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Graphitic hollow carbon calabashes

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Abstract

Graphitic carbon calabashes, a new structure of carbon, have been found among the solid carbon spheres synthesized by a mixed-valent oxide-catalytic carbonization (MVOCC) process. The calabashes are as large as 0.8 μm and are constructed by graphitic carbon shells of thicknesses ∼ 10 nm. The calabash can be hollow or filled with a carbon core. Oxygen gas has been found to be trapped inside the calabashes, suggesting they could be used for gas/energy storage.

Carbon is probably the most versatile element because it can form various structures. The successful growth of diamond films, fullerene molecule C_{60} and its family [1], carbon nano-tubes [2], and carbon onion [3] has excited many researchers and raised many speculations about their potential applications [4–14]. The variety of structures produced by carbon are determined by its unique hybridization sp^1, sp^2 and sp^3 bonding. One of the most striking features of carbon is that it can form pentagonal and heptagonal carbon-rings, and the combination of the two basic structural units with the hexagonal carbon-rings can form a variety of geometrical configurations. In this Letter, we report the finding of hollow graphitic carbon calabashes in the carbon products synthesized by a mixed-valent oxide-catalytic carbonization (MVOCC) process.

The MVOCC process uses natural gas (methane) as the source of carbon for synthesis of carbon products [7–14]. Natural gas flowed through a quartz tube placed inside a horizontal cylindrical furnace. The MnO_2 catalysis was placed at the end of the gas inlet. As the temperature increased at a rate of 9°C/min, decomposition of CH_4 occurred when the chamber temperature reached 900–1050°C; carbon solid spheres and calabashes were formed on the wall of the quartz tube. Although carbon spheres were the most dominant product, carbon calabashes were found using transmission electron microscopy (TEM).

Fig. 1a is a bright-field TEM image of the carbon calabashes with spherical and dumbbell shapes. The carbon calabash has the size of ∼ 0.8 μm, which is much larger than any of the fullerenes known. A careful examination of the image shows that the wall of the calabash is fairly uniform in thickness (see arrowheads 1 and 3). The calabash can be an hollow enclosed shell or filled with a carbon core, and in some cases the separation between the carbon shell and its core is almost equal distance (see arrowhead 3). The carbon calabashes and spheres stand by themselves without any contact or encapsulation with the MnO_2 catalyst. Chemical microanalysis using energy-dispersive X-ray spectroscopy (EDS) showed no Mn present in the carbon structures. The shell

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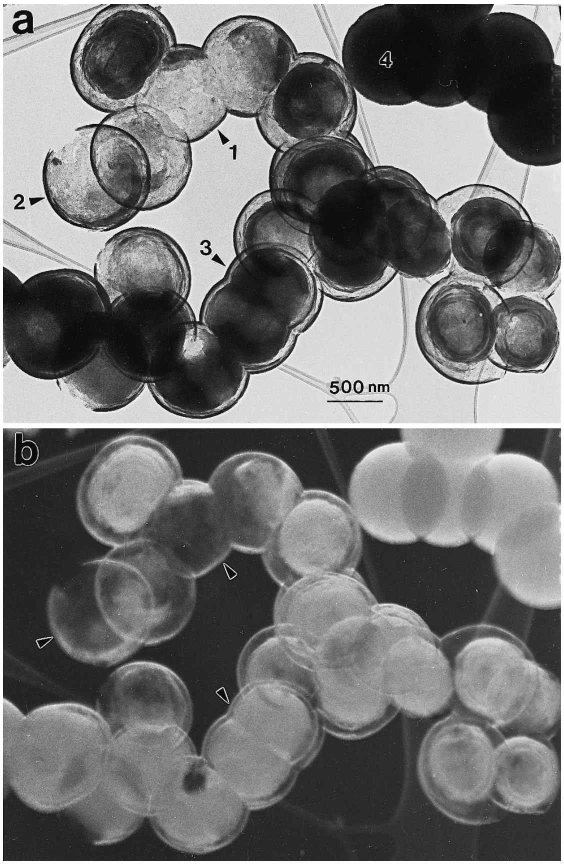

Fig. 1. (a) Bright-field and (b) dark-field TEM images of carbon calabashes found in carbon spheres synthesized by MVOCC. Arrowheads 1, 2, 3 and 4 indicate a spherical calabash, dumbbell calabash, dumbbell calabash containing a solid core and solid carbon spheres, respectively. The images were recorded at 200 kV using a Hitachi HF-2000 TEM equipped with a field emission source. The dark-field image was recorded by selecting the (101) and (112) reflection rings.

structure of the carbon calabash is also clearly revealed by the dark-field TEM image (Fig. 1b) since the image contrast is directly related to the projected density of carbon and from which the hollow shell structure is apparent. The core structure of the calabashes and the solid carbon spheres are clearly revealed. The solid spheres are composed of graphitic flakes and their growth model has been proposed [15–18].

The graphitic shell of the calabashes is best seen in the high-resolution TEM image (Fig. 2a). The calabash shell is rather uniform and the shell thickness is ∼ 10 nm. A sharp drop in the image contrast right inside the inner wall of the shell indicates that the calabash is hollow. Electron diffraction pattern shows that, if the electron beam is positioned at the center of a calabash (Fig. 2b), two broad rings corresponding to graphite (101) and (112) are observed; the absence of the (002) reflection indicates

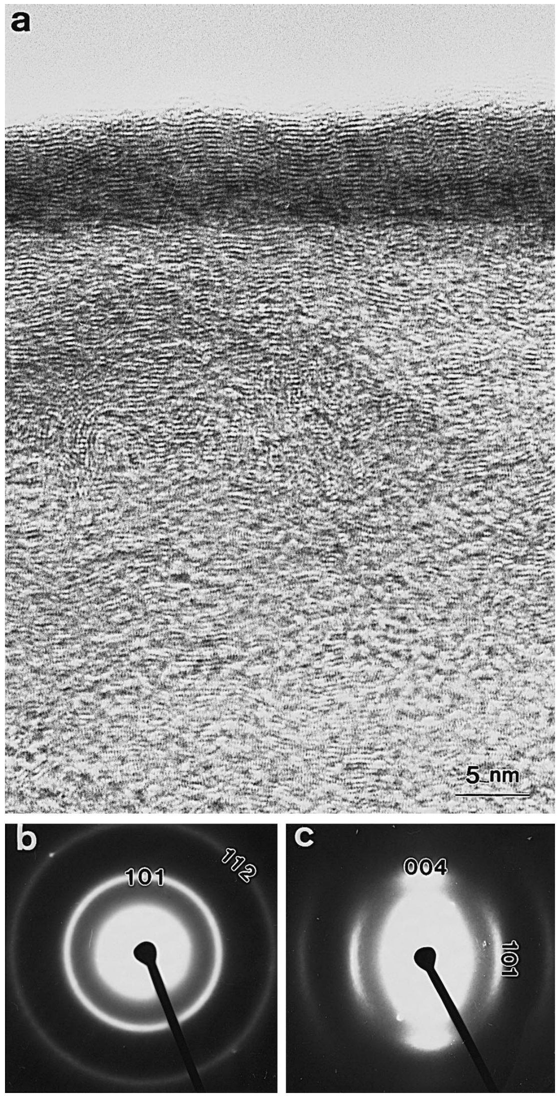

Fig. 2. (a) High-resolution TEM image recorded from a carbon calabash, showing a hollow shell structure. Electron diffraction patterns recorded from a hollow spherical carbon shell when the electron probe was positioned at (b) the center and (c) the edge of the calabash. The (002) reflection was over exposured in (c).

that the local (001) graphite plane is nearly perpendicular to the electron beam. The continuous (101) and (112) rings mean the random twist among (001) graphitic layers forming the shell. When the electron beam is positioned at the edge of the calabash (Fig. 2c), the pattern shows an arc-shape of the (002) and (004) reflections due to the curvature of the graphitic layers, thus, the (001) plane is nearly parallel to the electron beam, in agreement with the result provided by the TEM image. The elliptical shape of the (101) reflection is due to the spherical shape of the graphitic layers, and it indicates that the size of the graphitic layer is large [19]. This elliptical shape is a distinct difference from the diffraction pattern recorded from a solid carbon sphere composed of small-size graphitic flakes [15–18].

From the TEM images presented above it can be concluded that the carbon calabashes are either hollow or containing a carbon core. It is our interest to find the type of gas enclosed inside the calabashes. To probe this phenomenon from a single carbon calabash, EDS in TEM was employed. The electron beam was focused to a size of 30 nm, so that the chemical composition of the carbon calabash, as shown in the inset of Fig. 3, can be detected near its center and at its edge. In reference to the carbon K line, the oxygen K line in the EDS spectrum acquired from the center of the calabash shell (Fig. 3a) is apparently stronger than that in the spectrum acquired from the edge of the shell (Fig. 3b). The

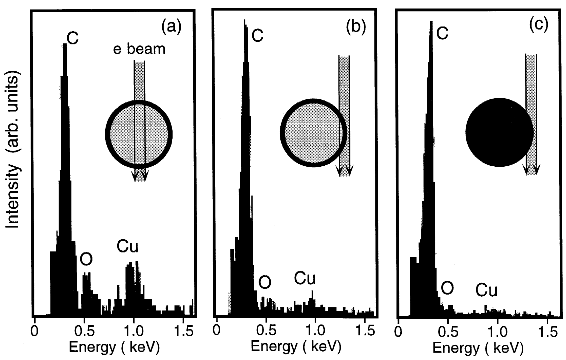

Fig. 3. Energy-dispersive X-ray spectra acquired from (a) the center of a carbon calabash, (b) the edge of the calabash, and (c) the edge of a solid carbon sphere. The Cu L line came from the copper grid used in TEM analysis. The relative intensity of the Cu L line with respect to that of the carbon K line depends on the specimen thickness, but the relative magnitude of O K line to C K line is the intrinsic property of the local region.

EDS spectrum acquired from the edge of a solid carbon sphere (Fig. 3c) shows a negligible oxygen peak, indicating that the oxygen adsorbed on the carbon surface, if any, is vanishingly small. Quantitative analysis of Fig. 3a gives the atom ratio of $[n_O/n_C]_{(a)} = (2.3 \pm 0.3)\%$, where the oxygen signal is contributed by the adsorbed oxygen and the oxygen gas enclosed inside the shell. In the case of Fig. 3b, $[n_O/n_C]_{(b)} = (0.5 \pm 0.3)\%$, and the oxygen signal is dominated by the adsorbed oxygen on the shell. With consideration the large size of the calabash in comparison to the beam size, the volume density of oxygen ρ_O enclosed inside the shell is determined by

$$\rho_O \approx \frac{r_o - r_i}{r_i}\{[n_O/n_C]_{(a)} - 2[n_O/n_C]_{(b)}\}\rho_C , \quad (1)$$

where r_o and r_i are the outer and inner radii of the shell, respectively, and ρ_C is the atom volume density of graphite. From the kinetics of gases, the partial pressure of oxygen is given by

$$P_O = \frac{\rho_O}{N_A} RT , \quad (2)$$

where N_A is the Avogadro's number, R the gas constant and T temperature. For $T = 300$ K and $(r_o - r_i)/r_i = 0.04$, Eq. (2) yields $P_O \approx 2.4 \times 10^5$ N/m^2. This means that the oxygen partial pressure inside the calabash is ~ 2.4 atmospheric pressure. This is a reasonable number with consideration of our experimental condition.

The gases trapped inside the hollow carbon calabashes can be oxygen, hydrogen and/or CH_4. If the trapped oxygen were in solid state and were distributed uniformly on the surface of the inner shell, there would be no difference between the EDS spectra acquired when the electron probe was positioned at the center and at the edge of the shell. The oxygen could be provided by the MnO_x catalysis during the carbonization process.

From the literature, a curling graphitic carbon particle is believed to be nucleated from a pentagonal atom ring, and its growth gives a quasi-icosahedral spiral shell carbon particle [20,21]. A pentagonal carbon ring produces an inward surface with positive curvature, resulting in spiral growth. This has been proposed as the nucleation of fullerenes and solid carbon spheres [15–18,20,21]. The structure of the carbon calabashes reported here is, however, different from either the carbon onion [3], the fullerenes, or the graphitic carbon sphere [15–18]. The most striking feature of the carbon calabashes is the large-size, hollow-shell graphitic structure. The growth of a large hollow calabash may require the formation of a large graphitic spherical layer at least for the most inner wall of the shell. For a diameter of 600 nm, it requires 6.8×10^7 atoms to construct a single enclosed layer. The energetically unfavorable growth of the large hollow shell cannot be interpreted by the spiral growth model. Therefore, our study here demonstrates a new carbon structure whose growth mechanism remains to be investigated.

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