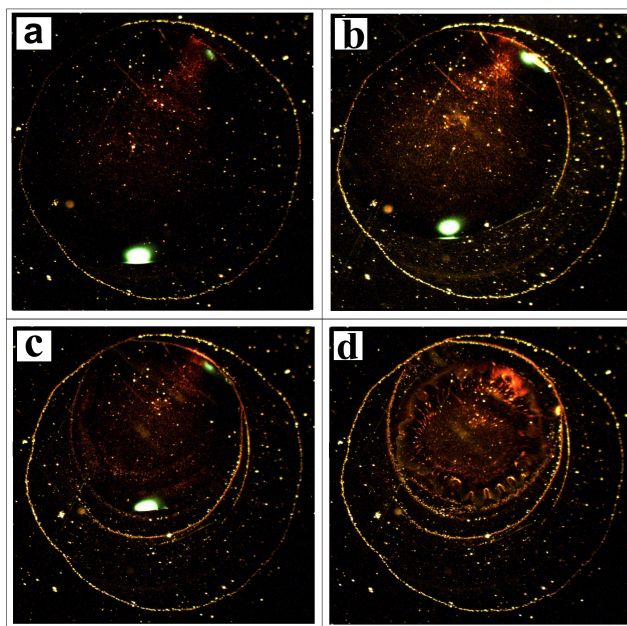


Figure 2: The evolution of distribution of fullerene C_{60} particles and formation of concentric ring consisting of mC_{60} nanoaggregates on a surface of glass substrate in process of thermal evaporation of organic solvent (xylene) at room temperature from a volume of C_{60} solution droplet with a volume of $V \approx 80$ ml. The concentration of C_{60} in the initial solution was ~ 0.24 mg/ml. The image was taken with an optical binocular microscope of the brand "Motic B1-220A" with a digital camera for continuous recording of images.

Next, we investigated the structural and morphological features of rings formed from colloidal particles of fullerene C_{60} by field emission scanning electron and atomic-force microscopies. Figure 3 shows a 2D-SEM image of a small randomly selected region inside the ring shown in Figure 2. It can be seen that after the complete evaporation of xylene from droplet of C_{60} solution on the surface of the substrate large porous mC_{60} aggregates of quasispherical and elongated spherical (i.e. ellipsoidal) shapes were aggregated (see Figure 3,a). The length of the major and minor axis of ellipsoidal mC_{60} aggregates, which chaotically oriented relative to the ring, is 1900 nm and 1250 nm, respectively (see Figure 3, b). It is easy to see that synthesized large porous nanostructured mC_{60} aggregates consist of smaller intermediate discrete C_{60} aggregates with geometrical dimensions in diameter $\sim 80 \div 220$ nm. The mechanism

of the formation of nanoscale fractal aggregates of fullerenes in the initial molecular solution of C_{60} in nonpolar organic solvents and the determination of their fractal dimension were studied in detail in [40].

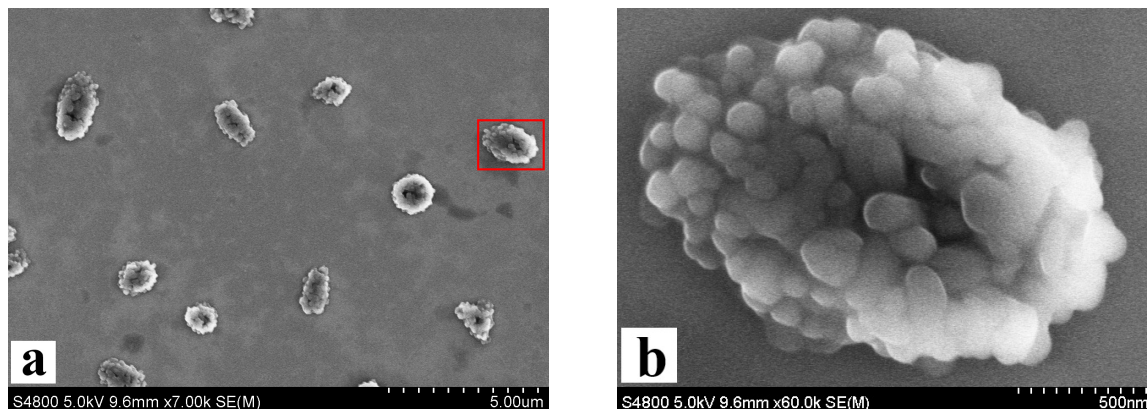


Figure 3: (a) SEM image of mC_{60} nanoaggregates synthesized inside the ring after the complete evaporation of organic solvent (xylene) from a volume droplet of solution of fullerene C_{60} on a planar surface of glass substrate and (b) magnification of the area inside the box in (a). The concentration of fullerene C_{60} in the solution was $\sim 0.24 \text{ mg/ml}$.

Figure 4 shows AFM image of mC_{60} aggregates synthesized in the process of thermal evaporation of xylene from a volume droplet of C_{60} colloidal solution. It should be particularly noted that insignificant varying the concentration of fullerene C_{60} in an initial drop did not affect the course of the process of mutual self-aggregation of fullerene particles, but led to noticeable changes in the finite geometric dimensions as well as to a dense arrangement of the synthesized mC_{60} aggregates on the substrate surface. At a higher initial concentration of C_{60} in a droplet ($\sim 0.32 \text{ mg/ml}$), after complete thermal evaporation of xylene, mC_{60} fullerene aggregates with a denser arrangement on the substrate surface are synthesized. Their geometric dimensions in diameter vary in the range of $\sim 1800 \div 4000 \text{ nm}$ and height reaches up to $\sim 300 \text{ nm}$.

Figure 5 shows the evolution of the time variation of the concentration of C_{60} particles inside an isolated evaporating droplet of a solution of fullerene in xylene deposited on the surface of a flat substrate at room temperature. The initial droplet volume at time $t = 0 \text{ min}$ is 80 microliters. It can be seen that at the initial stage of the evaporation of an organic solvent from a drop the concentration of C_{60} particles in a drop increases almost linearly, hence, mutual aggregation of the particles of the solute does not occur (stage I). Further, upon reaching the fullerene particles concentration in the droplet up to a certain critical value (C_{min}^{agg}) close to the saturation concentration of C_{60} in xylene, the so-called phase of active self-aggregation of C_{60} particles in the evaporating droplet occurs (stage II). It is at this stage of the self-aggregation of C_{60} particles that all the solute passes into a large aggregative state. Further, until the complete evaporation of xylene from the drop, continuing the process of self-aggregation of discrete nanoparticles, the final sizes of the formed mC_{60} aggregates reach the maximum possible value (stage III).

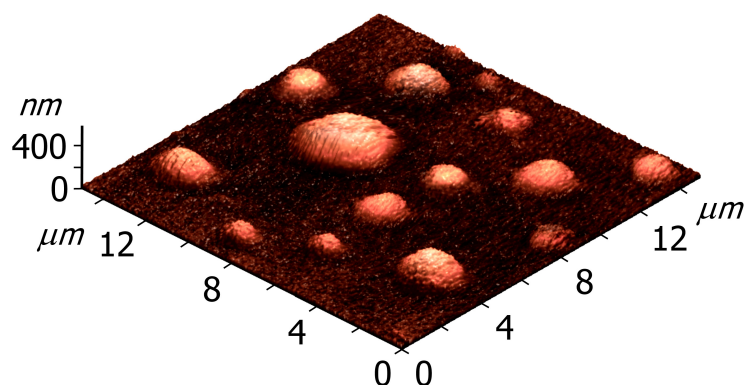


Figure 4: Three-dimensional (3-D) AFM image of a large porous nanostructured mC₆₀ aggregates synthesized in a volume of evaporating microdroplets of colloidal solution of fullerene C₆₀ on a planar surface of glass substrate in normal atmosphere. The concentration of fullerene C₆₀ in the solution was $\sim 0.32 \text{ mg/ml}$.

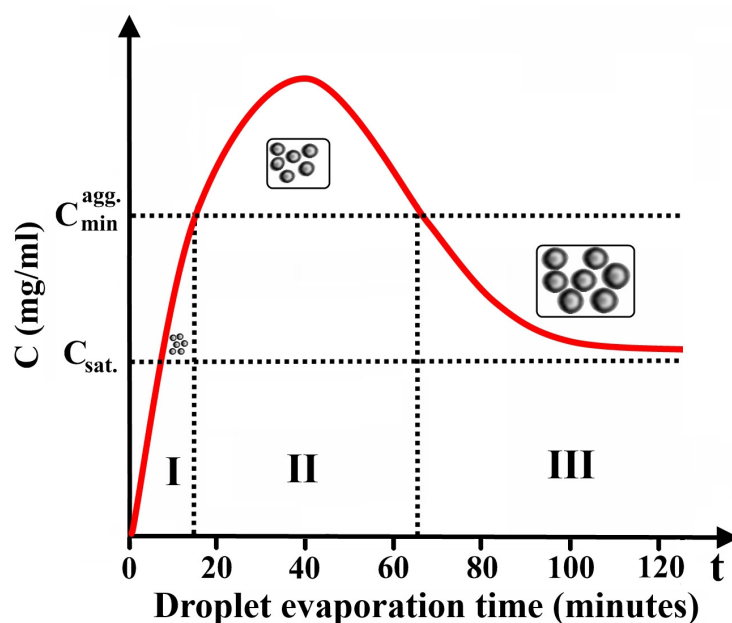


Figure 5: The scheme of self-assembly of C₆₀ particles in the volume of an evaporating drop of a fullerene solution and the formation of mC₆₀ aggregates. The initial concentration of fullerene C₆₀ in the solution was $\sim 0.36 \text{ mg/ml}$.

Thus, on the basis of the analysis of the conducted studies, the following characteristic features of a drop of mC₆₀ solution evaporating into the surrounding medium at room temperature can be distinguished: it is open, i.e. there is an exchange of energy and matter with the environment; contains an ensemble of aggregated particles; there is an initial (unordered) and final (ordered) state of the ensemble; the transition

from the initial particles state to the final colloidal state takes a finite time (~ 120 minutes) and is completely irreversible; the transition is initiated by the evaporation of the solvent (xylene), which leads to a decrease in the volume of the solution, as a result of which the capillary forces perform work on the ordering of the system and are dissipated by friction forces. Thus, the supply of energy to the solution of a droplet from the external environment occurs during the process of xylene evaporation and stops when the solvent is completely evaporated.

Thus, the obtaining experimental results by us may be practically useful for the development of new promising areas for the synthesis of bulk (3-D) nanomaterials which differ in size, shape, and morphological properties, for the needs of modern nanotechnology.

4 Conclusions

A new accelerated method for the obtaining of large nanostructured porous mC_{60} aggregates of quasispherical and elongated spherical shape from fullerene C_{60} molecules was developed and implemented. The method is based on the self-aggregation particles of C_{60} in a volume of an evaporating drop of colloidal solution of fullerene on a flat surface at room temperature. When a microdroplet of a C_{60} fullerene solution located on a horizontal substrate is evaporated, capillary flows arise both in the volume and in the near-surface layers of the evaporating drop that transfer particles of matter dissolved in droplets. At the same time, inside the droplet with decreasing volume diffusion of fullerene particles occurs, they are deposited on a substrate, and C_{60} particles interact with each other. All these processes lead to the fact that, after complete evaporation, drops of the C_{60} colloidal solution form an annular precipitate with a characteristic structure on the substrate. Herewith as a result of complete thermal evaporation of the xylene from a drop of solution of fullerene on the standard substrate surface nanostructured and porous mC_{60} aggregates of large geometrical sizes (up to ~ 4000 nm in diameter) are synthesized. In turn, mC_{60} aggregates consist of smaller intermediate discrete C_{60} aggregates with geometrical dimensions in diameter $\sim 80 \div 220$ nm. Prolonged (within three months) microscopic observations of the state of the synthesized mC_{60} aggregates allowed us to conclude that they have a high structural stability. The reported process of formation of porous nanostructured mC_{60} aggregates by the evaporation of single droplets of a nanoparticle solution seems to offer some new possibilities of producing new nano- and micro-sized functional materials/thin films for micro- and optoelectronics, solar cells, LED displays, and biochips. In addition, the proposed method can be used for evaluating the structural changes of biological fluids in biochemical probes and medical diagnostics. Further studies will focus on obtaining more complex objects and a theoretical description of the laws of self-organization processes of carbon nanoscale particles (fullerenes C_{60} and C_{70} , single-walled nanotubes) in an open dissipative system at different temperature, the study of new mechanisms of nanostructured materials' formation on a solid substrate.

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