

Supporting Information

Construction of 1T@2H MoS₂ heterostructures in situ from natural molybdenite with enhanced electrochemical performance for lithium-ion batteries

ChengLong Peng, Mingming Shi, Fei Li, Yang Wang, Xueqin Liu, HuaSheng Liu and Zhen Li*

Engineering Research Center of Nano-Geomaterials of Ministry of Education, Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan, Hubei 430074, P. R. China

E-mail: zhenli@cug.edu.cn

Additional figures discussions

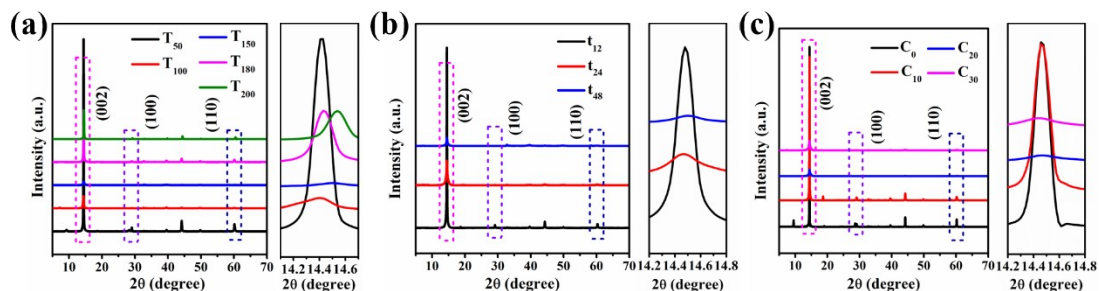


Fig. S1 XRD patterns of 1T@2H MoS₂ prepared under different conditions: (a) different reaction temperature; (b) different reaction time; (c) different reaction concentrations of sodium hydroxide.

Fig. S1a shows that as the temperature increases, the characteristic peak intensity first increases and then decreases. The characteristic peak intensity is the lowest at 150°C, indicating that the optimal reaction temperature for expansion is 150°C. In addition, the grain size is calculated by the Scherrer formula $D=K\lambda/(\beta\cos\theta)$, $D_{50}=50.13$ nm, $D_{100}=24.00$ nm, $D_{150}=21.35$ nm, $D_{180}=57.82$ nm, $D_{200}=49.35$ nm. When the reaction temperature is 150°C, the grain size is the smallest, proving that molybdenite expands most fully under this condition. Similarly, the optimal reaction time is 24 h, and the sodium hydroxide concentration 25 mol L⁻¹ (Fig. S(b-c) †).

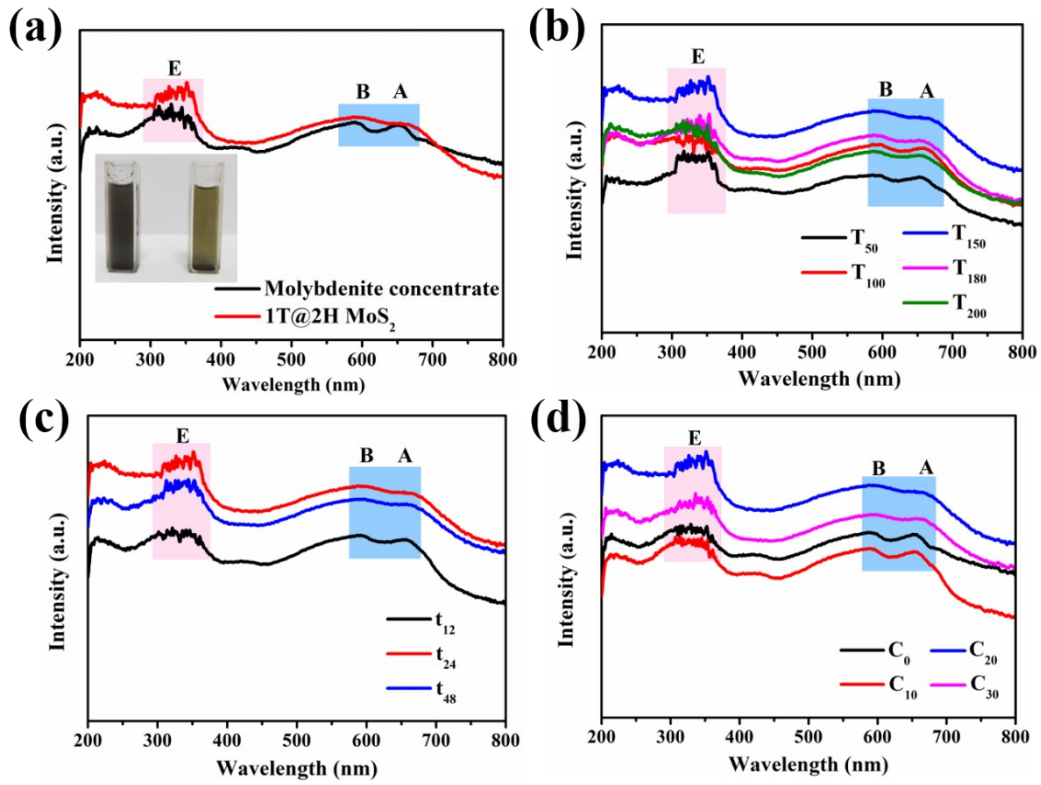


Fig. S2 UV-Vis absorption spectra: (a) molybdenite concentrate and 1T@2H MoS₂; (b) the preparation of the 1T@2H MoS₂ at different reaction temperatures; (c) The preparation of the 1T@2H MoS₂ at different reaction time; (d) The preparation of the 1T@2H MoS₂ at different reaction concentrations of sodium hydroxide.

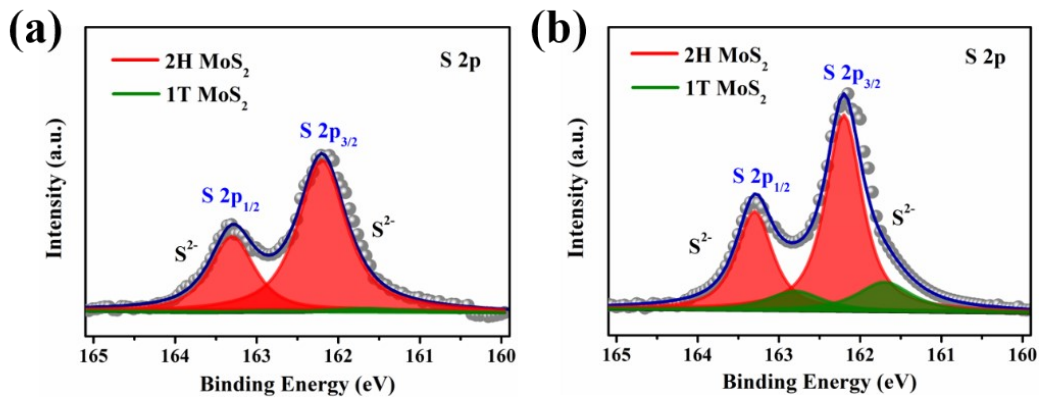


Fig. S3 (a) S 2p spectra of molybdenite concentrate. (b) S 2p spectra of 1T@2H MoS₂.

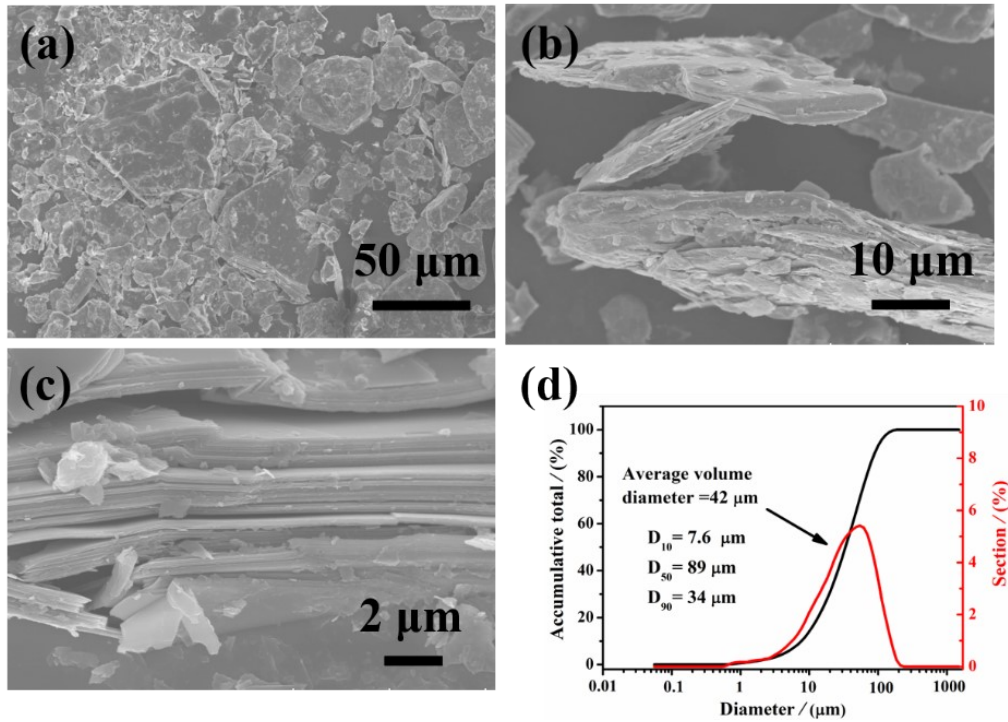


Fig. S4 (a-c) SEM diagram of molybdenite concentrate. (d) Particle size distribution diagram of molybdenite concentrate.

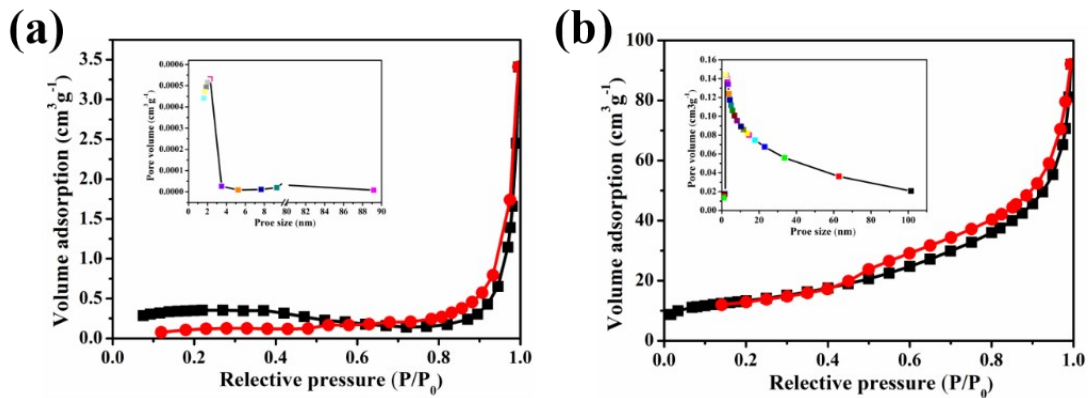


Fig. S5 N₂ isothermal adsorption-desorption and pore size distribution curve (insert): (a) molybdenite concentrate; (b) 1T@2H MoS₂.

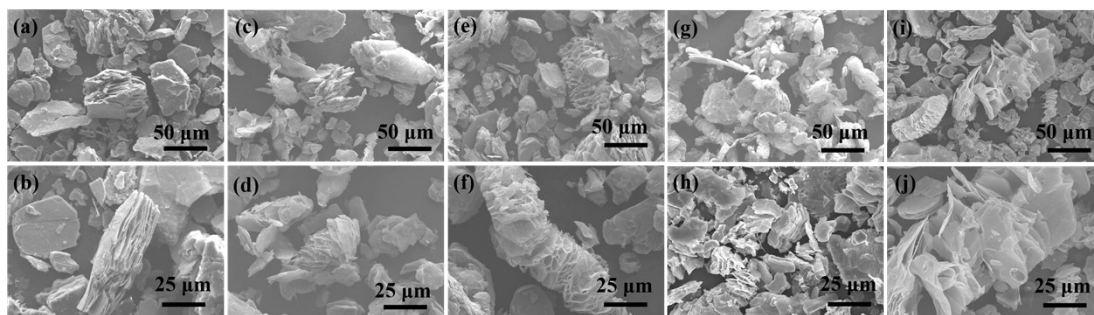


Fig. S6 1T@2H MoS₂ prepared at different temperatures: (a-b) 50°C; (c-d) 100°C; (e-f) 150°C; (g-h) 180°C; (i-j) 200°C.

When the reaction temperature was 150 °C, the molybdenite concentrate expanded most fully.

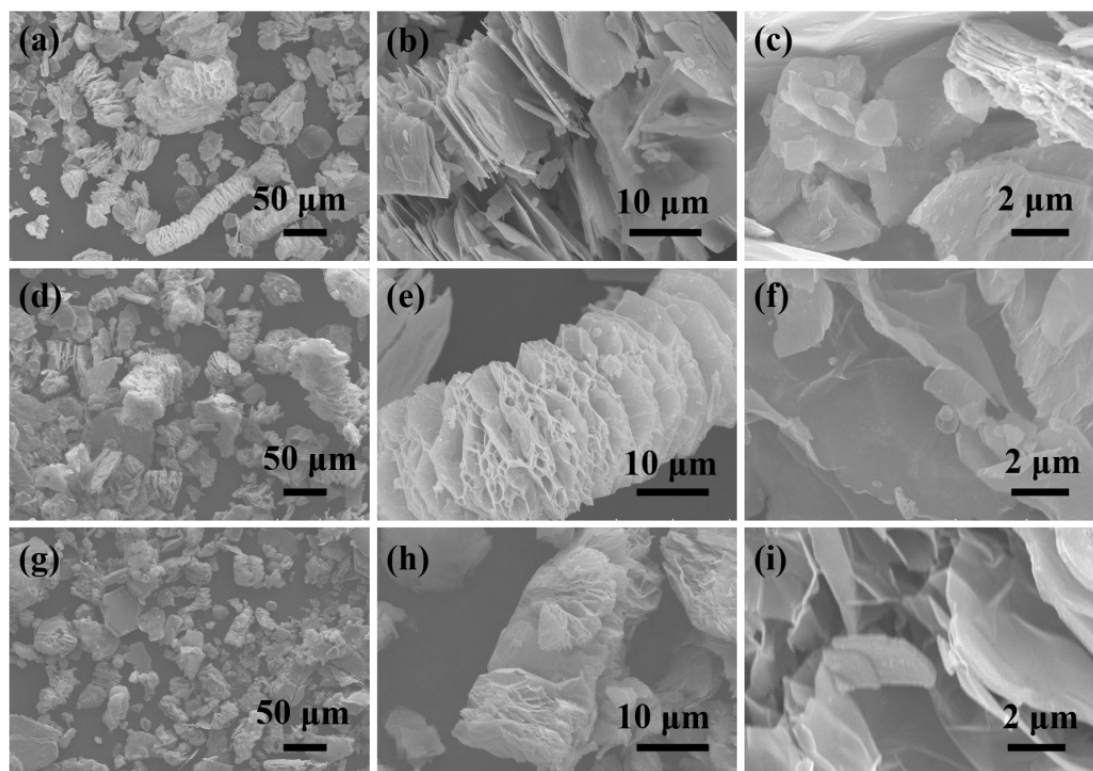


Fig. S7 1T@2H MoS₂ prepared at different time: (a-c)12 h; (d-f) 24 h; (g-i) 48 h.

When the reaction time was 24 h, the molybdenite concentrate expanded the most fully.

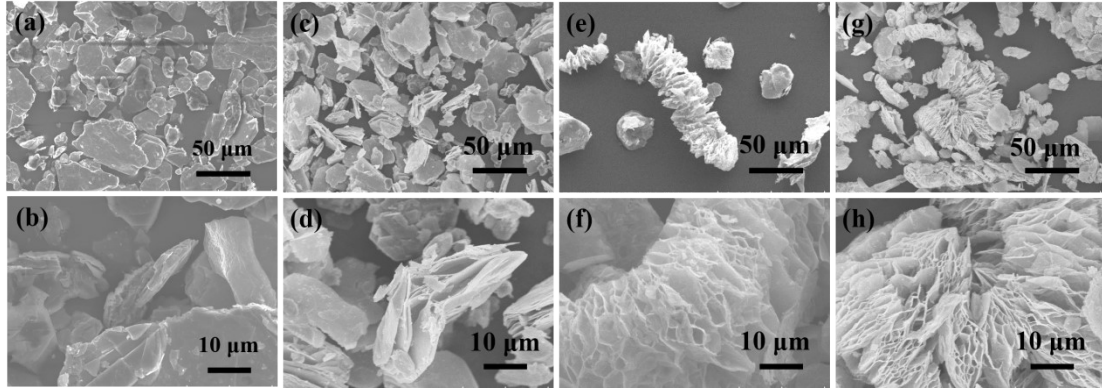


Fig. S8 1T@2H MoS₂ prepared at different reaction concentrations of sodium hydroxide: (a-b) 0 mol L⁻¹; (c-d) 12.5 mol L⁻¹; (e-f) 25 mol L⁻¹; (g-h) 37.5 mol L⁻¹.

When sodium hydroxide concentration was 25 mol L⁻¹, the molybdenite concentrate expanded the most fully.

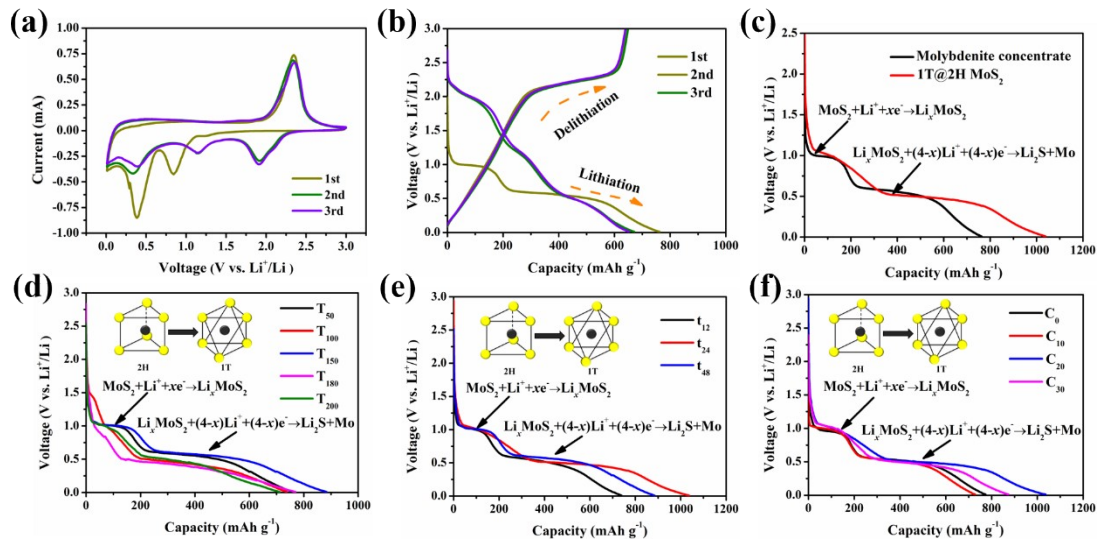


Fig. S9 (a) CV curves of molybdenite concentrate. (b) Charging and discharging curves of molybdenite concentrate in the first three cycles. (c) The first cycle discharge curves of molybdenite concentrate and 1T@2H MoS₂. (d) The first cycle discharge curves at different reaction temperatures. (e) The first cycle discharge curves at different reaction time. (f) The first cycle discharge curves of different sodium hydroxide concentrations.

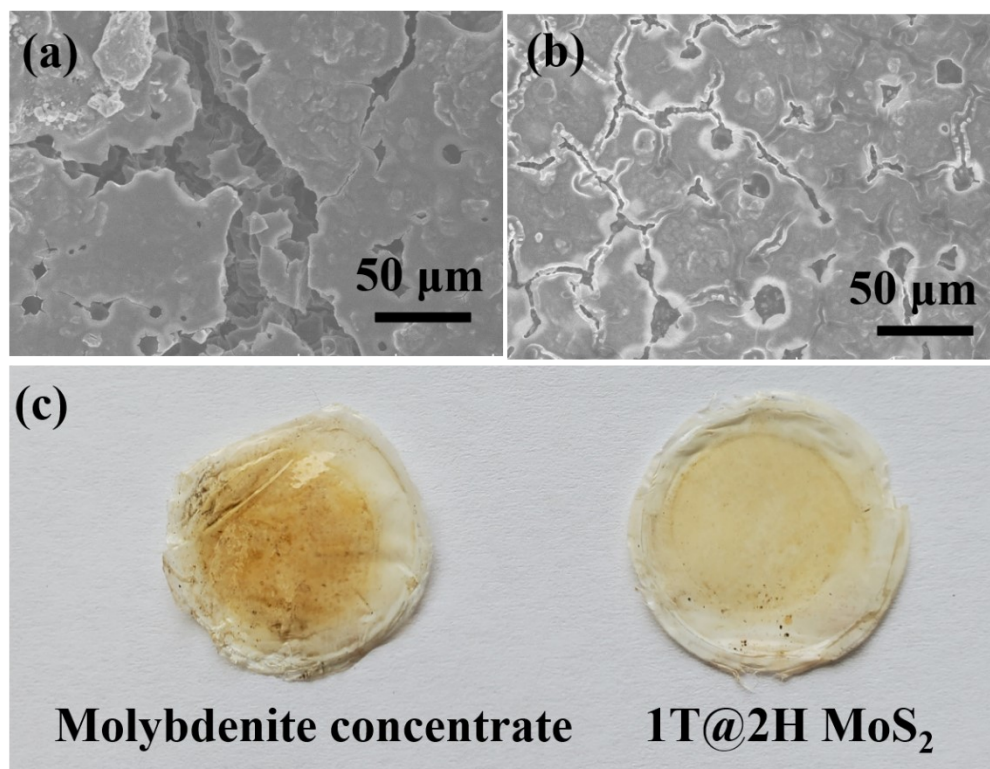


Fig. S10 (a) SEM images of the molybdenite concentrate. (b) 1T@2H MoS₂ electrode after 120 cycles at a current density of 100 mA g⁻¹. (c) Separators color contrast after 120 cycles.

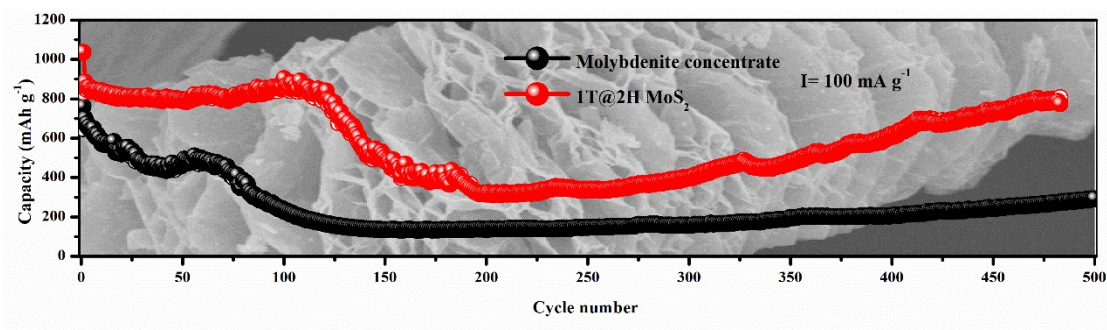


Fig. S11 Comparison diagram for the long-cycle performance of molybdenite concentrate and 1T@2H MoS₂.

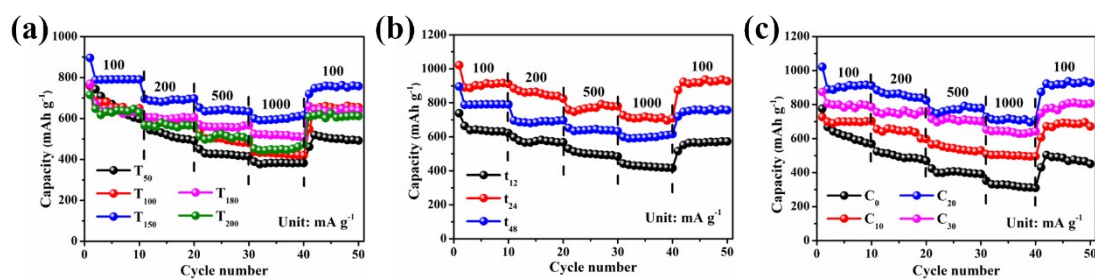


Fig. S12 1T@2H MoS₂ rate performances: (a) different reaction temperature; (b) different reaction time; (c) different sodium hydroxide concentrations.

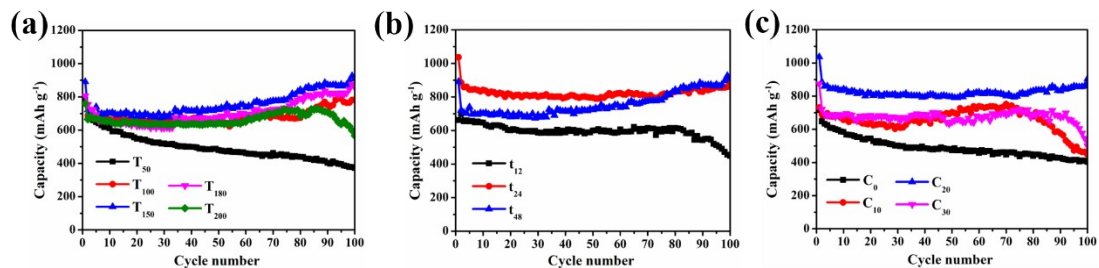


Fig. S13 Cycling performance of 1T@2H MoS₂: (a) different reaction temperature; (b) different reaction time; (c) different sodium hydroxide concentrations.

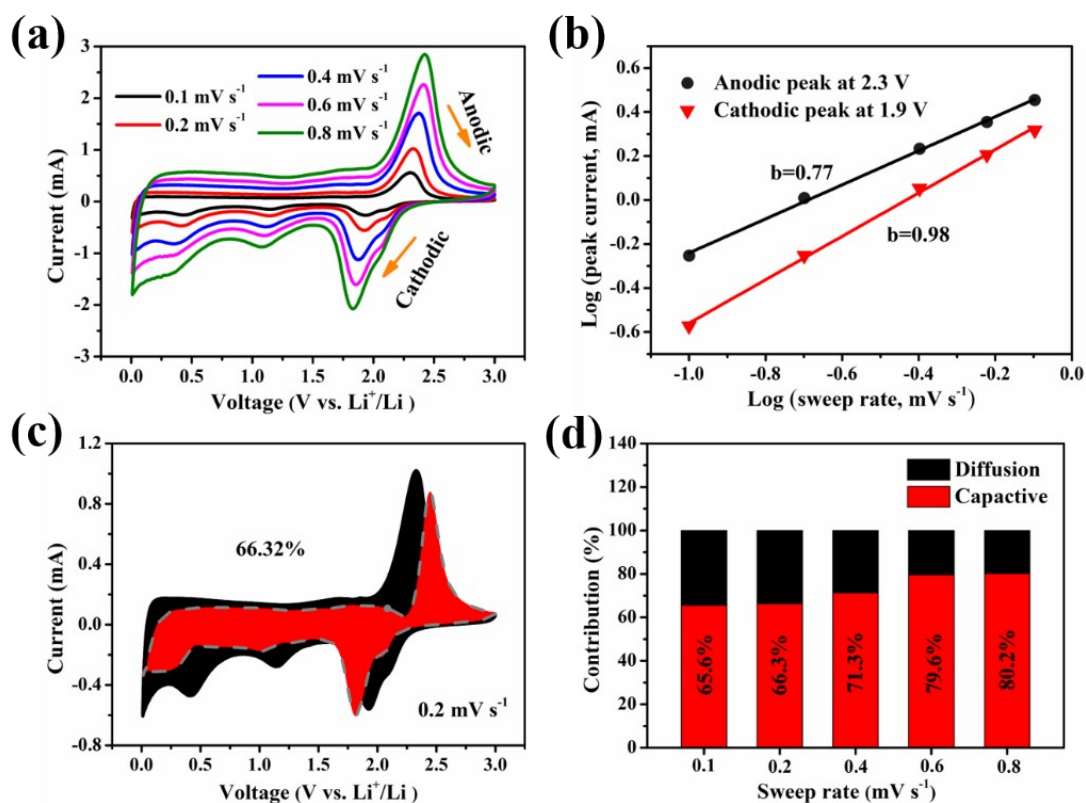


Fig. S14 Electrochemical kinetics analysis of molybdenite concentrate: (a) CV curves measured at different scan rates from 0.1 to 0.8 mV s⁻¹; (b) log(*i*) vs. log(*v*) plots at oxidation and reduction state; (c) CV curve with capacitive and diffusion-controlled contributions at 0.2 mV s⁻¹; (d) bar chart showing the contribution ratio of capacitive and diffusion-controlled capacities at different scan rates.

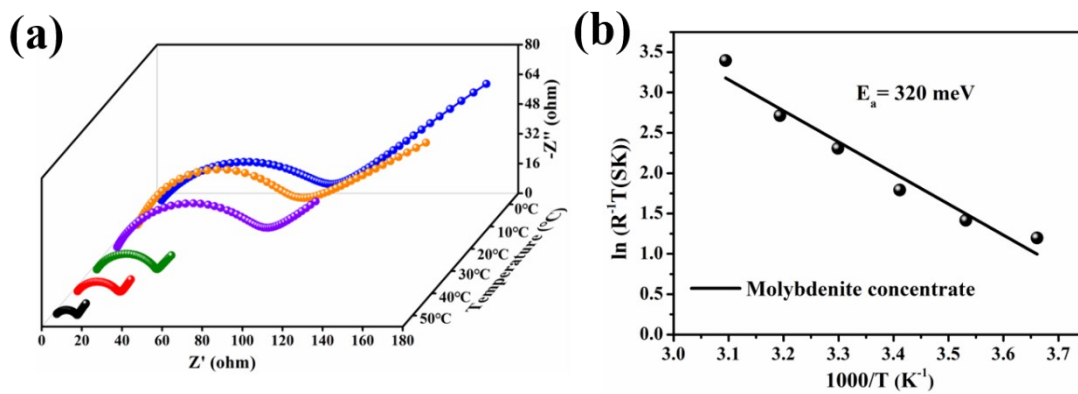


Fig. S15 (a) Temperature-dependent Nyquist plots of molybdenite concentrate. (b) Reciprocal bulk and interface impedance as a function of the reciprocal temperature of molybdenite concentrate.

Table S1 Sample number of 1T @2H MoS₂ prepared under different conditions.

Reaction conditions	Sample number	Detailed parameter
Temperature (°C)	T ₅₀	50°C
	T ₁₀₀	100°C,
	T ₁₅₀	150°C,
	T ₁₈₀	180°C,
	T ₂₀₀	200°C
Time (h)	t ₁₂	12 h
	t ₂₄	24 h
	t ₄₈	48 h
Concentration (mol L ⁻¹)	C ₀	0 mol L ⁻¹
	C ₁₀	12.5 mol L ⁻¹
	C ₂₀	25 mol L ⁻¹
	C ₃₀	37.5 mol L ⁻¹

Table S2 The electronic conductivity of molybdenite concentrate and 1T@2H MoS₂ at the different reactions.

Sample number	The resistivity ($\Omega\cdot\text{cm}$)	Electrical conductivity (s/cm)
Molybdenite concentrate	Over More than a range $>5\times 10^5$	Over More than a range $<10^{-5}$
Commercial MoS ₂	4.52×10^{-4}	2.21×10^{-4}
T ₅₀	88070	1.13×10^{-5}
T ₁₀₀	2	0.5
T ₁₅₀	0.2	5
T ₁₈₀	0.9	1.111
T ₂₀₀	1.4	0.714
t ₁₂	10.2	9.8×10^{-2}
t ₂₄	0.1	10
t ₄₈	0.2	5
C ₁₀	9404	1.06×10^{-4}
C ₂₀	0.1	10
C ₃₀	0.125	8

Table S3 XRF comparative analysis of molybdenite concentrate and 1T@2H MoS₂.

Sample name	Sum. of conc.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	MnO	Fe ₂ O ₃
		CuO	ZnO	MoO ₃	RuO ₂	PbO	Rh	As ₂ O ₃	BaO	F
Molybdenite concentrate	100		6.04	0.38	12.3	35.92	0.13	0.36	0.04	1.14
		0.25	0.14	41.74	0.13	0.07		0.06	0.31	0.85
1T@2H MoS ₂	100	2.52	1.68	0.16	0.49	42.07	0.03	0.15	0.03	1.18
		0.21	0.06	50.29	0.15	0.06	0.82			

Table S4 Compared lithium-ion storage performances with other reported natural molybdenite, synthetic MoS₂, and MoS₂ based anode materials.

Electrode material	Method	Morphology	Capacity (mAh g ⁻¹) after cycles (Y) at (z) current density	References
1T@2H MoS ₂	Expansion	Bukly worm-like	788 (485) (0.1 A g ⁻¹) 832 (120) (0.1 A g ⁻¹)	This work
Pure natural molybdenite	Flotation (different binders)	Flakes	234 (100) (0.2 A g ⁻¹); 580 (CMC)	1
PEO/molybdenite	Exfoliated/ Solution Process	Nanocomposite	953 (50) (0.05 A g ⁻¹)	2
MoS ₂	Hydrothermal	Nanoflakes	780 (40) (0.04 A g ⁻¹)	3
MoS ₂	Impregnation	Wire-like Arrays	876 (100) (0.1 A g ⁻¹)	4
MoS ₂	Hydrothermal	3D Flower-like Spheres	947 (50) (0.1 A g ⁻¹)	5
MoS ₂	Hydrothermal	Hollow Nanoparticles	902 (80) (0.1 A g ⁻¹)	6
MoS ₂	Hydrothermal	Worm-like	845 (50) (0.1 A g ⁻¹)	7
MoS ₂ @C/RGO	Exfoliation / Solution Process	A robust 3D bulky	1189 (200) (0.2 A g ⁻¹)	8

References

1. S. J. Li, H. H. Tang, P. Ge, F. Jiang, J. H. Zhou, C. Y. Zhang, H. S. Hou, W. Sun and X. B. Ji, *ACS Appl. Mater. Interfaces*, 2018, **10**, 6378-6389.
2. J. Xiao, D. Choi, L. Cosimbescu, P. Koech, J. Liu and J. P. Lemmon, *Chem. Mater.*, 2010, **22**, 4522-4524.
3. C. Q. Feng, J. Ma, H. Li, R. Zeng, Z. P. Guo and H. K. Liu, *Mater. Res. Bull.*, 2009, **44**, 1811-1815.
4. H. Liu, D. W. Su, R. F. Zhou, B. Sun, G. X. Wang and S. Z. Qiao, *Adv. Energy Mater.*, 2012, **2**, 970-975.
5. T. Yang, Y. J. Chen, B. H. Qu, L. Mei, D. N. Lei, H. N. Zhang, Q. H. Li and T. H. Wang, *Electrochim. Acta*, 2014, **115**, 165-169.
6. M. Wang, G. D. Li, H. Y. Xu, Y. T. Qian and J. Yang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1003-1008.
7. H. Y. Wang, B. Y. Wang, D. Wang, L. Lu, J. G. Wang and Q. C. Jiang, *RSC Adv.*, 2015, **5**, 58084-58090.
8. S. C. Li, P. Liu, X. B. Huang, Y. G. Tang and H. Y. Wang, *J. Mater. Chem. A*, 2019, **7**, 10988-10997.

Table S5 The resistance value, the Warburg factor σ and diffusion coefficient D of molybdenite concentrate and MoS₂ were obtained.

Electrode	Molybdenite concentrate	1T@2H MoS ₂
R _e (Ω)	3.36	3.10
R _{ct} (Ω)	47.25	37.78
σ	28.16	17.08
D	2.15×10 ⁻¹¹	5.81×10 ⁻¹¹

Table S6 The fitting values of molybdenite concentrate were from the EIS spectrum at different temperatures.

Component	Temperature (°C)					
	0	10	20	30	40	50
R _e (Ω)	5.13	3.61	3.24	3.07	2.79	2.06
R _{ct} (Ω)	82.42	68.72	48.85	30.17	20.77	10.82

Table S7 The fitting values of 1T@2H MoS₂ were from the EIS spectrum at different temperatures.

Component	Temperature (°C)					
	0	10	20	30	40	50
R _e (Ω)	3.09	2.91	2.65	2.18	1.45	1.186
R _{ct} (Ω)	64.46	48.01	38.84	29.67	20.51	10.32