

## Superior cycle and rate performance of a novel sulfur cathode by immobilizing sulfur into porous N-doped carbon microspheres

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## **Experimental section**

### **Preparation of N-doped carbon microspheres (NCMSs):**

NCMSs were prepared using the dopamine as raw material.<sup>1</sup> In a typical synthesis of poly-dopamine (PDA) microspheres with size about 300 nm, 2.4 ml of ammonia aqueous solution (NH<sub>4</sub>OH, 30%) was added into 360 ml of ethanol aqueous solution (v:v, 4:9) under mild stirring at room temperature for 30 min. Dopamine hydrochloride (1.50 g) was dissolved in deionized water (20 mL) and then dropped into the above mixture solution, after adding the dopamine solution, the mixture solution was allowed to proceed for 60 h at room temperature. After that, the PDA microspheres were formed and then separated by centrifugation. The obtained PDA microspheres were washed with water for three times and then placed in the furnace whose temperature was increased to 800 °C at a heating rate of 5 °C min<sup>-1</sup> and kept for addition 1 h for further calcination in Ar to obtain NCMSs.

### **Preparation of porous NCMSs**

The obtained NCMSs were mixed with KOH at a weight ratio of 1:4, followed by thermal treatment at 700 °C for 1 h in Ar after the furnace temperature was increased to 700 °C at a heating rate of 5 °C min<sup>-1</sup>. After cooling down to room temperature, the resulted powder was washed with HCl (1 M) for three times and then washed with deionized water for another three times to remove the excess KOH. The final solid product was separated by filtration and dried at 80 °C for 12 h to obtain porous NCMSs.

### **Synthesis of NCMSs/S composites**

The porous NCMSs and sulfur were thoroughly mixed with a mass ratio of 50:50 by hand-milling for 1 h. The mixture was then sealed in a glass container and heated at 155 °C for addition 30 h after the furnace temperature was increased to 155 °C by a heating rate of 0.5 °C min<sup>-1</sup>. After cooling down to room temperature, the NCMSs/S composites were obtained.

### **Materials characterization**

Powder X-ray diffraction (XRD) was carried out using a Bruker D8 ADVANCE powder diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA at a step of 0.020° s<sup>-1</sup>. Data were recorded ranging from 10° to 60°. The morphology and the element dispersive spectroscopy (EDS) mapping of the composites were measured by scanning electron microscopy (SEM, JP-2000). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were recorded on Philips Tecnai-F20.

The Burnauer-Emmett-Teller (BET) surface areas measurement and pores features were carried out by measuring the N<sub>2</sub> adsorption/desorption isotherms at 77 K on a 3H-2000PS1 surface area analyzer.

The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analyses (TGA) were conducted using a thermo gravimetric analyzer(TGA-Q50, TA) in Ar at a scan rate of 5 °C min<sup>-1</sup> from room temperature to 600 °C. Raman spectra were recorded at room temperature on LabRAM Aramis (Horiba Jobin Yvon Company) Raman spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra spectrometer using a focused monochromatized Al K $\alpha$  radiation ( $\lambda = 1486.6$  eV).

### Electrochemical test

The composite electrodes consisted of 80% NCMSs/S composite, 10% acetylene black and 10% polyvinylidene fluoride (PVDF) by weight and were prepared by coating the mixture on aluminum foils with typical NCMSs/S composite loading of  $\sim 2.0$  mg cm<sup>-2</sup>. The 2025 coin cells were used in the test with lithium foil as the counter electrode, polypropylene micro porous membrane as the separator (Celgard 3501, Hoechst Celanese). The electrolyte was 1.0 mole bis(trifluoromethane)-sulfonamide lithium salt (LiTFSI, 99.95% trace metals basis, Aldrich) per liter of 1,3-dioxolane (DOL) + dimethoxymethane (DME) in a 1:1 volume ratio. The cells were assembled in an argon-filled glove box. The assembled cells were cycled between 2.8 and 1.5 V at different rates using a LAND-CT2001A battery testing instrument. The cyclic voltammogram (CV) measurements were performed on an Autolab electrochemical system in a voltage range of 1.5 to 2.8 V vs. Li/Li<sup>+</sup> at a scan rate of 0.1 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) data of the coin cells were acquired at room temperature by a Versa-stat 3 electrochemical workstation (Princeton Applied Research) after a desired number of discharge cycles, with the frequency ranging from 100 kHz to 100 mHz by imposing an alternate current with an amplitude of 10 mV on the electrode. The specific capacity was calculated on the basis of the mass of the sulfur in the NCMSs/S nanocomposites.

Reference:

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1. K. L. Ai, Y. L. Liu, C. P. Ruan, L. H. Lu and G. Q. Lu, *Adv. Mater.*, 2013, **25**, 998.

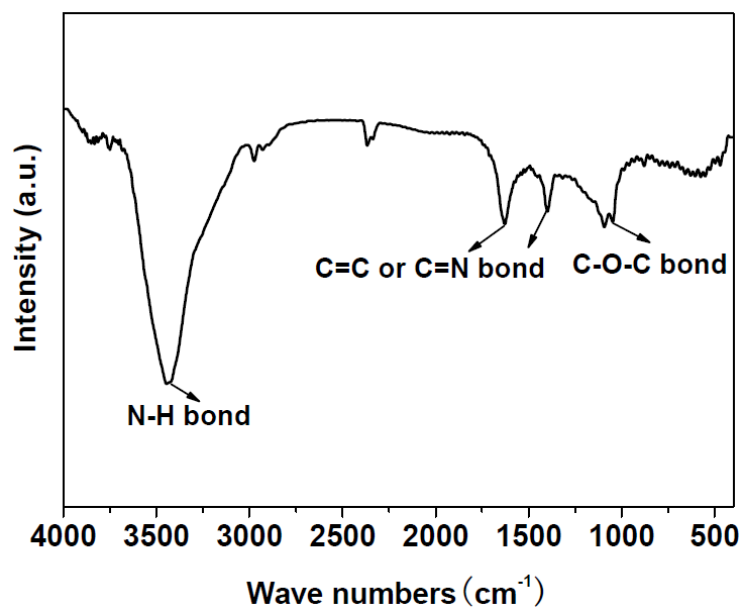


Fig. s1. The IR spectra of the obtained porous NCMSs and NCMSs/S composites.

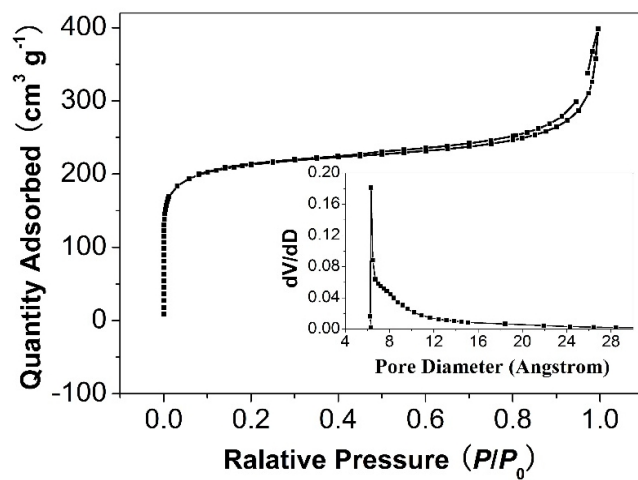


Fig. s2 The N<sub>2</sub> adsorption-desorption isotherms and pores sizes distribution of the porous NCMSs.

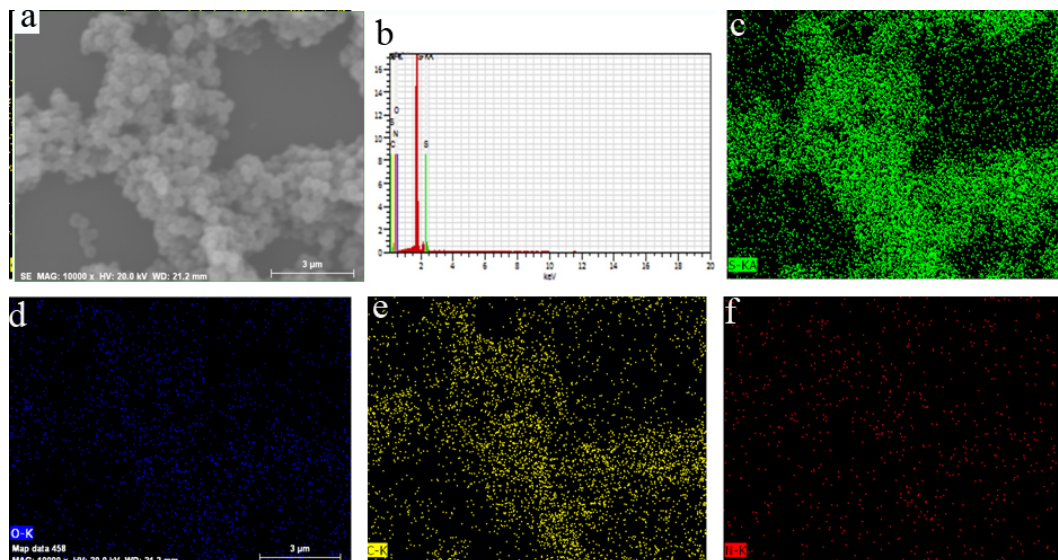


Fig. S3. (a) SEM image of the NCMSs/S composites, (b) Energy dispersive spectroscopic (EDS) line scanning of the region of full SEM images, the corresponding EDS mapping of (c) sulfur (d) oxygen, (e) carbon and (f) nitrogen.

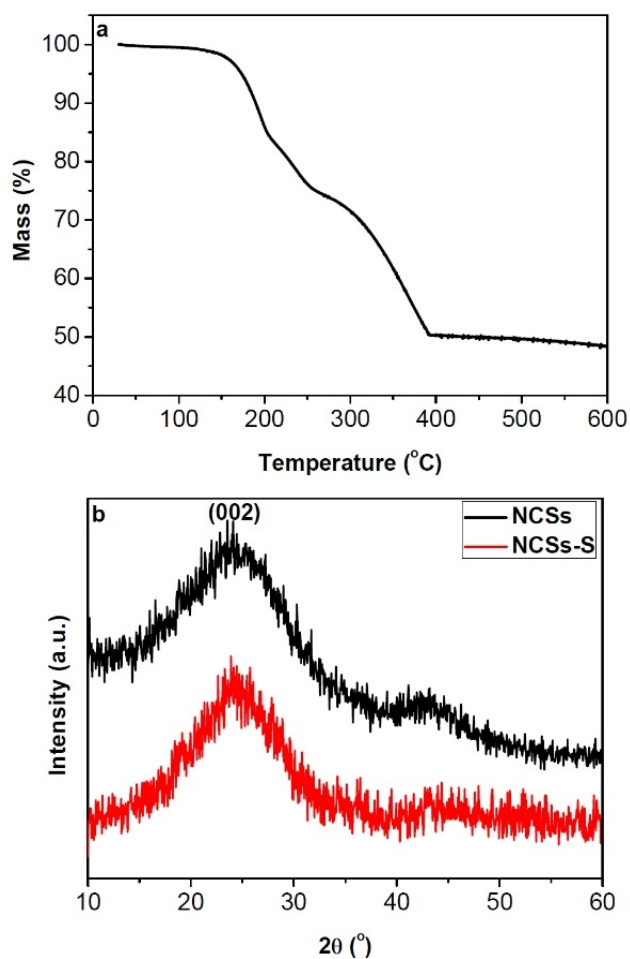


Fig. S4. (a) The TGA of the NCMSs/S composites and (b) the XRD patterns of the NCMSs and NCMSs/S composites.

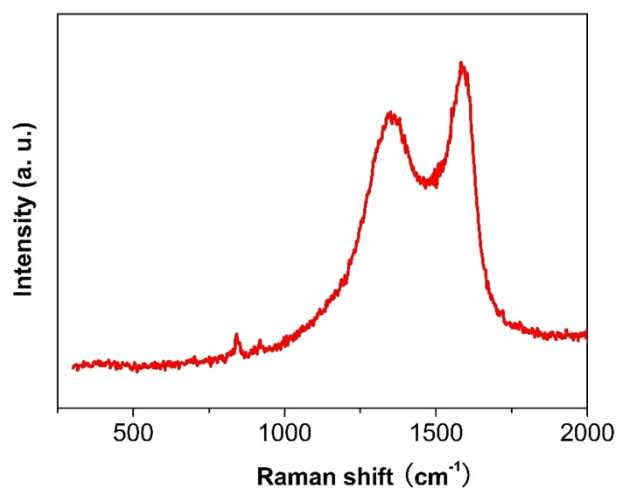
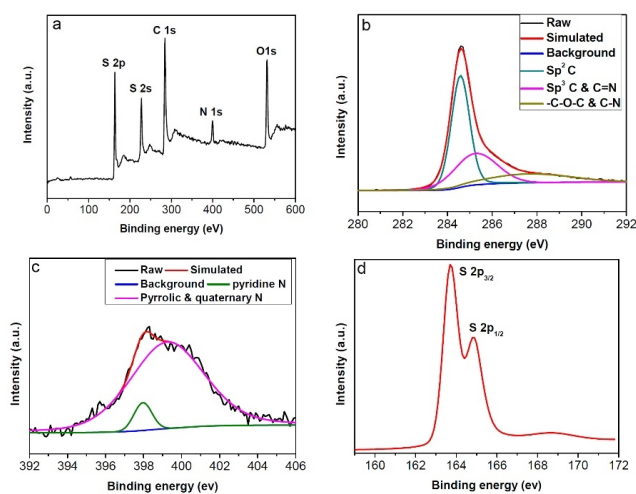


Fig. S5. The Raman spectrum of the obtained NCMs/S composites.



5 Fig. s6. (a) The XPS results and high-resolution XPS spectra of (b) C1s, (c) N1s and (d) S2p of the obtained NCMs/S composites.

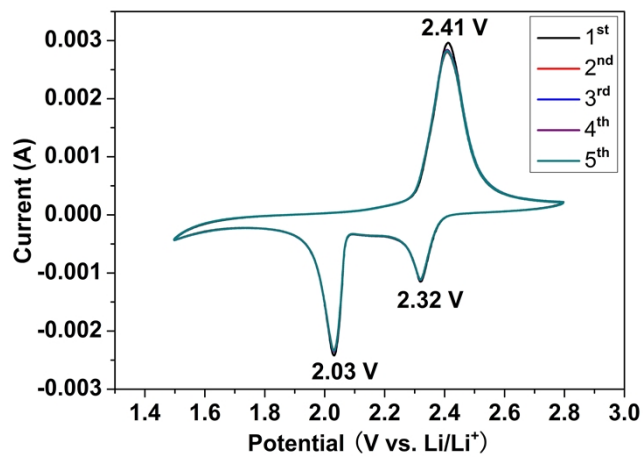


Fig. s7. Typical cyclic voltammograms at a sweep rate 0.1 mV s<sup>-1</sup> of the NCMs/S composites.

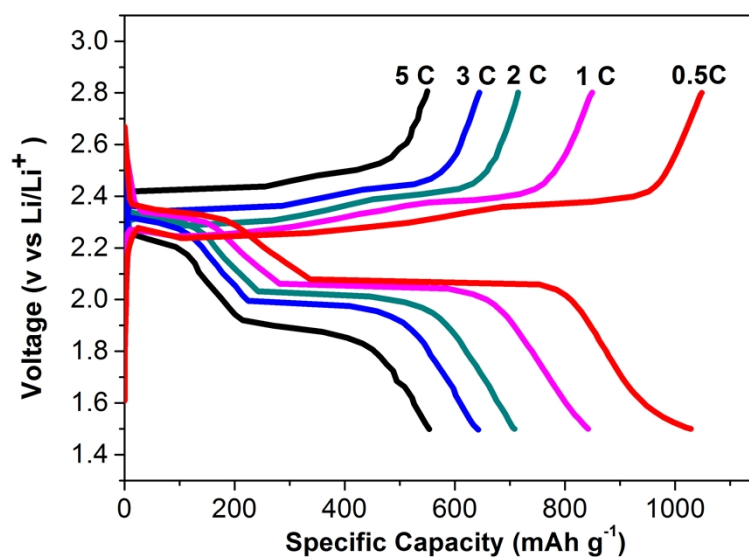


Fig. s8. The voltage vs. capacity profiles at various rates.

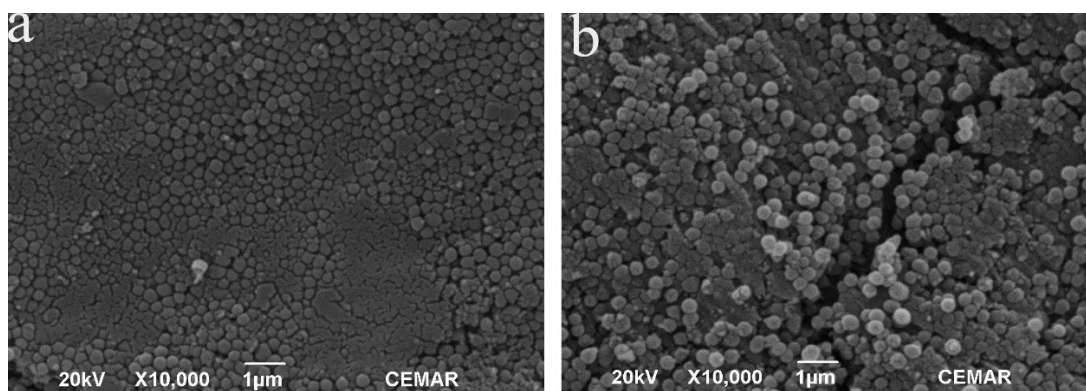


Fig. s9. The SEM images of the electrodes: (a) fresh and (b) cycled for 100 cycles at 0.2 C rate.

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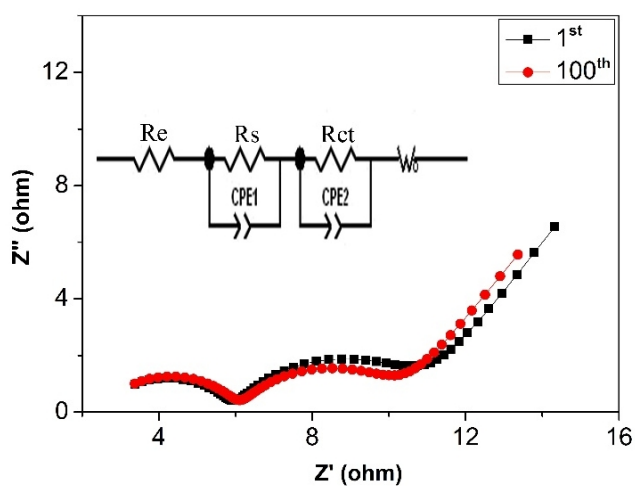


Fig. s10. EIS spectra of the NCMSs/S composites at different cycles after charging to 2.8 V at 0.2 C rate.