

Supporting Information

N-Doped Graphene-Cobalt Nickel Sulfide Aerogel as Sulfur Host for Lithium-Sulfur Batteries

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1. Supplementary Text

1. Experimental sections

1.1. Synthesis of CNS/N-rGO

Graphene oxide (GO) was prepared by using natural flake graphite powder (325 mesh, MACKLIN) as a raw material according to the modified Hummer's method.^{S1} The freeze-dried GO was collocated into 2 mg mL⁻¹ suspension and evenly dispersed by sonication at room temperature. Typically, 1 mmol Co(NO₃)₂·6H₂O, 0.5 mmol Ni(NO₃)₂·6H₂O, and 0.48 g thiourea were added to the 30 mL GO dispersions and sonicated for 30 minutes, and then 0.24 g ascorbic acid was added to the mixture and stirred evenly. Next, the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and then hydrothermally reacted at 150 °C for 12 h. The product was washed with deionized water and ethanol, and then freeze-dried for 48 h to produce CNS/N-rGO. Finally, the CNS/N-rGO was heat-treated at a heating rate of 10 °C min⁻¹ to 900 °C for 1 h in an Ar atmosphere. Co-Ni-O/rGO (CNO/rGO) was also prepared through an identical procedure without adding thiourea during the process. In addition, the CoS₂/N-rGO or NiS₂/N-rGO were prepared by adding 1.5mmol Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O, and 0.48g thiourea into the 30 mL GO dispersions. rGO material was purchased from the Sixth Element (Changzhou) Materials Technology Co. Ltd.

1.2. Synthesis of CNS/N-rGO/S

CNS/N-rGO and sublimed sulfur were ground together at a mass ratio of 1:3, and then the mixture was heat-treated at 155 °C for 12 h in an Ar atmosphere to obtain a CNS/N-rGO/S sample. At this heat temperature, the melting sulfur has the lowest viscosity and easily diffuses into the pores of the carbon material by the capillary

action. For comparison, CNO/rGO/S, rGO/S, CoS₂/N-rGO/S and NiS₂/N-rGO/S samples were also prepared using CNO/rGO, rGO, CoS₂/N-rGO and NiS₂/N-rGO as host materials under the same conditions, respectively.

1.3 Structural Characterizations

The morphologies and microstructure of the materials were visualized by field-emission scanning electron microscopy (SEM, FEI QUANTA 200F) and transmission electron microscopy (TEM, FEI, Titan G2 ETEM), and the energy dispersive X-ray spectroscopy (EDS) was used to characterize the element distribution on the CNS/N-rGO surface. TGA (NETZSCH, STA 2500 Regulus) analysis is to heat the material to 800 °C under N₂ flow, and the weight reduction during the 200 to 350 °C process is the sulfur content of sulfur matrix composites. Brunauer–Emmett–Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size distribution were analyzed using the N₂ adsorption/desorption isotherm by Micromeritics ASAP 2460 apparatus. Raman spectra were adopted to observe on a HORRIBA Jobin Yvon HR Evolution spectrometer using a 532 nm (green) laser excitation. X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance equipped with a Cu-K α radiation ($\lambda=0.15406$ nm). X-ray photoelectron spectroscopy (XPS) was carried out on X-ray photoelectron spectroscopy (XPS) analysis of the valence state of elements in the sample was carried out on a Thermo Fisher Scientific ESCALAB250Xi Spectrometer. UV–visible spectrometer (Lambda 750) in the range of 200–800 nm was used to measure the adsorption of the sulfur host on polysulfide.

1.4 Electrochemical Measurements

The electrochemical tests of the cathode of Li-S batteries were assembled in an Ar-filled glove box using CR2032 coin cells. The cell was formed by using a lithium metal as the anode, a Celgard 2500 membrane as the separator, and the electrolyte of 1.0 M LiTFSI + 1 wt% LiNO₃ dissolved in a mixture of 1,2-dimethoxymethane and 1,3-dioxolane (DME/DOL= 1:1, v/v). The cathode was prepared by mixing the CNS/N-rGO/S composites, conductive carbon black, and polyvinylidene difluoride (PVDF) binder with a weight ratio of 75:20:5 in N-methyl-2-pyrrolidone (NMP) to form uniform slurry. Subsequently, the slurry was coated onto Al foil and dried at 60 °C for 12 h under vacuum oven. The mass loading of sulfur in the cathode was ~ 2 mg cm⁻². Galvanostatic charge-discharge and cycle performance tests of the batteries were carried out using a Neware BTS8 batteries testing system in the potential range of 1.7-2.8 V. Using CHI 660E electrochemical workstation, the cyclic voltammetry (CV) curves were conducted at a scanning rate of 0.1 mV s⁻¹ in the voltage range from 1.7 to 2.8 V. All of the experiments in the electrochemical tests were carried out at room temperature. All specific capacity values were obtained based on the mass of elemental sulfur.

1.5 Visualized adsorption test

0.05 M Li₂S₆ solution was prepared by mixing Li₂S and sulfur powders in a DME/DOL mixture solution (1:1, v/v) at a molar ratio of 1:5. The solution was heated at 50 °C for 24 h with vigorous stirring to obtain the Li₂S₆ solution. Then, as-prepared Li₂S₆ solution (0.05 M) was added into 5 mL DME/DOL solution (1:1, v/v) and diluted to 2 mM Li₂S₆ solution, and then 20 mg rGO, CNO/rGO and CNS/N-rGO

were added to three glass vials and stirred for 30 min. It is noteworthy that all the above operations were carried out in the glove box filled with Ar.

1.6 Symmetric cell assembly and measurements

The preparation of symmetrical cell is that each main material (rGO, CNO/rGO, CNS/N-rGO, CoS₂/N-rGO or NiS₂/N-rGO) and PVDF binder were dispersed in NMP at a mass ratio of 3:1, and then the slurry was stirred uniformly and coated on the Al foil. After drying, the Al foil was punched into electrode disks with a diameter of 12.0 mm. During the assembly, the disks were used as a cathode electrode and anode electrodes, and 40 μ L 0.5 M Li₂S₆/DME was added as the electrolyte, while the control cell of CNS/N-rGO without Li₂S₆ was also assembled. CV curves of symmetrical cells were carried out at a scanning rate of 50 mV s⁻¹ in a potential window of -0.8 to 0.8 V. Moreover, CNS/N-rGO also measured CV profiles at different scan rates of 10-200 mV s⁻¹ in the voltage range of -0.8 to 0.8 V.

Figure Captions:

Fig. S1. (a) Cycle voltammograms of NiS₂/N-rGO/S cathode at a scan rate of 0.1mV s⁻¹. (b) Cycle voltammograms of CoS₂/N-rGO/S cathode at a scan rate of 0.1mV s⁻¹.

Fig. S2. (a) Galvanostatic discharge/charge curves of the NiS₂/N-rGO/S and CoS₂/N-rGO/S cathodes at 0.2 C. (b) Cycling performance and Coulombic efficiency of the NiS₂/N-rGO/S and CoS₂/N-rGO/S cathodes at 0.5 C for 300 cycles.

Fig. S3. Nyquist plots of the initial CNS/N-rGO/S and after 300 cycles at 0.5 C.

2. Supplementary Figures

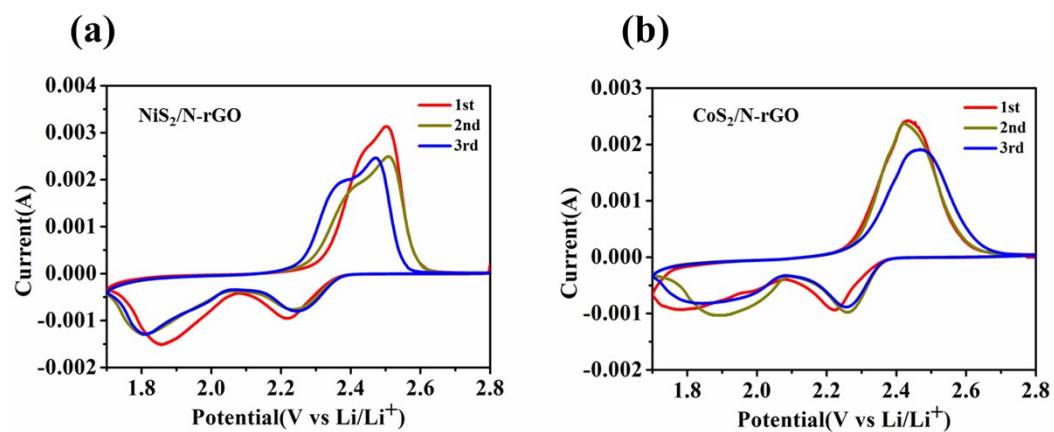


Fig. S1. (a) Cycle voltammograms of NiS₂/N-rGO/S cathode at a scan rate of 0.1mV s⁻¹. (b) Cycle voltammograms of CoS₂/N-rGO/S cathode at a scan rate of 0.1mV s⁻¹.

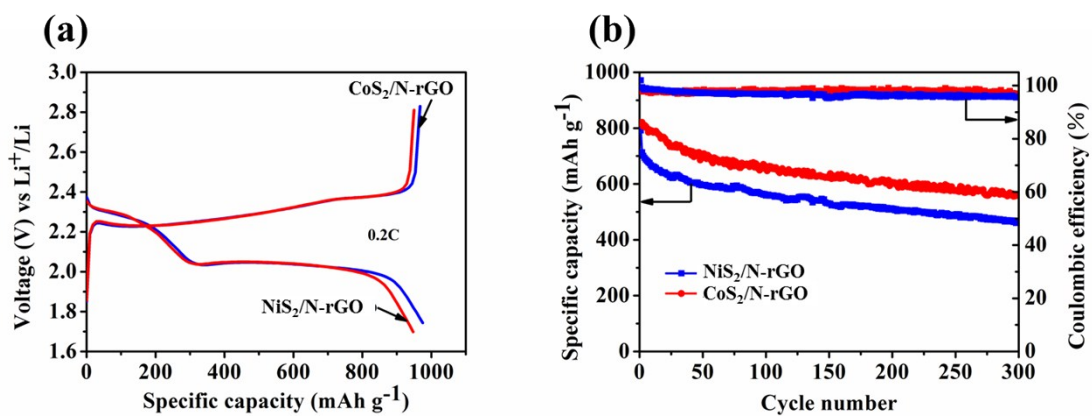


Fig. S2. (a) Galvanostatic discharge/charge curves of the NiS₂/N-rGO/S and CoS₂/N-rGO/S cathodes at 0.2 C. (b) Cycling performance and Coulombic efficiency of the NiS₂/N-rGO/S and CoS₂/N-rGO/S cathodes at 0.5 C for 300 cycles.

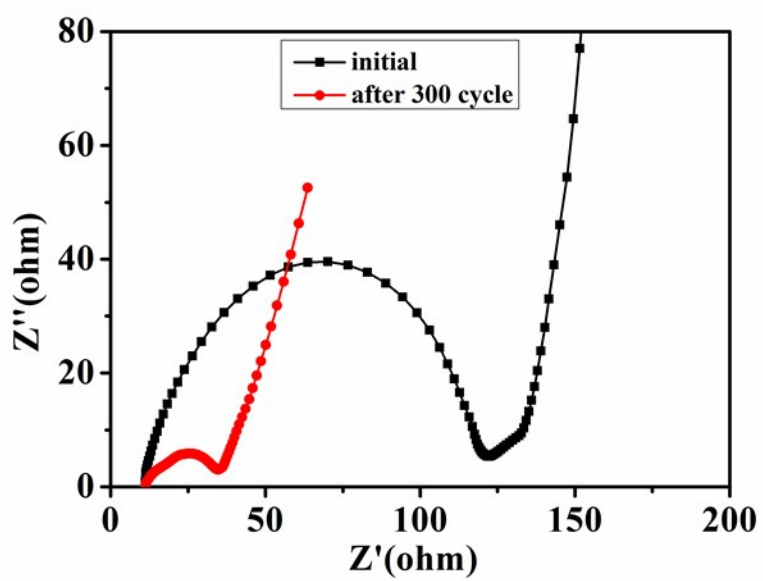


Fig. S3. Nyquist plots of the initial CNS/N-rGO/S and after 300 cycles at 0.5 C.

References

- [S1] S. Moussa, G. Atkinson, M. SamyEl-Shall, A. Shehata, K.M. AbouZeid and M.B. Mohamed, *J. Mater. Chem.*, 2011, **21**, 9608–9619.