

以常壓熱化學氣相沉積法成長奈米碳管之研究

韓世澤、姚品全

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

摘要

本研究以常壓熱化學氣相沉積法(atmospheric thermal CVD) 成長奈米碳管。藉溶膠-凝膠法(sol-gel)將觸媒先驅物旋轉塗佈於矽基板，經由線上還原，(In-Situ reduction)以化學氣相沉積法成長奈米碳管。由我們的研究可觀察到幾個現象：(1)前處理時間、氣體流量、溫度、氣體種類、混合比等參數可用以控制奈米碳管之直徑，(2)800 ~ 900 之前處理溫度有利於奈米碳管之成長，(3)以氫氣作為前處理之氣體比氫好，(4)700 ~ 900 之溫度有利於奈米碳管之成長，(5)添加氫氣比不添加時，可以成長更完美型態的CNT，(6)氫氣、乙炔混合比例相當時有利於奈米碳管之成長，(7)添加氫氣，作用時間約10-20分鐘後有利於奈米碳管之成長，(8)如要控制奈米碳管之成長方向，未來可能需瞭解氫氣、氫氣和乙炔流量之效應。

關鍵詞：觸媒，化學氣相沉積法，奈米碳管

目錄

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
.	vii	圖目錄
.	xiv	第一章 緒論
.	1	1.1 前言
.	2	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
.	19	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
.	31	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、氫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
.	60	4.1.4 前處理時間對CNT成長之影響
.	61	4.1.5 不同參數對CNT成長之影響
.	65	4.1.6 前處理作用溫度之影響
.	68	4.2 成長奈米碳管
.	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
.	78	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氫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

參考文獻

- [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, 以溶膠凝膠法製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.