

The Effects of Chemical Solution Post-Treatment on the Properties of Thermal Chemical Vapor Deposited Carbon Nanotubes

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ABSTRACT

In this work, thermal chemical vapor deposition was utilized to grow carbon nanotubes (CNTs) on Si type, catalyst metal is Ni, methane (CH₄) was the main source for carbon, and argon was used as the carrier gas. CNTs were synthesized from carbon atoms obtained from catalytic thermal decomposition of methane. A simple acid treatment method was applied to functionalize the surface and to modify the structures of multi-walled carbon nanotubes (CNTs) grown on silicon substrates by thermal chemical vapor deposition (thermal CVD) using sulfuric acid (H₂SO₄). Scanning electron microscopy (SEM), Raman spectroscopy, and energy dispersive spectrometer (EDS) were employed to investigate the mechanism causing the modified field emission (FE) properties of the CNT film. From our experimental data, it is found that after 20 min of H₂SO₄ treatment the emitted currents were enhanced by more than one order of magnitude compared with those of the untreated CNTs. We can see that after using H₂SO₄ of 20 min, the emission current density of CNTs reached 9.44 mA/cm². The method provides a simple, economical, and effective way to enhance the CNT field emission properties.

Keywords : carbon nanotubes (CNTs)、emitted currents、thermal chemical vapor deposition (thermal CVD)

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REFERENCES

- [1] S. Iijima, Helical microtubules of graphitic carbon, *Nature*, 354(7) (1991) 56-58.
- [2] M. R. Falvo, G. J. Clary, R. M. Taylor II, V. Chi, F. P. Brooks, Jr., S. Washburn and R. Superfine, Bending and buckling of carbon nanotubes under large strain, *Nature (London)*, 389(6651) (1997) 582-584.
- [3] G. Che, B. B. Lakshmi, E. R. Fisher and R. Martin, Carbon nanotubule membranes for electrochemical energy storage and production, *Nature (London)*, 393 (1999) 346-347.
- [4] N. Hamada, S. Sawada and A. Oshiyama, New one-dimensional conductors-graphitic microtubules, *Phys. Rev. Lett.*, 68(10) (1992) 1579-1581.
- [5] T. Guo, P. Nikolaev, A. G. Rinzler, D. Tomanek, D. T. Colbert and R. E. Smalley, Self-assembly of tubular fullerenes, *J. Phys. Chem.*, 99 (1995) 10694-10697.
- [6] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shirashi and H. W. Kroto, The production and structure of pyrolytic carbon nanotubes (PCNTs), *J. Phys. Chem. Solids*, 54 (1993) 1841.
- [7] A. Sarkar, H. W. Kroto and M. Endo, Hemi-toroidal networks in pyrolytic carbon nanotubes, *Carbon*, 33 (1995) 51.
- [8] M. Endo, K. Takeuchi, K. Kobori, K. Takehashi, H. W. Kroto and A. Sarkar, Pyrolytic carbon nanotubes from vapor-grown carbon fibers, *Carbon*, 33(7) (1995) 873-881.
- [9] W. K. Hsu, J. P. Hare, M. Terrones, H. W. Kroto, D. R. M. Walton and P. J. F. Harris, Condensed phase nanotubes, *Nature*, 377 (1995) 687.
- [10] W. K. Hsu, M. Terrones, J. P. Hare, H. Terrones, H. W. Kroto and D. R. M. Walton, Electrolytic formation of carbon nanostructures, *Chem. Phys. Lett.*, 262 (1996) 161-166.
- [11] S. H. Jo, Y. Tu, Z. P. Huang, D. L. Carnahan, D. Z. Wang and Z. F. Ren, Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties, *Appl. Phys. Lett.*, 82 (2003) 3520-3522.
- [12] Z. L. Wang, R. P. Gao, W. A. de Heer and P. Poncharal, In situ imaging of field emission from individual carbon nanotubes and their structural damage, *Appl. Phys. Lett.*, 80(5) (2002) 856.
- [13] J. M. Bonard, K. A. Dean, B. F. Coll and C. Klinke, Field emission of individual carbon nanotubes in the scanning electron microscope, *Phys. Rev. Lett.*, 89 (2002) 197602.
- [14] H. Folwer and L. Nordheim, Electron emission in intense electric fields, *Proc. R. Soc. London, Ser A*, 119 (1928) 683.
- [15] P. G. Collins and A. Zettl, Unique characteristics of cathode carbon-nano tube-matrix field emitters, *Phys. Rev. B*, 55 (1997) 9391.
- [16] S. Han and J. Ihm, First-principles study of field emission of carbon nanotubes, *Phys. Rev. B*, 66 (2002) 241402.
- [17] V. I. Trefilov, D. V. Schur, B. P. Tarasov, Yu. M. Shul'ga, A. V. Chernogorenko, K. Pishuk and S. Yu. Zaginaichenko, Fullerenes is a basis of materials for future, Kiev, (2001) 148.
- [18] E. G. Rakov, *Uzpekhi Khim.*, 69 (2000) 41.
- [19] M. Terrones, W. K. Hsu, H. W. Kroto and D. R. Walter, Nanotubes: A revolution in materials science and electronics, *Top. Curr. Chem.*, 199 (1999) 189.
- [20] C. Journet and P. Bernier, Production of carbon nanotubes, *Appl. Phys. A: Mater. Sci. Process.*, 67(1) (1998) 1-9.
- [21] P. M. Ajayan, Nanotubes from carbon, *Chem. Rev.*, 99 (1999) 1787.
- [22] S. Iijima and T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, *Nature*, 363 (1993) 603.
- [23] K. Tohji, T. Goto, H. Takahashi, Y. Shinoda, N. Shimizu, B. Jayadevan, I. Matsuoka, Y. Saito, A. Kasuya, T. Ohsuna, K. Hiraga and Y. Nishina, Purification procedure for single-walled nanotubes, *J. Phys. Chem.*, 101(11) (1997) 1974-1978.
- [24] S. Bandow, A. M. Rao, K. A. Williams, A. Thess, R. E. Smalley and P. C. Eklund, Purification of single-wall carbon nanotubes by microfiltration, *J. Phys. Chem. B*, 101 (1997) 8839.
- [25] E. Dujardin, T. W. Ebbesen, A. Krishnan and M. M. J. Treacy, Wetting of single shell carbon nanotubes, *Adv. Mater.*, 10 (1998) 1472.
- [26] 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 and R. E. Smalley, Large-scale purification of single-wall carbon nanotubes: process, product, and characterization, *Appl. Phys. A*, 67 (1998) 29.
- [27] K. B. Shelmov, R. O. Esenaliev, A. G. Rinzler, C. B. Huffman and R. E. Smalley, Purification of single-wall carbon nanotubes by ultrasonically assisted filtration, *Chem. Phys. Lett.*, 282 (1998) 429-434.
- [28] A. C. Dillon, T. Gennett, K. M. Jones, J. L. Alleman, P. A. Parilla and M. J. Heben, A simple and complete purification of single-walled carbon nanotube materials, *Adv. Mater.*, 11 (1999) 1354.
- [29] Z. J. Shi, Y. F. Lian, F. H. Liao, X. Zhou, Z. Gu, Y. Zhang and S. Iijima, Purification of single-wall carbon nanotubes, *Solid State Commun.*, 112 (1999) 35.
- [30] I. W. Chiang, B. E. Brinson, R. E. Smalley, J. E. Margrave and R. H. Hauge, Purification and characterization of single-wall carbon nanotubes, *J. Phys. Chem.*, B, 105 (2001) 1157.
- [31] J. M. Moon, K. H. An, Y. H. Lee, Y. S. Park, D. J. Bae and G. S. Park, High-yield purification process of single-walled carbon nanotubes, *J. Phys. Chem. B*, 105 (2001) 5677-5681.

- [32] S. Niyogi, H. Hu, M. A. Hamon, P. Bhowmik, B. Zhao, S. M. Rozenzhak, J. Chen, M. E. Itkis, M. S. Meier and R. C. Haddon, Chromatographic purification of soluble single-walled carbon nanotubes (s-SWNTs), *J. Am. Chem. Soc.*, 123 (2001) 733.
- [33] A. R. Harutyunyan, B. K. Pradhan, J. P. Chang, G. G. Chen and P. C. Eklund, Purification of single-walled carbon nanotubes by selective microwave heating of catalyst particles, *J. Phys. Chem. B*, 106 (2002) 8671.
- [34] M. T. Martínez, M. A. Callejas, A. M. Benito, W. K. Maser, M. Cochet, J. M. Andreu, J. Schreiber, O. Chauvet and J. L. G. Fierro, Microwave single walled carbon nanotubes purification, *Chem. Commun.*, (2002) 1000.
- [35] S. H. Jo, Y. Tu, Z. P. Huang, D. L. Carnahan, D. Z. Wang and Z. F. Ren, Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties, *Appl. Phys. Lett.*, 82 (2003) 3520-3522.
- [36] K. B. Shelimov, R. O. Esenaliev, A. G. Rinzler, C. B. Huffman and R. E. Smalley, Purification of single-wall carbon nanotubes by ultrasonically assisted filtration, *Chem. Phys. Lett.*, 282 (1998) 429-434.
- [37] Z. J. Shi, Y. F. Lian, F. H. Liao, X. H. Zhou, Z. N. Gu, Y. G. Zhang and S. Iijima, Purification of single-wall carbon nanotubes, *Solid State Commun.*, 112 (1999) 35-37.
- [38] G. S. Duesberg, M. Burghard, J. Muster, J. Philipp and S. Roth, Separation of carbon nanotube by size exclusion chromatography, *Chem. Commun.*, 3 (1998) 435-436.
- [39] 周貝倫著, 「純化程序對奈米碳管表面特性影響之研究」, 國立中央大學碩士論文, 2006年。
- [40] Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita and T. Hayashi, Growth and structure of graphitic tubules and polyhedral particles in arc-discharge, *Chem. Phys. Lett.*, 204 (1993) 277-282.
- [41] H. Dai, A. G. Rinzer, P. Nikolaev, A. Thess, D. T. Colbert and R. E. Smalley, Single-wall nanotubes produced by metal catalyzed disproportionation of carbon monoxide, *Chem. Phys. Lett.*, 260 (1996) 471-475.
- [42] Y. H. Lee, S. G. Kim and D. Tomanek, Catalytic growth of single-wall carbon nanotubes: an ab initio study, *Phys. Rev. Lett.*, 78 (1997) 2393-2396.
- [43] M. Endo and H. W. Kroto, Formation of carbon nanofibers, *J. Phys. Chem.*, 96 (1992) 6491-6944.
- [44] R. T. K. Baker and P. S. Harries, The Formation of Filamentous carbon, in *Chemistry and Physics of Carbon*, ed. by P. L. Walker and P. A. Throer, Marcel Dekker, New York, Vol. 14 (1978) 83-165.
- [45] R. T. K. Baker, M. A. Braker, P. S. Harries, F. S. Feates and R. J. Waite, Nucleation and growth of carbon deposits from nickel catalyzed decomposition of acetylene, *J. Catal.*, 26 (1972) 51-62.
- [46] A. Oberlin, M. Endo and T. Koyama, Filamentous growth of carbon through benzene decomposition, *J. Cryst. Growth*, 32 (1976) 335-349.
- [47] T. Baird and J. R. Fryer, Carbon formation on iron and nickel foils by hydrocarbon pyrolysis reactions at 700 ° C, *Carbon*, 12 (1974) 591-602.
- [48] W. A. DeHeer, A. Chatelain and D. Ugarte, A carbon nanotube field-emission electron source, *Science*, 270 (1995) 1179-1180.
- [49] A. Oberlin, M. Endo and T. Koyama, High resolution electron microscope observations of graphitized carbon fibers, *Carbon*, 14 (1976) 133-157.
- [50] C. Journet and P. Bernier, Production of carbon nanotubes, *Appl. Phys.*, 67 (1998) 1-9.
- [51] J. Kong, A. M. Cassell and H. J. Dai, Chemical vapor deposition of methane for single-walled carbon nanotubes, *Chem. Phys. Lett.*, 292 (1998) 567-574.
- [52] R. T. K. Baker and J. J. Chudzinski, Filamentous carbon growth on nickel – iron surfaces-effect of various oxide additives, *J. Catal.*, 64 (1980) 464-478.
- [53] R. T. K. Baker, P. S. Harries, R. B. Thomas and R. J. Waite, Formation of filamentous carbon from iron and chromium catalyzed decomposition of acetylene, *J. Catal.*, 30 (1973) 86-95.
- [54] R. T. K. Baker and R. J. Waite, Formation of carbonaceous deposit from the platinum-iron catalyzed decomposition, *J. Catal.*, 37 (1975) 101-105.
- [55] M. Jung, K. Y. Eun, J. K. Lee, Y. J. Baik, K. R. Lee and J. W. Park, Growth of carbon nanotubes by chemical vapor deposition, *Diam. Relat. Mater.*, 10 (2001) 1235-1240.
- [56] S. Xie, W. Li, Z. Pan, B. Chang and L. Sun, Self-assembly of shape-controlled nanocrystals and their in-situ thermodynamic properties, *Mater. Sci. Eng.*, 286 (2000) 11-15.
- [57] X. H. Chen, S. Q. Feng, Y. Ding, J. C. Peng and Z. Z. Chen, The formation conditions of carbon nanotubes array based on FeNi alloy island films, *Thin Solid Films*, 339 (1999) 6-9.
- [58] C. J. Lee, J. Park, S. Y. Kang and J. H. Lee, Growth of well-aligned carbon nanotubes on a large area of Co-Ni co-deposited silicon oxide substrate by thermal chemical vapor deposition, *Chem. Phys. Lett.*, 323 (2000) 554-559.
- [59] M. Terrones, N. Grobert, J. P. Zhang, H. Terrones, J. Olivares, W. K. Hsu, J. P. Hare, A. K. Cheetham, H. W. Kroto and D. R. M. Walton, Preparation of aligned carbon nanotubes catalysed by laser-etched cobalt thin films, *Chem. Phys. Lett.*, 285 (1998) 299-305.
- [60] Q. Liang, Q. Li, D. L. Chen, D. R. Zhou, B. L. Zhang and Z. L. Yu, Carbon nanotube prepared in the atmosphere of partial oxidation of methane, *Chemical Journal of Chinese Universities-Chinese*, 21(4) (2000) 623-625.
- [61] K. Hernadi, A. Fonseca, J. B. Nagy, A. Siska and I. Kiricsi, Production of nanotubes by the catalytic decomposition of different

carbon-containing compounds, *Appl. Catal. A: Gen.*, 199 (2000) 245-255.

- [62] W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao and G. Wang, Large-scale synthesis of aligned carbon nanotubes, *Science*, 274 (1996) 1701-1703.
- [63] Z. W. Pan, S. S. Xie, B. H. Chang, L. F. Sun, W. Y. Zhou and G. Wang, Direct growth of aligned open carbon nanotubes by chemical vapor deposition, *Chem. Phys. Lett.*, 299 (1999) 97-102.
- [64] A. P. Li, F. Muller, A. Birner, K. Nielsch and U. Gosele, Hexagonal pore arrays with a 50-420 nm interpore distance formed by self-organization in anodic alumina, *J. Appl. Phys.*, 84 (1998) 6023-6026.
- [65] H. Masuda, H. Yamada, M. Satoh and H. Asoh, Highly ordered nanochannel-array architecture in anodic alumina, *Appl. Phys. Lett.*, 71 (1997) 2770-2772.
- [66] H. Masuda and M. Satoh, Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask, *Jpn. J. Appl. Phys. Part 2*, 35 (1996) L126-129.
- [67] P. E. Nolan, M. J. Schabel and D. C. Lynch, Hydrogen control of carbon deposit morphology, *Carbon*, 33 (1995) 79-85.
- [68] P. Pinheiro, M. C. Schouler, P. Gadelle, M. Mermoux and E. Dooryhee, Effect of hydrogen on the orientation of carbon layers in deposits from the carbon monoxide disproportionation reaction over Co/Al₂O₃ catalysts, *Carbon*, 38(10) (2000) 1469-1479.
- [69] A. A. Khassin, T. M. Yurieva, V. I. Zaikovskii and V. N. Parmon, Effect of metallic cobalt particles size on occurrence of CO disproportionation: Role of fluidized metallic cobalt-carbon solution in carbon nanotube formation, *React. Kinet. Catal. Lett.*, 64 (1998) 63-71.
- [70] S. H. Tsai, C. W. Chao, C. L. Lee and H. C. Shin, Bias-enhanced nucleation and growth of the aligned carbon nanotubes with open ends under microwave plasma synthesis, *Appl. Phys. Lett.*, 74 (1999) 3462-3464.
- [71] Z. P. Huang, J. W. Xu, Z. F. Ren, J. H. Wang, M. P. Siegal and P. N. Provencio, Growth of highly-oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition, *Appl. Phys. Lett.*, 73 (1998) 3845-3847.
- [72] Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Klemic and M. A. Reed, Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot, *Appl. Phys. Lett.*, 75 (1999) 1086-1088.
- [73] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell and H. Dai, Self-oriented regular arrays of carbon nanotubes and their field emission properties, *Science*, 283 (1999) 512-514.
- [74] Y. K. Kwon, Y. H. Lee, S. G. Kim, P. Jund, D. Tomanek and R. E. Smalley, Morphology and stability of growing multiwall carbon nanotubes, *Phys. Rev. Lett.*, 79 (1997) 2065-2068.
- [75] D. H. Oh and Y. H. Lee, Stability and cap formation mechanism of single-walled carbon nanotubes, *Phys. Rev. B*, 58 (1998) 7407-7411.
- [76] V. L. Kuznetsov, A. N. Usoltseva, A. L. Chuvilin, E. D. Obratsova and J. M. Bonard, Thermodynamic analysis of nucleation of carbon deposits on metal particles and its implications for the growth of carbon nanotubes, *Phys. Rev. B*, 64 (2001) 235401-1.
- [77] S. H. Jo, Y. Tu, Z. P. Huang, D. L. Carnahan, D. Z. Wang and Z. F. Ren, Effect of length and spacing of vertically aligned carbon nanotubes on field emission properties, *Appl. Phys. Lett.*, 82 (2003) 3520-3522.
- [78] Z. L. Wang, R. P. Gao, W. A. de Heer and P. Poncharal, In situ imaging of field emission from individual carbon nanotubes and their structural damage, *Appl. Phys. Lett.*, 80(5) (2002) 856-858.
- [79] J. M. Bonard, K. A. Dean, B. F. Coll and C. Klinker, Field emission of individual carbon nanotubes in the scanning electron microscope, *Phys. Rev. Lett.*, 89 (2002) 1976021-24.
- [80] Juntao Li, Wei Lei, Xiaobing Zhang, Xuedong Zhou, Qilong Wang, Yuning Zhang and Baoping Wang, Field emission characteristic of screen-printed carbon nanotube cathode, *Appl. Surf. Sci.*, 220 (2003) 96 – 104.
- [81] S. L. S. Jacoby, J. S. Kowalik and J. T. Pizzo, *Iterative Methods for Nonlinear Optimization Problems*, Prentice Hall, Inc., Englewood Cliffs, New Jersey, (1972) 79-83.
- [82] R. H. Fowler and L. W. Nordheim, Electron emission in intense electric fields, *Proc. Royal Soc. London*, 119 (1928) 173-181.
- [83] 詹博舜, 「鉻酸與硝酸後處理對熱化學氣相沉積奈米碳管薄膜表面型態與場發射特性之影響」。大葉大學電機工程系碩士論文, 2008年。
- [84] 李世凱, 「使用熱化學氣相沉積在矽奈米絲上合成奈米碳管」。大葉大學電機工程系碩士論文, 2009年。