Catalyst-Free Synthesis of Carbon Nanofibers by Ultrasonic Spray Pyrolysis of Ethanol

Jianfeng Bao[1], Naoki Kishi[1], Ishwor Khatri[1], Tetsuo Soga[1], Takashi Jimbo[2]*

[1]Depertment of Frontier Materials, Nagoya Institute of Technology,

Nagoya 466-8555, Japan

[2]Research Center for Nano-Device and System, Nagoya Institute of Technology,

Nagoya 466-8555, Japan

Abstract

We synthesized carbon nanofibers (CNFs) at atmospheric pressure by ultrasonic spray pyrolysis of ethanol without a catalyst. The morphology of carbon deposited on silicon and quartz substrates strongly depended on the position of the substrate in the reaction tube. CNFs with typical bamboo-like structures were formed downstream in the reaction tube, whereas amorphous carbon films were formed in the center of the reaction tube. The growth of these CNFs may be explainable in terms of a mechanism based on the autocatalytic chemical vapour deposition of 3D graphene flakes. As-grown samples were characterized by scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy.

Keywords: Carbon materials, Chemical vapour deposition.

1. Introduction

Carbon nanofibers (CNFs) [1] have attracted considerable attention as promising carbon materials because of their high aspect ratio, small radii of curvature, low chemical activity, and mechanical toughness properties. They are expected to be applied for various applications such as in electron field emission source [2], probe tip [3], and fuel cells [4].

Chemical vapour deposition (CVD) is a promising technique for mass producing CNFs because it is a simple, low cost fabrication process. Synthesizing CNFs by CVD generally requires using transition metals as catalysts. Aoki *et al*. have grown amorphous CNFs by thermal CVD with CuNi alloy films as a catalyst in a mixture of acetylene and helium [5]. CNFs have also been synthesized by plasma-enhanced CVD using Fe, Ni, Co, and their alloys (e.g., FeCo) as catalysts CNF [6, 7].

Zhang *et al.* recently synthesized CNFs without using transition metal catalysts by ultrasonic spray pyrolysis. CNFs that are several tens of nanometers in diameter have been produced using graphite, fullerene, or boron as nucleating site [8, 9]. Deng *et al*. developed a simple method for synthesizing CNFs that involves non-catalytic thermal decomposition of acetylene on a copper substrate [10]. Several methods have been reported for synthesizing CNFs using non-transition metal catalysts, but the details of these methods have not been clarified. Therefore further study of non-catalyst CVD for synthesizing CNFs is required.

This paper reports synthesis of CNFs by ultrasonic spray pyrolysis of ethanol without using a catalyst. The morphology of carbon deposition on substrates strongly depended on the position of the substrate in the reaction tube. CNFs with typical bamboo-like structures were obtained downstream in the reaction tube.

2. Experimental

Fig. 1 shows the schematic diagram of ultrasonic spray pyrolysis. This method is described in Ref.11. Ethanol was placed in a medication cup and pure nitrogen gas was used to transport the precursor mist generated in the atomization chamber to a quartz tube (length: 65 cm; diameter: 28 mm) in the furnace. Silicon and quartz substrates (size: 10 mm × 10 mm) were cleaned in acetone and methanol, washed in de-ionized water, and dried using nitrogen blower. Substrates were placed in quartz boats, which were placed at three different positions (position1, 2, and 3 in Fig. 1). When the furnace temperature was set to 850^{o}C, a thermocouple measured temperature of 890^{o}C, 820^{o}C, and 570^{o}C at position 1, 2 and 3 in the quartz tube; respectively. Both ends of the quartz tube were then closed by quartz joints; one ends was connected to a nebulizer and other end was connected to water bubbler. A constant nitrogen flow with a flow rate of 0.5 L/min was applied until the temperature reached 700^{o}C -1000^{o}C. After the furnace reached the set temperature, the nitrogen flow rate was increased to 1L/min and this state was maintained for 5 min. An ethanol mist was passed through the reaction tube for 1h. After deposition, the furnace was turned off and allowed to cool to room temperature. The center of the quartz tube was black after the deposition, while the quartz tube near position 3 was slightly blackened but transparent. As-produced samples were characterized by field emission scanning electron microscopy (FE-SEM; JEOL-7001F), scanning electron microscopy (SEM; Hitachi s-3000H), transmission electron microscopy (TEM; Hitachi JEM-Z2500), and Raman spectroscopy (JASCO NRS-1500W). Raman measurements were performed 532-nm-wavelength excitation.

3. Results and discussion

Fig. 2(a) shows a photograph of as-produced samples formed on quartz substrates at 850^{o}C. The quartz substrates at position 1 and 2 appear to be completely black, whereas the substrate at position3 is transparent. Figs. 2(b)-(d) show FE-SEM images of the as–grown samples at position 1, 2, and 3, respectively. The samples at position 1 and 2 have amorphous carbon films with carbonaceous nanoparticles on their surface, whereas the sample at position 3 clearly exhibit CNFs. Fig. 3 shows a SEM image of as-grown CNFs on the silicon substrate at position 3. Similar results were observed on the silicon substrates.

To investigate the temperature dependence of carbon deposition, the furnace temperature was varied in the range 700-1000^{o}C. Deposition of amorphous carbon films was observed on the samples at positions 1 and 2 in the range of 800-1000^{o}C. In contrast, CNFs formed on the sample at position 3 for temperatures between 800 and 900^{o}C.

Fig. 4(a) show a TEM image of CNFs synthesized at 850^{o}C; they exhibit bamboo-like (i.e., hollow-fibril) morphology. The CNFs are about 20 nm in diameter. As shown in Fig. 4(b), these CNFs are open consisting of fringes with a low degree graphitization and small sheets.

The as-grown samples synthesized at 850^{o}C were characterized by Raman spectroscopy. As shown in Fig. 5, two distinct peaks were observed at about 1350 and 1597 cm^{-1}, corresponding respectively to the D- and G-band of graphite. The broadening of these lines into bands implies that the CNFs have a low crystallinity and are composed of small sheets with a low degree of graphitization. The D band may be associated with structural defects and disorder in the CNFs. The G band is due to vibration of sp^2 bonded carbons in a 2D hexagonal lattice [12]. The prominent D band

in Fig. 5 indicates a low graphitization degree and presence of a many defects and disorder. Samples at position 1, 2, and 3 have intensity ratio I_G/I_D of 0.84, 0.89, and 1.07, respectively; the I_G/I_D ratio of the sample at position 3 is considerably higher than those position 1 and 2.

The growth mechanism of these bamboo-like CNFs from only ethanol is currently unclear. However, based on various studies [8-10,13], we consider that the growth mechanism of the present CNFs is closely related to autocatalytic 3D graphene flakes (i.e., graphene sheets that are curved, bent, flat, rolled, or wrinkled) by Deng *et al*. [8]. It has been suggested that carbon molecules rapidly combine to form long, branched carbon chains. Small cyclic structures with long carbon chains form from these large chains.

4. Summary

We have synthesized CNFs on silicon and quartz substrates by ultrasonic spray pyrolysis using ethanol only. These CNFs are several tens of nanometers in diameter and have a bamboo-like structure with an open tip or end. Carbon deposition on the present substrates strongly depended on the substrate location in the reaction tube. We found that CNFs with typical bamboo-like structures were formed downstream in the reaction tube.

References

[1] A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth 1976; 32: 335-49

[2] K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, and W. I. Milne, Appl. Phys. Lett 2002; 80: 2011-13.

[3] H. Cui, S. V. Kalinlin, X. Yang, and D. H. Lowndes, Nano Lett 2004; 4: 2157-61

[4] Jui-Hsiang Lin, Tse-Hao Ko, Miao-Yu Yen, Energy &Fuels 2009; 23: 4042-46.

[5] Katsunori A, Tetsurou Y, Hiroshi F, Takashi I, Shinichi H, Mamoru F, Kenjiro O, Takashi H, Jpn. J. Appl. Phys 2006; 45: 5329-31.

[6] Vladimir l. Merkulov, A. V. Melechko, M. A. Guillorn, M. L. Simpson Appl. Phys. Lett 2002; 80: 4816-18.

[7] K. D. Sorge, K. L. Klein, A. V. Melechko, C. L. Finkel, O. Malkina, Th. Leventouri, J. D. Fowlkes, P. D. Rack, M. L. Simpson, J. Appl. Phys 2008; 104: 033909-16.

[8] Zhang J, Khatri I, Kishi N, Soga T, Jimbo T, IEICE Transactions on Electronics 2009; E92-C: 1432-37.

[9] Zhang J, Khatri I, Kishi N, Soga T, Jimbo T, Materials Letters 2010; 64: 1243-45.

[10] Da Deng, Jim Yang Lee, Chem. Mater 2007; 19: 4198-04.

[11] Khatri I, Soga T, Jimbo T, Adhikari S, Ram A H, Umeno M, Diamond Rel Mater 2009; 18: 319-23.

[12] A. C. Ferrari, J. Robertson, Phys. Rev. B 2000; 61: 14095-07

[13] Z. L. Wang, Z. C. Kang, J. Phys. Chem. 1996; 100: 17725-31.

Figure captions

Fig. 1 Schematic of ultrasonic spray pyrolysis set-up used to synthesize CNFs.

Fig. 2 (a) Photograph of as-produced samples deposited on quartz substrates at positions 1, 2, and 3. FE-SEM images of the samples on quartz substrates placed at positions (b) 1, (c) 2, and (d) 3. The furnace temperature was set to 850°C.

Fig. 3 Typical SEM image of samples synthesized on silicon substrate at position 3. The furnace temperature was set to 850°C.

Fig. 4 Typical TEM images of CNFs at position 3 observed at (a) low and (b) high magnifications. The furnace temperature was set to 850°C.

Fig. 5 Raman spectra of as-grown samples located at positions 1, 2, and 3 on quartz substrates. The furnace temperature was set to 850°C.

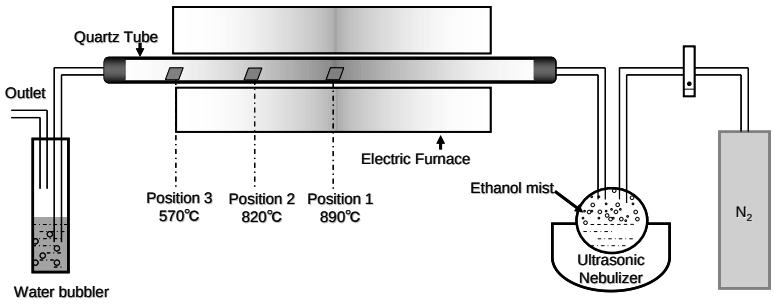

Fig. 1 Bao. J *et al*.

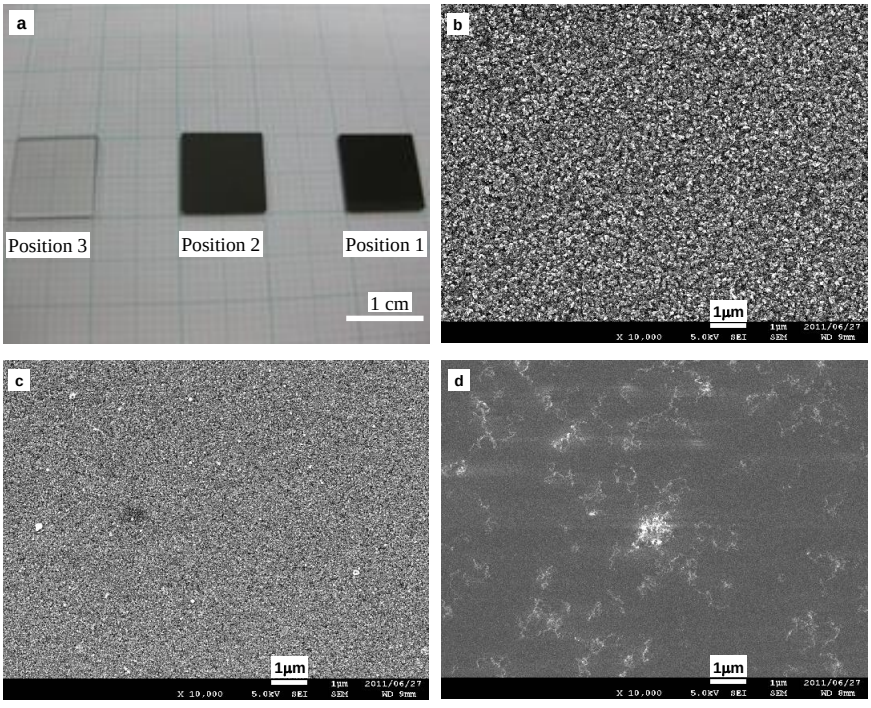

Fig. 2 Bao. J *et al*.

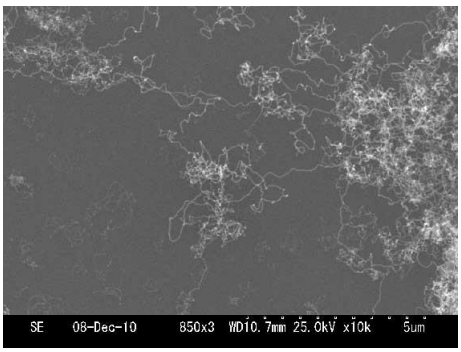

Fig. 3 Bao. J *et al*.

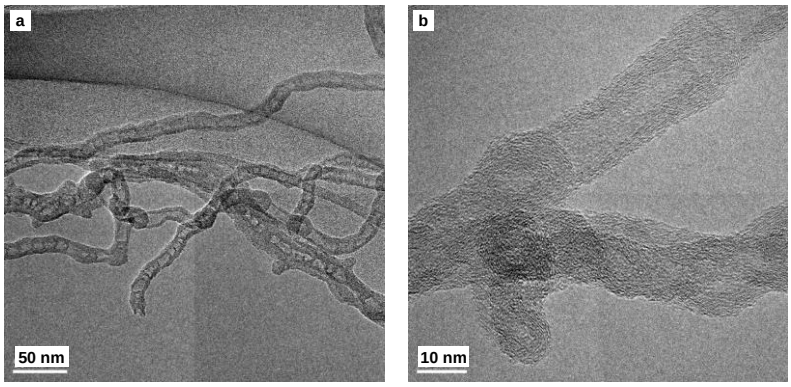

Fig. 4 Bao. J *et al*.

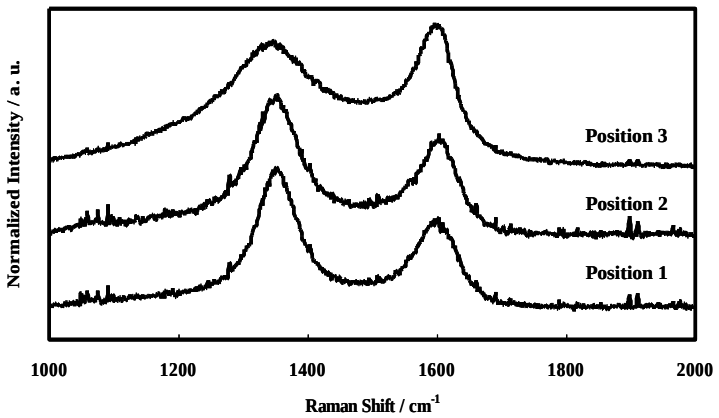

Fig. 5 Bao. J *et al*.