

Electronic Supporting Information (ESI)

ZnO-graphene-polyaniline nanoflowers: Solution synthesis, formation mechanism and electrochemical activity

Susanta Bera, Atanu Naskar, Moumita Pal and Sunirmal Jana*

Sol-Gel Division, CSIR-Central Glass and Ceramic Research Institute
196 Raja S.C. Mullick Road, P.O. Jadavpur University, Kolkata-700 032, West Bengal, India

1. Experimentals

1.1 Synthesis of Graphene Oxide (GO)

Graphene oxide (GO) was synthesized from graphite powder (Sigma Aldrich, size <20 micron) adopting modified Hummer's technique.¹ For this synthesis, ~5 g of graphite powder, 2.5 g of NaNO₃ (Merck, 99%) as well as 150 mL of conc. H₂SO₄ (98%, Merck, GR) were taken together and stirred the mixture in an ice bath for 3 h. After that 20 g of KMnO₄ (Merck, 98.5%) solid was added **slowly**. To allow chemical **reaction**, the aliquot was stirred **vigorously** for about 1 h. During **the stirring** at room temperature, 250 mL of distilled water was added and raised the temperature **of the container** to ~ 100°C for 30 min by using a heating cum stirring magnetic stirrer. In the next, warm distilled water (500 mL) was added to the aliquot and subsequently, 10 mL of H₂O₂ (30 wt%, Merck) were **slowly** added. After that the solution was filtered and washed with 250 mL aqueous HCl (1: 10 volume ratio) solution for removal of metal ions followed by final washings that had been done by using distilled water. It is noted that the resultant solid mass was taken out by centrifugation and the precipitated mass was dried in an air oven at 55°C for a day. The final product, graphene oxide (GO) was appeared as non-shiny blackish brown coloured material.

1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, **1958**, *80*, 1339.

1.2 Synthesis of ZnO-chemically converted graphene (ZG) and pristine ZnO

ZnO-chemically converted graphene, ZnO-CCG (ZG) was prepared by following a facile low temperature (95°C) solution process using as-synthesized graphene oxide (GO) with zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, ZA, Sigma-Aldrich, $\geq 98\%$) in dimethyl formamide (DMF) solvent medium. In this synthesis, 30 mg of GO was uniformly dispersed in 40 ml of DMF by ultrasonication for ~ 60 min **duration**. Then, **950 mg** of ZA was dissolved in 200 ml DMF by rigorous stirring. Then, the dispersed GO was added into the ZA solution during the continuously stirring and the mixture was heated at 95°C for 9 h in an air oven. It is worthy to mention that for the ZG nanocomposite, the product was washed by centrifugation using ethanol and distilled water as washing liquids. The sample was dried at $\sim 55^\circ\text{C}$ in an air oven. Pristine ZnO was also prepared in the similar preparative condition without using GO in the precursor.

1.3 Synthesis of ZnO-chemically converted graphene-polyaniline (ZnO-CCG-PANI) and ZnO-polyaniline (ZP) inorganic-organic hybrids

The ZnO-CCG-PANI nanocomposites were prepared by varying ZG to aniline monomer weight ratio (R); 20: 1, 14 : 1, 7 : 1 and 3 : 1 in the precursors and the corresponding inorganic-organic hybrids are termed as ZGP20, ZGP14, ZGP and ZGP3, respectively. The required amount of ZG was dispersed in ethanol and water (weight ratio, 1 : 1) by stirring for 30 min and an aqueous solution of **ammonium persulfate** [$(\text{NH}_4)_2\text{S}_2\text{O}_8$ **abbreviated as APS**] was added to the mixture after cooling the system, 5 – 10°C for 6 h duration. In this synthesis, the APS was taken with respect to aniline monomer. The molar ratio of aniline to APS was 1:1 for the products, ZGP20, ZGP14, ZGP and ZGP3. The resultant precipitates were washed several times by vacuum filtration using ethanol and deionized water. Finally, the precipitates were dried at room temperature under a desiccator activated with magnesium sulfate as moisture adsorbent. To understand the solvent effect, two additional ZGP samples were also prepared using water and ethanol separately and designated as ZGPW and ZGPE, respectively. Keeping all the preparative parameters fixed, we have also prepared ZnO-PANI (ZP) nanocomposite using pristine ZnO to aniline monomer weight ratio, 7 : 1 in the precursor. On the other hand, pure polyaniline (PANI) was also synthesized from aniline monomer under the identical condition as maintained for ZGP sample preparation where water and ethanol was used in 1 : 1 (**weight ratio**).

2. Characterizations

2.1 Materials properties

The crystalline phase was determined by X-ray **diffraction** (XRD) study using an X-ray diffractometer (Philips PW 1730 X-ray diffraction unit employed with nickel-filtered CuK_α radiation source, wavelength 1.5418 Å) and the diffraction angle was chosen in the 2θ range, 10° - 80° . The surface morphology of nanocomposites were checked with the help of field emission scanning electron microscope (FESEM, ZEISS, SUPRA™ 35VP) while transmission electron microscope (TEM/high resolution TEM (HRTEM), TEM-selected area electron diffraction (TEM-SAED) and TEM-energy dispersive X-ray spectroscopy (TEM-EDS) mapping of Zn, O and N were also performed on nanocomposites using an ultra high-resolution field emission gun (UHR-FEG) TEM instrument (model JEM 2100 F, JEOL) at a 200 kV electron source. For each sample preparation, the material was dispersed in methanol, followed by ultrasonication for ~2 h duration. Finally, it was carefully placed on a carbon coated 300 mesh Cu grid. The excess liquid was allowed to evaporate in air. Using atomic force microscope (AFM, Nanosurf Easy scan 2, Switzerland), a tentative roughness / thickness of ZG sample and the petals of the hierarchical nanoflowers of ZGP was also analyzed. FTIR vibrations were measured by IR spectrometer (Nicolet 5700, Thermo Electron Corporation). The number of scans for each experiment was 100 when the wavenumber resolution was 4 cm^{-1} . Using a micro-Raman spectrometer (Renishaw inVia Raman microscope), Raman spectral study of the samples was performed. In this measurement, an argon ion laser with an incident wavelength of 514 nm was used as an excitation source. The X-ray photoelectron spectra (XPS) of GO, ZG and ZGP was measured with the help of PHI Versaprobe II Scanning XPS microprobe surface analysis system using Al-K_α X-rays ($h\nu$, 1486.6 eV; ΔE , 0.7 eV at room temperature). The energy scale of the spectrometer has been calibrated with pure (Ag) samples. The XPS analysis chamber pressure was better than 5×10^{-10} mbar. The position of C 1s peak has taken as standard with the binding energy of 284.5 eV.

2.2 Electrical property and electrochemical activity

The current-voltage (I–V) characteristics of ZG, ZGP and PANI samples were measured using an Agilent make (two-channel precision source) measurement unit (model, B2902A) with a GW Instek dual-range DC power supply (model, SPD-3606). Electrochemical measurement of ZG,

ZGP and ZP samples was carried out with the help of Metrohm, Autolab AUt 85930 instrument using standard three-electrode cell. In this measurement, a Pt wire and an Ag/AgCl/3M KCl electrode were taken as the counter electrode and reference electrode, respectively. The working electrode was prepared from the slurry of sample and polyvinylidene fluoride as binder (PVDF) in n-methyl pyrrolidinone (NMP, solvent). Then, the slurry was coated on cleaned nickel foil and dried at 110°C in an air oven for 5 h. It is noted that an aqueous solution of 1M KOH was used as an electrolyte for measurement of the electrochemical activity of the samples.

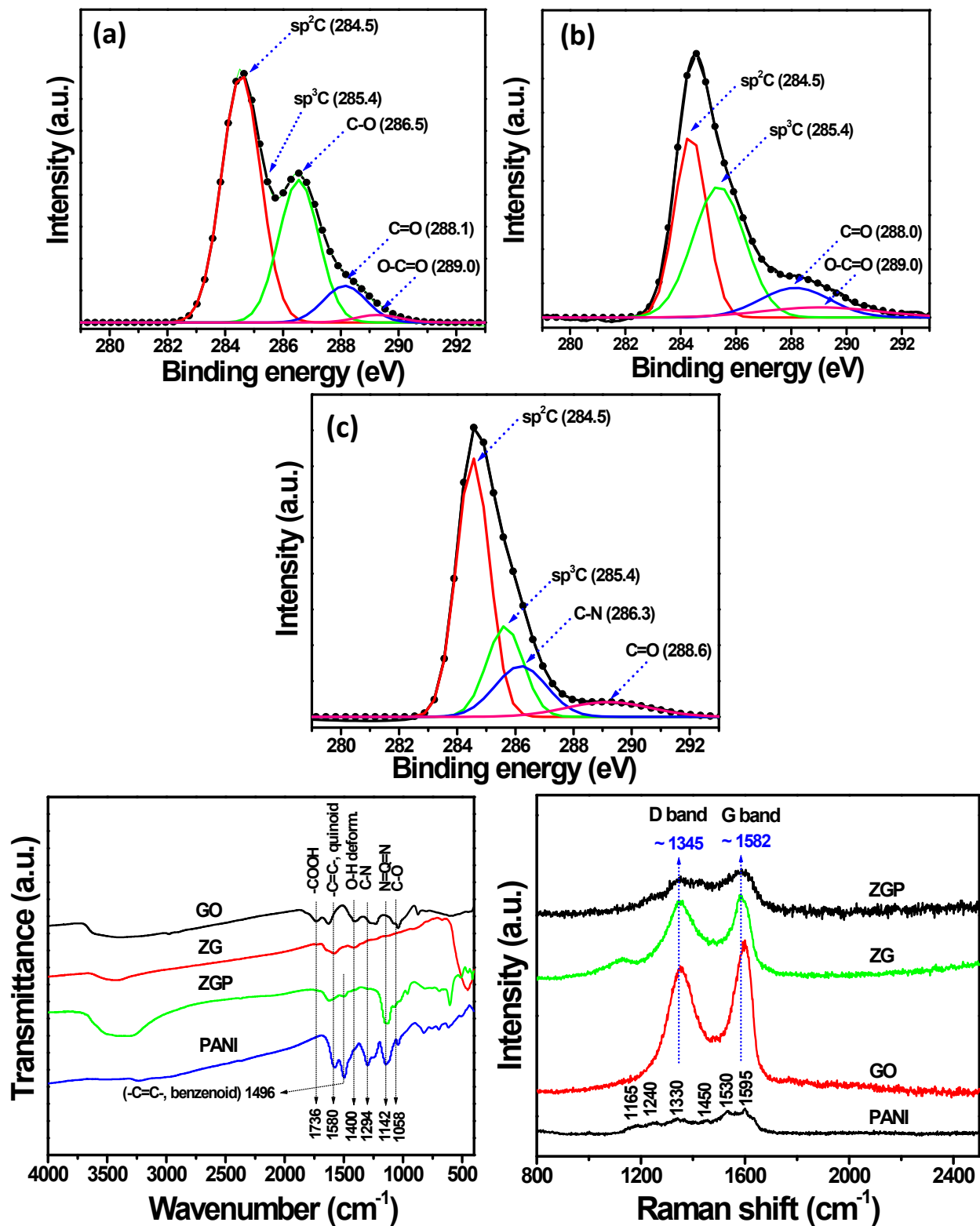


Figure S1: XPS signals of C 1s for (a) GO, (b) ZG and (c) ZGP. FTIR (d) and Raman spectra (e) of ZG and ZGP along with the precursor materials.

In GO sample, the asymmetric XPS signal of C1s (**Fig. S1a**) can be resolved into four Gaussian fitted components (with a broad shoulder) appeared at ~ 284.5 eV (I), ~ 285.4 eV (II), ~ 286.5 eV (III), ~ 288.1 eV (IV) and ~ 289.0 eV (V), ascribe to C-C bonded carbon (sp^2C , I) and (sp^3C , II), epoxy or hydroxyl (C-O, III), carbonyl (C=O, IV) and carboxyl (O-C=O, V), respectively.^{1,2} It is worthy to note that the asymmetric signal of C1s in ZG and ZGP samples was also resolved into Gaussian fitted components and all the components are present in ZG nanocomposite but in comparison GO, the intensity of the components for oxygen-containing functional groups are found to be decreased **greater** extent in ZG nanocomposite (**Fig. S1b**), indicating the conversion of GO to chemically converted graphene (CCG) occurred in ZG nanocomposite.^{1,2} It is also important to note that the intensity of C=O related components with respect to sp^2C/sp^3C is noticed to **diminish** further in some extent for ZGP sample. Moreover, a new signal is observed at ~ 286.3 eV, ascribed to the presence of C-N group.³ Further, a shifting of the binding energy of C=O group towards higher energy (**Fig. S1c**) is also noticed. **It is mentioned that** the binding energy peak position is higher than that of the XPS peak energy of pure PANI, reported in the literature.⁴ This XPS result clearly demonstrates **the** chemical complexation/interaction that happened between PANI and ZG moiety in ZGP nanocomposite.^{3,4}

The FTIR spectra of ZG and ZGP composites along with GO and PANI used as the precursors are given in **Figure S1 (d)**. In the precursor GO, the presence of C–O stretching (~ 1060 cm^{-1}), C-OH stretching (~ 1225 cm^{-1}), O-H deformation (~ 1400 cm^{-1}) and C=O stretching of carboxylic groups (~ 1735 cm^{-1}) are distinctly observed.^{1,2} In addition, a skeletal vibration of unoxidized graphitic domains in GO is found at ~ 1620 cm^{-1} . However, the intensity of oxygen containing functional groups is found to be decreased to a greater extent or nearly disappear in ZG nanocomposite. Moreover, a new vibration at ~ 1570 cm^{-1} in the ZG sample is noticed. This can be assigned to the characteristic skeletal vibrations of graphitic domains of chemically converted graphene (CCG)^{1,2} and implies the conversion of GO to CCG took place in the ZG nanocomposite. In PANI, the presence of N=Q=N (Q denotes quinoid ring) mode (~ 1140 cm^{-1}), C-N stretching mode (~ 1295 cm^{-1}), C=C stretching vibration of benzenoid rings (~ 1495 cm^{-1}) and C=C stretching of quinoid rings (~ 1580 cm^{-1})⁴⁻⁷ are observed. In the FTIR spectrum of ZGP sample, it is noted that some FTIR peaks at ~ 1580 , ~ 1294 and ~ 1142 cm^{-1} for polyaniline (PANI) are found to be shifted towards lower frequency region, compare to pure PANI. This shifting of FTIR vibrations of PANI in the ZGP nanocomposite can cause due to

complexation/interaction of ZG NPs with PANI in the ZGP sample.^{4,5} It is worthy to note that in both the nanocomposites, the existence of FTIR vibrations in 400-600 cm⁻¹ wavenumber region, suggests the presence of hexagonal ZnO.^{1,2}

Raman spectra of ZG and ZGP nanocomposites along with GO are displayed in **Figure S1e**. In this Figure, two characteristic Raman peaks are found at ~1350 cm⁻¹ (D band, as a breathing mode of k-point phonons in A_{1g} symmetry) and at ~1598 cm⁻¹ (G band, assigned to E_{2g} phonon of sp² carbon atoms) in precursor GO.^{1,2} However, in ZG and ZGP samples, the shifting of both G and D bands towards lower energy regions is observed. It is noted that the peak position of the G and D bands in ZG and ZGP samples is found at ~1345 cm⁻¹ and ~1580 cm⁻¹, respectively (**Fig. S1e**). In this respect, about ~18 cm⁻¹ shifting of G band and ~5 cm⁻¹ shifting of D band is noticed compare to GO. These shifting particularly in ZG can be accounted for the conversion of GO to CCG via the chemical interaction/complexation of CCG with the inorganic moiety (ZnO/Zn²⁺).^{1,2} On the other hand, the Raman peaks located at ~ 1165 cm⁻¹, ~ 1240 cm⁻¹, ~ 1330 cm⁻¹, ~ 1450 and 1530-1595 cm⁻¹ in pure PANI can be attributed to the Raman scatterings of C-H benzoid or quinoid, C-N benzoid, C-N⁺, C=N quinoid and C=C quinoid, respectively.⁸ However, the D and G bands in ZGP nanocomposite are found to be broadened compare to ZG sample. This spectral broadening of G and D bands in ZGP sample can be considered due to the chemical interaction that can happen between the ZG and the electron donating PANI in the ZGP nanocomposite.⁹ The assumption is justified from the AFM and TEM studies.

1. S. Bera, M. Ghosh, M. Pal, N. Das, S. Saha, S.K. Dutta and S. Jana, *RSC Adv.*, 2014, **4**, 37479–37490.
2. S. Bera, M. Pal, A. Naskar and S. Jana, *J. Alloys Compd.*, 2016, **669**, 177–186.
3. G. Ning, T. Li, J. Yan, C. Xu, T. Wei, Z. Fan, *Carbon* 2013, **54**, 241–248.
4. Y. Lin, D. Li, J. Hu, G. Xiao, J. Wang, W. Li, Xianzhi Fu, *J. Phys. Chem. C*, 2012, **116**, 5764–5772
5. H. Zhang, R. Zong, and Y. Zhu, *J. Phys. Chem. C*, 2009, **113**, 4605–4611.
6. D. Ghosh, S. Giri, M. Mandal, C. K. Das, *RSC Adv.*, 2014, **4**, 26094–2610.
7. S. Chatterjee, R. K. Layek, A. K. Nandi, *Carbon*, 2013, **52**, 509–519.
8. X. Xia, Q. Hao, W. Lei, W. Wang, D. Sun, X. Wang, *J. Mater. Chem.*, 2012, **22** 16844–16850.
9. Z. Pei, L. Ding, M. Lu, Z. Fan, S. Weng, J. Hu, P. Liu, *J. Phys. Chem. C*, 2014, **118**, 9570–9577.

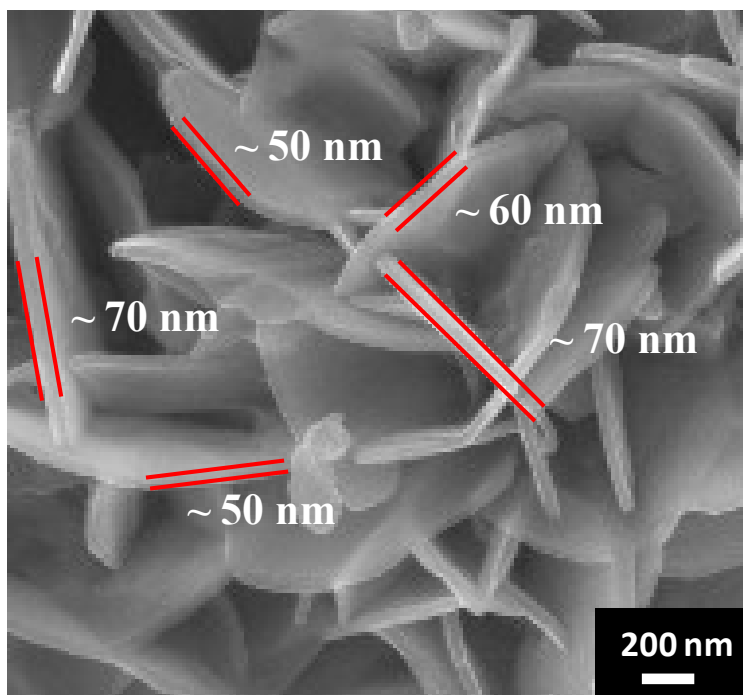


Figure S2: FESEM image of ZGP nanocomposite (ZG to aniline monomer weight *ratio*, 7 : 1 used in the precursor)

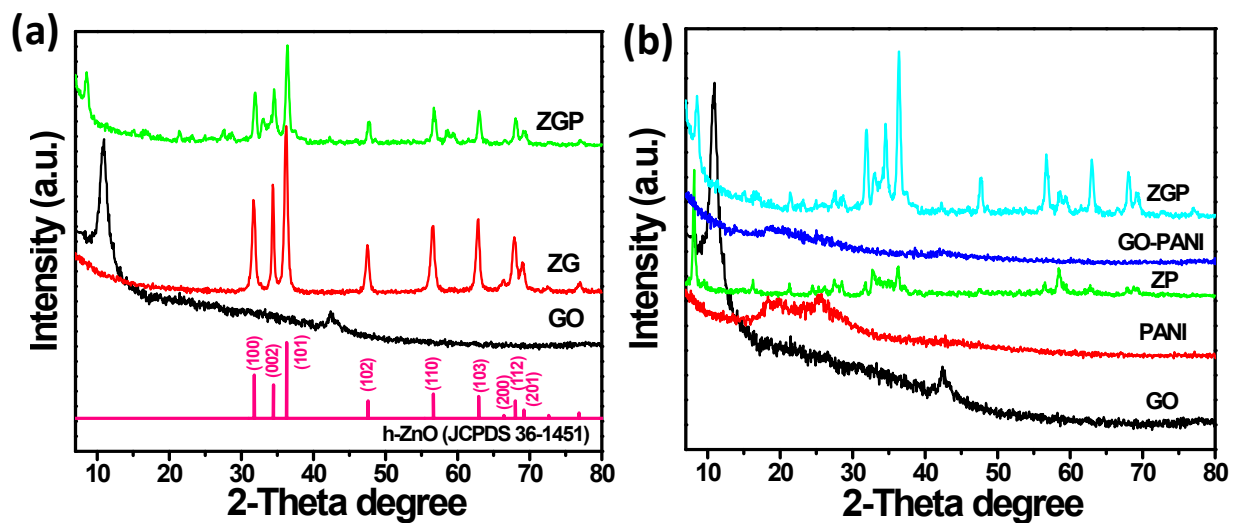


Figure S3: XRD patterns of (a) ZG, ZGP and precursor GO with (b) other nanocomposites and precursor materials.

The XRD pattern (**Fig. S3a**) of GO shows a strong diffraction (2θ) peak at 2θ , 10.9° (interlayer spacing, 8.12 \AA) along (002) plane and a weak intensity peak at 42.4° of its (100) crystal plane¹. It is noted that these XRD peaks are **fully** disappeared in ZG sample, implying that a complete conversion of GO to chemically converted graphene (CCG) is occurred in the nanocomposite. However, in ZG nanocomposite, different XRD peaks are found and these are well matched with hexagonal ZnO (h-ZnO). After introduction of PANI to the ZG nanocomposite forming ZGP, all the XRD peaks of ZG nanocomposite remain at the similar peak positions for h-ZnO but some additional peaks are observed (**Fig. S3b**) at $\sim 8.5^\circ$, $\sim 18.6^\circ$, $\sim 21.3^\circ$, $\sim 27.4^\circ$, $\sim 28.5^\circ$ and $\sim 32.7^\circ$. It is worthy to note that similar XRD peaks are found in ZP sample but the intensity of the peaks of h-ZnO in ZP is relatively low compare to ZGP. On the other hand, the characteristic XRD peaks of PANI^{2,3} are found at $\sim 18.6^\circ$ and 25.4° in pure PANI and the intensity of these peaks is relatively low in GO-PANI.² In this work, the XRD peak appeared at $\sim 8.5^\circ$, $\sim 21.3^\circ$, $\sim 27.4^\circ$, $\sim 28.5^\circ$ and $\sim 32.7^\circ$ for PANI can be attributed as a result of interaction of PANI with ZnO NPs in ZP and ZGP samples.^{4,5} It is known that the growth of PANI is possible along different crystallographic planes in presence of a crystalline metal oxide or ice.^{6,7} This can be the reason for the observation of more XRD peaks of PANI in ZP and ZGP samples. However, it is not clear at this moment for the disappearance of the 2θ peak at 25.4° in ZP and ZGP samples.

1. S. Bera, M. Ghosh, M. Pal, N. Das, S. Saha, S.K. Dutta and S. Jana, *RSC Adv.*, 2014, **4**, 37479–37490.
2. U. Rana and S. Malik, *Chem. Commun.*, 2012, **48**, 10862–10864.
3. Q. Hao, H. Wang, X. Yang, L. Lu, and X. Wang, *Nano Res.*, 2011, **4**, 323–333.
4. V. Eskizeybek, F. Sari, H. Gülce, A. Gülce and A. Avcı, *Appl. Catal. B*, 2012, **119–120**, 197–206.
5. K. G. B. Alves, J. F. Felix, E. F. de Melo, C. G. dos Santos, C. A. S. Andrade, C. P. de Melo, *J. Appl. Polym. Sci.*, 2012, **125**, E141–E147
6. S. Giri, D. Ghosh and C. K. Das, *Adv. Funct. Mater.*, 2014, **24**, 1312–1324
7. I. Y. Choi, J. Lee, H. Ahn, J. Lee, H. C. Choi and M. J. Park, *Angew. Chem. Int. Ed.*, 2015, **54**, 10497–10501.

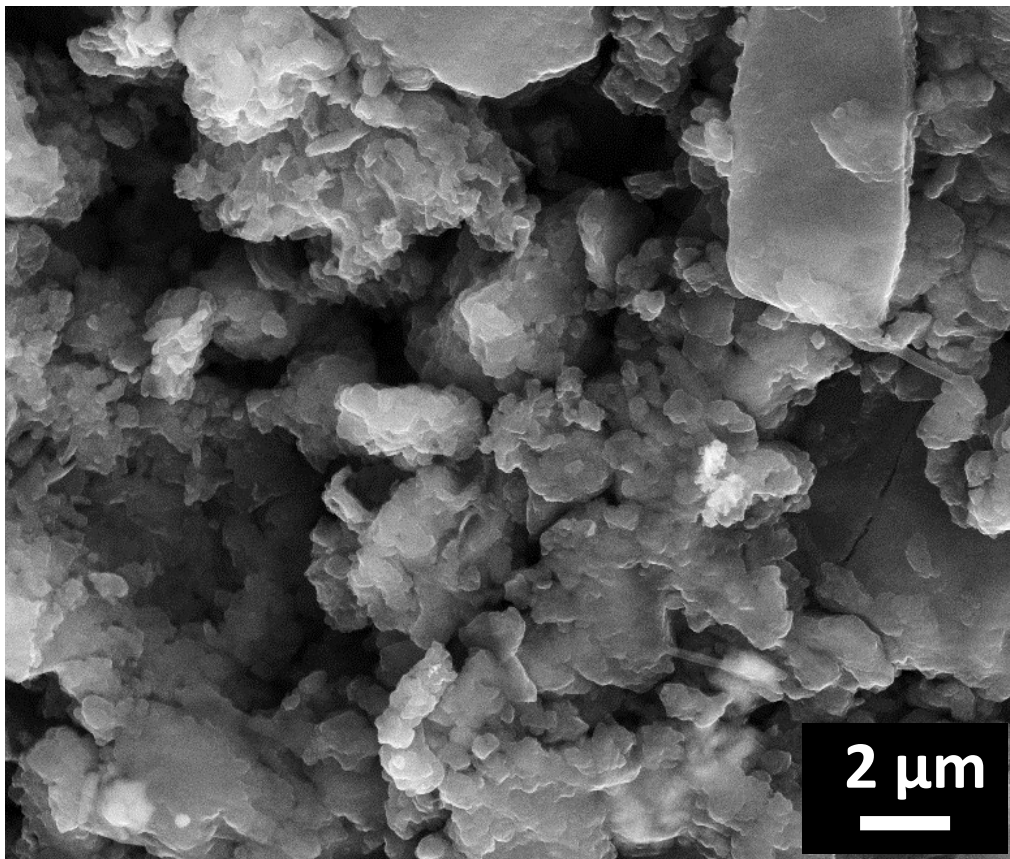


Figure S4: *FESEM image of GO-PANI*

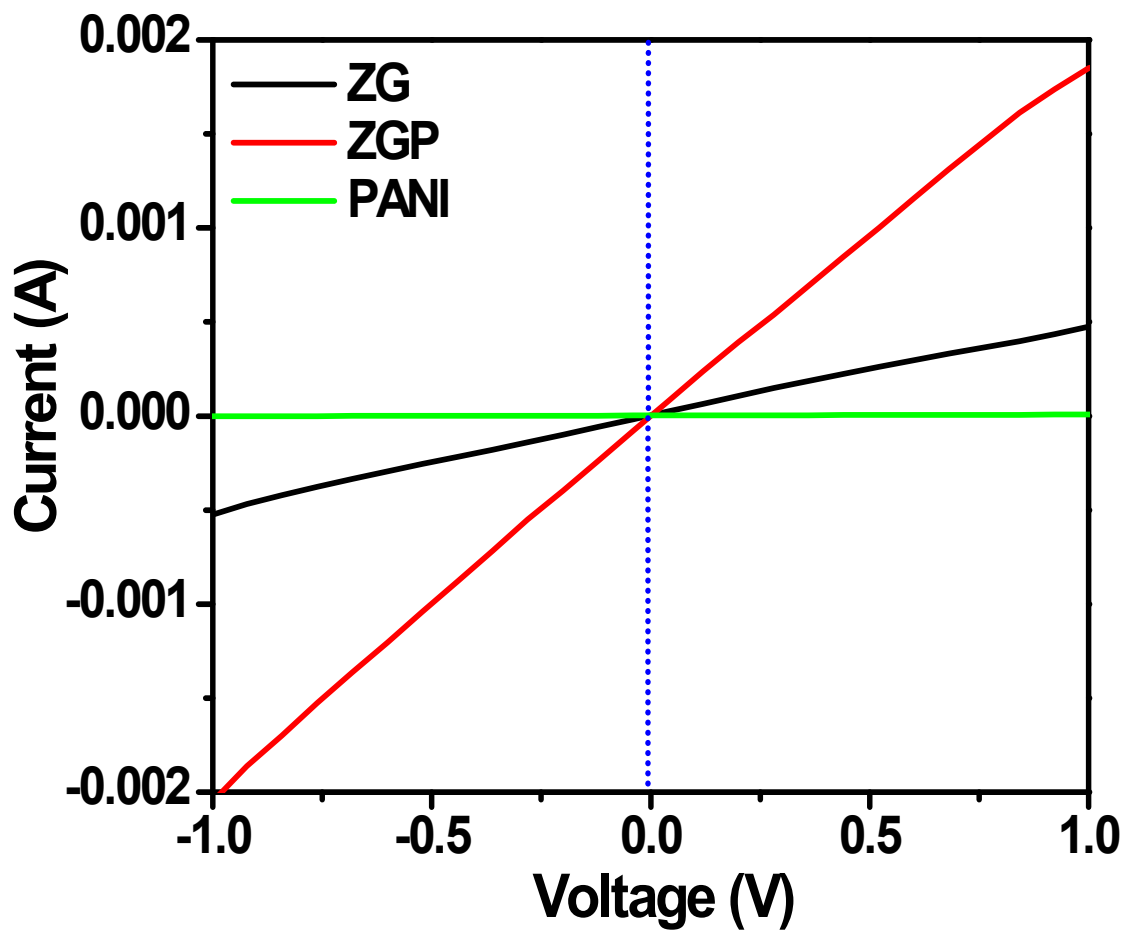


Figure S5: *I-V* curves of ZG, ZGP and PANI samples.

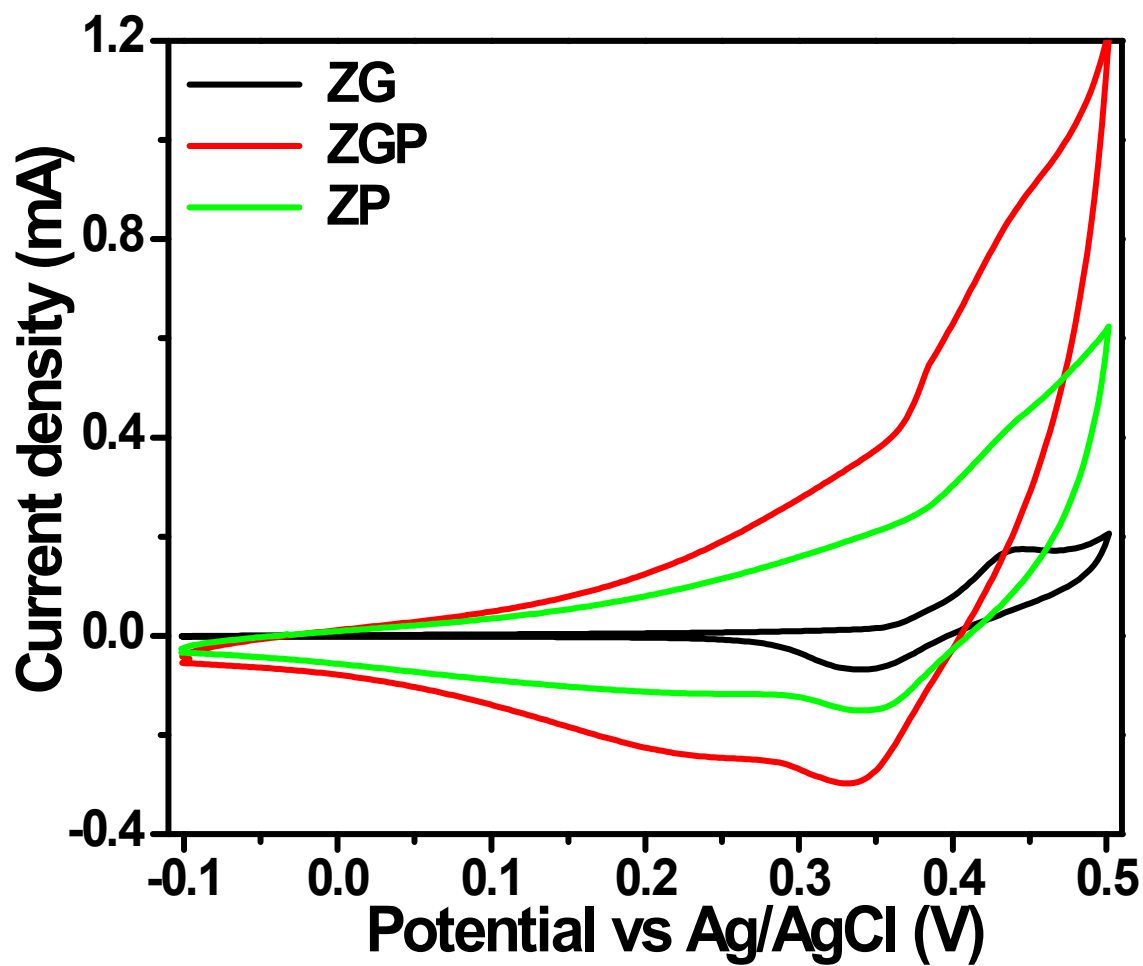


Figure S6: Cyclic voltammetry (CV curves) of ZG, ZGP and ZP at a scan rate 10 mVs^{-1} .