

# Generation of giant carbon hollow spheres from C<sub>60</sub> fullerene by shock compression

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## Abstract

We report on the generation of carbon hollow spheres up to several  $\mu$  m in diameter on an internal hollow surface of the recovered sample from C<sub>60</sub> fullerene powder after shock-compression up to 57 GPa. Scanning electron microscopy demonstrates see-through spheres, a collapsed one like a **Ping-Pong** ball and bowl type objects, suggesting that the spheres are empty. Raman spectroscopy reveals that the carbon hollow spheres are in highly graphitized state, of which crystalline size is several hundred of nm. The possible formation mechanism is proposed.

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## 1. Introduction

Starting from the discoveries of C<sub>60</sub> fullerene [1], nanotubes [2] and carbon onions [3], the research on the synthesis and properties of new carbon materials has seen a considerable growing interest in the last decade. Laser vaporization, resistive heating, arc-discharge, and electron irradiation etc. have been utilized for the production.

Shock compression is one of experimental methods to instantaneously change carbon materials into a condition of high temperature and high pressure. It has been reported that tapped C<sub>60</sub> powders, of which initial density is 75 % of bulk crystal, transformed to disordered carbon near 25 GPa and an amorphous carbon above 50 GPa by shock compression [4]. Utilizing shock compression and rapid quenching (SCARQ) technique [5-7], on the other hand, transparent amorphous diamond and nanocrystalline diamond ceramics were fabricated from a C<sub>60</sub> thin film above 50 GPa, indicating that the quenching speed is an important factor to control the products.

In the present study, we report a discovery of highly graphitized hollow spheres up to several  $\mu$  m in diameter generated locally in a recovered sample from C<sub>60</sub> fullerene powder after shock-compression.

## 2. Experimental procedure

The specimen utilized is C<sub>60</sub> fullerene powder with the purity of 99.9 % from MER co. The powder was set into a stainless capsule (10-mm diameter and 4-mm thick) and subjected to shock loading twice using a powder gun with a 20-mm diameter bore. The capsule composed of C<sub>60</sub> fullerene powder was at first condensed to 18 GPa (Cu with flyer velocity of 0.92 km/s), of which pressure is lower than the critical pressure (20 GPa) to collapse C<sub>60</sub> fullerene molecules [8]. The density of the shocked C<sub>60</sub> powder was 97.5 % of the crystal density, which is relatively high density [4]. The capsule was then compressed to 57 GPa (W with flyer

velocity of 1.72 km/s). We had a recovered specimen of 4 mm in thickness and characterized by using a scanning electron microscope (SEM). Raman measurements were done with a micro-Raman spectroscope (SPEX Raman-500) using an Ar (488 nm) laser. A x50 microscope objective was used to focus the laser with a spot approximately 2  $\mu$  m in diameter and to collect the scattered light.

### 3. Results and discussion

An optical image of the recovered sample of several mm in size is shown in Fig. 1a. The sample corresponds to a part of the original circular specimen. Most of the area of the sample looks gray by the naked eye. An upper part of the sample denoted by an arrow had flaked off after the shock compression and then the inner structure appeared as shown in a SEM micrograph of Fig. 1b. The flaked part consists mainly of flat areas but hollow areas exist near the boundary of the flaked part (Fig. 1c). In a magnified view of the hollow area, we can find spherical particles, ranging 1-5  $\mu$  m in diameter (Fig. 1d).

The flaked part of the specimen was investigated by the micro-Raman spectroscopy with a spatial resolution of 2  $\mu$  m. Fig. 2 shows Raman spectra for a flat area and a spherical particle. A Raman spectrum of highly-oriented pyrolytic graphite (HOPG) is also shown for comparison. Raman spectrum for the flat area is clearly a doublet at 1580  $\text{cm}^{-1}$  (G peak) and 1360  $\text{cm}^{-1}$  (D peak), which is characteristic for a disordered carbon but the spherical particle is almost singlet similar to that of HOPG, indicating that the spherical particles are in a highly graphitized state. Applying a least squares algorithm, the Raman spectra were deconvoluted into two Lorentzian peaks. The intensity ratio of the D peak to the G peak ( $I(D)/I(G)$ ), which is related to phonon correlation length, for the flat area and the spherical particle are 0.78 and 0.015 respectively. Using the formula obtained by Knight and White [9], which gives an inverse linear relationship between the planer crystalline size ( $L_a$ ) and the intensity ratio  $I(D)/I(G)$ , the  $L_a$  for the flat area

and the spherical particle are estimated to be 5.6 and 290 nm respectively. One should note that the  $\lambda$  for the spherical particle is near the order of its diameter.

Interesting images of the spherical particles are obtained in the flaked area. In Fig. 3, we can find see-through particles as denoted by black arrows, suggesting that the particles are empty. This is supported by an image of a spherical particle denoted by a white arrow, which has partly collapsed like a **Ping-Pong** ball. Another evidence can be seen by a photo of the different area of Fig. 4. We find several circular images like bowls which probably correspond to the bottom part of the spherical particles destroyed for some reason. Also the ashes of the upper part of the particles which was crashed flat can be seen as indicated by white arrows.

The above results strongly suggest that the particles generated on an internal hollow surface of the shock compressed specimen are hollow spheres. It is noteworthy because the formation of such a carbon hollow sphere like a **Ping-Pong** ball up to several  $\mu$  m in diameter has not reported so far as far as we know. Well-known spherical particles of carbon onions composed of concentric graphite layers are usually less than 100 nm in diameter and are considered to have a structure such like a type of  $C_{60}@C_{240}@C_{540}@C_{960}...$ [10,11].

In the present experimental condition, the shock state reach to 57 GPa and 3000 K [12], and then the  $C_{60}$  fullerene molecules should transform at first to  $sp^3$ -bonded carbon as the shocked-state is in a diamond phase of the phase diagram [13]. If we utilized the SCARQ technique, the  $sp^3$ -bonded carbon structure would be quenched. However, the cooling speed in this case of shock compression is rather slow, and then the  $sp^3$ -bonded carbon structure transforms to  $sp^2$ -bonded carbon structure due to residual heat after the shock-pressure release.

A question then arises as to how the carbon hollow spheres such like a structure similar to **Ping-Pong** balls are formed. One should note that the size of the hollows of the particles are too large to be formed by the mechanism proposed for the formation of polyhedral graphitic particles from liquid-like droplets. [14,15]. Also, one should remember that the carbon hollow spheres formed in the present study are in a highly graphitized state. To proceed the

graphitization, a temperature high enough to give a high degree of structural fluidity is necessary. However, in that case the particle would become a droplet due to surface tension [16].

To form a remarkably large hollow in the condition of high degree of structural fluidity, a force to balance with the surface tension is necessary similar to the case of soap bubbles. So, we propose a possible formation mechanism of the carbon hollow spheres consisting of two steps: (1) the formation of hollow spherical carbon bubbles in a liquid phase; and (2) the graphitization of the liquid carbon bubble. The growth of graphite layers begins at the surface and then progress toward the center [16]. Liquid phase in the first step may be produced locally at grainboundaries of  $C_{60}$  fullerene substrate where the shock-temperature is considered to be higher than that of bulk because of its high compressibility and friction [12]. Further investigation are necessary to clarify as to how the carbon liquid bubbles are formed.

#### 4. Conclusions

We have shock-compressed  $C_{60}$  fullerene powder up to 57 GPa. The recovered sample was investigated by scanning electron microscopy and Raman spectroscopy. We have discovered the generation of highly graphitized hollow spheres on the internal hollow surface of the sample. Liquid carbon bubble formation and consecutive graphitization is proposed as a possible formation mechanism. The graphitized carbon spheres obtained in the present study may be one of the most stable capsules at high temperatures.

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## Figure caption

Fig.1 (a) an optical image of the recovered sample after shock compression from C<sub>60</sub> powder. Upper part of the sample denoted by an arrow had flaked off. SEM micrographs of (b) the flaked area and (c) a magnified view of an area denoted by an arrow in photo (b). (d) spherical particles, ranging 1-5  $\mu$  m in diameter, in the hollow area of photo (c) denoted by an arrow.

Fig.2 Raman spectra for a flat area and a spherical particle in the flaked part, and a HOPG. Raman spectrum for the flat area is clearly a doublet at 1580 cm<sup>-1</sup> and 1360 cm<sup>-1</sup> but for a spherical particle is almost singlet similar to that of HOPG.

Fig.3 A SEM micrograph of the spherical particles. See-through particles, of which backgrounds can be seen, are denoted by black arrows. A hollow surface similar to the one given to a **Ping-Pong** ball is seen for a spherical particle denoted by a white arrow.

Fig.4 A SEM micrograph of bowl type objects which probably correspond to the bottom part of the spherical particles destroyed for some reason. Also the ashes of the upper part of the particles which was crashed flat can be seen as indicated by white arrows.

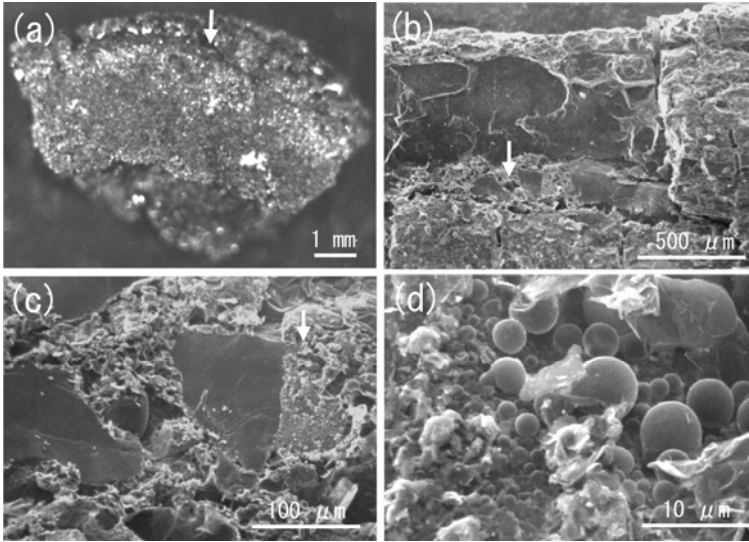


Fig. 1

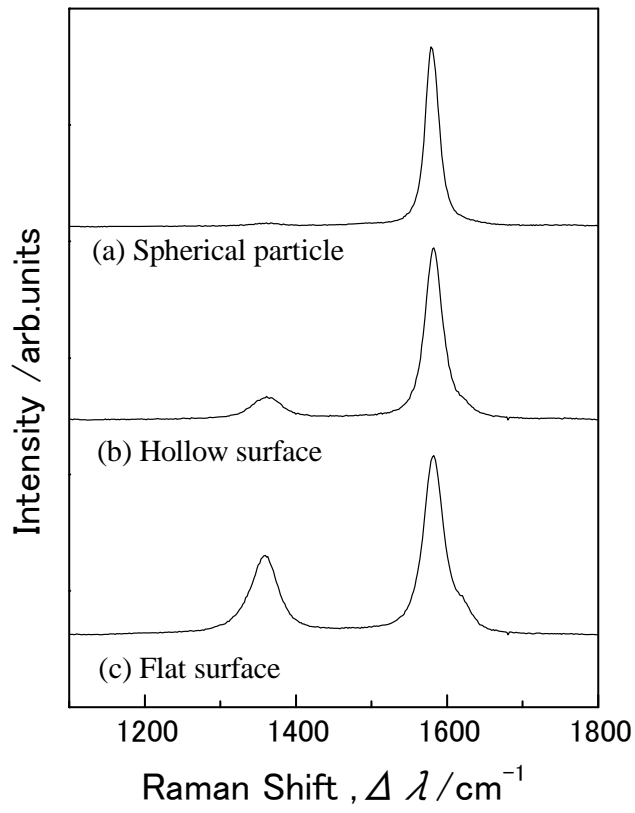


Fig. 2



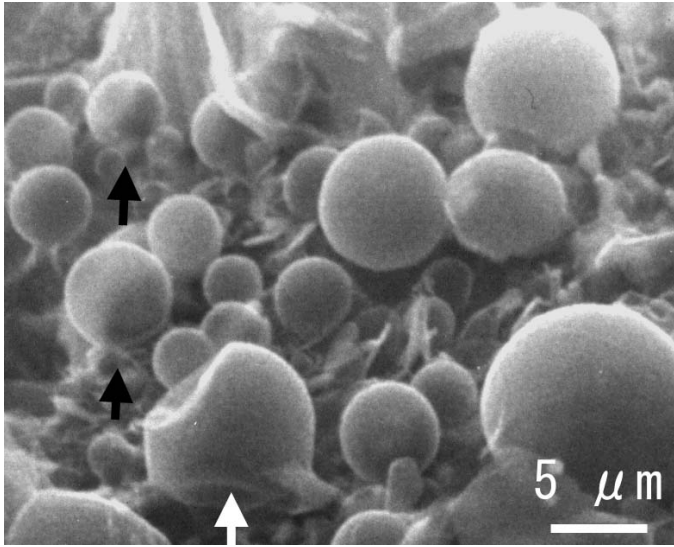


Fig. 3

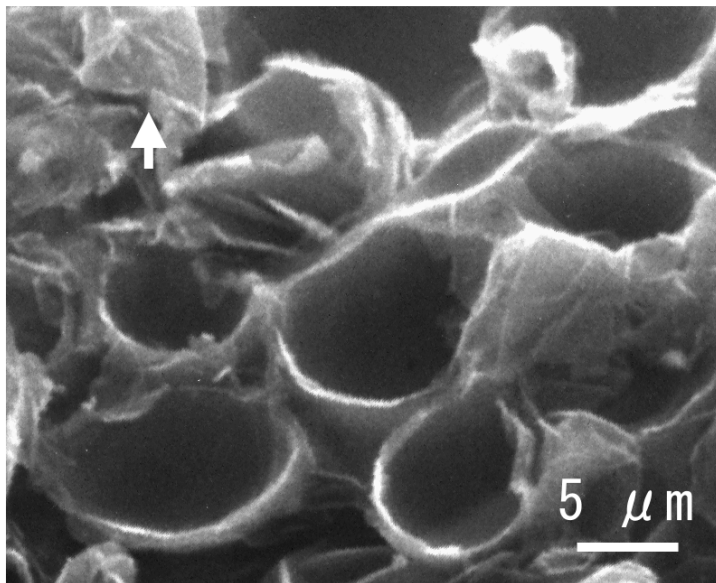


Fig. 4