Vol 15 No 11, November 2006
1009-1963/2006/15(11)/2761-04
Chinese Physics
© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

Photoluminescence of multiwalled carbon nanotubes excited at different wavelengths

Yuan Yan-Hong(袁艳红)[a)b)†], Miao Run-Cai(苗润才)[c)], Bai Jin-Tao(白晋涛)[b)], and Hou Xun(侯 洵)[b)d)]

[a)] *Department of Arts & Science, Shanghai Dianji University, Shanghai 200240, China*
[b)] *Institute of Photonics & Photon-Technology, and Provincial Key Laboratory of Photoelectronic Technology, Northwest University, Xi'an 710069, China*
[c)] *Shaanxi Yulin College, Yulin 719000, China*
[d)] *State Key Laboratory of Transient Optics & Photonics, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Sciences, Xi'an 710068, China*

(Received 19 December 2005; revised manuscript received 23 June 2006)

In this paper the multiwalled carbon nanotubes (MWNTs) were synthesized by a chemical vapour deposition and the SEM graph shows that the sample has good construction. The micro-Raman spectrum shows the characteristic line of the MWNTs and an additional line produced by the defects on the outer surface of MWNTs. The photoluminescence (PL) spectra observed experimentally are variable under different excitation wavelengths and the strong excitation wavelength dependence of luminescence indicates a distribution of emitters which include electron π in excited states and the Van Hove singularities. The absorption spectra confirm the transition channels which are consistent with the PL emission.

Keywords: multiwalled carbon nanotubes, photoluminescence, excitation
PACC: 7865V, 7855

1. Introduction

As a new one-dimensionality structure of the carbon family,[1] carbon nanotubes (CNTs) have attracted considerable attention because of their unique structure, which may lead to various optical and electronic applications.[2−6] For instance, they have large nonlinear optical responses, and may thus be used for electro-optical devices. The CNTs have been deposited by using several growth techniques, including arc discharge,[7] laser vaporization,[8] pyrolysis,[9] and plasma-enhanced or thermal chemical vapour deposition (CVD).[10,11] The optical fundamental properties of CNTs have been investigated for relative long time, which include their absorption and photoluminescence (PL).[7,12] For example, PL with different colors including green, yellow, and red were observed.[7,8,13,14] However, in previous researches on PL, light and electronic beams were mainly used as excitation sources. Only a single fixed wavelength was employed for light excitation. Few investigations were concerning about the differences among the PL of CNTs under the excitations at different wavelengths and the mechanism of PL spectra variation. In the present work, MWNTs were synthesized by a CVD and the SEM graph of the sample was achieved. Meanwhile, its Raman spectrum was measured to identify the MWNTs structure. The PL spectra at different excitation wavelengths were carried out at room temperature experimentally in order to determine the dependence of the PL spectra on the excitation wavelength. To analyse the PL mechanism and the transition process, the absorption spectra were also detected.

2. Experimental results

The MWNTs were synthesized by a CVD method over a dispersed iron catalyst that is deposited on quartz substrates.[15] The synthesis apparatus consists of a quartz tube reactor inside a combined pre-heater and furnace set-up. A syringe pump allows the continuous injection of a xylene–ferrocene liquid into a preheat section that is operated at ∼200°C. The xylene-ferrocene vapours are carried from the pre-heater into the reaction zone of the furnace by an Ar/10% H_2 car-

†Corresponding author. E-mail: xjcjyyh@163.com

rier gas that also controls the partial pressure inside the quartz tube reactor. The reaction zone is typically 700°C, with an Ar/H_2 flow rate of 6l/min. The micrograph of sample MWNTs by a scanning electron microscope (SEM JSM-6700F) is showed in Fig.1. The SEM result shows that the most nanotubes are 30 to 50μm long and their diameters distributes within the range 50 nm. The MWNTs have very clean surface.

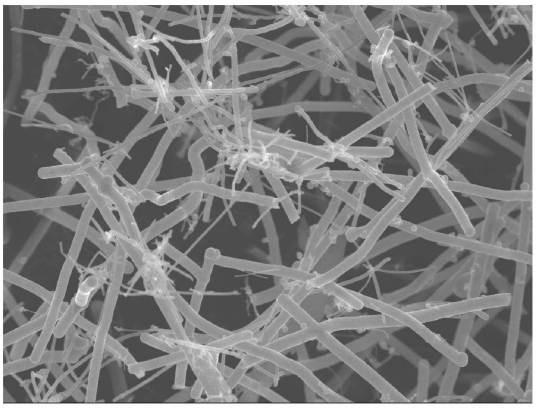


Fig.1. SEM micrograph of MWNTs, the diameter within the range 50 nm.

Figure 2 is the micro-Raman spectrum for the MWNTs which was carried out by the Raman spectrometer HR800. The excitation is a He–Ne laser with wavelength at 632.8 nm. The multiwall structure of CNTs is identified by a clear G-line at 1586 cm^{-1}.[16,17] But there is no second order peak at 1720 cm^{-1}. The peak at 1330 cm^{-1} was also observed, which is resulted from the defective outer graphite sheets of MWNTs.[18] It should be noticed that the relative intensity of 1330 cm^{-1} peak is larger than that of 1586 cm^{-1} peak, which indicates that there are some more defects on the wall surface. Therefore, Raman spectrum analysis provides definite evidence that the MWNTs have good crystallinity (1586 cm^{-1}) and some defects on the wall surface (1330 cm^{-1}).

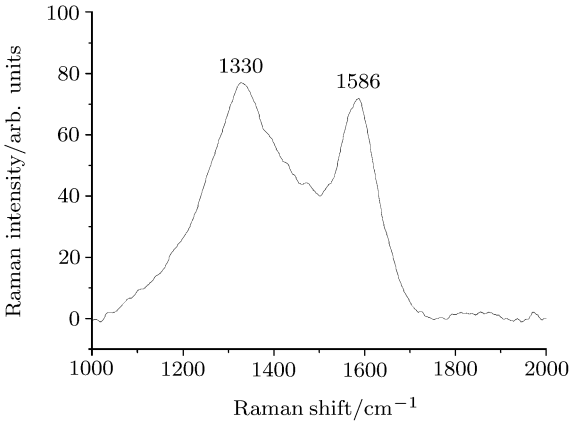


Fig.2. Raman spectrum of MWNTs.

The absorption spectra are shown in Fig.3 which were measured by a Cary 5000UV–VIS–NIR spectrometer. It can be obtained from Fig.3(a) that there is an intensive absorption peak at 240 nm (5.18eV). Most researchers consider that this peak results from the MWNTs electron transition of $\pi - \pi^*$.[19] To analyse the absorption in the range between 400 nm to 760 nm in Fig.3(a), we scan them again with high sensitivity and which is shown in Fig.3(b). By careful observation, one will find three small peaks which are located at 440 nm (2.82 eV), 610 nm (2.04 eV) and 660 nm (1.88 eV) respectively. An absorption band (660 nm–760 nm) is observed from the figure. The transition rate for absorption is proportional to the initial density of electronic states. The density of the states corresponding to the locations where there are small peaks is greater than that in the other region. These ranges of energy with high associated density of states are called Van Hove singularities (VHS).[20]

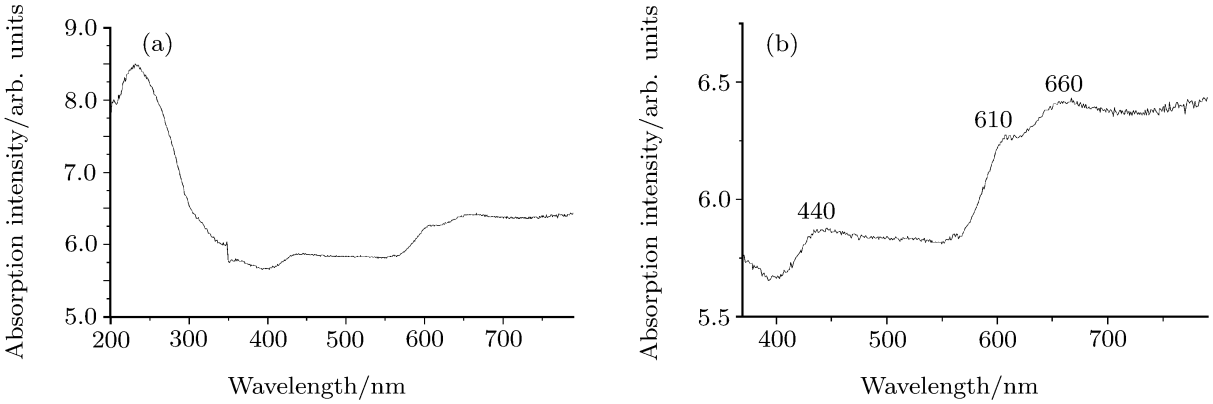


Fig.3. (a) Absorption spectrum of MWNTs, (b) Absorption spectrum of MWNTs.

The PL spectra under different excitation wavelengths were carried out at room temperature by a HITACHI F4500 visible–ultraviolet spectrophotometer. The PL spectrum, observed on excitation at 248 nm (4.97 eV), consists of a structured band, peaking at approximately 480 nm (2.57 eV), as shown in Fig.4(a). As the excitation at 514 nm was used instead of that at 248 nm, the different fluorescence was achieved which have two peaks at 750 nm and 860 nm respectively. One of them is intensive but the other is relatively weak. It should be noted that the PL spectra are variable under different excitation wavelengths. The strong excitation wavelength dependence of luminescence indicates a distribution of emitters. As explained by the absorption spectra in Fig.3, the excitation at 248 nm in Fig.4(a) results in transition of the MWNTs electron $\pi - \pi^*$, but the excitation process in Fig.3(b) takes place mainly in the some defects on the MWNTs surface.[13] This means that the MWNTs electrons in the excited states experience radiative transitions and form the PL spectrum in Fig.4(a), but the defects on the MWNTs surface results in the formation of the PL spectrum in Fig.4(b).

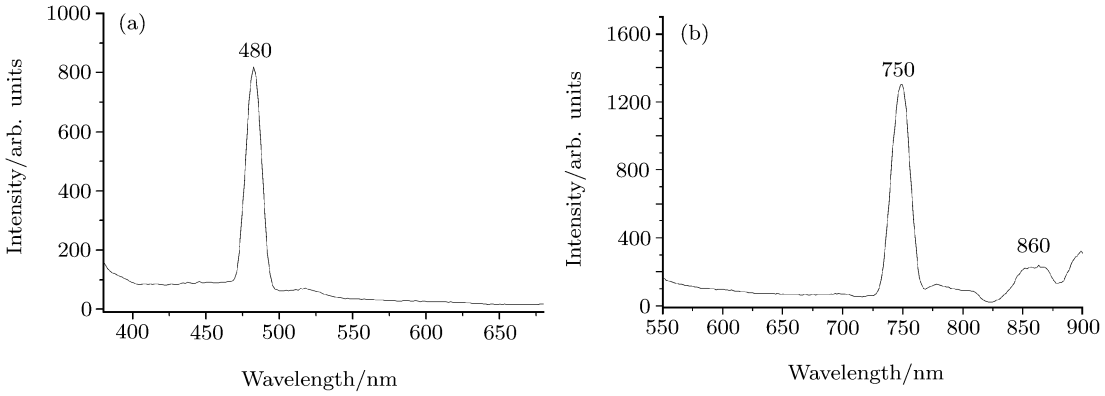


Fig.4. (a) PL spectrum from MWNTs excited at 248 nm, (b) PL spectrum from MWNTs excited at 514 nm.

3. Conclusion

In conclusion, the MWNTs were synthesized by a CVD and the SEM graph shows that the most nanotubes are 30 to 50μm long and their diameters distributes within the range 50 nm. The MWNTs structure is also identified by a clear Raman peak at 1586 cm^{-1}. Another peak at 1330 cm^{-1} shows the defects on the surface of the outer graphite sheets of MWNTs. The absorption peak at 240 nm was observed experimentally and it can be assigned the MWNTs electron transition of $\pi - \pi^*$. Meanwhile, an absorption band and three small peaks in the region between 400 nm–760 nm were also found and these peaks demonstrate the VHS in MWNTs. The PL spectra under different excitation wavelengths were carried out at room temperature experimentally and the PL spectra are variable under different excitation wavelengths. The strong excitation wavelength dependence of luminescence indicates a distribution of emitters. The excitation at 248 nm results in transition of the MWNTs electron $\pi - \pi^*$ and the MWNTs electrons in the excited states experience radiative transitions and form the PL spectrum peaking at 480 nm. But the excitation at 514 nm takes place mainly in the some defects on the MWNTs surface and which produces the PL spectrum peaking at 750 nm and 860 nm respectively.

References

[1] Tang N S, Yan X H and Ding J W 2005 *Acta Phys. Sin.* **54** 333 (in Chinese)

[2] Qu Y Y and Fang Y 2005 *Acta Phys. Sin.* **54** 578 (in Chinese)

[3] Zhang Z Y and Wang T H 2004 *Acta Phys. Sin.* **53** 942 (in Chinese)

[4] Chen C S, Chen X H, Li X Q, Zhang G, Yi G J, Zhang H and Hu J 2004 *Acta Phys. Sin.* **53** 531 (in Chinese)

[5] Liu L F, Zhou W Y, Zhu P P, Cui M Q and Wang G 2004 *Chin. Phys.* **13** 1922

[6] Dou X Y, Zhou Z P, Tan P H, Zhou J J and Wang G 2005 *Chin. Phys.* **14** 2068

[7] Brennan M E, Coleman J N, Drury A, Lahr B, Kobayashi T K and Blau W J 2003 *Opt. Lett.* **28** 266

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

[9] Terrones M, Grobert N, Olivares J, Zhang J P, Terrones H, Kordatos K, Hsu W K, Hare J P, Townsend P D, Prassides K, Cheetham A K, Kroto H W and Walton D R M 1997 *Nature* **388** 52

[10] Ren Z F, Huang Z P, Xu J W, Wang J H, Bush P, Siegal M P and Provencio P N 1998 *Science* **282** 1105

[11] Sung S L, Tsai S H, Tseng C H, Chiang F K, Liu X W and Shih H C 1999 *Appl. Phys. Lett.* **74** 197

[12] O'Connell M J, Bachilo S M, Huffman C B, Moore V C, Strans M S, Haroz E H, Rialon K L, Boul P J, Noon W H, Kittrell C, Ma J, Hauge R H, Weisman R B and Smalley R E 2002 *Science* **297** 593

[13] Riggs J E, Guo Z, Carroll D L and Sun Y P 2000 *J. Am. Soc.* **122** 5879

[14] Sun Y, Wilson S R and Chuster D I 2001 *J. Am. Soc.* **123** 5348

[15] Andrews R, Jacques D, Rao A M, Derbyshire F, Qian D, Fan X and Dickey E C 1999 *Chem. Phys. Lett.* **303** 467

[16] AndoY, Zhao X and Kaneto K 1999 *J. Inorganic Materials* **1** 77

[17] Kawashima Y and Katagiri G 1999 *Phys. Rev.* B **59** 62

[18] Kasuya A, Sasaki Y, Staito Y, Kohji Y K and Nishina Y 1997 *Phys. Rev. Lett.* **78** 4434

[19] Pichler T, Knupfer M, Golden M S, Fink J, Rinzler A and Smalley R E 1998 *Phys. Rev. Lett.* **80** 4729

[20] Guo J, Yang C, Li Z M, Bai M and Liu H J 2004 *Phys. Rev. Lett.* **93** 17402