Supporting Information

Efficient Trapping and Catalytic Conversion of Polysulfides by VS₄ Nano-sites for Li-S Batteries

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Experimental section

Preparation of free-standing NT arrays: The free-standing NT host was prepared by a chemical vapor deposition (CVD) method, as reported previously.¹ Carbon paper (CP) was pretreated by coating a thin Al₂O₃ layer by atomic layer deposition. The resulted CP was then fixed inside a vertical quartz tube of a chemical vapor deposition furnace. The furnace was heated up to 856 °C under Ar with a flow rate of 240 sccm. After the temperature reached 856 °C, a ferrocene solution (0.02 g mL⁻¹) was introduced into the tube at a flow rate of 250 μ L/min for 8 min. The growth of NTs was finished by introducing an imidazole solution B (0.2 g mL⁻¹) into the tube under the same condition for ~25 min.

Preparation of free-standing VS@NT host: The free-standing NT host was soaked in 70% nitric acid aqueous solution and subsequently transferred into a 50 ml Teflon-lined autoclave by heating at 100 °C for 2 h. The obtained hydroxylated NT host was washed with ethanol and distilled water alternately for several times. The VS@NT was prepared by using a facile hydrothermal method, as reported elsewhere.² In a typical synthesis, 1.2 mmol sodium orthovanadate was dissolved in 40 mL distilled water with continuous stirring for 30 min, followed by addition of 6 mmol thioacetamide. The solution together with the hydroxylated NT was transferred into a 50-mL Teflon-lined autoclave and heated at 200 °C for 20 h. After the hydrothermal process, the VS@NT free-standing host was washed with distilled water and dried at 80 °C for 12 h.

Materials characterizations: The morphologies were characterized using field emission scanning electronic microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL 2010 FEG). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to analyze the elemental composition and valence state. X-ray diffraction (XRD, Bruker D8 advanced) and Raman spectroscopy (HORIBA Scientific LabRAM) were used to analyze the structure, composition and chemical bonds of these samples. UV–Vis spectra were recorded using a spectrophotometer (Varian Cary 50 Conc). The nitrogen sorption isotherm was recorded on a gas sorptometer (Micromeritics 3Flex 3500).

Polysulfide adsorption Observations: Li₂S₄, Li₂S₆ and Li₂S₈ solutions were prepared by mixing Li₂S and S with a molar ratio of 1:3, 1:5 and 1:7, respectively, into a 1:1 (v/v) DOL/DME mixture. Scrapping of the free-standing hosts, 5 mg of NT or VS@NT powder was separately added into a solution of 5 mmol·L⁻¹ Li₂S₄, Li₂S₆ or Li₂S₈.

Symmetric cell measurements: The electrodes for symmetrical cells were fabricated using the free-standing hosts directly without introduction of elemental sulfur. Two identical VS@NT electrodes (or two NT electrodes) were used as working and counter electrodes with 50 μ L of electrolyte (0.5 mol·L⁻¹ Li₂S₆ and 1 mol·L⁻¹ LiTFSI in 1:1 DOL/DME (v/v)). The CV measurements of the symmetrical cells were performed at a rate of 50 mV·s⁻¹ between -1.0 V and 1.0 V.

*Li*₂*S nucleation tests:* Li₂S₈ electrolyte (0.20 mol L⁻¹) was prepared by mixing sulfur and Li₂S at a molar ratio of 7: 1 in a 1:1 DOL/DME (v/v) solutions followed by vigorous mixing for 24 h. A consistent amount of 20 mL Li₂S₈ electrolyte was first distributed into the cathode and then 25 mL LiTFSI (1.0 mol L⁻¹) without Li₂S₈ was dropped onto the lithium anode compartment. The batteries were galvanostatically discharged to 2.06 V under 0.112 mA and held potentiostatically at 2.05 V until the current was below 0.01 mA for nucleation and growth of Li₂S. Based on Faraday's law, the energy was collected to evaluate the nucleation/growth rate of Li₂S on various host surfaces.

Electrochemical Characterizations: Standard CR2032-type coin cells were assembled in an Ar-filled glove box with oxygen and moisture content below 1 ppm. The electrolyte was 1.0 M LiTFSI dissolved in mixed solvents of DOL and DME (v/v = 1:1) with 1 wt% of LiNO₃ as an additive. 40 μ L sulfur-containing solution (20 mg·mL⁻¹ sulfur in CS₂) were dropped onto the *VS@NT host.* To control the loadings of sulfur in the VS@NT cathode, the same process was repeated. The regular sulfur loading is ~1.2 mg·cm². Electrodes with high areal sulfur loadings of 3.2-16.0 mg·cm⁻² were also prepared to test the stability of cycling performances. The galvanostatic charge/discharge tests and GITT curves of the cells were measured on a Land T2001A battery testing station with a voltage range of 1.7 to 2.8 V. Through a VMP3 electrochemical workstation, the CV was performed at a scan rate of 0.1 mV·s⁻¹ and the EIS was tested with a frequency range of 200 kHz to 0.1 Hz.

Calculation details: The structure optimization and electronic band calculation were performed with Vienna ab initio simulation package.³ The Perdew-Burke-Ernzerhof generalized functional of gradient approximation was used for the exchange-correlation term.⁴ The projector-augmented wave method was employed to represent the ion-electron interactions.⁵ The van der Waals interactions were corrected by using DFT-D3 method of Grimme.⁶ The energy cutoff was set to 500 eV, and the energy and force convergence criteria were set to be 10^{-5} eV and 10^{-2} eV/Å respectively. A two dimensional model was utilized to calculate the binding energy between the Li-S clusters and substrate, where a monolayer VS_4 (110) surface was chosen. The substrate was set by a supercell consisting of 40 atoms. To avoid the interactions between the periodical images, the vacuum layer was set to at least 15 Å.



Figure S1. (a,b) SEM images of NT array on carbon paper.



Figure S2. (a)-(d) TEM images with different magnifications of VS@NT host.



Figure S3. (a) FESEM images and corresponding elemental mappings with element distributions of (b) C, (c) V, and (d) S; (e) EDX spectrum of VS@NT host.



Figure S4. XPS spectra for the VS@NT host: (a) survey spectrum, (b) C 1s, (c) V 2p and (d) S 2p.



Figure S5. UV-Vis curves of Li_2S_6 solution before/after adding VS@NT host.



Figure S6. Cyclic voltammograms of symmetric cells with identical electrodes of NT and VS@NT in electrolytes with/without adding Li_2S_6 .



Figure S7. Potentiostatic discharge curves of a Li_2S_8 / DOL/DME solution at 2.05 V on different surfaces.

Notes: The cells were discharged galvanostatically at 0.112 mA to 2.06 V and kept potentiostatically at 2.05 V until the current was below 0.01 mA. The whole process of Li_2S nucleation/growth lasted for 600 min approximately. Based on Faraday's law, the energy was collected to evaluate the nucleation/growth rate of Li_2S on various host surfaces.



Figure S8. Comparison of the peak potentials for lithiation/delithiation reactions of VS@NT/S and NT/S cathodes.



Figure S9. GITT curves as functions of time for (a) VS@NT/S and (b) NT/S cathodes.



Figure S10. Electrochemical impedance spectra of NT/S and VS@NT/S cells before/after cycling.



Figure S11. Cyclic performance of VS@NT cathode without sulfur loading.



Figure S12. Discharge/charge voltage curves of rate performances for NT/S cathode

(1 C= 1672 mA/g).



Figure S13. Photographs showing separators obtained from (a) VS@NT and (b) NT cells disassembled after long-term cycling.



Figure S14. (a,b) SEM images of VS@NT cathode with sulfur loading of 6.4 mg cm^2 after 200 cycles.



Figure S15. Cycling performance of VS@NT/S cathodes with sulfur loadings of 13.3 $mg^{2}cm^{2}$ at 0.12 C and 16 $mg^{2}cm^{2}$ at 0.1 C for 50 cycles.

	Sulfur	Current		Initial	Areal	Decay		
Host	loading	density	Cycle	capacity	capacity	rate (%	Year	Ref
materials	(mg cm ⁻²)	(C)	S	(mAh g ⁻¹)	(mAh cm ⁻²)	per cycle)		
NiS@C-HS	2.3	0.5	300	723	1.66	0.013	2017	7
$C@WS_2$	1.2	0.5	500	1180	1.42	0.0313	2017	8
rGO-VS ₂	2.56	0.1	100	1015	2.6	-	2017	9
G-VS ₂	5	0.2	50	1000	5.1	-	2018	10
CNF@VS ₂ /	5.6	0.1	<50	1150	6.25	-	2018	11
CNT@GN								
MoS ₂ -Flakes	1.5	0.5	300	956	1.434	0.056	2017	12
MXene/1T-2H	1	0.5	300	1014.1	1.01	0.07	2018	13
MoS ₂ -C								
CNTs/CoS-	1	1	1000	982	0.98	0.031	2018	14
NSs								
Co_3S_4	~4	0.1	50	~1000	~4	-	2017	15
nanotubes								
Hollow Co ₃ S ₄	3.5	0.2	150	1012	3.54	0.126	2017	16
Nanoboxes								
Co ₉ S ₈ /C	3	0.5	300	~850	~2.55	-	2017	17
CoS ₂ - G	2.9	0.1	30	1130	3.28	-	2016	18
TiS ₂ -	12	-	200	1030	12.36	0.18	2018	19
polysulfide								
PS-ReS ₂	3.3	0.5	300	~925	~3.05	0.063	2016	20
@CNF								
SnS ₂ -ND@G	10	0.2	100	1133	11.3	0.3	2018	21
	6.4	0.2	200	944.9	6.05	0.15	-	
VS@NT	9.6	0.1	120	1356	13.02	0.23		This
	13.3/16	0.12/0.	50	750/	9.97/10.24	0.4/0.42		work
		1		640				

Table S1. Performance comparisons with recent works on MS-based materials as Li-S batteries electrodes.

Host Name	Sulfur loading (mg cm ⁻²)	Current density	E/S Ratio (mL g ⁻¹)	Areal capacity (mAh•cm ⁻²)	Gravimetric Energy Density (Wh•kg ⁻¹)	Current collector	Ref
S/PCNF/C NT	12	0.6 mA cm ⁻²	20	13.5	109.7	PCNF	22
S/CNT/NF C	8.1	0.25 C	30	8	65.7	CNT/NFC	23
S@NG-CN T	4.7	0.5 C	10	5.17	191.9	NG/CNT	24
S@NCFF	3	0.2 C	20	2.4	76.7	CFF	25
SN-HCSs/S	2.5	0.05 c	32	3.5	89.2	NCF	26
S@CNF/ rGO	20.3	1.7 mA cm ⁻²	15.6	15.5	93.4	CNF/rGO	27
S@CNTF	7.1	0.1 C	11	9	210.5	CNT foam	28
G-HPC/S	3.6	0.5 C	11	4.26	196.8	GO sheet	29
NCF– S@rGO	8.8	0.1 C	9	6.6	150.9	melamine foam	30
MWCNT-S	3.1	0.5 C	9.5	3.56	170	MWNCT fim	31
SWCNT/C NF-S	16	0.1 C	15	12.3	96.6	SWCNT/ CNF film	32
PCF/VN/S	8.1	0.1 C	20	10.61	127.4	PCF	33
VS@NT-S	9.6	0.1 C	8	13.02	243.4	СР	This work

Table S2. Comparisons with recent works on free-standing high sulfur loading fibrous electrodes.

Note:

Weights of all cell components except cell housing components were included for the calculations. Several assumptions were established in purpose of easier calculation as well as comparison: i) the density of electrolyte equals 1 g·mL⁻¹; ii) nominal voltage of the batteries equals 2.15 V; iii) 50 wt.% lithium excess accords to the stoichiometric ratio of sulfur; iv) the Separator (Celgard 2400) weight equals 0.9 mg·cm⁻².

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