

## Electronic Supporting Information

### **Novel scalable synthesis of highly conducting and robust PEDOT paper for high performance flexible solid-supercapacitor**

*Bihag Anothumakkool<sup>ab</sup>, Roby Soni<sup>ab</sup>, Siddheshwar N. Bhange<sup>a</sup>, and Sreekumar Kurungot<sup>ab\*</sup>*

<sup>a</sup>Physical and Materials Chemistry Division, CSIR - National Chemical Laboratory, Pune-411008, Maharashtra, India.

<sup>b</sup>Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bhawan, 2, Rafi Marg, New Delhi – 110 001, New Delhi, India.

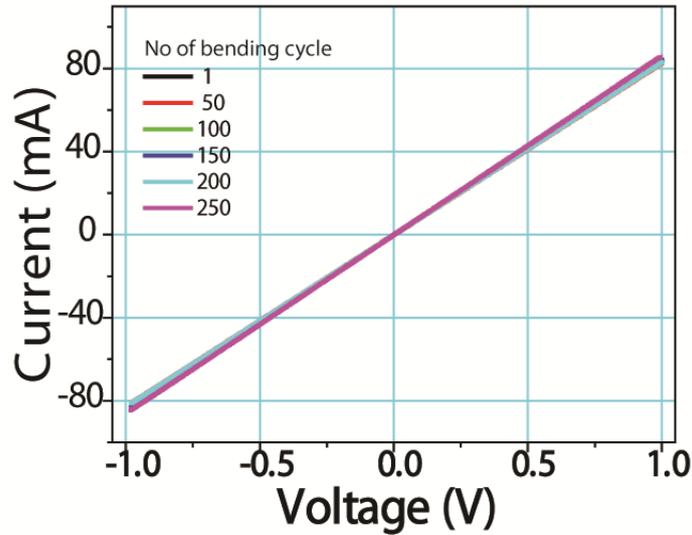


Figure S1. I-V polarization at after various bending cycles on PEDOT-p-5

### Calculations

The following equation<sup>1</sup> was used for calculating the areal/volumetric capacitance of the PEDOT from the cyclic voltammogram.

$$C = 2 * \frac{Q}{(E_1 - E_2) * A \text{ or } V} \text{----- (1)}$$

$Q(\text{charge}) = \frac{\int_{E_1}^{E_2} I(E)dE}{v}$ , is the average charge obtained by the integration of cathodic and anodic parts of the voltammogram

$E_1 - E_2$  = Potential window (1.2 V)

$v$  = Scan rate (mV/s)

$A$  = Area of the single paper electrode

$V$  = Volume of the single paper electrode

The following equation was used for calculating the areal/volumetric capacitance of the PEDOT from the chrono charge-discharge profile :

$$C = 2 * \left( \frac{I \Delta t}{\Delta V * A \text{ or } V} \right) \text{----- (2)}$$

$\Delta t$  = Discharge time

$\Delta V$  = Potential window

$I$  = Constant current used for charging and discharging

$A$  = Area of the single paper electrode

$V$  = Volume of the single paper electrode or PEDOT alone

- Multiplication of the capacitance by a factor of 2 is included in the above equations for converting the capacitance in terms of single electrode.

Energy density ( $E_d$ ) and power density ( $P_d$ ) for the whole device were calculated from the capacitance value obtained from the charge-discharge method.

$$\text{Volumetric Energy density } E_v (Wh\ cm^{-3}) = \frac{1}{2} * \frac{C_v V^2}{3600}$$

$C_v (F)$  = Volumetric capacitance for the whole device calculated from the charge-discharge method

V= Voltage window

$$\text{Volumetric Power density } P_v (W\ cm^{-3}) = \frac{E_v}{t}$$

t = Discharge time in hour calculated from the discharge curve

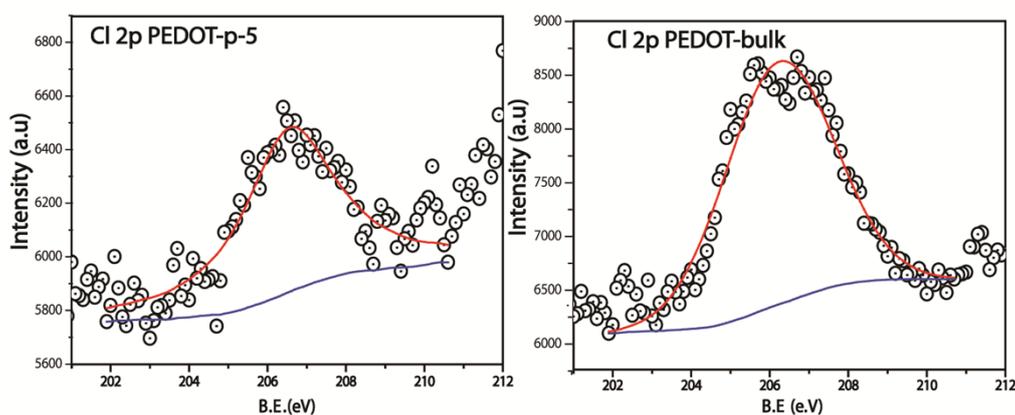


Figure S2: Cl 2p of a) PEDOT-p-5 and b) PEDOT-bulk.

### Detailed XPS analysis

Table S1: Peak parameters of PEDOT-p-5

Peak	Position (eV)	Area	FWHM (eV)
0 (S2p 3/2)	162.32	2983.91	1.79
1(S2p 1/2)	163.63	1421.95	3.62
2 (S $\delta^+$ )	166.27	2026.22	4.29

<b>Cl 2p</b>	<b>206.55</b>	<b>2702.51</b>	<b>2.84</b>
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Table S2: Peak parameters of PEDOT-bulk

<b>Peak</b>	<b>Position (eV)</b>	<b>Area</b>	<b>FWHM (eV)</b>
<b>0 (S2p 3/2)</b>	<b>162.31</b>	<b>12945.40</b>	<b>1.95</b>
<b>1(S2p 1/2)</b>	<b>163.73</b>	<b>6291.28</b>	<b>2.03</b>
<b>2 (S<sup>δ+</sup>)</b>	<b>166.20</b>	<b>5619.56</b>	<b>4.57</b>
<b>Cl 2p</b>	<b>206.23</b>	<b>7880.31</b>	<b>3.27</b>

Doping level is calculated by the following two methods:

**First method**

By taking the ratio of the area under the peak of Cl 2p to S 2p.

Doping level = (Area of Cl 2p/ASF of Cl 2p) / (Area of S2p/ASF of S 2p)

ASF (atomic sensitivity factor, which is 0.54 for S 2p and 0.73 for Cl 2p)

**Second method**

Doping level = Area under the peak of S<sup>δ+</sup>/ Total area under the peak of S 2p

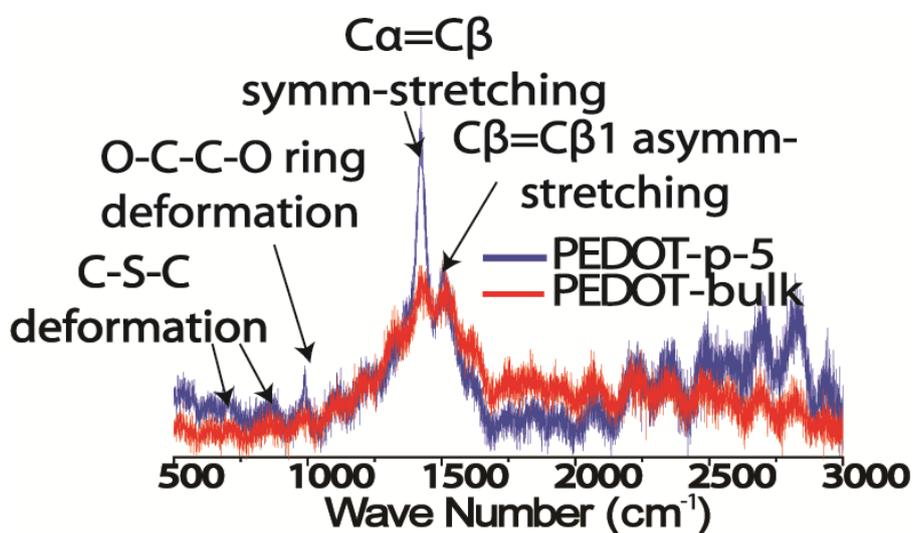


Figure S3. Raman spectra of the various samples.

In Raman spectra (Figure S3), a strong peak at  $1426\text{ cm}^{-1}$  corresponds to  $C\alpha=C\beta$  symmetric stretching of PEDOT appears. Peaks at  $1358$  and  $1497\text{ cm}^{-1}$  represent the  $C\beta=C\beta_1$  stretching. The other characteristic peak observed at  $981\text{ cm}^{-1}$  corresponds to the oxyethylene ring deformation and the two peaks appeared at  $705$  and  $852\text{ cm}^{-1}$  correspond to the symmetric and asymmetric C-S-C deformation of PEDOT respectively. It is interesting to note that the intensity of the  $C\alpha=C\beta$  symmetric stretching peak at  $1426\text{ cm}^{-1}$  is much higher in PEDOT-p than that of PEDOT-bulk. This could be a combined effect of more crystallinity as well more doping level as found by XRD and XPS in case of PEDOT-p-5 compared PEDOT-bulk.

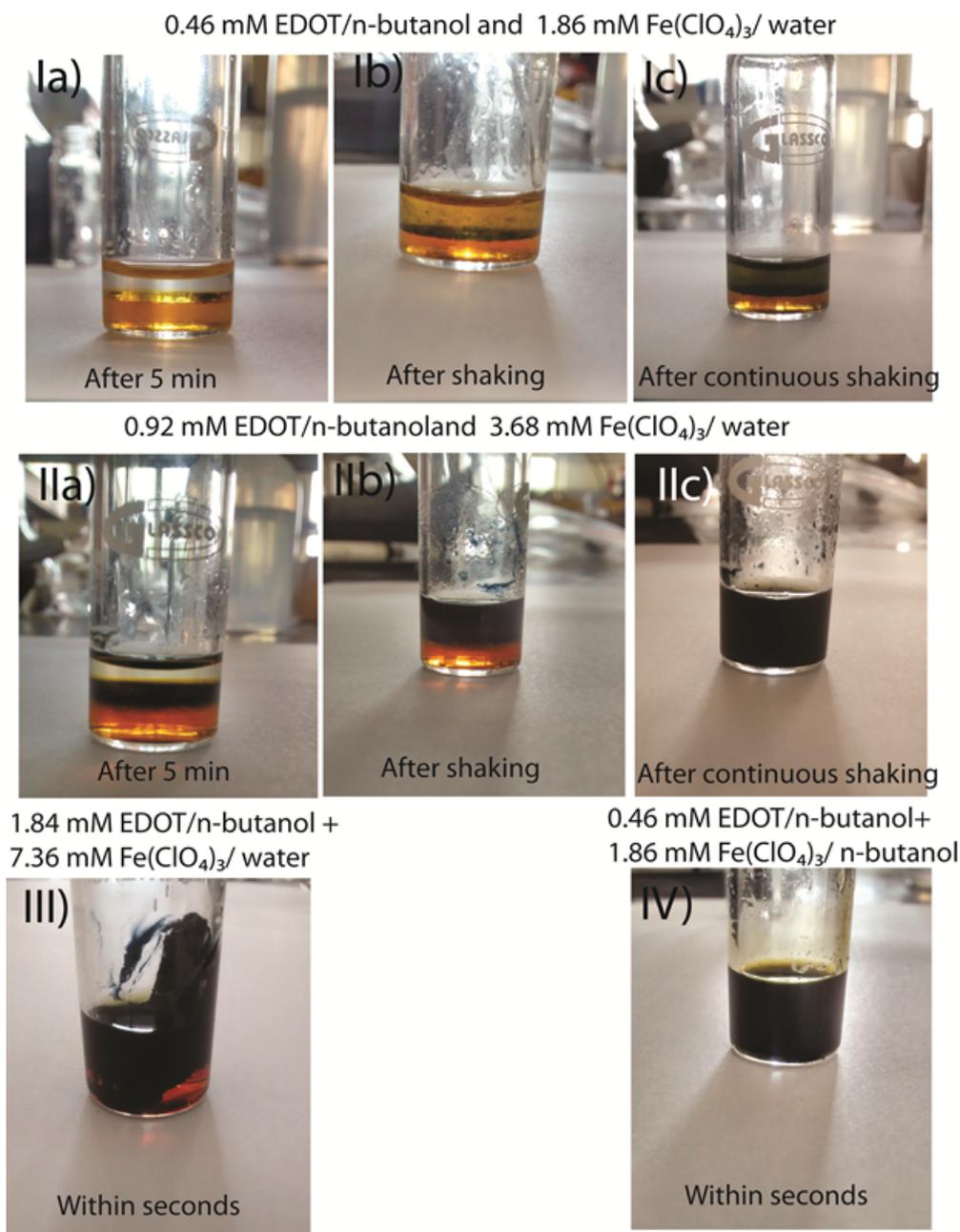


Figure S4. Pot syntheses of PEDOT in various conditions. I) 0.46 mM EDOT II) 0.92 mM EDOT, III) 1.84 mM EDOT in n-butanol after adding to  $\text{Fe}(\text{ClO}_4)_3$ /water solution, IV) formation of PEDOT in n-butanol by mixing 0.46 mM EDOT with  $\text{Fe}(\text{ClO}_4)_3$  in n-butanol.

Images shown in **Figure S3** give insights on the mechanism of interfacial polymerization in the cellulose paper. In **Figure S3I to S3III**, the experiments were carried out by changing the concentration of the monomer (EDOT) from 0.46 mM to 1.84 mM in n-butanol, while keeping 4 times higher molar concentration for  $\text{Fe}(\text{ClO}_4)_3$  in water with the monomer. n-Butanol/EDOT was further added slowly through the walls of a vial to the aqueous phase. In **Figure S3 Ia**, even after 5 min, there is no visible polymerization happens

as there is very less interface is available, and, overall the polymerization rate is found to be less. No bulk polymerization is found in the organic phase as there is no diffusion of  $\text{Fe}(\text{ClO}_4)_3$  from the aqueous phase to the organic phase owing to the less solubility of  $\text{Fe}(\text{ClO}_4)_3$  in n-butanol compared to water. Possible interfacial polymerization rate is very less under static condition, even though it can be increased further by shaking, which creates large number of droplets of n-butanol inside the aqueous phase. **Figure S3 Ib & Ic** show the presence of PEDOT, which is formed at the interface of the droplets after the shaking and join together during settling. It can be seen that some PEDOT is formed in the organic phase as well, which is obvious due to the diffusion of  $\text{Fe}(\text{ClO}_4)_3$  into the organic phase during the shaking process.

While going from low to high concentration, bulk polymerization in the organic phase is happening at a faster rate, which is due to the easy diffusion of the high concentrated  $\text{Fe}(\text{ClO}_4)_3$  from water to the organic phase through the interface. This gradual change is visible from the **Figure S3 I-III**. Thus, concentration has a key role in the surfactant-free interfacial polymerization carried out here. Hence, we used the EDOT concentration of 0.46 mM, which will preferably result in the interfacial polymerization. However, lengthy reaction time as well as poor yield (**Figure S3 I**) makes the pot synthesis less viable choice. High concentration can result in higher yield, but the bulk polymerised PEDOT will be predominant in such cases (**Figure S3 III**). For comparison, PEDOT formation in pure n-butanol has also been carried out (**Figure S3 IV**), and the reaction is found to be very fast as compared to that in aqueous/organic mixture while maintaining the same concentration. The conductivity of the formed PEDOT formed in this case is measured and is found to be 10 times lesser than PEDOT-bulk (31 S/cm) compared to PEDOT-p-5

Table S3. Four-probe conductivity data

Sample	Conductivity (S cm <sup>-1</sup> )
<b>PEDOT-p-5</b>	<b>375</b>
<b>PEDOT-bulk</b>	<b>31</b>

By transferring the experiments (**Figure S3 I**) judiciously on a cellulose paper, formation of extremely uniform and highly conducting interfacial polymerised PEDOT in short duration with excellent yield could be ensured. This is clearly due to the dominance of

the interfacial polymerization compared to the bulk polymerization resulted from the enhanced interface formed along the cellulose fibers having thin layer of water layer. However, increasing the concentration can result in bulk polymerization in this case. **Figure S4** clearly elucidates this difference. When we used 4 times higher concentration of  $\text{Fe}(\text{ClO}_4)_3$  instead of multi-layer coating, as we found in experiment in **Figure S3 I-III**,  $\text{Fe}(\text{ClO}_4)_3$  easily diffuses to the organic phase and trigger polymerization there. This results in higher sheet resistance for the formed PEDOT.

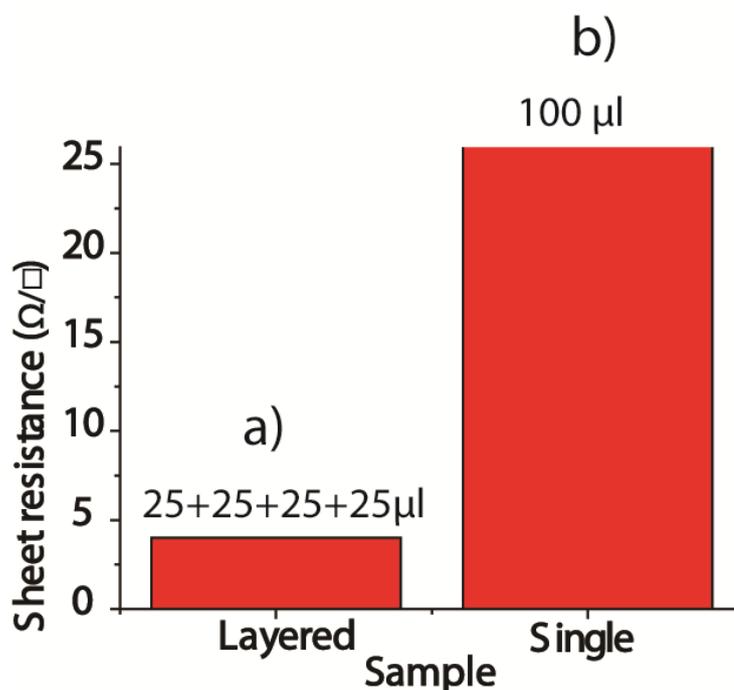


Figure S5. Comparative sheet resistance of the PEDOT samples which are polymerised by (a) multi-layer coating (4 times) and (b) by single coating of 4 time's higher concentration of  $\text{Fe}(\text{ClO}_4)_3$ .

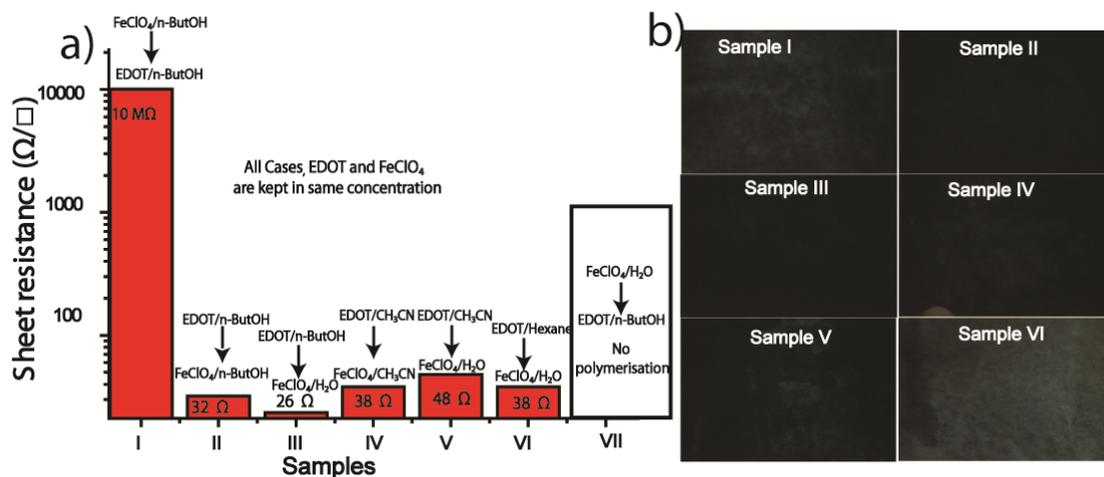


Figure S6. a) PEDOT polymerization on the cellulose paper through various solvent combinations and b) optical images of the corresponding PEDOT papers.

After optimising the concentration of  $\text{Fe}(\text{ClO}_4)_3$  to 0.46 mM from the previous experiments, coatings were carried out on cellulose paper having an area of 9 cm x 11 cm. **Figure S5** shows the sheet resistance data of the various experiments. In **Sample I**, the reaction was carried out in pure n-butanol and as we found previously in the case of pot synthesis (**Figure S3 IV**), is the present process resulted into low conducting PEDOT. The paper is showing a sheet resistance of around 10  $\text{M}\Omega/\square$  and this high value is associated with the low yield of PEDOT as well as its low conductivity. On the other hand, when we coated  $\text{Fe}(\text{ClO}_4)_3$  in n-butanol initially on the cellulose paper, followed by EDOT/n-butanol (**Sample II**), drastic improvement in the conductance has been observed and the sheet resistance is found to be decreased to 32  $\Omega/\square$ . This improvement is clearly attributed to the hydrophilic nature of  $\text{Fe}(\text{ClO}_4)_3$  which absorbs moisture after removal of n-butanol, which results in triggering the interfacial polymerization. In this case, we observed that the sheet resistance was varying according to the humidity conditions in the atmosphere. **Sample III** (PEDOT-p-1) was derived purely through interfacial polymerization which resulted in very low sheet resistance among the all samples as the  $\text{Fe}(\text{ClO}_4)_3$  was dissolved in water. As we found in the previous case of pot synthesis, the concentration of  $\text{Fe}(\text{ClO}_4)_3$  plays a crucial role for confining  $\text{Fe}(\text{ClO}_4)_3$  in the aqueous phase (**Figure 2**). Thus, the preferred interfacial polymerization helps to achieve very low sheet resistance. In **Sample VII**, we used the same combination as that of **Sample III** and the only difference was that EDOT/n-butanol was coated initially on the cellulose paper which was followed by coating of  $\text{FeClO}_4$  in the aqueous phase. As expected, there is no polymerization occurring in the aqueous phase due to the insolubility of EDOT in this phase.

One question can be arisen in this contest as what about the conductivity of PEDOT produced in a solvent where both EDOT and  $\text{Fe}(\text{ClO}_4)_3$  are soluble and possesses high dielectric constant and polarity (e.g. acetonitrile,  $\epsilon = 37.5$ ,  $D = 3.9$ ) compared to butanol? To answer this, we carried out such an experiment in acetonitrile (**Sample IV**). Due to the relatively fast polymerization in this case, non-uniform polymer film over the cellulose paper has been formed and displayed a conductivity value which is substantially lower than that of the polymer formed by the interfacial polymerization process. However, the PEDOT synthesised in acetonitrile is superior in terms of the conductivity ( $38 \Omega/\square$ ) compared to the PEDOT formed in pure n-butanol ( $10 \text{ M}\Omega/\square$ ). This is due to the high dielectric constant in the former case, which helps for better doping of the counter ions in PEDOT. There is no possibility of interfacial polymerization in water/acetonitrile combination as the both solvents are miscible with each other and such an experiment rather results into a sample possessing high sheet resistance (**Sample V**). This further confirms that, not only high dielectric constant but interfacial polymerization (which slows down the polymerization rate) also is crucial for better attaining chain packing and doping for ensuring an overall improvement on the conductivity of the PEDOT.

Second question that can arise is, what will the outcome of a PEDOT formed through interfacial polymerization at an interface of water with another immiscible solvent (like hexane)? **Sample VI** shows that the sheet resistance of PEDOT-p formed at the interface of water/hexane ( $38 \Omega/\square$ ), which is far less than **Sample I** which is formed in butanol ( $10 \text{ M}\Omega$ ). However, the above value less than that measured on the water/butanol based system due to the low dielectric constant of the total interface compared to the later. In conclusion butanol/water at proper concentration gives pure interfacial polymerization at a boundary which possesses highest dielectric constant in total compared to the other combinations experimented here. Further this polymerization yield is many folds higher in the cellulose paper due to the enhanced surface area on the fibers.

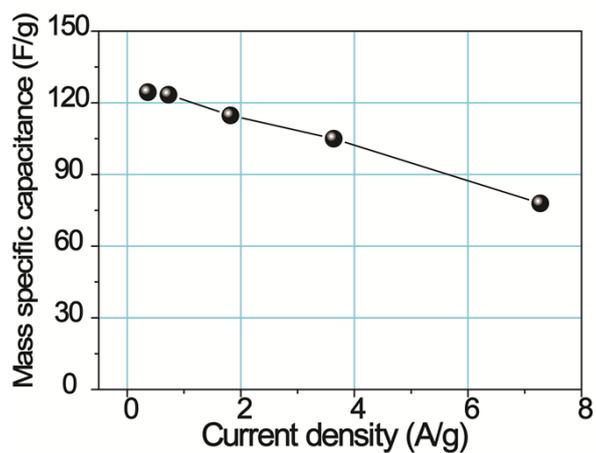


Figure S7. Mass specific capacitance of PEDOT-p-5 at varying current density values.

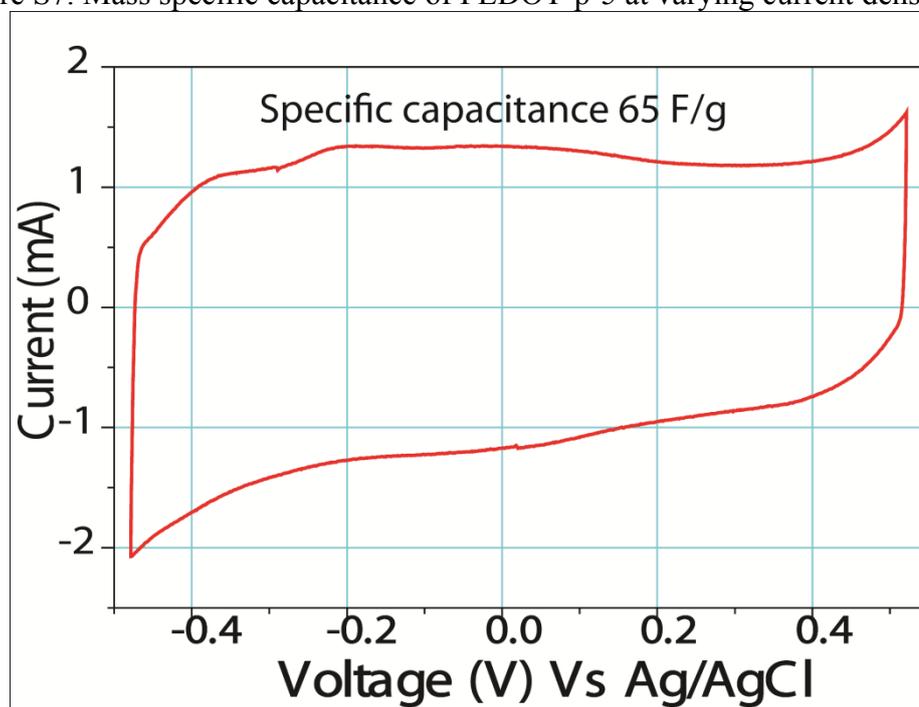


Figure S8. CV profile at 10 mV/s of PEDOT-bulk coated on a solid current collector.

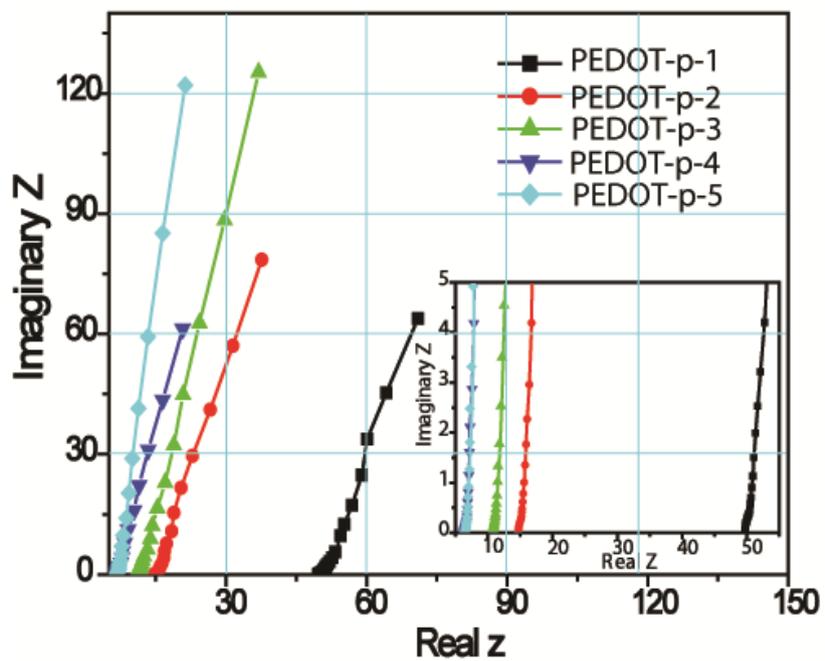


Figure S9. Nyquist plot of various solid-state devices made from PEDOT-p-1 to PEDOT-p-5

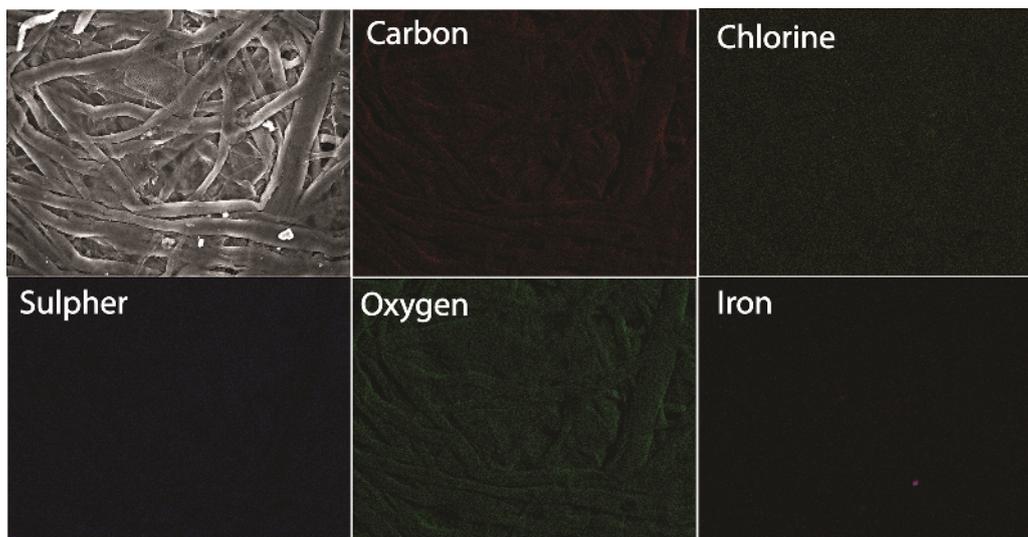


Figure S10: EDAX mapping of PEDOT-p-5.

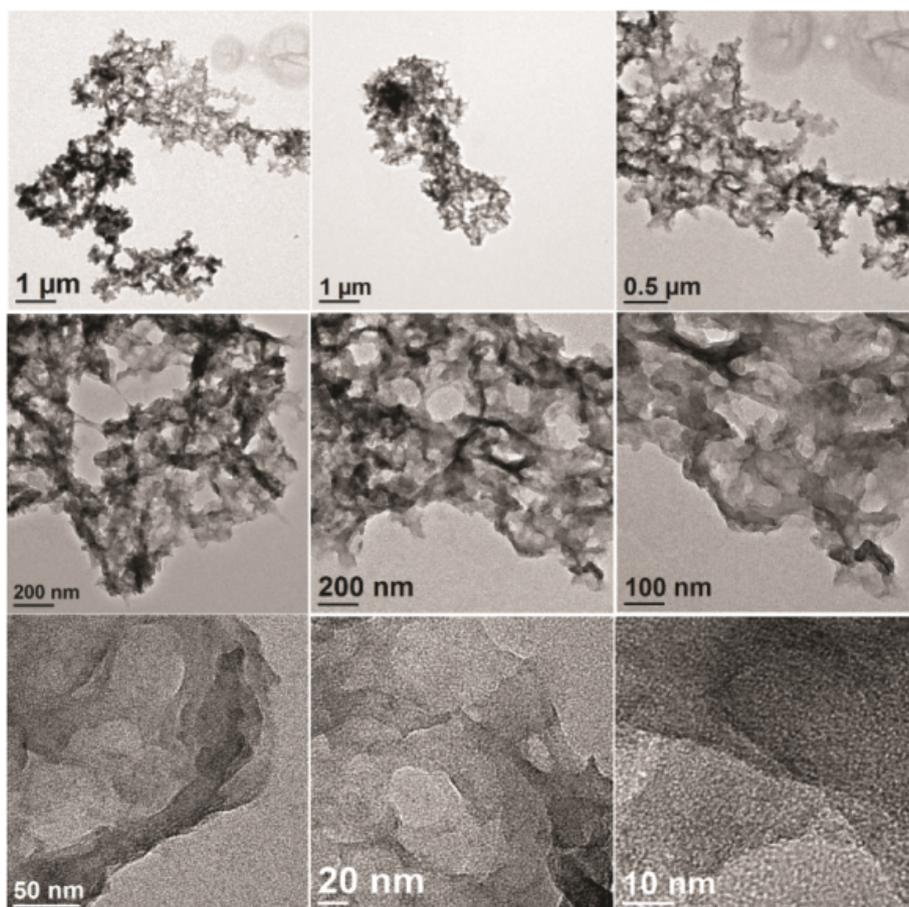


Figure S11. TEM images of PEDOT-p at various magnifications

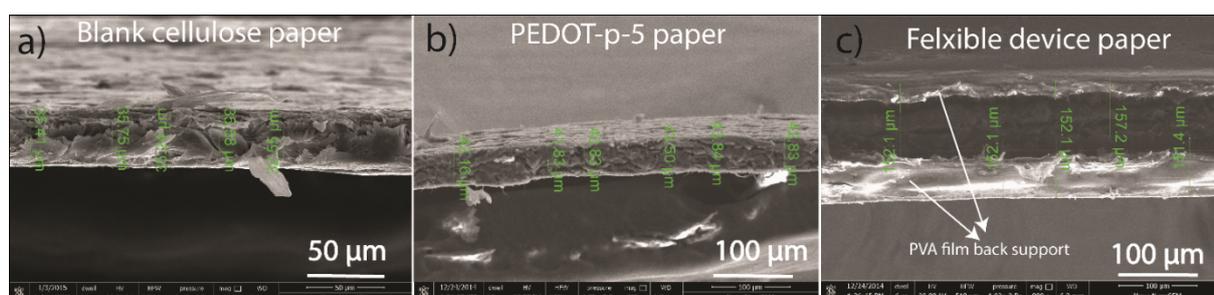


Figure S12. SEM cross-sectional images of a) cellulose paper, b) PEDOT-p-5 and c) the device made from PEDOT-p-5.

To confirm the thickness of PEDOT-p-5 obtained from screw gauge measurements ( $8 \mu\text{m}$ ), we have carried out the SEM imaging of the cross-section of the cellulose paper and PEDOT-p-5. Blank cellulose paper shows an average thickness of  $35 \mu\text{m}$  and  $42.5 \mu\text{m}$  for PEDOT-p-5. Thus, PEDOT film thickness comes around  $7.5 \mu\text{m}$ , which is almost similar to the value obtained from the screw gauge measurements ( $8 \pm 1 \mu\text{m}$ ). Little higher value obtained during the screw gauge measurements is due to the surface roughness of the cellulose fibers. Even

though the volumetric capacitance calculated by considering the PEDOT thickness as 7.5  $\mu\text{m}$  will show a little high value, we used 8  $\mu\text{m}$  as a PEDOT thickness for the calculation of the capacitance as it is measured by the conventional method. In case of the device, the thickness measured from the screw gauge is 170  $\mu\text{m}$ , but the same measured from the SEM measurements it is found to be 153  $\mu\text{m}$ . This difference is probably due to the solvent evaporation under high vacuum in the sample chamber. Thus, we used 170  $\mu\text{m}$  as our device thickness for calculating the volumetric capacitance and volumetric energy density.



Figure S13 . Preparation of four PEDOT-p-1 of 100  $\text{cm}^2$  simultaneously using roll coat methode.

(1) Chen, W.; Fan, Z.; Gu, L.; Bao, X.; Wang, C. Enhanced Capacitance of Manganese Oxide Via Confinement inside Carbon Nanotubes. *Chem. Commun.* **2010**, *46*, 3905-3907.