Conductive V$_2$O$_3$ electrocatalyst on carbon hollow sphere to accelerate polysulfides conversion for long-cycle and high-rate lithium sulfur batteries

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1. Experimental section

1.1 Synthesis of C-HS

Nano SiO_2 microspheres were prepared using the Stober method [1]. Under stirring, 20 mL of anhydrous ethanol and 2 mL of NH_4OH (28 wt%) solution were mixed for 30 minutes. Then, 3 mL of tetraethyl orthosilicate (TEOS) was added, followed by continuous stirring at room temperature for 12 hours. The products were washed several times with anhydrous ethanol and deionized water through centrifugation and then vacuum dried at 80 °C for 12 hours to obtain SiO_2 nanoparticles.

0.3 g of SiO_2 nanoparticles were dispersed in 30 mL of deionized water and 60 mL of anhydrous ethanol by ultrasonic treatment for 30 minutes. Then, 0.3 g of cetyltrimethylammonium bromide (CTAB) and 2 mL of NH_4OH (28 wt%) were added to the solution, followed by stirring at room temperature for 30 minutes. Next, 0.4 g of resorcinol (R) was added and stirred for 10 minutes. After that, 0.6 mL of formaldehyde (F) solution was added and stirred for 12 hours. The resulting mixture was centrifuged, and the products were washed several times with anhydrous ethanol and deionized water through centrifugation, followed by vacuum drying at 80 °C for 12 hours to obtain SiO_2 particles coated with RF resin.

The black powder obtained was calcined at 850 °C for 4 hours in a tube furnace under an argon gas (Ar) atmosphere to obtain C-HS. The black powder was etched in a 10% hydrofluoric acid (HF) solution for 12 hours. Then, the products were washed several times with anhydrous ethanol and deionized water through centrifugation and vacuum dried at 80 °C for 12 hours.

1.2 Synthesis of V$_2$O$_3$/C-HS composite

Weighed 0.06 g of C-HS, 0.025 g of ammonium metavanadate (NH$_4$VO$_3$), 0.015 g of sodium dodecyl sulfate (SDS), and 0.024 g of tartaric acid (T) were added to 15 mL deionized water and stirred for 24 hours. The mixture was dried at 120 °C under atmospheric pressure for 10 hours to obtain a black powder. The obtained powder was further calcined at 800 °C for 2 hours in a tube furnace under an argon gas (Ar) atmosphere to get V$_2$O$_3$/C-HS material.

1.3 Synthesis of C-HS@S and V$_2$O$_3$/C-HS@S

Sulfur was loaded into C-HS and V$_2$O$_3$/C-HS materials by a fusion method. The prepared C-HS and V$_2$O$_3$/C-HS composite materials were manually ground for 30 minutes with sublimed sulfur in a mass ratio of 1:3 and thoroughly mixed, obtaining a black mixture. The mixture was then loaded into a reaction vessel and filled with argon gas. It was heated at 155 °C for 12 hours. Finally, under an argon atmosphere, further heating at 250 °C for 30 minutes was conducted to evaporate the excess sulfur on the surface, obtaining the positive electrode material.

2. Battery performance test

Weigh 70% electrode active material, 20% acetylene black, and 10% polyvinylidene fluoride (PVDF) binder in mass ratio, put them into a grinding bowl, and grind and stir evenly. Add a suitable amount of N-methyl-2-pyrrolidone (NMP) and continue grinding for 30 minutes to obtain a uniformly mixed electrode slurry. Apply the slurry evenly onto aluminum foil, dry in a vacuum oven at 80 °C for 12 hours, then cut the dried electrode pieces to prepare a 12 mm diameter disc. CR2032

button cells were used for electrochemical performance testing on the composite electrode material. Celgard2400 was used as the separator. The electrolyte used was a 1.0 M LiTFSI solution (solvent: DME: DOL=1:1, with 2.0% LiNO$_3$ added).

The assembled battery was subjected to charge and discharge performance testing using the LAND CT2001A battery testing system. The testing was conducted as constant current charge/discharge, and the voltage windows range was set at 1.7-2.8 V. The ambient temperature for battery charge and discharge was room temperature. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed using the Shanghai CHI660E electrochemical workstation. The scan potential range was set at 1.7-2.8 V, with a scan rate of 0.1-0.5 mV s^{-1}. The frequency range for EIS testing was 0.01~100 kHz, with an alternating current voltage amplitude of 0.005 V. The electrochemical performance testing was performed at room temperature.

3. Assembly and test of symmetrical batteries

Weigh 70% of V$_2$O$_3$/C-HS and C-HS materials, 20% of acetylene black, and 10% of polyvinylidene fluoride (PVDF) binder in mass ratio, put them into a grinding bowl, and grind and stir evenly. Add a suitable amount of N-methyl-2-pyrrolidone (NMP) and continue grinding for 30 minutes to obtain a uniformly mixed electrode slurry. Apply the slurry evenly onto aluminum foil, dry in a vacuum oven at 80 °C for 12 hours, then press and cut the dried electrode sheet to prepare a 12 mm diameter disc. Two identical electrode pieces were used as the positive and negative electrodes of the button battery. The electrolyte used was a 0.2 M Li$_2$S$_6$ solution (solvent: DME:

DOL=1:1). The scan potential range for the symmetrical battery was -1.5-1.5 V, with a scan rate of 0.1 mV s^{-1}.

4. Lithium sulfide adsorption experiment

Prepare a 0.5 mM Li$_2$S$_6$ solution (solvent: DME: DOL=1:1) and add 3 mL of the lithium sulfide solution to a flask with 15 mg of the sample. Let it stand for 30 minutes, 6 hours, and 24 hours, and take photographs to record the color of the solution. Take the upper clear liquid and measure the absorbance of the solution using the TU-1901 Dual-Beam UV-Visible Spectrophotometer, measurement range: 200 nm-600 nm.

Li$_2$S deposition experiment: Coat the V$_2$O$_3$/C-HS and C-HS materials on aluminum foil. Use lithium foil as the counter electrode and the Celgard2400 membrane as the separator. Drop 25 μL of 0.2 M Li$_2$S$_6$ solution (solvent: DME: DOL=1:1) on the positive electrode side, and drop 25 μL of DME: DOL=1:1 solution on the negative electrode side. The battery is discharged at 0.112 mA until 2.07 V and then maintained at 2.05 V for discharge.

5. DFT calculation

In this study, the electronic exchange-correlation function is described using the GGA-PBE approximation. The plane wave pseudopotential method is used with ultrasoft pseudopotentials. The plane wave cutoff energy is set to 381 eV. The (110) surface of V$_2$O$_3$ is chosen as the adsorption substrate. To accurately describe the interaction between lithium sulfide and V$_2$O$_3$, the TS DFT-D correction method is employed to consider van der Waals interactions. The convergence criterion for forces

is set to 0.03 eV Å^{-1}, and the energy convergence criterion is set to 1.0e^{-5} eV atom^{-1}. The corresponding K-point is set to the Gamma point.

6. Sample Characterization

The XRD detection was carried out using a Bruker D8 Advance X-ray diffractometer, with a copper target as the target material（λ= 0.15418 nm), voltage 40 kV, current 30 mA, testing range 10°~80°, scanning speed 20°·min-1, testing temperature 25 ℃. SEM detection was performed using JSM-6701F scanning electron microscope with an accelerated voltage of 10 kV. TEM detection was performed using JEM-2010F transmission electron microscopy. XPS detection uses the Thermo Scientific K-Alpha XPS system. The test condition is vacuum test. Data correction was performed with C1s=284.80 eV to detect the composition of the prepared sample and the bonding methods of different elements. The specific surface area test uses a fully automatic specific surface area and pore size analyzer produced by the American Mike Company. Its model is ASAP2460. Before the test, the sample will be pretreated at 150 ℃ to avoid interference from impurities. The Raman detection uses the Raman spectrometer produced by HoribaJobinYvon in France, whose model is LabRAMHR800, and the excitation wavelength is 532 nm. The sulfur load of the positive electrode material was analyzed using a DSC-TGA Q500 synchronous thermal analyzer, with a protective atmosphere of argon and a heating rate of 10 ℃·min-1. The testing range was from room temperature to 600 ℃.
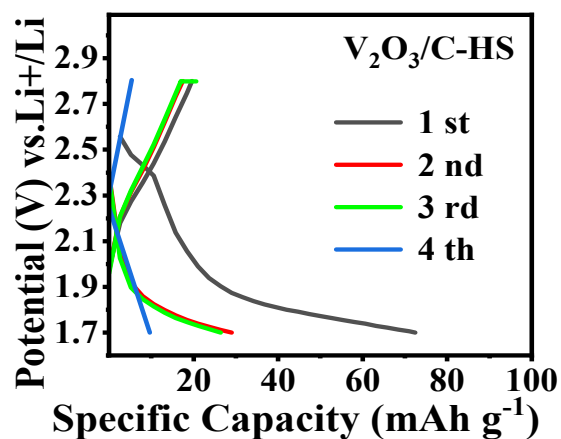
Fig. S1 The galvanostatic charge and discharge curves of V_2O_3/C-HS electrode with same electrolyte (at current density of 0.06 mA g^{-1}).
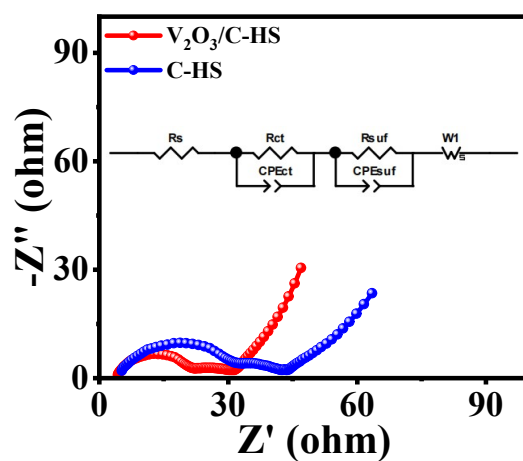
Fig. S2 EIS curves of C-HS and V_2O_3/C-HS after cycling test, and the illustration is the analog circuit diagram of battery impedance.
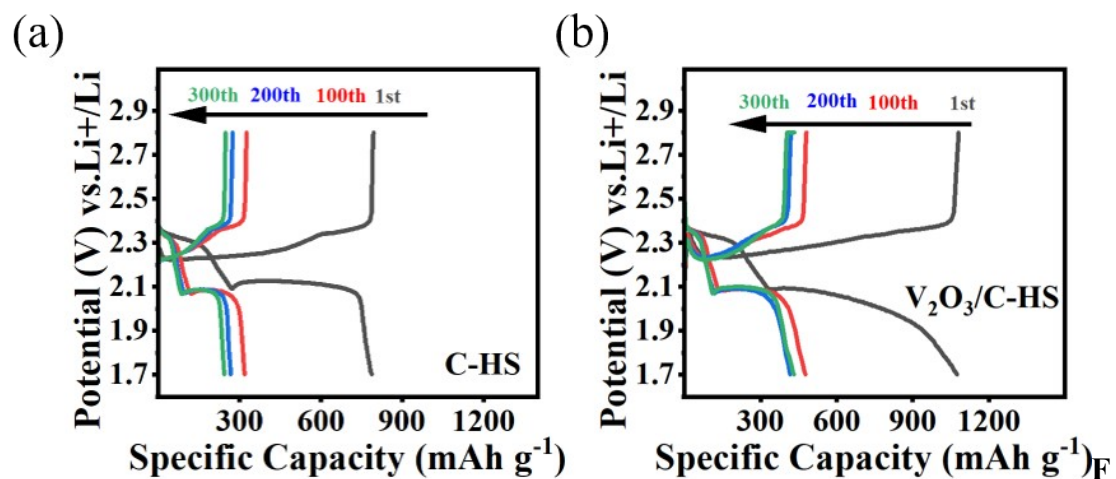
Fig. S3 Charge and discharge voltage profiles of C-HS and V_2O_3/C-HS at 0.2 C of different cycles.
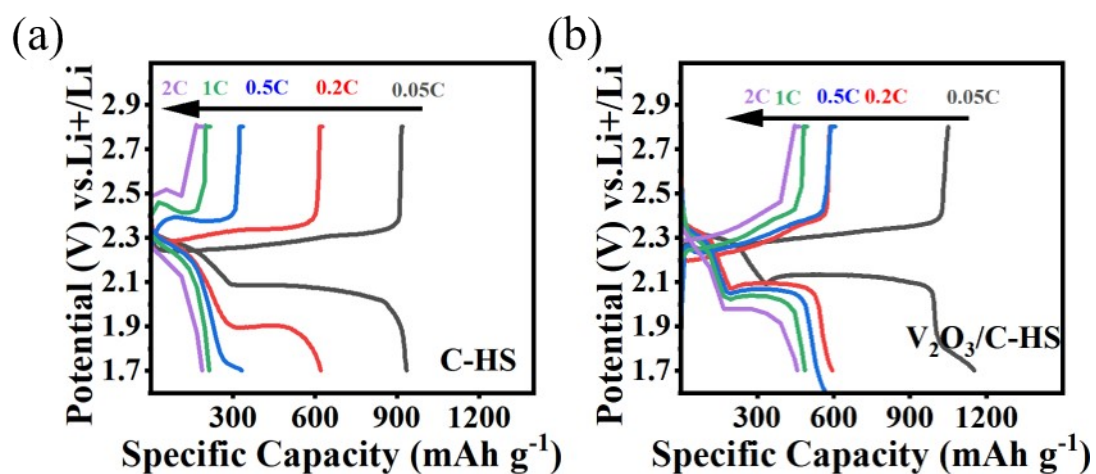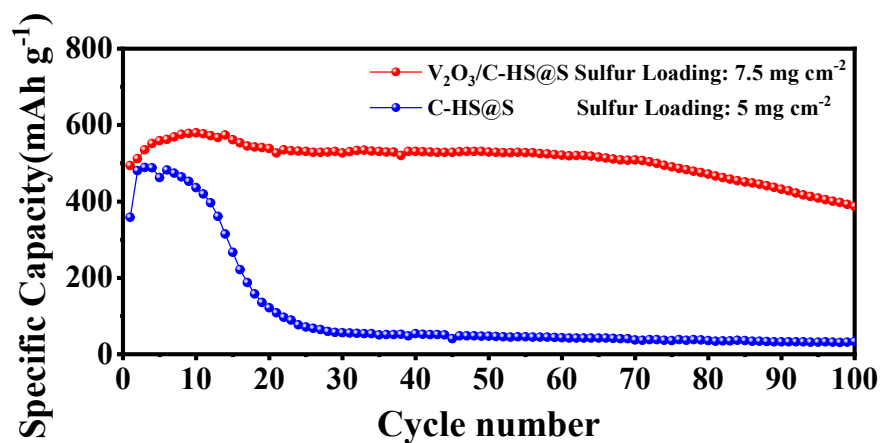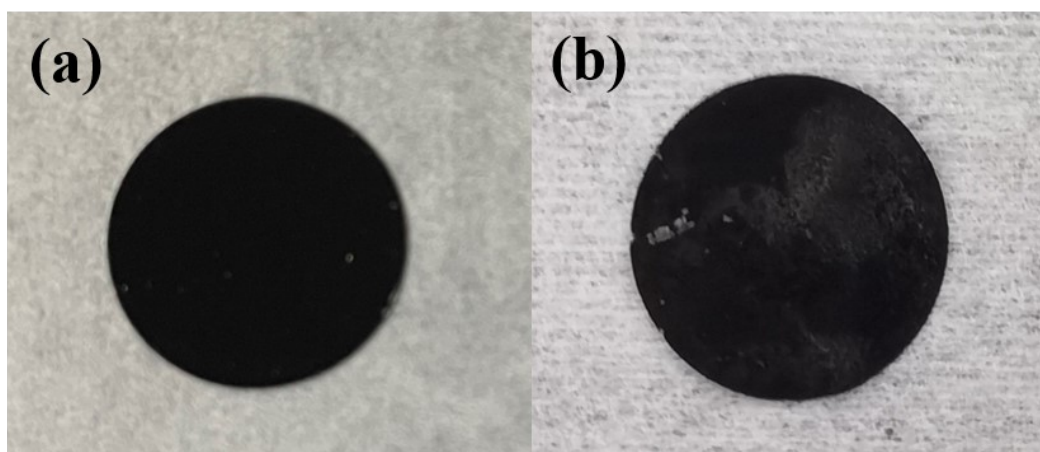

Fig. S4 Charge and discharge voltage profiles of C-HS and V_2O_3/C-HS at different current density.
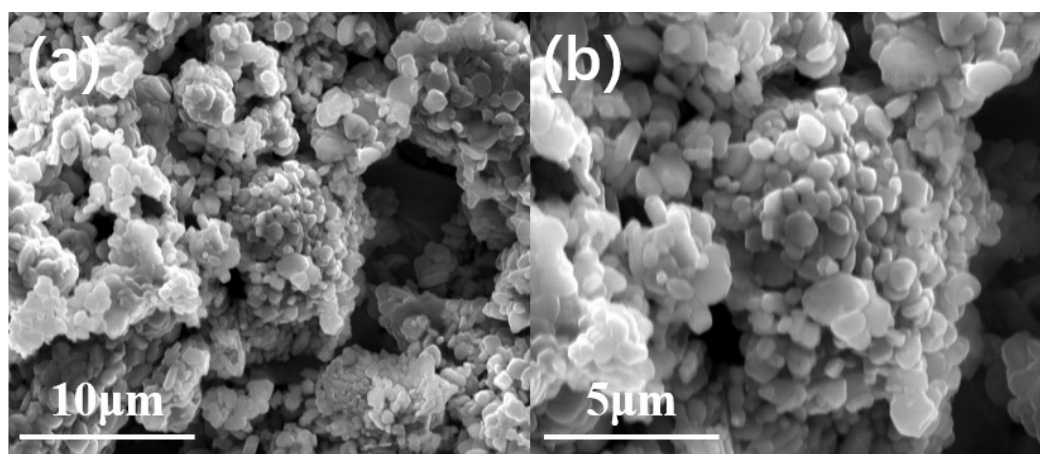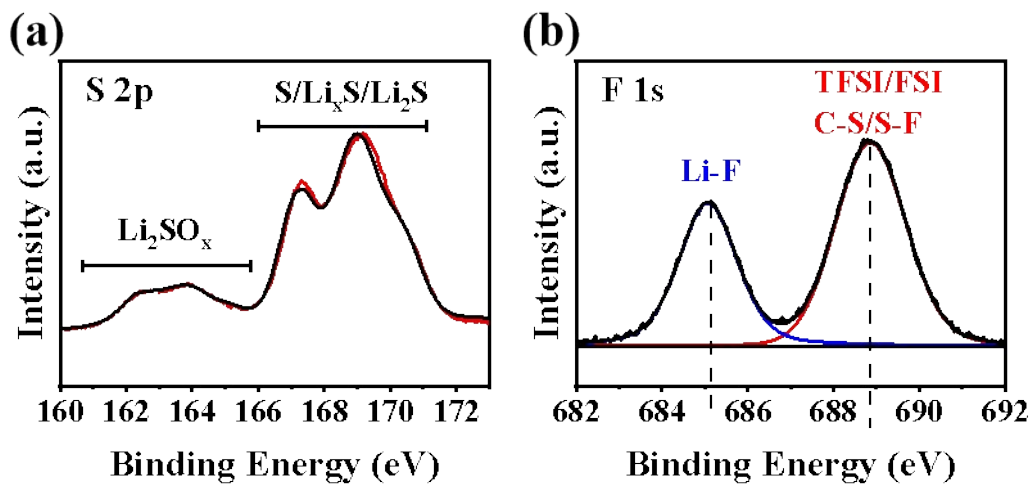
Fig. S5 Cycling performance of V_2O_3/C-HS@S and C-HS@S in high sulfur loading at current density of 0.2 C.
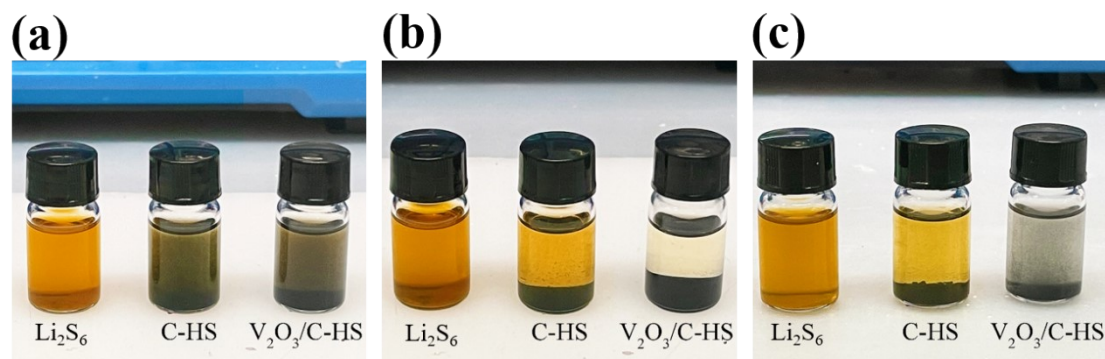

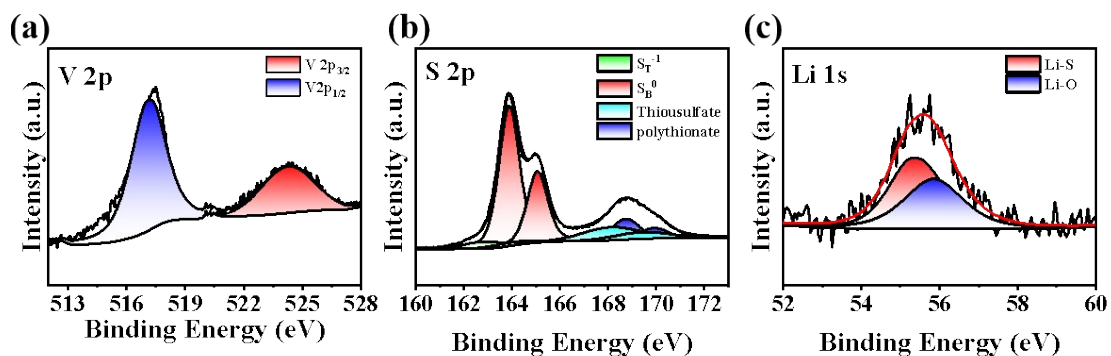**Fig. S6** V_2O_3/C-HS@S cathode disc before cycling test (a); after 500 cycles.

Fig. S7 SEM images of V_2O_3/C-HS@S cathode disc after 500 cycles.
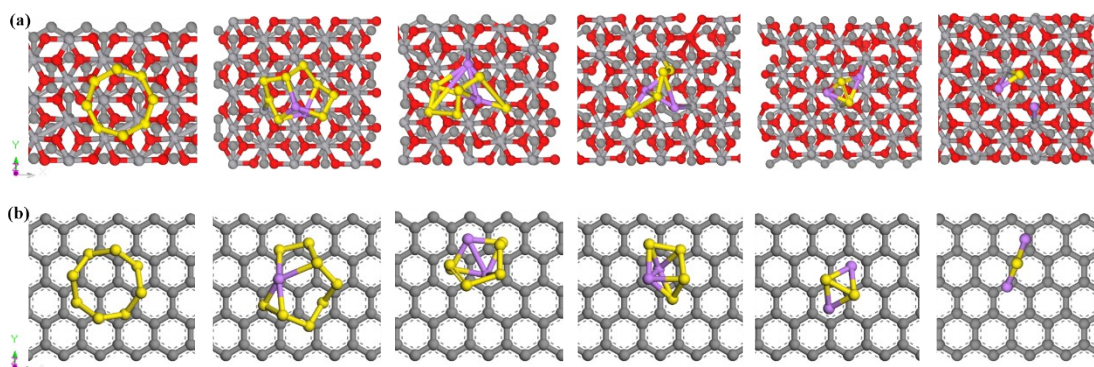
Fig. S8 High resolution XPS spectra of S 2p (a), and F 1s (b) of V_2O_3/C-HS@S electrode after cycle.

Fig. S9 LiPSs adsorption test after 0.5 h (a), 12 h (b), and 24 h (c). Form left to right are isolated, C-HS and V_2O_3/C-HS.

Fig. S10 High resolution XPS spectra of V 2p (a), S 2p (b) and Li 1s (c) of V_2O_3/C-HS after adsorbed Li_2S_6.

Fig. S11 Stable adsorption models for lithium polysulfides on the surface of V_2O_3/C-HS and C-HS.
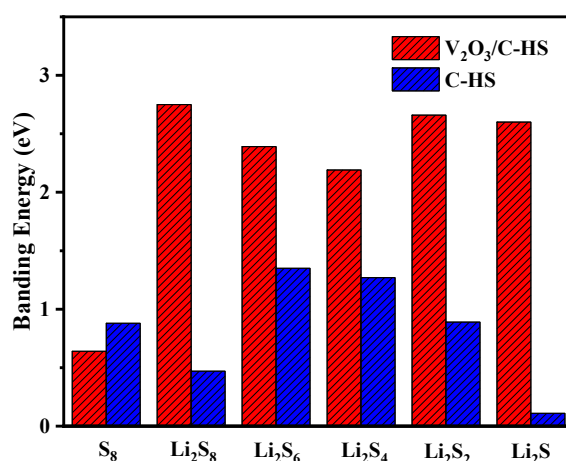
Fig. S12 Adsorption energy to LiPSs of V_2O_3/C-HS and C-HS.

Table S1 Parameters identification by modeling the impedance spectra in Figure 4e.

Cathode materials	Rs (ohm)	Rct (ohm)	D_{Li+} (cm^2 s^{-1})
C-HS	3.19	73.43	4.37×10^{-14}
V_2O_3/C-HS	1.83	49.87	5.00×10^{-14}

Table S2 Parameters identification by modeling the impedance spectra

Cathode materials	Rs (ohm)	Rct (ohm)	Rsuf (ohm)
C-HS	3.96	30.11	31.96
V_2O_3/C-HS	3.93	18.73	23.18

Table S3 presents performance comparison of different composite as sulfur host materials in lithium-sulfur batteries.

Cathode materials	Sulfur content in the cathode (wt%)	Maximum discharge capacity (mAh g^{-1})	Final capacity (mAh g^{-1})	Capacity-keeping rate (%)	Reference
V_2O_3/C-HS@S	75	1153 (0.05 C)	433 (300 cycles, 0.2 C)	99.67	This work
V_2O_3/C-HS@S	75	665 (2 C)	298 (300 cycles, 2 C)	99.73	This work
V_2O_5/C	66	1350 (0.1 C)	900 (50 cycles, 0.5 C)	99.19	[2]
S-C-V_2O_5	30	1300 (0.1 C)	750 (10 cycles, 0.1 C)	94.41	[3]
S/C/PN-V_2O_5	60	1095 (0.1 C)	666 (50 cycles, 0.1 C)	98.95	[4]
CNTs/V_2O_5/S	68.5	710 (0.1 C)	515 (100 cycles, 0.1 C)	99.63	[5]
Mg@V_2O_3	66.6	1325.8 (0.1 C)	600 (130 cycles,1 C)	99.39	[6]
V_2O_5-MWCNT/S	68.3	1200 (0.2 C)	700 (200 cycles, 0.2 C)	99.73	[7]

Reference

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