A temperature window for the synthesis of single-walled carbon nanotubes by catalytic chemical vapor deposition of CH_4 over Mo-Fe/MgO catalyst*

OUYANG Yu,CHEN Li[1], LIU Qi-xin[2] and FANG Yan[3]**

1. *Department of Physics, Linyi Normal University, Shandong 276005,China*
2. *Department of Applied Physics, College of Science, Shandong University of Science and Technology, Shandong 276005, China*
3. *Beijing key lab. for nanophotonics and nanostucture, Capital Normal University, Beijing 100037,China*

(Received 11 September 2007)

A temperature window of single-walled carbon nanotubes (SWCNTs) growth has been studied by Raman spectroscopy. The results presented when temperature lower than 750 °C, there were few SWCNTs formed, and when temperature higher than 900 °C, mass amorphous carbons were formed in the SWCNTs bundles due to the self-decomposition of CH_4. The temperature window of SWCNTs efficiently growth is between 800 and 900 °C, and the optimum growth temperature is about 850 °C. These results were supported by transmission electron microscope images of samples formed under different temperature. The temperature window is important for large-scale production of SWCNTs by catalytic chemical vapor deposition method.

CLC numbers: TB383 **Document code:** A **Article ID:** 1673-1905(2008)02-0096-3
DOI 10.1007/s11801-008-7115-6

Since single-walled carbon nanotubes (SWCNTs) were discovered in 1993 [1], they have generated significant research activities due to their particular microstructures, unique properties and great potential applications in many fields. A single-walled nanotube can be described as a single layer of a graphite crystal that is rolled up into a seamless cylinder, with both ends capped with hemispheres made of hexagonal and pentagonal carbon rings. With remarkable properties, SWCNTs can be explored to be used in novel applications like actuators [2], pressure sensors [3], flow sensors [4], nanoscale electronics [5] and hydrogen storage [6].

Because SWCNTs possess so many unique properties, the synthesis of SWCNTs becomes a subject of a significant global research effort. Up to now, a number of methods for preparing SWCNTs have been reported, such as electric arc discharge [7], laser ablation methods [8] and catalytic chemical vapor deposition (CCVD) [9-13]. Among them, the CCVD method is becoming a dominant way for scaling up the production of SWCNTs at relatively low cost. In the CCVD method, methane, acetylene, hexane, alcohol and other hydrocarbons are used as carbon feedstock. The catalysts are generally supported on Al_2O_3 or MgO and consist of Fe, Co, Mi, Mo or mixtures of those metals.

In the synthesis of SWCNTs by CCVD method, the temperature plays a key role. In this paper, we report the synthesis of SWCNTs by catalytic decomposition of methane over Mo-Fe/MgO catalyst and give a temperature window using Raman spectroscopy. With the relatively intensity of *D* band to the *G* band (I_D/I_G) and the transmission electron microscopy images of samples, we obtain that the optimum synthetic temperature is about 850 ℃.

A mixture of $Mg(NO_3)_2 \cdot 6H_2O$, ammonium molybdate, citric acid, H_2O and $Fe(NO_3)_2 \cdot 9H_2O$ at a weight ratio of 10: 0.07:4:1:1.6 was stirred for 6 hours at 90 ℃ and dried at 150℃ overnight, then grounded into a fine powder. Finally, the powder was calcined in air (air flow: 30 ml/min) for 30 minutes at 550 ℃ before used for SWCNTs growth.

The growth of SWCNTs was carried out in a fluidized-bed which is shown in Fig.1. In a typical experiment, about 100 mg catalyst was put into the quartz tube. The temperature was raised to the setting value in Ar atmosphere at a flow rate of 200 ml/min before CH_4 was introduced into the reactor at 60 ml/min for 30 min, then CH_4 was turned off and the furnace was cooled to room temperature in an Ar flow. The impurities were removed by concentrate HCI.

The Raman spectra were recorded by an RM 2 000 spec-

* This work has been supported by the National Natural Science Foundation of China and Natural Science Foundation of Linyi, China.

** E-mail: ouyangyu1976@tom.com

trophotometer at room temperature and in a back-scattering geometry, with Ar laser at 514.5 nm.

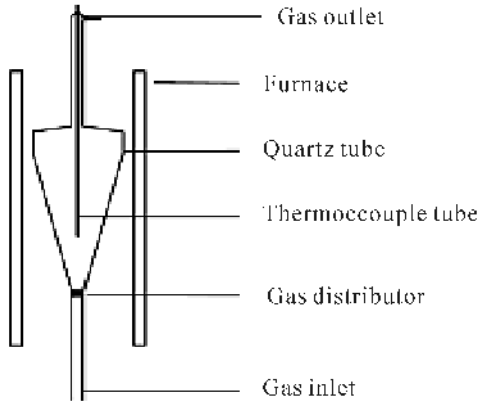

Fig.1 Sketch map of the fluidized bed reactor

Fig.2 shows Raman spectra for materials grown at different growth temperature (a : 700 ℃ ; b : 750 ℃ ; c : 800 ℃ ; d : 850 ℃ ; e : 900 ℃ ; f : 950 ℃). In Fig.2(a), only the G band (tangential mode), D band (related to disordered graphite or amorphous) and a shoulder at 1604 cm^{-1} (the fundamental E_{2g} mode of graphite) are presented. In the lower wavenumber region (100-300 cm^{-1}), the radial breath modes (RBM) which represent the existence of SWCNTs are hardly shown. The data shows no SWCNTs are formed and there are only poorly multi-walled carbon nanotubes (MWCNTs) and organized carbon in the sample. The relatively high intensity of the D band relative to G band (I_D/I_G=0.7) indicates mass amorphous carbon content or more defect concentration in the MWCNTs. These conclusions are supported by TEM image (Fig.3(a)).

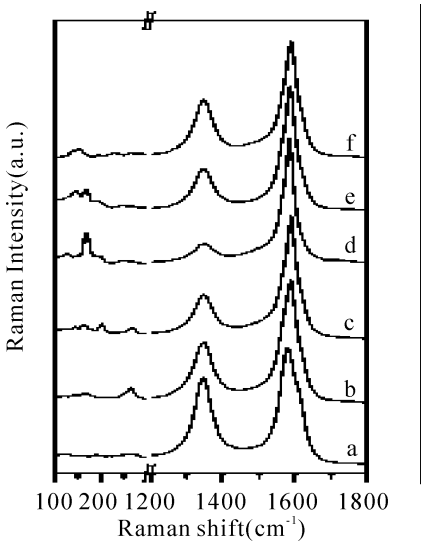

Fig.2 Raman spectra from samples grown at the designated temperature.
(a) 700 ℃; (b) 750 ℃; (c) 800 ℃; (d) 850 ℃; (e) 900 ℃; (f) 950 ℃

When temperature increases to 750 ℃,Raman spectrum of the sample (Fig.2(b)) shows a broad, weak RBM at 266 cm^{-1}. This revealed that SWCNTs was formed at 750 ℃. From TEM image (Fig.3(b)), we can observe that there are a few single SWCNT and SWCNTs bundle at point A among MWCNTs. According to the equation $\omega_{RBM}=6.5+223.75/d_t$ (cm^{-1})[14], the diameter of SWCNTs synthesized at 750 ℃ is about 0.86 nm, which accords with the result of TEM image (Fig.3(b)). The intensity ratio, I_D/I_G is observed to decrease with increasing temperature (at 750 ℃, the I_D/I_G is 0.46).

Raman spectrum of the sample grown at 800 ℃ (Fig.2 (c)) is typical for SWCNTs. In the lower wavenumber region (100-300 cm^{-1}), several RBM band are presented. According to the formula, the peaks at 142, 162, 203 and 273 cm^{-1} correspond to the SWCNTs with diameter of 1.73, 1.44, 1. 14 and 0.84 nm, respectively. The TEM image (Fig.3(c)) reveals that the product consisted of single and bundle SWCNTs with different diameters. The intensity ratio becomes lower with I_D/I_G = 0.33 and the TEM presents that only a few amorphous carbons in the SWCNTs bundle.

The RBM modes are observed as a strong band at 167 cm^{-1} and a set of very weak bands at 128, 145, 179, 250 and 269 cm^{-1} in the Raman spectrum at 850 ℃ (Fig.2(d)). The relatively lower intensity, I_D/I_G = 0.15, indicates a lower amount of amorphous carbon content or a lower defect concentration in the SWCNTs. This can be observed from TEM image in Fig.3(d). As shown in Fig.3(d), the SWCNTs in the bundle have even diameters and appear clean and uncoated. All the results show high-quality SWCNTs have been synthesized at 850 ℃.

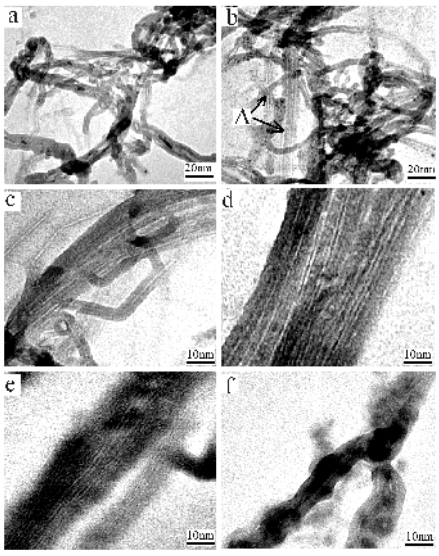

Fig.3 Transmission electron microscope images of samples formed at
(a) 700 ℃, (b) 750 ℃, (c) 800 ℃, (d) 850 ℃, (e) 900 ℃ and (f) 950 ℃

With increasing growth temperature to 900 and 950 ℃, more and more amorphous carbons are formed in the SWCNTs bundles due to the self-decomposition of CH_4. This is shown both in Raman spectra Fig.2(e) and Fig.2(f) and TEM images Fig.3(e) and Fig.3(f). The spectra show the I_D/I_G increasing rapidly with increasing growth temperature. The TEM images present SWCNTs coated by mors and more amorphous carbons, when temperature increases to 950 ℃, SWCNTs are hardly observed.

In order to study the influence of growth temperature on the purity of prepared tube samples, we give the curve (Fig. 4) showing the dependence of I_D/I_G on the growth temperature. From Fig.4, two kinds of I_D/I_G distributions can clearly be distinguished. From 700 ℃ to 850 ℃, the I_D/I_G decreases with increasing growth temperature. After the temperature higher than 850 ℃, the I_D/I_G increases with growth temperature. In the former stage, SWCNTs is formed gradually with increasing growth temperature and the content of SWCNTs in the products increases. In the latter stage, the high growth temperature causes CH_4 self-decomposition. With increasing growth temperature, more and more amorphous carbons formed, when growth temperature increases to 950 ℃, only a few SWCNTs in the results and coated by plenty of amorphous carbons.

A temperature window of single-walled carbon nanotubes

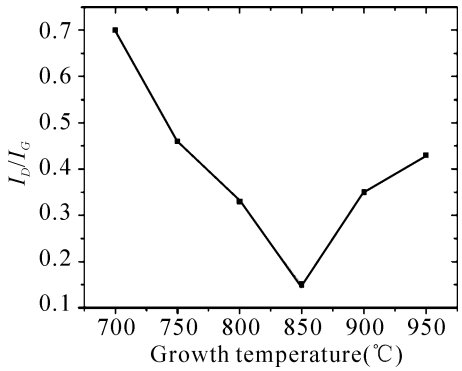

Fig.4 Influence of growth temperature on the resulting intensity ratio I_D/I_G

growth by catalytic chemical vapor deposition of CH_4 over Mo-Fe/MgO catalyst has been studied. The results suggested when temperature lower than 750 ℃, there was few SWCNTs formed, and when temperature higher than 900 ℃, more and more amorphous carbons were formed in the SWCNTs bundles due to the self-decomposition of CH_4. The temperature window of single-walled carbon nanotubes efficiently growth is between 800 to 900 ℃, and the optimum growth temperature is about 850 ℃.

References

[1] S.Iijima, and T.Tchihashi, Nature ,**363** (1993),603.

[2] R.H. Baughman, C. Cui, and A.A. Zakhidov, Science, **284** (1999), 1340.

[3] Q. Zhou, J.R. Wood, and H.D.Wagner, Appl. Phys. Lett., **78** (2001) ,1748.

[4] P.Kral, and M.Shaprio, Phys. Rev. Lett., **86** (2001),131.

[5] M. Kruger, M.R. Buitelaar, and T. Nussbaumer, Appl. Phys. Lett., **78** (2001), 1291.

[6] N. Rajalakshmi, K.S. Dhathathreyan, and A. Govindaraj, Electrochim. Acta, **45** (2000), 4511.

[7] Journet C, Master WK, and Bernier P, Nature,**388**(1997),756.

[8] Thess A, Lee R, and Nikolaev P, Science, **273** (1996),483.

[9] Li Qingwen, Yan Hao, and Cheng Yan, J. Mater. Chem., **12** (2002), 1179.

[10] Alan M. Cassell, Jeffrey A. Raymakers, Jing Kong, and Hongjie Dai, J. Phys. Chem. B, **103** (1999),6484.

[11] J.-F. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z. Konya, A. Fonseca, Ch. Laurent, and J. B.Nagy, Chem. Phys. Lett., **317** (2000),83.

[12] Jason H. Hafner, Michael J. Bronikowski, Bobak R. Azamian, Pavel Nikolaev, Andrew G. Rinzler, Daniel T. Colbert, Ken A. Smith, Richard E. Smalley Chem. Phys. Lett., **296** (1998), 195.

[13] G.L.Hornyak, L.Grigorian, A.C.Dillon, P.A.Parilla, K.M. Jones, M.J.Heben J. Phys. Chem. B, **106** (2002), 2821.

[14] S.C.Lyu, B.C.Liu, T.J.Lee, Z.Y.Liu, C.W.Yang, C.Y.Park, C.J.Lee, Chem. Commun., **734** (2003).