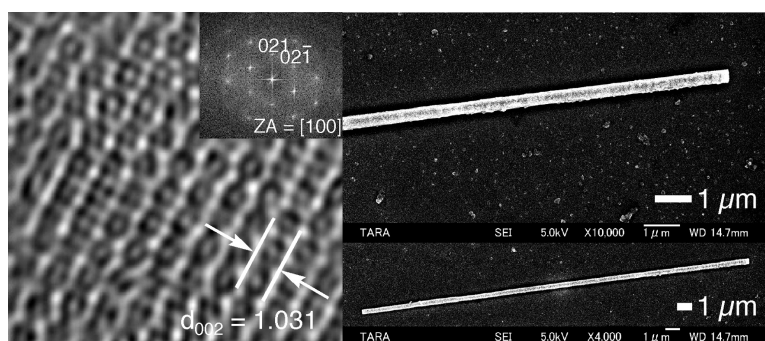


Nanorods of Endohedral Metallofullerene Derivative

Takahiro Tsuchiya, Ryotaro Kumashiro, Katsumi Tanigaki, Yoichiro Matsunaga, Midori O. Ishitsuka, Takatsugu Wakahara, Yutaka Maeda, Yuta Takano, Motoki Aoyagi, Takeshi Akasaka, Michael T. H. Liu, Tatsuhisa Kato, Kazutomo Suenaga, Jong S. Jeong, Sumio Iijima, Fumiko Kimura, Tsunehisa Kimura, and Shigeru Nagase

J. Am. Chem. Soc., **2008**, 130 (2), 450-451 • DOI: 10.1021/ja7110396n

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

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

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- 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](#)

Nanorods of Endohedral Metallofullerene Derivative

Takahiro Tsuchiya,[†] Ryotaro Kumashiro,[‡] Katsumi Tanigaki,^{*,‡} Yoichiro Matsunaga,[†] Midori O. Ishitsuka,[†] Takatsugu Wakahara,[†] Yutaka Maeda,[†] Yuta Takano,[†] Motoki Aoyagi,[†] Takeshi Akasaka,^{*,†} Michael T. H. Liu,[§] Tatsuhisa Kato,^{||} Kazutomo Suenaga,^{*,⊥} Jong S. Jeong,[⊥] Sumio Iijima,[⊥] Fumiko Kimura,[#] Tsunehisa Kimura,^{*,#} and Shigeru Nagase[∇]

Center for Tsukuba Advanced Research Alliance, Department of Chemistry, University of Tsukuba, Tsukuba 305-8577, Japan, Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan, Department of Chemistry, University of Prince Edward Island, Prince Edward Island CIA4P3, Canada, Department of Chemistry, Josai University, Sakado 350-0295, Japan, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan, and Department of Theoretical Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

Received November 17, 2007; E-mail: akasaka@tara.tsukuba.ac.jp

One-dimensional (1D) nanostructures with well-controlled composition and crystallinity have become the focus of intensive research on the structure–property relationships and the scientific and technological applications due to their dimensional anisotropy.¹ The field of nanoscale electronics has received a growing interest with fundamental issues on operating principles and valuable fabrication techniques of nanoscale devices.² Meanwhile, endohedral fullerenes have attracted special interest since they could lead to new spherical molecules with unique structures and properties that are unexpected for empty fullerenes.³ Among them, endohedral metallofullerenes is of particular interest from the point of view of its application as a building block of future nanoscale-electronic devices and conducting materials, because of a narrow band gap and paramagnetic character.⁴ Recently, formation of crystalline fibers of C₆₀ with a diameter of submicrometers by a liquid–liquid interfacial precipitation method was reported,⁵ and it was revealed to show *n*-channel enhancement-type FET.⁶ The formation of crystals of endohedral metallofullerene, however, remains difficult. Recently, we have successfully obtained the columnar crystals of endohedral metallofullerene derivative La@C₈₂(Ad) (Ad = adamantylidene) by slow evaporation of the CS₂ solution and clarified its packing structure.⁷ Chemical derivatization may be one of the efficient stepping stones for accomplishing the orderly alignment of endohedral metallofullerenes followed by crystallization.

In this Communication, we report for the first time the preparation and characterization of the nanorods of the endohedral metallofullerene derivative La@C₈₂(Ad) as a well-arrayed 1D nanostructure, which showed the *p*-type FET property and oriented with the nanorod axis perpendicular to the magnetic field.

The endohedral metallofullerene derivative La@C₈₂(Ad) was formed and isolated by the selective reaction of La@C₈₂ with 2-adamantane-2,3-[3*H*]-diazirine as reported previously.⁷ The nanorods of La@C₈₂(Ad) were prepared by a liquid–liquid interfacial precipitation method. After the two layers became homogeneous, needlelike precipitates (nanorods) were obtained, whereas the needlelike precipitates could not be obtained by using the same method for pristine La@C₈₂.

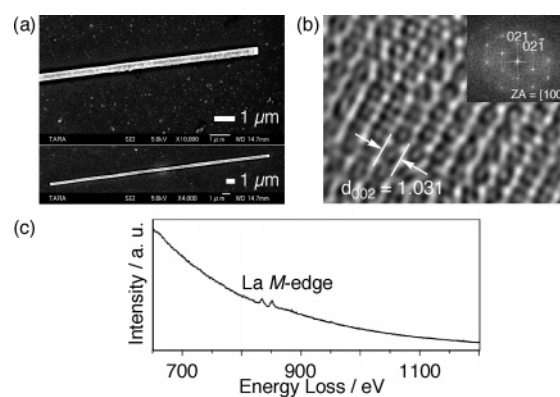


Figure 1. (a) SEM image of the nanorods of La@C₈₂(Ad) formed by the liquid–liquid interfacial precipitation method; (b) Fourier-filtered HRTEM image of the nanorods. Inset: selected area electron diffraction pattern; (c) EELS spectrum of the La@C₈₂(Ad) nanorod.

Structural analyses of the nanorods of La@C₈₂(Ad) were performed by means of measurements of a scanning electron microscope (SEM), a high-resolution transmission electron microscope (HRTEM), and electron spin resonance (ESR) spectroscopy measurements. First, the contour of the La@C₈₂(Ad) nanorods was observed by SEM, as shown in Figure 1a. It shows the fine needlelike shape, which has 0.1–5 μm width and aspect ratio of ca. 30:1. SEM observation of the precipitates obtained from the pristine La@C₈₂ was also performed; however, no needlelike precipitate was found so far, and only an amorphous substance was observed. Thus, functionalization of endohedral metallofullerenes plays an important role in the preparation of the nanorod of endohedral metallofullerenes. The TEM image of the La@C₈₂(Ad) nanorods in Figure 1b shows the close-packed crystalline structure of La@C₈₂(Ad) with the endohedral feature. The selected area electron diffraction pattern (SAEDP) is shown in the inset of Figure 1b. The existence of the La atom was finally confirmed by the typical electron energy loss (EELS) spectrum for the edge of the nanorods showing the La *M*-edge (Figure 1c). These observations clearly suggest that the fine needlelike precipitates are single-crystalline fibers of La@C₈₂(Ad), that is, the nanorods of La@C₈₂(Ad). To shed light on the magnetic property of the nanorods, the ESR experiment has been performed. A piece of the La@C₈₂(Ad) nanorods exhibited an ESR spectrum which resembled that of a single-crystal sample⁸ in appearance at the temperature range from 6 K to room temperature. A magnetic intermolecular coupling

[†] University of Tsukuba.

[‡] Tohoku University.

[§] University of Prince Edward Island.

^{||} Josai University.

[⊥] National Institute of Advanced Industrial Science and Technology (AIST).

[#] Kyoto University.

[∇] Institute for Molecular Science.

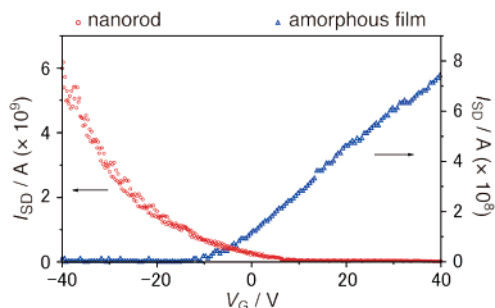


Figure 2. I_{SD} curve of nanorod and amorphous film of La@C₈₂(Ad).

averaged out the octet structure due to the La nucleus hyper-fine-coupling into a single broad line having the line width of ca. 25 G at 6 K.⁹ The anisotropic character of the g -value line width was inherited from the anisotropic magnetic intermolecular interaction in the single crystal. The g -value and the position of the spectrum center varied with the rotation of the nanorod around the magnetic field of the ESR apparatus, and the line width decreased with an increase of temperature. The ESR properties of the nanorods also could be understood from the partially aligned single-crystal sample.

In this context, the physical properties of the La@C₈₂(Ad) nanorods are of great interest. To clarify the FET property of the La@C₈₂(Ad) nanorods, the SiO₂/doped-Si substrates with thickness of an oxidized layer of 200 nm were prepared.^{9,10} La@C₈₂(Ad) nanorods were dispersed in 2-propanol as a very diluted solution, and the obtained suspension was spread on the FET substrate. The source and drain electrodes were fabricated by Ag paste. The observation shows that all the actions were p -type (Figure 2, red) and were exceptional, considering that C₈₂-endo-hedral derivatives show only an n -type action in general. For having complete confirmation, we have prepared thin films of La@C₈₂(Ad) (Figure 2, blue) and La@C₈₂¹¹ separately on FET substrates and have measured FET actions. The FET actions were very different from that of La@C₈₂(Ad) nanorod and the n -type actions were observed. These experiments unambiguously show that the p -type action was intrinsic to the rod shape of La@C₈₂(Ad).⁹ Since the Ag electrodes were employed for this experiment, the p -type action would be explained by the work function of Ag and the HOMO level of La@C₈₂(Ad).⁷ Therefore, the observed p -type action is most probably due to the nanointerfacial contact between the electrodes and La@C₈₂(Ad) nanorod or the special electronic states such as the lowering of work function in the rod-shape La@C₈₂(Ad). The thin films¹² and whisker⁶ of other empty fullerenes are well-known to show n -type semiconductivity. Consequently, the p -type behavior of the La@C₈₂(Ad) nanorods is unique within the fullerene FETs. This finding may offer good prospects in the search for future nanoelectronics devices.

Controlling the arrangement and positioning of the nanorods is a crucial task to realize the FET devices. In this context, it is an interesting subject to orient the nanorods in a magnetic field.¹³ In an attempt to orient the La@C₈₂(Ad) nanorods, we carried out the experiment for the magnetic orientation in the magnetic field. The suspension of the La@C₈₂(Ad) nanorods in isopropyl alcohol was placed in a magnetic field at 12 T, and the solvent was slowly vaporized at room temperature. The orientation was monitored by an optical microscope. Figure 3 shows that the La@C₈₂(Ad) nanorods orientate perpendicularly to the magnetic field. This

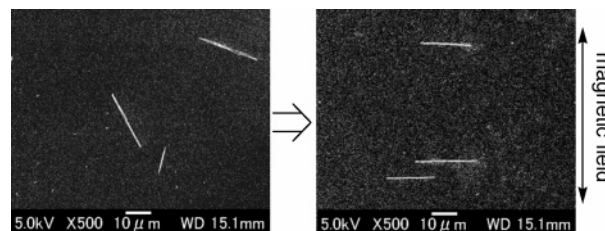


Figure 3. SEM observation for the magnetic orientation of nanorods of La@C₈₂(Ad).

observation indicates that the nanorods of La@C₈₂(Ad) have a negative magnetic anisotropy (i.e., the magnetic susceptibility in the direction parallel to the rod axis is smaller than that in the direction perpendicular to the rod axis). The molecular origin of this anisotropy is unknown at present time. These orientations of nanorods were observed in the magnetic field at the region of ≥ 3 T. Clearly, the construction of the nanostructures would be controllable by the appropriate choice of nanorods.

Acknowledgment. This work was supported in part by a Grant-in-Aid, the 21st Century COE Program, Nanotechnology Support Project, from the Ministry of Education, Culture, Sports, Science, and a grant from the Association for the Progress of New Chemistry and Mitsubishi Chemical Corporation.

Supporting Information Available: Complete ref 7, materials and methods, VT-ESR spectra of La@C₈₂(Ad) nanorod, and illustration of FET substrate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Zhang, H.; Wang, D.; Yang, B.; Moehwald, H. *J. Am. Chem. Soc.* **2006**, *128*, 10171–10180. (b) Cheng, J. Y.; Zhang, F.; Chuang, V. P.; Mayes, A. M.; Ross, C. A. *Nano Lett.* **2006**, *6*, 2099–2103. (c) Patzke, G. R.; Kumiech, F.; Nesper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446–2461. (d) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001**, *291*, 630–633. (e) Hu, J.; Odem, T. W.; Lieber, M. C. *Acc. Chem. Res.* **1999**, *32*, 435–445.
- (2) (a) Cai, L.; Cabassi, M. A.; Yoon, H.; Cabarcos, O. M.; McGuinness, C. L.; Flatt, A. K.; Allara, D. L.; Tour, J. M.; Mayer, T. S. *Nano Lett.* **2005**, *5*, 2365–2372. (b) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature* **2001**, *409*, 66–69. (c) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851–853. (d) Collet, J.; Vuillaume, D. *Appl. Phys. Lett.* **1998**, *73*, 2681–2683.
- (3) *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T.; Nagase, S., Eds.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 2002.
- (4) Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **1996**, *214*, 57–63.
- (5) Miyazawa, K.; Kawasaki, Y.; Obayashi, A.; Kuwabara, M. *J. Mater. Res.* **2002**, *17*, 83–88.
- (6) Ogawa, K.; Kato, T.; Ikegami, A.; Tsuji, H.; Aoki, N.; Ochiai, Y.; Bird, J. P. *Appl. Phys. Lett.* **2006**, *88*, 112109/1–112109/3.
- (7) Maeda, Y.; et al. *J. Am. Chem. Soc.* **2004**, *126*, 6858–6859.
- (8) Nara, R.; Maeda, Y.; Wakahara, T.; Tsuchiya, T.; Takeuchi, K.; Fukushima, M.; Akasaka, T.; Kato, T. Abstract of the 30th commemorative fullerene-nanotubes general symposium, 2006, 156.
- (9) See Supporting Information.
- (10) Hiroshiba, N.; Kumashiro, R.; Tanigaki, K.; Takenobu, T.; Iwasa, Y.; Kotani, K.; Kawayama, I.; Tonouchi, M. *Appl. Phys. Lett.* **2006**, *89*, 152110/1–152110/3.
- (11) Hiroshiba, N.; Tanigaki, K.; Kumashiro, R.; Ohashi, H.; Wakahara, T.; Akasaka, T. *Chem. Phys. Lett.* **2004**, *400*, 235–238.
- (12) (a) Nagano, T.; Sugiyama, H.; Kuwahara, E.; Watanabe, R.; Kusai, H.; Kashino, Y.; Kubozono, Y. *Appl. Phys. Lett.* **2005**, *87*, 023501/1–023501/3. (b) Shibata, K.; Kubozono, Y.; Kanbara, T.; Hosokawa, T.; Fujiwara, A.; Ito, Y.; Shinohara, H. *Appl. Phys. Lett.* **2004**, *84*, 2572–2574. (c) Kubozono, Y.; Rikiishi, Y.; Shibata, K.; Hosokawa, T.; Fujiki, S.; Kitagawa, H. *Phys. Rev. B* **2004**, *69*, 165412/1–165412/7. (d) Haddon, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 3041–3042. (e) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming, R. M. *Appl. Phys. Lett.* **1995**, *67*, 121–123.
- (13) Kimura, T. *Polym. J.* **2003**, *35*, 823–843.

JA710396N