

# Composite supercapacitor electrodes made of activated carbon/PEDOT:PSS and activated carbon/doped PEDOT

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**Abstract.** In this paper, we report on the high electrical storage capacity of composite electrodes made from nanoscale activated carbon combined with either poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or PEDOT doped with multiple dopants such as ammonium persulfate (APS) and dimethyl sulfoxide (DMSO). The composites were fabricated by electropolymerization of the conducting polymers (PEDOT:PSS, doped PEDOT) onto the nanoscale activated carbon backbone, wherein the nanoscale activated carbon was produced by ball-milling followed by chemical and thermal treatments. Activated carbon/PEDOT:PSS yielded capacitance values of  $640 \text{ F g}^{-1}$  and  $26 \text{ mF cm}^{-2}$ , while activated carbon/doped PEDOT yielded capacitances of  $1183 \text{ F g}^{-1}$  and  $42 \text{ mF cm}^{-2}$  at  $10 \text{ mV s}^{-1}$ . This is more than five times the storage capacity previously reported for activated carbon–PEDOT composites. Further, use of multiple dopants in PEDOT improved the storage performance of the composite electrode well over that of PEDOT:PSS. The composite electrodes were characterized for their electrochemical behaviour, structural and morphological details and electronic conductivity and showed promise as high-performance energy storage systems.

**Keywords.** Carbon materials; composite materials; electrodeposition; energy storage and conversion; thin films; conducting polymers.

## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the best known *p*-conjugated conducting polymers. Because of their excellent properties (Ryu *et al* 2004; Snooke *et al* 2010) (high conductivity, high stability, transparency in the oxidized state and relatively low bandgap), PEDOT and its derivatives have developed into one of the most important materials from both fundamental and practical perspectives and are now utilized in several applications, such as LEDs, organic solar cells and electrochromic devices Wang and Wong (2006). During the initial stages of development, PEDOT that was synthesized using the conventional oxidative chemical/electrochemical method was insoluble in water. However, the solubility problem was overcome using a water-soluble polyelectrolyte, poly(styrenesulfonic acid) (PSS) (Yang *et al* 2008). PSS was also found to help in keeping the PEDOT segments dispersed in water. PSS also acts as the charge-balancing dopant for PEDOT, thus providing the desired electrical properties. When processed with organic solvents such as glycerol and dimethyl sulfoxide (DMSO), conductivity of the films is enhanced by two orders of magnitude (Antje *et al* 2009). This phenomenon was initially attributed to the screening effects of polar solvents on Coulomb interaction between positively charged PEDOT

grain and negatively charged PSS dopant (Alexandre 2007) or to a solvent-induced conformational change in the PEDOT chain, which increases the interchain interaction. Recent investigations indicate that this conductivity enhancement is due to morphological changes in the film structure and a phase-segregation process. Thus, the dispersion of PEDOT segments is attributed to the water solubility of PSS and Coulombic interactions between PEDOT and PSS, which promote hydrophilicity through dipole interactions.

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) consists of a conducting polythiophene derivative that is electrostatically bound to a PSS polyanion. Since this polymer has high electrical conductivity, processibility, high stability, flexibility and good transparency, it has found a wide variety of applications including polymeric anodes for organic photovoltaics, light-emitting diodes (Pingree *et al* 2008), flexible electrodes, supercapacitors (Huang *et al* 2006) and electrochromic devices.

Research in the area of supercapacitors has been done on composites for a wide number of materials especially with carbon-related materials. The major carbon materials that are looked upon are carbon nanotubes (CNTs), graphene and activated carbon. Specific capacitances of up to as high as  $300 \text{ F/g}$  in an aqueous electrolyte has been achieved for activated carbon electrodes (Zheng and Jow 1995). Activated carbon fibres modified by ruthenium chloride showed up to  $180 \text{ F/g}$  offering good characteristics for use in supercapacitors (Wang and Hu 2005). Activated carbon fibres with high

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surface area and highly mesoporous structure have been prepared from polyacrylonitrile with NaOH activation. These yielded up to 371 F/g making them suitable for high performance EDLCs (Xu *et al* 2008). Very high surface area activated carbon (3000 m<sup>2</sup>/g) yielded up to 300 F/g for use in supercapacitors (Obreja 2008). PEDOT/carbon nanotubes (CNTs) composite supplied lower capacitance values of 100 F g<sup>-1</sup> (Frackowiak *et al* 2006) with a perfect stability during cycling. Additional advantage of the PEDOT/CNTs composite was a possibility of operating in acidic, alkaline and organic electrolytic solutions. Composite electrodes of PEDOT and CNTs were prepared (Lota *et al* 2004) by (a) direct polymerization on ultrasonically dispersed CNTs (130 F g<sup>-1</sup>) and (b) electrochemical deposition of polymer onto the CNTs (150 F g<sup>-1</sup>). Also, a negatively charged CNT suspension and PEDOT was co-deposited (Peng *et al* 2006) and gave capacitances of at least 0.5 F cm<sup>-2</sup>.

An electrode made of PEDOT-carbon composite exhibited high specific capacitance due to the semiregular, macroporous nature of the electrode film. The composite electrode was prepared with multi-walled carbon nanotubes by chemical or electrochemical polymerization of PEDOT on nanotubes and the capacitance is reported as 60–160 F/g (Kelly *et al* 2009; Sharma and Zhai 2009). An important work was reported on enhancement of double-layer capacitance behaviour and electrical conductivity in layered PEDOT based nanocomposite (Murugan *et al* 2005). Also there are works done on PEDOT and related materials such as PEDOT-graphene composite (Xu *et al* 2009), PEDOT-CNTs composites (150 F g<sup>-1</sup>) (Lota *et al* 2004) and activated carbon-PEDOT composites (158 F g<sup>-1</sup>) (Selvakumar and Bhat 2008). These advances give a way for many other combinations of carbon-conducting polymer composites for energy storage and other applications.

In our paper, we developed composite electrodes with high electrical storage capacity made from nanoscale activated carbon combined with either poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or PEDOT doped with multiple dopants such as ammonium persulfate (APS) and dimethyl sulfoxide (DMSO). The composites were fabricated by electropolymerization of the conducting polymers (PEDOT:PSS, doped PEDOT) onto the nanoscale activated carbon backbone. The composite carbon-doped PEDOT electrodes showed high specific capacitance, which is more than five times the storage capacity previously reported for activated carbon-PEDOT composites. Further, the use of multiple dopants in PEDOT improved storage performance of the composite electrode well over that of PEDOT:PSS.

## 2. Materials and methods

### 2.1 Preparation of activated carbon

Graphite powder is taken and subjected to rotary ball milling for 11 h with the usage of balls made up of tungsten carbide,

hardness of balls being 14 on Moh scale and speed of rotation of the mill being 300 rpm. 1 g of the ball milled graphite is mixed with 20 ml of HNO<sub>3</sub> and ultrasonicated for 3 h at 60 °C. A given volume of the supernatant is taken and further mixed with equal parts of H<sub>2</sub>SO<sub>4</sub> and ultrasonicated for 3 h at 60 °C. The resulting solution containing carbon particles is washed sufficiently with de-ionized water to remove traces of acid and air dried.

### 2.2 Electropolymerization of PEDOT:PSS

PEDOT monomer and PSS was purchased from M/s Sigma-Aldrich. PEDOT was not distilled before use. Electropolymerization was carried out in a 3-electrode set up with the working electrode as titanium, saturated calomel as reference electrode and platinum as counter electrode with the voltage being 1.8 V and polymerization times being 25, 50 and 100 s. The electrolyte consisted of 0.05 M PEDOT and 0.005 g PSS in 10 ml of distilled water.

### 2.3 Electropolymerization of doped PEDOT

PEDOT was multiple doped with 0.01 M (ammonium persulfate (APS), a common oxidant for polymerization) and 5 microlitres of dimethyl sulfoxide (DMSO). APS and DMSO were added to 0.05 M PEDOT solution in 10 ml water and further electropolymerized at 1.8 V for different time intervals (15, 25, 50 and 100 s).

### 2.4 Preparation of activated carbon/PEDOT:PSS and activated carbon/doped PEDOT composites

Composite studies were carried out on activated carbon (ball milled size, 150 nm chemically treated) by depositing PEDOT:PSS and doped PEDOT onto it and then comparing the results. 2 mg of activated carbon in 10 ml of isopropanol was electrophoretically deposited on titanium (cathode), anode being platinum rod. Conditions were 20 V for 20 min. Subsequently, the layer was annealed in air at 100 °C for 3 h. Both polymers were electrodeposited on activated carbon at 1.8 V for 100 s. Cyclic voltammetry (CV) studies on the composite electrodes were carried out in 0.1 M LiClO<sub>4</sub> in acetonitrile at various scan rates.

## 3. Results and discussion

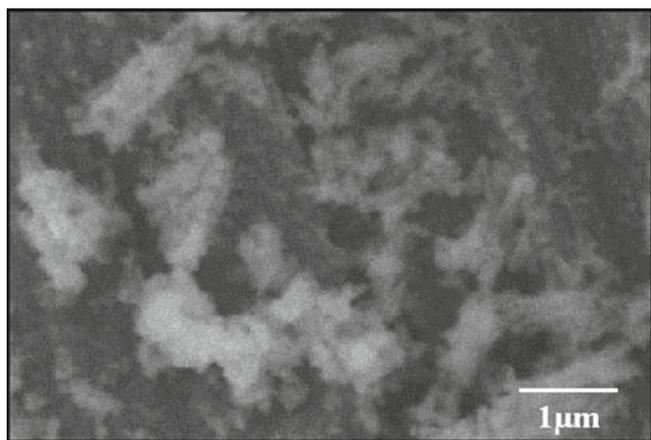
The activated carbon, as described in § 2.1, was analysed for its particle size using SEM and the average particle size was 150 nm. In our reported studies (Nandhini *et al* 2012), this activated carbon was made as an electrode by electrophoretic deposition and tested for its specific capacitance using CV studies in 0.1 M KOH. The activated carbon yielded a specific capacitance of 413 F g<sup>-1</sup> at 100 mV s<sup>-1</sup>. The activated

carbon was further used as a conducting and high surface area backbone for electrodepositing PEDOT:PSS and doped PEDOT polymers.

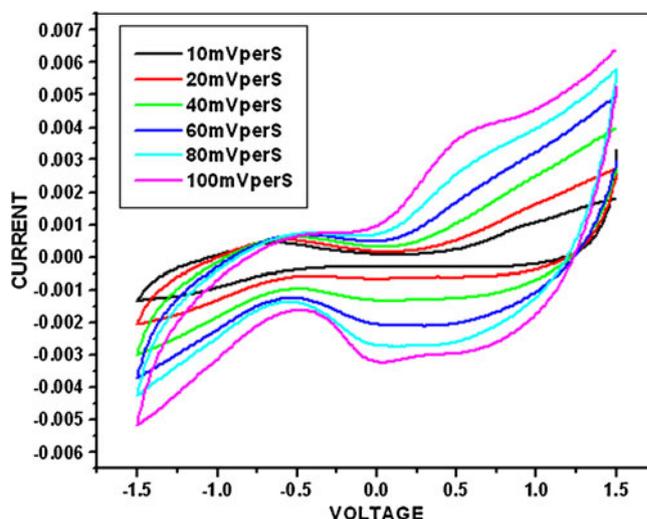
Initial studies were carried out on electropolymerized PEDOT:PSS on titanium substrates as outlined in § 2.2 which shows that optimum polymerization time is 50 s. This yields maximum specific and area capacitances of  $197 \text{ F g}^{-1}$  and  $24.6 \text{ mF cm}^{-2}$ . The morphology shows a porous globular structure. The Raman spectra of PEDOT:PSS has major peaks at  $1440 \text{ cm}^{-1}$  which corresponds to the  $C_\alpha = C_\beta$  stretching of the structure and at  $1596 \text{ cm}^{-1}$  corresponding to the asymmetric stretching of  $C_\alpha = C_\beta$  bond.

Figure 1 shows SEM image of the activated carbon–PEDOT:PSS composite which was synthesized as per § 2.4. The activated carbon/PEDOT:PSS composite yielded capacitance values of  $640 \text{ F g}^{-1}$  and  $26 \text{ mF cm}^{-2}$  at  $10 \text{ mV s}^{-1}$ . The electrochemical CV curves are shown in figure 2. The high value of specific capacitance is because the activated carbon provides a high surface area, porous and conductive backbone for electropolymerization and this kind of morphology maximizes the faradaic interactions with the electrolyte.

Surface current profile measurements of the PEDOT:PSS thin film/doped PEDOT thin film and the activated carbon–PEDOT:PSS composite/activated carbon-doped PEDOT composite were carried out in a scanning electrochemical microscope (SECM, make: Sensolytics) with the help of  $10 \mu\text{m}$  wider platinum microelectrode, Ag/AgCl reference electrode and  $0.1 \text{ M LiClO}_4$  in acetonitrile as the electrolyte. The activated carbon–PEDOT:PSS/activated carbon-doped PEDOT composite yielded higher values of current reinforcing the role played by the nanoscale activated carbon in providing a conductive backbone (figures 3(a, b) and 4(a, b)). The current scale on each graph is on the right top and a darker shade on the 3-D plot shows higher value of current. PEDOT was doped with various dopants like DMSO, sorbitol



**Figure 1.** High magnification SEM image of activated carbon–PEDOT:PSS composite showing polymer film deposited over underlying carbon backbone.

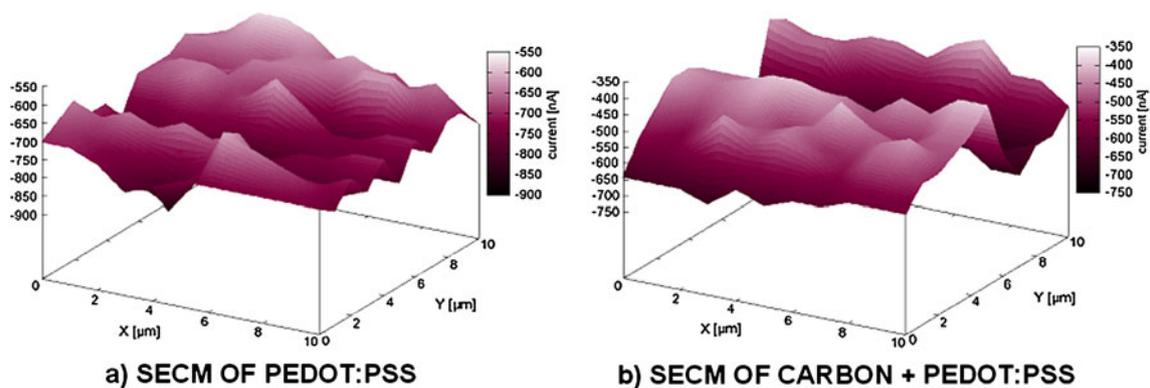


**Figure 2.** CV curves of activated carbon–PEDOT:PSS composite at various scan rates in  $0.1 \text{ M LiClO}_4$  in acetonitrile. Calomel electrode is used as reference. Scan rates are varied from  $10 \text{ mV s}^{-1}$  to  $100 \text{ mV s}^{-1}$ .

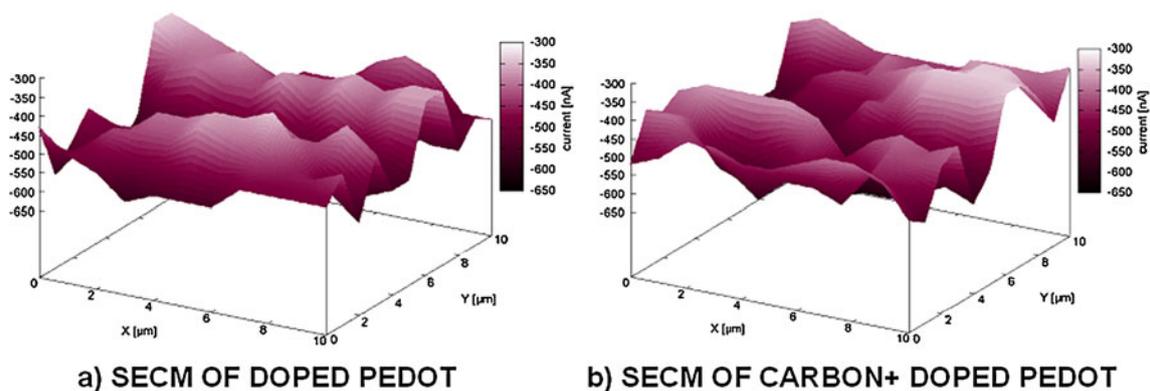
and APS and the electrochemical performance of the electrodeposited thin films were individually measured. Based on the CV studies,  $0.01 \text{ M APS} + 5 \mu\text{l}$  of DMSO was chosen as the doping media for PEDOT. Films were polymerized as per § 2.3 and polymerization for 25 s gave the optimum electrochemical data ( $230 \text{ F g}^{-1}$  at  $10 \text{ mV s}^{-1}$ ).

Composite electrodes of the activated carbon-doped PEDOT were synthesized as per § 2.4. The activated carbon/doped PEDOT composite yielded capacitance values of  $1183 \text{ F g}^{-1}$  and  $42 \text{ mF cm}^{-2}$  at  $10 \text{ mV s}^{-1}$ . The electrochemical CV curves are shown in figure 5. The morphology of the activated carbon-doped PEDOT composite is shown in figure 6. Doping PEDOT with multiple dopants can affect the self-discharge characteristics. Self-discharge, to a large extent, is dependant on the internal resistance/impedance of the active layer in the electrode. Thus, on account of higher electrode/active mass conductivities (figures 3 and 4, which are also representative of lower internal resistance), we expect self-discharge to be within acceptable limits even with multiple doping.

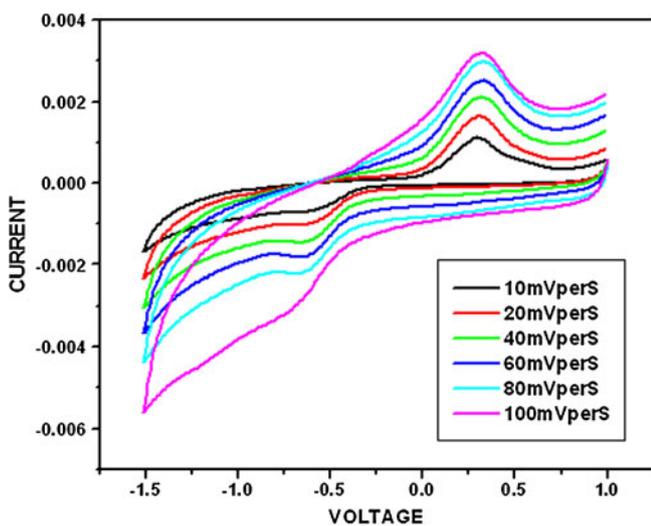
FTIR data for both activated carbon/PEDOT:PSS and activated carbon/doped PEDOT composite is shown in figure 7. The appearance of additional peaks is shown for the composites when compared to FTIR of carbon alone. The nanoscale activated carbon-doped PEDOT composite electrodes showed high specific capacitance, which was more than five times the storage capacity previously reported for activated carbon–PEDOT composites. The large capacitance values that we have achieved is due to high surface area provided by the nanoscale activated carbon together with its conductivity and this provides an optimum backbone for polymer deposition. Thus, surface area for faradaic interactions of the porous conducting polymer with the electrolyte



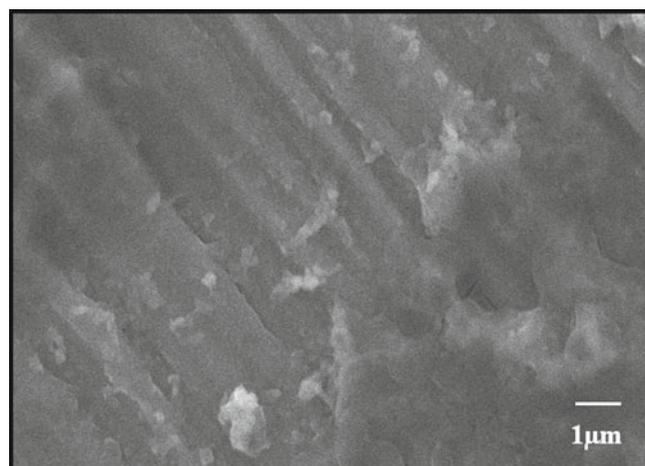
**Figure 3.** SECM 3-D current plot for PEDOT:PSS and activated carbon–PEDOT:PSS composite. Current bar in nA is shown on top right of plot. Darker shade indicates higher values of current.



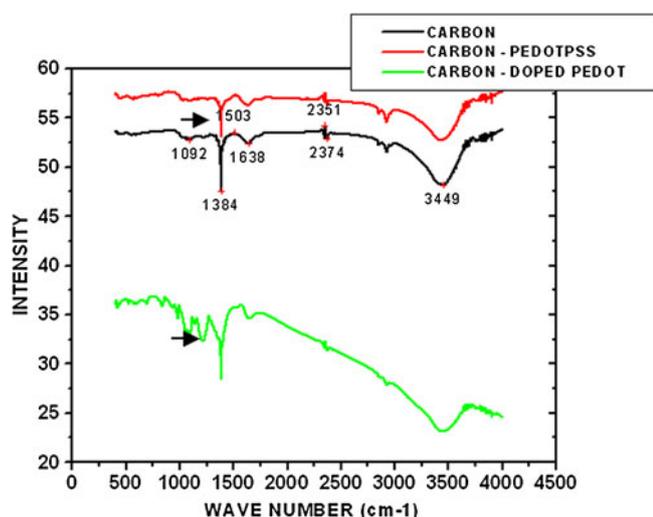
**Figure 4.** SECM 3-D current plot for doped PEDOT and activated carbon-doped PEDOT composite. Current bar in nA is shown on top right of plot. Darker shade indicates higher values of current.



**Figure 5.** CV curves of activated carbon-doped PEDOT composite at various scan rates in 0.1 M LiClO<sub>4</sub> in acetonitrile. Calomel electrode is used as reference. Scan rates are varied from 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup>.



**Figure 6.** SEM image of activated carbon-doped PEDOT composite showing polymer film deposited over underlying carbon backbone.



**Figure 7.** FTIR data for carbon alone, activated carbon–PEDOT:PSS composite and activated carbon-doped PEDOT composite. Upon composite formation, additional peaks appear in FTIR spectrum (shown by arrows).

is also enhanced. Further, the use of multiple dopants in PEDOT improved the storage performance of the composite electrode well over that of PEDOT:PSS.

#### 4. Conclusions

In conclusion, we were able to successfully synthesize composite supercapacitor electrodes with high electrical storage capacity made from nanoscale activated carbon combined with either PEDOT:PSS or PEDOT doped with multiple dopants such as APS and DMSO. The nanoscale activated carbon-doped PEDOT composite electrodes showed high specific capacitance of  $1183 \text{ F g}^{-1}$ , which is more than five times the storage capacity previously reported for activated carbon–PEDOT composites. Further, the use of multiple dopants in PEDOT improved the storage performance of the composite electrode well over that of PEDOT:PSS ( $640 \text{ F g}^{-1}$ ).

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