

Synthesis of Carbon Nanotube by Thermal CVD

韓世澤、姚品全

E-mail: 9500952@mail.dyu.edu.tw

ABSTRACT

Nano-Sized nickel particles were deposited on silicon substrates by sol-gel process as the catalysts for the growth of carbon nanotubes using atmospheric thermal CVD process. The results show that several parameters which incluning during the synthesis has prominent effect on the diameter and morphology of the carbon nanotube. The pretreatment mode, ambient gases, its flow rate and synthesis temp. A pretreatment temperature of 800 ~ 900 is adequate for CNT growth. Ammonia is a better pretreatment gas than hydrogen in reduning the content of amorphous carbonaceous by produce. The optimal temperature range for CNT growth lies between 700 to 900 . Addition of hydrogen, had better effect on nanotube quality than those without H₂ addition. Under proper ratio of H₂/C₂H₂,CNT grows at considerable rate. It took about 10~20 minutes for complete CNT growth under H₂ containing ambient. For better control of the orientation of as grown CNTs. more detail information about the effect of NH₃ H₂ and C₂H₂ would be necessary.

Keywords : catalyst, chemical vapor deposition,carbon nanotubes

Table of Contents

封面內頁 簽名頁 授權書	iii 中文摘要
	iv 英文摘要
	v 謝誌
vi 目錄	x 表目錄
vii 圖目錄	xiv 第一章 緒論
	1 1.1 前言
	1 1.2 研究動機及目的
	2 第二章 文獻探討
	4 2.1 MWNTs及SWNTs的合成
	4 2.2 奈米碳管的結構
	4 2.3 奈米碳管的成長機制
	24 2.4 奈米碳管之純化方法
	29 2.4.1 過濾法
	29 2.4.2 氧化法
	30
2.4.3 層析法	31 2.5 溶膠-凝膠法簡介
	31 2.6 添加氫氣成長奈米碳管之機制
	38 2.6.1 添加氫氣對碳沉積型態之影響
	38 第三章 實驗設備與方法
	43 3.1 CNT成長裝置實驗步驟
	43 3.1.1 Thermal CVD 系統
	43 3.1.2 實驗方法
	44 3.1.3 觸媒之溶膠-凝膠法及旋轉塗佈法
	45 3.2 實驗分析儀器與注意事項
	47 3.2.1 掃描式電子顯微鏡
	47 3.2.2
高解析穿透式電子顯微鏡	48 3.2.3 Raman Spectrum
	50 第四章 結果與討論
	53 4.1 前處理對CNT成長特性之影響
	53 4.1.1 鎳觸媒經前處理後之型態
	53 4.1.2 使用氫氣、氮氣及其混合氣體之比較
	56 4.1.3 未前處理無法成長奈米碳管
	61 4.1.5 不同參數對CNT成長之影響
60 4.1.4 前處理時間對CNT成長之影響	65 4.1.6 前處理作用溫度之影響
	72 4.2.1 成長奈米碳管時還原氣體之影響
	72 4.2.2 成長奈米碳管添加氫氣作用時間影響
	72 4.2.3 成長奈米碳管添加氫氣作用溫度影響

... 82 4.2.4 合成奈米碳管乙炔氫氣氬氣等氣體流量比例影響	85 4.2.5 前處理及奈米碳管成長
參數之關係	88 第五章 結論及未來展望
... 89 5.1 結論	89 5.2
未來展望	90 參考文獻
	91

REFERENCES

- [1] S. Iijima. (1991). Helical microtubules of graphite carbon. *Nature*. 354:56. [2] S. Iijima and T. Single-shell. (1993). Carbon nanotube of 1nm diameter. *Nature*. 363:603-604. [3] D.S. Bethune, C. H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers. (1993) Electronic structure simulations of carbon nanotubes. *Nature*. 363:605. [4] M. Tomita, Y. Saito and T. Hayashi, *Jpn. J. Appl. Phys.* 32 (1993) L280 [5] C. Guerret-Piecourt, Y. L. Bouar, A. Loiseau and H. Pascard. (1994). *Nature*. 372:761. [6] Y. Saito and Yoshikawa. (1993). *J. Crystal Growth*.134:154. [7] Y. Tanaka, K. Okahara, M. Okada and T. Yamaba. (1992). *Chem. Phys. Lett.*, 191:2204. [8] T. W. Odom, J. L. Huang, P. Kim and C. M. Lieber. (1998). Atomic structure and electronic properties of single walled carbon nanotubes. *Nature*. 391: 62. [9] M. M. J. Treacy, T. W. Ebbesen and J. M. Gibson. (1996). Exceptionally high Young ' s modulus observed for individual carbon nanotubes. *Nature*. 381: 678. [10] W. A. de Heer, A. Chatelain and D. Ugarte. (1995). A Carbon Nanotube Field-Emission Electron Source. *Science*.270:1179. [11] C. Niu, E.K. Sichel, R. Hoch, D. Moy and H. Tennent. (1997). High Power Electrochemical Capacitors Based on Carbon Nanotube Electrodes. *Appl. Phys. Lett.* 70:1480. [12] W.Z. Li, J.G. Wen, Y. Tu, Z.F. Ren. (2001).Effect of gas pressure on the growth and structure of carbon nanotubes by chemical vapor deposition. *Appl. Phys. A*. 73:259. [13] (2002).*Appl. Phys.A*. 74:397-402. [14] (2005).*CPL*. 403:320-323. [15] APL. 86(2005)23109. [16] APL. 83.(25)(2003)5307. [17] W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, G. Wang. (1996). Large-scale synthesis of aligned carbon nanotubes. *Science*. 274:1701-1703. [18] Z. W. Pan, S. S. Xie, B. H. Chang, C. Y. Wang, L. Lu, W. Liu, W. Y. Zhou, W. Z. Li, L. X. Qian. (1998). Very long carbon nanotubes. *Nature*. 394:631. [19] USP. 5830326 [20] USP. 5753088 [21] P. M. Ajayan, T. Ichihashi and S. Iijima. (1993). Distribution of pentagons and shapes in carbon nano-tubes and nano-particles. *Chem. Phys. Lett.* 202:284. [22] X. K. Wang, X.W. Lin, V.P. Dravid, J. B. Ketterson and R. P. H. Chang. (1995).Carbon nanotubes synthesized in a hydrogen arc discharge. *Appl. Phys. Lett.* 66:2430. [23] Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita and T. Hayashi. (1993). *Chem. Phys. Lett.* 304:277. [24] Yahachi Saito, New Diamond and Frontier Carbon Technology Vol.9, NO. 1 (1999) [25] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy dela chapelle, S. Lefrant, P. Deniard, R. Lee & J. E. Fischer. (1997). Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature*. 388:756 [26] Ching-Hwa Kiang. (2000). Growth of Large Diameter Single-Walled Carbon Nanotubes. *J. Phys. Chem. A*. 104:2454 [27] C. H. Kiang, W. A. Goddard, . (1996). *Phys. Rev. Lett.* 76:2515 [28] T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R. E. Smalley. (1995).Catalytic growth of single-walled nanotubes by laser vaporization. *Chem. Phys. Lett.* 243:49 [29] Ivanov, V. ,Nagy, J.B. et al. (1994). The study of carbon nanotubes produced by catalytic method. *Chem. Phys. Lett.* 223:329. [30] R. sen, A. Govindaraj and C. N.R. Rao. (1997). Carbon nanotubes by the metallocene route. *Chem. Phys. Lett.* 267:276 [31] W. Z. Li, et al.(1996). Large-Scale Synthesis of Aligned Carbon Nanotubes. *Science*. 274:1701 [32] Shoushan Fan m et al. (1999). Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties. *Science*. 283:512 [33] Shaoming Huang , Liming Dai , and Albert W. H. Mau. (1999). Patterned Growth and Contact Transfer of Well-Aligned Carbon Nanotube Films. *J. Phys. Chem. B*. 103:4223 [34] Pavel Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D.T. Colbert, K. A. Smith, R. E. Smalley. (1999). *Chem. Phys. Lett.* 313: 97 [35] H. M. Cheng, F. Li and G. Su, H. Y. Pan and L.L. He, X. Sun and S. Dresselhaus. (1998). Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons. *Appl. Phys. Lett.* 72:3282 [36] Kroto, H.W., Heath, J.R., OBrien, S.C., Curl, R.F. and Smalley, R.E. , " C60: Buckminsterfullerene " , *Nature* 318, pp.162-163, 1985. [37] 謝力宜, 工業材料雜誌,185 期, pp.124-127, 2002. [38] Kin-Tak Lau, David Hui, " The revolutionary creation of new advanced materials-carbon nanotube composites " , Composites : Part B 33, pp.263-277, 2002. [39] A. Fonseca et al., " Model Structure perfectly Graphitizable Coiled Carbon Nanotubes " , Carbon 33, No.12, pp.1759-1775, 1995. [40] M. Ahlskog et al., " Ring formations from catalytically synthesized carbon nanotubes " , *Chemical Physics Letters* 300, pp.202-206, 1999. [41] Sumio Iijima et al., " Metal-free production high quality multi-wall carbon nanotubes, in which innermost nanotubes have a diameter of 0.4nm " , *Chemical Physics Letters* 356, pp.595-600, 2002. [42] R. Setton and N. Setton , " Carbon nanotubes: . Toroidal structures and limits of model for the construction of helical and s-shaped nanotubes " , *Carbon* 35, pp.497, 1997. [43] L. P. Biro et al., " From straight carbon nanotubes to Y-branched and coiled carbon nanotubes " , *Diamond and Related Materials* 11, pp.1081-1085, 2002. [44] <http://www.stut.edu.tw/nano/N14.htm> [45] Alan M, " Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers " , *Nature* 395, pp.878 ~ 881, 1998. [46] Z.W.Pan et al., " Direct growth of aligned open carbon nanotubes by chemical vapor deposition " , *Chem. Phys. Lett.* 299, pp.97 ~ 102, 1999. [47] Alan M et al., " Chemical vapor deposition of methane for single-walled carbon nanotubes " , *Chemical physics letters* 292, pp.567 ~ 574, 1998. [48] M. Grujicic et al., " An atomic-scale analysis of catalytically-assisted chemical vapor deposition of carbon nanotubes " , *Materials Science and Engineering* B94, pp.248,2002. [49] 唐炯文, 以化學氣相沉積法成長直立陣列碳奈米管之研究,國防大學中正理工學院兵器系統工程 研究所碩士論文,2000. [50] Morinubo Fundo et al., *Carbon nanotubes*, pp.97, 1996. [51] 謝峰欣, 利用sol-gel製作矽質薄膜之研究, 中國文化大學材料科學與製造研究所碩士論

文, (2001). [52] C. Jeffrey Brinker et al., Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing , pp.96,45. [53] 陳文章等人, 以溶膠凝膠法制備有機無基混成材料, 化工46 , 58(1999)59. [54] 李元堯, 21 世紀尖端材料-奈米碳管, 化工技術期刊-奈米材料與應用專輯, 11(3), 140-159, 民國92 年. [55] Katoh R, Tasaka Y, Sekreta E, Yumura M, Ikazaki F, Kakudate Y, Fujiwara S, 1999, Sonochemical production of a carbon nanotube, Ultrasonics Sonochemistry, 6, 185-187. [56] L. S. K. Pang, J. D. Saxby, S. P. Chatfield. (1993). Thermogravimetric analysis of carbon nanotubes and nanoparticles. J. Phys. Chem.. 97:6941. [57] B. C. Satishkumar, A. Govindaraj, J. Mofokeng, G. N. Subbanna, C. N.R. Rao.(1996). The decoration of carbon nanotubes by metal nanoparticles. J. Phys. B. 29:4925. [58] R Saito.(1998). Physical properties of Carbon Nanotubes, 77-79. [59] M.S.Dresselhaus, 2002, "Abstract for Symposium on Nanostructured Materials " MIT , 175th Anniversary of KTH , April 11-12, Single Nanotube Spectroscopy, Cambridge MA 02139. [60] A Jorio, A.G.Souza, G.Dresselhaus, M.S.Dresselhaus, 2002, "G-band Raman Spectra of Isolated Single Wall Carbon Nanotube:Diameter and Chirality", Sependence, Mat.res. soc.symp.proc. vol.706. [61] A.Maroto Valiente et al. In situ study of carbon nanotube formation by CH decomposition on an iron-based catalyst, Carbon 38, pp.2005-2006, 2000.