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High-Yield Carbon Nanorods Obtained by a Catalytic Copyrolysis Process

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Carbon nanorods were produced with a yield of about 90% by the copyrolysis of C_6H_6 and C_5H_6 at 600 °C under the cocatalysis of Fe and Mg. Many novel Y-junction carbon nanorods were found in the products. The obtained carbon nanorods have a diameter in the range of 200–350 nm and are several micrometers in length. The effects of reactants, catalysts, and the temperature were investigated, and the experimental results indicate that C_5H_6 and cocatalysts Fe and Mg play crucial roles in the formation of carbon nanorods. The possible formation mechanism of the carbon nanorods is discussed.

Introduction

In recent years, the development of 1D materials has become a focus in nanoscale research because their special characteristics differ from those of respective bulk crystals.[1−8] Among these 1D nanomaterials, carbon materials have been especially emphasized because of their various structures and correspondingly unique performance.[9−17] So far, carbon nanotubes,[18,19] nanowires,[20] nanoribbons,[21] and nanofibers[22] have been largely synthesized with various methods. In addition, carbon rods have largely been applied in anodic materials of batteries because of their performance (large discharge capacity, small irreversible capacity or high Coulombic efficiency, and low discharge potential for obtaining high voltage) and the low cost for mass production.[23] The great success of the microelectronics industry has been based on the miniaturization of a few basic device elements in which different types of junctions are used;[24] therefore, Y-junction carbon nanorods with a complex three-point junction structure have been proposed as the building blocks of nanoelectronics. Various methods have been used for the preparation of carbon nanorods. Liu et al. have prepared carbon nanorods by the arc discharge method.[25] Thien-Nga's group have fabricated the carbon nanorods on a high-T^c substrate via chemical vapor deposition (CVD).[26] Template methods have been used to synthesize carbon

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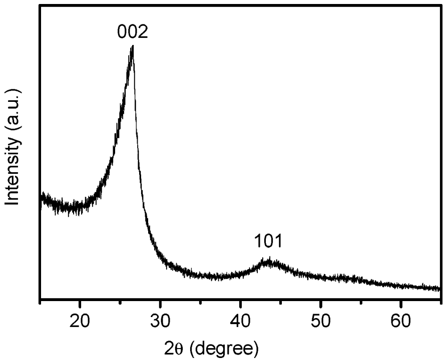

Figure 1. Typical X-ray powder diffraction pattern of the products.

nanorods.[27] Chen et al. have prepared carbon nanorods using the electron beam-induced route.[28] However, to our knowledge, a high-yield preparation of carbon nanorods by a catalytic copyrolysis method has not been reported. Here, we report that carbon nanorods with a yield of about 90% have been prepared using the copyrolysis of C_6H_6 and C_5H_6 under the cocatalysis of Fe and Mg at 600 °C in the autoclave; ca. 40% Y-junction carbon nanorods were found for the first time in the products.

Experimental Section

All of the reagents used were of analytical purity (Shanghai Chem. Co.). In a typical experimental procedure, 10 mL of C_6H_6 and 5 mL of C_5H_6 together with a mixture of 0.25 g of Mg and 0.25 g of Fe powder were placed into a 20-mL stainless steel autoclave. The autoclave was tightly sealed and heated on an electric stove at a rate of 20 °C/min and maintained at 600 °C for 12 h, and then it was naturally cooled to room temperature. The product in the autoclave was collected and washed with absolute ethanol, dilute hydrochloric acid, and distilled water several times. Finally, the product was dried in a vacuum at 50 °C for 4 h. The final products were characterized by powder X-ray diffraction (XRD, Rigaku D with Cu Kα^1 radiation wavelength of $\lambda = 1.54178$ Å), scanning electron microscopy (SEM, HITACHIX-650 and JEOL JSM-6700F), transmission electron microscopy (TEM, HITACHI 800), high-resolution transmission electron microscopy (HRTEM, JEOL 2010 using an accelerating voltage of 200 kV), and Raman spectroscopy (RS, Spex 1403 Raman spectrometer with an argon ion laser at an excitation wavelength of 514.5 nm).

Result and Discussion

A typical XRD pattern of the products is shown in Figure 1. The intense peaks at ca. 26.4 and 43.4° can be indexed to (002) and (101) diffraction planes of hexagonal graphite (JCPDS card files, no. 41-1487), respectively. No impurity is observed in the XRD pattern.

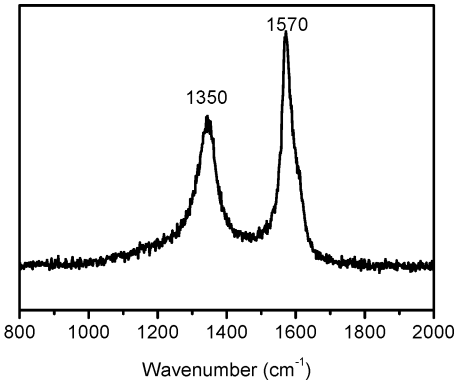

Figure 2. Raman spectrum of the products.

Figure 2 shows the Raman spectrum of the carbon nanorods. Two strong peaks exist at 1350 and 1570 cm^{-1}, corresponding to the typical Raman peaks of graphitized carbon nanorods. The peak at 1570 cm^{-1} corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2D hexagonal lattice, such as in a graphene layer.[29] The peak at 1350 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The peak is relatively high, indicating that in the basal planes 2D disorder exists, which is quite common in pyrolytic production.[30]

Figure 3a and b shows SEM images of a typical sample of carbon nanorods, indicating the large quantity of carbon nanorods obtained via this approach. The yield of carbon nanorods estimated through SEM and TEM observation of the products is about 90%. These carbon nanorods have diameters ranging from 200 to 350 nm and lengths ranging from hundreds of nanometers to several micrometers. It is worth noting that many Y-junction carbon nanorods (marked with arrows in Figure 3b) can be found in the products. The TEM images of the products and a typical Y-junction carbon nanorod are shown in Figure 3c and d, respectively. The ratio of the Y-junction carbon nanorods in the products is estimated to be about 40% by the large number of TEM and SEM observations. Because Y-junction carbon nanotubes have displayed interesting nonlinear electric properties,[31,32] we proposed Y-branch switches with the aim of realizing low switching voltages in a single-mode, coherent regime of operation.[33−35] Therefore, we consider the Y-junction carbon nanorods to be very significant to the building of the future nanoelectronic industry. Figure 3e shows a TEM image of an individual carbon nanorod with a diameter of ca. 300 nm. The selected-area electron diffraction (SAED) pattern (inset of Figure 3e) exhibits a pair of small but strong arcs for 002 and a weak ring for 101 plane diffractions. The appearance of 002 diffractions as a pair of arcs indicates some orientation of the 002 planes in the carbon nanorods.[25,36] The ED analysis is consistent with the XRD results. Besides the carbon nanorods, a small quantity of carbon nanotubes (Figure 3f) can be observed in the product.

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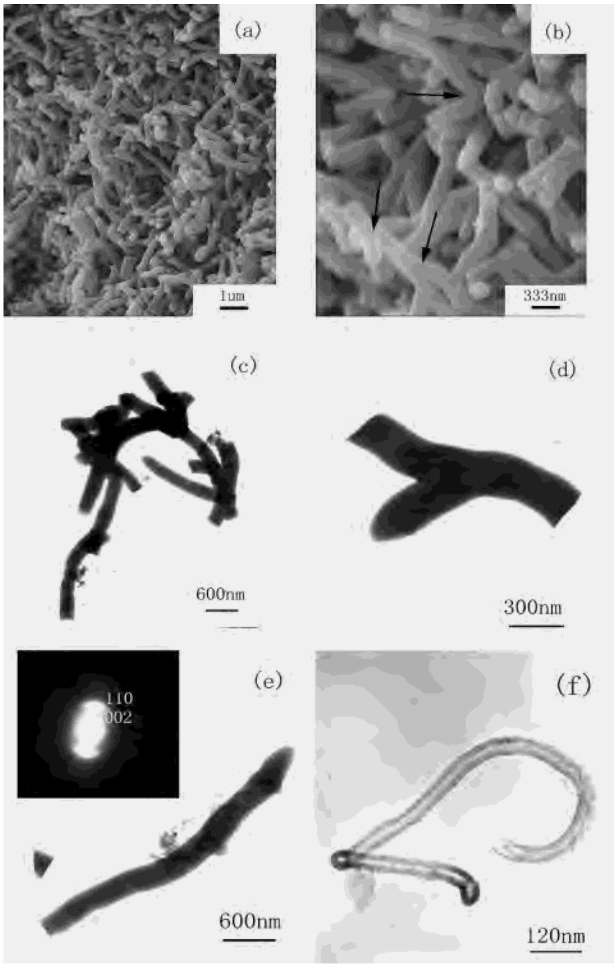

Figure 3. (a) Low-magnification and (b) field-emission SEM images of the as-prepared sample. (c and d) TEM images of the sample and typical Y-junction carbon nanorods, respectively. (e) TEM image and (inset) SAED pattern of an individual carbon nanorod. (f) Typical TEM image of the carbon nanotube.

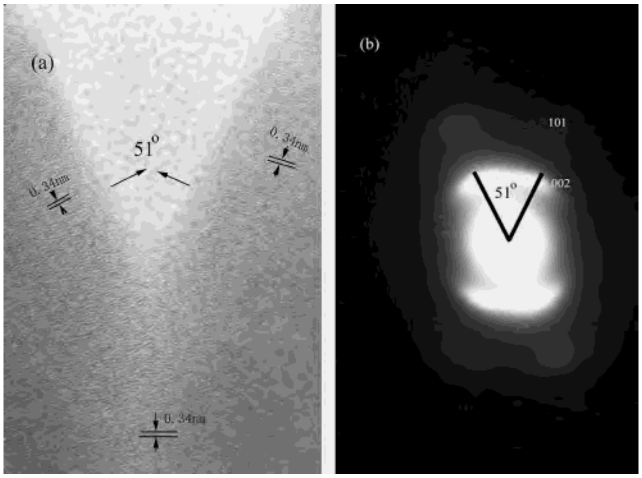

Figure 4. (a) HRTEM image and (b) SAED pattern of the junction of a Y-like carbon nanorod.

The structural characterization of the Y-junction carbon nanorod was investigated in detail by HRTEM and SAED. Typical images are shown in Figure 4. It can be seen that the carbon nanorods are formed from graphitic layers, although the carbon nanorods are not well crystallized. Moreover, the irregular graphite layers are almost perpendicular to the respective axis of the Y-like carbon nanorod, and their interlayer spacing is ca. 0.34 nm, which is typical for the (002) lattice distance in hexagonal carbon. A carbon nanorod with a similar microstructure was reported in the literature.[26] The SAED (Figure 4b), taken at the junction of the Y-like carbon nanrod, exhibited strong arcs for 002 diffractions and weak arcs for 101 diffractions. At the same time, it also reflected the disorder of the stacked carbon layers. The further observation of the SAED found that it consisted of two pairs of strong arcs for 002 diffractions, implying two different orientations of the 002 planes in the Y-junction carbon nanorod. It is worth noting that the angle of the strong arcs was almost consistent with the Y-junction angle. On the basis of the HRTEM and SAED analyses, the results suggest that the junction was formed by curving carbon layers. These observations were similar to those in the Y-junction carbon nanotubes report.[18]

The reactions involved in our experiment are fairly complex. To study the influences of the reactants and catalysts on the formation and yield of carbon nanorods, we carried out a series of experiments (as shown in Table 1) with a process similar to that mentioned in the Experimental Section. From experiment no. 1, it was found that the products did not contain carbon nanorods; mainly, carbon nanotubes were observed when only C_6H_6 was used as the starting material. This result is similar to that in our previous report.[30] When C_5H_6 was added to the reaction system, some carbon nanorods could be found in the products, and when the C_5H_6 quantity increases, the yield of carbon nanorods correspondingly increases (experiment no. 2). The yield of ca. 90% carbon nanorods can be obtained when 10 mL of C_6H_6 is added to 5 mL of C_5H_6 in experiment no. 3. Although C_5H_6 was very important for the formation and yield of carbon nanorods according to the above experiments, when the amount of C_5H_6 increased, the yield of carbon nanorods decreased in experiment no. 4; it is worth noting that the yield of carbon nanorods obviously decreased when the reactants did not contain C_6H_6 in experiment no. 5. This shows that C_6H_6 and C_5H_6 have a synergetic effect on the production of carbon nanorods. That is, the proper ratio of C_5H_6 and C_6H_6 is a very important factor in carbon nanorod formation. However, the catalysts also have important influence on the formation of carbon nanorods. When the catalysts are absent from the reaction system (no. 8), the carbon nanorods cannot form. Moreover, the results of experiments 3, 6, and 7 show that a high yield of carbon nanorods was obtained only when Fe and Mg powder were added simultaneously to the reaction system. We think that this is a synergetic effect of cocatalysts Fe and Mg. The phenomenon of the synergetic effect of catalysts can be also found in some reports.[37,38] Except for the above relative factors, the reaction temperature is also an important factor in carbon nanorod formation. When the reaction temperature

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Table 1. Products Obtained by the Following Experiments at 600 °C for 12 h; and Ratios of the Products Estimated through Large Numbers of SEM and TEM Observations of the Products[a]

expt no.	reactant	catalyst	approximate contents of various products
1	C_6H_6 (15 mL)	Fe and Mg	75% NTs + 25% carbon particles
2	C_6H_6(12 mL) + C_5H_6(3 mL)	Fe and Mg	40% NTs + 50% NRs + 10% carbon particles
3	C_6H_6 (10 mL) + C_5H_6 (5 mL)	Fe and Mg	90% NRs + 10% NTs
4	C_6H_6 (5 mL) + C_5H_6 (10 mL)	Fe and Mg	30% NRs + 70% carbon particles
5	C_5H_6 (15 mL)	Fe and Mg	5% NRs + 95% carbon particles
6	C_6H_6 (10 mL) + C_5H_6 (5 mL)	Fe	85% carbon spheres + 15% NTs
7	C_6H_6 (10 mL) + C_5H_6 (5 mL)	Mg	90% carbon spheres + 10% NTs
8	C_6H_6 (10 mL) + C_5H_6 (5 mL)		carbon particles

[a] NRs and NTs are abbreviations for carbon nanorods and nanotubes, respectively.

is below 400 °C and other conditions are kept constant, we cannot obtain any carbon products. Some short carbon nanorods are produced when the temperature is increased to 500 °C. When the reaction temperature is further increased, longer carbon nanorods can be obtained in larger quantity. In the end, the ca. 90% yield of carbon nanorods is produced at 600−700 °C. However, carbon particles are formed when the reaction temperature is increased to 800 °C. In addition, the entire yield of the carbon nanorods is changed by altering the conditions of the reaction, but it is interesting that the proportion of Y-junction carbon nanorods is almost identical to that of whole carbon nanorods.

Although the exact formation mechanism of carbon nanorods is not very clear, we can tentatively use a mechanism that is similar to Gamaly and Ebbesen's model[39] to discuss the formation of carbon nanorods. In this model, the velocity of carbon atom distribution on the surface of catalysts mainly influences the formation of carbon nanorods. In the reaction process, the starting materials are first pyrolyzed into carbon atoms with the reaction temperature increasing,and then the carbon atoms form a homogeneous system under the assistance of catalysts. Next, some carbon atoms that are attached to the surface of the catalysts form graphite layers as a cap, which may be considered to be seed structures for the growth of carbon nanorods. It is well known that the carbon atom's moving velocity is correlative with many factors, including the concentration of carbon atoms, the catalyst category, and the temperature. Thus, with the reaction temperature increasing, part of C_5H_6 will be pyrolyzed into carbon atoms first because the pyrolysis temperature of C_5H_6 is much lower than that of C_6H_6. Because of the different pyrolysis speeds of C_5H_6 and C_6H_6, the carbon atoms' concentration is influenced by the ratio of C_5H_6 to C_6H_6. That is, the ratio of C_5H_6 to C_6H_6 has an indirect relationship with the moving speed of the carbon atoms. In addition, the catalyst category and temperature also are influences on the distribution speed of the carbon atoms in our experiments. When carbon atoms with moderate velocities are distributed on the surface of the catalysts, the graphite layers form carbon nanorods. When their velocity is slow, the graphite layers form carbon nanotubes. However, when the velocity is high, the graphite layers form carbon particles. The above discussion well explains the experimental results; of course, because of the complexity of the experimental process, the exact formation mechanism of carbon nanorods still needs further research.

Conclusions

In summary, C_6H_6 and C_5H_6 together with cocatalysts Fe and Mg powder were successfully used to synthesize a yield of about 90% carbon nanorods at 600 °C for 12 h. The yield of carbon nanorods with diameters in the range of 200−350 nm and lengths in the range of 0.8−6 μm was ca. 90%. Many Y-junction carbon nanorods that we found in the products are significant to the basic building units for nanoelectronic devices. The experimental results show that the synergic effect of C_5H_6 and C_6H_6 and cocatalysts Fe and Mg affected the yield of the carbon nanorods. In addition, the possible formation mechanism of the carbon nanorods was discussed.

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