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Branched carbon nanofibers synthesized by an improved floating catalytic method

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In recent years, carbon nanotubes (CNTs) have been extensively studied because of their unique excellent properties and potential applications [1, 2]. One application near to practical use is to utilize their electric conductivity by incorporating them in resin, thus improving its electric conductivity. The requirement for the structure of carbon nanotubes in this application is not strict. It is expected that these CNT/resin composites will apply to the areas such as electrostatically painting for automobile parts, preventing the electronic devices from electrostatic discharge and shielding electromagnetic wave [3]. Compared with granular additives such as carbon black, the fiber-like shape is considered to be the better additives, because the fiber-like shape additives are easier to connect with each other and form a network in the matrix. In this viewpoint, branched carbon nanotubes or nanofibers additives are expected to decrease the amount that is needed, because the branched fibers can be considered as partly already connected fibers.

Branched CNTs were observed occasionally in some CVD processes [4, 5]. In that case, the splitting of catalytic particles is responsible for the formation of branched CNTs. However, the splitting of catalyst particles rarely takes place and is difficult to control. Another method to produce branched nanofibers is to grow nanofibers on the formerly-grown carbon nanofibers being sprayed with catalyst slurry [6], but such a method tends to form a network, and the product is difficult to be dispersed in subsequent treatment. In this letter, we report the synthesis of branched carbon nanofibers by an improved floating catalytic method.

The floating catalytic method to synthesize VGCF, carbon nanofiber or carbon nanotube was developed by Endo [7]. In this method, metal-organic compound as precursor of catalyst and carbon source were vaporized [8] or injected [9] into reaction tube and carbon nanotubes were grown continually. In the present research, branched carbon nanofibers were synthesized by similar floating catalytic process using ferrocene as catalyst precursor and benzene as carbon source, besides, TEOS was also carried into the reaction tube to promote the formation of branched carbon nanofibers. The synthesis was carried out in a quartz reaction tube at 1323 K with an inner diameter of 35 mm and a length of 1300 mm. The flow rates of hydrogen and argon, as the carrier gases, were 400 sccm and 800 sccm, respectively. The vaporization rates of benzene, TEOS and ferrocene were measured to be 4.7×10^{-3} mol/min, 1.6×10^{-4} mol/min, 5.8×10^{-5} mol/min, according to the mass change after reaction. The soot-like products were blown out by the flowing gas and collected near the outlet of the reaction tube. As a comparison, similar experiments in the same conditions as above without TEOS addition were also carried out. The as-prepared products were analyzed using field emission scanning electron microscopy (FESEM) (Jeol, JSM-6700F), transmission electron microscopy (TEM) (Jeol, JEM-200CX) and X-ray diffraction (XRD) (Rigaku D/max RB).

Fig. 1 shows the FESEM images of the as-prepared product. It can be seen that many branched nanofibers are present in the as-prepared product. Several nanofibers, with a diameter of about 100 nm and a length ranging from lower than 1 micrometer to several micrometers, protrude out from a core. Such morphology dominates in the product. Fig. 1B with a higher magnification shows a branched nanofiber consisting of four long nanofibers with length of about 700 nm, and two short nanofibers with length of about 200 nm, and several other half-ball-like particles. It is interesting to note that the four long nanofibers grow out in four completely different directions with angles of about 90 °.

Fig. 2 shows TEM micrographs of the as-prepared products. From Fig. 2A, we can see that a branched nanofiber consists of 10 nanofibers, while another two branched nanofibers consist of 4 or more nanofibers but shorter than the first one. Some particles were also observed, usually adhered to longer fibers. It can be seen that each nanofiber has a hollow tube in the center with a diameter of several nanometers, and catalyst particles were observed in the tips of some nanofibers shown in Fig. 2B. Many black particles with size of about 10 nm were also observed in the core (the bottom left image shows the center part clearly), which are considered to be Fe catalyst particles from contrast distinction, because SiO_2 has similar contrast with carbon nanofibers.

Complete oxidation of the as-prepared products in air at 873 K results in light brown color particles with 94%

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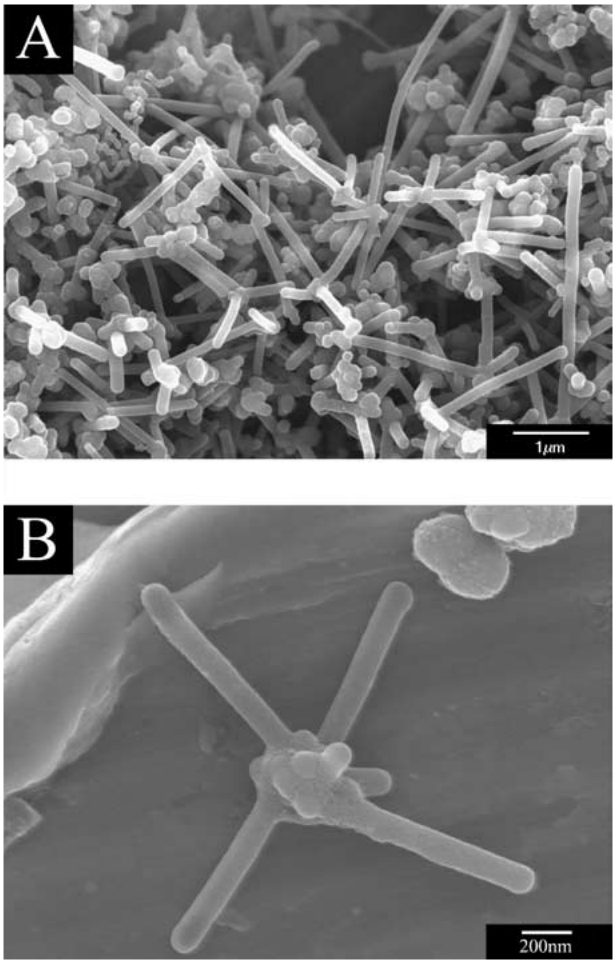

Figure 1 FESEM images of the as-synthesized products.

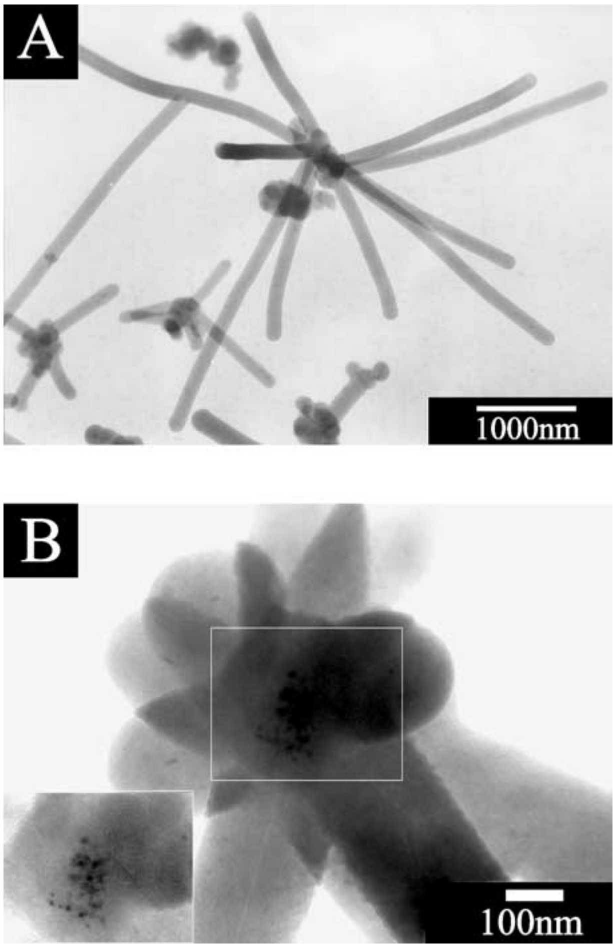

Figure 2 TEM images of the as-synthesized products. (B: The TEM image of the center part in the white frame is show in bottom left with appropriate contrast and lightness).

weight loss. Analyses indicate that the residue consists of iron oxide and amorphous silica. From Fig. 2B, we can find that Fe particles are located mainly in the center of the cores and FESEM observation of incomplete oxidized samples suggest that SiO_2 particles are also located mainly in the center.

We also synthesize straight carbon nanofiber (shown in Fig. 3) using only benzene and ferrocene without TEOS. There is almost no distinct difference between the nanofibers in branched nanofibers with the straight nanofibers except the length and diameter, which indicate that they take the similar growth mechanism. The growth mechanism of carbon nanofiber is considered to be like this. First, hollow carbon nanotubes with diameter of several nanometers grow with the catalytic effect of iron. Subsequently the decomposition of benzene deposits pyrolytic carbon on the thin hollow tube, resulting in thickening of nanotube to diameter of about 100 nanometers or more, depending on parameters like temperature and concentration of benzene [10]. Therefore, carbon nanofibers are mainly composed of pyrolytic carbon from the direct decomposition of benzene, thus exhibiting a poor graphitization degree.

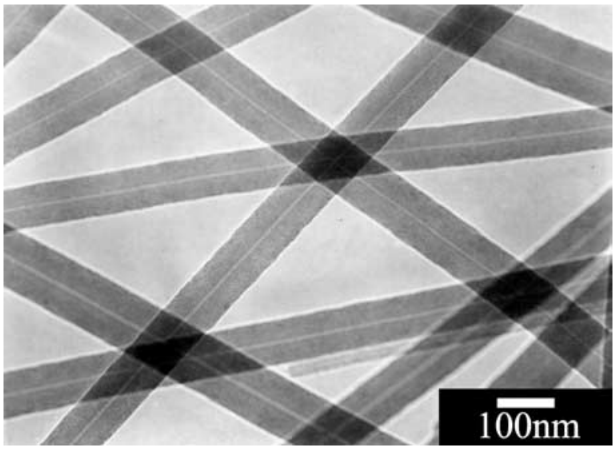

Figure 3 TEM images of carbon nanofibers synthesized without TEOS addition.

Here we provide a growth mechanism for this unique structure as shown in Fig. 4. In the first stage, Fe clusters decomposed from ferrocene collide with SiO_2 particles, which formed from the decomposition of TEOS, resulting in Fe-SiO_2 composite aggregation. Since mole ratio of Fe/SiO_2 is about 1/3, SiO_2 acts as the matrix and small Fe particles are distributed both on its surface and interior. In the next stage, after it is carried into the reactor zone, several CNTs catalytically grow from it just as the similar mechanism described in [10]. In this catalytic growth process, Fe particles on the surface act as catalyst of carbon nanotubes and Fe-SiO_2 composite aggregation core act as the substrate. In the last stage, with pyrolytic carbon deposition from benzene on the carbon nanotubes and the surface of the core, the diameters of carbon nanotubes increase and the aggregation

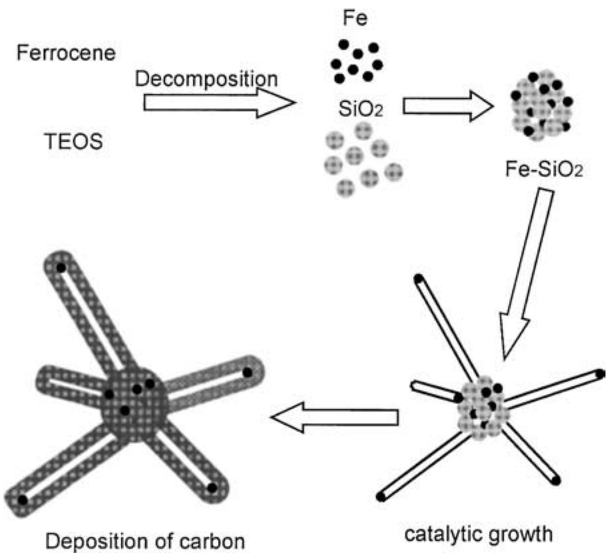

Figure 4 Model of branched carbon nanofibers growth mechanism.

core are thus also covered by a thick carbon layer, which makes almost all Fe particles look like they only exist in the center of the core shown as Fig. 2B. Although there are dozens of Fe particles at one Fe-SiO_2 composite aggregation, only several carbon nanofibers are catalytic growth from it. One reason is that the Fe particles which embedded in the interior of the aggregation may have no opportunity to contribute to the growth of carbon nanotube, because only the Fe particles on the surface will get the opportunity to contact the carbon source.

The distinct difference between the nanofibers synthesized with and without TEOS in length indicates that the growth of carbon nanofibers in this process is lower than that by pure Fe particles. It may because some nanofibers follows "bottom-growth" mechanism, so that the carbon source around the composite aggregation will totally consume soon and then the supply rate of carbon source is limited by the rate of carbon diffuse from the atmosphere to the surface of Fe particles. Another result of this in carbon nanofibers tend to grow in different direction as shown in Fig. 1. In the case of pure Fe act as catalyst, the top can move in the atmosphere easily and get enough carbon sources, which result in long length.

In summary, we synthesize branched CNTs nanostructure by co-decomposing benzene and TEOS using floating catalytic method. The branched carbon nanofibers are expected to have an application as electric conductive addition to resin or paint. The properties and possible application in resin matrix composites are under examination.

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References

1. E. THOSTENSON, Z. REN and T. W. CHOU, *Comp. Sci. Technol* **61** (2001) 1899.
2. HONGJIE DAI, *Surf. Sci.* **500** (2002) 218.
3. Hyperion homepage (http://www.fibrils.com/ApplicationsPage.htm).
4. N. M. RODRIGUEZ, *J. Mater Res.* **8** (1993) 3233.
5. B. GAN, J. AHN, Q. ZHANG, S. F. YOON, RUSLI, Q. F. HUANG and H. YANG, *Diamond Relat. Mater.* **9** (2000) 897.
6. Showa Denko Ltd., Kokai-Tokkyo-Koho, Heisei 7-150419.
7. A. OBERLIN, M. ENDO and T. KOYAMA, *J. Cryst. Growth* **32** (1976) 335.
8. H. M. CHENG, F. LI, G. SU, H. Y. PAN, L. L. HE and X. SUN, *Appl. Phys. Lett.* **72** (1998) 3282.
9. R. ANDREWS, D. JACQUES, A. M. RAO, F. DERBYSHIRE, D. QIAN, X. FAN, E. C. DICKEY and J. CHEN, *Chem. Phys. Lett.* **303** (1999) 467.
10. T. KATO, K. HARUTA, K. KUSAKABE and S. MOROOKA, *Carbon* **30** (1992) 989.

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