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Electronic Supplementary Information



Fig. S1 (a, b) SEM images of PAN nanofibers.



Fig. S2 Digital photos of the flexible film: (a, b) PAN@ZIF-67 nanofibers, (c) CNF@Co@C composites.



Fig. S3 SEM images of the PAN@ZIF-67/ZIF-8 nanofibers (a, b) and PAN@ZIF-8 nanofibers (c, d).

Note: PAN@ZIF-67/ZIF-8 nanofibers were synthesized as well through same procedure of the PAN@ZIF-67 nanofibers but using 1 mmol $Co(NO_3)_2.6H_2O$ and 1 mmol $Zn(NO_3)_2.6H_2O$ dissolved in 20 deionized water, meanwhile, 1.3 g 2-MIM was dissolved into 20 ml deionized water as well. In addition, PAN@ZIF-67/ZIF-8 nanofibers were synthesized as well through same procedure of the PAN@ZIF-67 nanofibers but using 2 mmol $Zn(NO_3)_2.6H_2O$ dissolved in 20 deionized water, meanwhile, 1.3 g 2-MIM was dissolved into 20 ml deionized water as well.



Fig. S4 (a-c) SEM images of the CNF@Co@C composites.



Fig. S5 XRD pattern of the CNF@Co@C composites.



Fig. S6 (a, b) SEM images of the CNF@CoS₂@C composites, TEM (c) and HRTEM (d) images of the CNF@CoS₂@C composites.



Fig. S7 EDX spectrum of the CNF@CoSSe@C composites.



Fig. S8 SEM image of the CNF@CoSe2@C composites.



Fig. S9 XRD patterns of the CoSSe@C cmposites at different mass ratio between $CNF@CoS_2@C$ and Se powder.



Fig. S10 SEM images of the CoSSe@C composites at different mass ratios between CNF@CoS2@C and Se powder : (a, b) 2:1; (c, b) 3:1; (e, f) 4:1.



Fig. S11 EDX elemental mapping images of the CoSSe@C composites at different mass ratio between CNF@CoS2@C and Se powder: (a, b) 2:1; (c, b) 3:1; (e, f) 4:1.



Fig. S12 TGA curves of the CNF@CoSSe@C composites.



Fig. S13 (a) XPS survey spectrua of the CNF@CoSSe@C composites, (b) high-resolution C 1s spectra of the CNF@CoSSe@C, CNF@CoS2@C, CNF@CoSe2@C composites.



Fig. S14 Electrochemical performance of the CoSSe@C cmposites at different mass ratio between CNF@CoS2@C and Se powder.



Fig. S15 CV profiles of the electrodes at 0.5 mV s⁻¹: (a) CNF@CoS₂@C, (b) CNF@CoSe₂@C.



Fig. S16 GCD profiles of the electrodes at 1.0 A g⁻¹: (a) $CNF@CoS_2@C$, (b) $CNF@CoSe_2@C$.



Fig. S17 The differential capacity curves of the CNF@CoSSe@C electrode at 1.0 A g⁻¹.

Note: In Fig. S17a, two obvious cathodic peaks located at about 0.98 and 0.74 V agree with the CV results. As the cycle continues from 2 nd to 20 th cycle, a peak at about 1.47 V disappeared and meanwhile two new peaks at about 1.57 and 2.04 V were found. During the charging process from 1st to 20th cycle (Fig. S17b), the peaks at about 1.82 and 1.91 V are due to the stepwise desodiation process generating the single CoSSe or mixed CoS and CoSe structure. From 50th to 200 th cycle, an obvious anodic peak at 1.55 V appears. The appearance and transfer of these new redox peaks maybe raised by the continuous activation behaviors of the electrode material during the repeated Na⁺ de-intercalation.



Fig. S18 SEM images for the CNF@CoSSe@C film as binder-free anode after cycling.



Fig. S19 GCD profiles of the electrodes at different rates: (a) $CNF@CoS_2@C$, (b) $CNF@CoSe_2@C$.



Fig. S20 The cycling performance of the pure carbon at 20.0 A g^{-1} with a voltage window of 0.01-3.0V.



Fig. S21 In-situ Nyquist plots of the CNF@CoSSe@C composites at predetermined cycles.



Fig. S22 Scan rate-dependent CV curves (a), the plots of $\log i$ and $\log v$ at each redox peak (b), capacitive charge contribution (dark green shadow) at 2.0 mV s⁻¹ (c), and the normalized percentage of capacitive contributions at distinct scan rates (d) for the CNF@CoS₂@C electrode.



Fig. S23 Scan rate-dependent CV curves (a), the plots of $\log i$ and $\log v$ at each redox peak (b), capacitive charge contribution (dark green shadow) at 2.0 mV s⁻¹ (c), and the normalized percentage of capacitive contributions at distinct scan rates (d) for the CNF@CoSe₂@C electrode.



Fig. S24 Ex-situ XPS spectra of the CNF@CoSSe@C electrode at predetermined voltage states:(a) XPS Survey spectra; (b) High-resolution C 1s spectra.



Fig. S25 In-situ Nyquist plots of the CNF@CoSSe@C composites with respect to predetermined potentials within the 1st cycle.



Fig. S26 The surface slab models of the CoSSe, CoS₂, and CoSe₂.



Fig. S27 The Na⁺ migration energy barriers of the CoSSe, CoS₂ and CoSe₂ models.



Fig. S28 XRD pattern of the NVP@C.



Fig. S29 GCD profiles (a) and cycling performance (b) of the NVP@C cathode at 0.1 A g⁻¹.

Materials	Voltage	Rate	Cycle	Capacity	Ref.
	window (V)	(A g ⁻¹)	number	(mAh g ⁻¹)	
Cu-CoSe ₂ microboxes	0.01-3.0	1.0	500	374.0	1
CoSe ₂ @NC@TiO ₂	0.01-3.0	0.2	200	374.0	2
CoSe ₂ @CNF	0.01-3.0	2.0	1000	370.0	3
CoSe ₂ /WSe ₂ @@C/CNs	0.01-3.0	0.5	200	277.0	4
P-CoSe ₂ /C	0.01-3.0	0.2	200	322.0	5
Multishell CoSe ₂	0.01-3.0	1.0	2000	319.0	6
N-CNT/rGO/CoSe ₂	0.3-2.9	10.0	10000	264.0	7
Hollow microflower-	0.5-3.0	1.0	1690	220.0	8
like CoSe ₂					
CoS ₂ /Sb ₂ S ₃ @NC/CNT	0.01-3.0	0.5	200	360.1	9
rGO-CoS ₂ -GNCSs	0.4-2.9	1.0	400	412.3	10
f-Ti ₃ C ₂ /CoS ₂ @NPC	0.01-3.0	10.0	8000	104.1	11
AGC-CoS ₂ /NCNFs	0.01-3.0	3.2	1000	148.0	12
SnS ₂ -CoS ₂ @C	0.2-3.0	5.0	500	402.5	13
Cu-CoS ₂ @CuxS	0.4-2.6	0.3	300	385.0	14
CoS2@MCNFs	0.4-2.9	1.0	900	620.0	15
CNF@CoSSe@C	0.01-3.0	20.0	13000	158.2	This work

Table S1 Comparison of cycle lifespan and specific capacity of the CNF@CoSSe@C with previous reported CoS₂- and CoSe₂-based anodes in SIBs systems.

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