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## Supporting Information

### High-Rate, Ultra-Long Cycle-Life Lithium/Sulfur Batteries enabled by Nitrogen-doped Graphene

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#### Experimental details

**Preparation of graphene oxide (GO).** Graphite oxide was synthesized according to the literature reported by Xu *et al.*<sup>1,2</sup> Briefly, natural graphite powder (20 g) was put into an 80 °C solution of concentrated H<sub>2</sub>SO<sub>4</sub> (30 mL), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 g), and P<sub>2</sub>O<sub>5</sub> (10 g), and then kept for 6 h to pre-oxidize the graphite powder. After cooling to room temperature, 3.5 L de-ionized (DI) water was added into the mixture, which was then filtrated, washed and vacuum dried before storage. Subsequently, the dried pre-oxidized graphite was oxidized using a modified Hummers' method: Firstly, the pre-oxidized graphite powder (0.5 g) was put into concentrated H<sub>2</sub>SO<sub>4</sub> (12 mL, 0 °C),

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followed by gradually adding  $\text{KMnO}_4$  (1.5 g) under vigorous stirring. Secondly, the mixture was stirred at 35 °C for 2 h, and then diluted with DI water (24 mL). Successively, the resultant mixture was stirred at an elevated temperature of 80 °C for 0.5 h. After cooling to room temperature, an additional 70 mL DI water was added, and shortly, 1.25 mL 30%  $\text{H}_2\text{O}_2$  was added. Lastly, the mixture was washed with 5 wt% HCl aqueous solution (125 mL) to remove metal ions, followed by washing with DI water three times and centrifugation. Dialysis was carried out to further remove the remaining metal species.

**Preparation of N-doped graphene sheets.** The freeze dried GO powder was loaded into a silica tube reactor placed in a horizontal tube furnace and connected to a gas feed system. Initially, a flow of Ar gas (99.99 %) was maintained over the bed to get rid of air and  $\text{H}_2\text{O}$ . Then the flowing gas was switched to  $\text{NH}_3$  with a flow rate of 30  $\text{cm}^3 \text{min}^{-1}$ . The furnace was heated from room temperature to 750 °C at a rate of 30 °C  $\text{min}^{-1}$ , held at this temperature for 30 minutes. Finally, the furnace was allowed to cool down under a flowing Ar gas.

**Preparation of S@NG nanocomposite.** The S@NG nanocomposite was prepared by a chemical deposition method in an aqueous solution mentioned below:  $2\text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 + 6\text{HCOOH} = 4\text{S} + 6\text{HCOONa} + 3\text{H}_2\text{O}$ . 50 mL of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (2.7 g) and  $\text{Na}_2\text{S}_2\text{O}_3$  (0.89 g) aqueous solution was added to 150 mg of N-doped graphene aqueous solution to form a blended solution under vigorous stirring. The N-doped graphene sheets were dispersed in water by strong sonication for 1 h. The as-prepared blended solution was stirred for another 2 hours and then directly titrated into 50 mL

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of 2 mol/L HCOOH solution at a rate of 30~40 drops/min and stirred for overnight. Finally, the precipitate was filtered and washed with DI water several times to eliminate salts and impurities. After filtration, the precipitate was dried at 60 °C in a drying oven for 48 hours.

**Electrochemical Measurements.** To prepare the cathodes, S@NG and S@GS composite materials were first mixed with PVDF binder (92 : 8 by weight) in NMP solution under vigorous stirring overnight. The mixture was then spread evenly on the aluminum foil and roll-pressed to produce electrode films with an average sulfur loading of 0.8 mg cm<sup>-2</sup>, which were heated at 50 °C for 24 hours under vacuum before using to fabricate the coin cells. 2025 type coin cells were fabricated in an argon filled glove box using lithium foil as the anode.

**Electrolyte Preparation.** The electrolyte solution was prepared by dissolving stoichiometric amount of Li<sub>2</sub>S and sulfur (nominal Li<sub>2</sub>S<sub>8</sub>, [S] = 0.2 M), commercial LiTFSI (1 M), and LiNO<sub>3</sub> (1 wt%) in DOL/DME solvent. We used 20 μL of the electrolyte (containing ~0.128 mg S) to assemble each cell.

**Material Characterization.** SEM was measured on a Quanta 400 FEG field-emission scanning electron microscope. TEM was measured on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. XRD was collected with a Bruker D8 diffractometer. TG measurement was performed using a TG/DTA 6200. Electrochemical measurements were carried out using a Land CT2001 automatic battery tester. The NEXAFS experiments were carried out at two separate beam lines at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory

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(LBNL).

**Preparation of samples for electrical properties measurements.** 5 mg of the powder sample was produced to be a pellet using a hydraulic press. The sheet resistance of the samples was measured using a “four point probe”. The thickness of the pellets was measured using a microcalliper.

Table S1. Comparisons of electrical properties between graphene sheets (GS) and N-doped graphene sheets (NG).

| Powder | Sheet resistance ( $\Omega/\square$ ) | Resistivity ( $\Omega\cdot\text{cm}$ ) | Conductivity (S/cm) |
|--------|---------------------------------------|--|---------------------|
| NG     | 9.9                                   | $3.67 \times 10^{-3}$                  | 272.2               |
| GS     | 52.1                                  | $1.93 \times 10^{-2}$                  | 51.8                |

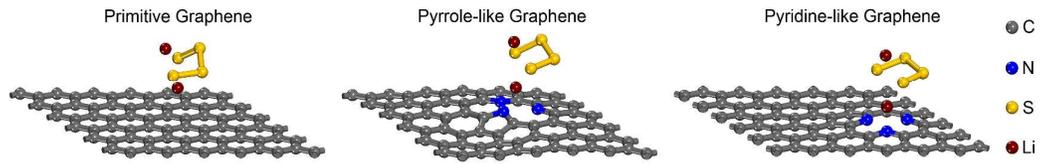
### Computational methods

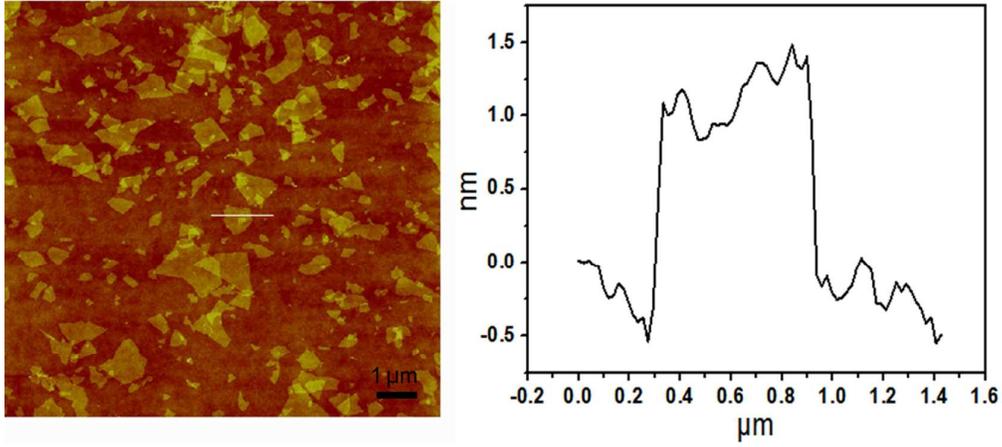
First-principles calculations were performed using Vienna *ab initio* simulation package (VASP)<sup>3</sup>, with the exchange-correlation potential described by PW91 version<sup>4</sup> of the generalized gradient approximation. The projector-augmented wave (PAW) approach<sup>5</sup> with a cutoff energy of 400 eV is used to describe the electron-ion interactions. We adopted a 6×6 supercell to model graphene with a 16 Å vacuum in the vertical direction. Brillouin zone is sampled by a 1×1×1 *k*-point grid for relaxation and 5×5×1 for static calculations.

Herein, two typical N-doped graphene configurations, pyrrole-like (N-5) and pyridine-like (N-6) NG,<sup>6, 7</sup> are considered. And a primitive graphene case is for comparison.<sup>7</sup> The binding energy ( $E_{\text{bind}}$ ) of a lithium polysulfide cluster is defined as

$$E_{\text{bind}}(\text{Li}_2\text{S}_x) = E_{\text{NG}} + E_{\text{Li}_2\text{S}_x} - E_{\text{NGLi}_2\text{S}_x} \quad (x = 4, 6 \text{ and } 8)$$

where  $E_{\text{NG}}$ ,  $E_{\text{Li}_2\text{S}_x}$ , and  $E_{\text{NGLi}_2\text{S}_x}$  are the total energies of graphene host,  $\text{Li}_2\text{S}_x$  clusters and NG-  $\text{Li}_2\text{S}_x$  composite, respectively. A larger positive value means a higher stability.





**Figure S1**, The tapping-mode atomic force microscope (AFM) image of the as-prepared graphene oxide sheets and its corresponding height.

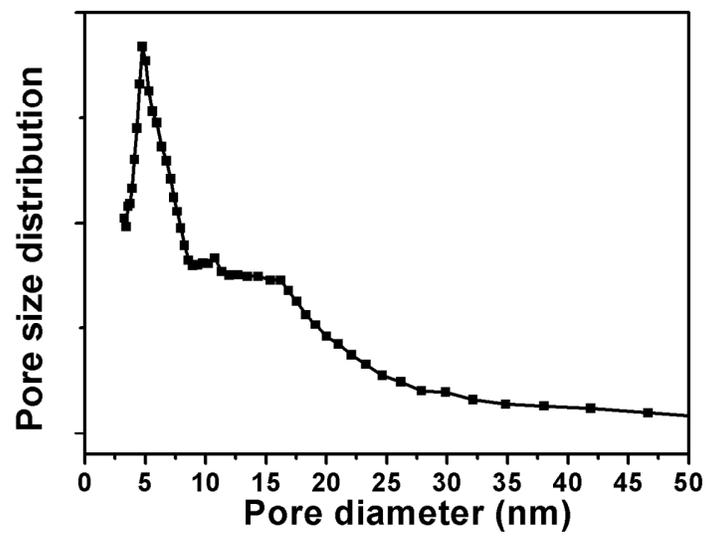
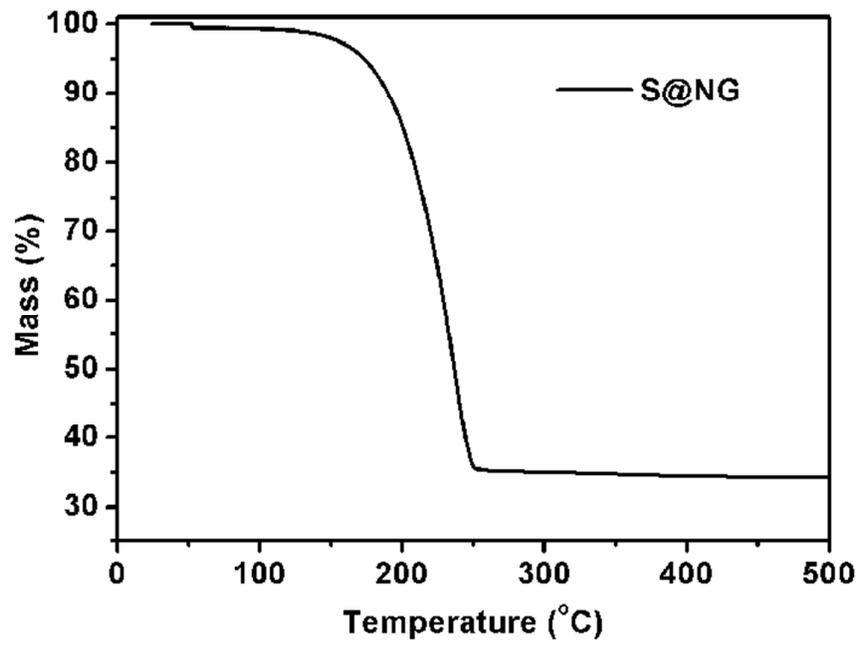
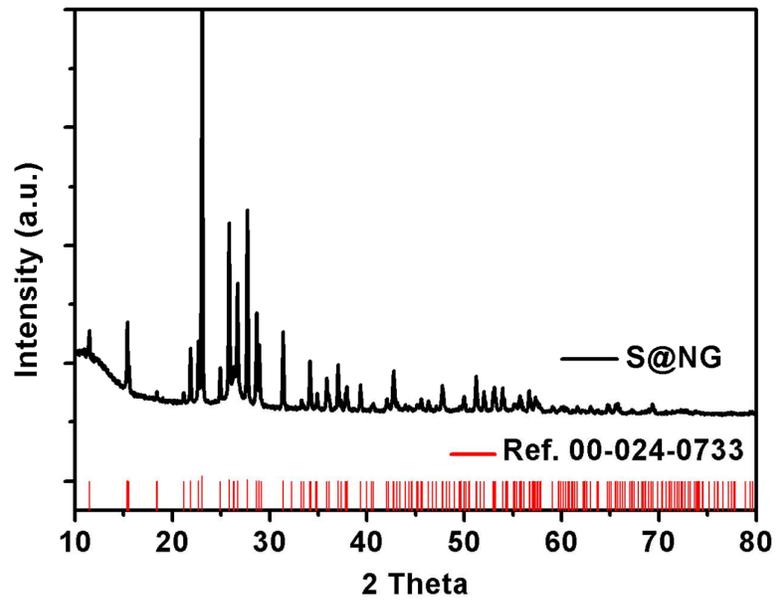


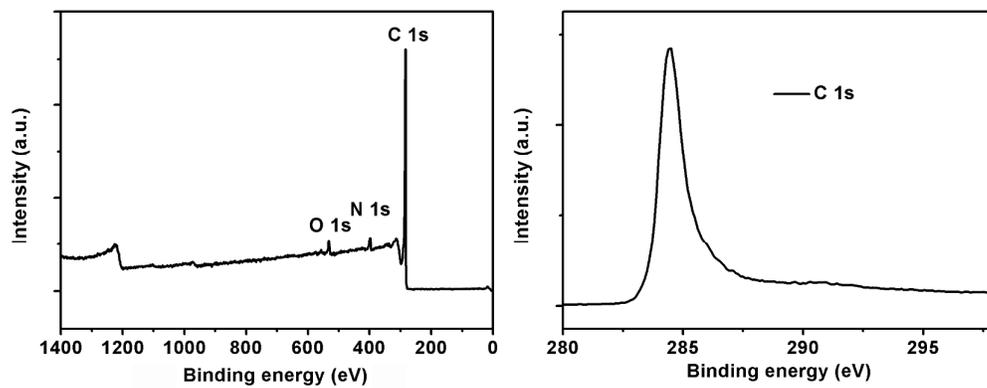
Figure S2, Pore distribution of the NG sheets.



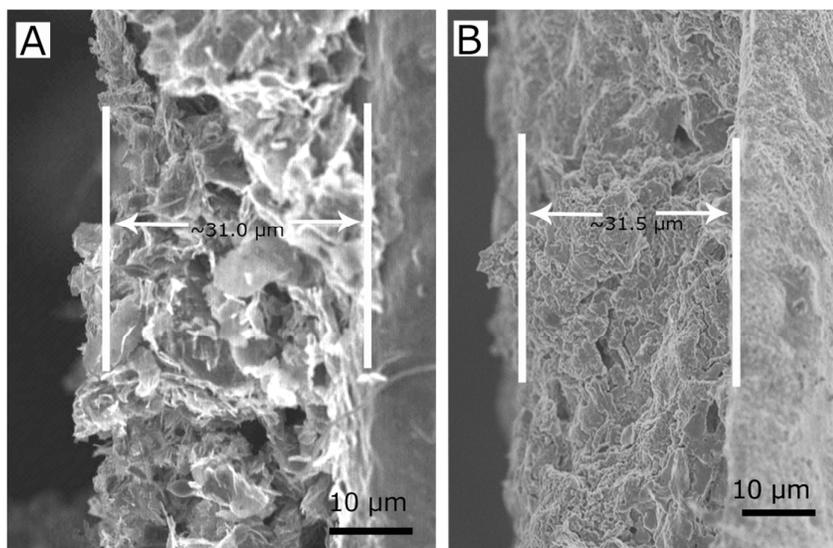
**Figure S3**, TGA trace of the S@NG nanocomposite.



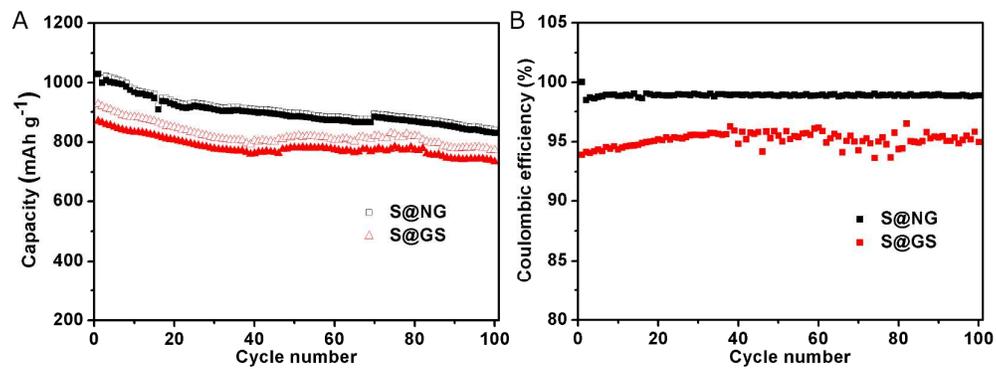
**Figure S4**, XRD pattern of the S@NG nanocomposite.



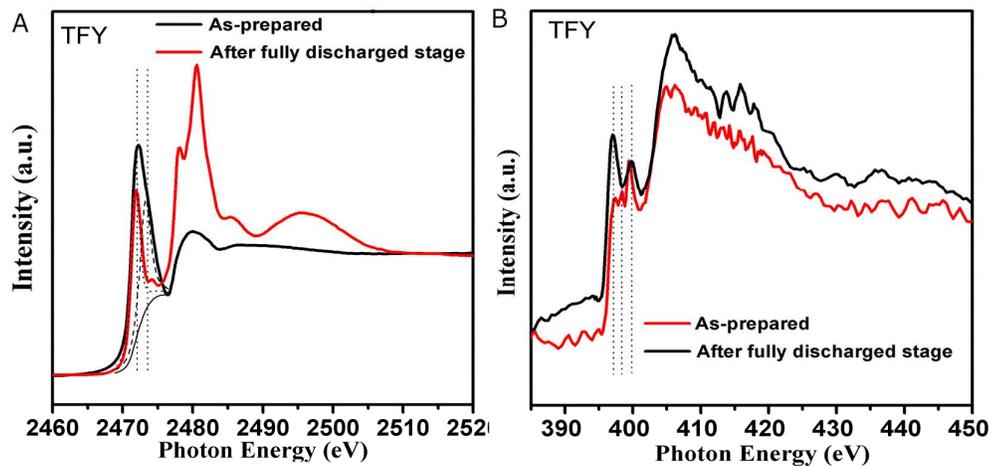
**Figure S5**, XPS spectrum of the NG sheets and high-resolution C 1s XPS spectrum.



**Figure S6,** Thickness comparisons of the S@NG electrode film (A) before lithiation and (B) after 100 cycles discharge/charge and at fully discharge state.



**Figure S7,** (A) Capacity and (B) Coulombic efficiency comparisons between the S@NG cell and the S@GS cell cycled at 0.5 C.



**Figure S8**, TFY-NEXAFS spectra of the S K-edge (A) and N K-edge (B) of the S@NG cathode materials before (at charged state) and after 200 charge/discharge cycles (at discharged state).

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## References

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