Quick synthesis of highly aligned or randomly oriented nanofibrous structures composed of $C_{60}$ molecules via self-assembly

Shunji Kurosu, Takahiro Fukuda and Toru Maekawa

Bio-Nano Electronics Research Centre, Toyo University, 2100, Kujirai, Kawagoe, Saitama 350-8585, Japan
E-mail: maekawa@toyo.jp

Received 23 February 2013
Accepted for publication 8 March 2013
Published 25 March 2013
Online at stacks.iop.org/ANSN/4/025003

Abstract

Assemblies, which are composed of nanoparticles such as nanofibres, have been intensively studied in recent years. This has particularly been the case in the field of biomedicine, where the aim is to develop efficient methodologies for capturing and separating target biomolecules and cells and/or encouraging bio-chemical reactions, utilizing the extremely high surface area to volume ratio of assemblies. There is an urgent need for the development of a quick synthesis method of forming nanofibrous structures on the surface of biomedical microchips and devices for the investigation of the interactions between biomolecules/cells and the nanostructures. Here, we produce nanofibrous structures composed of $C_{60}$ molecules, which are aligned in one direction or randomly oriented, by dissolving $C_{60}$ molecules and sulphur in benzene and evaporating a droplet of the solution on a glass substrate under appropriate conditions. The synthesis time is as short as 30 s. Sulphur is extracted and nanofibres are crystallized by leaving them in supercritical carbon dioxide.

Keywords: $C_{60}$ fullerene, sulphur, self-assembly, fibres, solution growth

Classification numbers: 2.00, 4.00, 4.02, 5.00, 5.12, 5.16

Online supplementary data available from stacks.iop.org/ANSN/4/025003/mmedia

1. Introduction

Nanofibrous structures have been intensively studied in recent years, particularly in the biomedical field, with the aim of developing efficient methodologies for capturing and separating target biomolecules and cells [1,2] and/or encouraging bio-chemical reactions [3] utilizing their extremely high surface area to volume ratio. The effect of nanomaterials on cellular behaviour has also been investigated in order to understand the viability, morphology and differentiation of cells [4–7]. There is an urgent need to develop a quick synthesis method of forming nanostructures on the surface of bio-medical microchips and devices so that the immobilization of biomolecules on the nanostructures, the separation of target cells and the growth behaviour of cells on the nanostructures can be investigated [8,9].

Nanostructures are commonly created by so-called top-down ultra-fine fabrication techniques such as photolithography, x-ray lithography and etching [10,11], whereas they can also be formed via bottom-up self-assembly processes like those in biological systems [11,12]. $C_{60}$ fullerene was discovered by Kroto et al [13] and since then, polymerization of $C_{60}$ molecules has been successfully performed by several methods such as photon irradiation, electron irradiation, bridging by foreign atoms or molecules, chemical reactions and the application of high pressure and/or high temperature [14]. One-dimensional chains and two-dimensional films have been produced by polymerization of $C_{60}$ molecules [14].

It is well known that $C_{60}$ fullerene molecules are soluble in organic solvents [15] and that $C_{60}$ crystals can be formed by the free evaporation method [16]. The lattice
structures change depending on the type of solvent in which the $C_{60}$ molecules are dissolved and the temperature of the crystals [17]. The slow evaporation method and the liquid–liquid interfacial precipitation (LLIP) method were invented for the formation of fibrous clusters composed of $C_{60}$ molecules, which are usually called fullerene nanowhiskers (FNWs) [18–20]. It is also known that crystals are formed by $C_{60}$ molecules and sulphur [21–24].

In this paper we produce nanofibres composed of $C_{60}$ molecules, which are aligned in one direction or randomly oriented, by dissolving $C_{60}$ molecules and sulphur in benzene and evaporating a droplet of the solution under appropriate conditions. The synthesis time is as short as 30 s. The present methodology may well be utilized for the formation of nanofibres on biomedical microchips and devices.

2. Experimental details

The outline of the experimental procedure is shown in figure 1. We used benzene as a solvent. $C_{60}$ molecules and sulphur powder were mixed with benzene, sonicating the solution for 5 min at 23 °C and 1 atm. The concentration of $C_{60}$ molecules in benzene was set at 0.6 μmol ml$^{-1}$, while that of sulphur was changed: 0, 1.55, 3.10 or 6.19 μmol ml$^{-1}$. 60 μl of the above solution, the temperature of which was set at 23 °C, was dropped onto the surface of a glass substrate, the dimensions of which were 20 mm (length) ×20 mm (width) ×1 mm (height). The initial temperature of the glass substrate was set at 23, 35, 40, 45, 50, 60, 70, 80, 90 or 100 °C by a heater installed at the bottom of the substrate. The evaporation process was observed by a CCD camera (CCD-F9000, Shimadzu Co.) and recorded on the hard disk of a computer and videotape. After the solvent had completely evaporated, the structures of the deposit on the glass substrate were observed and analysed by a scanning electron microscope (SEM) (JSM-7400F, JEOL), transmission electron microscope (TEM) (JEM-2200FS, JEOL) and the selected area electron diffraction (SAED) method (JEM-2200FS, JEOL). Elementary mappings of the deposit were also carried out by energy-dispersive x-ray spectroscopy (EDS) (JED-2300T, JEOL). The deposit on the glass substrate was placed in supercritical carbon dioxide and the structural changes were observed and analysed by SEM, TEM, EDS and SAED.

3. Results and discussion

We found that nanofibres composed of $C_{60}$ molecules, which were aligned in one direction, were formed during the evaporation process. Nanofibres were most efficiently produced when the concentration of sulphur was 3.10 μmol ml$^{-1}$ and the substrate temperature was 50 °C. Note that the concentration of $C_{60}$ molecules in benzene was fixed at 0.6 μmol ml$^{-1}$. An SEM image of typical aligned nanofibres is shown in figure 2(a), where the concentration of sulphur in the solution was 3.10 μmol ml$^{-1}$ and the substrate temperature was 50 °C. The orders of the width and length of typical aligned nanofibres were, respectively, ~100 nm and ~100 μm. A movie of the droplet’s evaporation process is shown in supplementary data 1, (available from stacks.iop.org/ANSN/4/025003/mmedia) where it is clearly shown that the circumference of the droplet was moving outwards on the glass substrate and fibres were formed aligning in a perpendicular direction to the circumference during the evaporation process. It took approximately 30 s for the droplet to evaporate completely. When the substrate temperature is 50 °C, the circumference of the droplet evaporates faster than the central part, which makes the local surface temperature along the circumference lower than that at the centre. Note that the initial temperature of the droplet of the solution was 23 °C. As a result, the surface tension along the circumference becomes higher than that at the central part of the surface of the droplet, which induces outwards circumferential motion; known as Marangoni convection [25–27]. $C_{60}$ molecules and sulphur are also transported outwards and coagulate with each other to form nanofibres near the circumference of the droplet due to supersaturation and those fibres align in a perpendicular direction to the circumference of the droplet while it moves outwards. We carried out elementary analysis of nanofibres (see figure 2(b) for an SEM image and EDS mappings of fibres). Sulphur was evenly distributed in the fibres and the element ratio of carbon to sulphur was 19:1. It is well known that $S_8$ is stably formed by sulphur and crystals composed of $C_{60}$ and $S_8$ grow under equilibrium conditions [28, 29]. A TEM image and SAED pattern of a nanofibre are shown in figure 2(c). The nanofibres’ internal structures were amorphous. It is therefore inferred from the elementary and structural analyses that sulphur clusters $S_8$ may be acting as the nucleation sites to form $C_{60}$–sulphur clusters, noting that the element ratio of $C_{60}$ to $S_8$ was 2.5:1, and that nanofibres grow via cluster–cluster aggregations. $C_{60}$–sulphur clusters are randomly located inside the nanofibres due to the fast evaporation process.Aligned nanofibres were formed only when the substrate temperature was set at 23 up to 50 °C and the concentration of sulphur was 1.55 and 3.10 μmol ml$^{-1}$, but the quantity of aligned nanofibres was largest when the substrate temperature was 50 °C and the concentration of sulphur...
Figure 2. SEM, TEM, SAED and EDS images of nanofibres composed of C$_{60}$ molecules. (a) An SEM image of nanofibres composed of C$_{60}$ molecules. Nanofibres were formed most efficiently when the concentration of sulphur was 3.45 $\mu$mol ml$^{-1}$ and the initial substrate temperature was 50 $^\circ$C. Nanofibres are aligned in one direction perpendicular to the circumference of a droplet of the solution during the outwards movement of the circumference (see supplementary data 1 for the movie). (b) A TEM image and EDS mappings of nanofibres. Nanofibres are composed of carbon and sulphur. (c) A TEM image and SAED pattern of a nanofibre. The internal structure of the nanofibre is amorphous. (d) An SEM image of buckypaper composed of randomly oriented nanofibres. A sheet composed of randomly oriented nanofibres was created by disturbing the circumferential motion with a step set on the glass substrate.

was 3.10 $\mu$mol ml$^{-1}$ as mentioned. When the substrate temperature was lower than 50 $^\circ$C, the speed of outwards motion of the circumference of the droplet was lower than that at 50 $^\circ$C and as a result, fibres were not so efficiently aligned in one direction although fibres were formed near the circumferential region, whereas when the substrate temperature was higher than 50 $^\circ$C, the speed of outwards motion of the circumference of the droplet and evaporation was so high that few fibres were formed. When the sulphur was not dissolved in benzene, no nanofibres were produced, but dendritic structures were formed by C$_{60}$ molecules due to fast evaporation of benzene (see supplementary data 2 (available from stacks.iop.org/ANSN/4/025003/mmedia for a TEM image of a dendritic structure). It is supposed that the trapping of C$_{60}$ molecules by sulphur clusters and the outwards motion of the circumference of a droplet are necessary for the nucleation and growth of aligned nanofibres. Sulphur clusters may be acting as nucleation sites to form C$_{60}$–sulphur clusters such as (C$_{60}$)$_n$S$_8$ ($n=2$ or 3 according to the elementary analysis) since S$_8$ attracts C$_{60}$ molecules [28, 29] (see supplementary data 2 for the potential curves) and the temperature of the substrate needs to be higher than that of a droplet of the solution for the induction of outwards motion of the circumference of the droplet by the Marangoni effect.

As we mentioned, nanofibres grew in a perpendicular direction to the circumference of a droplet during the outwards movement of the circumference, which suggests that sheets composed of randomly oriented nanofibres may be formed rather than aligned ones if the motion of the circumference of a droplet is disturbed or stopped by force. An SEM image of typical randomly oriented nanofibres is shown in figure 2(d), where the circumferential motion was stopped by placing a step on the glass substrate.

Supercritical fluids are often used in nanotechnology as well as chemical, electronic and environmental sciences and engineering [30]. Reactions are encouraged, chemicals are extracted, semiconductors are cleaned and nanomaterials and nanostructures can be produced efficiently [31–36] utilizing supercritical fluids. We left nanofibres in supercritical carbon dioxide at 36 $^\circ$C for 2 h to observe the change in the internal structures of the nanofibres. Note that the internal structures of the nanofibres were amorphous as mentioned (see figure 2(c)) and that the critical temperature of carbon dioxide is 31.0 $^\circ$C [37]. An SEM image, EDS mappings and SAED pattern of the nanofibres after the supercritical fluid treatment are shown in figure 3. It is clearly shown that
sulphur was extracted from the nanofibres and fcc lattice structures were formed by C$_{60}$ molecules in the nanofibres.

The present methodology is so simple and the synthesis time is so short that it may well be applied to the synthesis of other nanomaterials composed of carbon nanotubes and graphenes and to the development of nano-/micro-mechanical, -electronic and -biomedical devices.

4. Conclusions

We produced nanofibres composed of C$_{60}$ molecules by dissolving C$_{60}$ molecules and sulphur in benzene and evaporating a droplet of the solution on a glass substrate. Aligned nanofibres were formed by setting the initial concentrations of C$_{60}$ molecules and sulphur in benzene and the initial temperatures of the solution and substrate at appropriate values. It is supposed that sulphur is necessary for nucleation of fibres, whereas the temperature of the substrate needs to be higher than that of a droplet of the solution for the alignment of nanofibres. The internal structures of the nanofibres were amorphous, but sulphur was extracted and the fibres were crystallized by leaving them in supercritical carbon dioxide. The advantage of the present methodology is its simplicity and speed. Nanofibres can be formed directly on biomedical microchips and devices. The present methodology may well be extended to the following research areas: (a) investigation of the effect of other assistance molecules such as metallocenes mixed with benzene or other organic solvents on the nucleation and formation process of nanofibres; (b) synthesis of nanofibres composed of other types of fullerene molecules, carbon nanotubes, graphenes, magnetic nanoparticles and quantum dots; (c) creation of different patterns formed by fullerene molecules by an active control of convective motion in the solution; and (d) surface modifications of the fibres with bio-compatible materials.

Acknowledgments

Part of the present study has been supported by a Grant for the Programme for the Strategic Research Foundation at Private Universities S1101017 organized by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, since April 2011.

References

[1] Zhang N et al 2012 Adv. Mater. 24 2756
[2] Kim J H, Hwang E T, Kang K K, Tatavarty R and Gu M B 2011 J. Mater. Chem. 21 19203
[3] Li D, Frey M W and Baeumner A J 2006 J. Membr. Sci. 279 354
[4] Poland C A, Duffin R, Kinloch I, Maynard A, Wallace A H, Seaton A, Stone V, Brown S, Macnee W and Donaldson K 2008 Nature Nanotechnol. 3 423
[5] Ryman-Rasmussen J P et al. 2009 Nature Nanotechnol. 4 747
[6] Donaldson K, Aiiken R, Tran L, Stone V, Duffin R, Forrest G and Alexander A 2006 Toxicol. Sci. 92 5
[7] Shimazaki J O, Nadejima S, Takaku S, Kanehira K, Sonezaki S and Taniguchi A 2010 Health 2 1456
[8] Aki A, Nihei Y, Asai H, Ukai T, Morimoto H, Nakajima Y, Hanajiri T and Maekawa T 2008 Sensors. Actuator B 131 285
[9] Hughes A D and King M R 2010 Langmuir 26 12155
[10] Li X M, Reinholds D and Calama M C 2007 Chem. Soc. Rev. 36 1350
[11] Mijatovic D, Eijkel J C T and van den Berg A 2005 Lab Chip 5 492
[12] Whitesides G M and Grzybowski B 2002 Science 295 2418
[13] Kroto H W, Heath J R, O’Brien S C, Curl R F and Smalley R E 1985 Nature 318 162
[14] Kadish K M and Ruoff R S 2000 In Fullerenes: Chemistry, Physics, and Technology (New York: Wiley-Interscience)
[15] Kratschmer W, Lamb L D, Fostiropoulos K and Huffman R D 1990 Nature 347 354
[16] Korobov M V, Stukalin E B, Mirakyan A L, Neretin I S, Slovokhotov Y L, Dzyabchenko A V, Ancharov A I and Tolochko B P 2003 Carbon 41 2743
[17] Yao M, Andersson B M, Stenmark P, Sundqvist B, Liu B and Wågberg T 2009 Carbon 47 1181
[18] Miyazawa K, Uwasaki Y K, Obayashi A and Kuwabara M 2002 J. Mater. Res. 17 83
[19] Miyazawa K 2002 J. Am. Ceram. Soc. 85 1297
[20] Cha S I, Lee D Y, Miyazawa K and Wakahara T 2009 J. Phys.: Conf. Ser. 159 012011
[21] Roth G, Adelmann P and Knitter R 1993 Mater. Lett. 16 357
[22] Talyzin A and Jansson U 1999 Thin Solid Films 350 113
[23] Grell A S, Masin F, Céolin R, Gardette M F and Szwarc H 2000 Phys. Rev. B 62 3722
[24] Takabashi H, Matsubara E, Belosludov R V, Matsubara S, Sato N, Muramatsu A, Kawazoe Y and Tohji K 2002 Mater. Trans. 7 1530
[25] Napolitano L G 1984 Science 225 197
[26] Maekawa T and Tanasawa I 1988 Int. J. Heat Mass Trans. 31 285
[27] Nikolov A D, Wasan D T, Chenguara A, Koczo K, Policello G A and Kolossvary I 2002 Adv. Colloid Interface Sci. 96 325
[28] Buravov L L, D’yachenko O A, Konovalikhin S V, Kuszch N D, Lavrent’ev L P, Spitsyna N G, Shilov G V and Yagubskii E B 1994 Russ. Chem. Bull. 43 240
[29] Gardette M-F, Chilouet A, Toscani S, Allouchi H, Agafonov V, Rouland J-C, Szwarc H and Céolin R 1999 Chem. Phys. Lett. 306 149
[30] Hauthal W H 2001 Chemosphere 43 123
[31] Fukuda T, Ishii K, Kurosu S, Whitby R and Maekawa T 2007 Nanotechnology 18 145611
[32] Fukuda T, Maekawa T, Hasumura T, Rantonen N, Ishii K, Nakajima Y, Hanajiri H, Yoshida Y, Whitby R and Mikhalkovsky S 2007 New J. Phys. 9 321
[33] Fukuda T, Watabe N, Whitby R and Maekawa T 2007 Nanotechnology 18 415604
[34] Hasumura T, Fukuda T, Whitby R L D, Aschenbrenner O and Maekawa T 2010 Chem. Phys. Lett. 492 304
[35] Hasumura T, Fukuda T, Whitby R L D, Aschenbrenner O and Maekawa T 2011 J. Nanopart. Res. 13 53
[36] Hayasaki Y, Fukuda T, Hasumura T and Maekawa T 2012 Adv. Nat. Sci.: Nanosci. Nanotechnol. 3 035010
[37] Somayajulu G R 1989 J. Chem. Eng. Data 34 106