



Polyaniline/partially exfoliated multi-walled carbon nanotubes based nanocomposites for supercapacitors



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ABSTRACT

In the present study, polyaniline (PANI)/partially exfoliated multi-walled carbon nanotubes (Px-MWCNT) nanocomposites were investigated for supercapacitor application. Nanocomposites with varying weight/weight ratio of PANI and Px-MWCNT were prepared by *in-situ* polymerization of aniline over Px-MWCNT. Transmission and scanning electron microscopic analysis showed that the MWCNT was partial unzipped along the length of tubes. The morphology of PANI/Px-MWCNT nanocomposites exhibited wrapping of PANI over Px-MWCNT. Symmetric supercapacitors containing PANI/Px-MWCNT nanocomposites as the electrode material were fabricated. The electrochemical characterization of the nanocomposites was carried by two electrode method (unit cell configuration). Cyclic voltammetric analysis showed a synergistic increase in specific capacitance of the nanocomposites. Charge-discharge cycle study indicated that nanocomposites have greater charge-discharge rate capability than pure PANI. The observed result is attributed to the shorter diffusion length of ions in the nanocomposites as compared to that of pure PANI. The electrochemical impedance spectra of supercapacitors were resolved into real and loss capacitances. The loss capacitance indicated that the time constant of the nanocomposites decreases with increase in the Px-MWCNT content. The supercapacitors showed enhanced stability during continuous charge-discharge cycling as the Px-MWCNT content in the nanocomposites increased. PANI-50 and PANI-25 nanocomposites based supercapacitors exhibited 91% and 93% capacitive retention after 2000 charge-discharge cycle while pure PANI showed only 67% capacitance retention for the same number of cycles.

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1. Introduction

In order to achieve a wide range of energy density, power density and long life cycle performance, supercapacitors are promising candidates to a variety of energy applications [1]. Supercapacitors are divided into two categories; electric double layer capacitors (EDLC) and pseudocapacitors (PC) depending on the electrode material used for device fabrication [2]. The former constitutes high surface area carbon materials whereas the latter constitutes metal oxides and conducting polymers [3–5]. In EDLC materials, charge separation takes place at the electrode/electrolyte interface and charge storage mechanism is electrostatic in nature. In PC materials, fast reversible faradic redox reaction takes place and the reaction involves the whole active material [5–7]. This makes pseudocapacitors to achieve greater capacitance and energy densities than EDLC [8].

Even though, conducting polymers are attractive materials for PC, due to high specific capacitance, controllable electrical conductivity, fast charge-discharge process and low cost, they show poor cycling stability due to swelling and shrinkage of the polymer backbone during charge-discharge process [9]. This drawback can be minimized to a large extent by adding nanofillers like carbon nanotubes (CNT) or graphene to conducting polymers. Fine coating of polymer over carbon nanofillers reduces swelling and shrinkage and improves the cycling stability of the polymer [10]. Moreover; the introduction of carbon nanofillers into the polymer matrix enhances the capacitive energy storage capability, mechanical and thermal properties of nanocomposites [11].

Various conducting polymers have been reported for supercapacitor application and the majority of research works reported till date is based on polyaniline, polypyrrole and polythiophene, due to their reasonably high specific capacitance, high stability, light weight and low material cost [12,13]. Amongst, polyaniline (PANI) has been paying a great attention to the researchers due to its high specific capacitance, good environmental stability, excellent electrical conductivity and easy synthesis process [13].

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Polyaniline composites containing single walled carbon nanotubes (SWCNT) [14], multiwalled carbon nanotubes (MWCNT) [15] and graphene have been well explored for application in supercapacitors [16,17]. Liu et al. reported on graphene nanoribbon-carbon nanotubes (GNR-CNT) hybrid composite with polyaniline. The PANI-GNR-CNT composites (at 95/5 wt/wt) exhibited a specific capacitance of 890 F g^{-1} with a solid electrolyte [18]. Wang et al. recently reported the enhancement in capacitance of partially exfoliated MWCNT as compared to pure MWCNT and graphene [19]. The enhancement of capacitance was attributed to partial exfoliation which increases the surface area and increases the accessibility of electrolyte to innermost concentric tubes of carbon nanotubes. Full exfoliation of MWCNT which leads to graphene ribbons show lower specific capacitance than partially exfoliated MWCNTs due to stacking of graphene layer and poor diffusion of ions into graphene layers.

In this paper, preparations of PANI/Px-MWCNT nanocomposites by simple in-situ polymerization of aniline over Px-MWCNT have been reported. The nanocomposites were used as the electrode material for supercapacitor fabrication. The electrochemical comparison of PANI/Px-MWCNT with PANI/MWCNT based nanocomposite has also been reported.

2. Experimental section

2.1. Reagents and materials

MWCNT was procured from Nanocyl, Belgium (grade 3100) having a purity above 95%. Conducting carbon (CC) powder (Vulcan XC-72) and carbon paper were procured from Toray, Japan. Teflon suspension was supplied by Hindustan Fluorocarbon Corporation India. Sulphuric acid (98%), hydrogen peroxide (30%), hydrazine hydrate (64%), potassium permanganate (KMnO_4) (99%), hydrochloric acid (HCl) and ammonium peroxydisulfate (APS), were purchased from Merck, India and used as received. Aniline (99%) was purchased from Fischer Scientific and distilled prior to use.

2.2. Synthesis of Px-MWCNT and PANI/Px-MWCNT nanocomposites

Px-MWCNT was synthesized following reported procedure [19,20]. In a typical process, MWCNT (200 mg) was dispersed in H_2SO_4 (20 mL, 98%) by probe sonication for 15 min. It was then stirred at rt for 1 h followed by slow addition of KMnO_4 (1 g). The reaction mixture was further stirred at 60°C for 1 h to yield oxidized Px-MWCNT. It was cooled to rt and quenched with deionized water (50 mL) containing H_2O_2 (3 mL, 30%). The oxidized MWCNT was filtered and washed with excess of deionized water. The Px-MWCNT was obtained by reduction of oxidized Px-MWCNT using aqueous hydrazine hydrate and NH_4OH followed by washing with deionized water and filtration. Prior to polymerization; Px-MWCNT was sonicated by probe sonication for 10 min in aqueous solution of 1 M HCl. The PANI to Px-MWCNT ratios were maintained as 0.75:0.25 (PANI-75), 0.50:0.50 (PANI-50) and 0.25:0.75 (PANI-25). The aniline was added into 1 M HCl solution containing Px-MWCNT and the solution was cooled to $0-5^\circ\text{C}$ in an ice bath. APS (0.025 M) was dissolved separately in 200 mL of 1 M HCl and pre-cooled to a temperature range of $0-5^\circ\text{C}$. Later, APS (1 M HCl) solution was added slowly in the aniline solution with stirring, and the reaction was continued for 12 h. The dark blackish green precipitate of PANI/Px-MWCNT nanocomposite was then recovered by filtration and dedoped using 2 M ammonia solution with constant stirring for 24 h. Finally the product was washed with deionized water, methanol followed by soxhlet extraction in acetone to remove low molecular weight impurities. The nanocomposites were dried in a temperature controlled oven at 60°C

for 5 h. Pure PANI sample was also prepared by following the same procedure in absence of Px-MWCNT.

2.3. Preparation of electrodes

PANI/Px-MWCNT nanocomposites and CC were mixed with Teflon suspension to form well dispersed paste. This paste was applied on $2 \text{ cm} \times 2 \text{ cm}$ carbon paper with uniform coating and dried for 12 h at 60°C . The amount of various ingredients used for 4 cm^2 area electrode is given in Table 1.

2.4. Preparation of unit cell

Unit cells were prepared by placing the capacitor grade separator paper in between two electrodes. Unit cells were soaked in 1 M H_2SO_4 for 24 h and then sealed in self-sealing pouch. The sealed unit cells were used for various electrochemical characterizations.

2.5. Characterization

Fourier transform infrared (FTIR) spectra of Px-MWCNT and PANI/Px-MWCNT nanocomposite samples were taken with attenuated total reflection (ATR) mode by a JASCO FTIR - 4200, Japan, over a scanning range from 500 to 4000 cm^{-1} , with a nominal resolution of 2 cm^{-1} . For each spectrum 16 runs were collected and averaged. Raman spectra were collected using Jobin Yvon spectrometer (HR 800 micro-Raman) on powder samples of nanocomposites with incident laser excitation wavelength of 514 nm. Field emission gun-scanning electron microscopic (FEG-SEM) analysis of PANI/Px-MWCNT nanocomposites was conducted on a Carl Zeiss Supra-55VP field emission electron microscope. High resolution transmission electron microscopy (HRTEM) was carried out by a JEOL JEM 1200 EX operated at an accelerating voltage of 120 kV with a high resolution. Electrochemical characterizations were carried out using an Eco chimie Autolab PGSTAT30.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of nanocomposites are shown in Fig. 1. The spectrum of Px-MWCNT show two peaks at 1383 cm^{-1} and 1580 cm^{-1} which correspond to weak C–H band of sp^3 hybridized methyl impurities formed during unzipping of MWCNT and C=C aromatic ring stretching respectively [21,22]. PANI shows peaks at 1591 and 1496 cm^{-1} corresponding to C=C stretching vibrations of the quinonoid and benzenoid rings respectively [23] and this result confirms the emeraldine structure of PANI. The peaks at ~ 1300 and 1166 cm^{-1} are attributed to C–N stretching vibration of benzene ring and stretching of C=N (–N= quinoid =N–) respectively. The band at $\sim 3410 \text{ cm}^{-1}$ is due to the N–H stretching vibration in the benzene ring. The C=C stretching of quinonoid peak at 1591 cm^{-1} for pure PANI shifts to

Table 1
Electrode composition of supercapacitors.

Electrode composition (weight in mg)	Px-MWCNT	PANI-25	PANI-50	PANI-75	PANI
PANI	-	-	-	-	5.0
PANI/Px-MWCNT	-	5.0	5.0	5.0	-
Px-MWCNT	5.0	-	-	-	-
CC	2.5	2.5	2.5	2.5	2.5
PTFE	0.5	0.5	0.5	0.5	0.5

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