Electronic Supplementary Information (ESI)

Graphene Oxide / Polyaniline Nanostructures: Transformation of 2D sheet to 1D Nanotube and *in-situ* Reduction

Utpal Rana and Sudip Malik *

Polymer Science Unit, Indian Association for the Cultivation of Science, 2A & 2B Raja S. C. Mullick Road., Jadavpur, Kolkata – 700032, India.

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1) Experimental Section

Materials:

Powdered flake graphite (12500, 500 mesh) was purchased from Sigma Aldrich. Aniline monomer (Merck Chemicals) was distilled under pressure. Ammonium persulphate ($(NH_4)_2S_2O_8$, APS, Rankem chemicals) as a radical oxidant for PANI, $KMnO_4$, $NaNO_3$, sulphuric acid(98%) were purchased from commercial sources as analytical pure reagents. All aqueous solutions were prepared in 18MΩ water obtained by the purification of deionized water with a Millipore Milli-Q system.

Apparatus and characterizations

The FTIR spectra were recorded in an FTIR-8400S instrument (Shimadzu) using the KBr pellets of the samples. Fluorescence studies of all samples were carried out in a Horiba Jobin Yvon Fluoromax 3 spectrometer. Raman was recorded with a Renishaw in Via Raman Microscope 1000 operating at 785 nm with a charge-coupled device detector. The UV-Vis spectra of all samples were studied with Hewlett-Packard UV-Vis spectrophotometer (model 8453). XRD of the all samples were measured on Bruker AXS diffractometer (D8 advance) using CuKα radiation (λ=1.54 Å), a generator voltage 40 kV and current 40 mA. Samples were scanned in the range of $2\theta = 5^o - 40^o$ at the scan rate of 0.5sec/step with a step width of 0.02^o. Thermo gravimetric analysis (TGA) was done with TA thermal analysis system at heating rate 10 ^oC/min under N_2 environment.

2.a) Synthesis of GO:

Graphite oxide was synthesized from powdered flake graphite (12500, 500 mesh) by a modified Hummers method. A 500ml conical flask equipped with a magnetic stirring bar was charged with 50 mL of H_2SO_4 and cooled to 0-5 °C by immersion in an ice bath. Graphite (1.0g) was then added slowly with vigorous stirring while maintaining the reaction mixture at 0-5 °C. After the addition, graphite flakes formed a well dispersed black slurry, 1.0g of $NaNO_3$ was added slowly over 15min at 0-5 °C and then 5.0g $KMnO_4$ slowly was added. The mixture was allowed to warm to room temperature (RT) and stirred for 2 h. Water (110 mL) was then added, and the solution was stirred for 30 min. while the temperature was raised to 90 °C. The mixture was poured into 200 mL of water, after which 7 mL of H_2O_2 was slowly added. The colour of the solution changed from dark-brown to yellow. The solution was then filtered using Millipore filter paper. The material was redispersed in water and centrifuged at 15000 rpm washed with water until the pH of the solution was neutral. The resultant GO material was dried in a vacuum desiccators overnight at RT and stored in the ambient environment.[1]

FTIR: γ O-H peak at 3400 cm^{-1}, γC=O stretch at 1724 cm^{-1}, C=C at 1622 $cm^{-1,}$ C-OH peak at 1345 cm^{-1}, C-O-C peak at 1224 cm^{-1}, C-O stretching at 1049 cm^{-1}, and aromatic C-H peak at 832 cm^{-1}

3) Synthesis of GO-PANI: PANI composites have been prepared typically by the dispersion of aniline (102mg, 1.1mmol) and required amount of GO in water with sonication for 30 mins followed by stirring for one hour to make GO dispersion. After cooling the mixture at 10^0C, aqueous solution of ammonium persulphate ($(NH_4)_2S_2O_8$, APS, 250mg,1.1mmol) was added over 30 min and the mixture was allowed to stand for 24 hrs at low temperature. The resultant precipitate was filtered and washed ten times with water and methanol to remove APS and oligoaniline. Finally, it was dried under vacuum for 24 hrs to receive GO-PANI composites.

Table S1: Preparation of Polyaniline using different GO concentration.

Name of composite	**An [mmol]**	**GO [wt% w.r.t An]**	**[GO]:[An] (w/w)**	**APS [mmol]**	**[An]/[APS]**	**Yield mg**	**I_q/I_b #**	**D/G $^{\$ \alpha}$**
(GP_{50})	102mg [1.1]	51 mg [**50**]	0.50:1	250 mg [1.1]	1:1	130	1.002	-
(GP_{25})	102mg [1.1]	26 mg [**25**]	0.25:1	250 mg [1.1]	1:1	115	1.006	1.12
(GP_{10})	102mg [1.1]	10.2mg [**10**]	0.10:1	250 mg [1.1]	1:1	98	1.015	1.11
(GP_{5})	102mg [1.1]	5.1 mg [**5**]	0.05:1	250 mg [1.1]	1:1	90	1.008	1.08
(GP_{1})	102mg [1.1]	1 mg [**1**]	0.01:1	250 mg [1.1]	1:1	84	1.01	1.09

[#] Data taken for Fig. S2

[$] The ratio was calculated from Fig4a. [α] D/G for GO was 0.76.

4) FESEM images of GO and GO/PANI composites:

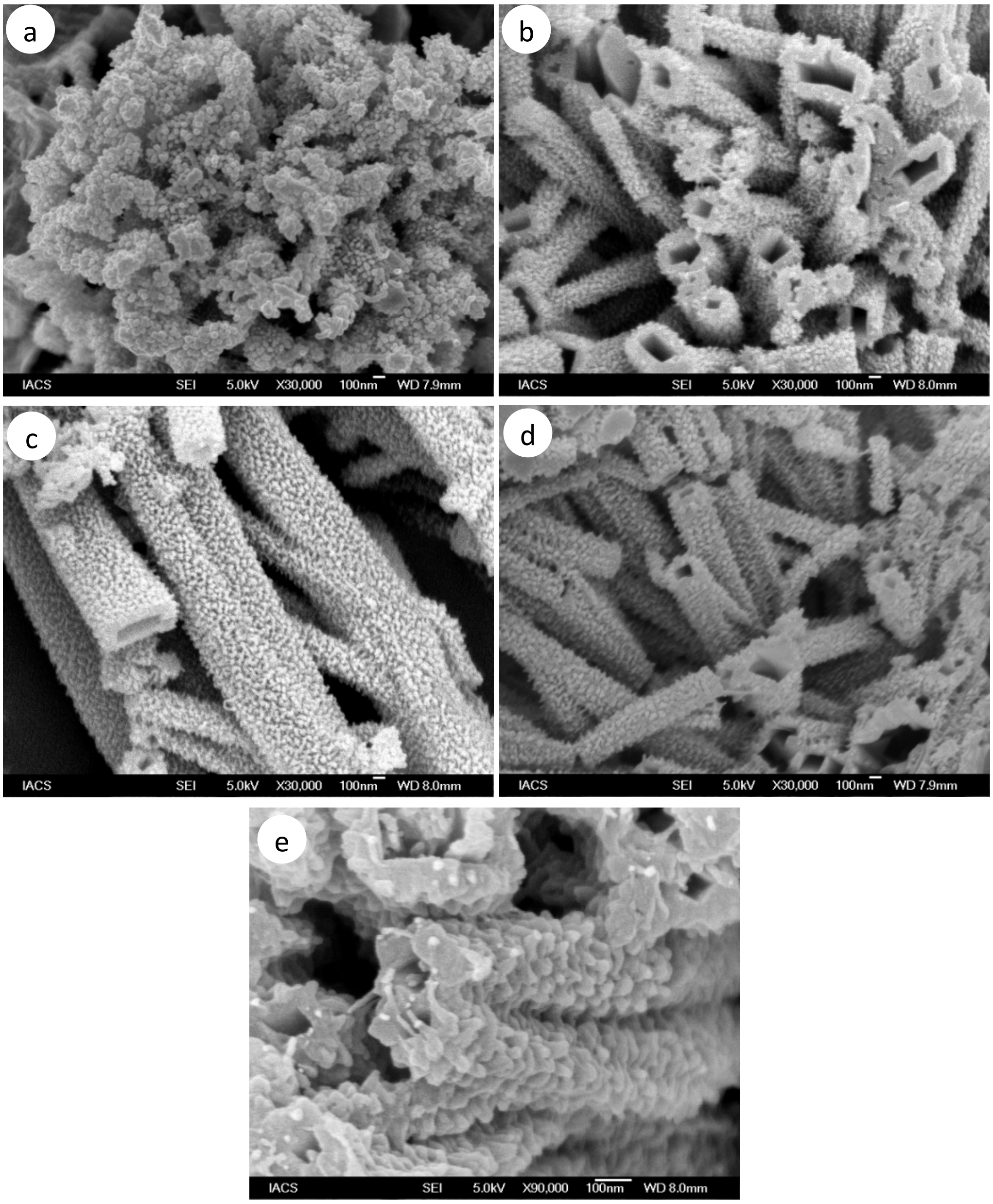

Fig. S1. Additional FESEM images GO/PANI composites synthesized at different weight ratio of GO to aniline (w/w): a) GP_{50}, b) GP_{25}, c) GP_{10}, d) GP_5 and e) GP_1.

5) HRTEM observations:

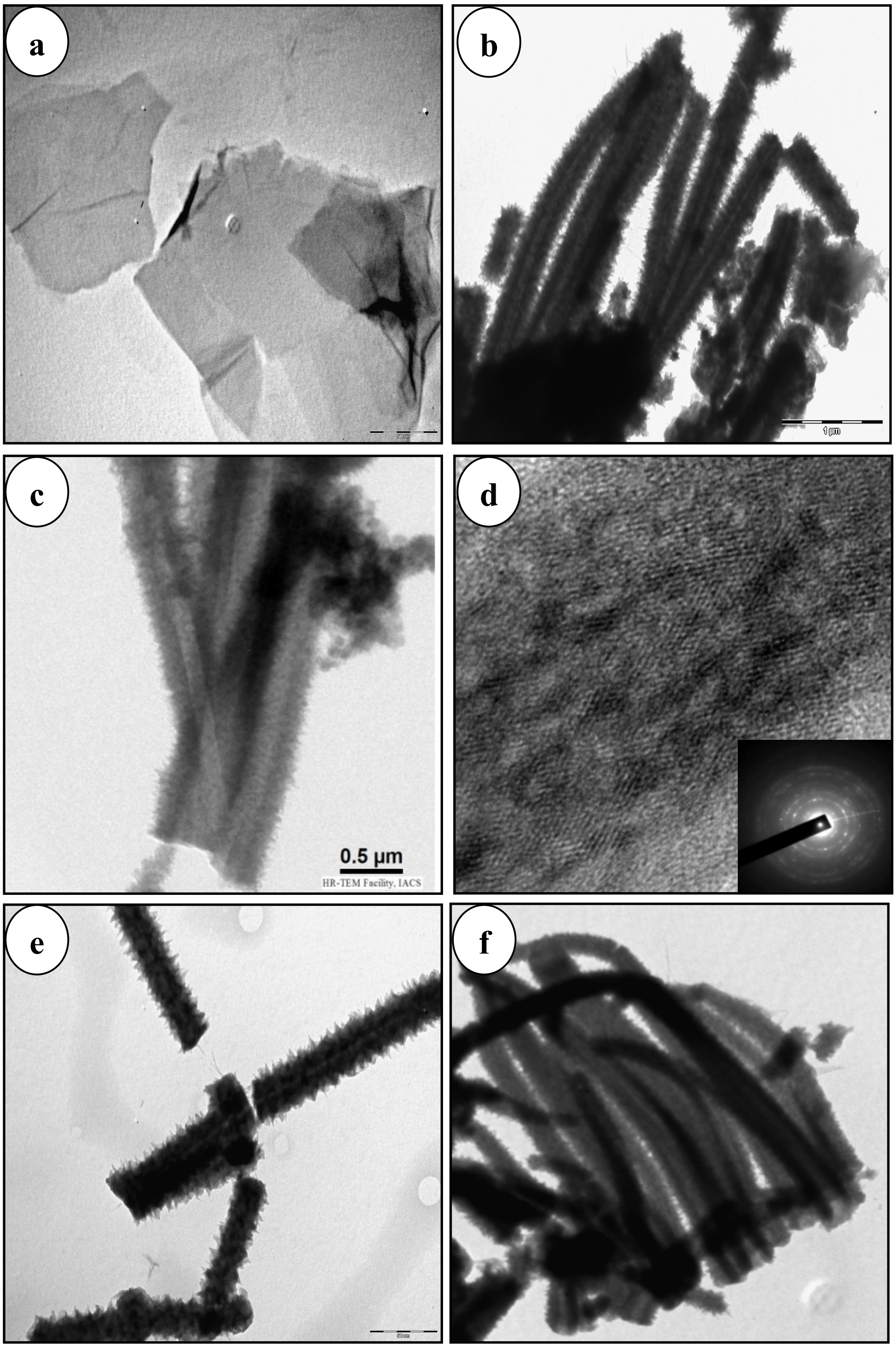

Fig. S2. HRTEM images of GO and GO/PANI composites synthesized at different weight ratio of GO to aniline (w/w): a) GO, b) GP_{25}, c) GP_{10}, d) GP_{10}, e) GP_5 and f) GP_1.[2]

6) X-ray diffraction:

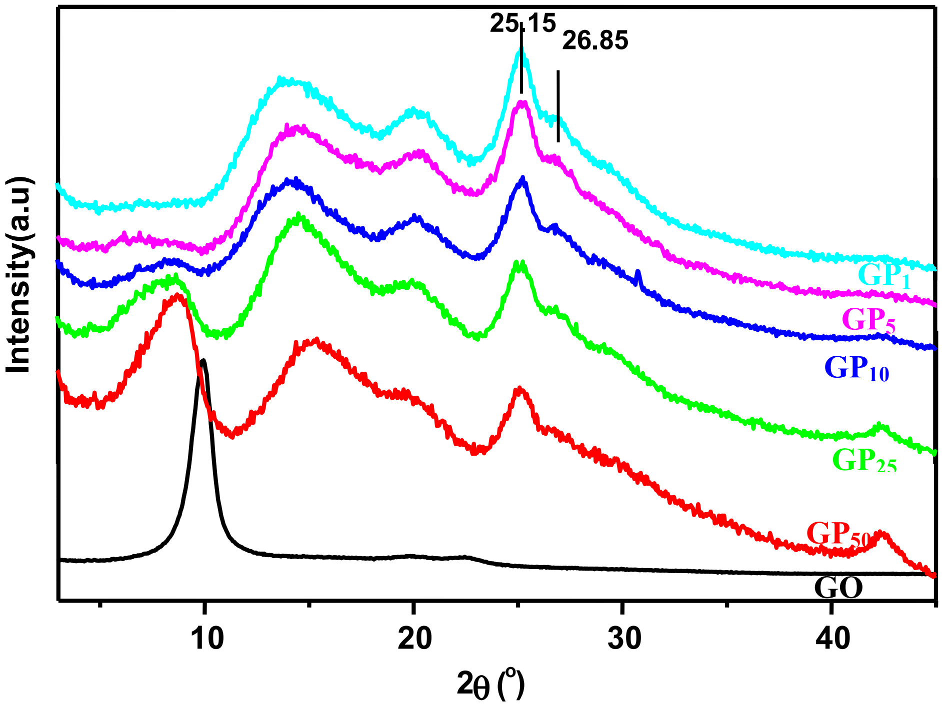

Fig.S3. X-ray diffraction studies of GO and GO/PANI synthesized using different weight of GO.

7) Thermogravimetric analysis of GO and GO/PANI composite :

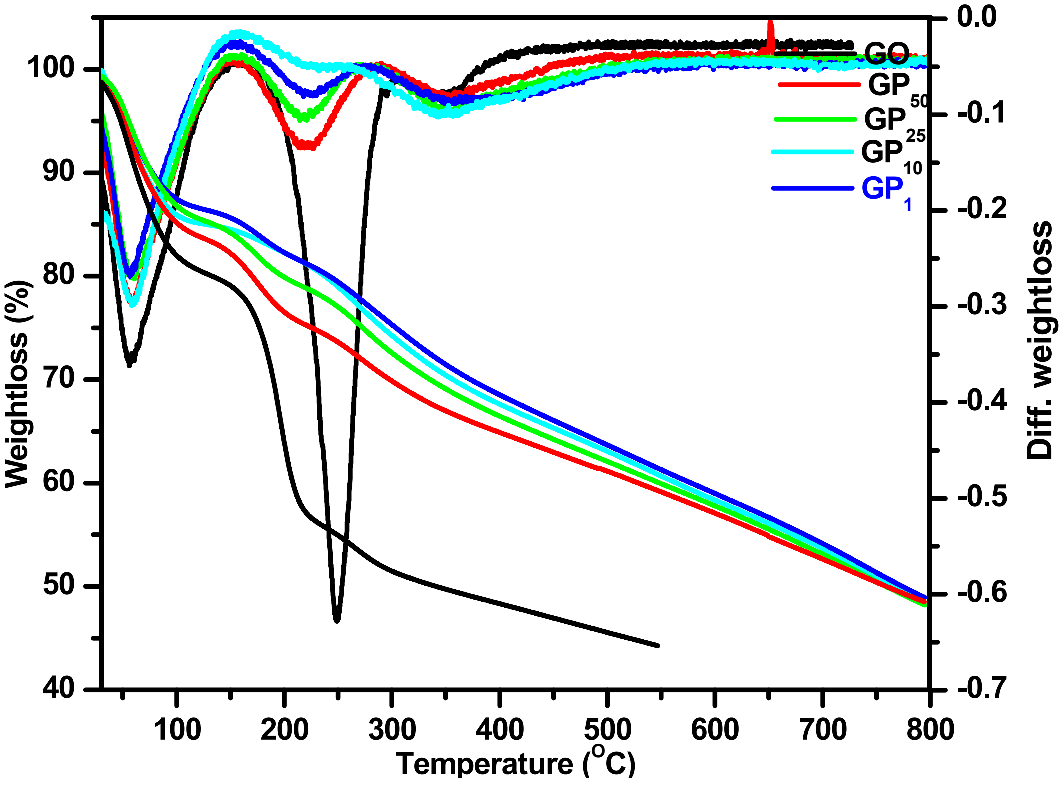

Fig.S4. TGA analysis of GO and GO/PANI synthesized using different weight of GO. [3]

8) **FT-IR studies**:

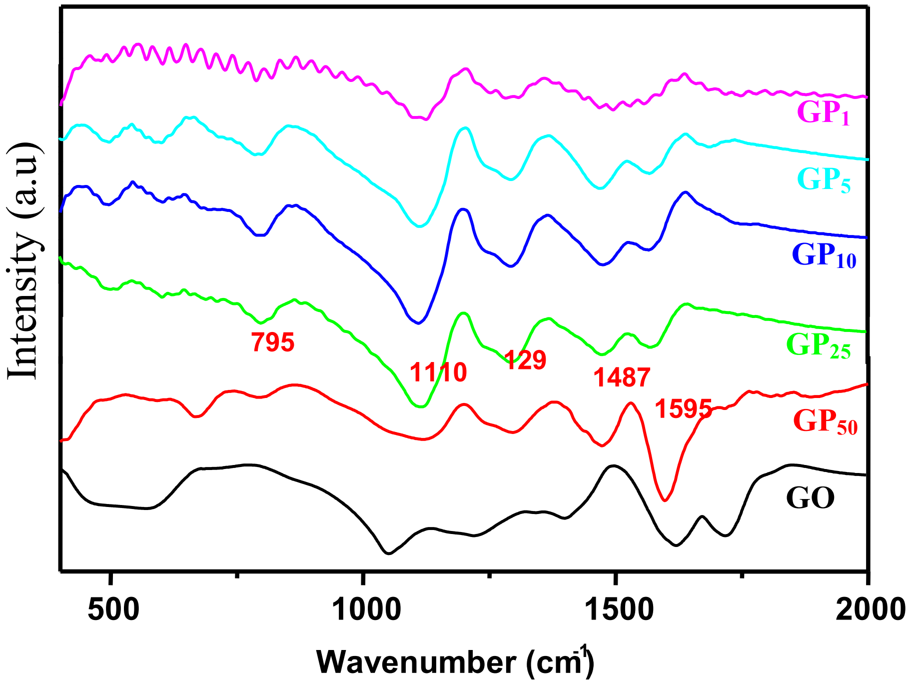

Fig.S5. FT-IR-spectral analysis of GO/PANI synthesized at the different amount of GO.

9) Photoluminescence Spectroscopy study of GO/PANI composites:

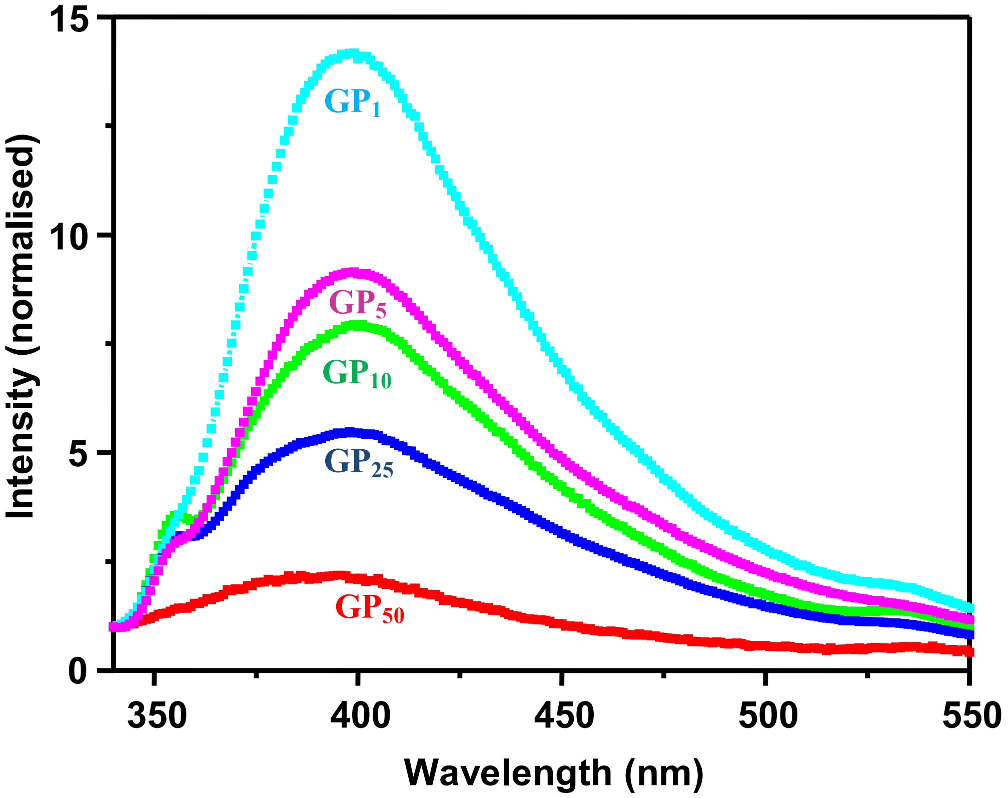

Fig.S6. Photoluminescence-spectral analysis of GO/PANI synthesized using different amount of GO. (path length = 1.0 cm, λ_{ex}=310 nm , concentration= 0.1mg/ml.). GO is fluorescence inactive whereas emission peaks are observed for all composites, indicating *in-situ* reduction of GO in GO/PANI composites. Moreover, normalised fluorescence spectral analysis provides that with decreasing the concentration of GO the intensity of the peak gradually increases due to generation of more and more amount of RGO at the lower ratio of GO to aniline.[4]

10) Cyclic Voltammetry of GO and GO/PANI composite:

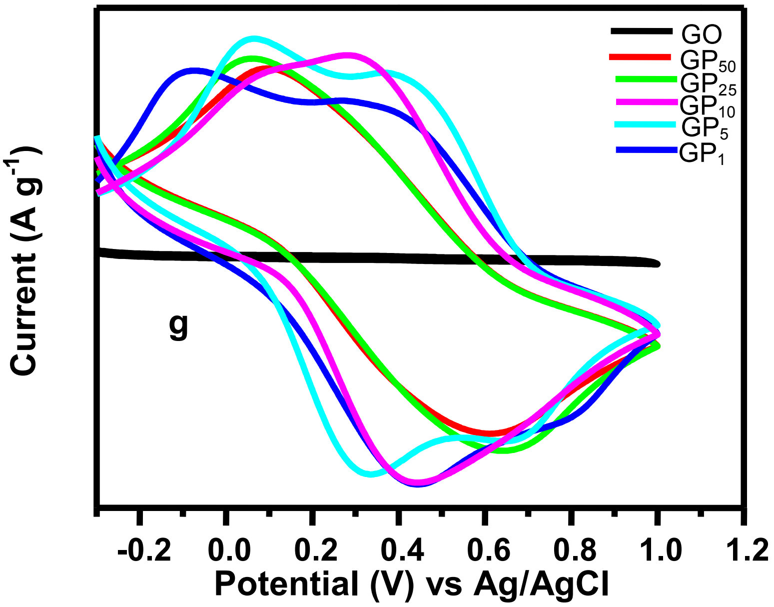

Fig.S7. Cyclic Voltametry of GO and GO/PANI synthesized using different amount of GO. Scan speed 50 mV/S.

Two couples of redox peaks appear in the CV curve of the GO/PANI electrode, which are attributed to the transitions between a semiconducting state (leucoemeraldine form) and a conducting state (polaronic emeraldine form) and the Faradaic transformation of emeraldine-pernigraniline, respectively.

However, compared with the GO electrode, the current density response and the CV curve area of the GO/PANI electrode are both much larger than those of the GO electrode. This indicates that the electrochemical performances of the GO-PANI hybrid papers are remarkably enhanced owing to the addition of PANI coating on the surface of the GO paper.

10) I-V curves of different composition:

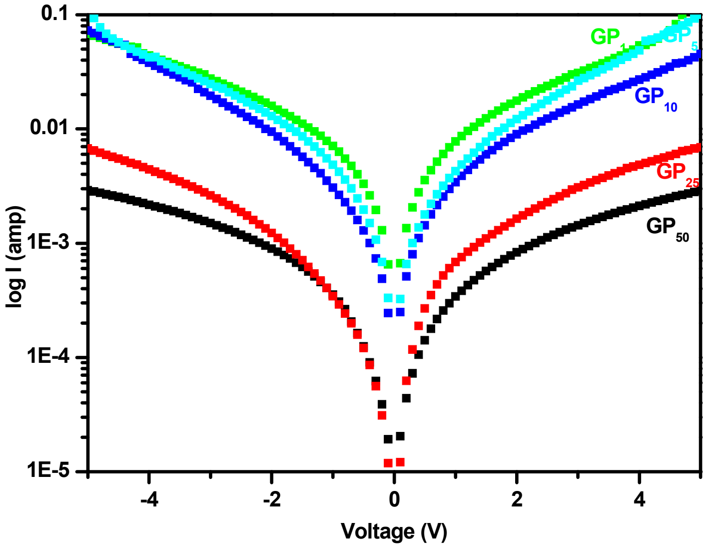

Fig.S8. I-V curve of GO/PANI synthesized using different amount of GO. I-V curves at different concentration of GO plotted in semi log scale to clearly show the symmetric nature of the curves and reduction behaviour of GO to partially reduced graphene oxide. [5]

11) References:

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5. J. M. Mativetsky, E. Treossi, E. Orgiu, M. Melucci, G. P. Veronese, P. Samori and V. Palermo, *J. Am. Chem. Soc*. 2010, **132**, 14130.