

Novel Bridged Carbon Nanofibers Grown by Cleaving Carburized Iron Substrates

Takeshi HIKATA*, Soichiro OKUBO, Risa UTSUNOMIYA, Yugo HIGASHI and Teruaki MATSUBA

We developed a novel growth method for carbon nanofibers (CNFs), such as carbon nanotubes (CNTs), and multi-layered graphene sheets, where the metal nanoparticle catalyst and template substrates were not used for growth of the CNFs. The CNFs were grown with the bridge formation between the cleaved crack walls through the carburizing heat treatment of the high purity iron oxide foils in an acetylene gas flow. We indicate a possibility that the bridging growth CNFs (BG-CNFs) are formed by division of an unknown novel iron phase including a large amount of carbon as a solid solution. We introduce the new fabrication process of BG-CNFs and possibility for the practical use.

Keywords: carbon nanotube, graphene, iron, carburize, bridge, carbon nanofiber, oxide

1. Introduction

Carbon nanotubes (CNTs) and graphene are expected as industrial materials for future electric wires and devices. They have excellent properties, with lighter weight, higher strength and high conductivity, compared with conventional metals⁽¹⁾⁻⁽⁷⁾. For practical applications, the primary properties of these carbon nanomaterials should be reflected in the scale of each application, and we have studied and developed CNT growth methods for electric wire applications^{(8), (9)}. In this report, we introduce the novel growth method of CNFs, and show possibilities for applications.

2. Problems of the Present Growth Method for CNTs and Graphene Sheets

CNTs are generally grown on a metal nanoparticle catalyst by providing a carbon source gas as shown in Fig. 1⁽¹⁾⁻⁽⁵⁾. The nanoparticles have a diameter of a few nm, and CNTs are grown in harmony with the diameters of the nanoparticles. It is difficult to keep stable conditions on the tiny metal nanoparticles for the carbon source supply and the growth of CNTs. Thus, novel control methods for a more stable growth of CNTs are desired.

Recently, graphene has been researched actively for such as transparent conductive films and electronic devices^{(6), (7)}. Figure 2 shows the multi-layered graphene sheet

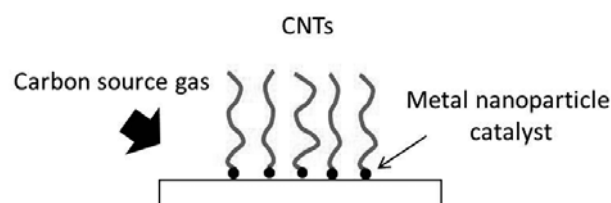


Fig. 1. Growth model of CNTs

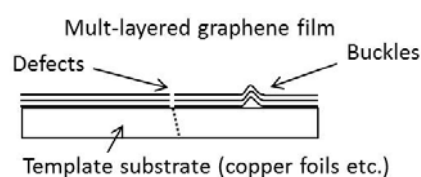


Fig. 2. Growth model of multi-layered graphene films

on a template substrate, such as copper or silicon. The graphene sheets have defects and kinks by mismatching between the graphene sheet and the template substrate. Therefore, the mismatching problems need to be solved.

3. Bridge Grown Method

In this report, we introduce a novel growth method of CNTs and multi-graphene sheets without using the metal nanoparticles and template substrates⁽¹⁰⁾.

The bridge grown method has novel features that the bridging growth CNFs (BG-CNFs) are grown in the cracks of the cleaved substrates as shown in Fig. 3.

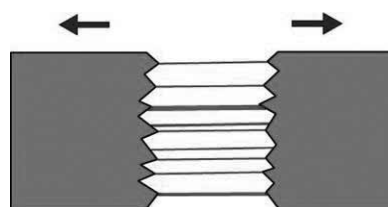


Fig. 3. Growth model of BG-CNFs

4. Experimental and Results

High-purity electrolytic iron foils (purity of 4-5N), were used as the starting material with a thickness of 50–80 μm . The iron sample was placed at the center bottom of a quartz glass tube in an electric tubular furnace. Heat treatment was performed at two steps: oxidation and carburization (including reduction). First, the iron foil was oxidized by heat treatment for 1 min. at 850°C in air. Oxidation doubled the thickness of the iron foil from 50 μm to about 100 μm . We analyzed the oxidized iron samples by X-ray diffraction (XRD) and identified them as iron oxide composed of hematite (Fe_2O_3) and magnetite (Fe_3O_4).

Next, we heated the iron oxide samples to 850 °C at a rate of 10 °C/min and maintained this temperature for 10 min. under nitrogen (N_2) gas with a flow rate of 700 mL/min. The gas flow was changed to a mixture of 5% acetylene (C_2H_2) in N_2 with a flow rate of 740 mL/min. Samples were heat treated at 850°C under the acetylene gas flow. A N_2 gas flow was then used to decrease the temperature in the furnace.

Samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), XRD and Raman spectroscopy. Samples for TEM were prepared by dividing the sample at a crack with BG-CNFs by bonding it to a TEM grid and then removing part of the heat-treated sample. Raman spectra were acquired using a laser excitation of 532 nm with an incident power of 0.4 mW and spot size of 1 μm .

Photo 1 shows an SEM photograph of the surface of a carburized sample with BG-CNFs in the cracks. Almost all the BG-CNFs were formed linearly to the bridged direction between the cleaved cracks as shown in **Photo 2**. The ends of the BG-CNFs were connected completely to the walls in the cracks.

We observed the structure of the BG-CNFs by TEM, and confirmed that the BG-CNFs were composed of carbon through energy dispersive X-ray spectroscopy (EDX) and electron diffraction (ED) analysis. TEM images revealed that the BG-CNFs had two shapes, tubular, bridging growth carbon nanotubes (BG-CNTs), and sheets, bridging growth carbon nanosheets (BG-CNSs).

Photo 3 shows a BG-CNF with a root connected to a cracked wall and the opposite side was free and a broken

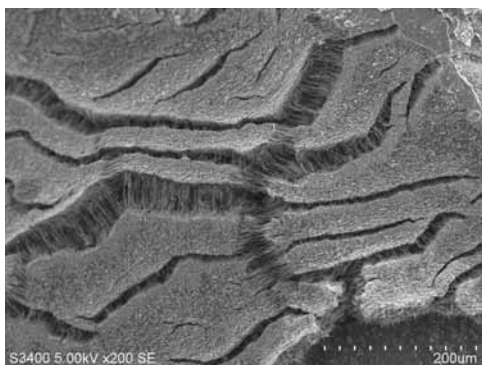


Photo 1. CNFs grown at cracks in the carburized iron substrate

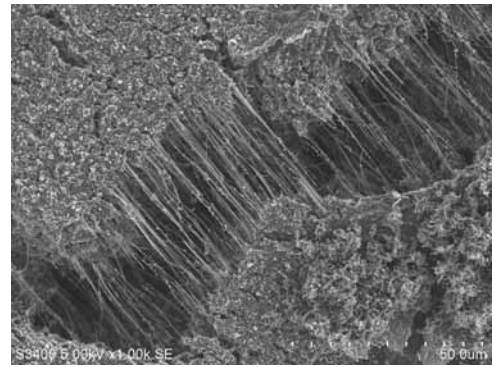


Photo 2. CNFs bridging grown between crack walls in the carburized iron substrate

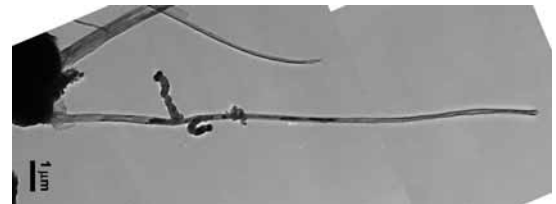
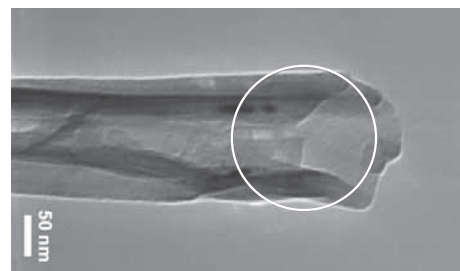
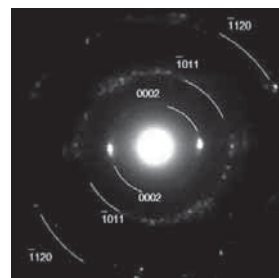


Photo 3. A TEM photograph of BG-CNT

end. The broken end indicates the tubular shape as shown in **Fig. 4**. The ED pattern obtained around the top end indicates that the BG-CNT is composed of multi-layered graphene layers as shown in **Fig. 4 (2)**.



(1)



(2)

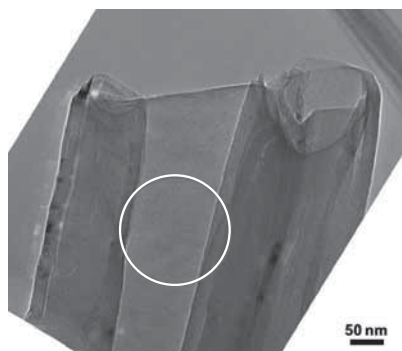
Fig. 4. (1) TEM photograph and (2) electron diffraction pattern of the edge of the BG-CNF in **Photo 3**

Photo 4 shows a BG-CNS with flat and scrolled structures. The top end was cleaved with a horizontal straight line, as shown in **Fig. 5**. The ED analysis on the flat area of the top end of the BG-CNS indicated it was composed of multi-layered graphene.

We analyzed the structure of the BG-CNFs by Raman spectroscopy, as shown in **Fig. 6**. In the Raman spectra of BG-CNFs in the cracks, the G- and D-bands that are related to graphite structure and defects, respectively, can be used to evaluate crystal phase and defect concentration. This



Photo 4. A TEM photograph of the BG-CNS



(1)



(2)

Fig. 5. A TEM photograph and electron diffraction pattern of the edge of the BG-CNS in **Photo 4**

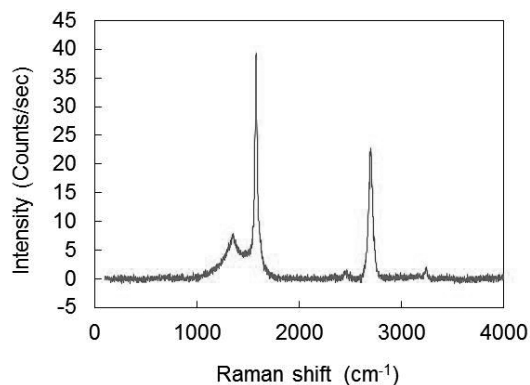


Fig. 6. Raman analysis of the BG-CNF in a crack of the carburized iron substrate.

data indicates that BG-CNFs are composed of crystal of multi-layered graphene structure, rather than amorphous carbon.

Tension experiments for the carburizing samples in the heat treatment furnace were performed by Professor Jun-ichi Fujita's group of Tsukuba University. They demonstrated that the BG-CNFs were formed on the cleaved surface of the sample by tension deformation in carburizing heat treatment with acetylene gas flow.

5. Growth Mechanism of BG-CNFs

We considered the growth mechanism of BG-CNFs. We paid attention to BG-CNFs in a sector shaped crack, as shown in **Photo 5**. BG-CNFs were formed along the opened trajectory into a sector form. It indicates that BG-CNFs were grown with each speed at different places according to the cleaving motion with the sector form.

In the conventional growth process of CNTs, a carbon source gas decomposes and shifts to solid carbon (CNTs) on a metal nanoparticle catalyst. Therefore, the CNTs grow with the speed in accordance with the supplied carbon quantity.

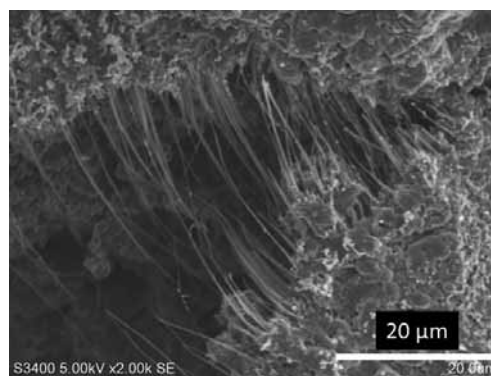


Photo 5. BG-CNFs grown in the sector-shaped cracks

On the other hand, BG-CNFs grow according to the spreading speed at the cleaved crack walls. Therefore, it seems that the growth mechanism of the BG-CNFs is different from the conventional CNT growth on metal nanoparticles.

At the phase diagram of Fe-C, carbon concentration of atomic ratio is less than 25% of Fe_3C . Therefore, it is difficult to explain the growth of BG-CNFs by cleaving iron substrates according to the conventional Fe-C phase diagram. **Photo 1** shows that the BG-CNFs have grown in the cleaved cracks of the carburized iron substrate. This result suggests the possibility that an unknown special iron phase has appeared by the heat treatment.

We observed the inside structure in the heat treated samples for clarifying the mechanism of the formation of BG-CNFs through heat treatment of iron oxide in acetylene. **Figure 7** shows a SEM photograph of the polished cross section of the heat treated sample for 2 minutes at $850^{\circ}C$ in a 5% acetylene gas flow. The structure is composed of porous iron, and the precipitated carbon in the pores. Therefore, the carbon is deposited in pores of the iron, as shown in the pattern diagram at the upper right of **Fig. 7**. On the other hand, **Fig. 8** shows a SEM photograph of the polished cross section of the heat treated sample for 10 minutes at $850^{\circ}C$ in a 5% acetylene gas flow. The iron is broken into small particles dispersed in the carbon matrix. Therefore, the pattern of iron and carbon is reversed, as shown in comparison of the pattern diagrams in **Figs. 7 and 8**. It indicates that the iron substrate was broken into small pieces by the precipitation of the inside carbon as the carburizing progressed. Generally, it is known that precipitated material is cementite (Fe_3C) from Fe-C alloy, according to the Fe-C phase diagram. Therefore, it is difficult that this carbon precipitation phenomenon is explained by the usual Fe-C phase diagram.

Thus, we paid attention to the iron oxide used as a starting material, and supposed the mechanism as follows. The dense iron oxide (Fe_2O_3 , Fe_3O_4) is reduced to a porous iron oxide ($Fe_{1-x}O$) and then the porous iron, includes a

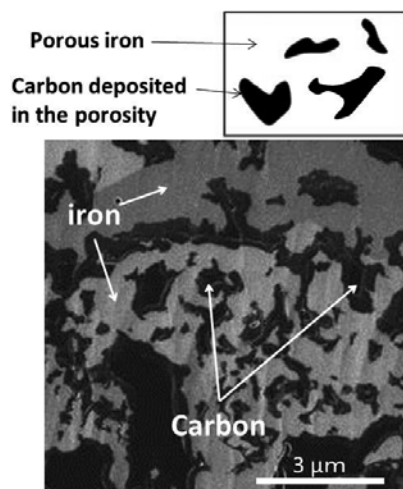


Fig. 7. SEM photograph and the pattern diagram of the cross section in the sample for carburized heat treatment for 2 minutes at $850^{\circ}C$

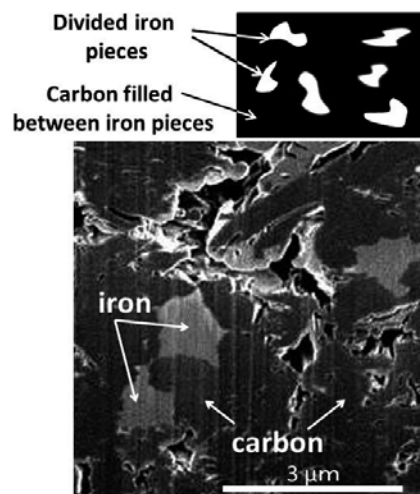


Fig. 8. SEM photograph and the pattern diagram of the cross section in the sample for carburized heat treatment for 10 minutes at $850^{\circ}C$

large amount of the atom vacancy through the secession of the oxygen by heat treatment in the acetylene gas flow. Next, the atomic vacancy is filled by the penetration of the carbon atom, and then the carbon is precipitated with breakup into smaller pieces of iron, as shown in **Fig. 8**. Therefore, we consider the possibility of a special iron phase, including much amount of carbon to be associated with the growth of BG-CNFs.

On the other hand, when we used the iron samples with the lower purity of 3N, the carburized samples could not be kept in a sheet form, and broke into fine powder. This experiment demonstrates the use of high purity iron over 4N is essential for the BG-CNF growth by cleaving the iron substrates.

6. Possibility of BG-CNFs for Applications

BG-CNFs have novel features in the growth process and mechanism compared with general CNT and graphene growth methods. CNT growth does not need to use metal nano-particles involved with handling difficulty. Multi-layered graphene growth does not need the template substrates involved with the surface mismatching problems. BG-CNFs are grown directly by tension in midair between the cleaved separated substrates. Therefore, it can be easily moved to arbitrary places after the growth of BG-CNFs.

For practical use, form control of BG-CNFs is required. However, current growth processes have a difficulty in controlling the cross section of BG-CNFs because the cross section shape of a BG-CNF is configured by the uncontrollable cleaved surface of the carburized iron. We will research the processes to form the controllable cleaved points for BG-CNFs.

7. Conclusion

We have heretofore recognized the CNT growth on a metal nano-particle as a limited phenomenon in nano-scale. However, we discovered BG-CNFs grown by cleaving the carburized iron substrates as a bulky scale phenomenon.

BG-CNFs have been grown by cleaving the carburized iron substrates. We suppose the possibility that the special iron structure including extra-large amounts of carbon has been formed by reducing and carburizing the iron oxide.

The mechanism of these phenomena is not clear related to the growth of BG-CNFs. We will seek to solve the mechanism, which could lead to the development of a novel fabrication process for long CNT and graphene wires.

8. Acknowledgment

This study was carried out as a collaborative investigation with Professor Jun-ichi Fujita and Dr. Katsuhisa Murakami of Tsukuba University and Professor Sadahiro Tsurekawa of Kumamoto University. The authors are grateful to their great contributions toward the investigation of BG-CNFs.

References

- (1) A. Oberlin, M. Endo, and T. Koyama, *J. Cryst. Growth* **32**, 335 (1976)
- (2) K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, *Science* **306**, 1362 (2004)
- (3) Y. Li, I. A. Kinloch and A. H. Windle: *Science*, **304**, 276 (2004)
- (4) N. Behabtu, C. Young, D. Tsentelovich, O. Kleinerman, X. Wang, A. Ma, A. Bengio, R. Waarbeek, J. Jong, R. Hoogerwerf, S. Fairchild, J. Ferguson, B. Maruyama, J. Kono, Y. Talmon, Y. Cohen, M. Otto, and M. Pasquali, *Science*, **339**, 182 (2013)
- (5) R. Zhang, Y. Zhang, Q. Zhang, H. Xie, W. Qian, and F. Wei: *ACS Nano*, **7**, 6156 (2013)
- (6) A. K. Geim and K. S. Novoselov, *Nat. Mater.* **6**, 183 (2007)
- (7) S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, and S. Iijima, *Nat. Nanotech.* **5**, 574 (2010)
- (8) T. Hikata, K. Hayashi, T. Mizukoshi, Y. Sakurai, I. Ishigami, T. Aoki, T. Seki and J. Matsuo, *APEX*, **1**, 034002 (2008)
- (9) T. Hikata, *SEI Technical Review*, **67**, 3 (2008)
- (10) T. Hikata, S. Okubo, Y. Higashi, T. Matsuba, R. Utsunomiya, S. Tsurekawa, K. Murakami, J. Fujita, *AIP Advances*, **3**, 042127 (2013)
- (11) J. Fujita, E. Iida, T. Hikata, S. Okubo, and K. Murakami, "Graphitic Fiber Growth Observed within Cleavage Gap of Oversaturated Carburized Iron," SS13.90, MRS2013, Dec.1-6,2013, Boston, USA.
- (12) S. P. Matthew, T. R. Cho, and P. C. Hayes, *Metall. Trans.* **B21**, 733 (1990)

Contributors (The lead author is indicated by an asterisk (*).)

T. HIKATA*

- Dr. Eng.
Assistant General Manager, New business
Frontier R&D Laboratories



S. OKUBO

- Assistant General Manager, New business
Frontier R&D Laboratories



R. UTSUNOMIYA

- Chief senior staff, Material R&D Laboratories, Nissin Electric Co., Ltd.



Y. HIGASHI

- Material R&D Laboratories, Nissin Electric Co., Ltd.



T. MATSUBA

- Material R&D Laboratories, Nissin Electric Co., Ltd.

