

二组元酞菁固相混合法裂解合成直立碳纳米管

况云华 李克智* 李贺军 许占位 王永杰

(西北工业大学超高温复合材料国防重点实验室, 西安 710072)

摘要: 通过向两种金属酞菁的混合物添加一定量的硫粉, 在 800~950 °C 裂解合成了大面积的直立碳纳米管。采用场发射扫描电镜(FE-SEM)、高分辨透射电镜(HRTEM)和拉曼光谱对产物进行了观察和表征, 结果显示: 所合成的碳纳米管(直径为 15~35 nm, 长度为 200~800 nm)管身平直, 具有很好的石墨化程度, 且杂质很少。采用两种金属酞菁($M(II)Pc$, $M=Fe, Co$)进行混合裂解时, 既可以提供碳源, 而且可以产生相当均匀的催化剂颗粒, 有利直立碳纳米管的沉积。这种将两种酞菁进行固相混合裂解的方法, 相当安全高效, 有利于大规模生产直立碳纳米管。

关键词: 直立碳纳米管; 酞菁; 热化学气相沉积; 硫

中图分类号: O614.81; O613.51

文献标识码: A

文章编号: 1001-4861(2009)06-0951-05

A Solid-state Hybrid Method to Synthesize Straight Carbon Nanotubes by Pyrolysis of Two Mixed Metal Phthalocyanines

KUANG Yun-Hua LI Ke-Zhi* LI He-Jun XU Zhan-Wei WANG Yong-Jie

(National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an, Shaanxi 710072)

Abstract: Straight carbon nanotubes (CNTs) were synthesized in large scale through thermal chemical vapor deposition (TCVD) by pyrolysis of two mixed metal phthalocyanines with a certain amount of sulfur at 800~950 °C. The results by field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy (Raman) reveal that the as-synthesized CNTs (15~35 nm in diameter, 200~800 nm in length) are quite straight and well-graphitized with nearly no defects. Two kinds of mixed transition metal phthalocyanines ($M(II)Pc$, $M=Fe, Co$) were used as carbon source to obtain uniform catalysts favoring the growth of the straight CNTs. The solid-state hybrid method is quite safe and efficient for synthesis of straight carbon nanotubes in large scale.

Key words: straight carbon nanotubes; phthalocyanine; thermal chemical vapor deposition (TCVD); sulfur

Since carbon nanotubes (CNTs) were reported by Iijima^[1] in 1991, they have been attracted great interest due to their unique electronic, mechanical, chemical and biological properties. The CNTs applied in nano-electrical devices^[2-4] and nanocomposites should be relatively straight. However, the CNTs easily tangle together because of their agglomerated nature, curved

form and length of several microns, thus severely limiting the electrical transmission properties and mechanical strength of the materials. Therefore, it is very important and necessary to synthesize straight CNTs in order to examine their theoretical performances and potential applications.

Several methods have been developed for synthesis

收稿日期: 2008-12-08。收修改稿日期: 2009-04-08。

国家自然科学基金(No.90716024)和西北工业大学博士论文创新基金资助。

*通讯联系人。E-mail: likezhi@nwpu.edu.cn

第一作者: 况云华, 男, 25 岁, 硕士研究生; 研究方向: 碳纳米管制备及其功能应用。

of CNTs. Among them chemical vapor deposition(CVD) has been received a great deal of attention due to the advantages of low-cost, easy-control and large-scale production. Some efforts have been taken in synthesizing straight CNTs by CVD, most of which have been concerned with the possibility of synthesizing straight CNTs with alloy catalysts^[5-8]. However, the preparation of alloy catalysts is relatively complicated and high in cost. Additionally, the synthesized CNTs by using these alloy catalysts through CVD are usually several microns long and easy to tangle together.

Recently, many works have been reported by using organometallic phthalocyanines as precursors to synthesize CNTs. The usage of these organometallic compounds^[9,10] turns out to be a crucial factor for promoting the uniform morphologies and the yield of the CNTs, but most of experiments with phthalocyanines as precursors use H_2 to protect from the agglomeration of the catalyst and carbon atoms. H_2 is a very inflammable and explosive gas, so it sets severe demands on equipment. Some research work^[11,12] reported that sulfur is a good substitute to replace the important role of H_2 . The sulfur has obvious advantages as cheap and easily available, thus favoring for safety and energy saving. This work aims at developing a relatively simple and low-cost method to fabricate straight CNTs through CVD. A mixture of two kinds of metal phthalocyanines is used as a precursor to replace alloy catalysts in this work. The precursor is consisted of Iron(II) phthalocyanine(Fe(II)Pc) and Cobalt(II) phthalocyanine(Co(II)Pc) mixed with a certain amount of sulfur to promote the catalytic activities of the mixture. The as-synthesized CNTs(15~35 nm in diameter) with an average length of several hundred nanometers are extremely straight with almost no defects.

1 Experimental

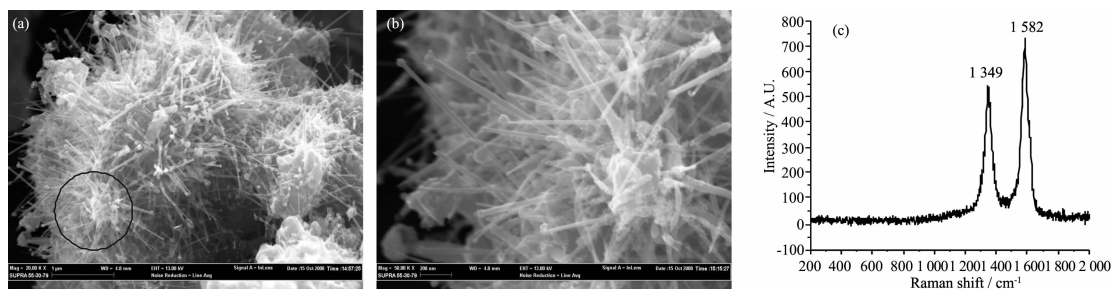
The metal phthalocyanines of Fe(II)Pc and Co(II)Pc (analytically pure) were obtained from Alfa Aesar Company, and the sulfur was C.P. reagent with a purity of > 95.5%. They were evenly mixed in advance by a certain percentage(the mass ratio of Fe(II)Pc, Co(II)Pc and S is 1:1:2). The mixed metal phthalocyanines serve as both

the catalyst precursor and carbon source. The sulfur added into the phthalocyanines mixture was used for preventing the metal catalysts from being agglomerated and for activating the surface of the metal catalysts^[11,12].

The experiments were carried out in an electrical-resistance CVD furnace with two independently heating zones. The reaction chamber was a quartz tube with 30 mm in diameter and 1 700 mm in length. The CVD process was carried out for 3 h(including temperature-increasing stage for 2 h and isothermal deposition stage for 1 h). The mixture(typically total of 0.2 g) of Fe(II)Pc, Co(II)Pc and sulfur were placed in a quartz boat at the low temperature zone(usually at 700 °C), while there was a substrate located at the high temperature zone(at 800~950 °C) for collecting the CNTs, and nitrogen(N_2) was supplied as the carrier gas(200 mL · min⁻¹). After the CVD reaction progress was over, the system was slowly cooled down to room temperature under N_2 flow. An entirely black product was observed and characterized by using ZEISS SUPRA55 field emission scanning electron microscopy (FE-SEM), JEOL JEM-3010 high-resolution transmission electron microscopy(HRTEM), and Raman spectrometer(RENISHAW invia, with 514.5 nm excitation).

2 Results and discussion

Typical FE-SEM images of the as-synthesized product without any purification are shown in Fig.1. Fig.1(a) indicates that a large scale of well-dispersed, straight CNTs, just like growing on an oasis, is synthesized. As can be seen from Fig.1(b), the diameter and average length of the CNTs range from 15 to 35 nm and from 200 to 800 nm, respectively. It is also shown that the wall surfaces of the straight CNTs are quite clean and smooth. The Raman spectrum in Fig.1(c) reveals that there are two main Raman bands at 1 349 cm⁻¹(D band) and 1 582 cm⁻¹(G band), which are characteristic peaks of CNTs. The G band originates from well-ordered graphite carbon structure, while the D band indicates the defective structure of graphite sheets. The intensity of the G mode(1 582 cm⁻¹) is higher than that of the D mode(1 349 cm⁻¹), indicating that the as-synthesized CNTs are well-graphitized and have a high purity.



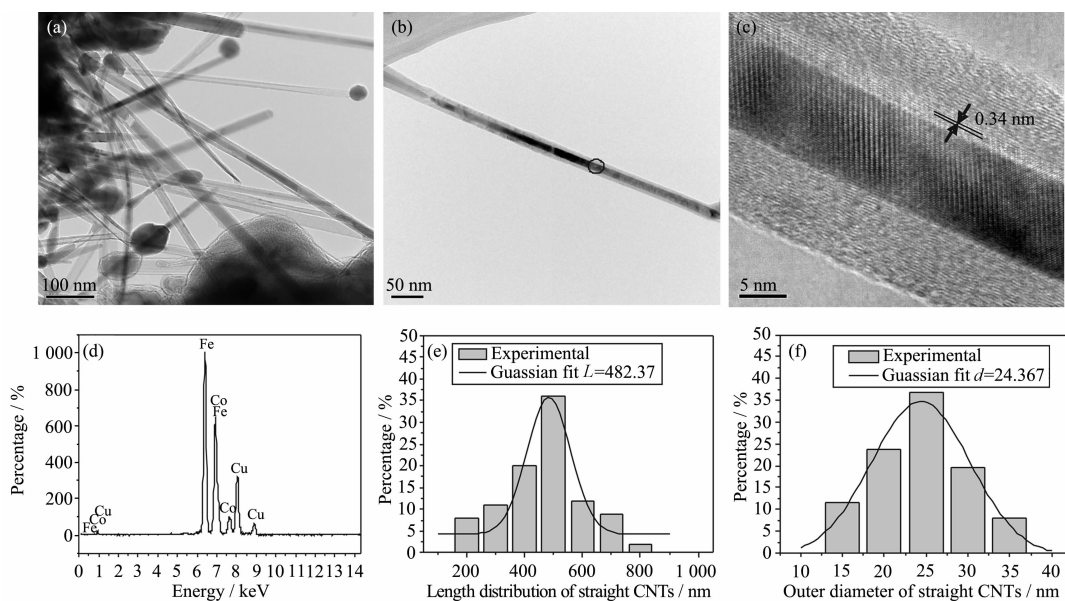
(a) The macro morphology of the straight CNTs; (b) The magnification of the sphere area in (a); (c) Raman spectrum of as-synthesized CNTs

Fig.1 SEM images and Raman spectrum of the CNTs produced by catalytic decomposition for the mixture of Fe(II)Pc and Co(II)Pc with sulfur at 950 °C for 1 h under N₂

In the TEM and HRTEM observation and examination of the as-synthesized CNTs, a mass of straight CNTs are detected in Fig.2(a). The walls of them are very smooth and clear. The TEM and HRTEM images of some typically straight CNTs(in Fig.2(b) and Fig.2(c)) demonstrate that they are straight, well-graphitized, multi-walled nanotubes comprised of well-ordered graphene layers(normally 10~20 layers) with less amorphous carbon. The graphitic sheets of the CNTs(in Fig.2(c)) are parallel, and the interlayer distance between neighboring graphitic sheets is 0.34 nm in accordance with the ideal graphitic interlayer

space.

From Fig.2(b and c), it is not difficult to find that the inner parts of straight CNTs are mainly filled with metal catalysts(in Fig.2(c)).The mixed catalytic(Fe and Co) particles are enwrapped in the tubes, the crystallization of which is very good and the catalytic particles are fairly uniform in Fig.3(c). EDS spectra(in Fig.3(d)) of the sphere in Fig.3(b) confirms that these straight CNTs are filled with the mixture particles of iron and cobalt, so they might be used for promoting the complex permeability of microwave absorbing composites^[13,14] after some furthermore treatment.



(a) TEM; (b) HRTEM of a typical straight CNTs in 50 nm; (c) HRTEM in 5 nm; (d) EDS of the sphere in (b); (e), (f) the length distribution and the outer diameter distribution

Fig.2 Images of the as-synthesized CNTs by pyrolysing the mixture of Fe(II)Pc and Co(II)Pc with sulfur at 950 °C for 1 h in the presence of N₂

The results of such a series of characterizations show that the catalyst particles play a crucial role in the

growth of straight CNTs, as found in reference^[15]. When only one kind of transition metal is used as catalyst

(shown in Fig.3 (a)), the growth rate of CNTs along the circumference of catalyst particles is not uniform due to different catalytic activities on the surface of different metal nanoparticles, and this causes the carbon nanotubes to curve towards the lower growth rate side^[16]. Conversely, when two kinds of mixed metal catalysts are used for producing large alloy catalysts, with the help of an appropriate amount of sulfur, the surface energy of

the alloy metal can be reduced efficiently. As a result of the synergetic effect of two kinds of mixed metal catalysts (shown in Fig.3 (b)), the circumference of smaller alloy catalysts is so uniform that carbon atoms pyrolyze from the mixture of Fe(II)Pc and Co(II)Pc are more efficiently deposited on the alloy catalysts surface equally in all directions, so it is easier and more beneficial to making CNTs grow straightly.

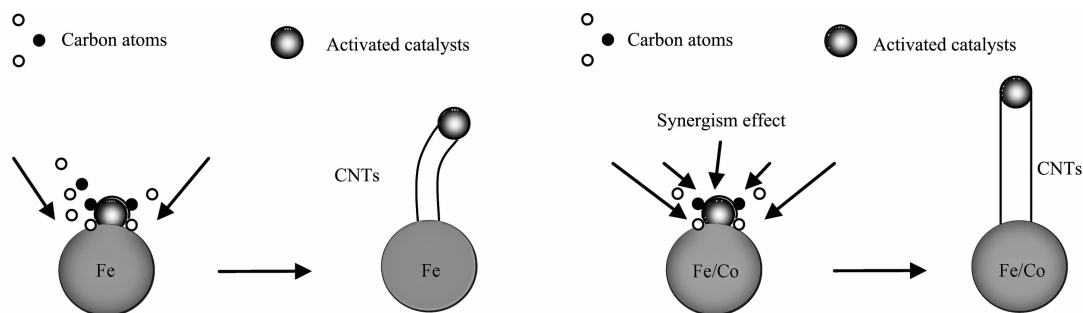


Fig.3 Growth mechanism schematics of curved CNTs and straight CNTs

The length and diameter distribution images in Fig.2(e) and Fig.2(f) reveal that the length of straight CNTs ranges from 200 nm to 800 nm (the Gaussian fit length is 482 nm), and the outer diameter is from 15 nm to 30 nm (the Gaussian fit diameter is 24 nm). These scale parameters make them suitable for application in a nanoelectrical device and nanocomposites^[17,18].

This simple and safe method has been used to synthesize straight CNTs by pyrolysis of Fe(II)Pc and Co(II)Pc added with some sulfur. Firstly, the organometallic phthalocyanine mixture is proved to be a key factor for promoting the morphologies (shape and uniformity) and the high yield of the CNTs (in our experiment, 0.05 g CNTs could be obtained from the phthalocyanine mixture weight of 0.2 g). Secondly, the mixture of transition metal (Fe and Co in our work) catalysts is more uniform and efficient for synthesizing straight CNTs than one metal catalyst does, because the former can promote the uniformity of catalyst particles, which is beneficial for straight CNTs growth. Finally, solid-state hybrid synthesis of straight CNTs is very simple and safe. Additionally, sulfur particles play an interesting role in the growth of straight CNTs. When more sulfur is added into the mixture, the CNTs seems to be a little more curved, but we have not identified how the sulfur influ-

ence the morphologies of these CNTs. Can we control the morphology (straight or curved) of carbon nanotubes by changing the content of sulfur added into mixture? Further work is needed to investigate this interesting phenomenon.

3 Conclusions

A large mass of well-dispersed, straight CNTs (with 15~35 nm in diameter) was synthesized by catalytically pyrolyzing the metal phthalocyanine mixture of Fe(II)Pc and Co(II)Pc with some amount of sulfur. This solid-state hybrid method of growing straight carbon nanotubes is simpler, safer and more efficient than using alloy catalysts methods, and has a better morphology than using one metal as the catalyst precursor.

References:

- [1] Iijima S. *Nature*, **1991**, *354*(7):56~58
- [2] Hamada N, Sawada S, Oshiyama A. *Phys. Rev. Lett.*, **1992**, *68*(10):1579~1581
- [3] Harigaya K, Fujita M. *Phys. Rev. B*, **1993**, *47*(24):16563~16569
- [4] Zou X P, Abe H, Shimizu T, et al. *Phys. E*, **2004**, *24*(1~2):14~18
- [5] Chen P, Zhang H B, Lin G D, et al. *Carbon*, **1997**, *35*(10~

- 11):1495~1501
- [6] Alvarez W E, Kitiyanan B, Borgna A. *Carbon*, **2001**,**39**(4): 547~558
- [7] PENG Feng(彭 峰), JIANG Jian-Cheng(江剑城), LEI Jian-Guang(雷建光). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2002**,**18**(2):1025~1029
- [8] TANG Chang-Xing(唐长兴), QU Mei-Zhen(瞿美臻), ZHOU Gu-Ming(周固民), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2003**,**19**(9):1025~1029
- [9] Liu B C, Lee T J, Lee S H, et al. *Chem. Phys. Lett.*, **2003**, **377**(1~2):55~59
- [10] Wu J S, Hamaoui B E, Li J X, et al. *Small*, **2005**,**1**(2):210~212
- [11] Demoncey N, Stephan O, Burn N, et al. *Synthetic. Met.*, **1999**, **103**(1~3):2380~2383
- [12] Wei J Q, Zhu H W, Yi J, et al. *Carbon*, **2007**,**45**(11):2152~2155
- [13] Melanie D, Tomoya K, Masanori K, et al. *Surf. Sci.*, **2007**, **601**(18):4366~4369
- [14] Lin H Y, Zhu H, Guo H F, et al. *Mater. Res. Bull.*, **2008**,**43** (10):2697~2702
- [15] Yang Y, Hu Z, Tian Y J, et al. *Nanotechnology*, **2003**,**14**(7): 733~737
- [16] Ivanov V, Nagy J B, Lambin P, et al. *Chem. Phys. Lett.*, **1994**,**223**(4):329~335
- [17] Chico L, Crespi V H, Benedict L X, et al. *Phys. Rev. Lett.*, **1996**,**76**(6):971~974
- [18] Sitharaman B, Shi X F, Walboomers F X, et al. *Bone*, **2008**, **43**(2):362~370