

Effect of aqueous electrolytes for TiO₂/MWNTs nanocomposites thin film electrode Supercapacitor

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Abstract

Research in carbon nanotubes has been tremendous growth in recent years; however, technological advances are limited by lack of continuous and scalable synthesis methods. Here we present two step cost effective chemical route approach via a 'dip and dry' has been demonstrated for the deposition of multiwalled carbon nanotubes (MWNTs) thin film onto a stainless steel (SS) substrate and Chemical bath deposition (CBD) method has been used for TiO₂ onto MWNTs. Thin films were characterized using structural and surface morphological studies by XRD, FESEM and TEM. Uniform and porous coating of TiO₂ on MWNTs has been confirmed using FESEM and TEM. The electrochemical performance of the TiO₂/MWNTs electrode has been evaluated by varying different aqueous electrolytes using cyclic voltammetry. The cyclic voltammetry of TiO₂/MWNTs electrode has been achieved within -0.9 to 0.9 V (V, vs, Ag/AgCl) potential range in 1 M aqueous different electrolyte such as NaOH, NaCl, KCl, Na₂SO₄, KOH and H₂SO₄ at the scan rate of 50 mVs⁻¹. The cyclic voltammetry study shows H₂SO₄ electrolyte gave the largest current than the other electrolytes.

Keywords: Multiwalled carbon nanotubes, TiO₂, Thin Film, Electrolyte, Supercapacitor

1. Introduction

The growing demand for energy and power sources, supercapacitors are attracting great interest because of having high power density than dielectric capacitors and the high energy density than rechargeable batteries [1, 2]. Such types of supercapacitors have been used in a variety of applications such as electric automobiles, electric motorcycles, and electric bicycles, greater advantage in digital communication, pulse power application and short term power sources for mobile electronic devices [3, 4]. According to the charge storage mechanism, supercapacitor electrode materials are divided into two categories. The charge storage of a

supercapacitor is based on two different mechanisms. The first is electric double layer capacitance (EDLC), where charges are stored at the electrode-electrolyte interface via the formation of a Helmholtz double layer (HDL) upon polarization, which takes advantage of the electro-ionic charge storage induced in the electrochemical double layer of high surface area. Carbon-based materials of various forms have been used as EDLC electrode materials [5,6]. However, the low specific capacitance of carbon materials severely limits their energy density. The second is pseudo capacitance, where charges are stored via a redox mechanism. Transition metal oxides and conducting polymers exhibit pseudocapacitive behavior [7,8,9]. In general, metal oxides can provide higher energy density for electrochemical supercapacitors than carbon materials and better electrochemical stability than polymer materials. The key to develop supercapacitors with high energy and power density is to design and synthesize high-performance hybrid electrode materials.

MWNTs have a novel carbon nanostructure with a densely packed honeycomb with three dimensional porous nanostructure, due to its unique properties such as large specific surface area, high electrical conductivity, excellent electron transfer rate and high mechanical strength expands a highly promising material for many applications in nanoelectronics, flexible electronics, batteries, supercapacitors, solar cells, gas and chemical sensors.

Recently, hybrid electrode materials using various transition metal oxides and multiwall carbon nanotubes (MWNTs) have attracted much attention for supercapacitor applications in order to take advantage of both charge storage mechanisms. To date, various hybrid electrode materials combining metal oxides and MWNTs such as Co₃O₄/MWNT, [10,11] MnO₂/MWNT[12,13], TiO₂/MWNT[14], NiO/MWNT[15,16], and V₂O₅/MWNT[17,18] etc. have been extensively investigated for

supercapacitors. In the present investigation, we report comparative studies on the supercapacitive performance of MWNTs, TiO₂ and TiO₂/MWNTs hybrid thin film electrodes. TiO₂ has been studied as an electrode material for supercapacitors that offers low cost, low environmental impact, a variable oxidation state and high theoretical capacity. However, there are limits to its practical specific capacitance and capacity retention owing to the poor electrical conductivity of TiO₂ nanoparticles. In order to increase their electrical conductivity and specific capacitance, TiO₂ nanoparticles have been decorated on a MWNTs network. Decoration of TiO₂ nanoparticles on MWNTs opens a pathway for the investigation of new chemistry and electrochemistry within a confined one-dimensional interspace. MWNTs are an attractive form of carbon that can be used as an electrode material for supercapacitors with EDLC behavior. MWNTs exhibit superb characteristics such as high electrical conductivity, a large surface area, high mechanical stability and provide a conducting pathway for electrochemical reactions [19].

In the present investigation, a facile approach has been proposed for the decoration of TiO₂ nanoparticles onto the surface of MWNTs for use as a high-performance electrode material for supercapacitors by combining dip-coating and chemical bath deposition (CBD) methods. In this report, attention has been focused on: (i) Preparation of MWNTs solution, (ii) Functionalized the MWNTs, (iii) the synthesis of TiO₂ nanoparticles on SS and MWNTs/SS substrates using a simple and low-cost chemical bath deposition (CBD). (iv) Comparative studies of different electrolyte for TiO₂/MWNTs on SS substrates as supercapacitor electrode materials.

2 Experimental details

2.1 Coating of MWNTs thin film on SS substrate

Carbon nanotubes (MWNTs) (>95% purity, outer diameter from 15 to 20 nm and length from 5 to 15 μm) were purchased from Nano Amor (Houston, TX). These MWNTs were refluxed in H₂O₂ at 60 for 48 h to remove amorphous carbon derivatives and to generate oxygenated functional groups. The oxidized MWNTs are thoroughly washed with double distilled water and then dried in oven at 90 C for 12 h. The 0.125 g of oxidized MWNTs were sonicated in TritonX-100 and in 25 ml double

distilled water (1:100, Tx-100: water) for 1 h to obtain stable dispersion. Well cleaned stainless steel substrates were dipped in MWNTs solution for 10 min. The MWNTs gets adsorbed on the surface of stainless-steel substrate (SS). This process was repeated by 6–7 times to deposit MWNTs onto SS substrate. Further these MWNTs coated stainless steel substrate were dried under IR lamps to evaporate the solvents and to make it ready for further deposition of TiO₂

2.2 Coating of TiO₂ nanoparticles on MWNTs/SS substrate

TiOSO₄ (100 mM) was dissolved in double distilled water, in which the complexing agent H₂O₂ was added to maintain the pH 2 [26]. MWNTs coated SS substrates were dipped in this solution. The solution was kept at room temperature (300 K) where the solution color was red. After few minutes, the yellowish precipitation is started in the bath. During precipitation, a heterogeneous reaction occurred and titanium oxyhydroxide nanodots were deposited on the MWNTs coated substrates. The substrates coated with nanodots were removed after 4 h from the bath, washed with double distilled water, dried in air and preserved in an air tight desiccators. The films were annealed at 723 K for 2 h, in order to remove oxyhydroxide phase to pure oxide and to improve the crystallinity of deposited films.

2.3 Characterization techniques

The amount of TiO₂ loaded on MWNTs was measured by commonly used weight difference method using a sensitive microbalance. The structure of the prepared samples was characterized by X-ray diffraction (XRD; RIGAKU RINT 2000 model) with Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$) with an diffraction angle 2θ between 20° and 80°. Surface morphologies of TiO₂/MWNTs films were examined by using field emission scanning electron microscopy (FE-SEM, Model: Hitachi S 4800) attached with an energy dispersive X-ray analysis (EDAX) to measure the sample composition. Transmission electron microscopy (TEM) and High resolution TEM (HRTEM) were carried out by using PHILIPS CM200. Electrochemical measurements were conducted in a three electrode cell which consist of a 25 ml beaker equipped with a reference electrode (vs, Ag/AgCl), counter electrode (platinum), and a working electrode (TiO₂/MWNTs)

thin film) using potentiostat (Gamry Instrument PWR600).

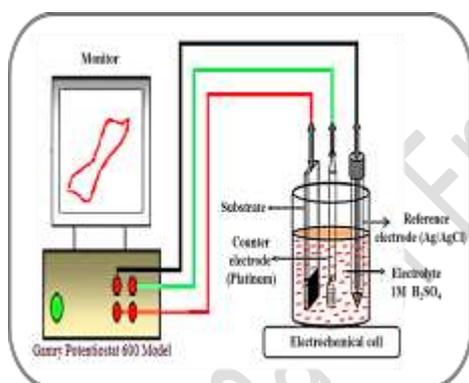
2.4 Electrochemical study

Cyclic voltammetry (CV) was performed to investigate supercapacitive performance of TiO₂/MWNTs electrodes in different electrolytes NaOH, NaCl, KCl, Na₂SO₄, KOH and H₂SO₄ within a potential window of -0.9 to + 0.9 V (vs, Ag/AgCl) as shown in fig. 1.

The specific capacitance of the samples was estimated from the integrated charge from the CV data using the equation.

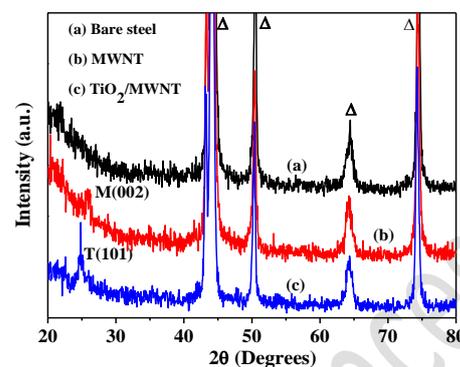
$$C_s = \frac{1}{mv(V_c - V_a)} \int_{V_a}^{V_c} I_m dV$$

Where, C_s is the specific capacitance (F.g⁻¹), v is the potential scan rate (mVs⁻¹), (V_c -V_a) is the potential range (-0.9 to 0.9 V (vs,Ag/AgCl) and I_m denotes the response current (mAcm⁻²) based on the mass of the TiO₂ /MWNTs material.



3. Results and discussion

3.1. Structural and compositional analysis



XRD patterns of the bare steel, MWNTs, and TiO₂/MWNTs nanocomposite thin films are shown in Fig.2. The XRD pattern of bare steel or stainless steel (SS) is shown as a reference. The characteristic graphitic (00 2) peak of the MWNTs at 25.8 ° was clearly observed in MWNTs thin films . The reflection along (1 01) obtained at 24.42° is characteristic peak for anatase phase of TiO₂ nanodots (JCPDS 01-1047). The low intensity diffraction peak indicates that the TiO₂ coated onto the MWNTs has a nanocrystalline nature [15]. This phase is feasible for supercapacitor application because the protons can easily permeate through the bulk of the TiO₂ material, and the entire electrode can be used for energy storage. Moreover, the peaks obtained at 43.66 °, 50.32°, 64.30° and 74.46° result from the contribution of the stainless steel substrate and are marked with triangle. Since the stainless steel and TiO₂ peak intensities are much higher than MWNTs, detection of carbon is not possible by using XRD analysis of the TiO₂/MWNTs composite film. There were no other contamination or impurity peaks observed in XRD analysis.

3.2. Surface morphological analysis

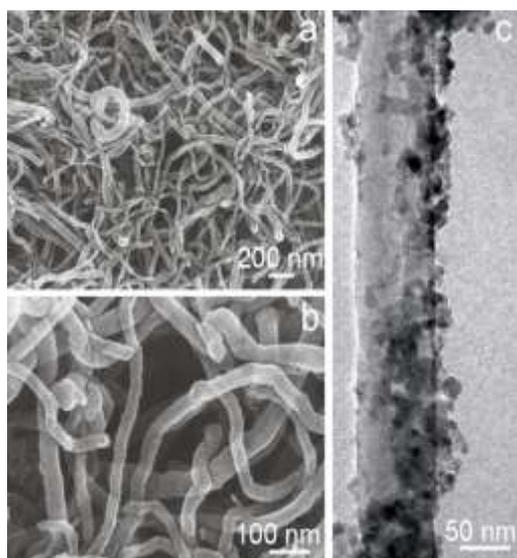


Fig.3 presents FESEM images of $\text{TiO}_2/\text{MWNTs}$ thin films at two (200 nm and 100nm) different magnifications. No aggregation and alignment of bundles of MWNTs due to van der Waals interactions is observed as seen from Fig.3(a and b). Means no aggregation of TiO_2 was observed in the porous area between MWNTs network. However from Fig. 3(c), the films exhibit uniform coating of TiO_2/MWNT nanocomposite on substrate surface with rough surface. The outside surface of the MWNTs is uniformly spotted with TiO_2 nanodots (less than 10 nm) indicating that the nucleation occurs predominantly on the exterior surfaces of the MWNTs [15].

3.3. Supercapacitive studies

The CV curves were measured in 1 M different electrolyte within a potential window ranging from -0.9 to $+0.9$ V (vs, Ag/AgCl). Fig.4. presents the cyclic voltammetry curves of MWNTs, TiO_2 and $\text{TiO}_2/\text{MWNTs}$ composite at a 0.05 V s^{-1} scan rate. The shape of the CV indicates that the capacitance characteristic is different from the electric double layer capacitance, where the shape is normally close to an ideal rectangular shape. From the curves, it is observed that redox peaks are present for the TiO_2 and $\text{TiO}_2/\text{MWNTs}$ curves, indicating that the capacity results mainly from a pseudocapacitive capacitance, which is based on a redox mechanism. There are generally two parallel mechanisms proposed, based on the adsorption and intercalation involving surface and bulk phenomena during the charge storage in TiO_2 .

The electrolyte used in the supercapacitor must have a maximum possible decomposition voltage, a broad range of potentials of electrochemical stability and should be stable in the temperature range extending from 248 to 342^0 K. The resistance of the supercapacitor cell is strongly dependent on the resistivity of the electrolyte used and size of the ions from the electrolyte that diffuse into and out of the pores of the microporous electrode particles. Organic electrolytes have a higher resistance but the subsequent power reduction is usually offset by the gain in higher cell voltage. This is usually not a problem for an aqueous electrolyte, such as sodium hydroxide, potassium hydroxide or sulfuric acid with the resistivity of $1-2 \Omega \text{ cm}$. Aqueous electrolytes are cheaper, easier to purify and have a lower resistance, but they limit the cell voltage to typically 1 V, thereby limiting the maximum achievable power.

Furthermore, the acidic electrolytes have the problem of corrosion of electrode due to the acidic nature. In the present case, the aqueous electrolytes like H_2SO_4 , NaOH, KOH, NaCl, KCl, Na_2SO_4 etc. have been tested for $\text{TiO}_2/\text{MWNTs}$ thin film electrodes and the electrolyte was chosen which was able to give maximum capacitance. CV of the $\text{TiO}_2/\text{MWNTs}$ thin film electrode in aqueous electrolytes viz. 1.0 M solution of H_2SO_4 , NaOH, KOH, NaCl, KCl, and Na_2SO_4 were studied in the voltage range of -0.9 V to $+0.9$ V (vs,Ag/AgCl) at the scan rate of 50 mVs^{-1} . In all the cases, the electrode exhibited symmetric CV characteristics in forward and reverse sweeps (shown in the Fig 4). The H_2SO_4 electrolyte gave the largest current than the other electrolytes. Hence, all the supercapacitive properties of thin film electrode were tested in H_2SO_4 electrolyte.

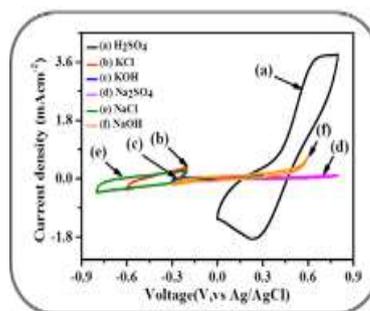


Fig. No. 4.

4. Conclusions

In conclusion we described MWNTs and TiO₂/MWNTs nanocomposites hybrid thin film electrodes via a chemical bath deposition method and applied them as electrochemical capacitive electrodes. The porous network of MWNTs was generated by a dip-coating method, which provided a conducting pathway for electrochemical reactions, and coating of TiO₂ nanoparticles on the MWNT network was prepared by the CBD Method. The cyclic voltammetry study shows H₂SO₄ electrolyte gave the largest current than the other electrolytes. Thus, these encouraging results of cyclic voltammetry suggest that the TiO₂/MWNTs nanocomposites can serve as promising electrode materials in 1M H₂SO₄ electrolyte for high performance supercapacitors.

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