# Electronic Supplementary Information

# Superior Catalytic Activity of Nitrogen-Doped Graphene Cathode for High Energy Capacity Sodium-Air Batteries

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## Experimental details:

### Synthesis of Graphene Nanosheets (GNSs)

Graphene nanosheets (GNSs) were prepared by the oxidation of graphite powder using the modified Hummers' method.[1] Typically, graphite powder (1 g), sodium nitrate (0.75 g) and potassium permanganate (4.5 g) were added to concentrated sulphuric acid (37.5 mL) and stirred for 2 h in an ice water bath. Then the mixture was stirred for five days at room temperature. 100 mL of 5 wt% $H_2SO_4$ and 3 g of 30 wt% $H_2O_2$ were added into the above mixture in sequence under stirring with interval of 1 h. After stirring for 2 h, the sample was filtered and washed until the pH=7. The as-received sample was dried and heated at 1050 $^{o}$C for 30 s under Ar to produce GNSs.[2]

### Physical Characterizations

The morphology of the discharge products of GNSs and N-GNSs electrodes were characterized by a Hitachi S-4800 field emission scanning electron microscopy (FESEM). Raman scattering (RS) spectra were recorded on a HORIBA Scientific LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser. The XRD pattern was recorded by a Bruker-AXS D8 Discover diffractometer employing a Cu-Kα source (λ=1.5374 Å).

### Electrochemical Measurements

Swagelok type cells were used to test the battery performance. GNSs or N-GNSs and PVDF (Alfa Aesar) with a weight ratio of 9:1 were casted onto a separator (Celgard 3500) as cathode. The electrodes were cut to 3/8 inch in diameter and the loadings of GNSs or N-GNSs were ~0.3 mg. The electrolyte was 0.5 mol $dm^{-3}$ $NaSO_3CF_3$ dissolved in diethylene glycol dimethyl ether ($C_6H_{14}O_3$, diglyme, DEGDME). The discharge/charge characteristics were performed using an Arbin BT-2000 battery station in a voltage range of 1.8-3.6 V in a 1 atm oxygen atmosphere at room temperature (25 °C). Cyclic voltammetry (CV) measurements were carried out using a CHI 600c electrochemical work station at a scan rate of 2 mV $s^{-1}$ in a voltage range of 1.8-3.6 V at room temperature. In order to study the cycleability of batteries utilizing GNSs and N-GNSs electrodes, the batteries were discharged at a current density of 75 mA $g^{-1}$, delivering a discharge capacity of 1150 mAh $g^{-1}$, and then proceeded the charge process until voltage reached to 3.6 V. Electrochemical impedance spectra were recorded in the frequency range of 0.01-$10^5$ Hz using a VMP3 Potentiostat (BioLogic Science Instruments). The resulted spectra were fitted by ZView software.

## References

1 W. Hummers, R. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339; M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara, M. Ohba, *Carbon*, 2004, **42**, 2929.

2 H. Schniepp, J.-L. Li, M. McAllister, H. Sai, M. Herrera-Alonso, D. Adamson, R. Prud'homme, R. Car, D. saville, I. Aksay, *J. Phy. Chem. B*, 2006, **110**, 8535.

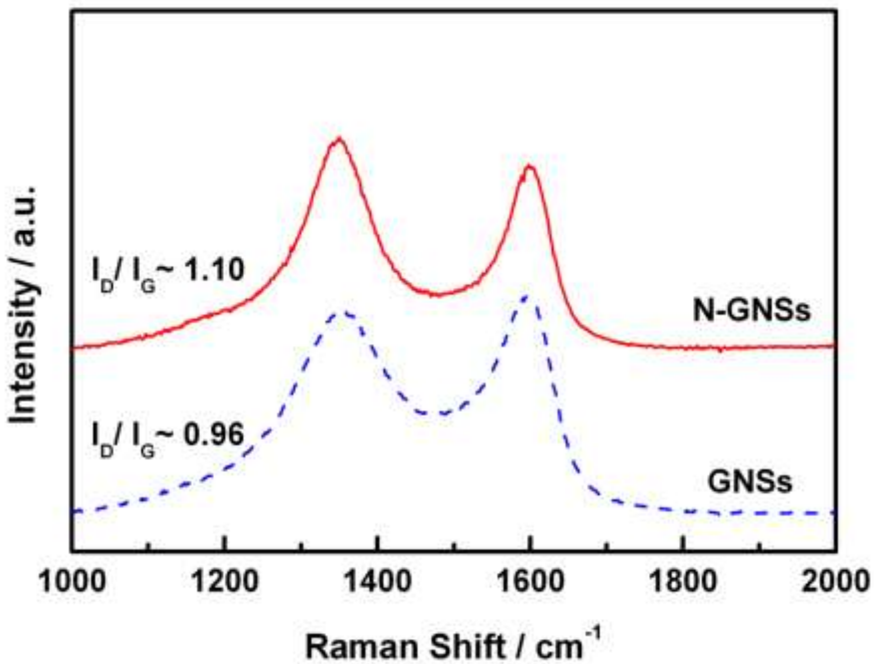


**Fig. S1** Raman spectra of GNSs and N-GNSs.

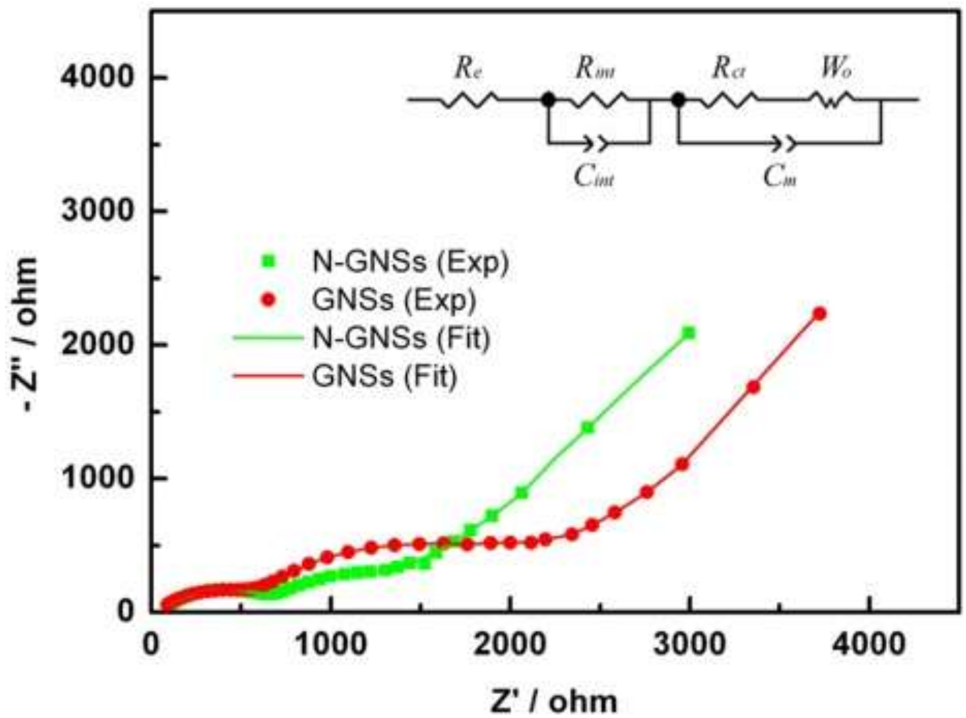


**Fig. S2** Measured and calculated electrochemical impedance spectra of GNSs and N-GNSs electrodes after discharge at 75 mA $g^{-1}$. The inset is the equivalent circuit used for the analysis of the impedance plots.

**Table S1**. Dependence of equivalent-circuit parameters for GNSs and N-GNSs electrodes.

| | $R_e$/Ω | $R_{int}$/F | $C_{int}$/Ω | $R_{ct}$/Ω | $C_m$/F | $W_o$/Ω |
|---|---|---|---|---|---|---|
| N-GNSs | 36.4 | 655.6 | $2.46e^{-6}$ | 663.7 | $47.9e^{-6}$ | 0.274 |
| GNSs | 38.0 | 517.1 | $5.76e^{-6}$ | 1556.0 | $94.4e^{-6}$ | 0.284 |

$R_e$ is the ionic resistance of electrolyte; $R_{int}$ and $C_{int}$ are the interfacial resistance and capacitance of film on the interface between electrode/electrolyte, respectively; $R_{ct}$ is the charge-transfer resistance while $C_m$ is the parallel capacitance for the semicircle accordingly, and $W_o$ is the finite length Warburg resistance.[1]

**References**

1 X. Yang and Y. Xia, *J. Solid State Electrochem.*, 2010, **14**, 109; M. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, U. Heider and L. Heiderb, *J. Electrochem. Soc.*, 1999, **146**, 1279; J. Song, H. Lee, Y. Wang and C. Wan, *J. Power Sources*, 2002, **111**, 255.

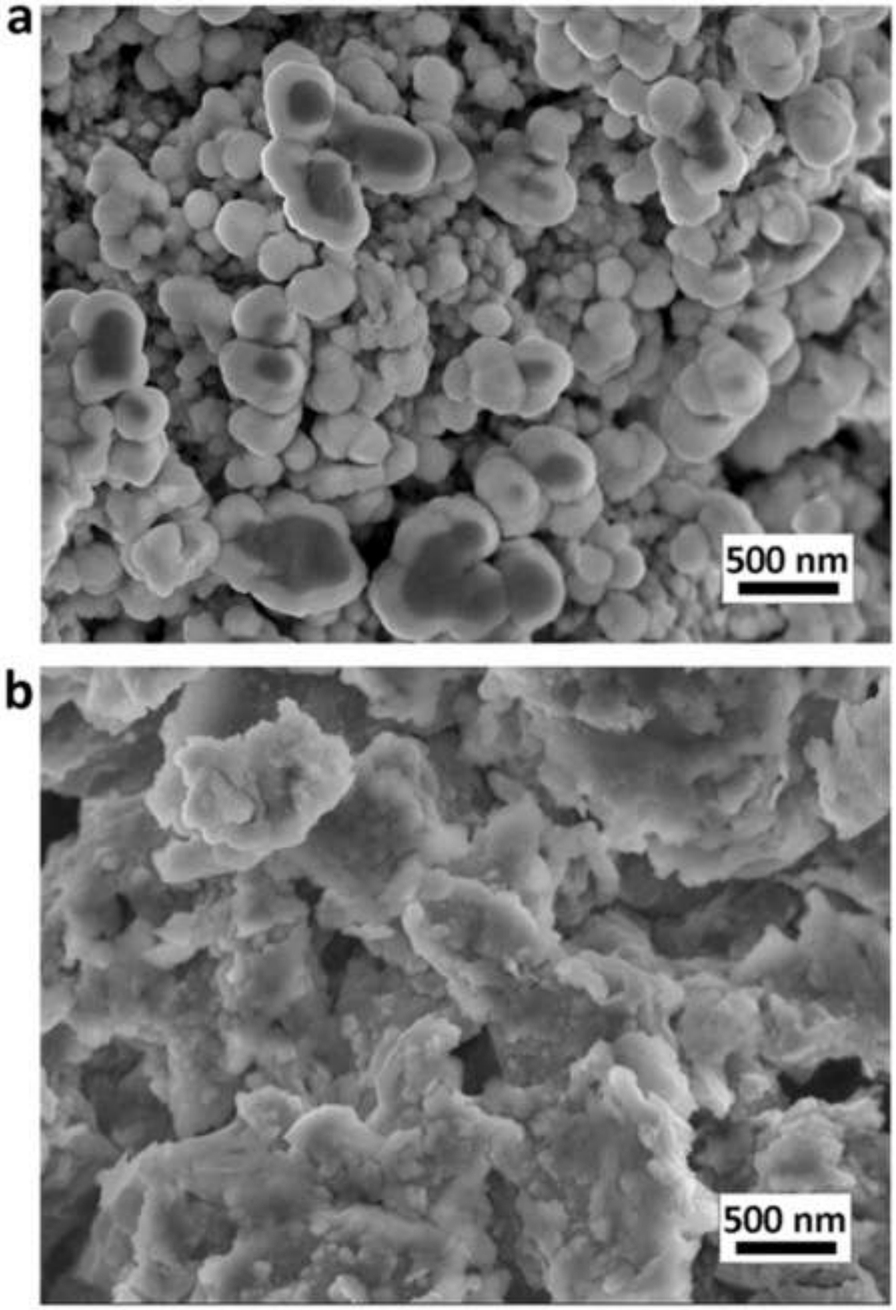


**Fig. S3** SEM images of discharge products on N-GNSs electrodes at (a) 150, and (b) 300 mA $g^{-1}$.

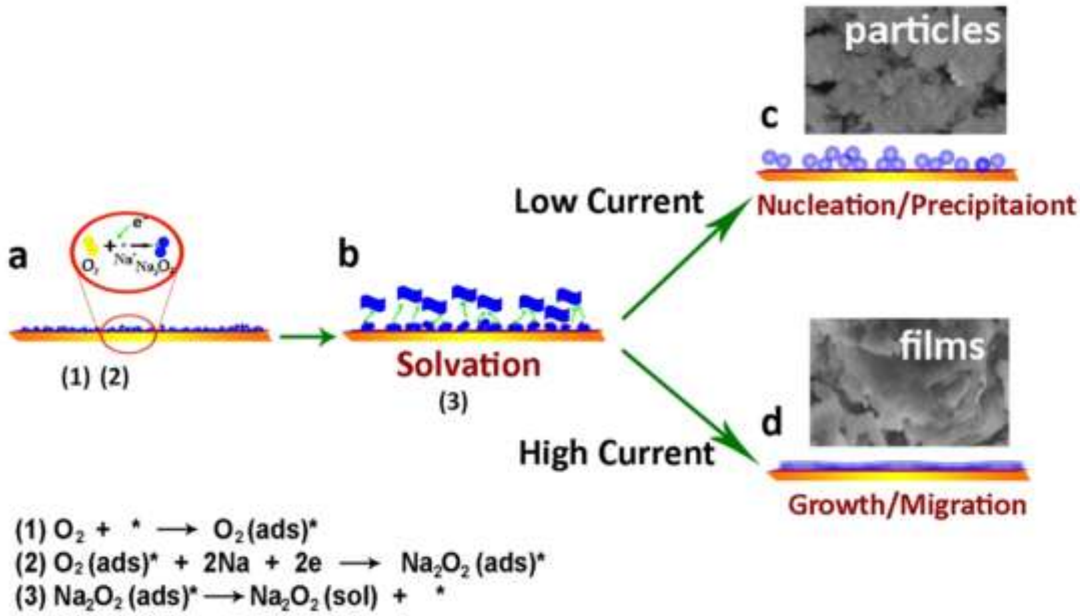


**Fig. S4** Schematic of the growth of discharge product nanostructures on N-GNS electrodes.