Unusual Shapes of C_{60} Crystals Formed at Liquid–Liquid Interfaces

Hu Yan,*[1] Tsubasa Kagata,[1] Takuya Uchida,[2] Takayuki Uematsu,[1] Yu Iriyama,[2] and Hidenori Okuzaki*[1]
[1]*Laboratory of Organic Robotics, Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-4-37 Takeda, Kofu 400-8511*
[2]*Division of Interdisciplinary Sciences, University of Yamanashi, 4-4-37 Takeda, Kofu 400-8510*

(Received August 10, 2009; CL-090738; E-mail: yanhu@yamanashi.ac.jp, okuzaki@yamanashi.ac.jp)

We have found some unusually shaped C_{60} crystals which formed at liquid–liquid interfaces when *m*-xylene and ethanol were used as good and poor solvents, respectively. The crystals coexisted with large amounts of needle-like or whisker-like crystals which likely form at the initial stage of mixing the two solvents, probably indicating that this system follows Ostwald rule of stages like well-studied isoxazolone dye which has two polymorphs, i.e., the least stable needle-like one with a small size and the most stable rhombic crystal with a large size.

In 1985 Kroto et al. discovered C_{60} and named it Buckminsterfullerene (to date simply fullerene) after Richard Buckminster Fuller or after the Fuller Dome (also geodesic dome).[1] Since the discovery the unique physical and chemical properties of the C_{60} have attracted great attention.[2] One application is utilization of C_{60} crystals, usually prepared by physical vapor depositions, as an n-type semiconductor in organic field effect transistors.[3,4] Fullerences prepared by physical vapor deposition have been well studied in terms of crystal structure and have been found to be a face-centered cubic phase with a lattice constant, *a* of 14.13 Å.[5–8]

In contrast to the physical vapor deposition, solvent-based crystallization provides rich polymorphism in the C_{60} crystals thanks to recrystallization at the liquid–liquid interface, as reported by Miyazawa et al.[9,10] The solution-based method can give various crystal polymorphs such as micrometer- or nanometer-scaled whiskers,[9,10] tubes,[11] wires,[12] rods,[13] and trees.[14] Recently, Sathish et al. observed transformation of 2D nanosheets of the C_{60} crystal into 1D nanorods,[15] and Masuhara et al. reported various shapes of the fine C_{60} crystal with a monodispersity.[16]

Shinohara et al. investigated C_{60} crystallization at liquid–liquid interfaces in short time-scale by using a microfluidic device and observed in situ metastable phases of the C_{60} crystals formed in very short time-scale.[17] As a result, the C_{60} crystals, solvent-contained face-centered cubic phase with a lattice constant *a* of 23.3 Å, showed various shapes such as tubes, spheres, open-ended hollows columns, stars, branches, and trees, which was considered to be not observed in usual flask experiments due to Ostwald rule of stages.[17]

In the Ostwald rule of stages,[18] the least stable phase of crystal forms first because it is kinetically favored, and finally the most stable phase forms being thermodynamically most favored. Transition between the least stable phase and the most stable phase usually occurs via solvent, i.e., dissolution and recrystallization. A good example for such phase transition which follows the Ostwald rule of stages is a yellow isoxazolone dye which is utilized as a filter dye in photographic films.[19]

Herein we report some unusual shapes of C_{60} crystals formed at liquid–liquid interfaces, observed in flask experiments. We also preliminarily discuss on polymorphism and phase transition which follows the Ostwald rule of stages.

We prepared C_{60} crystals by using *m*-xylene and ethanol as good and poor solvents, respectively, according to a modified procedure reported by Miyazawa et al.[9] Crystallization was typically performed as follows: *m*-xylene solution containing 0.14 mmol % of C_{60} (99.9%, Aldrich) was prepared at room temperature. After addition of ethanol with a volume ratio of 1:2 or 1:1 against the *m*-xylene solution, the solution was placed in a refrigerator (5 °C) for several days. The C_{60} crystals were separated from the solution and observed by scanning electron microscopy (SEM, JEOL JSM-6510) after drying and Au/Pd-sputtering.

After addition of ethanol the solution was placed in a refrigerator for seven days giving mainly needle-like crystals. The crystals were less than 1-μm wide and several tens μm long and were observed with a few giant block measuring less than 10 μm in width and several tens μm in length as shown in Figures 1–3.

In Figure 1, there are two kinds of two branched C_{60} crystals where the length of the two branches is almost the same. Other large, thick, and unbranched blocks were also observed. The C_{60} crystal in the center of the image is symmetric and has an angle of 60° between the two branches with a thickness of 1.5 μm, and the cross sections of the branch ends are hexagonal. Such symmetric branches are to the best of our knowledge rare in crystal-

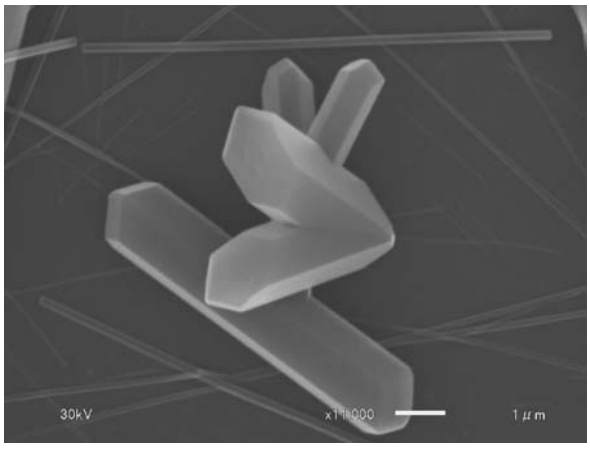

Figure 1. SEM image of the C_{60} crystals formed at *m*-xylene–ethanol interfaces (volume ratio of ethanol against *m*-xylene solution of C_{60} is 1:2). A few unusual shapes of the C_{60} crystals were observed among a large number of long needle shapes of the C_{60} crystals. The C_{60} crystal at the center of the image has an angle of 60° between the two branches with a thickness of 1.5 μm and the cross sections of the branch ends are hexagonal. Scale bar is 1 μm.

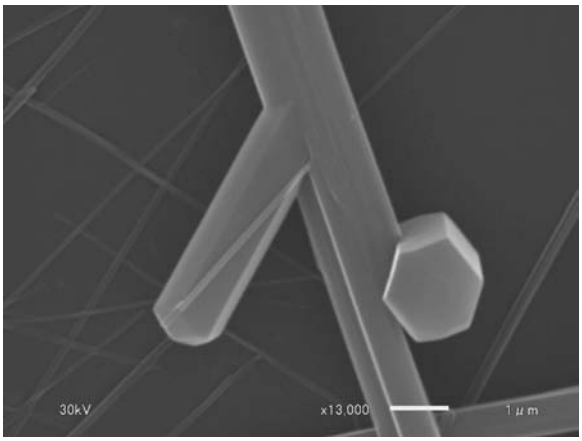

Figure 2. SEM image of the C_{60} crystals formed at *m*-xylene–ethanol interfaces (volume ratio of ethanol against *m*-xylene solution of C_{60} is 1:2). A few unusual shapes of the C_{60} crystals were observed among a large number of long needle shapes of the C_{60} crystals. The C_{60} crystal at the center of the image has an angle of 45° between the two branches. The end cross sections of the block-like C_{60} crystal which may fuse on the branched one is perfectly hexagonal. Scale bar is 1 μm.

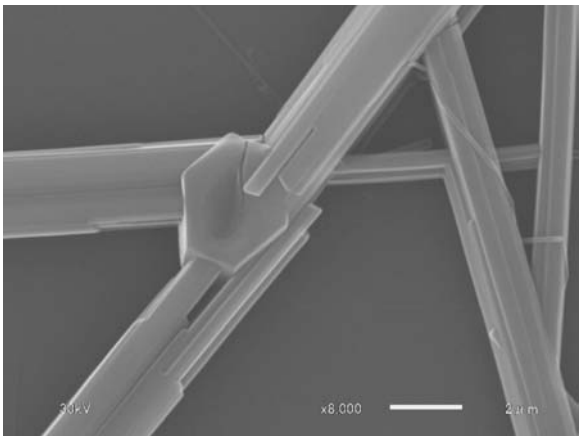

Figure 3. SEM image of the C_{60} crystals formed at *m*-xylene–ethanol interfaces (volume ratio of ethanol against *m*-xylene solution of C_{60} is 1:1). A few unusual shapes of the C_{60} crystals were observed among a large number of long needle shapes of the C_{60} crystals. Three thick and long rod-like C_{60} crystals may fuse on a block. Among them two rods fuse to each other with an angle of 180°, and the two rods fuse on a third rod with angles of 135 and 45°, respectively. Scale bar is 2 μm.

lization at liquid–liquid interfaces. It should be noted, not scientifically but artistically, that the unusual shapes of the crystals seem to resemble micrometer-scale wood carvings made by a skilled carpenter.

In Figure 2, there is one branched C_{60} crystal which fused vertically with another block-like crystal. The long branch and the block have the same diameter of 1.5 μm. The other branch is thin and short. The giant crystal in Figure 3 is more complicated in shape. Three thick and long rod-like C_{60} crystals may fuse on a block-like one. Among them two rods fuse to each other with an angle of 180°, and the two rods fuse to a third rod with angles of 135 and 45°, respectively. Noting that the ratio of the poor solvent against the good solvent crucially influences the morphology of the C_{60} crystals formed at the liquid–liquid interfaces.[20]

The relationship between the needle-like crystals and the giant crystals of unusual shape is preliminarily but likely discussed in terms of polymorphism which follows Ostwald rule of stages like the case of isoxazolone dye.[19] The needle-like crystals which may be a metastable phase can be observed immediately after addition of the poor solvent, ethanol, while giant crystals which may be the stable one only can be observed after placing the solution in the refrigerator for several days. And some traces after dissolution of the needle-like crystals were also observed. It is speculated that the first formed needles provide a solute source for propagation of the giant crystals. The exact mechanism, however, can be verified only based on X-ray diffraction and differential scanning calorimetric measurements of the C_{60} crystal which has to date failed to provide sufficient information due to limited amount of the giant crystals at this stage.

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162.
2 A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Plasta, A. P. Ramirez, A. R. Kortan, *Nature* **1991**, *350*, 600.
3 K. Itaka, M. Yamashiro, J. Yamaguchi, M. Haemori, S. Yaginuma, Y. Matsumoto, M. Kondo, H. Koinuma, *Adv. Mater.* **2006**, *18*, 1713.
4 H. Yan, T. Kagata, H. Okuzaki, *Appl. Phys. Lett.* **2009**, *94*, 23305.
5 A. F. Hebard, R. C. Haddon, R. M. Fleming, A. R. Kortan, *Appl. Phys. Lett.* **1991**, *59*, 2109.
6 J. A. Dura, P. M. Pippenger, N. J. Halas, X. Z. Xiong, P. C. Chow, S. C. Moss, *Appl. Phys. Lett.* **1993**, *63*, 3443.
7 R.-F. Xiao, *J. Cryst. Growth* **1997**, *174*, 821.
8 M. Tan, B. Xu, H. Li, Z. Qi, Y. Xu, *J. Cryst. Growth* **1997**, *182*, 375.
9 K. Miyazawa, Y. Kuwasaki, A. Obayashi, M. Kuwabara, *J. Mater. Res.* **2002**, *17*, 83.
10 S.-H. Lee, K. Miyazawa, R. Maeda, *Carbon* **2005**, *43*, 887.
11 K. Rauwerdink, J.-F. Liu, J. Kintigh, G. P. Miller, *Microsc. Res. Tech.* **2007**, *70*, 513.
12 J. Geng, W. Zhou, P. Skelton, W. Yue, I. A. Kinloch, A. H. Windle, B. F. G. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 2527.
13 Y. S. Woo, D. Y. Jeon, I. T. Han, Y. J. Park, H. J. Kim, J. E. Jung, J. M. Kim, N. S. Lee, *J. Appl. Phys.* **2003**, *94*, 6789.
14 S. I. Cha, D. Y. Lee, K. Miyazawa, T. Wakahara, *J. Phys.: Conf. Ser.* **2009**, *159*, 012011.
15 M. Sathish, K. Miyazawa, J. P. Hill, K. Ariga, *J. Am. Chem. Soc.* **2009**, *131*, 6372.
16 A. Masuhara, Z. Tan, H. Kasai, H. Nakanishi, H. Oikawa, *Jpn. J. Appl. Phys.* **2009**, *48*, 050206.
17 K. Shinohara, T. Fukui, H. Abe, N. Sekimura, K. Okamoto, *Langmuir* **2006**, *22*, 6477.
18 W. Ostwald, *Z. Phys. Chem.* **1897**, *22*, 289.
19 E. Aret, H. Meekes, E. Vlieg, G. Deroover, *Dyes Pigm.* **2007**, *72*, 339.
20 K. Hotta, K. Miyazawa, *J. Phys.: Conf. Ser.* **2009**, *159*, 012021.

Published on the web (Advance View) September 12, 2009; doi:10.1246/cl.2009.988