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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^{o}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 (8kW. 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

Jafar Khan Kasi, Ajab Khan Kasi, and Muzamil Bokhari are with Department of Physics, University of Balochistan, Quetta 87300 Pakistan (e-mail: jafarkhankasi@gmail.com, ajabkasi@gmail.com, mouzimail@gmail.com).

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/Al_2O_3 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 $(NO_3)_2 \cdot 6H_2O$ 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 election 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/Al_2O_3 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.

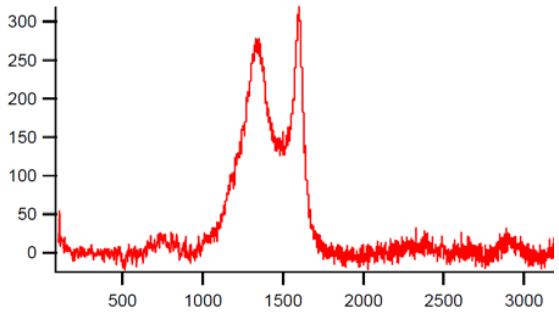

Fig. 1 Raman spectra of the MWCNTs at growth temperatures of 750°C measured by 532nm

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.

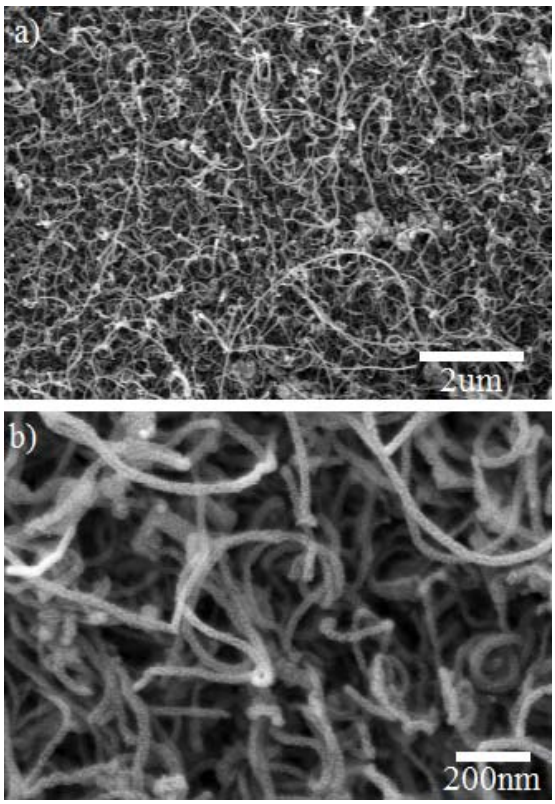

Fig. 2 SEM images of MWCNTs at the surface of electrode

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 mVs^{-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 mV $.s^{-1}$, 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.

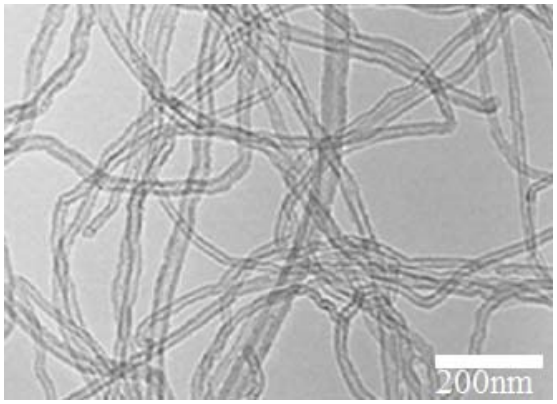

Fig. 3 TEM image of MWCNTs

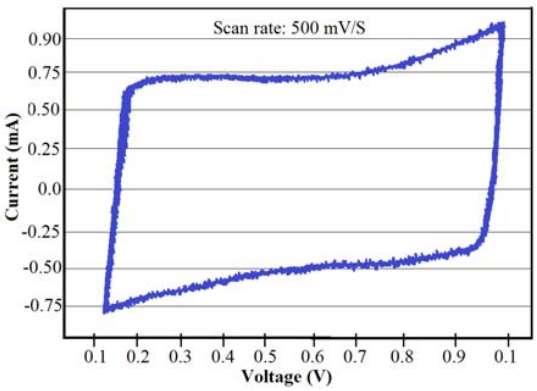

Fig. 4 CVs of the nanotubes thin film supercapacitor cycled from 0V to +1V

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 F. g^{-1} and 22kW. 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.

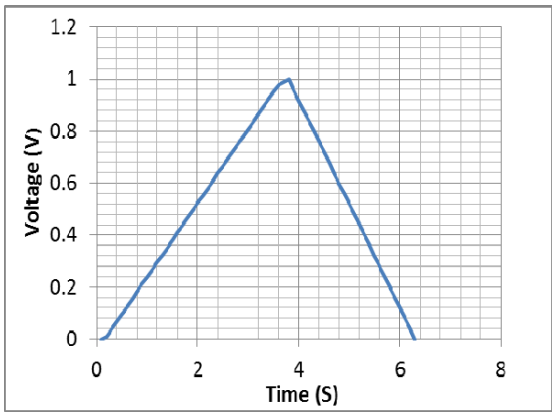

Fig. 5 Charge/discharge curves of the nanotube thin film supercapacitor

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.

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Jafar Khan Kasi was born on February 07, 1973 in Quetta, Pakistan. He earned Post Graduate Diploma in Computer Science in 1996, Master of Science degree in Physics from University of Balochistan, Pakistan with distinguished positions. In 2010 he earned MS degree in the field of Microelectronics Technology from Asian Institute of Technology (AIT), Thailand. In August 2012 he earned his Doctoral Degree in microelectronics from Asian Institute of Technology, Thailand.

He has been teaching in Physics Department, University of Balochistan, Pakistan as Assistant Professor since 2007. His area of interest is Electronics, Microelectronics fabrication, circuit theory, digital electronics and nanotechnology. He has succeeded to publish 28 international articles in journals and conference proceedings.