Large-Scale Synthesis of Carbon Nanotubes and Their Applications to the Counter Electrodes of Dye-Sensitized Solar Cells

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ABSTRACT

The ideal counter electrodes of Dye-Sensitized Solar Cells(DSSC) must meet the following requirement: (1).Good electrical conductivity to reduce the series resistance (RS), (2).Excellent chemical stability to protect from corrosive electrolytes and take part in undesired electrochemical reactions, (3).To reduce the over-potential of the redox couples (mediator, i.e. I-/I3- in typical DSSC) and (4).High surface area for mass transfer. Fullerenes family such as C60 and carbon nanotubes(CNTs) have better electron affinity for fast transfer of photocurrent(electron shuttle),. Carbon nanotubes have high porosity, large surface area with good electric conductivity and relatively easy synthesized in lab. Scale. Accordingly, in this study, we had fabricated multiwalled carbon nanotubes(MWNT) based counter electrode of DSSC in endeavor for cell performance improvement. MWNTs were synthesized by atmospheric thermal chemical vapor deposition over Co-Mo/MgO by using C2H2 as carbon source and H2/NH3 as reducing ambient at 700~900oC. The major products were multiwalled carbon nanotubes with diameter around 7~13 nm. The as-synthesized MWNTs with high carbon yield are easily purified and processed. The optimal pretreatment temperature is 800 oC. For higher nanotube density, reaction temperature of 800~900oC is desirable. As the growing temperature is increased, the diameter of MWNT is larger. One of the production yield is 0.733 g-CNT/hr whose growth rate is fastest at the very start of 10min.(0.057 g-CNT/min. g-cat). After purification of the as-grown MWNTs, finely dispersed CNTs were anchored on the ITO glasses as the counter electrode of DSSC. After fabrication of TiO2 working electrode dyed with mercurochrome. The assembled DSSC was tested for I-V character under illumination. It revealed that CNT-based counter electrode own superior VOC and ISC under identical conditions. In comparison with the traditional Pt-counter electrode(VOC=0.49 V and ISC=1.86 mA), the CNT-counter electrode possessed higher cell performance with VOC=0.65 V and ISC=3.05 mA. After keeping the [KI]/[I2] to 5/1, the influence of different electrolyte concentration were invesitagted. The results shows that there is optimal value of [KI]/[I2]=0.3 M/0.06 M. Under the given electrolyte value, the DSSC have VOC=0.65 V and ISC=3.05 mA. Besides, it shows that under identical [KI]/[I2] ratio, the VOC is always kept the same. By varying the [I2] and keeping [KI]=0.3 M, the ISC will increase as the [I2] is increased. The equivalent solar cells circuit analysis shows that the series resistance under best cell performance in this study is Ro=138 Ω, with ideal factor n=0.56 in comparison to that of Pt-counter electrode with Ro=190 Ω, n=0.4. As a conclusion, the CNTs is effective increase the electron transfer property of counter electrode of DSSC.

Keywords : MgO ; Chemical vapor deposition ; Dye-Sensitized ; Counter electrodes ; family ; after

Table of Contents

REFERENCES

[1]. S. Iijima ,“ Helical microtubules of graphite carbon ”, Nature,vol.354,no.7, pp-56.58, 1999.
[2]. D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J.vazquez, R. Beyers, Nature, 363, 605-609 (1993).
[3] J. Kong, M. Cassell and H. G. Dai,“ Chemical vapor deposition of methane for single-walled carbon nanotubes ”, Chemical Physics Letters, 292, 567-574 (1998).
[4] C. Dillon, P. A. Parilla, J. L. Alleman, J. D. Perkins and M. J. Heben,“ Controlling single-wall nanotube diameters with variation in laser pulse power ”, Chemical Physics Letters, 316, 13-18 (2000).
[5] Subramoney,“ Novel Nano Carbons-Structure, Properties, and Potential Applications ”, Advanced Materials, 1(15), (1157-1171) 1998.
[6] A. Rao,“ Nanostuctured From of Carbon-An Overview ”, International School of Solid State Physics-18th course: the three faucets Nanostructured Carbon for Advanced Applications (NATO-ASI), 2000, Italy.
[7] T. W. Ebbesen, P. M. Ajayan, H. Hiura, and K. Tanigaki, Nature, 367, 519 (1994).
[8] T. W. Ebbesen and P. M. Ajayan, Nature, 358, 220 (1992).
[9] r, J. M. Planeix, V. Brotons, B. Coq, and J. Castaing, Chem. Phys. Lett., 226, 364 (1994). J. M. Lambert, P. M. Ajayan, P. Bernie [10] R. Saito, G. Dresselhaus, M. S. Dresselhaus, "Physical Properties of Carbon Nanotubes ", Imperial College Press, 1998, p75 [11]. C. Journet, P. Bernier, Appl. Phys. A, 67（1998）1.
[12] H. Dai, A. G. Rinzer, P. Nikolaev, A Thess, D. T. Colbert, and R. E.Smalley, Chem. Phys. Lett. ,260, 471 (1996).
[13] Rao, A. M. et al., Science 275, 1997, 187.

[14] P. M. Ajayan, O. Stephan, C. Colliex, D. Trauth, Science, 265, 1212 (1994).
[15] Alan M.Cassell, Jeffrey A. Raymakers, Jing Kong, Hongjie Dai, 1999,Joural Physical Chemistry B , 103, pp. 6484-6492 [16] J. F. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z.Konya, A. Fonseca, C. h. Laurent, J. B. Nagy, 2000, Chemical Phycics etters, 317, pp. 83-89 [17] M. J. Bronikowski, P. A. Willis, D. T. Colbert, K. A. Smith, R. E. Smalley, 2001, Journal Vacuum Science Technol. A, 19, pp. 1800-1805 [18] P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T.Colbert, K. A. Smith, R. E. Smalley, 1997, Chemical Physics Letters,313, pp. 91-97 [19] R. Andrews, D. Jacques, A. M. Rao, F. Derbyshire, D. Qian, X. Fan, E.C. Dickey, J. Chen, 1999, Chemical Physics Letters, 303, pp. 467-474 [20] Md. Shajahan , Y.H. Mo , A.K.M. Fazle Kibria , M.J. Kim , K.S. Nahm , Received 20 August 2003; accepted 30 April 2004 Available online 9 June 2004 , Carbon 42 (2004) 2245 – 2253 [21] 吳榮宗著, 「工業觸媒概論」, 國興出版社, 1989 [22] T. W. Ebbesen, P. M. Ajayan, H. Hiura and K. Tanigaki, "Purification. of carbon nanotubes". Nature,367, (1994) 519.
[23] 李元堯, 「21 世紀的尖端材料- 奈米碳管」, 化工技術, 第120期, 第140~159 頁, 民國九十二年。
[24] M. Yumura, S. Ohshima, K. Uchida, Y. Tasaka, Y. Kuriki, F. Ikazaki,Y. Saito, and S. Uemura, 1999, Diamond and Related Materials, 8, p.785 [25] K. Bladh, L.K.L. Falk, F. Rohmund, On the iron-catalysed growth of single-walled carbon nanotubes and encapsulated metal particles in the gas phase, Appl. Phys. A 70 (2000) 317 – 322 [26] A. Fonseca1, et al., Synthesis of single-and multi-wall carbon nanotubes over supported catalysts, Appl. Phys., A 67 (1998) 11-22 [27] Jose E. Herrera, et al., Relationship between the Structure/Composition of Co – Mo Catalysts and Their Ability to Produce Single-Walled Carbon Nanotubes by Disproportionation, Journal of Catalysis, 204 (2001) 129 – 145 [28] Ping ’ an Hu, et al., Synthesis of single-walled carbon nanotubes using MgO as a catalyst support, Synthetic Metals 135 – 136 (2003) 833 – 834 [29]Solar Energy Mater.,and Solar Cells.,44(1996)99-117 [30]Solar Energy Mater.,and Solar Cells.,79(2003)459-469 [31]簡匯宏, 以化學氣相沉積法在氧化鎂觸媒載體上成長單層奈米碳管, 大同大學材料工程研究所碩士論文,2004.
[32]J.Am.Chem.SOC.,115(1993)6382-6390 [33]J.Photochem.,and Photobio.A:Chemistry,164(2004)179-182 [34]Electrochimica Actr.,51(2006)3814-3819 [35] J.Photochem.,and Photobio.A:Chemistry,145(2001)107-112 [36]Synthetic Metal.,77(1996)47-49
[37]J.Electrochem.Soc.,144(1997)876 [38]Chemistry Letter,32(2003)28-29 [39]黃調元,半導體元件物理與製作技術(第二版),國立交通大學出版社