

# 奈米碳管電漿後處理對場發射特性之影響

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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(CNT)，主要的碳原子來源為甲烷(CH<sub>4</sub>)，並以Ar當載氣，將CH<sub>4</sub>帶入爐管中反應，利用觸媒熱分解效應將CH<sub>4</sub>分解成碳原子並成長出典型的CNT。之後利用CF<sub>4</sub>及Ar對典型的CNT進行電漿後處理。我們也用拉曼光譜、SEM、EDS、TEM來分析經過電漿處理後的CNT微結構。從實驗數據得知，電漿處理後的CNT頂端的被修改，而且非晶質碳也被移除。這些因素會導致場發射電流的增大。另外，從場發射的分析，經過CF<sub>4</sub>電漿處理2分鐘的場發射電流達到9.5 mA/cm<sup>2</sup>，而Ar電漿處理2分鐘後場發射電流只有3 mA/cm<sup>2</sup>。這個相當大的差異可以歸因於CF<sub>4</sub>電漿處理之後所發現的聚集現象，這聚集現象可以提供許多的場發射點。

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. Kroto, H. W., Heath, J. R., O' Brian, S. C., Curl, R. F., & Smalley, R. E. (1985). C<sub>60</sub>: Buckminsterfullerene. *Nature*, Vol. 318 (6042), pp. 162-163.
2. Kratschmer, W., Lamb, L. D., Fostiropoulos, K., & Huffman, D. R. (1990). Solid C<sub>60</sub>: A new form of carbon. *Nature*, Vol. 347, pp. 354-358.
3. Maiti, Brabec, C. J., Roland, C., & Bernholc, J. (1995). Theory of carbon nanotube growth. *Phys. Rev. B*, Nov 15; Vol. 52(20), pp. 14850-14858.
4. Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, Vol. 354, Nov. 7, pp. 56-58.
5. Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature*, Vol. 363, pp. 603-605.
6. 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*, Vol. 363, pp. 605-607.
7. 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*, Vol. 273, pp. 483-487.
8. Dresselhaus, M. S., Dresselhaus, G., & Saito, R. (1995). *Physics of carbon nanotubes*. Carbon, Vol. 33, pp. 883-891.
9. Peter J. F. Harris, (1999). *Carbon Nanotubes and Related Structure*. Cambridge University Press, Chapter 4.2: Electronic properties of nanotube. pp. 16 – 54.
10. Dresselhaus, M.S.; Dresselhaus, G.; Eklund, P.C. (1996) *Fullerenes and Carbon Nanotubes*, Academic, San Diego.
11. Charlier, J. C., & Issi, J. P. (1998). Electronic structure and quantum transport in carbon nanotubes. *Applied Physics A: Materials Science & Processing*, Vol. 67, pp. 79-87.
12. Haus, M. D., Dresselhaus, G., Eklund, P., & Saito, R. (1998). Carbon nanotubes. *Physics World*, Vol. 11, pp. 33-38.
13. Mintmire, J. W. &

White, C. T. (1998). First-principles band structures of armchair nanotubes. *Applied Physics A: Materials Science & Processing*, Vol. 67, pp. 65-69.

14. K. Tohji, T. Goto, H. Takahashi, Y. Shinoda, N. Shimizu, B. Jeyadevan, I. Matsuoka, Y. Saito, A. Kasuya, T. Ohsuna, K. Hiraga, Y. Nishina, J. (1997) *Phys. Chem.* Vol.101, pp. 1974.

15. S. Bandow, A.M. Rao, K.A. Williams, A. Thess, R.E. Smalley, P.C. Eklund, J. (1997) *Phys. Chem. B* Vol.101 pp. 8839.

16. E. Dujardin, T.W. Ebbesen, A. Krishnan, M.M.J. Treacy, *Adv.Mater.* 10 (1998) pp. 1472.

17. A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macias, P.J. Boul, A.H. Lu, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, R.E. Smalley, (1998) *Appl. Phys. A* Vol 67 pp.29.

18. K.B. Shelmov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman, R.E. Smalley, (1998) *Chem. Phys. Lett.* Vol 282 pp. 429.

19. A.C. Dillon, T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla, M.J. Heben, *Adv. Mater.* 11 (1999) , pp.1354.

20. Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, (1999) *Solid State Commun.* 112 , pp.35.

21. I.W. Chiang, B.E. Brinson, R.E. Smalley, J.E. Margrave, R.H. Hauge, J. (2001) *Phys. Chem. B* 105, pp.1157.

22. J.M. Moon, K.H. An, Y.H. Lee, Y.S. Park, D.J. Bae, G.S. Park, J. (2001) *Phys. Chem. B* 105, pp.5677.

23. S. Niyogi, H. Hu, M.A. Hamon, P. Bhowmik, B. Zhao, S.M. Rozenzhak, J. Chen, M.E. Itkis, M.S. Meier, R.C. Haddon, *J. Am. Chem. Soc.* 123 (2001) , pp.733.

24. A.R. Harutyunyan, B.K. Pradhan, J.P. Chang, G.G. Chen, P.C. Eklund, *J. Phys. Chem. B* 106 (2002) , pp.8671.

25. M.T. Martinez, M.A. Callejas, A.M. Benito, W.K. Maser, M. Cochet, J.M. Andre's, J. Schreiber, O. Chauvet, J.L.G. Fierro, *Chem. Commun.* (2002); , pp.1000.

26. E. Va'zquez, V. Georgakilas, M. Prato, *Chem. Commun.* 2002; 230

Jo, S. H., Y. Tu, Z. P. Huang, D. L. Carnahan, D.Z. Wang and Z. F. Ren (2003) Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties. *Applied Physics Letters*, 82(20) , pp.3520-3522.

27. Shelimov, K.B.; Esenaliev, R.O.; Rinzler, A.G.; Huffman, C. B.; Smalley, R.E. *Chem. Phys. Lett.*, 282, (1998)429.

28. Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima. *Solid State Communications*, Vol.112, (1999) , pp.35-37.

29. Duesberg, G.S.; Burghard, M.; Muster, J.; Philipp, J.; Roth, S. *Chem. Commun.*, 1998, (1998) , pp.435.

30. S. H. Jo, Y. Tu, Z. P. Huang, D. L. Carnahan, D. Z. Wang, Z. F. Ren, *Appl. Phys. Lett.* 82 (2003) 3520.

31. Z. L. Wang, R. P. Gao, W.A. de Heer, P. Poncharal, *Appl. Phys. Lett.* 80 (2002) 856.

32. J. M. Bonard, K. A. Dean, B. F. Coll, C. Klinke, *Phys. Rev. Lett.* 89 (2002) 197602.

33. H. Folwer and L. Nordheim, (1928) *Proc. R. Soc. London, Ser A*, Vol.119, pp.683

34. P.G. Collins and A.Zettl, (1997) *Phys. Rev. B* 55, pp.9391

35. S. Han and J. Ihm, *Phys. Rev. B*, Vol.66, 241402 (2002); Changwook Kim, Bongsoo Kim, Seung Mi Lee, Chulsu Jo and Young Hee Lee, *Phys. Rev. B*, Vol.65, pp.418, 36.

V.I.Trefilov, D.V.Schur, B.P.Tarasov, Yu.M.Shul'ga, A.V.Chernogorenko, .K.Pishuk, S.Yu.Zaginaichenko. *Fullerenes is a basis of materials for future?*. Kiev, 2001, pp.148.

37. E.G.Rakov. *Uzpekhi Khim.*, (2000), Vol. 69, N 1, pp.41.

38. Terrones M., Hsu W.K., Kroto H.W., Walter D.R. (1999) *Top. Curr. Chem.*, Vol 199, pp. 189.

39. Journet C., Bernier P. (1998) 1 *Appl. Phys. A: Mater. Sci. Process*, A67(1),.

40. Ajayan P. M.. *Chem. Rev.*, (1999)1787.

41. S. Iijima; Ichihashi, (1993) *T. Nature*, Vol 363, pp. 603.

42. A. Wadhawan, R.R. Stallcup, J.M. Perez, (2001) *Appl. Phys.* Vol.78 , pp. 108.

43. Q.H. Wang, T.D. Corrigan, J.Y. Dai, R.P.H. Chang, A.R. Krauss, *Appl. Phys. Lett.* 70 (1997) 3308.

44. C.Y. Zhi, X.D. Bai, E.G. Wang, *Appl. Phys. Lett.* 81 (2002) 1690.

45. H. Burbert, S. Haiber, W. Brandl, G. Marginean, M. Heintze, V. Brunser, (2003) *Diamond Relat. Mater.*, Vol.12 , pp. 811.

46. Ke Yu, Ziqiang Zhu, Yongsheng Zhang, Qiong Li, Weiming Wang, Laiqiang Luo, Xianwen Yu, Honglei Ma, Zhenwen Li, Tao Feng (2004). Change of surface morphology and field emission property of carbon nanotube films treated using a hydrogen plasma. *Applied Surface Science*, Vol. 225, pp. 380 – 388.

47. Y. W. Zhu, F. C. Cheong, T. Yu , X. J. Xu, C. T. Lim, J. T. L. Thong, Z. X. Shen, C. K. Ong, Y.J. Liu, A.T.S. Wee, C. H. Sow (2005). Effects of CF4 plasma on the field emission properties of aligned multi-wall carbon nanotube films. *Carbon*, Vol. 43, pp. 395-400.

48. 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*, Vol. 204, pp. 277-282.

49. Dai, H., Rinzler, 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.*, Vol. 260, pp. 471-475.

50. Lee, Y. H., Kim, S. G., & Tomanek, D. (1997). Catalytic growth of single-wall carbon nanotubes: an ab initio study. *Phys. Rev. Lett.*, Vol. 78, pp. 2393-2396.

51. Endo, M., & Kroto, H. W. (1992). Formation of carbon nanofibers. *Journal of Physical Chemistry*, Vol. 96, pp. 6491-6944.

52. Baker, R. T. K., & Harries, P. S. (1978). The formation of filamentous carbon. *Chemistry and Physics of Carbon*, New York: Marcel Dekker, Vol. 14, pp. 83-165.

53. 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*, Vol. 26, pp. 51-62.

54. Oberlin, A., Ento, M., & Koyama, T. (1976). Filamentous growth of carbon through benzene decomposition. *Journal of Crystal Growth*, Vol. 32, pp. 335-349.

55. Baird, T., & Fryer, J. R. (1974). Carbon formation on iron and nickel foils by hydrocarbon pyrolysis reactions at 700 ° C. *Carbon*, Vol. 12, pp. 591-602.

56. Oberlin, A., Ento, M., & Koyama, T. (1976). High resolution electron microscope observations of graphitized carbon fibers. *Carbon*, Vol. 14, pp. 133-157.

57. Journet, C. et al., (1998). Production of carbon nanotubes. *Applied Physics*, Vol.67, pp. 1-9.

58. Alan, M. et al., (1998). Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chem. Phys. Lett.*, Vol. 292, pp. 567-574.

59. Yacaman, M. J., Yoshida, M. M., Rendon, L., & Santiesteban, J. G. (1993). Catalytic growth of carbon microtubules with fullerene structure. *Appl. Phys. Lett.*, Vol. 62, pp. 202-204.

60. Baker, R. T. K., & Chludzinski, J. J. (1980). Filamentous carbon growth on nickel – iron surfaces—effect of various oxide additives. *Journal of Catalysis*, Vol. 64, pp. 464-478.

61. 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*, Vol. 30, pp. 86-95.

62. Baker, R. T. K., & Waite, R. J. (1975). Formation of carbonaceous deposit from the platinum-iron catalyzed decomposition. *Journal of Catalysis*, Vol. 37, pp. 101-105.

63. 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*, Vol. 10, pp.1235-1240.

64. 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*, Vol. 286, pp. 11-15.

65. 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, Vol. 339, pp. 6-9. 66. 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*, Vol. 323, pp. 554-559. 67. Terrones, M. et al., (1998). Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films. *Chemical Physics Letters*, Vol. 285, pp. 299-305. 68. 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*, Vol. 21(4), pp. 623-625. 69. 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*, Vol. 199, pp. 245-255. 70. 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*, Vol. 274, pp. 1701-1703. 71. 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*, Vol. 299, pp. 97-102. 72. Li, A. P., Muller, F., Birner, A., Nielsch, K., & Gosele, U. (1998). Hexagonal pore arrays with a 50-420 nm inter-pore distance formed by self-organization in anodic alumina. *J. Appl. Phys.*, Vol. 84, pp. 6023-6026. 73. Masuda, H., Yamada, H., Satoh, M., & Asoh, H. (1997). Highly ordered nanochannel-array architecture in anodic alumina. *Appl. Phys. Lett.*, Vol. 71, pp. 2770-2772. 74. Masuda, H., & Satoh, M. (1996). Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask. *Jpn. J. Appl. Phys.*, part 2, Vol. 35, L. 126-129. 75. Nolan, P. E., Schabel, M. J., & Lynch, D. C. (1995). Hydrogen control of carbon deposit morphology. *Carbon*, Vol. 33, pp. 79-85. 76. 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*, Vol. 38(10), pp. 1469-1479. 77. 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*, Vol. 64, pp. 63-71. 78. 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.*, Vol. 74, pp. 3462-3464. 79. 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.*, Vol. 73, pp. 3845-3847. 80. 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.*, Vol. 75, pp. 1086-1088. 81. Fan, S., Chapline, M. G., Franklin, N. R., Tomblor, T. W., Cassell, A. M., & Dai, H. (1999). Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties. *Science*, Vol. 283, pp. 512-514. 82. 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.*, Vol. 79, pp. 2065-2068. 83. Oh, D. H., & Lee, Y. H. (1998). Stability and cap formation mechanism of single-walled carbon nanotubes. *Phys. Rev. B*, Vol. 58, pp. 7407-7411. 84. Kuznetsov, V. L., Usoltseva, A. N., Chuvilin, A. L., Obratsova, 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*, Vol. 64, pp. 235401-1. 85. Lieberman, M. A., and A. J. Lichtenberg, "Principles of plasma discharges and materials processing," John Wiley & Sons Inc., 1994. 86. Xiao, H. (2001). "Introduction to semiconductor manufacturing technology," Prentice Hall Inc..