Optimization of the liquid–liquid interfacial precipitation method for the synthesis of C₆₀ nanotubes

DORRA MAHDAOUI^{1,2,*} , CHIKA HIRATA², NABIL OMRI¹, TAKATSUGU WAKAHARA², MANEF ABDERRABBA¹ and KUN'ICHI MIYAZAWA³

¹Laboratory of Materials, Molecules and Applications, Preparatory Institute for Scientific and Technical Studies, University of Carthage, BP 51, 2075 La Marsa, Tunis, Tunisia

²National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan

³Department of Chemical Sciences and Technology, Graduate School of Chemical Sciences and Technology, Tokyo University of Science, 12-1-203, Ichigaya Funakawara-Machi, Shinjuku-Ku, Tokyo 162-0826, Japan

*Author for correspondence (mahdaoui.khiaridorra@hotmail.fr)

MS received 28 August 2017; accepted 5 February 2018; published online 7 December 2018

Abstract. Tubular fullerene nanowhiskers called ‘fullerene nanotubes’ are composed of C₆₀ fullerene molecules (C₆₀ NTs) are synthesized at room temperature using the liquid–liquid interfacial precipitation method in the pyridine and isopropyl alcohol (IPA) system. The growth control of fullerene nanotubes is important for their chemical and physical properties as well as for their future applications. In the present study, we investigated the effect of light, water, solvent ratio and temperature on the synthesis of C₆₀ nanotubes. A marked development in the yield of C₆₀ NTs was achieved using dehydrated solvents, a solution with a volume ratio of 1:9 for pyridine: IPA, a growth temperature equal to 5°C and by illuminating the C₆₀-pyridine solution with ultraviolet light (wavelength 302 nm) for 102 h. The synthesized fullerene nanotubes were characterized by different analytical techniques including Raman and Fourier transform infrared spectroscopy, optical microscopy, focussed ion beam scanning electron microscopy and transmission electron microscopy.

Keywords. Fullerene nanotubes; liquid–liquid interfacial precipitation method; solution growth; solvent; temperature; light.

1. Introduction

Since the discovery of fine single crystalline fibres composed of fullerene C₆₀, known by ‘C₆₀ nanowhiskers’ (C₆₀ NWs), in a lead zirconate titanate (PZT) colloidal solution added with C₆₀ [1], many researchers were working to synthesize one-dimensional nanostructures using fullerene molecules to utilize their various novel properties characteristic to the nanodimension. Fullerene C₆₀ nanotubes (C₆₀ NTs) were synthesized for the first time by Liu *et al* using the holes of a porous alumina membrane as the synthetic template; thus prepared C₆₀ NTs were polycrystalline in nature [1,2]. However, the liquid–liquid interfacial precipitation method (LLIP method) is the first established method to fabricate the single-crystal fullerene nanofibres composed of C₆₀ or C₇₀ [3–5]. Fullerene C₆₀ and C₇₀ nanofibres not only can be synthesized by this method, but also the two-component nanofibres composed of C₆₀ and C₇₀. In addition, C₆₀ NFs containing various derivatives of C₆₀ such as C₆₀ (2-methoxycarbonyl-N-methylpyrrolidine)₂, (n²-C₆₀)Pt(PPh₃)₂, C₆₀C₃H₇N, C₆₀[C(COOC₂H₅)₂] and so on, can be synthesized by LLIP method [6–8].

Fullerene nanofibres are pure carbon semiconductors, which behaved like an electron accumulator to accept and

release electrons [9]. Generally, they are described as either non-tubular or tubular. Non-tubular crystalline fullerene nanofibres are called fullerene nanowhiskers (FNWs). However, fullerene nanotubes (FNTs) are long FNFs with tubular structure. On an average, FNTs are >300 nm thick [10]. Another very important property of this material is its flexibility; actually, Young's modulus of C₆₀ NTs was estimated to be 62–107 GPa, which is 1.1–3.3 times larger than that of C₆₀ nanowhiskers [11]. This flexible nature of C₆₀ NTs makes them usable as the light cantilever beams for micro-electro-mechanical systems (MEMS) applications [12]. In addition, C₆₀ nanotubes have wide applications in the field of electronics, optics, catalysts, energy and environment for recovering various useful metals from waste solutions [12,13]. Thanks to all these properties, as different synthesis methods were established to prepare such fullerene C₆₀ NTs, such as solution evaporation [14], template technique [2], surfactant-assisted method [15] and liquid–liquid interfacial precipitation method [16]. Using the LLIP method, many researchers consider that FNWs and nanotubes nucleate at the interface between the good and poor solvents. They are usually grown at or below room temperature. After several days, fullerene nanofibres (FNFs) are fully grown and during this time, the poor solvent slowly diffuses into the fullerene-rich

phase, increasing its hydrophilicity [17]. Compared to other synthesis methods, the LLIP method is simple and financially not costly, but its poor reproducibility and modest yields are problematic.

In this work, we report modified approach based on LLIP method to produce significantly higher yield of C_{60} NTs. The growth of C_{60} NTs was studied as a function of solvent's nature and ratio, effect of UV irradiation time light and temperature. These results shown in further sections could be useful in their future applications.

2. Experimental

To prepare C_{60} NTs and to study the effect of water in pyridine, isopropyl alcohol, IPA (as-received, Wako Pure Chemical Industries Ltd., Japan) was used as a poor solvent of fullerene C_{60} and pyridine (as-received, Wako Pure Chemical Industries Ltd., Japan) as a good solvent. The water content of as-received pyridine was measured to be 0.04% by a Karl Fischer titrator (Coulometer 831 KF). The content of water in prepared pyridine solutions was set to be <4.50 mass% H_2O . Pyridine and IPA were used without further purification.

In a typical procedure, crushed C_{60} fullerene powder (99.5% pure MTR Ltd.) was freshly dissolved in pyridine (Wako) by applying a solubility factor of 0.3 mass% to form C_{60} -saturated pyridine solution. The use of C_{60} fullerene powder (99.5% pure MTR Ltd.) is based on the experimental procedures described in ref. [16]. For maximum fullerene C_{60} solubilization, the prepared C_{60} -pyridine solutions were stored at 5°C; then, fullerene solutions were filtered to remove the undissolved C_{60} powder (450 nm pores, Puradisc TM, Whatman Inc., Clifton, USA). The next step is to put these solutions in quartz glass bottles for better light absorption; then, expose it to UV (UVM-57) 302 nm at different irradiation times to understand the effect of light on the growth of C_{60} NTs. A nine-fold to six-fold volume of excess isopropanol was slowly layered at top of this phase to form the liquid–liquid interface. The interface was prepared in a water bath set at 5°C, where both IPA and C_{60} -pyridine solutions were cooled at the same temperature before mixing. The mixtures were sonicated for 1 min, shaken 10 times by hand to get homogeneous precipitation of embryo crystals of fullerene C_{60} [18], and sonicated using an ultrasonic bath (UNIT Cool thermo UCT 1000) for 1 min. The resulting mixtures were stored in incubators with three different temperature settings of 5, 10 and 20°C to grow the C_{60} NTs. The prepared nanotubes are dried under vacuum.

To express the efficiency of our synthesis, a calculation of yield is necessary. In this study, yield is described by the following expression (equation (1)):

$$Y = \frac{m_s}{m_{th}} \times \frac{n_{NTs}}{n_s} \times 100, \quad (1)$$

where m_s is the mass of synthesized C_{60} NTs, m_{th} the theoretical mass of dissolved C_{60} in pyridine solution, n_{NTs} the

number of specimens C_{60} NTs and n_s the total number of samples.

The C_{60} NTs obtained were characterized by optical microscopy (Nikon-ECLIPSE-ME 600) and JEOL JEM 2800 transmission electron microscopy (TEM) (The University of Tokyo, Tokyo, Japan) at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR; Perkin Elmer, mode: Spectrum two) and Raman (Photon Design) analyses were done for the fibrous precipitates and pure C_{60} powder (99.5% pure MTR Ltd.). The as-grown NTs were then thinned using a focussed beam (FIB) equipped with a scanning electron microscope (SEM) (FIB-SEM, Hitachi NB5000) [19]. The SEM and TEM samples were prepared by dispersing the C_{60} NTs through low agitation and depositing a few drops of solution containing C_{60} NTs on the microgrid. The samples were air-dried for few hours before microscopic investigation.

3. Results and discussion

3.1 Characterization of the obtained C_{60} nanotubes

As shown in the optical micrograph of figure 1, long tubular fibres with brownish and metallic colours were obtained in bottles. These tubular fibres grew to the order of millimetres in length.

The infrared spectrum in figure 2 measured for pristine C_{60} and C_{60} nanotubes shows sharp absorption bands with similar positions. The frequencies measured for C_{60} NTs present four strong lines (524, 575, 1183 and 1429 cm^{-1}). Lines of C_{60} powder are included in table 1. Weak features at 667 cm^{-1} are common to the C_{60} and C_{60} nanotubes spectra and may be due to some contaminants.

Furthermore, Raman spectrometry is a very useful method to know the vibrational state of fullerene molecules. Figure 3 shows Raman spectrum of C_{60} molecules and C_{60} NTs well-dried at room temperature. Since the Raman spectrum of C_{60}

Figure 1. Optical micrograph for the as-prepared C_{60} NTs.

Figure 2. Absorbance FTIR spectra of pristine C_{60} (black curve) and C_{60} (red curve) nanotubes.

Table 1. Observed C_{60} powder infrared line position (cm^{-1}).

V IR (cm^{-1})	Assignment
524	F_{1u} IR active
575	F_{1u} IR active
1182	F_{1u} IR active
1426	F_{1u} IR active

Figure 3. Raman spectra of C_{60} (black curve) and pristine C_{60} (red curve) nanotubes.

NTs strongly resembles that of pristine C_{60} crystals. From the infrared and Raman studies, we can prove that the synthesized C_{60} NTs are composed of only C_{60} molecules.

Figure 4. TEM image of C_{60} nanotubes prepared using 1 (C_{60} -pyridine without water addition):9 (IPA) solvent ratio; its inner diameter is ~ 357 nm.

1 : 9 1 : 8 1 : 7 1 : 6 1 : 5

Figure 5. A liquid-liquid interfacial precipitation of C_{60} fullerene nanotubes using different C_{60} -pyridine:IPA ratios.

To confirm the tubular structure of the synthesized fibres, TEM observations were conducted and the results are presented in figure 4.

As a result, we can confirm that we have successfully synthesized long and tubular fibres composed of C_{60} molecules (C_{60} NTs).

3.2 Effect of solvent ratio on C_{60} NTs growth

As shown in figure 5, long and feathery, light yellow ball of C_{60} FNTs are successfully synthesized in solutions with solvent ratios of C_{60} -pyridine:IPA, 1:9, 1:8 and 1:7 mixtures. On the other hand, mixtures with high amount of good solvent 1:6 and 1:5 do not allow the formation of C_{60} NTs. These results confirm those results previously found [10]. The high yield and faster growth of C_{60} NTs (figure 6) are obtained using 1:9 volume of excess isopropanol. It is noticed that high volume of alcohol provides faster formation of FNTs with higher yield.

Figure 6. Time of growth (hours) of C₆₀ NTs fabricated at different solvent ratios at the same experimental conditions.

It is known that IPA is a bad solvent for fullerene because C₆₀ will not dissolve with polar solvent. At room temperature, the solubility of fullerene C₆₀ in this alcohol is 0.0021 mg ml⁻¹ [20]; on the other hand, C₆₀ shows better solubility in pyridine reaching 0.89 mg ml⁻¹ [21]. So, when a solution of poor solvent was injected into a good solvent, C₆₀ colloids with narrow size distributions were immediately formed [22,23]. This phenomenon may be due to repulsive interaction after addition of polar IPA into non-polar C₆₀-pyridine solution. So, the size of C₆₀-pyridine colloids decreases and there is no aggregation [24]. In fact, C₆₀ colloids play an important role in the nucleation and crystal growth process. Hence, when the volume of the added IPA decreases, the hydrophobic interaction between the two kinds of solvents is not strong enough for C₆₀ colloids size decrease; hence, the formation of C₆₀ NTs becomes harder and slower.

A general decrease in fullerene C₆₀ NTs inner diameter from 1:9 to 1:7 solvent ratios was observed through FIB SEM analyses (figure 7). This result is related to the stability of C₆₀

Figure 7. FIB-SEM images of the C₆₀ NTs by the use of solutions with different volume ratios of C₆₀-saturated pyridine and IPA. Pyridine:IPA (v/v) = (a) 1:9, (b) 1:8 and (c) 1:7; inner diameters are (a) ~357, (b) ~256 and (c) ~144 nm.

seeds. In the crystal growth process, C_{60} seeds are crystal seeds encapsulated with an outer layer of pyridine.

The growth direction of C_{60} NTs is (110) resulting in one-dimensional structure [3,16]. According to the growth mechanism proposed by Piao *et al* [25] during the growth mechanism, the molecules of fullerene prefer the corners of the rectangle cross-section, thanks to the relatively higher energy of these sites; then, C_{60} molecules prefer the edge sites of the cross-section. Finally, the latest sites occupied by these molecules are the central portion of the cross-section, and this crystal growth process will end at the equilibrium point, when the C_{60} seeds are too stable to supply fullerene molecules to the central portion. When the volume ratio of good/poor solvent is 1:9, the solubility of C_{60} molecules in the two solvents is poor; so when a crystal seed is formed and starts to grow, it will suffer from C_{60} concentration depletion. After the nucleation, fullerenes molecules are preferably attached to the corners and edge sites and not the central portions. According to this mechanism, the formation of hexagonal tubes with well-defined hollow interiors is obtained. Further, if the volume ratio of good:poor increases, the concentration of C_{60} in solution increases and becomes high enough to absorb the concentration depletion effect in the central portion of the

growing faces, leading to the decrease in the inner diameter of C_{60} NTs [15,26].

3.3 Effect of water on C_{60} NTs growth

Figure 8 shows optical microscopy images of the fullerene precipitates that were formed using pyridine with different amounts of water (H_2O). Long C_{60} NTs were successfully synthesized when the percentage of added water does not exceed 0.48%. In addition, some images show the granular precipitation, other than fullerene nanotubes. Examples of this granular precipitation are indicated by the white arrows. Those crystals become less with decrease in the water content in pyridine. The formation of this kind of particles means isotropic crystal growth of C_{60} [18]. So, the modes of isotropic and anisotropic crystal growths of C_{60} are strongly related to the percentage of water in pyridine.

The addition of water has a negative effect on the synthesis of C_{60} NTs, this is due to the reduction of interaction forces between C_{60} molecules and pyridine molecules in the solution. Furthermore, the solubility of fullerenes is reduced by the presence of water in the good solvent. In binary (nonpolar–polar) solvents, when the polarity increases, the

Figure 8. Optical micrographs of C_{60} precipitates formed by using pyridine with different H_2O contents: (a) 0.05, (b) 0.48 and (c) 4.2 mass% H_2O .

Figure 9. TEM images of C_{60} precipitates formed by using pyridine with different H_2O contents: (a) 0.048, (b) 0.4475 and (c) 4.2 mass% H_2O .

solubility decreases, because pyridine is capable of forming hydrogen bonds with water, so that the concentration of pyridine, which will interact with C_{60} molecules will be lower. In our previous work, we found that the concentration of C_{60} molecules decreases with increase in water in pyridine solution. In addition, we noticed that the solubility of C_{60} in pyridine decreases significantly when the amount of water in pyridine exceeds 0.557%. These results explain the failure of FNT synthesis when the percentage of water in pyridine is $>0.48\%$ [27]. Really, if the solubility of fullerenes decreases in the presence of water, C_{60} molecules will be removed during the filtration step, so, only small amount of fullerene will participate in C_{60} NT synthesis. Hence, the yield of C_{60} NTs synthesis decreases by increasing the water content in pyridine solution (figure 8).

The second negative effect of water on the synthesis of C_{60} NTs is the formation of granular crystals. Actually, the formation of these crystals is due to the strong interaction between water in pyridine solution and IPA molecules, these two polar solvents are able to form complicated water–IPA molecular cluster that hinders the inter-diffusion between pyridine and IPA as stated in a water–methyl alcohol system [28]. As a result, the driving force of tubes formation will be decreased by the addition of water and leads to the formation of these granular crystals [29].

Further, a decreasing tendency in the inner diameter of C_{60} NTs resulting from the increase in the amount of water in pyridine was observed through TEM analysis (figure 9). In this work, the inner diameter values of C_{60} NTs were measured according to three percentages of added water

(0.05, 0.48 and 4.2%). The results of these measurements are presented in figure 10. As seen, the value of the mean inner diameter decreases from 320 nm until it reaches zero for 4.2% of added water.

C₆₀ NTs with different inner diameters are obtained when the C₆₀ seeds have different equilibrium points. The stability of suppliers is related to the number of fullerenes it contains. The smallest suppliers are composed of a small number of fullerene molecules, which will suffer from C₆₀ depletion; as a result, these spheres are more stable and unable to provide a high fullerene number to the crystal growth.

Figure 10. Mean inner diameter of C₆₀ NTs as a function of water content (mass%) in pyridine.

Solvent polarity plays a significant role in the aggregation process of C₆₀ in the solution. The aggregation numbers and sizes of the aggregates in neat solvents like pyridine are small. On the contrary, in mixed solvents and neat polar liquids, the aggregates are large [30]. After IPA injection, the most stabilized sphere-like fullerene particles with smallest diameter encapsulated with an outer layer of pyridine were formed from the small aggregates. As a result, these stable fullerenes reach the equilibrium point easily and they are not able to supply C₆₀ to the central portion. However, from large aggregates, we can only form large sphere-like fullerene particles, these are unstable C₆₀ seeds and capable to provide fullerene to the central portion. In general, if the amount of water increases in pyridine solution, formation of large aggregates occurs that contributes to the production of unstable C₆₀ seeds. On the other hand, the addition of water negatively affects the protection layer of pyridine outside the fullerene particles; this is due to the reduction of interaction forces between C₆₀ molecules and pyridine molecules in solution. In fact, the protection layer of pyridine extends the duration of the C₆₀ supply stage, which means low supersaturation at the face and the formation of C₆₀ NTs with large inner diameter [24]. So, the supersaturation of C₆₀ at the crystal face is a function of water content in pyridine.

3.4 Effect of UV irradiation on C₆₀ NTs growth

It was reported that the yield and growth rate of C₆₀ NTs are more significantly promoted by irradiation with ultraviolet light (wavelength 302 nm) compared with that of illuminated with visible light (436 nm) [10]. In this work, we chose

Figure 11. Optical photographs of C₆₀ NTs formed in the vicinity of pyridine/IPA after UV irradiation: (a) 0, (b) 48, (c) 87 and (d) 102 h.

wavelength of 302 nm for different times of irradiation from 0 to 102 h. As can be seen in figure 11, no C₆₀ NTs were observed for the first series of non-irradiated solutions (a). However, the use of UV light with increasing the duration of C₆₀-pyridine solutions exposure, produce more abundant yield of NTs.

The growth process of C₆₀ nanotubes is controlled by the properties of the charge transfer (CT) adducts of C₆₀-pyridine solution and their aggregation profile on the nucleation. Really, one of the most fascinating and remarkable properties of fullerenes is the ability to accept electrons [31].

Figure 12. Comparison of yield (%) of growth between C₆₀ NTs fabricated after UV exposure: (a) 0, (b) 48, (c) 87 and (d) 102 h.

In addition, its low energy first excited singlet state makes this molecule ready to accept multiple electrons and become a potential electron accumulator [32]. Further, the existence of a nitrogen atom with its lone electron pair in pyridine molecule allows it to have the character of an electron donor. Therefore, CT complex may exist in C₆₀-pyridine system under certain conditions. The existence of CT complex is exemplified by the colour change of the C₆₀-pyridine solution. When fullerene C₆₀ molecule is dissolved in pyridine, the colour of C₆₀-pyridine solution is purple-pinkish at the beginning, but turns into burgundy over the time [33]. This colour change is accelerated by UV irradiation, hence, UV light stimulates the aggregation process, resulting in the phase transition of the C₆₀-pyridine colloid. In fact, when CT complexes are formed, pyridine is adsorbed by fullerene molecules. In this case, pyridine acts as a surfactant around fullerene molecules [34]. Such interaction between C₆₀ and pyridine plays an important role in the nucleation and crystal growth process. Thus, the irradiation time of UV light played an important role in the synthesis of C₆₀ NTs and the optimal irradiation time was about 102 h. As shown in figure 12, the crystallization and yield of C₆₀ NTs may be reinforced by increasing the duration of C₆₀-pyridine solution exposure to UV light.

3.5 Effect of incubation temperature on C₆₀ NTs growth

The yield of the synthesized C₆₀ NTs was gauged depending on three incubation temperatures (5, 10 and 20°C). We have successfully synthesized FNTs for the different temperatures. However, the temperature variation affects significant yield of the synthesis. The results of these

Figure 13. Optical photographs of C₆₀ NTs formed in the vicinity of pyridine/IPA after incubation at (a) 5, (b) 10 and (c) 20°C.

Figure 14. Comparison of yield (%) of growth between C₆₀ NTs fabricated after incubation at (a) 5, (b) 10 and (c) 20°C.

measurements are presented in figures 13 and 14. It is observed that the growth yield of FNTs tends to increase with decrease in the incubation temperature. The optimum incubation temperature to obtain a maximum of FNTs was 5°C.

In the previous work, Ringor *et al* [10] indicate that the decrease in solubility of C₆₀ molecules in the pyridine–IPA mixture due to the decrease of temperature is the main cause for the raise in yield of the synthesis. Contrary to this idea, the solubility of C₆₀ in pyridine increases with decreasing temperature [27]. After IPA addition, C₆₀–pyridine colloids will be formed and pyridine appears to act as a surfactant around fullerene molecules protecting them from this polar solvent. So, when poor solvent is added, crystal seeds were formed and acted as the fullerene suppliers in the crystal growth process. Really, if the solubility of C₆₀ in pyridine–IPA increases; as a result, the number and the stability of colloids are more important. Thus, the yield of C₆₀ NTs increases.

4. Conclusions

In summary, the yield and growth rate of FNTs are notably improved by varying different parameters, such as volume ratio, nature of solvents, irradiation time and incubation temperature.

It was found that C₆₀ NTs with high yield and faster growth were synthesized using dehydrated mixtures of 1:9 (C₆₀–pyridine–IPA) solvent ratios. Furthermore, the addition of water in pyridine has a negative effect on the yield of the synthesis also on the inner diameter of C₆₀ NTs, which reaches zero when the percentage of water is more or equal to 4.2%. In addition, an optimum irradiation time equal to 102 h was set for this synthesis. At 5°C, the growth of FNTs was ameliorated.

Acknowledgements

Part of this research was supported by Japan Society for the Promotion of Science JSPS KAKENHI (grant number 26600007). TEM analysis of this work was conducted at Advanced Characterization Nanotechnology Platform of Tokyo University, supported by ‘Nanotechnology platform’ of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

- [1] Miyazawa K, Obayashi A and Kuwabara M 2001 *J. Am. Ceram. Soc.* **84** 3037
- [2] Liu H, Li Y, Jiang L, Luo H, Xiao S, Fang H *et al* 2002 *J. Am. Chem. Soc.* **124** 13370
- [3] Miyazawa K, Kuwasaki Y, Obayashi A and Kuwabara M 2002 *J. Mater. Res.* **17** 83
- [4] Miyazawa K and Suga T 2004 *J. Mater. Res.* **19** 3145
- [5] Miyazawa K, Minato J, Yoshii T, Fujino M and Suga T 2005 *J. Mater. Res.* **20** 688
- [6] Miyazawa K, Mashino T and Suga T 2003 *J. Mater. Res.* **18** 2730
- [7] Miyazawa K, Minato J, Mashino T, Nakamura S, Fujino M and Suga T 2006 *Nukleonika* **51** S41
- [8] Miyazawa K and Suga T 2004 *J. Mater. Res.* **19** 2410
- [9] Zhang X, Jiao K, Piao G, Liu S and Li S 2009 *Synth. Met.* **159** 419
- [10] Ringor C L and Miyazawa K 2008 *Diamond Relat. Mater.* **17** 529
- [11] Kizuka T, Saito K and Miyazawa K 2008 *Diamond Relat. Mater.* **17** 972
- [12] Miyazawa K 2009 *J. Nanosci. Nanotechnol.* **9** 41
- [13] Miyazawa K and Ringor C 2008 *Mater. Lett.* **62** 410
- [14] Wang B L, Liu B, Liu D, Yao M, Hou Y, Yu S *et al* 2006 *Adv. Mater.* **18** 1883
- [15] Ji H X, Hu J S, Tang Q X, Song W G, Wang C R, Hu W P *et al* 2007 *J. Phys. Chem. C* **111** 10498
- [16] Minato J, Miyazawa K and Suga T 2005 *Sci. Technol. Adv. Mater.* **6** 272
- [17] Rauwerdink K, Liu J F, Kintigh J and Miller G P 2007 *Microsc. Res. Tech.* **70** 513
- [18] Miyazawa K and Hotta K 2010 *J. Cryst. Growth* **312** 2764
- [19] Miyazawa K, Kuriyama R, Shimomura S, Wakahara T and Tachibana M 2014 *J. Cryst. Growth* **388** 5
- [20] Heymann D 1996 *Carbon NY* **34** 627
- [21] Ruoff R S, Tse D S, Malhotra R and Lorents D C 1993 *J. Phys. Chem.* **97** 3379
- [22] Nath S, Pal H, Palit D K, Sapre A V and Mittal J P 1998 *J. Phys. Chem. B* **102** 10158
- [23] Bokare A D and Patnaik A 2005 *J. Phys. Chem. B* **109** 87
- [24] Qu Y, Yu W, Niu N, Liang S, Li G and Piao G 2012 *Condens. Matter Phys.* <https://doi.org/10.5402/2012/140842>
- [25] Krueger G C and Miller C W 1953 *J. Chem. Phys.* **21** 2018

- [26] Andrievsky G V, Klochkov V K, Bordyuh A B and Dovbeshko G I 2002 *Chem. Phys. Lett.* **364** 8
- [27] Mahdaoui D, Abderrabba M, Hirata C, Wakahara T and Miyazawa K 2016 *J. Sol. Chem.* <https://doi.org/10.1007/s10953-016-0497-3>
- [28] Guo J H, Luo Y, Augustsson A, Kashtanov S, Rubensson J E, Shuh D K *et al* 2003 *Phys. Rev. Lett.* <https://doi.org/10.1103/91.157401>
- [29] Miyazawa K and Hotta K 2011 *J. Nanopart. Res.* <https://doi.org/10.1007/s11051-010-0132-y>
- [30] Nath S, Pal H, Sapre A V and Mittal J P 2003 *J. Photosci.* **10** 105
- [31] Imahori H, Hagiwara K, Akiyama T, Taniguchi S, Okada T and Sakata Y 1995 *Chem. Lett.* 265
- [32] Kuciauskas D, Lin S, Seely G R, Moore A L, Moore T A, Gust D *et al* 1996 *J. Phys. Chem.* **100** 15926
- [33] Cheng J, Fang Y, Huang Q, Yan Y J and Li X Y 2000 *Chem. Phys. Lett.* **330** 262
- [34] Mrzel A, Mertelj A, Omerzu A, Copic M and Mihailovic D 1999 *J. Phys. Chem. B* **103** 11256