Synthesis of Polygonized Carbon Nanotubes Utilizing Inhomogeneous Catalyst Activity of Nonspherical Fe₃O₄ Nanoparticles

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The synthesis of novel carbon nanotubes (CNTs) with polygonal cross sections by heating a powder mixture of ferrocene, oxalic acid, and the alkali metal potassium at mediate temperatures (480-500 °C) is reported. This kind of special polygonized CNTs has two distinctive characters: first, ribbonlike polygonized CNTs have diameters between 60 and 200 nm, and the lengths as long as several microns; second, the edge of polygonized CNTs is well-graphitized, the wall of which is amorphous. On the basis of evidence that the formation of polygonized CNTs appears to be strongly determined by inhomogeneous catalytic activity of nonspherical Fe₃O₄ nanoparticles, we propose the possible growth model.

1. Introduction

The discovery of carbon nanotubes (CNTs)¹ has stimulated intense interest in the fields of synthesis and technological applications due to their fascinating electronic, mechanical, and chemical properties.^{2,3} Up to now, various shapes of CNTs, such as straight, curved, helical, zigzag, and bamboo-shaped, have been prepared from various carbon resources,^{4–6} all of them are one-dimensional cylinderlike carbon materials. Conventionally, CNTs are generally believed to be perfect rolled graphene sheets, because CNTs with circular cross sections are assumed to minimize the strain energy of free, isolated nanotubes.

Several kinds of semiconductor nanomaterials, such as ZnO,^{7,8} Sb₂S₃/Sb₂Se₃,⁹ GaN,¹⁰ and carbon nanocoils,¹¹ can form polygonal nanoprisms, but the formation of polygonized CNTs is very difficult. Recently, several theoretical analyses have shown that polygonization of the single-walled CNTs (SWNTs) may be induced by flattening the tubes against each other in microbundles as the inter-tube van der Waals interaction increased.^{12,13} Furthermore, the polygonized CNTs have ever been observed under high pressure,^{14,15} or synthesized through CO₂ laser ablation.¹⁶

SWNTs with different cross sections exhibit different $\sigma^* - \pi^*$ hybridization which occur locally at the polygonized edges, and consequently different electronic properties, such as metal/insulator character.^{17,18} Tamura et al.¹⁹ reported that a type of large paramagnetic persistent current is revealed in polygonal CNTs through calculation of the persistent current-induced magnetic moment. In general, the transformation of the cross section induces modifications of the electronic band structure, leading to modulation of the transport properties, which could have potential applications in nanoelectronics.¹⁵

In this paper, we report the synthesis of a novel structure of CNTs with polygonal cross sections, which are not in the form of bundles, but which exist separately. The unique microstructure characteristics and possible growth model for this kind of polygonized CNTs are also discussed.

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2. Experimental Section

Ferrocene (98%), oxalic acid (99.95%), ethanol, hydrochloric acid (analytically pure), and metallic potassium (98%, chemically pure) were all used as purchased. The typical reaction begins by heating a mixture of 5.00 g of $H_2C_2O_4$, 0.50 g of $Fe(C_5H_5)_2$, and 3.75 g of metallic K in a stainless steel autoclave with a capacity of 15 mL at a temperature of 480-500 °C for 10 h, and then allowing it to cool to room temperature naturally. The as-prepared products were gray and spongy, were washed with ethanol and distilled water; it was designated as Sample 0 (S0). A part of the S0 sample was then treated with 4.0 mol/L HCl aqueous solution, the precipitate was collected by use of a microfilter, it was then washed with distilled water several times until the pH value was about 6, and it was finally dried in an oven at 110 °C; it was designated as Sample 1 (S1).

The XRD pattern was recorded in the 2θ range of $10-70^{\circ}$ by using a Rigaku (Japan) D/max-yA X-ray diffractometer equipped with graphite monochromatized Cu Ka radiation $(\lambda = 1.54187 \text{ Å})$. The morphology and structure of CNTs were observed by a Hitachi model H-800 transmission electron microscope (TEM) with electron diffraction and a JEOL-2010 high-resolution transmission electron microscope (HRTEM) with an energy dispersive X-ray detector, using an accelerating voltage of 200 kV. For TEM and HRTEM observations, the products were separated in ethanol by ultrasonic dispersion and then transferred onto carbon-coated copper grids. The Raman spectrum was taken on a LABRAM-HR Confocal Laser Micro-Raman spectrometer using an Ar⁺ laser with 514.5 nm at room temperature. The thermogravimetric analysis (TGA) was recorded on a Shimadzu TGA-50H (heating rate: 10 °C/min, N2 floating rate: 30 mL/min).

3. Results and Discussion

The XRD pattern of the as-prepared sample (S0) is shown in Figure 1. The reflection indexed with 111, 220, 311, 222, 400, 422, 511, 440 (labeled as \bullet) can correspond to face-centered cubic Fe₃O₄ (PDF standard cards, JCPDS 89-0688). The reflection peaks indexed with 210, 002, 201, 220, 031, 131,



Figure 1. X-ray diffraction pattern of the as-prepared sample (S0).



Figure 2. X-ray diffraction pattern of the S1 sample after the treatment with HCl aqueous solution.

221, (labeled as \checkmark) can correspond to primitive orthorhombic Fe₃C (PDF standard cards, JCPDS 72-1110). The reflection peaks indexed with 002 (labeled as \blacksquare) can correspond to hexagonal graphite (PDF standard cards, JCPDS 41-1487).

Figure 2 shows the XRD pattern of the S1 sample. It shows a strong peak at $2\theta = 26.3^{\circ}$, corresponding to the (002) reflection of hexagonal graphite (PDF standard cards, JCPDS 41-1487), and the other two weak peaks arose from (101) and (004) reflection. It is obvious that after the treatment with HCI aqueous solution, the main product is hexagonal graphitic-like carbon. The XRD of the S1 sample shows two relatively broad diffraction peaks of (002) and (101), indicating the existence of disordered and low graphitized structure.

A Raman spectrum is usually used to investigate the vibrational properties of carbon structures, which also allows us to draw further conclusions about the degree of crystallization.²⁰ The peak at ~1596 cm⁻¹ (G band) corresponding to an E_{2g} mode of graphite is related to the vibration of sp²-bonded carbon atoms in a 2-dimensional hexagonal lattice, while the peak at ~1346 cm⁻¹ (D band) is related to the defects and disorders in the hexagonal graphitic layers.²¹ In Figure 3, the value of I_D/I_G is calculated to be 0.85, which means that the S1 sample has relative disorder and a low graphitization degree,²² in agreement with the XRD pattern.

Figure 4 shows typical TEM images of polygonized CNTs of the S1 sample synthesized at 500 °C. First, the diffraction contrast of the TEM image (Figure 4a) proves they are nanotubes. Then from the open section of nanotubes, we can see a clear hexagonal outline, which is in contrast to the earlier



Figure 3. Typical Raman spectrum of the S1 sample.



Figure 4. TEM images of polygonized CNTs of the S1 sample synthesized at 500 °C. (a) Polygonized CNTs with hexagonal cross sections; (b) quadrigonal CNTs with an obvious edge between two sides, a corresponding typical SAED pattern is also shown in (b); (c,d) polygonized CNTs with quasi-hexagonal cross sections.

observations of nearly circular tubes. In Figure 4b, edges due to the connecting of two sides of CNTs can be clearly observed, revealing its characteristics of a quadrangle. The selected area electron diffraction (SAED) pattern of the sample exhibits two diffraction rings, corresponding to (002) and (101) reflections of hexagonal graphite (Figure 4b, insert). In addition, Figure 4, parts c and d, shows the polygonized CNTs with quasihexagonal cross sections.

Figure 5, parts a-c, shows TEM images of ribbonlike polygonized CNTs of an S1 sample synthesized at 480 °C, which have diameters between 60 and 200 nm and lengths as long as several microns, indicating features of softness and flexibility. Figure 5c depicts the magnified image of the boxed area of Figure 5b, in which edges can be observed more clearly. Figure 5d is the HRTEM image of the boxed area of Figure 5c, in which it is found that the edge of polygonized CNTs is wellcrystallized but the wall is amorphous, features which are different from those of other ordinary CNTs. The interlayer spacing (0.35 nm) of the edge agrees well with the (002) lattice distance in hexagonal graphite.



Figure 5. TEM and HRETM images of polygonized CNTs of the S1 sample synthesized at 480 °C. (a-c) Ribbonlike polygonized CNTs as long as several microns, and (c) is the magnified image of the boxed area of (b); (d) HRTEM image of the boxed area of (c), showing the different lattice structure between edge and wall of polygonized CNTs.

It is well-known that ferrocene is a highly volatile organometallic compound with excellent vaporizability. Up to now, ferrocene has been widely used for the growth of CNTs.^{23,24} In the present work, ferrocene was reduced to atomic iron and cyclopentadienyl group by metallic K (eq 1).²⁴

$$Fe(C_5H_5)_2 + 2K \rightarrow Fe + 2K^+ + 2C_5H_5^-$$
 (1)

When heated over 100 °C, $H_2C_2O_4$ is easily decomposed to CO₂, CO, and H_2O (eq 2), and then CO and CO₂ were deoxidized to carbon by metallic K. Hata et al.²⁵ had reported that the activity and lifetime of the catalysts can be dramatically enhanced by the addition of a controlled amount of water vapor in the growth of SWNTs. Therefore, in our reaction system, H_2O might act as an effective mediator of catalysts.

$$H_2C_2O_4 \rightarrow CO + CO_2 + H_2O \tag{2}$$

If the experiment was done using only ferrocene, it would be decomposed to amorphous carbon, iron carbide, and organic gas at 450 °C, in which iron carbide was encapsulated by amorphous carbon. If the experiment was done by using oxalic acid and metallic potassium, the products were mainly potassium carbonate, graphene shells, and amorphous carbon. Combined with above experimental truths, we could infer that the synthesis of polygonized CNTs is the synergism of oxalic acid and ferrocene—the carbon source of oxalic acid is catalyzed by iron originating from ferrocene.

The polygonal particles in the as-prepared products (S0) were observed to be quadrigonal, pentagonal, and hexagonal by TEM, as shown in Figure 6, parts a and b. The corresponding EDX spectrum (Figure 7) shows Fe, Cu, C, and O peaks, in which Fe and O signals originated from the polygonal particles and C and Cu signals originated from carbon-coated copper grids, respectively. The EDX spectrum analysis associated with the XRD result of the S0 sample can confirm that the polygonal particles are Fe₃O₄. The TEM image of Figure 6c shows a representative hexagonal open end in the morphology of a hexagonal CNT, which reveals a polygonal particle surrounded by a hexagonal outer shell of carbon, indicating that the



Figure 6. (a-b) TEM image of polygonal catalyst particle; (c) TEM image of a catalyst particle surrounded by a hexagonal carbon nanotube; (d) HRTEM image of polygonized CNTs, showing the different lattice of structure between edge and wall.



Figure 7. Typical EDX spectrum of polygonal particles.

polygonal particles might act as a catalyst for the formation of CNT. These results indicated there are some kinds of relations between the shape of the catalyst particles and polygonal sections of CNTs. Recently, El-Sayed et al.²⁶ reported that transition-metal nanoparticles are very attractive to use as catalysts due to their high surface-to-volume ratio and their high surface energy, which makes their surface atoms very active. They also pointed out that during the early stages of reaction, the catalytic activity is inhomogeneous, dependent on the shape of the nanocatalyst used, and particularly dependent on the fraction of surface atoms on corners and edges.

The edge of polygonized CNTs is well-graphitized, but the wall is non- graphitized, as clearly shown in the HRTEM image of Figure 6d. On the basis of Stiakaki's computation²⁷— chemisorption energy of corners is higher than that of edges of catalyst particles, we put forward the following explanation. The growth of the edge and wall of polygonized CNTs is controlled by the corner and edge of the polygonal catalyst particle, respectively. Compared with the edge, the corner of the catalyst particle has better catalytic activity, and therefore it can induce quicker deposition of carbon atoms and better crystallization on the edge of polygonized CNTs.

Now, we would suggest the possible growth model of polygonized CNTs-a polygonal catalyst particle acts as a

SCHEME 1: Schematic Illustration for the Growth Model of Hexagonal CNTs^{*a*}



^{*a*} (A) Iron atoms were oxidized and agglomerated into hexagonal Fe₃O₄ particles; (B) forming initial carbon shell by the deposition of carbon atoms, in which more atoms were inclined to aggregate on the corner of catalyst tarticle; (C) keep growing upward along the side; (D) finally forming hexagonal CNTs.



Figure 8. TGA curve of the S1 sample in a dynamic N₂ atomsphere.

substrate that governs the shape of the CNTs, causing the transverse cross section of the CNTs polygonal, which is similar to the base growth model.²⁸ Let's take hexagonal catalyst particles as an example. Scheme 1, parts a-d, illustrates the possible growth process of hexagonal CNTs. (a) First, iron atoms originating from ferrocene should be oxidized and agglomerate into small clusters. At moderate temperatures, small clusters are easy to aggregate to form large hexagonal Fe₃O₄ nanoparticles. (b) Then carbon atoms preferentially deposit on the boundary of the Fe₃O₄ nanoparticle to form the initial carbon shell, but due to the better catalyst activity of the corner, most of carbon atoms are inclined to aggregate on the corner rapidly, causing the graphitization at the edge of CNTs. (c) This continues growing upward along the side. (d) It eventually terminates with the formation of hexagonal CNTs.

Figure 8 shows a typical TGA curve of an S1 sample in a N_2 atmosphere, in which there is a gradual decrease in the weight loss curve, indicating that the products have a relatively high thermal resistance in a N_2 atmosphere.

4. Conclusion

In conclusion, we have successfully synthesized fascinating polygonized CNTs by introducing oxalic acid, ferrocene, and the alkali metal potassium at mediate temperature of 480-500 °C. The possible growth model that polygonal Fe₃O₄ nanoparticles act as templates which control the cross sections of the polygonized CNTs is proposed. One of the unique characters

of this kind of special CNTs is that the graphitization degree of edges is better than that of walls, which can be explained by the different catalytic activity between the corner and edge of the polygonal catalyst particle. The yield of polygonized carbon nanotubes was only 5-10% of the S1 sample, because it is difficult to control the catalytic activity of Fe₃O₄ nanoparticles. Our experimental result represents the first step toward synthesizing multiple- (or single-) wall CNTs with a polygonal catalyst nanoparticles, which also serve as templates for the growth of CNTs.

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