Supplementary Information

$FeSe_2/MoSe_2$ heterostructures: Interface engineering for enhanced high-rate sodium-ion storage

Manshu Han[a,*], Baofeng Mu[a], Yu Li[a,*], Zhehui Shen[a], Zixin Li[a], Rongyun Jiang[b], Minghua Chen[a], Qingguo Chen[a,*]

[a] *Key Laboratory of Engineering Dielectric and Applications (Ministry of Education), School of Electrical and Electronic Engineering, Harbin University of Science and Technology, Harbin 150080, P. R. China;*

[b] *School of Science, Tianjin Chengjian University, Tianjin, 300384，P. R. China.*

* Corresponding authors:

E-mails: hanmanshu@hrbust.edu.cn (Manshu Han); 13124501781@163.com (Yu Li); qgchen@263.net (Qingguo Chen).

1. Materials and chemicals

Selenium powder (Se) was purchased from Sinopharm Chemical Reagent. Ferrous phosphate ammonia-hexahydrate ($(NH_4)_2Fe(SO_4)\cdot 6H_2O$), sodium molybdate ($Na_2MoO_4$), hydrazine hydrate ($N_2H_4\cdot H_2O$) anhydrous citric acid were purchased from Aladdin. All chemicals were used directly and without any purification.

2. Material synthesis

2.1 Preparation of $FeSe_2$

The synthesis of $FeSe_2$ is based on the method of Mazumder with optimization.[17]

Specifically, add 2 mmol $(NH_4)_2Fe(SO_4)_2$-$6H_2O$, 20.8 mmol citric acid, and 4 mmol Se powder to 44 ml deionized water and stir well. After that, 16 ml of $N_2H_4 \cdot H_2O$ was added dropwise to the mixed solution, stirred vigorously, and sonicated for 1 h. The resulting $FeSe_2$ solution was extracted by centrifugation with deionized water and anhydrous ethanol at 10,000 rpm for 10 min 6 times and dried in an oven to obtain $FeSe_2$.

2.2 Preparation of spherical $FeSe_2/MoSe_2$ heterostructures

A typical procedure involves placing 2 mmol Na_2MoO_4 into 20 ml of deionized water and stirring for 10 minutes, labeled as solution A. 4 mmol Se was put into 10 ml of hydrazine hydrate and stirred for 20 min, marked as solution B. Next, Solution A is added drop by drop to solution B and stirred. Finally, the $FeSe_2$ obtained in the first step by hydrothermal was incorporated. Finally, 10 mmol, 20 mmol, and 30 mmol of $FeSe_2$ obtained by the first step of hydrothermal treatment were put into them for comparison in different proportions (5:1,10:1,15:1) and the hydrothermal reaction was performed at 200°C for 24 h. The different ratios of $FeSe_2/MoSe_2$ (5:1,10:1,15:1) were named FM-5, FM-10 and FM-15.

3. Structural characterization

For the $FeSe_2$, $MoSe_2$, and $FeSe_2/MoSe_2$ heterostructures, the crystal structures were measured by X-ray diffraction (XRD, Brucker AXS/D8 Advance powder diffractometer equipped with Cu K_α radiation, λ = 1.541 Å). The Raman spectrums measurement with a Witec Alpha 300 R confocal Raman microscope. Scanning

electron microscopy (SEM, Hitachi/SU8020) was used to analyze the morphology features. Atomic resolution images and elemental distribution were characterized by high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G^2 F20) and an energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) measurements were performed by Thermo Scientific ESCALAB 250Xi at Al-$K\underline{\alpha}$ source ($h\nu$ = 1486.6 eV).

4. Electrochemical measurement

A CR2032-type coin cell with $FeSe_2/MoSe_2$ as active material was assembled for battery testing. The anode material was prepared by mixing the active material ($FeSe_2/MoSe_2$ powder), conductive additive (Super P), and binder (carboxymethyl cellulose (CMC)) in a 7:2:1 weight ratio and dissolving them in deionized water for 6 h. The copper foil surface was coated with slurry and subsequently dried under vacuum at 60°C for 12 h. The half cells were assembled in a closed glovebox filled with argon gas, using a sodium thick plate as the counter electrode, glass fiber, and 1.0 M $NaClO_4$ (EC: DMC=1:1 vol% with 5% FEC) as separator and electrolyte, respectively. Cyclic voltammetry (CV) measurements were conducted using an electrochemical workstation (CHI660E) with a voltage range of 0.1 to 2.5 V. Cycle, rate and Galvanostatic intermittent titration technique (GITT) were tested at 200 mA current with a battery test system model CT-4008. Electrochemical impedance spectra were measured using a Parstat 3000A Princeton workstation in the frequency range of 0.01 to 100 kHz.

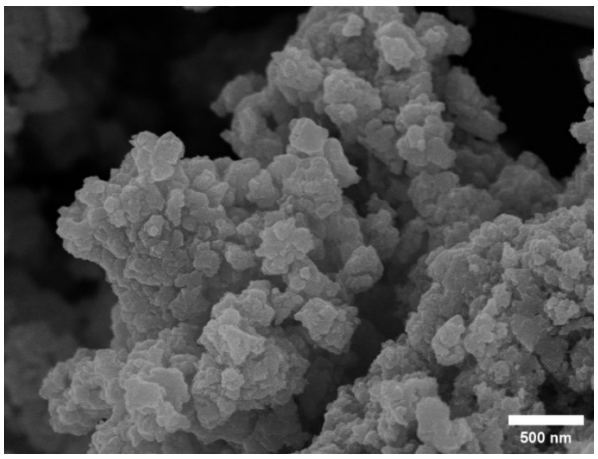

Fig. S1. SEM images of $MoSe_2$.

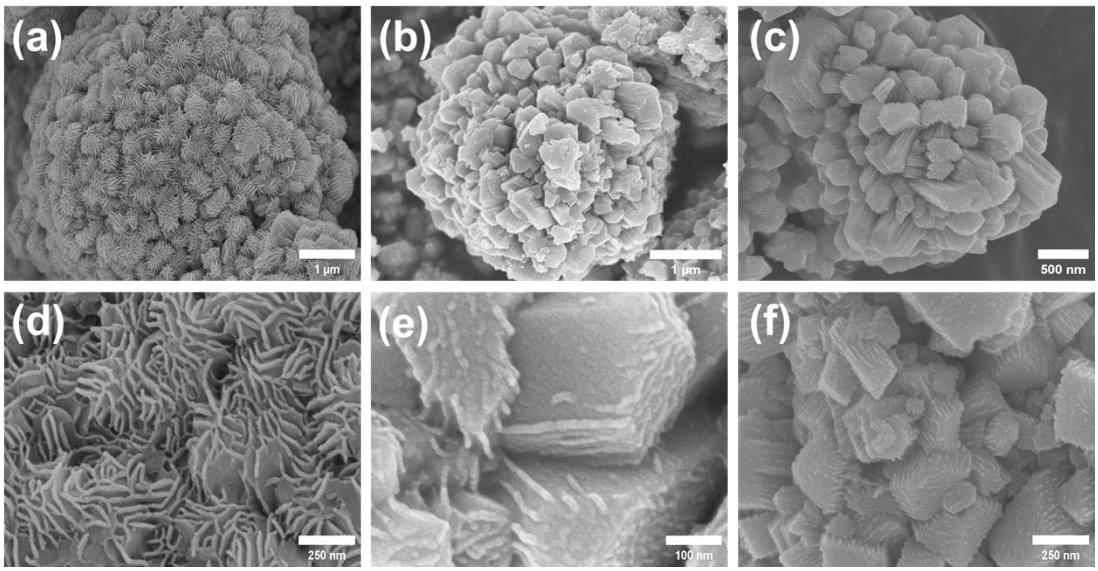

Fig. S2. SEM images for different ratios of $FeSe_2/MoSe_2$. (a, d) for FM-5, (b, e) for FM-10 and (c, f) for FM-15.

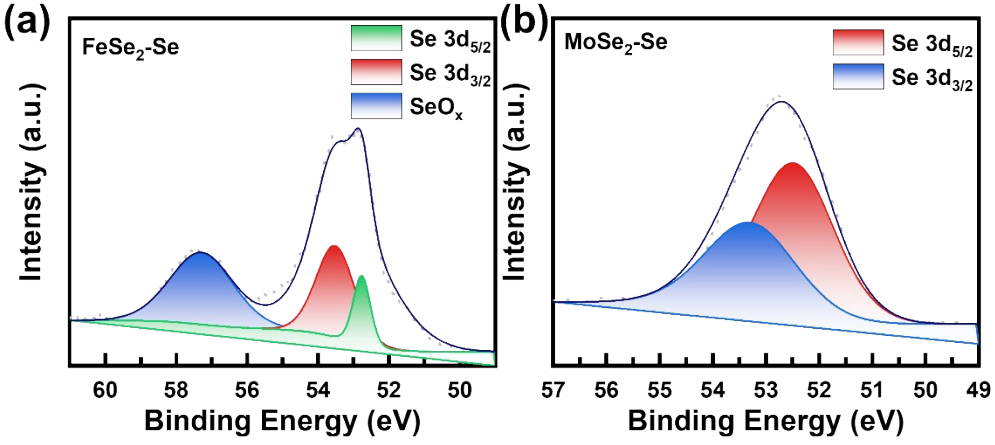

Fig. S3. (a, b) XPS of the Se elements in $FeSe_2$ and $MoSe_2$, respectively.

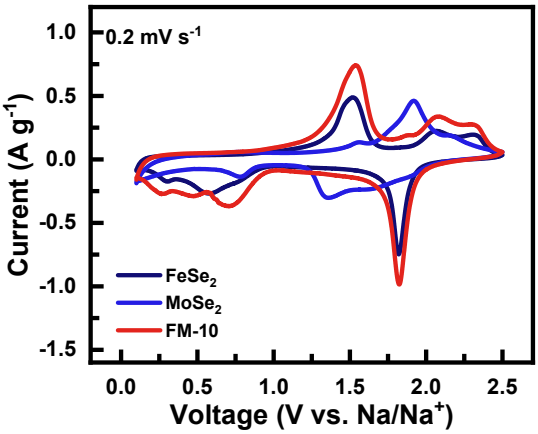

Fig. S4. CV curves of $FeSe_2$, $MoSe_2$ and FM-10 at 0.2 mV s^{-1}.

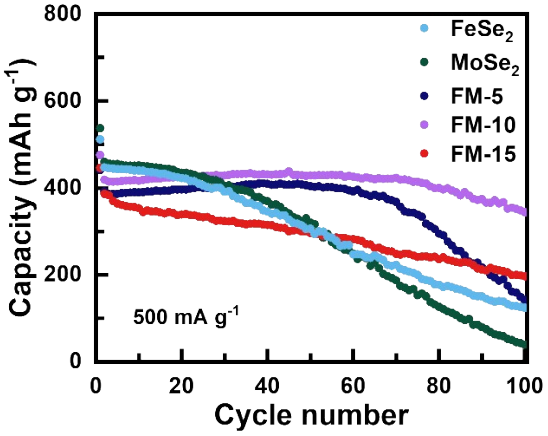

Fig. S5. Cycling characteristics of $FeSe_2$, $MoSe_2$, and different ratios of $FeSe_2/MoSe_2$ heterostructures at a current density of 500 mA g^{-1}.

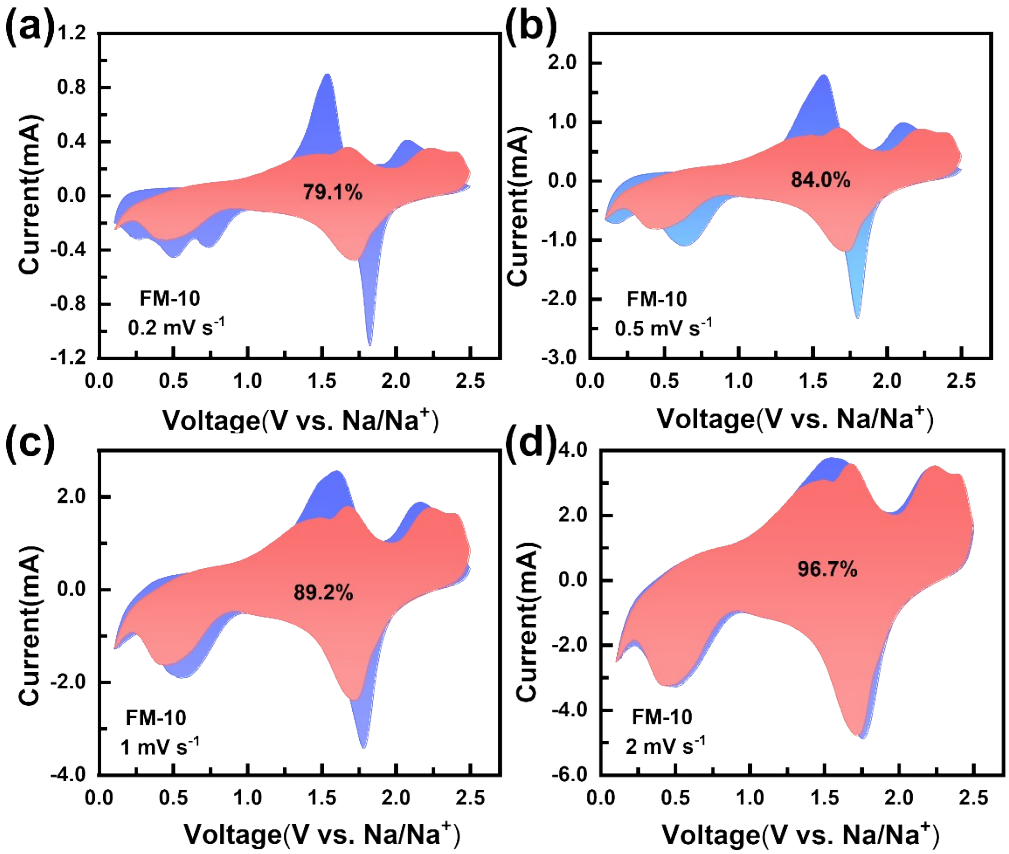

Fig. S6. Capacitive charge contributions for FM-10 at a scan rate of 0.2, 0.5, 1, and 2 mV s^{-1}.

Table S1. $FeSe_2$ and other anodes employed in SIBs with remarkable durability.

Materials	Morphology	CE	Voltage [V]	Current density [mA g^{-1}]	Cycles (n)	Capacity [mAh g^{-1}]	Year[Ref.]
$FeSe_2$/N-C	Rod-like	97.00%	0.5-3	100	100	439.2	2018[15]
$FeSe_2$@C	Hollow nanocube	89.30%	0.01-3	100	100	450	2017[14]
$FeSe_2$@rGO	Nanoparticles	98.30%	0.01-3	100	100	468.8	2018[28]
$FeSe_2$@C	flower-like nanosheets	≈100%	0.5-3	100	30	239	2022[38]
CNT/$FeSe_2$/C	Core shell	≈100%	0.01-3	100	100	450	2020[13]
$FeSe_2$@NC	spherical	≈100%	0.5-3	200	200	410.3	2022[23]
$CoSe_2$-$MoSe_2$/rGO	Rod-like	≈100%	0.01-3	100	200	533.5	2021[34]
$MoSe_2$/C	Nanosheets	≈100%	0.01-2.5	200	100	354	2018[39]
CNT/$MoSe_2$/C	Nanosheets	93.50%	0.01-3	100	100	484	2019[40]
HC@$MoSe_2$/WS_2@NC	spherical	≈100%	0.01-3	200	100	415	2024[42]

Fe_3Se_4-CoSe-C	Hierarchical porosity	≈100%	0.01-3	1000	100	400	2025[43]
$FeTiO_3/TiO_2$	spherical	≈100%	0.01-3	100	400	278	2024[44]
MX-Sb/Sb_2S_3@C-1.0	Nanosheets	≈100%	0.01-3	100	200	355	2024[45]
NCSe@NCSeO-YS	spherical	92%	0.01-3	200	50	446	2025[46]
$FeSe_2/MoSe_2$	spherical	≈100%	0.1-2.5	100	50	505.2	This work
				500	100	378.3	

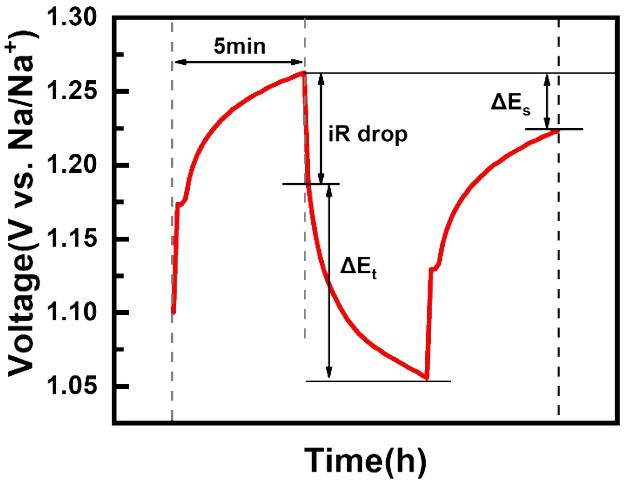

Fig. S7. E vs. t curves for the FM-10 electrodes for a single GITT.

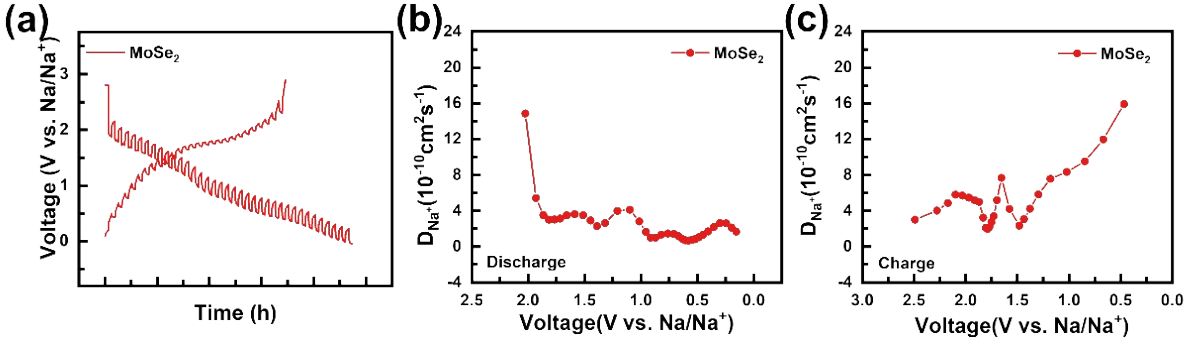

Fig. S8. (a) GITT curves measured at $MoSe_2$ electrodes. (b-c) Na^+ diffusion coefficients of $MoSe_2$ during charging and discharging.