Electronic Supplementary Information (ESI)

Reduced Graphene Oxide/Fe_3O_4/Polyaniline Nanostructures as Electrode Materials for All-Solid-State Hybrid Supercapacitor

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Synthesis of Graphene Oxide (GO)

Graphite oxide (GO) was synthesized by a modified Hummers method from graphite powdered.[S1, S2] Following the typical synthesis of GO according to our earlier report. Briefly, 1.0g of graphite powdered slowly added to a 500mL conical flask placed in an ice bath (0-5 ^{o}C) equipped with 50 mL of conc. H_2SO_4 and a magnetic bar 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 with continuous stirring. The mixture was allowed to warm at room temperature (25 ^{o}C) and stirred for additional 2h. Again conical flask with reaction mixture placed in an ice-bath and 110 mL water was then added very slowly while the temperature was not raised more than 90 °C. The mixture was again poured into 200 mL of water, after which 7 mL of 30% H_2O_2 was added carefully 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.

Table S1 Preparation of rGF and rGFP

Composite	Aniline	GO	$FeCl_2$	$FeCl_3$	Reaction time	Reaction temperature
rGF	0 µL	10 mg	100 mg	0 mg	12 h	25^{o}C
RGFP	100 µL	10 mg	100 mg	0.8 mg	24 h	25^{o}C

Previous work report (Table S2)

Materials	Specific capacitance	Energy density	Power density	Cyclic stability	Electrolyte & Devices	References
rGO/Fe_3O_4/Polyaniline	283.4 F/g at current density of 1 A/g	35.1 Wh/kg	1128 W/kg	78% after 5000th cycles	H_3PO_4/PVA gel electrolyte and solid-state device	This work
Graphene/Polyaniline	210 F/g at current density of 0.3 A/g	~19.1 Wh/kg	~1400 W/kg	High cyclic stability	1M H_2SO_4 electrolyte and solid-state device	Ref S3
MnO_2 template based PANI nanotubes	528 F/g at current density of 1 A/g	84 Wh/kg	182 W/kg	------	Ionic liquid/H_2SO_4 gel electrolyte and solid-state device	Ref S4
Stretchable polyaniline/graphene electrode	261 F/g at current density 0.38 A/g	23.2 Wh/kg	399 W/kg	89% after 1000th cycles	H_3PO_4-PVA gel electrolyte and solid-state device	Ref S5
Fe_3O_4@Carbon Nanosheet	586 F/g at current density of 0.5 A/g	18.3 Wh/kg	351 W/kg	70.8% (5000th cycles)	KOH/PVA gel electrolyte and all solid-state device	Ref S6
Fe_3O_4/rGO nanocomposites	480 F/g at 5 A/g in three electrode system	67 Wh/kg	5506 W/kg	100% after 1000th cycles	1M KOH electrolyte and three electrode system	Ref S7
Porous Graphene/Polyaniline Nanocomposite	864 F/g at current density of 1 A/g three electrode system	24.02 Wh/kg	400.33 W/kg	85.6% after 500th cycles	PVA/H_2SO_4 gel electrolyte and all solid-state device	Ref S8
CNT/graphene and Mn_3O_4-NPs/graphene	72.6 at current density of 0.5 A/g	32.7 Wh/kg	----	86.0 % after 10000th cycles	Potassium polyacrylate (PAAK)/KCl gel electrolyte	Ref S9
Fe_3O_4 NPs on Graphene sheets	220.1 at current density of 0.5 A/g	----	----	Stable after 3000th cycles	1M KOH electrolyte and three electrode system	Ref S10

Different scan speed cyclic voltammetry study

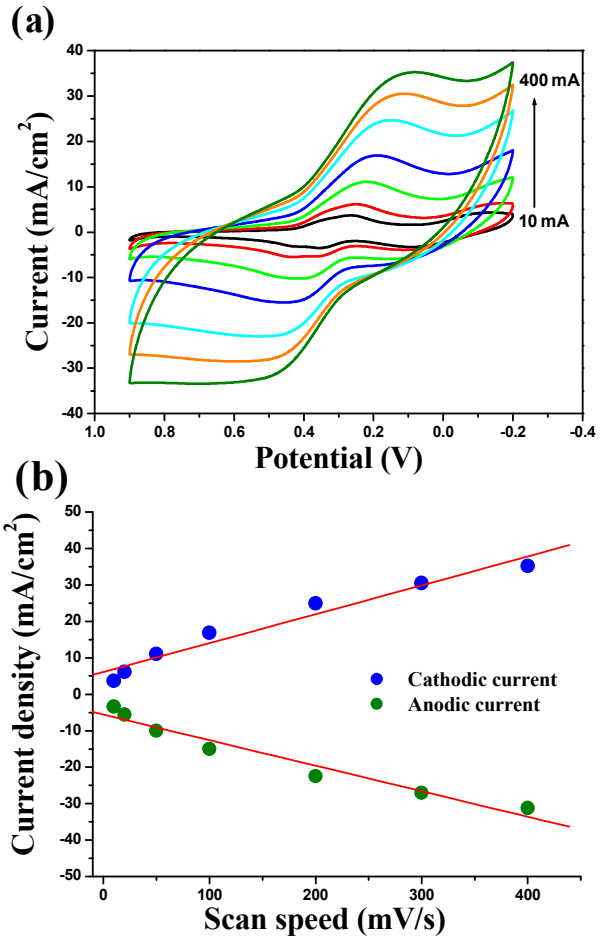

Figure S1 Scan dependent CV study of rGO/Fe_3O_4/PANI composite in two electrode system at 25 ^oC temperature

Synthesis of rGO/PANI

Synthesis of rGO/PANI composite: Graphene oxide (GO) was dispersed in water (10 mg in 10 mL). Aniline (108 mg, 1.0 mmol) was added to GO aqueous dispersion with continuous stirring for 30 min at 25 ^{o}C. After that, 5.0 mL of aqueous $FeCl_3$ solution (1.0 mmol) was added drop wise to resulting GO-aniline mixture with stirring at same temperature for 30 min. The resulting suspension was kept in low temperature (0-5 ^{o}C) for 24h with mechanical stirring. Finally, green color precipitate was thoroughly washed with water, methanol and dried under vacuum at 60 ^{o}C temperature over night and get greenish-black rGO/PANI powder.

Electrochemical study of rGO/PANI composite

Electrochemical study: Electrochemical measurements of rGO/PANI composite were carried out by using same instrument (CHI6087E electrochemical workstation (CHI, USA)) by two-electrode system. Cyclic voltammetry (CV) and Galvanostatic charge-discharge studies were performed within the potential range of (-0.2 to 0.9 V) and specific capacitance (C_s), energy density (E) and power density (P) were calculated by following equation 1, 2 and 3 respectively. The electrochemical results (2-electrodes method) were showed in **Figure S3** and compared in **Table S4**.

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

$$E = \frac{1}{2} \times \Delta \mathrm{V}^2 \times C_s \ (W\,h/kg) \quad \text{----------} \quad \textbf{(2)}$$

$$P = \frac{E}{\Delta t} \ (W/kg) \quad \text{----------} \quad \textbf{(3)}$$

2-Electrode electrochemical study of rGO/PANI composite

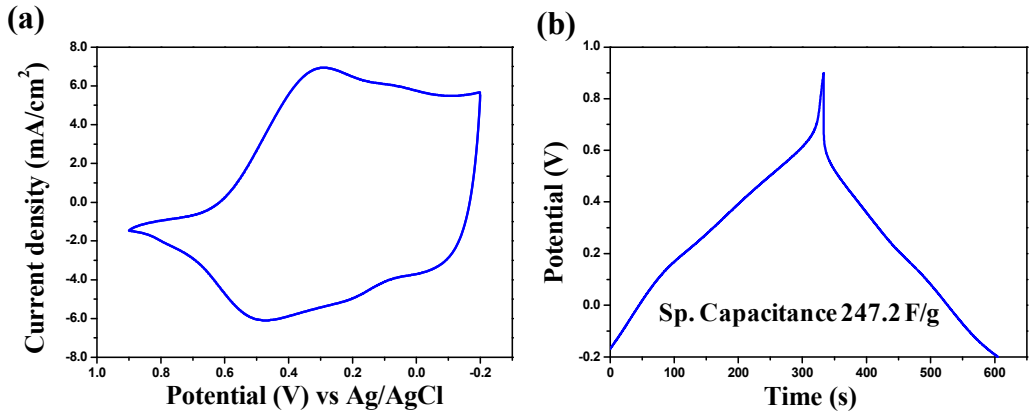

Figure S2 All-solid-state electrochemical measurement carried out by **two electrode system** for rGO/PANI composites (a) CV study at scan speed 50 mV/sec; (b) GCD measurement at 1A/g current density.

Table S4 Comparable electrochemical study for all composites (Two electrode)

[#]*Composite*	*Discharge time (Δt in sec)*	*Specific Capacitance (C_s in F/g)*	*Energy density (E in W h/kg)*	*Power density (P in W/kg)*
GO	*6.1*	*~ 5.5*	*~1.0*	*590*
rGO/Fe_3O_4	*73.1*	*~ 66.5*	*11.2*	*551.5*
rGO/Fe_3O_4/PANI	*312.2*	*~ 284*	*47.7*	*550.0*
rGO/PANI	*271.9*	*~ 247*	*41.5*	*549.4*

[#] *GCD data for all composites are at 1.0 A/g current density.*

Electrochemical performance of synthesized composite using three electrode system

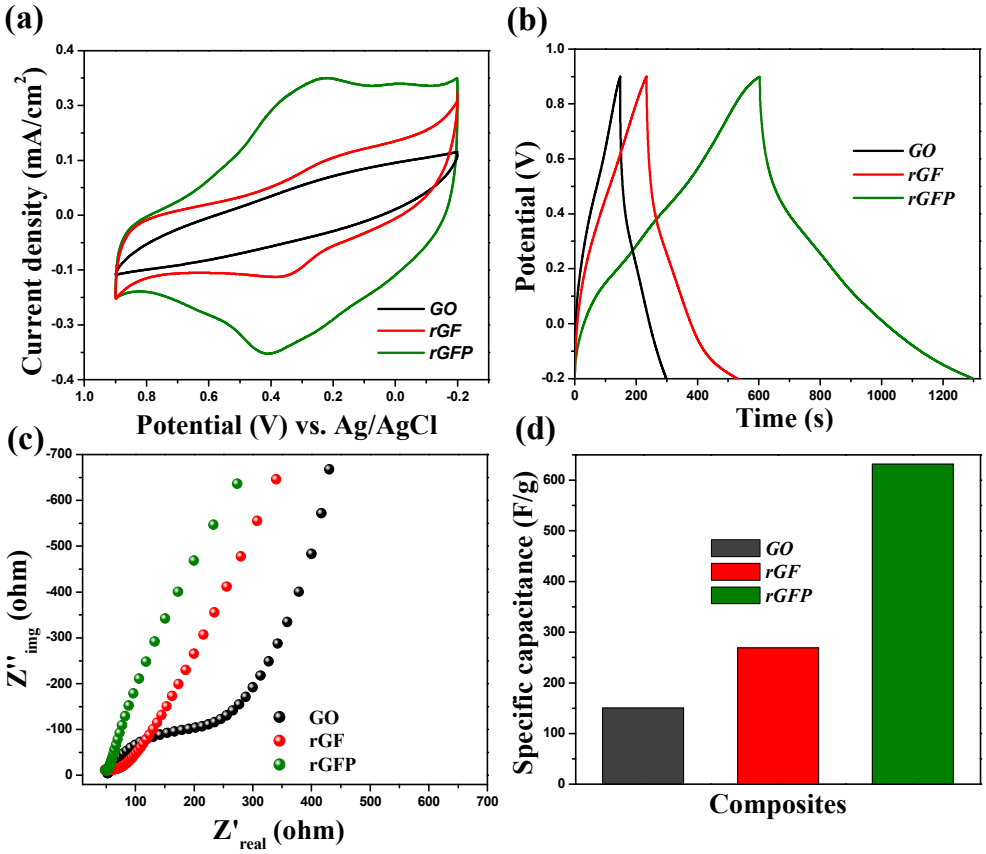

Figure S3 Electrochemical measurement (3- electrode) of synthesized composites (a) CV study (scan rate of 50 mV/s); (b) GCD study (at 1 A/g current density); (c) electrochemical impedance study (Nyquist plot, at 0.1 - 100000 Hz range); (d) Bar plot for specific capacitance. All measurement was done in 0.5 M H_3PO_4 aqueous solution.

Table S3 Electrochemical performance of synthesized composite using **three electrode system**

Composite	*Sp. Capacitance (C_s)**	*Energy density (E)**	*Power density (P)**
GO	*136.9 F/g*	*23 Wh/kg*	*549.8 W/kg*
rGO/Fe_3O_4	*269.2 F/g*	*45.2 Wh/kg*	*549.5 W/kg*
rGO/Fe_3O_4/PANI	*631.7 F/g*	*106.1 Wh/kg*	*549.6 W/kg*

** Electrochemical data (C_s, E and P) at current density 1 A/g*

TEM and XRD study after 5000th GCD cycles

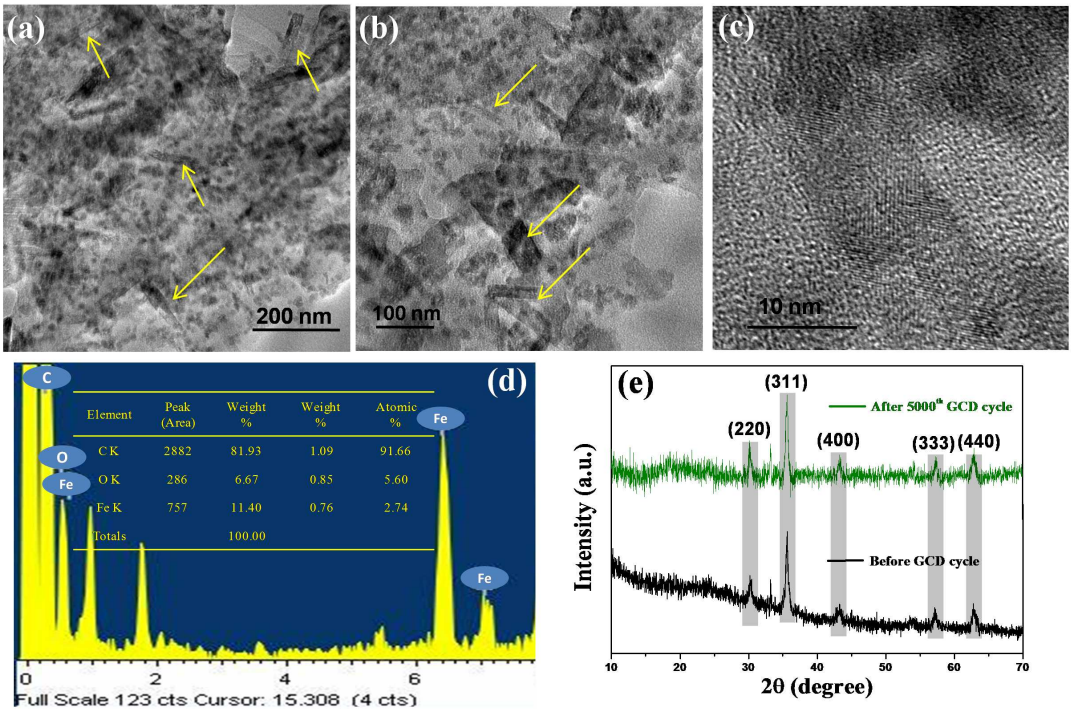

Figure S4 (a)-(c) Low and high resolution TEM image; (d) EDX pattern and (e) Powder XRD signature of rGFP composite after 5000th cycles.

Stress-Strain measurement of prepared device

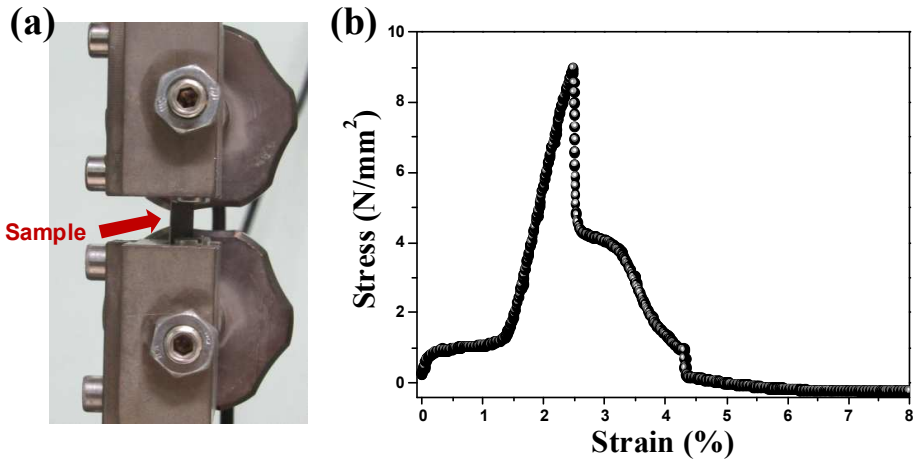

Figure S5 (a) One instrumental snap short; (b) Stress-strain relationship curve of as prepared all solid state supercapacitor device

BET study of synthesized composite

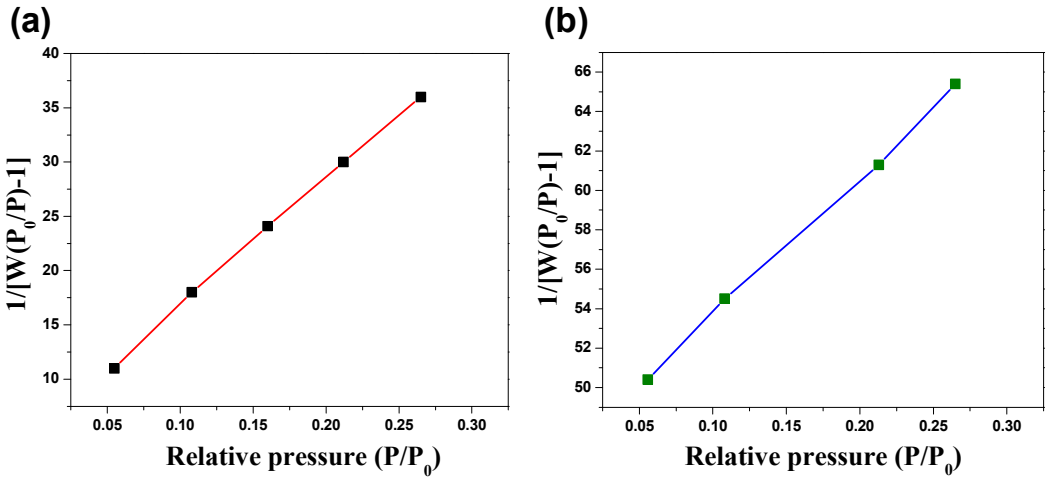

Figure S6 BET curve for (a) rGO/Fe_3O_4 and (b) rGO/Fe_3O_4/PANI

Table S6 Surface area of synthesized composite

Composite	***Surface area (m^2/g)***
rGO/Fe_3O_4	*28.278*
rGO/Fe_3O_4/PANI	*29.731*

Potential window optimization for rGO/Fe_3O_4/PANI composite

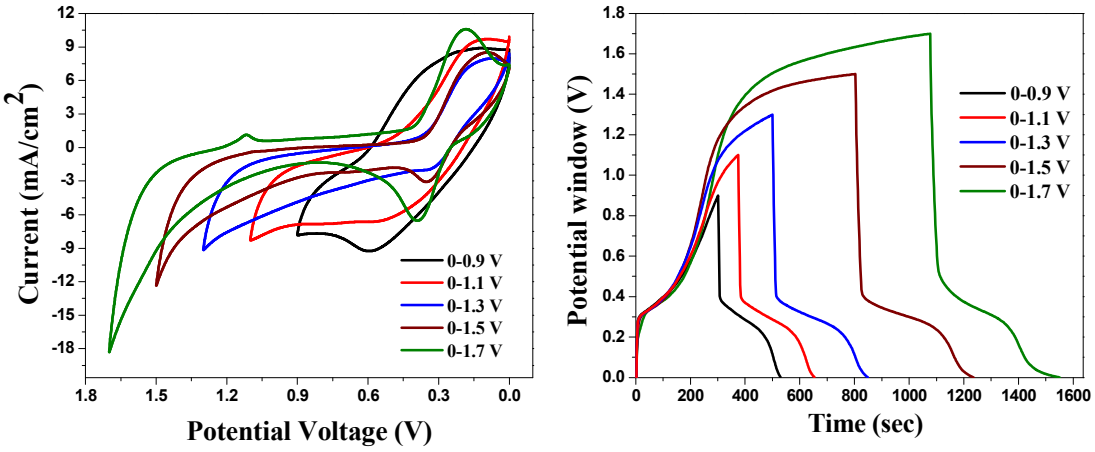

Figure S7: Electrochemical potential windows optimization study (a) CV curves of rGO/Fe_3O_4/PANI composite an in different potential windows (0-0.9 to 0-1.7 V) at scan rate of 50 mV/s; (b) GCD curves obtained over different voltages (0-0.9 to 0-1.7 V) at a current density of 1 A/g.

To identify the optimum potential window, we have performed CV and GCD studies. In CV measurements, when the potential window is increased from 0-0.9 V to 0-1.7 V, the area under curve is decreased. It indicates that upto a certain voltage, synthesized rGO/Fe_3O_4/PANI composites behave as good capacitive material. Similarly in GCD results, with increasing potential window, voltage drop is increased and at the same time the charging time is more over discharging time. GCD study supports that upto a certain voltage, rGO/Fe_3O_4/PANI composites behave as low voltage drop capacitive material. From CV and GCD results, it is concluded that 0-1.3 V potential window is the optimum operating potential window for rGO/Fe_3O_4/PANI ternary composite.

References

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