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Multiwalled Carbon Nanotubes Filled with Transition Metal Oxides as Supercapacitor Materials

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Abstract: Manganese oxide (MnO_2), nickel oxide (NiO), copper oxide (CuO) and iron oxide (Fe_2O_3)/multiwalled carbon nanotubes (MWCNTs) nanocomposites for supercapacitor electrodes were synthesized by wet chemical method using acid treated MWCNTs and respective salts. Structural and morphological characterizations of metal oxides encapsulated in MWCNTs were carried out using transmission electron microscopy (TEM) and energy dispersive x-ray (EDX). The electrochemical performances of MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs on aqueous electrolytic supercapacitor were investigated using cyclic voltammetery (CV), galvanostatic charge-discharge. The MnO_2/MWCNTs and NiO/MWCNTs nanocomposite electrodes showed more significant capacitive behavior than other electrode materials of Fe_2O_3/MWCNTs, CuO/MWCNTs and pure MWCNTs. The average specific capacitance (SC) of the pure MWCNTs, NiO/MWCNTs and MnO_2/MWCNTs nanocomposites electrodes were found to be 68.56, 134.40 and 302.41 F/g, respectively.

Key words: Supercapacitor · Nanocomposites · Specific capacitance · Metal oxides

INTRODUCTION

The electrochemical capacitor (EC, also named as supercapacitor) is a novel type of energy storage device whose capacitance is 20–200 times higher than that of an electrolytic capacitor [1, 2]. The supercapacitor has several advantages of high power density, long cycle life, short charge time and safety over the battery and attracts great interests for energy storage devices [3].

Depending on charge-storage mechanism, they are basically classified into two types: electric double layer capacitors (EDLCs) based on carbon electrodes and pseudocapacitors with certain metal oxides (RuO_2, IrO_2, NiO, CoO_x, SnO_2 and MnO_2) [4, 5] or conducting polymers as electrode materials [6]. Carbon materials with high specific surface area, such as activated carbon, activated carbon fibers, carbon aerogels/foams and carbon nanotubes (CNTs) are the main electrode materials for supercapacitor application [7-9].

CNTs are attractive materials for electrodes of electrochemical energy storage devices due to their high conductivity, chemical stability, low mass density and large surface area. CNTs are mainly classified in to two groups; single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) where both of them have been recognized as potential electrode materials for supercapacitors. The capacitance of CNT-based supercapacitor electrodes can be improved by various techniques such as activating CNTs with heat/acid treatment [10] modification of CNTs with conducting polymers [11] or with certain transition-metal oxides [12, 13].

Ruthenium oxides are widely used in electrochemical supercapacitors due to their high specific capacitance (SC) and prominent properties, [14, 15]. However, the high cost of ruthenium (Ru) has retarded its commercial acceptance as electrode materials in electrochemical capacitors. Recent researches have been focused on

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cheap transition metal oxides with acceptable electrochemical properties. Manganese dioxide (MnO_2) [16], nickel oxide (NiO) [17], iron Oxide (Fe_2O_3) [18] and copper oxide (CuO) [19] are the candidates on account of their electrochemical behavior, low cost and environmental compatibility. However, the specific surface areas of these metal oxides in general are not high enough for high capacitance. The CNTs have been introduced to yield high conductivity and large specific surface area [12, 20].

In our previous study, the electrochemical properties of MnO_2/MWCNT and NiO/MWCNT were comparatively investigated [21]. In this paper the structural and electrochemical screening of different cheap metal oxides such as MnO_2, NiO, Fe_2O_3 and CuO encapsulated in MWCNTs using wet chemical method are studied. The main advantages of the wet chemical method are its flexibility and the level of experimental control so that a wide variety of materials can be introduced into the nanotubes.

The supercapacitive behavior of these nanocomposites electrodes have been studied using cyclic voltammetry (CV) and galvanostatic charge-discharge measurements and the results were compared with that of pure MWCNTs electrodes and discussed. However, based on developed knowledge, the supercapacitance properties of the nanocomposites material prepared by filling MnO_2, NiO, Fe_2O_3 and CuO particles in MWCNTs have has attracted great attentions.

EXPERIMENTAL

Materials: MWCNTs used in this study were produced by catalytic decomposition of methane using Ni/TiO_2 based catalyst. These MWCNTs were treated with multi-step purification process and 99.9 wt% of the impurities were removed. A detail experimental procedure for the synthesis and purification were explained elsewhere [22-26]. Nitric acid solution (supplied by Sigma-Aldrich) was prepared to open the close tips of MWCNTs. Manganese nitrate (supplied by ACROS, 98%), nickel nitrate (supplied by Fluka), Iron nitrate (supplied by ACROS) and copper nitrate (supplied by ACROS) were the metal oxide precursor. KOH (supplied by Fisher Scientific) aqueous solution has been used as electrolyte. Acetylene black (AB) and polytetrafluoroethylene (PTFE) (both supplied by Aldrich) have been used as the conductor and the binder, repectively.

Synthesis Method and Fabrication of Supercapacitor Cell: Purified MWCNTs were sonicated in nitric acid solution (supplied by Sigma-Aldrich) for 30min. After the sonication procedure, MWCNTs sample was refluxed under constant agitation of 350rpm in 40mL of 50wt% HNO_3 at 120 °C for 3 hrs in order to open the close end tips of MWCNTs, followed by washing with distilled water for several times. The acid treated MWCNTs are thus called as-opened MWCNTs.

MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs nanocomposites were prepared by wet chemical reduction method using a Mn, Ni, Fe and Cu salts and pretreated MWCNTs. As-opened MWCNTs were dispersed in a solution of manganese nitrate, nickel nitrate, Iron nitrate and copper nitrate separately by ultrasonic agitation. The as-synthesized products of MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs were centrifuged and washed repeatedly with distilled water and ethanol to remove the excess nitrate ions. The prepared nanocomposites were then dried in an oven at 70°C for 12hrs followed by annealing under the flow of argon gas at 450°C for 2hrs.

The electrochemical properties and capacitance measurements of these electrodes were studied using a symmetric two-electrode system with 6M KOH aqueous solution as electrolyte. A working electrode (Cathode) and counter electrode (Anode) were prepared by the coating of a slurry composed of 92wt% metal oxides/MWCNTs as the active material, 5wt% acetylene black (AB) and 3wt% polytetrafluoroethylene (PTFE) solution with ethanol on a stainless steel mesh (diameter: 19mm).

Two pieces of polypropylene sheets and a glass fiber filter paper as separators immersed in the electrolyte placed between the two electrodes were used.

Characterization and Electrochemical Testing: The morphology of the nanocomposites were investigated using transmission electron microscopy (TEM) system (Philips, model CM12). Energy dispersive x-ray (EDX) systems (Supra-35VP and EDX Falcon System) were served for the elemental analysis purpose. CV and galvanostatic charge-discharge spectroscopy measurements have been carried out using electrochemical workstation instrument (WonATech, Model: WBCS 3000-WL). Voltammetry testing was carried out at constant potentials scan rate of 5mV/s between -0.3 to 0.3V charge-discharge test was conducted at constant current scan rate of 10 mA/cm^2.

RESULTS AND DISCUSSION

TEM and EDX Investigation MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs Nanocomposites: Fig. 1 (a and b) show one of the low-magnified TEM images of pure MWCNTs before and after acid treatment, respectively. These images revealed that during the oxidation process in nitric acid solution, the end tips of the tubes were opened. This evidence is in agreement with the results reported by Zhao and co-workers [27]. Hollow cavities of MWCNTs are filled with MnO_2, NiO, Fe_2O_3 and CuO nanoparticles which are clearly visible in Fig. 1 (c), (e), (g) and (I), respectively. The size of the encapsulated particles are about 10-100 nm in length.

The resulting metal oxides/MWCNTs nanocomposites are further characterised using EDX to examine their chemical composition. EDX scans obtained from individual nanocomposites indicated that the particles compositions comprised solely of metal and oxygen. Fig. 1 (d) reveals the elements of C, Mn and O as the components of MnO_2/MWCNTs nanocomposite. EDX spectra of NiO/MWCNTs nanocomposite in Fig. 1 (f), exhibits the presence of elements Ni, O and C. As shown in Fig. 1 (h), it is found that the nanocomposite of Fe_2O_3/MWCNTs includes elements of Fe, O and C. Fig. 1 (j) shows that the nanocomposite of CuO/MWCNTs is composed of elements of Cu, O and C. The appearance of Au in the analysis of NiO/MWCNTs and MnO_2/MWCNTs nanocomposites (Fig. 1 (d and f), respectively) is due to use of different apparatus (EDX Falcon System) which needed coating of the sample with a conducting layer of Au before analysis.

Cyclic Voltammetry Study on MWCNTs, MnO_2/ MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs Nanocomposites Electrodes: Fig. 2 shows the cyclic voltammetery (CV) behavior of the pure MWCNTs and MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO/MWCNTs nanocomposites at a potential scan rate of 5mV/s.

CV curves of pure MWCNTs reveals no current peaks and furthermore it is nearly symmetric with respect to the zero-current line. This indicates that the electrodes have the characteristic of a capacitor with constant charging and discharging rates over a complete cycle. However, there are oxidation peaks observed in the CV for metal oxides/MWCNTs electrodes, which are attributed to redox reactions due to the functional groups on MWCNTs [28].

There is a reasonable symmetry to the curves for MWCNTs electrodes, which may be resulted by the capacitance arising solely due to the double layer. However, in metal oxide/MWCNTs electrodes, the lack of symmetry to the curves is probably due to combination of double layer and pseudo capacitances contributing to the total capacitance [29]. The area of the curves gradually increases by addition of Fe_2O_3, CuO, NiO and MnO_2, which is indicating an enhancement of the specific capacitance for different electrode materials. Therefore, these transition metal oxides/MWCNTs electrodes were proved to be closer to an ideal capacitor than the pure MWCNTs electrode. Also these types of electrodes follow similar properties of CNTs [30]. The CV curve for MnO_2/MWCNTs and NiO/MWCNTs nanocomposite electrodes show more rectangular shape and more significant capacitive behavior than other electrode materials. This is due to higher pseudocapacitive behavior of NiO and MnO_2 than Fe_2O_3, CuO. Hence, hereafter it would be focused only on the electrochemical properties of MnO_2/MWCNTs and NiO/MWCNTs.

The NiO/MWCNTs curve had an oxidation peak approximately at 0.05 V and a reduction peak around -0.1 V; however, the MWCNTs curve had neither oxidation nor reduction peaks. It could be an indication of electrochemical oxidation and reduction on the NiO/MWCNTs electrode when the EC was being charged or discharged. After filling MnO_2 in to MWCNTs, it was clearly found that larger oxidation peaks at 0.45V and non-significant reduction peaks around 0.0 V occurred. These confirmed that there were electrochemical oxidation and reduction on the NiO/MWCNTs and MnO_2/MWCNTs electrodes when the supercapacitor was being charged or discharged. The effective capacitance of an electrode is estimated from the area included in the curve [2]. As shown in CV curves, it is clear that the capacitance of the MnO_2/MWCNTs as a positive electrode in the alkaline EC was larger than those of the NiO/MWCNTs and pure MWCNTs positive electrodes. The CV curve of MnO_2/MWCNTs is larger than NiO/MWCNTs because of higher pseudocapacitive properties and electrochemical stability of MnO_2 than NiO. The capacitive behavior of MnO_2/MWCNTs is higher than pure MWCNTs, because the MnO_2/MWCNTs nanocomposite takes the advantages of both pseudocapactive and electric double layer capacitive behavior. However the pure MWCNTs have only the electric double layer capacitive behavior during charging and discharging of the electrode.

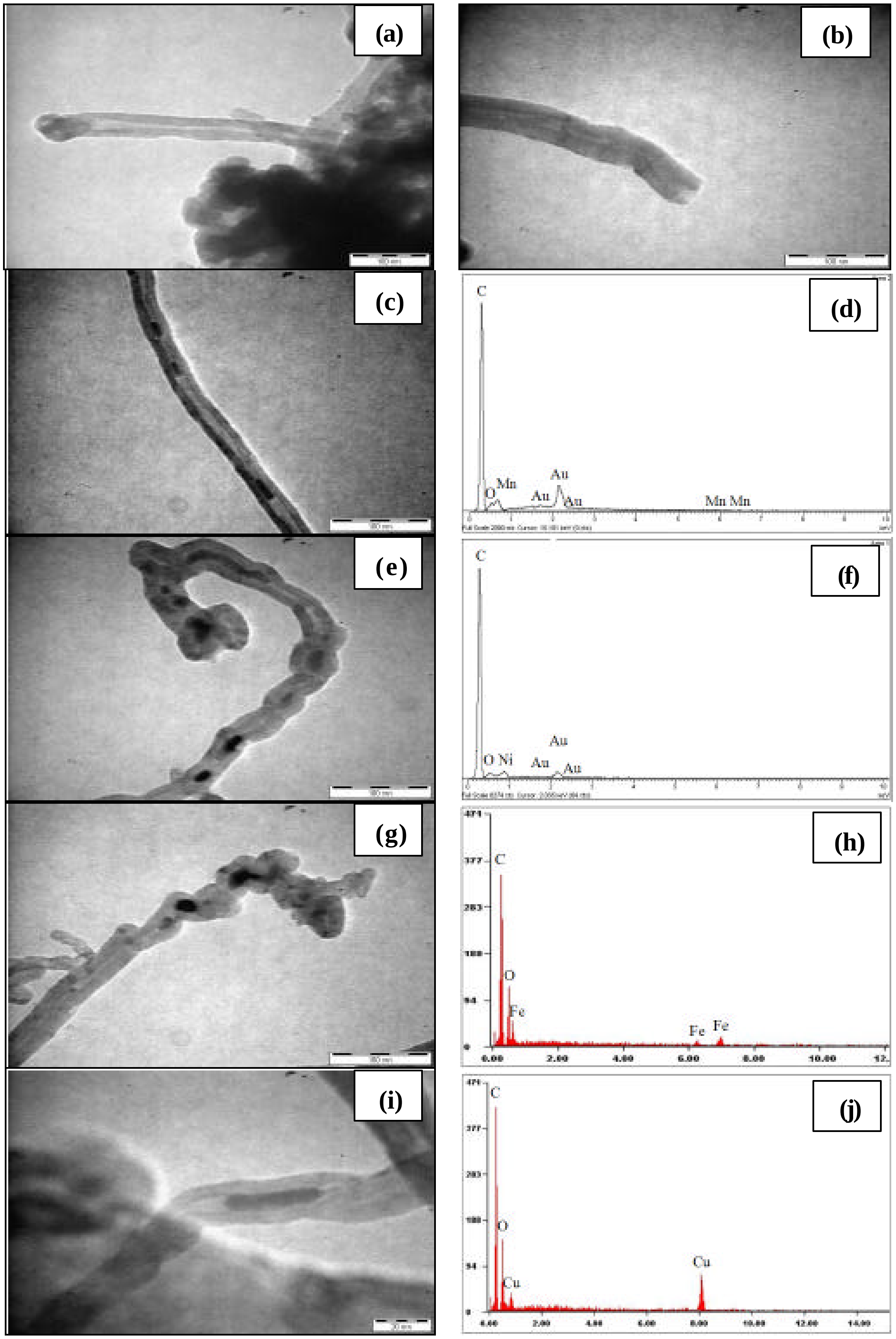

Fig. 1(a-j): Fig. 1(a), (b), (c), (e), (g) and (i): TEM images of MWCNTs, opened tip MWCNTs, MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO, respectively. (d), (f), (h) and (j): EDX spectra of MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs and CuO, respectively

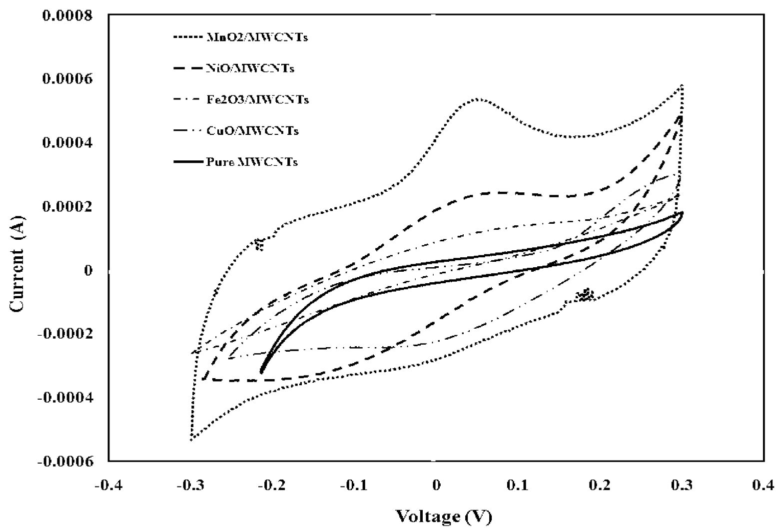

Fig. 2: Cyclic voltammograms of MnO_2/MWCNTs, NiO/MWCNTs, Fe_2O_3/MWCNTs, CuO/MWCNTs and MWCNTs in 6 M KOH solution at constant scan rate (5mV/s).

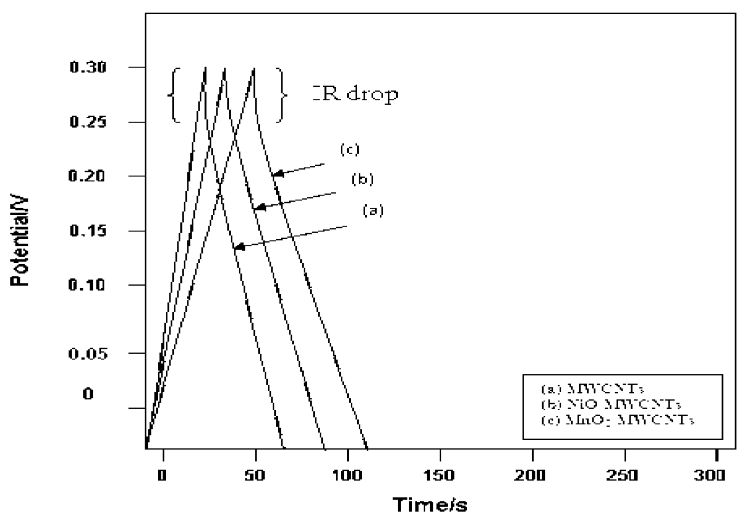

Fig. 3: Galvanostatic charge-discharge curves of the (a) MWCNTs, (b) NiO/MWCNTs and (c) MnO_2/MWCNTs at current density of $10 mA/cm^2$ in 6M KOH aqueous electrolyte.

Galvanostatic Charge–Discharge Study on MWCNTs, NiO/MWCNTs and MnO_2/MWCNTs Nanocomposites Electrodes: The charge–discharge properties of acid-treated MWCNTs, NiO/MWCNTs and MnO_2/MWCNTs electrodes were investigated by galvanostatic charge discharge in 6 M KOH solutions. At constant current density of 10 mA/cm^2, the galvanostatic charge–discharge curves of the MWCNTs, NiO/MWCNTs and MnO_2/MWCNTs are illustrated in Fig. 3 (a, b and c), respectively. The symmetry of the charge and discharge characteristics showed good capacitive behavior of the nanocomposites electrodes.

The SC has been evaluated from the charge-discharge curves, according to equation (1) introduced by Fan and co-workers [15]:

$$C_S = \frac{Q_{com} - Q_{MWCNTs}}{\Delta V \times M} = \frac{I \times (t_{com} - t_{MWCNTS_s})}{\Delta V \times M} \quad (1)$$

Where C_s (F/g) is the SC of the NiO/MWCNTs and MnO_2/MWCNTs nanocomposite electrode based on NiO and MnO_2, respectively; Q_{com} and Q_{MWCNTs} are discharge capacities of each nanocomposites and MWCNTs electrodes, respectively; I is discharge current (in Fig. 3, I =10 mA/cm^2); t_{com} and t_{MWCNTs} are discharge times for composites and CNTs electrodes, respectively; ΔV is potential window (in this paper, $\Delta V = 0.3$ V); M is the loading mass of NiO and MnO_2. The SCs of NiO/MWCNTs and MnO_2/MWCNTs nanocomposites electrodes based on NiO and MnO_2 were calculated by obtaining their discharge time from Fig. 3. The average SCs measurements using the two electrodes techniques of the pure MWCNTs, NiO/MWCNTs and MnO_2/MWCNTs nanocomposites electrodes were 68.56, 134.40 and 302.41 F/g, respectively. An increase in the capacitance of MWCNTs is mainly due to the diffusivity of the electrolyte ions into electroactive materials [29] and the electrolyte ions accessibility to the sidewalls and central core of the nanotubes [13] after opening MWCNTs. The enhancement of the SCs attributed to the presence of NiO and MnO_2 encapsulated in the MCWNTs, which in turn modify the microstructure and morphology of MCWNTs, allowing the metal oxides to be available for the electrochemical reactions and improves the efficiency of the nanocomposites. The IR of composite electrodes drops, the trends for all curves are similar and not obvious, the curves are also shown in Fig. 3. These imply further that MnO_2/MWCNTs composite electrode has excellent capacitive properties with relatively small overall resistances due to high conductivity of CNTs [15].

CONCLUSION

Low cost transition metal oxides such as MnO_2, NiO, Fe_2O_3 and CuO were encapsulated MWCNTs with the same mass ratio by a simple method. TEM images showed the distribution of metal oxide particles of size of about 10 to 100 nm in the cavity of MWCNTs which were achieved by wet chemical method. The MnO_2/MWCNTs and NiO/MWCNTs nanocomposite electrodes due to have higher pseudocapactive properties and electrochemical stability showed more significant capacitive behavior than other electrode materials of Fe_2O_3/MWCNTs, CuO/MWCNTs and pure MWCNTs. The average SCs measurements made by the two electrodes techniques of the pure MWCNTs, NiO/MWCNTs and MnO_2/ MWCNTs nanocomposites electrodes were 68.56, 134.40 and 302.41 F/g, respectively. Both NiO/MWCNTs and MnO_2/MWCNTs nanocomposites were the promising materials to be used as positive electrode in alkaline electrochemical supercapacitor. However, the capacitance properties of MnO_2/MWCNTs were better than NiO/MWCNTs.

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