Supporting Information

Double-walled N-doped carbon@NiCo₂S₄ hollow capsules as SeS₂ hosts for advanced Li-

SeS₂ batteries

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1. Experimental section

1.1. Synthesis of $NiCo_2S_4$ hollow capsule

Firstly, the uniform NiCo-precursor was prepared by a modified co-precipitation method. In a typical procedure, 2 mmol of nickel (II) acetate tetrahydrate and 4 g of polyvinylpyrrolidone (PVP, molecular weight-58000) were simultaneously added into 90 ml of anhydrous ethanol and stirred to completely dissolve at room temperature. The mixed solution was then reflux at 90 °C for 4 h. After cooling down to room temperature, the sediments were collected by centrifugation and washed with ethanol, then dried at 60 °C overnight. Secondly, 80 mg of as-prepared NiCo-precursor was dispersed into 0.04 mol L⁻¹ thioacetamide solution, and then transferred into a Teflon-lined stainless steel autoclave for heating 6 h at 120 °C. The final products were obtained by filtration, washed several times with ethanol and deionized water, and dried at 60 °C for further using.

1.2. Synthesis of double-walled N-doped carbon@NiCo $_2S_4$ substrate material

40 mg of NiCo₂S₄ hollow capsule was re-dispersed in 10 mM Tris buffer solution (pH = 8.5, 50 mL) with ultrasoniced for 20 min. After that, 20 mg dopamine hydrochloride was added into the dispersion liquid and stirred at room temperature for 3 h. Then the resultants were collected by filtration and washed three times with deionized water. The dried products were annealed in a N₂ atmosphere at 400 °C for 2 h with a heating rate of 1 °C/min to achieve NiCo₂S₄@NC.

1.3. Synthesis of double-walled N-doped carbon@NiCo₂S₄-SeS₂ composite

Briefly, 75 mg of SeS₂ and 30 mg of NiCo₂S₄@NC were thoroughly mixed in an agate mortar by wet grinding. The mixture was heated at 180 °C for 12 h under N₂ atmosphere, and then the temperature was increased to 200 °C for 20 min to remove the residual SeS₂ on the surface of NiCo₂S₄@NC. For comparison, NiCo₂S₄-SeS₂ and NC-SeS₂ composites were also prepared with the same weight ratio.

2. Physical characterizations

The morphologies and microstructure were detected by Field-emission scanning microscope (FESEM, JSM-7800F, Japan) and transmission electron microscopy (TEM, JEM-2100, Japan). XRD measurements were conducted using a Powder X-ray diffraction (XRD, MAXima-X XRD-7000) with Cu Ka radiation ($\lambda = 1.5406$ Å). Element composition and bonding information were collected by TEM (JEOL, JEM-2100F) with EDS spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively. Raman characterization was performed using a LabRAM HR Evolution (Horiba) Raman microscope with an excitation laser of 532 nm. Thermogravimetric (TGA) analysis was carried out by using Q50 (USA) to determine the contents of carbon and SeS₂. The BET specific surface area and pore size distribution were performed by Quadrasorb evo 2QDS-MP-30 (Quantachrome Instruments, USA). The UV-Vis spectra were collected on Shimadzu UV-2550 spectrophotometer.

3. Electrochemical measurements

The working electrode was fabricated by fully mixing 75 wt% NiCo₂S₄@NC-SeS₂, 15 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP), and then the homogeneous slurry was coated on the aluminum foil. After drying at 60 °C for 12 h, it was used as the cathode, lithium foil and Celgard 2400 were employed as the anode and separator, respectively, to assembled CR3025 coin cells in an Ar-filled glovebox. The electrolyte was composed of 1 M Lithium bis (trifluoromethanesulfonyl) sulfonimide (LiTFSI) solution in a mixture of 1, 3-dioxolane (DOL) and dimethoxymethane (DME, 1:1, v/v) with 0.1 M LiNO₃ additive. Galvanostatic discharge-charge cycling and cyclic voltammogram (CV) tests were conducted

by Land Instruments testing system (Wuhan Kingnuo Electronic Co., China) and an Arbin instruments within a cell voltage of 1.7-2.8 V, respectively. Electrochemical impedance spectroscopy (EIS) was carried out on Zahner electrochemical workstation (Zennium, IM6, Germany). However, the symmetric cells were assembled by using individual NiCo₂S₄ or NC both as anode and cathode. Besides, the Li_2S_6 was prepared by the reaction of sulfur powder and lithium sulfide at a molar ratio of 1:5. Polyselenide can be prepared by the lithiation of the elemental selenium. The CV curves of symmetric cells were collected between the voltage ranging from -0.8-0.8 V at a scan rate of 50 mV s⁻¹. The current densities were calculated by the theoretical capacity of SeS₂, namely, 1 C is equal to 1345 mAh g⁻¹.

4. Supplementary Figures



Fig. S1. Nyquist plots of individual $NiCo_2S_4$ and NC electrodes and the corresponding equivalent electrical circuits for the EIS

Samples	$\operatorname{Rct}(\Omega)$	$\operatorname{Rs}(\Omega)$	$Zw(\Omega)$
NiCo ₂ S ₄	2.035	39.64	17.08
NC	5.308	43.04	22.9

Table S1. Fitting parameters of NiCo₂S₄ and NC electrodes obtained from EIS



Fig. S2. Schematic illustration of the procedure for preparing the NiCo₂S₄@NC-SeS₂ composite.



Fig. S3. (a, b) FESEM, (c) TEM images and (d) XRD pattern of the NiCo-precursor.



Fig. S4. (a, b) FESEM and (c, d) TEM images of $NiCo_2S_{4.}$



Fig. S5. XRD pattern of NiCo₂S_{4.}



Fig. S6. XPS pattern of NiCo₂S₄@NC.



Fig. S7. Raman spectra of NiCo₂S₄ and NiCo₂S₄@NC hollow capsule.



Fig. S8. TGA curve of NiCo₂S₄@NC hollow capsule in the oxygen atmosphere.



Fig. S9. (a, c) N₂ adsorption-desorption isotherms and (b, d) pore-size distributions of the NiCo₂S₄@NC-and NiCo₂S₄@NC-SeS₂ composite. The specific surface areas of NiCo₂S₄@NC and NiCo₂S₄@NC-SeS₂ are 44.5 and 21.5 m²g⁻¹, respectively.



Fig. S10. FESEM images and TGA curves of (a) the NiCo $_2S_4$ -SeS $_2$ and (b) the NC-SeS $_2$ composites in the nitrogen atmosphere.



Fig. S11. (a) CV curve at the scan rate of 0.1 mV s^{-1} and (b) charge/discharge profiles of pure NiCo₂S₄ electrode at 0.1 C.



Fig. S12 (a) Rate capabilities and (b) cycling performance of the NiCo₂S₄@NC-SeS₂ electrode with high SeS₂ loading of 5 mg cm⁻². The electrode delivers a reversible discharge capacities of about 989.6, 830.9, 714.4, 548.5 mAh g⁻¹ as the current density increase from 0.1 C to 1.0 C. When continues charge and discharge at 0.5 C for 150 cycles, the capacity can still maintain 527.6 mAh g⁻¹ with the average capacity decay of around 0.17 % per cycle.

Samples	Content of Se _x S _y (wt.% / mg cm ⁻²)	Theoretical capacity (mAh g ⁻¹)	Initial capacity (mAh g ⁻¹)	Cycle numbe r	Decay rate (per cycle)
CMK-3/SeS ₂ @PD ^[1]	70/2.6-3	1342	1234 at 0.2 A g ⁻¹	500	0.11%
Co-N-C/SeS ₂ ^[2]	66.5	1345	1193.5 at 0.1 C	200	0.08%
HMC@TiN/SeS ₂ ^[3]	70/1	1121	990 at 0.1 C	200	0.15%
	70/5		960 at 0.1 C	80	/
CoS ₂ @LRC/SeS ₂ ^[4]	70/2.3-3	1123	1015 at 0.2 A g ⁻¹	400	0.11%
MWCNT/SeS ₂ ^[5]	70	1342	>1200	50	/
			at 0.05 A g ⁻¹		
SeS ₂ @MCA ^[6]	49.3/1.5-2		1150 at 0.05 A g ⁻¹	250	/
NiCo ₂ S ₄ @NC-SeS ₂	66.7/2	1345	1205.1 at 0.1 C	800	0.038 %

Table S2. The comparisons of cathode materials for Li- Se_xS_y batteries



Fig. S13. (a) Charge/discharge profiles of the Se-based electrode at 0.1 C, (b) polyselenium entrapment by $NiCo_2S_4$ hollow nano-capsules and (c) UV-vis absorption spectra of polyselenium solution after adding $NiCo_2S_4$.



Fig. S14. The separators of $NiCo_2S_4@NC-SeS_2$ electrode after 500 cycles and the separators of $NiCo_2S_4$ -SeS₂, and CN-SeS₂ electrodes after 350 and 450 cycles, respectively.



Fig. S15. EDS elemental mappings and EDS spectra of lithium metal from (a-c) NiCo₂S₄@NC-SeS₂ electrodeafter 500 cycles, (d-f) NiCo₂S₄-SeS₂ and (g-i) NC-SeS₂ electrodes after 350 and 450 cycles, respectively, insets are SEM images of the corresponding lithium metal.



Fig. S16. CV curves of NiCo₂S₄ and NC symmetric cells with and without Li₂S₆.

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