Electronic Supplementary Material (ESI) for Nanoscale
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Supplementary Information

MIL-47(V) derived hierarchical lasagna-structured V_2O_3@C hollow microcuboid as an efficient sulfur host for high-performance lithium-sulfur batteries

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ESI includes experimental section, 17 figures, 3 tables and 10 references.

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Experimental section

Visualized adsorption tests

Li_2S_6 solution (5 mmol L^{-1}) was prepared by mixing lithium sulfide and sulfur with mole ratio 1:5 and then dissolved in 1,2-dimethoxyethane (DME). 10 mg of V_2O_3@C, commercial V_2O_3 and amorphous carbon framework were dispersed in 3 mL Li_2S_6 solution, respectively. The whole experiment was conducted in an argon-filled glove box.

Fabrication of symmetric cell and cyclic voltammetry test

Symmetric cell was assembled with V_2O_3@C (or amorphous carbon framework for comparison) electrode as both working and counter electrode and 20 μL electrolyte (using DOL/DME (1:1, vol.%) as the solvent with 0.5 mmol L^{-1} Li_2S_6 and 1 mmol L^{-1} LiTFSI). Cyclic voltammetry (CV) test of the symmetric cell was conducted with voltage range of -1.0 V to 1.0 V.

Li_2S nucleation measurement

The cell of nucleation measurement was assembled with cathode material load on carbon-fiber-paper (CP) without sulfur, Celgard 2400 membrane as the separator, lithium tablets as the anode, Li_2S_8 (0.2 mol L^{-1}, 20 μL) as catholyte and LiTFSI (1 mol L^{-1}, 25 μL) as anolyte. Li_2S_8 with a concentration of 0.2 mol L^{-1} was prepared by dissolving sulfur and lithium sulfide (molar ratio 7:1) in tetraglyme, followed by vigorous stirring for 24 hours. CP was punched into circle disk with a diameter of 14 mm and coated with V_2O_3@C or commercial V_2O_3 with the areal density of 1.5 mg cm^{-2}. The batteries were galvanostatically discharged to 2.06 V at 0.112 mA and then maintained potentiostatically at 2.05 V until the current was below 10^{-5} A. Use the Faraday's law to evaluate the nucleation/growth rule of Li_2S.

Theoretical calculation

The theoretical calculations were performed with periodic boundary conditions used Materials Studio 2017 (from Accelrys Inc.). For V_2O_3, the (104) surface were used as the contact facet with sulfur species, according to the HRTEM characterization results. The spin-polarized first-principles calculations were performed based on density functional theory (DFT) as implemented in the DMol^3 module with the Perdew-Burke-Ernzerhof (PBE) functional method. The cut-off

energy for the basis function was 300 eV. Structural relaxations were performed until all the residual forces on atoms were less than 0.02 $eV \cdot Å^{-1}$. The convergence criteria for the energy calculation and geometric optimization were set as below: a maximum force tolerance of 10^{-6} eV and an energy tolerance of 10^{-5} eV.

Figures

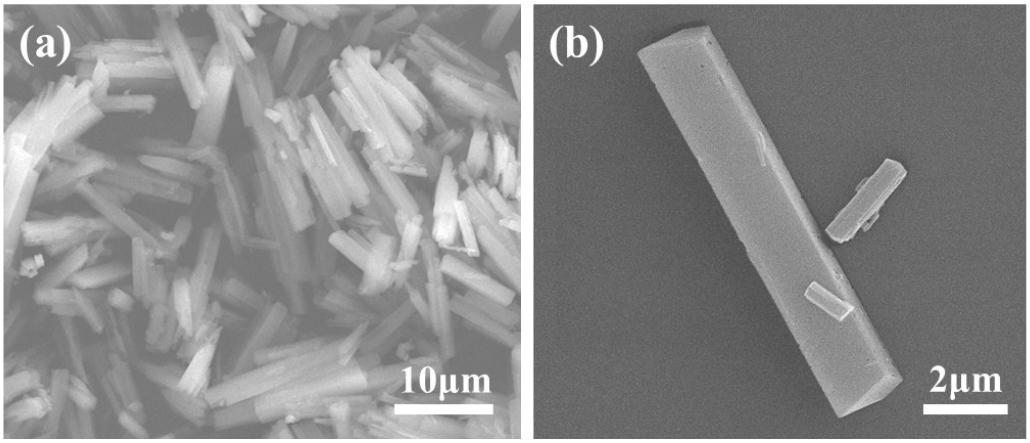

Fig. S1† SEM image of MIL-47.

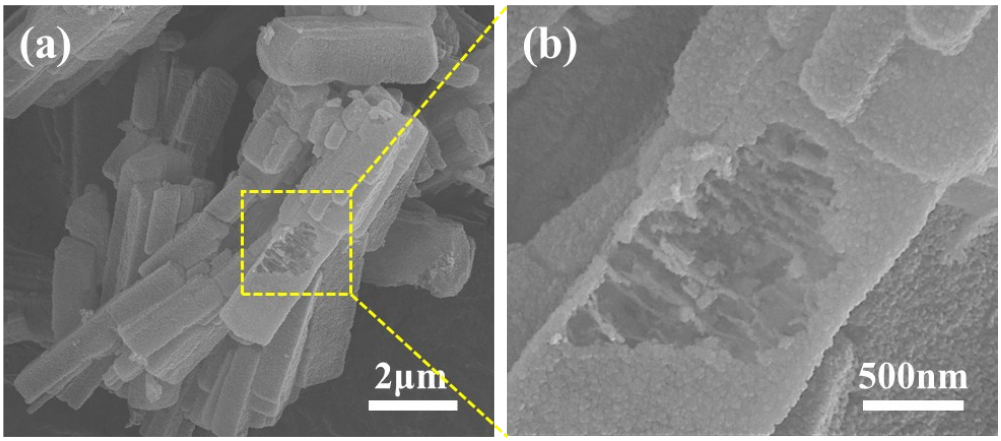

Fig. S2† (a) SEM image of V_2O_3@C host. (b) The larger version of the marked area in (a).

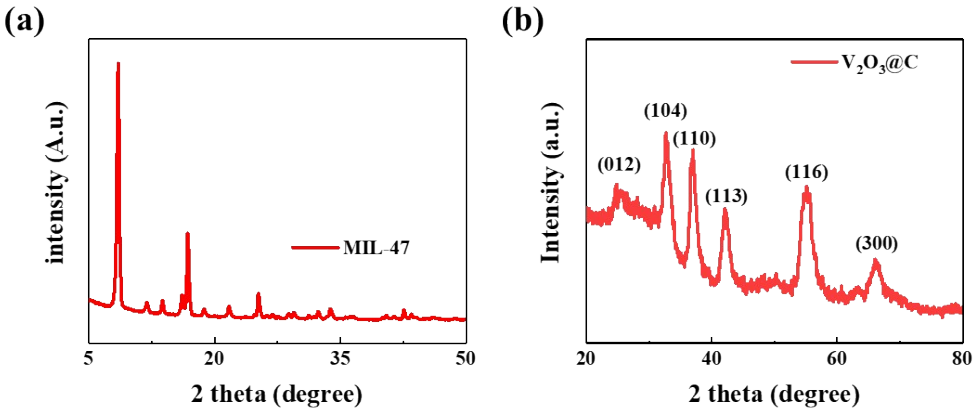

Fig. S3† XRD pattern of (a) MIL-47 and (b) V_2O_3@C with the corresponding crystal plane.

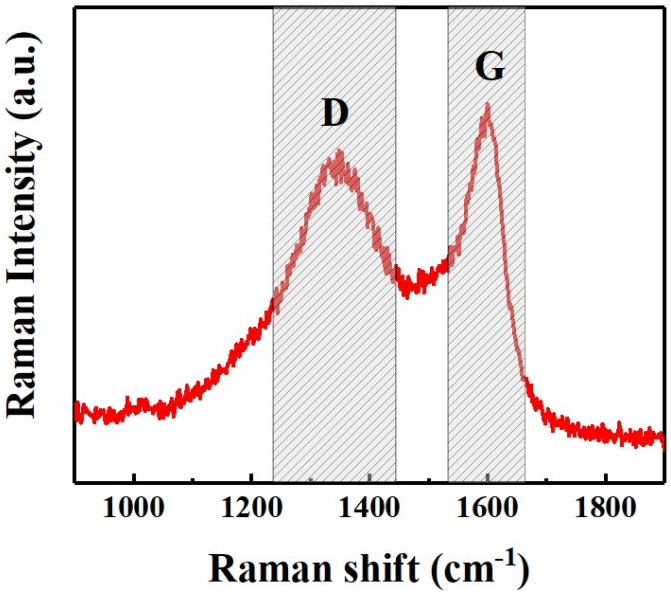

Fig. S4† Raman spectrum of V_2O_3@C.

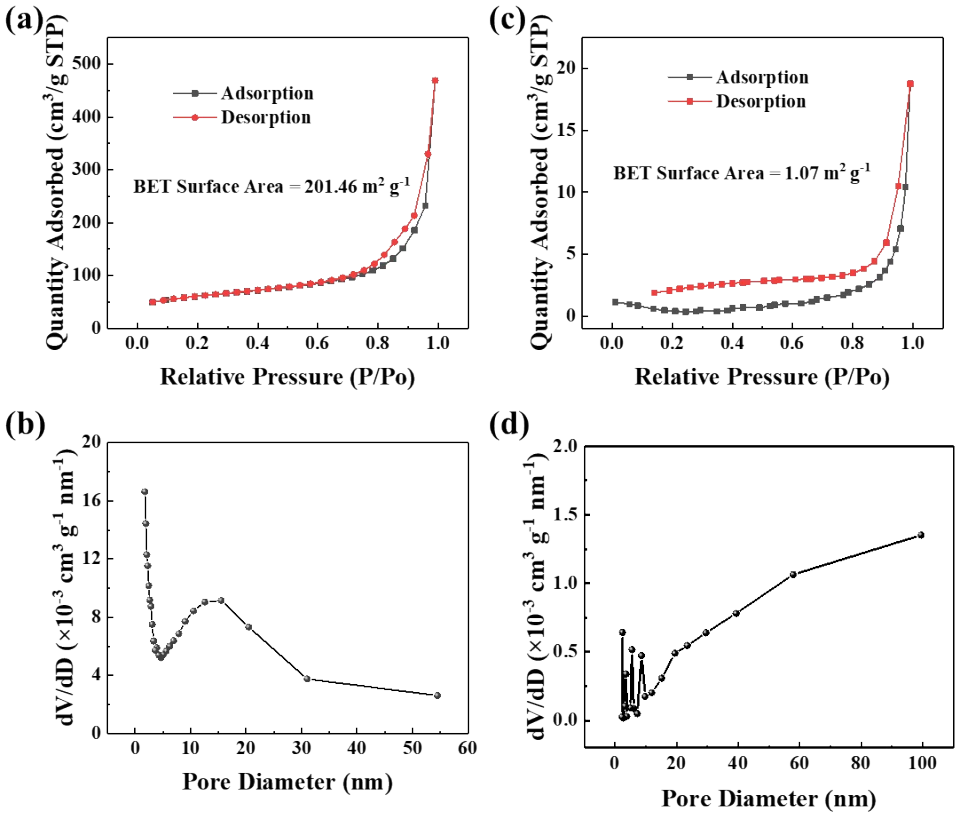

Fig. S5† Nitrogen adsorption/desorption isotherms combined with the distribution curves of pore size of (a, b) V_2O_3@C and (c, d) commercial V_2O_3.

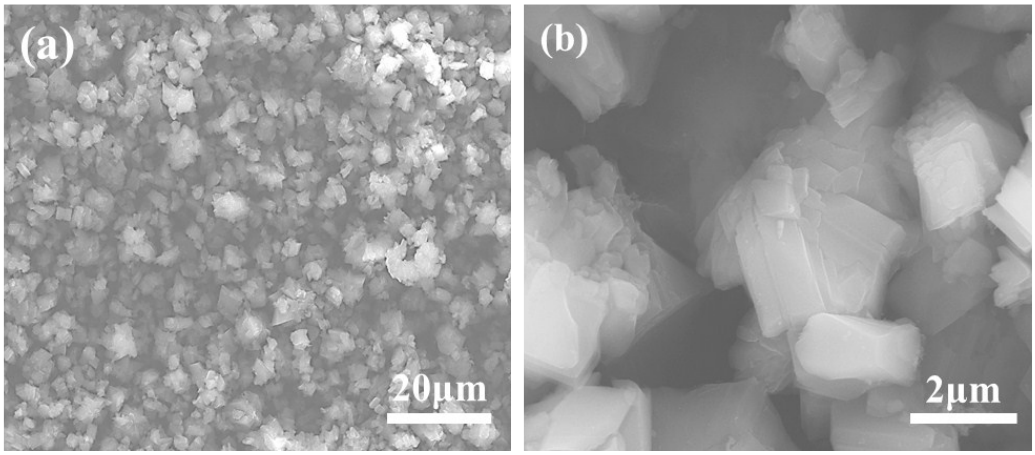

Fig. S6† SEM image of commercial V_2O_3.

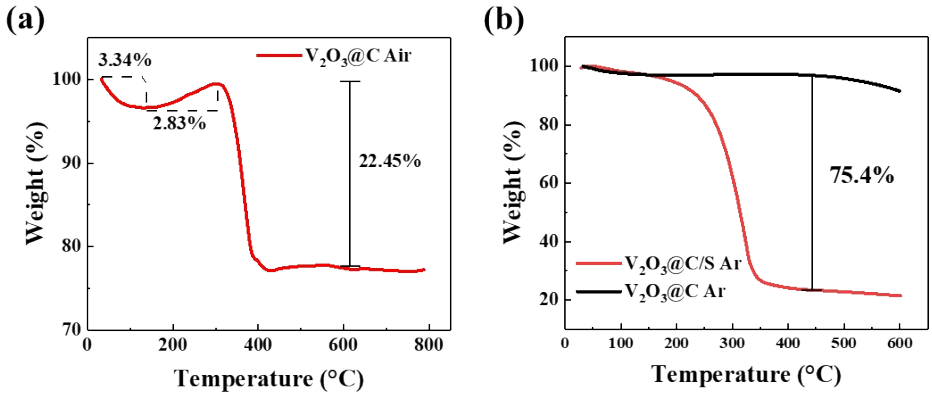

Fig. S7† TGA curves of (a) V_2O_3@C in air and (b) V_2O_3@C/S and V_2O_3@C in argon.

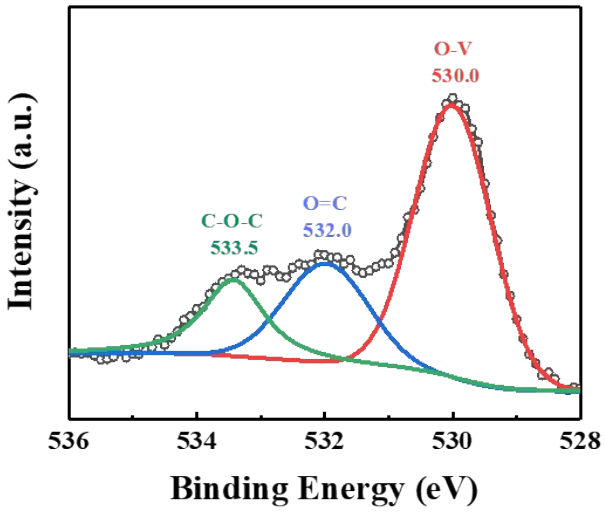

Fig. S8† XPS spectra of O 1s for V_2O_3@C.

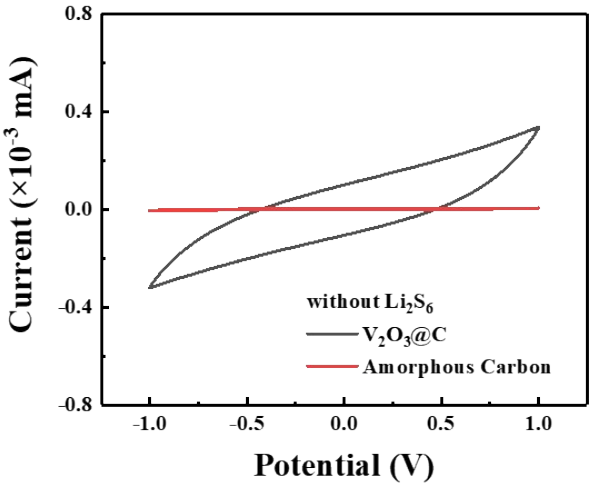

Fig. S9† CV curves of symmetric cells using the electrolyte without Li_2S_6 additives within -1.0~1.0 V at a scan rate of 50 mV s^{-1}.

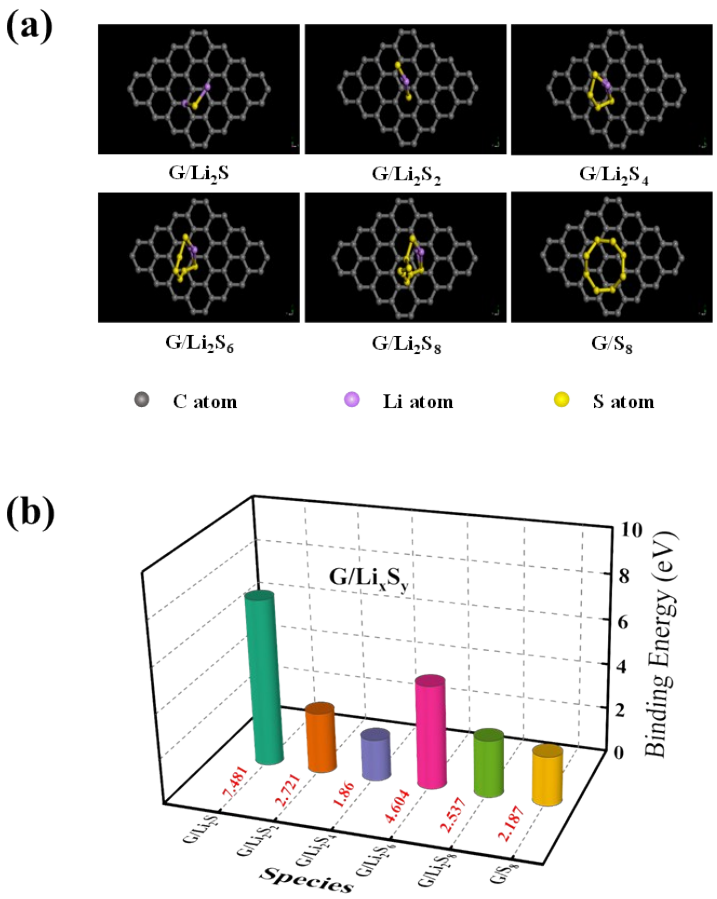

Fig. S10† (a) Top views of the optimal configurations of sulfur species adsorbed on graphene. (b) Binding energies of Li_xS_y molecules with graphene surface.

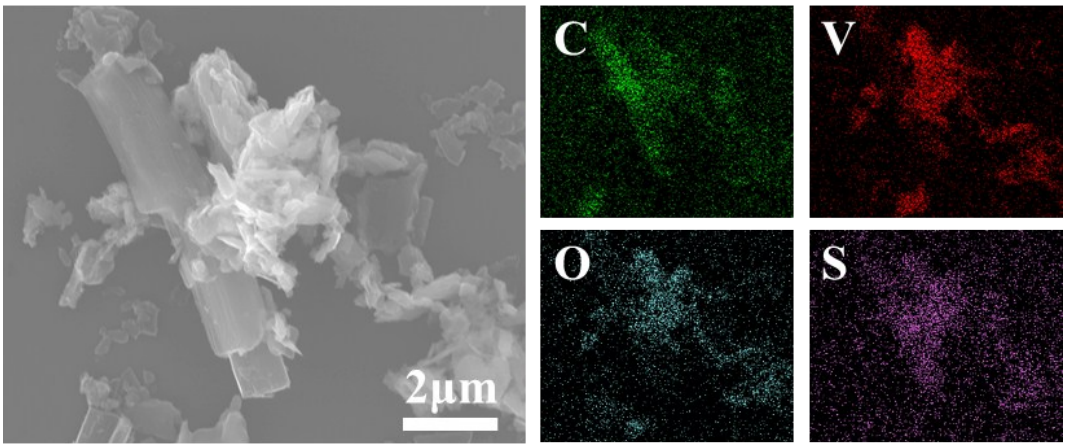

Fig. S11† SEM image and element mapping of V_2O_3/C/S.

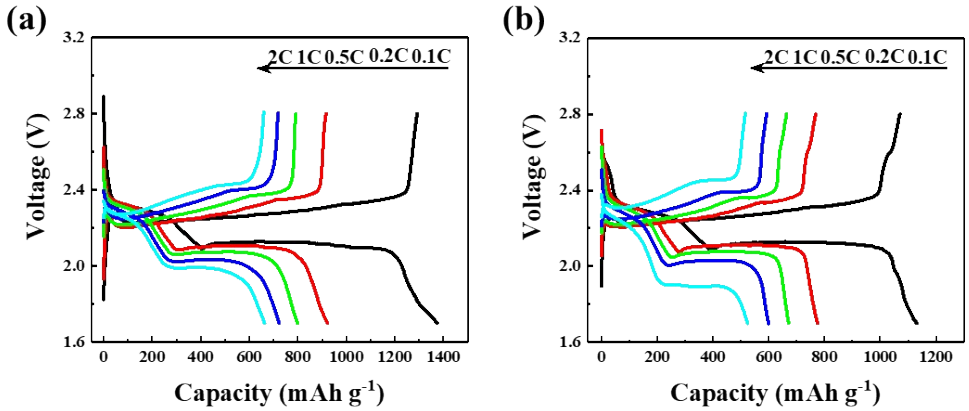

Fig. S12† Galvanostatic charge/discharge profiles at current rates ranging from 0.1 C to 2 C of (a) V_2O_3@C/S and(b) V_2O_3/C/S.

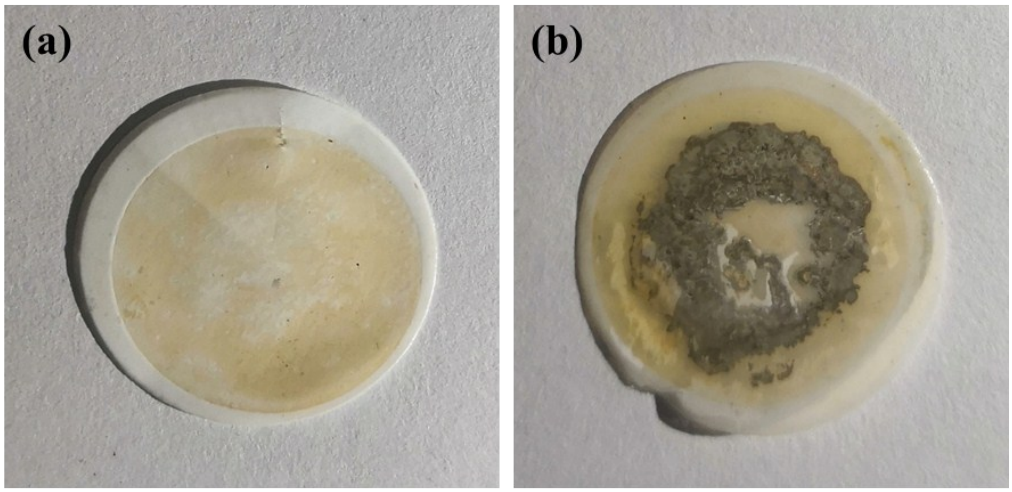

Fig. S13† Examination of the separators from disassembled (a) V_2O_3@C/S and(b) V_2O_3/C/S batteries after 200 cycles at 0.2 C.

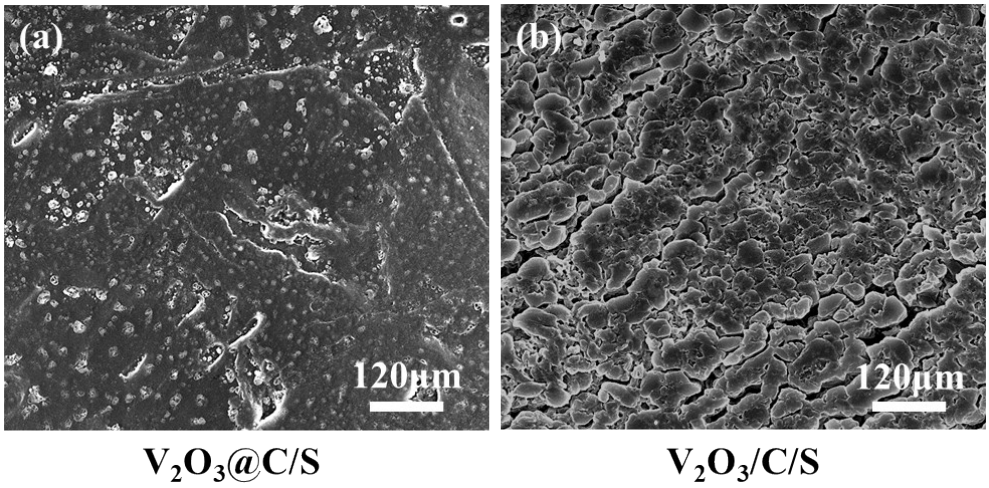

Fig. S14† Examination of the lithium electrodes from disassembled (a) V_2O_3@C/S and(b) V_2O_3/C/S batteries after 200 cycles at 0.2 C.

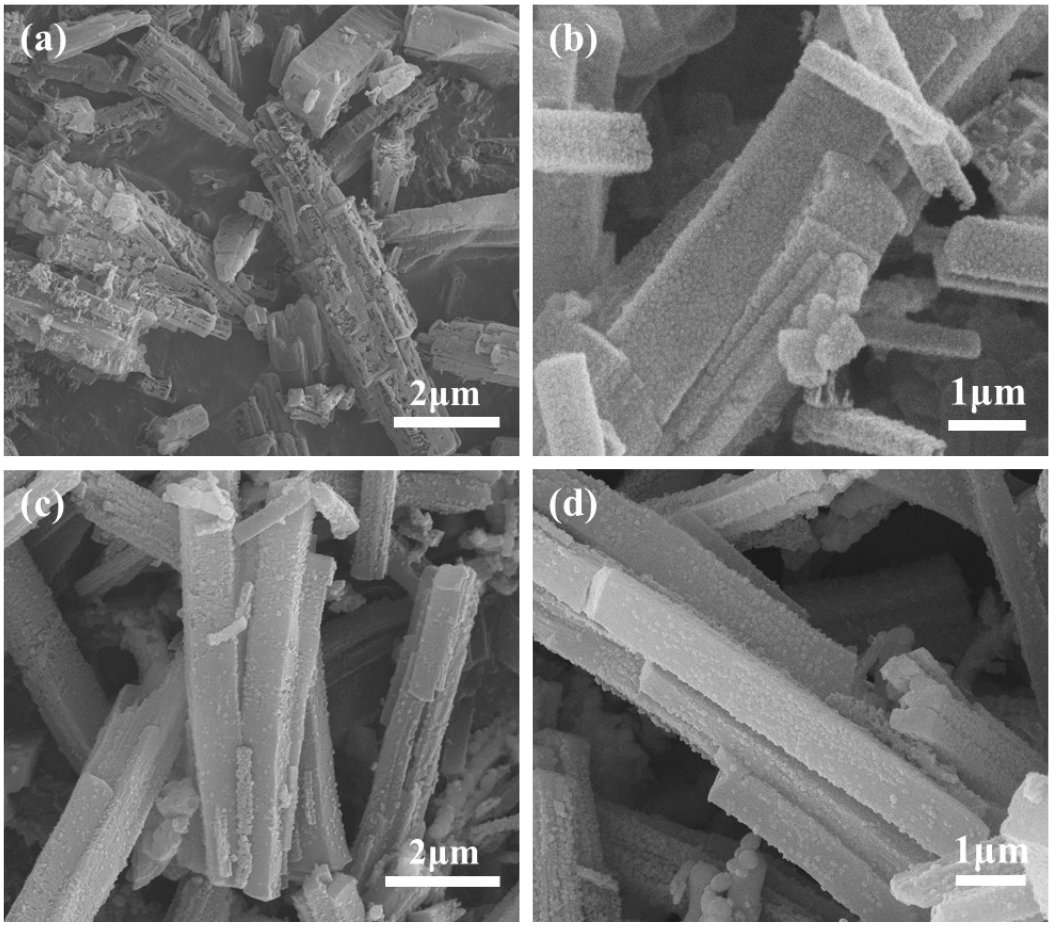

Fig. S15† SEM images of V-MOFs with VCl_3 and H_2BDC in different proportions, (a) 1: 0.25, (b) 1: 0.5, (c) 1: 0.75, (d) 1: 1.

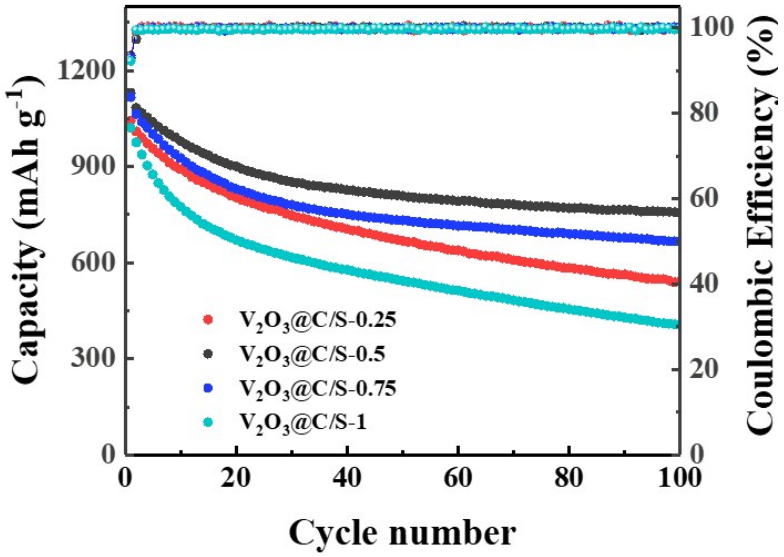

Fig. S16† The electrochemical performances of the V_2O_3 NP@C/S cathodes with VCl_3 and H_2BDC in different proportions at 0.2 C.

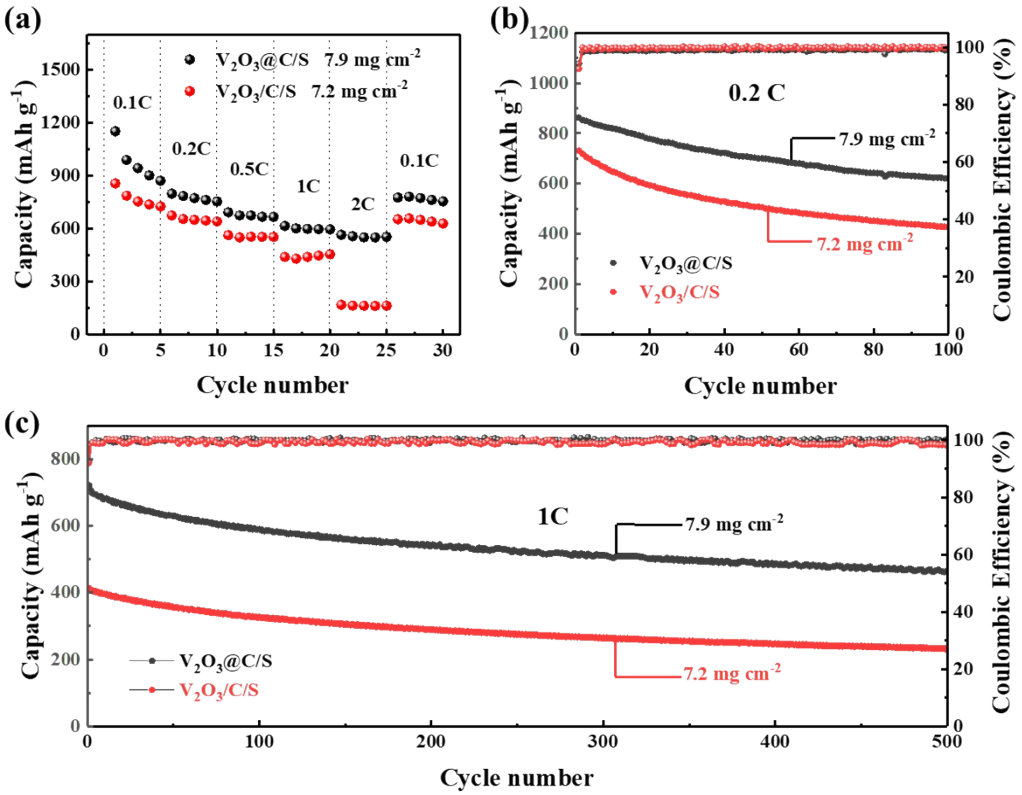

Fig. S17† (a) Rate capabilities of the V_2O_3@C/S and V_2O_3/C/S cathodes from 0.1C to 2C with a sulfur mass loading of 7.9 and 7.2 mg cm^{-2}, respectively. (b) Cycling performances of the V_2O_3@C/S and V_2O_3/C/S cathodes at 0.2C with a sulfur mass loading of 7.9 and 7.2 mg cm^{-2}, respectively. (c) Long-term cycling performance of the V_2O_3@C/S and V_2O_3/C/S cathode at 1C with a sulfur mass loading of 7.9 and 7.2 mg cm^{-2}, respectively.

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Table S1† Binding energies of sulfur species on the (104) plane of V_2O_3 and on graphene, respectively.

Species	Binding Energy (eV)	Species	Binding Energy (eV)
G/Li_2S	-7.481	V_2O_3/Li_2S	-5.287
G/Li_2S_2	-2.721	V_2O_3/Li_2S_2	-7.928
G/Li_2S_4	-1.860	V_2O_3/Li_2S_4	-6.625
G/Li_2S_6	-4.604	V_2O_3/Li_2S_6	-6.520
G/Li_2S_8	-2.537	V_2O_3/Li_2S_8	-7.579
G/S_8	-2.187	V_2O_3/S_8	-5.828

Table S2† Comparation of the electrochemical performance of V_2O_3@C/S with the reported literatures.

Materials	**Sulfur loading (mg cm^{-2})**	**S content (wt%)**	**Initial capacity ($mAh\ g^{-1}$)**	**Cycles**	**Capacity Decay (% per cycle)**	**Ref.**
V_2O_3@C/S	**3.7/7.9**	**78.4**	**961/721(1C)**	**1000 /500**	**0.037/0.07**	**This work**
S/VCM	1.5-1.6	55.9	1006(1C)	100	0.84	[1]
S@G/G-V_2O_3	3.6	78.3	1203(0.2C)	70	0.26	[2]
S@3VO_2–1VN/G	2.8	61.8	~807(1C)	100	0.36	[3]
VO_2 HS@S	1.64	71	576(1C)	200	0.12	[4]
VO_2@rGO/S	1.5	76.1	1071 (1C)	200	0.14	[5]
VO_2/G/S	1.4~2.0	70.0	860(2C)	200	0.14	[6]
VO_2(P)-NCNT/S	4.8	-	~1000(1C)	200	0.09	[7]
S-V_2O_3	1	66	~900(0.2C)	160	0.2	[8]
VO_2(p)-V_2C/S	4.8	72.7	~1250(0.2C)	200	0.3	[9]
VO_2@S	~1.5	67.2	1061(1C)	200	0.26	[10]

Table S3† EIS Fitting results of the two electrodes before and after cycling.

Components	Before cycle		After cycle	
	V_2O_3@C/S	V_2O_3/C/S	V_2O_3@C/S	V_2O_3/C/S
R_Ω (Ω)	4.40	3.72	4.47	3.80
R_s (Ω)	2.82	9.53	1.81	2.62
R_{ct} (Ω)	35.75	76.06	13.90	41.43
R_{total} (Ω)	42.97	89.31	20.18	47.85

$R_{total} = R_\Omega + R_s + R_{ct}$

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