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Original article

Growth of carbon nanotubes on a finely dispersed nickel metal and study its electrochemical application

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ABSTRACT Growth of Carbon nanotubes (CNTs) were obtained by Chemical Vapour Deposition (CVD) technique. Castor oil was vapourised above its boiling point and pyrolysis of oil was carried out by passing vapours over finely dispersed nickel metal at 650 °C. After characterization study of carbon material, scanning electron microscope (SEM) image revels that there is a growth of densely packed nanotubes with average diameter 30 – 40 nm. The XRD study of purified carbon nanotubes shows graphitic nature of carbon. Electrochemical application of CNTs obtained was studied in Supercapacitor. Cyclic Voltammetry (CV) was used to study the capacitive behaviour of carbon nanotubes in KOH electrolyte. A capacitance of 9.89 F/g (based on the weight of the carbon material) was obtained.

KEYWORDS Carbon nanotube, castor oil, pyrolysis, nickel metal, capacitance

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1. Introduction

Supercapacitors or electric double-layer capacitors (EDLCs), are the new generation of energy storage devices to store electrical charges and provide high power densities and long cyclic life compared to other storage devices (e.g., Li-ion, lead acid, and alkaline batteries). These capacitors are intermediate systems that mainly use high dielectric materials to store more energy in a shorter time. Owing to high charging–discharging rate, large power density, as well as excellent longevity, supercapacitors have been widely seen as some of the most prospective energy storage devices [1, 2].

Supercapacitor known as "electric double-layer capacitor" utilizes the phenomenon called electric double layer whereby electricity is stored at the interface of a solid electrode and a liquid electrolyte. Hence, due to the accessible electrode/electrolyte interface and a low electrical resistance of nanotubes, a high power is expected for devices built with electrodes from these materials [3, 4]. Various carbonaceous materials have been discussed as electrode materials in supercapacitor. CNT possess many unique properties such as high mechanical strength [5], capillary properties [6], remarkable electrical conductivity and, more importantly, high specific surface area [7] which makes it a promising material for supercapacitor applications.

It is widely accepted that CNMs of various different morphologies are synthesized from plants parts as well as plant derivatives by the process of Chemical Vapor Deposition (CVD) under pyrolytic conditions [8, 9]. Researchers have also successfully prepared carbon nanotubes (CNTs) from vegetable sources by a modified traditional process [10, 11].

Hydrocarbons which are derived from fossil fuels have been used as precursor for CNT [12]; but greater availability and low cost of natural precursor sources might be advantage. Sharon et al have obtained various forms of graphitic carbon by pyrolysis of camphor [13–15].

In this paper, we report on the preparation of CNT by low temperature (650 °C) CVD of Castor oil (derived from castor seed) over finely dispersed Ni metal as a catalyst. Our point of interest was to see whether abundant growth of CNT can be brought by using a finely dispersed Ni catalyst and to study its capacitive behaviour.

2. Experimental: synthesis of carbon material

Metals particles such as Ni, Co, Fe are known for their catalytic role in growth of CNTs [16]. Ni metal catalyst was prepared by thermal decomposition method. Mixture of Ni $(NO_3)_2$ and urea (1:3 weight ratio) was prepared in aqueous medium [17]. The solution was then heated at around 500 °C at the flash point of urea. The decomposition of urea is highly exothermic and large amounts of ammonia and carbon dioxide are liberated and fine nickel oxide is obtained. The explosive gas blows off the material resulting into ultra-fine crystallite powder. The nickel oxide was reduced in H_2 at

600 °C for 2 hours yielding a very fine metal powder which was used as catalyst to grow CNT by CVD of castor oil. In CVD unit two furnaces with heating zones were used.

Initially H_2 gas was allowed to pass through quartz furnace to make oxygen free atmosphere. Carrier gas H_2 was allowed to flow into the quartz tube with a fixed flow rate (6 ml/min). After 15 min of flow, the furnace was switched on to reach the desired temperature 650 °C. When the desired temperature in the second zone was reached the oil was heated in the first zone to 400 °C so as to vaporize the oil. Temperature of the second zone of furnace was also maintained at this pyrolyzing temperature for 3 h to insure maximum deposition. At the end of the desired time, the furnace was switched off which allows one to cool for overnight at room temperature.

Carbon material formed inside the quartz boat was collected and purified by treating with 50 % HCl for 24 h, in order to separate the CNT from Ni catalyst [18]. After that CNT were filtered of and finally washed with distilled water to neutral pH and dried in an air at 400 °C to remove amorphous carbon. This Carbon material was characterized by SEM, XRD and Raman spectra.

This way of carbon nanotubes synthesizing on a finely dispersed nickel metal was studied from the point of view of its electrochemical applications. All electrochemical measurements were performed with a potentiostat. With the help of potentiostat, voltage was applied for measuring of the current-voltage characteristics of the carbon material.

A set of half-cell electrode assembly of configuration "Pt / carbon nanotubes / electrolyte/ Pt" was made and specific capacitance was measured by cyclic voltammetry with the scan rate 20 mV/s, in 30 % KOH electrolyte. Pt plate and saturated calomel electrode were used as the counter and reference electrode respectively.

3. Results and discussion

3.1. SEM study

Microstructure and morphology of the carbon material was studied by SEM image (Fig. 1). SEM image shows that the CNT are densely packed. The average diameter of CNTs is in the range of 30 to 40 nm. It is well known that such high surface area material is very useful to assemble capacitor for better capacitance. Usually carbon nanotubes produced by CVD method are mixed with nanotubes of disordered structure and amorphous carbon [19].

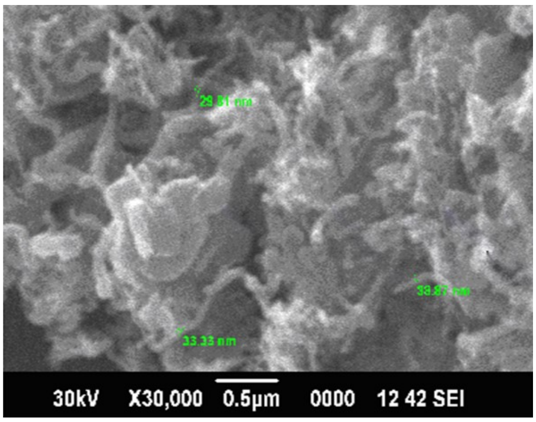

FIG. 1. SEM of CNT synthesized from Castor oil

3.2. Spectroscopic studies

3.2.1. Interpretation of XRD patterns. XRD shows similar diffracted pattern peak (002) with graphite sheet, but not identical (Fig. 2) [20]. XRD (Fig. 2) spectrum suggests the presence of graphitic carbon which can be indicated by the sharp peak at $2\theta = 26.45$ (002) [21] along with 44.40 (101) and 54.25 (004) values. Presence of broad peak attributed to partial crystalline nature of carbon.

3.2.2. Raman spectroscopy. The G-band and D-band which are characteristic for graphitic nature of carbon are prominent in Raman spectrum (Fig. 3). The G-band at 1584 cm^{-1} originates from ordered graphitic nature of carbon while D-band at 1354 cm^{-1} is due to disordered carbon. Raman spectrum showed well resolved D-band characteristic peak due to destabilization of graphitic plane [22]. These peaks are slightly shifted from its original position at 1580 cm^{-1} of G-band and 1340 cm^{-1} for D-band, respectively. The prominent G-band characteristic peak corresponds to tangential vibration in all sp^2 carbon atoms in materials.

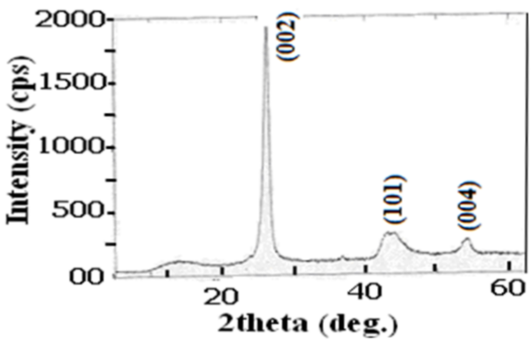

FIG. 2. XRD of CNT synthesized from Castor oil

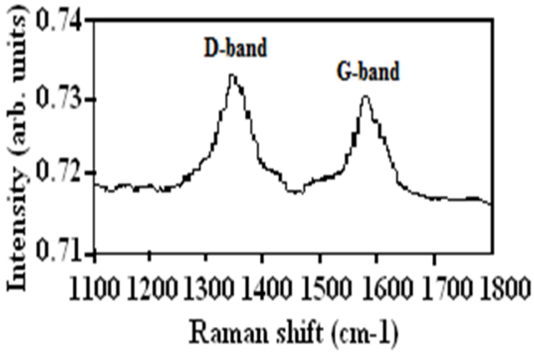

FIG. 3. Raman spectra of CNT synthesized from Castor oil

3.3. Electrochemical characterization

With the help of potentiostat instrument, electrochemical study of carbon nanotubes was carried out for three electrode system in 30 % KOH electrolyte. Cyclic voltammetry study of CNT material was carried out at 20 mV/S scan rates. Potential window, where no prominent oxidation-reduction peak observed (that is -0.4 to $+0.4$) was used for CV (Fig. 4); which indicates that the carbon material is stable in provided potential range. Capacitance was calculated from CVs at low scan rate, namely, 20 mV/s scan rate [23].

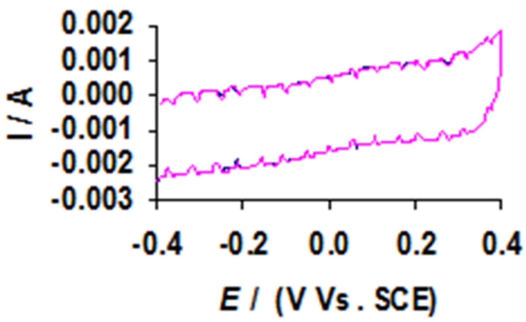

FIG. 4. CV of CNT in 30 % KOH; weight of electroactive material – 5 mg

From a potentiodynamic sweep, the capacitance (C) was calculated by considering equation, $C = \frac{dQ}{dE}$, where $\frac{dQ}{dE}$ is the rate of change of the surface charge density of the double layer with electrode potential.

Capacitance of the supercapacitor or electrochemical double layer capacitor was tested and specific capacitance of carbon nanotubes derived from castor oil was calculated on the basis of weight of the electroactive material taken (5 mg).

Hence, specific capacitance 9.89 F/g was reached for CNTs obtained from castor oil. Though CNT are known for their high surface area; its unorganized structure may lead to less accessibility to electrolyte solution. The surface area of those non-accessible pores will not contribute to the total double-layer capacitance of the material [24, 25].

4. Conclusion

Growth of carbon nanotubes on a finely dispersed nickel metal was very effective method. Highly dense carbon nanotubes (CNTs) were obtained by pyrolysis of castor oil vapours. Supercapacitor was assembled by using CNT electrode and electrochemical study was performed in 30 % KOH electrolyte and specific capacitance of 9.89 F/g was reached for this device.

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