

Electrochemical Performance of Carbon Nanotube Based Supercapacitor

Jafar Khan Kasi, Ajab Khan Kasi, Muzamil Bokhari

Abstract—Carbon nanotube is one of the most attractive materials for the potential applications of nanotechnology due to its excellent mechanical, thermal, electrical and optical properties. In this paper we report a supercapacitor made of nickel foil electrodes, coated with multiwall carbon nanotubes (MWCNTs) thin film using electrophoretic deposition (EPD) method. Chemical vapor deposition method was used for the growth of MWCNTs and ethanol was used as a hydrocarbon source. High graphitic multiwall carbon nanotube was found at 750°C analyzing by Raman spectroscopy. We observed the electrochemical performance of supercapacitor by cyclic voltammetry. The electrodes of supercapacitor fabricated from MWCNTs exhibit considerably small equivalent series resistance (ESR), and a high specific power density. Electrophoretic deposition is an easy method in fabricating MWCNT electrodes for high performance supercapacitor.

Keywords—Carbon nanotube, chemical vapor deposition, catalyst, charge, cyclic voltammetry.

I. INTRODUCTION

CARBON Nanotubes (CNTs), has revolutionized the modern scientific research due to their exceptional electrical and mechanical properties. CNTs have wide variety of potential applications in scientific and commercial fields such as energy, medicine, automobile, aerospace, and chemical industry. Since the pioneer works regarding CNT, nanotechnology with carbon nanomaterials (CNMs) has been developed very rapidly [1]-[4]. The potential applications of CNMs are in different nanoscale devices such as in field effect transistors, nanosensors and interconnect for many devices due to its one dimensional nanostructure and robust conductivity [5]-[8]. Carbon nanotubes are synthesized by different techniques such as arc discharge, laser ablation and chemical vapor deposition (CVD). Out of three main techniques, CVD method is the most promising method because it gives high yield mass, high controllability in diameter, quantity, and growth direction. The basic principle of CNT growth in CVD is the physical and chemical characteristic of the hydrocarbon source and metal catalyst and appropriate conditions. The dissociation of carbon source molecule with the interaction of catalyst leads the formation of CNTs. So the diameter of the CNT is dependent on catalytic particle size, and it is very difficult to control the size of nano metal catalyst for uniform size and distribution for CNTs growth [9]-[12]. Use of porous

alumina as a template is one of the easiest approaches to produce CNTs with dimension control. For porous alumina template, anodic aluminum oxide (AAO) membrane can be fabricated by simple method of two electrodes setup [13]-[20].

Carbon Nanotubes are used for electrochemical energy storage due to low mass density, remarkable chemical stability, electronic conductivity and very high surface area. A wide range of potential applications has been reported for electrochemical energy and conversion system such as for supercapacitor [21]-[23], hydrogen storage in fuel cell [24] and for Li-ion batteries [25]-[26]. Electrochemical capacitor has the ability to provide a tremendous amount of energy in short period of time. Most of the supercapacitor surface area has microporous which is not capable to support an electrical double layer, consequently shows bad frequency response. The main hindrance for the frequency response and power density of the supercapacitor is the resistivity of electrodes, contacts, and electrolyte [27]. Niu et al. used MWCNTs as electrodes for improving of frequency response and power density [27]. They reported the better frequency response (100Hz) and power density ($8\text{kW} \cdot \text{kg}^{-1}$). To get a high power density supercapacitor internal resistance and contact resistivity should be reduced. An et al. achieved high power density by single wall carbon nanotube (SWCNTs) with heat treatment and lowered the contact resistivity by using polished Nickel foil [28]. Yoon et al. directly synthesized CNTs on metal collector to reduce the contact resistivity [29]. In this paper we report the electrode coated with MWCNTs thin film using electrophoretic deposition (EPD) method. The supercapacitor fabricated from these electrodes showed a considerably small equivalent series resistance (ESR), and a high specific power density. Electrophoretic deposition is one of the attractive and easy methods in fabricating CNT electrodes for high performance supercapacitor.

II. EXPERIMENTAL DETAIL

A. Materials

The dimensions of the nickel foil (sheet) used as electrodes for supercapacitor in the experiment were 10mm x 10mm x 0.1mm. For CNT growth 99.99% pure ethanol was used as hydrocarbon source and Fe/ Al_2O_3 as catalysts.

B. Fabrication of CNT

In this study, MWCNTs were synthesized through chemical vapour deposition method. Analytical grade ethanol (99.99%) was used as hydrocarbon source and Ar was used as carrier gas for the fabrication of CNT. The catalyst powder Fe/ Al_2O_3 was

put into the ceramic boat and placed in the quartz tube. Subsequently, Ar gas with a flow rate of 500 sccm was allowed. The temperature was raised to the 750°C and ethanol vapor was switched into the furnace by Ar carrier gas at flow rate of 500 sccm for 20 min. MWCNTs were synthesized at the surface of the catalyst powder by deposition of carbon atoms from decomposition of ethanol vapors at atmospheric pressure. The ethanol supply was then shut off and the furnace was cooled to room temperature. The synthesized MWCNTs along with Fe/Al₂O₃ were treated with concentrated nitric acid to extract the MWCNTs. Subsequently the carbon nanotubes were collected by filtration. Finally carbon nanotubes were washed by deionized water and dried.

C. Preparation of Electrodes

For the supercapacitor two electrodes of nickel foil with the dimension of 10mm x 10mm were cut. Prior to electrodes preparation, a colloidal suspension of MWCNTs and dimethylformamide (DMF) was formed. 10 ml of CNTs - DMF suspension was ultrasonicated for one hour to get a stable form for long time.

For electrochemical applications, Mg(NO₃)₂·6H₂O were added into the suspension as electrolyte for electrophoretic deposition. The two electrodes were put into suspension parallel placing filter paper as separator between them. The electrochemical performance of the supercapacitor was analyzed in a two-electrode system using cyclic voltammetry (CV) and galvanostatic charge/discharge on a potentiostat/galvanostat, and electrochemical impedance spectroscopy (EIS) on a frequency response detector.

D. Characterization of CNTs

For the characterization of fabricated CNTs structures, size and morphology, field emission scanning electron microscope (FESEM, Hitachi S-4700), transmission electron microscopy (TEM; Philips CM 120), and Raman spectroscopy (DXR, Smart Raman, Thermo Scientific) were used.

III. RESULTS AND DISCUSSION

A. Fabrication and Characterization of CNT

In this research, MWCNTs were fabricated at the surface of Fe/Al₂O₃ catalyst powder under different conditions. Highly pure ethanol was used as hydrocarbon source. Growth temperature was kept 750°C. Fig. 1 shows Raman spectra of the MWCNTs synthesized at 750°C temperature by using an Ar ion laser with a wavelength of 532 nm (2.45 eV). The typical Raman spectra for the carbon materials are composed of two peaks, which can be assigned to disorder-induced (D) mode at about 1350 cm⁻¹ and C-C stretching (G) mode of graphite structure at about 1590 cm⁻¹, respectively [30].

The intensity ratio of G-band to D-band is usually used for evaluating the quality of the produced carbon nanomaterials (CNMs). For CNMs, the higher ratio of intensity of G-band to D-band reflects the higher crystallinity and purity of the produced CNMs. At 750°C, the G-Band rises over the D-band indicating the growth of graphitic structure of CNTs. Fig. 2

shows SEM image and the Fig. 3 shows the TEM image of the purified MWCNTs obtained by CVD method and grown by EPD at a thin film.

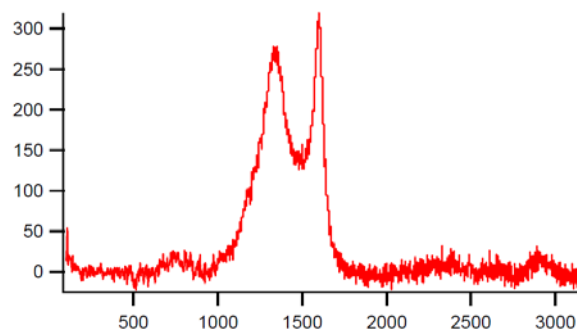


Fig. 1 Raman spectra of the MWCNTs at growth temperatures of 750°C measured by 532nm

The grown carbon nanotubes have uniform structure, with average diameter of about 20 nm. The equally distributed nanostructures making open space between nanotubes, such a porous structure provide high surface area for easy access of solvated ions to the electrodes/electrolyte interface.

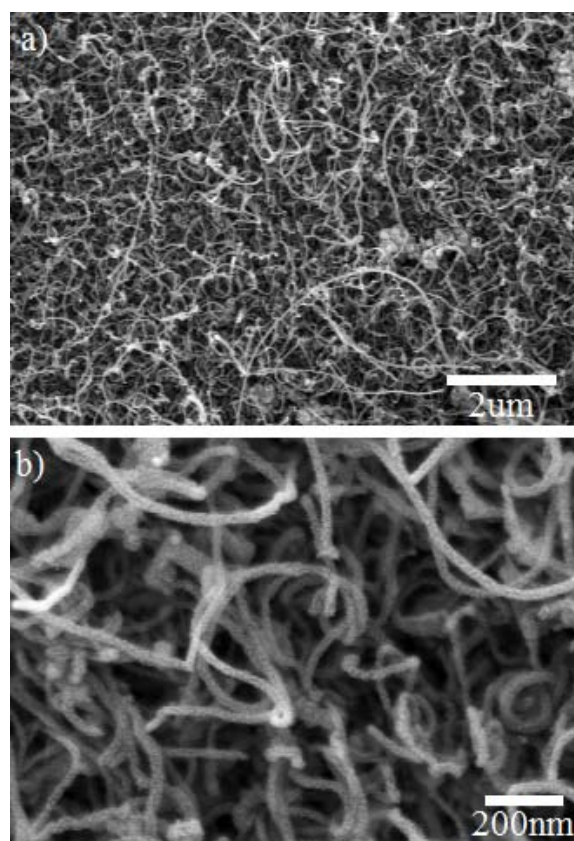


Fig. 2 SEM images of MWCNTs at the surface of electrode

B. Cyclic Voltammetry (CV) Measurements

The current response profile of the cyclic voltammetry curves at a scan rate of 50 mV·s⁻¹, 100 mV·s⁻¹, 500 mV·s⁻¹ and 1000 mV·s⁻¹ were taken. In all scan rates the CV curves show a

nearly rectangular shape, a clear proof of well-developed capacitance properties. Even at a very high scan rate of $1000 \text{ mV} \cdot \text{s}^{-1}$, the CVs still retain their rectangular shape. Fig. 4 shows the CV of the nanotubes thin film supercapacitor cycled from 0 V to +1 V. The outstanding CV shape at different scan rate exposes a very rapid current response on voltage reversal at each end potential, and the straight rectangular sides represent a very small equivalent series resistance of the electrodes and also the fast diffusion of electrolyte in the films.

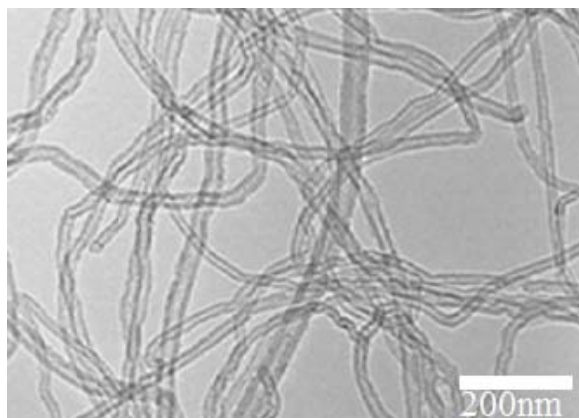


Fig. 3 TEM image of MWCNTs

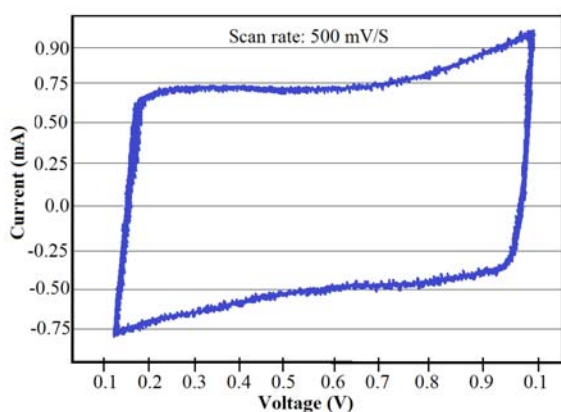


Fig. 4 CVs of the nanotubes thin film supercapacitor cycled from 0V to +1V

The supercapacitor was cycled for 50 times and no degradation was observed at all. The specific capacitance and the specific power density were obtained as $20 \text{ F} \cdot \text{g}^{-1}$ and $22 \text{ kW} \cdot \text{kg}^{-1}$ respectively. Fig. 5 shows a typical charge /discharge curve of the nanotube thin film supercapacitor. Beside the above mentioned characteristics the EPD thin films, supercapacitor electrode also showed a remarkable frequency response which means a better power performance. The main reason of the better response of the supercapacitor electrodes is the easy access of the electrolyte to the entire thin films surface through nanoporous structures made by EPD. In the EPD process the MWCNTs were driven and accumulated by the electrical field. These carbon nanotubes uniformly deposited and bound with the nickel foil. The good adhesion of the MWCNTs and the

nickel foil were formed by the formation of magnesium hydroxide from magnesium ions at the surface of the EPD cathode. The adhesion between the carbon nanotubes and nickel foil were enhanced by post deposition heat treatment. The carbon nanotubes also provide the excellent conductivity which reduces the internal resistance and ultimately the ESR.

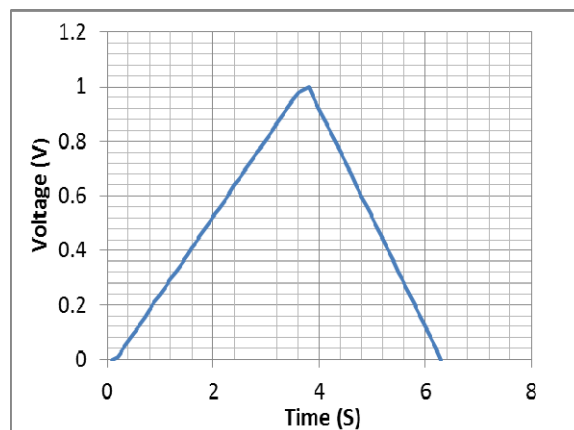


Fig. 5 Charge/discharge curves of the nanotube thin film supercapacitor

IV. CONCLUSIONS

In this research we successfully fabricated MWCNTs thin film electrode through electrophoretic deposition. For the growth of carbon nanotube CVD process was adopted and analytical grade ethanol was used as carbon precursors. The most appropriate temperature of CNT synthesis for our experimental setup was 750°C . The supercapacitor constructed from carbon nanotube based electrodes performed a significantly small ESR, a high specific power density and superior frequency response.

REFERENCES

- [1] A. Oberlin, M. Endo and T. Koyama, "Filamentous growth of carbon through benzene decomposition", *Journal of Crystal Growth*, vol. 32, pp. 335, January 1976.
- [2] S. Iijima, "Helical microtubes of graphitic carbon", *Nature*, vol. 354, pp.56-58, November 1991.
- [3] S. Iijima and T. Ichihashi, "Single-Shell Carbon Nanotubes of 1-nm Diameter", *Nature*, vol. 363, pp.603-605, June 1993.
- [4] D. S. Bethune, C. H. Klang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, "Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls", *Nature*, vol. 363, pp.605-607, June 1993.
- [5] Q. Ngo, B. A. Cruden, A. M. Cassell, G. Sims, M. Meyyappan, J. Li and C.Y. Yang, "Thermal Interface Properties of Cu-Filled Vertically Aligned Carbon Nanofiber Arrays", *Nano Letters*, vol. 4, pp. 2403-2407, December 2004.
- [6] A. P. Graham, G.S. Duesberg, R.V. Seidel, M. Liebau, E.Unger, W.Pamler, F. Kreupl, and W. Hoenlein, "Carbon Nanotubes for Microelectronics", *Small*, vol. 1, pp.382-390, April 2005.
- [7] O. M. Kuttel, O. Groening, C. Emmenegger and L. Schlapbach, "Electron Field Emission From Phase Pure Nanotube Films Grown in a Methane/Hydrogen Plasma", *Applied Physics Letters*, vol. 73, pp.2113-2115, October 1998.
- [8] J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han and M. Meyyappan, "Bottom-up approach for carbon nanotube interconnects", *Applied Physics Letters*, vol. 82, pp.2491-2493, April 2003.
- [9] J. K. Kasi, A. K. Kasi, M. Bokhari, N. Afzulpurkar, "Synthesis of Unique Structures of Carbon Nanotube at Anodic Aluminum Oxide Template"

- Applied Mechanics and Materials, vol. 421, pp. 319-323, September, 2013.
- [10] M.A. Ermakova, D.Y. Ermakov and G.G. Kuvshinov, "Effective catalysts for direct cracking of methane to produce hydrogen and filamentous carbon: Part I. Nickel catalysts", *Applied Catalysis A: General*, vol. 201, pp.61-70, June 2000.
- [11] N.M. Rodriguez, A. Chambers and R.T.K. Baker, "Catalytic engineering of carbon nanostructures", *Langmuir*, vol. 11, pp. 3862-3866, October 1995.
- [12] N.M. Rodriguez, M. S. Kim, F. Fortin, I. Mochida and R.T.K. Baker, "Carbon deposition on iron-nickel alloy particles", *Applied Catalysis A: General*, vol. 48, pp.265-282, January 1997.
- [13] A. K. Kasi, M.W. Ashraf, J.K. Kasi, S. Tayyaba and N. Afzulpurkar, "Low cost nano-membrane fabrication and electro-polishing system", *World Academy of Science, Engineering and Technology*, vol. 64, pp.56-58, April 2010.
- [14] M. Hasan, A. K. Kasi, J. K. Kasi and N. Afzulpurkar, "Anodic aluminum oxide (AAO) to AAO bonding and their application for fabrication of 3D microchannel", *Nanoscience and Nanotechnology Letters*, vol. 4, pp. 569-573, December 2012.
- [15] H. Masuda and K. Fukuda, "Ordered Metal Nanohole Arrays made by two step Replication of Honeycomb structures of Anodic Alumina", *Science*, vol. 268, pp.1466-1468, June 1995.
- [16] J. K. Kasi, A. K. Kasi, N. Afzalpurkar, M. Hasan, S. Pratontep and A. Poyai, "Fabrication of three dimensional AAO structures", *Nanoscience and Nanotechnology Letters*, vol. 4, pp. 537-543, December 2012.
- [17] M. K. McQuaig Jr., A. Toro, W. Van Geertruyden and W.Z. Misiolek, "The effect of high temperature heat treatment on the structure and properties of anodic aluminum oxide", *Journal of Material Science*, vol. 46, pp.243-253, January 2011.
- [18] A. K. Kasi, J. K. Kasi, N. Afzulpurkar, E. Bohez and A. Tuantranont, "Continuous voltage detechement and etching (CVDE) technique for fabrication of nano-porous AAO tubular membrane", *Nanoscience and Nanotechnology Letter*, vol. 4, pp. 530-536, December 2012.
- [19] C. R. Martin, "Nanomaterials: A Membrane-Based Synthetic Approach", *Science*, vol. 266, pp.1961-1966, December 1994.
- [20] A.K. Kasi, N. Afzulpurkar, J.K. Kasi, A. Tuantranont and P. Dulyaseree, "Utilization of cracks to fabricate anodic aluminum oxide nanoporous tubular and rectangular membrane", *Journal of Vacuum Science and Technology: B*, vol. 29, pp.D1071-D1077, July 2011.
- [21] M. Hughes, M. S. P. Shaffer, A. C. Renouf, C. Singh, G. Z. Chen, D. J. Fray, A. H. Windle, "Electrochemical Capacitance of Nanocomposite Films Formed by Coating Aligned Arrays of Carbon Nanotubes with Polypyrrole", *Advanced Materials*, vol. 14, pp. 382- 385, March 2002.
- [22] M. Hughes, G. Z. Chen, M. S. Shaffer, D. J. Fray, A. H. Windle, "Electrochemical Capacitance of a Nanoporous Composite of Carbon Nanotubes and Polypyrrole", *Chemistry of Materials*, vol. 14, pp.1610-1613, February 2002.
- [23] B. J. Yoon, S. H. Jeong, K. H. Lee, H. S. Kim, C. G. Park, and J. H. Han, "Electrical properties of electrical double layer capacitors with integrated carbon nanotube electrodes," *Chemical Physics Letters*, vol. 388, pp. 170-174, April 2004.
- [24] C. Nutzenadel, A. Zuttel, D. Chartouni, L. Schlapbach, "Electrochemical storage of hydrogen in nanotube materials", *Electrochemical and Solid-States Letters*, vol. 2, pp. 30-32, January 1999.
- [25] A. S. Claye, J. E. Fischer, C. B. Huffman, A. G. Rinzler and R. E. Smalley, "Solid-State Electrochemistry of the Li Single Wall Carbon Nanotube System" *Journal of Electrochemical Society*, vol.147, pp. 2845-2852, April 2000.
- [26] H. C. Shin, M. L. Liu, B. Sadanadan and A. M. Rao, " Electrochemical Insertion of Lithium into Multi-Walled Carbon Nanotubes Prepared by Catalytic Decomposition", *Journal of Power Sources*, vol. 112, pp.216-221. October 2002.
- [27] C. M. Niu, E. K. Sichel, R. Hoch, D. Moy and H. Tennent, "High Power Electrochemical Capacitors Based on Carbon Nanotube Electrodes", *Applied Physics Letters*, vol. 70, pp. 1480-1482, January 1997.
- [28] K. H. An, W. S. Kim, Y. S. Park, J. M. Moon, D. J. Bae, S. C. Lim, Y. S. Lee and Y. H. Lee, "Electrochemical Properties of High-Power Supercapacitors Using Single-Walled Carbon Nanotube Electrodes", *Advanced Functional Materials*, vol. 11, pp. 387-392, October 2001.
- [29] B.J. Yoon, S.H. Jeong, K.H. Lee, H.S. Kim, C.G. Park and J.H. Han, "Electrical properties of electrical double layer capacitors with integrated carbon nanotube electrodes", *Chemical Physics Letter*, vol. 388, pp. 170-174, April 2004.
- [30] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M. S. Dresselhaus, "Structural (n,m) Determination of isolated single-wall carbon nanotubes by resonant Raman scattering", *Physical Review Letter*, vol. 86, pp. 1118-1121, February 2001.

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