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Preparation and Capacitive Properties of Nickel-manganese Oxides/Multiwalled Carbon Nanotube/Poly (3,4-ethylenedioxythiophene) Composite Material for Electrochemical Supercapacitor

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Abstract: Nickel-manganese oxides/multiwalled carbon nanotubes/poly (3,4-ethylenedioxythiophene) (NMO/MWCNTs/PEDOT) nanocomposite was prepared by in chemical oxidation method and served as electrode material in supercapacitor. Binary nanocomposites of NMO/MWCNTs and pure MWCNTs electrodes were also prepared for comparative purpose, their physical and electrochemical performances were investigated. Well encapsulation of NMO nanoparticles inside cavities of MWCNTs and uniform coating of NMO/MWCNTs with PEDOT were observed with Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDAX). The electrochemical properties were determined by Cyclic Voltammetry (CV) and Charge-discharge (CD) tests in 6 M KOH aqueous electrolytes. The Specific Capacitance (SC) value of the NMO/MWCNTs/PEDOT was significantly resulted larger than NMO/MWCNTs and Pure MWCNTs.

Keywords: Nickel-manganese oxides, MWCNTs, PEDOT, nanocomposite, electrochemical properties, supercapacitor

INTRODUCTION

There has been a great deal of interest in recent years on the ability to control nanoscale structures using simple routes by the preparation of conducting polymer based nanocomposite for several applications including chemical sensors (Li *et al.*, 2007), lithium batteries (Vadivel Murugan *et al.*, 2008), fuel cells (Barroso-Bujans *et al.*, 2008) and Electrochemical Supercapacitors (ESCs) (Liu 2008; Lota *et al.*, 2007; Peng *et al.*, 2008; Suppes *et al.*, 2008). In particular, a comparison of the application of either conjugated polymers or transition metal oxides individually with their MWCNTs based nanocomposites as positive electrodes in supercapacitor suggests that when these polymer/oxide materials and MWCNTs are combined at the "nanoscale" level, many properties can be achieved such as enhanced charge storage ability due to synergistic effects emerge. Of the various transition metal oxide /MWCNTs nanocomposite materials that have been investigated over the years, Although RuO_2/MWCNTs is the material that presents the highest specific capacitance values (Zheng *et al.*, 2007; Kim *et al.*, 2005), it has the inherent disadvantage of being both expensive and toxic (Liu, 2008).

Conducting polymers after carbon materials and metal oxides are the third group of candidate materials for supercapacitors due to their good electrical conductivity large pseudocapacitance and relatively low cost. The most commonly used conducting Polymers Include Polyaniline (PANI), Polypyrrole (Ppy) and poly (3,4-ethylenedioxythiophene) (PEDOT). Combination of polymers with MWCNTs and metal oxides such as; PANI/MWCNTs (Wu *et al.*, 2007), PPy/MWCNTs (Wang *et al.*, 2007a), PEDOT/MWCNTs (Chen *et al.*, 2009), MnO_2/CNTs/PANI (Yuan *et al.*, 2008) and MnO_2/CNTs/PPy (Sivakkumar *et al.*, 2007) have shown great potential as hybrid electrode materials in supercapacitors previously.

In view of finding an inexpensive alternate to RuO_2, manganese oxide (MnO_2) (Ko and Kim, 2009) and Nickel Oxide (NiO) (Xie *et al.*, 2008) have recently been prepared by both chemically and electrochemically by other researchers and it was found to possess capacitive characteristics with acceptable values of specific capacitance. Among the conducting polymers, PEDOT, as a member of polythiophene family, has drawn a wide interest in ESCs application because of its fast charge/discharge ability, wide potential window and environment-friendly feature as well as high room temperature conductivity (easily up to 500 Scm^{-1}) (Chen *et al.*, 2009; Czardybon and Lapkowski, 2001; Murugan *et al.*, 2006).

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MnO_2 /MWCNTs and NiO/MWCNTs nanocomposites were successfully synthesized separately in our previous work (Kiamahalleh *et al*., 2009) and their electrochemical behaviors were completely described. The purpose of this study is to encapsulate mixed NMO inside MWCNTs with the same procedure with our previous work and to maximize its electrochemical utilization for charge-storage. For this purpose, nanostructured NMO/MWCNTs nanocomposite was coated by PEDOT by chemical oxidation polymerization method. Material characterization was carried out by TEM, EDAX, CV and CD cycling. The results showed that higher the specific capacitance values, higher power density of the prepared NMO/MWCNTs/PEDOT nanocomposite were demonstrated. To our knowledge, synthesizing NMO/MWCNTs/PEDOT nanocomposite as electrode for electrochemical supercapacitors has not yet been reported.

MATERIALS AND METHODS

Materials: The NMO/MWCNTs nanocomposite used as composite backbone in this study was synthesized by filling the NMO particles inside the cavities of the MWCNTs using wet chemical method. The complete description of filling process has been explained in our previous work (Kiamahalleh *et al*., 2009). EDOT (supplied by Sigma-Aldrich) and Iron (III) chloride. Hexahydrate ($FeCl_3.6H_2O$) from Bendosen have been served as monomer and oxidant reagent, respectively for oxidative polymerization. The solvent for making solution of monomer is Acetonitrile which has been provided by Sigma-Aldrich). All chemicals were of analytical reagent grade. Water used in this investigation was distilled water.

Synthesis: Polymerization of conducting polymers by a chemical method appears definitively easier than the electrochemical one (Frackowiak *et al*., 2006). Because of a limited solubility of the EDOT monomer in aqueous medium, the polymerization was performed in aprotic medium such as Acetonitrile (AN) with Fe (III) playing the role of oxidant (Lota *et al*., 2004). Constant concentration of EDOT (0.7M) was prepared by dissolving in 20 mL Acetonitrile. The solution was sonicated in the ultrasonic bath due to better solubility of EDOT in acetonitrile. In the case of the direct polymerization of PEDOT on NMO/MWCNTs nanocomposite, the nanocomposite was dispersed in the reaction mixture using an ultrasonic bath. Then, ($FeCl_3.6H_2O$) dissolved in 20 mL distilled water (1.5 M) was dropped into the solution under constant stirring and the polymerization was allowed to proceed for 4 h at 25°C. The product was filtered under gravity and then washed carefully with distilled water and acetonitrile (Frackowiak *et al*., 2006). Finally it was dried overnight at 70°C in the oven to obtain doped NMO/MWCNT/PEDOT nanocomposite.

Characterizations: The products were characterized using TEM (Philips, model CM12). EDAX analysis was recorded to discover the composition elements using (Supra-35VP field emission scanning electron microscope).

Electrodes and supercapacitor preparation: The nanocomposite electrodes materials were prepared by dry mixing NMO/MWCNTs/PEDOT or composites The paste was spread onto the stainless steel mesh collectors and then pressed. These electrodes were dried in the air at 70°C for one day and then used as the working electrode in the supercapacitor assembly. The working electrode has been separated with the MWCNTs counter electrode by two sheets of glass fiber and one sheet of polypropylene in the middle. The working electrode and counter electrode with the separators between them were packed in the Teflon cell as supercapacitor cell has been 6M KOH aqueous solutions served as electrolyte.

RESULTS AND DISCUSSION

TEM illustrates pure MWCNTs with no extra material on the outer surface (Fig. 1a) and a uniform coating of MWCNTs with PEDOT (Fig. 1c). Presenting of the metal oxide particles inside MWCNTs are interestingly supported by Fig. 1a and EDAX analysis (Fig. 1b) proves the composition of the sample after filling NMO inside MWCNTs. As shown in Fig. 1c the uniform deposition of PEDOT on the MWCNTs is similarly demonstrated by Transmission Electron Microscopy (TEM) which the uniformity of the coated PEDOT on MWCNTs is consistent with results by Chen *et al*. (2009). The result of EDAX analysis in Fig. 1d similarly with the result by Cho *et al*. (2008) clearly indicates that the EDOT was successfully polymerized by the Fe (III) which was simultaneously and carefully removed from the nanocomposite due to wash with distilled water and acetonitrile. As the internal cavity is well discernible in TEM images, we conclude that the coating with PEDOT takes place only at the outer surface of the MWCNTs and the inner cavities of the MWCNTs were filled partially only with NMO particles.

Typically, the uniform coating of MWCNTs with a conducting polymer has been reported in the literature (Konyushenko *et al*., 2006; Han *et al*., 2005;

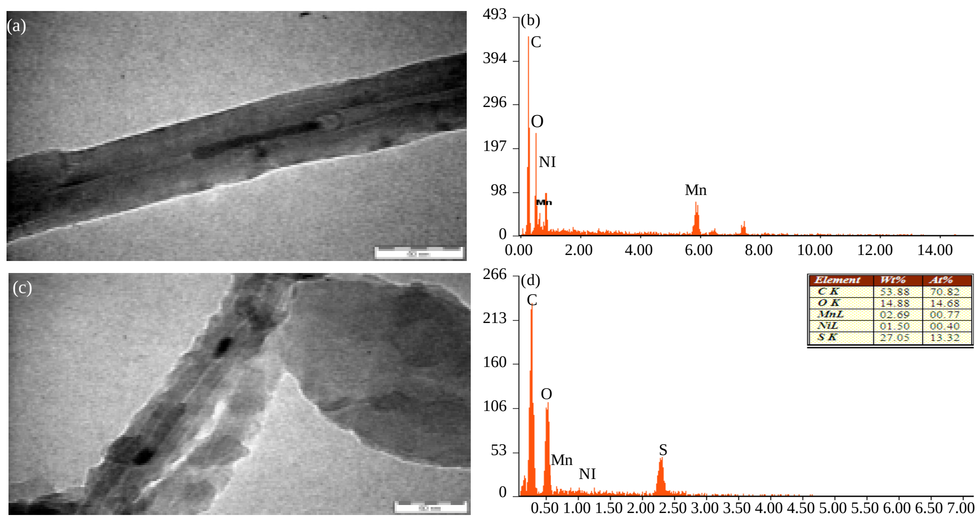

Fig. 1: (a) TEM image (b) EDAX of NMO/MWCNTs (c) TEM image and (d) EDAX of NMO/MWCNTs/PEDOT

Deng *et al*., 2005; Peng *et al*., 2006), in agreement with the present results. However, to our knowledge the preparation of coated PEDOT on encapsulated MWCNTs with transition metal oxides has not been studied yet. The surface of the MWCNTs has also been modified by oxidation in nitric acid in our previous study (Kiamahalleh *et al*., 2009) and production of carboxylic fictionalization group are consistent with previous researches (Han *et al*., 2005; Qu *et al*., 2005; Karim *et al*., 2005), to enhance the deposition of conducting polymer such as PEDOT.

PEDOT due to its high molar mass presents a moderate value of capacitance in comparison with PPY, PANI, etc. (Lota *et al*., 2004). The presence of carbon in the bulk electrode materials for supercapacitor allows the electronic conduction of the electrode to be improved when PEDOT is in its insulating or less conducting state. For these reasons, it is profitable to use a non-tubular carbon material such as acetylene black as surface area-enhancing component which makes the nanocomposite bulk more accessible for ions transferring and improves the electronic conduction of NMO/MWCNTs/PEDOT electrodes.

The pure MWCNTs, NMO/MWCNTs and NMO/MWCNTs/PEDOT are respectively used to make asymmetric supercapacitor and their electrochemical properties are compared by means of the CV.

In all the experiments, the CV curves of the two-electrode cells using NMO/MWCNTs and NMO/MWCNTs/PEDOT nanocomposite electrodes present a typical rectangular shape independently of the

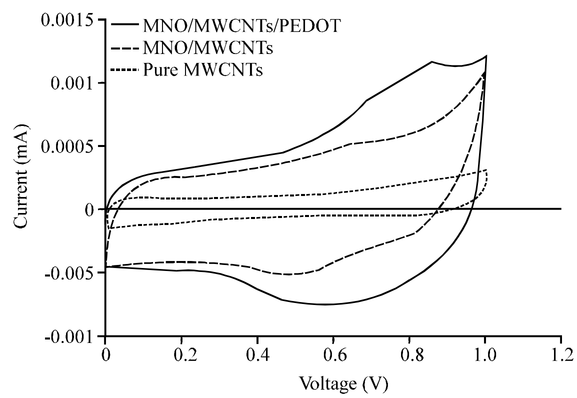

Fig. 2: CV curves of the (a) Pure MWCNTs electrode (b) NMO/MWCNTs electrode and (c) NMO/MWCNTs/PEDOT electrode at constant scan rates in 6M KOH

composition, however the status of reduction peaks are different in each curves. It is due to different electrochemical behavior of the nanocomposite materials used in the electrodes (Peng *et al*., 2006). Figure 2 compares the voltammograms of pure MWCNTs, NMO/MWCNTs and NMO/MWCNTs/PEDOT electrodes similarly made using same electrolyte.

The MWCNTs present the typical box-like curve, expected for an ideal capacitor.

However, there are oxidation peaks observed in the CV for NMO/MWCNTs electrodes and NMO/MWCNTs /PEDOT which are attributed to redox reactions due to the metal oxides (NuLi *et al*., 2009) inside and functional

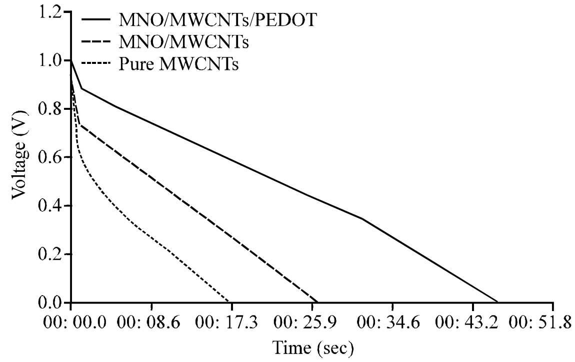

Fig. 3: The CD curve of Pure MWCNTs electrode, NMO/MWCNTs electrode and NMO/MWCNTs/PEDOT electrode at constant scan rates in 6M KOH

groups on the MWCNTs (Frackowiak *et al.*, 2000). NMO/MWCNTs/PEDOT nanocomposite shows the widest potential window in comparison with other electrode materials. It is interesting to observe that the NMO/MWCNTs/PEDOT nanocomposite electrode shows higher SC than that of the NMO/MWCNTs and pure MWCNTs electrode. The difference in SC originates from a Faradaic pseudo-capacitance of the transition metal oxides and conducting polymer applied in nanocomposites (Ko *et al.*, 2009).

The galvanostatic CD behaviors of the different electrodes have been studied with an applied constant current of 10 mA in the potential range between 0 and 1 V. The symmetry and linear of the charge and discharge characteristics show good capacitive behavior (Fig. 3).

The discharge capacitance C is calculated from the linear part of discharge curves using the following formula (Eq. 1) purposed by Wang *et al.* (2007b):

$$C = I \times \Delta t \times \Delta V^{-1} \quad (1)$$

where, i is the current and Δt is the time interval for the change in voltage ΔV. In two-electrode system, the specific capacitance C_m is obtained by Eq. 2:

$$C_m = \frac{2C}{m} \quad (2)$$

where, m is the mass of the nanocomposite material on the electrode.

The average SC measured using the three electrochemical techniques for the symmetric arrangement of the pure MWNTs and asymmetric arrangement of NMO/MWCNTs electrodes and NMO/MWCNTs/PEDOT were 77.75, 311.90 and 526.55 F g^{-1}, respectively. The capacitance values thus obtained here from PEDOT based nanocomposite (526.55 F g^{-1}) is comparatively more than literature values of 160 F g^{-1} (Lota *et al.*, 2004) from MWCNTs/PEDOT in the asymmetric supercapacitor configuration and this is due to presence of NMO particles as the promising electroactive materials.

The further increase in the supercapacitance properties of polymer/metal oxide-filled MWCNTs is due to uniform coating of polymer over functionalized MWNTs (Estaline Amitha*et al.*, 2009) and metal oxide particles encapsulated inside MWCNTs (Nam *et al.*, 2009) which in turn modify the microstructure and morphology of MWNT, allowing the polymer and metal oxides to be available for the electrochemical reactions and improves the efficiency of the nanocomposites. The progressive redox reactions occurring at the surface and bulk of NMO/MWCNTs/PEDOT through Faradiac charge transfer between electrolyte and electrode result in the enhancement of the specific capacitance of PEDOT and NMO filled in MWCNTs from pure MWCNTs.

CONCLUSION

In summary, we have reported a uniform PEDOT coating on the surface of NMO/MWCNTs using simple oxidation polymerization. MWCNTs play a role of an excellent support for conducting polymers. Their unique microtextural, mechanical and conducting properties allow to form a supercapacitor material with an accessible electrode/electrolyte interface for efficient charge propagation. Electron microscopy images showed the well uniform structured of PEDOT coated on NMO/MWCNTs. Electrochemical testing showed the good cycleability of the hybrid nanocomposite materials. It was concluded the coating of PEDOT on NMO/MWCNTs nanocomposite improved the SC value by 214.65 and it was 448.80 F g^{-1} higher compared to the pure MWCNTs electrode. All of above results suggest that the synthetic NMO/MWCNTs/PEDOT nanocomposite has an excellent electrochemical performance as a potential electrode for the supercapacitor.

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