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Synthesis and Characterization of Molybdenum Doped MnO_2 /CNT Composite and Its Electrochemical Application

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Abstract

A simple method for synthesizing Mo doped MnO_2 /CNT composite has been reported. During chemical co-precipitation of polymer, metal salts have been added in the ultrasonicated carbon nanotubes (CNTs) where metals incorporated in Mo- MnO_2 via self-assembly process. The structural features of composite were characterized by FTIR spectroscopy and UV- Visible spectroscopy. The peaks observed show that metal oxide is in its doped state. The X- Ray diffraction technique also reveals the crystalline nature of the composite and indicates successful incorporation of metal elements in the composite structure. The morphological characteristics were studied by scanning electron microscopy (SEM). It is observed that nanocomposite has uniform deposition of metal oxide onto CNTs surface. The characteristics of the nanocomposite as a promising candidate for applications in supercapacitor.

Keywords: Molybdenum, MnO_2, CNT, Composite.

Introduction

The expanding request in vitality and the diminishing accessibility of fossil fuels and in addition the worry about a worldwide temperature alteration have empowered incredible examination endeavours on maintainable and ecological inviting advancements in energy conversion and storage. Supercapacitors (SCs) are the promising energy storage source and have pulled in much consideration in perspective of a number of important elements including higher power density, speedier charging/releasing rate and more cycling stability contrasted with traditional capacitors or batteries[1], which make them promising in an extensive variety of utilizations from crossover vehicles and compact hardware to military gadgets [2]. Carbon-based materials that store the charge electrostatically utilizing reversible adsorption of electrolytic particles onto dynamic materials on the anode are basically utilized as dynamic cathode materials for SC application [3, 4]. Carbon based materials as Charcoal, carbon nanotube (CNT) etc. have been introduced into the polymer matrix to obtain add on features like upgraded mechanical strength, improved electrochemical activity and longer cyclic stability [5-8]. CNTs are 1-dimensional with carbon skeleton. CNTs offers special electronic, thermal and reinforcement characteristics which makes them attractive filler material for polymer based composites. As per charge-discharge phenomenon, supercapacitors can be distributed into electrical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs dependent on carbon can acquire increased repetitive time period but comparatively degraded specific capacitance. Competing with EDLCs, pseudocapacitors incorporated with oxide of metals or conductive polymers have considerable improved specific capacitance credited to their reducing and oxidising characteristics . furthermore, needs such as adaptability and leanner width have been raising for portable, hybrid, compact advance electronics and alternative means of transportation etc. while counting on oxides, an extreme exercise on oxide of ruthenium-integrated supercapacitors has been grown due to their up marked specific capacitance; in spite of these, expensiveness and toxicity constraints their practical applications[9]. In this paper a fresh route for preparation of binary transition metal oxide/ carbon materials is proposed for power

accumulating appliances using a easy, cheap and environment supportive process.

Manganese oxide referred as leading electrode substance in different power accumulating fields. Doping other oxides of transition metal can hybridize the storage capacity of manganese oxide by activating simultaneous transportation of electrons and positive charge holes

Materials and Methods

Material Used

All chemicals like ammonium molybedate $(NH_4)_6Mo_7O_{24}$,, Potassium permanganate ($KMnO_4$) were of ACS grade purchased from Merck Germany. Carbon nano tube (CNTs) having diameter 9.5-12 nm and length 1.5 µm was obtained from Nanocyl, Belgium. Ultrapure water purified with Milli-Q plus system (Millipore Co.) was frequently utilized for purpose of rinsing and preparing solutions.

synthesis of composite

In First step, commercial multi-walled CNT were oxidized in the mixture of HNO_3 and H_2SO_4 (3:1 volume ratio) by ultrasonication for 1 h. The acid-treated CNT were then collected by filtration and moisture eliminated by keeping at 100 ^oC for 12 h in oven. In the second step, Mo–MnO_2 was coated onto the acid treated CNT by the reaction of $KMnO_4$ at room temperature. Typically, 0.003 mol of $KMnO_4$ and 0.00085 mol of $(NH_4)_6Mo_7O_{24}$ were dispersed well in 35 mL of deionized water, succeeded by mixing with 0.1g of CNT and 2 mL concentrated HNO_3 (16 mol L^{-1}) under vigorous stirring using magnetic stirrer. The suspension was transferred to a Teflon-interlined autoclave (50 mL), kept at specific temperature (140^oC) for 3 h, and let to cool down to normal temperature. After rinsing using 30 mL of double distilled water and 30 mL of ethyl alcohol thrice, brown black precipitates were procured and kept in oven at 60 ^{o} C for 12 hrs. The yield of the final Mo doped MnO_2 /CNT composite was 85%.

Characterizations

IR spectra (KBr pellet) was obtained by using Fourier transform infrared spectrophotometer FTIR (Perkin Elmer spectrum BXII FTIR) and Field emission electron microscopy (FESEM, JEOL-JSM-5600LV @ accelerating voltage 20kv) was employed to check the surface characteristics of composites. The well ordeal arrangement of structure were inspected through XRD. XRD data was taken on a Xpert PRO make Philips via CuKα basis and fitted with an X'celerator detector (PW 3050/60). Statistics was evaluated at 2θ with diverging intensity. The diffractogram was at 2θ in the range 20–80°. UV-Vis absorptive works were carried in the 200-800 nm limits applying standard spectrometer (Perkin-Elmer, Lambda-45).

Preparation of the Electrodes

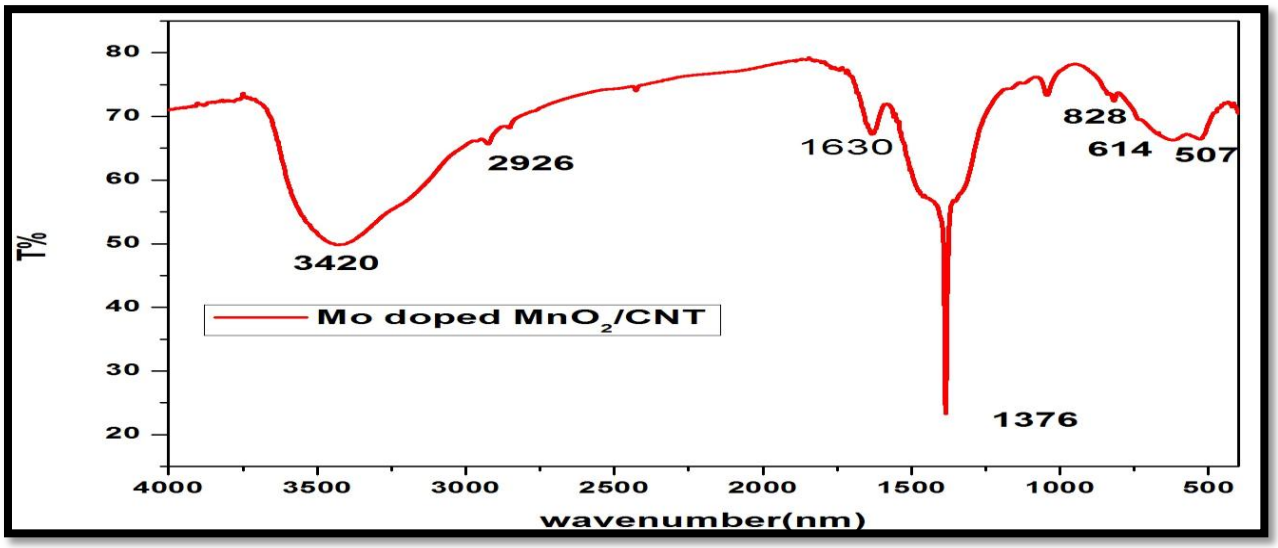
Supercapacitor electrodes were developed by addition of the obtained banana biochar, activated charcoal and binder (PVDF) in an optimized weight% ratio of 80:15:5. The developed paste coated on a graphite electrode with a brush on an effective area of 1 cm ×1 cm and then dried in oven at 45 °C for 30 mins. Electrochemical studies were performed in a electrode trio cell constitution in 1 M Na_2SO_4 electrolyte with Pt wire acting as counter electrode, and Ag/AgCl as reference electrode.

Result and Discussion

FTIR Analysis

The FTIR spectrum of Mo doped MnO_2 /CNT composites are displayed in Fig. 1 . A wide band at 3435 cm^{-1} corresponding to water molecule illustrating that the hydroxyl group adhere on the surface of CNT. The spiky tip of peak at 2917 cm^{-1} corresponds to the aliphatic C-H stretching vibrations, thoug the band peak at 1643 cm^{-1} agrees to extending mode of O-H group and C=O stretching vibration of ester[10]. The two strong peaks near 614 cm^{-1} and 507 cm^{-1} were credited to the symmetric Mn–O vibrations, thus point to the rise of a well-formed tetragonal geometry with an interstitial vacancies comprising of 2 × 2 tunnels in these Mo–MnO_2 samples[11]. At other view, the Mo-O stretching mode,37 found at 828 cm^{-1} for the reacting materials, is seen as a shoulder on the upper-wave number of the Mn-O starching peak [12]. So, There is little probability of inducing comparatively higher Mo^{6+} (0.87 Å) into the tunnel of α-MnO_2.

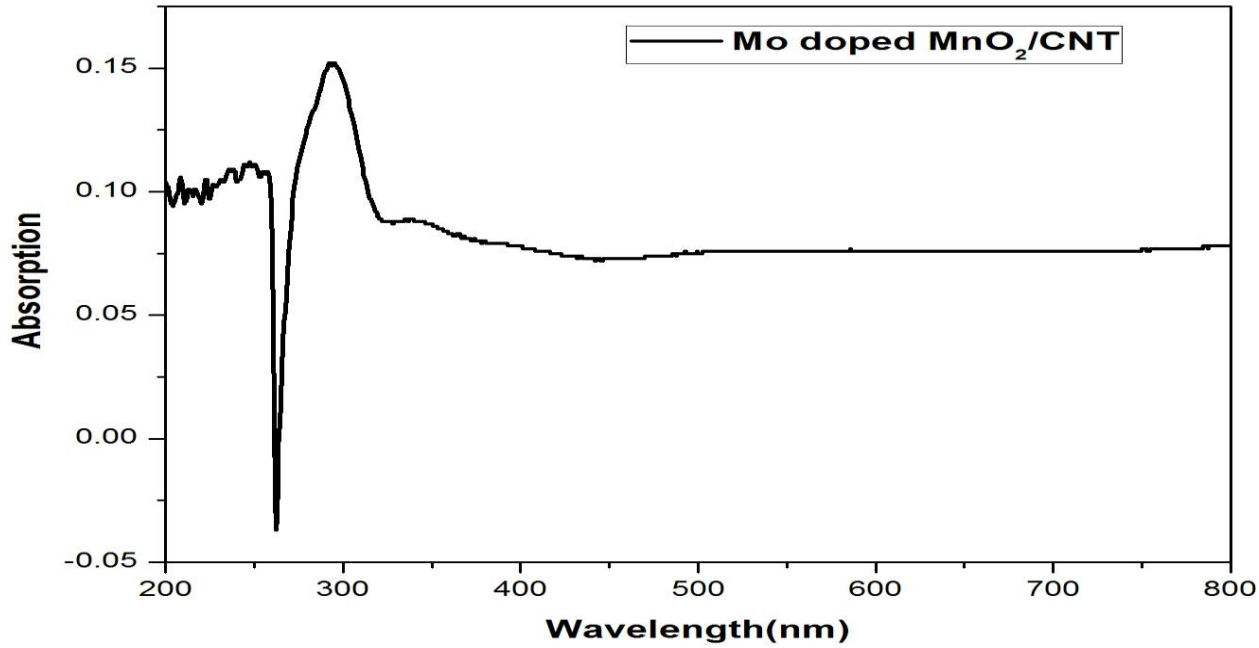
Fig. 1. FTIR Spectra of Mo–MnO_2 /CNT Composite



UV-vis Spectroscopy

The Ultra-violet visible spectra of Mo–MnO_2 /CNT composites prepared were recorded in ethanol and illustrated in Fig. 2. The absorption band observed at 293 nm is indicate Mn in crystallization state that has a valence of +2 which indicates charge transfer interactions between oxygen anion and manganese cation (+2) [13, 14]. In case of the Mo–MnO_2 /CNT composites, a broad tail is observed in absorbance band may indicate that Mo^{6+} incrporated in the MnO_2 channels.

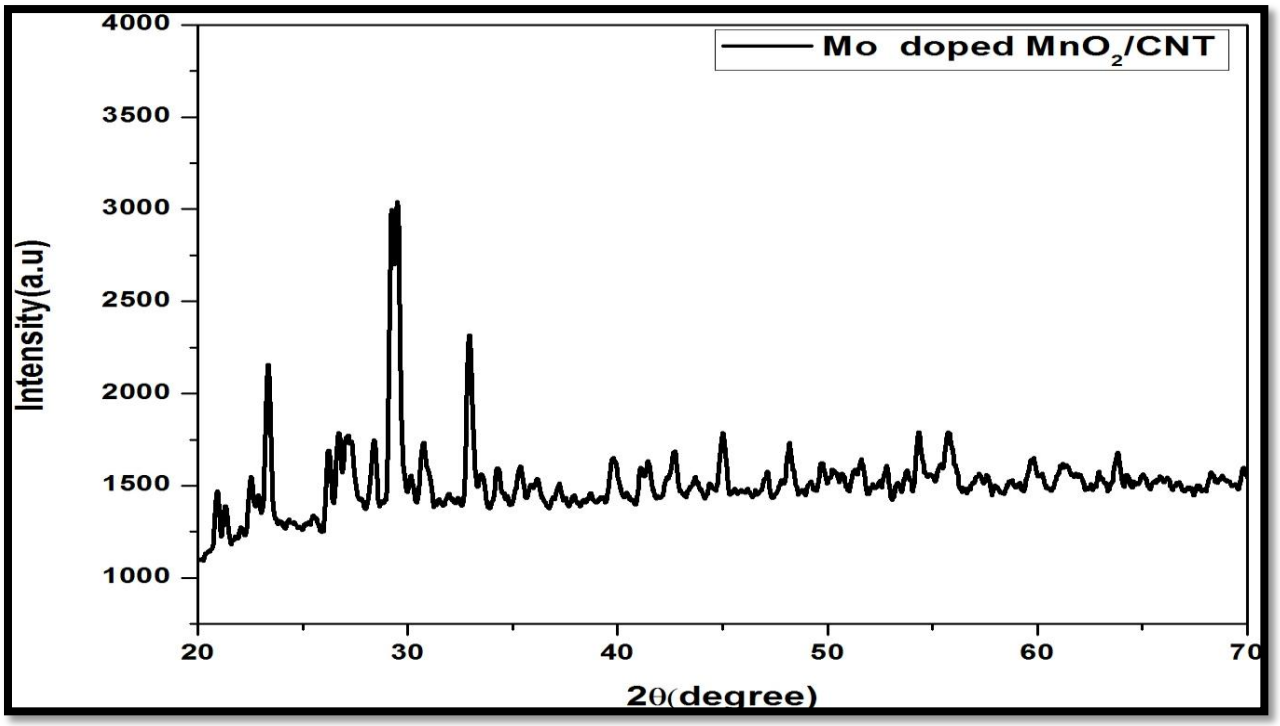
Fig. 2. UV-VIS spectra of Mo–MnO_2 /CNT Composite



X-ray Diffraction Studies

The X-ray powder diffraction (XRD) given in Fig. 3. The XRD of α-MnO_2 are accredited to a cryptomelane-shape manganese oxide with a 2 × 2 tunnel (4.6 Å × 4.6 Å) (JCPDS 29-102 [15].The XRD models of α-MnO_2 were in good agreement with those of cryptomelane structure. Respective of six-coordinated high-valent dopant positive charged ions, viz Mo^{6+} (0.73 Å) , framework replacement can take place, which supposed to cause the formation of manganese vacancies.

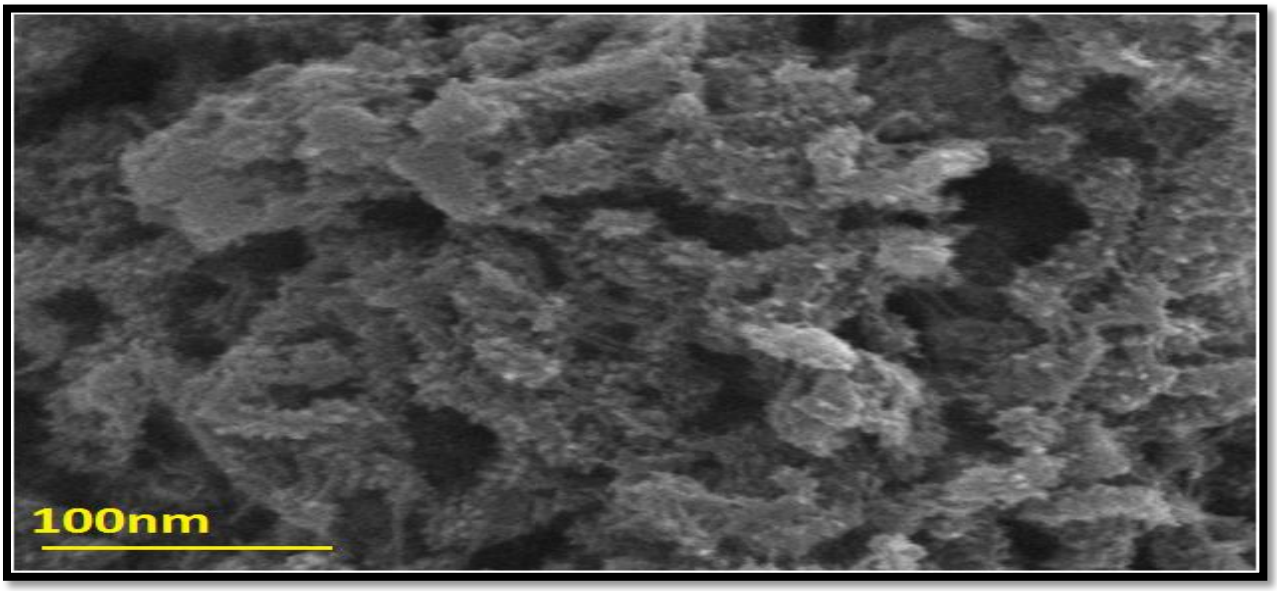
Fig. 3. XRD pattern of Mo–MnO_2 /CNT Composite



Scanning Electrone Microscopy

SEM micrographs of the Mo doped MnO_2/CNT composites are shown in Fig. 4. The micrographs reveal that MnO_2 directly grows on the surface of CNT in the form of inter connected nano flakes [16]. Whereas, in the case of Mo doped MnO_2/CNT nano needles/nanorods are visible at different dopant concentration [16, 17]. Figure shows needles-like growth of nano architectures mixed with MnO_2 nanoflakes after Mo doping at lower concentration.

Fig. 4 . FESEM Micrographs of Mo–MnO_2 /CNT Biochar Composite



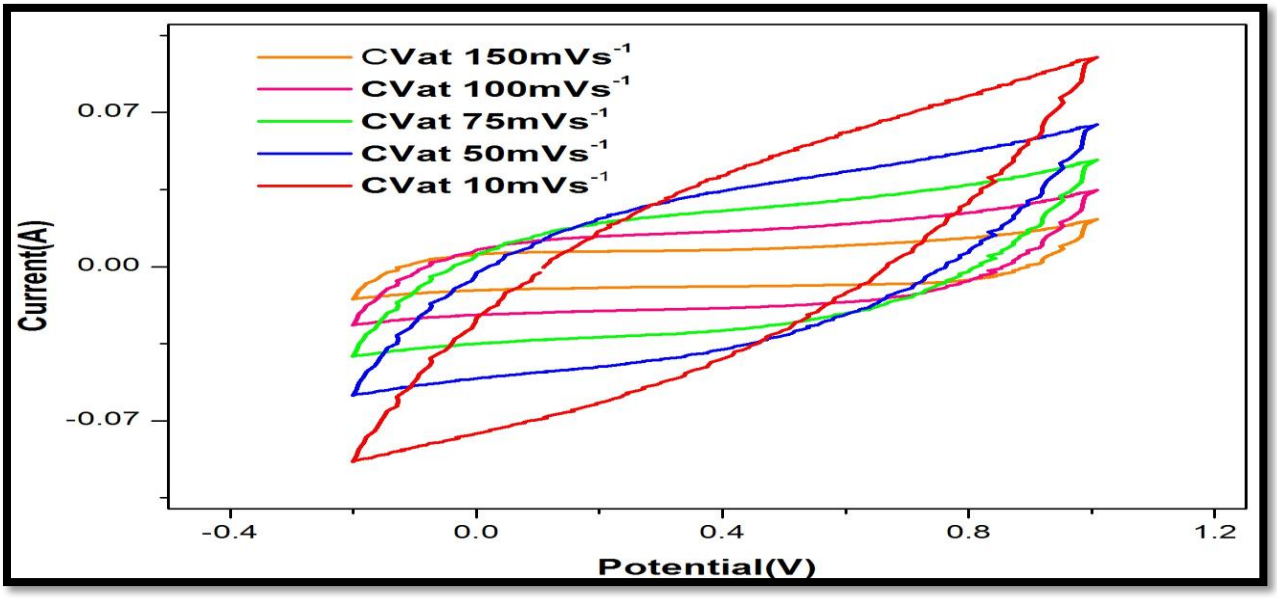
Electrochemical Studies

As prepared Ce doped MnO_2/CNF was subjected to cyclic voltammetry (CV) was measured in a potential varying between -0.2 V to 1.0 V in 1 M Na_2SO_4 at several potential ranges. The capacitance value of each sample was computed applying following equation.

$$C = \Delta i / m\Delta V \quad (1)$$

I designated for discharge current (A), Δt given for discharge time (s), ΔU shows potential variation of the electrodes during discharge (V), m is the total mass of material in electrodes (g), and C is the specific capacitance (F g^{-1}). As seen in the **Fig.5,** the shape of all the *voltammograms* were quasi-rectangular in the potential range. Cyclic *voltammograms* of the banana biochar sample was recorded at 150 mV s^{-1}, 100 mV s^{-1} ,75 mV s^{-1}, 50 mV s^{-1} and 10 mV s^{-1} scan rate respectively. The current value highest for the sample at 150 mV s^{-1} and lowest for 10 mV s^{-1}. From the plot, it is able to deduce that banana biochar has the highest specific capacitance value of 217 F g^{-1} at scan rate of 150 mVs^{-1} sand 833 F g^{-1} at 100 mVs^{-1}. The percentage loss of specific capacitance is only 38.3.7% as scan rate increases 20 times therefore the sample was stable at high scan rates also.

Fig. 5. Cyclic voltametric curves Mo doped MnO_2/CNT composite with scan rates from 10 to 150mVs^{-1}



Conclusion

This study presents a facile rout to synthesize Mo doped MnO_2/CNT composite via co-precipitation methods. The above work pronounces outstanding electrochemical properties of prepared composites as supercapacitor electrode material. An enhancement of (833F g^{-1}) specific capacitance in Mo doped MnO_2/CNT has been achieved on introducing cerium in Mo doped MnO_2/CNT. The doping concentration of cerium was averred to posses reportable effect on structural and electrochemical activity of the Mo doped MnO_2/CNT electrode materials.

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