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Experimental Investigation on the Synthesis of Nanostructures Based on Fullerene C_{70} and Their Stability

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Abstract

Nanostructures based on fullerene C_{70} are of great interest due to their wide application in modern branches of science and technology. In this work, a method for synthesizing nanostructures of various dimensions (nanoaggregates and nanowhiskers) of fullerene C_{70}, based on the self-organization of C_{70} molecules during the evaporation of droplets of a solution of fullerene in ethylbenzene on the substrate surface, is proposed and implemented for the first time. It has been established that the onset of C_{70} nanowhisker synthesis during evaporation of C_{70} solution droplets on the substrate surface depends on the substrate temperature. Experimental evidence is presented that an increase in both the C_{70} concentration in the solution and the substrate temperature leads to an increase in the geometric dimensions of C_{70} nanowhiskers. The stability of the resulting nanostructures to high temperatures has been determined. The results obtained provide the necessary information on the role of solution concentration and substrate temperature in the synthesis of one-dimensional nanomaterials.

Keywords: Fullerene C_{70}; Solution Droplet; Self-Organization; Nanostructure; Nanowhisker; Stability

Introduction

Fullerenes continue to hold significant potential as nanoscale raw materials for molecular engineering, novel materials, and supramolecular chemistry [1]. This potential is attributed to their high symmetry, novel π-conjugated systems, and unique chemical and physical properties. Consequently, supramolecular nanostructures based on fullerenes, such as nanowhiskers [2], nanotubes [3-5], nanorods [6], nanowires [7], and nanolayers [8], are of particular interest.

In modern science, nanowhiskers are defined as thread-like crystals with a cross-section of up to 100 nm and a length significantly exceeding the cross-section [9]. Currently, metallic, inorganic, and carbon nanowhiskers are of particular interest; they can be obtained naturally or through synthetic methods. Nanowhisker synthesis is achieved using various techniques, including molecular beam epitaxy, vapor deposition, laser ablation, magnetron deposition, and chemical epitaxy in high vacuum, among others [10,11]. Nanowhiskers exhibit several times greater strength than conventional crystals, along with high conductivity, flexibility, water-repellent properties, and corrosion resistance [12]. Semiconductor nanowhiskers are widely employed in the development of device elements across fields such as microelectronics, optoelectronics, nanoengineering, solar energy, biomedicine, nanoelectromechanics, and gas sensors [13-16].

Light fullerenes (C_{60}/C_{70}) are hollow, spherical or ellipsoidal carbon molecules with diameters of less than 1 nm, composed of sp2 carbon atoms arranged in truncated icosahedral structures. A notable property of fullerene molecules is their ability to self-assemble in pure solvents over time, leading to the formation of nanoclusters with various shapes and sizes [17]. The solvent's nature plays a crucial role in this self-assembly process. The molecular self-assembly, reactivity, and electron-acceptor characteristics of fullerenes offer unparalleled advantages in applications such as electrocatalysts and supercapacitors [18]. Furthermore, fullerenes possess high photosensitivity, electron mobility, antioxidant activity, and radical scavenging capabilities [19]. These properties make them highly attractive for a wide range of applications, including photodetectors, sensors, solar cells, LEDs, biomedicine, and drug delivery systems [20-22].

Since the discovery of C_{60} fullerene nanowhiskers (C_{60}NWs) by Miyazawa KI, et al. [23], these structures have found applications across various fields. The synthesis method involves adding a poor solvent to a saturated solution of C_{60}, which leads to the formation of a liquid-liquid interface. This results in a supersaturated solution where C_{60} crystal nuclei form at the interface, leading to the synthesis of elongated C_{60}NWs. Although this method was initially "static" (without external influence), later developments introduced "dynamic" approaches (such as ultrasound and manual mixing) and other modified techniques [24]. Similarly, C_{70} fullerene nanowhiskers (C_{70}NWs) were synthesized using the same methods based on C_{70} fullerenes [25].

The formation of nanowhiskers from nanoscale fullerenes relies on bottom-up technology, where precise regulation and control of NWs size and structure are crucial. Notably, when fullerene NWs synthesized in solution are transferred to a solid substrate, their morphology undergoes significant changes [26]. This change is caused by the self-assembly of fullerene nanoparticles during the evaporation of drops of a colloidal solution (containing nanostructures) of fullerene on the substrate surface. In our opinion, if one-dimensional nanostructures are synthesized using molecular solutions of fullerene on the surface of a solid substrate, it is possible to control their morphology. In addition, the stability of fullerene nanostructures synthesized on the substrate surface is considered very important and is currently poorly studied. Therefore, it is very important to study the processes that occur during the evaporation of fullerene molecular solution droplets on the surface of a solid substrate, control the size and morphology of synthesized nanostructures, as well as their stability.

In this work, scientific results on the synthesis of C_{70} fullerene nanostructures (nanoaggregates and nanowhiskers) on the substrate surface by evaporation of a microdroplet of C_{70} molecular solution and their structural stability characteristics are described.

Materials and Methods

In the experiments, fullerene C_{70} powders with high purity of ~99.8% (Sigma-Aldrich, USA) were used, and dichlorobenzene ($C_6H_4C_{12}$, Sigma-Aldrich) was used as an organic solvent. The solubility of C_{70} powders in dichlorobenzene at room temperature is approximately 18.5 mg/mL. The mixture of dichlorobenzene and C_{70} powders, contained within a hermetically sealed glass vessel, was subjected to continuous mechanical stirring for 1 hour at a frequency of approximately 2.0 Hz, using a MS-11H programmed laboratory magnetic stirrer (WIGO, Poland). The magnetic stirrer is used for mixing low-viscosity liquid (dichlorobenzene) and soluble substances (C_{70}) at different frequencies (0÷40 Hz) at the room temperature. Subsequently, the C_{70} solution was sonicated for 20 minutes using a DC-120H ultrasonic bath. The DC-120H ultrasonic bath is made of stainless steel with wire basket and lid. Its temperature range is from Ambient to 70°C, it can affect the solution at 40 KHz frequency.

A thermostatically controlled table with an accuracy of ±1°C was employed for heat treatment experiments utilizing the Peltier effect. The temperature of the glass substrate was monitored with an accuracy of ±2% using a thermocouple connected to an MS8217 digital multimeter.

Droplets of C_{70} solution were applied to the substrate surfaces using a VITLAB pipette dispenser (VITLAB GmbH, Germany) under controlled laboratory conditions. The solution and ambient temperature were approximately ~23±1°C, and the droplets were protected from convective air currents until complete evaporation.

In the experiments, a "Motic B1-220A" optical binocular microscope with a digital camera was used to record continuous images of dispersed phase rings. The maximum possible magnification in the Motic B1-220A microscope is 1000x.

We employed a JSM-IT200 high-resolution scanning electron microscope (JEOL, Tokyo, Japan) to investigate the morphological features and accurately measure the geometrical dimensions of one-dimensional C_{70} nanowhiskers (C_{70}NWs) and nanoaggregates. In the electron microscope, control functions such as switching the cathode to the operating mode, focusing the image, eliminating astigmatism, adjusting brightness and contrast are automated. The JSM-IT200 microscope implements the mode of studying samples even under controlled low vacuum conditions. The pressure in the sample chamber studied under the microscope can vary from 10 to 100 Pa.

Experimental Results and Their Discussion

The shape of a droplet of fullerene solution with a volume of V ≈ 40÷50 µL on a flat surface resembles the shape of a segment of a sphere. It is noteworthy that the base area of the droplet remains constant throughout the thermal evaporation process. However, the contact angle (α) of the droplet gradually decreases until it reaches zero degrees. This behavior is attributed to strong capillary flows induced by the Marangoni effect along the droplet-air interface and the Rayleigh-Bénard effect within the evaporating droplet volume (Figure 1). These effects lead to significant capillary flows, facilitating the assembly of fullerene nanoparticles and the subsequent synthesis of various nanostructures.

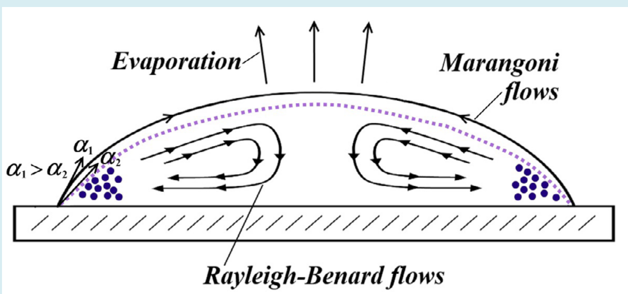

Figure 1: A Schematic Illustration of the Currents Occurring Inside the Evaporating Droplet of C_{70} Solution.

Figure 2 shows an SEM image of the structures formed by the evaporation of droplets of C_{70} solution in dichlorobenzene at room temperature (~24 ± 1°C) on a base surface. Due to the constant base area of the microdroplet, the residue left after complete solvent evaporation resembles a coffee ring, indicating a trace of nanostructures. The temperature gradient, resulting from the rapid cooling of the surface and near-surface layers of the droplet, plays a crucial role in this process. Upon complete solvent evaporation, ellipsoidal C_{70} aggregates were observed on the substrate surface (Figure 2). The average polar and equatorial diameters of these C_{70} aggregates were ~1500 nm and ~900 nm, respectively. The resulting C_{70} aggregates are porous and consist of discrete intermediate nanoaggregates with an average diameter of ~50÷60 nm.

Figure 3 presents an SEM image of C_{70} nanoaggregates synthesized at ~24±1°C after heating to ~185°C on the substrate surface. The image reveals that the overall appearance and dimensions of the nanoaggregates, which exhibit a porous and fractal structure, were maintained during the synthesis. However, several porous cracks were observed in the nanoaggregates, which we attribute to the complete evaporation of solvent molecules throughout the volume of the nanoaggregates at this elevated temperature.

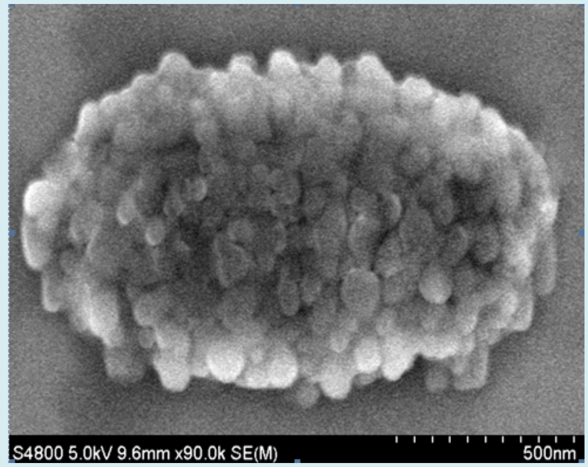

Figure 2: SEM Image of C_{70} Aggregates Formed from the Evaporation of an Organic Solvent in a Microdropleto C_{70} Solution at Room Temperature (~24 ± 1°C).

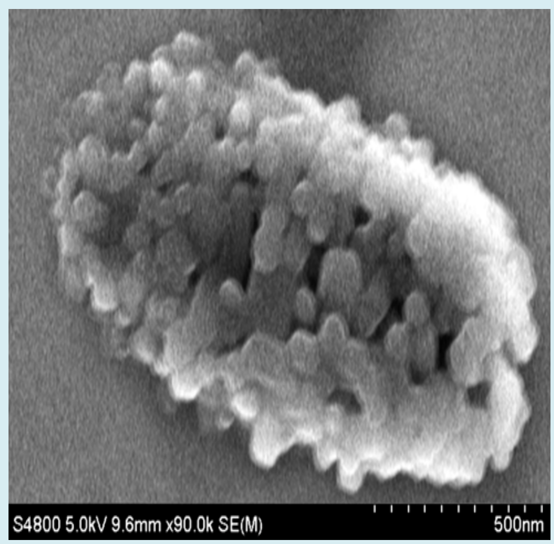

Figure 3: SEM Image of C_{70} Nanoaggregates after Heating to ~185°C on the Substrate Surface.

To synthesize one-dimensional C_{70} structures, the evaporation process of a C_{70} solution droplet on a substrate was conducted at various temperatures. When the solid substrate was heated to ~32°C, nanostructured filaments (whiskers) of C_{70} fullerene with an optimal shape were synthesized on the substrate surface (Figure 4). The concentration of C_{70} fullerene in the initial droplet of the solution was ~5.6 mg/mL. At 32°C, the intense solvent evaporation from the microdroplet creates a temperature gradient that helps overcome certain energy barriers in the formation of C_{70} nanowires (C_{70}NWs). In this case, the average geometric dimensions of the C_{70}NWs were ~1.5 μm in width and ~9 μm in length.

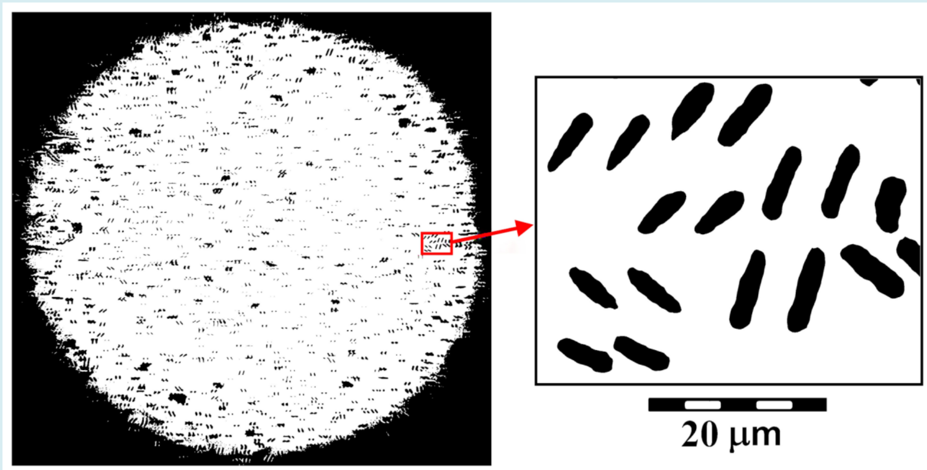

Figure 4: Optical Microscopic Image of One-Dimensional Structures Synthesized from the Evaporation of a C_{70} Molecular Solution in Dichlorobenzene (with a Fullerene C_{70} Concentration of ~5.6 Mg/Ml) on the Substrate Surface.

Figure 5 shows an SEM image of C_{70} nanowires (C_{70}NWs) synthesized on a horizontally oriented substrate heated to 36°C. The initial concentration of C_{70} in the droplet was ~2.5 mg/mL. During the evaporation of the droplet, strong capillary currents in both the volume and surface layers of the droplet initiate the self-assembly of fullerene particles and the synthesis of C_{70} filaments. The C_{70}NWs depicted in Figure 5 have a molecularly flat surface. The average geometric dimensions of these NWs were ~1.75 μm in length and ~100 nm in width. These results indicate that the size of the C_{70} nanowhiskers can be adjusted by varying the initial concentration of fullerene in the solution.

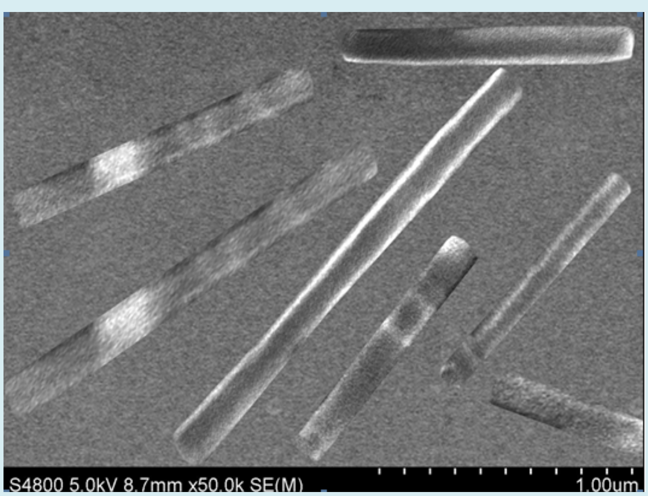

Figure 5: SEM Image of Nanowhiskers Synthesized from the Evaporation of a C_{70} Molecular Solution Droplet on the Base Surface at T≈36°C.

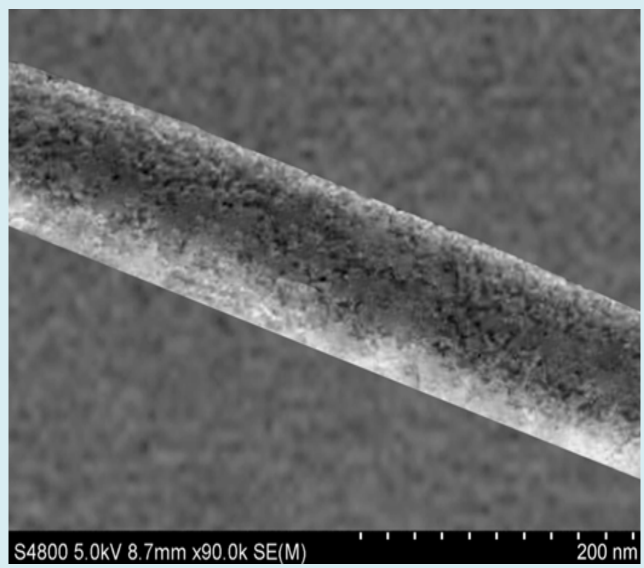

Figure 6: SEM Image of C_{70} Nanowhiskers Synthesized at T≈36°C, Following Heating to ~185°C on the Substrate Surface.

Figure 6 presents an SEM image of C_{70} nanowhiskers synthesized at ~36°C on the base surface, followed by heating to ~185°C. The image shows that, at this temperature, the overall appearance and dimensions of the C_{70} nanowhiskers were preserved, although small nanocraters were observed on their surface. This indicates that the C_{70} nanowhiskers are sufficiently resistant and stable as one-dimensional structures at elevated temperatures.

The experiments revealed that the geometric dimensions of the formed C_{70} nanowhiskers (C_{70}NWs) can be controlled by varying both the substrate temperature and the concentration of fullerene. Specifically, an increase in substrate temperature accelerates the formation and growth of crystalline nanowhiskers, while also significantly enlarging their geometric dimensions. Table 1 presents the experimental results, illustrating the changes in the geometric dimensions of the synthesized C_{70}NWs. It is easy to see from the table that by increasing the concentration of C_{70} by 1.2 times, the average length of the synthesized C_{70}NS can be increased to 1.45 times, and the average diameter to 1.12 times.

C/(mg/ mL)[a]	T/(°C)[b]	Average length (µm)	Average width (nm)
2.5	32	1.25	85
	36	1.75	100
	40	2.1	118
3	32	1.48	94
	36	1.9	122
	40	3.05	133

[a]*Concentration of C_{70} in solution.* [b]*The substrate temperature (T) is maintained constant until the droplet is completely evaporated.*

Table 1: Variation in the Average Size of Synthesized C_{70} Nanowhiskers (C_{70}nws) as a Function of Substrate Temperature and C_{70} Concentration.

Conclusion

For the first time, as a result of self-organization of C_{70} fullerene molecules in the volume of evaporation of solution droplets, synthesis of nanostructures of different dimensions (nanoaggregates and nanowhiskers) was carried out. Synthesis of C_{70} fullerene-based nanostructures using droplet evaporation on the substrate surface is a cost-effective and versatile method. By changing the initial fullerene concentration and substrate temperature, it is possible to adjust the morphology of C_{70} nanostructures according to desired values, which is one of the main scientific novelties of the research. Electron microscopic measurements confirmed that ellipsoidal nanoaggregates were synthesized during droplet evaporation on the substrate surface at room temperature, while one-dimensional C_{70} nanowires (C_{70}NWs) were formed during droplet evaporation on a heated substrate surface at 32°C. The average polar and equatorial diameters of C_{70} nanoaggregates are ~1500 nm and ~900 nm, respectively, and the structure is porous, consisting of discrete intermediate aggregates with an average diameter of ~50÷60 nm. The results of controlling the average geometrical dimensions of C_{70}NWs by changing the experimental conditions are also presented and analyzed. In addition, the structural stability of C_{70} nanoaggregates and C_{70}NWs after heating to ~185°C on a solid substrate surface was determined. The proposed method has proven effective for synthesizing micro- and nanoscale fullerene-based whiskers, which can be applied in various "bottom-up" technology processes.

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