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SELF-ORGANIZATION OF FULLERENE C_{60} MOLECULES IN VOLUME OF EVAPORATING DROPLETS

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C_{60} фуллереннинг икки компонентли эритувчилар (бензол ва ацетонитрил) аралашмасидаги эритмалари ҳона ҳароратидаги силлиқ таглик сиртида жойлашган томчисининг буғланаётган ҳажмида тартибланган наноагрегатлар ҳосил бўлишининг эффектив методи кўрсатилган. C_{60} фуллеренни наноагрегатлари синтези – нисбатан катта структуралар кичиклари ҳисобидан ўсишига асосланган Оствальд етилишининг физик-кимёвий механизмлари таклиф этилди.

Продемонстрирован эффективный метод формирования упорядоченных наноагрегатов фуллерена C_{60} в объеме испаряющихся капель фуллерена в смесях двухкомпонентных растворителей (бензола и ацетонитрила) на плоской поверхности подложки при комнатной температуре. Предложен конкретный физико-химический механизм синтеза наноагрегатов фуллерена C_{60} − оствальдовское созревание, согласно которому относительно большие структуры растут за счет меньших.

An efficient method of formation of the ordered fullerene C_{60} nanoaggregates in the volume of evaporating fullerene droplets in mixtures of two-component solvents (benzene and acetonitrile) on a flat substrate surface at room temperature is demonstrated. The specific physical-chemical mechanism of the synthesis of fullerene C_{60} aggregates in the volume of the evaporating droplet of solution, so called Ostwald ripening, according to which relatively large structures grow at the expense of smaller ones, has been proposed.

I. INTRODUCTION

Currently, nanoparticles and nanomaterials, in particular, nanoagregates of fullerenes C_{60} and C_{70}, are expected to play a crucial role in the newest bio and chemical technologies [1-2], modern medicine [3], solar energy [4] and other branches of science and technology [5-8] in the near future. Unlike other well-known allotropic forms of carbon (diamond, carbyne, graphite, ...), fullerene C_{60} is well soluble in most low-polar organic solvents (for example, benzene, toluene, carbon disulfide, tetralin, etc.), but practically not soluble in polar solvents like alcohols [9]. In addition, an aqueous dispersion of fullerene C_{60} can be relatively easily obtained by slow evaporation of the organic component of the solvent with the gradual addition of distilled water in small amounts to a solution of C_{60} [10]. Fullerene C_{60} has high lipophilicity [11], and is a nontoxic substance [12], having powerful antioxidant properties due to its high activity as free radicals acceptor [13].

At the same time, there are new experimental data [14-16] which reveal that C_{60} molecules have tendency to self-assembling and formation of large negatively charged $(C_{60})_m$ aggregates (where m is a number of fullerene molecules in aggregate) of different shapes and sizes in a wide range of mono- and multi-component organic and inorganic solvents. Aggregation of fullerene molecules in solutions may cause significant changes

in their chemical and physical properties and result in a dramatic change in their medical and biological, technical and other applications. One of the most important tasks of modern nanotechnologies is the development of relatively inexpensive highly efficient selective methods for the synthesis of new nanoscale structures and nanomaterials with new physical properties, as well as the generation of various functional devices based on them.

In this work, the self-organization of fullerene C_{60} molecules in the volume of evaporating droplets of fullerene solutions in mixtures of benzene and acetonitrile on the flat surface of a mica at room temperature have been experimentally investigated for the first time.

II. EXPERIMENTAL DETAILS

To prepare the initial molecular solution of C_{60}, from which the investigated droplet were subsequently selected, we used crystalline powders of high purity fullerite C_{60} (>99.8%, SES Research, USA) and the organic solvents benzene (C_6H_6, Sigma-Aldrich) and acetonitrile (C_2H_3N, Sigma-Aldrich). Weighing of the dry crystalline powder C_{60} was carried out using electronic scales EP 214C (Ohaus Explorer Pro, Switzerland) with ~0.1 mg readability.

To prepare the molecular solutions of fullerene of necessary concentration, powders of C_{60} were dissolved in mixtures two-component solvents benzene and acetonitrile with volume proportions 0.9:0.1 respectively and kept at room temperature (~ 25°C) in test tubes for 36 hours without external mechanical influences. It can be noted that within 36 hours in the initial fullerene solution, self-aggregation of C_{60} molecules and synthesis of $(C_{60})_m$ nanoaggregates was not detected.

We have used the atomic force microscope (AFM) Solver Next (NT-MDT, Russia) with atomic resolution to determine morphological features and dimensional characteristics of $(C_{60})_m$ aggregates synthesized in volume of evaporating droplets of fullerene C_{60} on the mica surface. For establishing a final distribution of particles of the solid phase on the surface of mica deposited from a drop of the C_{60} solution we have used optical binocular microscope Motic B1-220A (Speed Fair Co., Ltd., Canada) with 1000×magnification and with a digital camera for continuous image recording.

III. RESULTS AND DISCUSSIONS

Phenomena in evaporating liquid droplets of nanoscale particles are very perspective for use in modern technology, such as in medical diagnostics, cosmetics, inkjet printing, coating, deposition of materials, agriculture, food industry, or spills of liquids. In the course of experimental studies of the evaporation of droplets deposited on the flat surface of horizontally mounted mica and contained both pure organic solvents and C_{60} fullerene solutions in mixtures of two-component organic solvents, we found the following main regularities of droplet behavior:

– drops taken from pure organic solvents (benzene, toluene, acetonitrile, tetrahydrofuran, carbon disulfide, ...) or their mixtures in any volume proportions retained the value of the edge angle α throughout the thermal evaporation, but gradual narrowing the area of the "drop-substrate" contact was observed, up to the complete disappearance of the drop itself;

– if the drop contained molecular or nanosized particles (for example, fullerene $(C_{60})_m$ nanoaggregates), then after the solvent evaporates from the droplet, the droplet base area remains constant and the "pinning" mode of the contact line is realized - the edge angle of the droplet gradually decreases up to $\alpha \approx 0°$. In this case, due to the influence of the known Rayleigh-Benard and Marangoni effects both in the volume and in the near-surface layers of the evaporating drop of the C_{60} solution (Fig. 1*b*), strong capillary flows arise (so-called Rayleigh-Benard flows and Marangoni flows). The latter directly initiates the mutual approach of C_{60} molecules and the synthesis of $(C_{60})_m$ aggregates according to the scheme $C_{60}+C_{60}+ ...+C_{60} \rightarrow (C_{60})_m$. The above regularity of the behavior of a droplet of the C_{60} solution on the surface of the substrate (mica) is maintained throughout the evaporation of the organic solvent.

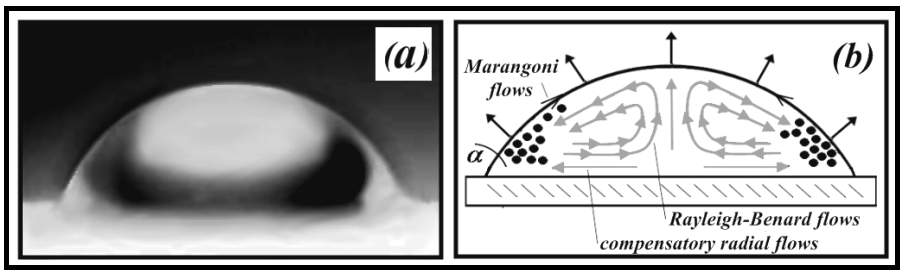


Fig. 1. A photograph of a drop of fullerene C_{60} solution with the base diameter $d \approx 10$ mm lying on the surface of a mica (*a*) and a schematic illustration of the appearing flows inside the evaporating droplet (*b*), leading to the self-organization of C_{60} fullerene molecules. The arrows inside the drop and above the drop indicate the directions of the Rayleigh-Benard flows and the evaporation of the solvent, respectively. The arrows on the "drop-air" interface line indicate the directions of the Marangoni flows.

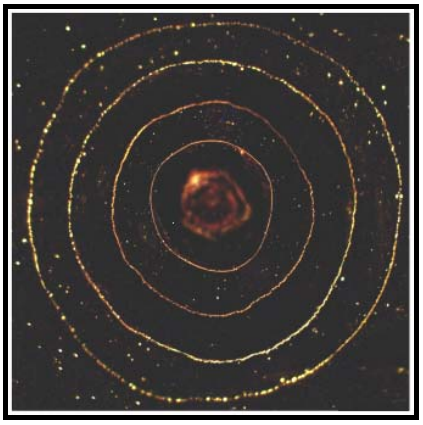


Fig. 2. The final distribution of particles of the solid phase deposited on the surface of mica from a drop of the C_{60} fullerene solution in a mixture of benzene and acetonitrile in volume proportion of 0.9:0.1, after complete thermal evaporation of the solvents at room temperature. The initial concentration of C_{60} in the drop is ~0.36 mg/ml, the drop radius is $R \approx 3.0$ mm, the height of the drop is $h \approx 1.9$ mm.

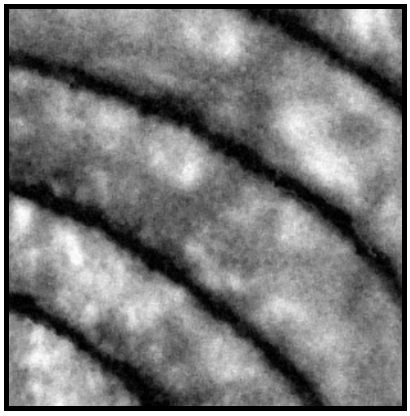


Fig. 3. An enlarged optical micrograph of the peripheral part of the final distribution of fullerene nano-aggregates $(C_{60})_m$ synthesized in the volume of evaporating droplets of fullerene solutions in mixtures of benzene and acetonitrile on the mica surface.

As the mixtures of organic solvents (benzene and acetonitrile) evaporated from the droplet of C_{60} solution sitting on the surface of a mica, self-organization of the C_{60} molecules occurred and the characteristic rings (see Fig. 2) containing nanoaggregates of fullerene $(C_{60})_m$ in four different dimensional ranges gradually formed.

Self-organization is a collective process in which the whole ensemble of C_{60} fullerene nanoparticles participates. It is not difficult to see that the C_{60} molecules, which didn't participate in the synthesis of initial $(C_{60})_m$ nanoaggregates, as the droplets evaporated, moved further along the surface of mica together with the organic solvents, and eventually accumulated in the central part of the "dried drop" as a solid "circular" disk.

Figure 3 shows an image of the peripheral part of the final distribution of $(C_{60})_m$ nanoaggregates synthesized on the mica surface. The fact that the molecular solution of C_{60} used in the drop experiments was initially homogeneous (that is, the chemical composition and physical properties of the solution throughout the volume were identical). In this case a probable factor capable of initiating the transport of particles in the droplet volume (the effect, similar to the Marangoni and Rayleigh flows) and lead to the synthesis of $(C_{60})_m$ nanoaggregates, in our opinion is the presence of a significant temperature gradient (up to 5°C) between volume and near-surface layers of an evaporating drop of a C_{60} solution. The appearance of the above-mentioned temperature gradient in the droplet volume is probably associated with a sharp cooling of its surface and near-surface layers as a result of intensive evaporation of the organic solvents (benzene and acetonitrile) into the environment.

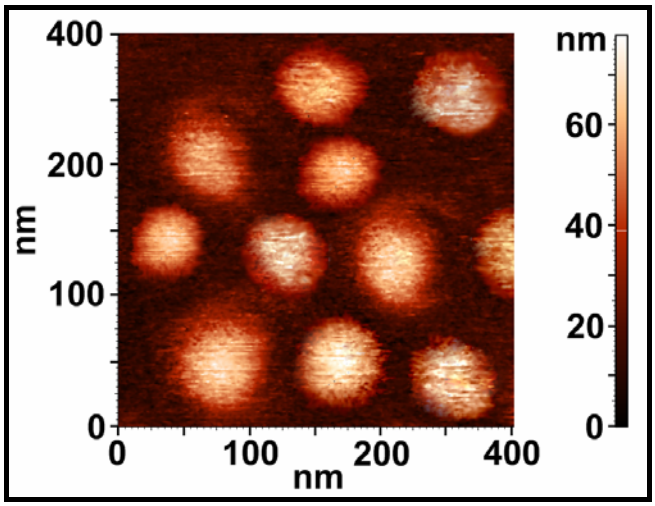


Fig. 4. Atomic force microscope image of a monomolecular close-packed $(C_{60})_m$ nanoaggregates synthesized on the mica surface at a room temperature. Concentration of fullerene C_{60} in initial equilibrium solution was ~0.9 mg/ml.

Figure 4 shows the high-resolution image obtained by the atomic force microscopy of $(C_{60})_m$ nanoaggregates synthesized in the volume of evaporating droplets of fullerene solutions in mixtures of benzene and acetonitrile on the mica surface. Drying droplets of fullerene C_{60} on a surface of a substrate can exhibit complex transitory structures during the process of evaporation of a solvent. The evaporation of solvents can drive the creation

of nanoaggregates $(C_{60})_m$ of various morphologies and sizes as well as the formation of nanoaggregate monolayers on a flat substrate (mica) surface. In this case, a substrate can dramatically influence the process of self-aggregation of molecules C_{60}, which during evaporation of the solvent, migration of molecules C_{60} on the substrate usually continues and induces further self-assembly processes. It can be noted that by controlling the concentration of nanoparticles, one can control the size of the synthesized nanoaggregates, which can reach hundreds of nanometers.

IV. THE PROBABLE MECHANISM FOR THE FORMATION OF $(C_{60})_m$ NANOAGGREGATES ON THE SUBSTRATE SURFACE

When organic solvent in a colloidal droplet evaporates, the fullerene concentration increases. That changes the physical and chemical properties of the droplet and affects on the droplet formation. Individual C_{60} molecules, as well as dimers $2C_{60}$ and trimers $3C_{60}$, arising in the volume of a drop to maintain equilibrium in the system, will be deposited on the surface of larger particles. At the same time, smaller fullerene clusters will have to dissolve further to compensate the substance that has left the solution. As a result of this self-organization of the fullerene molecules in the volume of the evaporating solution droplet takes place, larger aggregates (for example, $(C_{60})_m$, where $m>n$) grow due to both the Coulomb and Van der Waals attraction of smaller nanoparticles. Thus, continuous diffusion transfer of C_{60} molecules from smaller $(C_{60})_n$ clusters to larger aggregates of $(C_{60})_m$ occurs inside the evaporating drop of C_{60} fullerene solution in the binary mixtures of toluene with tetrahydrofuran. This phenomenon is well known under the general name "Ostwald ripening".

Based on the analysis of the results obtained, the following characteristic features of the evaporating droplet of C_{60} solution can be identified:

– it is an open dissipative system, that is, energy and matter are exchanged with the environment;

– this is an ensemble of aggregated particles, there is an initial (unordered) and final (ordered) state of the ensemble. The transition from the initial molecular state of C_{60} to the final cluster $(C_{60})_m$ takes a finite time, depending both on the volume of the initial drop and the type of solvent used, and on the initial temperature of the drop;

– the self-organization processes of the C_{60} nanoparticles according to the $C_{60}+C_{60}+\cdots+C_{60} \rightarrow (C_{60})_m$ scheme is irreversible: the transition from the initial molecular state of C_{60} to the final aggregate nC_{60} is initiated by the evaporation of the solvent. So the energy supply to the drop of the C_{60} solution from the external medium occurs during the evaporation of the solvent and terminates by the completion of evaporation of the solvent.

The obtained scientific results made it possible to reveal both the basic regularities of an organic solvent evaporation from a drop of a C_{60} fullerene solution and the working mode of synthesis of thin 2-D films from $(C_{60})_m$ nanoaggregates on a flat surface of a substrate.

V. CONCLUSIONS

A new accelerated method for the synthesis of $(C_{60})_m$ aggregates of a spherical shape from fullerene C_{60} molecules has been developed and implemented. The method is based on the self-aggregation of C_{60} molecules in the volume of the evaporating drop of the fullerene solution at room temperature. The proposed method can also be used for the

synthesis of thin (≤100 nm) two-dimensional (2-D) films based on C_{60} molecules on the mica surface for the needs of high-efficiency solar energy.

It has been established that the most likely motive force for the self-aggregation of C_{60} molecules in an evaporating droplet volume of solution due to the thermal action is the presence of strong temperature gradients both in the volume and in the near-surface layers of the evaporating drop.

The physical mechanism of self-aggregation of C_{60} molecules and formation of large $(C_{60})_m$ nanoaggregates, so-called Ostwald ripening, according to which relatively large structures grow at the expense of smaller ones, has been proposed. The most important factor determining the ordering of fullerene molecules and the formation of $(C_{60})_m$ nanoaggregates in the volume of evaporating droplets is the velocity on the contact line along the substrate, depending on the type of organic solvent used in the preparation of the initial C_{60} solution.

On the basis of the proposed method, a thin semiconductor fullerene C_{60} film with a thickness of ~100 nm was obtained, which can be used as a photoactive layer for solar cells and photodetectors.

Prolonged (for six months) microscopic observations of self-aggregation processes of fullerene C_{60} in the experiments have allowed one to establish that synthesized thin films of $(C_{60})_m$ nanoaggregates are stable to external mechanical and thermal influences.

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