第 24 卷第 9 期 无 机 化 学 学 报 Vol.24 No.9
2008 年 9 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 1424~1427

一步法溶剂热催化合成纳米碳纤维

王百年[1,2] 陈祥迎*[,2] 钱逸泰[1]
([1]中国科学技术大学化学与材料科学学院,合肥 230026)
([2]合肥工业大学化学工程学院,合肥 230009)

摘要:利用四氢呋喃为溶剂和碳源,通过溶剂热催化方法在 500 ℃一步合成了纳米碳纤维,X-射线衍射(XRD)分析显示此法合成的碳纤维晶型为碳的六方石墨相,场发射电镜(FESEM)和透射电镜(TEM)照片进一步表明碳纤维平均直径为 100 nm,长度达几百纳米至几微米,高分辨电镜照片揭示产品中碳的晶间距为 0.34 nm;产品纯度通过热重法(TGA)分析;同时,拉曼光谱图显示在 1 347 和 1 584 cm^{-1} 处有 2 个强峰,这与石墨相碳的典型拉曼光谱图是一致的。

关键词:碳纳米纤维;溶剂热法;催化剂
中图分类号:O612.4; O613.72 **文献标识码**:A **文章编号**:1001-4861(2008)09-1424-04

One-pot Catalytic Solvothermal Approach for Carbon Nanofibers Preparation

WANG Bai-Nian[1,2] CHEN Xiang-Ying*[,2] QIAN Yi-Tai[1]
([1]*College of Chemistry and Material Science, University of Science and Technology of China, Hefei* 230026)
([2]*School of Chemical Engineering, Hefei University of Technology, Hefei* 230009)

Abstract: Carbon nanofibers have been synthesized through a one-pot catalytic solvothermal approach using tetrahydrofuran as the solvent and carbon source at 500 ℃. XRD patterns show that the as-prepared carbon nanofibers are of hexagonal graphite. Field-emission scanning electron microscopy(FESEM) and TEM images indicate that the carbon nanofibers have an average diameter of 100 nm and length ranging from hundreds of nanometers to several micrometers. High-resolution transmission electron microscopy (HRTEM) images reveal that the products consist of graphite layers with interlayer spacing of about 0.34 nm. The purity of the carbon nanofibers is also examined by thermal gravimetric analysis (TGA). The Raman spectrum has two strong peaks at 1 347 and 1 584 cm^{-1}, corresponding to the typical Raman peaks of graphitized carbon nanofibers.

Key words: carbon nanofibers; solvothermal; catalyst

Carbon materials are found in a variety of forms such as graphite, diamond, carbon nanofibers, fullerences and carbon nanotubes. A world-wide intensive research efforts have been paid on the carbon materials since the discovery of carbon nanotubes by Iijima in 1991[1] Carbon nanofibers(also known as carbon filaments) represent an important class of graphite-related materials from the scientific and commercial viewpoints [2,3]. Carbon nanofibers have shown promising potential applications as hydrogen storage media, semi-fuel cell application and functional fillers for various kinds of composite materials[4-8] because of their unique properties, such as high thermal stability, electrical conductivity and excellent mechanical properties.

收稿日期:2008-03-22。收修改稿日期:2008-06-21。
国家自然科学基金(No.20431020)资助项目。
*通讯联系人。E-mail:cxy@ustc.edu.
第一作者:王百年,男,35 岁,讲师;研究方向:无机纳米材料合成。

Floating catalyst method[9], thermal chemical vapor deposition[10], and plasma-enhanced Chemical Vapor Deposition(CVD)[11] were conventionally used to synthesize carbon nanofibers. Recently, some convenient approaches have been developed to prepare nano-scale carbon materials. For instance, Lee et al.[12] obtained the amorphous carbon nanowires by heating a pressed tablet of graphite powder mixed with nickel. Carbon materials with different morphology such as hollow spheres, nanotubes were fabricated in this group using various methods previously[13~15]. Herein, we present a simple catalytic route to prepare carbon nanofibers. In addition, some porous carbon structures are also found to coexist with the carbon nanofibers. The reaction process may be formulated as follows:

$$4C_4H_8O(\text{tetrahydrofuran}) + 3Fe\text{–}Ni \rightarrow 16C\ (\text{graphite}) + Fe_3O_4 + 16H_2 + Ni$$

1 Experimental

1.1 Sample preparation

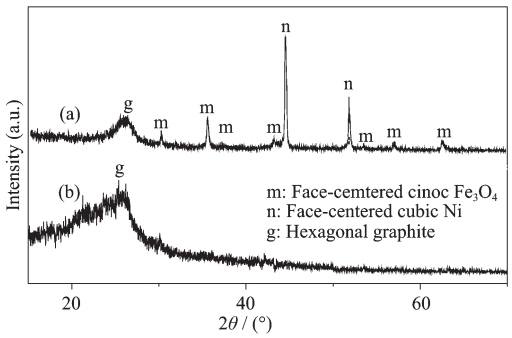
In a typical run, equal mole of micro-sized iron and nickel powders and 12 mL tetrahydrofuran were loaded into a 20 mL stainless steel autoclave. The autoclave was then sealed and maintained at 500 ℃ for 10 h. After cooling to the room temperature, dark precipitates and some residual gases were obtained. The black products were collected and divided into two parts: one part was washed with distilled water and absolute ethanol several times; the other was washed with 3 mol·L^{-1} HNO_3 solution. The two parts were then dried in vacuum at 50 ℃ for 4 h, respectively for further characterization.

1.2 Sample characterization

XRD patterns were recorded by using a Philips XPert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation (λ = 0.154 1874 nm), scanning from 10°~70°(2θ) in speed of 8.000° ·min^{-1}. Field emission scanning electron microscopy(FESEM) image was taken at 10 kV with a JEOL JSM6700F scanning electron microscope. Transmission electron microscopy(TEM) images and selected area electron diffraction (SAED) patterns were carried out on a Hitachi Model H-800 transmission electron microscope. High-resolution transmission electron microscopy (HRTEM) images were examined on a JEOL-2010 transmission electron microscope. The thermal gravimetric analysis (TGA) was conducted using a Shimadzu TGA-50H analyzer (purified air stream 50 mL min^{-1}, heating rate 10 ℃·min^{-1}). The Raman spectrum was studied using a French Labram-HR confocal laser micro Raman Spectrometer with an argon-ion laser at 514.5 nm.

2 Results and discussion

Fig.1 shows the XRD patterns of the as-prepared products with different treatments. Fig.1a is the XRD pattern of the products washed with distilled water and ethanol. The reflection peaks in Figure 1a can be indexed as face-centered cubic(fcc) Fe_3O_4 denoted as "m" (PDF No. 19-0629), face-centered cubic(fcc) Ni denoted as "n"(PDF No. 04-0850), and hexagonal graphite denoted as "g"(PDF No. 41-1487). Fig.1b shows the typical XRD pattern of the products washed with diluted HNO_3 solution, which can be indexed as pure hexagonal graphite. In contrast to the standard hexagonal graphite(PDF No. 41-1487), the XRD pattern in Fig. 1b is weak and broad, indicating its poor crystallinity.



(a) Washed with distilled water and ethanol for several times;
(b) After diluted HNO_3 solution treatment then washed with distilled water and ethanol

Fig.1 XRD patterns of the products with different treatments

The panoramic view on the as-prepared sample is shown in Fig.2, which reveals that the sample is composed of a large number of carbon nanofibers. The carbon nanofibers have an average diameter of 100 nm and length ranging from hundreds of nanometers to several micrometers.

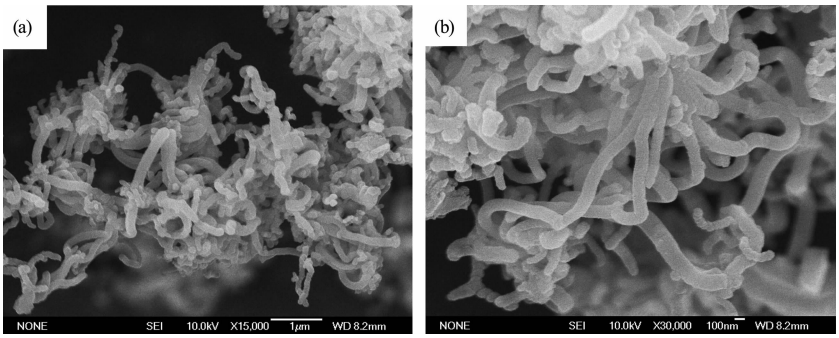


Fig.2 (a~b) Field emission SEM image of carbon nanofibers

Fig.3a demonstrates an individual carbon nanofiber with a diamter of 70 nm. The SAED pattern in Fig.3a reveals that there exists a pair of small but strong (002) arcs, together with a weak(100) ring, which indicates the orientation of the 002 planes in the carbon nanofibers. A further analysis by HRTEM in Fig.3b shows that the interlayer spacing of the carbon nanofibers is about 0.34 nm, in agreement with the 002 plane lattice parameters of graphitized carbon. In the process of TEM and HRTEM observations, some porous carbon structures were also detected. Fig. 3c shows a representative TEM image of the novel porous carbon structures with an average diameter of 160 nm and length up to hundreds of nanometers. The SAED pattern (the inset of Fig.3c) indicates the crystallinity of the porous carbon structures. Fig.3d shows the typical HRTEM image, which is similar to that of carbon nanofibers.

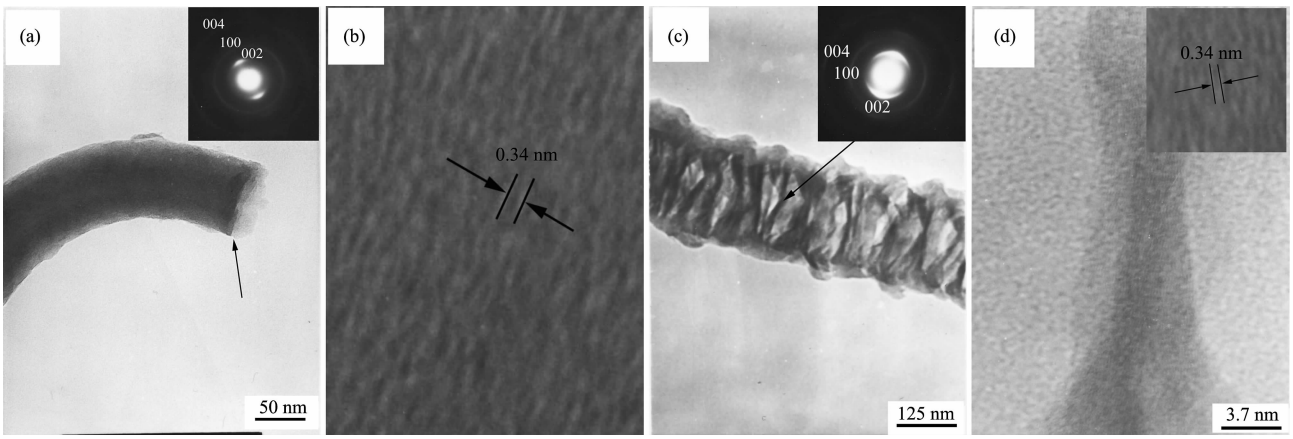


Fig.3 (a) A representative TEM image of the porous carbon structure; (b) High-resolution TEM image of the porous carbon structure; (c) High-resolution TEM and SAED pattern (inset) image of an individual CF; (d) Typical HRTEM image, which is similar to that of CFS.

The typical Raman spectrum (Fig.4) shows that there exist two strong peaks at 1 347 and 1 584 cm^{-1}. The peak at 1 347 cm^{-1} can be assigned to the vibrations of carbon atoms with dangling bonds in plane termination of disordered graphite[16]. The peak at 1 584 cm^{-1} corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite layer[16].

The TGA curve for the as-prepared carbon nanofibers after washing with distilled water and absolute ethanol is illustrated in Fig.5. The curve shows a

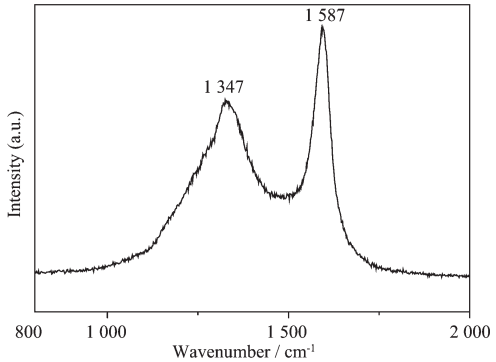


Fig.4 Raman spectrum of CFS with two graphite peaks at 1 347 and 1 584 cm^{-1}

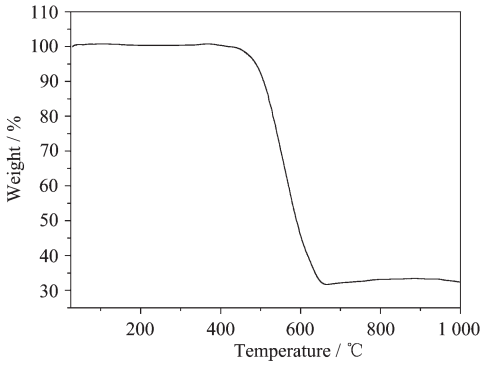


Fig.5　TGA curve of the as-prepared CFS

weight-decreasing profile up to 500 ℃. The weight loss is caused by the oxidation of carbonaceous elements expect carbon nanofibers in TGA measurement because the carbon oxides(such as CO, or CO_2) will disperse out easily. When increasing the temperature to 530 ℃, a sudden weight drop occurs due to the gasification of the carbon nanofibers and other carbonaceous impurities to carbon oxide or carbon dioxide. The calculated purity of the as-prepared carbon nanofibers is about 68% from the TGA curve, which probably contains some undissolved iron oxide or nickel formed in the process of carbon nanofibers.

The reaction temperature and Ni powders are found to play significant roles in the formation of carbon nanofibers. When the reaction is carried out below 500 ℃, the as-prepared carbon nanofibers are poorly crystallized. Ni functions as a catalyst in the reaction. When the reaction is carried out without Ni powders, the product obtained is much less than that with Ni.

As for the formation mechanism of carbon nanofibers prepared from tetrahydrofuran in this study, it is believed that it is to some extent similar to that proposed by Baik et al. [10]. The growth of carbon nanofibers in this study probably consists of the following sequential steps: the decomposition of tetrahydrofuran on the metal catalysts, the diffusion of carbon species, and the precipitation of carbon atoms from the supersaturation state to form carbon nanofibers. Carbon nanotubes have been reported by this group from different carbon sources such as hexachorobenzene [13], ethanol [14], and benzene [15] suggesting that the carbon sources perhaps have important influences on the morphology of the final products. It was also reported that the growth of tubular structure with flat graphitic sheet depended on the crystal orientation of the catalysts[17,18]. Therefore, it is believed that the carbon source and catalyst play key roles in determining the morphology of the products.

3　Conclusions

In summary, car bon nanofibers have been prepared through a simple catalytic route at 500 ℃. As tetrahydrofuran acts both solvent and carbon source, this method avoids the separation of raw material from solvent and simplifies the operation process.

References:

[1] Iijima S. *Nature*, **1991**,**354**(6348):56~8

[2] Sato R, Dresselhaus G, Dresselhaus M S. *Physical Properties of Carbon Nanotubes*, Singapore: Imperial College Press, **1998.**

[3] Dresselhaus M S, Dresselhaus G. *J. Electroceram.*, **1997**,**1**(3): 273~86

[4] Koyama T, Endo M. *Jpn. J. Appl. Phys.*, **1974**,**13**(7):1933~9

[5] Koyama T, Endo M. *Jpn. J. Appl. Phys.*, **1974**,**13**(7):1175~6

[6] Poirier E, Chahine R, Bose T K. *Int. J. Hydrogen Energy*, **2001**, **26**(8):831~5

[7] Fan Y Y, Liao B, Liu M, et al. *Carbon*, **1999**,**37**(10):1649~51

[8] Bessette R R, Medeiros M G, Patrissi C J, et al. *J. Power Sources*, **2001**,**96**(1): 240~4

[9] Ci L J, Wei J Q, Wei B Q, et al. *Carbon*, **2001**,**39**(3):329~35

[10]Yoon Y J, Baik H K. *Diam. Relat. Mater.*, **2001**,**10** (3 ~7): 1214~7

[11]Chen Y, Guo L P, Johnson D J, et al. *J. Crystal Growth*, **1998**, **193**(3):342~6

[12]Tang Y H, Wang N, Zhang Y F, et al. *Appl. Phys. Lett.*, **1999**, **75**(19):2921~3

[13]Jiang Y, Wu Y, Zhang S Y, et al. *J. Am. Chem. Soc.*, **2000**,**122** (49):12383~4

[14]Liu J W, Shao M W, Chen X Y, et al. *J. Am. Chem. Soc.*, **2003**,**125**(27):8088~9

[15]Shao M W, Li Q, Wu J, et al. *Carbon*, **2002**,**38**(40):2961~3

[16]Dresselhuas M S, Dresselhaus G, Pimenta MA, et al. *Ana nlytic Applications of Raman Spectroscopy*. Oxford **1999**, Chapter 9

[17]Kuang M H, Wang Z L, Bai X D, et al. *Appl. Phys. Lett.*, **2000**,**76**(10):1255~7

[18]Oberlin A, Endo M, Koyama T. *J. Cryst. Growth*, **1976**,**32**(2): 335~49