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Synthesis of Multiwall Carbon Nano Tube by Using Eucalyptus Oil, its Characterization and Capacitance Study

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Abstract:- Multiwall Carbon nanotube (MWCNTs) are extensively studied in last few decades because of their great potential and wide applications in different fields like supercapacitors, gas sensors electronic devices, magnetic materials rechargeable batteries solar energy absorption pigment for ceramics, biosensors, fuel cell etc. Synthesis of MWCNTs was carried out by using chemical vapour deposition (CVD) method. In present work we used natural renewable green precursor i.e. eucalyptus *(Eucalyptus globulus)* oil for the synthesis of MWCNTs. CVD was carried out at 750^0C temperature with the flow rate 20 ml per hour of the precursor on Ni-Co catalyst in H2 atmosphere. The characterisation of synthesized MWCNTs was done by Infrared spectroscopy (IR) X-ray diffraction (XRD), Scanning electron microscopy (SEM), High resolution transmission electron microscopy (HRTEM) and Raman spectroscopic analysis. Surface area and Pore volume measured by Brunauer- Emmet-Teller (BET) technique. Capacitance study was done by using potentiostat (CHI110A). We confirmed the MWCNTs with diameter range 30 nm to 70 nm, surface area 163.89 cc, pore volume 0.248 cc and specific capacitance 214 F/g.

Keywords*: Multiwall carbon nano tube (MWCNT), Chemical vapour deposition (CVD) Eucalyptus oil, Specific capacitance, Brunauer- Emmet- Teller (BET).*

1. Introduction

The discovery of carbon nanotubes (CNTs) by Sumio Iijima in 1991 has sparked significant research to understand their structure and physical properties. Researchers have utilized both direct measurement and predictive modelling methods to characterize CNTs. Through this research, many of the fundamental and remarkable properties of CNTs have been uncovered. Today, CNTs are widely used in various applications due to their extensive properties (1,2). They are of basically two type's single walled carbon nano tube (SWCNT) and multiwall carbon nanotube (MWCNT) (3,4). Electronic properties of CNTs were significantly useful so they used in various electronic devices, while their structural geometry makes them a new and exciting material of precision-controlled drug delivery. They having exceptionally high tensile strength and stiffness so can be utilised where extraordinary mechanical properties are needed. They extensively used into the fabrication of nanotube composite materials. The manufacturing charge/cost of the CNTs is one of the great tasks. The conventional method used for the production of MWCNTs like arc discharge and laser ablation methods have disadvantage like less yield as compare to the starting material used, monotonous parameters to control and large time of production. The pyrolysis of oils, is an economical and simple method for production of CNTs at low temperatures. Fabrication and characterization of MWCNTs using pyrolysis techniques are described at present work. Our main interest is in the synthesis of MWNTs by a chemical vapour deposition (CVD) by making use of natural precursor i.e., Eucalyptus oil as carbon source so process designed to produce high-purity aligned nanotubes in bulk and with good quality CNTs at low-cost. Unsaturated hydrocarbons such as acetylene, ethylene, propylene and ethylene, have significantly higher reactivity than saturated hydrocarbons, so it is possible to conduct the catalytic pyrolysis processat low temperatures (5-7). Under the condition of catalytic pyrolysis, these unsaturated hydrocarbons are

able to under goes thermal and catalytic traction that form heavy hydrocarbon, which include condensed aromatics (8). This work focuses on the use of renewable, globally clean and cheap natural precursor as a source for the synthesis of carbon nanotubes (CNTs). Traditional carbon sources for CNTs synthesis often require the use of chemical products that are harmful and increase the number of steps needed for additional purification, leading to additional costs. Edible oils derived from plant seeds have been identified as a potential natural source for CNTs synthesis. These oils are globally available, renewable and relatively inexpensive. In addition, they are considered to be clean and environmentally friendly, making them an attractive alternative to traditional carbon sources. The use of edible oils in CNTs synthesis has been a topic of research in recent years. Studies have shown that edible oils can be used as a carbon source in the production of CNTs with similar properties to those synthesized using traditional carbon sources. The process of synthesizing CNTs using edible oils involves the pyrolysis of the oil under controlled conditions. The use of edible oils has been found to result in CNTs with high purity and high yield. In conclusion, the use of renewable, globally clean and cheap natural products such as edible oils derived from plant seeds presents an attractive alternative to traditional carbon sources for CNTs synthesis. This approach has the potential to reduce the use of harmful chemical products and the number of steps required for additional purification, resulting in a more environmentally friendly and cost-effective process.

2. Materials and Methods

2.1. Materials

MWCNTs were synthesized from natural precursor as carbon source i.e., *Eucalyptus globulus* oil. Raw Eucalyptus was collected from Kalyan market (near to college campus). Eucalyptus is medicinal plant easily grow in the in this tropical condition. Medicinally it is used for cough syrups and vapor baths, used to treat sinusitis, and also for to relive nose and chest congestion. Raw oil is enriched with carbon source so its directly use as carbon source for synthesis of MWCNTs (9,10). High purity of Hydrogen gas was provided by gas-world corporation Ulhasnagar, Kalyan. All other chemical reagents used for the experiment were of analytical grade purity, purchased from Merck, India and were directly used without any further purification (Nickel nitrate hexahydrate (Ni (NO3)3.6H2O), Cobalt nitrate hexahydrate (Co (NO3)3.6H2O), Glycine (C2H5NO2), Conc. Hydrochloric acid (HCl). Double distilled water required for the synthesis was prepared in our college laboratory.

2.2. Preparation of mixture of catalysts

A Ni-Co oxide is prepared using solution combustion method mixing by Nickel nitrate hexahydrate (Ni(NO3)3.6H2O), Cobalt nitrate hexahydrate (Co(NO3)3.6H2O), and Glycine (C2H5NO2) in 1:1:2 ratio in 30 ml distilled water heated at 550^0C in muffle furnace for 1 hour. Prepared Ni-Co oxide reduced in CVD furnace at 700^0C in presence of hydrogen atmosphere with flow rate 20ml/min for 90 min. The prepared Ni-Co catalyst used for the synthesis of MWCNTs.

2.3. Methods

The low yield methods in the synthesis of CNTs by other methods are slow and energy consuming because of that they increase the cost for production. The high cost of production limits the applications of CNTs on large scale. CVD method have been investigated over the years with advanced technique and alternative precursors (carbon source) such as natural oil help to reduce, CNTs cost and dependence on non-renewable carbon source. This research work was mainly focused on plant seed oil-based precursors, which used for synthesis of CNTs. The steps involved in synthesis of CNTs using biomass precursor are illustrated in figure 1. The raw Eucalyptus oil was filtered to remove any suspended impurities. In CVD unit two furnaces with heating zones were used. The precursor Eucalyptus oil was kept in quartz boat in furnace - A and catalyst in fine powder form of Ni-Co catalyst was kept in the quartz boat in furnace – B (Figure1). Carrier gas H2 was allowed to flow into the quartz tube with a fixed flow rate (6ml/min). After 15 min of flow, furnace-B was switched on to reach the desired temperature 750ºC. When the desired temperature was reached the oil was heated in furnace-A to 400ºC so as to vaporize the oil. Temperature of furnace B was also maintained at this pyrolyzing temperature for 2 hours to insure maximum deposition. At the end of the desired time the furnaces were switched off and allowed to cool at room temperature. MWCNTs formed inside the quartz boat was collected (11,12). Synthesized MWCNTs were treated with 50%

Conc. HCl to remove the catalytic impurities, amorphous carbon and metals present for 24 hours. Finally, the MWCNTs were filtered and washed with distilled water several times to reach neutral pH i.e.,7 and dried in an oven at 120°C and powdered. MWCNTs was then characterized by FTIR, XRD, SEM, HR-TEM and BET.

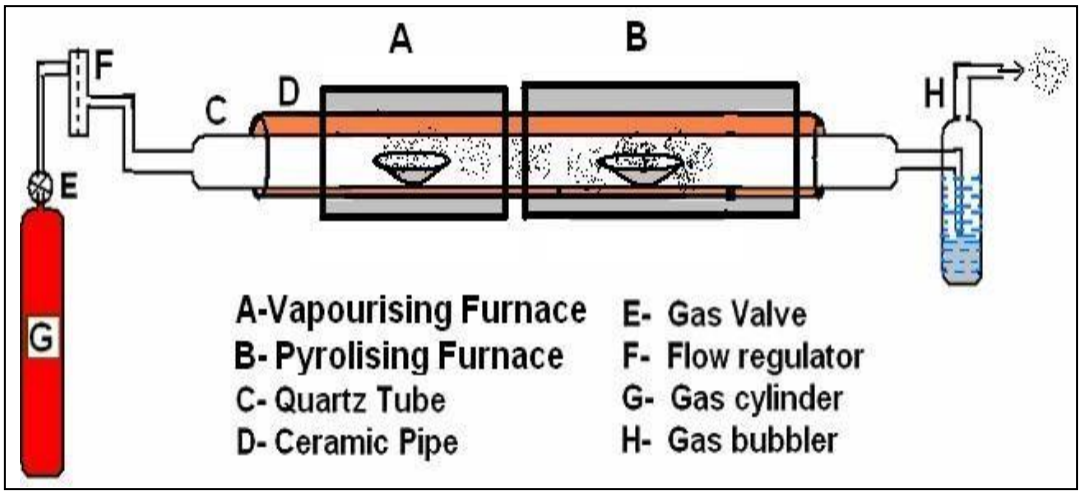

Figure 1. Schematic Diagram of CVD Furnace used in Synthesis of CNTs Using Eucalyptus Oil

3. Characterization

Purified MWCNTs obtained by CVD technique were characterized using following analytical instruments:

The chemical structure of the samples was examined using a FTIR Spectroscopy Jasco model No. 4100 in a wavenumber range of 400–4000 cm^{-1} set up at B. K. Birla College, Kalyan, India.

3.1. X-ray diffraction (XRD)

XRD patterns were recorded using a D2 phaser second generation X-ray diffractometer (Bruker, Bremmen, Germany) with a Cu Ka radiation (λ = 1.5418 Å) at a scanning speed of 10°/min from 10° to 80°.

3.2. Raman Analysis

Raman spectra were collected using the Laser Raman Spectroscopy HR800-UV confocal micro-Raman spectrometer, Horiba Jobin Yvon, France at SAIF, IIT Bombay in a range of 500–3000 cm^{-1}.

3.3. Surface Area Analysis (BET Analysis)

Surface area were analysed by nitrogen adsorption analyses implemented on single port Brunauer– Emmett–Teller (BET) analyzer (smart instrument, dombiwali, India).

3.4. Field Electron Gun -Scanning Electron Microscope (FEG-SEM)

The morphology of all samples was visualized by a FEG-SEM model of JSM—5410, courtesy of JEOL, USA at SAIF, IIT Bombay with an accelerate voltage of 30 kV.

3.5. High Resolution -Transmission Electron Microscopy (HR-TEM300)

The morphology of all samples was visualized by the HR-TEM of 300Kv Model: Tecnai G2, F30 at SAIF, IIT Bombay.

4. Results and Discussion

Eucalyptus oil is easily available low-cost natural carbon enriched source so it can be used for the synthesis of CNTs. Raw Eucalyptus oil is directly used for the synthesis at 750 °C and hydrogen as carrier gas for 1 hour deposition time. Simple method of purification is implied, synthesis is completed without release of nay toxic gas in atmosphere. To get more structural information about the synthesized MWCNTs, FT-IR, XRD, SEM, HR-TEM, TGA and BET of the powdered samples were performed and the results are represented as follows:

4.1. FT-IR Analysis

The FT-IR spectra of MWCNTs synthesized by using Eucalyptus oil as carbon source were shown in figure 2. It is seen that the band observed graphitic carbon material with induced characteristic peaks at 3153, 2630, 1384, 1145, 1099,714 and 835 cm^{-1}. Similar type of bands has been also reported by many other researchers for MWCNTs produced from different source. The band at around 3153 cm^{-1} are due to the –OH vibrational stretching mode of hydroxyl functional group (13). The band at around 2630 cm^{-1} are assigned to the -CH stretching mode. The peaks observe at 1384cm^{-1} are assign to C-H bending and 1145 and 1099 cm^{-1} are assigned for bending vibration mode of functional group attached to -OH atom like conjugated C-O stretching, C-O stretching in carboxylic groups, and carboxylate moieties (14). The band at around 714 cm^{-1} and band at around 835 cm^{-1} are assigned to the C=C bending mode.

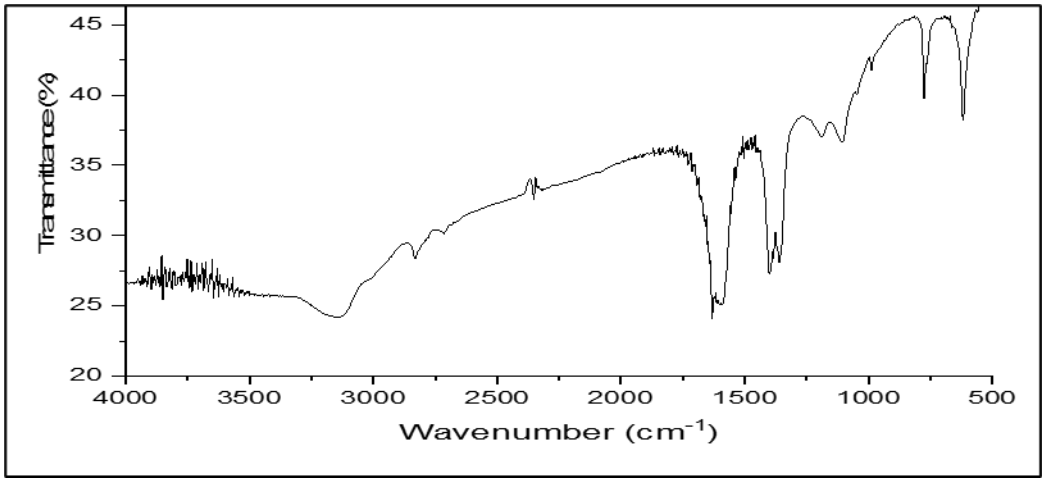

Figure 2. FT-IR Spectrum of MWCNTs Synthesized using Eucalyptus oil.

4.2. XRD Analysis

The XRD pattern of MWCNTs Synthesized using Eucalyptus oil were shown in figure 3. XRD profiles of the purified MWCNTs shows the diffraction peak at 2θ = 25.75° indexed as [111] reflection for characteristic graphitic carbon according to PDF JCPDS: 01-075-2078 (15). The low intensity peak at 44.41° is attributed due to the graphite like structure corresponding to the [010] plane. In addition, the positions and relative intensities of peaks present in figure 3, related with metallic particles at 2θ = 56.35° and 78.59° indicate the presence of metallic particles in MWCNT with plane [222] and [-110] respectively.

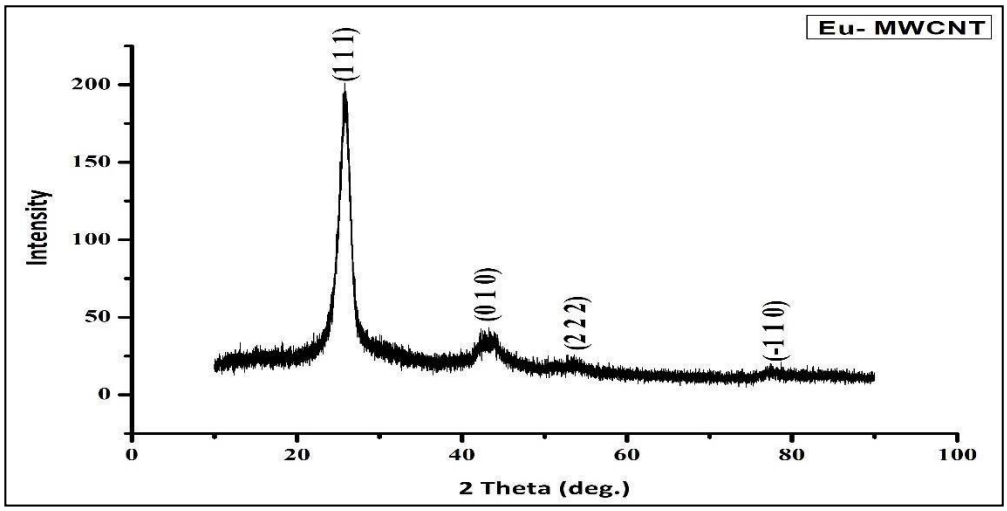

Figure 3. XRD Pattern of MWCNTs Synthesized using Eucalyptus oil

4.3. Raman Analysis

The Raman spectra of MWCNTs Synthesized using Eucalyptus oil were shown in figure 4. Spectrum profiles of the purified MWCNTs shows four separate peaks at 1347.96, 1576.39, 2682.73 and 2937.58 cm^{-1}. Which correspond to D and G Band respectively**.** The peak intensity of these two bands, as an index to determine the crystallinity and degree of graphitization of carbon nano materials (16,17). The D mode which corresponds to sp^2 hybridized carbon and G band is due to the C–C stretching in the graphitic material. The second order D-band (also called the 2D-band), peaks at 2682 cm^{-1} are due to asymmetrical C–H stretching vibrations of the CH2 group (18). The intensity ratio of the D band to the G band (ID/IG) is often used to estimate the defect concentration in carbon materials. The low value of ID/IG ratio indicates high graphitization and high value of ID/IG ratio is usually ascribed to the presence of defects on MWCNTs. The ID/IG ratio of R-CNFs is 0.58 indicates a high graphitization.

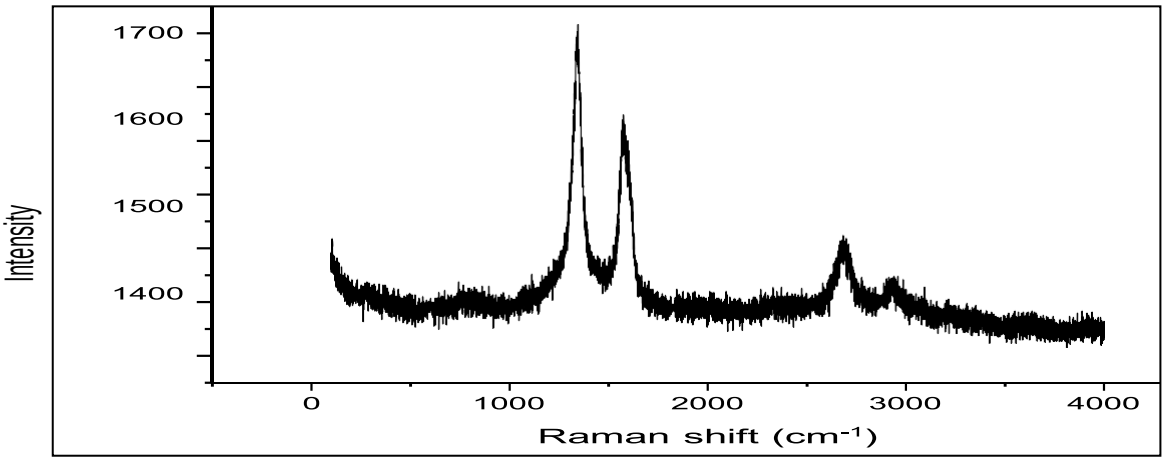

Figure 4. Raman Spectra of MWCNTs Synthesized using Eucalyptus oil

4.4. SEM Analysis

The scanning electron microscopy image of the as-grown MWCNTs over Ni-Co bimetallic catalyst surface as base at 750 °C under the flow of hydrogen by CVD method. SEM image clearly reveals that CNTs grew nicely on the surface of the catalyst with heterogeneous diameter. The SEM image of MWCNTs Synthesized using Eucalyptus oil shown in figure 5. The outer diameters and tube length size distribution of MWCNTs using SEM image were observed in detailed. SEM analysis shows that the tube outer diameter and length of the MWCNTs are in the range of 30-70 nm and tube length is approximately 5 microns respectively.

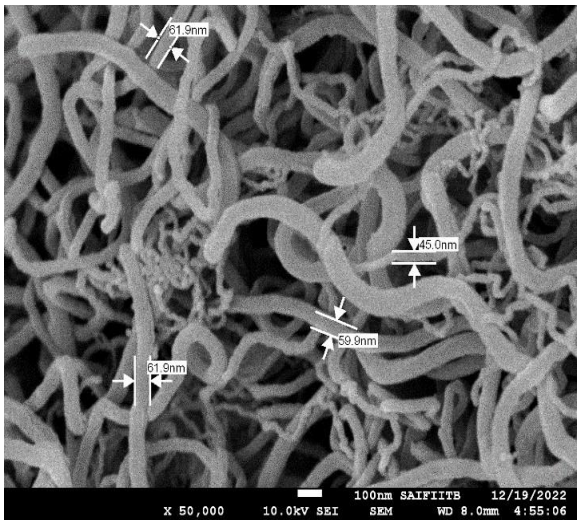

Figure 5. SEM Images of MWCNTs Synthesized using Eucalyptus oil

4.5. EDX Analysis

To find the elemental proportion of MWCNTs Synthesized using Eucalyptus oil, the EDX spectra of were analyzed. The EDX image of MWCNTs Synthesized using Eucalyptus oil were shown in figure 6. The EDX image of the purified MWCNTs indicate that MWCNTs contained different elements such as Carbon, Oxygen, Nickel, Cobalt and. The weight percentage of these elements were 96.19, 3.28, 0.33 and 0.28 respectively. From the weight percentage of the element's high purity of MWCNT is confirmed.

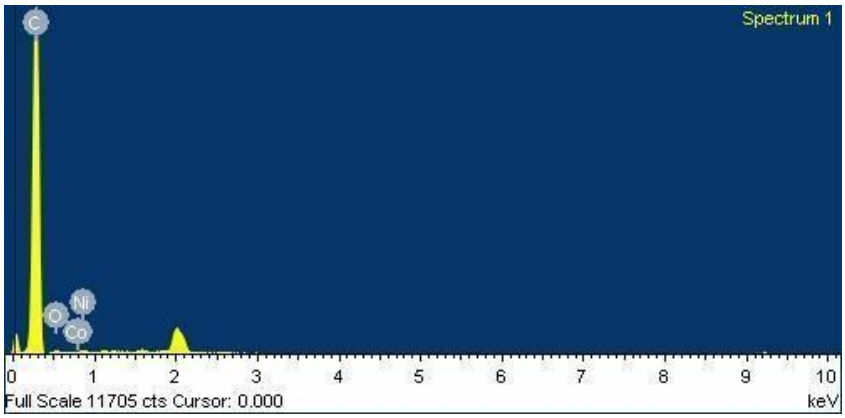

Figure 6. EDX Image of MWCNTs Synthesized using Eucalyptus oil

4.6. TEM Analysis

The carbon nanotubes obtained was characterized by HR-TEM to determine their morphologies. The results showed that very dense rope-like carbon nanostructures were grown from the surface of the dark catalyst clusters. Upon further magnification, the rope-like tubular carbon structure with a hollow core was visible, which confirmed the formation of CNTs. Figures 7 (a-d) demonstrate the HRTEM images of MWCNTs synthesized at 750 °C using Eucalyptus oil. These images provide a clear visual representation of the morphology of the CNTs, highlighting their unique and complex structure. Overall, the HR-TEM analysis revealed the successful synthesis of MWCNTs with desirable morphologies and characteristics. It can be observed from HRTEM images that the nanotubes formed are of multi-walled type composed of around 30 to 40 walls and most graphene layers grow perpendicularly to the growth axis of the tubes. The average outer diameter of the nanotube ranges from 20-60 nm and inner diameter is about 5 to 15 nm.

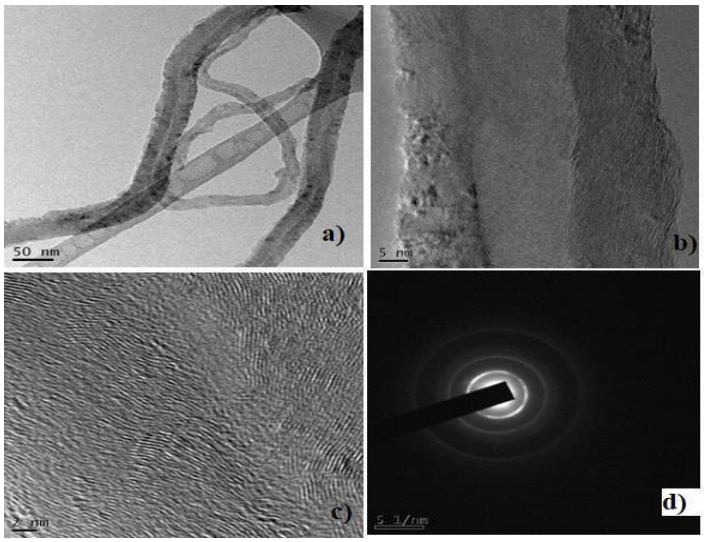

Figure 7.TEM Image of MWCNTs Synthesized using Eucalyptus oil

4.7. Surface Area Analysis

The specific surface area of the MWCNTs is obtained by the N2 adsorption using the BET method. The specific surface area of as was 113.84 m^2/g., which increases after acid treatment and observe surface area of as purified MWCNTs was 163.89 m^2/g.

4.8. Electrochemical Measurements

Electrochemical performance measurement by cyclic voltammetry technique on CHI1101A electrochemical workstation (CH Instrument Pvt. Ltd. India). To investigate the electrochemical properties, the synthesized functional carbon electrode material was fabricated using active carbon material (MWCNTs), carbon black as conductive additive and polyvinylidine fluoride (PVDF) as used as binder in the ratio 80:10:10 dissolve in NMP solvent. Initially all three materials were grind together in mortar pastel for proper mixing after ensuring proper dispersion, the slurry was prepared by adding required amount of NMP solvent. Prepared slurry coated on the activated Ni-foam sheet with surface area 1 cm^2, the prepared working electrode was dried in oven for 3 hours at 120 ^{0}C. The measurement was carried out in 6M KOH aqueous solution by three electrode system. MWCNT coated Ni-foam as working electrode, Ag/ AgNo3 reference electrode and platinum wire as counter electrode. Cyclic voltammogrames (CV) were measured at the scan rate 10, 20, 30, 40, 50, and 100 mVs^{-1}. The specific capacitance values calculated and were found to be 214,193,176,161,149,109 F/g. The electrochemical stability was tested by CV at a scan rate of 50 mVs^{-1} for 1000 cycles.

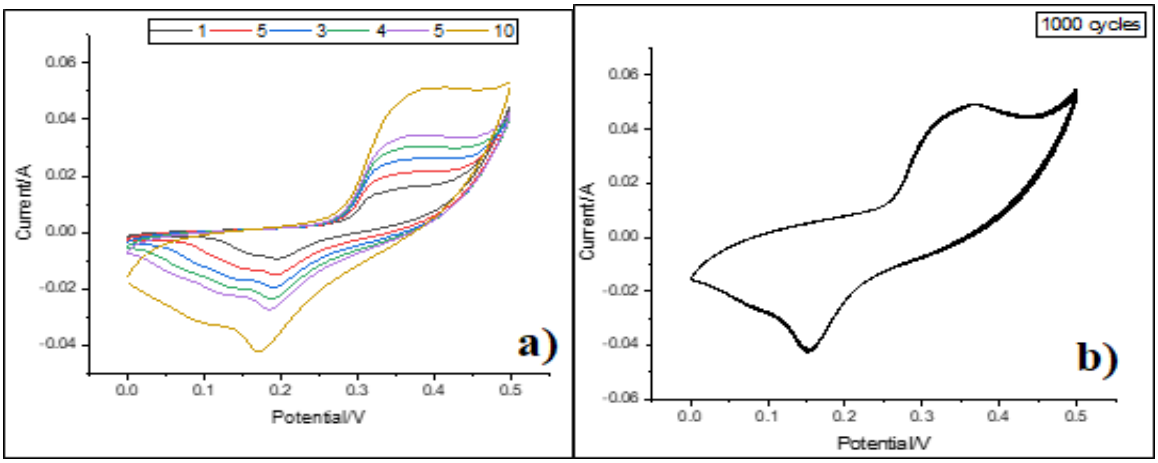

Figure 8. CV plot of MWCNTs Synthesized using Eucalyptus oil (a) Scan rate (b) Stability curve

5. Conclusion

We successfully synthesize MWCNTs at a temperature of 750^{o}C using Eucalyptus oil on Ni-Co bimetallic catalyst support. CNTs morphology and structure were investigated by FT-IR SEM, HR- TEM, XRD, BET and Raman spectroscopy. It was found that temperature was enough to transform hydrocarbon source into carbon nanotubes using plant oil Eucalyptus oil. MWCNTs obtained with heterogeneous diameter, very good quality and yield and purity up to 98% at this temperature. The MWCNTs grown also has high surface area 163.89 m^2/g and pore volume 0.245 cc. so can be useful for their potential application in different fields. Thus, we could grow good crystalline MWCNTs from renewable carbon source Eucalyptus oil at low temperature by CVD without release of any toxic chemicals.

Acknowledgments

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