



INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

CHROMIUM DOPED POLYANILINE/MWCNTS NANOCOMPOSITE FOR SUPERCAPACITOR ELECTRODE MATERIALS

Chapal Kumar Das*, Benorita Prusty, Munesh Chandra Adhikary, Swinderjeet Kalra

Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302, India

P.G. Department of Applied Physics and Ballistics Fakir Mohan University, Balasore-756019, Orissa

³Department of Chemistry, Dayanand Anglo-Vedic (D.A.V.) College, Kanpur, India

ABSTRACT

In this study we have prepared Cr-doped polyaniline/MWCNTs [Cr-PANI-CNT] nanocomposite by simple in-situ polymerization method where ammonium persulphate used as oxidant in HCl medium. The probable interaction between the Cr with both MWCNTs and PANI is investigated by Fourier transform infrared spectroscopy (FTIR) analysis. The morphological analysis of the nanocomposite was studied by FESEM and TEM analysis. The electrochemical performance of the nanocomposite was characterized by three electrode method. The nanocomposite showed the highest specific capacitance of 328 F/g at 10 mV/s scan rate.

Keywords: Polyaniline; MWCNTs; doping; supercapacitor

INTRODUCTION

Recently supercapacitors have attracted extensive interest as a possible basis for energy-storage or conversion devices. This is due to their relatively higher power density as well as long cycle life compared to batteries, and their comparatively better energy density compared with conventional dielectric capacitors. Such devices could be applied in a large range of applications, including consumer electronics, public transportation, electric vehicles, memory back-up systems, industrial power and military devices [1, 2]. On the basis of the charge storage mechanism, supercapacitors can be divided into two categories: electrical double layer capacitors (EDLC) and redox supercapacitors. Energy storage in an EDLC is because of the charging of the electrical double layer at the electrode–electrolyte interface; on the other hand, a redox supercapacitor uses faradic reactions in addition to the double-layer charge [3, 4]. Polyaniline (PANI) is one of the most significant conducting polymers due to their electrical conductivity, easy synthesis, and environmental stability [5]. The wide range of electrochemical, optical, and electrical properties makes PANI potentially attractive for applications as a synthetic metal [6]. Among conducting polymers PANI is unique in that its electrical properties can be reversibly controlled by both protonation and charge-transfer doping. Various carbonaceous materials, like

mesoporous carbon, carbon fibers, and carbon nanotubes (CNTs) have been considered for EDLCs [7, 8]. CNTs are attractive electrode materials for electrochemical capacitors because of their outstanding properties, high aspect ratio, strong mechanical strength, and high chemical stability [9, 10].

In recent years, PANI doped with various transition metal ions has attracted much more research attention due to their potential practical applications like redox-active catalyst [11], corrosion inhibitor [12] etc. Various research articles were also available on transition metal doped PANI in presence of both multi-walled carbon nanotubes (MWCNTs) as well as single-walled carbon nanotubes (SWCNTs) for supercapacitor applications [13, 14]. To the best of our knowledge there is no research articles were available on chromium (Cr) doped PANI in presence of MWCNTs. So, in this article we have prepared Cr-doped PANI/MWCNTs [Cr-PANI-CNT] nanocomposite by in situ polymerization techniques for supercapacitor application.

MATERIALS AND METHODS

Materials Used

The aniline was supplied by Merck, Germany. The ammonium persulfate (APS) and HCl was also supplied by Merck, Germany. The chromium (III)

chloride [CrCl₃] was purchase from Sigma-Aldrich. MWCNTs were obtained from Iljini Nanotechnology, South Korea. Cetyl triethylammonium bromide was purchase from Loba Chemie Pvt., Ltd. Mumbai, India.

Synthesis of polyaniline

In a 200 ml of beaker, 100 ml of 1 M HCl solution and 1 ml of aniline monomer was added. In another beaker we have taken 2 g of APS and dissolved in 50 ml of aniline solution. The APS solution was then added slowly to the aniline solution. Then the total solution was stirred for 6 h at room temperature. When the polymerization was completed, the total solution was then filtered, washed and dried [15].

Synthesis of Cr-PANI-CNTs nanocomposite

In a 200 ml of 1 M HCl solution, we have taken CTAB and MWCNTs and sonicated for 1 h. In another beaker dissolved 1 ml of aniline in 50 ml of 1 M HCl solution. This solution was then added to the MWCNTs solution and stirred for 30 minutes. Then we have added the CrCl₃ solution to the above solution and stirring for another 30 minutes. Lastly, added 2 g solution of APS into the previous solution. Then the whole solution was stirred for 6 h at room temperature. After that, total solution was kept at 5 °C for 6 h for complete polymerization. Total solution was then filtered, washed and dried for 12 h and we get the Cr-PANI-CNT nanocomposite [13].

Characterization

The FTIR analysis of the nanocomposite was carried out with a Nexus 870 FTIR instrument, Thermo Nicolet, in the range of 400 to 4000 cm⁻¹. Field emission scanning electron microscope (Carl Zeiss-SUPRA 40 FESEM) was used to examine the surface morphology of the nanocomposite. The high-resolution transmission electron microscopy (HRTEM) JEOL 2100 was used to check the coating of the doped PANI in MWCNTs surface. The electrochemical characterization of the nanocomposite was carried out by three electrode system, platinum was used as counter electrode, and calomel electrode was used as reference electrode. Here 1 M KCl was used as electrolyte. The specific capacitance of the nanocomposite was calculated by the help of following equation [16-18]:

$$\text{Specific Capacitance } (C_{sp}) = (I_+ - I_-) / \nu m \quad (1)$$

where, I_+ and I_- signifies the maximum current in the positive and negative voltage scan, ν is the scan rate and m is the mass of the nanocomposite.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectrum of pure PANI and Cr-PANI-CNT nanocomposite is shown in Figure 1. Pure PANI shows the characteristic peaks at 1496 and 1551 cm⁻¹ are assigned to the benzene ring and the quinoid ring vibration, respectively. The adsorption peaks at 3410, 1292, 1116, and 786 cm⁻¹ correspond to the adsorption of the N-H stretching, C-N stretching of the secondary aromatic amine, aromatic C-H in-plane bending and out-of plane C-H bending vibrations, respectively [19, 20]. The Cr-PANI-CNT nanocomposite showed the same type of characteristic peaks but there is some peak shifting. The characteristic peak at 1551 cm⁻¹ shifted to 1522 cm⁻¹, the peak 1292 cm⁻¹ shifted to 1312 cm⁻¹ and the peak at 1116 cm⁻¹ shifted to 1110 cm⁻¹, respectively. This peak shifting behavior is due to the doping effect and also there is the good interaction between the MWCNTs with the Cr-doped PANI.

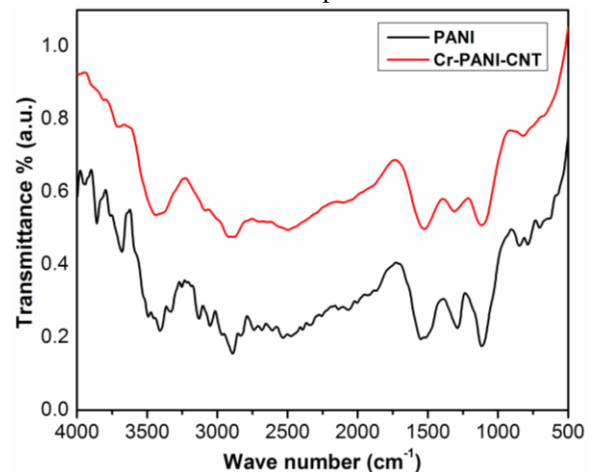


Figure 1: FTIR spectra of pure PANI and Cr-PANI-CNT nanocomposite

FESEM Analysis

The FESEM images of the pure PANI and the Cr-PANI-CNT nanocomposite are shown in Figure 2. Figure 2(a) represents the FESEM image of pure PANI. It can be seen that PANI showed the granular like morphology. On the other hand Figure 2 (b) stands for FESEM images of Cr-PANI-CNT nanocomposite. It is observed that the MWCNTs surface is fully coated by Cr-doped PANI. This type of morphology may enhance the electrochemical

properties of the nanocomposite.

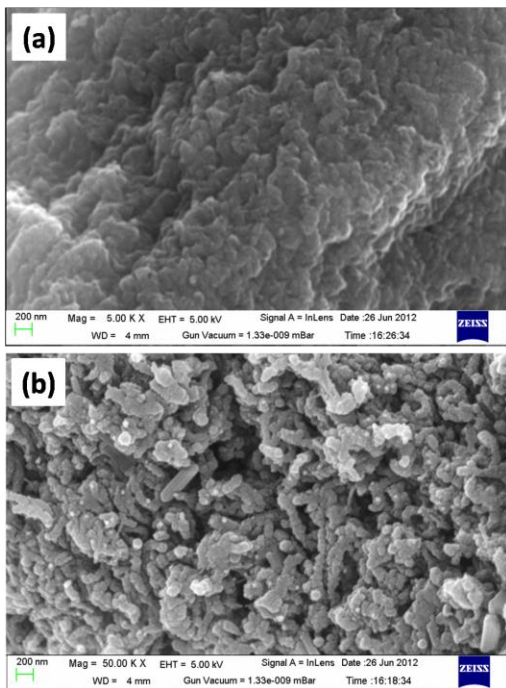


Figure 2: FESEM images of (a) pure PANI, and (b) Cr-PANI-CNT nanocomposite

TEM Analysis

The TEM micrographs of pure PANI and Cr-PANI-CNT nanocomposite are presented in Figure 3. PANI shows its granular like morphology, illustrates in Figure 3 (a). Figure 3 (b) represents the TEM image of the Cr-PANI-CNT nanocomposite. It can be seen that the MWCNTs surface is uniformly coated by Cr-doped PANI. This result is in good agreement with the FESEM morphology.

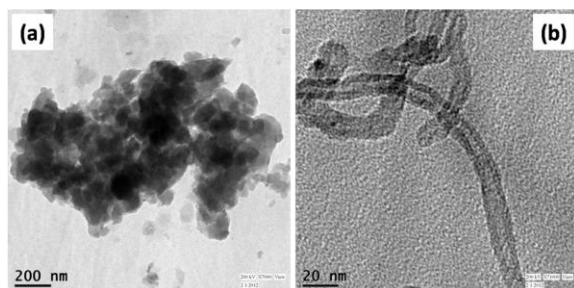


Figure 3: TEM images of (a) pure PANI and (b) Cr-PANI-CNT nanocomposite

Electrochemical Characterization

The electrochemical characterization of the Cr-PANI-CNT nanocomposite along with pure PANI was

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examined by cyclic voltammetry (CV). The electrochemical characterizations were carried out by three electrode system. 1 M KCl solution was used for all the electrochemical tests. The CV was taken in the voltage range between -0.8 V – 0.8 V. The cyclic voltammogram of pure PANI and Cr-PANI-CNT nanocomposite at a scan rate of 10 mV/s are shown in Figure 4. The Cr-PANI-CNT nanocomposite showed the highest specific capacitance value of 328 F/g at 10 mV/s scan rate. On the other hand pure PANI showed the specific capacitance of 175 F/g at the same scan rate. The highest specific capacitance of the nanocomposite is achieved is due to the presence of MWCNTs. Transition metal doping also enhances the specific capacitance of the nanocomposite. Uniform coating of MWCNTs by Cr-doped PANI may also be the reason for increase in the specific capacitance of the Cr-PANI-CNT nanocomposite.

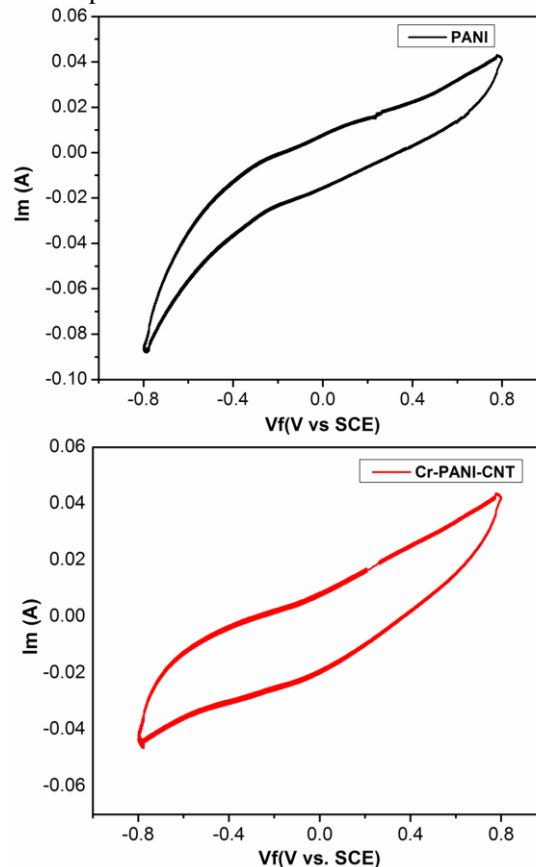


Figure 4: Cyclic voltammogram of pure PANI and Cr-PANI-CNT nanocomposite

The energy density of the Cr-PANI-CNT nanocomposite and pure PANI were calculated by the help of following equation:

$$\text{Energy Density (E)} = \frac{1}{2} (CV^2) \quad (2)$$

where, C denotes the specific capacitance and V is the operating voltage.

On the other hand, the power density of the pure PANI and Cr-PANI-CNT nanocomposite were determined by the following equation:

$$\text{Power Density (P)} = E/t \quad (3)$$

where, t is the time in sec for complete the cycle.

The Cr-PANI-CNT nanocomposite showed the highest energy density of 116.62 Wh/kg at 10 mV/s scan rate. On the other hand pure PANI showed the energy density of 62.22 Wh/kg at the same scan rate. The maximum power density of 1311.975 W/kg was obtained for the Cr-PANI-CNT nanocomposite at 10 mV/s scan rate. Whereas, pure PANI achieved the power density of 699.975 W/kg at the same scan rate.

The cyclic stability of the Cr-PANI-CNT nanocomposite along with pure PANI were carried out in 1 M KCl solution and at a current density of 1 A/g and shown in Figure 5. The Cr-PANI-CNT nanocomposite show specific capacitance retention of 76 % after 500 cycles. However, pure PANI shows specific capacitance retention of 71 % after 500 cycles. The highest cyclic stability of the nanocomposite is due to the doping effect.

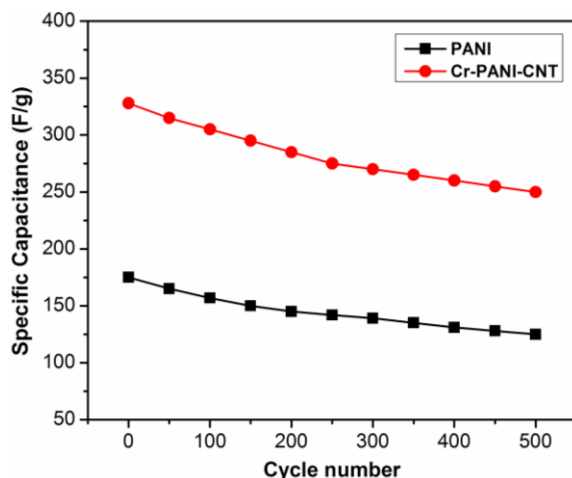


Figure 5: Plot of specific capacitance vs. cycle number of PANI and Cr-PANI-CNT nanocomposite

CONCLUSION

We have prepared Cr-doped PANI/CNT nanocomposite by in situ polymerization method. From the morphological analysis it is confirmed that the MWCNTs surfaces are fully coated by Cr-doped PANI. The nanocomposite showed the highest specific capacitance of 328 F/g at 10 mV/s scan rate. Highest energy density of 116.62 Wh/kg at 10 mV/s scan rate and highest power density of 1311.975 Wh/kg at 10 mV/s scan rate was obtained from Cr-PANI-CNT nanocomposite. The specific capacitance of 76 % after 500 cycles was obtained for Cr-PANI-CNT nanocomposite.

ACKNOWLEDGEMENTS





We are thankful to IIT Kharagpur for instrumental facilities.

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Author Bibliography

	<p>Prof. Chapal Kumar Das. (Corresponding author) Professor in Materials Science centre, IIT Kharagpur, Kharagpur- 721302, West Bengal, India.</p> <p>He has prodedced 32 Ph.D. students and 46 M.Tech. students. He has phublished around 370 research articles in International Journals and also published 19 Book chapters. He has visited abrod 49 times.</p>
	<p>Benorita Prusty (First Author) She is a Research Scholar in Physics at Post Graduate Department of Applied Physics and Ballistics under Fakir Mohan University, Balasore, Odisha, India.</p>
	<p>Munesh Chandra Adhikary (Second Author) He, at present working as Reader & Head at Post Graduate Department of Applied Physics and Ballistics under Fakir Mohan University, Balasore, Odisha, India after completing 25 years of Education Service.</p>
	<p>Swinderjeet Singh Kalra (Third Author) Department of Chemistry, D. A-V College Kanpur 208001, India He has written about 10-15 Books on the Basic Chemistry and Mathematics.</p>