Electronic Supplementary Material (ESI) for ChemComm.

**Electronic Supplementary Information (ESI)**

# Graphene Quantum Dots doped Polyaniline Nanofiber as High Performance Supercapacitor Electrode Materials

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## Experimental Section

### Materials

Graphite powdered (12500, 500 mesh), Ammonium persulphate [$(NH_4)_2S_2O_8$ (APS)] were purchased from Sigma Aldrich and used without further purification. Merck Chemicals supplied Aniline, (distilled under reduced pressure and store at 5 °C in dark place before use), $H_2O_2$ (30% v/v), $KMnO_4$ and $NaNO_3$. Sulphuric acid (98%) was purchased from commercial sources as analytical pure reagents. All solutions were prepared in deionised water (18 MΩ cm, Millipore Milli Q water system).

### Synthesis of Graphene Oxide (GO)

Graphite oxide (GO) was synthesized by a modified Hummers method from graphite powdered.[S1] Following the synthesis of GO according to our earlier report. Briefly, 1.0g of graphite powdered slowly added to a 500mL conical flask equipped with 50 mL of conc. $H_2SO_4$ and a magnetic bar. The conical flask placed in an ice bath (0-5 °C) with vigorous stirring while maintaining the reaction mixture fixed. After the addition, graphite powered formed well dispersed black slurry and stirring continue for 2-3h. 1.0g of $NaNO_3$ and 5.0g $KMnO_4$ was added very slowly one by one at 0-5 °C. The mixture was allowed to warm at room temperature (25 °C) and stirred for 2h. Again conical flask with reaction mixture placed in an ice-bath and 110 mL water was then added slowly while the temperature was not raised more than 90 °C with constant stirring for 30 min. The mixture was poured into 200 mL of water, after which 7 mL of 30% $H_2O_2$ was added through inner wall of the conical flask. Immediately the colour of the solution changed from dark brown to pale yellow. The solution was then filtered using Millipore filter paper to get pale yellow residue. The residue was redispersed in water and centrifuged at 15000 rpm washed several times with water until the pH of the solution was neutral. The resultant solid material was dried in vacuum at 25 $^{o}$C and stored in the ambient environment to get pure GO.

**Synthesis of Graphene Quantum Dots (GQD)**

Synthesized flake shaped GO was dispersed in water (4 mg/mL) with sonication followed by stirring. 40 mL of 30% $H_2O_2$ was subsequently added to 5 mL of GO suspension. The resulting mixture reacted at 90 $^{o}$C with vigorous stirring for 12h. Unreacted $H_2O_2$ and water was removed by rotary evaporation at 60$^{o}$C. Ethanol was added as a poor solvent to precipitate out and wash the GQD. Finally GQD was purified by dialysis.

**Table S1: Preparation of GQD/PANI composite with different GQD weight ratio**

| *Composites* | *Aniline [mmol]* | *GQD [wt%]* | *GQD:Ani (w/w)* | *APS [mmol]* | *Yield (mg)* | *$C_s$ [F /g]** |
|---|---|---|---|---|---|---|
| *GQDP0* | *100 mg [1.1]* | *0 mg* | ------ | *250* | *27* | *205.7* |
| *GQDP5* | *100 mg [1.1]* | *5 mg* | *0.05: 1* | *250* | *91* | *332.89* |
| *GQDP10* | *100 mg [1.1]* | *10* | *0.1:1* | *250* | *96* | *1044.34* |
| *GQDP15* | *100 mg [1.1]* | *15* | *0.15:1* | *250* | *103* | *776.67* |
| *GQDP20* | *100 mg [1.1]* | *20* | *0.2:1* | *250* | *106* | *319.34* |

* All specific capacitance are at 1 A/g current density

## Characterization of GQD and GQDP composite

Surface morphology as well as over all morphology of GQDP composite were characterized by FESEM (JEOL, JSM 6700F) instrument operating at 5 kV. To reduce the surface potential, samples were coated with platinum for 90 s. TEM imaging of GQDP composites carried by HRTEM (JEOL, 2010EX) instrument, an accelerating voltage of 200 kV and. Small amount of water dispersed samples were spread on a 200 mesh Cu-grid coated with a holey carbon support AFM topologies of synthesized GQDs was recorded using atomic force microscopy (Veeco, model AP0100) in noncontact mode at a tip resonance frequency of 300 kHz. The well dispersed water sample spread on freshly cleaved mica surface at ambient conditions. UV-vis spectroscopy of GQDs and GQDP composites were done by Agilent (model 8453) UV-vis spectrophotometer. Fluorescence spectra of GQDs obtain by using Horiba Jobin Yvon Fluoromax 3 instrument. The FTIR spectroscopy was carried out in a FTIR-8400S instrument (Shimadzu) using KBr pellets. Raman studies were performed using a Raman triple spectrometer (model T-64000, Horiba-Jobin Yvon) fitted with a synapse detector. The samples were excited with a 514.5 nm laser (Spectra Physics, model Stabilite 2017). Powered WXRD analysis were performed by using a Bruker AXS diffractometer (D8 advance) using CuK$_{\alpha}$ radiation ($\lambda$=1.54 Å), a generator voltage of 40 kV and a current of 40 mA. XPS study was performed by using a focused monochromatized A1 K$_{\alpha}$ X-ray source (1486.8 eV) in Omicron Nano-Technology 0571 XPS instrument.

## Electrochemical measurements

All electrochemical experiments like cyclic voltammogram (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) study was done by a CHI6087E electrochemical workstation (CHI, USA) by a conventional three-electrode system. In present study modified glassy carbon electrode (GCE) as a working electrode, a saturated calomel electrode (SCE) as the reference electrode, Pt wire electrode as the auxiliary electrode and 0.5 M $H_2SO_4$ as a electrolyte were used. Prior to use the GCE (3 mm in diameter, surface area of 0.07 $cm^2$) were carefully polished with 1, 0.3, and 0.05 μm alumina powder and sequentially washed through water and ethanol with sonication at room temperature until a mirror finish was obtained. The specific capacitance ($C_s$), energy density, (E) and power density (P) were calculated from the discharge curve based on equation (1), (2) and (3) respectively.

$$\mathrm{C_s} = \frac{i \times \Delta \mathrm{t}}{\Delta \mathrm{V} \times \mathrm{m}} \quad \text{(F/g)} \qquad \text{........................} (1)$$

$$E = \frac{C_s \times \Delta V^2}{7.2} \text{ (W h /kg)} \qquad \text{........................} (2)$$

$$P = E \times 3600/t \text{ (W /kg)} \qquad \text{........................} (3)$$

Where, ‘i’ = current (A); ‘$\Delta$t’ = discharge time (s), ‘$\Delta$V’ = voltage windows (V) and ‘m’= mass of GQDP composites (g).

## UV-vis and PL study of GQDs

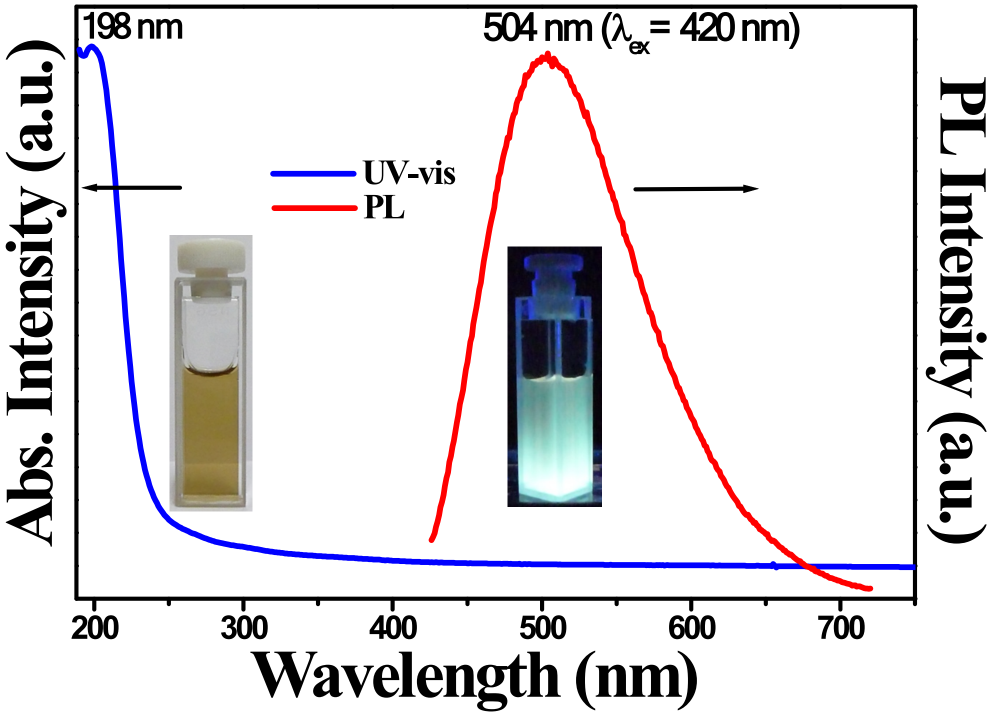

**Fig.S1**: UV-vis and PL spectra of water well dispersed GQD.

## XRD study of Graphite, GO and GQD

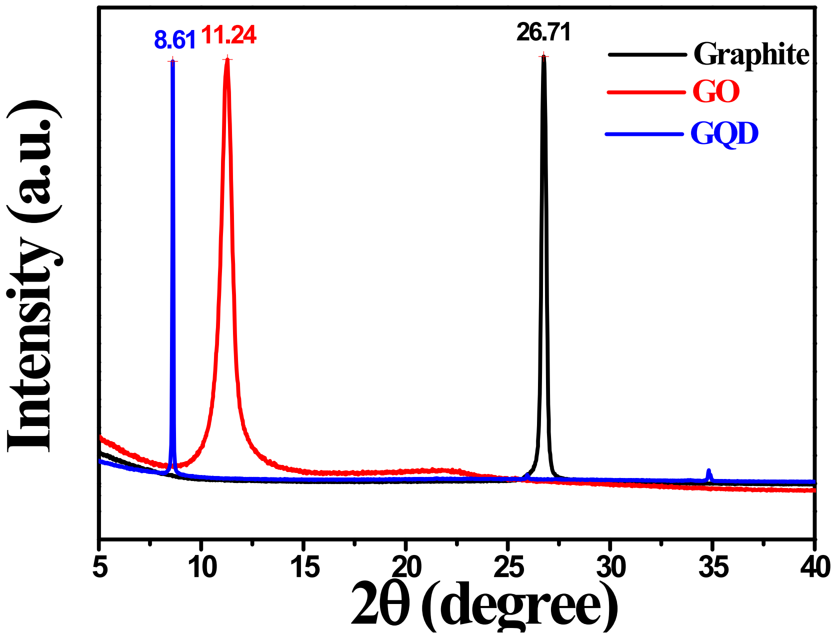

**Fig.S2**: XRD pattern of synthesized graphite, GO and GQDs

**FTIR study**

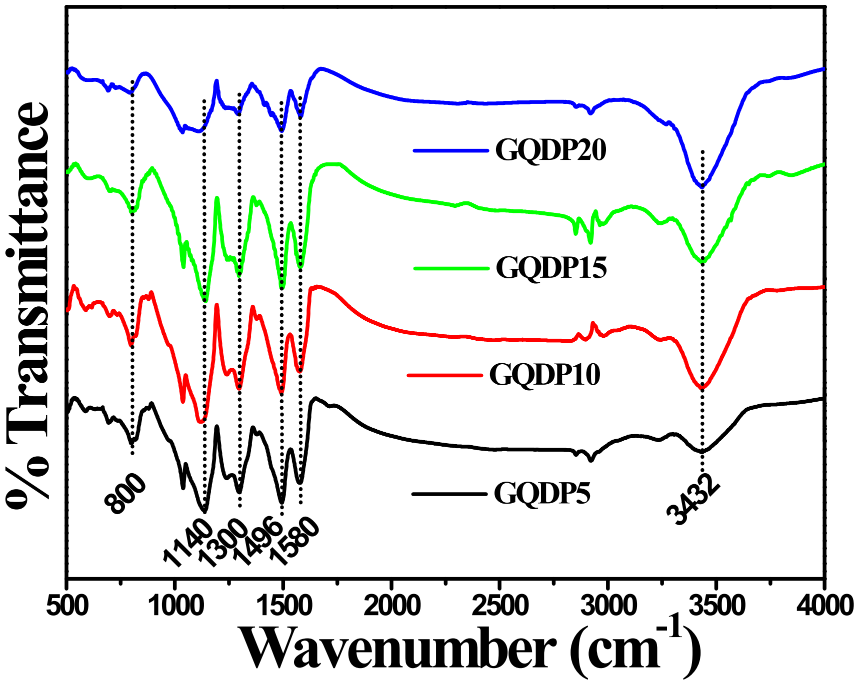

**Fig.S3**: FTIR spectra of synthesized GQDP composites

**XPS study of GQDP composites**

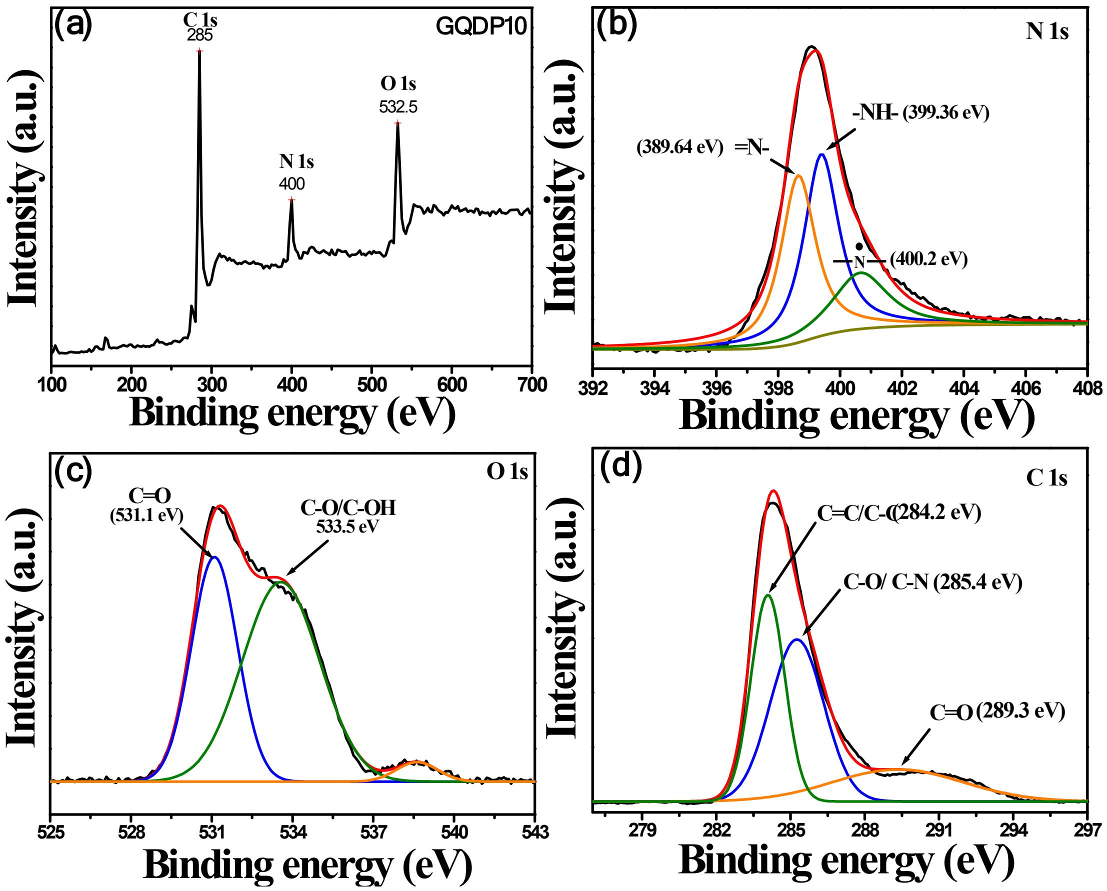

**Fig.S4** XPS study of GQDP10 composite (a) whole scan (b) deconvolution spectra of N1s, (c) O1s and (d) C1s.

The C1s (~285 eV) peak of GQDP10 composite deconvolate into three Gaussian sub-peaks position at ~284.2 eV (C=C/C-C), 285.4 eV (C-O/C-N) and 289.3 eV (C=O) in Fig.S3. Again deconvolate N1s peak shown in Fig.S4 that contains two sub-peaks at ~531.1 eV (C=O) and 533.5 eV (C-O/ C-OH).

### XRD study of GQDP composites

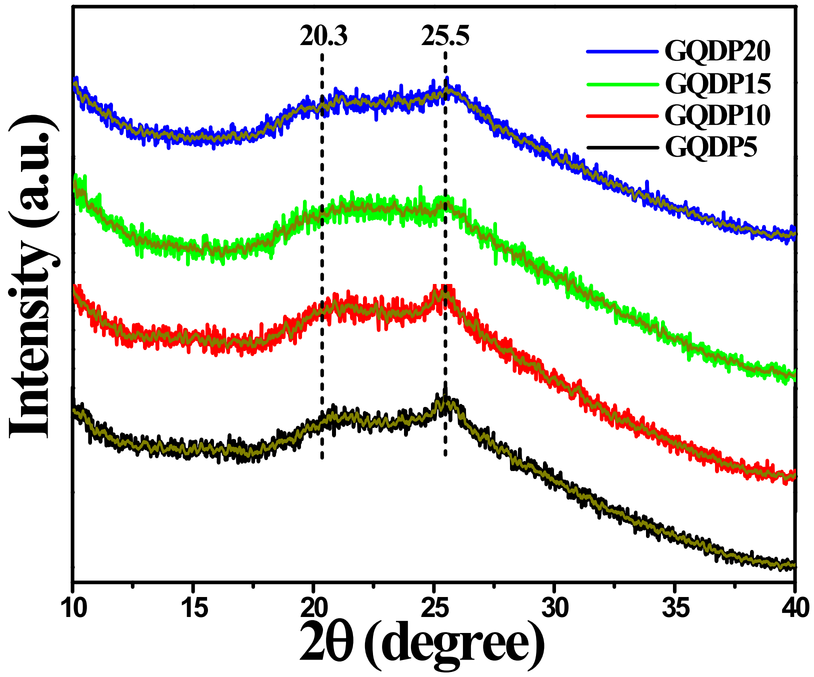

**Fig.S5** Powder XRD study of synthesized GQDP composites.

### Raman Study of GQDP composites

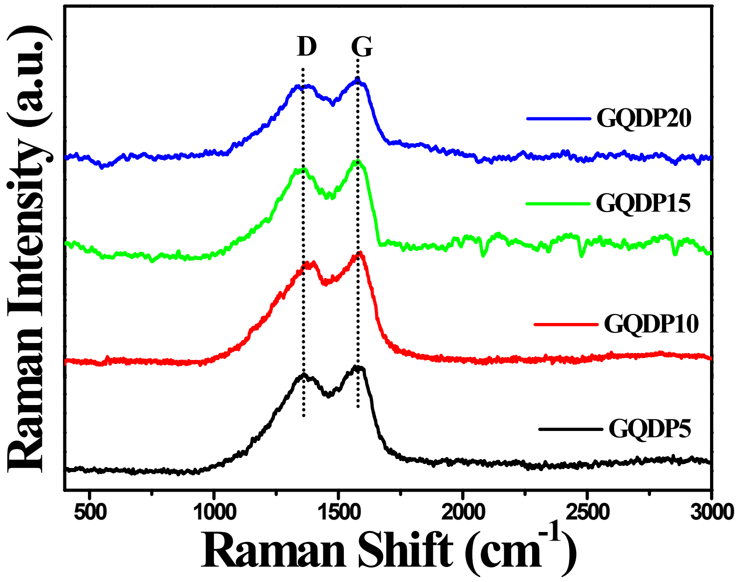

**Fig.S6** Raman study of synthesized GQDP composite under 514 nm laser

Raman spectra of GQDP composites shows GQDs are involve for PANI formation as a soft doping materials. All GQDP composites have D and G band at 1355 and 1580 cm$^{-1}$ respectively. D band related to defects or edge areas and G band corresponds to the vibration of sp$^2$-hybridized carbon. GQDs have some fluorescence behaviour which makes noise in region of 2000-3000cm$^{-1}$. In all composites have higher ID/IG ratio (<1.0) suggested that GQDs intercalation with PANI.

## CV plot of GQDP10 composite with different scan rate

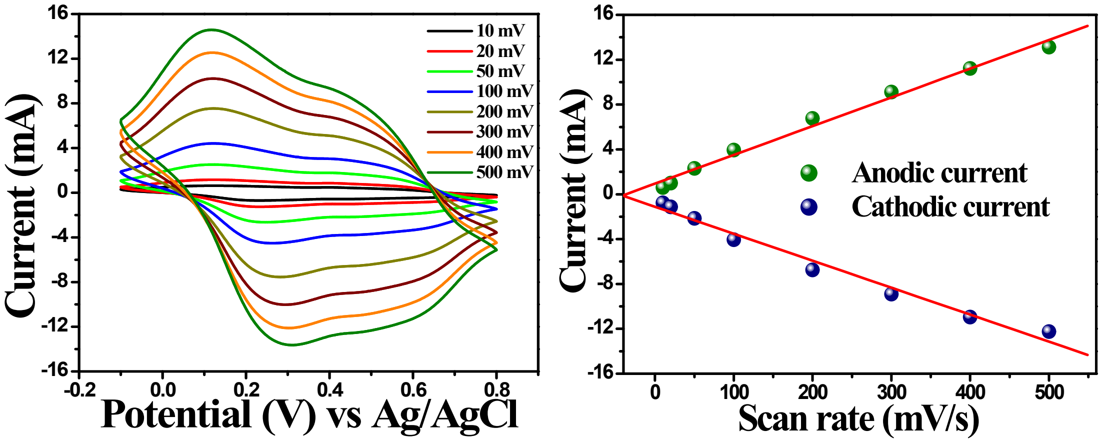

**Fig.S7** Scan dependent CV study of GQDP10 composite in 0.5 M $H_2SO_4$ electrolyte by 3 electrode cell at 25 °C

## Specific capacitance of GQDP composite

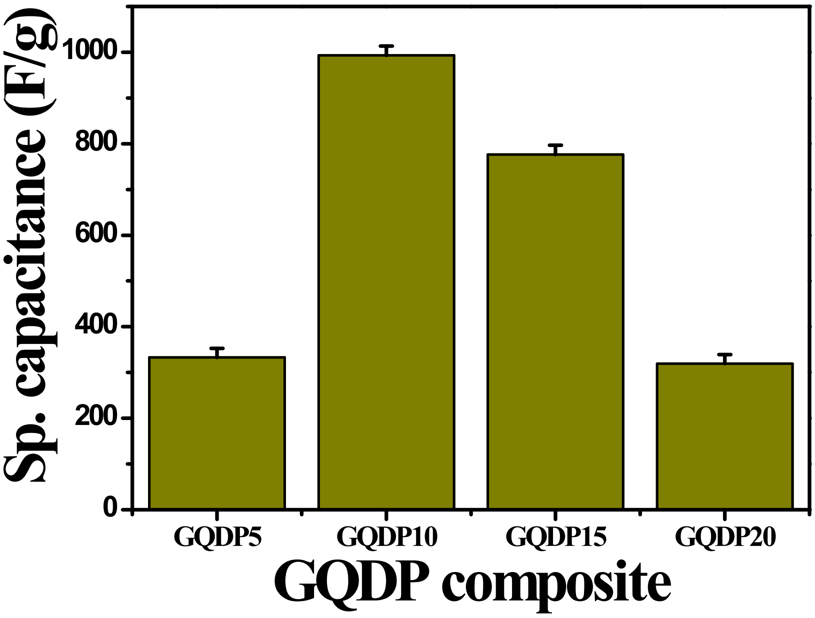

**Fig.S8**: Specific capacitance value of different GQDP composites.

## Impedance study

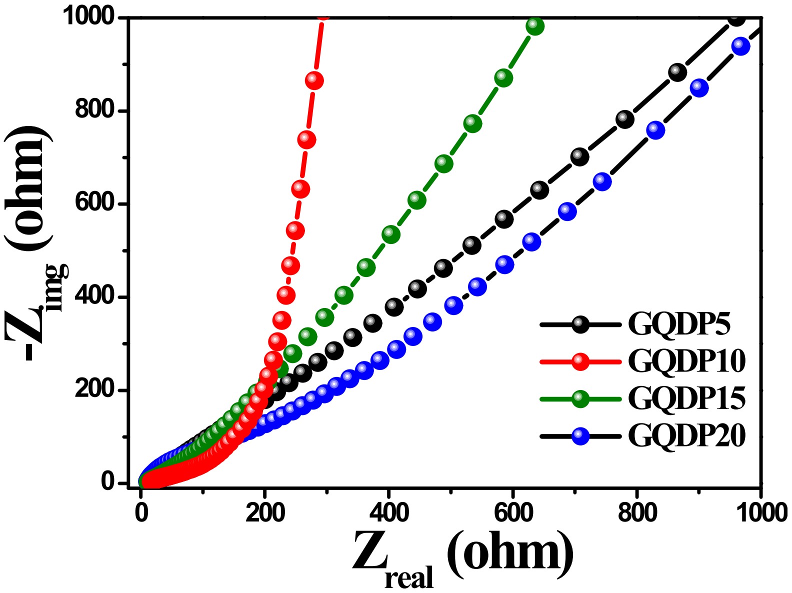

**Fig.S9** Impedance study of GQDP composites.

## Previous report about supercapacitor

| Materials | Preparation method | Current density | $C_s$ (F/g) | Ref | Remark |
|---|---|---|---|---|---|
| **GQD/PANI** | Chemical oxidative polymerization | 1 A/g | 1044 | **This work** | 1. Simple solution process to make GQD/PANI composites.<br>2. Good Specific capacitance value with small voltage drop |
| **rGO-PANI** | Chemical oxidative polymerization | 1 A/g | 533 | **S2** | Specific capacitances value comparable less |
| **Graphene-PANI paper** | Electro-polymerization | 1 A/g | 763 | **S3** | Polymerization technique is different with low specific capacitance value |
| **PANI** | Chemical-Vapor-Induced in Situ Polymerization | 1 A/g | 2136 | **S4** | Electrode fabrication processes is really different and laborious. |
| **Porous nanorod PANI-graphene** | Chemical oxidative polymerization | 1 A/g | 878.57 | **S5** | Specific capacitances value comparable less |
| **GQDs/PANI** | Electrochemical polymerization | 15.0 $\mu A/cm^{-2}$ | 667.5 $\mu F/ cm^{-2}$- | **S6** | Separately, PANI as positive active material and GQDs as negative active material are used |

## References

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