

Preparation and Characterization of Carbon Nanotubes for Supercapacitor Applications

V.Thirumal¹, A.Pandurangan², R.Jayavel³, C.Sekar⁴, K.S.Vengatesh¹,
S.R.Krishnamoorthy¹, N.S Palani¹, R. Ilangovan^{*1}.

¹ Department of Nanoscience and Technology, Alagappa University, Karaikudi – 630 004, Tamil nadu, India.

² Department of Chemistry, Anna University, Chennai – 600 025, Tamil nadu, India.

³ Center for Nanoscience and technology, Anna University, Chennai – 600025, Tamil nadu, India.

⁴ Department of Bioelectronics and Biosensor, Alagappa University, Karaikudi – 630 004, Tamil nadu, India.

Corresponding author: rajangamilangovan@gmail.com

Abstract— Recent advancements in nanotechnology have proposed the Carbon nanotubes as electrode material for the Supercapacitor applications due to their unique properties. Synthesis of Carbon nanotube in Catalytic Chemical vapor deposition (CCVD) is the easiest and economic way of production in a larger scale. The synthesized MWCNTs were characterized by X – ray diffraction (XRD). The morphological characterizations were carried out by the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) and also the structure of MWCNTs were analysed using Raman spectroscopy. The Electrochemical performance of MWCNTs was carried out with Modified Glassy Carbon (GC) Electrodes (MWCNTs – GCE). A cyclic voltammograms obtained for bare GCE and MWCNTs – MGCE in 0.1M KCl containing $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1 mM) and specific capacitance was measured. The electrochemical impedance spectroscopy (EIS) showed that the resistance (Rct) value of the system was 16 for MWCNTs–GCE. The highest value 168 F g⁻¹ of specific capacitance was measured at 500 mV/s scan rate.

Keywords- MWCNT, CVD, Supercapacitor, CV, Impedance spectroscopy, Specific Capacitance

I. INTRODUCTION

Carbon nanotubes have a novel structure, a narrow distribution size, highly accessible surface area, low resistivity, and high stability [1, 2]. They are broadly classified into single walled carbon nanotubes (SWNTs) and multi walled carbon nanotubes (MWNTs). Nowadays, CNT attracts significantly attention of the scientific community because of their remarkable optical, electronic, thermal, mechanical and chemical characteristics. Arc discharge, Chemical vapor Deposition (CVD) and laser ablation methods are the most commonly used techniques for the synthesis of the CNTs. The chemical vapor deposition CVD method is a controllable process for the selective synthesis of CNTs either individually or in bulk [3–7]. CVD method has been believed as the most suitable bulk synthesis method in terms of quality of both single walled CNTs (SWCNTs) and Multi walled CNTs (MWCNTs) [8]. Recently, the CNTs have been used for fabrication of supercapacitors, batteries, fuel cells, solar cells, Polymer nanocomposites, sensors and biological applications [9].

The single-walled and multiwalled carbon nanotubes (SWNT and MWNT) have been recognized as potential electrode materials for energy storage device like Supercapacitors for storing huge amount of energy [10, 11]. The most significant advantage of Supercapacitors are alternative to traditional batteries due to their miniature size, high power density, long life cycle, high energy density, high efficiency, fast charging and discharging, wide operating temperature, Safe and Light weight. These are having the potential for reducing waste disposal to the environment [12, 13]. CNTs based hybrid supercapacitors also developed with activated carbon electrodes. Hence, Carbon/Carbon based supercapacitors have been largely investigated because of their low cost, high cycling life and high capacitance [14, 15]. The development of supercapacitors has flexible, conformable energy storage devices are also of great interest to the emerging high energy storage devices [16, 17, and 18].

In the present work, catalytic chemical vapor deposition (CCVD) have been employed for the preparation of high yield and impurity-free multiwalled carbon nanotubes through the decomposition of methane and acetylene over an MgO supported Fe–Co catalyst. The Synthesized carbon nanotubes were characterized and tested as the electrode materials for supercapacitors application. Cyclic voltammetry measurements were carried for the bare glassy carbon electrode (GCE) and modified glassy carbon electrode (MGCE) with MWCTs to measure specific capacitance for the supercapacitor application.

II. EXPERIMENTAL

A. Catalyst preparation

The Fe-Co/ MgO bimetallic catalyst were prepared by impregnation method. Sample powder was ground and calcined at 300 °C in a muffle furnace for 4 hours [19, 20].

B. Preparation of carbon nanotubes CNTs-CCVD.

Preparation of CNTs was carried out in a horizontal electric tubular furnace under atmospheric pressure in CCVD method. The catalyst (about 100 mg) was spreaded over the quartz boat and it was placed in the centre of the furnace. The experiment was carried out at 700 °C and reaction time was 20 minutes, for CNT production in tubular furnace. After the furnace was reached temperature to 300 °C, the argon (Ar) (99.99 %) gas was introduced at rate of 84 ml min⁻¹ for 30 min. Hydrogen (H₂) (99.99 %) gas started to flow with a rate of 100 ml min⁻¹ when the temperature reached 550 °C for 45 min for the reduction of catalyst. Argon (Ar) gas was passed at the rate of 60 ml min⁻¹ for 45 min at the 565 °C. Then the synthesis was started with the introduction of acetylene (C₂H₂) (99.99 %) and argon at 700 °C with a flow rate of the 60 ml min⁻¹ for 20 min. After completion the reaction, the flow of Acetylene (C₂H₂) gas was stopped and the quartz tube was allowed to cool to room temperature under Argon (Ar) atmosphere with flow rate of 60 ml min⁻¹. The final product black fine powder was obtained in from the quartz tube and it was subjected to further purification process.

C. Purification of MWCNTs.

The above obtained Carbon Nanotubes (CNTs) were purified by acid and heat treatment method. Hydrochloric acid (10 ml) was added to 60 ml of distilled water with CNTs in stirring for 10 hrs. The HCl treatment was used to remove both the metal catalysts and the amorphous carbon. After stirring, the CNTs solution was filtered through whatman filter paper to separate the CNTs powders. Finally the filtered material was dried at 100 °C for 4 hours in air atmosphere and then annealing at 400 °C for in 2 hrs in muffle furnace. The pure CNT fine powder was then weighed and it was characterized by SEM, TEM and Raman analysis.

III. CHARACTERIZATIONS

A. Characterization of CNTs.

Crystallographic structures and Phase formation of the Purified MWCNTs were determined by a powder X-ray diffraction (XRD) system X'PERT- PRO model with Cu K radiation ($\lambda = 0.15406$ nm). The Surface morphology structure was analyzed by Scanning electron microscope (SEM) model JEOL - JSM-6390 instrument and Transmission Electron Microscopy (TEM), model (JEOL 3010) operated at 300 KV. Raman spectra were observed with a laser - Raman spectroscopy (Model STR) using a laser excitation line at 514.5 nm, with 1 μ m focus spot in order to avoid photo decomposition of the samples.

B. Electrochemical characterizations

The electrochemical measurements, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were performed in three electrode cell with mirror polished 0.07 cm² glassy carbon (GC) as the working electrode, Pt wire as the counter electrode and 0.1 M KCl Ag/AgCl as the reference electrode (CHI Model 6018D, USA) electrochemical workstation. CV measurements were carried out in 0.1 M KCl containing 1mM [Fe(CN)₆]^{3-/4-} as redox probe under air atmosphere at room temperature, the potential range between -0.2 to 0.8 V at a scan rate of 50 mV/s to 500 mV/s. The electrochemical impedance measurements were made by applying a.c potential amplitude of 5 mV over the d.c potential 200 mV in the frequency range between 100 KHz to 1 Hz.

IV. RESULT AND DISCUSSION

A. X – Ray Diffraction (XRD)

The XRD pattern of the purified multiwalled Carbon nanotubes (MWCNTs) is shown in the figure 1(a). The pattern showed a sharp diffraction peaks at $2\theta = 25.9^\circ$ with additional peaks 45° and 75.20° are attributed to the diffraction peaks correspond to (002), (100) and (110) respectively. The diffraction peak corresponds to (002) shows carbon phase and diffraction patterns typically well graphitized. The XRD pattern was conformed that the carbon nanotubes are in well crystalline hexagonal structure. The Raman analysis is most effective technique to evaluating the structure of CNTs. Figure.1 (b) shows the MWCNTs the major peaks at 1563 cm⁻¹, 1340 cm⁻¹

correspond to disorder (D) band and graphitic (G) band respectively. The G-band observed around 1563 cm^{-1} is assigned to the Raman allowed phonon E_{2g} (stretching) mode. The strongest peak of G-band in the spectrum indicates low defects and ID/IG intensity ratio value 0.17 the formation of good crystalline arrangement of hexagonal lattice [23]. So the major peaks (D and G) confirmed and the presence of crystalline graphitic carbon of MWCNTs.

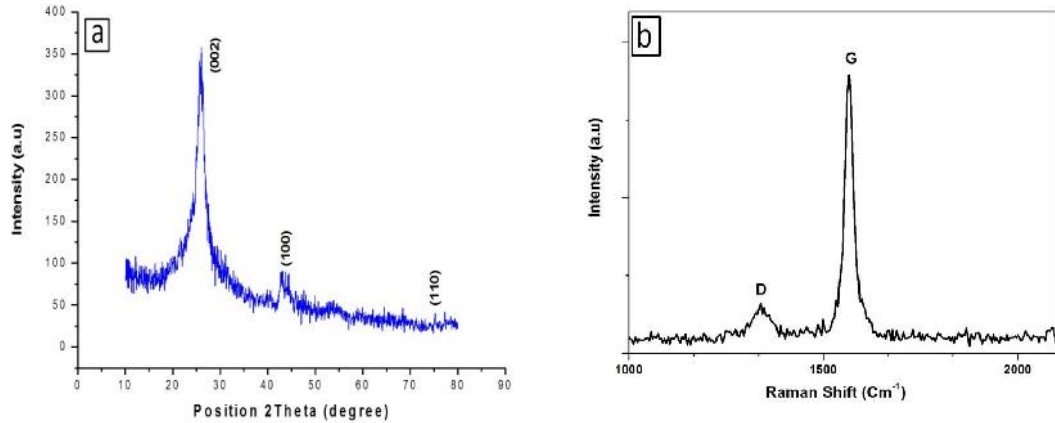


Fig.1 (a) the XRD pattern and (b) Raman spectrum of the purified multi walled carbon nanotubes (MWCNTs)

B. SEM ANALYSIS

The SEM images of as-synthesized CNT grown on Fe-Co/MgO catalyst at $800\text{ }^{\circ}\text{C}$ are shown in Fig 2 (a) and 2 (b). The synthesized MWCNTs are in the average diameter range of $50 - 100\text{ nm}$ and length is about $3.5 - 5\text{ }\mu\text{m}$. This image also clearly indicated the formation of CNT on the surface of tube like structure. The CNTs were not affected even after acid treatment purification. The SEM images show the good yield for Fe-CO/MgO catalyst. Also figure 4.2(b) shows the cluster of the CNT but there in uniform size. Transmission Electron Microscopy (TEM) images of purified MWCNTs were showed in fig. 2 (c) and 2 (d) for the multiwalled carbon nanotubes. The fig. 2 (c) shows very long multi walled carbon nanotubes with uniform diameter. The plenty fine graphitic walls were clearly visualized by TEM image Fig. 2 (d). The diameter of the multiwalled carbon nanotubes was found as 21 nm .

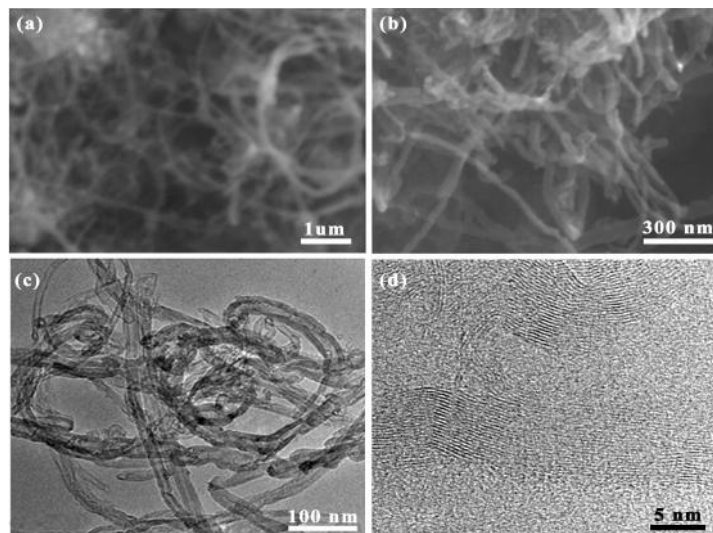


Fig. 2 (a) (b) SEM images of MWCNTs and (c)(d) TEM images of MWCNTs.

C. Cyclic Voltammetry studies

The electrochemical behavior of CNTs based supercapacitor electrode has been characterized by cyclic voltammetry. Fig. 3 (a) showed cyclic voltammograms curves obtained for bare glassy carbon electrodes in 0.1M KCl containing $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1 mM) and the I–V curve was recorded at the scan rate was varied from 50 to 500 mVs^{-1} . Fig. 3 (a) showed the redox peak currents are proportional to the square root of scan rate due to the increase of scan rate for the current density.

Electrochemical impedance spectroscopy (EIS) was used to measure the impedance of the glassy carbon electrode and MWCNTs at the potential 200 mv. The charge transport process in MWCNTs modified GC electrode has been studied by monitoring charge transfer resistance (R_{ct}) at the electrode electrolyte interface impedance spectra fig.3 (b). The R_{ct} value for bare GC, and MWCNTs modified glassy carbon electrodes have been estimated as 172 and 16 $\Omega \text{ cm}^{-2}$, respectively. The R_{ct} value of carbon nanotubes modified electrode was nearly 10 times higher than that of unmodified glassy carbon electrode. It may due to the high surface area and good catalytic activity of MWCNTs facilitate the charge transfer reaction of ferri or ferro cyanide reaction. Therefore, the impedance angle at low frequency region is nearly 45° and shows an ideal capacitance behavior.

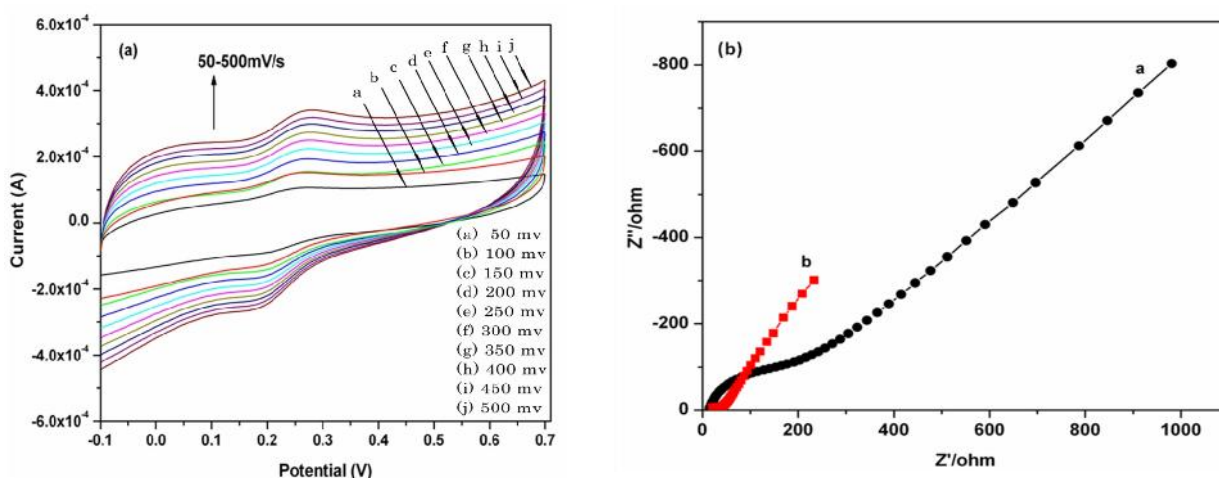


Fig. 3 (a) Cyclic voltammogram of MWCNTs modified GCE in 0.1 M KCl containing 1mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as redox couple. 3(b) Electrochemical impedance spectra of (a) bare GCE and (b) MWCNTs modified GCE in 0.1 M KCl containing 1mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as redox probe.

D. Supercapacitor – Specific Capacitance

The electrochemical measurements on supercapacitors the specific capacitance (C_{sp}), was calculated from current Vs voltage cyclic voltammograms curve were using cyclic voltammetry at scan rate 500 mV s^{-1} high specific capacitance 168 Fg^{-1} for MWCNTs.using the formula $C_{sp} = [(I(A) / (dV/dt)) \times m]$; where I is the current in amperes, dV/dt is the voltage scan rate in V/s , and m is the mass in milligrams of the active carbon material and their vales using from CV curve slope. The modified GC electrodes with MWCNTs resistance was low and good conductance.

V. Conclusion

Multi walled carbon nanotubes (MWCNTs) have been synthesized successfully by Catalytic chemical vapor deposition (CCVD). The XRD and Raman results were confirmed the carbon phase and carbon nanotubes crystallize hexagonal structure. The SEM and TEM showed the morphology of MWCNTs. The electrochemical measurements (Cyclic Voltammetry) were the rectangular shape for bare GCE and MWCNTs modified GC electrode. The charge transfer resistance (R_{CT}) value is 172 $\Omega \text{ cm}^{-2}$ and 16 $\Omega \text{ cm}^{-2}$ for bare glassy carbon electrode. The result indicated faster charge transport, which also could be responsible for its high specific capacitance (SC) values. The specific capacitance value (168 F g^{-1}) is the highest value for MWCNTs.

Acknowledgments

The authors wish to thank Dr.A.Pandurangan, Director, Institute of Catalysis and Petroleum Technology (ICPT) and R.Ragavan,Research Scholar, Department of chemistry, Anna University, Chennai for providing lab facilities to carried out the research work.

References:

- [1] S. Iijima, *Nature*, 354 (1991) 56.
- [2] C.M. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, *Appl. Phys. Lett.* 70 (1997) 1480.
- [3] P. F. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-first Century*, Cambridge University Press (1999).
- [4] M. S. Dresselhaus et al, *The Science of Fullerenes and Carbon Nanotubes: Their Properties and Applications*, Academic Press (1996).
- [5] T. W. Ebbesen ed., *Carbon Nanotubes – Preparation and Properties*, CRC Press (1996).
- [6] M. S. Dresselhaus et al eds., *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, Springer-Verlag (2000).
- [7] T. W. Ebbesen, *Carbon Nanotubes*, *Ann. Rev. Mater. Sci.* 24 (1994) 235; *Physics Today* 381(1996) 678.
- [8] B. Zheng, Y. Li, and J. Liu, CVD synthesis and purification of single-walled carbon nanotubes on aerogel-supported catalyst, *Applied Physics A*, vol. 74 (2002) 345–348.
- [9] Mukul Kumar, Yoshinori Ando, *Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production*, *J. Nanoscience and Nanotechnology*, 10 (2010) 3739–3758.
- [10] A. Burke, *Ultracapacitors: why, how, and where is the technology.* *J. Power Sources*, 91 (2000) 37-50.
- [11] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, New York, (1999).
- [12] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, and F. Beguin, *Carbon* 37(1999) 61.
- [13] I. Capek, *Dispersions, novel nanomaterial sensors and nanoconjugates based on carbon nanotubes*, *Advances in Colloid and Interface Science*, 150 (2009) 63.
- [14] D. Lozano-Castello, D. Carzorla-Amoros, A. Linares-Solano, S. Shiraishi, H. Kurihara and A. Oya, *Carbon*, 41 (2003) 1765.
- [15] F. Lufrano, P. Staiti, *Mesoporous carbon materials as electrodes for electrochemical supercapacitors*, *Int. J. Electrochem. Sci.* 5 (2010) 903 – 916.
- [16] J.R. Miller, A.F. Burke, *Electrochemical capacitors: Challenges and opportunities for real world applications.* *Electrochem. Soc. Interf.* 17 (2008) 53–57.
- [17] J.R. Miller, & P. Simon, *Electrochemical capacitors for energy management*, *Science*, 321 (2008) 651–652.
- [18] B.E. Conway, *Electrochemical Capacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic, Plenum, 1999.
- [19] Beh Hoe Guan, Irmawati Ramli, Noorhana Yahya, Lim Kean Pah., *Purification of Carbon nanotubes synthesized by catalytic decomposition of methane using bimetallic Fe-Co catalysts supported on MgO*, *IOP Conf. Series: Materials Science and Engineering* 17 (2011) 012025.
- [20] J.W. Seo, K. Hernadi, C. Miko and L. Forro, “Behaviour of transition metals catalysts over laser-treated vanadium support surfaces in the decomposition of acetylene”, *Applied Catalysis A: General*, 260 (2004) 87-91.
- [21] M.S.Dresselhaus, G.Dresselhaus, R.Saito, A. Jorio, *Physics Reports*, 409 (2005), 47-99
- [22] A.M. Rao, E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, et al. *Diameter-selective Raman scattering from vibrational modes in carbon nanotubes.* *Science* 275 (1997) 187–191.
- [23] John H. Lehman, Mauricio Terrones, Elisabeth Mansfield, Katherine E. Hurst, Vincent Meunier, *Carbon*, 49 (2011) 2581 – 2602.