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The Synthesis of C_{70} Fullerene Nanowhiskers Using the Evaporating Drop Method

Sagdulla A. Bakhramov [1], Urol K. Makhmanov [1,2,*] and Bobirjon A. Aslonov [1]

[1] Institute of Ion-Plasma and Laser Technologies, Uzbekistan Academy of Sciences, Tashkent 100125, Uzbekistan
[2] Faculty of Physics, National University of Uzbekistan, Tashkent 100174, Uzbekistan
* Correspondence: urolmakh@gmail.com

Abstract: Semiconductor nanowhiskers, particularly nanostructured whiskers based on zero-dimensional (0D) C_{70} fullerene, are being actively discussed due to the great potential of their application in modern electronics. For the first time, we proposed and implemented a method for the synthesis of nanostructured C_{70} fullerene whiskers based on the self-organization of C_{70} molecules during the thermal evaporation of C_{70} droplets on the substrate surface. We found that the onset of the synthesis of C_{70} nanowhiskers upon the evaporation of drops of a C_{70} solution in toluene on the substrate surface depends on the substrate temperature. We have provided experimental evidence that an increase in both the C_{70} concentration in the initial drop and the substrate temperature leads to an increase in the geometric dimensions of C_{70} nanowhiskers. The obtained results provide useful vision on the role of solute concentration and substrate temperature in the synthesis of one-dimensional materials.

Keywords: C_{70} fullerene; evaporating drop; self-organization; nanostructure; filamentous whisker

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1. Introduction

In nanoscience, nanowhiskers are considered to be filamentous crystals with a transverse size of up to 100 nm and a length that is an order of magnitude or greater than the transverse size. Semiconductor nanowhiskers are widely used today to create miniature elements of devices in microelectronics [1,2], optoelectronics [3,4], nanoengineering [5,6], solar energy [7–9], biomedicine [10], nanoelectromechanics [11,12] and gas sensing [13,14]. To date, there are various methods [15–17] for obtaining nanowhiskers of a wide range of semiconductor materials, such as growth using molecular beam epitaxy, vapor deposition, laser ablation, growth catalysts, magnetron deposition, chemical epitaxy in a high vacuum and others.

Carbon nanomaterials (fullerene, carbon nanotube and graphene) are becoming key components of nanotechnologies for the development of complex functional nanostructures. Light fullerenes (C_{60}/C_{70}) are a hollow sphere/ellipsoid carbon molecule less than 1 nm in diameter, with sp^2 carbon atoms located on a curved surface at the vertices of a truncated icosahedron. They have unique physical properties, particularly optical and electrical ones. A remarkable property of fullerene molecules is their ability to self-assemble over time in pure solvents to form clusters of various shapes and sizes [18,19], and the nature of the solvent plays an important role in this process [20]. Intermolecular self-assembly, reactivity and electron affinity properties give fullerenes incomparable advantages in applications such as electrocatalysts and supercapacitors [21]. In addition, they have a suitably high photosensitivity, electron mobility, antioxidant activity and radical scavenging [22–24]. The latter leads to a range of applications, including photodetectors [25], sensors [26], solar cells [27], LEDs [28], biomedicines [21] and drug delivery [29].

Since the discovery of C_{60} fullerene nanowhiskers (C_{60}NWs) by the Miyazawa group in 2001 [12,30], applications in various fields have been found. A poor solvent is added to a saturated well-dissolved solution of C_{60} and a liquid–liquid interface is formed in the middle. As a result, a supersaturated solution is formed, C_{60} embryo crystals are nucleated at the liquid–liquid interface and long C_{60}NWs are synthesized. Although this method was initially "static" (without external influence), later "dynamic" (ultrasound, manual mixing, etc., effects) and other modified methods were developed [31,32]. Similarly, C_{70} fullerene nanowhisker (C_{70}NW) structures were synthesized on the basis of C_{70} fullerene in the same ways [33]. It is known that NWs formed on the basis of nanosized fullerenes are based on bottom-up technology. Traditional and newly developed strategies for the synthesis of one-dimensional micro/nanostructures based on fullerenes and their practical applications are considered in [34,35]. In this case, the regulation and control of the size and structure of one-dimensional structures is of great importance. Specialists have now found that the morphology and size of fullerene micro- and nanostructures can be easily controlled by adjusting experimental parameters such as good/poor solvent systems, solvent ratios, temperature, area size of liquid–liquid interface and various treatments [34–37]. The elliptical shape of C_{70} molecules renders them anisotropically polarizable, and the spherical shape of C_{60} renders it isotropic [38]. This diversifies the physico-chemical properties of the micro/nanostructures synthesized on their basis [39]. In particular, when NWs synthesized in a solution are transferred to the surface of a solid substrate, changes in their morphology occur. It should also be taken into account that the evaporation of droplets of fullerene solutions on the surface of a solid substrate leads to self-organization processes [40,41]. In this regard, there is a need to study the processes occurring in the volume of the evaporation of droplets of fullerene solutions.

In this paper, we consider the synthesis of nanostructured C_{70} fullerene whiskers on the surface of a substrate by evaporating a microvolume drop of a C_{70} solution. Experimental methods for controlling the geometric dimensions of the synthesized nanowhiskers are discussed.

2. Results

In our experiments, the shape of the initial drop of a fullerene solution with a volume of $V \approx 40–50\ \mu L$ on a wetted flat substrate is approximately represented by a spherical cap (see Figure 1, left). It can be noted that the drops of the fullerene solution always retain a constant area of the base of the drop throughout the entire duration of the thermal evaporation. But the contact angle (φ) of the drop gradually decreases until it disappears. The fullerene drop is protected from convective air flows until complete evaporation; the drop thermal evaporation direction is perpendicular on the surface of the spherical cap. Due to the Marangoni effect along the "droplet–air" interface and the Rayleigh–Benard effect along the evaporating droplet volume (Figure 1, right), strong capillary flows appear and start the assembly of fullerene particles as well as the synthesis of different nanostructures based on them.

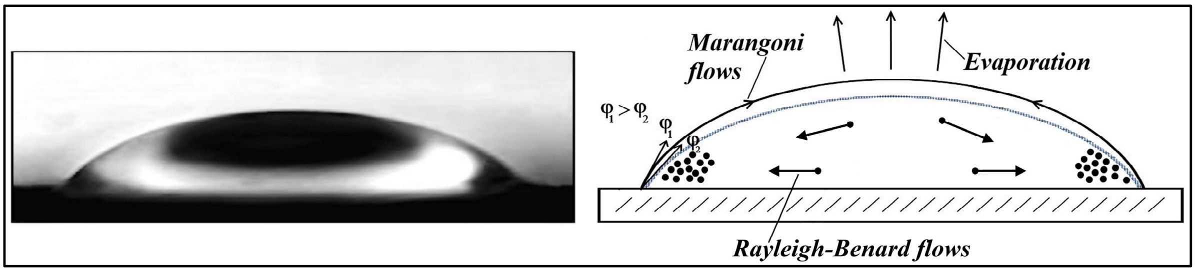

Figure 1. A photograph of the lateral microdroplet profiles of a C_{70} solution (**left**) and a schematic representation of the appearing flows inside the evaporating droplet (**right**).

The SEM image of the structures formed during the evaporation of droplets of a C_{70} solution in toluene on the substrate surface at room temperature (~24 ± 1 °C) is shown in Figure 2. Due to the constant base area of the microdroplet, a trace of C_{70} nanostructures remains along the base of the drop, similar to a coffee ring, during the entire thermal evaporation of the solvent. An important role is played by the temperature gradient that occurs when the surface and near-surface layers of the droplet cool sharply as a result of intense toluene evaporation. It can be seen that after the complete evaporation of toluene from a microdroplet of the C_{70} solution, large quasi-spherical C_{70} aggregates are formed on the surface of the optical glass substrate. At the same time, the average geometric dimensions in the diameter of C_{70} aggregates are ~600 nm. The resulting C_{70} aggregates are porous and consist of discrete intermediate nanoaggregates with sizes up to ~40–45 nm in diameter. The most probable, from our point of view, is the following fundamental mechanism of the self-organization of C_{70} fullerene molecules in the volume of the evaporating solution droplets and the formation of quasi-spherical nanoaggregates. A drop of a C_{70} solution always tends to minimize its total surface energy. The latter can be achieved, in particular, as a result of the self-organization of C_{70} molecules. Let us assume that two intermediate fullerene formations with diameters d_1 and d_2 ($d_2 >> d_1$) are localized in the volume of an evaporating drop of a C_{70} solution. Then, each of these nanosized particles will tend to establish a thermodynamic equilibrium with the surrounding solution. In accordance with the well-known Gibbs–Thomson relation [42], the solubility of a larger spherical C_{70} cluster with an average diameter d_2 in a solution will be noticeably lower than the similar solubility parameter for a smaller C_{70} fullerene formation with the diameter d_1. Then, individual C_{70} molecules, appearing as a result of the dissolution of the smaller formation d_1 into drops, will be deposited on the surface of larger particles d_2 to maintain the equilibrium in the system. At the same time, smaller fullerene formations will be forced to dissolve further to compensate for the C_{70} molecules that have left the drop. As a result, inside the evaporating drop of the C_{70} fullerene solution, a continuous diffusion transfer of the dissolved substance (C_{70} molecules) occurs from smaller C_{70} formations to larger quasi-spherical nanoaggregates.

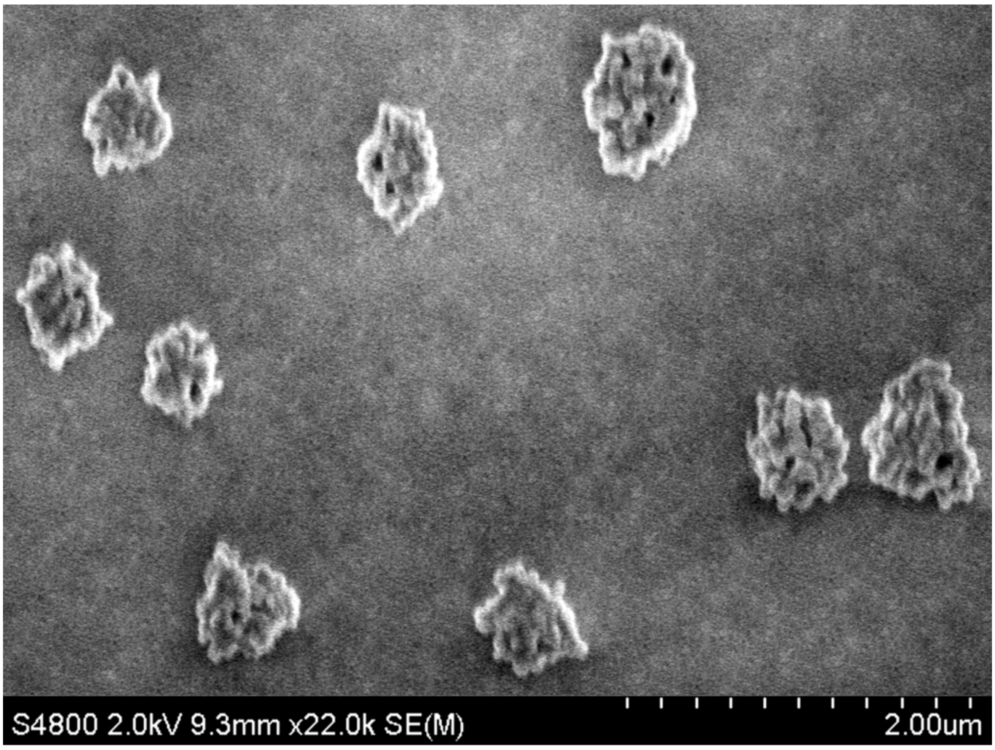

Figure 2. SEM image of C_{70} aggregates formed by thermal evaporation of organic solvent from the volume of microdroplet of a C_{70} solution at room temperature (~24 $\pm$ 1 °C). The initial concentration of fullerene C_{70} in the solution was ~1.1 $\times$ 10^{-3} mol·L^{-1}.

We studied the process of the evaporation of a C_{70} solution droplet on the substrate surface at different substrate temperatures in order to synthesize one-dimensional C_{70}

structures. When the K-8 optical glass substrate was heated to 28 °C, nanostructured filaments (nanowhiskers) of C_{70} fullerene of an optimal shape were synthesized on the substrate surface (see Figure 3). The concentration of fullerene C_{70} in the initial drop of the solution was ~1.1 × 10^{-3} mol·L^{-1}. In this case, the temperature gradient in the process of the intensive evaporation of the solvent from a microdroplet at a temperature of 28 °C made it possible to overcome some of the energy difficulties in the formation of C_{70}NWs. We could observe that X- and V-shaped C_{70}NWs were mainly synthesized in the volume of an evaporating drop of the C_{70} molecular solution on a substrate (see Figure 3). The average geometric dimensions of C_{70}NWs are ~105 nm in width and ~750 nm in length. At the same time, we could observe that the maximum length and width of the resulting C_{70}NWs reached the values ~1.7 µm and ~200 nm, respectively.

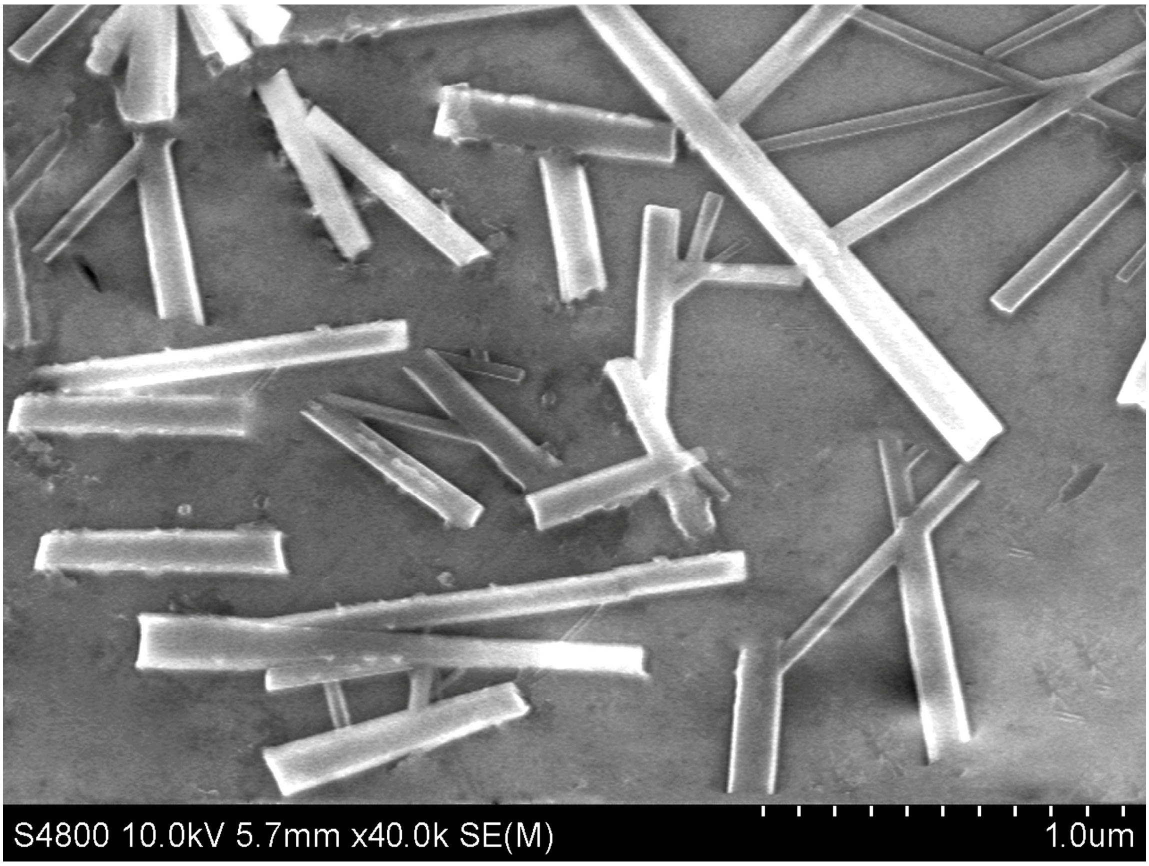

Figure 3. SEM image of C_{70}NWs synthesized in a volume of the evaporating droplet of C_{70} molecular solution on the smooth surface of a substrate at T ≈ 28 °C. The concentration of fullerene C_{70} in the initial drop of the solution was ~1.1 × 10^{-3} mol·L^{-1}.

A SEM image of C_{70}NWs, synthesized on a surface of a horizontally located glass substrate heated to T = 36 °C, is presented in Figure 4. In experiments with a fixed concentration of C_{70} (~1.1 × 10^{-3} mol·L^{-1}) in a drop of the working solution, the effect of increasing the temperature of the substrate on the ongoing processes of the evaporation drop was studied. It was established that an increase in the substrate temperature not only led to a more accelerated nucleation and growth of C_{70}NWs but also to a noticeable increase in the final geometric dimensions of the synthesized C_{70}NWs. Therein, the distribution of C_{70}NWs on the substrate surface was getting denser. At the same time, the average length and width of the resulting C_{70}NWs reached the values ~1.8 µm and ~175 nm, respectively. The presented results proved that the size of nanowhiskers can be controlled by changing the substrate temperature at a fixed concentration of C_{70} in the working drop.

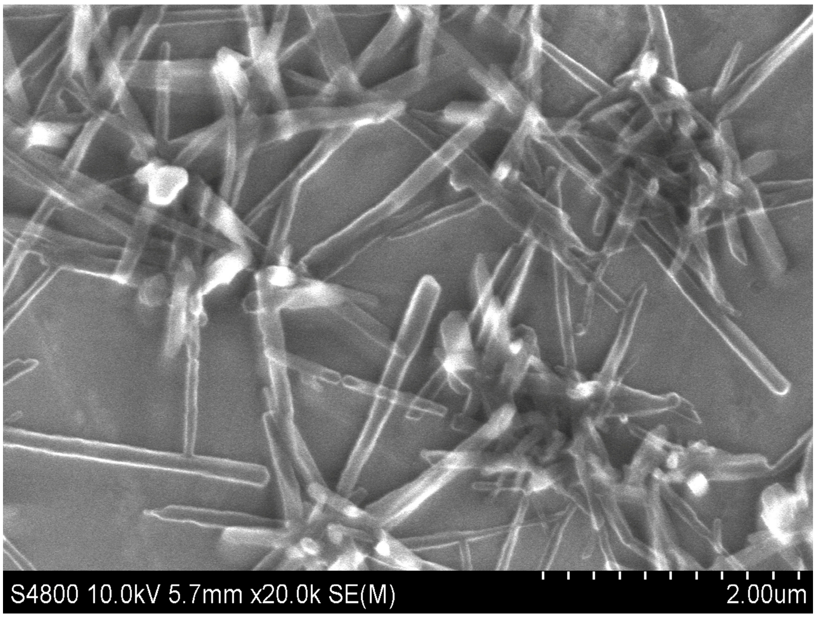

Figure 4. SEM image of C_{70}NWs synthesized in the volume of an evaporating droplet of the C_{70} molecular solution on the flat substrate at T ≈ 36 °C. The concentration of fullerene C_{70} in the initial drop of the solution was ~1.1×10^{-3} mol·L^{-1}.

Under the same conditions, we studied the effect of the initial concentration on the size of the synthesized nanoparticles. Figure 5 presents a SEM image of nanostructured whiskers of C_{70} fullerene synthesized on the smooth surface of a substrate heated to T ≈ 36 °C. An increase in the fullerene concentration (up to ~1.5×10^{-3} mol·L^{-1}) in the initial droplet led to a noticeable increase in the final C_{70}NW size. It was easy to observe that the longest C_{70}NWs had a size of ~28 μm in length, ~2 μm in width, as well as the shortest length and width of ~6 μm and ~200–250 nm, respectively (Figure 5). So, it was shown that the geometric dimensions of the C_{70}NWs can be controlled by changing the initial concentration of the fullerene solution.

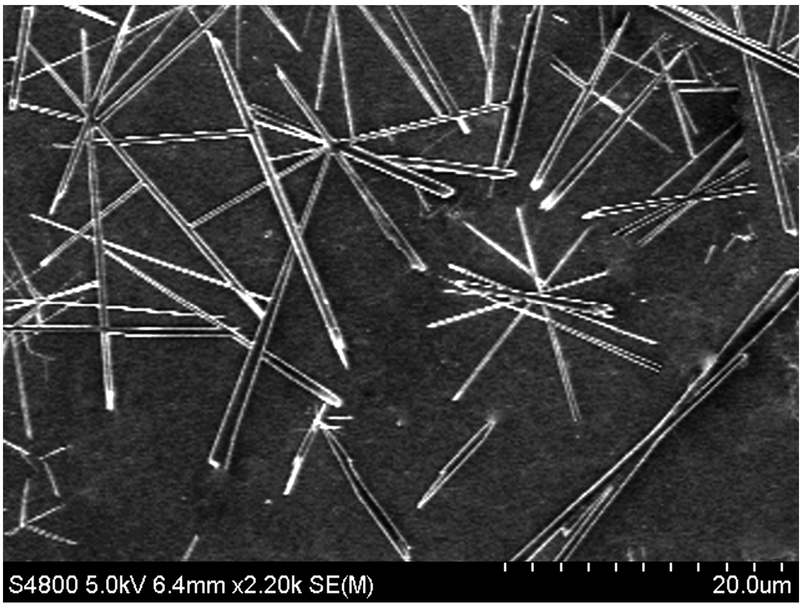

Figure 5. SEM image of filamentous crystalline structures (nanowhiskers) of C_{70} fullerene, synthesized on the substrate surface at T ≈ 36 °C. The concentration of fullerene C_{70} in the initial drop of the solution was ~1.5×10^{-3} mol·L^{-1}.

The experimental results reflecting the change in the geometric dimensions of the synthesized C_{70}NWs at a fixed concentration of C_{70} fullerene with different substrate temperatures are presented in Table 1.

Table 1. Evolution of changes in the average sizes of synthesized C_{70}NWs depending on the substrate temperature.

C/(mol·L^{-1}) [a]	T/(°C) [b]	Average Length/µm	Average Width/nm
~1.1×10^{-3}	28	0.75	105
	32	1.35	152
	36	1.8	175

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

The thermal and temporal stability of C_{70}NWs is also very important for the investigation of their structure and further applications. In our case, a TEM observation was performed on synthesized C_{70}NWs. When the synthesized nanowhiskers were stored at room temperature for 2 months, microscopic observations revealed practically no changes in their morphology and structure (see Figure 6, left). The TEM image of stored C_{70}NWs (with a diameter of ~72 nm) after heating at ~120 °C for 15 min is shown in Figure 6 (right). This result indicates that the C_{70} nanowhiskers got thinner at ~120 °C. In addition, while the overall integrity of the nanowhiskers was preserved, traces similar to nanosized "craters" appeared on their surface.

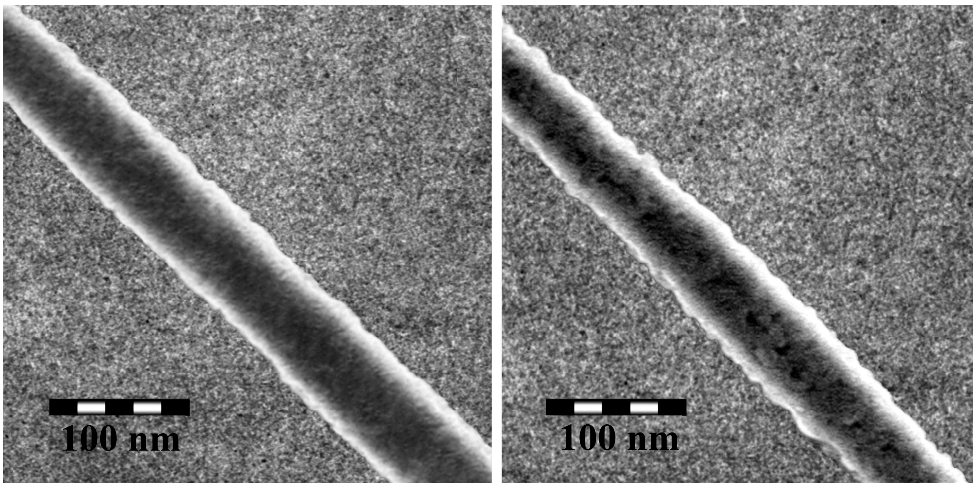

Figure 6. TEM images of C_{70}NWs taken 2 months after synthesis: no heating (**left**) and after heating at ~120 °C (**right**).

The results of this work can be used to predict and control the geometric dimensions of nanostructured whiskers based on different macromolecules. In addition, this method is useful in the synthesis of one-dimensional, two-dimensional and three-dimensional structures from a zero-dimensional material consisting of only one component, through various combined and/or separate processes. Note that synthesized C_{70}NWs are a separate class of materials that exhibit the combined properties of both C_{70} fullerene and nanostructures. The next steps are to develop structural and functional materials using synthesized fullerene-based one-dimensional nanounits. Although today there are many approaches to create new functional materials based on C_{70} fullerene, combining and reorganizing independent knowledge and facts with practical applications will lead to great progress in material science. The electrical properties, superconductivity and energy storage properties of fullerene C_{70}NWs are still unexplored and thus represent an excellent area for future research. These amazing properties allow them to be effectively used in many future concrete applications such as photocatalysis, solar cells, energy storage, photodynamic therapy, drug and gene delivery, electrocatalysis and sensors.

3. Discussion

We presented an experimental method for the synthesis of cost-effective and compatible C_{70}NWs in the volume of an evaporating droplet on a substrate. Our electron microscopic measurements confirm the formation of one-dimensional C_{70}NWs during the evaporation of a drop on the surface of a substrate heated from 28 °C. The difference in substrate temperature with respect to the temperature of the deposited droplet and the environment creates additional thermodynamic forces acting on C_{70} particles, which ultimately ensure the synthesis of nanowhiskers based on them. It was found that changing both the concentration of fullerene in the initial drop and the substrate temperature provides an opportunity to tune the geometric dimensions of C_{70}NWs to the desired value.

At a fixed concentration of C_{70} (~1.1×10^{-3} mol·L^{-1}) in an initial drop, changing the substrate temperature from T_1 = 28 °C to T_2 = 36 °C led to a noticeable increase in the final geometric dimensions of the synthesized C_{70}NWs. In this case, the ratio of the average length (~1.35 μm) to width (~152 nm) of the synthesized C_{70}NWs was about 9:1. At a fixed substrate temperature (T = 36 °C) with a relatively high concentration of fullerene (~1.5×10^{-3} mol·L^{-1}), C_{70}NWs with a maximum length and width of ~28 μm and ~2 μm, respectively, were synthesized. It was shown that the method used is effective for the synthesis of micro- and nanosized whiskers, which can be used for various purposes of "bottom-up" technology.

4. Materials and Methods

In our experiments, we used high-purity (~99.8%) powders of fullerene C_{70} (Sigma-Aldrich, Saint Louis, MO, USA) as well as the organic solvent toluene ($C_6H_5CH_3$, Sigma-Aldrich). The mixture of "toluene + C_{70} powders", located in a hermetically sealed glass flask, was dissolved with continuous mechanical stirring at a frequency of ~1.5 Hz for 1.5 h using a programmable laboratory magnetic stirrer of the MS-11H brand, WIGO (Pruszkow, Poland). Thereafter, the C_{70} solution was sonicated for 15 min using an ultrasonic bath brand, DC-120H. Further, dosed drops of the C_{70} molecular solution were taken using a VITLAB dosing pipette (VITLAB GmbH, Grossostheim, Germany).

A standard K-8 optical glass with a surface roughness of $\leq$7 nm was used as a substrate. Before each experiment, the surface of the used glass substrate was plasma, cleaned at the nanolevel using a Plasma Cleaner device (Harrick Plasma, «PDC-002», Ithaca, NY, USA).

For experiments on heat treatment, a thermostatically controlled table was used with the possibility of heating up to 140 °C on a Peltier effect. The temperature was programmed with an accuracy of 1 °C. Using a thermocouple built into the MS8217 digital multimeter, the temperature on the glass substrate was controlled with an error of $\pm$2%.

Drops of the C_{70} solution were placed on a heated substrate using a VITLAB piston micropipette (VITLAB GmbH, Grossostheim, Germany) under laboratory conditions. In this case, the temperature of the solution and the environment was ~23 $\pm$ 1 °C, and the drops were protected from convective air currents until complete evaporation.

We used a high-resolution scanning electron microscope (hereinafter SEM) brand, JSM-IT200 (Joel, Tokyo, Japan), and a transmission electron microscope (hereinafter TEM), LEO-912 AB (Carl ZEISS, Oberkochen, Germany), to establish the morphological features and determine the exact geometrical sizes of one-dimensional C_{70}NWs.

5. Conclusions

For the first time, we proposed the evaporating drop method for producing nanostructured C_{70}NWs. In this case, the self-organization of the C_{70} molecules occurs upon the thermal evaporation of the toluene from the C_{70} droplets located on the surface of a flat glass substrate. The optimal substrate temperature for the start of the synthesis of C_{70} fullerene nanowhiskers in the volume of droplet evaporation was experimentally established. It was shown that the geometric dimensions of the synthesized C_{70}NWs can be controlled both by changing the C_{70} concentration in the initial droplet and by changing the temperature of the substrate used. A selective synthesis of fullerene nanowhiskers was carried out. The results of this work can be used to predict and control the geometric dimensions of nanostructured whiskers of various kinds, which will have great potential in applications such as nano- and microelectronics, solar cells, nonlinear optics, sensors and electromechanics.

Author Contributions: Conceptualization, U.K.M.; methodology, U.K.M.; investigation, U.K.M. and B.A.A.; writing—original draft preparation, U.K.M.; writing—review and editing, S.A.B. and U.K.M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ogawa, K.; Kato, T.; Ikegami, A.; Tsuji, H.; Aoki, N.; Ochiai, Y.; Bird, J.P. Electrical properties of field-effect transistors based on C_{60} nanowhiskers. *Appl. Phys. Lett.* **2006**, *88*, 112109. [CrossRef]
2. Larsen, C.; Barzegar, H.R.; Nitze, F.; Wagberg, T.; Edman, L. On the fabrication of crystalline C_{60} nanorod transistors from solution. *J. Nanotechnol.* **2012**, *23*, 344015. [CrossRef]
3. Joyce, H.J.; Gao, Q.; Tan, H.H.; Jagadish, C.; Kim, Y.; Zou, J.; Smith, L.M.; Jackson, H.E.; Yarrison-Rice, J.M.; Parkinson, P.; et al. III–V semiconductor nanowires for optoelectronic device applications. *Prog. Quantum. Electron.* **2011**, *35*, 23–75. [CrossRef]
4. Kausar, A.; Ahmad, I.; Maaza, M.; Eisa, M.H.; Bocchetta, P. Polymer/Fullerene Nanocomposite for Optoelectronics-Moving toward Green Technology. *J. Compos. Sci.* **2011**, *6*, 393. [CrossRef]
5. Miyazawa, K. Synthesis and properties of fullerene nanowhiskers and fullerene nanotubes. *J. Nanosci. Nanotechnol.* **2009**, *9*, 41–50. [CrossRef]
6. Salhi, B.; Hossain, M.; Mukhaimer, A.; Al-Sulaiman, F.A. Nanowires: A new pathway to nanotechnology-based applications. *J. Electroceram.* **2016**, *37*, 34–49. [CrossRef] [PubMed]
7. Hochbaum, A.I.; Yang, P. Semiconductor Nanowires for Energy Conversion. *Chem. Rev.* **2010**, *110*, 527–546. [CrossRef]
8. Zhang, G.; Finefrock, S.; Liang, D.; Yadav, G.G.; Yang, H.; Fang, H.; Wu, Y. Semiconductor nanostructure-based photovoltaic solar cells. *Nanoscale* **2011**, *3*, 2430–2443. [CrossRef]
9. Sun, K.; Kargar, A.; Park, N.; Madsen, K.N.; Naughton, P.W.; Bright, T.; Jing, Y.; Wang, D. Compound Semiconductor Nanowire Solar Cells. *IEEE J. Sel. Top. Quantum Electron.* **2011**, *17*, 1033–1049. [CrossRef]
10. Okuda-Shimazaki, J.; Nudejima, S.; Takaku, S.; Kanehira, K.; Sonezaki, S.; Taniguchi, A. Effects of fullerene nanowhiskers on cytotoxicity and gene expression. *Health* **2010**, *2*, 1456–1459. [CrossRef]
11. Akiyama, T. Development of Fullerene Thin-Film Assemblies and Fullerene-Diamine Adducts towards Practical Nanocarbon-Based Electronic Materials. *Bull. Chem. Soc. Jpn.* **2019**, *92*, 1181–1199. [CrossRef]
12. Miyazawa, K. Synthesis of fullerene nanowhiskers using the liquid–liquid interfacial precipitation method and their mechanical, electrical and superconducting properties. *Sci. Technol. Adv. Mater.* **2015**, *16*, 013502. [CrossRef] [PubMed]
13. Kausar, A. Polymeric nanocomposites reinforced with nanowhiskers: Design, development, and emerging applications. *J. Plast. Film. Sheeting* **2020**, *36*, 312–333. [CrossRef]
14. Zhang, W.D.; Zhang, W.H. Carbon Nanotubes as Active Components for Gas Sensors. *J. Sens.* **2009**, *2009*, 160698. [CrossRef]
15. Naumova, O.V.; Nastaushev, Y.V.; Svitasheva, S.N.; Sokolov, L.V.; Zakharov, N.D.; Werner, P.; Gavrilova, T.A.; Dultsev, F.N.; Aseev, A.L. Molecular-beam epitaxy-grown Si whisker structures: Morphological, optical and electrical properties. *Nanotechnology* **2008**, *19*, 225708. [CrossRef]
16. Zhang, X.; Dubrovskii, V.G.; Sibirev, N.V.; Cirlin, G.E.; Sartel, C.; Tchernycheva, M.; Harmand, J.C.; Glas, F. Growth of Inclined GaAs Nanowires by Molecular Beam Epitaxy: Theory and Experiment. *Nanoscale Res. Lett.* **2010**, *5*, 1692–1697. [CrossRef]
17. Xia, M.; Guo, H.Y.; Hussain, M.I. Controllable Combustion Synthesis of SiC Nanowhiskers in a Si–C–N System: The Role of the Catalyst. *Appl. Sci.* **2020**, *10*, 252. [CrossRef]
18. Sathish, M.; Miyazawa, K.; Hill, J.P.; Ariga, K. Solvent Engineering for Shape-Shifter Pure Fullerene (C_{60}). *J. Am. Chem. Soc.* **2009**, *131*, 6372–6373. [CrossRef]
19. Makhmanov, U.K.; Kokhkharov, A.M.; Bakhramov, S.A.; Erts, D. The formation of self-assembled structures of C_{60} in solution and in the volume of an evaporating drop of a colloidal solution. *Lith. J. Phys.* **2020**, *60*, 194–204. [CrossRef]
20. Mchedlov-Petrossyan, N.O. Fullerenes in molecular liquids. Solutions in "good" solvents: Another view. *J. Mol. Liq.* **2011**, *161*, 1–12. [CrossRef]

21. Xu, T.; Shen, W.; Huang, W.; Lu, X. Fullerene micro/nanostructures: Controlled synthesis and energy applications. *Mater. Today Nano* **2020**, *11*, 100081. [CrossRef]
22. Lin, Y.; Wang, J.; Zhang, Z.G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar Cells. *Adv. Mater.* **2015**, *27*, 1170–1174. [CrossRef] [PubMed]
23. Sabirov, D.S.; Terentyev, A.O.; Bulgakov, R.G. Polarizability of fullerene [2+2]-dimers: A DFT study. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14594–14600. [CrossRef] [PubMed]
24. Itaka, K.; Yamashiro, M.; Yamaguchi, J.; Haemori, M.; Yaginuma, S.; Matsumoto, Y.; Kondo, M.; Koinuma, H. High-Mobility C_{60} Field-Effect Transistors Fabricated on Molecular-Wetting Controlled Substrates. *Adv. Mater.* **2006**, *18*, 1713–1716. [CrossRef]
25. Tang, Q.; Zhang, G.; Jiang, B.; Ji, D.; Kong, H.; Riehemann, K.; Ji, Q.; Fuchs, H. Self-assembled fullerene (C_{60})-pentacene superstructures for photodetectors. *SmartMat* **2021**, *2*, 109–118. [CrossRef]
26. Bairi, P.; Minami, K.; Nakanishi, W.; Hill, J.P.; Ariga, K.; Shrestha, L.K. Hierarchically Structured Fullerene C_{70} Cube for Sensing Volatile Aromatic Solvent Vapors. *ACS Nano* **2016**, *10*, 6631–6637. [CrossRef]
27. Roy, J.K.; Kar, S.; Leszczynski, J. Optoelectronic Properties of C_{60} and C_{70} Fullerene Derivatives: Designing and Evaluating Novel Candidates for Efficient P3HT Polymer Solar Cells. *Materials* **2019**, *12*, 2282. [CrossRef]
28. Grebinyka, A.; Grebinyk, S.; Prylutska, S.; Rittere, U.; Matyshevska, O.; Dandekar, T.; Frohm, M. C_{60} fullerene accumulation in human leukemic cells and perspectives of LED-mediated photodynamic therapy. *Free Radic. Biol. Med.* **2018**, *124*, 319–327. [CrossRef]
29. Kazemzadeh, H.; Mozafari, M. Fullerene-based delivery systems. *Drug Discov. Today* **2019**, *24*, 898–905. [CrossRef]
30. Miyazawa, K.I.; Obayashi, A.; Kuwabara, M. C_{60} nanowhiskers in a mixture of lead zirconate titanate sol–C_{60} toluene solution. *J. Am. Ceram. Soc.* **2001**, *84*, 3037–3039. [CrossRef]
31. Hotta, K.; Miyazawa, K. Synthesis and growth investigation of C_{60} fullerene nanowhiskers. *J. Phys. Conf. Ser.* **2009**, *159*, 012021. [CrossRef]
32. Kobayashi, K.; Tachibana, M.; Kojima, K. Photo-assisted growth of C_{60} nanowhiskers from solution. *J. Cryst. Growth* **2005**, *274*, 617–621. [CrossRef]
33. Miyazawa, K. C_{70} Nanowhiskers Fabricated by Forming Liquid/Liquid Interfaces in the Systems of Toluene Solution of C_{70} and Isopropyl Alcohol. *J. Am. Ceram. Soc.* **2002**, *85*, 1297–1299. [CrossRef]
34. Bao, L.; Xu, T.; Guo, K.; Huang, W.; Lu, X. Supramolecular Engineering of Crystalline Fullerene Micro-/Nano-Architectures. *Adv. Mater.* **2022**, *34*, 2200189. [CrossRef] [PubMed]
35. Baskar, A.V.; Benzigar, M.R.; Talapaneni, S.N.; Singh, G.; Karakoti, A.S.; Yi, J.; Al-Muhtaseb, A.H.; Ariga, K.; Ajayan, P.M.; Vinu, A. Self-Assembled Fullerene Nanostructures: Synthesis and Applications. *Adv. Funct. Mater.* **2022**, *32*, 2106924. [CrossRef]
36. Ariga, K.; Shresth, L.K. Fullerene Nanoarchitectonics with Shape-Shifting. *Materials* **2020**, *13*, 2280–2295. [CrossRef]
37. Kim, J.; Park, C.; Choi, H.C. Selective growth of a C_{70} crystal in a mixed solvent system: From cube to tube. *Chem. Mater.* **2015**, *27*, 2408–2413. [CrossRef]
38. Cui, D.; MacLeod, J.M.; Rosei, F. Planar Anchoring of C_{70} Liquid Crystals Using a Covalent Organic Framework Template. *Small* **2019**, *15*, 1903294. [CrossRef]
39. Sabirov, D.S.; Terentyev, A.O.; Cataldo, F. Bisadducts of the C_{60} and C_{70} fullerenes with anthracene: Isomerism and DFT estimation of stability and polarizability. *Comput. Theor. Chem.* **2016**, *1081*, 44–48. [CrossRef]
40. Bakhramov, S.A.; Makhmanov, U.K.; Kokhkharov, A.M. Synthesis of nanoscale fullerene C_{60} filaments in the volume of an evaporating drop of a molecular solution and preparation of thin nanostructured coatings on their basis. *Appl. Sol. Energy* **2019**, *55*, 309–314. [CrossRef]
41. Makhmanov, U.K.; Kokhkharov, A.M.; Bakhramov, S.A.; Esanov, S.A. Synthesis of fullerene C_{60} nanotubes in the volume of an evaporating drop of colloidal solution. *Rom. J. Phys.* **2022**, *67*, 601–609.
42. Shao-Horn, Y.; Sheng, W.C.; Chen, S.; Ferreira, P.J.; Holby, E.F.; Morgan, D. Instability of Supported Platinum Nanoparticles in Low-Temperature Fuel Cells. *Top. Catal.* **2007**, *46*, 285–305. [CrossRef]