Co₃Se₄ Nanoparticles Anchored on Inverse-Opal Skeleton as Sulfur Host for High-Performance Li-S Batteries

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Experimental Section

Materials and chemicals

All the reagents were utilized in their as-received state without undergoing additional purification steps. They include selenium powder (Shanghai Macklin Biochemical Co., Ltd. 99%), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O) (Shanghai Macklin Biochemical Co., Ltd. 99%), a sodium oleate (Adamas Reagent Co., Ltd. 99%) and tetraethyl orthosilicate (TEOS) (Shanghai Aladdin Biochemical Technology Co., Ltd. 99.8%).

Preparation of Cobalt oleate (Co-OL) and SiO₂ opal template

Generally, 5 mmol of $CoCl_2 \cdot H_2O$ and 10 mmol of sodium oleate were introduced into the mixed solution composed of 10 mL of ethanol, 10 mL of distilled water and 20 mL of hexane. The solution was condensed at 70°C for 5h and then cool down to ambient temperature. The upper organic layer was rinsed multiple times with deionized water to eliminate the by-product, sodium chloride (NaCl). After a specific interval of standing, the upper transparent organic mixture was treated with methanol and acetone in turn, and the cobalt oleate can be obtained after 12 h freeze-drying.

Silica nanospheres were synthesized via Stöber's approach. An appropriate amount of silica microspheres was dispersed in ethanol and dried for a week to obtain white solid with pearlescent luster. Then the obtained template was placed in an alumina porcelain boat and calcined at 800°C in Muffle furnace for 2h to enhance the mechanical strength. Finally, the silica opal template was obtained.

Preparation of Co₃Se₄/NC and NC

Firstly, 0.6 g of SiO₂, 0.5 g of Co-OL, 5 ml of oleamine (OA) and 0.5 g of selenium powder were mixed uniformly. Subsequently, the mixture was transferred into an alumina porcelain boat and subjected to calcination at 650 °C for 3 h within an Ar/H₂ atmosphere with the heating rate employed during this process of 5 °C/min. Subsequent to being cooled down to ambient temperature, the obtained sample was etched with HF solution to remove SiO_2 template and the Co_3Se_4/NC was obtained. The synthesis of N-doped carbon (NC) followed a procedure analogous to that of Co_3Se_4/NC , with the sole exception being the omission of selenium powder addition. And the final sample was treated with acid to remove active component.

Preparation of Co₃Se₄/NC/S and Co₃Se₄/NC/S cathode

The sulfur cathode was fabricated via the typical melting-diffusion approach. Co₃Se₄/NC was uniformly blended with sublimed sulfur in a proportion of 4:6. And then the mixture was set to a vacuum and kept at 155°C for 12 h, so the sulfur complex could be obtained. In the process of preparing the working cathode, the slurry was prepared through the process of mixing the Co₃Se₄/NC/S composite (70 wt.%), Cochin black (20 wt.%), and LA133 solution (10 wt.%). The acquired slurry was evenly applied onto an aluminum (Al) foil and then dried at a temperature of 60 °C for a duration of 12 h. Subsequently, the working electrodes were cut into circular discs, with the areal sulfur loading within the range of 1–1.5 mg cm⁻².

Characterization

The morphologies and microstructures of the samples were investigated using a scanning electron microscope (SEM, JSM-6700F) equipped with energy-dispersive X-ray analysis (EDS), along with a transmission electron microscope (TEM, FEI Talos F200x). To determine the sulfur content, thermogravimetric analyses (TGA, Hitachi 7200) were conducted under N₂ protection, with a heating rate set at 10 °C min⁻¹. The UV-vis adsorption test results were recorded via a UV-vis spectrometer (Shimadzu UV-2450 Spectrophotometer). X-ray diffraction (XRD) measurements were performed on a DX-2700 using Cu-K α radiation (λ =1.54056 Å) to examine the crystalline phases. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-ALPHA) experiments were executed to analyze the surface chemistry of the specimens. N₂ absorption-desorption examinations were carried out on an ASAP 2020 system. The relevant cell tests were accomplished on an electrochemical workstation (CHI 760E) and Landt CT 2001A battery cyclers.

Li-S Cell Assembly and Electrochemical Measurements

CR2016-type coin cells were assembled within an Ar-filled glovebox where the concentrations of water and oxygen were maintained below 0.1 ppm. A Celgard 2400 membrane served as the separator, and the electrolyte was composed of 1 M LiTFSI and 1 wt.% LiNO₃ dissolved in a 1:1 (v/v) mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME). The cells' cycling behavior was evaluated through galvanostatic charge-discharge tests within a voltage range of 1.7–2.8 V (relative to Li/Li⁺) at different current densities, employing a Landt CT 2001A battery testing system. The cathode's specific capacity was calculated based on the sulfur mass. Additionally, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were performed using a CHI 760E electrochemical workstation.

Lithium Polysulfide Adsorption Test

A 5 mM Li_2S_6 solution was synthesized by combining Li_2S and elemental sulfur in a 1:5 molar ratio within a mixed solvent of DOL and DME (volume ratio 1:1) in a glovebox. The mixture was thoroughly blended, heated, and continuously stirred for 48 hours. To assess Li_2S_6 adsorption, equal quantities of NC and Co_3Se_4/NC were introduced into 6 mL of the prepared Li_2S_6 solution and allowed to stand for 24 hours. The adsorption performance was evaluated qualitatively by measuring the absorbance using ultraviolet-visible spectroscopy.

Symmetrical Cell Measurements

Symmetrical cells were fabricated using Co_3Se_4/NC and reference electrodes, with Li_2S_6 solution serving as the electrolyte. Cyclic voltammetry (CV) tests were conducted on these cells within a voltage range of $-1.0\sim1.0$ V, employing varying scan rates of 1, 2, 3, 4, 5, 10, 20, and 50 mV·s⁻¹.

Li₂S Nucleation Test

The 0.25 M Li_2S_8 electrolyte was produced by reacting Li_2S with sulfur in a molar ratio of 1:7 within a mixed solvent of DOL and DME (volume ratio of 1:1). The mixture was continuously stirred for 48 hours under an inert Ar atmosphere to ensure complete dissolution

and homogeneity. The Co₃Se₄/NC and NC composite slurries were uniformly deposited onto aluminum foil substrates to serve as electrodes, with Celgard 2400 employed as the separator. For cell assembly, 25 μ L of the prepared Li₂S₈ catholyte was dispensed onto the cathode side, while 25 μ L of a Li-S base electrolyte was applied to the lithium anode side. The cells were subjected to galvanostatic discharge to 2.06 V at a constant current of 0.112 mA, followed by potentiostatic hold at 2.05 V to promote the nucleation and growth of Li₂S until the current decreased to below 10⁻⁵ A.

Computation Simulation

All simulations were executed via density functional theory (DFT) utilizing the Vienna Ab Initio Simulation Package (VASP). The computational framework adopted a plane-wave basis set with a kinetic energy cutoff of 450 eV, coupled with projector-augmented wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA). Partial orbital occupancy was addressed through the Gaussian smearing scheme with a broadening width of 0.1 eV. Self-consistency in electronic iterations was achieved when energy variations between consecutive steps fell below 1×10^{-51} eV, while structural relaxations were deemed converged when atomic forces dropped below 0.02 eV Å⁻¹. Long-range dispersion corrections were incorporated via Grimme's DFT-D3 approach. Surface Brillouin zone sampling was implemented using a $3 \times 3 \times 1$ Monkhorst-Pack k-point grid. Binding energies (E_b) were derived as $E_b = E_{ad-sub} - E_{ad} - E_{sub}$, where E_{ad-sub} , E_{ad} and E_{sub} correspond to the total energies of the optimized adsorbate-substrate complex, isolated adsorbate species, and pristine substrate, respectively.

The current-time transient behaviors of four fundamental electrochemical deposition mechanisms can be mathematically described as follows:

$$\frac{i}{2\text{DI:}} \frac{i}{i_m} = \left(\frac{t}{t_m}\right) \left\{ exp\left[\frac{t_m^2 - t^2}{2t_m^2}\right] \right\} \#(S1)$$

$$\frac{i}{2\text{DP}} = \left(\frac{t}{t_m}\right)^2 \left\{ exp\left[\frac{-2\left(t^2 - t_m^3\right)}{3t_m^2}\right] \right\} \#(S2)$$

$$3\text{DI}: \frac{i}{i_m} = \left(\frac{1.9542}{t/t_m}\right)^{1/2} \left\{ 1 - exp\left[-1.2564\left(\frac{t}{t_m}\right)\right] \right\} \#(S3)$$

$$3\text{DI}: \frac{i}{i_m} = \left(\frac{1.2254}{t/t_m}\right)^{1/2} \left\{ 1 - exp\left[-2.3367\left(\frac{t}{t_m}\right)^2\right] \right\} \#(S4)$$



Fig. S1 The (a) SEM image and (b) XRD pattern of SiO_2 nanospheres. (c) the SEM image of $Co_3Se_4/SiO_2@NC$.



Fig. S2 (a) The X-ray pattern of NC. The (b) SEM image and (c, d) elemental mapping and of NC.



Fig. S3 The (a), (b) SEM image, (c) TEM and (d) HR-TEM image of the Co₃Se₄/NC.



Fig. S4 TGA curve of the Co_3Se_4/NC sample at a heating rate of 10 °C min⁻¹ under air atmosphere

When the Co_3Se_4/NC was heated from 25 °C to 900 °C under air flow, carbon would be burned out, and the Co_3Se_4 were turned to Co_3O_4 , according to the following chemical reactions:

$$C(s) + O_2(g) = CO_2(g);$$

 $Co_3Se_4(s) + 6O_2(g) = Co_3O_4(s) + 4SeO_2(g)$

Thus, the Co_3Se_4 content in the NC is about $(MCo_3Se_4/MCo_3O_4) * 54.88\% = 48$ wt%.



Fig. S5 Nitrogen adsorption and desorption isotherms of NC.



Fig. S6 High-resolution XPS spectrum of Co_3Se_4/NC .



Fig. S7 High-resolution XPS spectra of N 1s of Co_3Se_4/NC .



Fig. S8 CV curves of symmetric cells tested at different scanning rates of Co₃Se₄/NC electrode.



Fig. S9 CV curves of symmetric cells tested at different scanning rates of NC.



Fig. S10. SEM images of the final Li_2S deposited on (a) Co_3Se_4/NC electrode and (b) NC electrode.

Note: As illustrated in Fig. S10, the Li₂S deposition on the NC electrode forms large twodimensional platelet-like morphology. These platelets aggregate into densely packed crystalline Li₂S layers during the deposition process, which impede the electrochemical reaction by limiting the exposure of active sites and reducing the effective contact area between the electrolyte and the electrode surface. In contrast, the Co_3Se_4/NC electrode exhibits a markedly different morphology. Instead of forming large platelets, Li₂S deposits as small, uniformly sized granules on the Co_3Se_4/NC surface, which aligns well with the growth modeling and thereby suppresses the passivation of Li₂S while enhancing its electrochemical activity. These results indicate a higher nucleation rate of Li₂S on the Co_3Se_4/NC surface compared to NC on account of the catalysis of Co_3Se_4 .



Fig. S11. (a) SEM image and (b-g) elemental mappings (h) XRD patterns and (i) TGA curves of Co₃Se₄/NC/S.



Fig. S12 CV curves at different scanning rates of the NC/S cathode.



Fig. S13 Relationships between peak current and the square root of scan rates for $Co_3Se_4/NC/S$ and NC/S cathodes.



Fig. S14 The EIS image and equivalent circuit of Li-S batteries with two cathodes.



Fig. S15 The R.R. values of $Co_3Se_4/NC/S$ and NC/S cathodes.



Fig. S16 GCD curves of different current densities from 0.2 C to 3 C.



Fig. S17 Cycling performance of the different sulfur cathodes at 0.5 C.

Materials	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
Co ₃ Se ₄ /NC	298.62	0.276
NC	315.25	0.285

Table S1 Specfic surface area and pore volume of Co₃Se₄/NC and NC.

Table S2 Lithium-ion diffusion rates (D_{Li^+} , cm⁻² s⁻¹) of Li-S batteries paired with different cathodes.

Sample	R1	R2	01
Co ₃ Se ₄ /NC/S	3.04×10 ⁻⁸	2.92×10 ⁻⁸	5.30×10 ⁻⁷
NC/S	1.06×10 ⁻⁸	1.21×10 ⁻⁸	2.37×10 ⁻⁷

Table S3 The EIS fitting results of Li-S batteries paired with different cathodes.

Sample	R_{Ω}	R _{ct}
Co ₃ Se ₄ /NC/S	1.6	44.1
NC/S	4.3	120.6