Micrometer-Sized Graphitic Balls Produced Together with Single-Wall Carbon Nanohorns

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We present in this report a new type of particles with micrometer-order sizes, which we called giant graphitic balls (GG balls). The GG balls are produced by CO_2 laser ablation of graphite together with single-wall carbon nanohorns. They have graphitic structures whose layers tend to align parallel with the GG-ball surfaces, resulting in polygonal-like arrangements. Comparing the GG-ball structure with that of the previously reported polygonal graphite-particles, the growth mechanism of the GG ball is discussed briefly.

Introduction

So far, various nanometer-sized carbonaceous materials with unique structures have been obtained by CO_2 laser ablation of graphite at room temperature. The representative one is the single-wall carbon nanohorn (SWNH), a type of single-wall carbon nanotube with diameters of 2−5 nm and length 40−50 nm.[1] The SWNHs always form the spherical aggregates named dahlia-like, bud-like, or seed-like after their morphologies, and have interesting properties.[1−4] The three types are selectively formed depending on the types and pressures of ambient-gases.[5] By increasing the ambient-gas pressure to 10^4 Torr, the polygonal graphite (PG) particles can be formed, which also have spherical shapes.[6,7]

In this report, we introduce a new type of carbonaceous material also formed by CO_2 laser ablation of graphite at room temperature. It was found to be formed together with SWNHs. Its structure is similar to that of the PG particles[6] but has larger sizes of micrometer orders. We call them giant graphitic balls (GG balls). In this paper, we show the structure of the GG ball, and its growth mechanism is briefly discussed.

Experimental Section

Dahlia-like SWNHs were produced by CO_2 laser ablation of a pure-graphite target (wavelength 10.6 μm, power density ~20 kW/cm^2, pulse width 500 ms, frequency 1 Hz) at room temperature in Ar gas at 760 Torr.[1] As-grown dahlia SWNHs were analyzed by a thermogravimetric (TG) measurement: The samples were heated from room temperature to 1000 °C at a heating rate of 10 °C/min in 100% O_2 atmosphere with a flow rate of 100 sccm. The TG measurement was stopped at 570 and 690 °C, and the residues were studied with a transmission electron microscope (TEM) (Topcon EM-002B), a scanning electron microscope (SEM) (Hitachi S4800), Raman spectrum (JASCO NRS-2000), and X-ray diffraction analysis (XRD) (Rigaku RINT-1500). To obtain the high-purity GG balls in large quantity, we treated the dahlia nanohorns in 100% O_2 gas at 690 °C for 10 min. To compare the structure with that of the GG ball, the Raman spectrum and XRD of pyrolytic graphite (Advanced Ceramics Corporation, Grade: ZYA) were measured.

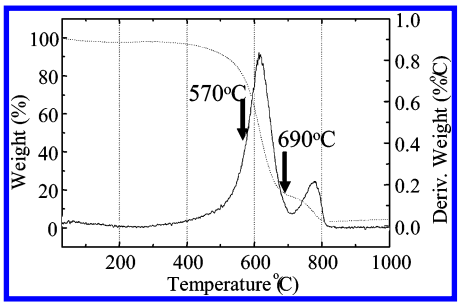

Figure 1. Results of TG analysis of dahlia-like SWNHs measured in 100% O_2 atmosphere. The temperature was increased at a rate of 10 °C/min. The dotted line is the weight−temperature curve, and the solid line is temperature derivatives of the weights. Arrows indicate the temperatures at which TG measurements were stopped.

Results and Discussion

The TG analysis of the dahlia-type SWNHs (Figure 1) indicated that two types of carbonaceous materials combusted at temperatures about 620 and 770 °C. When we stopped the TG measurements at 570 °C, the majority was SWNHs (Figure 2a) but that obtained by stopping at 690 °C was the large particles with sizes of micrometer orders (Figure 2b,c). A TEM image with high magnification (Figure 2d) indicated that they have layer structures similar to graphite, with the layers arranged parallel to the particle surfaces leading to the polygonal-like stacking. From these structural characteristics, we called them "giant graphitic-balls (GG balls)", which quantity was estimated from TG analysis (Figure 1) to be about 15%. The GG balls were not the materials produced in the course of temperature elevation during the TG measurements, but existed from the beginning. This was apparent because SEM and TEM images of as-grown SWNHs (Figure 3a,b) indicated that the GG balls were contained in the as-grown SWNHs, and that their structure (Figure 3c) has no clear difference from the GG balls (Figure 2d). The structure of the GG balls was further studied by measuring Raman spectra and XRD, and the results are shown in the following.

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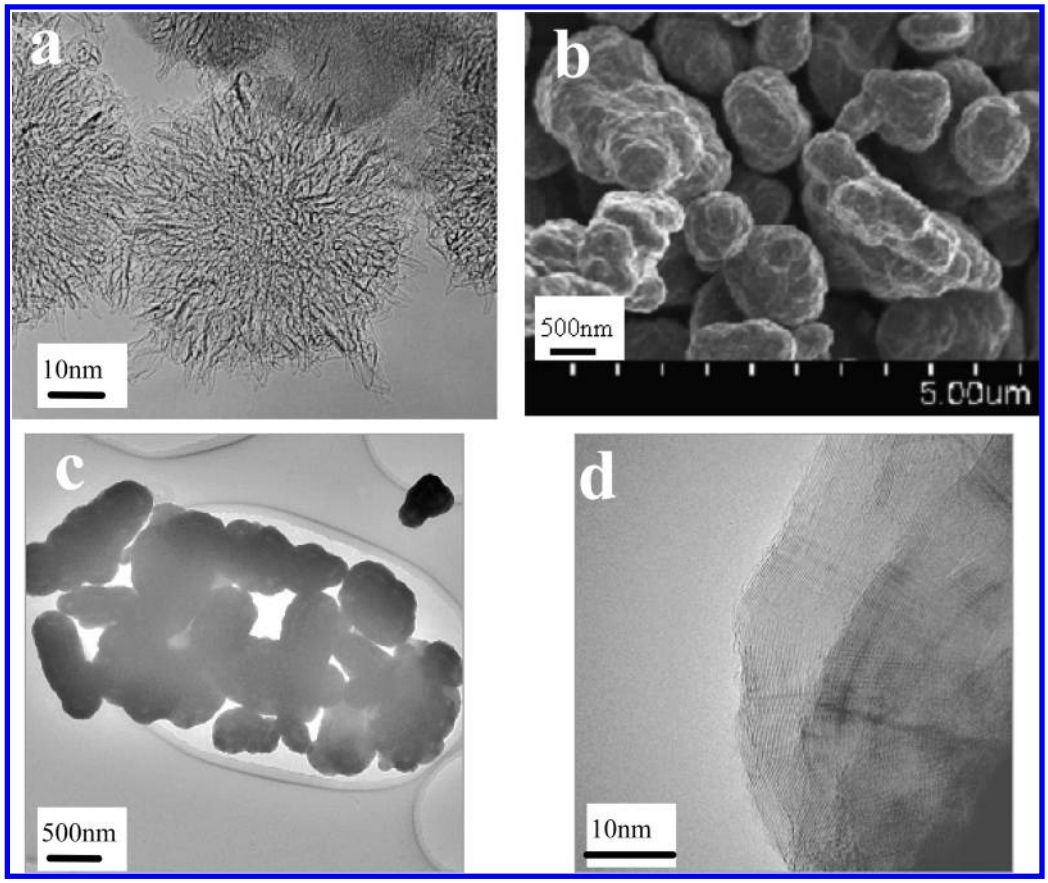

Figure 2. TEM image of the residue obtained by stopping the TG measurement at 570 °C, exhibiting dahlia-type SWNHs (a). An SEM image (b) and TEM images (c,d) of the residue obtained by stopping TG measurement at 690 °C showed that the residue materials were the GG-balls.

The Raman spectrum of the GG balls (Figure 4c), was completely different from those of as-grown SWNHs (Figure 4a) and the 570 °C residue (Figure 4b). The spectra of Figures 4a and 4b are typical Raman spectra of SWNHs[1] and the partially combusted SWNHs[5] that have holes at the tips and side-walls,[8] respectively. The spectrum of the GG balls had a distinct peak at 1580 cm^{-1} and a weak peak at 1360 cm^{-1} (Figure 4c). The peak at 1580 cm^{-1} indicated that the GG balls were graphitic because the peak coincides with the G band of highly oriented pyrolytic graphite[9] (Figure 4d). The small intensity of the D band reflects the small layer-domain sizes of the graphene sheets, and they were estimated to be 100−200 nm from the empirical rule using the intensity ratio of G and D bands.[9] The full width at half the peak height (fwhm) of the G band of the GG balls at 1580 cm^{-1} was 27 cm^{-1} (Figure 4c), which was larger than the 16 cm^{-1} of graphite (Figure 4d). This also indicates that the defective structures of the graphene sheets construct the GG balls.

The irregular stacking distances of the GG balls exhibited curious peaks in XRD data (Figure 5a): a main peak (A) and a shoulder (B), corresponding to the lattice constants of 3.44 and 3.36 Å, respectively. These distances are apparently larger than that of pyrolytic graphite (002), 3.34 Å (Figure 5b).[10] The large layer distances and broad width of peaks A and B indicate a little disordered layer stacking of the graphene sheets. The XRD analysis of the as-grown nanohorns (not shown) presented a peak and shoulder similar to those for the GG balls but with weaker intensities, which also suggested that the GG balls existed in the as-grown SWNHs.

We can conclude that the GG balls have graphitic structures with disorders in the graphite layer planes and layer stacking. The graphene layers tend to align parallel with the surface of GG balls, resulting in polygonal-like stacking.

The structure of the GG balls reminds us of PG particles,[6] which also have spherical shapes, but smaller sizes of about 300 nm. Its XRD result exhibited only one peak but no shoulder, which corresponded to the graphite (002) diffraction.[6] PG is formed by CO_2 laser ablation in Ar gas at high pressure (10^4 Torr), and its purity is high. In the ablation, the plume sizes are small due to the high Ar-pressure, that is, the carbon clusters are confined in a narrow space. These carbon clusters lead to the PG formation through the collisions among them.[11]

On the other hand, the GG balls were small in the production quantity, and they were formed together with dahlia-type and bud-type SWNHs. The GG balls were formed at lower pressure of 760 Torr where the confinement of carbon clusters in the plume was not so strong as at the pressure of 10^4 Torr.[11,12] These differences between the PG and GG balls indicate that the formation mechanism of GG balls might be different from PG ones. We think that the GG balls are initially fragments expelled from the graphite target by the strong laser beam irradiation.[13] The fragment temperature might exceed 5000 °C near the target surface[14] and cool to room temperature, during which the carbon fragments melt and are reconstructed to transform to GG balls. This formation model explains the various shapes and large sizes of the GG balls. The cooling process takes place from the outermost surface to the center of the particle gradually, thus the graphitic layer first grows in the surface and then expands to the core. This growth model is similar to that of carbon black[15] and polyhedral particles by arc discharge,[16] which can describe the formation of the concentric structure of GG balls.

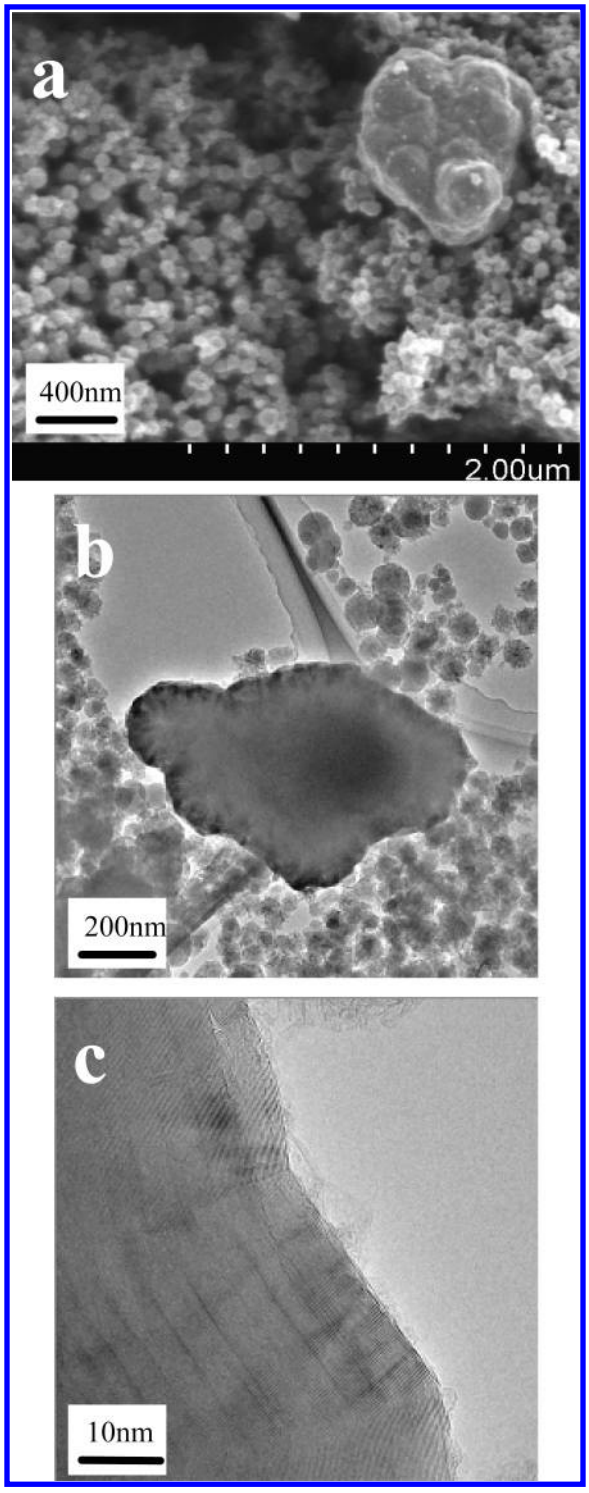

Figure 3. SEM and TEM images of the as-grown dahlia-type of SWNHs: SEM images (GG balls in upper right corner) (a), TEM image with low magnification (b), and TEM image with high magnification (c).

We also found GG balls together with nanohorns produced by laser ablation under various conditions: for example, at lower gas pressure of 450 or 200 Torr in Ar (ordinarily 760 Torr), or in 760 Torr of He gas atmosphere (ordinarily in Ar gas), or with 3.7 or 2.65 kW of laser power intensity (ordinarily 3.0 kW on a spot with 3-mm diameter). This confirms that the GG ball is the fragment expelled from the graphite target by laser ablation and will not be strongly affected by the gas pressure and laser power density we applied.

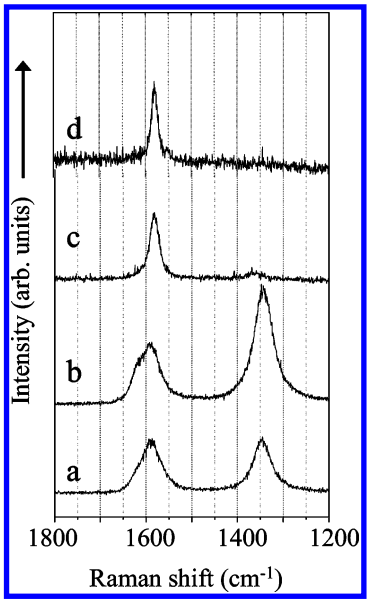

Figure 4. Raman spectra for the dahlia-like as-grown SWNHs (a), 570 °C residue (b), GG balls (690 °C residue) (c), and pyrolytic graphite (d).

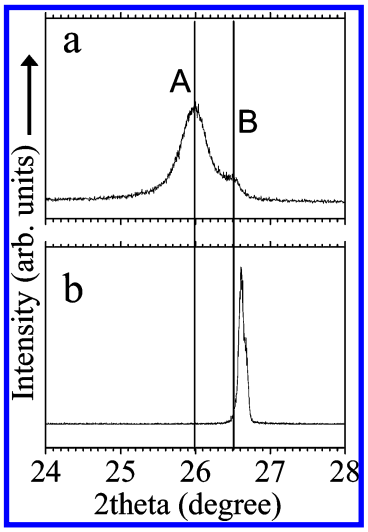

Figure 5. XRD data of GG balls (residues obtained when TG measurement was stopped at 690 °C) (a) and pyrolytic graphite (b).

Conclusion

We found a new type of carbonaceous particles in as-grown dahlia-type SWNHs. The particles, which we call giant graphitic (GG) balls, are produced by CO_2 laser ablation of graphite at 760 Torr together with SWNHs. In this study, we investigated the structures of GG balls and found that they are micrometer in size and irregular in shape. GG balls have graphitic layers arranged parallel with the ball surfaces. The graphitic layers were more or less defective, and they were stacked with a little disorder.

References and Notes

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