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Supporting Information

Ultrafine cobalt nanoparticles decorated carbon submicron-cubes enhance polysulfide trapping and redox kinetics in lithium-sulfur batteries

Zheng Huang,^a Qijun Han,^a Jishu Han,^a Lei Wang,^a and Qingliang Lv^{*ab}

^a Key Laboratory of Eco-chemical Engineering, Taishan scholar advantage and characteristic discipline team of Eco chemical process and technology, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.

^b College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R China.

*Corresponding authors.

E-mail: qinglianglv@qust.edu.cn.

1. Experimental Section

Synthesis of ZIF-67 submicron-cubes (SCs). In a typical synthesis, 292 mg of $Co(NO_3)_2 \cdot 6H_2O$ is dissolved in 10 mL of deionized water (DIW) containing 4 mg of cetyltrimethylammonium bromide (CTAB). Then this solution is rapidly injected into 70 mL of an aqueous solution containing 4.54 g of 2-methyimidazole (2-MIM) and stirred at room temperature for 30 min. The product is collected by centrifugation at 2500 rpm for 3 min, washed with ethanol several times.

Synthesis of hollow tannic acid-Co network submicron-cubes (TA-Co SCs). The as-prepared ZIF-67 SCs are first dispersed into 20 mL of ethanol, then poured into 300 mL of ethanol and DIW mixture solution containing 1 mg mL-1of tannic acid (TA) and stirred at room temperature for 10 min. The product is collected by centrifugation and washed with ethanol several times, which is then dried in an oven at 70 °C.

Synthesis of ultrafine cobalt nanoparticles decorated hollow carbon submicroncubes (Co@HCSs). The as-prepared TA-Co SCs powder is first annealed at 200 °C for 30 min and then further annealed at 600 °C for 1 h with a heating rate of 1 °C min⁻¹ under N₂ flow, and cooled down to room temperature naturally.

Synthesis of hollow carbon submicron-cubes (HCSs). 10 mg of the as-prepared Co@HCSs is added to 50 mL of 4 M HCl solution. After sonication for 5 min, the mixture is strongly stirred at room temperature for 12 h, washed by ethanol three times, and dried at 70 °C in a vacuum, producing the HCSs, washing until neutral and drying at 70 °C for 12 h.

Preparation of Co@HCSs/S and HCSs/S composites. Co@HCSs/S and HCSs/S electrodes are obtained via a melt-diffusion method. Typically, a mixture of sulfur powder and Co@HCSs and HCSs with a mass ratio of 3:1 is placed in the Teflon-lined autoclave, and then heated at 155 °C for 24 h to completely disperse the sulfur into the host material.

Material characterizations. X-ray diffraction (XRD, D-MAX 2500/PC, Cu K α , λ = 1.5406 Å) patterns of the as-prepared samples are collected with a powder X-ray diffractometer. Scanning electron microscope (SEM, JEOL-JSM7500F) and

transmission electron microscope (TEM, FEI Talos F200X G2, AEMC) are performed to investigate the morphology of Co@HCSs/S and HCSs/S. Thermogravimetric analysis (TGA) is carried out on a Shimadzu DRG60 thermal analyzer under N₂ flow and air. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) is conducted to measure the chemical states. All XPS spectrums are calibrated with C 1s using a binding energy of 284.6 eV. UV-Vis spectroscopy (Shimadzu UV 2450 Spectrometer) is performed to analyze the adsorption degree of Li₂S₆ on the host materials. The specific surface area of Co@HCSs/S and HCSs/S is assessed by N₂ adsorption-desorption sorption at 77 K on a Micromeritics ASAP 2460 analyzer.

Electrochemical measurements. Li-S battery assembly and electrochemical measurements. The electrodes are prepared by mixing sulfur host materials (Co@HCSs/S and HCSs/S), Super P, poly (vinylidene fluoride) binder with the weight ratio of 8:1:1 in moderate N-methylpyrrolidone (NMP). Then, the slurry evenly coated on a carbon cloth with the areal sulfur loading of 1.0-1.2 mg cm⁻² and the electrodes are dried overnight in an oven at 80 °C. The CR2032 coin cells are assembled using asprepared electrodes as cathodes, Celgard membrane as separator and 12 mm Li metal as anode in an argon-filled glovebox. The electrolyte is composed of 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and 0.2 M of LiNO₃ in a mixed solvent of DME and DOL (1:1, v/v). Galvanostatic discharge/charge (GCD) tests are conducted on a LAND test system (LAND CT2001A). Electrochemical impedance spectroscopy (EIS) tests are performed on Solartron 1470E with a voltage amplitude of 5.0 mV in a frequency range of 0.01~10⁵ Hz. Cyclic voltammetry (CV) measurements are conducted with a scanning rate of 0.1 mV s-1 in the voltage range of 1.6 to 2.8 V on a CHI760E electrochemical workstation. All the electrochemical measurements are implemented at 25 °C.

Symmetrical batteries test. The cathode and anode of the symmetrical battery are both as-prepared electrodes, the anode electrolyte is the conventional Li-S battery electrolyte, and the cathode electrolyte is 2 M Li_2S_6 . The CV measurements for symmetrical cells are performed at a sweep rate of 10 mV s⁻¹ in a voltage window of - 1.0-1.0 V.

Adsorption measurements of Li_2S_6 . To obtain the 2 mM Li_2S_6 solution, S and Li_2S with the molar ratio of 5:1 are dissolved in tetrahydrofuran solution, and stirred at 60 °C for 24 h. The same mass of Co@HCSs and HCSs are added into 2 mM of Li_2S_6 solution. The precipitate and supernatant of the mixture are further analyzed by XPS analysis and UV-Vis spectroscopy, respectively.

Li₂S nucleation and dissolution. The Co@HCSs or HCSs and polyvinylidene difluoride (PVDF) are fully ground in NMP solution at a ratio of 9:1, and then coated on the surface of carbon paper. Li₂S nucleation and dissolution experiments are used conventional 1 M LiTFSI electrolyte as anolyte and 0.2 M Li₂S₈ electrolyte as catholyte. For the Li₂S nucleation experiments, the batteries are first discharged galvanostatically to 2.06 V at 0.112 mA, and then remained discharged potentiostatically to 10⁻⁵ A at 2.05 V. For the Li₂S dissolution experiments, the batteries are first discharged galvanostatically to 1.7 V at 0.112 mA, and then charged at a voltage of 2.4 V until the current was less than 10⁻⁵ A.

2. Supplementary Figures



Fig. S1. SEM images of ZIF-67 SCs.



Fig. S2 XRD pattern of ZIF-67 SCs.



Fig. S3 TEM images of TA-Co SCs.



Fig. S4 XPS survey spectra of Co@HCSs and HCSs.



Fig. S5 TGA curves of Co@HCSs in air condition.



Fig. S6 TGA curves of Co@HCSs/S and HCSs/S.



Fig. S7 The S 2p XPS spectra of Co@HCSs-Li₂S₆.



Fig. S8 CV curves of symmetric cells.



Fig. S9 CV curves of Co@HCSs/S and HCSs/S electrodes at 0.1 mV s⁻¹.



Fig. S10 (a-c) Tafel curves of sulfur reduction and Li₂S oxidation process.



Fig. S11 (a-c) Peak current versus the square root of the scan rate (υ) for the cathodic reduction processes (Peak A, Peak B and Peak C).



Fig. S12 Li^+ diffusion coefficient of Co@HCSs/S and HCSs/S electrodes.



Fig. S13 The ΔE and Q_2/Q_1 values obtained from charge and discharge curves.



Fig. S14 The long-cycle performance of Co@HCSs electrodes at 0.5 C.



Fig. S15 The long-cycle performance of Co@HCSs/S electrodes.

3. Supplementary Table

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Cathada	Capacity	Cycle	Capacity	Reference	
Cathode	$(mAh g^{-1})$	time	decay rate		
S-YS-C/S	709	200	0.48%	Chem. Eng. J.,2019, 373: 382-392	
HPBC/Ni/S	907.3	200	0.16%	J. Alloys Compd., 2020, 832, 153692	
MnO2-HC-S	700	1000	0.039%	Appl. Surf. Sci., 2022, 585, 152498	
S-G/C/SiO ₂ -2	786.7	400	0.062%	Electrochimica Acta 2017, 255, 179-	
				186	
SACo/NC@S	777.9	300	0.09%	ACS Appl. Mater. Interfaces, 2022,	
				14 , 25337-25347	
C-NiCo ₂ O ₄ /PC	782.2	500	0.053%	Chem. Eng. J., 2023, 466 , 143187	
HPBC/Ni	907.3	200	0.16%	J. Alloys Compd., 2020, 832 , 153692	
Se@NC-TiO ₂	502	500	0.037%	Adv. Energy Mater., 2405532	
hPCN/S	879	200	0.1%	Chem. Eng. J., 2023, 465, 143035	
S@rGO-rGO	797.7	400	0.058%	Carbon, 2024, 222, 118966	
Co@HCSs	908.9	1000	0.049%	This work	

Table S1. Comparison of electrochemical performance of Co@HCSs with recently

reported advanced electrocatalysts at 0.5 C.

Table. S2 Fitted impendence parameters of Co@HCSs and HCSs.

	R _s	R _{ct}	Z _w
Co@HCSs	1.92	116.4	99.92
HCSs	2.205	177.6	165.8