Supercapacitor based on electropolymerized polythiophene and multiwalled carbon nanotubes composites

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Abstract. In this paper we have reported the synthesis of the composites of polythiophene (PTP)and carbon nano tubes (CNTs) by easy in-situ polymerization method. Structure and morphology of the PTP-CNT composites were examined by X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM).From the electrochemical studies, it was found that the electrochemical performance of pure PTP got improved due to the incorporation of CNTs into pure PTP in the composites. The CNTs incorporated binary composite electrode exhibited specific capacitance of 125F/g.

1. Introduction

Till date a considerable amount of researches has been carried out in order to develop of various types of lithium ion batteries, secondary batteries and supercapacitors. But these are not sufficient in meeting the present ever increasing demand of energy and recently safety issues associated with Li-ion batteries have raised serious concerns about their use in specialized applications such as for electric vehicles and aircrafts **[1-3]**. Thus, the development of supercapacitors seeks a huge attention of a great deal of research. Supercapacitors (SCs) haveattracted considerable attention over the past few decades in the field of energy storage.SCs, are also termed as ultracapacitors or electric double layer capacitor having unique properties, such as power supply in pulses, simple principle of working, faster charge-discharge rates and low maintenance cost **[4-5]**.

SCs have two types of capacitances arising from two types of mechanisms used for energy storage termed as electronic double layer capacitance (EDLC) and pseudo capacitance. In EDLC storage of charge employs absorption of ions at the electrode –electrolyte interface in a reversible way. Organic active materials possessing huge surface area and good electrical conductivity viz. activated carbon (AC), mesoporous carbon (MC), and carbon nanotubes (CNTs) etc. consist of EDLC [**6**]. Mechanism of charge storage in case of pseudocapacitors differs from that of EDLC in the sense that the former undergo reversible and rapid redox reactions (Faradic) at the surface of electro-active materials responsible for charge storage. Transition metal oxides such as MnO_2, FeO_4, RuO_2, FeO_4,TiO_2,CoO_4, V_2O_5, NiO etc. and the polymers such as polyaniline, polypyrrole and polythiophene (PTP), having a good conductivity, and their hybrid combinations shows a good redox capacitove nature**[7-8]**. However, they are often show instability during charge/discharge process. Also the typical time of response of redox capacitors are much longer than the EDL capacitors. Hence, the coupling of pseudocapacitors with the EDL capacitance through blending the carbon materials with low-cost pseudocapactive conducting polymers will show overall improvement in the capacitive properties of

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the hybrid. Actually the system is benefited from the synergetic merits of both EDL capacitance and pseudocapacitance, resulting in the supercapacitors with excellent performance**[9-10]**.

In the present work, we have prepared a organic-polymeric hybrid material composed of PTP and CNTs as the organic and carbon part respectively via in situ chemical oxidative polymerization of the thiophene monomers. The results obtained showed that the material exhibited enhanced electrochemical property as compared to its host materials.

2. Experimental

2.1. Preparation of PTP/ CNT composite

0.2g CNT was added to 50mL chloroform and was ultra-sounded for 1h. 12g $FeCl_3$ was added to the mixture and the solution was stirred for30mins. 1.0g thiophene monomer was added to the solution and was stirred for another 15h at the room temperature. The resulting black precipitate was separated from the aqueous supernatant by centrifugation at 10,000rpm for 15 min. After washing with water and methanol the precipitate was dried at 80^0C. Following the above method of preparation, three different composites of PTP/CNT were prepared by varying the CNT content in the composites viz. 2%, 6% and 10% (weight %) of the total content.

3. Characterization Techniques

FTIR spectra of the synthesized composite were recorded in the wavelength range of 400 to 4000 cm^{-1} using NEXUS 870 FTIR (Thermo Nicolet) to study the bonding properties in the resultant composites. Crystallographic study of the prepared composites were carried out using X-ray diffractometer (Brooker D8) with nickel-filtered CuKα target (λ= 1.5406 Å) at the scan rate of 0.5^0/min. Raman spectroscopy was employed to investigate the interaction of different species present in the composites and the characterization of the carbon nanotubes was donewith Micro Raman (Renishaw)spectro-photometer with 532 nm laser excitation. The morphological and microstructural studies of the synthesized composites were performed using FESEM and EDX (SUPRA 55 CARL ZEISS GERMANY).Thermal behavior was examined using Thermal Gravimetric Analysis (NETZSCH - 0798-M) technique in the temperature range 30-700 ^{0}C at the heating rate of 10^0C min^{-1} in nitrogen environment. In order to study the electrochemical properties of the synthesized composites, cyclic voltammetry (CV) and charging-discharging (CD) analysis were performed on the electrochemical workstation (CHI-760D) at room temperature. Specific capacitance, was calculated from CD using the following formula,

$$C_{sp} = 2*[I/ (m\ dv/dt)] \qquad (3.1)$$

Where, I- current density (mA); m- Mass of active materials(mg); V- potentialwindow (V) and dv/dt-slope of the discharge curve (V/s).

4. Results and Discussion

4.1. FTIR Analysis

Formation polythiophene and its composites with CNTs were studied with FTIR as shown in Figure 1. The FTIR spectra confirm the successful fabrication of polythiophene.The characteristic peak of PTP at 670cm^{-1}denotes the C-S stretching in the ring of thiophene **[11]**. The peak at 820cm^{-1} is due to the out of plane vibration of the C-H in the thiophene ring **[12]**. Peak at 1060 cm^{-1} is assigned to C-H in plane bending band. The other peaks at 1405cm^{-1} and 1530cm^{-1}belong to C=C asymmetric and symmetric stretching vibration of thiophene ring, respectively **[13]**.The low intense peak present in the range of 2800-3000cm^{-1} designating the C-H stretching vibration is not only present in neat PTP but also in the PTP-CNT composites. FTIR spectra of the PTP-CNT composites contain the PTP characteristic peaks. However, for PTP-CNT composites some absorption peaks of PTP have a slight shift, which indicates the presence of interaction between CNT and PTP and creation of some new atomic vibrations.

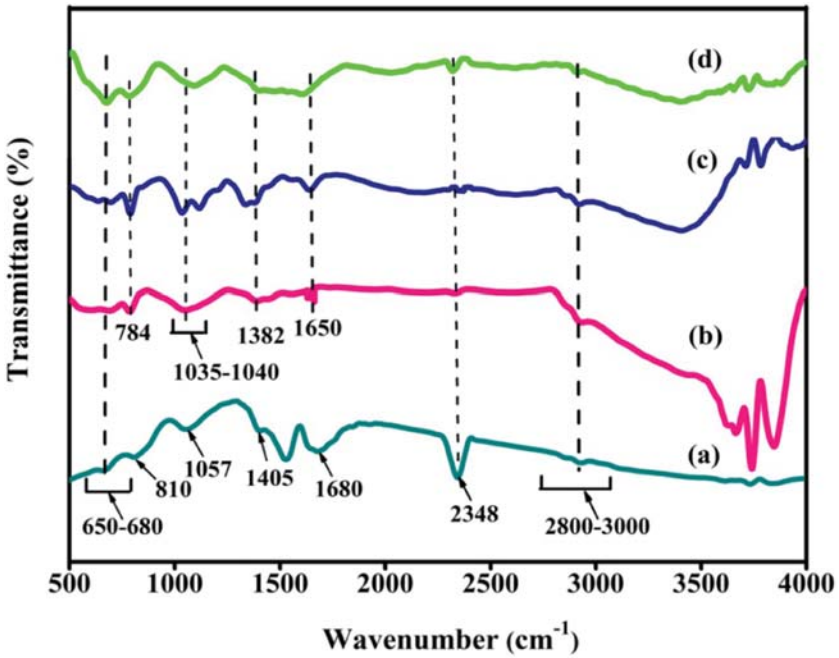


Figure 1.FTIR spectra for (a) Pure PTP and PTP-CNTs composites: with 2% (b) 6%(c) and 10% (d) CNTs.

4.2. X-Ray diffraction Analysis

The X-ray diffraction patterns for the PTP and PTP-CNTs composites at room temperatureare shown in Figure 2. For the PTP powder, the broad diffraction peak appearing at about 2ɵ= 15°, indicates an amorphous structure, which is in good agreement with the previous report **[13]**. The PTP-CNTs composites have diffraction peaks at 2ɵ=25° **[13]**. For PTP/CNT composites, the XRD spectra show that with an increase in the amount of CNTs in the PTP-CNTs composites the characteristic peak for CNTs increases and the PTP broad peak decreases.

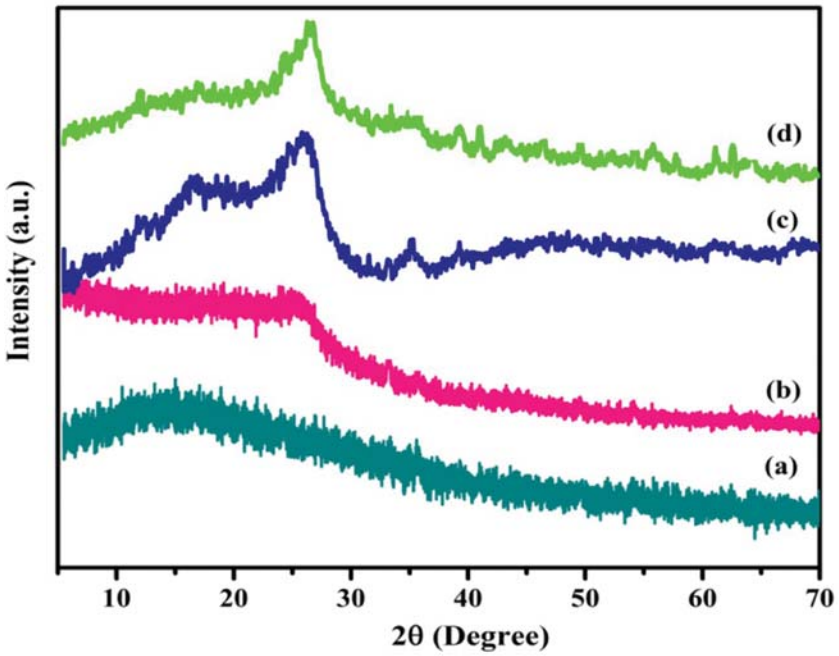


Figure 2. X-ray diffraction of PTP (a) and PTP-CNTs composites: with 2% (b) 6% (c) and 10% (d) CNTs.

4.3. Raman Spectroscopy

Raman spectra of the PTP and PTP-CNTs are shown in Figure 3. The bands at 1500cm^{-1} and 1425cm^{-1} correspondto the C=C stretching region of pure PTP. The band in the weaker range 1050cm^{-1}-1100cm^{-1} corresponds to the C-C stretching and C-H wagging componentswhile, 636cm^{-1} signifies the C-S-C ring deformation**[13]**. In the case of PTP-CNTswith an increase in the content of CNTs the intensity ofthe PTP also increases. Peak intensity of the G band and the D band isalso seen to increase with an increase in the CNTs content in the composites as shown in Figure (c) and Figure (d). PTP/CNT composites according to Figure 3 (c), exhibits the D band at 1325 cm^{-1} and the G band at 1425cm^{-1}.The D band is due to the crystal defects and disordered structures in the carbon material. While the G band is attributed to the phonon mode with E2g symmetry of graphite **[13]**.

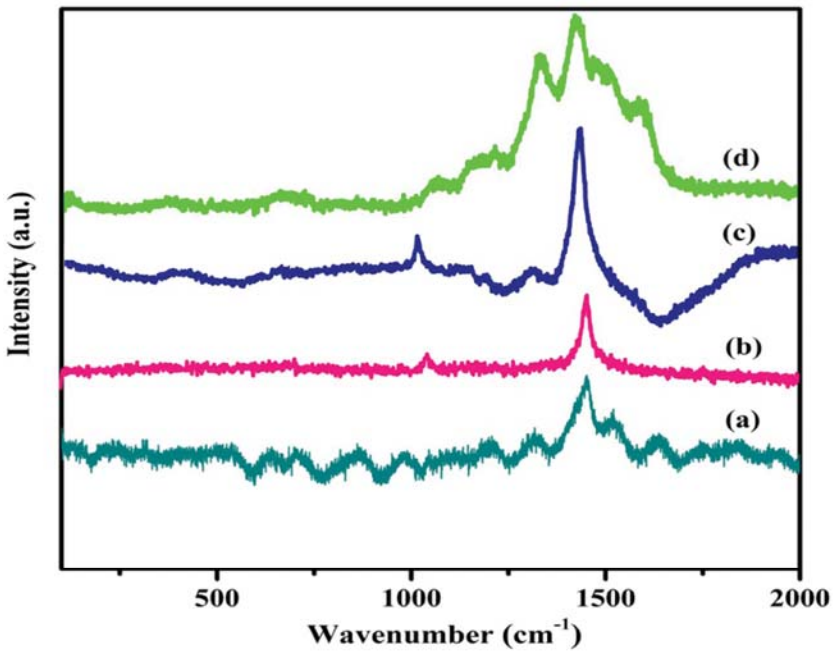


Figure 3. Raman spectra of PTP (a) and PTP-CNTs composites: with 2% (b) 6% (c) and 10% (d) CNTs.

4.4. FESEM Analysis

Figure4 presents the morphology and corresponding EDX images of the PTP and PTP-CNTs composites with 2% 6% and 10 wt. % CNTs. The small thread-fibrils like structures are observed in the pure PTP as shown in Fig. 4(a). Isolated CNTs are present in the PTP-CNTs composites over the entire range of the CNTs as shown in Figure 2(b)-(d). For the composite with low CNTs content as shown in Figure 2(b), the CNTs are well-covered by the PTP matrix. The CNTs are well dispersed on the surface of PTP particles and fills the inter-spaces between PTP particles, shown in Figure4(c) and (d). The distances between the nanotubes decrease with an increase in the CNTs content. The CNTs form a connective network wrapped around the PTP particles in the composites, shown in Figure4(d).EDX spectra for PTP and PTP-CNTs composites give the quantitative and qualitative estimate of the chemical constituents of pure PTP and PTP-CNTs composites.

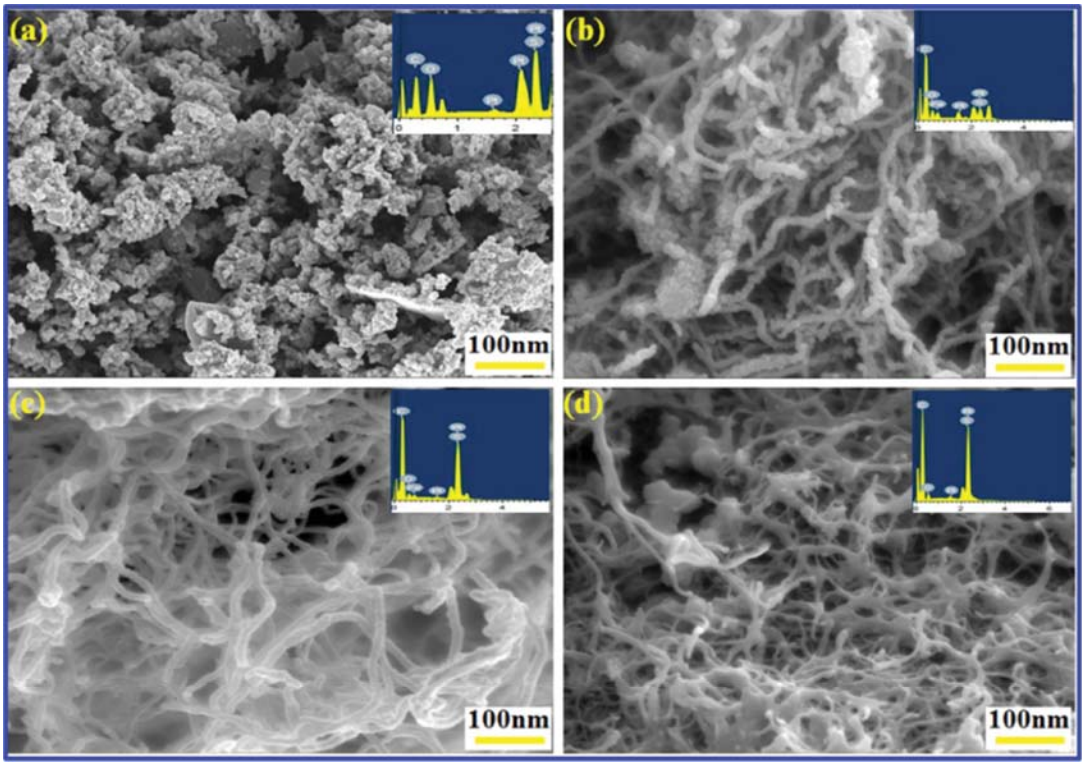


Figure 4. FESEM image of PTP (a) and PTP/CNT composites: with 2% (b) 6% (c) and 10% (d) CNTs.

4.5. Cyclic voltammetry

Figure 5 reveals the CV curves of PTP-CNTs at 5mV/s in 1M H_2SO_4 solution as electrolyte in the range -0.2V-0.8V. As shown inFigure 5a, the CV curves for the 2% CNTs shows low current response and shapes are not rectangular. As amount of CNTs increases current response and area of the loop increases.The CV curve shows non-rectangular shape andabsence of any redox pair both positive and negative sweep. Figure 5c shows CV curves of 10% CNTs composites which shows the higher area and higher current response as compared to other 2% and 6% CNTs composites. These show that 10% CNTs is having higher capacitance.

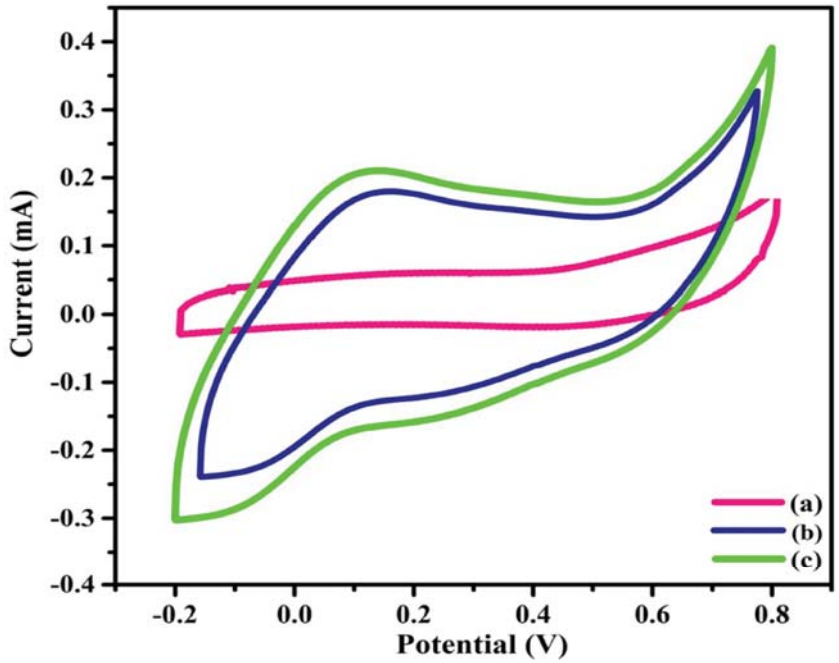


Figure 5. CVof PTP/CNT composites: with 2% (a) 6% (b) and 10% (c) CNTs.

4.6. Galvanostatic charge-discharge curves

The charge-discharge capability of PTP-CNT composites was examined by galvanostatic charge-discharge technique over the potential range 0V-0.8V at 1A/g current density as shown in Figure 6. The symmetrical and triangular characteristics of the charge-discharge curves indicate efficient electrochemical capability and redox process, thereby depicting better reversibility. The PTP-CNT composite electrodes showed that the values for capacitance reduced with an increase in the current density. The specific capacitance of PTP-CNT (10%) was calculated using equation (1) to be 125F/g at the current density of 1A/g.

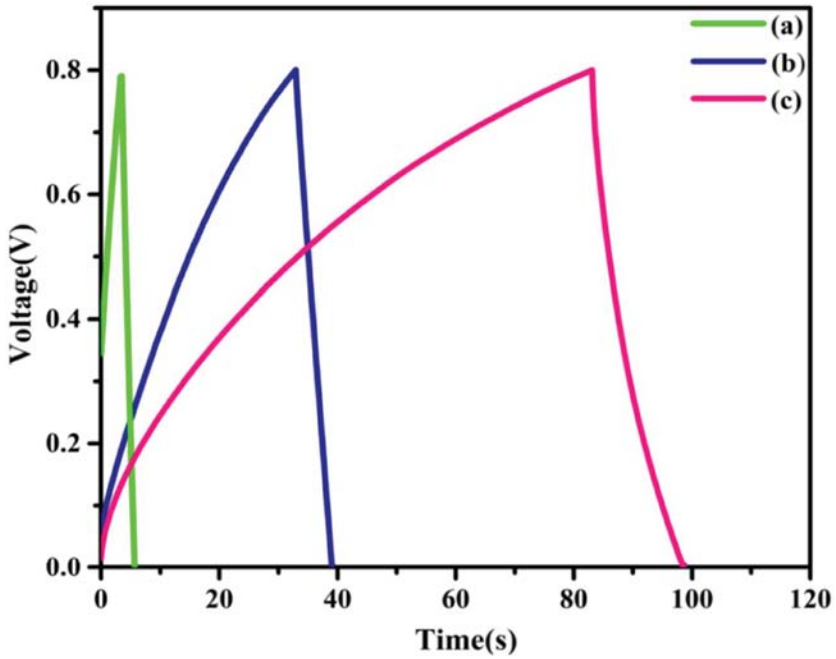


Figure 6. CD of PTP-CNTs composites: with 2% (a) 6% (b) and 10% (c) CNTs.

4.7.Thermal analysis

Thermal stability of the samples was investigated using TGA.The TGA measurement results for the PTP andthe PTP-CNTs composites with 2%,6% and 10%CNTs (in weight) areshown in Figure 7.The TGA curve for pure PTP inset Figure (a) shows that PTP is thermally unstable as compare to PTP-CNTs and it decomposes completely when the temperature reaches up to 600^0C. In case of PTP-CNTs composites, all the composites are stable up toa temperature of 350^0C.TGA plots of PTP-CNTs composites showweight loss in the temperature range of 300-350^0C which is due to the decomposition of PTP. It is observed that the weight loss decreases with an increasing in the CNTs content.

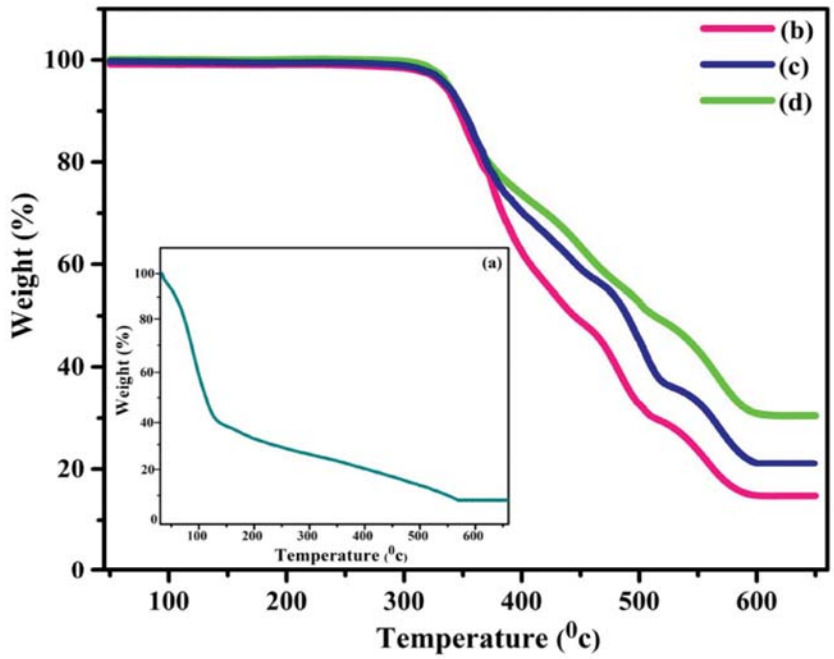


Figure 7. Thermal analysis of PTP (a) and PTP-CNTs composites: with 2% (b) 6% (c) and 10% (d) CNTs.

5. Conclusion

PTP-CNT composites with varying content of CNTs were successfully synthesized by using in-situ chemical oxidative polymerization and were characterized by IR, XRD, Raman and TGA analysis. Their supercapacitive performances were further investigated via electrochemical characterizations. IR and XRD analysis confirmed the presence of CNT in the PTP, morphological analysis confirmed the coating of CNTs over the PTP. CNTs were used as support material for the deposition of PTP matrix and they also acted as conductive wires interconnected between the PTP matrixes. CNTs not only provide highly conductive path resulting in the improvement of conductivity of the composites, but also maintains the mechanical strength and gives the specific capacitance up to 125F/g to the composite.

6. References

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