A New Carbon Reaction: Conversion of Isotropic Graphite into Carbon Nano-Onion Particles

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Abstract – This study describes a new carbon reaction method for nano-onion formation by using a high current electron beam system. Large nano-onion particle with diameter about 90 nm is observed on isotropic graphite after pulse irradiation at 30 kV for 100 times. Copper material in the cathode, has enhanced the formation of nano-onion during the irradiation, while the irradiation process with graphite cathode could not provide any formation of nano-onion. The present pulsed process consists of electron beam emission, Cu metal plasma, and high current up to 54 kA, which are considered as the essential factors for the reaction of nano-onion synthesis in this method. In this case, the current density is 17 kA/cm^2 and the energy is 78 J/cm^2 per pulse. The TEM observation on the irradiated sample after keeping for 2 year in the ambient atmosphere shows that the nano-onion particles from this method are relatively stable.

1. Introduction

Many researchers believe that diamond, known as the highest crystalline carbon, can be produced from soot (carbon black), which has very low crystalline structure, through modification of carbon atomic structure [1, 2]. As if supporting this ambitious "diamond from soot" project, several experiments have really shown that the atomic structure of carbon can be altered with highly dense current electron beam (EB) irradiation. Firstly, Ugarte has observed a structure transformation of carbon soot particles into quasi-spherical particles with concentric graphitic shells after irradiated by an intense electron beam in high-resolution electron microscope (HRTEM) [3]. The new carbon structure is then named as onion structure. Inspired by this phenomenon, Ozawa et al. have detected formation of spiral nanoparticles prior to transformation into onions during irradiation of electron beam in HRTEM onto nano-sized carbon black particles [4]. Furthermore, Banhart and Ajayan discovered that carbon onions can be transformed into diamond by heating at 700 °C under electron beam irradiation inside TEM [5]. More recently, Huang et al. have succeeded to form nano-diamond particle from nano-onion carbon with simultaneous EB irradiation and heating process up to 2000 °C inside a transmission electron microscope [6].

The experiment results reveal that the formation of nano-diamond from soot can be considered consisting of two-step carbon transformations, i.e., nano-onion and bucky-diamond formations. Hence, as the first step for realization of nano-diamond in mass production, fabrication of nano-onion particles in large amount should be required. Actually, there are several methods being proposed for preparation of carbon nano-onions. Besides electron irradiation method inside TEM, other methods have been proposed for the nano-onion formation, such as arc discharge of carbon electrodes in water [7], RF plasma enhanced CVD on methane gas [8], or shock wave treatment of carbon soot [9].

However, due to low impurity and productivity of product in the conventional methods, innovations for fabrication of commercial nano-onions in mass production are still open for investigation. This study introduces a new carbon reaction method for nano-onion formation with electron beam system. However, unlike the conventional irradiation method, which should be taken place under a focused electron beam in TEM, our method can be carried out without focusing electron beam, at low accelerating voltage to enable for mass production of nano-onion particles in the future.

2. Experimental procedure

Isotropic graphite crucible (IG-110, Toyo Tanso Co., Ltd.) and carbon black powder (#8500F, Tokai Carbon Co., Ltd.) have been used as starting materials for the nano-onion formation in the present experiment. The samples are irradiated by using low energy high current electron beam system by using 2 mm diameter Cu rod as the cathode, as shown schematically in Fig. 1. For commercial mass production of nano-onion particles, special designed system with automatic rotating 20 holders of crucibles has been manufactured by Nagata Seiki Co., Ltd. (Fig. 2).

The graphite crucible having inner hole diameter of 16 mm and depth of 20 mm, is placed under the cathode wire. The distance between tip of cathode wire and the bottom of crucible is 5 mm. In the case of carbon black powder, the thickness of the powder layer is about 3 mm. For preventing the scattering of the irradiated powder, a cover with hole is installed on the upper part of the crucible. In order to know the effect of starting material and Cu material on the formation of nano-onion, experiments with conditions shown in the Table have been conducted.

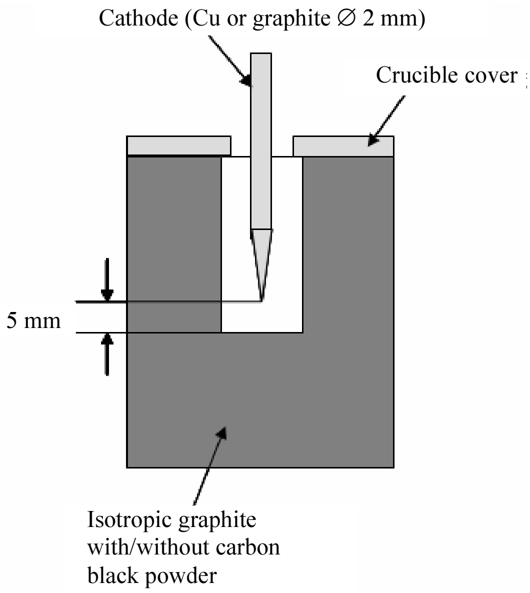


Fig. 1. Schematic illustration of the cathode position and the sample for the process

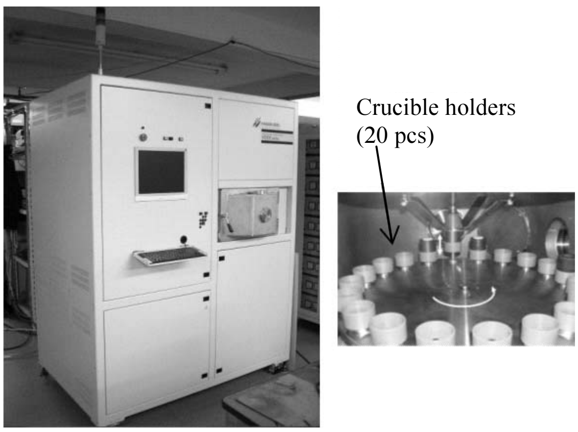


Fig. 2. High Density Electron Emision (HDEE) system for mass production of nano-onion particles. The system has dimension of 1.6×1×2.3 m

Table. Samples and type of the cathode

Sample	Cathode type
Isotropic carbon crucible only	Copper rod, ∅ 2 mm
Isotropic carbon crucible with carbon black powder	Graphite rod, ∅ 2 mm
Isotropic carbon crucible with carbon black powder	Copper rod, ∅ 2 mm

For this experiment, setting of cathode voltage, solenoid voltage, anode voltage, and Ar pressure are 30, 1.5, 4.5 kV, and 0.05 Pa, respectively. The pulse number is 100 pulses for each sample, with interval time of about 10 s between the pulses.

After the irradiation, nano-onion particles stuck on the inner wall of the crucible are observed with high resolution transmission electron microscope HRTEM (JEOL Co. Ltd., JEM2010). After keeping for 2 years, again the particles on the wall is observed to investigate the atmospheric weathering stability of nano-onions, using field emission TEM (JEOL Co. Ltd., JEM-2200FS) in Toyo University at Saitama Japan.

For evaluating the behavior of the electrical discharge during the irradiation pulse, the voltage and current oscillograph are recorded with TEKTRONIX TDS 2014 100 MHz digital oscilloscope.

3. Results and discussion

3.1. Electrical discharge behavior

The oscilographs of voltage and current during one pulse of the irradiation process are presented in Fig. 3 below. The voltage is measured from the capacitor divider (5 kV/div), and the current is measured from a Rogowsky coil installed at one cable of the totally six cables connected to the cathode (18 kA/div).

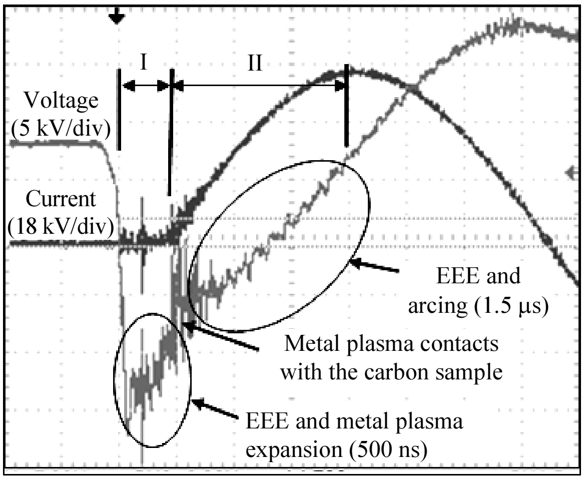


Fig. 3. The oscilographs of voltage and current during one pulse of the process. There are two regions with different discharge behaviors

There are two regions with different discharge behaviors. Region I could be corresponded to the process of explosive emission electron (EEE) to initiate metal plasma around the cathode tip. Almost no detected current in this region means that the metal plasma is still in the period of plasma expansion, as illustrated with darker colored plasma in Fig. 4.

Considering that velocity of the metal plasma is about 5×10^5 cm/s and the distance between cathode and crucible is about 5 mm, the time required for the plasma to reach the graphite crucible is approximately 1 μs, which fairly agrees to the value measured in the oscilograph.

Once the metal plasma reaches the graphite crucible after about 500 ns, a very high oscillating current starts (Region II). The oscillating current is generated as the characteristic of the equivalent LC circuit containing 3 μF capacitor in the pulse power supply and inductance in the cables connected to the cathode, as illustrated in Fig. 4. At 25 kV of pulse cathode voltage,

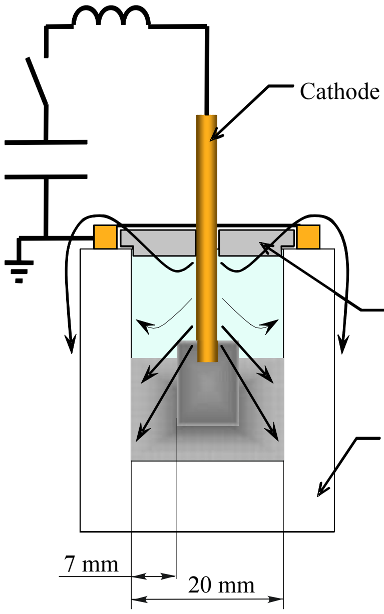


Fig. 4. Schematic illustration of the explosive emission electron to generate metal plasma around the cathode tip. The equivalent LC circuit in this system performs an oscillating high current after the metal plasma expansion

the total peak current of the oscillating current can reach up to about 54 kA. Assuming that the irradiated area by the metal plasma has radius of 1 cm on the bottom of the crucible, then the current density per pulse is about 17 kA/cm^2 corresponding to energy of 78 J/cm^2 measured by calorimeter. This energy is enough for evaporation of graphite to form carbon plasma.

Careful observation on the voltage in Region II, we can see that at the time when the current rises, there are also many small arcing for about 1.5 μs.

3.2. Formation of nano-onion particles

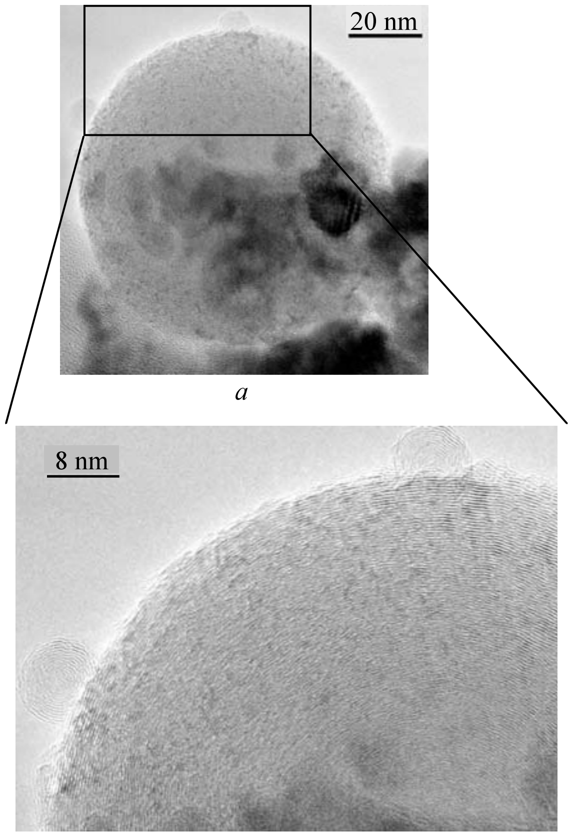
Figure 5 shows the HRTEM pictures of nano-onion particles produced after the high current electron beam irradiation on the isotropic graphite crucible only (without carbon black power) using copper rod cathode.

As shown in the Fig. 5, *a*, the diameter of the particle can reach until about 90 nm. Magnifying the picture, several small nano-onions with diameter about 8–10 nm are found on the surface of the large particle (Fig. 5, *b*).

However, in the case of graphite cathode on the carbon black as starting material, nano-onion particle could not be observed with HRTEM. Even though copper rod cathode is used for the irradiation on the carbon black powder, it is difficult to verify complete synthesis of nano-onion.

Figure 6 shows the nearest structure to nano-onion from carbon black powders, which could not be completely transformed into nano-onion structure.

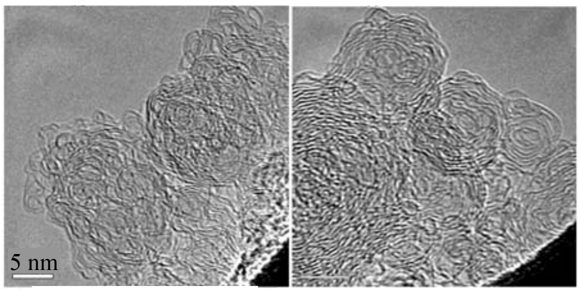
It should be mentioned that the accelerating voltage used in the present study is only 30 kV, which is much lower than the voltage commonly used in TEM.



a

b

Fig. 5. Diameter of the nano onion particle can reach until about 90 nm (*a*). Magnifying the picture, two small nano-onions having diameter about 8–10 nm are also found on the surface of the large particle (*b*)



Typical HR-TEM

The best onions that were found-quite few

Fig. 6. Typical structure of carbon black particles after the irradiation (left picture). The right picture shows that the carbon black particles could not be completely transformed into nano-onion.

Therefore, the mechanism of nano-onion generation should be rather different from nano-onion created in TEM at 200 kV as reported formerly by several researchers. The minimum energy which has to be transferred to a carbon atom in graphite to induce its permanent displacement is approximately 15 eV [10]. Calculating corresponding energy of the irradiating particles from the laws of momentum conservation, Banhart mentioned that electrons with their low mass need a threshold energy of 100 keV to induce structural alterations of the graphite lattice [11]. Hence, theoretically, the accelerating voltage in this work is not adequate to modify the structure of graphite.

This may come to the reason, why it is difficult to change carbon black powder into nano-onion in this method.

The formation mechanism can be described with three effects: breaking of carbon bonds by electron irradiation, knock-on of carbon atoms, increase of sample temperature [12]. In the present method, knock-on effect by the accelerated electron may be very minor, but temperature increase due to high current during the single pulse should be sufficient for vaporization of graphite.

The role of high temperature for carbon atomic structure modification has been performed firstly in the laser vaporization of graphite to produce a remarkably stable cluster consisting C_{60} [13]. Kroto et al. proposed that the stability of the carbon arises from the ability of a graphitic sheet to close into spheroidal shell, thereby eliminating its edges. This argument can be used to explain why the isotropic graphite, which has flat lamellar structure, is easier to form spheroidal shell of nano-onion compared to carbon black powders, which have lower crystalline structure.

The effect of Cu in the metal plasma for the present nano-onion synthesis is also essential. The same phenomenon has been observed by Tian et al., when they found Cu nanoparticles sputtered from copper electrodes had played an important role as catalyst for synthesis of carbon nanotubes in their arc plasma method [14].

Figure 7 shows the appearance of the nano-onion after 2 year storage in ambient atmosphere.

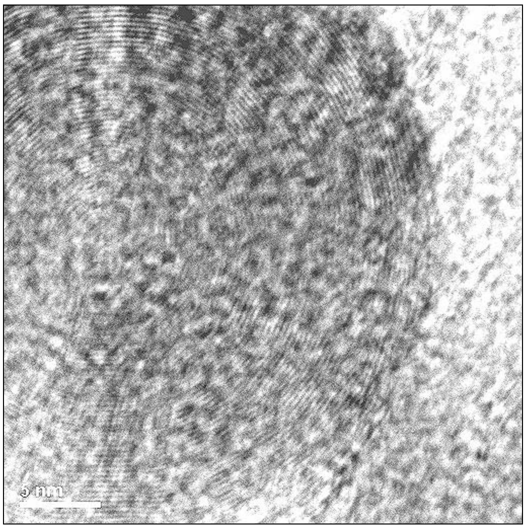


Fig. 7. Nano onion particles can be re-observed on the same isotropic crucible sample which has exhibited nano-onions after 2 year storage in the ambient atmosphere

It reveals that the nano-onion obtained in this method is relatively stable against weathering. The nano-onion particle can be re-observed by TEM on the same isotropic crucible sample which has exhibited nano-onion two years ago. Unfortunately, quality of the picture is not as good as high resolution TEM pictures, but large nano-onion about 40 nm can be remarkably observed from the pictures.

4. Conclusions

A new carbon reaction method for nano-onion formation by using a high current electron beam system has been presented. The test results can be summarized into the following conclusions:

1. Large nano-onion particle with diameter about 90 nm can be produced from isotropic graphite using pulse irradiation at 30 kV for 100 times.
2. The copper metal plasma plays an important role of catalyst for the nano-onion synthesis in this method. Electron beam emission, Cu metal plasma, and high current up to 54 kA, are also considered as the essential factors in the present method. A new carbon reaction to convert the isotropic graphite into carbon nano-onion particles can be done with 17 kA/cm^2 of current density and 18 J/cm^2 of energy density.
3. Result of TEM observation on the irradiated sample after keeping for 2 year in the ambient atmosphere shows that the nano-onion particles from this method are relatively stable.

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References

[1] E. Ōsawa, F. Banhart, L. Dai, T. Enoki, H. Naramoto, K. Narumi, A.I. Shames, A. Vul', and Ya, *Comprehensive Research on Novel Nano / Submicron Carbon Particles: Bucky-onion and Bucky-diamond*, Research Report of the Int. Joint Res. Program (NEDO Grant, 2004IT081, 2004–2006).
[2] F. Banhart and M.P. Ajayan, Adv. Mater. **9**/3, 261–263 (2004).
[3] D. Ugarte, Nature **359**, 707–709 (1992).
[4] M. Ozawa, H. Goto, M. Kusunoki, and E. Osawa, J. Phys. Chem. B. **106**, 29, 7135–7138 (2002).
[5] F. Banhart and P.M. Ajayan, Nature **382**, 433–435 (1996).
[6] J. Y. Huang, Nano Lett. **7**/8, 2335–2340 (2007).
[7] N. Sano, H. Wang, I. Alexandrou, M. Chhowalla, K.B.K. Teo, and G.A.J. Amaratunga, J. Appl. Phys. **92**, 2783–2788 (2002).
[8] X.H. Chen, F.M. Deng, J.X. Wang, H.S. Yang, G.T. Wu, X.B. Zhang, J.C. Peng, and W.Z. Li, Chem. Phys. Lett. **336**/3–4 201–204 (2001).
[9] K. Yamada, H. Kunishige, and A.B. Sawaoka, Naturwissenschaften **78**, 10, 450–452 (1991).

[10] F. Banhart, Reports on Progress in Phys. **62**, 1181–1221 (1999).
[11] F. Banhart, Phys. of the Solid State **44**/3, 388–392 (2002).
[12] I. Narita, T. Oku, K. Suganuma, K. Hiraga, and E. Aoyagi, J. Mater. Chem. **11**, 1761–1762 (2001).
[13] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature **318**/6042, 162–163 (1985).
[14] Y.J. Tian, Y.L. Zhang, Q. Yü, X.Z. Wang, Z. Hu, Y. F. Zhang, and K.C. Xie, Catalysis Today **89**/1–2, 233–236 (2004).