Promoting Fast Potassium Storage in CoSe₂/VSe₂ Non-Layered/Layered Heterostructured Nanofibers

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1. Experimental Section

1.1 Materials synthesis

The synthesis of Co(acac)₂/VO(acac)₂@PAN was carried out on an electrospinning equipment (ss-2535H, Ucalery). Typically, 1 g Co(acac)₂, 1 g VO(acac)₂, 0.5 g polyacrylonitrile (PAN) (M_w = 150,000, Macklin) and 0.5 g polymethyl methacrylate (PMMA) (Sigma) were added in 10 ml N,N-dimethylformamide (DMF) (>99.5%, SCR). After stirring for 24 h, the resulting solution was injected into a 20 ml of syringe connected to a stainless steel needle (gauge no.20) and electrospun at a rate of 0.05 mm·min⁻¹. The applied voltage and distance between the tip of needle and the aluminum foil

collector were 20 kV and 20 cm, respectively. After electrospinning, the obtained membrane was first stabilized at 220 °C in air for 2 h, and then carbonized at 600 °C in argon for 2 h at a ramping rate of 2 °C min^{-1}. Subsequently, 0.1 g of the treated membrane was placed at the downstream zone and 0.4 g selenium powder were placed at upstream zone of a tube furnace. The CoSe$_2$/VSe$_2$@NCNF was obtained after thermal treatment at 450 °C for 4 h under Ar/H$_2$ (95:5). CoSe$_2$@NCNF and VS$_{e2}$@NCNF were synthesized with the same method with adding only one kind of acetyl acetone salt in the solution.

1.2 Materials characterizations

Field emission scanning electron microscope (FE-SEM, FEI Inspect F50) and transmission electron microscope (TEM, JEM2010F) were used to characterize the morphology the samples. The composition and crystallographic information were analyzed by X-ray diffraction (XRD Bruker, D8 Advancer; Cu $K\alpha$, $\lambda = 1.54$ Å). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Escalab 250Xi) were used to confirm the chemical states of elements in the as-prepared samples. Thermogravimetric (TG) analysis was performed on a TGA/DSC thermal analyzer (NETZSCH STA 449 C) in air with a heating rate of 10 °C·min^{-1} from R.T. to 800 °C to determine the content of the active material. The Nitrogen adsorption/desorption isotherms and pore size distribution were conducted on a surface analyzer (Kubo-X1000; Builder), and the specific surface area and pore size distribution were obtained *via* the Brunauer–Emmett–Teller (BET) method and Barrett– Joyner– Halenda (BJH) model.

1.3 Electrochemical Measurement

The working electrodes consist of the active materials (CoSe$_2$/VS$_{e2}$@NCNF, CoSe$_2$@NCNF and VS$_{e2}$@NCNF), Super P carbon black and polyvinylidene fluoride (PVDF) at the weight ratio of 7:2:1.

The Cu foil was used as the current collector and the mass loading of active materials is controlled at 0.8-1 mg cm^{-2}. To test the potassium storage performance, the working electrode was sealed in a CR2032 coin-type cell with K metal as the counter and reference electrodes and 1 M KPF$_6$ dissolved in dimethyl ether (DME) as the electrolyte. The testing voltage window is 0.01-3 V for galvanostatic charge-discharge tests and cyclic voltammetry (CV) measurement. The electrochemical impedance spectrum (EIS) measurements were conducted in the frequency range from 100 kHz to 0.1 Hz. All the capacities were calculated based on the weight of CoSe$_2$/VSe$_2$@NCNF.

1.4 Theoretical calculation

First-principle calculations were performed via the Density Functional Theory (DFT) method coupled with the Vienna Ab-Initio Simulation Package (VASP, University of Vienna, Austria).[1] The generalized gradient approximation (GGA) in the formulation of Perdew−Burke−Ernzerhof (PBE) was used to treat the exchange and correlation energy.[2, 3] The cutoff energy of 450 eV was adopted for the wave basis sets. The adsorption energy of K (ΔE_{ads}) was defined as

$$E_{ads} = E_{total} - E_{base} - E_K$$

where E_{total} is the total energy of the substrate adsorbed with K atom, while E_{base} and E_K are the energy of clean substrate and K atom, respectively.
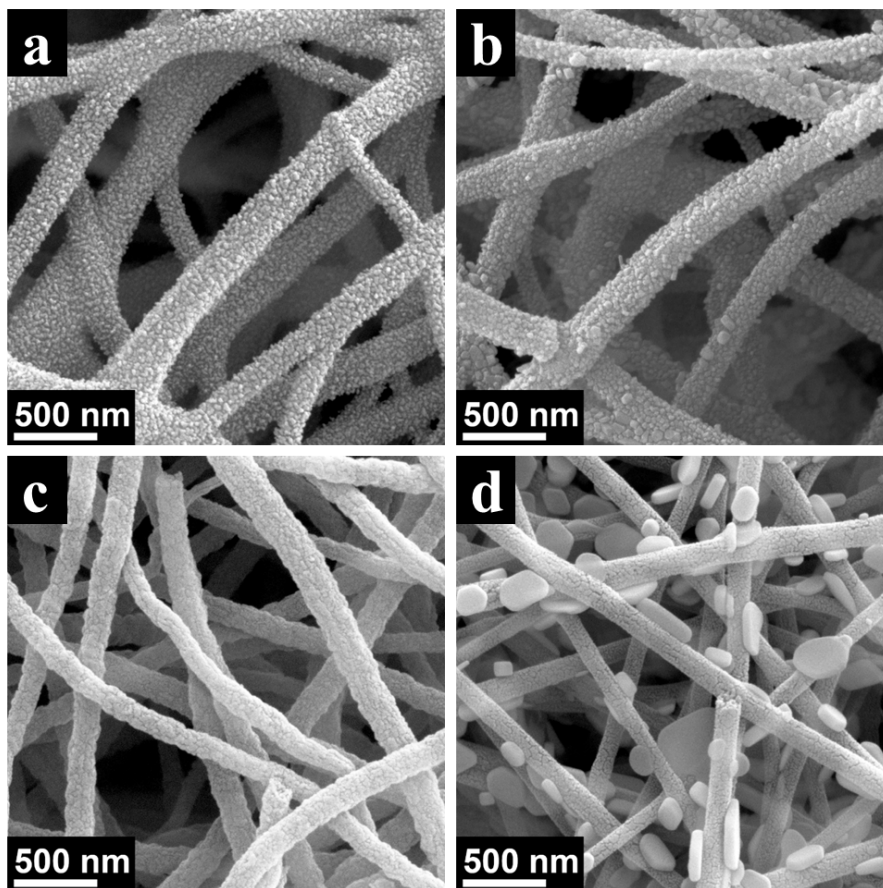
Figure S1 SEM images of (a) Co@NCNF, (b) CoSe$_2$@NCNF, (c) V@NCNF and (d) VSe$_2$@NCNF.
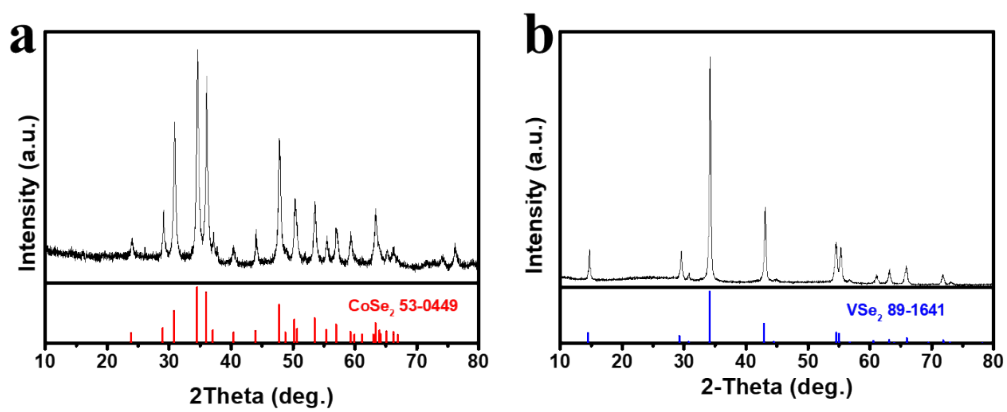

Figure S2 XRD pattern of (a) CoSe$_2$@NCNF and (b) VSe$_2$@NCNF.

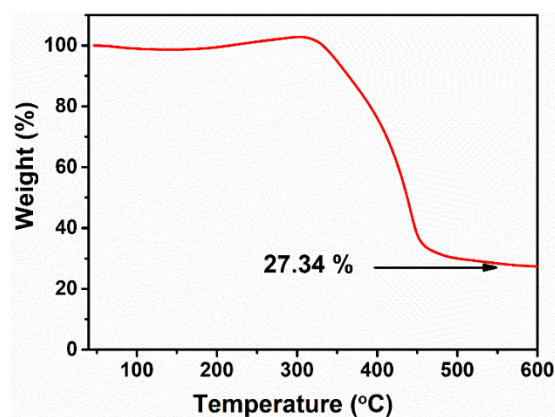**Figure S3**. TGA curves of CoSe$_2$/VSe$_2$@NCNF.

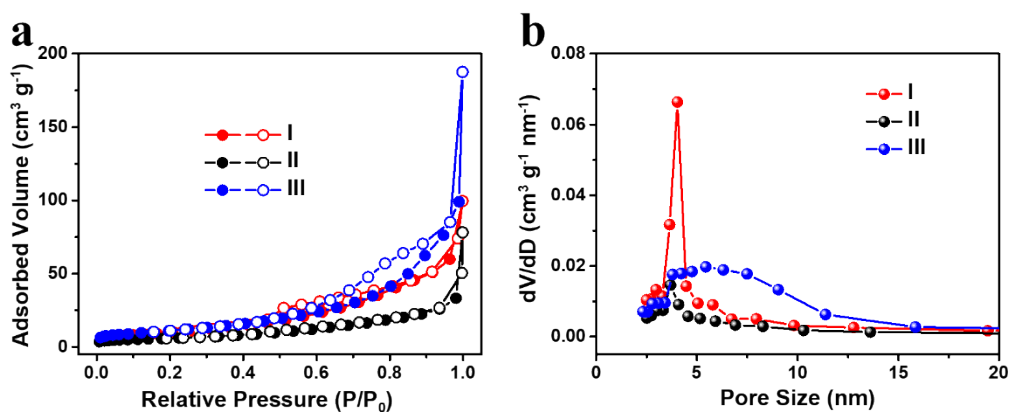**Figure S4** (a) N$_2$ adsorption-desorption isotherm and (b) the corresponding pore size distribution of (I) CoSe$_2$/VSe$_2$@NCNF, (II) CoSe$_2$@NCNF and (III) VSe$_2$@NCNF.
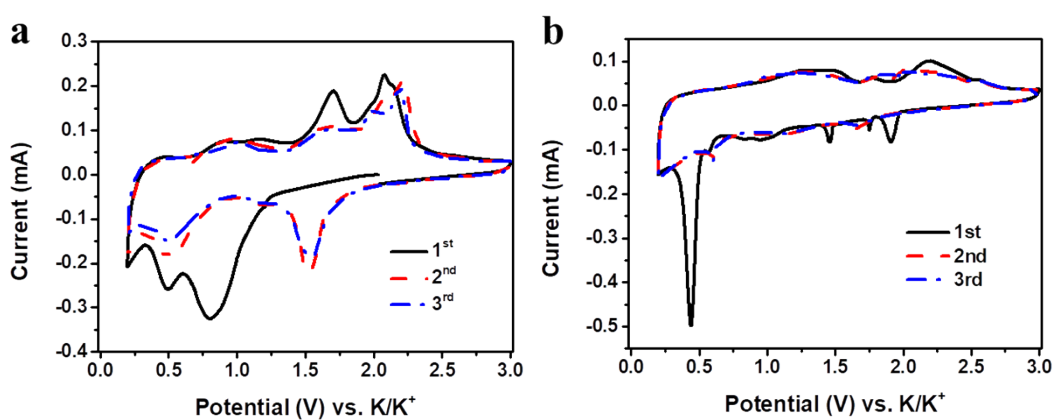
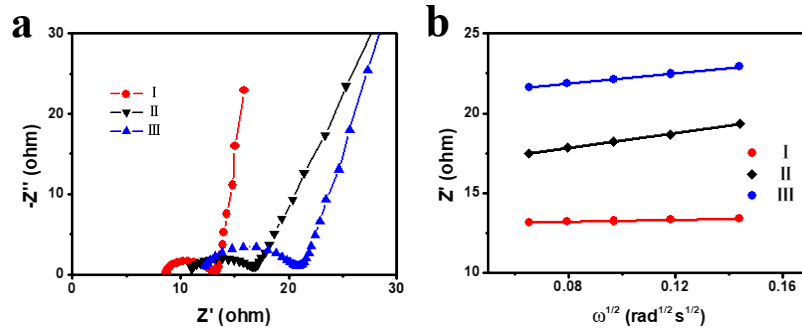**Figure S5** CV profiles of (a) CoSe$_2$@NCNF and (b) VSe$_2$@NCNF at the scan rate of 0.1 mV s^{-1}.

Figure S6. (a) The Nyquist plots, and (b) the linear relationships between Z' and $\omega^{-1/2}$ of (I) CoSe$_2$/VSe$_2$@NCNF, (II) CoSe$_2$@NCNF and (III) VSe$_2$@NCNF.

Table S1. Fitting data of the EIS results.

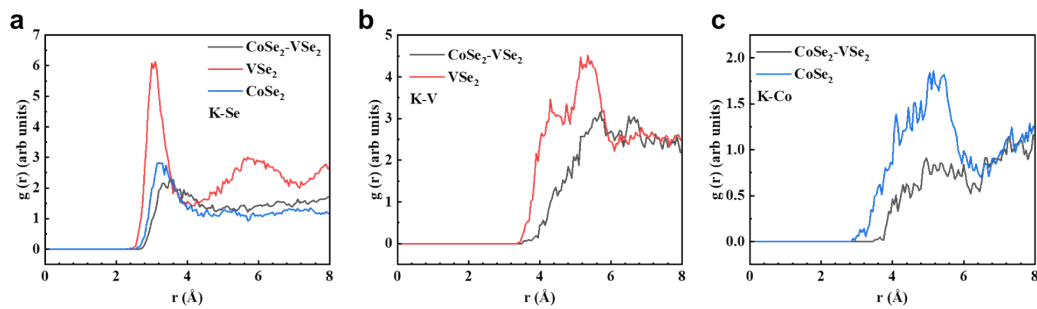| Sample	R_s (Ω)	R_{ct} (Ω)
CoSe$_2$/VSe$_2$@NCNF	8.37	4.91
CoSe$_2$@NCNF	10.39	6.77
VSe$_2$@NCNF	11.65	9.52

Figure S7 The calculated distribution functions of (a) K-Se atomic pairs in CoSe$_2$/VSe$_2$, VSe$_2$, and CoSe$_2$, (b) K-V atomic pairs in CoSe$_2$/VSe$_2$ and VSe$_2$, (c) K-Co atomic pairs in CoSe$_2$/VSe$_2$, and CoSe$_2$ at 1000 K.

Table S2. Comparison of the results in our study with those previously reported for PIBs.

Sample	ICE (%)	Current Density (A g^{-1})	Capacity (mAh g^{-1})	Reference
CoSe$_2$/VSe$_2$@NCNF	87.8	0.5	483	This Work
	-	5	325	
NbSe$_2$ NSs/G	-	5	140	[4]
WSe$_2$/MoSe$_2$	42.6	5	126	[5]
a-Bi$_2$S$_3$/c-Bi$_2$O$_3$	42.8	1	226	[6]
SnS$_2$/SnO$_2$	65.6	1	150	[7]
MoS$_2$/Ni$_3$S$_2$	59.6	5	184	[8]
MoSe$_2$-on-NC	-	5	171	[9]
Mo$_2$CT$_x$/MoSe$_2$	40.5	5	186	[10]
MXene/TiO$_2$	12.7	1	102	[11]
SnSe$_2$@C	60.4	1	200	[12]
Bi$_{0.4}$Sb$_{1.6}$Te$_3$	-	5	281	[13]
C-MoS$_{2-x}$/CNTs	40.7	5	170	[14]
Expanded graphite	60.4	500	182	[15]
Graphite	66.8	0.03	309	[16]

Reference

1.   P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953.

2. G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
4. J. Zhou, S. Zhao, F. Lv, H. Luo, S. Zhang, W. Zhang, F. Lin, W. Zhang, K. Wang, D. Wang and S. Guo, *Adv. Funct. Mater.*, 2024, DOI: 10.1002/adfm.202409301.
5. Z.-Y. Song, Y.-D. Cao, L.-L. Fan, J. Song, Y. Feng, H. Liu, C.-L. Lv and G.-G. Gao, *Rare Metals*, 2024, DOI: 10.1007/s12598-024-02906-3.
6. H. Yang, X. Zhang, W. Li, Y. Chen, X. Tang, Y. Wu, Q. Wei, X. Wang and H. Shu, *J. Mater. Chem. A*, 2024, **12**, 6093-6102.
7. G. Suo, D. Li, L. Feng, X. Hou, X. Ye, L. Zhang, Q. Yu, Y. Yang and W. Wang, *Journal of Materials Science & Technology*, 2020, **55**, 167-172.
8. J. Bai, J. Si, Y. Mao, H. Ma, P. Wang, W. Li, K. Xiao, G. Zhang, Y. Wei, X. Zhu, B. Zhao and Y. Sun, *J. Mater. Chem. A*, 2023, **11**, 12102-12113.
9. M. Ma, S. Zhang, Y. Yao, H. Wang, H. Huang, R. Xu, J. Wang, X. Zhou, W. Yang, Z. Peng, X. Wu, Y. Hou and Y. Yu, *Adv. Mater.*, 2020, **32**, 2000958.
10. Q. Jiang, W. Zhao, X. Xu, D. Ke, R. Ren, F. Zhao, S. Zhang, T. Zhou and J. Hu, *Chem. Commun.*, 2023, **59**, 13329-13332.
11. X. Zhang, J. Wang, Y. Jiang, M. Zhang, H. Min, H. Yang and J. Wang, *J. Mater. Chem. A*, 2024, **12**, 7598-7604.
12. Y. Huang, W. Wei, R. Haider, S. Ding, L. Wu, Y. Zhang, Y. Gu, W. Wen and X. Yuan, *Chem. Eng. J.*, 2024, **485**, 150037.
13. L. Zhang, J. Liu, Y. Zhai, S. Zhang, W. Wang, G. Li, L. Sun, H. Li, S. Qi, S. Chen, R. Wang, Q. Ma, J. Just and C. Zhang, *Adv. Mater.*, 2024, **36**, e2313835.
14. X. Wei, S. Tian, T. Wang, X. Zhang, J. Huang, P. Gao, Y. Feng, H. Zhang, J. Zhou and T. Zhou, *New J. Chem.*, 2024, **48**, 9110-9118.
15. K. Y. Zhang, H. H. Liu, M. Y. Su, J. L. Yang, X. T. Wang, E. Huixiang Ang, Z. Y. Gu, S. H. Zheng, Y. L. Heng, H. J. Liang, Y. Wang, S. Li and X. L. Wu, *J. Colloid Interface Sci.*, 2024, **664**, 607-616.
16. A. Xiao, Y. Chen, Z. Liu, R. Zhou, Y. Xue, Q. Zhang, J. Jiang, Q. Zhuang, Z. Ju and H. Song, *J. Alloys Compd.*, 2024, **981**, 173696.