Shape Control of Fullerene Microparticles by Using Ethylenediamine

Ken-ichi Matsuoka,[1] Satoshi Matsumura,[1] Tsuyoshi Akiyama*[1,2] and Sunao Yamada*[1,2,3]
[1]*Department of Materials Physics and Chemistry, Graduate School of Engineering,*
Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395
[2]*Department of Applied Chemistry, Faculty of Engineering, Kyushu University,*
744 Moto-oka, Nishi-ku, Fukuoka 819-0395
[3]*Center for Future Chemistry, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395*

(Received June 4, 2008; CL-080565; E-mail: t-akitcm@mbox.nc.kyushu-u.ac.jp)

[60,70]-Fullerene–ethylenediamine microparticles with sub-μm size were obtained by simply mixing fullerene and ethylenediamine in organic solvents under ambient condition. Amazingly, well-defined rhombic dodecahedral particles were obtained for C_{70}–ethylenediamine adducts only in the mixing ratio of C_{70}:ethylenediamine = 1:1000.

Fullerenes have been considered as a promising nanocarbon material for use in high-performance (photo)electronic devices.[1] To realize this, several approaches for tailor-made functionalization of fullerenes have been carried out, such as implanting organic functional groups,[2] solubilization,[3] and clustering.[4] Especially, fullerene clusters have been attracting much attention because assemblies of fullerenes exhibit high mobility of electrons.[5] The most popular method for the preparation of C_{60} clusters is sedimentation (precipitation) from a solution of C_{60} by the addition of a poor solvent.[6] As to C_{60} clusters, Kamat et al. reported a photoelectric conversion property of sub-μm C_{60} clusters.[6,7] Considering these recent developments, control of shapes and structures of fullerene clusters is an extremely attractive research goal to materialize tailor-made high-performance molecular electronic devices using fullerenes as a component.

In the meantime, early studies reported that the addition reaction between C_{60} and some aliphatic diamines generated cluster-like precipitates, though no morphological studies were described.[8–10] This addition reaction seems to be useful for the shape and size control of fullerene clusters. As a verification, we recently found that the reaction of C_{60} with a large excess of ethylenediamine (EDA) afforded uniform sub-μm spheres consisting of C_{60} and EDA. In addition, we also found that the resultant sub-μm spheres substantially enhanced photocurrent generation from a polythiophene film.[11]

In this study, we have investigated the effect of mixing ratio of fullerene (C_{60} and C_{70}) to EDA on the shape of resultant fullerene–EDA products. Amazingly, well-defined rhombic dodecahedral microparticles of C_{70}–EDA product was obtained only in the mixing ratio of C_{70}:EDA = 1:1000.

The preparation procedure of fullerene–EDA microparticles is as follows: In a typical case, 10 mL of toluene solution of C_{60} (14.4 mg, 2×10^{-3} mol dm^{-3}) and another toluene solution (10 mL) of EDA (100, 1000, and 10000 equiv to C_{60}) were prepared independently. The solutions were mixed at room temperature under sonication. The color of the mixed solution changed from brown to dark green. The period of color change depended on the ratio of C_{60} and EDA. The reaction mixture was left at room temperature for 30 min to 2 days (after completion of color changing). Resultant sub-μm powders of C_{60}–EDA products were collected by vacuum filtration and dried in vacuo, to obtain C_{60}–EDA microparticles, denoted as C_{60}PA, C_{60}PB, and C_{60}PC, respectively, where the mixing ratios of C_{60}:EDA were 1:100, 1:1000, and 1:10000, respectively. In the preparation of C_{70}–EDA products, 10 mL of *o*-dichlorobenzene/toluene (3/7 v/v) solution of C_{70} (16.8 mg, 2×10^{-3} mol dm^{-3}) was used instead of toluene solution of C_{60}. Resultant products, C_{70}PA, C_{70}PB, and C_{70}PC, with the mixing ratios (C_{70}:EDA) of 1:100, 1:1000, and 1:10000, respectively, by the same protocol as in the case of C_{60}–EDA preparation, were also sub-μm powders. It should be noted that the formation of C_{70}PB was exceptionally instantaneous, while other samples were formed in time courses.

Scanning electron microscopy (SEM) images of the fullerene–EDA adducts are shown in Figure 1. Randomly fused microparticles of C_{60}–EDA products were observed in the case of C_{60}PA and C_{60}PC. On the other hand, isolated spherical particles with the mean diameter of 325 ± 24 nm were observed in the case of C_{60}PB. A similar tendency could be seen in the case of C_{70}–EDA products. The roughly spherical microparticles of C_{70}–EDA products were observed in the case of C_{70}PA and

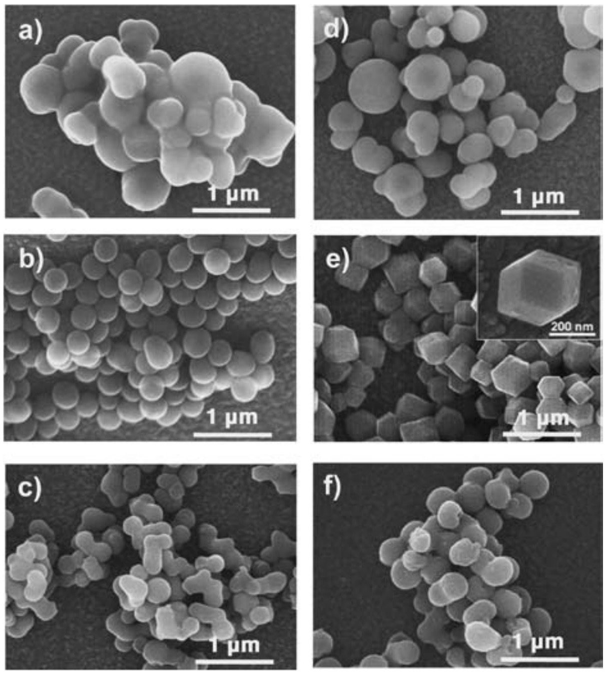

Figure 1. SEM images of fullerene–EDA adducts, a) C_{60}PA, b) C_{60}PB, c) C_{60}PC, d) C_{70}PA, e) C_{70}PB, and f) C_{70}PC.

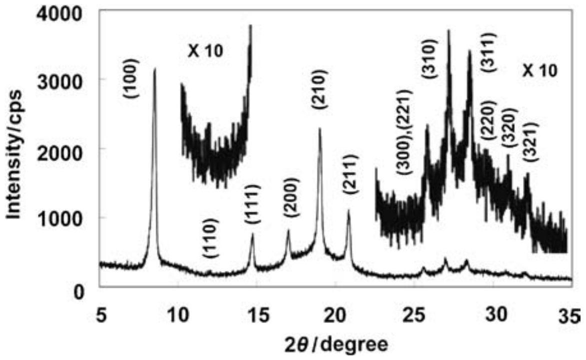

Figure 2. XRD pattern of C_{70}PB.

C_{70}PC. Note, however, that rhombic dodecahedral particles were observed in the case of C_{70}PB with highly regular dimensions. Sizes of C_{70}PB were in the range of 200–500 nm.

From elemental analysis of resultant fullerene–EDA products, the composition ratio of C_{60}:EDA in the case of C_{60}PB was estimated to be about 1:3. In the case of C_{70}PB, the ratio of C_{70}:EDA was also about 1:3. The reason for this similarity for the composition ratio is not clear at this stage. In the case of other fullerene–EDA adducts, the composition ratios of fullerene to EDA varied from 1:5 to 1:6.5. These values were relatively larger than that of fullerene–EDA adducts of C_{60}PB and C_{70}PB.

Powder X-ray diffraction (XRD) patterns of fullerene–EDA products were measured to investigate the structural properties. As to C_{70}–EDA products, C_{70}PB gave sharp peaks as shown in Figure 2, though other adducts showed much broader peaks. In the case of C_{60}–EDA products, on the other hand, all peaks were broad, yet the peaks of C_{60}PB were relatively sharp (see Supporting Information).[13] These results suggest that C_{70}PB has the highest structural regularity among the fullerene–EDA products in this study.

Rhombic dodecahedron holds four threefold axes and three fourfold axes, expressing cubic symmetry of $m3m$ point group class, and its twelve well-defined crystal faces can be indexed to {110} planes.[12] Considering the cubic symmetry of C_{70}PB, its peaks are assignable to a simple cubic lattice structure as indexed in Figure 2, and the lattice constant was estimated to be about $a = 10.4\,\text{Å}$.

Figure 3 shows absorption spectra of C_{70}–EDA products. All spectra were measured using an integration sphere. C_{70}PB showed a broad absorption band over the wide near-infrared (NIR) region with a shoulder at around 1100 nm. This broad absorption is probably due to a charge-transfer or electron-transfer interaction between EDA and C_{70}. On the contrary, other C_{70}–EDAs and all C_{60}–EDAs showed no appreciable absorption bands around NIR region different from the case of C_{70}PB (see Supporting Information).[13] These results suggest that in the case of C_{70}PB, the driving force for crystal structure formation is not only the well-known addition reaction between amine and fullerene but also steric and/or electrostatic interactions between C_{70} and EDA.

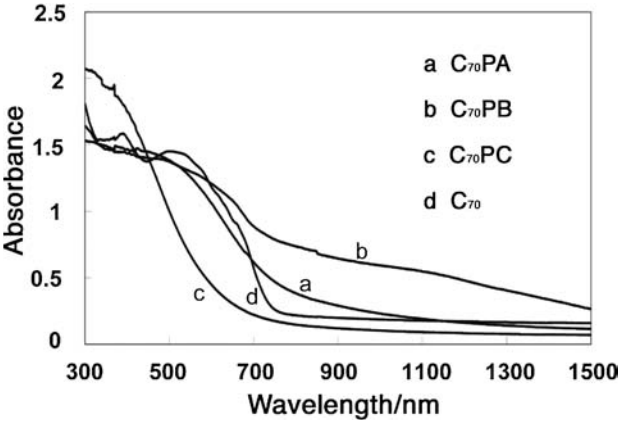

Figure 3. Absorption spectra of C_{70}–EDA products and C_{70} (measured in KBr pellet).

Although the detailed mechanism is still not clear, it implies that some specific interactions between C_{70} and EDA play an important role for the formation of rhombic dodecahedral particles. Further investigation is now in progress.

In this study, we have demonstrated that the control of fullerene–EDA interaction is a fascinating approach to organize fullerenes into specific objects. This approach seems to be applicable to the higher fullerenes, carbon nanotubes, and related compounds. We have already examined various combinations of fullerenes and aliphatic amines, and results will appear elsewhere.

References and Notes

1 a) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **1992**, *258*, 1474. b) S. Morita, A. A. Zakhidov, K. Yoshino, *Solid State Commun.* **1992**, *82*, 249.
2 a) F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf, C. Thilgen, *Helv. Chim. Acta* **1993**, *76*, 2445. b) M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519. c) G. P. Miller, *C. R. Chim.* **2006**, *9*, 952.
3 T. Andersson, K. Nilsson, M. Sundahl, G. Westman, O. Wennerström, *J. Chem. Soc., Chem. Commun.* **1992**, 604.
4 Y.-M. Wang, P. V. Kamat, L. K. Patterson, *J. Phys. Chem.* **1993**, *97*, 8793.
5 S. Kobayashi, T. Takenobu, S. Mori, A. Fujiwara, Y. Iwasa, *Appl. Phys. Lett.* **2003**, *82*, 4581.
6 P. V. Kamat, S. Barazzouk, S. Hotchandani, K. G. Thomas, *Chem.—Eur. J.* **2000**, *6*, 3914.
7 P. V. Kamat, S. Barazzouk, K. G. Thomas, S. Hotchandani, *J. Phys. Chem. B* **2000**, *104*, 4014.
8 T.-Y. Kuo, J. R. Hwu, T. M. Chang, U.S. Patent 5679861, **1997**.
9 A. Ulug, A. Mete, B. Ulug, *Fullerenes, Nanotubes, Carbon Nanostruct.* **1997**, *5*, 1651.
10 J. R. Hwu, T.-Y. Kuo, T. M. Chang, H. V. Patel, K.-T. Yong, *Fullerenes, Nanotubes, Carbon Nanostruct.* **1996**, *4*, 407.
11 K. Matsuoka, H. Seo, T. Akiyama, S. Yamada, *Chem. Lett.* **2007**, *36*, 934.
12 C. Yu, B. Tian, J. Fan, G. D. Stucky, D. Zhao, *J. Am. Chem. Soc.* **2002**, *124*, 4556.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

Published on the web (Advance View) August 2, 2008; doi:10.1246/cl.2008.932