

Supporting information

Controllable fabrication of vanadium selenium nanosheets for high-performance Na-ion battery anode

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Experimental Section

Synthesis of V₂Se₉

All chemicals including vanadyl acetylacetonate (98%), selenium powder (99.9%), oleylamine (OAm, 80-90%), absolute ethanol (99.5%), and hexane (99.99%) were directly used without further purification. The V₂Se₉ was prepared by a facile one-pot colloidal method. Typically, 15 mL OAm was added in a 50 mL three-neck flask. Subsequently, 1 mmol of vanadyl acetylacetonate and 2 mmol of selenium powder were quickly poured into the above three-neck flask with vigorous stirring. And then the solution was heated to 120 °C and stayed for 30 min under N₂ atmosphere to get rid of the water and oxygen. Next, the solution was heated to 180 °C and kept for 90 min to obtain the V₂Se₉. After turning off the heat source, the solution was cooled naturally to room temperature. After that, the obtained black precipitate was centrifuged, washed with a mixture of hexane and absolute ethanol (V: V=1:2) for several times. Finally, the sediment was dried in an oven and kept at 90 °C for 12 h.

Characterization

X-ray diffraction (XRD, Rigaku Ultima-IV X-ray diffractometer, Cu-K α radiation) was applied to examine the crystallographic characteristics of the samples. And the morphologies and microstructures were investigated *via* scanning electron microscopy (SEM, HITACHI-SU8010) and transmission electron microscopy (TEM, FEI, model Talos F200 S), respectively. The surface chemical compositions and electronic states were analyzed via X-ray photoelectron spectroscopy (XPS, Thermo Fisher, model ESCALAB 250 Xi). Element ratios were obtained from Inductively coupled plasma spectrometer (ICP, Agilent 720ES (OES)). N₂ sorption isotherms and the corresponding BET surface area was obtained from Micromeritics ASAP 2460.

Electrochemical Measurements

The electrochemical characteristics of the V₂Se₉ were evaluated by assembling CR2032-type cells in an argon-

filled glove box (water and oxygen content less than 0.01 ppm). A slurry, mixed 70 wt% V_2Se_9 , 20 wt% carbon nanotubes (CNTs), and 10 wt% poly(vinylidene fluoride) (PVDF) in a solvent of *N*-methylpyrrolidone (NMP), was spread on the copper foil (Semidiameter: 6 mm) as the working electrode. Then, 1 M NaPF₆ in diglyme electrolyte (DME) and the sodium metal were employed as electrolyte and counter electrode, respectively. Finally, the Galvanostatic charge and discharge (GCD) tests were performed using a NEWARE battery system with the voltage windows of 0.1-2.8 V vs. Na⁺/Na. The cyclic voltammetry (CV) was measured using CHI660E electrochemical workstation. Among them, the voltage ranges of CV were 0.1-3.0 vs. Na⁺/Na.

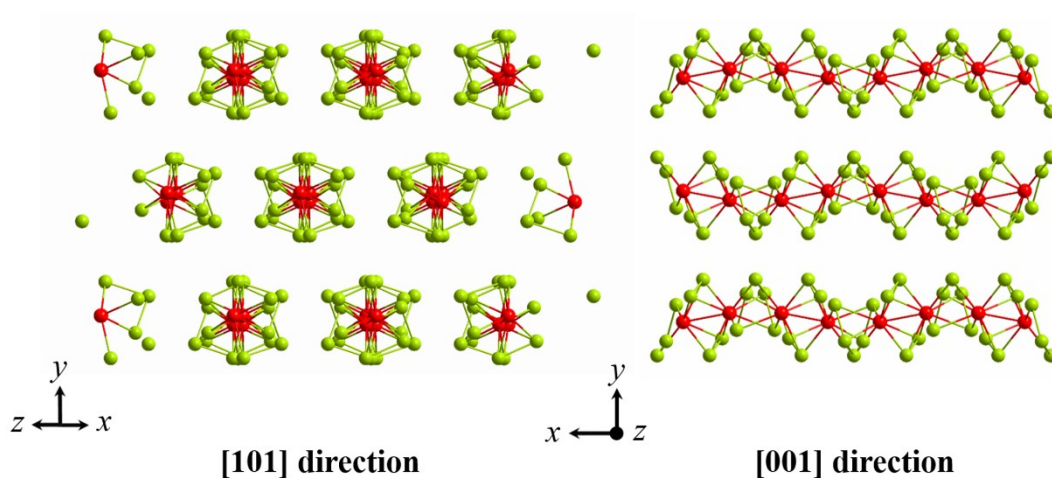


Fig. S1. Crystal structure diagram of V_2Se_9 along [101] and [001] crystal orientations (ball-stick model). Each V atom is bonded to eight Se atoms, and each Se atom is further bonded to two V atoms, and partial Se atoms bond with Se atoms.

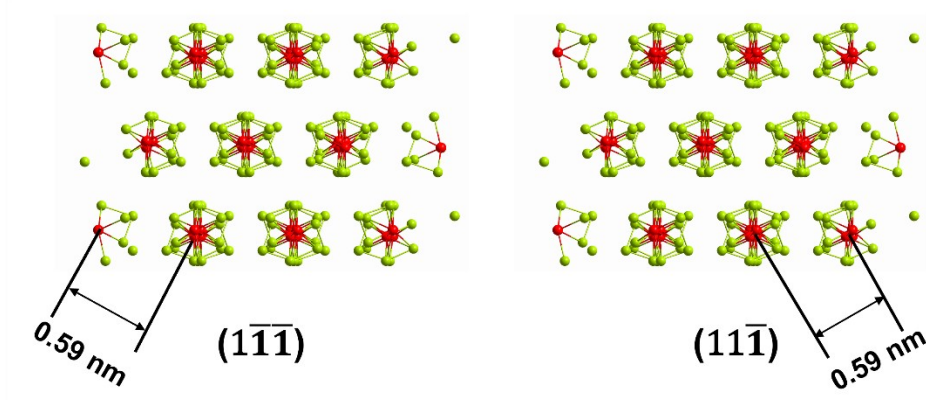


Fig. S2. Crystal structure diagram of V_2Se_9 in ($\bar{1}\bar{1}\bar{1}$) face and ($11\bar{1}$) face with corresponding crystal plane spacing.

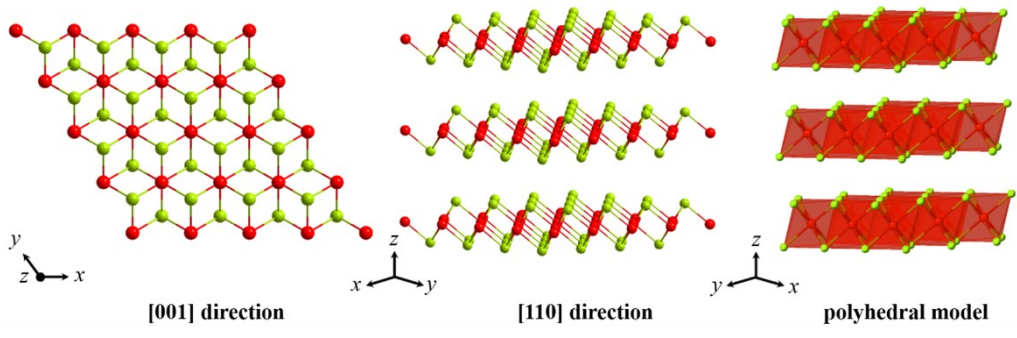


Fig. S3. Crystal structure diagram of VSe_2 along different crystal orientations (ball-stick model and polyhedral model). Each V atom is bonded to six Se atoms, while each Se atom is bonded to three V atoms to form $[VSe_6]$ octahedral structural units, which is parallel to the (001) crystal plane.

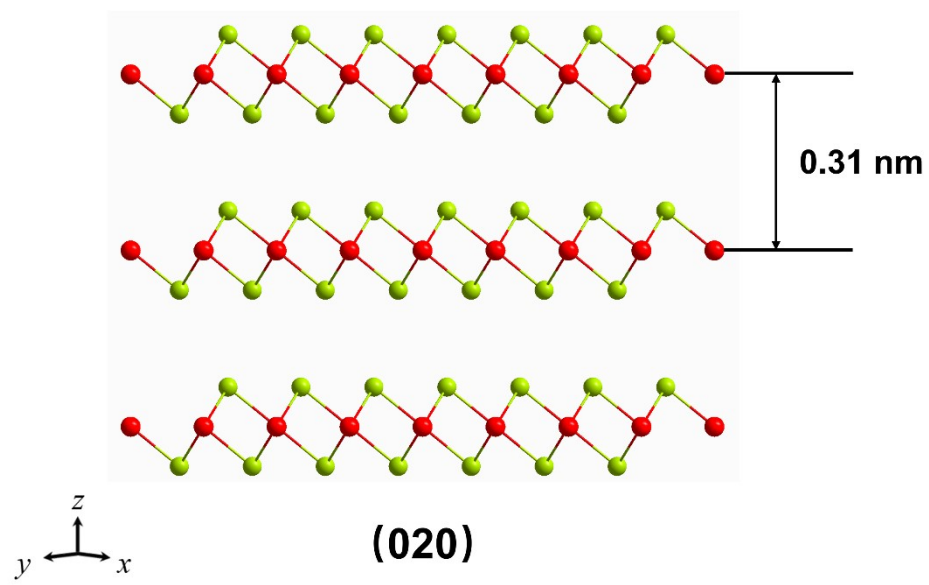


Fig. S4. Crystal structure diagram of VSe_2 and crystal plane spacing.

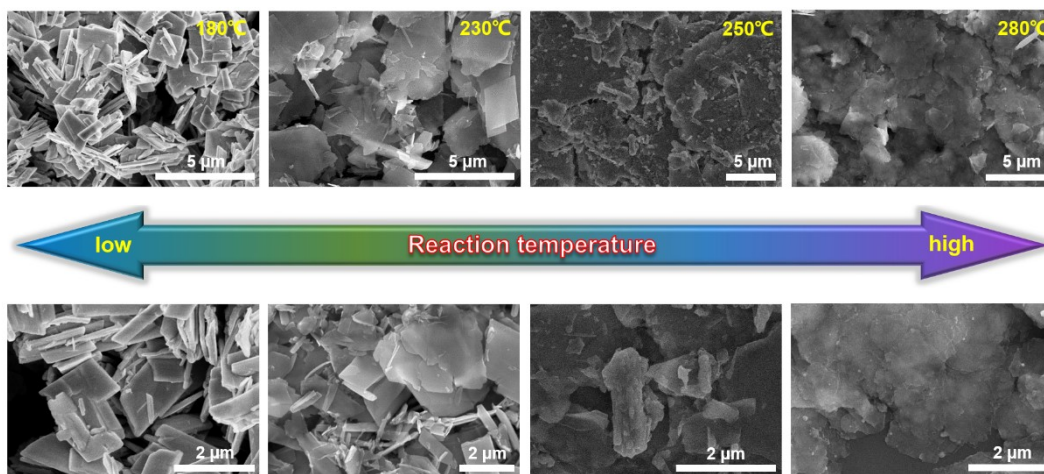


Fig. S5. SEM images of products as prepared at different reaction temperatures.

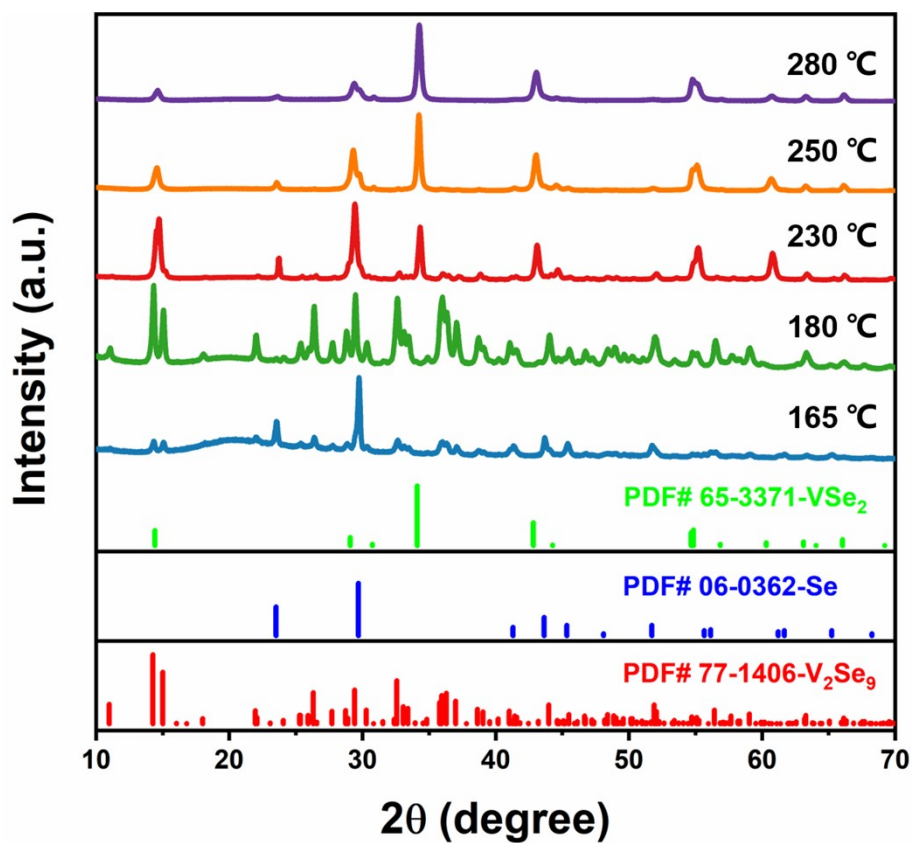


Fig. S6. XRD patterns of products as prepared at different reaction temperatures.

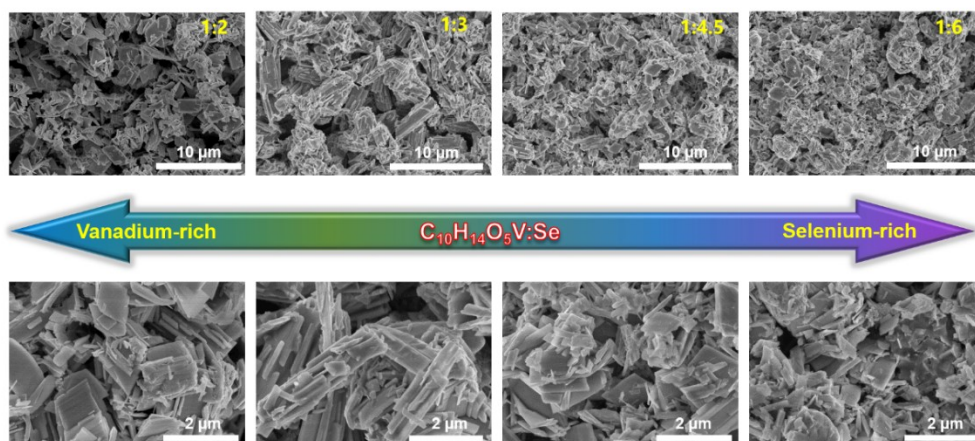


Fig. S7. SEM images of products as prepared at different molar ratio of vanadyl acetylacetonate and selenium powder.

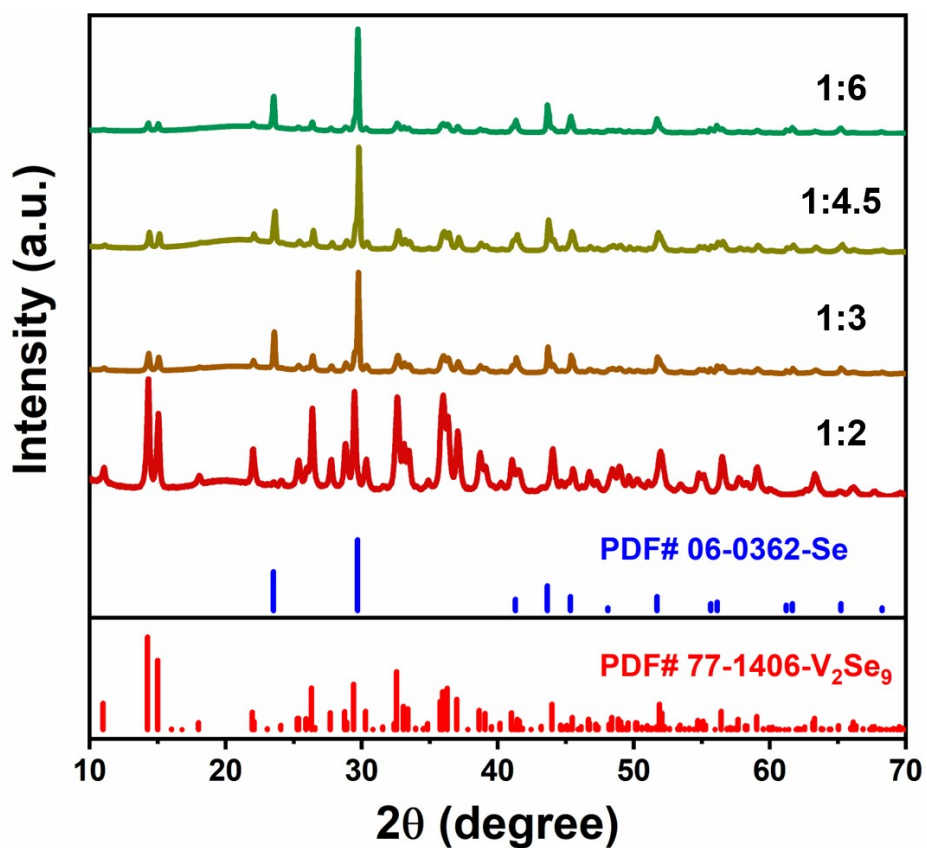


Fig. S8. XRD patterns of products as prepared at different molar ratio of vanadyl acetylacetonate and selenium powder.

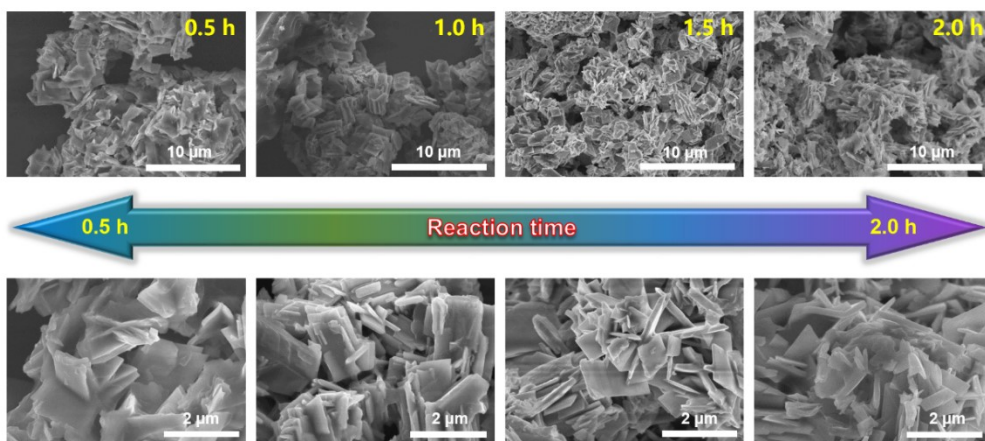


Fig. S9. SEM images of products as prepared at different reaction time.

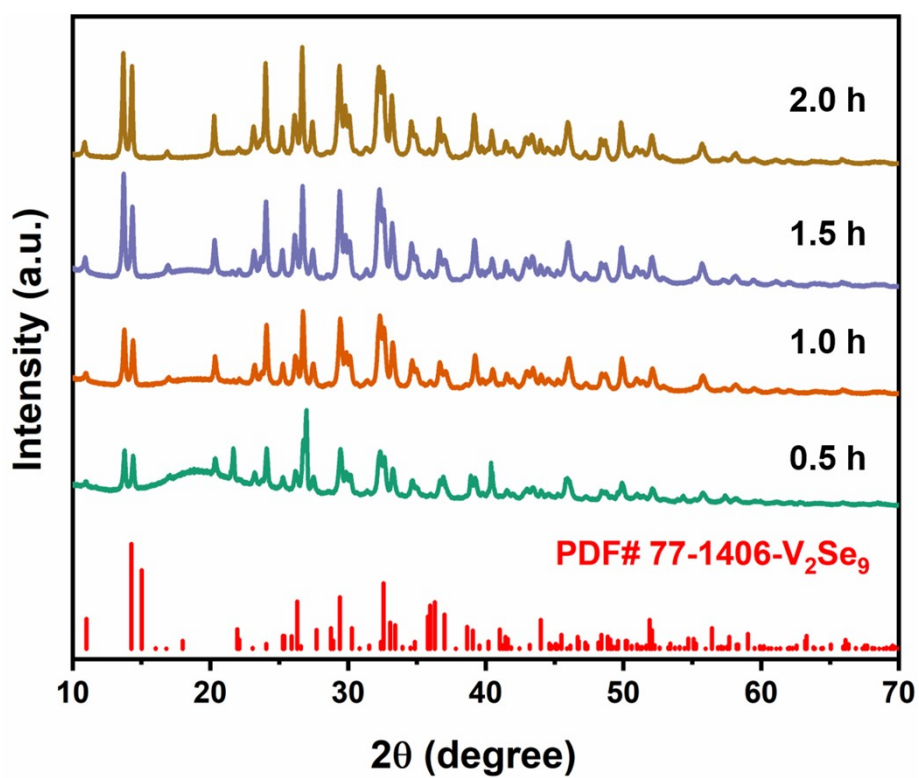


Fig. S10. XRD patterns of products as prepared at different reaction time.

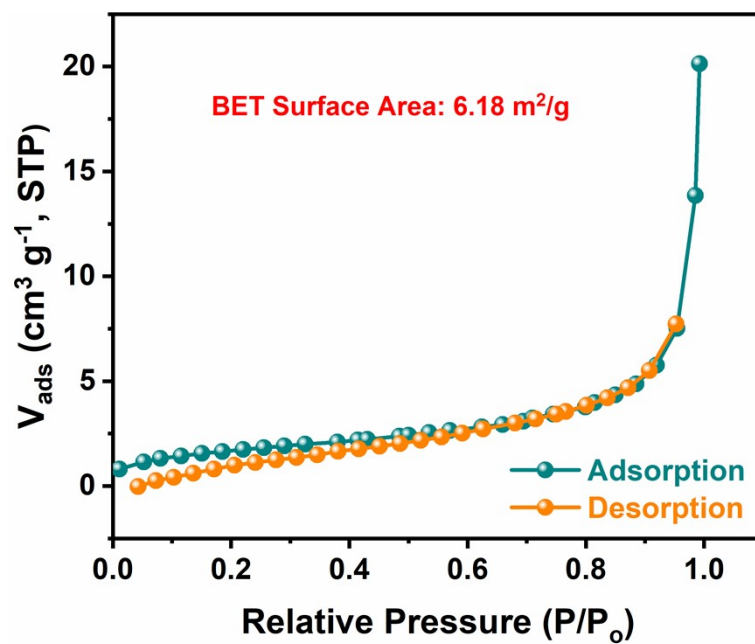


Fig. S11. N₂ sorption isotherms of V₂Se₉ materials.

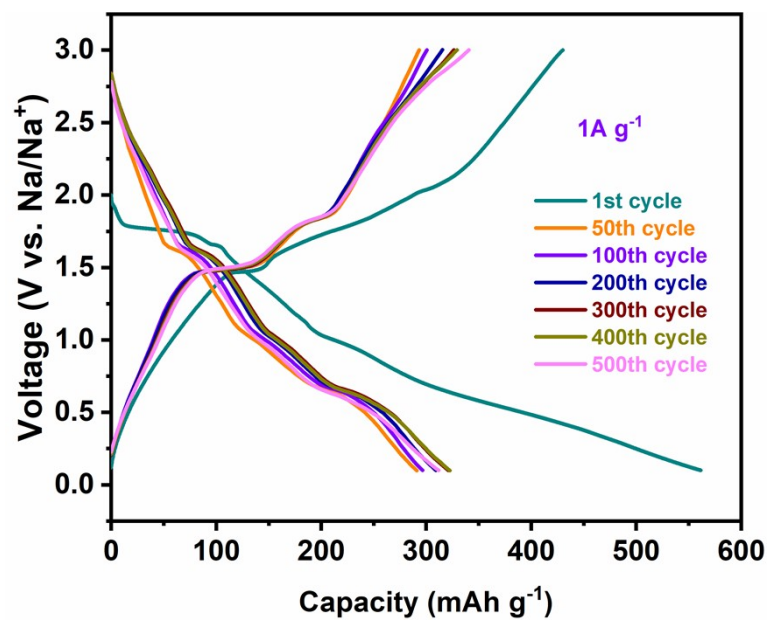


Fig. S12. Charge-discharge curves of V₂Se₉ anode at 1 A g⁻¹.

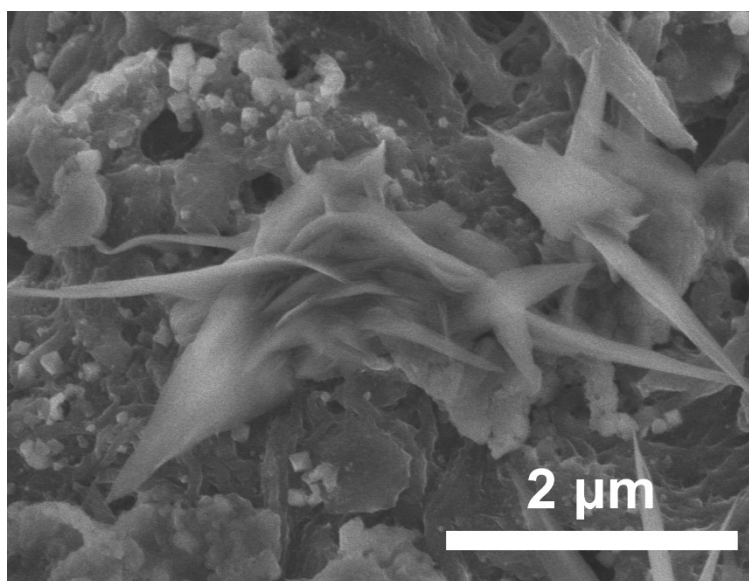


Fig. S13. SEM morphology of the V₂Se₉ electrode after cycled at 1 A g⁻¹.

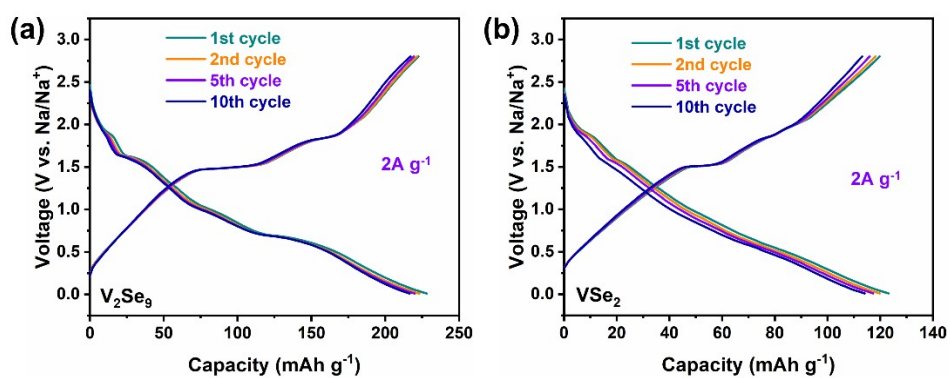


Fig. S14. Electrochemical performance of V₂Se₉ and VSe₂ anode at 2 A g⁻¹.

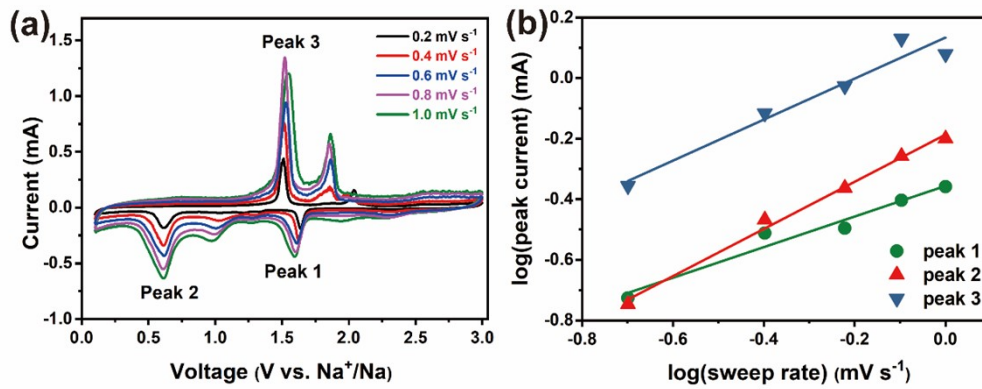


Fig. S15. The electrochemical Na^+ storage kinetic of V_2Se_9 . (a) CV curves at different scan rates with the corresponding $\log(i)$ versus $\log(v)$ plots (b) for anodic peaks and cathodic peaks. The current (i) and scan rate (v) obey a relationship of $i = av^b$ which also the formula for judging pseudocapacitive behavior. The values of i and v represent the peak current and scan rate, respectively, with a and b being constants connected to the matching results of i and v . Wherein, b as the judgment factor, the b -value of 1 indicates that the discharge-charge process is dominated by pseudocapacitive capacitance, and a b -value of 0.5 suggests that the electrochemical process is mainly controlled by ionic diffusion.

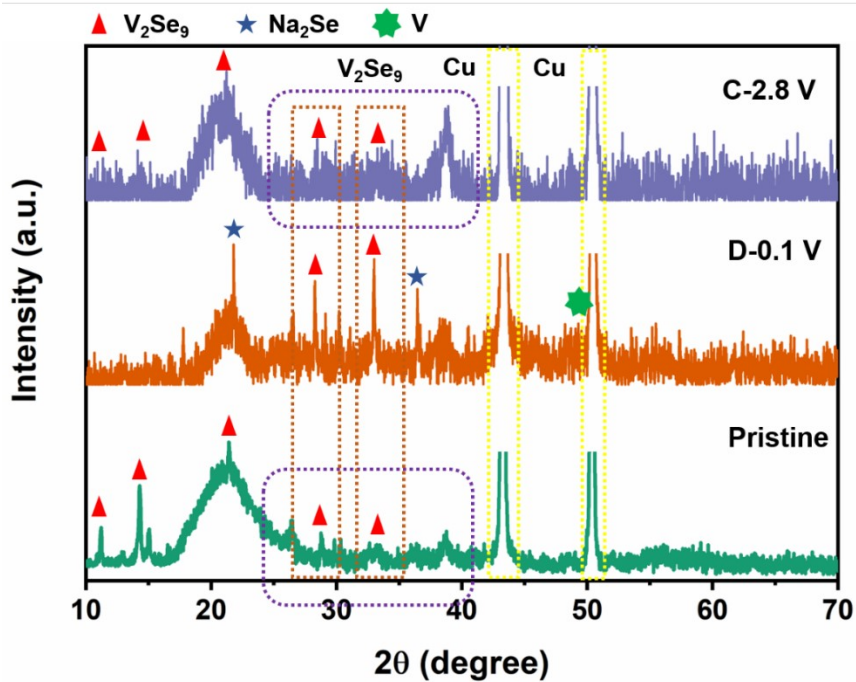


Fig. S16. Ex -situ XRD patterns of V_2Se_9 electrodes at different charge-discharge cutoff voltages.

Table S1 A comparison of the performance of our V2Se9 with VSe2 anodes in SIBs.

Samples (Before/after modification)	Voltage range (V)	Cycling performance (mAh g ⁻¹ /n/A g ⁻¹)	Ref.
VSe ₂ NSA VSe ₂ NSA/C	0.01-2.5	<300/50th/0.1 571/50th/0.1	1
VSe ₂ VSe ₂ /C	0.01-3	49/50th/0.1 467/50th/0.1	2
VSe ₂	0.01-3	~250/500th/1	3
VSe ₂ @MWCNT	0.01–2.7	469/200th/0.01	4
VSe ₂ VSe ₂ @3D-CN	0.01-3	<250/140th/0.2 ~460/140th/0.2	5
V2Se9	0.1-3	830/40th/0.05 311/500th/1	This work

References

- 1 F. Ming, H. Liang, Y. Lei, W. Zhang and H. N. Alshareef, *Nano Energy*, 2018, **53**, 11-16 11.
- 2 X. Yang and Z. Zhang, *Materials Letters*, 2017, **189**, 152-155.
- 3 Y. Yi, X. Du, Z. Zhao, Y. Liu, H. Guan, X. Liu, X. Pei, S. Zhang and D. Li, *ACS Nano*, 2022, **16**, 7772-7782.
- 4 Y. Jin, M. E. Lee, G. Kim, H. Seong, W. Nam, S. K. Kim, J. H. Moon and J. Choi, *Materials (Basel)*, 2023, **16**, 1253.
- 5 Z. Xue, Y. Feng, J. Lei, S. Wu, D. Xiong, L. Chen, Z. Feng, K. Wen, Z. Li and M. He, *Ionics*, 2023, **29**, 1127-1138.