Supporting Information

Polythiophene Derived Nickel Cobaltite Nanocomposite Showing Excellent Photo-switching and Photo-assisted Enhanced Supercapacitor Properties

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Instrumentation:

^{1}H NMR Spectra:

The ^{1}H-NMR spectra of the T, PT, PTNCO-1 and PTNCO-2 were recorded in $CDCl_3$ on a 500 MHz Bruker instrument.

Size Exclusion Chromatography (SEC):

The SEC experiment of PT was performed on a Waters instrument equipped with Waters 1515 pump, Waters 2414 differential refractive index detector, and three μ-Styragel columns. Here, polystyrene was used as the standard and tetrahydrofuran was used as the eluting solvent. The molecular weight range of the PS standards used for SEC analysis are 1320, 6770, 51200, 282000 and 791000 Da.

FTIR spectra:

The FTIR spectra of PT, NCO, PTNCO-1 and PTNCO-2 were measured using KBr pellets in a Perkin-Elmer FTIR (FT-IR-8400S) instrument.

Raman spectra:

The Raman spectra of PT, NCO, PTNCO-1 and PTNCO-2 were recorded using a Raman spectrometer (T64000, Horiba-Jobin Yvon) excited through a 514.5 nm laser.

X-ray diffraction study:

X-ray diffraction (XRD) experiments of PT, NCO, PTNCO-1 and PTNCO-2 were performed with a Bruker AXS diffractometer (model D8 Advance) using a Lynx Eye detector. The instrument was operated with 40 mA current at 40 kV voltage. Xerogels were kept on glass slides and were scanned in 2θ = 1-85° range at 0.3 s/step scan rate, with a step width of 0.02°.

Field Emission Scanning Electron Microscopy (FESEM):

The morphology of PT, NCO, PTNCO-1 and PTNCO-2 were monitored by FESEM instrument (FE-SEM, JEOL, JSM 6700 F). A small drop of THF solution (0.58 mg /mL) of

each sample was casted on microscopic cover slip at 30°C, then dried and finally preserved at vacuum for 2 days before the FESEM images were taken.

EDX Analysis:

EDX analysis of NCO, PTNCO-1 and PTNCO-2 were also performed by FESEM (JEOL, JSM 6700F) instrument.

High Resolution Transmission Electron Microscopy (HRTEM):

The morphology of PT, NCO, PTNCO-1 and PTNCO-2 were monitored by HRTEM instrument (JEOL, 2010EX) operated at an acceleration voltage of 200 kV and fitted with a charge-coupled device (CCD) camera. A small drop of THF solution of each sample was drop-casted on a carbon-coated copper grid at 30°C, then dried, and finally preserved at vacuum for 2 days before the HRTEM images were taken.

UV−vis and Photoluminescence (PL) Spectroscopy:

The UV−vis spectra of PT, PTNCO-1 and PTNCO-2 were taken in THF solutions (0.5 mg/mL) from 190 to 1100 nm using a UV−vis spectrophotometer (Hewlett-Packard, model 8453) at 30°C. The photoluminescence (PL) spectra of the samples in THF solutions (1 mg/mL) were recorded in a Fluoromax-3 instrument (Horiva Jovin Yvon) at 30°C. The sample was taken in a quartz cell of 1 cm path length. It was excited at 400 nm and the emission scans were recorded from 420 to 750 nm using a slit width of 2 nm with an increment of 1 nm wavelength having an integration time of 0.1 s.

TCSPC study:

The lifetime measurements were performed using the time correlated single photon counting (TCSPC, Horriba). The light emitting diode source of 403 nm was used for excitation and the emitted photon was measured at 580 nm

X-ray photoelectron spectrometry (XPS):

XPS spectrum of NCO and PTNCO-1 (cast from THF solution) were performed with an Omicron Nano Technology (model 0571) XPS spectrometer, using an aluminium anode and an Al Kα X-ray source (1486.8 eV).

N_2 adsorption/desorption studies of Nanocomposites:

Nitrogen adsorption and desorption isotherms of NCO, PTNCO-1 and PTNCO-2 were measured at 77 K using an Anton Paar Quanta Tec Inc. iSorb HP1 gas adsorption analyzer. The sample was degassed at 120°C for 3 h prior to the measurement.

DC-conductivity, current-voltage (*I-V*) and photo current measurements:

The dc-conductivity of PT, NCO, PTNCO-1 and PTNCO-2 were measured with Keithley source meter (model 2410) using films casted from dilute (2% w/v) solutions on ITO strip and was sandwiched with another ITO electrode. The conductivity values were calculated from the equation $\sigma = (1/R) \times (d/a)$ where R is the resistance, a is the area of the electrode, and d is the thickness of the samples. For both conductivity and *I-V* measurement the films were dried after keeping in vacuum for 2 days at 30°C to eliminate any moisture effect. For photocurrent measurement, Keithley source meter (model 2401) with 150 W xenon lamp source (Newport Corp., Springfield, OH; model 67005) was used for light illumination. PD and PDAg xerogel was dispersed in a 7:3 mixture of m-cresol and chloroform, followed by sonication for 1 hr. Then it was casted over the ITO glass and was dried under vacuum at 60°C for 24 hrs. Thin films were produced over the ITO and it was sandwiched with another ITO electrode for photocurrent measurement.

Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD) studies:

The above two experiments, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves of NCO, PTNCO-1 and PTNCO-2 were performed in a three-electrode system at room temperature using an electrochemical station (CHI600E). Glassy carbon electrode (GCE) was used as the working electrode, saturated Ag/AgCl electrode was used as the

reference electrode, Pt wire was used as the counter electrode. 1 (M) KOH was taken as the electrolyte for all the three electrodes. All the three electrodes were prepared by casting a slurry, containing 80% of the active material with 10% Carbon Black and 10% PVDF in (1:1) 1-methyl-2-pyrrolidone (NMP)/cresol medium, onto GCE. Then drop-casted GCE's were dried in vacuum at 50^{o}C for 48 h.

Solid State Supercapacitor (Two Electrode) and Device Fabrication:

The charge storage performance of PTNCO-1 both in dark and UV light (365 nm) irradiation condition were compared by processing CV and GCD tests in two electrode cell configurations containing two symmetrical electrodes. In this regard, we have used flexible carbon cloth where the above-mentioned slurry was deposited over 1 × 1 cm^2 area. The flexible carbon cloth paper having PTNCO-1 (mass loaded = 2.0 mg/cm^2) was used as the working electrodes. To understand the passage of light through the carbon cloth-based sandwiched supercapacitor we have measured transmittance data introducing a quartz plate into the sandwiched carbon cloth[S1] and also that of a quartz plate using UV-Vis spectrometer. The transmittance data shows that 87% transmittance through quartz plate and 20% transmittance through the sandwiched carbon cloth are observed. So, more than 20% transmittance of UV light (λ=365 nm) through the sandwiched carbon cloth is occurring. After deposition, electrodes were dried in vacuum at 50°C for 48 h. After that, the devices were fabricated by placing one surface coated electrode on the top of another such electrode in a head on fashion separated by PVA/KOH gel electrolyte. To produce the gel electrolyte, 100 mg of PVA was first dissolved in 25 mL of HPLC grade water by stirring the solution in an oil bath at 90°C for 1 h. Then aqueous KOH (~112 mg) solution (10 mL) was added drop wise into a previously prepared PVA solution under the same condition and kept it in oil bath for another 1 h to make the solution completely clear. Then it was allowed to cool at room

temperature to obtain PVA/KOH gel electrolytes.[S2] The fabricated devices were dried at 50°C for 48 h prior to electrochemical tests after carefully sealed with scorch tape.

Impedance Spectra (IS):

Impedance spectroscopic analyses of NCO, PTNCO-1 and PTNCO-2 were performed using the drop casted film (mass loaded = 2.0 mg/cm^2) from the same slurry composition as mentioned above on the nickel coin cell of area 1 cm^2 and then dried in a vacuum oven at 50°C for 24 h. Then both the electrodes were sandwiched with each other having the same PVA/KOH gel electrolyte separator in between them to fabricate the working electrode. Now this cell has been fitted between two copper plates with a thickness of 4 mm tightly with screws which act as current collectors. The spectra were recorded using CorrTest Potentiostat/Galvanostat in a symmetric two-electrode system within a frequency range of 100 kHz to 0.1 Hz at 0.5 V DC bias voltage. The experimental results were fitted and analysed using the Z-view software.

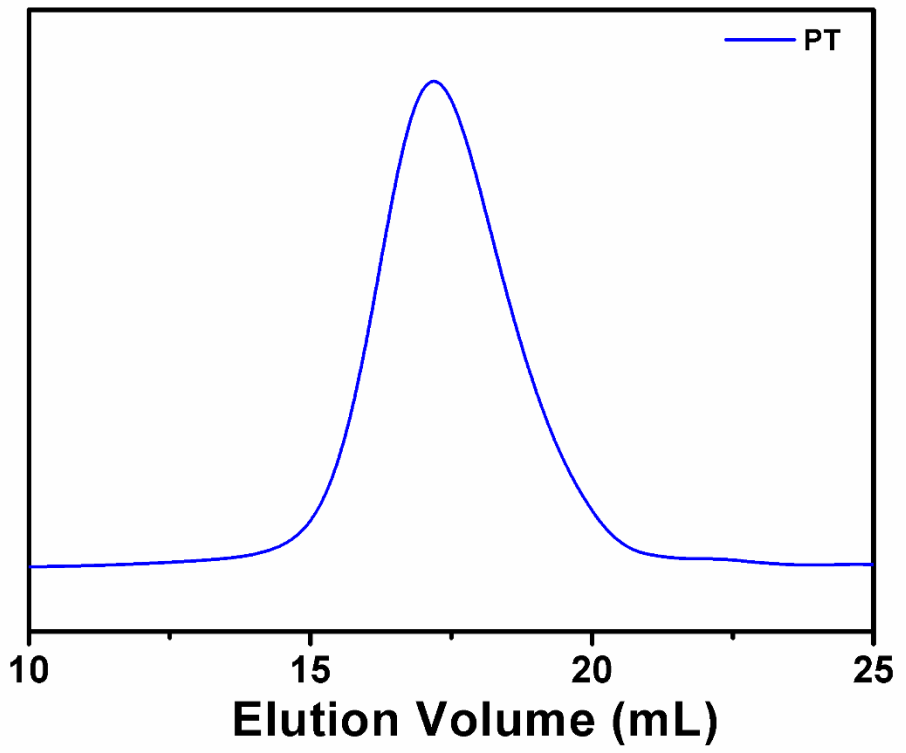

Fig. S1. SEC trace for PT in THF medium.

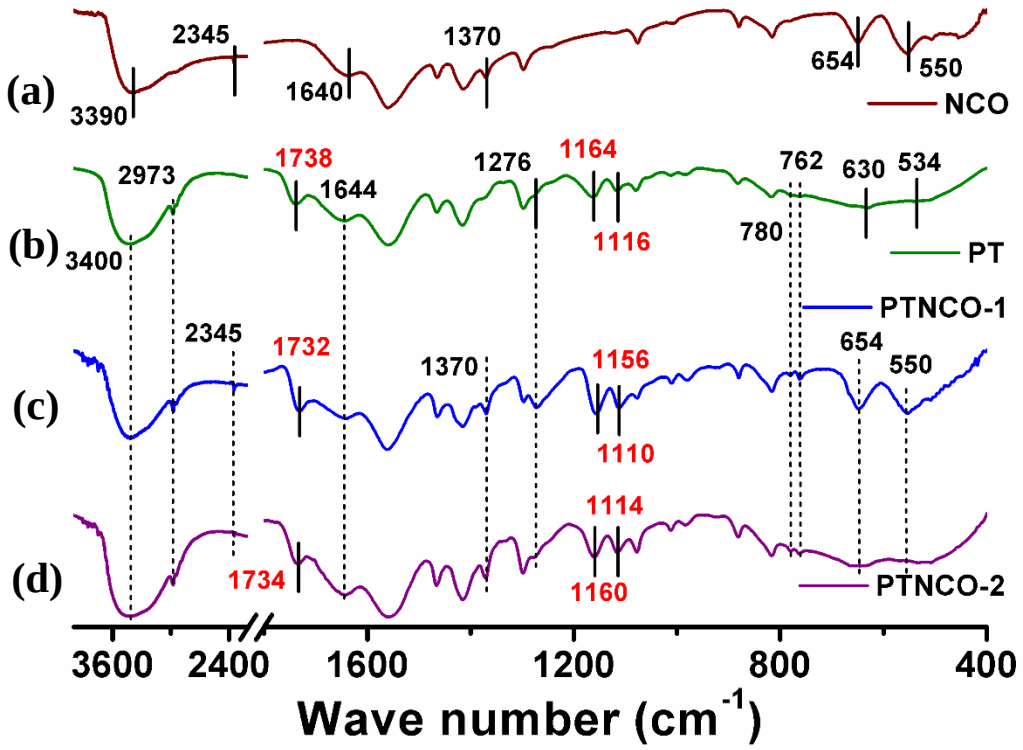

Fig. S2. FTIR spectra of (a) NCO, (b) PT, (c) PTNCO-1 and (d) PTNCO-2.

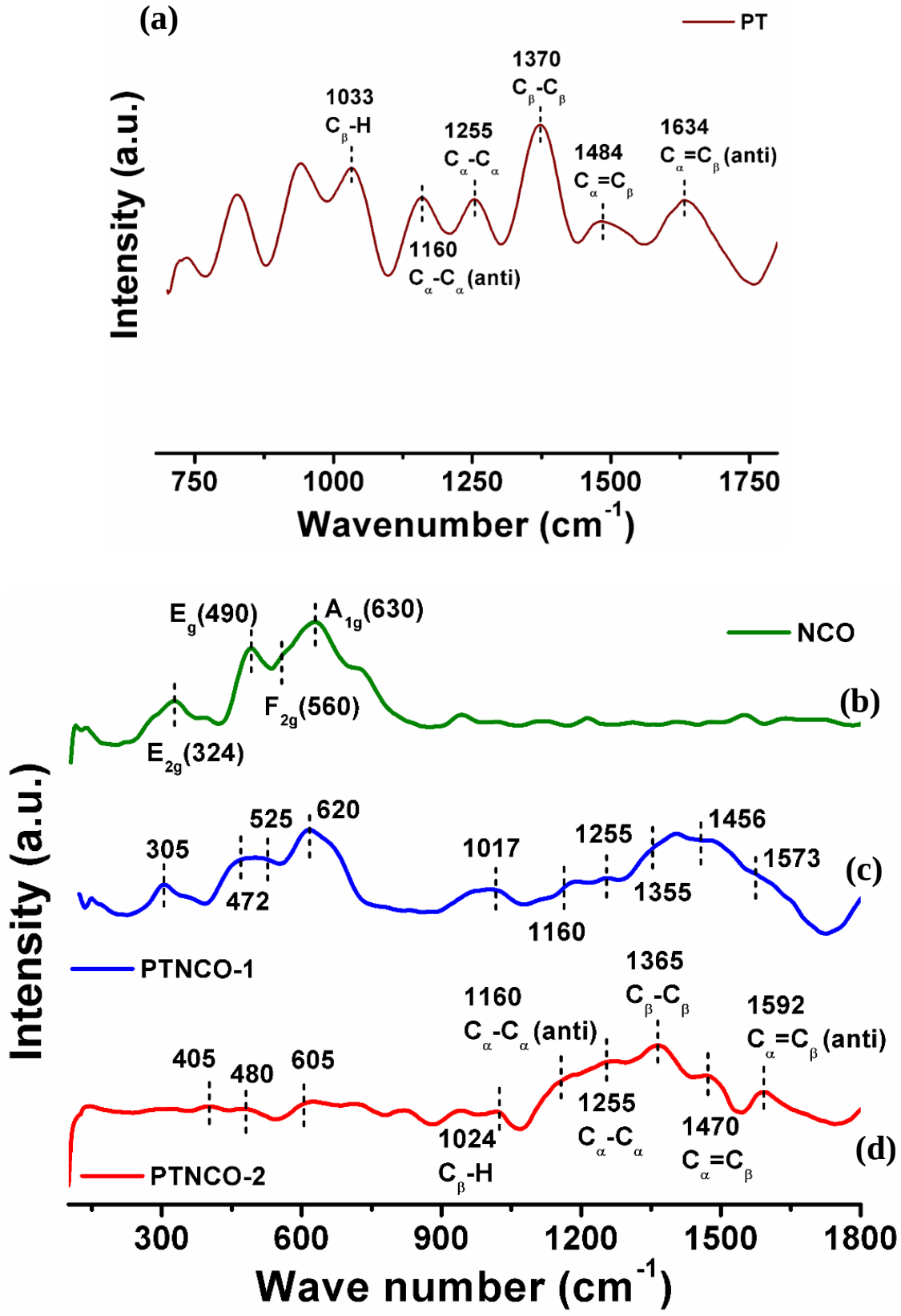

Fig. S3. RAMAN spectra of (a) NCO, (b) PT, (c) PTNCO-1 and (d) PTNCO-2.

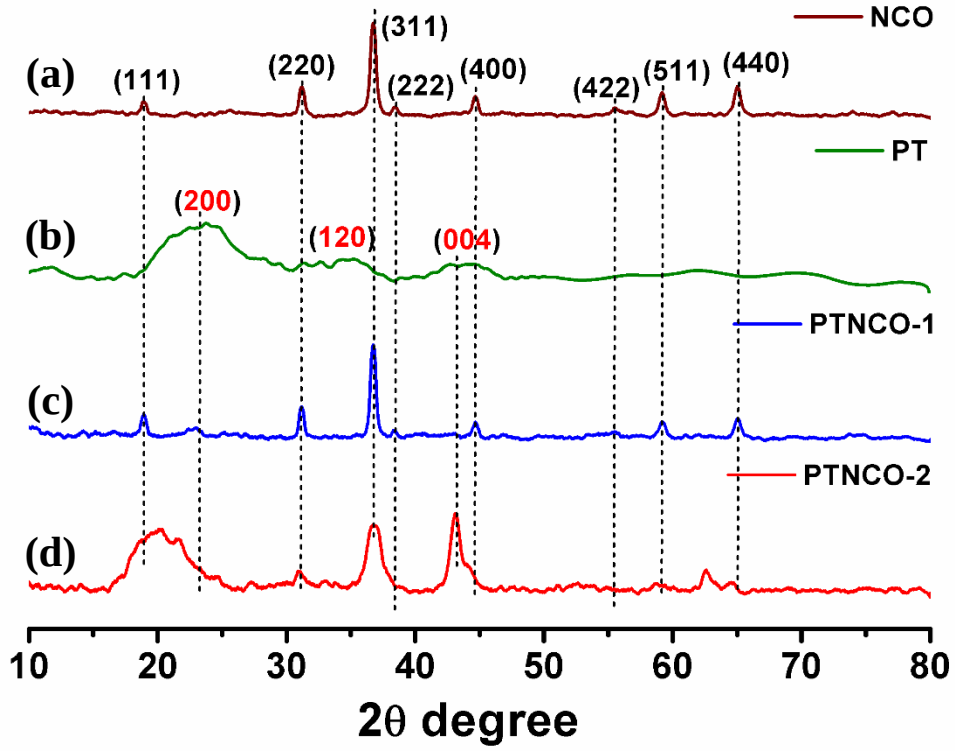

Fig. S4. XRD pattern of (a) NCO, (b) PT, (c) PTNCO-1 and (d) PTNCO-2.

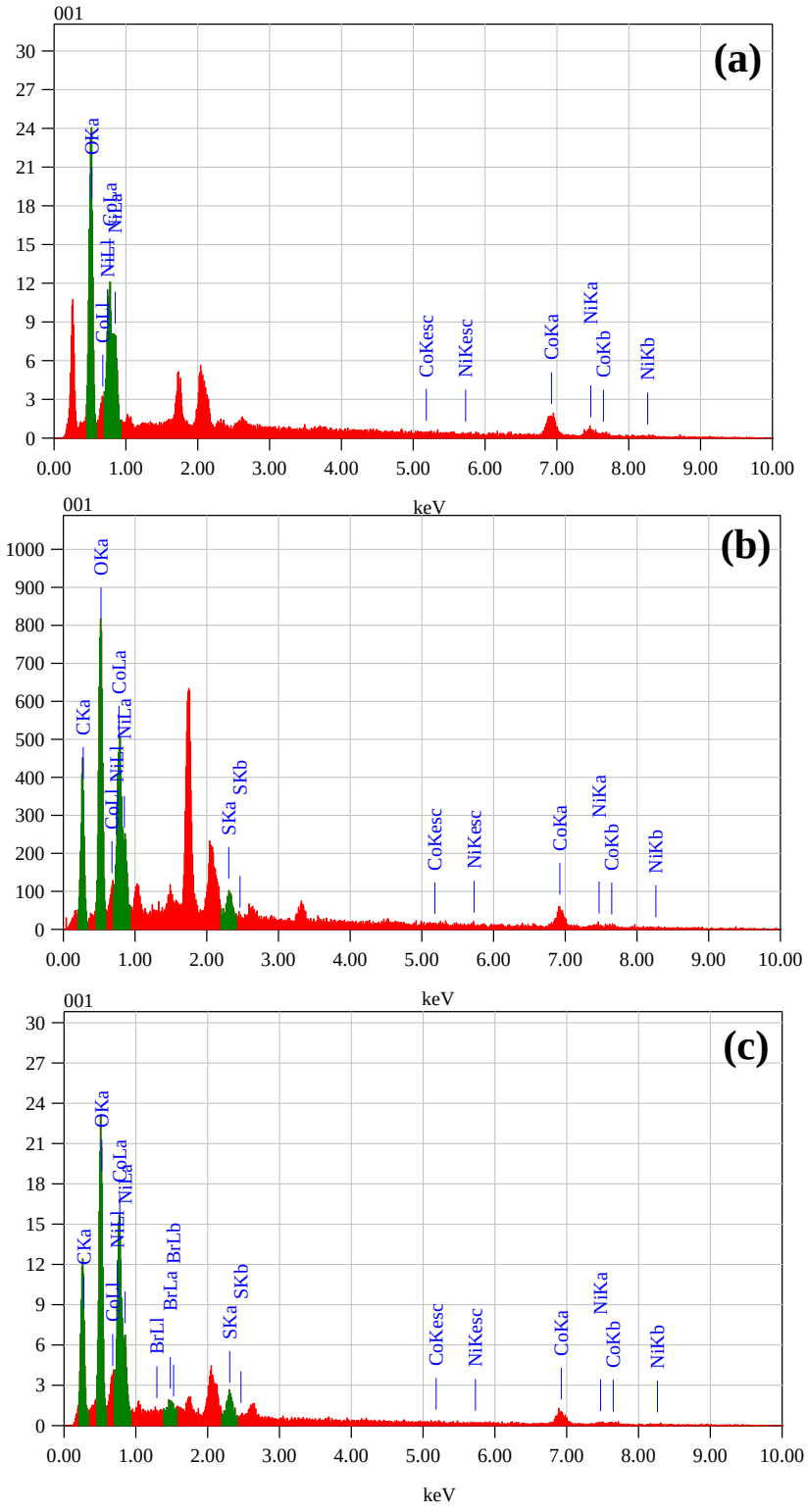

Fig. S5. EDX spectrum analysis of (a) NCO, (b) PTNCO-1 and (c) PTNCO-2.

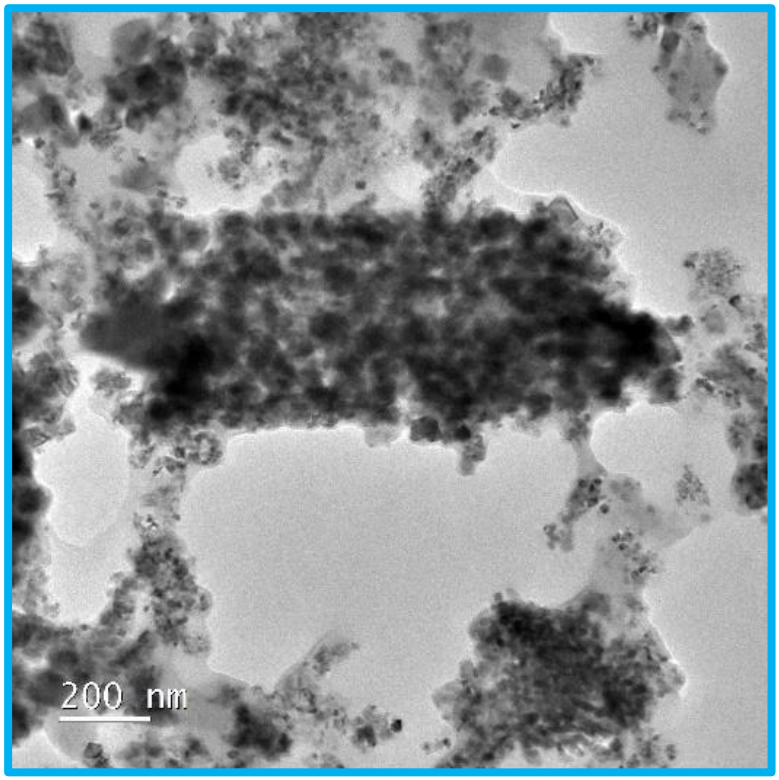

Fig. S6. HRTEM analysis of PTNCO-2

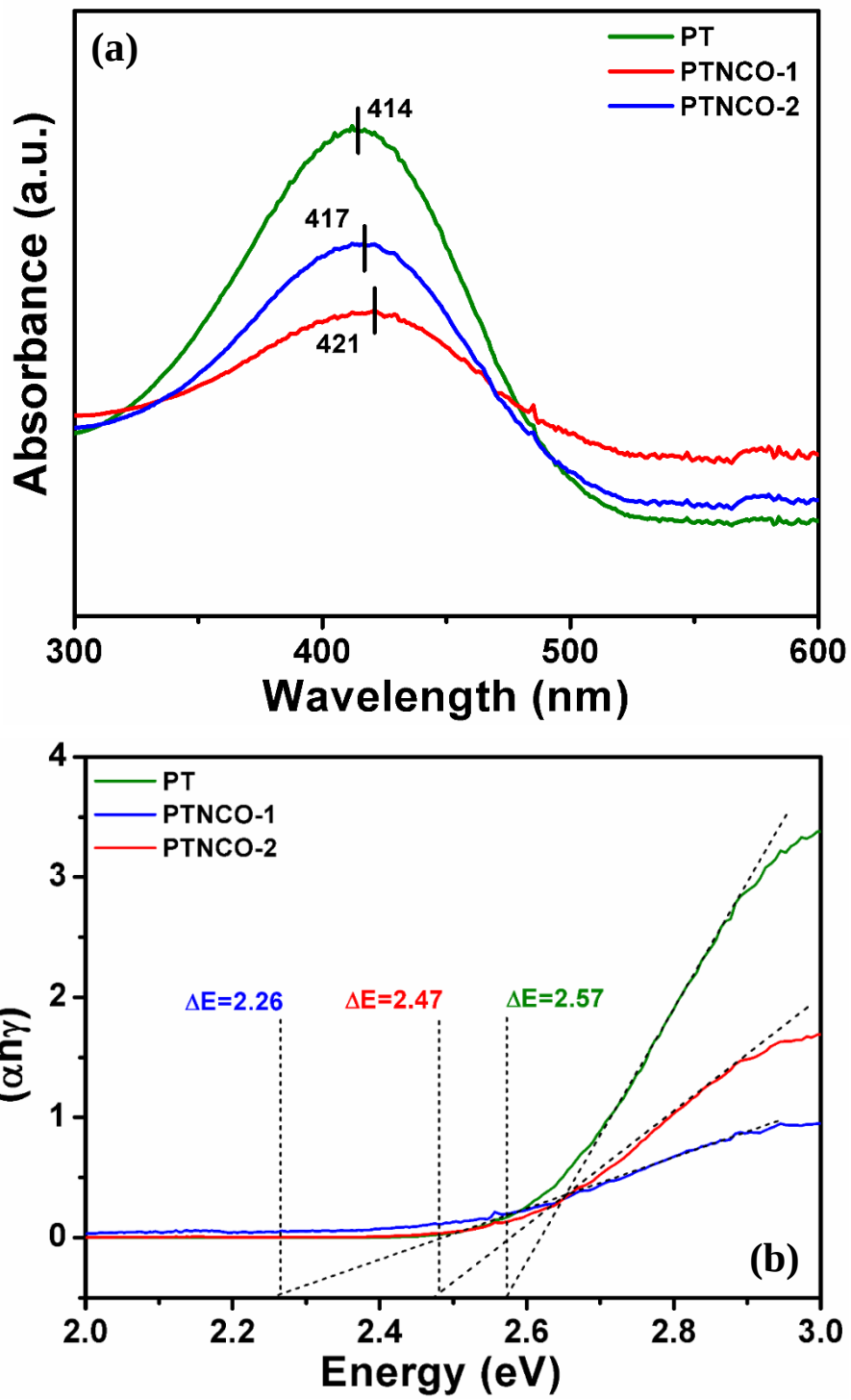

Fig. S7. Images of (a) UV–Vis spectra and (b) Tauc plot of PT, PTNCO-1 and PTNCO-2 in THF solution.

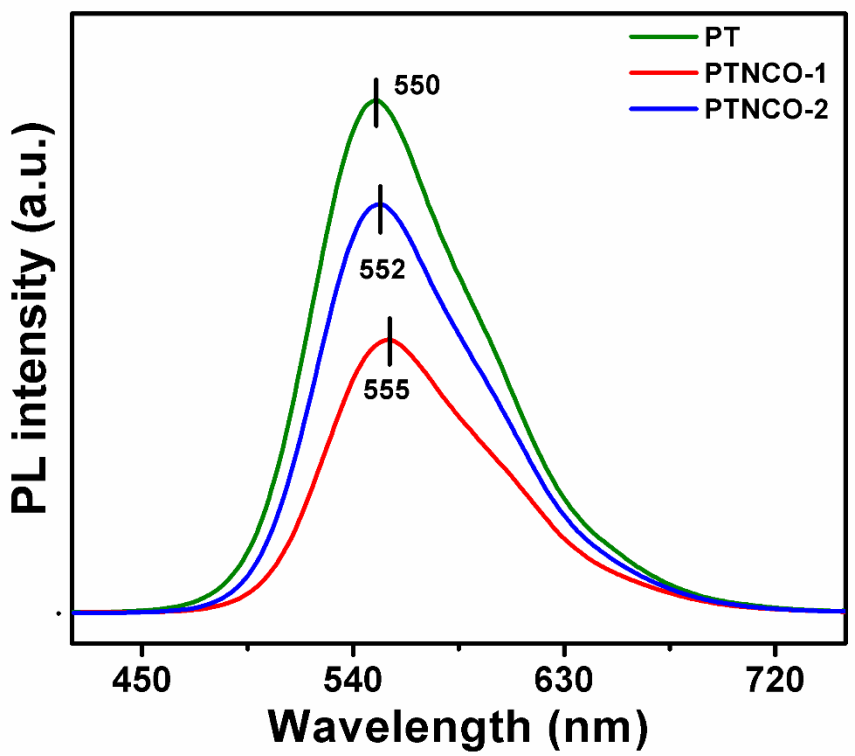

Fig. S8. Photo-luminescence spectrum of PT, PTNCO-1 and PTNCO-2 in THF solution.

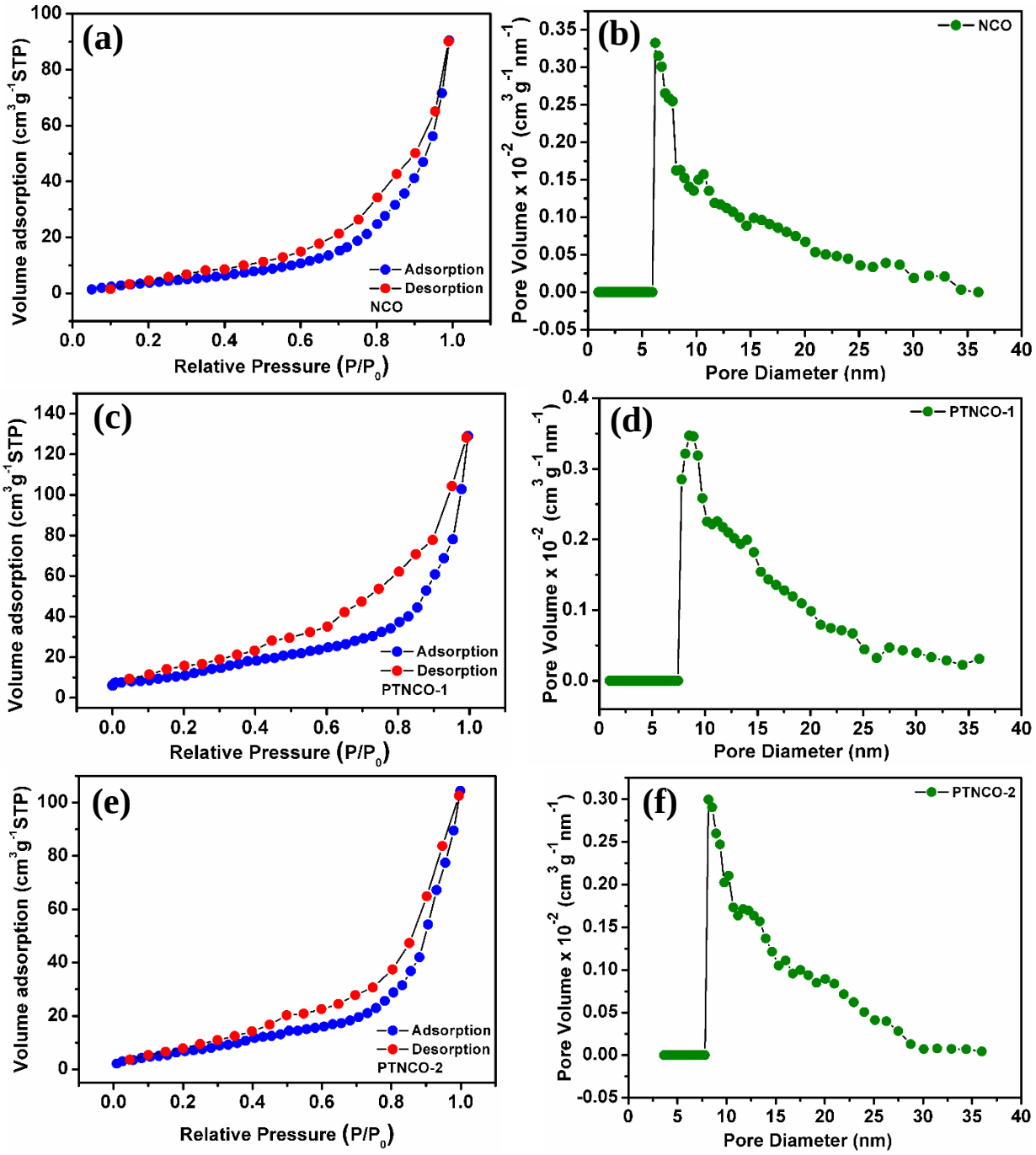

Fig. S9. N_2 adsorption / desorption isotherms of (a) NCO, (c) PTNCO-1 and (e) PTNCO-2, pore size distribution of (b) NCO, (d) PTNCO-1 and (f) PTNCO-2 by NL-DFT method.

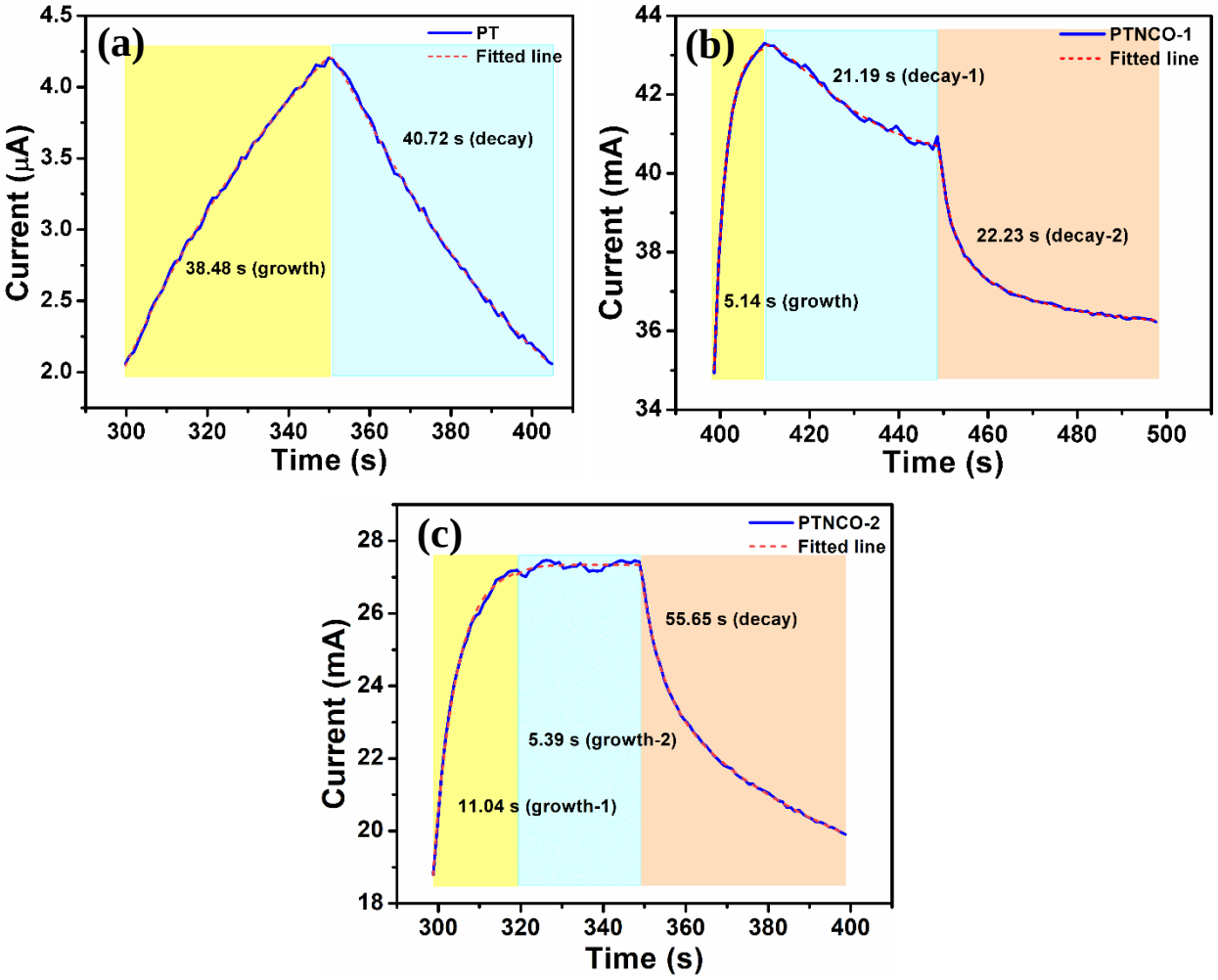

Fig. S10. Photo-switching curves fitted with biexponential function of equation (2) and (3) of (a) PT (b) PTNCO-1 and (c) PTNCO-2.

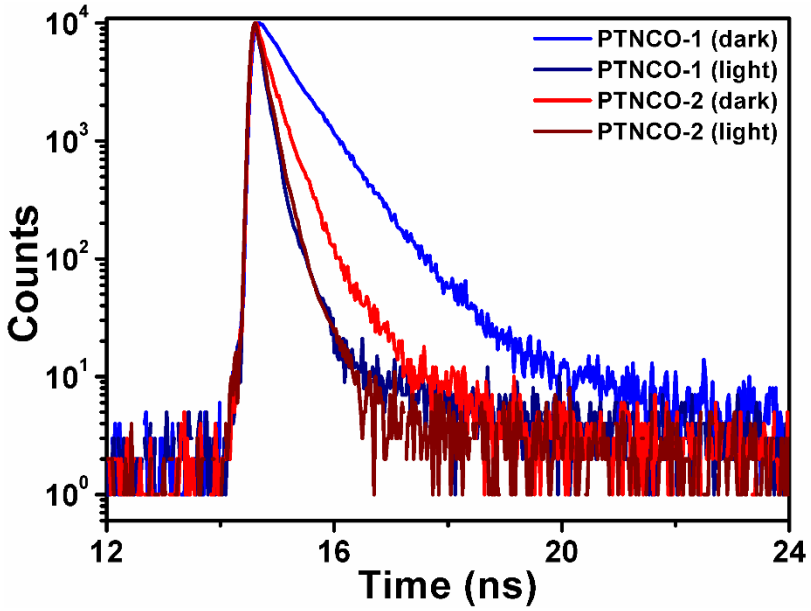

Fig. S11. TCSPC study of the PTNCO-1 and PTNCO-2 film before and after the irradiation of light (1 sun intensity).

Table S1: Fluorescence decay fitting parameters of photoactive electrodes at λ_{ex} of 403 nm deduced from bi-exponential fits.

Sample (film)	B_1	τ_1 (ns)	B_2	τ_2 (ns)	τ (ns)	χ^2
PTNCO-1 (dark)	97.26	0.441	2.74	2.06	0.451	1.130
PTNCO-1 (light)	98.05	0.037	1.95	0.618	0.038	1.075
PTNCO-2 (dark)	97.61	0.638	2.39	2.522	0.650	1.155
PTNCO-2 (light)	97.39	0.049	2.61	0.863	0.050	1.095

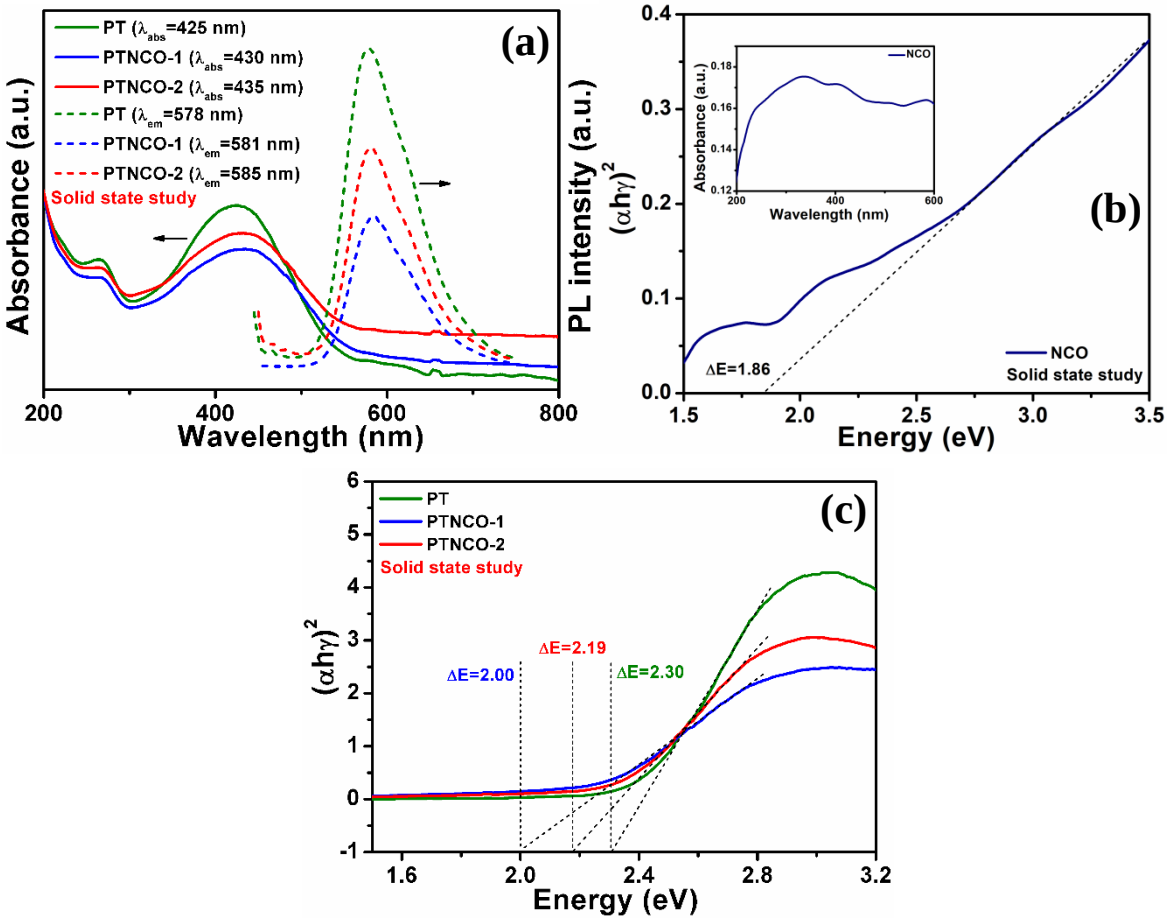

Fig. S12. Images of (a) UV–Vis and PL spectra of PT, PTNCO-1 and PTNCO-2, (b) Tauc plot of NCO and (c) Tauc plot of PT, PTNCO-1 and PTNCO-2 in solid state.

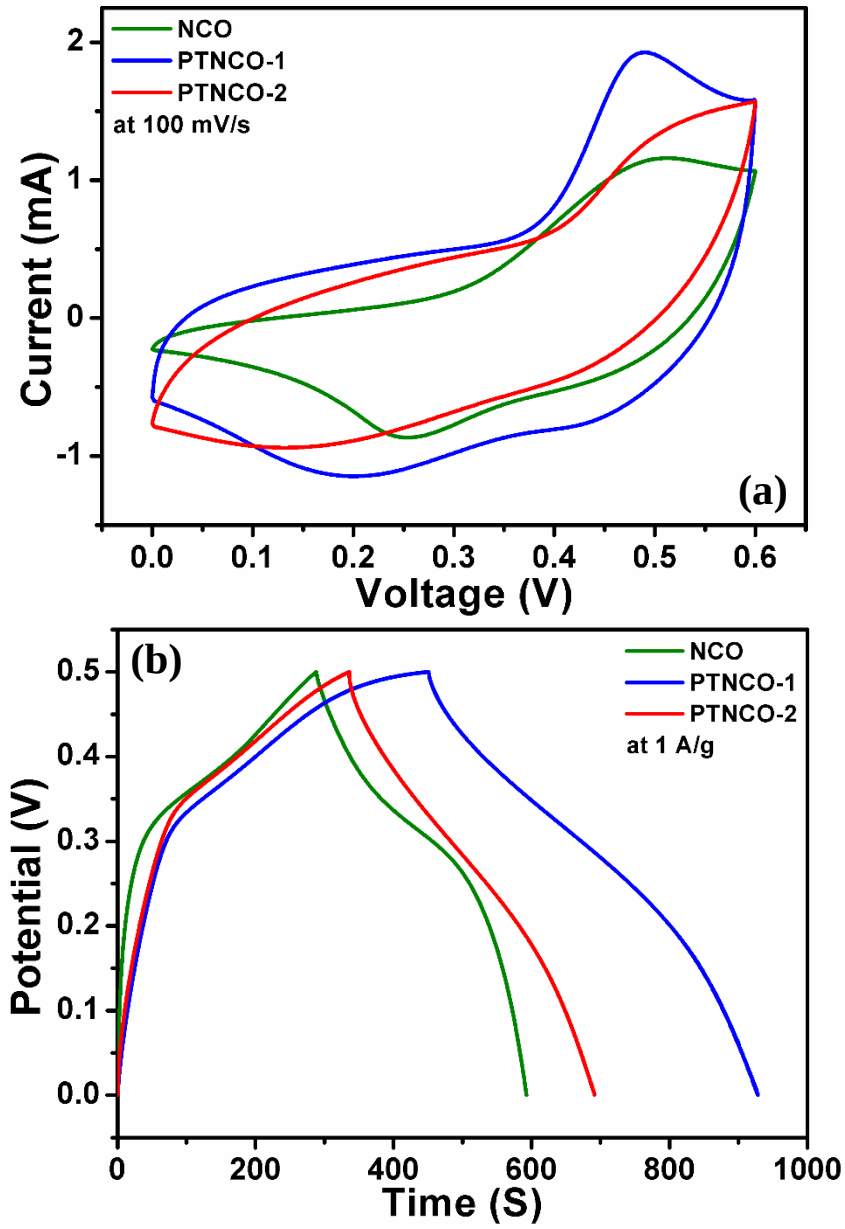

Fig. S13. Overlay of (a) Cyclic voltammograms of NCO, PTNCO-1 and PTNCO-2 at 100 mV/s scan rates and (b) GCD plots of NCO, PTNCO-1, and PTNCO-2 at 1 A/g current density.

Table S2: Comparison of C_S of $NiCo_2O_4$ nanostructured based supercapacitor (using three electrodes) with the literature data

Electrode Material	Working Electrode	Electrolyte	Specific Capacitance (F/g)	Measuring Condition	Ref.
$NiCo_2O_4$/rGO/PPy	Glassy carbon electrode	1(M) KOH	1547	0.5 A/g	S2
50% GNPLs/PTh	Silver plate	1(M) H_2SO_4	673	0.25 A/g	S3
$NiCo_2O_4$/PPy@CPF	Ni-foam	3(M) KCl	901	1 A/g	S4
Polythiophene/Al_2O_3	---	1(M) KCl	554.03	1 A/g	S5
$NiCo_2O_4$/NG	Ni-foam	6(M) KOH	1273.13	0.5 A/g	S6
$NiCo_2O_4$/GF	Copper sheet	6(M) KOH	1402	1 A/g	S7
$NiCo_2O_4$/g-C_3N_4	---	6(M) KOH	253	2 A/g	S8
$NiCo_2O_4$-ECN	Ni foil	6(M) KOH	596.8	2 A/g	S9
$NiCo_2O_4$/NPC	---	1(M) KOH	948.30	1 A/g	S10
$NiCo_2O_4$/YS/graphene	Ni foam	6(M) KOH	835.7	0.5 A/g	S11
$NiCo_2O_4$/PANI	Stainless steel wire meshes	0.5(M) H_2SO_4	439.4	5 mA/cm^2	S12
P3HT/SWCNTs	---	0.1 (M)$LiClO_4$ + CH_3CN	245.8	0.5 A/g	S13
PTNCO-1	**Glassy carbon electrode**	**1(M) KOH**	**958**	**1 A/g**	**This work**

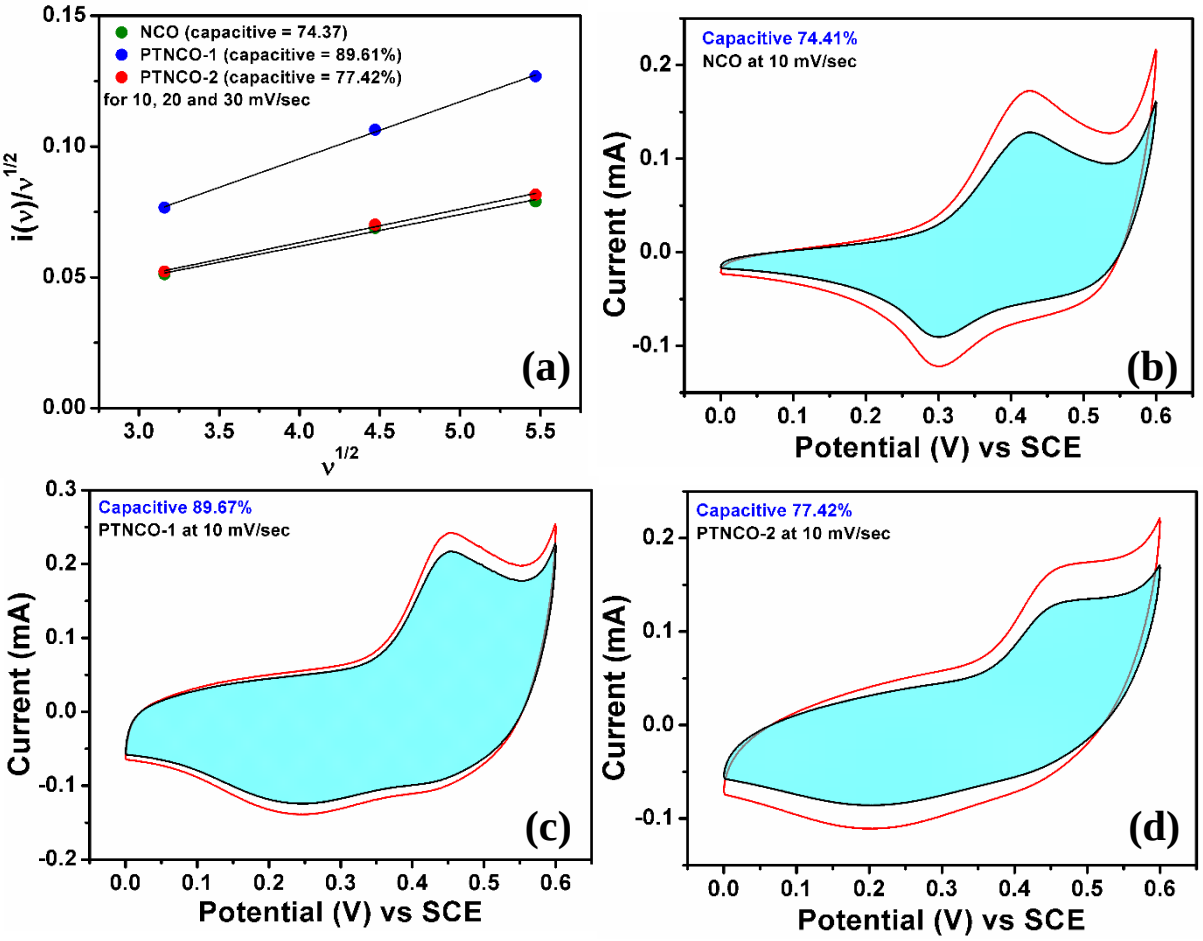

Fig. S14. Plot of (a) $i(\nu)/\nu^{1/2}$ vs $\nu^{1/2}$ for all three electrodes, Dunn method analysis of capacitance contribution of (b) NCO, (c) PTNCO-1 and (d) PTNCO-2 three electrodes at 10 mV/sec scan rate.

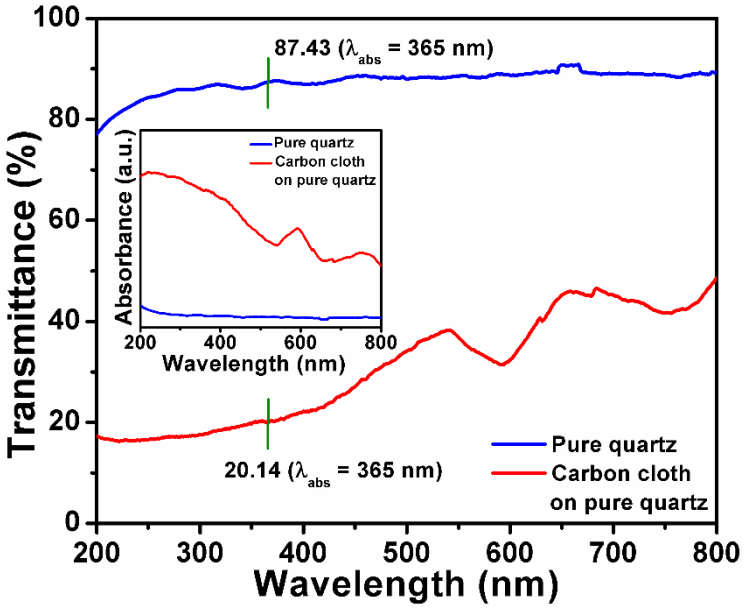

Fig. S15. Transmittance spectrum of carbon cloth on pure quartz. The absorbance spectrum of the corresponding transmittance is given in inset as well.

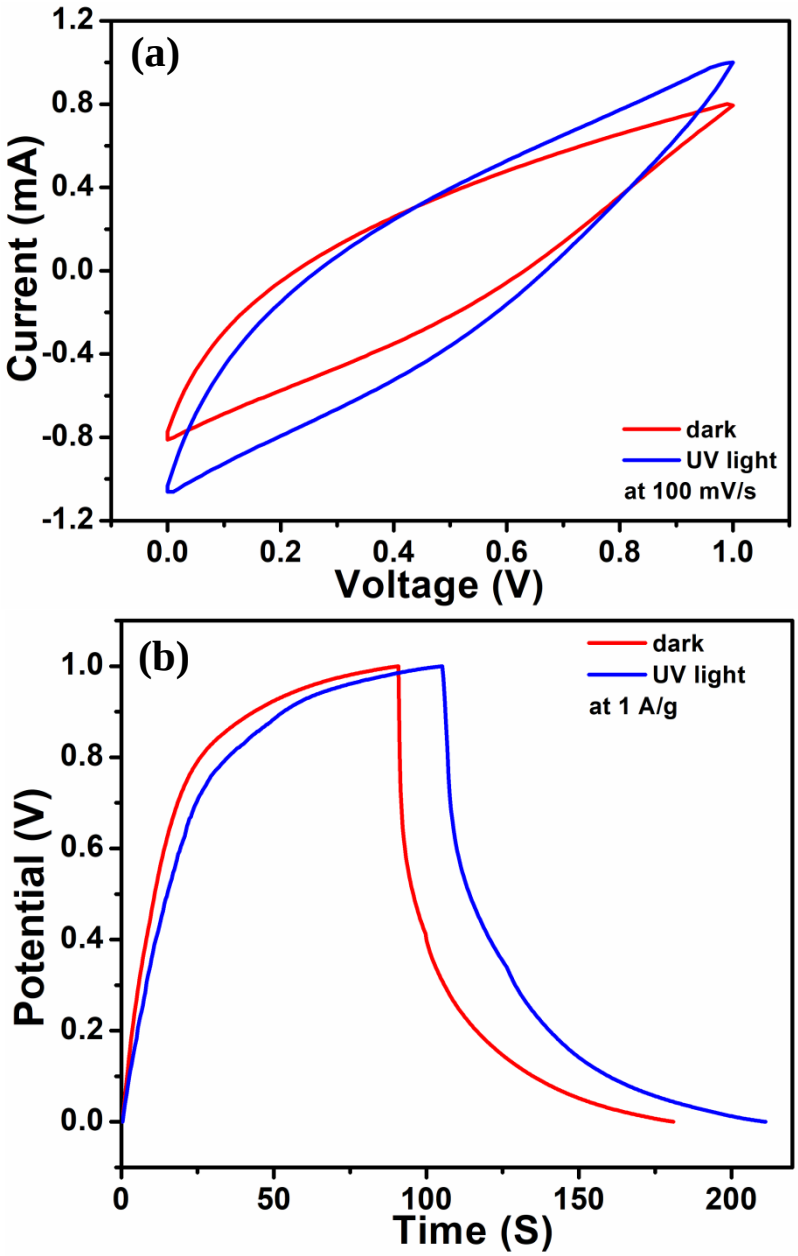

Fig. S16. Overlay of (a) Cyclic voltammograms at 100 mV/s scan rates and (b) GCD plots at 1 A/g current density of PTNCO-1 under dark and UV light condition at 2 electrode system.

Table S3: Comparison of C_S of $NiCo_2O_4$ nanostructured based supercapacitor electrodes (two) from literature data.

Electrode Material	Electrolyte	Specific Capacitance	Measuring Condition	Ref.
$NiCo_2O_4$/rGO/PPy	PVA-KOH	157 F/g	0.5 A/g	S2
$NiCo_2O_4$/PPy@CPF	PVA-KOH	118.6 F/g	1 A/g	S4
$NiCo_2O_4$/YS/graphene	6(M) KOH	88.25 F/g	1 A/g	S11
$NiCo_2O_4$/PPy asymmetric capacitor	2 (M) KOH	128.3 F/g	0.4 A/g	S14
$NiCo_2O_4$/PANI/MF asymmetric capacitor	3 (M) KOH	110 F/g	0.75 A/g	S15
$NiCo_2O_4$/MSBPC	PVA/KOH	60 F/g	1 A/g	S16
$NiCo_2O_4$@PPy	PVA/KOH	14.2 F/cm^3	63.7 mA/cm^3	S17
$NiCo_2O_4$@CNF55//N-rGO	PVA/KOH	134 F/g	1 A/g	S18
MWCNT/PTh	0.5(M) H_2SO_4	110 F/g	1 A/g	S19
CNT/PTh	1(M) KOH	0.057 F/g	0.2 A/g	S20
Mesoporouscarbon/PTh	1(M) H_2SO_4	66.3 F/g	0.5 A/g	S21
CNT/PTh	1(M) H_2SO_4	125 F/g	1 A/g	S22
PTNCO-1	**PVA-KOH**	**106 F/g**	**1 A/g**	**This work**

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