JOURNAL OF Materials CHEMISTRY Communication

Formation of carbon nanocapsules with SiC nanoparticles prepared by polymer pyrolysis

Takeo Oku,*† Koichi Niihara and Katsuaki Suganuma

Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

Carbon nanocapsules with SiC nanoparticles were produced by thermal decomposition of polyvinyl alcohol with SiC clusters at 500 °C in Ar gas atmosphere. High-resolution electron microscopy also showed the formation of carbon hollow structures such as nanoparticles, polyhedra, and clusters. The present work indicates that the pyrolysis of polymer materials with clusters is a useful fabrication method for the mass-production of carbon nanocapsules at low temperatures compared to the ordinary arc discharge method.

Carbon has various hollow-cage structures such as C_{60}, giant fullerenes, nanocapsules, bucky onions, nanopolyhedra, cones and nanotubes.[1–5] These structures show different physical properties, and offer the potential to study low-dimensional materials in isolated environments. Nanoclusters encapsulated within these carbon hollow-cage structures are intriguing for both scientific research and future device applications such as cluster protection, nano-ballbearings, nano-optical–magnetic devices, catalysis, and biotechnology.[6–9] The arc discharge method[10] is an ordinary method for the formation of hollow-cage structures. However, it is hard to separate these cages from carbon soot, and understanding of the formation process is difficult because of the coexistence of various carbon by-products and because of the high-temperature annealing.

The purpose of the present work is to prepare carbon nanocapsules with nanoclusters at low temperatures without using the arc discharge method. SiC nanoparticles with polyvinyl alcohol were selected for nanocapsule formation. Polyvinyl alcohol decomposes readily at elevated temperatures, and produces carbon-based materials. SiC is a hard material with a hardness of *ca.* 30 GPa. If the SiC nanoparticles are combined with slippery graphite, nano-ballbearings and solid-state lubricants can be obtained, which are similar in properties to the metal dichalcogenides produced by Rapoport *et al.*[8] To understand the formation mechanism of the nanocapsules, high-resolution electron microscopy (HREM) was carried out for microstructure analysis. These studies will provide guidelines for the design and synthesis of the carbon nanocapsules, which are expected as future nanoscale devices.

β-SiC nanoparticles (Sumitomo Cement Co. Ltd.) were dispersed in de-ionized water with polyvinyl alcohol (PVA-706, Kuraray Co., Ltd.)[9] at 60 °C. This polymer is a copolymer of polyvinyl alcohol and polyvinyl acetate. The solution with SiC and polyvinyl alcohol was dried in a drying oven prior to loading into the vacuum chamber. The annealing chamber was first evacuated to 1×10^{-6} Pa, and the samples were annealed at 500 °C for 30 min in an atmosphere of 0.12 MPa Ar gas.

Samples for HREM observation were prepared by dispersing the materials on a holey carbon grid. HREM observation was performed with a 200 kV electron microscope (JEM-2010) having a point-to-point resolution of 0.194 nm. The electron microscope is equipped with a TEM-IP system (PIXsysTEM), and imaging plates (IP) with the advantage of a large detection area of digital data were used to record the observed images. The detection area of the IP is 102×77 mm with a pixel size of 25×25 μm and an image depth of 0–16383 gray scale. The digital data were saved in digital data storage (DDS) by Digital Micro-Luminography (Fuji Film Co. Ltd.). For image processing and analysis of the observed HREM images, Image Gauge, L Process (Fuji Film Co. Ltd.), Digital Micrograph (Gatan Inc.) and Adobe Photoshop software were used.

A typical HREM image of as-prepared SiC nanoparticles with polyvinyl alcohol is shown in Fig. 1. The SiC particle size is in the range of 10–50 nm. An amorphous layer with a thickness of 1–5 nm is observed at the surface of the SiC nanoparticles as indicated by the arrows. This layer must be amorphous carbon, formed by decomposition of polyvinyl alcohol.

A HREM image of SiC nanoparticles prepared with polyvinyl alcohol annealed at 500 °C in Ar gas atmosphere is shown in Fig. 2(a). The particle size is 10–30 nm, and all particles are surrounded by graphite sheets as indicated by arrows A. Graphite sheets without any nanoparticles are also observed as indicated by arrows B. An enlarged HREM image of a nanoparticle is shown in Fig. 2(b). Lattice fringes with a distance of 0.25 nm which corresponds to the distance of {111} planes of β-SiC are observed in the clusters. The {002} planes of graphite grow epitaxially on the {111} planes of β-SiC, which divides the SiC nanoparticle.

Fig. 3(a) is a HREM image of double graphite-layered nanoparticles with a size of *ca.* 10 nm. These nanoparticles were formed by the decomposition of polyvinyl alcohol which consists of C, H, and O atoms. The polyvinyl alcohol has the general formula $[CH_2CH(OH)]_m[CH_2CH(OCOCH_3)]_n$, and

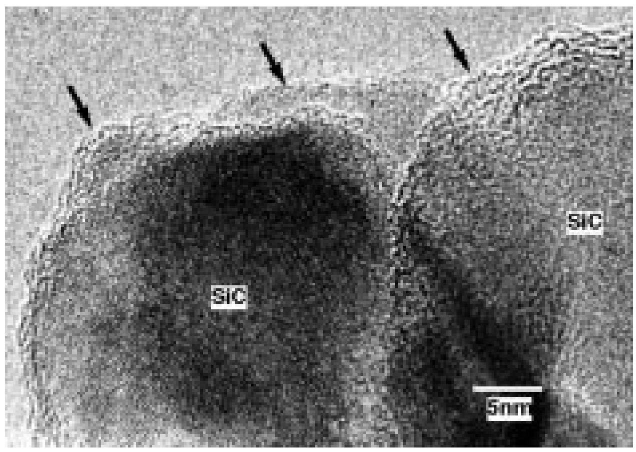

Fig. 1 HREM image of as-prepared SiC nanoparticles with polyvinyl alcohol

†E-mail: Oku@sanken.osaka-u.ac.jp

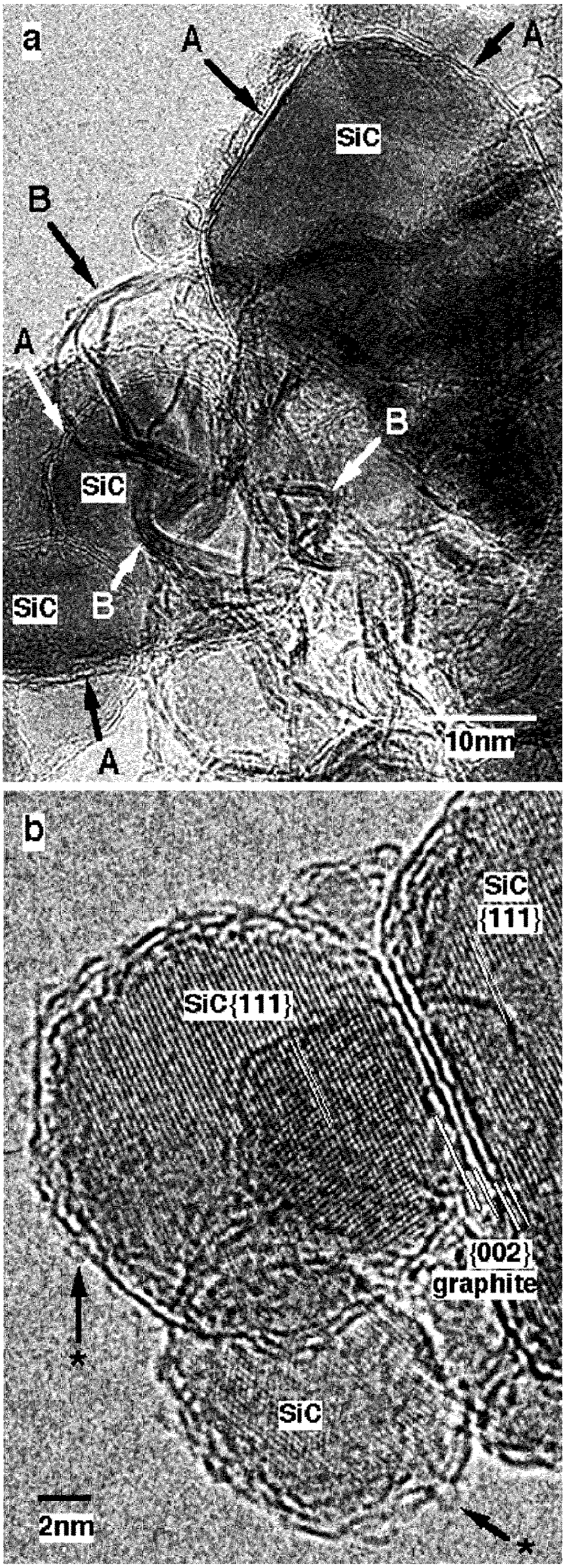

Fig. 2 (a) HREM image of annealed SiC nanoparticles with polyvinyl alcohol. (b) Enlarged HREM image of the nanocapsule.

it decomposes into H_2O and CO_2 at 120–170 °C in air. In the present work, only the carbon atoms remained in the sample after the pyrolysis of polyvinyl alcohol into H_2O and CO_2 in Ar atmosphere. A single wall polyhedron with flat graphite {002} planes is also observed at the graphite surface near the SiC nanoparticle as shown in Fig. 3(b). Weak contrast is observed inside the polyhedron, which might be due to the existence of amorphous carbon.

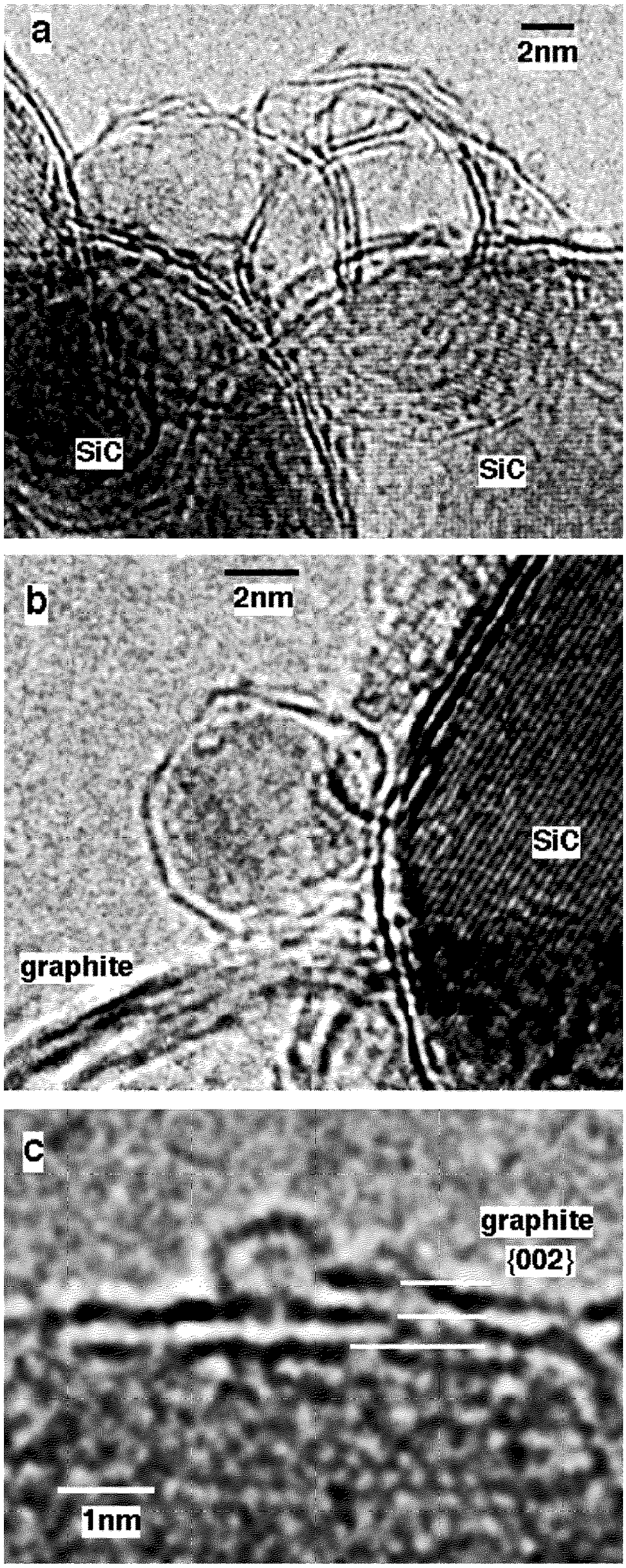

Fig. 3 HREM images of carbon hollow cages. (a) Double wall nanocages. (b) Single wall polyhedra. (c) Carbon cluster at nanocapsule surface.

Hollow carbon clusters with diameter in the range 0.7–1.0 nm are often observed as indicated by asterisks in Fig. 2(b). An enlarged HREM image of a carbon cluster is shown in Fig. 3(c). These are giant fullerenes derived from the

C_{60} series structures, which consist of 12 pentagons and arbitrary numbers of hexagons with 60+ carbon atoms.[6] In Fig. 3(c), the carbon cluster is connected at the step edge of the graphite sheets. Dark contrast corresponding to a carbon layer are observed, and the number of atoms is *ca.* 120, which is estimated from the size of the clusters (*ca.* 1 nm). In addition, dark contrast is observed inside the cluster, which indicates the existence of several atoms inside the carbon cluster.

Formation of the graphite layer around nanoparticles is useful for cluster protection against grain growth of nanoparticles. For various nanostructured materials, nanograins are needed to obtain various required properties such as mechanical, electronic, and magnetic properties. Similar formation of graphite layers had been reported in the SiC ceramics prepared from polysilastyrene at 1800 °C in Ar gas atmosphere[11] and by liquid phase sintering of SiC at 1700 °C in vacuum.[12] In addition, formation of carbon nanotubes had also been reported upon decomposition of SiC at 1700 °C in vacuum.[13] In these works, {002} planes of graphite sheets grow epitaxially on the {111} planes of β-SiC, which agrees well with the present results. The graphite structure was also produced by pyrolysis of a polyvinylidene chloride polymer at temperatures in the range 2100–2600 °C in an inert atmosphere.[14] In the present work, we have succeeded in producing carbon nanocapsules at 'low' temperature, 500 °C, in Ar gas atmosphere. Although carbon nanocapsules have previously been produced with the aid of catalytic effects of metal elements such as Fe, Co, and Ni,[6,9] these catalytic elements are not needed in the present work. By the ordinary arc discharge method, it is difficult to control the formation of nanocapsules. In the present work, the number of the graphite sheets is in the range of 1–3; this number can be controlled by altering the solution concentration of the polyvinyl alcohol.

In conclusion, carbon nanocapsules with SiC nanoparticles were produced by thermal decomposition of polyvinyl alcohol with SiC clusters at the low temperature of 500 °C in Ar gas atmosphere. Formation of carbon nanoparticles, polyhedra, and clusters were also observed by HREM. A HREM image of the nanocapsules showed that the graphite {002} planes were epitaxially grown on the {111} surface of the β-SiC. The present work indicates that the pyrolysis of polymer materials is a useful method for the formation of carbon nanocapsules at very low temperatures compared to the conventional methods. Since the polyvinyl alcohol has a pyrolysis temperature of *ca.* 120 °C, formation of carbon nanocapsules would be also expected at low temperatures below 100 °C. This kind of chemical process is also useful for large-scale production of nanocapsules with nanoclusters (semiconductors, metals, ceramics, *etc.*) from solution with colloids and metal complexes, which is expected to be applicable to future nanoscale devices.

The authors would like to acknowledge Prof. Y. Hirotsu and Dr. T. Ohkubo for allowing us to use the electron microscope. The authors would like to thank Mr. M. Ueshima for experimental help. This work is supported by The Mitsubishi Foundation.

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien and R. E. Smalley, *Nature* (*London*), 1985, **318**, 162.
2 S. Iijima, *Nature* (*London*), 1991, **354**, 56.
3 D. Ugarte, *Nature* (*London*), 1992, **359**, 707.
4 Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita and T. Hayashi, *Chem. Phys. Lett.*, 1993, **204**, 277.
5 A. Krishnan, E. Dujardin, M. M. J. Treacy, J. Hugdahl, S. Lynum and T. W. Ebbesen, *Nature* (*London*), 1997, **388**, 451.
6 Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, A. Kasuya and Y. Nisina, *J. Phys. Chem. Solids*, 1993, **54**, 1849.
7 J. Sloan, J. Cook, M. L. H. Green, J. L. Hutchinson and R. Tenne, *J. Mater. Chem.*, 1997, **7**, 1089.
8 L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S. R. Cohen and R. Tenne, *Nature* (*London*), 1997, **387**, 791.
9 Kuraray Co., Ltd., Osaka, Japan.
10 B. R. Elliott, J. J. Host, V. P. Dravid, M. H. Teng and J.-H. Hwang, *J. Mater. Res.*, 1997, **12**, 3328.
11 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature* (*London*), 1990, **347**, 354.
12 K. Suganuma, G. Sasaki, T. Fujita, M. Okumura and K. Niihara, *J. Mater. Sci.*, 1993, **28**, 1175.
13 C. M. Wang, M. Mitomo and H. Emoto, *J. Mater. Res.*, 1997, **12**, 3266.
14 M. Kusunoki, M. Rokkaku and T. Suzuki, *Appl. Phys. Lett.*, 1997, **71**, 2620.
15 P. J. F. Harris and S. C. Tsang, *Philos. Mag. A*, 1997, **76**, 667.

Communication 8/01912F; *Received* 9th *March*, 1998