1	Supplementary Information for				
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3	High lithiophilicity and Li diffusion rate on 1T phase transition metal				
4	dichalcogenides as effective Li regulating materials for dendrite-free metal anode				
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1 Experimental Section

2

Computational Methods: All DFT calculations were performed using software 3 package of Vienna ab initio simulation package (VASP)¹⁻³, based on the general 4 gradient approximation (GGA) exchange correlation functionals of Perdew-Burke-5 6 Ernzerhof (PBE).⁴ Projector augment wave (PAW) pseudopotential was used to describe the ion-electron interaction.^{5, 6} In both Li binding and diffusion energy 7 calculations, we considered the spin polarization and used vdW-DF2 functional to 8 include the van der Waals (vdW) interaction. For the electron wave expansion, a plane 9 wave of 500 eV was set as the cutoff energy. Single layer of 4*4 graphene, 3*3 h-BN, 10 3*3 sulfides (MoS₂, VS₂ and SnS₂) and 3*3 selenides (MoSe₂, VSe₂ and WSe₂), three 11 12 layers 4*4 Cu (111) facet and six layers 4*4 Li (001) facet were constructed with 20 Å vacuum distance to avoid layer interaction in z direction. Noted that the low index (111) 13 and (001) are the dominating surfaces for Cu and Li with the lowest surface energy 14 among the other possible crystal planes.^{7, 8} As 1T VS₂ owns metallic properties while 15 remains thermal dynamically stable at room temperature, we study 1T phrase VS₂ 16 throughout the whole study.9-11 17

18

19 For structure relaxation, the convergence criteria for electron self-consistent loop set to 20 be 10⁻⁶, while the Hellman–Feynman forces on atoms were less than 0.02 eV Å⁻¹. A 21 Gaussian smearing of 0.05 eV was adopted throughout the whole calculation. The 22 Brillouin zone was sampled by a k-points of 5*5*1 generated automatically using the 23 Monkhorst-Pack's technique.

24

25 The binding energy E_b between Li and substrate was calculated by the following 26 equation: $E_b = E_{Li/substrate} - E_{Li} - E_{substrate}$, where $E_{Li/substrate}$, E_{Li} and $E_{substrate}$ are the total energy of adsorbed Li atom on the substrate, single Li atom and pure substrate,
 respectively. The climbing image nudged elastic band (CI-NEB) method was adopted
 to study the diffusion barrier of Li on the substrates.¹² The two most stable and nearest
 Li adsorption sites of the substrate were selected as the initial and final state of the
 diffusion path during the CI-NEB calculation. The 3D visualization models were
 constructed using VESTA software.

7

8 The Bader charge analysis was conducted to determine the charge transfer and
9 accumulation quantitatively between Li and layered Li regulating materials using the
10 method developed by the Henkelman et al.¹³

11

Preparation of VS₂/NCNT and NCNT: All chemicals with analytical grade were 12 purchased from Sigma-Aldrich without further treatment and the deionized (DI) water 13 was used throughout the whole experiment. 15 mg of MWCNT was firstly dispersed 14 15 into 90 mL of DI water/IPA mixture (5:1 vol %) and sonicated for 3 h. Then, 200 mg 16 of dopamine was added into the CNT solution and stirred for 30 min to ensure even distribution. 100 mg Tris-HCl in 10 ml of DI water was added into the above solution 17 drop by drop and followed by vigorous stirring at room temperature for 24 h to 18 polymerize dopamine on CNT surface (PDA@CNT) as shown in Figure S1a and b, 19 which was later washed by DI water by centrifugation at 15000 rmp for 15 min each 20 21 round until the brownish is gone. 2 mmol of NH₄VO₃ in DI water/ammonia mixture 22 (7:3 vol %) was dropped into PDA-CNT and kept stirring for 3 h for ion adsorption, followed by freeze drying. The dried V5+@PDA@CNT was annealed in CVD furnace 23 at 300 °C for 30 min under 20 sccm Ar gas. The annealed composite is mixed with 500 24 mg sulfur powder and loaded into a semi-closed quartz tube for 25 min sulfurization at 25 26 530 °C under 50 sccm Ar and 15 sccm H₂ carrier gases to obtain final product of VS₂/NCNT. For NCNT, same experimental procedures were followed but without the
 V⁵⁺ ion introduction.

3

4 Material characterizations:

Scanning electron microscopy (SEM, JEOL 7100F), transmission electron microscopy 5 (TEM, JEOL 2010F) with the EDS element mapping were used to observe the 6 7 morphologies, structures and elemental distributions of VS₂/NCNT composites. Powder X-ray diffraction (XRD, PW1830) with Cu Karadiation (λ =1.5406 Å) was 8 applied to characterize the crystal structure at a scanning rate of 4.25° /min in the 20 9 range from 10° to 90°. The sulfur mass loading in the VS₂/CNT/S was determined by 10 thermogravimetric analysis (TGA, TA Q-50) at a heating rate of 5°C /min from room 11 12 temperature to 400°C under nitrogen protection. X-ray photoelectron spectroscopy (XPS, PHI 5600) was conducted to analyze the material composition and its elemental 13 valence states. Contact angle meter (Biolin Theta) was used to determine the wettability 14 15 of electrolyte of the separators.

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VS₂/ NCNT/ separator and VS₂/NCNT/S electrode preparation: Celgard 2500 17 membrane was used as the separator. To prepare the slurry for separator coating, 18 VS₂/CNT and PVDF were mixed (8:2 mass ratio) in NMP and uniformly coated on 19 separator by doctor blading. For VS₂/NCNT/S, sulfur was firstly infiltrated into the 20 21 VS₂/NCNT composites by 24 h melt diffusion at 155°C in a sealed container under 22 argon protection. Then VS₂/NCNT/S, carbon black (super P) and PVDF were mixed (7:2:1 mass ratio) in NMP and coated on aluminium foil by Doctor blading. The coated 23 separator and electrode were dried in the oven at 60°C overnight and punched into 24 25 circular discs in the diameter of 1.8 and 1.2 cm, respectively, for coin cell assembling.

1 Electrochemical measurements:

2 CR2032-type coin Li/Li symmetric cells were assembled in an argon gas filled glovebox with two lithium metal foils and blank separator or VS₂/ NCNT/ separator. 1 3 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in the mixture of dimethyl 4 ether (DME) and 1,3-dioxolane (DOL) in a volume ratio of 1:1 with 1 wt% lithium 5 nitrate (LiNO₃) was used as the electrolyte and 100 ul of the electrolyte was added in 6 7 each cell assembly (E/S ratio: ~50 ml g⁻¹) Full LSB cell was prepared with lithium metal foil as anode, VS₂/ NCNT/ separator, VS₂/ NCNT/S cathode. The galvanostatic 8 discharge/charge cycling tests were conducted by LAND CT2001A battery testing 9 10 system at room temperature. The cyclic voltammetry (CV) scans were conducted at a 11 scan rate of 0.1 mV/s with the same potential window of 2.8-1.8 V, and electrochemical 12 impedance spectroscopy (EIS) was performed at constant amplitude of 5mV in the 13 frequency range from 100 kHz to 0.01 Hz, both were carried out on an electrochemical 14 workstation (CHI 760E). 15 16 17 18 19 20 21 22 23 24 25 26

1 Supporting Figures







4 Figure S1. Li adsorption configurations on (a) graphene, (b) hBN, (c) Cu (111), (d)
5 Li (001), (e) TiS₂, (f) VS₂, (g) CrS₂, (h) CoS₂, (i) NiS₂, (j) NbS₂, (k) MoS₂, (l) TaS₂,
6 (m) WS₂, (n) ReS₂, (o) PtS₂, (p) TiSe₂, (q) VSe₂, (r) CrSe₂, (s) NbSe₂, (t) MoSe₂, (u)
7 TaSe₂, (v) WSe₂, (w) ReSe₂ and (x) PtSe₂.



2 Figure S2. Transmission Electron Microscope (TEM) Characterization of NCNT.

3 (a) Low and (b) high resolution of TEM image of polydopamine coated CNT.



2 Figure S3. Thermogravimetric analysis (TGA) curves of VS₂/ NCNT and NCNT

3 in air. Based on the results, the weight of vanadium oxide (V₂O₅) is 4.9% in the samples
4 of VS₂/ NCNT by increasing the temperature from 25°C to 600°C at the heating rate of
5 5°C/min, indicating 3.1wt% of VS₂ in the composite of VS₂/ NCNT.



2 Figure S4. X-ray photoelectron spectroscopy (XPS) characterization. (a) Full
3 spectrum of VS₂/ NCNT with the element indications of S2p, C1s, N1s, V2p, O1s and
4 V2s. (b) High resolution XPS spectrum of N1s.



7 Figure S5. Li nucleation overpotential. Voltage profiles of galvanostatic Li
8 deposition on (a) VS₂/ NCNT/ Cu and (b) blank Cu with the inset of the enlarged
9 voltage dip at 1.6 mAh cm⁻².





- 3 peaks indicate the high crystallinity of VS_2 in the composites.



2 Figure S7. Thermal gravimetric analysis (TGA) results of VS₂/NCNT/ S,
3 VS₂/NCNT and S. 58% of sample weight lost was found in the samples of
4 VS₂/NCNT/S by increasing the temperature from 25°C to 400°C at the heating rate of
5 5°C/min in N₂.





3 cell. (a) Schematic illustration of LSB cell configuration. (b) Charge-discharge profile
4 at 0.05 C in an initial cycle. (c) Cycling performance of the S and VS₂/NCNT/S cells at
5 0.2 C over 100 cycles.



- 2 Figure S9. Li₂S₆ adsorption test. UV-visible spectra of the samples of control (0.01
- 3 M Li_2S_6), NCNT and VS₂/NCNT.
- 4

- 5 Table S1. Adsorption energy, charge density and descriptor of transition metal
- 6 sulfides.

	Adsorption	Charge density	Descriptor, f
Transition metal sulfides	Energy (eV)	(e ⁻ /atom)	
TiS ₂	-3.62	0.03217	18.02
VS_2	-3.41	0.03216	19.07
CrS ₂	-4.07	0.03213	19.42
CoS ₂	-4.26	0.03214	22.00
NiS ₂	-3.08	0.03212	22.35

NbS ₂	-3.94	0.03233	20.32
MoS ₂	-1.94	0.03208	27.43
TaS ₂	-3.75	0.03232	20.55
WS ₂	-1.57	0.03216	32.33
ReS ₂	-2.02	0.03225	26.03
PtS ₂	-2.33	0.03228	31.24

¹

2 Table S2. Adsorption energy, charge density and descriptor of transition metal

3 selenides.

	Adsorption	Charge density	Descriptor, f
Transition metal sulfides	Energy (eV)	(e ⁻ /atom)	
TiSe ₂	-3.21	0.03209	20.48
VSe ₂	-2.98	0.03190	21.68
CrSe ₂	-3.50	0.03243	22.08
NbSe ₂	-3.50	0.03201	22.88
MoSe ₂	-1.66	0.03178	30.89
TaSe ₂	-3.35	0.03199	22.95
WSe ₂	-1.35	0.03165	36.11
ReSe ₂	-2.64	0.03240	29.07

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5 Reference

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