Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Data

Negative Photoresponse in ZnO - PEDOT: PSS nanocomposite and photogating effects.

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(a)

Concentration (% ZnO)	Wt of ZnO (mg)	Amount of PEDOT:PSS
0	0	1 mL (11 to 13 mg)*
10	1.222	1 mL
25	3.666	1 mL
35	5.92	1 mL
50	11	1 mL
60	16.5	1 mL
70	25.7	1 mL
80	44	1 mL
90	99	1 mL

(b)

Step	rpm	Coating Time (s)
1	250	30
2	500	30
3	750	40
4	1000	40
5	1250	40
6	1500	40

Table T1 a) ZnO-PEDOT: PSS sample details b) Spin Coating steps followed in preparing thin films

Nanocomposites of ZnO nanoparticles in PEDOT:PSS polymer were prepared by dispersing increasing concentrations (wt % ZnO) of ZnO in PEDOT:PSS as tabulated in table T1(a) and were spin coated on to glass coverslips, after bath sonication. Since nanoparticle loading appreciably changes viscosity of the various concentrations of NC, we have optimized the NC amount and spin conditions (i.e. number of steps, rpm and time) as presented in T1(b). Multiple step spin coating protocol was followed where the spinning speed is increased systematically for optimised time periods, after dropping 6 - 8 µL of the NC on the coverslips to ensure a uniform coating thickness and areal coverage across all concentrations. The above spin coating protocol results in thin films of thickness 1.5 µm ± 10% variation.

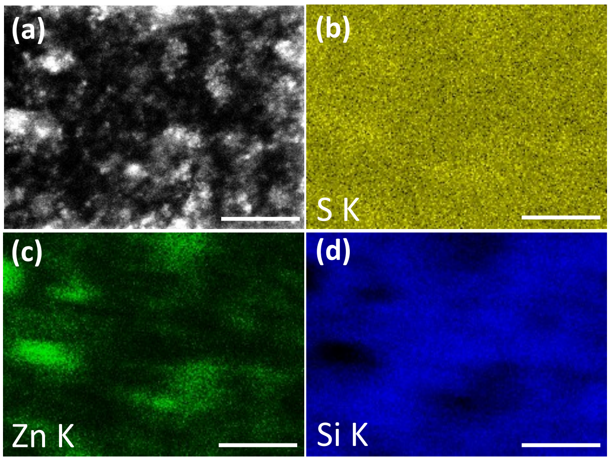

Figure S1: (a) SEM image and EDS elemental mapping of (b) sulphur (c) zinc and (d) silicon on the 50% ZNP nanocomposite thin film. The scalebar is 3 μm.

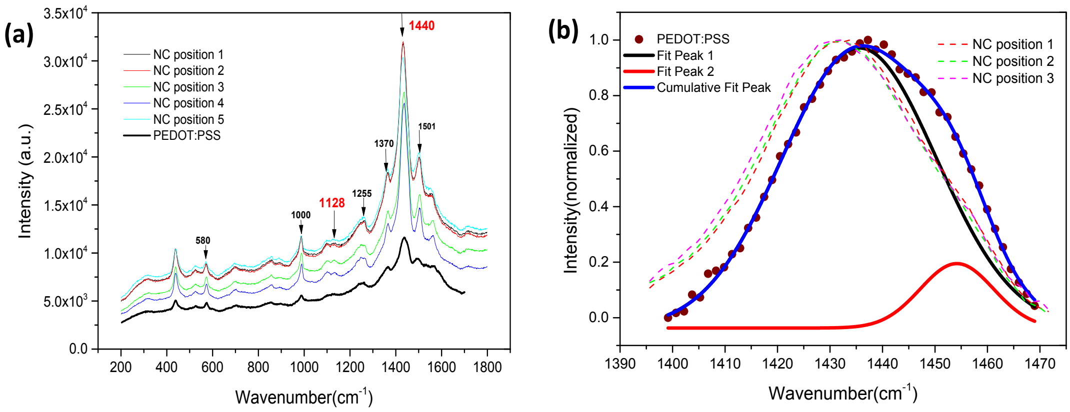

Figure S2: Raman spectra of a) bare PEDOT: PSS and at various regions on a 50% NC sample b) Close-up on spectra around the 1440 cm^{-1} peak ($C_\alpha = C_\beta(-O)$ stretching mode), normalized Raman spectrum of bare PEDOT:PSS (maroon dots), black and red solid lines shows deconvolution into two Gaussian peaks, blue line indicating the envelope. Dashed lines show normalized Raman spectra of 50% NC around The NC spectra are obtained at different positions of the same sample to probe possible variation in spectrum with distribution of ZNPs in PEDOT:PSS.

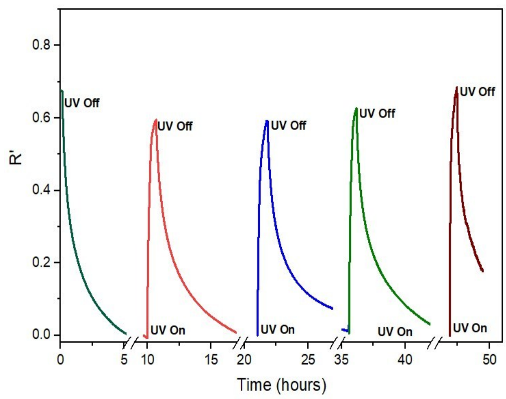

Figure S3: Repeatability of the negative PR over 5 cycles on a single 50% NC device.

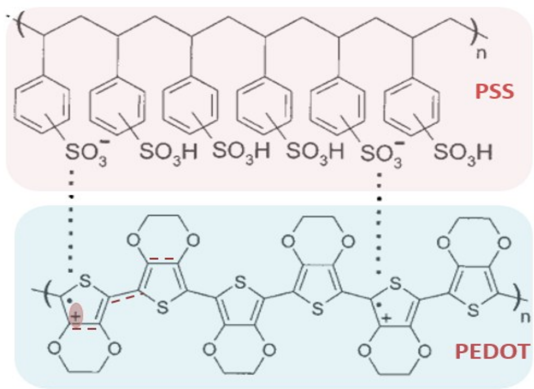

Figure S4: Schematic of PEDOT:PSS showing hole doping (PEDOT$^+$) of PEDOT.

PEDOT:PSS is a conducting polymer, in which delocalized positive charge (hole) is induced on PEDOT rendering the polymer conducting. The hole gets transferred along the PEDOT chain via a cooperative flip and shift of double bonds to the adjacent positions (red dashed line in figure S4). The PSS component maintains the necessary counterion and enhances the solubility of PEDOT in aqueous medium.

Morphologically, PEDOT:PSS consists of PEDOT rich grains isolated by insulating matrix of PSS[1] which suggests that the conductivity of PEDOT:PSS doesn't solely depend upon the intrinsic hole mobility along the PEDOT chain, but also on the transfer of charges between disconnected PEDOT islands through the PSS matrix [2]. The overall conduction is known to follow the variable range hopping (VRH) mechanism [3]. Figure S5(a) shows the temperature variation of resistance plot for bare PEDOT:PSS, suitably scaled to demonstrate their mutual linearity following the 3D VRH model from equation $\sigma(T) = \sigma_0\, exp\left[-\left(\frac{T_0}{T}\right)^{\alpha}\right]$, with α=1/4. Temperature variation of resistance in NC (figure S5(b)) also establishes the validity of the 3D VRH model around room temperature.

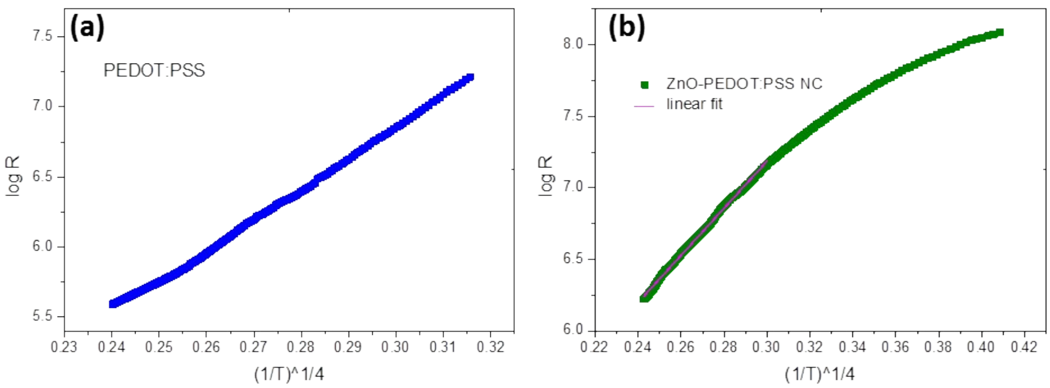

Figure S5: Temperature variation of resistance of a) bare PEDOT: PSS thin film b) 50% nanocomposite thin film. Red line shows the fit to the VRH model equation.

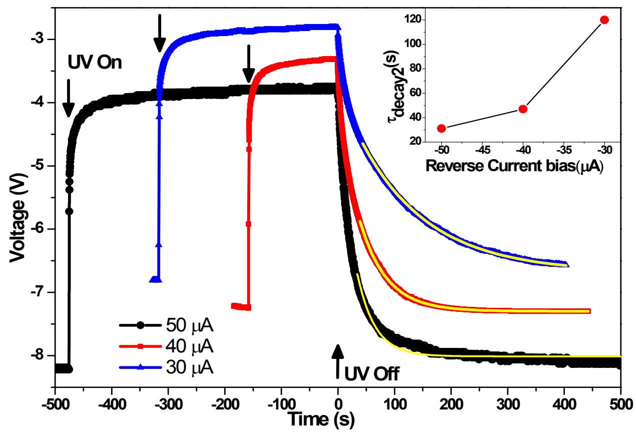

Figure S6: Time dependence of **positive** photoresponse of UV on-off illumination on a planar junction of *n* type ZnO thinfilm with PEDOT:PSS. The plots were acquired in the reverse bias regime, under constant reverse currents of -30, -40 and -50 μA. Down and up arrows indicate UV illumination on and off. The yellow lines are fits to the decaying PR within the data regions indicated. Inset shows decrease of decay τ with increasing reverse current. Constant current mode allows direct monitoring of change in accumulated junction charge (Q_J) with bias (V_J) following the relation $Q_J = C_J V_J$. Devices used for these measurements were fabricated following that in [4]

References:

1. Nardes, A.M., et al., *Microscopic Understanding of the Anisotropic Conductivity of PEDOT:PSS Thin Films.* Advanced Materials, 2007. **19**(9): p. 1196-1200.
2. de Kok, M.M., et al., *Modification of PEDOT:PSS as hole injection layer in polymer LEDs.* physica status solidi (a), 2004. **201**(6): p. 1342-1359.
3. Nardes, A.M., M. Kemerink, and R.A.J. Janssen, *Anisotropic hopping conduction in spin-coated PEDOT:PSS thin films.* Physical Review B, 2007. **76**(8).
4. Vempati, S., et al., *Unusual photoresponse of indium doped ZnO/organic thin film heterojunction.* Applied Physics Letters, 2012. **100**(16): p. 162104.