

TiO₂ coated MWCNT decorated by Fe₃O₄ nanoparticle as electrode material for Supercapacitor Application

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Abstract:- TiO₂ coated multi wall carbon nanotube (TiCN) and Fe₃O₄ based electrode material for the application in electrochemical devices has been produced through a simple approach. Morphological and electrochemical properties of the prepared nanocomposites were determined through field emission scanning electron microscopy (FESEM) and cyclic voltammetry (CV) and impedance analysis, respectively. Sol-gel technique was used to synthesize TiCN and in-situ chemical co-precipitation technique was used for the formation of magnetite particles (Fe₃O₄) on the surface of acid-modified multiwall carbon nanotube (MWCNT). Maximum specific capacitance obtained from CV is 221 F/g.

Keywords: Nanocomposites, Electrode, Carbon Nanotube, Specific capacitance, Cyclic Voltammetry, Supercapacitor

1. Introduction

Carbon nanotubes (CNTs) have generated an immense research interest in wide applications, because of their unique mechanical, electrical, and magnetic properties. Nowadays, super capacitors draw a significant amount of attention because of their high power application demands in many fields, such as electric vehicles, hybrid electric vehicles, mobile electronic devices, off-peak energy back-up systems etc. [1,2]. The interest is due to super capacitors being an energy storage device with no pollution, which means it can be used in the manufacturing of vehicles that are friendly to the environment. Supercapacitors are also well-known as a replacement of batteries and conventional capacitors, as their use has a lot of limitations, because the super capacitors have a very high power and energy density with a long cycle life [3,4]. Therefore, these days the research community is highly focused on this particular field of interest. There are many types of super capacitors, but the hybrid capacitor is desired for superior performance in various applications in modern science and technology. The hybrid capacitor is a new generation supercapacitor, and can be prepared by the hybridization of a double layer capacitor (non-Faradaic process) and a pseudo capacitor (Faradaic process). Thus, the design of the composites, combining electrical double layer capacitors (EDLCs, mostly carbon-based materials) and pseudocapacitors will take full advantage of their synergic effect and achieve the purpose of

developing high electrochemical electrode for supercapacitors. Over the past few years; CNTs have been considered to be a promising candidate for supercapacitor [5]. Spinel ferrites have also started to show their importance in the supercapacitor field [6]. Recently, Fe₃O₄ has emerged as a potentially promising supercapacitor material due to its low cost and environmentally benign nature [7, 8]. TiO₂ is another important candidate in the field of supercapacitor [9]. Therefore, we have prepared a novel composite based on CNT, Fe₃O₄ and TiO₂ for the application in supercapacitor.

2. Experimental Work

2.1. Materials

MWCNTs (Guangzhou Jiechuang Trading Co. Ltd., China) having an outer diameter of 20–30 nm and a length of 3–15 μm were used as components for the preparation of nanocomposites. HNO₃ and H₂SO₄, used for the acid modification of MWCNT, were obtained from Loba Chemie PVT, Ltd., India. FeSO₄·7H₂O and Fe(NO₃)₃·9H₂O has been used as a source of Fe²⁺ and Fe³⁺ ions required for the preparation of Fe₃O₄. These iron salts were purchased from Merck Ltd., India. Titanium (IV) n-butoxide and iso-propanol were bought from Sigma Aldrich, India. Sodium Hydroxide (NaOH) was used as a precipitating agent and taken from Loba Chemie Private Limited, India.

2.2. Preparation

Raw MWCNTs were functionalized through known acid modification method by using the mixture of HNO_3 and H_2SO_4 (3:1). In-situ coating of acid modified MWCNT was done by titanium(IV) n-butoxide via the sol-gel technique. Dispersion of acid modified MWCNT in isopropanol was prepared through sonication in presence of a cationic surfactant cetyltrimethylammonium bromide and then treated with titanium (IV) n-butoxide with continuous sonication for 30 min. Then distilled H_2O was added slowly to the mixture and kept under stirring at room temperature. Finally, the product was dried at 100°C and further annealed at 450°C to prepare TiCN.

Prepared TiCN was added into a required amount of water and dispersed through sonication. Then aqueous mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (molar ratio is 1:2) added to the TiCN dispersion. After sonication for some time, we added NaOH solution for making the precipitation of iron salts. After adding the precipitating agent we heated up the solution up to 50°C and stirred for 4 hours to complete the process of precipitation. Then, the mixture was cooled down to room temperature and filtered to obtain

the precipitate. The obtained product was washed several times by distilled water and ethanol. Then the sample was kept overnight at 100°C for the preparation of TiCN decorated by Fe_3O_4 (abbreviated as TiCN/ Fe_3O_4).

2.3 Characterization

A Carl Zeiss-SUPRATM 40 field emission scanning electron microscopy (FESEM) with an accelerating voltage of 5 kV was used to understand the morphology of the nanocomposites. Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD) analysis of the materials were carried out on Biologic sp-150 VMP-3 instrument using a three electrode system where platinum and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. The GC electrode was used as working electrode. The samples in 1% nafion solution of ethanol were deposited on the tip of the GC electrode and then dried. CV measurements were performed in the voltage range of 0.8 to -0.8 V versus SCE.

3. Result and Discussion

Figure 1 shows the representative FESEM image of the as synthesized nanocomposites.

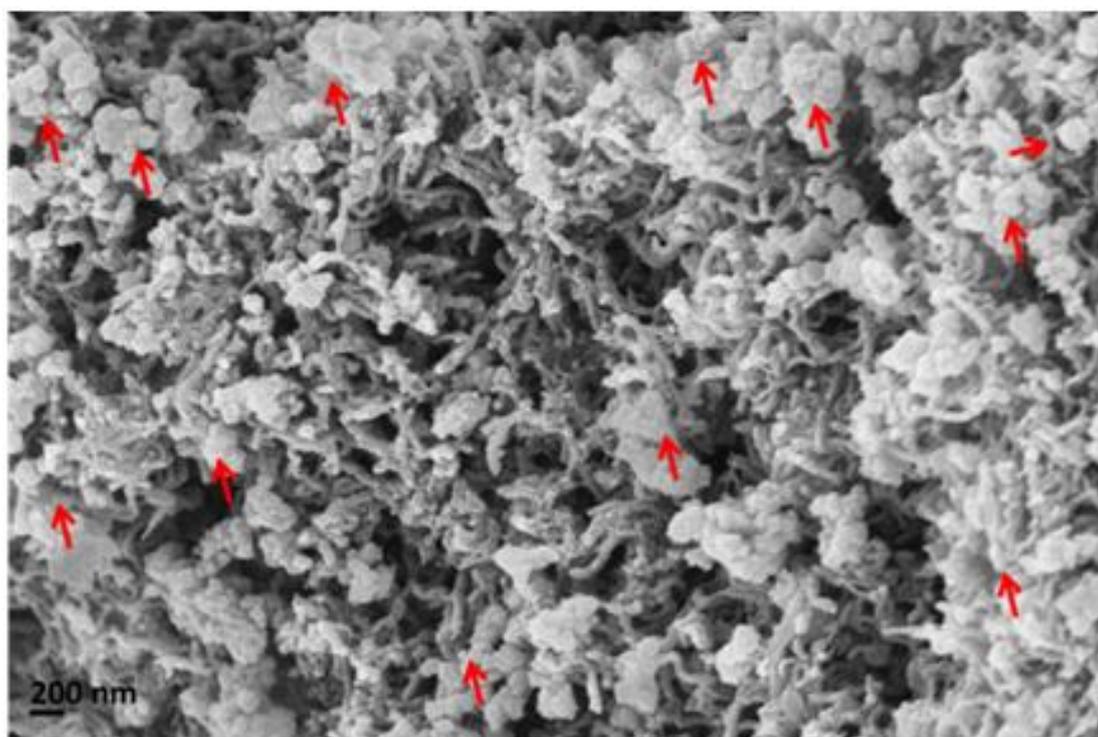


Figure 1. FESEM image of TiCN/ Fe_3O_4 nanocomposite

Tubular MWCNTs with TiO_2 coating is clearly visible from the image. Formation of Fe_3O_4 can also be confirmed from the FESEM image and shown by red arrows for better visibility. Wall of the MWCNTs looks thick

because of coating by TiO_2 . Fe_3O_4 is well distributed throughout the whole material with small agglomerated contents.

The electrochemical performance of the prepared material was investigated by means of cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) in 1 M aqueous KCl electrolyte. We have performed the CV analysis of TiCN/Fe₃O₄nanocomposite at various scan rates in the potential range of -0.8 V to 0.8 V. Resultant CV plot is shown in Figure 2a. The specific capacitance for the prepared nanocomposites was calculated by the equation 1:

$$C_{sp} = \frac{\int_{v1}^{v2} i(v)dv}{(V2-V1)vm} \dots\dots\dots 1$$

Where, C_{sp} is the specific capacitance obtained by CV measurements, the numerator calculates the total charge under the CV plot within the working potential range $V2$ and $V1$, v is the scan rate and m is the mass of the composite electrode materials. In case of three electrode cells, the

capacitance values are the capacitance per electrode. Specific capacitance calculated from the CV for the obtained material is 221 F/g at 2 mV/s. The CV-plot has two regions, the negative current zone denotes the reduction in cathode and the positive current region represents the oxidation in the anode. The shape of the plot is not perfectly rectangular, which indicates deviation from ideal supercapacitor behaviour. The plot contains some redox peaks which are due to the presence of TiO₂ and Fe₃O₄. This redox nature of the plot confirms the presence of pseudo capacitance, which contributes to the total specific capacitance of the material. Specific capacitances calculated by considering different scan rates for the same material. Specific capacitances of TiCN/Fe₃O₄nanocomposite are 185, 171, 158, 140 and 122 F/g at a scan rate of 10, 20, 50, 100 and 200 mV/s respectively. Specific capacitance values indicate good rate capability of the obtained nanocomposite.

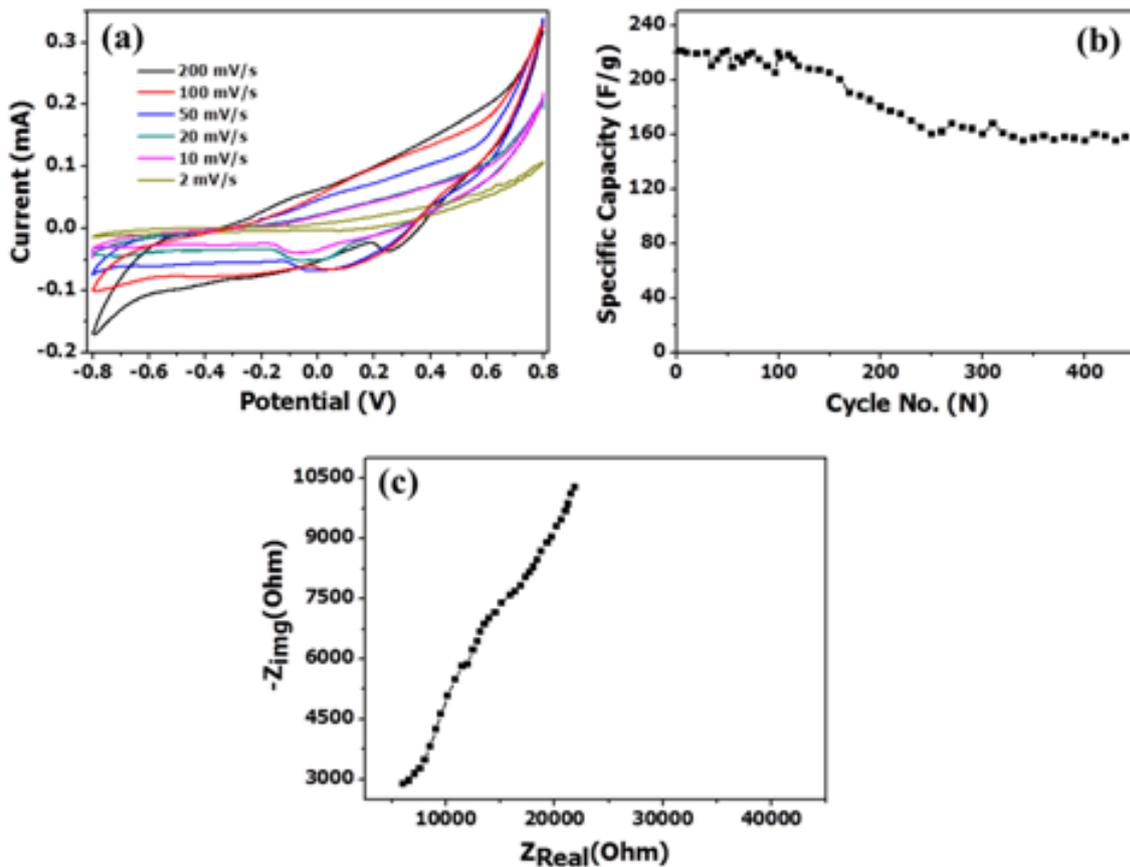


Figure 2. (a) CV plot, (b) cyclic stability and (c) Nyquist plot of TiCN/Fe₃O₄nanocomposite

Rate capability is an important aspect for the real application of supercapacitor. Specific capacity retains up to > 55% when scan rate has been raised from 10 mV/s to 200 mV/s. Decrease in specific capacitance with increase in scan rate is due to the diffusion effect of protons within the electrode material, which hampers the redox process of the inner

active sites at a high scan rate [10]. On the contrary, the peak current increased linearly with increasing the scan rate. This is due to the diffusion controlled doping and de-doping of the electrolyte ions and also the fast kinetics of the interfacial redox reaction [3]. Pristine MWCNT generally provides double-layer capacitance whereas; Fe₃O₄ and TiO₂

usually provide pseudo-capacitance. In the hybrid material, these two individual components contribute to the overall capacitance. Hence, because of the combined contribution of all the components, TiCN/Fe₃O₄ showed better capacitance properties than pristine MWCNT which is only 20-30 F/g [11].

To determine the performance of a hybrid supercapacitor, energy densities are very important to know. Therefore, we have determined the energy density by using the following equation:

$$\text{Energy density } (E) = 1/2(CV^2)$$

Where, C = specific capacitance in F/g, and V = operating voltage. Energy densities of the prepared TiCN/Fe₃O₄ are calculated as 78.6, 65.8, 60.8, 56.2, 49.8 and 43.4 Wh/kg at a scan rate of 2, 10, 20, 50, 100 and 200 mV/s respectively. Cycle performances were tested at 2 mV/s and it shows excellent performance up to 450 cycles as shown in Figure 2b. Initial specific capacity retains up to 70 % even after 450 cycles. So, in terms of specific capacitance, energy density and cycle stability the prepared electrode material performs well.

In addition, we have performed the EIS study and the corresponding Nyquist plot of TiCN/Fe₃O₄ is shown in Figure 2c. Nyquist plot is the plot of imaginary vs real component of the impedance study, and gives the frequency response of the electrode-electrolyte system [12]. The higher frequency region is associated with the electrolyte properties, and the mid frequency region corresponds to the electrode/electrolyte interface processes. The solution resistance (R_s) and charge transfer resistance (R_{ct}) are the intercept of the curve at high frequency and mid frequency with the real axis respectively. Impedance response of 45° straight line is known as the Warburg resistance (W) which signifies the mass transfer parameters of the electrochemical doping process [13]. The Nyquist plot of TiCN/Fe₃O₄ contains one small semicircle at high frequency region, and one straight line at low frequency region. For an ideal capacitor, this straight line should be parallel to the imaginary axis of the Nyquist plot. TiCN/Fe₃O₄ deviates from the behaviour of an ideal capacitor as the straight line is not perfectly parallel to the imaginary impedance axis. The observation is in good agreement with the CV results.

4. Conclusion

In conclusion, TiO₂ coated multi wall carbon nanotube (TiCN) and Fe₃O₄ based electrode material have been successfully synthesized through a simple and economic way. Formation of the hybrid material can be observed through FESEM images. Performance of the electrode material was determined by specific capacitance, rate capability, cyclic stability and Nyquist analysis. Specific capacitance of 221 F/g was achieved through three electrode measurement set up. Cyclic stability was measured up to 450 cycles and it shows amazing specific capacity retention of 70 %. The capacitance property of the nanocomposites is the result of both double layer capacitance and pseudocapacitance. Hence, the prepared nanocomposites can be used as efficient electrode materials for supercapacitor applications.

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