

**NANO IDEA**

**Open Access**

# Formation and reinforcement of clusters composed of C<sub>60</sub> molecules

Shunji Kurosu, Takahiro Fukuda, Yuichi Shibuya, Toru Maekawa\*

## Abstract

We carry out two experiments: (1) the formation of clusters composed of C<sub>60</sub> molecules via self-assembly and (2) the reinforcement of the clusters. Firstly, clusters such as fibres and helices composed of C<sub>60</sub> molecules are produced via self-assembly in supercritical carbon dioxide. However, C<sub>60</sub> molecules are so weakly bonded to each other in the clusters that the clusters are broken by the irradiation of electron beams during scanning electron microscope observation. Secondly, UV photons are irradiated inside a chamber in which air is filled at 1 atm and the above clusters are placed, and it was found that the clusters are reinforced; that is, they are not broken by electron beams any more. C<sub>60</sub> molecules located at the surface of the clusters are oxidised, i.e. C<sub>60</sub>O<sub>n</sub> molecules, where  $n = 1, 2, 3$  and  $4$ , are produced according to time-of-flight mass spectroscopy. It is supposed that oxidised C<sub>60</sub> molecules at the surface of the clusters may have an important role for the reinforcement, but the actual mechanism of the reinforcement of the clusters has not yet been clearly understood and therefore is an open question.

## Introduction

It is known that clusters composed of C<sub>60</sub> molecules such as chains and sheets can be formed by polymerising C<sub>60</sub> molecules via the irradiation of photons [1-13], application of high pressure and/or high temperature [3,5,6,14-17], or introduction of foreign atoms or molecules [18-20]. It is also known that C<sub>60</sub> molecules can be modified with oxygen atoms and molecules [21-30].

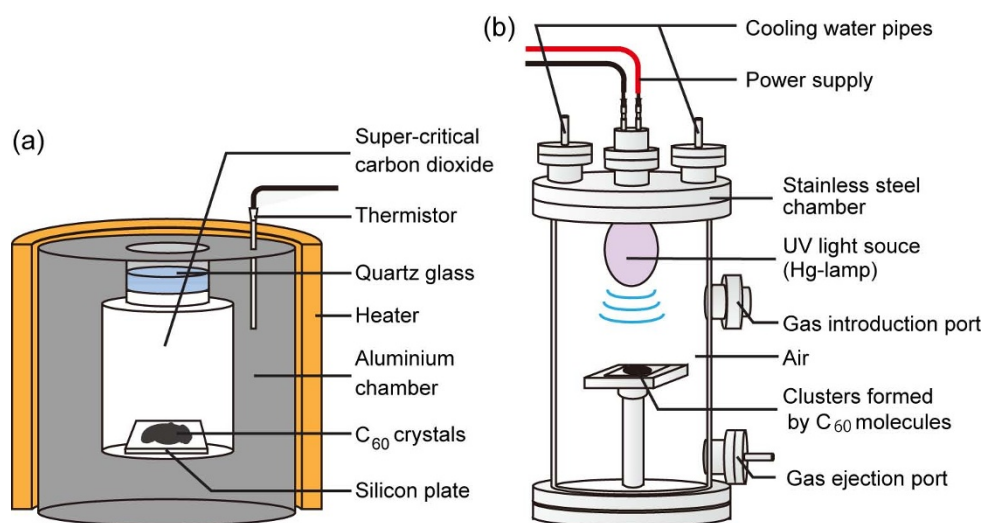
The gas-liquid coexistence curves terminate at the critical points [31]. Incident light cannot penetrate fluids as they approach their critical points, known as critical opalescence, due to the formation of large molecular clusters [31]. It was recently shown that fibres, fibre networks, sheets and helices composed of C<sub>60</sub> molecules were self-assembled by leaving C<sub>60</sub> crystals in ethane, xenon or carbon dioxide under supercritical conditions for 24 h [32]. Those structures were formed via van der Waals interactions between C<sub>60</sub> and the fluids' molecules.

In this letter, we create clusters composed of C<sub>60</sub> molecules via self-assembly in supercritical carbon dioxide and reinforce the clusters by attaching oxygen atoms to the surface of C<sub>60</sub> molecules.

## Experimental details

Figure 1 shows an outline of the experimental apparatuses. We carried out two experiments. First, clusters composed of C<sub>60</sub> molecules are produced by leaving C<sub>60</sub> crystals in carbon dioxide under supercritical conditions for 24 h [32] (see Figure 1a). The inner volume of the supercritical fluid chamber made of aluminium was 11.7 ml. Of the crystals composed of C<sub>60</sub> molecules, 0.2 mg was placed on the surface of a silicon plate set at the bottom of the supercritical fluid chamber and carbon dioxide of critical density was introduced into the chamber. The temperature of the fluid was set at 36.0°C by a heater installed around the chamber, which was regulated by a PID controller (C541, Technol Seven Co. Ltd., Tokyo, Japan). The temperature was monitored by a thermistor (SZL-64, Takara Thermistor Co. Ltd., Tokyo, Japan) embedded inside the chamber wall. Note that the critical temperature, pressure and density of carbon dioxide are respectively 31.0°C, 7.38 MPa and 468.0 kg m<sup>-3</sup> [33]. After the experiment, the fluid in the chamber was gradually released by controlling a valve switch. Clusters formed by C<sub>60</sub> molecules were observed by a scanning electron microscope [SEM] (JSM-7400F, JEOL, Tokyo, Japan). Secondly, the clusters formed on the silicon plate were moved to another chamber made of stainless steel for irradiation of UV light (Figure 1b). The inner height and diameter of the chamber were 500 and 254 mm. The clusters were placed 150 mm under an Hg

\* Correspondence: maekawa@toyo.jp  
Bio-Nano Electronics Research Centre, Toyo University, 2100, Kujirai, Kawagoe, Saitama, 350-8585, Japan



**Figure 1** Outline of the experimental apparatuses. **(a)** Supercritical fluid chamber. Crystals composed of C<sub>60</sub> molecules are placed on a silicon plate set at the bottom of the chamber. The chamber is then filled with carbon dioxide of critical density. The temperature is set at 36.0°C by a heater regulated by a PID controller. Crystals composed of C<sub>60</sub> molecules are left in the chamber for 24 h. Clusters formed by C<sub>60</sub> molecules are observed by an SEM. **(b)** UV light irradiation chamber. The clusters formed by C<sub>60</sub> molecules are placed in the chamber which is filled with air at 1 atm. After irradiation of UV light for 3 h, the clusters are observed by an SEM and mass spectroscopic analysis is carried out.

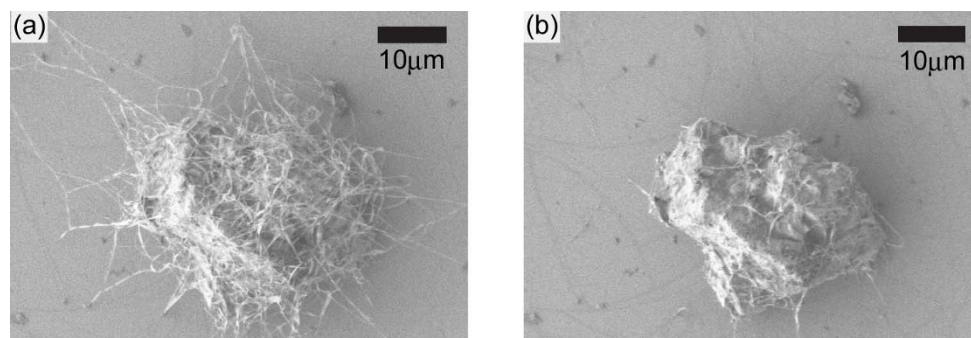
lamp (200 W, low-pressure Hg lamp, SEN Light Co. Ltd., Osaka, Japan). The chamber was filled with air at 1 atm and the air irradiated with UV light, the primary wavelengths of which were 184.9 and 253.7 nm, for 3 h. After the experiment, the chamber was vacuumed via the ejection port and fresh air was injected. The structures of the clusters were observed by an SEM. Mass spectroscopic analysis of the clusters was also carried out by matrix-assisted laser desorption ionisation time-of-flight mass spectroscopy (Brücker Daltonics, Autoflex, Bremen, Germany).

## Results

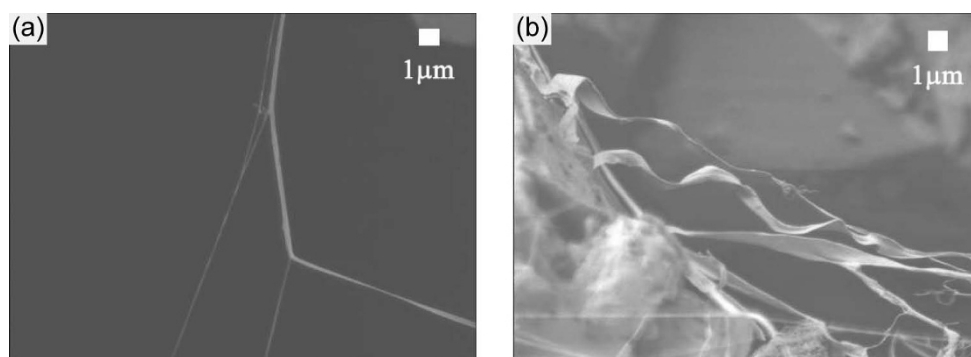
First of all, clusters such as fibres and helices were formed by C<sub>60</sub> molecules after having left the crystals composed of

C<sub>60</sub> molecules in carbon dioxide under supercritical conditions (36.0°C) for 24 h [32] (see Figure 2a). However, C<sub>60</sub> molecules were so weakly bonded to each other that the clusters were broken by electron beams during the SEM observation (Figure 2b; see also Additional file 1 for the movie). Note that the accelerating voltage, current and diameter of the electron beams were 1 kV,  $4.7 \times 10^{-2}$  nA and 2.0 nm, respectively, and therefore the energy flux of the electron beams was  $1.5 \text{ nW nm}^{-2}$ .

As mentioned, the clusters were placed in another chamber filled with air at 1 atm and irradiated with UV light in the chamber. Figure 3 shows the fibres and helices composed of C<sub>60</sub> molecules after irradiation of UV light for 3 h. Those structures were not broken by electron beams anymore even when the accelerating



**Figure 2** Formation of clusters. **(a)** Clusters formed by C<sub>60</sub> molecules after having left the crystals composed of C<sub>60</sub> molecules in carbon dioxide under supercritical conditions (36.0°C) for 24 h. **(b)** C<sub>60</sub> molecules were so weakly bonded to each other that the clusters were broken by the electron beams, the energy flux of which was  $1.5 \text{ nW nm}^{-2}$ , during the SEM observation.

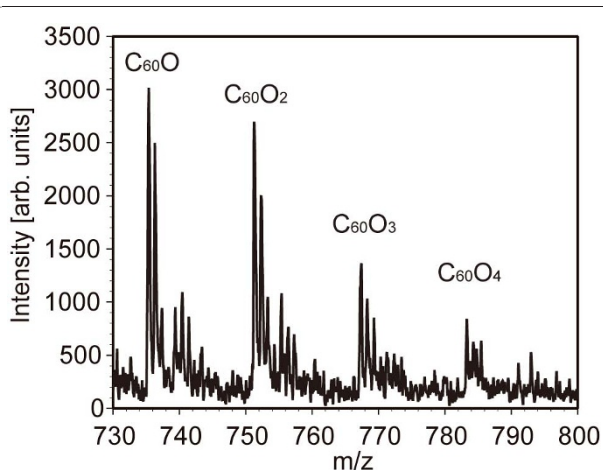


**Figure 3** Clusters after UV light irradiation for 3 h in a 1 atm air-filled chamber. (a) Fibres. (b) Helices. Those structures were not broken by electron beams any more.

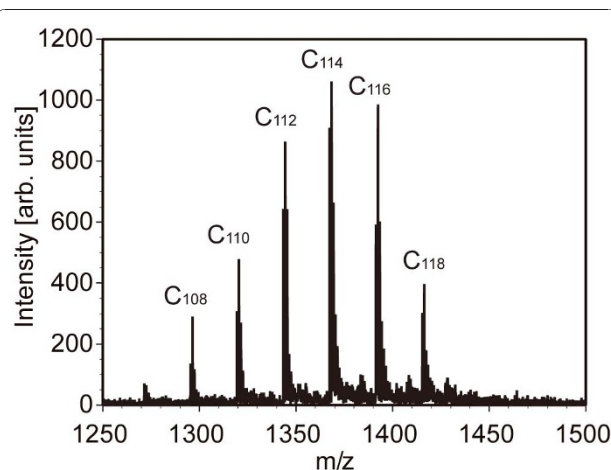
voltage was raised up to 10 kV (see Additional file 1 for the movie). Note that those structures were broken by electron beams when the clusters were placed in a vacuum chamber irradiated with UV light. Mass spectroscopic analysis of those clusters was carried out to investigate the component of the structures. Figure 4 shows the result of the mass spectroscopic analysis. Interestingly,  $C_{60}O_n$  molecules (where  $n = 1, 2, 3$  and 4), that is,  $C_{60}$  molecules to which oxygen atoms are bonded, but neither  $C_{120}$  nor  $C_{60}-O-C_{60}$  molecules were found. In other words, the reinforced clusters were not polymerised via a chemical bond. Note that when the chamber was vacuumed and UV light was irradiated, the clusters were broken as mentioned, but dimers such as  $C_{108}$ ,  $C_{110}$ ,  $C_{112}$ ,  $C_{114}$ ,  $C_{116}$  and  $C_{118}$  were created (see Figure 5). It is therefore supposed that air and irradiation of UV photons are essential for the reinforcement of clusters composed of

$C_{60}$  molecules. The dissociation energy of an oxygen molecule,  $O_2 \rightarrow O + O$ , is 5.1 eV [34]; therefore, it is supposed that oxygen molecules in the chamber were dissociated by photons of 184.9-nm wavelength, the energy of which is 6.48 eV, and oxygen atoms were bonded to  $C_{60}$  molecules. The order of the diameter of the clusters being 10 nm, it is supposed that  $C_{60}$  molecules located at the surface of the clusters were oxidised (see Figure 6) and the clusters somehow reinforced. It is inferred that oxidised  $C_{60}$  molecules located at the surface of the clusters may have an important role for the reinforcement of the clusters.

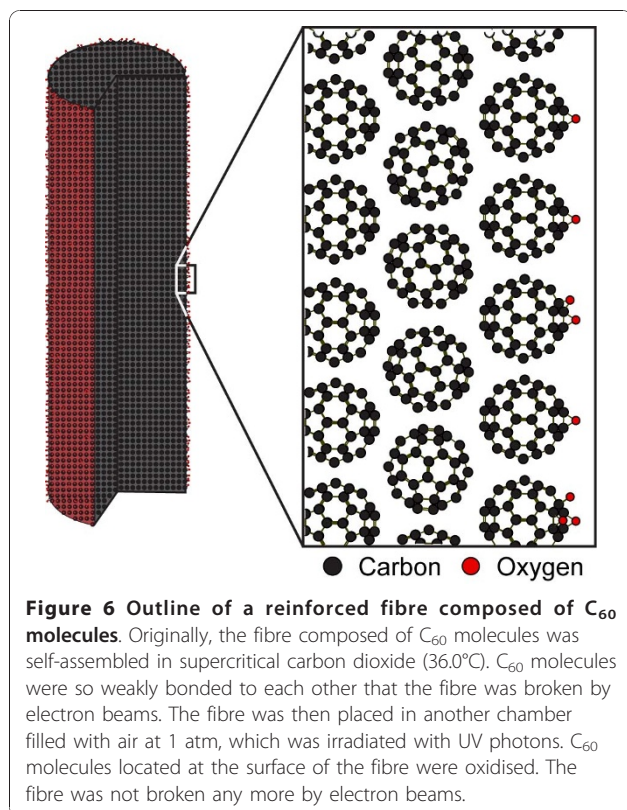
We will be investigating the mechanism of the reinforcement of the clusters, that is, the role of oxidised  $C_{60}$  molecules ( $C_{60}O_n$ ) located at the surface of the clusters, in the reinforcement process in detail, carrying out quantum mechanical calculations. We will also be measuring the electric, electronic, mechanical and thermal



**Figure 4** Time-of-flight mass spectroscopy. The clusters were composed of  $C_{60}$  molecules (not shown in the graph) and  $C_{60}O_n$  molecules ( $n = 1, 2, 3, 4$ ). It is supposed that oxygen atoms are bonded to  $C_{60}$  molecules at the surface of the clusters.



**Figure 5** Time-of-flight mass spectroscopy. The fibres and helices were broken by electron beams and dimers were formed when the clusters were placed in a vacuum chamber irradiated with UV light. The chamber was not filled with air.



properties of the fibres and helices so that the clusters may be utilised for the development of nano electron devices, nano/microelectromechanical systems and micro-total analysis systems.

## Summary

We carried out two experiments: (1) Crystals composed of  $C_{60}$  molecules were placed in supercritical carbon dioxide ( $36.0^{\circ}C$ ), and it was found that fibres, fibre networks and helices composed of  $C_{60}$  molecules were self-assembled. Since  $C_{60}$  molecules in the clusters were bonded to each other via van der Waals interactions [32], the clusters were easily broken by the irradiation of electron beams during the SEM observation. (2) The clusters were placed in another chamber filled with air at 1 atm and irradiated with UV photons. Oxygen molecules were dissociated by UV photons,  $C_{60}$  molecules at the surface of the clusters were oxidised, and  $C_{60}O_n$  molecules were created. The clusters were not broken by the electron beams any more. It is supposed that  $C_{60}O_n$  molecules located at the surface of the clusters may have an important role in the reinforcement process, but the actual mechanism of the reinforcement of the clusters has not yet been clearly understood and therefore is an open question.

## Additional material

**Additional file 1: Supplementary materials.** Supplementary Material 1 - SEM observation of clusters composed of  $C_{60}$  molecules which were self-assembled in supercritical carbon dioxide. The accelerating voltage of electron beams is 1.0 kV. The clusters are broken during the SEM observation. Supplementary Material 2 - SEM observation of clusters.  $C_{60}$  molecules located at the surface of the clusters were oxidised. The accelerating voltage of electron beams is 1.0 kV. The clusters are not broken any more during the SEM observation.

## Acknowledgements

Part of the present study has been supported by a Grant for High-Tech Research Centres organised by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. T. Fukuda would like to thank MEXT for their financial support.

## Authors' contributions

SK designed the study and carried out the experiment. TF participated in the design of the study and performed SEM observation and mass spectroscopic analysis. YS participated in the reinforcement experiment. TM participated in the design of the study, coordinated the study and wrote the manuscript. All authors read and approved the final manuscript.

## Competing interests

The authors declare that they have no competing interests.

Received: 25 August 2010 Accepted: 12 January 2011

Published: 12 January 2011

## References

1. Eklund PC, Rao AM, Zhou P, Wang Y, Holden JM: **Photochemical transformation of  $C_{60}$  and  $C_{70}$  films.** *Thin Solid Films* 1995, **257**:185.
2. Rao CNR, Govindaraj A, Aiyer HN, Seshadri R: **Polymerization and pressure-induced amorphization of  $C_{60}$  and  $C_{70}$ .** *J Phys Chem* 1995, **99**:16814.
3. Rao AM, Eklund PC, Venkateswaran UD, Tucker J, Duncan MA, Bendele GM, Stephens PW, Hodeau J-L, Marques L, Núñez-Regueiro M, Bashkin IO, Ponyatovsky EG, Morovsky AP: **Properties of  $C_{60}$  polymerized under high pressure and temperature.** *Appl Phys A* 1997, **64**:231.
4. Onoe J, Takeuchi K: **How many [2+2] four-membered rings are formed on a  $C_{60}$  molecule when photopolymerization is saturated?** *Phys Rev Lett* 1997, **79**:2987.
5. Rao AM, Eklund PC, Hodeau J-L, Marques L, Nunez-Regueiro M: **Infrared and Raman studies of pressure-polymerized  $C_{60}$ s.** *Phys Rev B* 1997, **55**:4766.
6. Onoe J, Takeuchi K: **Photo-induced coalescence of  $C_{60}$  molecules in a potassium-doped  $C_{60}$  film: mass spectral evidence.** *J Mass Spectrom* 1998, **33**:387.
7. Wågberg T, Jacobsson P, Sundqvist B: **Comparative Raman study of photopolymerized and pressure-polymerized  $C_{60}$  films.** *Phys Rev B* 1999, **60**:4535.
8. Fujitsuka M, Fujiwara K, Murata Y, Uemura S, Kunitake M, Ito O, Komatsu K: **Properties of photoexcited states of  $C_{180}$ , a triangle trimer of  $C_{60}$ .** *Chem Lett* 2001, **5**:384.
9. Dunsch L, Rapta P, Gromov A, Staško A: **In situ ESR/UV-vis-NIR spectroelectrochemistry of  $C_{60}$  and its dimers  $C_{120}$ ,  $C_{120}O$  and  $C_{120}OS$ .** *J Electroanal Chem* 2003, **547**:35.
10. Onoe J, Nakayama T, Aono M, Hara T: **Electrical properties of a two-dimensionally hexagonal  $C_{60}$  photopolymer.** *J Appl Phys* 2004, **96**:443.
11. Karachevtsev VA, Mateichenko PV, Nedbailo NY, Peschanskii AV, Plokhotnichenko AM, Vovk OM, Zubarev EN, Rao AM: **Effective photopolymerization of  $C_{60}$  films under simultaneous deposition and UV light irradiation: Spectroscopy and morphology study.** *Carbon* 2004, **42**:2091.
12. Alvarez-Zaucó E, Sobral H, Basiuk EV, Saniger-Blesa JM, Villagrán-Muniz M: **Polymerization of  $C_{60}$  fullerene thin films by UV pulsed laser irradiation.** *Appl Surf Sci* 2005, **248**:243.

13. Yamamoto H, Iwata N, Hashimoto R, Ando S: **Photon-assisted synthesis of C<sub>60</sub> polymers by laser irradiation.** *Appl Surf Sci* 2007, **253**:7977.
14. Oszlanyi G, Forro L: **Two-dimensional polymer of C<sub>60</sub>.** *Solid State Commun* 1995, **93**:265.
15. Persson P-A, Edlund U, Jacobsson P, Johnels D, Soldatov A, Sundqvist B: **NMR and Raman characterization of pressure polymerized C<sub>60</sub>.** *Chem Phys Lett* 1996, **258**:540.
16. Sundqvist B, Edlund U, Jacobsson P, Johnels D, Jun J, Launois P, Moret R, Persson P-A, Soldatov A, Wågberg T: **Structural and physical properties of pressure polymerized C<sub>60</sub>.** *Carbon* 1998, **36**:657.
17. Chen X, Yamanaka S, Sako K, Inoue Y, Yasukawa M: **First single-crystal X-ray structural refinement of the rhombohedral C<sub>60</sub> polymer.** *Chem Phys Lett* 2002, **356**:291.
18. Wang G-W, Komatsu K, Murata Y, Shiro M: **Synthesis and X-ray structure of dumb-bell-shaped C<sub>120</sub>.** *Nature* 1997, **387**:583.
19. Lebedkin S, Gromov A, Giesa S, Gleiter R, Renker B, Rietschel H, Krätschmer W: **Raman scattering study of C<sub>120</sub>, a C<sub>60</sub> dimer.** *Chem Phys Lett* 1998, **285**:210.
20. Komatsu KK, Wang G-W, Murata Y, Tanaka T, Fujiwara K: **Mechanochemical synthesis and characterization of the fullerene dimer C<sub>120</sub>.** *J Org Chem* 1998, **63**:9358.
21. Wood JM, Kahr B, Hoke SH, Dejarmell L, Cooks RG, Ben-Amotz D: **Oxygen and methylene adducts of C<sub>60</sub> and C<sub>70</sub>.** *J Am Chem Soc* 1991, **113**:5907.
22. Zhou P, Rao AM, Wang K-A, Robertson JD, Eloi C, Meier MS, Ren SL, Bi X-X, Eklund PC, Dresselhaus MS: **Photo-assisted structural transition and oxygen diffusion in solid C<sub>60</sub> films.** *Appl Phys Lett* 1992, **60**:2871.
23. Lebedkin S, Ballenweg S, Gross J, Taylor R, Krätschmer W: **Synthesis of C<sub>120</sub>O: A new dimeric [60] fullerene derivative.** *Tetrahedron Lett* 1995, **36**:4971.
24. Penn SG, Costa DA, Balch AL, Lebrilla CB: **Analysis of C<sub>60</sub> oxides and C<sub>120</sub>O<sub>n</sub> (n = 1,2,3) using matrix assisted laser desorption-ionization Fourier transform mass spectrometry.** *Int J Mass Spectrom Ion Processes* 1997, **169/170**:371.
25. Gromov A, Lebedkin S, Hull WE, Krätschmer W: **Isomers of the dimeric fullerene C<sub>120</sub>O<sub>2</sub>.** *J Phys Chem A* 1998, **102**:4997.
26. Krause M, Dunsch L, Seifert G, Fowler PW, Gromov A, Krätschmer W, Gutierrez R, Porezag D, Frauenheim T: **Vibrational signatures of fullerene oxides.** *J Chem Soc Faraday Trans* 1998, **94**:2287.
27. Heymann D, Bachilo SM, Weisman RB, Cataldo F, Fokkens RH, Nibbering NMM, Vis RD, Chibante LPF: **C<sub>60</sub>O<sub>3</sub>, a fullerene ozonide: Synthesis and dissociation to C<sub>60</sub>O and O<sub>2</sub>.** *J Am Chem Soc* 2000, **122**:11473.
28. Weisman RB, Heymann D, Bachilo SM: **Synthesis and characterization of the "missing" oxide of C<sub>60</sub>: [5,6]-open C<sub>60</sub>O.** *J Am Chem Soc* 2001, **123**:9720.
29. Resmi MR, Ma S, Caprioli R, Pradeep T: **C<sub>120</sub>O<sub>n</sub> from C<sub>60</sub>Br<sub>24</sub>.** *Chem Phys Lett* 2001, **333**:515.
30. Heymann D, Weisman RB: **Fullerene oxides and ozonides.** *CR Chim* 2006, **9**:1107.
31. Stanley HE: **Introduction to phase transition and critical phenomena.** Oxford: Oxford University Press; 1971.
32. Fukuda T, Ishii K, Kurosu S, Whitby R, Maekawa T: **Formation of clusters composed of C<sub>60</sub> molecules via self-assembly in critical fluids.** *Nanotechnology* 2007, **18**:145611.
33. Somayajulu GR: **Estimation procedures for critical constants.** *J Chem Eng Data* 1989, **34**:106.
34. Okabe H: **Photochemistry of small molecules.** New York: Wiley; 1978.

doi:10.1186/1556-276X-6-80

**Cite this article as:** Kurosu et al.: Formation and reinforcement of clusters composed of C<sub>60</sub> molecules. *Nanoscale Research Letters* 2011 **6**:80.

**Submit your manuscript to a SpringerOpen<sup>®</sup> journal and benefit from:**

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

---

Submit your next manuscript at ► [springeropen.com](http://springeropen.com)

---