JOURNAL OF Materials Communication CHEMISTRY

Formation and atomic structure of a tetrahedral carbon onion

Ichihito Narita,[a] Takeo Oku,[a] Katsuaki Suganuma,[a] Kenji Hiraga[b] and Eiji Aoyagi[c]

[a]*Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka, Japan 567-0047. E-mail: narita12@sanken.osaka-u.ac.jp*
[b]*Institute for Materials Research, Tohoku University, Aoba-ku, Sendai, Japan 980-8577*
[c]*High-Voltage Electron Microscope Laboratory, Tohoku University, Aoba-ku, Sendai, Japan 980-8577*

Received 27th March 2001, Accepted 14th May 2001
First published as an Advance Article on the web 24th May 2001

A carbon onion with a tetrahedral structure was produced by electron-beam irradiation of amorphous carbon, and structure models of C_{84} and C_{276} were optimized by molecular mechanics and semi-empirical molecular orbital calculation.

Various fullerene structures have been designed and produced[1–4] since the discovery of C_{60}.[5] These fullerene materials are good candidates for nanoscale devices such as single-electron devices, magnetic refrigerators, nano-diodes, nano-transistors, nano-ball bearings and insulator lubricants.[6,7] Ugarte showed that polyhedral graphitic structures were converted into quasi-spherical onions by electron-beam irradiation at an accelerating voltage of 300 kV.[1] Similar onion structures, which generally consist of quasi-spherical fullerene groups, have been discovered and studied in detail.[8–11]

The purpose of the present work is to produce new carbon onions by high-energy electron-irradiation of amorphous carbon, and to investigate the atomic structures and stability of the onion clusters by high-resolution electron microscopy (HREM) and molecular orbital/mechanics calculation. To confirm the proposed structure model, HREM image simulations were carried out.

For the formation of onion clusters, amorphous carbon produced from poly(vinyl alcohol) (PVA-706, Kuraray Co., Ltd.) was used. Samples for HREM observation were prepared by dispersing the materials on holey carbon grids. HREM observation was performed with a 1250 kV electron microscope (ARM-1250) having a point-to-point resolution of 0.12 nm. To compare observed images with calculated ones, HREM images were calculated by the multi-slice method using the MacTempas software.[12] The parameters used in the calculations are as follows: accelerating voltage = 1250 kV, radius of the objective aperture = 8.8 nm^{-1}, spherical aberration $C_s = 2.28$ mm, spread of focus $\Delta = 15$ nm, semi-angle of divergence $\alpha = 0.85$ mrad, under defocus values $\Delta f = -10$ to -90 nm, and crystal thickness $t = 2$ nm.

Atomic structures of the clusters were optimized by molecular mechanics calculation (MM3) and semi-empirical molecular orbital calculation (PM3) using Chem3D[13a] and CAChe.[13b] The energy levels and density of states were also calculated by first principles calculation with discrete variational (DV)–$X\alpha$ method.[14]

The amorphous carbon was irradiated by an electron beam for 30 min under a beam current of 100 μA cm^{-2} at 1250 kV. This beam current is *ca.* 20 times higher compared to that of ordinary HREM observation. A carbon onion with a tetrahedral structure was formed as shown in Fig. 1(a). The edge lengths of the first and second internal shell of the tetrahedral carbon onion are *ca.* 0.8 nm and 1.4 nm, respectively. The distance between onion layers is 0.35 nm. Although a similar structure consisting of $C_{264}@C_{660}@C_{1248}$ was calculated,[9] the size of the present tetrahedral carbon onion is smaller compared to the C_{264} onion. The present HREM result indicates that the carbon onion has a new tetrahedral structure.

At the center of the onion, there would be a tetrahedral carbon cluster, and the basic arrangements of carbon atoms are proposed, as shown in Fig. 1(b) and 1(c). Each vertex consists of a hexagonal ring (as indicated by a star mark), and three pentagonal rings exist around the vertex along the edge. Other parts are formed only by hexagonal rings. Edge lengths of the C_{84} and C_{276} in the optimized structures are 0.78 nm and 1.42 nm, respectively. The total numbers (N) of carbon atoms of the present tetrahedral onions are represented by the

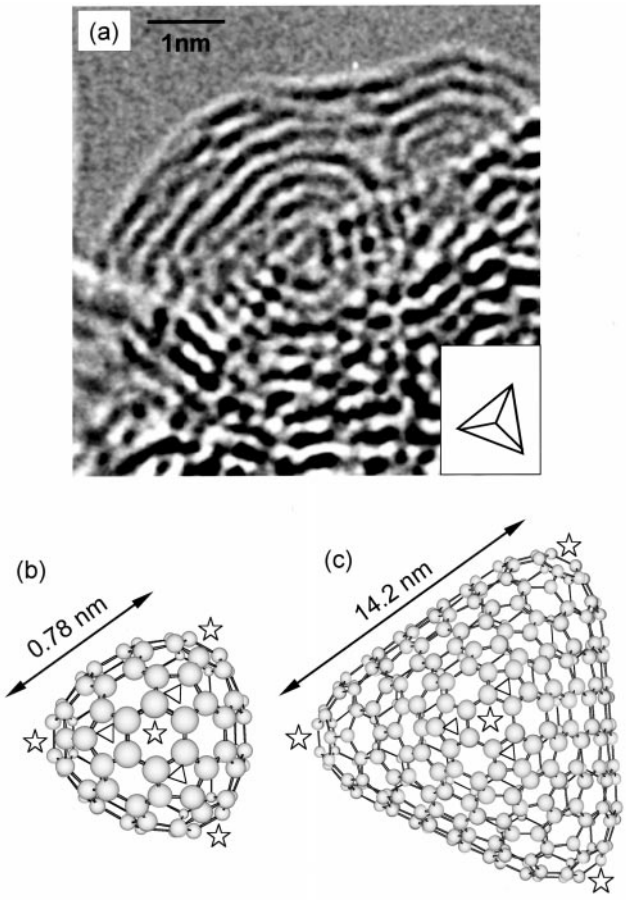

Fig. 1 (a) HREM image of tetrahedral carbon onion. Proposed structure models of (b) C_{84} and (c) C_{276}. (△: pentagonal ring, ☆: vertex (hexagonal ring)).

DOI: 10.1039/b102787p

Table 1 Steric energy and heats of formation on carbon clusters

n	C_N	Edge length/ nm	Steric energy/ kcal mol^{-1}	Heats of formation/ kcal mol^{-1}
1	C_{84td}	0.78	362	993
2	C_{168}	0.98	395	
3	C_{276}	1.42	389	
4	C_{408}	1.96	345	
	C_{60}		358	812
	C_{84d2}		335	967
	C_{84d2d}		355	968

equation: $N=12\,(n+2)^2-524$ ($n=1, 2, \ldots$). Edge lengths of the C_{84} and C_{276} agree with the first and second internal shell of tetrahedral carbon onion in the HREM image, respectively. Steric energy by molecular mechanics calculations and heats of formation by semi-empirical molecular orbital calculations on tetrahedral carbon clusters are summarized in Table 1. Steric energies of the C_{84} and C_{276} were 362 and 389 kcal mol^{-1}, respectively.

The smallest tetrahedral onion in the HREM image in Fig. 1 (a) agrees well with the calculated images of Fig. 2, based on the proposed structure model of $C_{84}@C_{276}$. In this optimized model, the distance between layers is close to the observed value of 0.35 nm. Further refinement has to be carried out in which the van der Waals interaction is considered.

Energy levels and density of states (DOS) of the C_{84} cluster were calculated, as shown in Fig. 3. Energy gaps of C_{60} and C_{84} are calculated to be 2.1 eV and 2.0 eV, respectively. The experimental energy gap of C_{60} is 1.7 eV.[15] The difference is *ca.* 0.4 eV between the present calculation and experimental data. Therefore, the energy gap of a C_{84} cluster would be *ca.* 1.6 eV, which is a little smaller compared to that of the C_{60} cluster.

The formation mechanism can be described with three effects: breaking of carbon bonds by electron irradiation; knock-on of carbon atoms; increase of sample temperature. In the present work, bond breaking and knock-on effect would be important. These effects cause fluidization of the structure, which provides a spherical structure because of the surface tension. In Fig. 1(a), two onions were observed, and they would collide during onion formation.

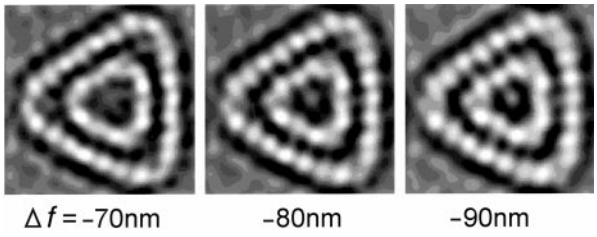

Fig. 2 Calculated HREM images of $C_{84}@C_{276}$ onion as a function of defocus values.

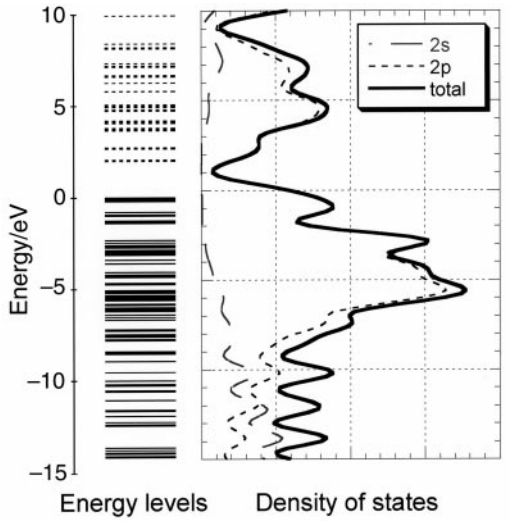

Fig. 3 Energy level diagram and density of states (DOS) of the C_{84} cluster.

There are two important theorems of Euler's rule[16] and the isolated pentagon rule (IPR)[17] in the formation of the fullerene. Even if the closed fullerene size becomes larger, the number of pentagonal rings is always 12 according to Euler's rule. Pentagonal rings do not adjoin to others based on the IPR when the size becomes bigger than C_{60}.

There are 24 structural isomers of C_{84},[18] and D_2-C_{84} and D_{2d}-C_{84} in the ratio of 2 : 1 are the main structural isomers. The first inside shell of the tetrahedral carbon onion is equivalent to the T_d-C_{84} structural isomer. Heats of formation of D_2-C_{84} and D_{2d}-C_{84} by PM3 calculation are 967 kcal mol^{-1} and 968 kcal mol^{-1}, respectively. This means that the spherical structure is more stable than the tetrahedral structure (heat of formation = 993 kcal mol^{-1}), and the Stone–Wales transformation[19] would be introduced during the growth of T_d-C_{84} according to Euler's rule and the IPR. The position of the pentagonal ring can be moved by this transformation keeping the fullerene size. Although this tetrahedral structure (T_d-C_{84}) might transform into a spherical structure (D_2-C_{84} and D_{2d}-C_{84}), the energy barrier between them would prevent the transformation. The barrier would be the van der Waals force from the outside shell and distortion due to the collision of two onions.

In summary, a tetrahedral carbon cluster with a new onion structure was produced by electron-beam irradiation, and new atomic structure models were proposed. Each vertex of the tetrahedral carbon cluster consists of a hexagonal ring, and three pentagonal rings exist around the vertex along the edge. Other parts are formed only by hexagonal rings. The electronic states were also calculated, and the energy gap of the C_{84} cluster would be smaller than that of C_{60}.

This work was partly supported by Grant-in-Aid, Ministry of Education, Science, Sports, and Culture of Japan.

Notes and references

1 D. Ugarte, *Nature*, 1992, **359**, 707.
2 H. Shinohara, H. Sato, Y. Saito, A. Izuoka, T. Sugawara, H. Ito, T. Sakurai and T. Matsuo, *Rapid Commun. Mass Spectrom.*, 1992, **6**, 413.
3 H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl and J. Worth, *Nature*, 2000, **407**, 60.
4 T. Oku, T. Hirano and K. Suganuma, *Mater. Sci. Eng. B.*, 2000, **74**, 210.
5 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
6 C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 542.
7 H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos and P. L. McEuen, *Nature*, 2000, **407**, 57.
8 F. Banhart and P. M. Ajayan, *Nature*, 1996, **382**, 433.
9 Q. Ru, M. Okamoto, Y. Kondo and K. Takayanagi, *Chem. Phys. Lett.*, 1996, **259**, 425.
10 H. Terrones and M. Terrones, *J. Phys. Chem. Solids*, 1997, **58**, 1789.
11 T. Oku, *J. Ceram. Soc. Jpn.*, 2001, **109**, S17.
12 *MacTempas*, Total Resolution, Berkeley, CA, 1996.
13 *Chem3D*, Fujitsu Corp., Chiba, Japan, 2001; *CACche*, Fujitsu Corp., Chiba, Japan, 2001.
14 H. Adachi, M. Tsukada and C. Satoko, *J. Phys. Soc. Jpn.*, 1978, **45**, 875.
15 Y. Wang, G. T. Hager and P. C. Eklund, *Phys. Rev. B*, 1992, **45**, 14396.
16 X. Liu, T. G. Schmalz and D. J. Klein, *Chem. Phys. Lett.*, 1992, **188**, 550.
17 H. Kroto, *Nature*, 1987, **329**, 529.
18 D. E. Manolopoulos and P. W. Fowler, *J. Chem. Phys.*, 1992, **96**, 7603.
19 A. J. Stone and D. J. Wales, *Chem. Phys. Lett.*, 1986, **128**, 501.