

Solvent tuned PANI-CNT composites as advanced electrode materials for supercapacitor application

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ABSTRACT

Composites of polyaniline and multiwalled carbon nanotube were prepared by *in-situ* chemical oxidative polymerization of the aniline monomer in 1M HCl and 1M HCl with 20% ethanol as solvent. The PANI-CNT composites were characterized by FTIR and XRD method. The surface morphology characterization of the composites was done by using scanning electron microscopy (SEM). Electrochemical behavior of prepared PANI-CNT composites was investigated by means of cyclic voltammetry. Specific capacitance of PANI-CNT composite using 0.02M aniline in 1M HCl (20% ethanol) and 1M HCl was 597.82 and 484.49 F/g respectively at scan rate of 2mV/s in 1M H₂SO₄. Copyright © 2012 VBRI Press.

Keywords: Carbon Nanotube; cyclic voltametry; polyaniline; supercapacitor.



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Introduction

Supercapacitor is an important device in the energy storage and conversion systems, and used in different applications such as in electric vehicles, uninterruptible power supplies, memory protection of computer electronics and cellular devices [1, 2]. Three types of materials are generally used in supercapacitor namely, carbon, metal oxides and conducting polymers [3, 4]. Compared to carbons and metal oxides, conducting polymers are less expensive to use for supercapacitor application because of ability to store energy through their redox processes. They present a continuous range of oxidation states with increasing electrode potential, thus presenting a pseudo-capacitive behaviour [5]. Moreover, they exhibit a three dimensional mechanism of charge storage which is a bulk process and this leads to large values of energy density [6–8]. But the conducting polymers have also disadvantage which include lower cycle life due to which it cannot be used for repeated redox processes. Among several kinds of conducting polymer such as polypyrrole (PPy), polyaniline (PANI), poly (3-methylthiophin) (polyMET), poly (1,5-diaminoanthraquinone) (polyDAAQ), poly (3,4-ethylenedioxythiophene) (PEDOT), etc., the PANI has been paid lots of attentions due to its ease of synthesis, chemical and environmental stability, good processability and also inexpensive.

Carbon nanotubes have unique structural, mechanical and electronic properties. Due to this they act as promising material for electrode of supercapacitors. But lower capacitance is the main disadvantage of CNTs. Taking in to account the attributes of both conducting polymer and CNTs it is reasonable to develop a composite of conducting polymer and CNTs. It has been also shown experimentally that the introduction of CNTs into a polymer matrix improves the electric conductivity as well as the mechanical properties of the original polymer matrix [9–11]. For the polymer-CNT composite to be used for any application like supercapacitor devices, the processibility and dispersion of the composite and the individual material in the solvent plays an important role. The monomer unit of conducting polymer has good dispersion in the protonic acid solution. But multiwalled carbon nanotubes do not have good processibility and dispersion in such solvents. For improved processibility of carbon nanotubes and its composites, it is better to utilize each bundle of the carbon nanotube. CNTs can be better dispersed by varying the solvent characteristics and use of organic solvents with aqueous solution of protonic acid is an option. The well dispersed carbon substrate provides more surface area for the uniform deposition of the polymer leading to overall enhanced energy storage in the polymer-carbon composites [12]. In this manuscript we report the preparation and characterization of some PANI-CNT composites by *in-situ* chemical oxidative polymerization by varying the solvent characteristics.

Experimental

Chemicals

Aniline (S.D.Fine-Chem.limited, 99.5%) was vacuum distilled prior to use. MWNT (99%) was purchased from Nanostructured and Amorphous Materials Inc. having outer diameter 20-40nm and length of 1-2 μ m and PVDF from Sigma-Aldrich. All other chemicals like hydrochloric acid (35.4%), ammonium peroxydisulfate (APS, 98%), ethanol (99.9%), sulphuric acid (98%), activated carbon, N, N-dimethyl formamide (DMF) were bought from S.D.Fine Chem. limited and used as received without further purification. All chemicals were of analytical grade. Solutions were prepared in deionized water.

Synthesis of PANI-CNT Composites

Weighed amount (0.2g) of CNT was dispersed in a solution of 1M HCl and 20% ethanol by means of ultrasonication for 1 hour. Different concentrations of aniline monomer in 1M HCl was added to the dispersed CNT solution and again ultrasonicated for 1 hour. To this solution 1M freshly prepared ammonium peroxydisulfate in 1M HCl was slowly added drop wise for about half an hour. The mixture was left for polymerization for 6 h at about 0-5 °C under constant stirring. The PANI-CNT composites were obtained by filtering and rinsing the reaction mixture with deionized water and methanol followed by drying the greenish black powder under vacuum at 60 °C for 24 h. Methanol washing is desirable to remove the oligomeric impurities. PANI-CNT composites without ethanol were also prepared by the procedure described above. In this

process CNT was only dispersed in 1M HCl alone and then ultrasonicated.

Preparation of electrodes

The PANI-CNT composite was mixed with 15wt. % of Activated Carbon as conductor and 5 wt. % of binder (PVDF) in N, N-Dimethyl formamide (DMF) solvent. The mixture was ultrasonicated for 1 hr and then stirred at ambient temperature to form slurry. The electrodes were fabricated by brush coating the slurry on 2 \times 2 cm² of graphite sheet as a current collector. The prepared electrode was dried in vacuum at 60 °C for 24h.

Characterization

Infrared spectrum was recorded by using Fourier transform infrared spectrophotometer (Shimadzu IR Affinity-I 8000 FT-IR spectrophotometer) to identify the chemical structure of the PANI-CNT composites. The infrared spectrums of the samples were compared with that reported in the literature. The scanning electron microscopy (SEM, JEOL-JSM-5600LV @ accelerating voltage 20kv) was used to examine the surface morphology and average thickness of deposited PANI over the surface of CNT. The ordered structures of PANI-CNT composites were studied by XRD method. X-ray diffraction data was obtained on a Philips (Xpert PRO) machine using CuK α source and fitted with an X'celerator detector (PW 3050/60). Data was collected at 2 θ with a step size of 0.017. PANI-CNT composite electrodes were tested in a beaker type three-electrode cell with a reference electrode (Saturated calomel electrode) and a counter electrode (Pt). Cyclic voltammetry measurements were carried out by means of potentiostat/galvanostat (CH Instruments 600C series). The electrolyte used was 1 M H₂SO₄ solutions and the geometric surface area of the working electrode was 2 \times 2 cm². Cyclic voltammograms were recorded in the voltage windows ranged from 0-0.8 V (vs. saturated calomel electrode) at different scan rates of 2, 5, 10 and 15mV/s.

Results and discussion

XRD and FTIR spectra

Fig. 1(a) represents the X-ray diffraction data of PANI-CNT composite. For PANI-CNT composite the diffraction peaks were observed at $2\theta = 14.90^\circ, 20.60^\circ, 25.48^\circ, 42.77^\circ$ and 64.29° which clearly indicate formation of PANI over the CNT and also no additional crystalline order has been introduced in the composite. The results are in agreement with the experimentally predicted values [13, 14]. **Fig. 1(b)** illustrates the FT-IR spectrum of PANI-CNT composite. The band at 1243.53 cm^{-1} is due to conducting form of polyaniline indicating that the polyaniline exists in conducting emeraldine salt form. The band at 1457.94 cm^{-1} and 1560.86 cm^{-1} show the benzenoid and quinoid ring vibrations respectively. The N-H stretching vibration band appears as a small peak at 3485.34 cm^{-1} . The band at 772.47 cm^{-1} and 1024.49 cm^{-1} can be assigned to aromatic C-H out of plane bending vibrations and aromatic C-H in plane bending vibrations respectively [15]. The values of FTIR spectra are in agreement with theoretical prediction [14-16].

Surface morphology

Surface morphology of the composites was examined by scanning electron microscopy (SEM). SEM images of PANI-CNT composites having 0.02, 0.25 and 0.5M of aniline monomer content in the initial polymerization solution prepared using 1M HCl and 20% ethanol as solvent are depicted in **Fig. 2(a-c)**.

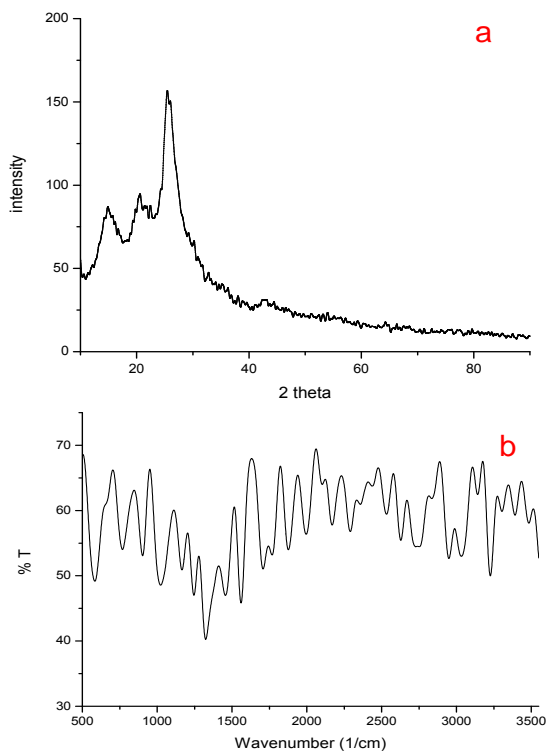


Fig. 1. (a) X-Ray diffraction and (b) FTIR spectra of PANI-CNT composite.

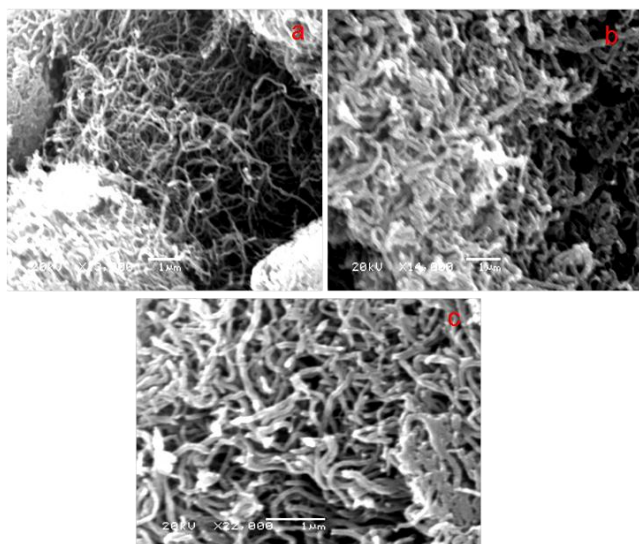


Fig. 2. SEM images of PANI-CNT composites having (a) 0.02, (b) 0.25 and (c) 0.5M aniline concentration prepared using 1M HCl and 20% ethanol.

Fig. 3(a-c) is the SEM micrographs of PANI-CNT composites having 0.02, 0.25 and 0.5M of aniline monomer

content in the initial polymerization solution prepared using 1M HCl alone. The average thickness of different PANI-CNT composites prepared using 1M HCl with 20% ethanol having 0.02, 0.05, 0.1, 0.25 and 0.5M aniline concentration in the initial polymerization solution is ~60-70, 80-90, 100-120, 150 and 200nm respectively. Similar composites were prepared using 1M HCl alone. In this work we are reporting only the PANI-CNT composites having 0.02, 0.25 and 0.5M of aniline monomer content in the initial polymerization solution. From the SEM images it is obvious that as the concentration of aniline in the initial polymerization solution increases the deposited polyaniline over the surface of CNT becomes thicker [17]. It has also been observed that PANI had a tendency to grow on itself when higher aniline content is used for polymerization. For both kinds of composites 0.02M aniline is the optimum concentration for deposition of thinnest layer. From SEM images it can be said that the composites prepared using 1M HCl and 20% ethanol has smoother surface morphology and lower average thickness compared to composites prepared using 1M HCl alone.

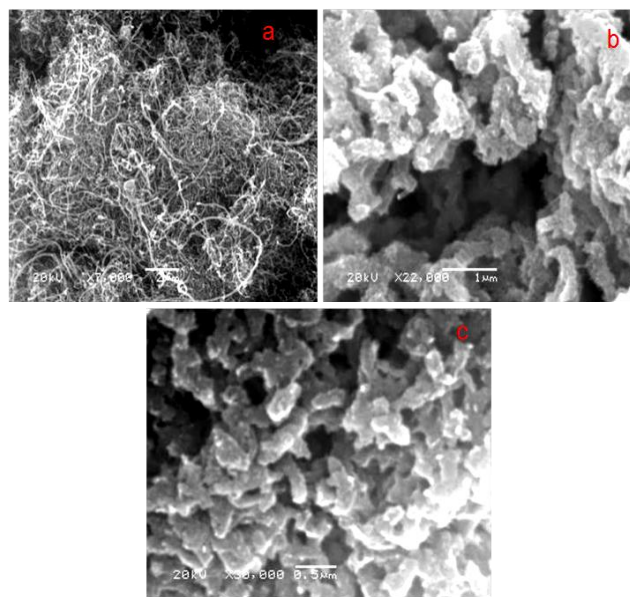


Fig. 3. SEM images of PANI-CNT composites having (a) 0.02, (b) 0.25, and (c) 0.5M aniline concentration prepared using 1M HCl alone.

Electrochemical characterization

Electrochemical measurements were performed using 1M H_2SO_4 aqueous electrolyte to examine the electrochemical performance of PANI-CNT composite electrodes. The cyclic voltammetry studies were carried out in the voltage window of 0-0.8 V at scan rates of 2, 5, 10 and 15mV/s.

Fig. 4 (a, b) shows cyclic voltammograms of PANI-CNT composites having thinnest layer prepared using 1M HCl with 20% ethanol and 1M HCl alone as solvent at scan rate of 2mV/s respectively. The specific capacitance of different PANI-CNT composites having 0.02, 0.25 and 0.5M aniline concentration prepared using 1M HCl with 20% ethanol, was 597.82, 375.72 and 353.53 F/g at 2 mV/s. For the composites prepared using 1M HCl alone having 0.02, 0.25 and 0.5M aniline concentration in the initial polymerization solution had the specific capacitance

of 484.49, 312.65 and 259.70 F/g at 2mV/s respectively. The PANI-CNT composite prepared using 0.02M aniline produced thinnest layer of PANI over surface of CNT and had highest specific capacitance for both kinds of composites because most mass of polyaniline worked as active mass. Moreover the thinner layer was better to reduce the contact resistances among the PANI-CNT composite strips and also between the PANI-CNT strips and current collector surface, would have the lowest electrode resistance so that it could show the highest specific capacitance along with the synergistic effect. On the other hand, for the thicker PANI layer it can be supposed that a penetration depth of ions in the PANI layer is not fully developed as much as the layer thickness so that some portions of the PANI mass are not worked as an active mass [12, 18]. In case of lower aniline concentration, PANI is deposited tightly over the surface of CNT which increases the degree of electron delocalization in this kind of composite. Due to increase in degree of delocalization, charge transfer takes place easily leading to enhanced specific capacitance. But in case of higher aniline concentration, the interaction between the deposited PANI and CNT become weak due to which the outer layer of PANI have loose contact with CNT. This affects the charge transfer ability of the composite and increases the resistance resulting in lower specific capacitance [19].

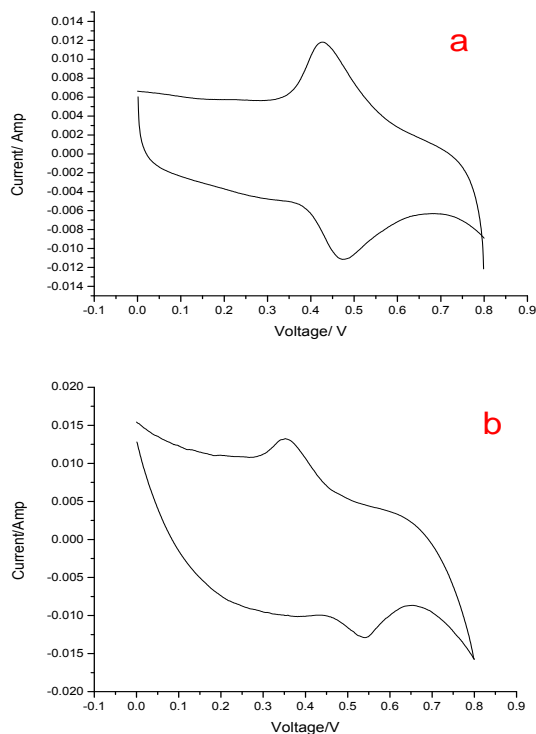


Fig. 4. Cyclic Voltammograms of PANI-CNT composites having thinnest PANI layer (a) prepared using 1M HCl (20% ethanol) and (b) 1M HCl.

Fig. 5 differentiates between specific capacitance values of different PANI-CNT composites prepared using 1M HCl with 20% ethanol and 1M HCl alone. The PANI-CNT composites prepared using 1M HCl with 20% ethanol had higher specific capacitance compared to the one prepared using 1M HCl alone. This can be explained that the mixture of solvent cause better dispersion of CNT in the polymer

matrix. The better dispersion of CNT results in separation of CNT bundles which provide a larger surface area for uniform and homogeneous deposition of conducting PANI layer. Probably the interaction between polymer molecules and CNT overcomes the Van der Waals interaction between CNT [20]. In such composites, CNT offer a good mechanical support to PANI and also ensures superior electronic conduction and enhanced reversibility. The uniformly dispersed MWNT adhere very well with the polyaniline. The large surface area provided to the composite material due to separation of MWNT bundles by better dispersion of CNT in 1M HCl with 20% ethanol allows excellent electrolyte access, low electrical resistance in the composite matrix and hence better storage of energy in the composite. Probably the increased numbers of active sites in the polymer composite material are available for better redox process. Also in such a composite the CNT wrapped by conducting PANI results in the formation of a charge transfer complex which increases the protonation of the polyaniline [21].

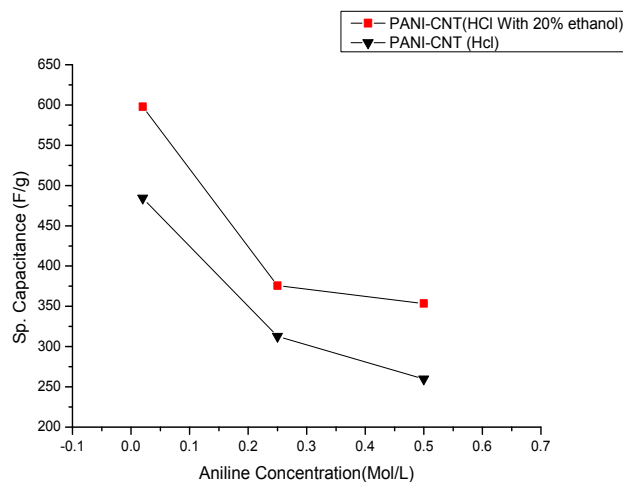


Fig. 5. Specific capacitance of PANI-CNT composites prepared using 1M HCl (20% ethanol) and 1M HCl.

Conclusion

The PANI-CNT composites were prepared by using chemical oxidative polymerization in 1M HCl with 20% ethanol as solvent had much smoother surface morphology and higher specific capacitance as compared to the composites prepared by 1M HCl alone. The phenomenon can be assigned due to better dispersion of CNT in the solvent using ethanol leading to separation of CNT bundles which provide a larger surface area for uniform and homogeneous deposition of conducting PANI layer. Also this composite electrode had good reversibility even at higher scan rates and can be proposed as an advanced electrode material for super capacitor application.

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