

Supporting Information

Nitrogen-doped and Crumpled Graphene sheets with Improved Supercapacitance

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Experimental section

All of the chemical reagents used in this work were of analytical grade and used without further purification.

Preparation of graphene oxide (GO) and thermally expanded graphene oxide (tGO)

GO was synthesized from natural graphite powder by a modified Hummers method.¹ Natural graphite powder (Alfa) was added into the mixture of HNO₃ aqueous solution (Fisher Scientific) and H₂SO₄ aqueous solution (Fisher Scientific) in an ice-water bath. KMnO₄ (Sigma-Aldrich) was added slowly into the suspension and reacted for 2 h under vigorous magnetic stirring. Deionized water and H₂O₂ aqueous solution (Fisher Scientific) were added into the system, followed by washing with HCl aqueous solution (Fisher Scientific). Graphene oxides were obtained after centrifuging (12000 rpm), washing with deionized water and sonicating for 30 min. As-prepared brown graphene oxide powders were thermally annealed in a tube furnace in N₂ at 800 °C for 2 h. After thermal expansion, a black fine powder was produced, i.e. thermally expanded graphene oxide (tGO).

Preparation of nitrogen-doped reduced graphene oxide (NRGO) and nitrogen-doped thermally expanded graphene oxide (NtGO)

In a typical experiment, 2.4 g of hexamethylenetetramine (HMT, Sigma-Aldrich) was dissolved in 15 ml of deionized water and stirred for a few minutes to form a transparent solution. 0.06 g of the as-synthesised tGO was ultrasonically dispersed in 15 ml of deionized water and then mixed with the above solution. The mass ratio of HMT to tGO is 40:1. The mixed suspension was sealed in a 40 ml Teflon lined stainless steel autoclave for a hydrothermal reaction at 180 °C for 12 h. N-doped thermally expanded graphene oxide (NtGO) powders were collected after centrifuging, washing with copious deionized water and drying. Nitrogen-doped reduced graphene oxide (NRGO) powders were obtained by following the same procedure but using GO instead of tGO.

Characterizations

The resultant products were characterized by X-ray diffraction (XRD, Rigaku D/max-2550V, Cu K α radiation), Environmental Scanning Electron Microscope (ESEM, Philips XL30 ESEM-FEG). Nitrogen adsorption isotherms were measured with a Micromeritics ASAP 2010 Analyzer, surface area was calculated by Brunauer-Emmett-Teller equation. Raman spectroscopy was recorded on a Renishaw laser Raman spectrometer with the excitation wavelength of 512 nm. X-Ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer (ThermoFisher-VG Scientific) using a monochromatized Al K α X-ray source (1486.6 eV).

Electrochemical Measurements

Cyclic voltammogram (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) tests were carried out using an Autolab potentiostat/galvanostat using a three-electrode cell. As-prepared samples and the binder (poly(vinylidene difluoride), PVDF, Aldrich) were mixed in a weight ratio of 90:10 with N-methyl-2-pyrrolidone (NMP) as the solvent. This mixed paste was

pressed on stainless steel mesh. The mass of the active materials in the working electrode was about 1 mg. Pt mesh (area is about $2 \times 2 \text{ cm}^2$) was used as counter electrode and Ag/AgCl (saturated KCl solution) was used as reference electrode. The electrolyte was 1 M H_2SO_4 . The cells were charged and discharged at a constant current in the fixed voltage range of 0.0-0.8 V. The applied voltage window of CV measurements was also in the range of 0.0-0.8 V. The capacitance retention tests were carried out at a constant current density of 1 A g^{-1} from 0.0 to 0.8 V for 2000 cycles. Electrochemical impedance spectroscopy (EIS) measurement were carried out by applying an AC voltage with 5 mV amplitude over a frequency range was from 0.01 Hz to 100 kHz at the open circuit potential. The equivalent circuit model was shown in Fig. S1. R_s , C_{dl} , R_F , C_F and R_w represent the solution resistance, double-layer capacitance, Faradaic resistance, pseudo-capacitance associated with potential-dependent coverage by adsorbed species involved in the Faradic reaction, and Warburg resistance which shows the diffusion control in the kinetics of electrode process, respectively.²

The specific capacitance C_{spec} (F g^{-1}) was calculated from the galvanostatic charge/discharge curves using the following equations:

$$C_{\text{spec}} = \int_{V_1}^{V_2} \frac{I_{\text{discharge}} dt}{m dV} \quad (1)$$

where $I_{\text{discharge}}$ is the discharge current, t is the discharge time, V is the voltage and m is the mass of active materials.

The energy (E) and power (P) density were calculated from charge-discharge curves at 1 A g^{-1} using Eq. (2) and Eq. (3) respectively

$$E = \frac{1}{2} C_{\text{spec}} \Delta V^2 \quad (2)$$

where C_{spec} is specific capacitance; ' ΔV ' is the potential window of discharge process.

$$P = \frac{\Delta V^2}{4mR_{\text{ESR}}} \quad (3)$$

where ' ΔV ' is the potential window of discharge process, R_{ESR} is equivalent series

resistance.

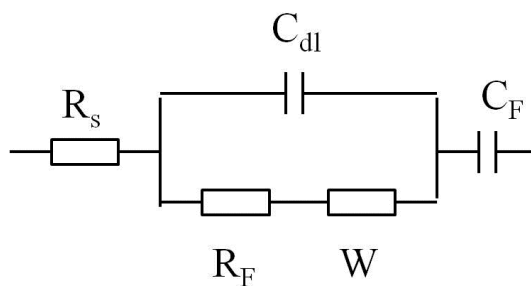


Fig. S1. The equivalent circuit model

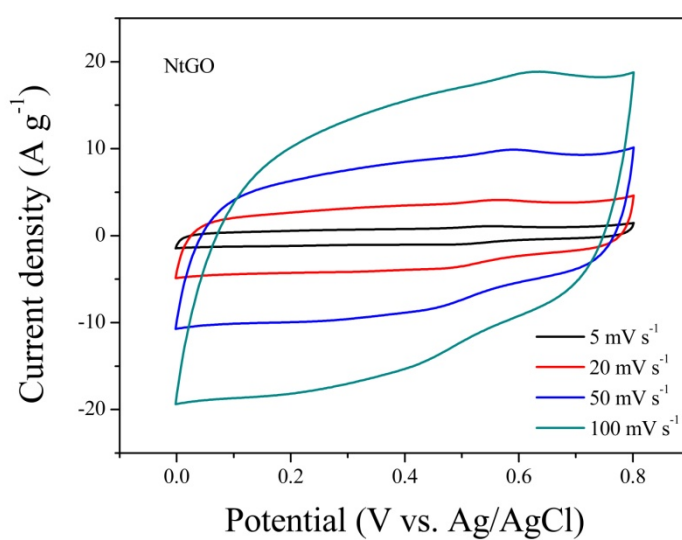


Fig. S2 CVs of NtGO samples between 0.0 – 0.8 V at various scan rates.

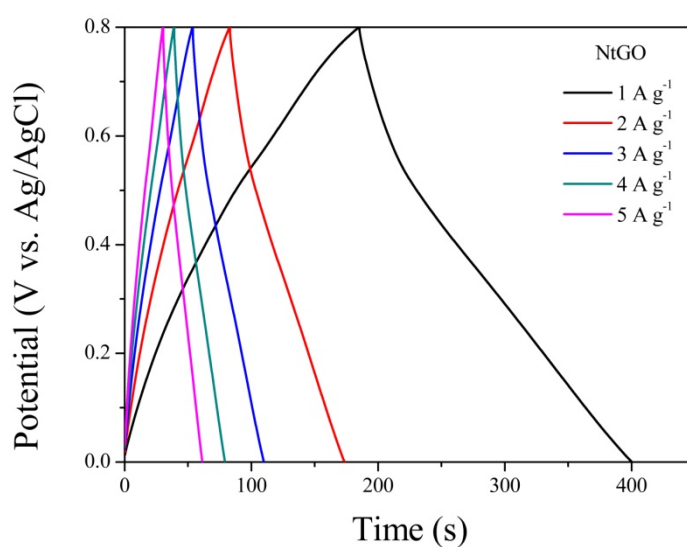


Fig. S3 Galvanostatic charge/discharge curves of NtGO samples between 0.0 – 0.8 V

at various discharge current densities.

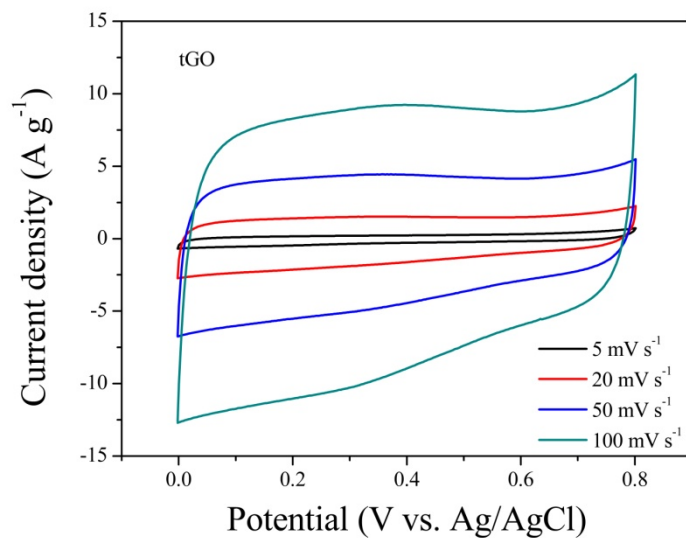


Fig. S4 CVs of tGO samples between 0.0 – 0.8 V at various scan rates.

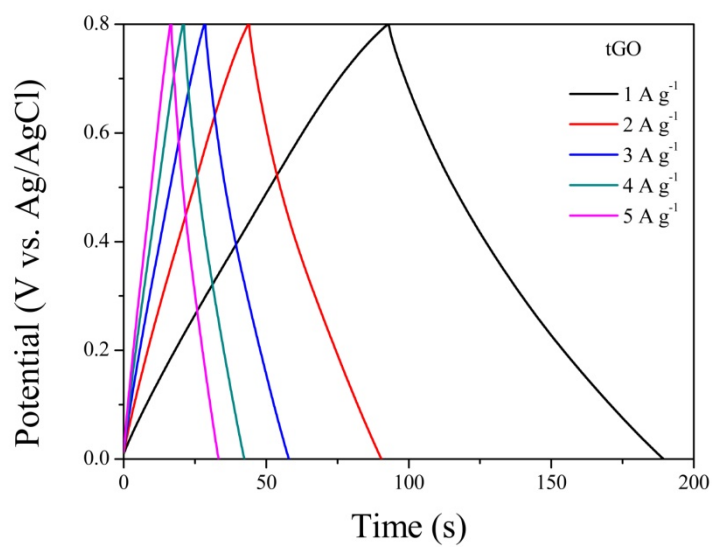


Fig. S5 Galvanostatic charge/discharge curves of tGO samples between 0.0 – 0.8 V at various discharge current densities.

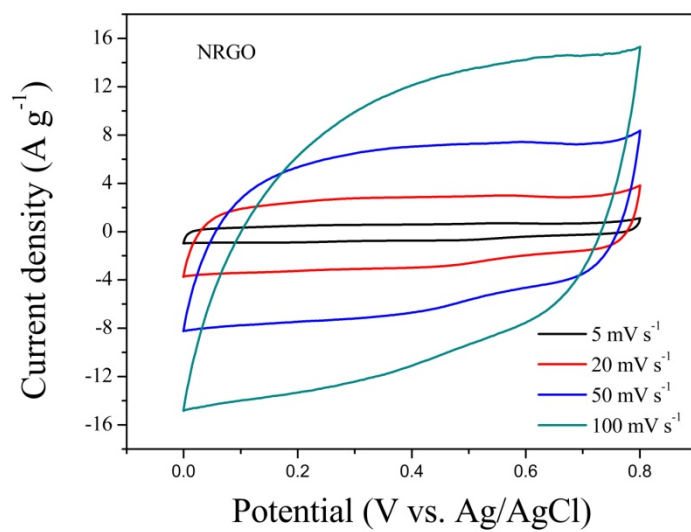


Fig. S6 CVs of NRGO samples between 0.0 – 0.8 V at various scan rates.

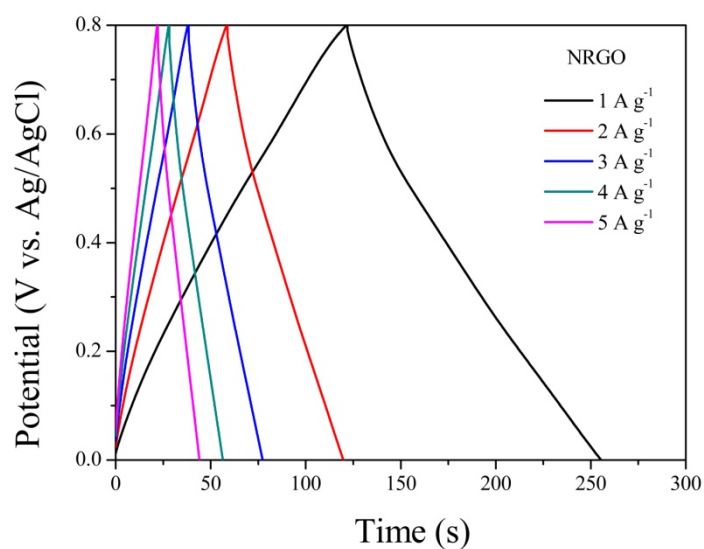


Fig. S7 Galvanostatic charge/discharge curves of NRGO samples between 0.0 – 0.8 V at various discharge current densities

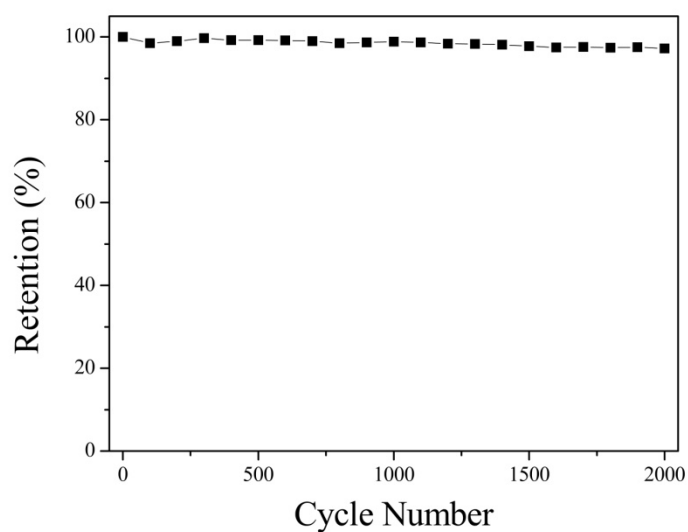


Fig. S8 Capacitance retention versus cycle number measure at a current density of 1 A g⁻¹ within the potential range from 0.0 – 0.8 V

Table S1 Atomic content of GO, tGO, NRGO and NtGO measured by XPS
(background type: Shirley)

	Atomic %		
	C1s	N1s	O1s
GO	62.30%	-	37.70%
tGO	85.18%	-	14.82%
NRGO	77.16%	9.67%	13.17%
NtGO	83.99%	5.26%	10.74%

Table S2 Parameters fitted from EIS spectra

Sample	R _s /ohm	C _{dl} / F	R _F /ohm	C _F /F	R _w /ohm
tGO	1.76	0.33 × 10 ⁻⁴	9.02	0.08	0.49
NRGO	0.17	1.58 × 10 ⁻⁴	4.50	0.10	0.21
NtGO	0.11	1.65 × 10 ⁻⁴	2.26	0.15	0.11

Table S3 Comparison of the capacitance of reported nitrogen-including graphene
(current density of 1 A g⁻¹)

Materials	Mass-normalized capacitance (F g ⁻¹)	Area-normalized capacitance (μF cm ⁻²)	Reference
Nitrogen-modified few layer graphene	227	N/A	3
Nitrogen-doped graphene	148	N/A	4
Nitrogen-doped graphene hydrogel	326	21	5
Nitrogen-doped graphene	110	N/A	6
Nitrogen-doped reduced graphene oxide	233	65	7
Nitrogen-doped graphene	230	67	8
N-doped graphene hollow spheres	311	N/A	9
Nitrogen-doped thermally expanded graphene	270	114	This work

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