

Supplementary Information

Poly [3-(2-hydroxyethyl)-2, 5-thienylene] grafted reduced graphene oxide: An efficient alternating material of TiO₂ for dye sensitized Solar Cell

Shreyam Chatterjee^a, Astam K. Patra^b, Asim Bhaumik^b and Arun K. Nandi*^a

^aPolymer Science unit, ^bDepartment of Materials Science, Indian Association for the
Cultivation of Science,
Jadavpur, kolkata- 700 032.

Experimental:

Preparation of acyl chloride functionalized reduced graphene oxide (frGO):

At first graphite oxide is prepared from graphite powder by oxidizing with KMnO_4 / NaNO_3 mixture in concentrated H_2SO_4 medium using Hummers method.¹ In this typical procedure, 75mg graphite oxide is dispersed in 75ml water (0.1% w/v). After sonication for 1 h in an ultrasonic bath (60W, frequency 28 KHz, Model AVIOC, Eyela), exfoliation of graphite oxide occurs and a clear brownish dispersion of graphene oxide (GO) is formed. Then the GO sample (40 mg) containing plenty active $>\text{COOH}$ groups on its basal planes and edges is refluxed with excess SOCl_2 (20 ml) for 24 h under, and then the residual SOCl_2 was removed by distillation under reduced pressure, and further dried under vacuum to yield the acyl chloride-functionalized reduced GO (frGO). It is reported that during functionalization by SOCl_2 GO gets reduced to rGO.

Covalent grafting of monomer 3-(2-hydroxyethyl)-2,5-thienylene (HET) with reduced graphene oxide (frGO):

The frGO is dispersed in 15 ml anhydrous THF, and the mixture is sonicated for 30 min in order to create a homogeneous dispersion. The dispersed sample is refluxed with 5mmol (0.64g = 445 μl) of 3-(2-hydroxyethyl)-2, 5-thienylene in the presence of a catalytic amount of triethylamine for 24 h under nitrogen atmosphere. The resulting reaction medium is diluted in excess THF. The resultant HET-g-rGO is collected by centrifuging the solution and is subsequently dried overnight under reduced pressure.

Oxidative polymerization of HET-g-rGO (PHET-g- rGO):

In a typical chemical oxidative polymerization process, the resultant HET-g-rGO and 20mmol (2.56g) FeCl₃ in 20 ml of dry chloroform is stirred in nitrogen atmosphere for 24 h at 30⁰C. The reaction medium is then diluted in excess methanol. The resultant product is collected by suction filtration and after washing with methanol for several times the product Poly [3-(2-hydroxyethyl)-2, 5-thienylene] grafted rGO (PHET-g- rGO) hybrid is dried in vacuum at 60⁰ C.

Hydrolysis of PHET-g-rGO:

Sodium hydroxide (400mg) mixed with a solution of PHET-g- rGO (750 mg) in DMF and the resulting mixture is stirred at 80⁰C for 4d. The thick solution was then filtered and poured into excess ethanol, which caused a solid to precipitate. The isolated solids were then washed with ethanol and deionised water to remove residual base. The resulting material is then vacuum-dried to get the weight percent of PHET in PHET-g-rGO. About 68% (w/w) PHET is grafted on the rGO part as determined from the hydrolysis of the PHET-g-RGO.

Thus the GPC (Waters 2414 RI detector and Water 515 HPLC pump) of the PHET is carried out in DMF using polystyrene as a standard giving the molecular weight (M_n) of 19468 with a 1.20 PDI.

Characterization:

TEM study has been made using a high resolution transmission electron micrograph (HRTEM, JEOL, Model-2010EX) directly under a voltage of 200 KV. Fourier transformed infrared (FTIR) spectra are made from a Perkin Elmer FTIR instrument (FTIR-8400S), UV-vis spectra is taken from Hewlett-Packard UV-vis Spectrophotometer (Model-8453). Fluorescence spectra are taken from Horiba Jobin Yvon Fluoromax 3

instrument. The samples were taken in a Quartz cell of path length one cm and were excited at 420 nm using slit width 2 nm both for excitation and emission with an increment of wavelength 1 nm having integration time 0.5 second. Nitrogen sorption isotherms were obtained using a Beckmann Coulter SA3100 surface area analyzer at 77 K. Prior to the measurement, the sample is degassed at 393 K for 12 h.

Conductivity and I- V Measurement:

The dc-conductivity of pure PHET and PHET-g-rGO are measured by taking the sample pallets between the two gold electrodes. The area of the samples and the thickness of the samples are measured by a screw gage. The conductivity (σ) of the samples are measured by an electrometer (Keithley, model 617) by two probe technique at 30°C using the equation: $\sigma = 1/R(l/a)$, where 'l' is the thickness and 'a' is the area and 'R' is the resistance of the sample. I-V characteristic curves of the samples are made by two-probe method using the same procedure by applying voltage from -5.0 to +5.0 V for both pure PHET and PHET-g-rGO nanocomposites and then measuring the current at each applied voltage.

Photocurrent Device Fabrication and Measurement:

For the photo current measurements, two gold electrodes of ~ 50 nm thicknesses are thermally deposited in circular form with a diameter of 1 mm through a shadow mask at a separation of 4 mm on the surface of pure PHET and PHET-g-rGO pallets. The photocurrent is measured by illuminating the samples with white light from a xenon lamp operating at 150 W using a spectral illuminator system (model 69907, New-port Corp, USA) under 5V bias conditions.

DSSC cell construction:

The PHET-g-rGO is dispersed in 1,4 dichloro benzene and film is casted on a ITO strip and is dried in air.. It is then immersed in a 0.5 mM ethanolic solution of a N719 (a ruthenium dye) for 12 h. The counter electrode is a graphite coated ITO glass plate (2x2 cm²-same type of ITO used as the substrate for pure PHET and PHET-g-rGO nanocomposites). The iodide-triiodide- based electrolyte solution, consisting of 0.5 M KI, 0.05 M I₂, and γ -butyrolactone are placed on the active electrode area drop-wise. The average active electrode area is ~ 0.72 cm². The electrodes are separated by a 60- μ m parafilm and sandwiched together with clips. A small space of bare ITO glass is uncovered for wire connection to the anode. The configuration of the solar cell is achieved by putting the pure PHET and PHET-g-rGO nanocomposites face of the ITO substrate on the top of the counter electrode in face-to-face fashion. The DC current between the two electrodes is measured using a Keithley source meter (model 2420). The currents are measured by illuminating with white light from a 150 W Xenon lamp source (Newport Corp. USA; model no. 69907). For all data, the corresponding illumination was 100 mW/cm². We have calibrated our sun simulator using the reference cell (Newport oriel instruments, USA; model – 91150V). After maintaining the fixed distance as a standard (6.9cm), where the reference meter (Newport oriel instruments, USA; model – 91150V) shows the illumination of 1 sun. So we have placed the sample in the same place in a sample holder.

Dye adsorption determination:

At first cell is dipped in a 0.5 mM ethanolic solution for 12 hr. After adsorption of the dye the concentration of the residual dye is measured by spectroscopic technique by a

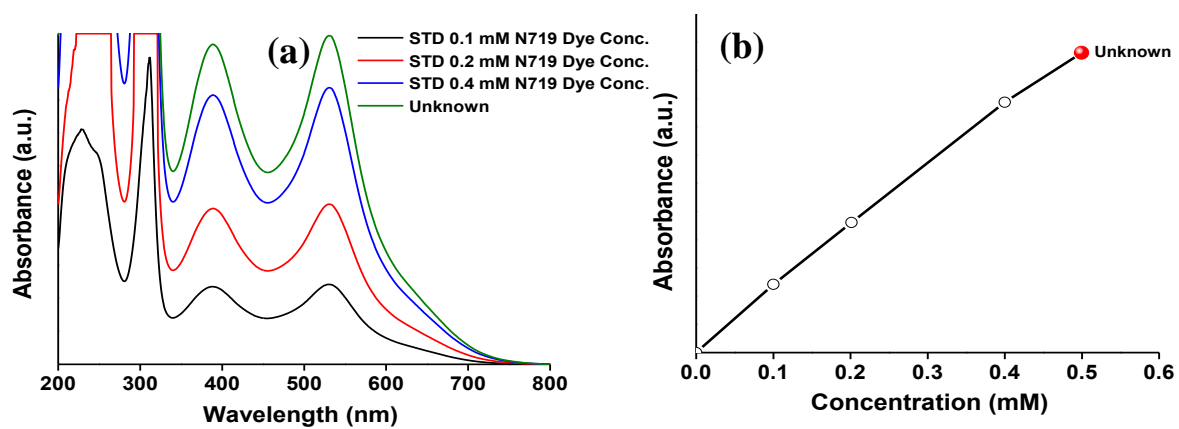
UV-Visible Spectrophotometer (Shimadzu Model UV 2401PC) in the quantitative mode. From this experiment the net dye adsorbed on the PHET-g-rGO surface in the DSC is 1.95×10^{-5} mmol/cm².

The 5 mL sample of N719 dye in the ethanol solution was collected for absorbance measurements using. Additionally, three known concentrations of N719 dye in ethanol solutions were prepared. These concentrations were 0.1 mM, 0.2 mM, and 0.4 mM respectively. These three samples were collected for absorbance measurements as well to generate a calibration curve. The absorbance spectra of all four samples can be found in Figure 1. Then using the 530 nm wavelength as λ_{max} all the data are calibrated and produced the best linear fit. From this absorbance vs. concentration data the unknown concentration of the dye is measured.

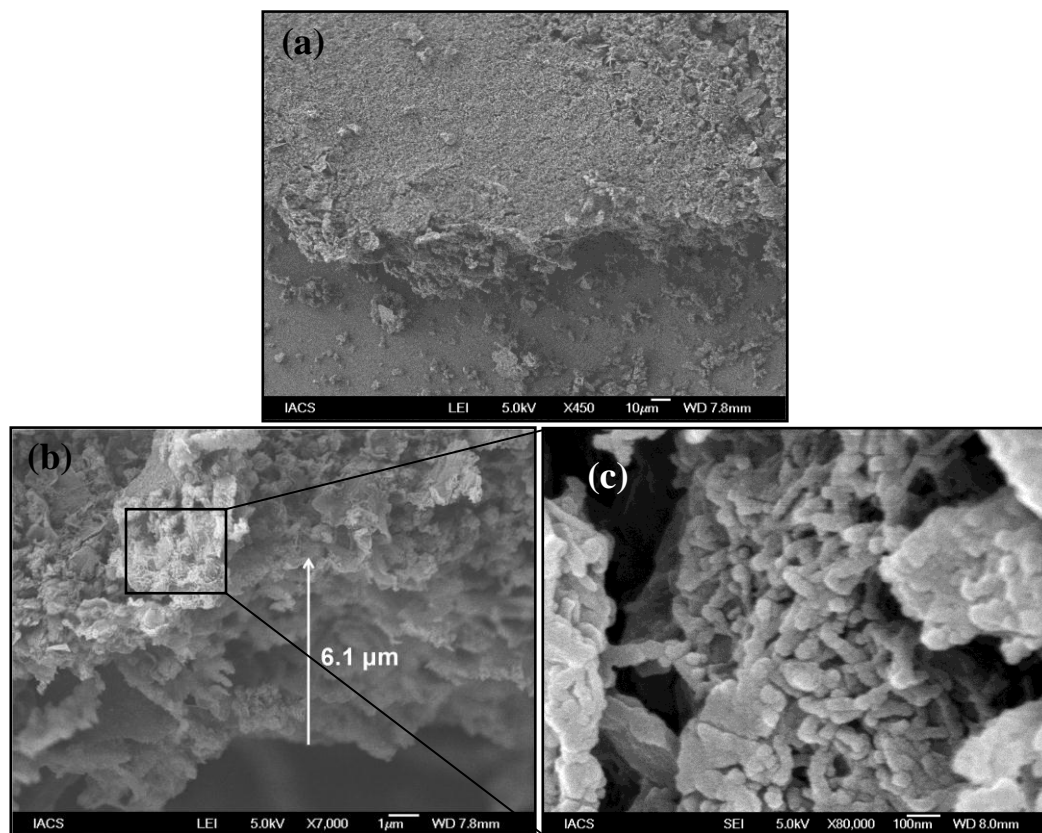
. We have compared the FT-IR spectra of PHET-g-rGO with the N719 sensitizer anchored PHET-g-rGO sample and it is included in the SIFig.3b of the revised manuscript. It is evident from the figure that 1728 and 1230 cm⁻¹ peak of PHET-g-rGO (for >C=O and C-O stretching vibrations, respectively) are shifted to 1722 and 1192 cm⁻¹ indicating supramolecular interaction (H-bonding) between the two components. Thus in our PHET-g-rGO system a physical adsorption of the dye occurs

References:

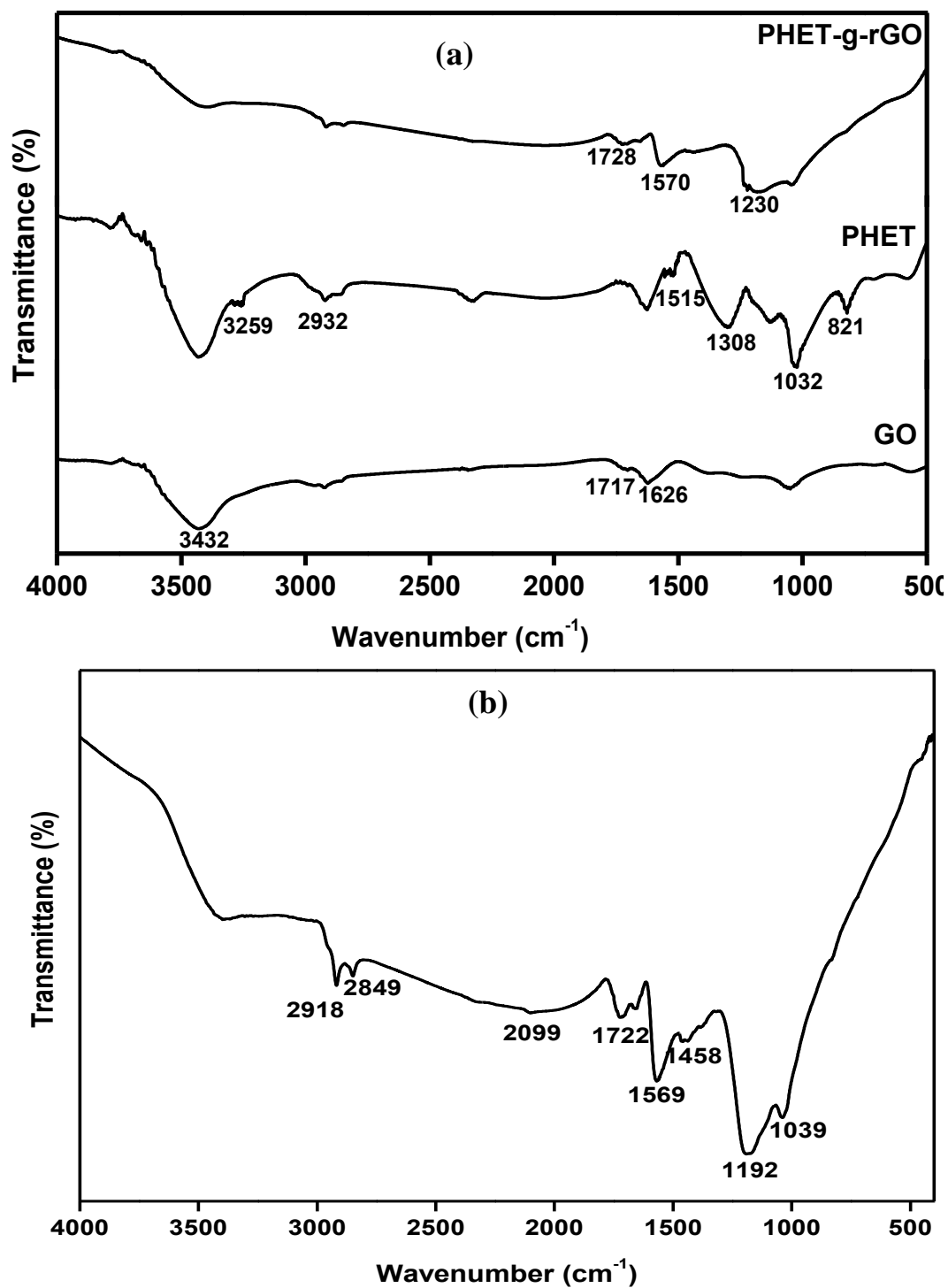
1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
2. W. Chen, L. Yan and P. R. Bangal *J. Phys. Chem. C* **2010**, *114*, 19885–19890.



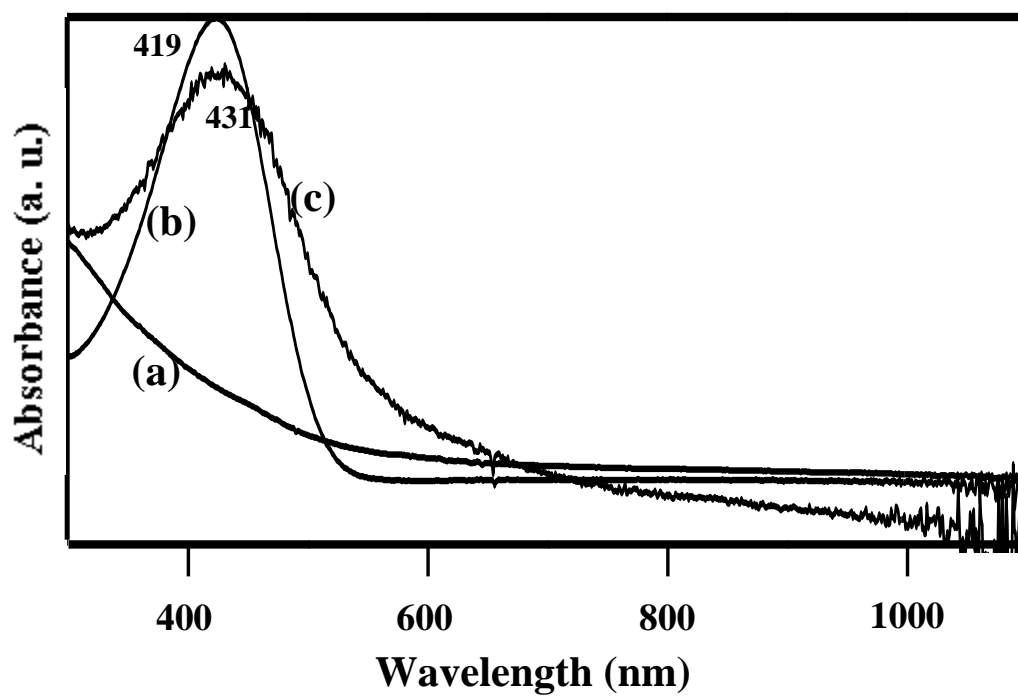
SI Fig. 1 (a) Absorbance spectra for N719 dye samples (b) Calibration curve for N719 dye samples at 530 nm along with the best fit curve



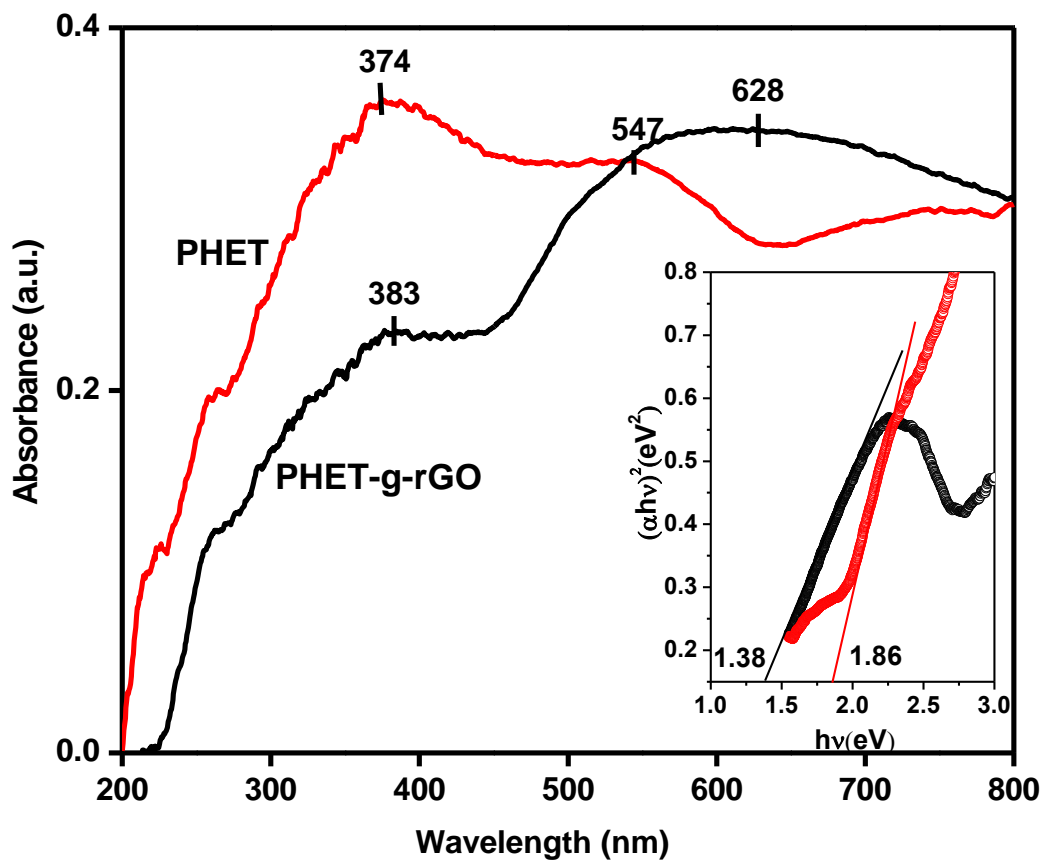
SIFig. 2(a) SEM image of the electrode **(b)** cross section and the thickness of the electrode **(c)** SEM images of the electrode showing the porous morphology of the electrode.



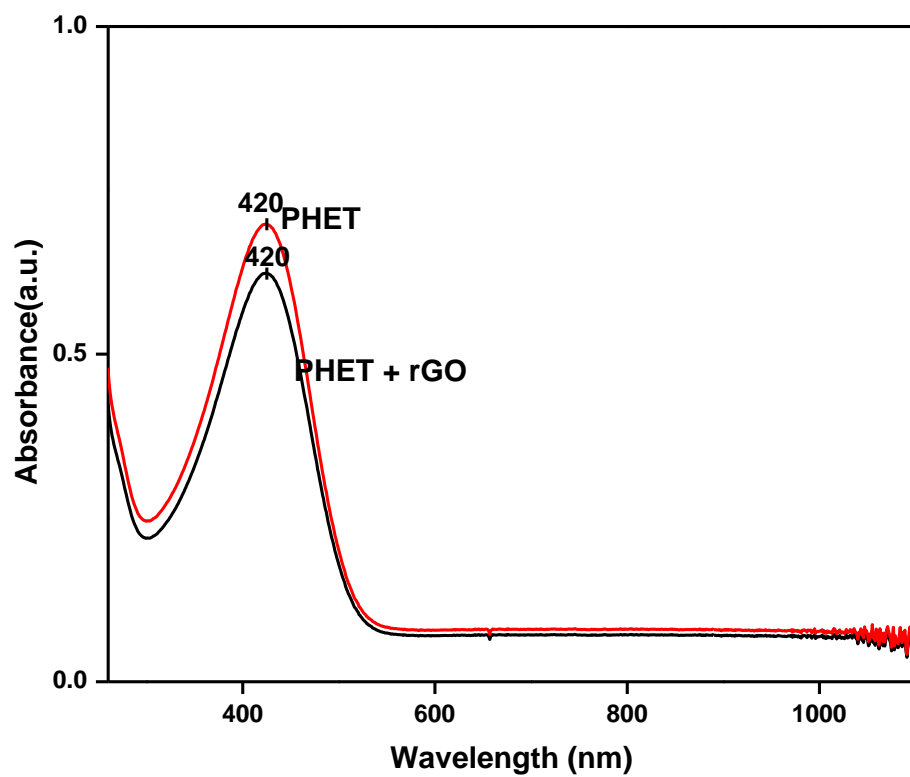
SIFig.3 FTIR spectra of pure (a) GO, PHET and PHET-g-rGO and (b) N719 dye adsorbed PHET-g-rGO



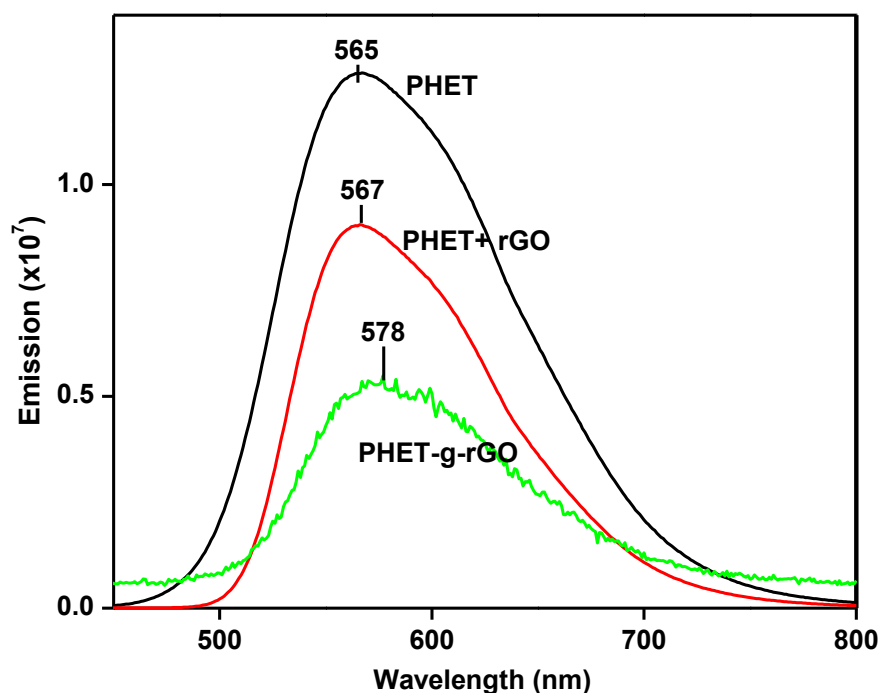
SIFig.4a UV-vis spectra of (a) pure GO (b) PHET and (c) PHET-g-rGO in N N' dimethyl formamide.



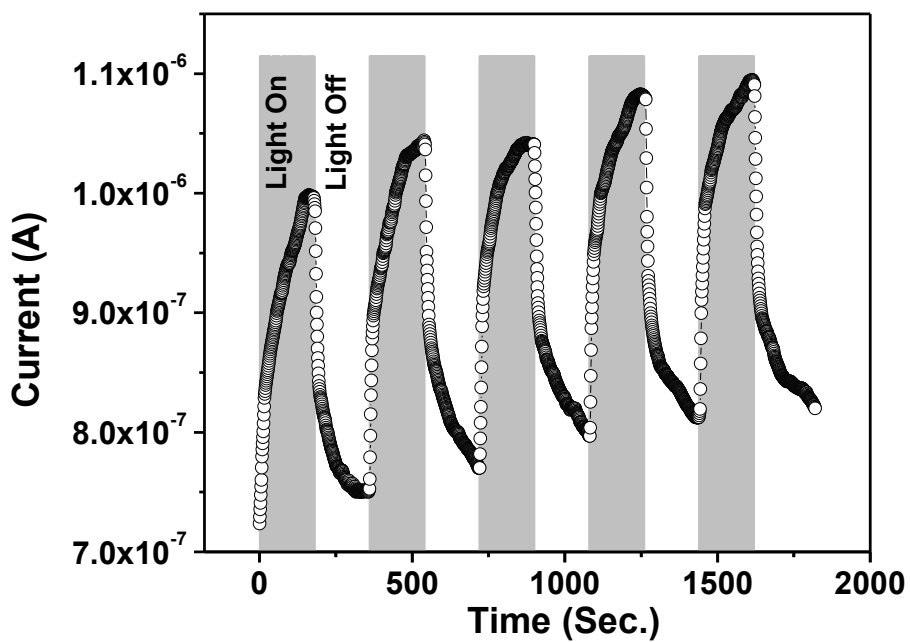
SI Fig. 4b UV-vis diffuse reflectance spectra of PHET and PHET-g-rGO, Inset: corresponding band gap energy calculation of the same systems from the spectra using Tauc's method.



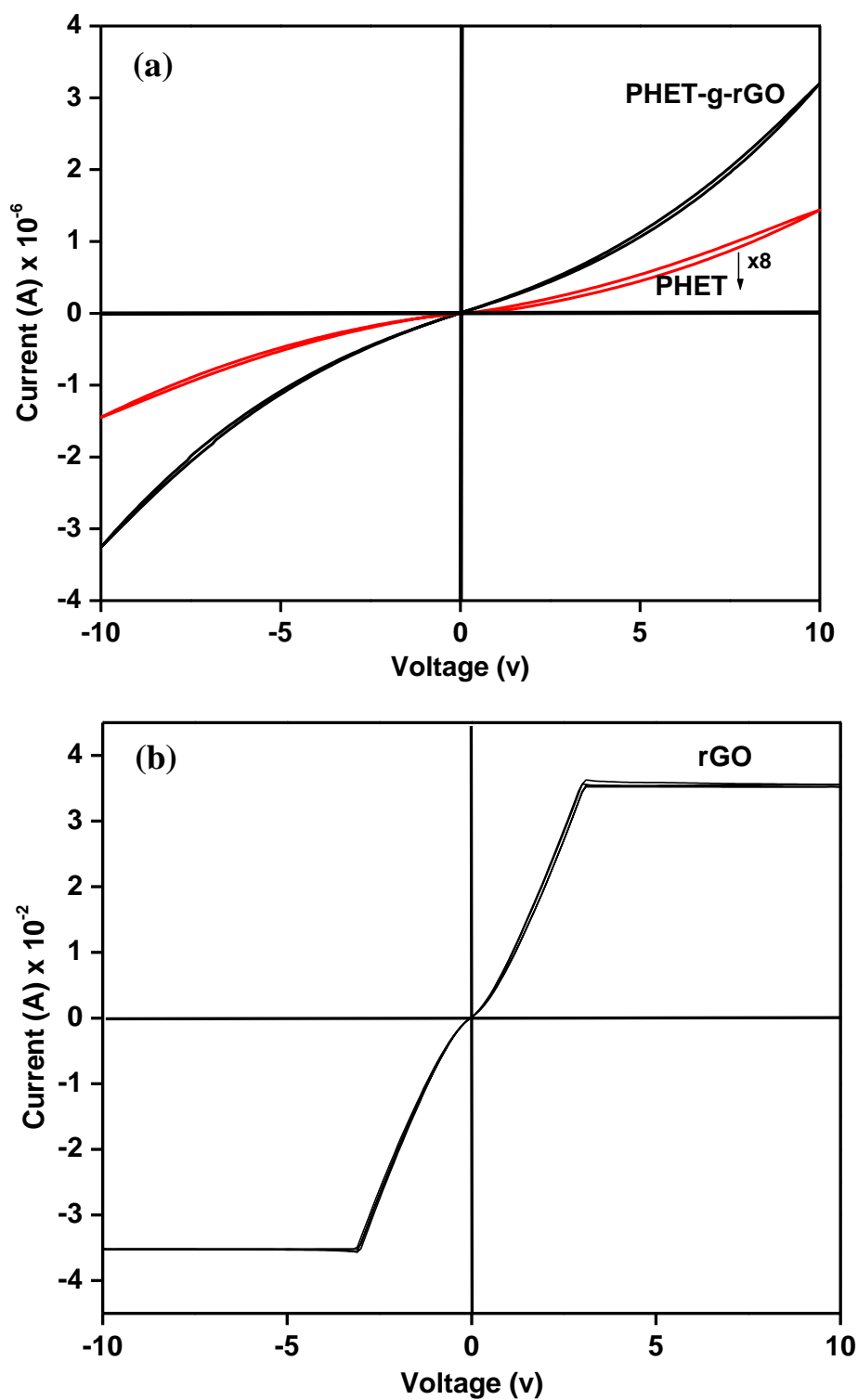
SIFig.4c UV-vis spectra of pure PHET and PHET+ rGO , there is no shifting in peak position.



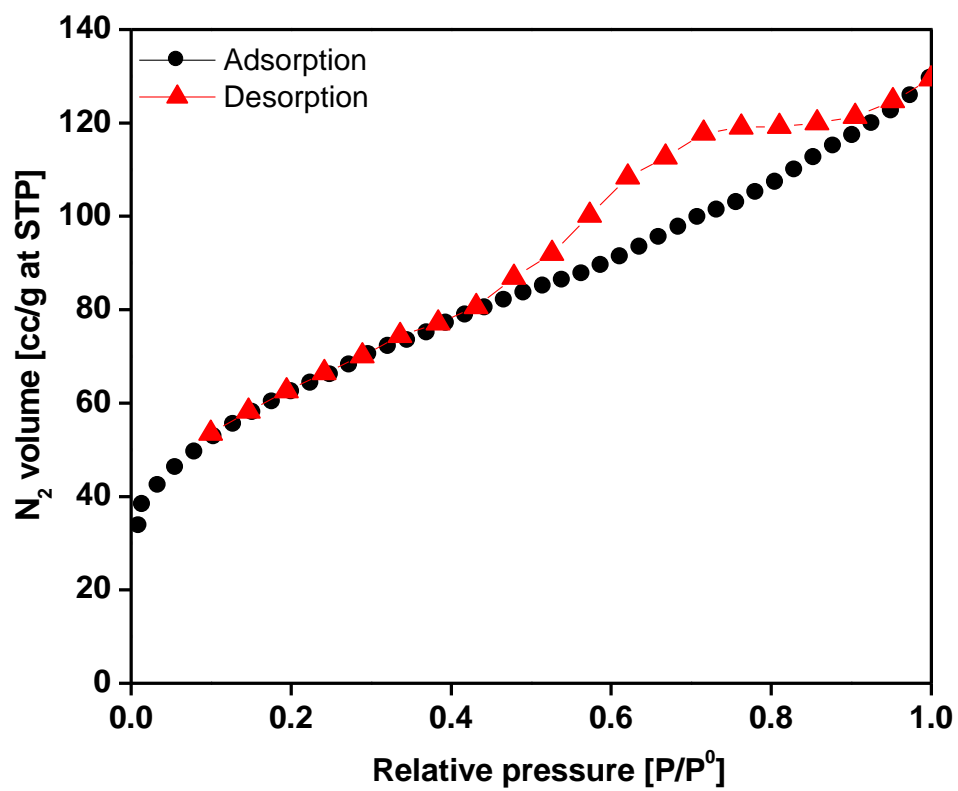
SI Fig. 5 PL spectra of PHET, PHET+ rGO and PHET-g-rGO



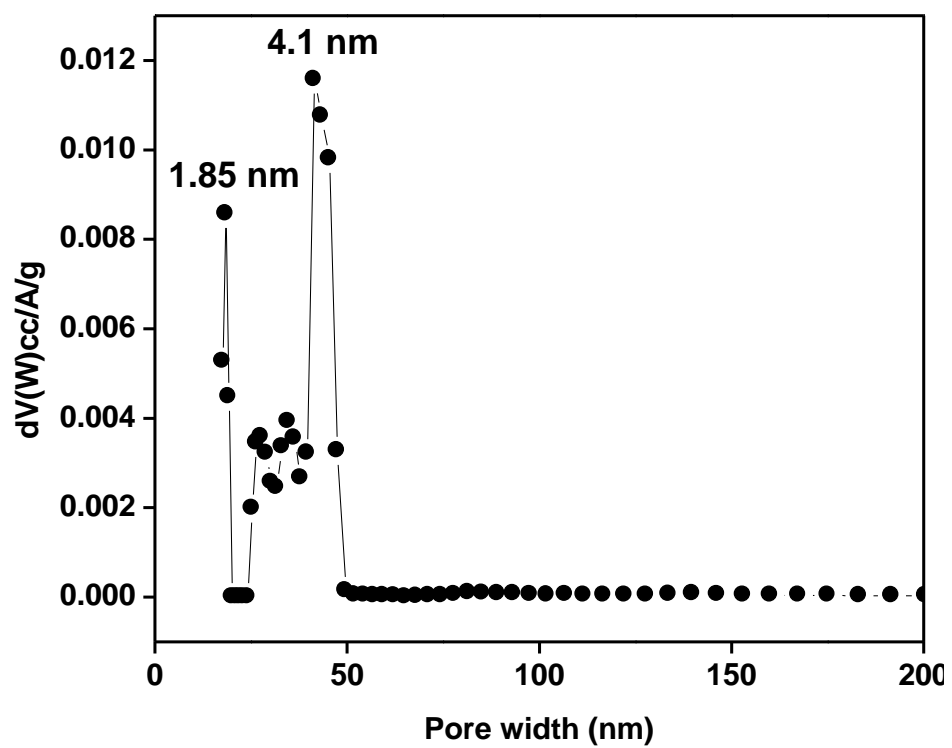
SIFig.6 Photocurrent cycles shows that the PHET-g-rGO composite can reversibly be turned “on” and “off” by switching the white light illumination “on” and “off” respectively



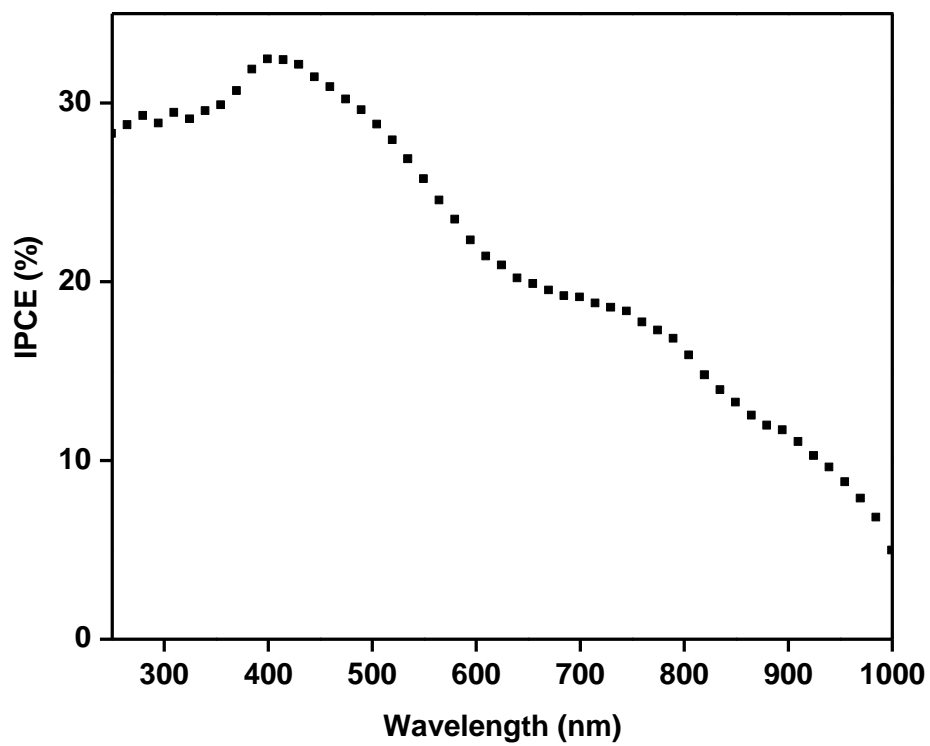
SI Fig. 7(a) Current (I) - Voltage (V) curve of the PHET(----) and PHET-g-rGO(----) in dark and **(b)** that of rGO in the dark



SIFig. 8 N₂ adsorption/ desorption isotherm at 77K for PHET-g-rGO



SI Fig. 9 The pore size distributions by NLDFT method of PHET-g-rGO



SIFig. 10 IPCE curve of the PHET-g-rGO based DSC

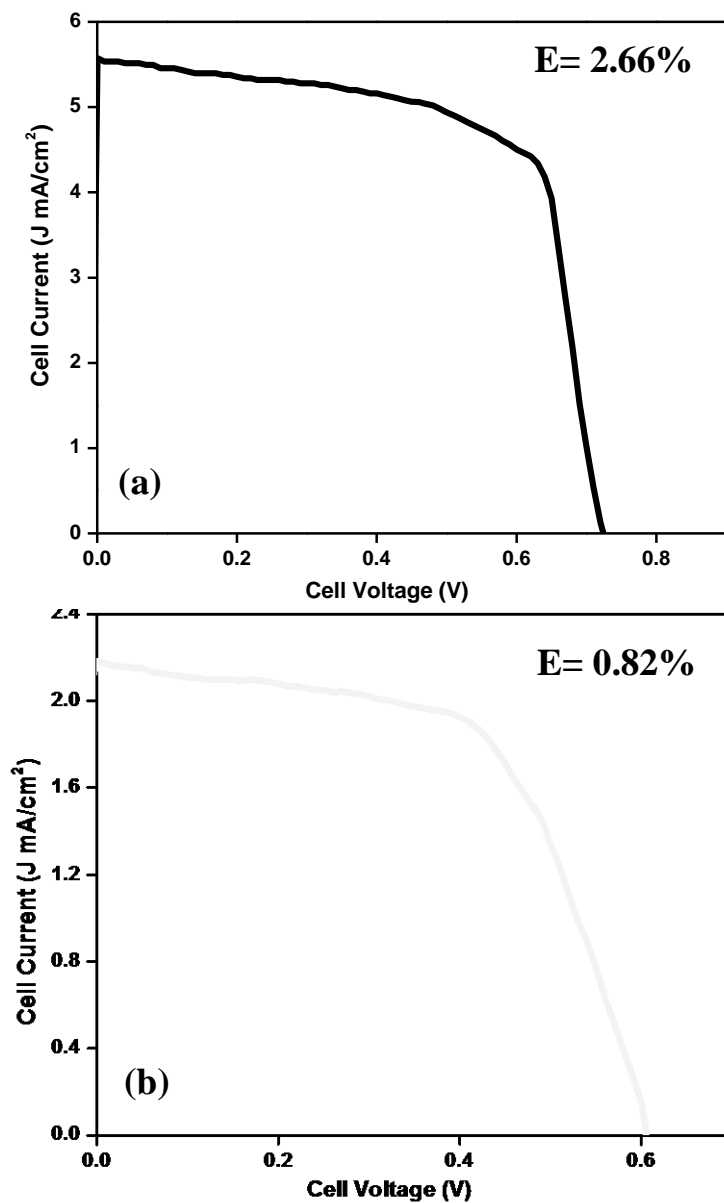


Fig.11 J-V characteristic curve of the (a) bulk TiO₂ based anode and graphite counter electrode and (b) PHET + rGO (i.e. simple mixing of PHET and rGO not the *in situ* grafting) based DSC