Asian Journal of Chemistry; Vol. 24, No. 6 (2012), 2695-2697

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Fabrication of Coiled Carbon Nanotubes by Chemical Vapour Deposition and Focused Ion Beam

JIANGLEI LU*, GUANGLONG WANG, FENGQI GAO and PENG QIU

Institute of Nanotechnology and Microsystems, Mechanical Engineering College, Shijiazhuang 050003, P.R. China

*Corresponding author: E-mail: ljianglei@163.com

(*Received*: 18 June 2011; *Accepted*: 17 January 2012) AJC-10975

A novel approach to fabricate coiled carbon nanotubes based on floating-catalyst chemical vapour deposition and focused ion beam was put forward. The numerous toroidal carbon nanotubes were synthesized and then accurately processed to coiled carbon nanotubes. The effect of catalysts on the synthesis of toroidal carbon nanotubes and the fabrication of coiled carbon nanotubes by focused ion beam machining techniques were discussed. This post-processing approach revealed the intrinsic relation between toroidal and coiled carbon nanotubes, which broke through the correspondingly isolated fabrication methods in the past. Compared with the recent improved methods, such as the fluidised-bed method, coprecipitation/reduction method and spray-pyrolysis method, *etc*., it could flexibly and accurately adjust the structural parameters, which laid the foundation for applications of coiled carbon nanotubes in the design of precise nanoelectromagnetic devices with special requests.

Key Words: Carbon nanotubes, Coiled carbon nanotubes, Toroidal carbon nanotubes, Chemical vapour deposition, Focused ion beam.

INTRODUCTION

Carbon nanotubes (CNTs) are structurally equivalent to a perfect graphite sheet rolled into a seamless hollow tube. Since carbon nanotubes were first observed by the transmission electron microscope in 1991, they have attracted considerable attention in recent years for their unique properties, such as excellent heat conductivity, metal-semiconductor conductivity, high specific surface area as well as the mechanical and chemical stability[1-3]. The structure of carbon nanotubes has various shapes including linear, V-shaped, Y-shaped, plait-like, worm-like, bamboo-like, toroidal carbon nanotubes (TCNTs) and coiled carbon nanotubes (CCNTs), *etc*. Among them, coiled carbon nanotubes have many merits due to the uniquely helical structure besides the intrinsic attributes of carbon nanotubes[4,5]. As a kind of nanoelectromagnetic material, they have potential applications ranging from conductive and high reinforcement material components to nanogenerators, nanotransformers, nanoswitches, energy converters and microsensors, *etc*.

In general, coiled carbon nanotubes are synthesized by the fixed-catalyst or floating-catalyst chemical vapour deposition (CVD)[6]. The morphology and quality of helical carbon species greatly depend on the selections of catalyst, carbon source, reaction temperature, gas flow rate, feedstock pressure, *etc*. Originally, coiled carbon nanotubes were synthesized in low yield as by-products in the catalytic decomposition of organic substances such as acetylene, toluene and pyridine. After the substrate material and catalytic activity were modified, the coiled carbon nanotubes yield has been extremely improved. Recently, many improved methods were reported to realize the controllable coiled carbon nanotubes production. Wang *et al*.[7], synthesized highly compressed and regular coiled carbon nanotubes by a spray-pyrolysis method. The high yield of coiled carbon nanotubes (90 vol. %) was realized by spray pyrolysis of the ethanol solution intermittently supplied into the reaction zone at 850 ºC. Liu *et al*.[8], synthesized the mixtures of regularly coiled and straight carbon nanotubes on the alumina supported Co catalysts under C_2H_2:H_2: N_2 at 750 ºC in a fluidised-bed. It was a promising technique for the large-scale synthesis of coiled carbon nanotubes. Qi *et al*.[9], synthesized high purity (99.21 wt. %) helical carbon nanotubes in large quantity over Fe nanoparticles by acetylene pyrolysis at 450 ºC and revealed the span of H_2 presence during the acetylene pyrolysis could influence coiled carbon nanotubes yield. However, coiled carbon nanotubes structural parameters including coil-pitch, coil-diameter and turn number could still not be flexibly and accurately controlled according to the application field (Fig. 1). The approach to fabricate coiled carbon nanotubes by chemical vapour deposition and focused ion beam (FIB) could well solve the problem in this paper.

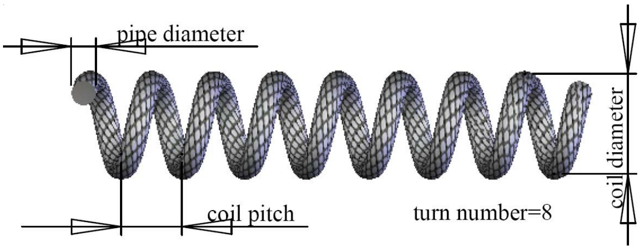

Fig. 1. Structural parameters of coiled carbon nanotubes

EXPERIMENTAL

The experimental scheme includes two sections. Toroidal carbon nanotubes are first synthesized by a floating catalyst chemical vapour deposition method and then processed to coiled carbon nanotubes by focused ion beam fabricating techniques. The schematic diagram of the apparatus used for synthesizing toroidal carbon nanotubes is shown in Fig. 2(a). The experimental setup is a three-section quartz tube (30 mm inner diameter) mounted in a two-stage furnace system. The A-section quartz tube put in the first furnace is used to sublimate the catalyst power. The small embedded quartz tube (10 mm inner diameter) placed in the B-section quartz tube is used as reactors in the second furnace. The C-section quartz tube includes a silicon substrate which is used to collect toroidal carbon nanotubes at a low temperature. The quartz tube is first flushed with argon flow for a while in order to eliminate oxygen. Ferrocene as catalyst precursor and sulphur as growth promoter are heated and carried into the reactor (1100 ºC) along with the gaseous mixture of argon and acetylene. This approach could synthesize toroidal carbon nanotubes with larger-scale and higher purity than other methods, such as laser ablation, solvent evaporation, solid-solution reaction, *etc*. It also laid the foundation for further machining toroidal carbon nanotubes by focused ion beam system[10].

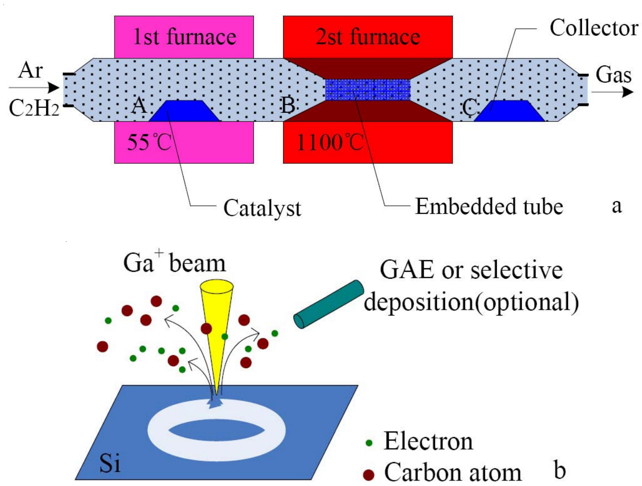

Fig. 2. Schematic diagrams of the apparatus used for synthesizing toroidal carbon nanotubes (a) and processing toroidal carbon nanotubes to coiled carbon nanotubes (b)

The focused ion beam system with scanning electron microscope (SEM) and nanomachining capabilities is used to further process toroidal carbon nanotubes to form coiled carbon nanotubes. The schematic diagram of focused ion beam used for processing toroidal carbon nanotubes is shown in Fig. 2(b). The system utilizes a finely focused high-energy beam of gallium ions (Ga^+) to hit the nanotube surface, which can produce some secondary electrons, secondary ions or neutral atoms. By determining the two-dimensional distribution of the generated amount, the SEM image of the nanotube wall surface can be accurately observed. By accelerating the gallium ions beam, large numbers of atoms sputter from the nanotube wall surface. The high aspect-ratio etching can be precisely performed by the gas assisted etching (GAE). By spraying hydrocarbon gas on the nanotube wall surface with the ion beam irradiation, carbon atoms are separated out and deposited on the site specific location. Synthetically utilizing focused ion beam imaging, milling and deposition techniques, numerous toroidal carbon nanotubes could be cut, twisted and welded to coiled carbon nanotubes with different structural parameters.

RESULTS AND DISCUSSION

Effect of catalysts on the synthesis of toroidal carbon nanotubes: Transition metals are generally used as the fixed-catalyst, such as iron, cobalt and nickel, *etc*. and combined with the catalyst carriers including graphite, silicon dioxide, titania, alumina, zeolite or molecular sieve material. The growth orientation and structural parameters of carbon nanotubes can be well controlled by the hole spacing effect of catalyst carriers although lacking of flexibility and accuracy. However, the yield is limited because the catalyst particles are rapidly surrounded by a dense tangle of nanotubes which prevent the feedstock gas from diffusing on the catalyst surface and limit the further nanotubes growth. The problem can be well solved by the floating-catalyst vapour deposition although the growth temperature is correspondingly higher. It commonly utilizes the organic metal as catalyst precursors and the sulphur or sulfocompound as growth promoters. Because the pyrolyzed metal particles are combined with some sulphur, the carbon atoms decompounded from hydrocarbons can not entirely cover the surface of metal particles[11]. So the mechanism of toroidal carbon nanotube synthesis in this research will be shown as following:

$$C_2H_2 \longrightarrow 2C + H_2 \quad (1)$$

$$Fe(C_5H_5)_2 + H_2 \longrightarrow Fe + 2C_5H_6 \quad (2)$$

$$nC + Fe \longrightarrow Fe\text{-catalyzed toroidal carbon nanotubes} \quad (3)$$

Three-dimensional nanostructures based on carbon nanotubes: The focused ion beam system has emerging applications for manipulating carbon nanotubes and fabricating complex three-dimensional nanostructures. The structure of carbon nanotubes tip for atomic force microscopy could be modified by the ion beam irradiation. When the ion beam scans the wall of bend metal-coated carbon nanotubes at precise angles for a few microseconds, carbon nanotubes vary along with the scanning orientation[12]. At higher beam currents, the focused ion beam system can complete the material sectioning at an atomic scale, whose function is similar to the milling machine. This precise milling can also be used for cutting carbon nanotubes[13,14]. The accelerated gallium ions scan on the material surface in a line and produce a trench with an inverse Gaussian shape. However, when the dose is increased, the trench becomes very sharp, narrow and unexpectedly deep. So focused ion beam system must be combined with the gas assisted etching technique to cut the high aspect-ratio material. carbon nanotubes can not only be cut to two segments, but also be welded together by focused ion beam deposition techniques. Instead of the gallium ion beam, when the accelerated carbon ion beam irradiates the two correlative carbon nanotubes, a larger amount of junctions can be achieved by amorphous carbons[15]. It was reported that the nanoflag was attached to an upright carbon nanotubes on a scanning probe microscope tip by the ion beam milling technique and platinum chemical vapour deposition[16]. So carbon nanotubes could be jointed to other materials in order to fabricate three-dimensional nanostructures and assemble nano electromechanical systems.

Coiled carbon nanotubes fabricated by focused ion beam machining techniques: Toroidal carbon nanotubes synthesized by the pyrolysis of acetylene in a floating-catalyst chemical vapour deposition system can be processed to coiled carbon nanotubes step by step with the focused ion beam cutting, imaging and welding techniques. The coiled carbon nanotubes fabricated by focused ion beam machining techniques is shown in Fig. 3. The focused ion beam system with SEM and nanomachining capabilities is utilized. Firstly, using the focused ion beam milling mode with the acceleration voltage of 10 kV and the current of 1000 pA, Gallium ions are focused down to 10-20 nm sized spot and continuously scan a narrow area on toroidal carbon nanotubes for several seconds (Fig. 3a). Carbon atoms are sputtered from nanotube surface so that the cutting process can be achieved (Fig. 3b). Secondly, using the focused ion beam imaging mode with accelerated gallium ions at 30 kV, the ion beam is 10 nm in diameter and scans the opening port of nanotube at precise angles with respect to the initial orientation for a few microseconds, then quickly transfers to the next point, which prevents the nanotubes surface from damaging. Meanwhile, the twist progress is real-time tracked by taking a SEM image in order to exactly control the twist angle. Then the semi-helical carbon nanotubes are fabricated (Fig. 3c). Using the same method, the numerous semi-helical carbon nanotubes can also be fabricated. Thirdly, using the focused ion beam deposition mode, one port of the semi-helical carbon nanotubes is welded with the other port of the second semi-helical carbon nanotubes in the coaxial orientation by the focused ion beam welding techniques (Fig. 3d). One by one, many semi-helical carbon nanotubes are jointed together to form coiled carbon nanotubes (Fig. 3e). Meanwhile, because some amorphous carbon and implanted gallium are deposited around the junction points of nanotubes in the cutting and welding process, they need to be further removed by the ion beam milling technique.

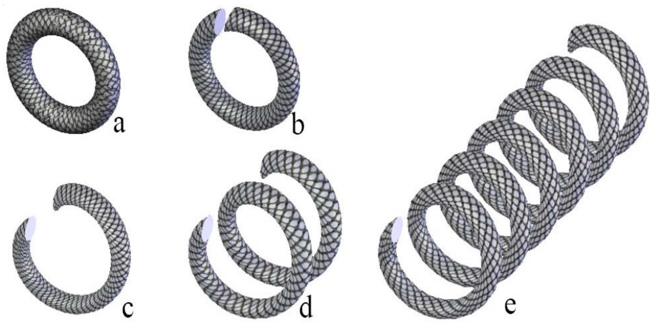

Fig. 3. Coiled carbon nanotubes fabricated by focused ion beam machining techniques

Conclusion

The post-processing approach to fabricate coiled carbon nanotubes based on chemical vapour deposition and focused ion beam reveals the intrinsic relation between toroidal carbon nanotubes and coiled carbon nanotubes. It requests many new techniques including focused ion beam milling, cutting and welding techniques, nanomanipulate techniques with high resolution. These techniques, especially the seamless junction of carbon nanotubes based on focused ion beam welding techniques, are recent research focuses and severe challenges. However, they break through the correspondingly isolated fabrication methods of toroidal carbon nanotubes and coiled carbon nanotubes in the past. This fabrication approach can meet special requests for precise nanoelectromagnetic devices along with the rapid development of nanomachining and nanomanipulate techniques in the future.

ACKNOWLEDGEMENTS

The authors thank Institute of Nanotechnology and Microsystems for providing the studying environment, experimental facility and technical support.

REFERENCES

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. Y. Gogotsi, *Science*, **330**, 1332 (2010).
3. P. Malik, A. Chaudhary and K.K. Raina, *Asian J. Chem.*, **21**, S095 (2009).
4. X.F. Li, K.T. Lau and Y. S. Yin, *Compos. Sci. Technol.*, **68**, 2876 (2008).
5. V. Gayathri, N.R. Devi and R. Geetha, *Int. J. Hydrogen Energy*, **35**, 1313 (2010).
6. J.Q. Huang, Q. Zhang and F. Wei, *Progr. Chem.*, **21**, 637 (2009).
7. J.N. Wang, L. F. Su and Z. P. Wu, *Cryst. Growth Des.*, **8**, 1741 (2008).
8. J. Liu and A.T. Harris, *J. Nanopart. Res.*, **12**, 645 (2010).
9. X.S. Qi, W. Zhong, Y. Deng, C.T. Au and Y.W. Du, *Carbon*, **48**, 365 (2010).
10. L. Song, L. J. Ci, L. F. Sun, C. Jin, L. Liu, W. Ma, D. Liu, X. Zhao, S. Luo, Z. Zhang, Y. Xiang, J. Zhou, W. Zhou, Y. Ding, Z. L. Wang and S. Xie, *Adv. Mater.*, **18**, 1817 (2006).
11. V. Bajpai, L. Dai and T. Ohashi, *J. Am. Chem. Soc.*, **126**, 5070 (2004).
12. Z.F. Deng, E. Yenilmez, A. Reilein, J. Leu, H. Dai and K.A. Moler, *Appl. Phys. Lett.*, **88**, 023119 (2006).
13. Y.H. Yoon, Y.H. Shin and J.W. Song, International Mechanical Engineering Congress and Exposition (IMECE), USA, pp. 547-550 (2006).
14. M.J. Kim, Continued Growth of Single-Walled Carbon Nanotubes from Open-Ended SWNT Substrates, RICE University, USA, pp. 29-30 (2006).
15. Z.X. Wang, L.P. Yu and W. Zhang, *Nucl. Phys. Rev.*, **22**, 47 (2005).
16. J. Jeon, H.C. Floresca and M.J. Kim, *J. Vac. Sci. Technol. B*, **28**, 549 (2010).