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Electrochemical Enhancement of Carbon Nanotubes Utilizing MnO_2 for Energy Storage Applications

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Abstract

Carbon nanotubes /Manganese oxide nanocomposites were prepared by two techniques a facile microwave-assisted technique and chemically synthesized technique. The structure, morphology, and electrochemical properties of prepared nanocomposites were investigated by the characterization measurements (XRD, FTIR, SEM) and electrochemical measurements. The XRD confirms the existence of MnO_2 on carbon nanotubes, which agrees with FTIR results where the fingerprint area of FTIR showed the incorporation of the metal oxide onto CNTs. SEM investigations show flower-like nano plates of MnO_2. Carbon nanotubes/MnO_2 nanocomposites show great enhancement in their electrochemical properties and larger value of specific capacitance than raw carbon nanotubes.

Keywords

Carbon nanotubes; MnO_2; Microwave-assistant; Electrochemical; Energy storage

1. Introduction

The demand for energy consumption has experienced significant growth owing to the rapid expansion of the global population and the international economy. Hence, there is a strong demand for efficient energy storage systems and consumer electronic devices[1]. Electrochemical energy storage (EES) devices have proven to be highly advantageous for the operation of portable electronic devices and hybrid electric vehicles. Among various emerging EES technologies, researchers are interested in developing electrochemical capacitors (ECs), and Li-ion batteries starting from their electrode materials[2].

In ECs, the capacitance arises from the adsorption of both anions and cations at the interface between the electrode and electrolyte. Consequently, it is highly dependent on the surface area of the electrode materials[3]. In the charging process, the direction of movement of both electrons and ions is reversed during the discharging process. Porous carbons, including activated carbon, carbon nanotubes (CNTs), carbon nanofibers (CNFs), mesoporous carbon, graphene, and graphene oxide, are considered standard electrode materials for electrochemical systems[4][5]. The performance of ECs electrodes depends on several main factors: specific surface area, pore size, electrical conductivity, and uniform distribution. However, carbon nanomaterials have some drawbacks as electrode material such as low volumetric energy density and low specific capacitance[6]. Recently a lot of researchers try to enhance the properties of these promising electrode

materials for energy storage application, they using Carbon nanomaterials based metal oxides nanocomposites to solve carbon nanomaterials problems[7][8][9]. Manganese oxide (MnO_2-based materials) have been intensively investigated as electrode materials for energy storage specially in ECs due to their high theoretical specific capacitance, good chemical, and thermal stability, environmental, natural abundance and low-cost preparation techniques[10][11].

In this study, we successed to improve the specific capacitance and generally electrochemical properties of multiwall carbon nanotubes (CNTs) by using MnO_2 utilizing two simple synthesis approach Microwave-assistant and chemical method the structure and morphological characterization of samples confirm the growth of MnO_2 on CNTs . A good agreement results with other reports were achieved where the nanocomposites of MWCNTs/MnO_2 exhibit promising properties for utilization in electrochemical energy storage applications.

2. Materials and techniques

Multiwall carbon nanotubes (CNTs) powder was obtained from Nanoridge-Houston-USA. Potassium permanganate, sulfuric acid and manganese chloride hexahydrate from loba-chemie PVT-LTD in India. X-ray diffraction (XRD) analyses were investigated by Philips (Model X-Pert). FTIR spectroscopic analysis was performed by the Nicolet 6700 FTIR spectrometer within the range of 400–4000 cm-1. The surface morphology of nanocomposites was morphology using a scanning electron microscope (SEM Model Quanta-250 FEG). Electrochemical studies were done using screen-printed electrodes (SPEs) with three-electrode system (working, counter and reference electrodes) Palmsens-4- potentiostat electrochemical workstation.

3. Experimental work

For microwave-assisted technique: Firstly, a pretreatment of CNTs were done by microwave-assisted route before being used. Briefly, CNTs solution (1.0 mg/ml) was stirred with a small droplet of surfactant for 5 min. then, CNTs solution was exposed to microwave radiation for 5 min with moderate power. The final MWCNTs powder was obtained after drying at 60 °C. Next, a 0.3 g of potassium permanganate (KMnO4) was added gradually while stirring to mixture of MnCl2.6H2O solution (10 mg/ml) and MWCNTs solution (1.0 mg/ml) for 20 min. Afterward, The mixture suspension was further irradiated with a microwave for 5 min, the mixture was filtered and dried at 60 °C to obtain the MWCNTs/MnO_2 nanocomposite. Fig. 1 illustrates the preparation steps of the nanocomposites.

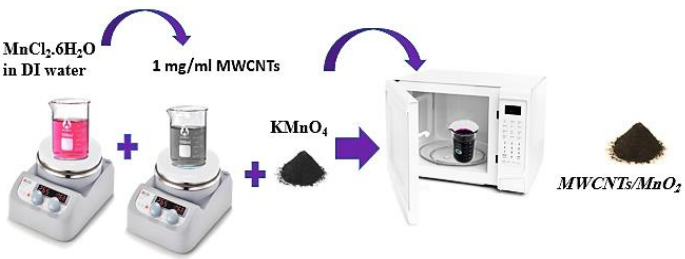

Fig. 1- Illustration of the microwave preparation method.

For chemical method: The CNTs /MnO_2 nanocomposites were prepared through a chemical reaction between the CNTs and KMnO4 by one–pot synthesis, followed by thermal treatment. In brief, 0.1 g of CNTs grind with 1 g of KMnO4 crystallites by a mortar and pestle to get a fine powder. This powder was then suspended in DI-water 100 ml and stirred at room temperature (~27 °C) for 9 h. After that, a few amount of concentrated H_2SO_4 (500 µl, 95– 98 wt%) was added to the system and the stir continued for an extra 60 min. Then, the mixture was heated in an oil bath at 80 °C for 60. The reaction mixture was then poured into 500 ml of DI water to cool down and dilute. The mixture was filtered, and the remaining solid was washed repeatedly with DI-water several times then dried at 80 °C for 6 h, finally the resultant powder named CNTs/MnO_2 as shown in Fig. 2.

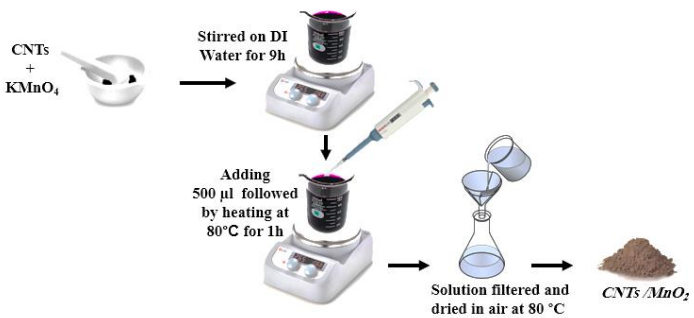

Fig. 2- Illustration of the chemical preparation method

4. Result and discussion

4.1 Structural characterizations by XRD

Structural characterisation of the as-synthesized nanocomposites were studied using the XRD s shown in Fig. 3 for raw material CNTs two significant characteristic peaks appeared at 26.28° and 44.88° which are related to (002), and (100) planes of graphite[12]. The XRD of MWCNTs / MnO2 shown broaden peaks around 22°, 37°, 42° and 56°, the pattern related to the pure orthorhombic gamma-phase of MnO_2 This result

completely agrees with Joint Committee on Powder Diffraction Standards (JCPDS) 14-0644 for gamma-phase of MnO2[13][14].

On another hand CNTs/ MnO_2 nanocomposite sample has a diffraction peaks of birnesstie type of (delta- phase) δ-MnO2 which are four broaden peaks at around 12°, 24°, 37°, and 66° corresponding to the crystal planes of (001), (002), (111), and (312), respectively. As in (JCPDS 42–1317) for birnessite-type of δ -MnO_2 phase[15].

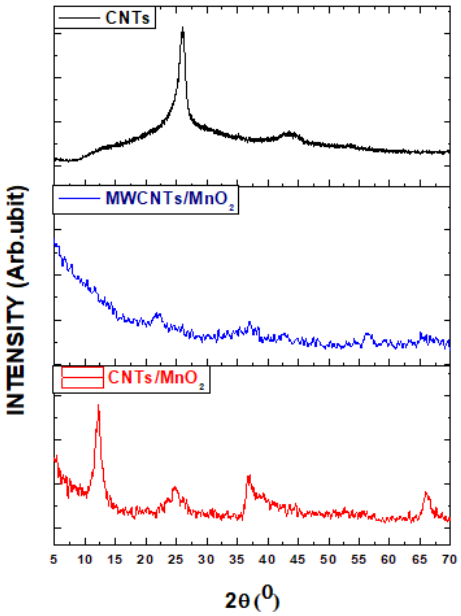

Fig. 3- XRD analysis of the synthesized nanocomposites.

4.2 FTIR analysis

Fourier Transform Infrared (FTIR) analysis plays a pivotal role in the characterization of intermolecular forces and the identification of chemical functional groups that arise from the formation of nanocomposites or mixtures involving various compounds. Consequently, the utilization of FTIR was necessary in this study, as depicted in Figure 4. The CNTs spectra showed the aromatic C=C at around 1600 cm^{-1} (the characteristic band of all carbon nanomaterials) beside some functional groups such as the O–H (3500 cm^{-1}), and C–O (1030 cm^{-1}). For the CNTs/MnO_2, and MWCNTs/MnO_2 nanocomposites a characteristic peak was obtained at 555 cm^{-1} and 430 cm^{-1} respectively, which is referred to the stretching vibrations of Mn-O[16], confirming the formation of CNTs /MnO_2 with complete agreement with XRD results .

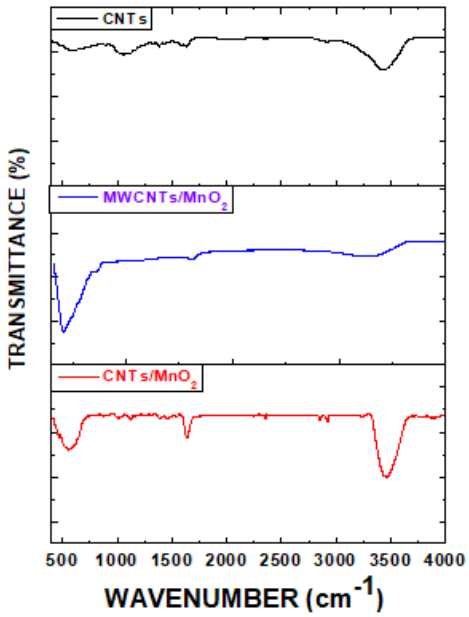

Fig.4- FTIR spectrum of CNTs, MWCNTs/MnO2 and CNTs/ MnO2.

4.3 Morphological analysis

The morphological features of the nanocomposites were explored using FESEM as shown in Fig. 5. The SEM image of the CNTs (Fig. 5a) demonstrated the tube structure with an obvious smoothness of the surface over the entire tube, While MnO2 nano-spheres were distinguished in the whole MWCNTs/MnO_2 nanocomposite, The sphere structure of MnO_2 exhibited a high spongy cluster structure referring to the high specific surface area (Fig. 5b). for the CNTs/ MnO_2 nanocomposite (Fig. 5c), we can see a uniform coating of MnO_2 layers along the carbon tubes and appeared on the surface of CNTs as cross-linked nanoflakes (flower shape) of MnO_2.

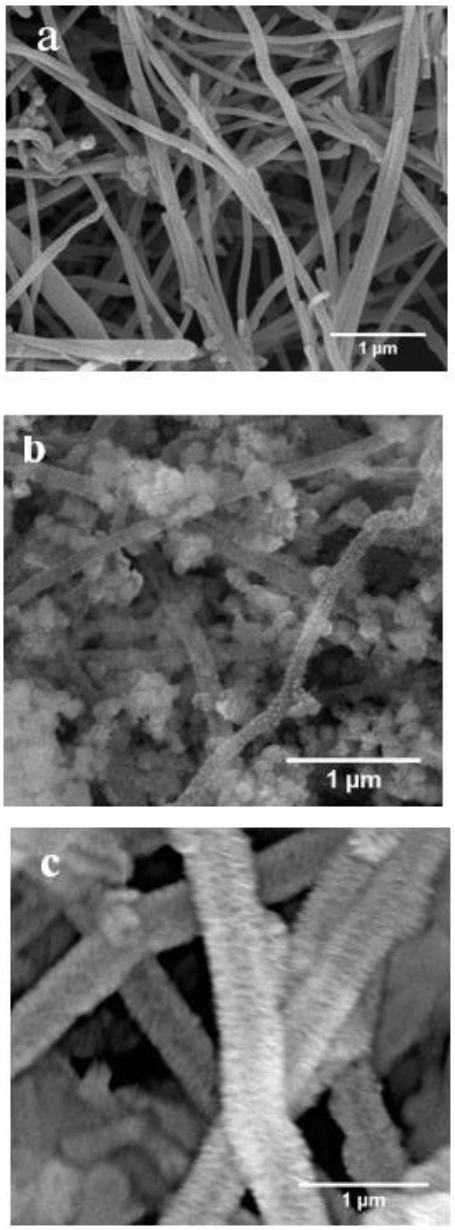

Fig. 5-SEM images of (a)CNTs ; (b) MWCNTs/MnO_2 ; (C) CNTs/MnO_2

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5. Electrochemical properties of nanocomposites

To have a better understanding of the electrochemical performance of the synthesized nanocomposites, screen-printed carbon electrodes (SPEs) were modified with a thin film of the composites. In briefly, 5.0 mg of the prepared nanocomposite was suspended in 1.0 ml of distilled water, and ultrasonicated for 30 min to get a homogenous suspended solution. the suspended solution (30 µl) was drop-casted on the electrode surface and left to dry at room temperature. For SPE characterization, CV measurement were conducted in ferricyanide $[Fe(CN)_6]^{-3/-4}$ (5.0 mM), as the standard redox probe in 0.1 M KCl (as the supporting electrolyte). Fig.6 summarizes the fabrication steps of the working electrode.

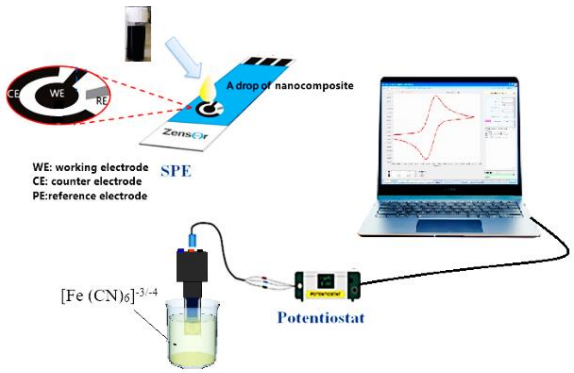

Fig.6-Steps of working electrode modification with the prepared nanocomposites

The storage of the electrical charge in the electrodes depends on double layer charging, faradaic processes, or a combination of both mechanisms. For carbon nanotubes electrodes the mechanism of charging-discharging process is due to the charge adsorption or accumulation at the interface between the electrode and the electrolyte, referring to the electric double layer (EDL) capacitance[2]. This process is electrostatic and non-faradaic. The specific capacitance could be given using the following equation[13]:

$$C = \frac{\int I\, dV}{2 \times v \times m \times \Delta V} \qquad (1)$$

where C is the specific capacitance (F/ g), v is the scan rate (V/s), m is the mass of the active material (g), ΔV is the potential window (ν) and I dV represents the area inside Cycle voltammetry curve. From equation 1 we can note that less area demonstrates the small specific capacitance. Consequently, the electrochemical behaviours of the prepared nanocomposites are characterized by cyclic voltammetry (CV). The good enhancement in the electrochemical performance is obtained when Carbon nanotubes electrode were modified with the MnO2 nanomaterial. This enhancement attributed to the enlarged surface area of electrode material.

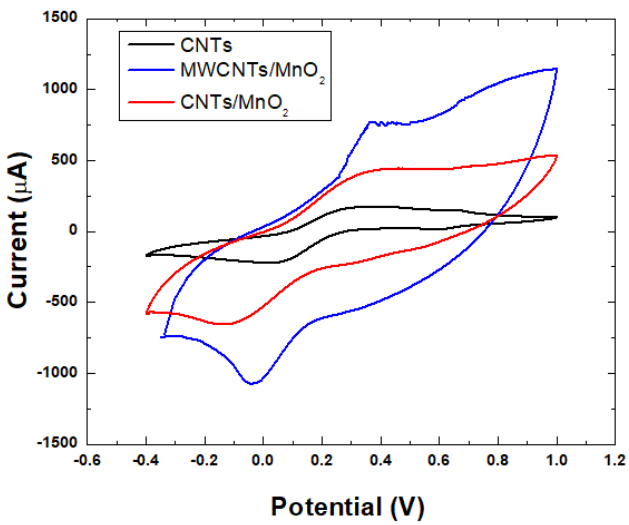

Fig .7- CV of prepared nanocomposites at scan rate

Thus, the prepared nanocomposites presented here are very promising feature in the electrochemical applications such as energy storage, sensors and biosensors. Voltammetric analysis of the fabricated nanocomposite was illustrated in Fig. 7. As reported in many researches before the CNTs has a quasi-rectangular voltammogram like a supercapacitor [17] while the MnO_2-based CNTs have a couple of oxidation/reduction peaks which

can be attributed to the surface functional group after treatment. CNTs have a high electric conductivity so they can offer a direct conductive path for MnO_2. Which lead to reducing the internal resistance within the nanocomposite itself. Additionally, the CNTs inter-tube pores demonstrate fast transport of the redox species from the solution to the surface of MnO_2.

Although the highest redox current was exhibited by the MWCNTs/MnO_2, the electrocatalytic function was more pronounced by the CNTs/MnO_2 modified electrodes. This electrocatalytic aspect was demonstrated by the observed shift of the redox peak towards the negative potential. The calculated electrochemical parameters shown in table 1. Where I_a is the anodic current I_c for the cathodic current, E_{oxd} for the potential of oxidation, E_{red} for the potential of reduction, ΔE is the change in the redox potential and SC specific capacitance.

Table 1 . Electrochemical parameters of prepared samples.

nanocomposites	I_a (μA)	I_c (μA)	$E_{oxd.}$ (V)	E_{red} (V)	ΔE (V)	SC (F/g)
CNTs	177	-230	0.15	-0.051	0.201	118
MWCNTs/MnO_2	780	- 1079	0.37	-0.046	0.41	447.5
CNTs/MnO_2	413	-280.6	0.35	-0.121	0.47	850.3

Conclusion

In summary, the present study reported the successful synthesis of MnO2/carbon nanotubes utilizing a two route with avoiding the use of complex and costly synthesis methods. Structural analysis using XRD and FESEM confirmed the synthesis of the MnO2/carbon nanotubes nanocomposites. The as-synthesized samples of CNTs /MnO2 and MWCNTs/MnO2 exhibited a distinguished porous structure. The fastest electron transfer as well the highest electrochemical performances were obtained by MWCNTs/MnO2 nanocomposite. Beside that the preparation time by using microwave-assistant as preparation method is more less than that for chemical method. Based on the electrochemical measurements, MWCNTs/MnO2 are beneficial and promising in various applications including the electrochemical energy storage systems, and the electrochemical sensor.

Acknowledgements

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