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Electronic Supplementary Material

NiS_2 coupling with CNT@3D rGO as sulfur host for enhancing the adsorption–catalytic conversion of polysulfides

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S1 Material characterization

The materials were characterized using an X-ray diffractometer (Bruker D8 Advance) equipped with Cu Kα radiation (λ = 1.5406 Å) under a Bragg–Brentano geometry with a step size of 0.02° and at a scan rate of 5.0(°)/min, a scanning electron microscope (Hitachi S-4800, operated at 5 kV), and a transmission electron microscope (Hitachi HT7700 TEM with an acceleration voltage of 120 kV). Raman spectra were recorded over the 2000–100 cm^{-1} range using a Renishaw in Via with a laser wavelength of 532 nm. The applied laser power was 5 mW as measured with a power meter at the sample location. A Thermo ESCALAB 250 X-ray photoelectron spectroscope (Al Kα 1486.6 eV) produced by the Thermo Fisher Technology Company was used to analyze the valence states of elements in catalysts and the valence bands of catalysts. All binding energies were calibrated with the C 1s peak (BE = 284.8 eV) as the standard. Elemental mapping images, selected-area electron diffraction (SAED) images and high-resolution transmission electron microscopy (HRTEM) images were obtained by a Hitachi HT7700 transmission electron microscopy with an acceleration voltage of 200 kV. The surface area analysis and pore size analysis were performed using Nova 2000E equipment from Conta Corporation. The samples were used for adsorption and desorption analysis in liquid nitrogen. A thermogravimetric analyzer (Setaram Labsys Evo SDT Q600) was used at a heating rate of 5 °C·min^{-1} from room temperature to 600 °C in flowing N_2 or air to analyze the contents of sulfur in composites.

S2 Electrochemical measurements

Electrochemical properties of 3D rGO/S, CNT/S, NiS_2/S, CNT@3D rGO/S, and NiS_2@CNT@3D rGO/S as cathode materials for lithium–sulfur batteries were investigated (CR2032). The above prepared samples (mass ratio of 75%), 15% carbon black, and 10% polyvinylidene fluoride binder

(PVDF) in N-methyl pyrrolidone (NMP, analytically pure, Aladdin's Reagent (Shanghai) Co., Ltd.) were rapidly stirred at room temperature to obtain a homogeneous slurry. The resulting slurry was uniformly coated onto aluminum foil (Aladdin's Reagent Ltd.) and initially dried in an oven at 60 °C for 30 min, followed by vacuum drying at 80 °C for 24 h. The dried cathodes were prepared as 12-mm-diameter electrode disks. The CR2032 coin cells were assembled in an argon-filled glovebox (O_2 < 0.01 ppm, H_2O < 0.01 ppm, Mikrouna, Super 1220/750/900). The mass of the dried cathode coating was approximately 2.46 mg per 12-mm electrode disk, excluding the Al current collector. The sulfur loading was approximately 1.2 mg·cm^{-2}. A total of 40 μL electrolyte was added to each CR2032 cell, corresponding to an electrolyte-to-sulfur (E/S) ratio of approximately 29.4 μL·mg^{-1}. The specific capacities (mAh·g^{-1}) and current densities (A·g^{-1}) were calculated based on the mass of sulfur. Lithium metal foil (Aladdin Reagent Shanghai Co., Ltd.) was used as the counter/reference electrode, and Celgard 2400 was employed as the separator. The electrolyte consisted of 1 mol·L^{-1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI; Sigma-Aldrich) dissolved in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v), containing 1% $LiNO_3$ as an additive. The discharge–charge tests were performed on a Neware battery test system at a constant temperature of 25 °C, with a potential range of 1.6–2.8 V. Cyclic voltammetry (CV) measurements were performed over a potential range of 1.6–2.8 V using an electrochemical workstation, including scan-rate-dependent measurements from 0.1 to 1.0 mV·s^{-1}. Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range of 0.01 Hz to 100 kHz using the same workstation. For the kinetic analysis, the scan-rate dependence of the characteristic redox peak currents was evaluated using the power-law relationship as follows:

$$i_p = av^b \tag{S1}$$

where i_p is the peak current, v is the scan rate, and both a and b are fitting parameters. The logarithmic form is:

$$\log i_p = b\log v + \log a \tag{S2}$$

The b-value was obtained from the slope of the linear relationship between $\log i_p$ and $\log v$. The surface-controlled and diffusion-controlled current contributions were further evaluated using the Dunn method:

$$i(V) = k_1 v + k_2 v^{1/2} \tag{S3}$$

where $i(V)$ is the current at a given potential V, and $k_1 v$ and $k_2 v^{1/2}$ represent the fitted surface-controlled and diffusion-controlled current contributions, respectively. The coefficients k_1 and k_2 were determined from the linearized relationship:

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \tag{S4}$$

The current contributions were evaluated across the CV potential window and integrated to estimate their respective percentages. This full-window analysis is distinct from the peak-specific b-value analysis.

S3 Density functional theory calculations

First-principles calculations of NiS_2 were performed using the Vienna Ab Initio Simulation Package (VASP) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional within the generalized gradient approximation (GGA). The projector augmented-wave (PAW) method was employed, and spin-unrestricted geometry optimizations were performed. The cutoff energy for the plane wave basis was set to 500 eV. The convergence threshold of the electronic self-consistency was specified as 1.0 × 10^{-6} eV, and the total energy change of the whole catalyst system between two

ionic relaxation steps was designated as less than 0.03 eV. The NiS_2 structural models were constructed using VESTA. The adsorption energy (E_{ads}) was expressed as:

$$E_{ads} = E_{surf+mol} - E_{surf} - E_{mol} \quad \text{(S5)}$$

where E_{surf} and E_{mol} are the single point energies of substrates and isolated molecules, respectively, and $E_{surf+mol}$ represents the energy of the combined systems upon adsorption.

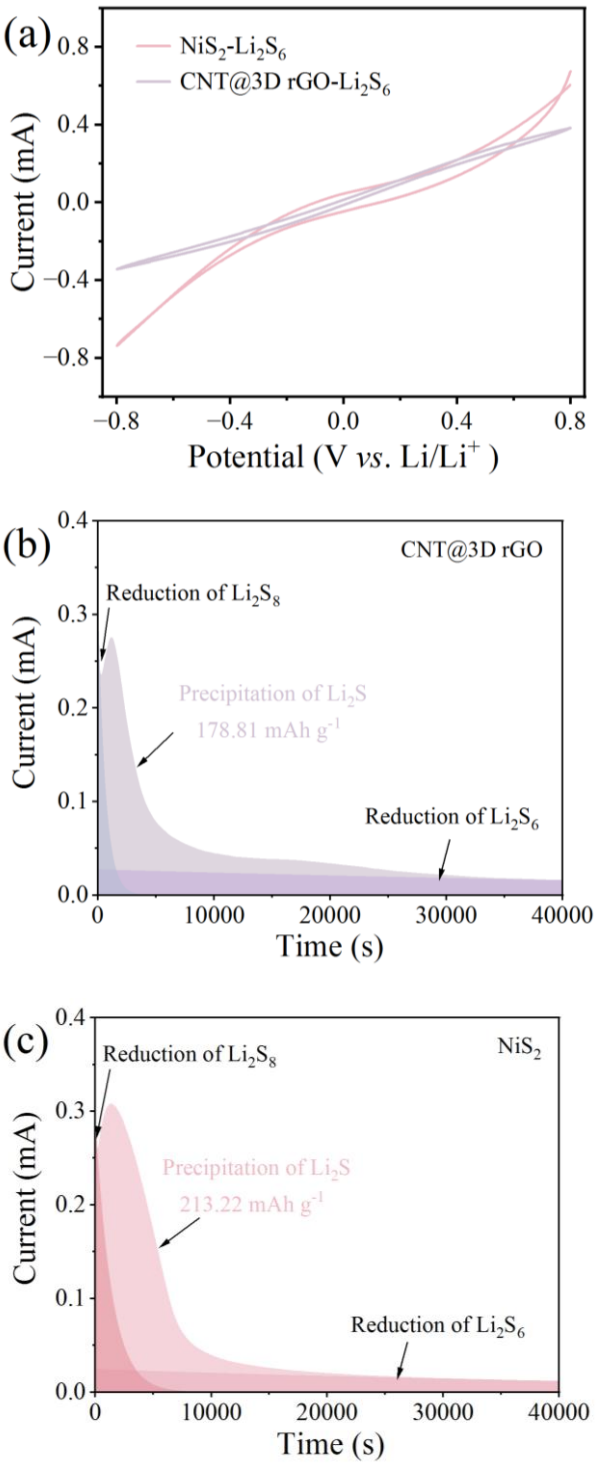

Fig. S1 (a) CV curves of Li_2S_6 symmetric cells with NiS_2 and CNT@3D rGO electrodes separately in the Li_2S_6-containing electrolyte. **(b)(c)** Potentiostatic Li_2S nucleation curves obtained using CNT@3D rGO and NiS_2, respectively.

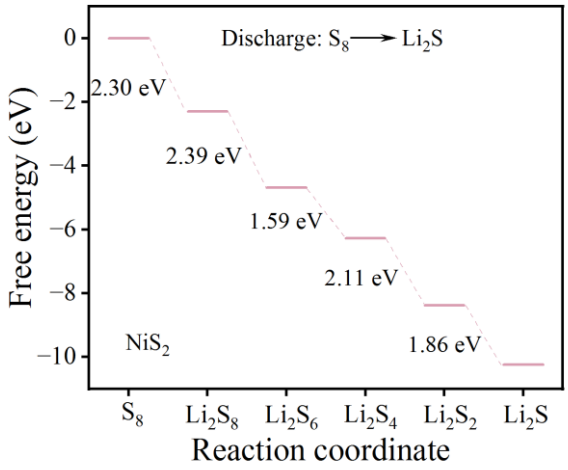

Fig. S2 Gibbs energy profile for the reduction process of the NiS_2 substrate.

Table S1 Comparison of the electrochemical performance of the present cathode with literature-reported lithium–sulfur battery cathodes

Material	Current density/($A \cdot g^{-1}$)	Cycle number	Capacity/($mAh \cdot g^{-1}$)	Ref.
NiS_2/KB@S	0.83	500	461	[31]
NiS_2/C	1.67	200	306	[50]
NiCoMn-S/CNT@S	0.33	80	826	[52]
NiS/NiSe	0.33	200	517	[53]
	1.67	500	462	[53]
NiCoP	0.33	200	550	[54]
NiO@Halloysite	0.33	100	855	[55]
	0.84	450	467	[55]
NiS_2@CNT@3D rGO/S	0.2	150	713	This work
	1.0	400	439	

Table S2 EIS fitting parameters of NiS_2/S, CNT@3D rGO/S, and NiS_2@CNT@3D rGO/S cathodes before and after cycling tests

Material	Before/after cycling test	R_1/Ω	R_{ct}/Ω	R_2/Ω
NiS_2/S	before	5.7	154.7	–
	after	7.3	191.5	1.2
CNT@3D rGO/S	before	8.7	277.8	–
	after	5.1	322.1	31.9
NiS_2@CNT@3D rGO/S	before	11.59	91.4	–
	after	5.7	96.9	8.1