Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Functionalization of Wet-Spun Graphene Films *via* Aminophenol Molecules for High Performance Supercapacitors

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Experimental Section

Materials: All the reagents were purchased from analytical grade and used as received. GO with average lateral size of 2 µm was purchased from Hangzhou Higher See Technology Inc.

1- Experiment

2.1- Synthesis of rGO and AP/rGO composite

Firstly, 1 mmol solution of OAP, PAP and MAP were prepared by dissolving 109 mg of each molecule in 60 ml of DI water and sonicated for at least 15 min in water bath to completely dissolve the substance. Then, the solution was transferred into a Teflon autoclave (100 ml volume) and added wet-spun GO film. The hydrothermal process was treated at 125 °C for 5 h. After that, the autoclave was naturally cooled to room temperature and washing of as-prepared N-doped reduced graphene oxide (N-rGO) was performed with ethanol and DI water to remove the unreacted precursors. After washing process, the sample was dried in an oven at 80 °C overnight and stored at room temperature for further characterization. The control sample of rGO was also prepared by the above process without adding AP molecules. All the chemicals used in this study were of analytical grades and used without any further purification.

2.2- Characterization

The as-prepared AP/rGO samples and rGO were analyzed under scanning electron microscope (SEM, Hitachi S-4800). Mechanical property test was carried on HS-3001C at a loading rate of 10% per min. Electron mobility was tested on Nanometrics HL5500 Hall system. Fourier-transform infrared (FT-IR) spectra were collected by Bruker, using the KBr pellet method. X-ray diffractometer (XRD, Rigaku, D/max-2500, using graphite monochromatized CuK α radiation). Raman spectra measurements were conducted on an inVia-Reflex microscope (Renishaw). Element composition of the samples was analyzed by X-ray photoelectron spectroscopy (PHI 5000C ESCA system (Physical Electronics) operated at 14.0 kV). The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed by CHI660e, CH Instruments, Inc. electrochemical work station using a two-electrode setup. By using a mixed cellulose esters membrane as separator (pore size 0.22µm), and 1 M H_2SO_4 as electrolyte. The weight of each electrode material was about 0.5 mg. Where, AP/rGO, Ag/AgCl (KCl, 0.1 M) and a Pt plate (0.5 mm diameter) were used as a working electrode, reference electrode and as the counter electrode respectively.

Calculations:

(1) The specific capacitance calculated by CV:

$$\mathrm{Cs} = \frac{\int \mathrm{IdU}}{\mathrm{m} \times \mathrm{u} \times (\mathrm{U}_2 - \mathrm{U}_1)}$$

Where Cs (F/g), m (g), u (V/s), U_2 and U_1 (V), and I (A) are the gram specific capacitance, the weight of single electrode, scan rate, high and low potential limit of CV tests, and the instant current of CV curves, respectively

(2) The specific capacitance calculated by GC:

$$\mathrm{Cs} = \frac{2 \times \mathrm{I} \times \mathrm{t}}{\mathrm{m} \times \Delta\mathrm{U}}$$

Where Cs (F/g), I (A), t (s), ΔU (V), and m (g) are the gram specific capacitance, the discharge current, the discharge time, the potential window and the weight of single electrode, respectively.

(3) The Energy density (E) calculation:

$$E = \frac{1}{3.6 \times 8} CU^2$$

Where, C and U are specific capacitance and potential window, respectively.

(4) The power density (P) calculation:

$$P=\frac{E}{\mathrm{t}}$$

Where E is energy density and t is the discharge time respectively.

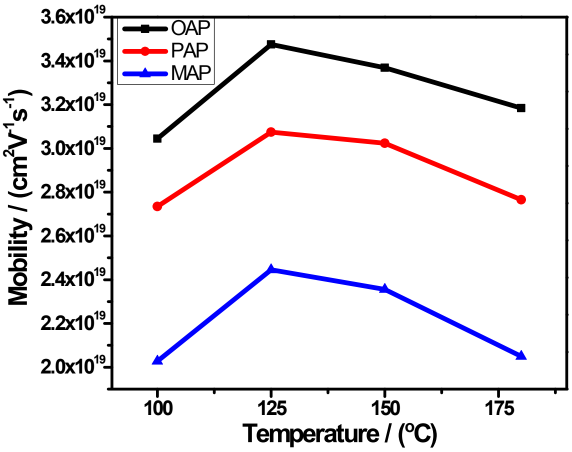


Fig. S1. The electron mobility of AP/rGO composites at different temperatures.

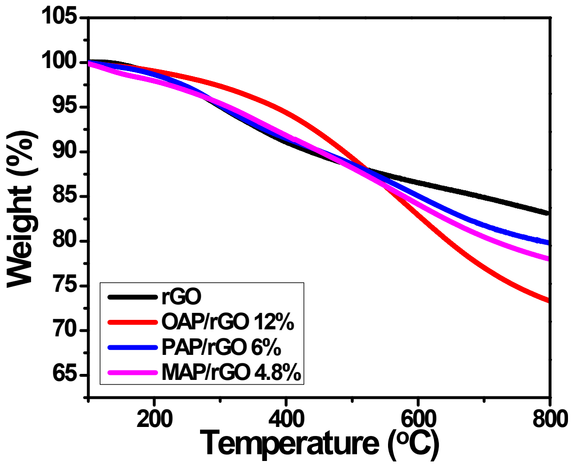


Fig. S2. The TGA curves of rGO and AP/rGO composites at heating rate 10 °C/min under N_2 atmosphere.

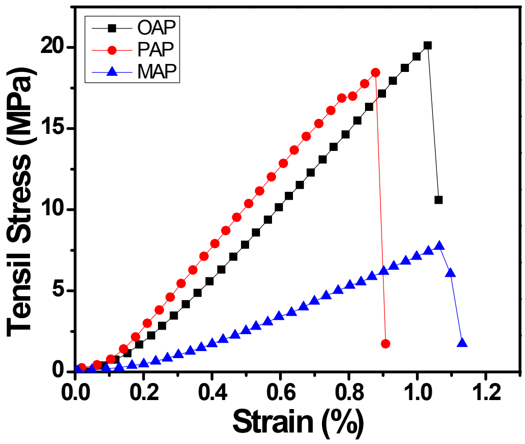


Fig S3. The Mechanical Behavior of AP/rGO composites.

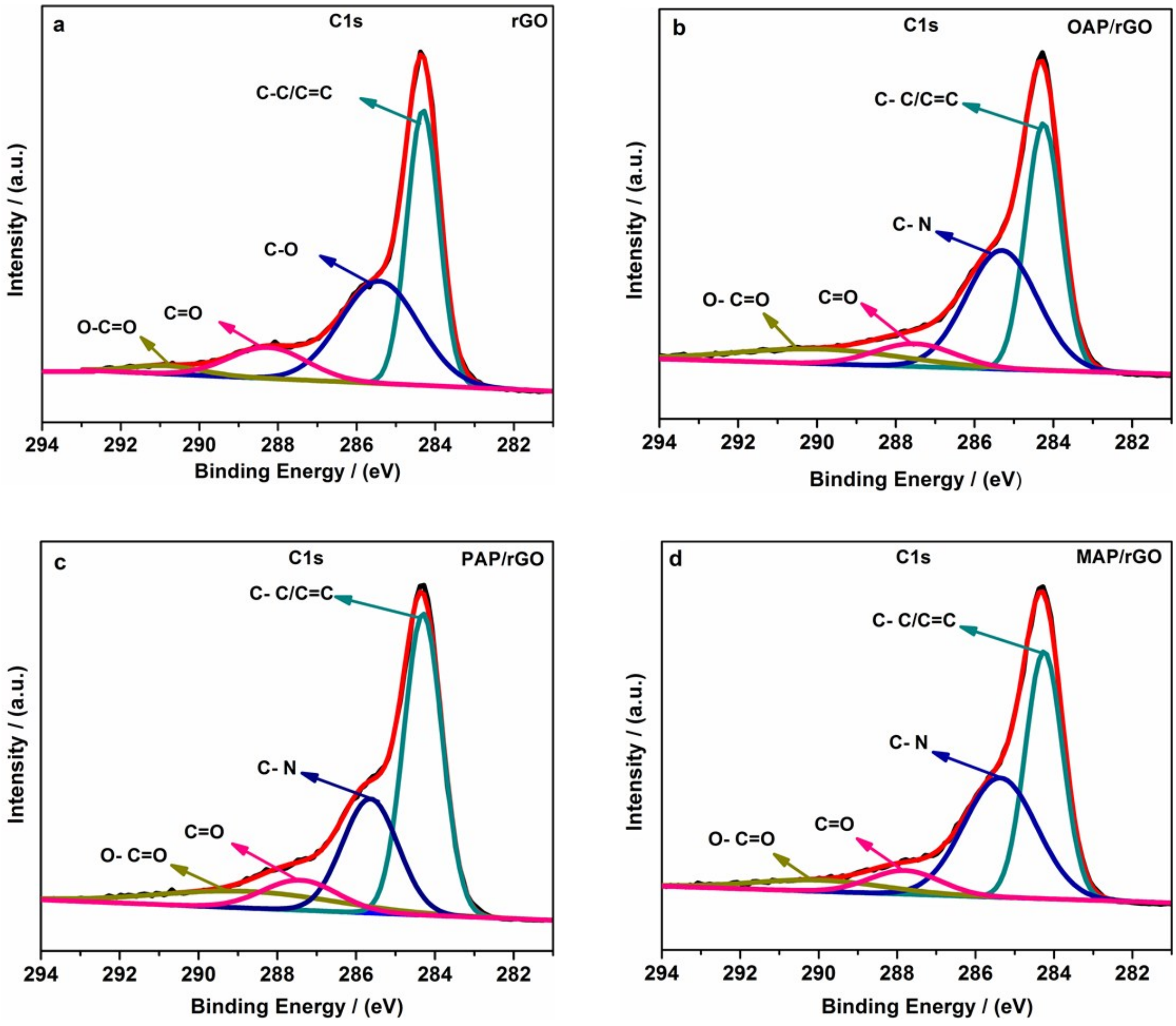


Fig. S4 High resolution C1s spectra of (a) rGO; (b) OAP/rGO; (c) PAP/rGO; and (d) MAP/rGO.

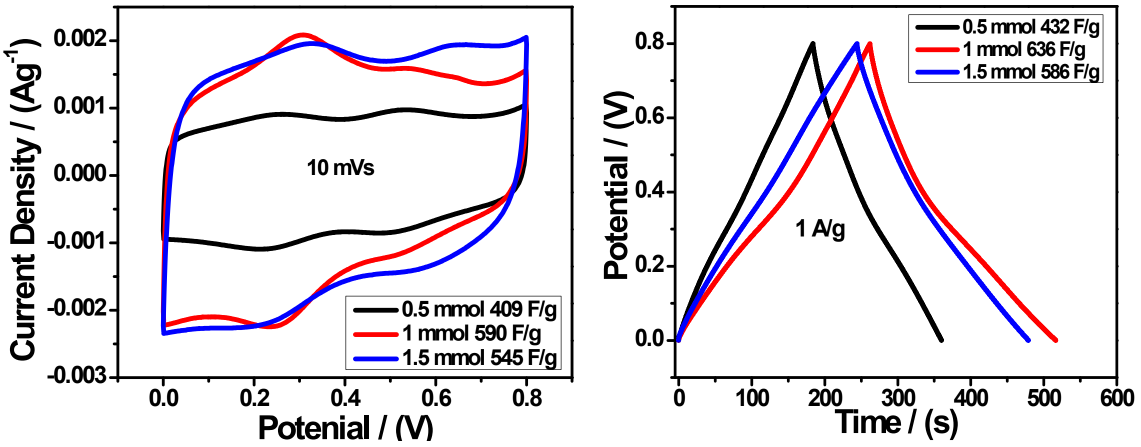


Fig. S5. CV and GCD measurements of OAP/rGO, PAP/rGO and MAP/rGO at different mole ratio.

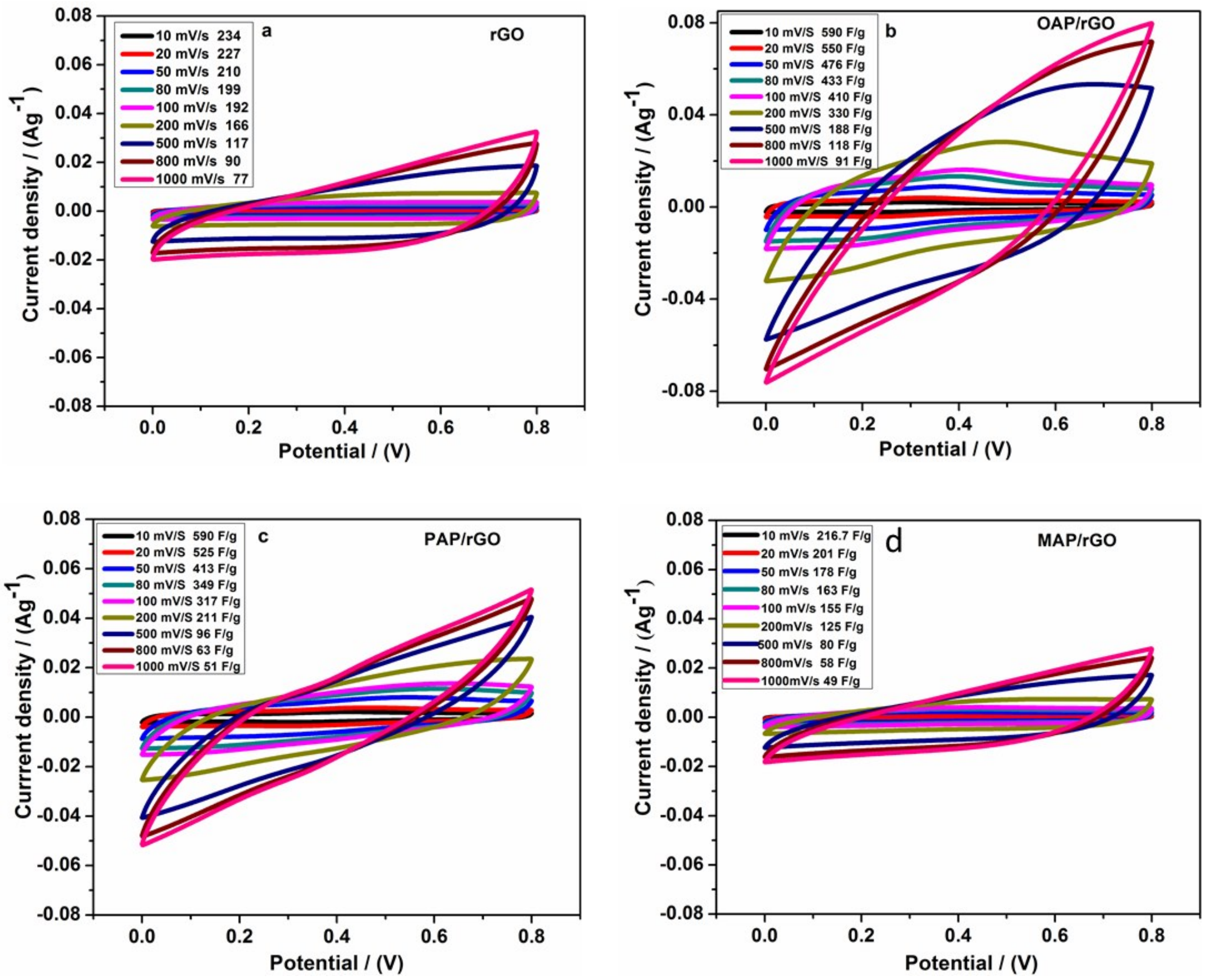


Fig. S6 CV measurements at different scan rates (a) rGO; (b) OAP/rGO; (c) PAP/rGO; and (d) MAP/rGO.

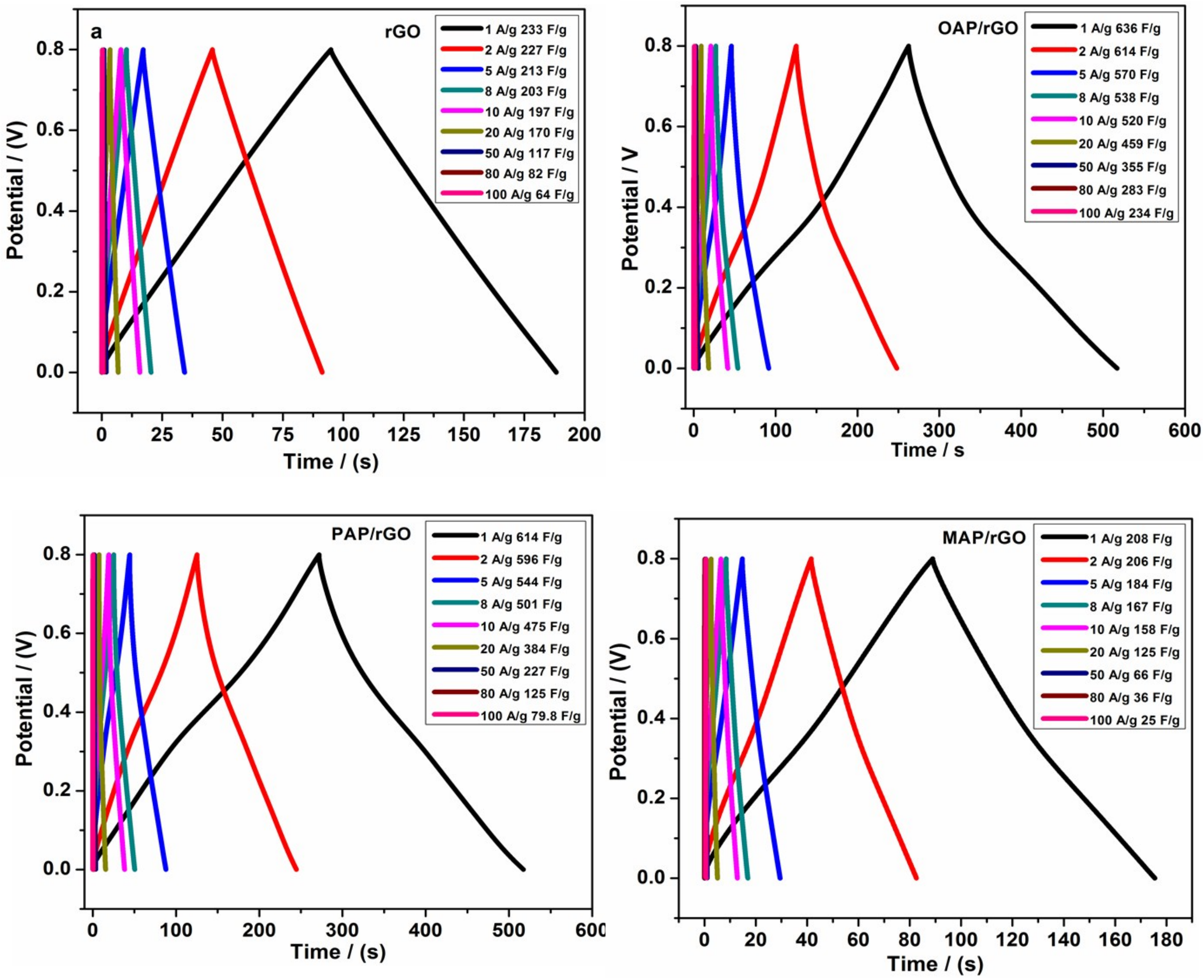


Fig. S7 (a) rate performance of rGO, OAP/rGO, PAP/rGO and MAP/rGO in CV measurements (b) rate performance of rGO, OAP/rGO, PAP/rGO and MAP/rGO in CV GCD.

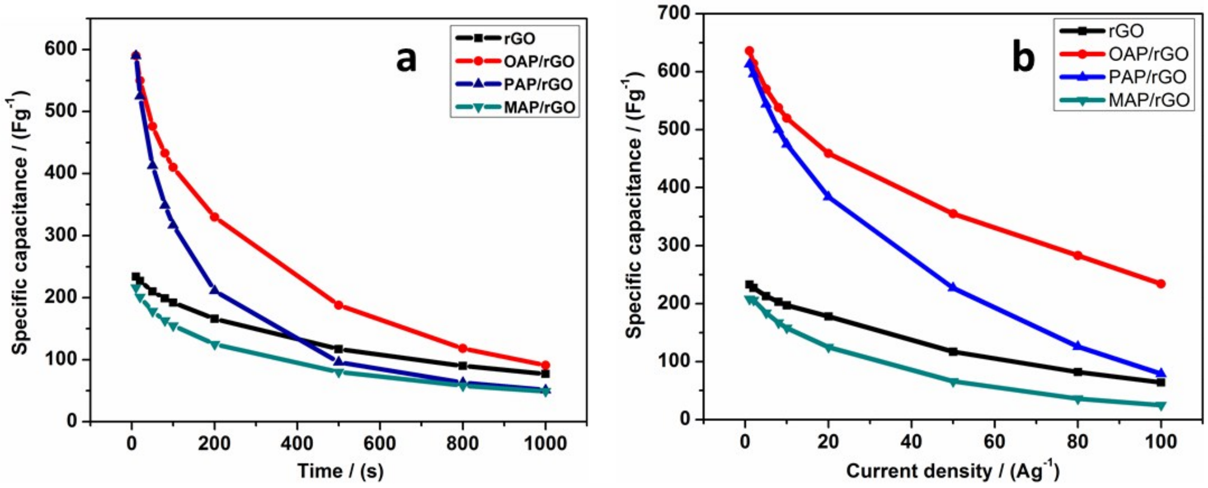


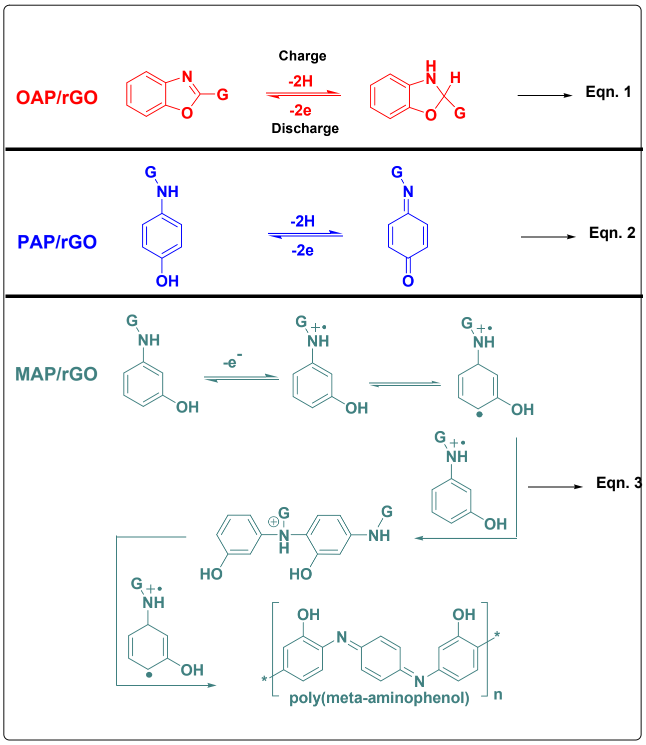
Fig. S8 GCD measurements of rGO, OAP/rGO, PAP/rGO and MAP/rGO at different current densities.

Table S1: Elemental composition of rGO and AP/rGO in C1s spectra of XPS analysis.

S.No	**Samples**	**C-C/C=C**	**C-O**	**C-N**	**C=O**	**O-C=O**
1	rGO	45.893	40.295	-	8.205	5.605
2	OAP/rGO	40.643	-	39.458	8.46	11.35
3	PAP/rGO	50.4	-	27.743	9.722	12.772
4	MAP/rGO	43.9	-	41.214	7.935	6.911

Table S2: Elemental composition of rGO and AP/rGO in N1s spectra of XPS analysis.

S. No	**Samples**	**C(at %)**	**O(at %)**	**N(at %)**	**Pyridinic-N**	**Pyrrolic-N**	**Amines Moiety**	**Quaternary-N**
1	rGO	79.9	19.9	-	-	-	-	-
2	OAP/rGO	80.43	14.45	5.12	28.04	34.11	33.24	4.59
3	PAP/rGO	77.68	19.95	5.32	22.19	31.22	33.79	12.78
4	MAP/rGO	78.08	15.03	5.82	26.48	48.1	20.35	4.70



Scheme S1. The Proposed Charge-Discharge mechanism of AP/rGO composites

Table S3: Comparison of electrochemical performance between AP/rGO and other N-rGO electrode materials

S. No.	Method	N-Source	(Cs) (F/g)	Scan rate (mV/s) / Current density (A/g)	Electrolyte	Temperature /time	Ref.
1	**Hydrothermal**	**Aminophenol isomers (OAP, PAP, MAP)**	**636** **614** **208**	**1 A/g**	**H_2SO_4 (1M)**	**125 ˚C/ 5 h**	**This work**
2	**Hydrothermal**	hydrazine hydrate	217	1 A/g	KOH (6M)	130 ˚C/ 5 h	1
3	**Hydrothermal**	Urea	245	0.25 A/g	KOH (6M)	180 ˚C/ 36 h	2
4	**Thermal method**	Urea choline chloride	383	1 A/g	KOH (6M)	200 ˚C/ 24 h	3
5	**Pyrolysis**	Melamine Formaldehye resin (FM)	296	1 A/g	H_2SO_4 (1M)	700 ˚C/ 2 h	4
6	**Hydrothermal**	urea	220	0.5 A/g	Na_2SO_4 (1M)	120 ˚C/ 12 h	5
7	**Hydrothermal**	1,2-ethanediamine	190.1	10 mV/s	KOH (5M)	180 ˚C/ 12 h	6
9	**Reflux**	*p*-phenylenediamine	316.54	10 mV/s	H_2SO_4 (2M)	90 ˚C/ 12 h	8
10	**Hydrothermal**	Amitrol	239	0.2 A/g	KOH (6M)	180 ˚C/ 8 h	9
11	**Hydrothermal**	1,4-butanediamine	268.8	0.3 A/g	KOH (6M)	180 ˚C/ 12 h	10
12	**Hydrothermal**	Hexamethylenetetraamine	161	0.5 A/g	KOH (6M)	180 ˚C/ 12 h	11

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