

# 熱化學氣相沉積奈米碳管之場發射特性

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## 摘要

本實驗利用熱化學氣相沉積法來成長奈米碳管，主要的碳原子來源為甲烷，並以氬氣當載氣，將甲烷帶入爐管中反應，利用觸媒熱分解效應將甲烷分解成碳原子並成長出碳管。本研究中，我們針對催化劑厚度與成長溫度以及不同的催化劑三種因素對於所成長奈米碳管的結構性質及場發射特性的影響來進行深入研究。我們使用拉曼光譜及SEM來分析的奈米碳管的結構性質，而奈米碳管的場發射特性則是在高真空狀況下施加很大的電場所量測得到。從拉曼光譜及SEM的分析我們發現，當催化劑鎳膜成長厚度愈厚時，催化劑鎳膜在成核時期所形成鎳催化顆粒會愈大，造成碳管數量變少，而碳管的直徑卻會逐漸增大。當溫度較低時，所提供的熱能可能並不足以將原子填補至適當的結晶位置，所以在奈米碳管中會形成較多的結晶缺陷。而當溫度被提高時，碳原子的表面遷移速率增大，因此可以幫助碳管的成長，石墨結晶化程度也較好。而且從不同催化劑(Fe,Co,Ni)比較當中，以鎳膜成長的奈米碳管的性質最佳。由F-N圖我們發現，鎳膜厚度增加的確會使功函數增大，場發射電流會因為所成長的碳管數量減少、碳管尖端電場增強效應減低、及碳管功函數增大三個因素同時作用而降低。這種場發射電流的改變不僅是因為所成長的碳管數量及直徑的改變所造成的，所成長碳管的結晶結構及功函數也會改變，造成電子發射難易程度的改變也是一個非常重要的因素。

關鍵詞：奈米碳管；場發射；熱化學氣相沉積

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## 參考文獻

1. Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, 354, 7, 56-58.
2. Radushkevich, L. V., & Lukyanovic, V. M. (1952). *Zh. Fiz. Khim.* 26, 88.
3. Hofer, L. J. E., Sterling, E., & MacCartney, J. T. (1955). *J. Phys. Chem.*, 59, 6210.
4. Kroto, H. W., Heath, J. R., O' Brian, S. C., Curl, R. F., & Smalley, R. E. (1985). C60: Buckminsterfullerene. *Nature*, 318 (6042), 162-163.
5. Kratschmer, W., Lamb, L. D., Fostiropoulos, K., & Huffman, D. R. (1990). Solid C60: A new form of carbon. *Nature*, 347, 354-358.
6. Maiti, Brabec, C. J., Roland, C., & Bernholc, J. (1995).

Theory of carbon nanotube growth. *Phys. Rev. B*, 15; 52(20), 14850-14858. 7. Kusunoki, M., Rokkaku, M., & Suzuki, T. (1997). Epitaxial carbon nanotube film self-organized by sublimation decomposition of silicon carbide. *Appl. Phys. Lett.*, 71(18), 2620-2622. 8. Zhang, Y., Gu, H., & Iijima, S. (1998). Single-wall carbon nanotubes synthesized by laser ablation in a nitrogen atmosphere. *Appl. Phys. Lett.*, 73(26), 3827-3829. 9. Ebbesen, T. W. (1997). Carbon Nanotubes: Preparation and properties. CRC Press, Boca Raton, 139-162. 10. Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature*, 363, 603-605. 11. Bethune, D. S., Kiang, C. H., deVries, M. S., Gorman, G., Saroy, R., Vazquez, J., & Beyers, R. (1993). Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer walls. *Nature*, 363, 605-607. 12. Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y. H., Kim, S. G., Rinzler, A. G., Colbert, D. T., Scuseria, G. E., Tomanek, D., Fischer, J. E., & Smalley, R. E. (1996). Crystalline ropes of metallic carbon nanotubes. *Science*, 273, 483-487. 13. Peter J. F. Harris, (1999). Carbon nanotubes and related structure. Cambridge University Press, Chapter 4.2: Electronic properties of nanotube. 16 – 54. 14. Charlier, J. C., & Issi, J. P. (1998). Electronic structure and quantum transport in carbon nanotubes. *Applied Physics A: Materials Science & Processing*, 67, 79-87. 15. Haus, M. D., Dresselhaus, G., Eklund, P., & Saito, R. (1998). Carbon nanotubes. *Physics World*, 11, 33-38. 16. Mintmire, J. W. & White, C. T. (1998). First-principles band structures of armchair nanotubes. *Applied Physics A: Materials Science & Processing*, 67, 65-69. 17. Dresselhaus, M. S., Dresselhaus, G., & Saito, R. (1995). Physics of carbon nanotubes. *Carbon*, 33, 883-891. 18. Jo, S. H., Tu, Y., Huang, Z. P., Carnahan, D. L., Wang, D. Z., & Ren, Z. F. (2003). Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties. *Appl. Phys. Lett.*, 82, 3520-3522. 19. Wang, Z. L., R. P. Gao, W. A. deHeer, P. Poncharal, (2002). In situ imaging of field emission from individual carbon nanotubes and their structural damage. *Appl. Phys. Lett.*, 80, 856-858. 20. Bonard, J. M., Dean, K. A., Coll, B. F., & Klinke, C. (2002). Field emission of individual carbon nanotubes in the scanning electron microscope. *Phys. Rev. Lett.*, 89(19), 4, 1976021-24. 21. Rinzler, A. G., Hafner, J. H., Nikolaev, P., Lou, L., Kim, S. G., Tomanek, D., Nordlander, P., Colbert, D. T., & Smalley, R. E. (1995). Unraveling nanotubes: field emission from an atomic wire. *Science*, 269, 1550-1553. 22. DeHeer, W. A., Chatelain, A., & Ugarte, D. (1995). A carbon nanotube field-emission electron source. *Science*, 270, 1179-1180. 23. Shyu, Y. M., & Hong, F. C. N. (2001). Low-temperature growth and field emission of aligned carbon nanotubes by chemical vapor deposition. *Mater. Chem. Phys.*, 72(2), 223-227. 24. Wang, Y. H., Lin, J., & Huan, C. H. A. (2002). Macroscopic field emission properties of aligned carbon nanotubes array and randomly oriented carbon nanotubes layer. *Thin Solid Films*, 405(1-2), 243-247. 25. Bonard, J., Salvetat, J., Stockli, T., de Heer, W. A., Forro, L., & Chatelain, A. (1998). Field emission from single-wall carbon nanotube films. *Appl. Phys. Lett.*, 73(7), 918-920. 26. Wang, Q. H., Corrigan, T. D., Dai, J. Y., & Chang, R. P. H. (1997). Field emission from nanotube bundle emitters at low fields. *Appl. Phys. Lett.*, 70(24), 3308-3310. 27. Sung, S. L., Tsai, S. H., Tseng, C. H., Chiang, F. K., Liu, X. W., & Shih, H. C. (1999). Well-aligned carbon nanotubes synthesized in anodic alumina by electron cyclotron resonance chemical vapor deposition. *Appl. Phys. Lett.*, 74(2), 197-199. 28. Saito, Y., & Uemura, S. (2000). Field emission from carbon nanotubes and its application to electron sources. *Carbon*, 38(2), 169-182. 29. Yumura, M., Ohshima, S., Uchida, K., Tasaka, Y., Kuriki, Y., Ikazaki, F., Saito, Y., & Uemura, S. (1999). Synthesis and purification of multi-walled carbon nanotubes for field emitter applications. *Diamond and Related Materials*, 8, 785-791. 30. Kuttel, O. M., Groning, O., Emmenegger, C., Nilsson, L., Mallard, E., Diederich, L., & Schlapbach, L. (1999). Field emission from diamond, diamond-like and nanostructured carbon films. *Carbon*, 37, 745. 31. 楊素華、藍慶忠 (2004)。科技發展。382期 , 71。 32. Saito, Y., Yoshikawa, T., Inagaki, M., Tomita, M., & Hayashi, T. (1993). Growth and structure of graphitic tubules and polyhedral particles in arc-discharge. *Chemical Physics Letters*, 204, 277-282. 33. Dai, H., Rinzer, A. G., Nikolaev, P., Thess, A., Colbert, D. T., & Smalley, R. E. (1996). Single-wall nanotubes produced by metal catalyzed disproportionation of carbon monoxide. *Chem. Phys. Lett.*, 260, 471-475. 34. Lee, Y. H., Kim, S. G., & Tomanek, D. (1997). Catalytic growth of single-wall carbon nanotubes: an Ab initio study. *Phys. Rev. Lett.*, 78, 2393-2396. 35. Endo, M., & Kroto, H. W. (1992). Formation of carbon nanofibers. *Journal of Physical Chemistry*, 96, 6491-6944. 36. Baker, R. T. K., & Harries, P. S. (1978). The formation of filamentous carbon. *Chemistry and Physics of Carbon*, New York: Marcel Dekker, 14, 83-165. 37. Baker, R. T. K., Braker, M. A., Harries, P. S., Feates, F. S., & Waite, R. J. (1972). Nucleation and growth of carbon deposits from nickel catalyzed decomposition of acetylene. *Journal of Catalysis*, 26, 51-62. 38. Oberlin, A., Ento, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. *Journal of Crystal Growth*, 32, 335-349. 39. Baird, T., & Fryer, J. R. (1974). Carbon formation on iron and nickel foils by hydrocarbon pyrolysis reactions at 700 °C. *Carbon*, 12, 591-602. 40. Oberlin, A., Ento, M., & Koyama, T. (1976). High resolution electron microscope observations of graphitized carbon fibers. *Carbon*, 14, 133-157. 41. Journet, C. et al., (1998). Production of carbon nanotubes. *Applied Physics*, .67, 1-9. 42. Alan, M. et al., (1998). Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chem. Phys. Lett.*, 292, 567-574. 43. Yacaman, M. J., Yoshida, M. M., Rendon, L., & Santiesteban, J. G. (1993). Catalytic growth of carbon microtubules with fullerene structure. *Appl. Phys. Lett.*, 62, 202-204. 44. Baker, R. T. K., & Chludzinski, J. J. (1980). Filamentous carbon growth on nickel – iron surfaces—effect of various oxide additives. *Journal of Catalysis*, 64, 464-478. 45. Baker, R. T. K., Harries, P. S., Thomas, R. B., & Waite, R. J. (1973). Formation of filamentous carbon from iron and chromium catalyzed decomposition of acetylene. *Journal of Catalysis*, 30, 86-95. 46. Baker, R. T. K., & Waite, R. J. (1975). Formation of carbonaceous deposit from the platinum-iron catalyzed decomposition. *Journal of Catalysis*, 37, 101-105. 47. Jung, M., Eun, K. Y., Lee, J. K., Baik, Y. J., Lee, K. R., & Park, J. W. (2001). Growth of carbon nanotubes by chemical vapor deposition. *Diamond and Related Materials*, 10, 1235-1240. 48. Xie, S., Li, W., Pan, Z., Chang, B., & Sun, L. (2000). Self-assembly of shape-controlled nanocrystals and their in-situ thermodynamic properties. *Materials Science and Engineering A*, 286, 11-15. 49. Chen, X. H., Feng, S. Q., Ding, Y., Peng, J. C., & Chen, Z. Z. (1999). The formation conditions of carbon nanotubes array based on FeNi alloy island films. *Thin Solid Films*, 339, 6-9. 50. Lee, C. J., Park, J., Kang, S. Y., & Lee, J. H. (2000). Growth of well-aligned carbon nanotubes on a large area of Co-Ni co-deposited silicon oxide substrate by thermal chemical vapor deposition.

Chemical Physics Letters, 323, 554-559. 51. Terrones, M. et al., (1998). Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. Chemical Physics Letters, 285, 299-305. 52. Liang, Q., Li, Q., Chen, D. L., Zhou, D. R., Zhang, B. L., & Yu, Z. L. (2000). Carbon nanotube prepared in the atmosphere of partial oxidation of methane. Chemical Journal of Chinese Universities-Chinese, 21(4), 623-625. 53. Hernadi, K., Fonseca, A., Nagy, J. B., Siska, A., & Kiricsi, I. (2000). Production of nanotubes by the catalytic decomposition of different carbon-containing compounds. Applied Catalysis A: General, 199, 245-255. 54. Li, W. Z., Xie, S. S., Qian, L. X., Chang, B. H., Zou, B. S., Zhou, W. Y., Zhao, R. A., & Wang, G. (1996). Large-scale synthesis of aligned carbon nanotubes. Science, 274, 1701-1703. 55. Pan, Z. W., Xie, S. S., Chang, B. H., Sun, L. F., Zhou, W. Y., & Wang, G. (1999). Direct growth of aligned open carbon nanotubes by chemical vapor deposition. Chemical Physics Letters, 299, 97-102. 56. Li, A. P., Muller, F., Birner, A., Nielsch, K., & Gosele, U. (1998). Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina. J. Appl. Phys., 84, 6023-6026. 57. Masuda, H., Yamada, H., Satoh, M., & Asoh, H. (1997). Highly ordered nanochannel-array architecture in anodic alumina. Appl. Phys. Lett., 71, 2770-2772. 58. Masuda, H., & Satoh, M. (1996). Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask. Jpn. J. Appl. Phys., part 2, 35, 126-129. 59. Nolan, P. E., Schabel, M. J., & Lynch, D. C. (1995). Hydrogen control of carbon deposit morphology. Carbon, 33, 79-85. 60. Pinheiro, P., Schouler, M. C., Gadelle, P., Mermoux, M., & Dooryhee, E. (2000). Effect of hydrogen on the orientation of carbon layers in deposits from the carbon monoxide disproportionation reaction over Co/Al<sub>2</sub>O<sub>3</sub> catalysts. Carbon, 38(10), 1469-1479. 61. Khassin, A. A., Yurieva, T. M., Zaikovskii, V. I., & Parmon, V. N. (1998). Effect of metallic cobalt particles size on occurrence of CO disproportionation. Role of fluidized metallic cobalt-carbon solution in carbon nanotube formation. Reaction Kinetic and Catalysis Letter, 64, 63-71. 62. Tsai, S. H., Chao, C. W., Lee, C. L., & Shin, H. C. (1999). Bias-enhanced nucleation and growth of the aligned carbon nanotubes with open ends under microwave plasma synthesis. Appl. Phys. Lett., 74, 3462-3464. 63. Huang, Z. P., Xu, J. W., Ren, Z. F., Wang, J. H., Siegal, M. P., & Provencio, P. N. (1998). Growth of highly-oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition. Appl. Phys. Lett., 73, 3845-3847. 64. Ren, Z. F., Huang, Z. P., Wang, D. Z., Wen, J. G., Xu, J. W., Wang, J. H., Calvet, L. E., Chen, J., Klemic, J. F., & Reed, M. A. (1999). Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot. Appl. Phys. Lett., 75, 1086-1088. 65. Fan, S., Chapline, M. G., Franklin, N. R., Tombler, T. W., Cassell, A. M., & Dai, H. (1999). Self-oriented regular arrays of carbon nanotubes and their field emission properties. Science, 283, 512-514. 66. Kwon, Y. K., Lee, Y. H., Kim, S. G., Jund, P., Tomanek, D., & Smalley, R. E. (1997). Morphology and stability of growing multiwall carbon nanotubes. Phys. Rev. Lett., 79, 2065-2068. 67. Oh, D. H., & Lee, Y. H. (1998). Stability and cap formation mechanism of single-walled carbon nanotubes. Phys. Rev. B, 58, 7407-7411. 68. Kuznetsov, V. L., Usoltseva, A. N., Chuvalin, A. L., Obraztsova, E. D. & Bonard, J. M. (2001). Thermodynamic analysis of nucleation of carbon deposits on metal particles and its implications for the growth of carbon nanotubes. Phys. Rev. B, 64, 235401-1. 69. Jacoby, S. L. S., Kowalik, J. S., & Pizzo, J. T. (1972). Iterative methods for nonlinear optimization problems. Prentice Hall, Inc., Englewood Cliffs, New Jersey, ISBN 0-13-.508199-X, 79-83. 70. Fowler, R. H., & Nordheim, L. W. (1928). Electron emission in intense electric fields. Proceedings of Royal Society of London, 119, 173-181.