Synergistic Adsorption and Catalysis Enabled by Hollow Co₉S₈-CoO Heterostructures for High-Performance Lithium-Sulfur Batteries

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1. Experimental

1.1 Synthesis of Hollow Co₉S₈-CoO, Co₉S₈, and CoO.

Initially, ZIF-67 was synthesized by combining cobaltous nitrate hexahydrate and 2methylimidazole in 100 mL of methanol at a molar ratio of 1:8. Subsequently, 0.2933 g of ZIF-67 was dispersed in 40 mL of ethanol, and 0.6011 g of thioacetamide was added to the suspension. The resulting mixture was refluxed at 80 °C for 30 min, followed by annealing at 450 °C in Ar to obtain the Co₉S₈-CoO hollow polyhedrons. Control sample of CoO was obtained through direct heat treatment of ZIF-67 under mixed atmosphere of Ar and air with a volume ratio of 95:5, while pure Co₉S₈ was obtained by adjusting the molar ratio of ZIF-67 and thioacetamide (1:4).

1.2 Synthesis of Co₉S₈-CoO@S, Co₉S₈@S, and CoO@S Composites

 Co_9S_8 -CoO@S composite was synthesized via a melt-infiltration method by mixing the hollow Co_9S_8 -CoO with sulfur at a mass ratio of 3:7. Co_9S_8 @S and CoO@S composites were prepared using Co_9S_8 and CoO and sulfur with the same mass ratio, following the same procedure.

1.3 Characterization

Crystal structure was analyzed by X-ray diffraction with Cu-K_{α} radiation (BRUKER, D8 ADVANCE). The microstructure and elemental composition of the materials were characterized using field-emission scanning electron microscopy (FEI, Nova Nano SEM 450) and transmission electron microscopy (FEI, Tecnai G2 F30). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo

Fisher K-Alpha spectrometer. UV-Vis absorption spectra were obtained using a UV-2600 spectrophotometer (Tian Mei).

1.4 Electrochemical Measurements

Sulfur electrode slurry was prepared by mixing 80 wt% active material, 10 wt% polyvinylidene fluoride (PVDF) binder, and 10 wt% carbon black in N-methyl-2-pyrrolidone (NMP). The obtained slurry was then coated onto aluminum foil and vacuum-dried at 60 °C for 24 h. CR2032 coin cells were assembled in an argon-filled glove box using 1 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) mixed with 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 by volume) containing 2 wt% LiNO₃. Electrochemical performance was evaluated using a LAND CT2001A battery testing system within a voltage window of 1.8-2.6 V to characterize cycling stability and rate capability. CV and EIS measurements were conducted using a CHI 660e electrochemical workstation.

Symmetrical cells were assembled by placing two identical electrodes on either side of a coin cell, with 30 μ L of Li₂S₆ solution added to each electrode. Cyclic voltammetry (CV) measurements were then performed using an electrochemical workstation within a voltage range of -1 to 1 V.

1.5 Li₂S₆ Adsorption Tests

Li₂S₆ solution was prepared by dissolving sulfur powder and lithium sulfide (Li₂S, 99.9 %) in a mixture of DME and DOL (volume ratio of 1:1) at a molar ratio of 5:1. The mixture was heated at 60 °C for 24 h in an argon-filled glove box. Subsequently, 15 mg

of Co_9S_8 -CoO, Co_9S_8 , and CoO materials were added to Li_2S_6 solution for 6 h. After adsorption, the supernatant was analyzed by UV-Vis spectroscopy.

1.6 Li₂S Nucleation Tests

 Li_2S_8 solution was prepared by dissolving Li_2S and S in a mixture of DOL and DME (volume ratio of 1:1) at a molar ratio of 1:7 under stirring at 60 °C for 24 h. Then, 20 μ L of Li_2S_8 solution was added to the cathode side, and 20 μ L of the lithium-sulfur electrolyte was added to the anode side. After standing for 12 h, the assembled coin cells were discharged at a constant current of 0.112 mA until a voltage of 2.06 V was reached, and then discharged at a constant voltage of 2.05 V until the current dropped below 0.01 mA.

Host Material	Rate/Number of Cycles	Discharge Capacity $(m \Delta h g^{-1})$	Capacity Retention	Sulfur Content	Sulfur Loading	Reference
		(IIIAII g)	(70)	(wt/0)	(ing cin)	
Co ₉ S ₈ -CoO	0.2 C/100	990.2	81.6	70	1.2-1.5	This work
	0.5 C/300	812.3	76.5			THIS WORK
CNT@TiON	0.2 C/100	842.2	80.6	70	1	[1]
MoS ₂ /Co ₄ S ₃	0.5 C/150	693.1	63	68	1	[2]
MoS ₂ -SnS	0.2 C/100	952.1	75	70	1	[3]
Fe ₃ C-Fe ₃ P	0.2 C/100	780.1	57	70	1	[4]
NiS ₂ /WS ₂	1 C/200	734.5	77	70	1	[5]
$V_{2}O_{3}/V_{8}C_{7}$	0.2 C/200	1028.3	96	78	1.2-1.5	[6]
ZnS-FeS/NC	0.2 C/200	822.2	67	70	1.02	[7]
Co/Mo	0.1 C/100	585.3	70	77	3.83	[8]
MoSe ₂ /MoO ₂	0.5 C/500	848.3	77	66	2.3	[9]
TiO ₂ /BaTiO ₃	0.5 C/500	541.2	60	60	1.8	[10]
Ni/Ni ₂ P@C	0.2 C/100	870.1	73	68	1.5	[11]
NiCo ₂ S ₄ @MoS ₂	0.1 C/300	865.1	77	74	1.5	[12]

 Table S1. Electrochemical performance comparison of lithium-sulfur batteries using various heterostructured catalysts

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Figure S1. XRD pattern of ZIF-67.



Figure S2. SEM image of ZIF-67.



Figure S3. Adsorption-desorption isotherms and pore size distribution of Co₉S₈-CoO.



Figure S4. SEM and TEM images of Co₉S₈-CoO@S.



Figure S5. XRD patterns of Co_9S_8 and CoO.



Figure S6. GCD curves of (a) $Co_9S_8@S$ and (b) CoO@S at different current densities.



Figure S7. Histogram of the specific capacity (Q_1 and Q_2) at 0.2 C of Co₉S₈-CoO@S,

Co₉S₈@S, and CoO@S.



Figure S8. CV curves at a scan rate of 0.1-0.4 mV s⁻¹ of (a) $Co_9S_8@S$ and (b) CoO@S.



Figure S9. Relationships between the peak currents of the (a) oxidation peak and (b, c) reduction peaks and the square root of the scanning rate for Co_9S_8 -CoO@S, $Co_9S_8@S$, and CoO@S.



Reaction coordinate

Figure S10. Relative activation energies of reduction reactions.



Figure S11. GITT voltage curves of (a) $Co_9S_8@S$ and (b) CoO@S.



Figure S12. Internal resistance of Co_9S_8 -CoO@S, $Co_9S_8@S$, and CoO@S.



Figure S13. EIS spectra of (a) $Co_9S_8@S$ and (b) CoO@S.



Figure S14. The corresponding fitting R_{ct} values of Co₉S₈-CoO@S, Co₉S₈@S, and CoO@S at different temperatures.



Figure S15. The deposition current versus time curves of Li_2S on (a) Co_9S_8 and (b) CoO.