MWCNTs/metal oxide nanocomposite as potential material for supercapacitors application in acidic and neutral media

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ABSTRACT

Supercapacitive properties of synthesised metal oxides nanoparticles (MO where M = Ni, Co, Fe) integrated with Multi-walled carbon nanotubes (MWCNT) on a basal plane pyrolytic graphite electrode (BPPGE) was investigated. Successful modification of the electrode with the MWCNT/MO nanocomposites was confirmed with TEM, SEM, EDX and XRD techniques. Supercapacitive properties of the modified electrodes in H_2SO_4 and Na_2SO_4 electrolytes was investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic constant current charge-discharge (CD) techniques. The specific capacitance (SC) values followed similar trend for the cyclic voltammetry and the electrochemical impedance studies and are slightly lower than galvanostaticresult.MWCNT-NiO based electrode gave best specific capacitance of 433.8 $mFcm^{-2}$ (ca 2119 F/g) in H_2SO_4.The electrode demonstrated high stabilities with no significant changes over 1000 cycles.

Keywords: MWCNT-metal oxide, nanocomposites, Electrochemical impedance, Galvanostatic charge-discharge, Specific capacitance.

1.0 INTRODUCTION

Studies had shown that the CNT/MO nanocompoiste modified electrodes exhibited huge capacitive current in some electrolytes [1,2]. Therefore, it becomes imperative to establishing the charge storage properties of these materials as a potential source for energy generation. This is in response to the increasing demands for clean energy technologies, where supercapacitors are considered to be the most promising energy storage and power output technologies [3] for portable electronics, electric vehicles, and renewable energy systems. In this work, we established the supercapacitive behaviour of three transition metals nanocompoiste such as Ni, Co and Fe oxides supported on MWCNT platform in acidic and neutral medium. Basal plane pyrolytic electrode (BPPGE) was used as the base electrode. Our motivation into this study was because of the scarce literatures on their supercapacitive properties especially, MWCNT-NiOnanocomposite modified electrode in acidic medium. Most literatures work found are carried out in the alkaline environment. Therefore, this work represents the first time a comparative study of the supercapacitive properties NiO, Fe_2O_3, Co_3O_4 nanoparticles chemically integrated into MWCNTs at a basal plane pyrolytic graphite electrode (BPPGE) platform is investigated in both acidic and neutral pH conditions. Our findings showed that the acid-functionalised MWCNTs significantly enhanced the supercapacitance of the synthesised nanooxide in the medium studied, as compared with other literature reports.

2.0 EXPERIMENTAL

2.1 Materials and reagents

Multi-walled carbon nanotubes (MWCNTs), obtained from Aldrich, was acid-digested using the known procedure [4]. $NiNO_3.6H_2O$, $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, H_2SO_4 and Na_2SO_4 were obtained from Sigma-Aldrich chemicals.

Ultra pure water of resistivity 18.2 MΩcm was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and used throughout for the preparation of solutions. A phosphate buffer solution (PBS, pH 7.0) was prepared with appropriate amounts of K_2HPO_4 and KH_2PO_4, and the pH adjusted with 0.1 M H_3PO_4 or NaOH. All electrochemical experiments were performed with nitrogen-saturated PBS. All other reagents were of analytical grades and were used as received from the suppliers without further purification.

2.1.1 Syntheses of metal oxide (MO) nanoparticles

Nickel oxide (NiO) nanoparticles were prepared using the method described by Xiang et al. [5]. Cobalt oxide nanoparticles were prepared using the method described by Yao et al [6]. The maghemite (Fe_2O_3) nanoparticles were synthesized by the method described by Sun et al. [7].

2.3 Electrode Modification and Pretreatments

The BPPGE surface was cleaned by gentle polishing on a carborundum paper and the surface was smoothened by adhesive tape. The electrode was then subjected to ultrasonic vibration in absolute ethanol to remove adhesives that might be trapped at the surface. BPPGE-MWCNT-MO nanocomposite electrode was prepared by casting 20 µL drop of the MWCNT/MO solution (20 mg MWCNT/MO in 1 ml DMF) onto the BPPGE, where MO can be NiO, Co_3O_4 or Fe_2O_3 nanoparticles. The electrode is dried in an oven at about 50 ^oC for about 5 min. The mass of the active material on the BPPGE (ca. 20 µg) was obtained using the Sartorius CP225D micro-balance with a readability of 0.01 mg.

3.0 RESULTS AND DISCUSSION

3.1 Comparative FETEM, HRSEM, EDX and XRD

Figure 1a, c and e is a typical TEM while Fig. 1b, d and f are the SEM micrograph showing the size distribution for the synthesised MWCNT-MO nanoparticles. The nanoparticles appeared crystalline with mono-disperse particles along the MWCNTs. The particle sizes are in the 10 – 30 nm range.

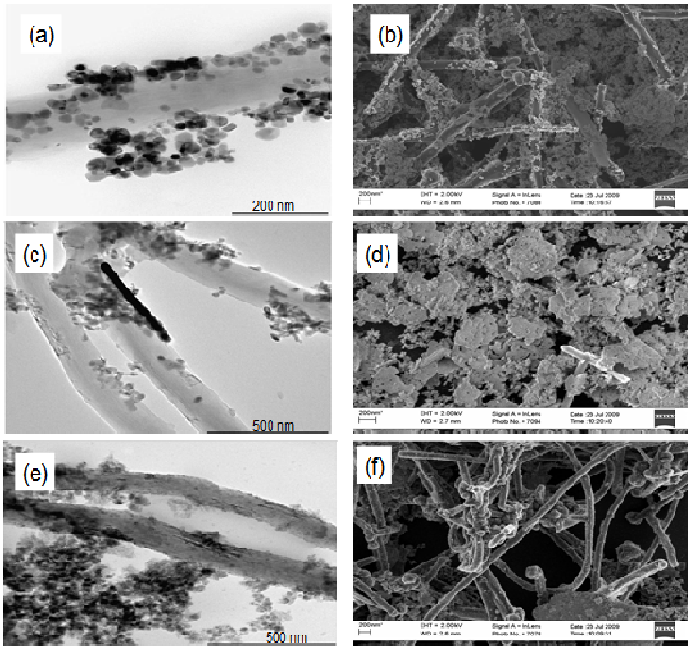

Figure 1: FETEM images of (a) MWCNT-NiO (c) MWCNT-Co_3O_4 and (e) MWCNT-Fe_2O_3nanocomposite. (b), (c) and (e) are their respective SEM images.

Figure 2 is the EDX profile of the electrodes. The presence of Ni, Co, Fe and oxygen peaks in (a), (b) and (c) showed that the electrodes were successfully modified with the respective metal nanoparticles and their oxide derivatives.

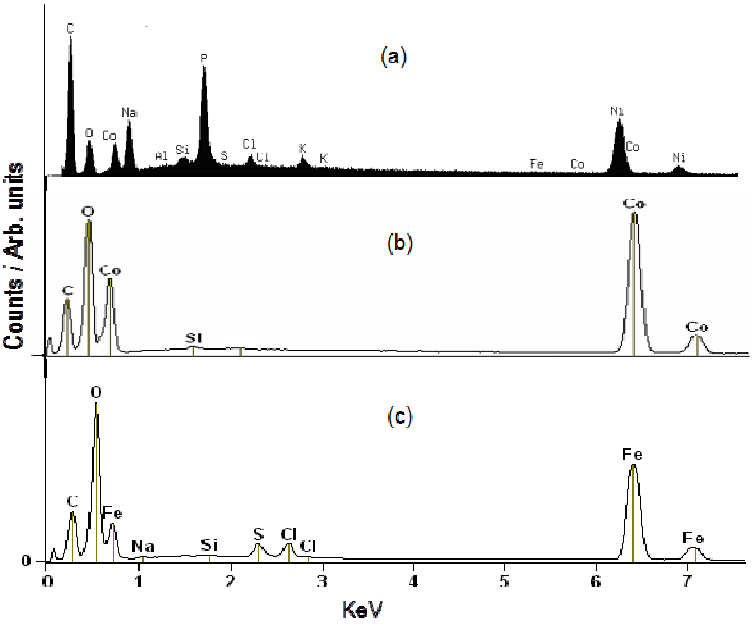

Figure 2:EDX spectra of (a) MWCNT-NiO, (b) MWCNT-Co_3O_4 and (c) MWCNT-Fe_2O_3.

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From the corresponding XRD spectra for the MO particles (not shown), the average crystal size of the particles were calculated to be ~ 21.5 nm (NiO), 22.8 nm (Co_3O_4) and 10.3 nm (Fe_2O_3). The values agreed within the range reported for the TEM.

3.2 Comparative cyclic voltammetric experiments

Figure 3 presents the comparative cyclic voltammograms of the bare BPPGE (i), BPPGE-MWCNT (ii), BPPGE-MWCNT-NiO (iii), BPPGE-MWCNT-Co_3O_4 (iv) and BPPGE-MWCNT-Fe_2O_3 (iv) electrodes in (a) 1 M H_2SO_4 and (b) 1 M Na_2SO_4 solutions (scan rate; 25 mVs^{-1}).

The CVs tend to be rectangular in H_2SO_4 than in Na_2SO_4 but the lack of perfect rectangular shape for the curves in both cases is attributed to the combination of double layer and pseudo-capacitances contributing to the total capacitance [8]. The specific capacitance (SC) was estimated from the cyclic voltammograms using the equation:Cfilm (Fcm^{-2}) =$I_{ch}/\nu A$(1)where Ich is the charging current, ν the scan rate and A is the area of the electrodein cm^2.

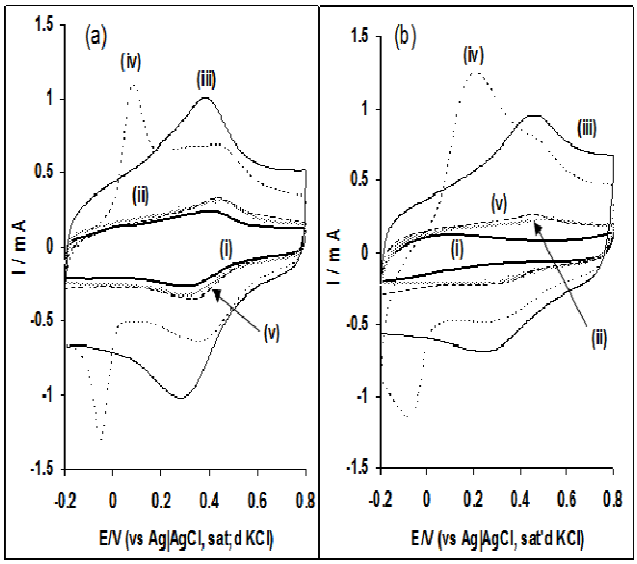

Figure 3:Comparative cyclic voltammograms of the bare BPPGE (i), BPPGE-MWCNT (ii), BPPGE-MWCNT-NiO (iii), BPPGE-MWCNT-Co_3O_4 (iv) and BPPGE-MWCNT-Fe_2O_3 (iv) electrodes in (a) 1 M H_2SO_4 and (b) 1 M Na_2SO_4 solutions (scan rate; 25 mVs^{-1}).

In H2SO4 solution, the SC values are: BPPGE-MWCNT-NiO (408.0 $mFcm^{-2}$) > BPPGE-MWCNT-Co_3O_4 (262.9 $mFcm^{-2}$) > BPPGE-MWCNT-Fe_2O_3 (134.8 $mFcm^{-2}$) > BPPGE-MWCNT (126.6 $mFcm^{-2}$) > BPPGE (100.8 $mFcm^{-2}$); and the trend is: BPPGE-SWCNT-NiO (329.8 $mFcm^{-2}$) > BPPGE-MWCNT-Co_3O_4 (248.0 $mFcm^{-2}$) > BPPGE-MWCNT-Fe_2O_3 (95.0 $mFcm^{-2}$) > BPPGE-MWCNT (87.0 $mFcm^{-2}$) > BPPGE (29.8 $mFcm^{-2}$) in Na_2SO_4 solution.

3.3 Electrochemical impedance studies

To further examine the electron transfer or capacitive behaviour of the MWCNT-MO electrodes in the electrolytes, electrochemical impedance spectroscopy (EIS) experiment was conducted at 0.3 V vsAg|AgCl, sat'dKCl.

Table 1:Impedance data obtained for MO nanocomposite modified electrodes in 1.0 M H_2SO_4 and 1.0 M Na_2SO_4 electrolytes at a fixed potential of 0.30 V.

Electrode	Impedimetric parameters					
	R_s (Ω cm^2)	CPE (μFcm^{-2})	*n*	R_{ct} (Ω cm^2)	C_{dl} ($mFcm^{-2}$)	f^o *(Hz)*
	1.0 M H_2SO_4					
BPPGE-SWCNT	0.62	429.00	0.49	1.13	92.2	794.0
-NiO	(0.40)	(35.88)	(4.01)	(0.57)	(5.35)	
BPPGE-SWCNT	0.69	679.90	0.52	1.57	70.7	631.0
-Co_3O_4	(0.35)	(30.16)	(3.70)	(0.71)	(6.84)	
BPPGE-SWCNT	0.57	37.86	0.43	4.90	34.2	501.0
-Fe_2O_3	(0. 59)	(28.06)	(2.85)	(0.63)	(7.68)	
	1.0 M Na_2SO_4					
BPPGE-SWCNT	1.36	13.15	0.40	6.48	44.1	158.5
-NiO	(0.34)	(28.66)	(2.79)	(0.44)	(5.70)	
BPPGE-SWCNT	1.48	7.42	0.38	9.64	34.9	125.9
-Co_3O_4	(0.38)	(35.08)	(3.00)	(0.60)	(8.35)	
BPPGE-SWCNT	1.31	2.40	0.39	23.76	18.55	125.9
-Fe_2O_3	(0. 30)	(18.21)	(1.63)	(0.46)	(6.60)	

From Table 1, BPPGE-MWCNT-NiO has the lowest Rct values, 1.13 and 6.48 Ωcm^2 in 1 M H_2SO_4 and 1 M Na_2SO_4 solutions respectively compared with the other MWCNT-MO modified electrodes. The result indicates faster charge transport in the NiO based nanocomposites which contributed to its high SC values. Bode plots of –phase angle (ϕ) vs log f at -1.0 Hz (not shown) gave phase angles of ~ 71.30 for BPPGE-MWCNT-NiO, BPPGE-MWCNT-Co_3O_4 and 63.40 for BPPGE-MWCNT-Fe_2O_3 in H2SO4 solution. The phase angle are lower ($\leq 58^0$) for the electrodes in Na_2SO_4 at the same frequency. The values further confirms the absence of ideal capacitive behaviour as the observed phase angles are less than the 90^o expected of an ideal capacitive properties.

The low-frequency differential capacitance (Cd) for each of the electrodes can be obtained from the slope ($1/2\pi Cd$) of the plot of the imaginary component of the impedance versus the reciprocal of the frequency (i.e., -Z" vs 1/f) (not shown) [9]. The Cd values of the electrodes in 1 M H_2SO_4 are BPPGE-MWCNT-NiO (184.4 $mFcm^{-2}$) > BPPGE-MWCNT-Co_3O_4 (174.9 $mFcm^{-2}$) > BPPGE-MWCNT-

Fe_2O_3 (131.5 $mFcm^{-2}$). However the values are lower in 1 M Na_2SO_4: BPPGE-MWCNT-NiO (106.8 mFcm-2) > BPPGE-MWCNT-Co_3O_4 (104.7 mFcm-2) > BPPGE-MWCNT-Fe_2O_3 (63.9 mFcm-2). The values are slightly lower and follows similar trend to data obtained from the cyclic voltammograms.

3.4 Comparative galvanostatic charge / discharge experiments

Galvanostatic discharge is the most reliable and accurate method for evaluating the supercapacitance of electrodes. The comparative current charge/discharge curves of the three BPPGE-MWCNT-MO electrodes conducted in (a) 1 M H_2SO_4 and (b) 1 M Na_2SO_4 solutions (current density of 0.1 mA cm^{-2}, potential range of - 0.2 to 0.8 V) is presented in Figure 4.

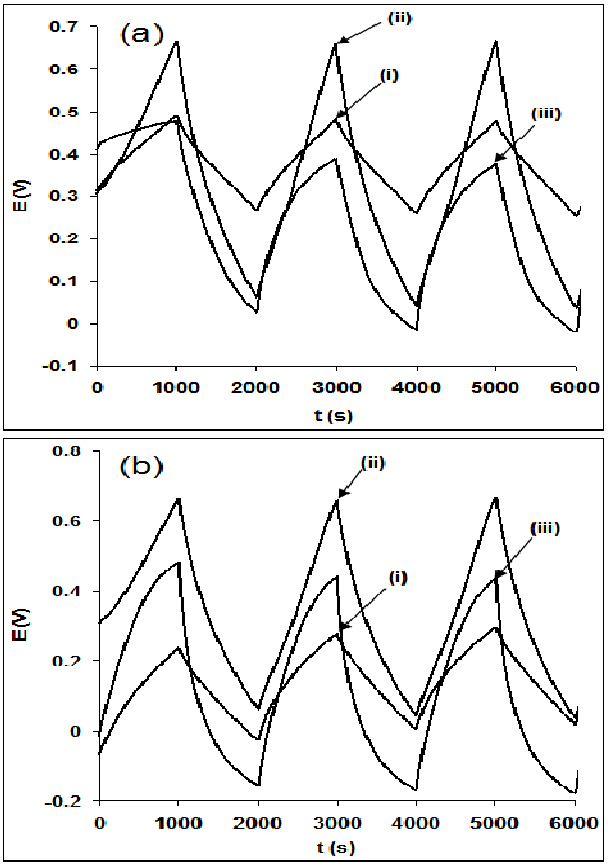

Figure 4:Typical examples of comparative galvanostatic charge discharge plot of BPPGE-SWCNT-NiO (i), BPPGE-SWCNT-Co_3O_4 (ii) and BPPGE-SWCNT-Fe_2O_3 (iii) electrodes in (a) 1 M H_2SO_4 and (b) 1 M Na_2SO_4 aqueous electrolytes, at an applied current density of 0.1 $mAcm^{-2}$.

The specific capacitance of the electrodes (SC) [10], was calculated using SC (Fcm^{-2}) = $\frac{I \times \Delta t}{\Delta E \times A}$ (2)

and the estimated SC is in the order of BPPGE-MWCNT-NiO (433.8 $mFcm^{-2}$) > BPPGE-MWCNT-Fe_2O_3 (335.0 $mFcm^{-2}$) > BPPGE-MWCNT-Co_3O_4 (235.7 $mFcm^{-2}$) in H_2SO4 solution; or BPPGE-MWCNT-NiO (334.2 $mFcm^{-2}$) > BPPGE-MWCNT-Fe_2O_3 (151.9 $mFcm^{-2}$) > BPPGE-MWCNT-Co_3O_4 (144.0 $mFcm^{-2}$) in Na_2SO_4 solution. The values are slightly higher compared with those obtained from CV experiment. The high capacitance of MWCNT-NiO has been related to the possible consequence of its high surface area and quality pore networks.

4.0 CONCLUSION

This study showed that supercapacitance of MWCNT-NiO was more enhanced in H_2SO_4 solution than the Na_2SO_4 electrolyte, possibly due to the high conductivity of the former.

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