References

[1] Heimann RB, Evsyukov SE, Kavan L. Carbyne and carbynoid structures. Dordrecht: Kluwer; 1999.

[2] Casari CS, LiBassi A, Ravagnan L, Siviero F, Lenardi C, Piseri P, et al. Chemical and thermal stability of carbyne-like structures in cluster-assembled carbon films. Phys Rev B 2004;69:075422.

[3] Wakabayashi T, Ong AL, Srelnikov D, Krätschemer WJ. Flashing carbon on cold surfaces. J Phys Chem B 2004;108:3686–90.

[4] Heath JR, Zhang QL, O'Brien SC, Curl RF, Kroto HW, Smalley RE. The formation of long carbon chain molecules during laser vaporization of graphite. J Am Chem Soc 1987;109:359–63.

[5] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. Phys Rev B 2000;61:14095–106.

[6] Kastner J, Kuzmany H, Kavan L, Dousek FP, Kurti J. Reductive preparation of carbyne with high yeld. An in ssitu Raman scattering study. Macromolecules 1995;28:344–53.

[7] Ferrari AC, Robertson J. Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon. Phys Rev B 2001;64:075414.

[8] Robertson J, O'Reilly EP. Electronic and atomic structure of amorphous carbon. Phys Rev B 1987;35:2946–57.

[9] Lucotti A, Tommasini M, Del Zoppo M, Castiglioni C, Zerbi G, Cataldo F, et al. Raman and SERS investigation of isolated sp carbon chains. Chem Phys Lett 2006;417:78–82.

[10] Strazzulla G, Baratta GA, Battiato S, Compagnini G. In: Cataldo F, editor. Polyynes: synthesis, properties, and applications. New York: Marcel Dekker; 2005. p. 271–84.

[11] Hlavaty H, Kavan L. Modification of electrochemical carbon by in situ generated carbenes. Carbon 1997;35:127–31.

[12] Ravagnan L, Bongiorno G, Bandiera D, Salis E, Piseri P, Milani P, et al. Quantitative evaluation of sp/sp2 hybridization ratio in cluster-assembled carbon films by in situ near edge X-ray absorption fine structure spectroscopy. Carbon 2006;44:1518–24.

[13] see for instance: Cataldo F. Synthesis of polyynes in a submerged electric arc in organic solvents. Carbon 2004;42:129–42.

Catalytic growth of giant single- and double-wall fullerene cages at low temperature

Z.M. Sheng, J.N. Wang *

School of Materials Science and Engineering, Shanghai Jiao Tong University, 1954 Huashan Road, Shanghai 200030, PR China

Received 4 March 2006; accepted 17 April 2006
Available online 16 May 2006

Keywords: Carbon nanoparticles; Heat treatment; Transmission electron microscopy

Since the discovery of C_{60} [1], there has been an immense interest not only in this fullerene cage but its varieties with larger sizes as well. However, wide exploration of the properties and applications of such material has been hindered as an efficient synthesis technique is still lacking. The synthetic processes described in the literature such as laser ablation [1] and arc discharging [2] take place at very high temperatures (>2600 °C) and result in a low yield of fullerenes of C_{60} and its close varieties. Higher fullerenes such as C_{180}, C_{240}, and C_{560} were rarely observed although they have been theoretically predicted [3]. Here we describe a catalytic method, for the first time, for production of giant fullerene cages of C_{1140} to C_{4570} with single- or double-wall structure. This was achieved by heat treatment of amorphous carbon containing uniformly distributed Fe nanoparticles at low temperatures of 1000–1350 °C.

The precursor used for heat treatment was fabricated by thermal pyrolysis. A gas mixture of C_2H_2 and iron pentacarbonyl [$Fe(CO)_5$] was introduced into a vertical quartz tube furnace set at 700 °C with N_2 as a diluting gas. In order to add $Fe(CO)_5$, N_2 and C_2H_2 gases flowed through the liquid carbonyl which was held at 0 °C. Typical flow rates were 30 l/h for N_2 and 20 ml/min for C_2H_2, yielding a production rate of ~5 g/h. For heat treatment, the obtained black powder was put in a corundum tube, and then the tube was evacuated and filled with argon to atmospheric pressure. The tube containing the sample was rapidly heated to a temperature of 1000–1350 °C at a heating rate of approximately 400 °C/min. After annealing for 0.5–2 h, the tube was cooled either in the furnace or in air.

X-ray diffraction (XRD) of the precursor suggests that crystallization of both carbon and iron was poor (Fig. 1(a)). High-resolution transmission electron microscopy (HRTEM) of the precursor shows that rather small iron particles with diameters of up to 3 nm were dispersed

* Corresponding author. Tel.: +86 21 62932015; fax: +86 21 62932587.
E-mail address: jnwang@mail.sjtu.edu.cn (J.N. Wang).

0008-6223/$ - see front matter

doi:10.1016/j.carbon.2006.04.019

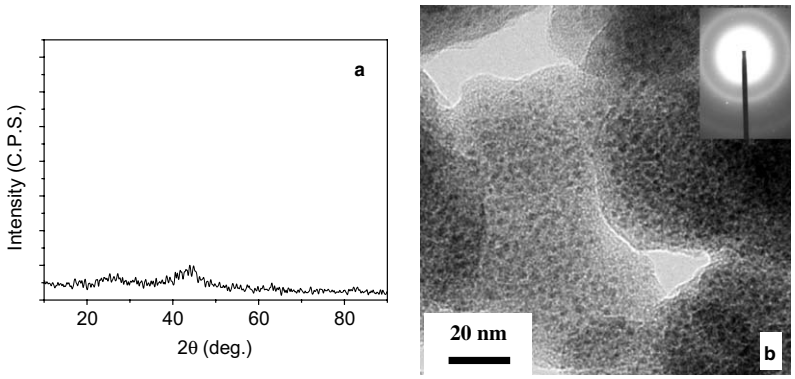

Fig. 1. Analysis of the precursor. (a) XRD pattern of the precursor with no strong peaks, indicating poor crystallization of carbon and iron. (b) HRTEM image of the precursor showing that rather small iron particles (up to 2–3 nm) were dispersed homogeneously in amorphous carbon, and SAED image (insert) indicating poor crystallization of Fe.

homogeneously in the matrix of carbon (Fig. 1(b)). XRD of the sample after heat treatment shows strong peaks (Fig. 2(a)), indicating that both carbon and iron crystallized with the formation of additional Fe_3C. HRTEM directly illustrates the change of the original amorphous carbon to crystalline carbon with a cage structure. The new carbon nanocages generally have diameters in the range of 3–6 nm, and consist of a shell made up of one or two graphitic layers and an empty core (Fig. 2(b)–(d)). They are generally aggregated and appear to have irregular shapes in TEM (Fig. 2(b) and (d)). Nevertheless, separate double-wall cages are seen to have a spherical shape (Fig. 2(c)). Separate single-wall cages with a diameter of as large as 12 nm were also observed, but only occasionally. Such cages illustrate a regular polyhedral shape (Fig. 2(e)). After heat treatment, the original fine iron particles (Fig. 1(b)) disappeared and were replaced by much larger iron or cementite (Fe_3C) particles encapsulated in graphitic cages. Within some of these cages, an empty space can be found between iron and graphitic layers (Fig. 3). Annealing at 1350 °C for 2 h followed by spontaneous cooling (with furnace power turned-off) led to almost complete transformation of the original amorphous carbon to crystalline carbon. In such sample, the volume fraction of the iron-free cages was estimated to be ~80% with the rest being the Fe- or Fe_3C-containing cages.

The cores of the cages without iron or cementite particles could be hollow. This suggestion is supported by the observations of the lack of structure and uniform translucent appearance to the electron beam, and similar structures of graphitic planes in multiple overlaid cage particles. If the cages were filled with amorphous carbon, then the cores will show variations of translucence and the structures behind the overlaid particles could not be clearly discerned due to the intervening crystalline material in the path of the electron beam. These hollow carbon nanocages are apparently different from the typical carbon nanoonions [4] with sequent graphitic layers down to the center, but fall in the fullerene category.

It is now well known that C_{60} has a football-like structure. The sizes of this fullerene and its varieties are related

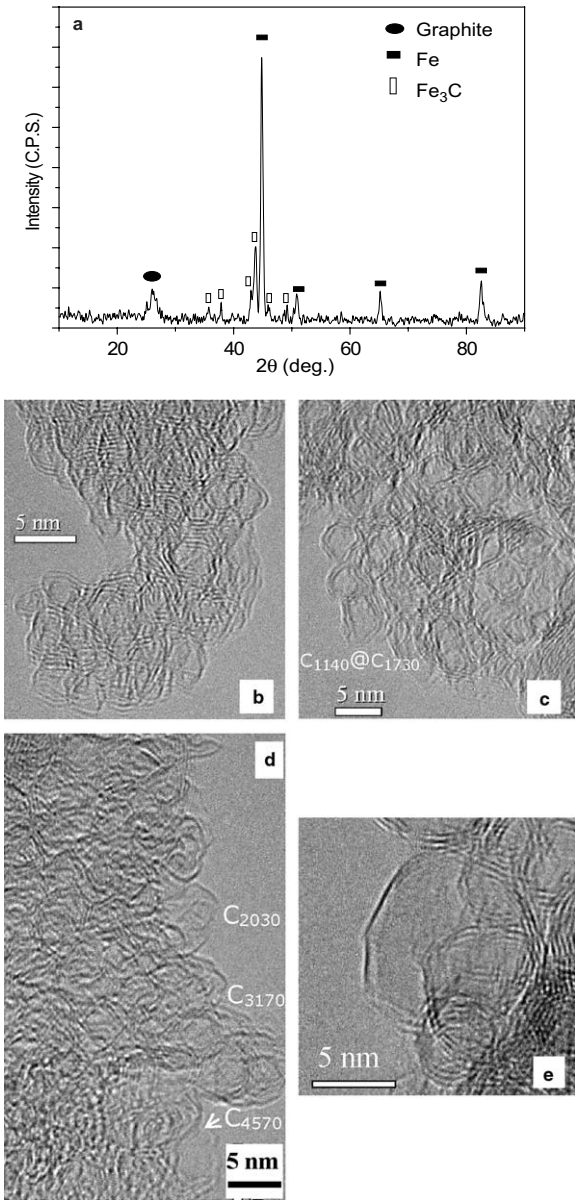

Fig. 2. XRD of the heat treated sample (1350 °C, 0.5 h, air cooling) showing peaks of graphite, α-Fe, and Fe_3C (a) and HRTEM images of fullerene cages with a double- (b, c) or a single-wall (d, e) structure.