第6期 2003年6月 无机化学学报 CHINESE JOURNAL OF INORGANIC CHEMISTRY Vol. 19, No. 6 Jun., 2003

研究简报

单壁纳米碳管的纯化研究

王新庆[1,2] 王 淼*[1,2] 李振华[4] 朱海滨[1] 王凤飞[1] 卢焕明[3] 何丕模[1]
([1]浙江大学物理系;[2]微系统研究与开发中心;[3]硅材料国家重点实验室;[4]力学系,杭州 310027)

关键词: 单壁纳米碳管 拉曼光谱 热重分析
分类号: O6130.71

Study on Purification of Single-Walled Carbon Nanotubes

WANG Xin-Qing[1,2] WANG Miao*[1,2] LI Zhen-Hua[4] ZHU Hai-Bin[1]
WANG Feng-Fei[1] LU Huan-Ming[3] HE Pi-Mo[1]
([1] *Department of Physics*; [2] *Micro System Center for Research and Development*; [3] *Department of State Key Laboratory of Silicon Materials*; [4] *Department of Mechanics, Zhejiang University, Hangzhou* 310027)

A purification method to remove the metal catalysts and impurity carbon materials from arc-discharge-grown single-walled carbon nanotubes (SWCNTs) has been developed. Microporous membrane and the oxidation in the air for the crude SWCNTs were used to eliminate the coexisting metal catalysts nanoparticles, carbon nanoparticles and amorphous carbon. Then we used the high resolution transmission electron microscopy (HRTEM) to characterize the crude SWCNTs prepared by arc-discharge method and the purified SWCNTs. The Raman spectra and the thermogravimetric analysis (TGA) were also utilized to analyze the approach of our purification for SWCNTs. With this method the SWCNTs with the purity more than 95% could be obtained.

Keywords: **single-walled carbon nanotube(SWCNTs)** **Raman spectra** **thermogravimetric analysis(TGA)**

0 Introduction

Since discovered by Iijima in 1991[1], carbon nanotubes have been actively and widely studied[2,3]. Due to their outstanding chemical, physical and mechanical properties, carbon nanotubes have and could been applied in many fields, such as field emission electron sources[4], scanning probes[5], chemical sensors[6], field-effect transistors[7], nano-electronic devices[8,9], and so on. Although SWCNTs possess many unique and technically important properties, lack of pure SWCNTs would limit the study of fundamental properties and development of more practical applications. Therefore, it is eager to find cheap and easy methods to obtain high-purity SWCNTs. In fact, long-term efforts have been dedicated to develop news procedures and optimize the conditions for enhanced production of high-purity SWCNTs without destroying the geometrical structure of SWCNTs[10,11].

收稿日期:2002-10-08。收修改稿日期:2002-12-16。
国家自然科学基金资助项目(No. 60271009),浙江省自然科学基金资助项目(No. 501109)。
★通讯联系人。E-mail: miaowang@css.zju.edu.cn
第一作者:王新庆,男,26岁,硕士研究生;研究方向:纳米碳管的制备及应用。

Nowadays, SWCNTs can be mainly synthesized by the laser ablation method[12], the d. c. arc-discharge methods[13, 14] using Ni/Co/Fe powders as a catalyst. With these methods, it' s inevitable to introduce the impurities contained metals and amorphous carbon in as-prepared SWCNTs. Metals used as catalysts for the growth of SWCNTs were present as nanoparticles and typically encased in carbon outer layers, so it' s difficult to remove them by an acid. All purification methods attempt to remove the metals and amorphous carbon without affecting SWCNTs. K. Tohji[10] et al. used hydrothermally initiated dynamic extraction method to purify SWCNTs and obtained the SWCNTs with over 95% purity, but the productivity of the purification is only 2%. I. W. Chiang[11] et al purified SWCNTs with acid reflux with water reflux and a two-stage gas phase oxidation process.

In our experiment, the SWCNTs for purification were prepared by arc-discharge using Y/Ni powders as catalysts, and keeping the mixture graphite anode at a given angle with a high purity graphite cathode[14]. In order to remove the metals and unwanted carbon, we adopted the purification process contained acid reflux with HNO_3, filtration with microporous membrane and oxidation in the air to get rid of the impurities in the SWCNTs materials. And the SWCNTs with the purity of more than 95% could be obtained and the productivity of this method is about 30%. Then the HRTEM (Philips CM200 ultratwin) was used to characterize the SWCNTs in the experiment, the TGA and Raman spectrum (excited with 532nm laser) were also used to analyze the influence of the purification approach on the purity of the SWCNTs.

1 Experiment

The SWCNTs for purification were prepared by arc-discharge using Y/Ni powders (Ni: 4. 2wt% and Y: 1wt%) as catalysts, and keeping the mixture graphite anode at a given angle (about 40 ~ 50℃) with a high purity graphite cathode[14]. Discharging for about five minutes at the arc current of 60 A, we can get more than one gram the crude SWCNTs, which could be seen in Fig. 1a.

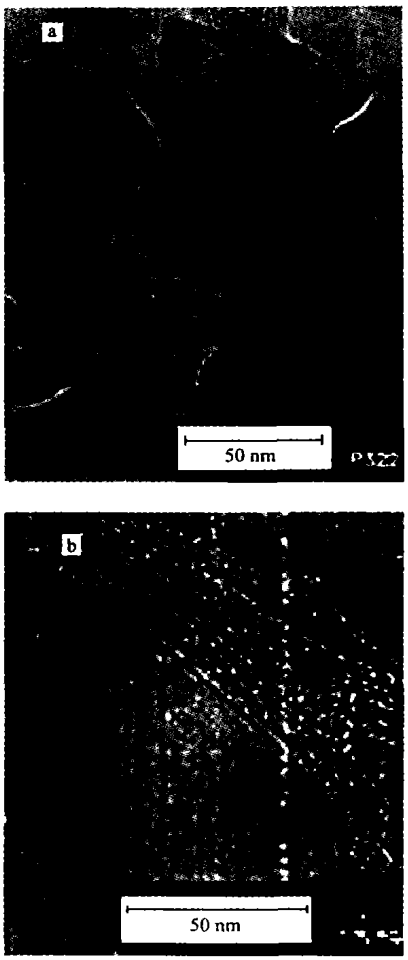

Fig. 1　High resolution transmission electron microscopy (HRTEM) photos of SWCNTs
(a) the crude SWCNTs; (b) the purified SWCNTs

In the experiment, approximately 100mg of crude materials was agitated in toluene by ultrasonic for an hour to extract the fullerenes and polyaromatic carbons. After drying, the insoluble solids were refluxed in 200mL 4mol · L^{-1} HNO_3 for 8h to partially eliminate the metal particles and amorphous carbons. Then the insoluble solids were dispersed in 200mL of aqueous solution of 0. 1% cationic surfactant, and using ultrasonic agitation for more than two hours to separate the metal particles and carbon nanospheres from the SWCNTs. The suspension was filtrated by microporous membrane with 0. 2μm pore, and most residual metal particles and carbon nanospheres would pass through the filter while the SWCNTs were trapped. The micro-

filtration process was repeated for three times to minimize the amount of residual metal particles and carbon nanospheres in the trapped SWCNTs. After drying at 60℃, the residual SWCNTs materials were oxidized in the air at 450℃ for half an hour to completely remove the carbon materials. In order to eliminate the residual metals, we soaked the SWCNTs in 37% HCl for two days. In addition, after each approach the deionized water must be used to wash the sample to avoid introducing other impurities, and a part of sample must be left for observation and analysis. Then we used the HRTEM to characterize the crude SWCNTs and the purified SWCNTs, and the Raman spectrum and the TGA were also used to analysis the purity of the SWCNTs.

2 Results and Discussion

In our experiment, though the methods we used to purified SWCNTs is similar to the usual[17], the conditions and the technics were changed and adopted to improve the purity and the productivity of the SWCNTs. The extraction in toluene was used to get rid of the fullerenes and polyaromatic carbons. The cationic surfactant and the ultrasonic agitation could make the SWCNTs well-dispersed in the aqueous solution, which is advantaged to separate the SWCNTs from the impurity. The oxidation at lower temperature also could decrease the loss of the SWCNTs. On all accounts, we could get the SWCNTs with the purity of 95%, and the productivity of this method is about 30%.

Fig. 1a is the HRTEM photo of the SWCNTs prepared at a helium pressure of 30000Pa and with arc current of 60A. The morphology and characteristics of the SWCNTs are shown in Fig. 1a and Fig. 1b, respectively. In Fig. 1a it can be seen that there are some metal particles and carbon nanospheres together with the SWCNT bundles. The SWCNTs usually exit in bundles due to the Van de Waals force between the individual SWCNTs. The diameter of the bundles usually is about 10 ~ 20nm. It should be point out that the structure and characteristics of the SWCNTs produced in this way are the same as that synthesized by the laser method, but the yield of our method is higher. Fig. 1b is the HRTEM photo of the purified SWCNTs. Comparing with Fig. 1a there are few black metal particles and carbon nanospheres in the purified SWCNTs.

Moreover, the above results have been confirmed by Raman spectra on the samples. In Fig. 2, the Raman spectra of the purified SWCNTs exhibits the characteristic frequencies of the SWCNTs. The scattering peaks of amorphous carbon and SWCNTs are observed around 1350cm^{-1} and 1588cm^{-1}, in which the peaks centered at 1588cm^{-1} and 1350cm^{-1} have been assigned to the E_{2g} mode of graphite[15] and the sp^2 mode of the amorphous carbon, respectively. The ratio of their peak height can reflect the purity of the SWCNTs of the deposits. In our experiment, the ratio of the intensity of the two peaks is large, which could prove that the SWCNTs after purification have high purity.

In order to give a detailed explain for the process of the purification for the SWCNTs, we also showed the Raman spectra of the crude SWCNTs near the cathode (a), the crude SWCNTs on the inner wall of evaporation chamber(b), the SWCNTs after refluxed in HNO_3 (c) and the purified SWCNTs (d) in Fig. 2. Comparing with the curve (a), the intensity of the peak at 1588cm^{-1} is higher than that in the curve (b), which showed the SWCNTs grown near the cathode are better than the others' with Ni as the catalyst[16]. The curve (c) is the Raman spectrum of the SWCNTs after refluxed in HNO_3. From it the intensity of the peak at 1588cm^{-1} decrease obviously[17], because the reflux with HNO3 would damage the structure of the partial SWCNTs. The Raman spectrum (d) of the purified SWCNTs, as compared with the curve (a) and (b), the peak centered at 1588cm^{-1} weakened because of the loss of partial SWCNTs. On the other hand, we also observed the Raman spectra of the crude SWCNTs and the purified SWCNTs in the low-frequency region, which were also shown in Fig. 2. There was a peak centered at 170cm^{-1} in this region. And the spectrum in this region is very sensitive to the nanotube diameter. In fact, $w = 223.75/d(\mathrm{nm})$, i. e., the frequency w is inversely proportional to the nanotube diameter.

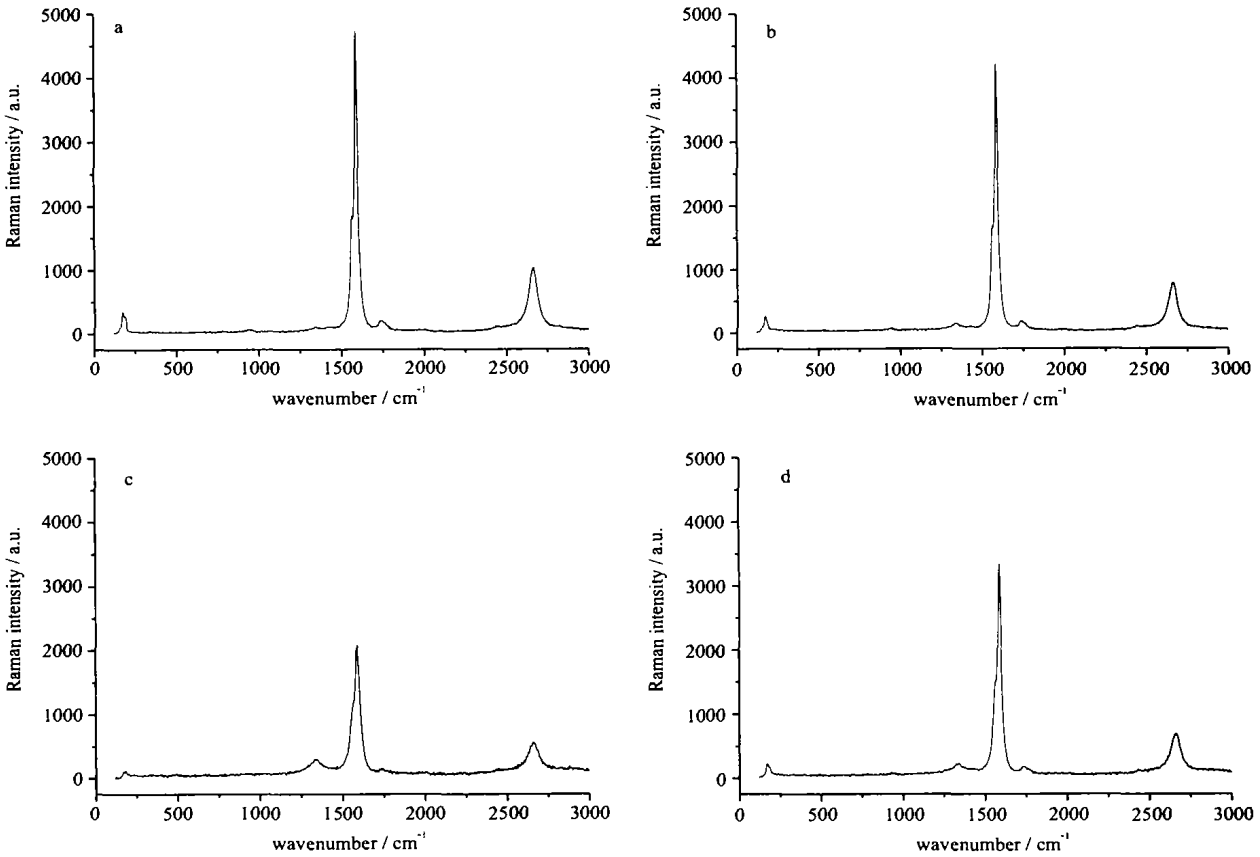

Fig. 2　Raman spectra of SWCNTs

(a) The crude SWCNTs near the cathode; (b) The crude SWCNTs on the inner wall; (c) The SWCNTs after refluxed with HNO_3; (d) The purified SWCNTs

According to the formula, the corresponding diameter, about 1. 30nm, of the SWCNTs can be obtained.

The TGA was also used to evaluate the crude and purified SWCNTs to illuminate the result of our method for the purification of SWCNTs. The data for the crude SWCNTs was shown in Fig. 3a. The carbonaceous fractions begin to combust at about 320℃ and are mostly removed by oxidation below 600℃. A small weight loss between 600℃ and 800℃ is due to the oxidation of surviving SWCNTs(~10% in weight) . But from the results of the observation of HRTEM and the analysis of Raman spectra, the content of SWCNTs in the soot should be more than 10%, we thought that the partial SWCNTs also be oxidized owning to the regional high temperature produced by the oxidation of carbonaceous fractions. The weight remaining after 810℃ corresponds to the weight of the oxidized metals

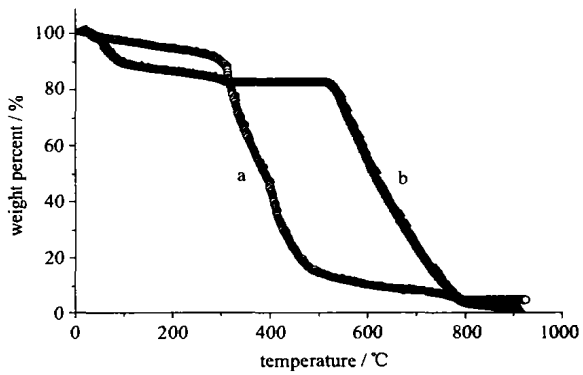

Fig. 3　Thermogravimetric analysis (TGA) of the SWCNTs

(a) the crude SWCNTs; (b) the purified SWCNTs

(~9%) . The curve with the weak color in Fig. 3b is the TGA data of the purified SWCNTs. A first thing to note is that the SWCNTs contained the water as much as 10% in weight for insufficient drying. At the temperature of 320℃, a small weight loss happens for the

existence of a little of carbonaceous, which could be seen in Fig. 1b. There is an evident weight loss in the TGA data at the beginning 550℃ and at the end of 850℃ because of the oxidation of the SWCNTs. At the 850℃ since the carbonaceous materials have been removed and the weight of the SWCNTs sample is the oxidized metals (about 1%).

3 Conclusions

From the results above, the purified SWCNTs photo and the analysis for the purification with the TGA and the Raman spectrum of SWCNTs, It could be concluded that the method we used is the one of the effective ways to purify the SWCNTs. The purified process contains the acid reflux with HNO_3, the microfiltration with the membrane (0.2μm) and the oxidation in the air. Finally, in spite of the loss of the partial SWCNTs, we could obtain the SWCNTs with the purity more than 95%.

References

[1] Iijima S. *Nature*, **1991**, **354**, 56.

[2] WANG Sheng-Gao(王升高), WANG Jian-Hua(汪建华), MAN Wei-Dong(满卫东), MA Zhi-Bin(马志彬), WANG Zhuan-Xin(王传新) *Wuji Huaxue Xuebao* (*Chinese J. Inorg. Chem.*), **2002**, **18**(6), 611.

[3] LU De-Yi(吕德义), XU Zhu-De(徐铸德), XU Li-Ping(徐丽萍), CHEN Wei-Xiang(陈卫祥), LIU Zong-Jian(刘宗健), GE Zong-Hua(葛忠华) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **2002**, **18**(5), 475.

[4] Yahachi S., Sashiro U. *Carbon*, **2000**, **38**, 169.

[5] Stanislaus S. W., Ernesto J., Adam T. W., Chin L. C., Charles M. L. *Nature*, **1998**, **394**, 52.

[6] Kong J., Franklin N. R., Zhou C. W., Chapline M. G., Peng S., Cho K., Dai H. J. *Science*, **2000**, **287**, 622.

[7] Martel R., Schmidt T., Shea H. R., Hertel T., Avouris Ph. *Appl. Phys. Lett.*, **1998**, **73**, 2447.

[8] Tans S. J., Verschueren A. R. M., Dekker C. *Nature*, **1998**, **393**, 49.

[9] Collins P. G., Zettl A., Hiroshi B., Thess A., Smalley R. E. *Science*, **1997**, **278**, 100.

[10] Journet C., Master W. K., Bernier P., Loiseau A., Chapelle M. L., Lefrant S., Denlards P., Lee R., Fischer J. E. *Nature*, **1997**, **388**, 756.

[11] Thess A., Lee R., Nikolaev P., Dai H. J., Petit P., Robert J., Xu C. H., Lee Y. H., Kim S. G., Rinzlev A. G., Colbert D. T., Scuseria G. E., Tomanek D., Fischer J. E., Smalley R. E. *Science*, **1996**, **273**, 483.

[12] Tohji K., Takahashi H., Shinoda Y., Shimizu N., Jeyadevan B., Matsuoka I. *J. Phys. Chem. B*, **1997**, **101**, 1974.

[13] Chiang I. W., Brinson B. E., Smalley R. E., Margrave J. L., Hauge R. H. *J. Phys. Chem. B*, **2001**, **105**, 1157.

[14] LI Zhen-Hua(李振华), WANG Miao(王 淼), WANG Xin-Qing(王新庆), ZHU Hai-Bin(朱海滨), LU Huan-Ming(卢焕明), Ando Y.(安藤义则) *Chinese Physics Letters*, **2002**, **19**(1), 91.

[15] Yahachi S. *New Diamond and Frontier Carbon Technology*, **1999**, **19**(1), 1.

[16] Jeong T., Kim W. Y., Hahn Y. B. *Chem. Phys. Lett.*, **2001**, **344**, 18.

[17] Dillon A. C., Gennett T., Jones K. M., Alleman J. L., Parilla P. A., Heben M. J. *Advanced Marerials*, **1999**, **11**(16), 1354.