

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/24305511>

# Solvent Engineering for Shape-Shifter Pure Fullerene (C-60)

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · MAY 2009

Impact Factor: 12.11 · DOI: 10.1021/ja902061r · Source: PubMed

CITATIONS

96

READS

40

4 AUTHORS, INCLUDING:



**Marappan Sathish**

Central Electrochemical Research Institute

44 PUBLICATIONS 1,485 CITATIONS

SEE PROFILE



**Jonathan P Hill**

National Institute for Materials Science

286 PUBLICATIONS 8,621 CITATIONS

SEE PROFILE



**Katsuhiko Ariga**

National Institute for Materials Science

623 PUBLICATIONS 21,426 CITATIONS

SEE PROFILE

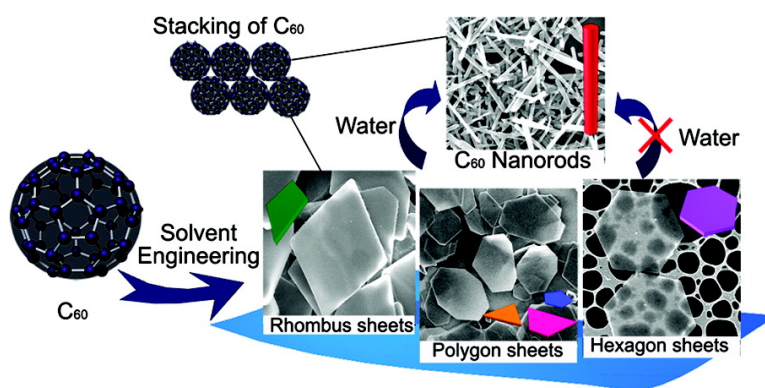
Communication

# Solvent Engineering for Shape-Shifter *Pure Fullerene (C)*

Marappan Sathish, Kun'ichi Miyazawa, Jonathan P. Hill, and Katsuhiko Ariga

*J. Am. Chem. Soc.*, **2009**, 131 (18), 6372-6373 • DOI: 10.1021/ja902061r • Publication Date (Web): 17 April 2009

Downloaded from <http://pubs.acs.org> on May 6, 2009



## More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

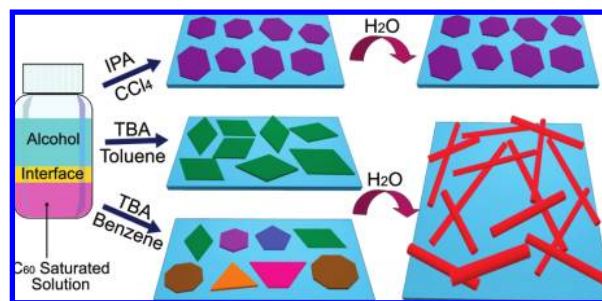
[View the Full Text HTML](#)

Solvent Engineering for Shape-Shifter *Pure Fullerene (C<sub>60</sub>)*Marappan Sathish,<sup>\*,†,‡</sup> Kun'ichi Miyazawa,<sup>\*,†</sup> Jonathan P. Hill,<sup>‡</sup> and Katsuhiko Ariga<sup>\*,‡</sup>*Fullerene Engineering Group and WPI Center for Materials Nanoarchitectonics (MANA), National Institute For Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan*

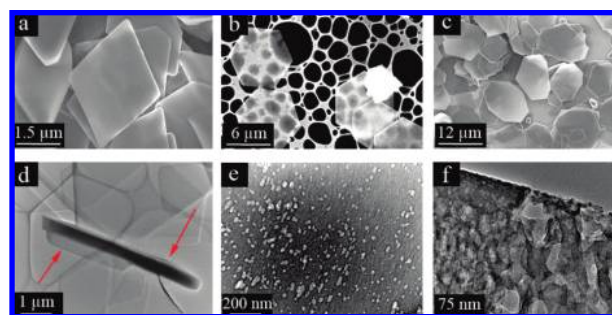
Received March 17, 2009; E-mail: MARAPPAN.Sathish@nims.go.jp; MIYAZAWA.Kunichi@nims.go.jp; ARIGA.Katsuhiko@nims.go.jp

Preparation of nano- and microstructures with predetermined morphologies through self-assembly is the key process of the bottom-up approaches to nanotechnology.<sup>1</sup> In particular, construction of shape-defined nanomaterials<sup>2</sup> of functional nanocarbons such as fullerenes<sup>3</sup> could lead to development of photoelectronic devices for ultrahigh information density processing. So far, shape control of nanostructures has been achieved by using the three fundamental strategies of crystallization/precipitation, template synthesis, and amphiphilic assembly. Crystallization and precipitation from appropriate solvents and/or at an interface result in crystals with well-defined shapes as seen in fullerene crystals<sup>4</sup> such as nanowhiskers.<sup>5</sup> However, there is usually no flexibility in shape modulation. Template synthesis<sup>6</sup> produces predesignated structures whose forms are inevitably restricted by the dimensions and forms of the templates. In contrast, self-assembly mainly based on specific amphiphilicity in a surrounding medium results in a selection of morphologies including nanotubes, nanofibers, and microspheres.<sup>7</sup> For example, assembly of alkyl-tail-attached C<sub>60</sub> derivatives in various solvents gives nanofibers, nanosheets, spheres, or flower-like nanoobjects.<sup>8</sup> Unfortunately, in the latter approach attachment of large functionless groups to the respective functional moieties is always required, and this feature is a distinct disadvantage for applications requiring a high density of functionality. As a useful technique for bottom-up nanotechnology, shape control of *pure* functional molecules remains challenging. Since our finding of microhexagon formation by pure C<sub>60</sub> molecules through precipitation from solution,<sup>9</sup> we have now successfully completed an investigation of solvent engineering for free control of microscopic shapes of pure C<sub>60</sub>. Here, we report controlled formation of two-dimensional (2D) crystals including hexagons and rhombi and their selective shape shifting (change or growth of crystals) into one-dimensional (1D) rods through solvent-dependent variations of the crystal lattice, *all involving pure C<sub>60</sub>* (Figure 1).

Interfacial precipitation of C<sub>60</sub> by addition of appropriate solvents (6 mL, isopropyl alcohol (IPA) or *tert*-butyl alcohol (TBA)) into saturated C<sub>60</sub> solutions (1 mL, benzene, toluene, CCl<sub>4</sub>, CS<sub>2</sub>, and *m*-xylene)) resulted in various 2D crystals (Figure 2). Scanning electron microscopy (SEM) images clearly demonstrate our control over the edge multiplicity between 3 and 8 of the polygonal nanosheets. Uniformly shaped rhombi (a) and hexagons (b) were obtained at TBA/toluene and IPA/CCl<sub>4</sub> interfaces, respectively, while polygon mixtures (c) were collected from the TBA/benzene interface. The former two cases exhibited a high uniformity in size and thickness of the structures obtained. Shape selection might originate in the dependence of the crystalline lattice obtained on the solvent used, although the detailed mechanism is still under investigation. Transmission electron microscopic (TEM) imaging (d) revealed a thin morphology of the rhombi. Closer TEM imaging



**Figure 1.** Selective precipitation of fullerene nanosheets and the structural transformation from 2D nanosheets to 1D nanorods.



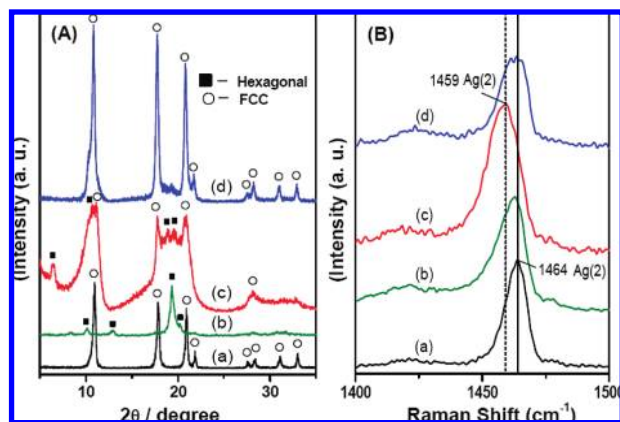
**Figure 2.** SEM images of 2D C<sub>60</sub> micro-objects prepared at (a) TBA/toluene, (b) IPA/CCl<sub>4</sub>, and (c) TBA/benzene interfaces. TEM images (d and e) and HR-TEM image (f) of 2D rhombus obtained at TBA/toluene interface.

(e) and high resolution TEM (HRTEM) imaging (f) also demonstrate the presence of numerous pores at the surface of the nanorhombi. We speculate that pore formation occurs by the evaporation of trapped solvent molecules from within the nanorhombi during drying. Interestingly, occasionally nanorhombi were found transformed to 1D structures through rolling up (Figure 2d) probably resulting from the release of high surface energy. Formation of 1D nanostructures (needles and rods) was also confirmed when CS<sub>2</sub> or *m*-xylene were cosolvents with TBA.<sup>10</sup>

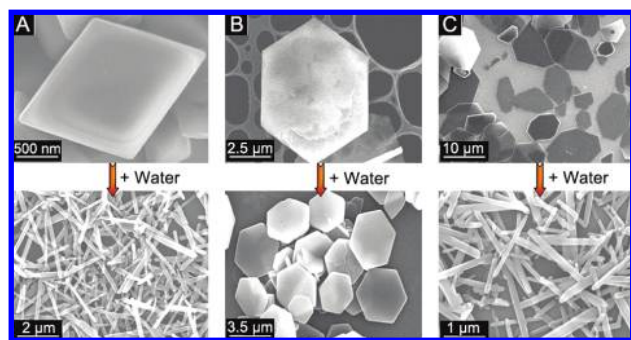
Although the X-ray diffraction (XRD) patterns (Figure 3A) of pristine C<sub>60</sub> powder (a) and the hexagon nanosheet from IPA/CCl<sub>4</sub> (b) can be assigned as fcc<sup>11</sup> and hexagonal<sup>9</sup> crystalline structures, respectively, the rhombus nanosheet from TBA/toluene (c) has a mixed crystalline lattice of fcc ( $a = 1.410$  nm) and hexagonal ( $a = 2.382$  nm and  $c = 1.089$  nm) (Figure 3A). In addition, complete drying upon heating under vacuum does not alter this mixed crystalline structure.<sup>10</sup> Mixed-shaped nanosheets from TBA/benzene also show characteristics of the mixed crystalline lattice.<sup>10</sup> Electron diffraction patterns of these nanosheets<sup>10</sup> confirmed this feature. Raman spectra (Figure 3B)<sup>10</sup> of the nanorhombi prepared in TBA/toluene (c) display a significant shift in the A<sub>g</sub>(2) mode peak to

<sup>†</sup> Fullerene Engineering Group.

<sup>‡</sup> MANA.



**Figure 3.** (A) XRD patterns and (B) Raman spectra: (a)  $C_{60}$  powder; (b) hexagonal nanosheets from IPA/ $CCl_4$ ; (c) rhombus nanosheets from TBA/toluene; (d) nanorods from water treatment of the nanorhombus.



**Figure 4.** SEM images of structural transformation of 2D fullerene nanosheets upon water treatment: (A) nanorhombus (from TBA/toluene) to nanorod; (B) inert nanohexagon (from IPA/ $CCl_4$ ); (C) mixed polygon (from TBA/benzene) to nanorod.

$1459\text{ cm}^{-1}$  as compared with that of  $C_{60}$  powder (a) and hexagonal nanosheets (b) (both at  $1464\text{ cm}^{-1}$ ). The clear presence of the fcc crystalline structure in the nanorhombi indicates the absence of polymerization so that the observed downshift to  $1459\text{ cm}^{-1}$  in the  $A_g(2)$  mode can be attributed to the presence of an accumulated strain<sup>12</sup> only present in rhombi nanosheets.

Exposure of these 2D nanosheets to water induced selective transformation into 1D nanorods (Figure 4). Nanorhombi from TBA/toluene (A) and mixed polygons from TBA/benzene (C) were converted to short nanorods upon exposure to water. Approximate matching in size of the nanorhombi (or mixed polygons) and nanorods suggested shape transfer through sheet rolling, which is also implied by the TEM image in Figure 2d. The shape shift is accompanied by changes in the XRD pattern to the fcc lattice (Figure 3A(d)), which is almost identical to the morphologically similar  $C_{60}$  nanowhiskers.<sup>5</sup> In addition, the Raman  $A_g(2)$  peak shifted back to  $1464\text{ cm}^{-1}$  (Figure 3B(d)), suggesting release of structural strains during the shape shift to nanorods. These observations indicate that the metastable nanorhombi which possess a strained mixed crystalline structure metamorphose into the more stable short nanowhisker (nanorods) probably through stimulation by some additional hydrophobic interaction between  $C_{60}$  molecules upon contact with water. In contrast, the stable nanohexagon of a single lattice (and so less strain) does not undergo shape shifting (Figure 4B).

This research clearly demonstrates controlled formation of 2D nanosheets of various shapes (hexagons, rhombi, and mixed

polygons) and selective shape shifting (change or growth of crystals) to nanorods (short nanowhiskers) *all from pure  $C_{60}$  molecules* by very simple solvent treatment. This technically innovative concept based on our findings represents a new methodology in fullerene-based bottom-up nanotechnology.

**Acknowledgment.** This work was in part supported by the World Premier International Research Center (WPI) Initiative on Materials Nanoarchitectonics, MEXT, Japan.

**Supporting Information Available:** Synthetic details and additional characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Kaschak, D. M.; Lean, J. T.; Waraksa, C. C.; Saupe, G. B.; Usami, H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 3435–3445. (b) Zhang, S. *Nat. Biotechnol.* **2003**, *21*, 1171–1178. (c) Kovtyukhova, N. I.; Mallouk, T. E. *Adv. Mater.* **2005**, *17*, 187–192. (d) Ariga, K.; Nakanishi, T.; Hill, J. P. *Curr. Opin. Colloid Interface Sci.* **2007**, *12*, 106–120. (e) Ariga, K.; Hill, J. P.; Lee, M. V.; Vinu, A.; Charvet, R.; Acharya, S. *Sci. Technol. Adv. Mater.* **2008**, *9*, 014109.
- (2) (a) Wang, Z.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 15954–15955. (b) Wang, Z.; Ho, K. J.; Medforth, C. J.; Shelnutt, J. A. *Adv. Mater.* **2006**, *18*, 2557–2560. (c) Wang, Z.; Li, Z.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 2440–2441.
- (3) (a) El-Khouldy, M. E.; Ito, O.; Smith, P. M.; D'Souza, F. *J. Photochem. Photobiol. C* **2004**, *5*, 79–104. (b) D'Souza, F.; Maligaspe, E.; Zandler, M. E.; Subbaiyan, N. K.; Ohkubo, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2008**, *130*, 16959–16967. (c) Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, H.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481–1483. (d) Yamamoto, Y.; Fukushima, T.; Suna, Y.; Ishii, N.; Saeki, A.; Seki, S.; Tagawa, S.; Taniguchi, M.; Kawai, T.; Aida, T. *Science* **2006**, *314*, 1761–1764. (e) Yoo, E. J.; Kim, J.; Hosono, E.; Zhou, H.-S.; Kudo, T.; Honma, I. *Nano Lett.* **2008**, *8*, 2277–2282.
- (4) (a) Tanaka, N.; Kitagawa, T.; Kachi, T.; Kizuka, T. *Ultramicroscopy* **1993**, *52*, 533–538. (b) Pekker, S.; János, A.; Mihály, L.; Chauvet, O.; Carrard, M.; Forró, L. *Science* **1994**, *265*, 1077–1078. (c) Rauwerdink, K.; Liu, J.-F.; Kintigh, J.; Miller, G. P. *Microsc. Res. Tech.* **2007**, *70*, 513–521. (d) Larsson, M. P.; Kjelstrup-Hansen, J.; Lucyszyn, S. *ECS Trans.* **2007**, *2*, 27–38. (e) Nurmawati, M. H.; Ajikumar, P. K.; Renu, R.; Sow, C. H.; Valiyaveetil, S. *ACS Nano* **2008**, *2*, 1429–1436. (f) Shin, H. S.; Yoon, S. M.; Tang, Q.; Chon, B.; Joo, T.; Choi, H. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 693–696. (g) Lu, G.; Li, L.; Yang, X. *Small* **2008**, *4*, 601–606. (h) Hasobe, T.; Sandanayaka, A. S. D.; Wada, T.; Araki, Y. *Chem. Commun.* **2008**, 3372–3374. (i) Tan, Z.; Masuhara, A.; Kasai, H.; Nakanishi, H.; Oikawa, H. *Jpn. J. Appl. Phys.* **2008**, *47*, 1426–1428. (j) Ji, H.-X.; Hu, J.-S.; Wan, L.-J.; Tang, Q.-X.; Hu, W.-P. *J. Mater. Chem.* **2008**, *18*, 328–332. (k) Chong, L. C.; Solan, J.; Wagner, G.; Silva, S. R. P.; Curry, R. J. *J. Mater. Chem.* **2008**, *18*, 3319–3324. (l) Geng, J.; Zhou, W.; Skelton, P.; Yue, W.; Kinloch, I. A.; Windle, A. H.; Johnson, B. F. G. *J. Am. Chem. Soc.* **2008**, *130*, 2527–2534.
- (5) (a) Miyazawa, K.; Kuwasaki, Y.; Obayashi, A.; Kuwabara, N. *J. Mater. Res.* **2002**, *17*, 83–88. (b) Sathish, M.; Miyazawa, K.; Sasaki, T. *Chem. Mater.* **2007**, *19*, 2398–2400. (c) Miyazawa, K. *J. Nanosci. Nanotechnol.* **2009**, *9*, 41–50.
- (6) (a) Liu, H.; Li, Y.; Jiang, L.; Luo, H.; Xiao, S.; Fang, H.; Li, H.; Zhu, D.; Yu, D.; Xu, J.; Xiang, B. *J. Am. Chem. Soc.* **2002**, *124*, 13370–13371. (b) Cha, S. I.; Miyazawa, K.; Kim, J.-D. *Chem. Mater.* **2008**, *20*, 1667–1669. (c) Bai, R.; Ouyang, M.; Li, Z.-Z.; Yang, L.-G.; Shi, M.-M.; Wu, G.; Wang, M.; Chen, H.-Z. *J. Mater. Chem.* **2008**, *18*, 4318–4323.
- (7) (a) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944–1947. (b) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature (London)* **2002**, *419*, 702–705. (c) Kawauchi, T.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 10560–10567. (d) Tsunashima, R.; Noro, S.; Akutagawa, T.; Nakamura, T.; Kawakami, H.; Toma, K. *Chem.—Eur. J.* **2008**, *14*, 8169–8176.
- (8) (a) Nakanishi, T.; Schmitt, W.; Michinobu, T.; Kurth, D. G.; Ariga, K. *Chem. Commun.* **2005**, 5982–5984. (b) Nakanishi, T.; Ariga, K.; Michinobu, T.; Yoshida, K.; Takahashi, H.; Teranishi, T.; Möhwald, H.; Kurth, D. G. *Small* **2007**, *3*, 2019–2023. (c) Nakanishi, T.; Michinobu, T.; Yoshida, K.; Shirahata, N.; Ariga, K.; Möhwald, H.; Kurth, D. G. *Adv. Mater.* **2008**, *20*, 443–446. (d) Shen, Y.; Wang, J.; Kuhlmann, U.; Hildebrandt, P.; Ariga, K.; Möhwald, H.; Kurth, D. G.; Nakanishi, T. *Chem.—Eur. J.* **2009**, *15*, 2763–2767.
- (9) Sathish, M.; Miyazawa, K. *J. Am. Chem. Soc.* **2007**, *129*, 13816–13817.
- (10) See Supporting Information.
- (11) David, W. I. F.; Ibberson, R. M.; Matsuo, T. *Proc. R. Soc. London, Ser. A* **1993**, *442*, 129–146.
- (12) Kuzmany, H.; Pfeiffer, R.; Hulman, M.; Kramberger, C. *Philos. Trans. R. Soc. London, Ser. A* **2004**, *362*, 2375–2406.

JA902061R