SYNTHESIS AND IN-SITU FILLING OF COAL-DERIVED CARBON NANOTUBES BY ARC DISCHARGE METHODE

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Abstract

Filled carbon nanotubes (CNTs) and thin-walled carbon nanotubes (TWNTs) were synthesized from coal-derived electrodes doped with transition metals like Fe, Ni, and Cr by the arc-discharge method. Transmission electron microscopy (TEM) studies reveal that long and continuous nanowires can be fabricated in the cavities of coal-derived CNTs. On the basis of the experimental results, the effects of the carbonization conditions of coal-derived electrodes on the formation and filling of TWNTs are discussed in terms of the specific chemical structure and texture of coal.

Key words: carbon nanotubes, coal, in-situ filling, arc discharge

1. Introduction

Since the first report in 1993 [1], the fabrication of CNTs filled with diverse materials has drawn enormous attention around the world, behind which the driving force is because the introduction of foreign materials into CNTs may substantially enhance or change their physical properties [2] as well as the properties of encapsulated materials [3] that lead to promising applications of these filled CNTs in many fields [4-6]. Up to now, various materials, such as metals [7-10] and their oxides or compounds [11-12], C_{60} [13] etc., have been successfully inserted into the hollow cavities of CNTs. For these purposes, several methods have been employed to bring the filling to success. One approach is to selectively open the tubes by oxidation treatments [14] before the filling operation, which is normally termed as two-step process. However, this two-step method has some obvious drawbacks, including low filling yields, limitation in the range of filling materials allowed, and irreversible damages to CNTs. Another approach is to fill CNTs in situ, i.e., to fill the tubes with foreign materials during their growth stage, which has been attempted using various techniques such as arc-discharge method [7-10] and catalytic hydrocarbon pyrolysis method [15-17].

Here we report the synthesis and *in-situ* filling of CNTs from carbons derived from coal, the cheapest natural carbon source, by the arc-discharge method. The feasibility of preparing nanomaterials from coal has been proved to be possible since the preparation of fullerene from coal was first reported by Pang et al. [18] In the past decade, our group has developed efficient techniques for preparation of fullerenes and CNTs from Chinese coals [19-23]. Previous results have shown that the plasma arcing of coal-based carbon has chemical and process advantages over high purity graphite in the formation of carbon nanomaterials due to the special chemical structure and texture of coal and/or coal-derived carbons. In this letter we extend our work to *in-situ* fill CNTs with transitional metal Fe, Cr and Ni by the arc-discharge method. It is very interesting to note that thin-walled nanotubes (TWNTs), mainly double-walled CNTs, are also obtained unexpectedly. This may make it possible for producing CNTs-modular nanowires and TWNTs in high efficiency and lower costs. This paper presents the experiment results about the synthesis of filled CNTs and TWNTs from coal, and the influence of carbonization conditions of coal-derived electrodes are discussed.

2. Experimental

For the arc method adopted in this study, coal needs to be converted into carbon rods first. A typical anthracite coal from Yang Quan coal mine of China was used. The as-received coal was crushed and sieved to 150 μm before use. The coal powder and Fe or NiO or Cr_2O_3 powder was finely mixed with coal tar as binder respectively, and subsequently pressed into a mould to form three kinds of metal-doping coal rods. The weight ratio of coal powder to metals is shown in Table 1. The metal-dopted coal rods were carbonized in an electric furnace in flowing N_2 to make electrodes. The furnace was first ramped at 5 K/min to 873 K, and then at 3 K/min to 1073 K and kept at 1073 K for 2 h. Finally, the coal-based carbon rods with a diameter of *ca.* 10 mm and a length of *ca.* 200 mm were obtained.

Table 1 The weight ratio of coal powder to metal catalysts

Metal or Metal oxide powder	Metal or Metal oxide: Coal powder
Fe	1.00: 3.00
NiO	1.00: 5.09
Cr_2O_3	1.00: 9.83

The coal-derived carbon rods were used as the anode in the arc-discharge experiments. The cathode was made of high purity graphite rod with a diameter of 16 mm and a length of 30 mm. Before the arc experiments, a cage made of iron wires was put inside the arc reactor, of which in the middle were the two carbon electrodes. During the arcing process, the distance between two electrodes was manually adjusted to maintain the arc to be stable, and the formed TWNTs deposited on the cage surface. All of the arc-discharge experiments were carried out with direct current of 50-90 A and voltages of 30-50 V in He at 0.05-0.06 MPa. For each run, the arc-discharge experiment normally lasted about 10 min.

After arc discharge was finished, the wire cage was taken out of the arc reactor, and the web-like materials deposited on the cage surface were directly peeled off and placed on a carbon copper grid for TEM (JEM-2000EX) examination. The deposits on the cathode were collected and dispersed in ethanol with ultrasonic treatment for 5 min and several drops of the suspension were placed on a carbon coated copper grid for TEM investigation.

3. Results and discussion

The low-magnification TEM examination reveals that the deposits taken from cathode consist of numerous filled CNTs that are about 10-100 nm in diameter and up to several micrometers in length, together with empty CNTs, metal-encapsulated nanoparticles and amorphous carbon particles with various shapes and sizes. Fig. 1 shows some typical TEM images of filled CNTs obtained by using the coal-derived anodes doped with transition metals like Fe, Ni, and Cr. These CNTs are frequently seen to be completely filled with foreign materials from the tip to the end. This is the case especially for Ni catalyst, a large number of long and continuous nanowires are found in the cavities of CNTs, though they are contaminated with other forms of impurities as mentioned above. Fig. 1c shows a long and continuously filled nanowire of *ca.* 2.6 μm in length, which was obtained from Ni-containing anode. This kind of true nanowires should have potential application in the magnetic wave shielding and micro-electronics fields. According to literature [7], the Ni-based and Fe-based filling is mainly crystalline metallic carbide and the Cr-based filling is mainly single crystal, further detailed examinations about these filled CNTs in our case are still in progress.

The results presented here clearly show that filled CNTs, which previously are mainly fabricated from high purity graphite doped with specific metals, can be synthesized from coal-derived carbon doped with iron group metals in relatively high yield by arc-discharge method. Moreover, it is interesting to note that abundant thin-walled carbon nanotubes (TWNTs) with a quite good purity, which differs from the MWNTs and SWNTs reported previously, are found in the web-like deposits collected from the surfaces of the iron wires cage, as shown in Fig. 2. In most cases, the length of these nanotubes is over a few micrometers, and with a diameter varying from 2 nm to 5 nm. The HRTEM examination and Raman spectroscopy study reveal that most of these TWNTs are double-walled nanotubes. It is well known that SWNTs form readily into bundles with several isolated tubules [24]. For the TWNTs reported here, it is not uncommon that most of these nanotubes do not gather together or, if any, ropes form only with a limited number of tubes, typically two or three. And their average diameters are a little larger than usual SWNTs.

The formation mechanism of these filled CNTs and TWNTs is not known at this moment. An attempt has been made to figure out the influence of catalysts and carbonization conditions of coal-derived carbon on the formation of TWNTs. In a series of subsequent arc-discharge experiments, the coal-based carbon rods carbonized at 1173 K were used as electrodes while other conditions remained unchanged. It has been found that abundant MWNTs and metal-encapsulated nanoparticles are formed, together with some TWNTs (shown in Fig. 2**c**). This implies that with coal-derived carbons as the carbon source, the carbonization conditions, especially the heat treatment temperature during the carbonization process, is one crucial parameter for the formation of filled CNTs and TWNTs. It is known that coal is a molecular solid rather than a lattice solid like graphite [25]. For coal-derived carbon rods that have chemical structures resembling graphite crystalline in the domain of 1-10nm, the basic units in the

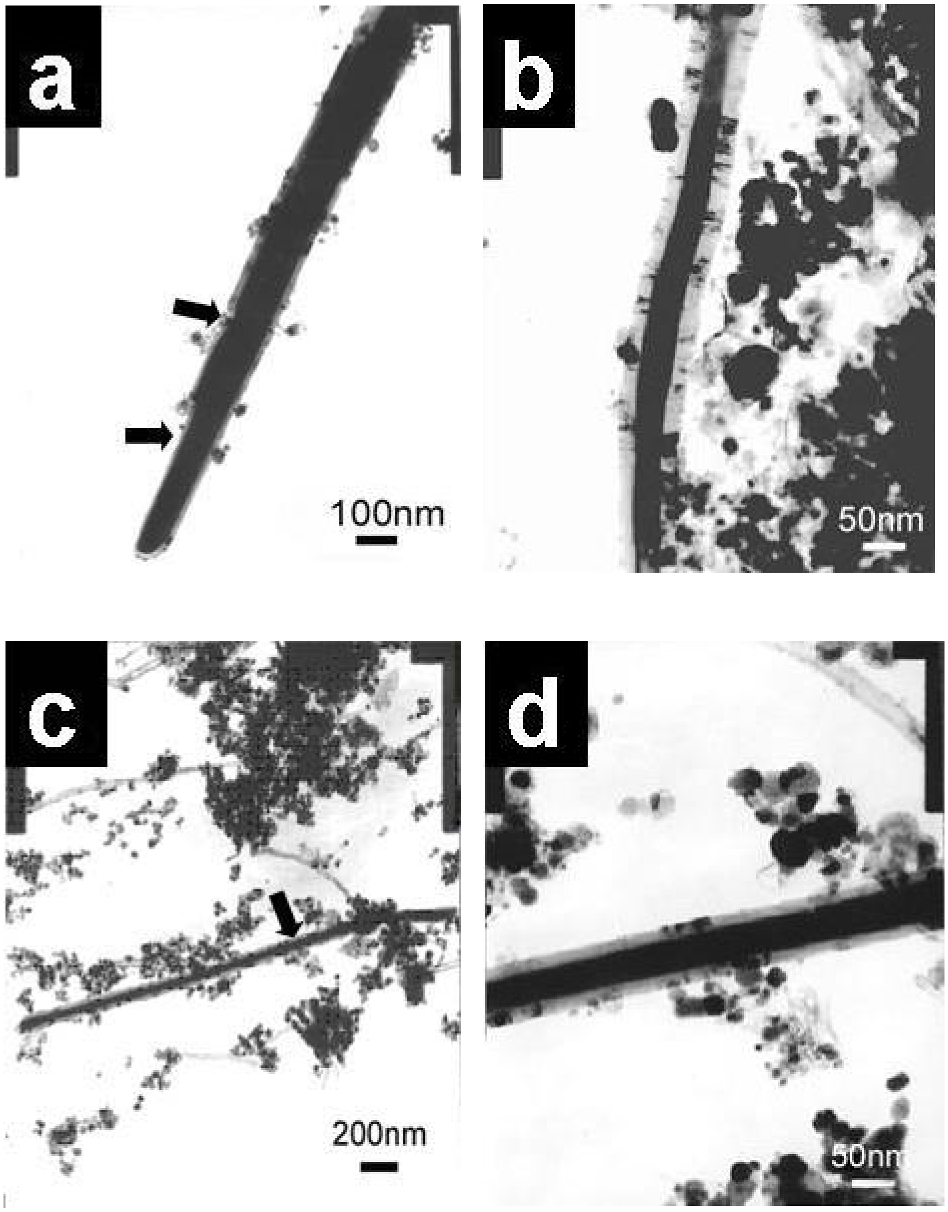

Fig. 1 TEM images of CNTs completely filled with metal-based materials. (a) One CNT of about 1.5 μm in length that is filled with continuous Cr species, in which sudden changes in the tube diameter are marked by arrows; (b) A CNT filled with Fe species; (c) A typical image of Ni-species filled CNT or nanowire with a uniform diameter and a length over 2.6 μm; (d) A high magnification image of the arrow-marked section of the Ni-filled CNT shown in Fig. 1c.

chemical structure are small graphitic crystallites containing a few layer planes that are joined together by a variety of weak bonds. Thus, it can be easily envisioned that the textures and properties of coal could be altered to various degrees due to the breakage of weak bonds and formation or regeneration of small graphitic crystallites during the carbonization process as the carbonization temperature varies. As a consequence, the structure units in coal-derived carbons may vary, and they will break up in different ways during the arcing process, leading to diverse active species that takes part in the formation process of filled CNTs and TWNTs.

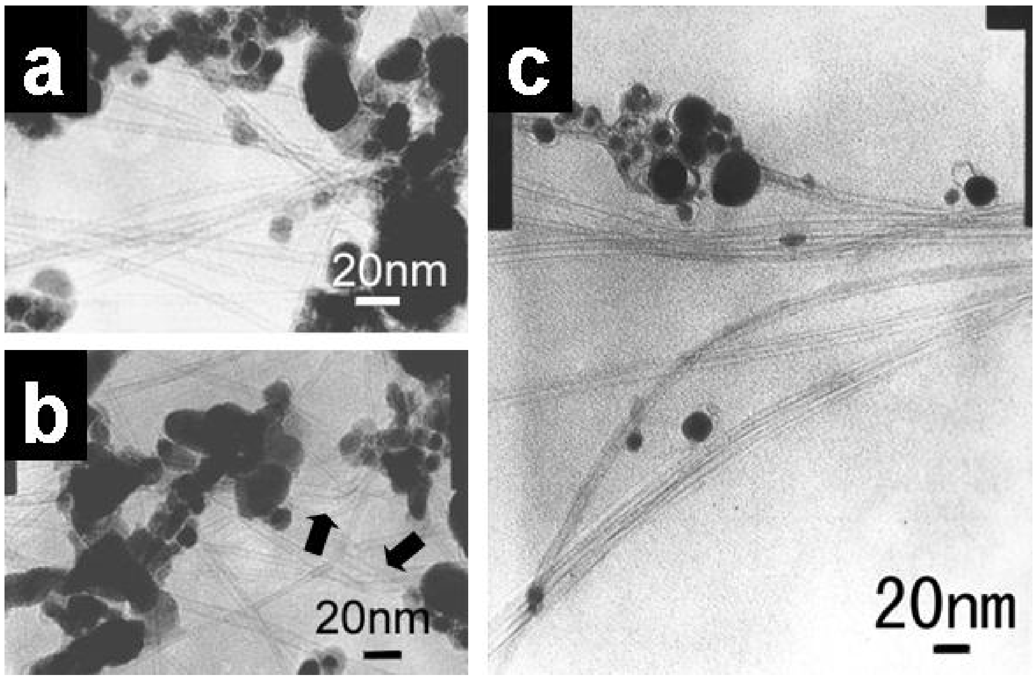

Fig. 2. TEM images of nanotubes with thin walls; (a) An image showing many thin-walled nanotubes with a big diameter exist in discrete state; (b) Some thin-walled nanotubes with distorted sections, as pointed by black arrows; (c) Nanotubes with thin walls, which was prepared from coal-derived carbon rods obtained at 1173 K.

The preliminary work presented here has shown that it is possible to prepare metal-filled CNTs from coal-derived carbons doped with transitional metals such as Fe, Cr and Ni, at the same time, CNTs with only a few walls or thin-walled CNTs are also obtained in the same experiment, which is not expected. It should be noted that these two different products are formed in different positions. Right now, the purity of the carbon nanomaterials and the selectivity towards a specific product is far from satisfactory. It is hoped that after further optimizing the preparation conditions of the coal-derived carbon rods, it would be feasible to selectively prepare metal-filled CNTs and TWNTs in a more efficient way. The related work is in progress now.

4. Conclusions

In this work, in-situ filled CNTs and TWNTs with a relatively high purity are fabricated from coal-derived carbon by arc-discharge method with transitional metals such as Fe, Ni and Cr as catalyst. Some continuous nanowires with a length over 2.6 μm have been synthesized successfully. The results obtained so far lead one to believe that the carbon electrode used in arcing process is the key parameter for the formation of metal-filled CNTs and TWNTs, and the properties of the coal-based carbon rods can be altered, to some degree, by varying the carbonization conditions especially the heat treatment temperature. We believe that the present work is a step toward efficient-production of cheap CNTs-modular nanowires and TWNTs. And more work is needed to clarify the mechanism involved in this process and to establish the optimum conditions for more efficient production of metal-filled MWCNTs or TWNTs.

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References

[1] Ajayan PM, Iijima S. Capillarity induced filling of carbon nanotubes. Nature 1993; 361: 333-335.
[2] Mintmire JW, Dunlap BI, White CT. Are fullerene tubules metallic? Phys Rev Lett 1992; 68: 631-634.
[3] Ruoff RS, Lorents DC, Chan B, Malhotra, Subramoney S. Single crystal metals encapsulated in carbon nanoparticles. Science1993; 259: 346-348.
[4] Frank S, Poncharal P, Wang ZL, de Heer WA. Carbon nanotube quantum resistors. Science 1998; 280: 1744-1746.
[5] Ebbesen TW, Lezec HJ, Hiura H, Bennett JW, Ghaemi HF, Thio T. Electrical conductivity of individual carbon nanotubes. Nature 1996; 382: 54–56.
[6] Monthioux M. Filling single-wall carbon nanotubes. Carbon 2002; 40: 1809-1823.
[7] Guerret-Plecourt C, Le Bouar Y, Loiseau A, Pascard H. Relation between metal electronic structure and morphology of metal-compounds inside carbon nanotubes. Nature 1994; 372: 761-765.
[8] Loiseau A, Pascard H. Synthesis of long carbon nanotubes filled with Se, S, Sb and Ge by the arc method. Chem Phys lett 1996; 256: 246-252.
[9] Demoncy N, Stephan O, Brun N, Colliex C, et al. Filling carbon nanotubes with metals by the arc-discharge method: the key role of sulfur. Eur Phys J 1998; B4: 147-157.
[10] Demoncy N, Stephan O, Brun N, Colliex C, et al. Sulfur: the key for filling carbon nanotubes with metals. Synthetic Metals 1999; 103: 2380-2383.
[11] Sloan J, Hammer J, Zwiefka-Sibley M, Green MLH. The opening and filling of single walled carbon nanotubes(SWNTs). Chem Comm 1998, 347-348.
[12] Sloan J, Wright DM, Woo HG, Bailey S, et al. Capillarity and silver nanowire formation observed in single walled carbon nanotubes. Chem Comm 1999, 699-700.
[13] Smith BW, Monthioux M, Luzzi DE. Encapsulated C_{60} in carbon nanotubes. Nature 1998; 396: 323-324.
[14] Harris PJF. Carbon Nanotubes and Related Structures. Cambridge, UK, Cambridge University Press. 1999, pp170-172.

[15] Mayne M, Grobert N, Terrones M, Kamalakaran R, Ruhle M, Kroto HW, Walton DRM. Pyrolytic of aligned carbon nanotubes from homogeneously dispersed benzene-based aerosols. Chem Phys Lett 2001; 338: 101-107.
[16] Grobert N, Terrones M, Osborne AJ, Terrones H, Hsu WK, Trasobares S, Zhu YQ, Hare JP, Kroto HW, Walton DRM. Thermolysis of C_{60} thin film yields Ni-filled tapered nanotubes. Appl Phys 1998; A67: 595-598.
[17] Terrones M, Grobert N, Zhang J P, Terrones H, Olivares J, IIsu WK, Hare JP, Cheetham AK, Kroto HW, Walton DRM. Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. Chem Phys Lett 1998; 285: 299-305.
[18] Pang LSK, Vasslalo AM, Wilson MA. Nature 1991; 352: 480.
[19] Qiu JS, Zhou Y, Wang LN, Tsang SC. Formation of Carbon Nanotubes and Encapsulated Nanoparticles from Coals with Moderate Ash Content. Carbon 1998; 36: 465.
[20] Qiu JS, Zhou Y, Yang ZG, Wang DK, Guo SC, Tsang SC, Harris PJF. Preparation of fullerenes using carbon rods manufactured from Chinese hard coals. Fuel 2000; 79: 1303-1308.
[21] Qiu JS, Zhou Y, Yang ZG, Wang LN, Zhang F, Tsang SC, Harris PJF. Preparation of fullerenes from several Chinese coals. Mol Mater 2000; 13: 377-384.
[22] Qiu JS, Zhang F, Han HM, Zhou Y, Hu DS, Tsang SC, Harris PJF. Carbon nanomaterials from eleven caking coals, Fuel 2002; 81: 1509-1514.
[23] Qiu JS, Li YF, Wang YP, Wang TH, Zhao ZB, Zhou Y, Li F, Cheng HM. High-purity single-walled carbon nanotubes synthesized from coal by arc discharge. Carbon 2003; 41: 2170-2173
[24] Thess A, Lee R, Nikolaev P, Dai HJ, Petit P, Robert J, Xu CH, Lee YH, Kim SG, Rinzler AG, Colbert DT, Scuseria GE, Tománek D, Fischer JE, Smalley RE. Crystalline Ropes of Metallic Carbon Nanotubes. Science 1996; 273: 483-487.
[25] Wilson MA, Pathey HK, Kalman J. New developments of carbon nanotubes from coal. Fuel 2002; 81: 5-14.