Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

An optimized conducting polymer nucleation scheme for solid-state supercapacitors on paper

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Electronic Supplementary Information (ESI) :

Specific areal capacitance (C_A) and cell capacitance (C_{cell}) were calculated from the charge-discharge curves according to the following equations.

Specific areal capacitance (C_A) = $(i/A_{single})(\Delta t/\Delta V)$ (for 3-electrode configuration).

A_{single} is the area of single electrode

Cell capacitance (C_{cell}) = $(i/A_{two})(\Delta t/\Delta V)$ (for 2-electrode configuration).

A_{two} is the total area of both the electrodes.

Volumetric stack capacitance (F/cm^3) was calculated by considering the total volume of the cell (both the electrodes and also the electrolyte).

Volumetric stack capacitance (C_{vol}) = $(i/v_t)(\Delta t/\Delta V)$

Energy density (E) = $\frac{1}{2}C_{vol}V^2$ (in mWh/cm^3)

Power density (P) = $E/\Delta t$ (in mW/cm^3).

Where i is the discharge current density, A_{single} and A_{two} are the area of the single and two electrodes in cm^2 respectively, C_{cell} is the cell capacitance, C_{vol} is the volumetric stack capacitance, v_t is the total volume of the cell (both the electrodes and the electrolyte), V is the potential window, Δt is the discharge time.

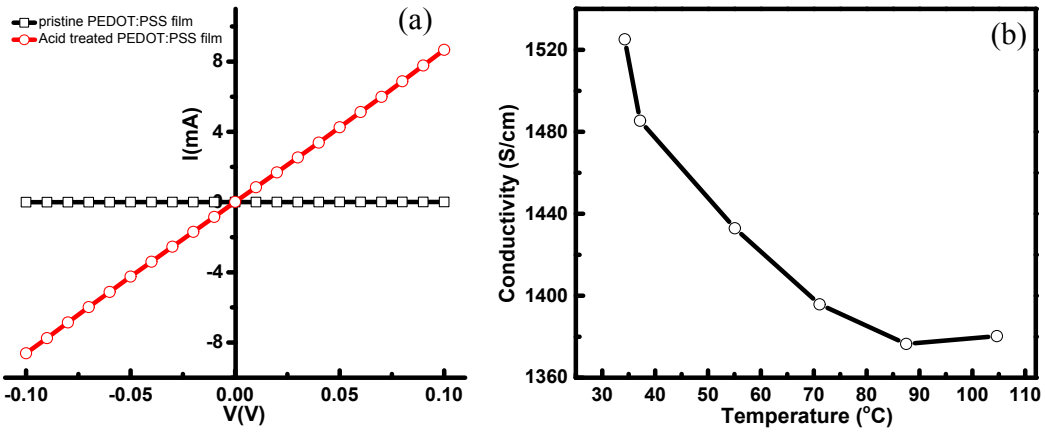

Fig. S1 (a) I-V data of pristine (black curve) and acid treated (red curve) PEDOT:PSS films. (b) 4-probe temperature dependent conductivity of acid treated PEDOT:PSS films, decrease in the conductivity with increasing temperature is signature for metallic type conductivity.

Four-probe electrical conductivity of the acid treated PEDOT:PSS sample was measured in the temperature range of 30−105 ºC in the inert gas (Ar) atmosphere using a commercial setup (Ozawa Science), data is shown in Fig. S1b. It has been well documented in the literature that the conductivity of the PEDOT:PSS films can be enhanced through treatment with various organic solvents such as DMSO, ethylene glycol, etc. Recently, inorganic acids such as sulphuric acid was employed to treat the PEDOT:PSS films in order to achieve the higher values of conductivity. Xia et al., have reported the maximum conductivity of the PEDOT:PSS up to 3065 S/cm after treating the films with 1M H_2SO_4 for multiple times and employed as a transparent electrode in fabricating organic photovoltaic devices.[1]

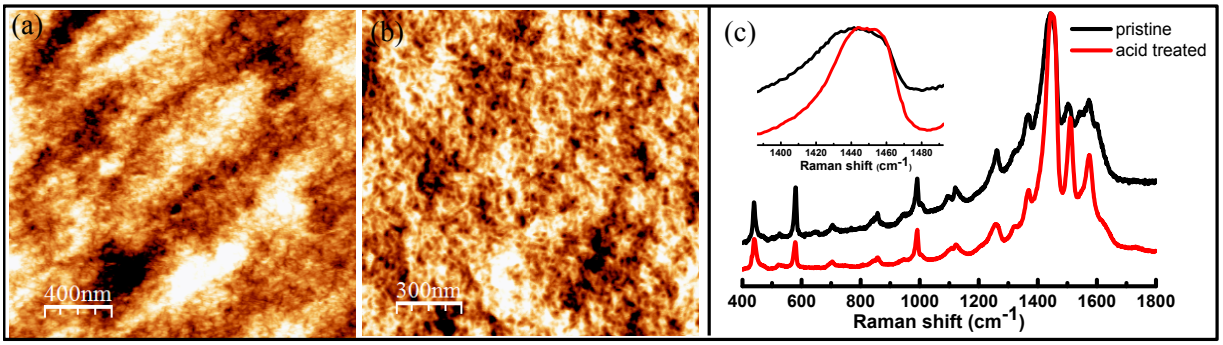

Fig. S2 AFM topography of the PEDOT:PSS films (a) before and (b) after acid treatment (dropping 100 µL of 1M H_2SO_4 on 1cm^2 area film followed by heating at 140 ºC for 5 minutes and washing with water and drying). (c) Raman spectra of pristine (black curve) and acid treated (red curve) PEDOT:PSS films, inset shows the red shift of the 1440 cm^{-1} peak after the acid treatment.

The surface acid treatment of the PEDOT:PSS films resulted in the relatively long chains of the PEDOT when compared with the pristine film (compare the AFM topography in Figs. S2a and S2b). Similar kind of observations were made in the literature to explain the enhancement in the electrical conductivity of PEDOT:PSS after acid treatment.[1]The peak at 1440 cm^{-1} corresponds to $C_\alpha = C_\beta$ stretching mode which is seen red shifted after the acid treatment, indicating the doped state of the PEDOT which is more conducting than the neutral form.[2] The doped state of PEDOT (oxidized form) and also the conformational changes up on the acid treatment are responsible for the enhanced electrical conductivity of the PEDOT:PSS films.

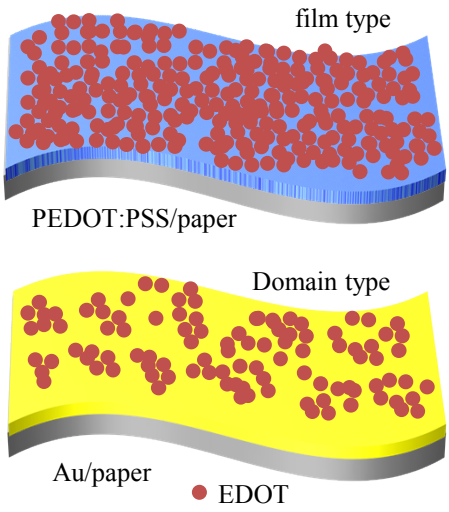

Fig. S3 Initial stage of adsorption of EDOT monomers on PEDOT:PSS/paper and Au/paper surfaces.

Though, the adsorption of EDOT on Au/paper seems to be domain type, it has resulted in the formation of micro globular deposits of PEDOT, a kind of three-dimensional growth. Fig S3 is the schematic representation of the initial stage of adsorption of EDOT monomers over the two nucleation layers. In our case, we have found that the amount of electrodeposited PEDOT is more or less same either on PEDOT:PSS or Au layers. The typical mass loading of electrodeposited PEDOT was found to be 0.95 and 0.9 mg/cm^2 over the PEDOT:PSS and Au layers, respectively for 15 minutes deposition. Based on this, we can attribute the difference in the capacitance to the morphology difference in the electrodeposited PEDOT over the two different nucleation layers.

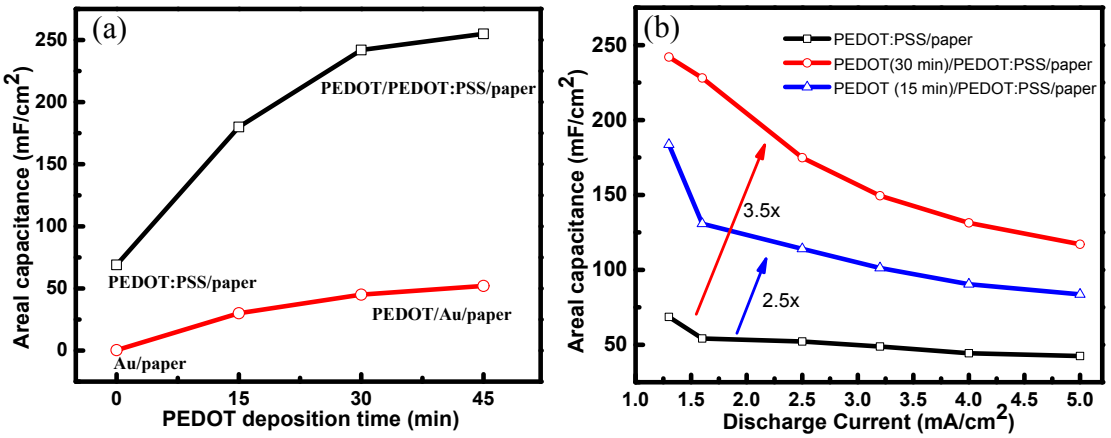

Fig. S4 (a) Areal capacitance vs. PEDOT deposition time over the PEDOT:PSS/paper and Au/paper. (b) Comparison of areal capacitance of PEDOT/PEDOT:PSS/paper with PEDOT:PSS/paper at different discharge current densities.

S. No.	Electrode	Configuration	Electrolyte	Areal capacitance (mF/cm^2)	Volumetric capacitance (F/cm^3)	Gravimetric capacitance (F/g)	Energy density (mWh/cm^3)	Power density (mW/cm^3)	ESR ($\Omega\ cm^2$)	Source
1.	Au/paper	3-electrode	1M H_2SO_4	0.3	30	-	-	-	7	Fig. S4
2.	PEDOT(15 min)/Au/paper	3-electrode	1M H_2SO_4	30	189	35	-	-	10	Fig. 4, Fig. S4
3.	PEDOT(30 min)/Au/paper	3-electrode	1M H_2SO_4	45	197	41	-	-	9	Fig. 4, Fig. S4
4.	PEDOT:PSS/paper	3-electrode	1M H_2SO_4	69	138	73	-	-	11	Fig. S4
5.	PEDOT(15 min)/PEDOT:PSS/paper	3-electrode	1M H_2SO_4	184	282	95	-	-	9	Fig. 3, Fig. S4
6.	PEDOT(30min)/ PEDOT:PSS/paper	3-electrode	1M H_2SO_4	242	327	110	-	-	6	Fig. 3, Fig. S4
7.	PEDOT(30 min)/PEDOT:PSS/paper	2-electrode	PVA/H_2SO_4 gel	32	133	-	1.4	29.5	22	Fig. 5
8.	PEDOT(30 min)/Au/paper	2-electrode	PVA/H_2SO_4 gel	14	58	-	0.61	15.5	19	Fig. S5
9.	PEDOT(30min)/ PEDOT:PSS/paper	2-electrode	[EMIM][TFSI]/ P(VDF-HFP)	11	46	-	2.3	75	56	Fig. 6
10.	PEDOT:PSS/paper	2-electrode	[EMIM][TFSI]/ P(VDF-HFP)	6	12	-	0.53	20	52	Fig. S6

Table S1. A list of PEDOT/paper electrodes investigated in this study.

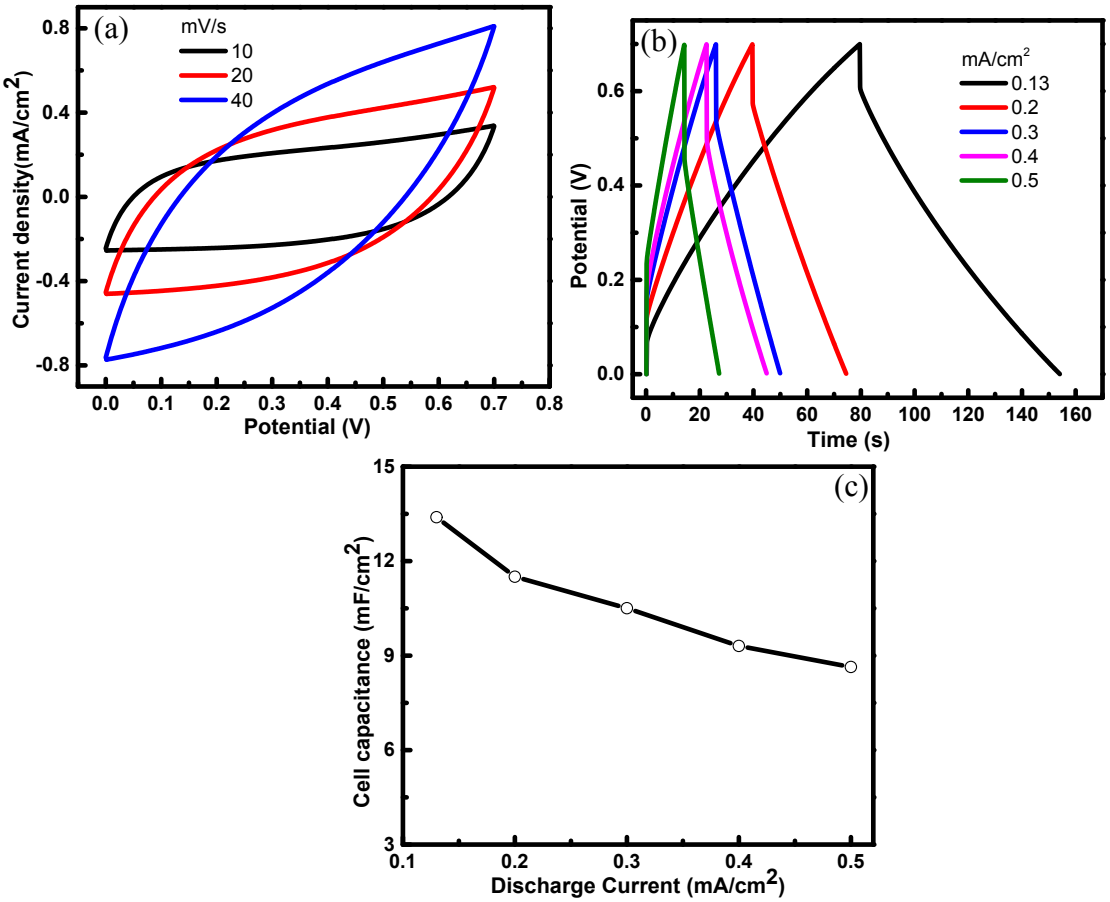

Fig. S5 (a) CV and (b) charge-discharge curves for the solid state symmetric PEDOT/Au/paper supercapacitor using PVA/H_2SO_4 gel electrolyte. (c) Cell capacitance of the solid state device at different discharge current densities.

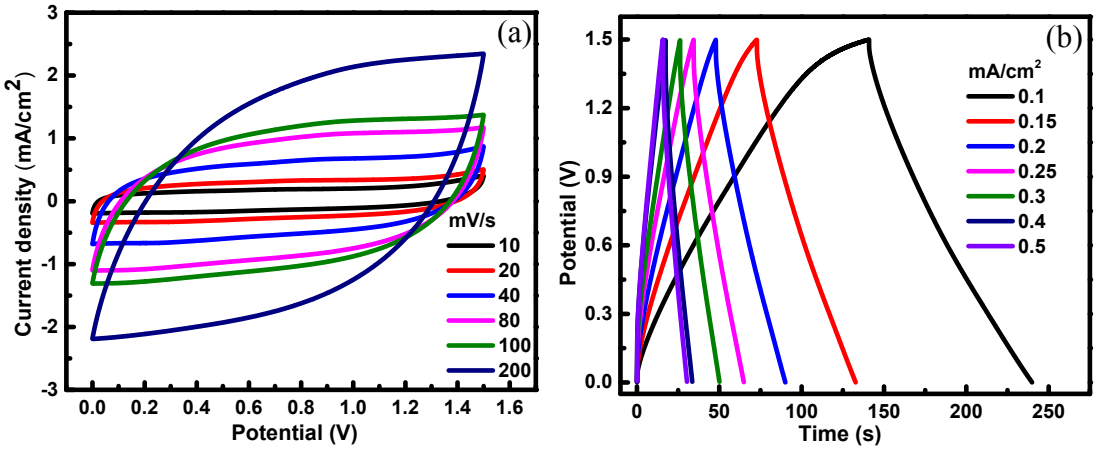

Fig. S6 (a) CV and (b) charge-discharge curves for the solid state symmetric PEDOT:PSS/paper electrodes using P(VDF-HFP)/[EMIM][TFSI] ion gel electrolyte.

References

1 Y. Xia , K. Sun and J. Ouyang, *Adv. Mater.*, 2012, **24**, 2436-2440.

2 M. Reyes-Reyes, I. Cruz-Cruz and L. Lopez-Sandoval, *J. Phys. Chem. C*, 2010, **114**, 20220-20224.