Correlated Charge Carrier like Photoresponse of Polymer Nanowires

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Supporting Information

Chemically synthesized polypyrrole nanowires[1] were used for this study. We have done detail photoconduction measurements on nanowires synthesized using 50, 100, 200 and 400 nm pore diameter polycarbonate membrane. Nanowires having diameter up to 200 nm show switching transition at low temperature while, 400 nm diameter nanowire does not show switching transition and behaves like a bulk sample. We found that large photoresponse is also observed up to 200 nm diameter nanowire. In the main text we have presented mainly the photoconduction property of polypyrrole nanowires synthesized using 200 nm pore diameter polycarbonate membrane; results of other lower diameter nanowires show qualitative resemblance with that observed for 200 nm diameter. Bellow, we have discussed about the photoconduction property of 50, 100 and 400 nm diameter nanowires.

These nanowire containing membranes are ~10 μm long and no detectable transmission of laser light is observed through the other end of the membrane containing nanowires even in the absence of the gold contact pads (more than 95% of 632.8 nm laser light can penetrate through 10 nm gold layer[2]). The porosity of Track-etch membrane is usually between 14-16%. In our case we found that for 200 nm pore diameter membrane, the average diameter of the nanowires is 225 nm and the nanowires cover $\sim$ 14% of the total membrane area (see Fig. S1a).[3] We used this effective area in the calculation of responsivity and external photoconductive gain.

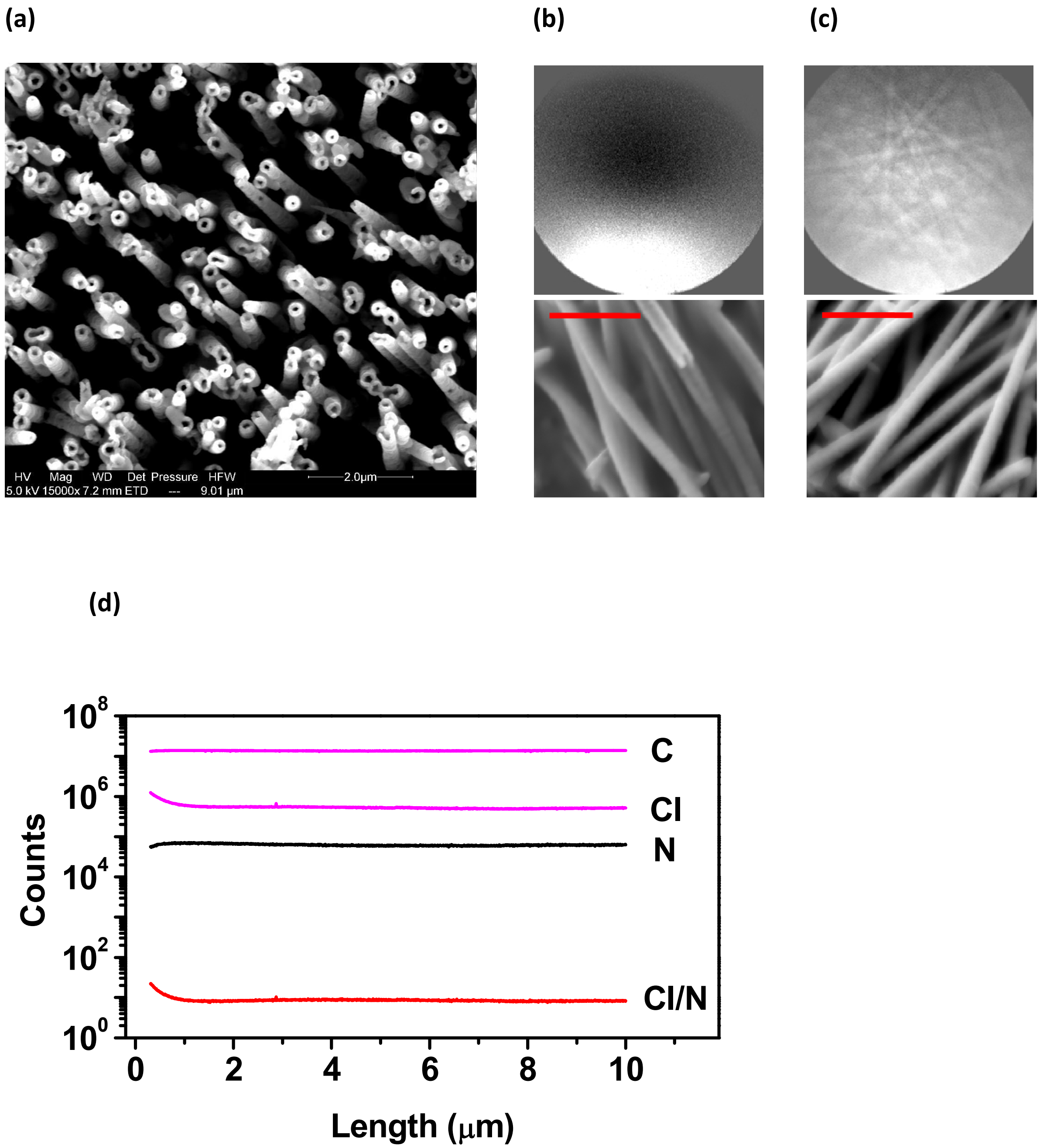

Fig. S1(a) SEM image of the PPy nanowires synthesized using 200 nm pore diameter membrane. The average diameter of the nanowires is ~225 nm. **(b)** Electron backscatter diffraction (EBSD) pattern of PPy nanowires, synthesized using 100 nm pore diameter membrane is shown in the upper panel. Corresponding SEM image (scale bar 500 nm) is shown in the lower panel. **(c)** For reference, EBSD of Cobalt nanowires (SEM image shown in the lower panel, scale bar 500 nm), synthesized using similar 100 nm pore diameter membrane is shown. The observed Kikuchi bands indicate its crystalline nature, whereas, in PPy nanowires no such pattern is observed. **(d)** Secondary ion mass spectroscopy (SIMS) data of 100 nm diameter nanowire showing homogeneous chemical composition along the length of the nanowires.

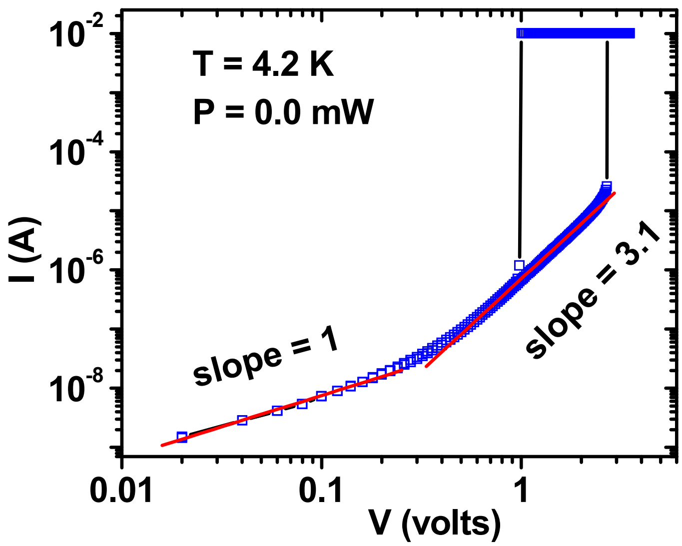

Fig. S2 I-V characteristics (in absence of laser illumination) showing linear (< 250 mv) and non-linear (> 400 mV) regions below the switching transition. In the non-linear region, it shows a power-law dependent I-V characteristics, I αV^{β} with β=3.1. After switching transition the current increases abruptly and gets limited by the current compliance of the source meter, which is set to 10 mA.

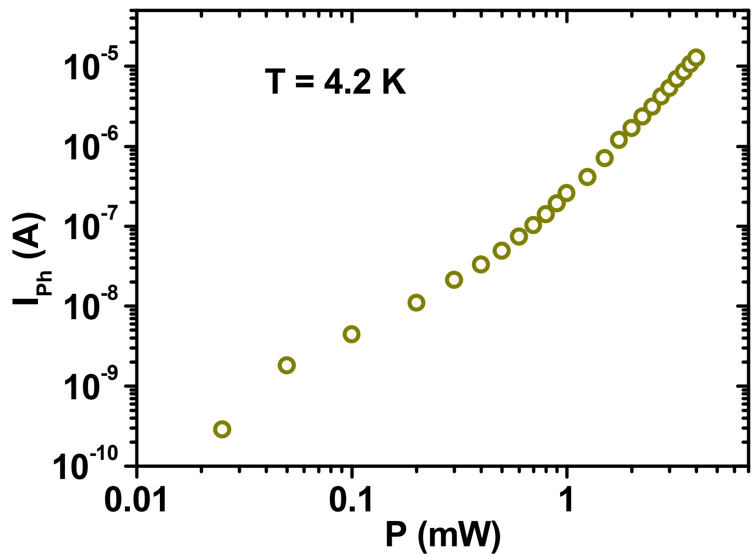

Fig. S3 Measured photocurrent at 4.2 K as a function of laser power has been plotted in the log-log scale. The photocurrent increases superlinearly with increasing power both in the linear and nonlinear regions.

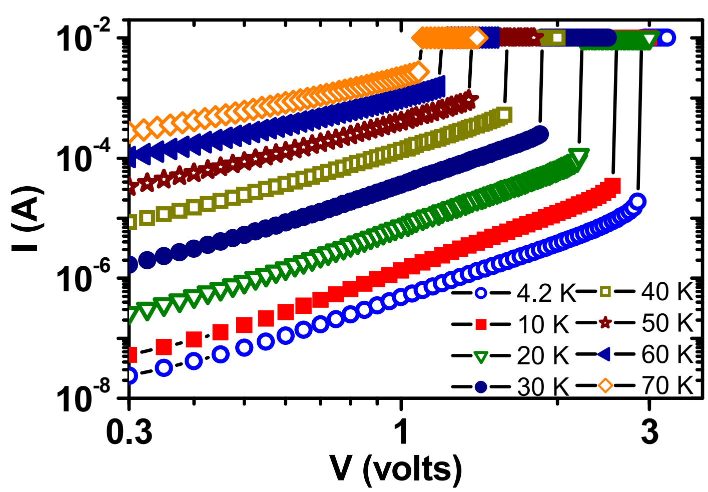

Fig. S4 I-V characteristics (in absence of laser illumination) showing switching transition, have been plotted in log-log scale for various temperatures. Above ~80 K the switching behavior vanishes.

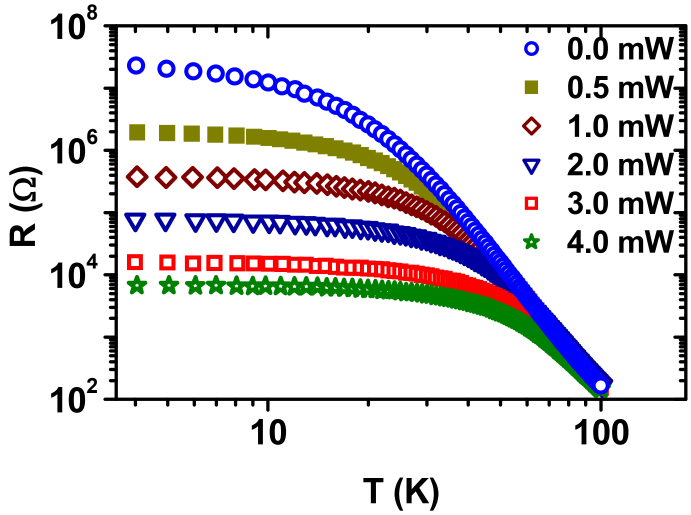

Fig. S5 Resistance (measured in the linear region of the *I-V* characteristics by applying 100 mV bias) as a function of temperature for different values of *P*. It is clear that the temperature dependence of resistance becomes weaker with increasing *P*. Above ~80 K the effect of P becomes negligibly small.

In the swiched state the effect of light is measured by driving current and measuring voltage in presence (V_{light}) and absence (V_{dark}) of light. The relative change ((V_{dark} – V_{light}) / V_{light}) was found to be very low compared to that below the switching transition.

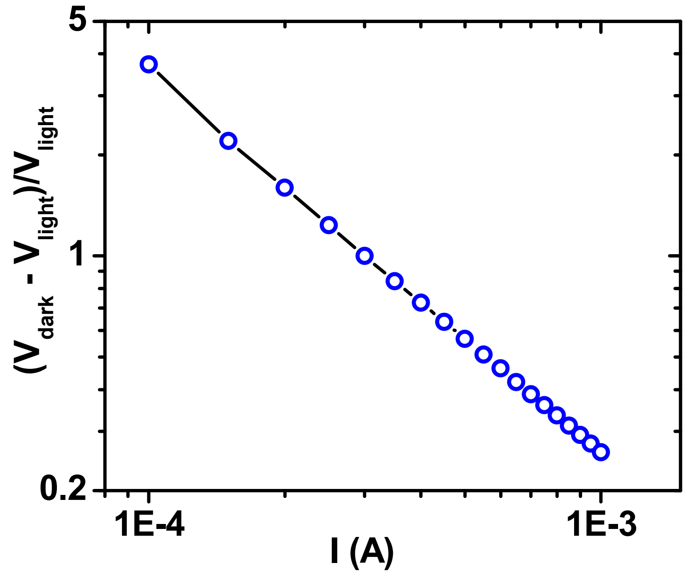

Fig. S6 Relative change in voltage for P = 4 mW in the switched state as a function of bias current. At 4.2 K, in absence of light, switching transition in this sample takes place above 2.6E-5 ampere bias current. For a fixed bias current the voltage generated across the sample in absence of light is high compared to that in presence of light. The relative change decreases rapidly with increasing bias current.

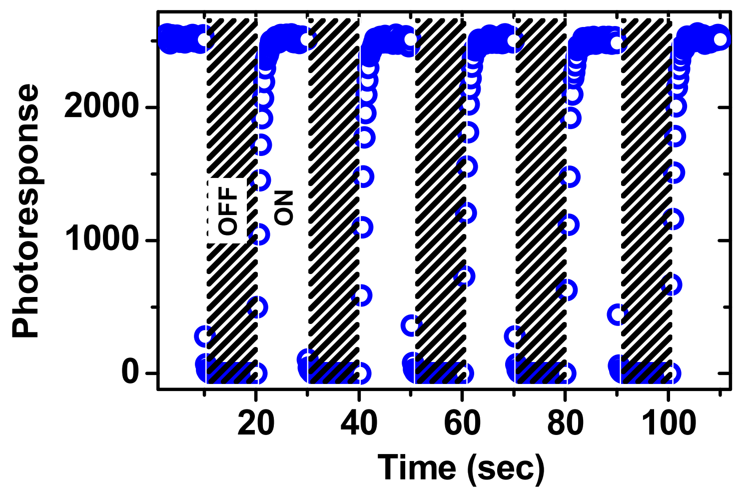

Fig. S7 Photoresponse of PPy nanowires synthesized using 200 nm pore diameter membrane, biased by 100 mV at 4.2 K, by switching on/off a 4 mW laser illumination.

External Photoconductive Gain and Responsivity:

External photoconductive gain (G_{ext}) defined as the ratio of photocurrent (in electrons per second) to number of incident photons at that wavelength,[4] is calculated using the relation, $G_{ext}=hc\ I_{ph}/e\lambda I_{\lambda}S$, where I_{ph} is the photocurrent, I_{λ} is the light intensity, S is the effective illuminated area, h is the Plank's constant, c is the velocity of light, e is electronic charge and λ is the wavelength of the light. Responsivity is defined as photocurrent flowing through the sample divided by incident optical power, I_{ph}/P.

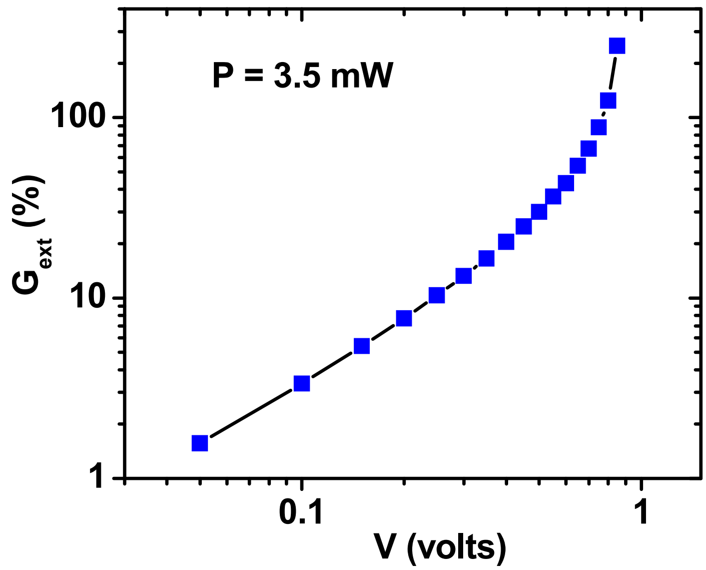

Fig. S8 External gain as a function of bias voltage has been plotted in log-log scale. It is clear that external gain increases superlinearly with increasing bias.

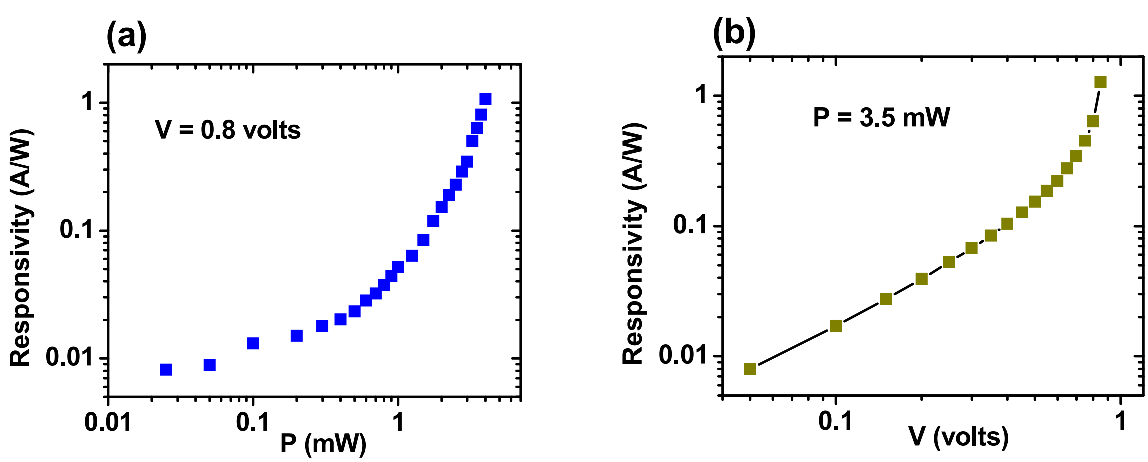

Fig. S9 Responsivity at T= 4.2 K is plotted in log-log scale **(a)** as a function of *P* for 0.8 volts bias and **(b)** as a function of bias voltage for *P*= 3.5 mW.

Comparison of photoresponse of different diameter nanowires:

Polypyrrole nanowires up to 200 nm diameter show clear switching transition, negative differential resistance and noise enhancement at low temperature.[5-6] Nanowires synthesized using 400 nm pore diameter template do not show switching transition and behave like bulk. At low temperature, large photoresponse is observed up to 200 nm diameter nanowire, while 400 nm diameter nanowire and bulk sample do not show considerable photoresponse.

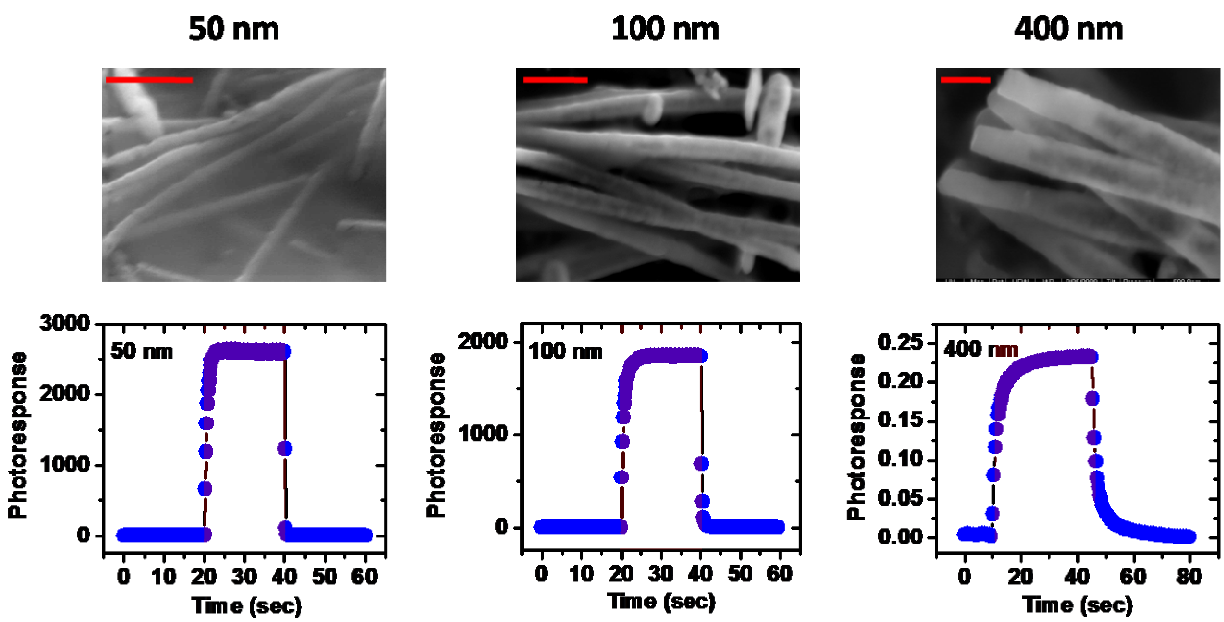

Fig. S10 SEM images of polypyrrole nanowires synthesized using 50 nm, 100 nm and 400 nm pore diameter templates (scale bar 500 nm). Images are taken after removing the polycarbonate template. The corresponding photoresponse in presence of 4 mW laser illumination (shaded region) are shown. The observed photoresponse is large for 50 nm and 100 nm but for 400 nm diameter nanowires, it is negligible (~10^4 times less). This is consistent with our observation of switching transition in low diameter nanowires. We observed clear switching transition in 50, 100 and 200 nm diameter nanowires but 400 nm diameter nanowires do not show switching transition and behave like bulk polymer. Bulk polypyrrole (measured in form of a pellet) does not show any significant change of resistance upon illumination.

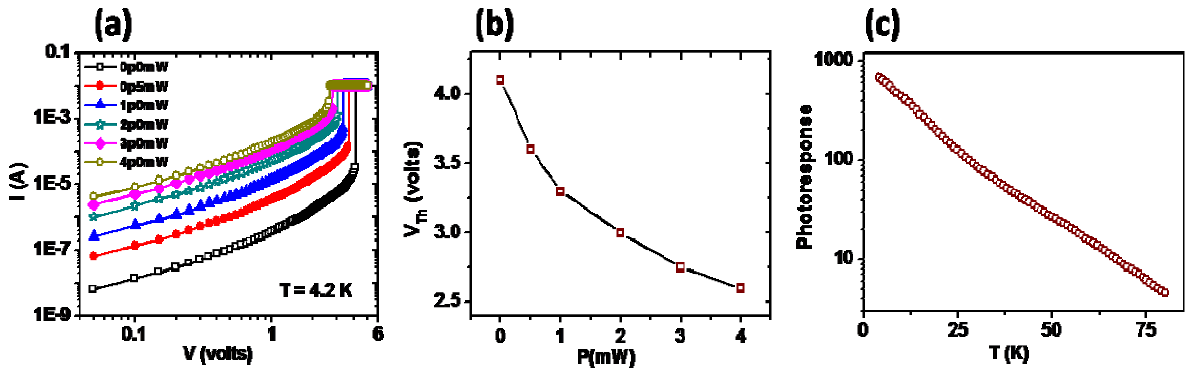

Fig. S11 (a) Current-voltage characteristics of nanowires synthesized using 100 nm pore diameter membrane, measured at 4.2 K for various laser powers. **(b)** Variation of threshold voltage as a function of laser power. **(c)** Temperature dependence of photoresponse measured at 20 mV bias in presence of 4 mW laser illumination. Like other nanowires showing switching transition, photoresponse decreases rapidly with increasing temperature.

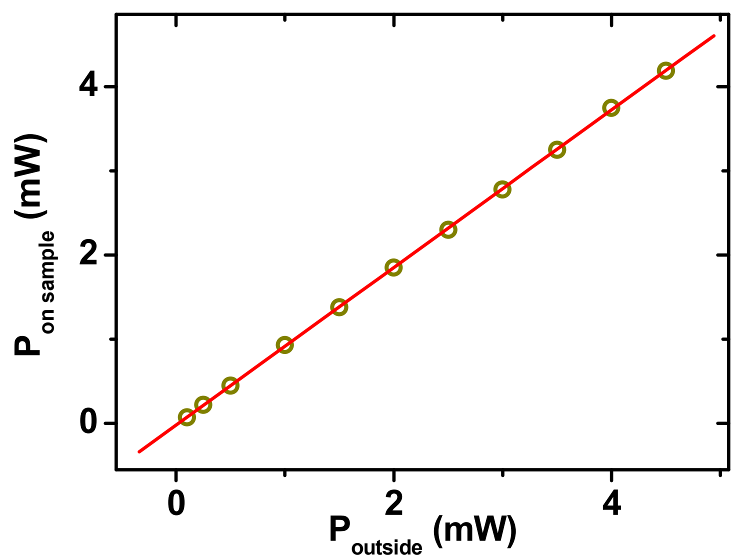

Fig. S12 Calibration curve (symbol) for actual laser power falling on the sample ($P_{on\ sample}$) inside the cryostat as a function of the laser power outside the cryostat ($P_{outside}$). A linear relationship between $P_{on\ sample}$ and $P_{outside}$ is observed over the entire range.

Ruling out filamentary conduction:

In our earlier publications[5, 6] we have shown that the observed switching is not due to filamentary conduction. If switching is due to the formation of conducting filament, then the switching to low resistive state will occur when the conducting filament will extend from one electrode to another electrode.[7-9] So if the separation between these electrodes increases then one needs larger bias voltage to establish a filamentary path between them. However, we have observed that larger diameter nanowires are longer but the switching threshold voltage is smaller than low diameter short nanowires. If the switching is due to the formation of conducting filament, then the switching threshold should not show systematic variation on the diameter of the nanowires[6] rather should depend on the length of the nanowires. Also in the case of filamentary conduction, noise in the high resistive state is higher than the low resistive state,[7] whereas we see an enhancement of noise in the low resistive switched state.[5-6] In our recent publication, we have shown that, switching threshold increases if we incorporate gold nanoparticles in these system;[10] if the switching transition is due to the formation of conducting filament then incorporation of gold nanoparticle will enhance the formation of filamentary path and the switching threshold should decrease. The observed switching transition cannot be explained by movement of Oxygen ion (often observed in filamentary conduction) or on the basis of a redox reaction because in these case the change in conductance is permanent whereas, we see a reproducible switching transition even after several thermal cycles.

Reference

1. Rahman, A.; Sanyal, M. K.; Gangopadhayy, R.; De, A.; Das, I. Evidence of a Ratchet Effect in Nanowires of a Conducting Polymer. *Phys. Rev. B* **2006,** 73, 125313.

2. Sze, S. M. *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, **1981**), p. 762.

3. Rahman, A.; Sanyal, M. K. Negative Capacitance in Wigner Crystal Forming Polymer Nanowires. *Appl. Phys. Lett.* **2009,** 94, 242102.

4. Konstantatos, G; Sargent, E. H. Nanostructured Materials for Photon Detection. *Nat. Nano.* **2010,** 5, 391-400.

5. Rahman, A.; Sanyal, M. K. Novel Switching Transition of Resistance Observed in Conducting Polymer Nanowires. *Adv. Mater.* **2007,** 19, 3956-3960.

6. Rahman, A.; Sanyal, M. K. Observation of Charge Density Wave Characteristics in Conducting Polymer Nanowires: Possibility of Wigner Crystallization. *Phys. Rev. B* **2007,** 76, 045110.

7. Asamitsu, A.; Tomioka, Y.; Kuwahara, H.; Tokura, Y. Current Switching of Resistive States in Magnetoresistive Manganites. *Nature* **1997,** 388, 50-52.

8. Sakamoto, T.; Sunamura, H.; Kawaura, H.; Hasegawa, T.; Nakayama, T.; Aono, M. Nanometer-Scale Switches Using Copper Sulfide. *Appl. Phys. Lett.* **2003,** 82, 3032.

9. Szot, K.; Speier, W.; Bihlmayer, G.; Waser, R. Switching the Electrical Resistance of Individual Dislocations in Single-Crystalline $SrTiO_3$. *Nat. Mater*. **2006,** 5, 312-320.

10. Sarma, A.; Sanyal, M. K.; Rahman, A.; Satpati, B. Hybrid Nanotubes: Single Step Formation of Homogeneous Nanotubes of Polypyrrole-Gold Composites and Novel Switching Transition of Resistance beyond Liquid Nitrogen Temperature. *J. Appl. Phys.* **2012,** 112, 044304.