

Supporting Information

Hierarchical Nanoarchitected Hybrid Electrodes Based on Ultrathin MoSe₂ Nanosheets on 3D Ordered Macroporous Carbon Frameworks for High-Performance Sodium-Ion Batteries

Yuanlin Liu^{b,†}, Nana Wang^{a,c,†}, Xunhua Zhao^a, Zhiwei Fang^a, Xiao Zhang^a, Yuanyue Liu^a, Zhongchao Bai^{a,c,*}, Shixue Dou^c, Guihua Yu^{a*}

Contents:

1. **Experimental Section**
2. **Fi. S1.** SEM images of SiO₂.
3. **Figure S2.** a) XRD pattern of the MoO₂@C.
4. **Figure S3.** a, b) SEM images 3DOM MoO₂@C. c, d) TEM images.
5. **Figure S4.** SEM images of 3DOM MSC.
6. **Figure S5.** a,) XRD pattern. b, c) SEM images and d, e) TEM images of MoP@C.
7. **Figure S6.** a) XRD pattern. b, c) SEM images and d, e) TEM images of MoS₂@C.
8. **Figure S7.** a) XRD pattern. b, c) SEM images and d, e) TEM images of Mo₂C@C.
9. **Figure S8.** XRD patterns of MSC and C-MSC.
10. **Figure S9.** XPS spectra of MSC: Se 3d.
11. **Figure S10.** SEM images of pure MoSe₂.
12. **Figure S11.** XRD pattern of the C-MSC nanocomposite after full oxidation at 600 °C in air.
13. **Figure S12.** The electrochemical performance of MSC and MS as anode materials for SIBs. a) CV curves of MSC at a scan rate of 0.1 mV s⁻¹ for the first three cycles. b) MS at a scan rate of 0.1 mV s⁻¹ for the first three cycles. c) CV curves of C-MSC and MSC at the third cycle.
14. **Figure S13.** a) Discharge/charge curves of MSC at 0.5 A g⁻¹. c) Discharge/charge curves of MS at 0.5 A g⁻¹.
15. **Figure S14** Charge-discharge curves of 3D-C at a current density of 0.5 A g⁻¹.
16. **Figure S15.** Discharge capacities of C-MSC with different areal loadings.

17. **Figure S16.** SEM images of C-MSC composite as anode materials for SIBs. a,b) after 100 cycles at the current density of 0.5 A g^{-1} .
18. **Figure S17.** Nyquist plots for the electrodes made of C-MSC, MSC, MS.
19. **Figure S18.** SEM images of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$.
20. **Figure S19.** The electrochemical performances of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material for SIBs. a) Cycling stability at 0.1 A g^{-1} . b) Discharge/charge profiles at different cycles under a current density of 0.1 A g^{-1} . c) Rate performance and d) XRD pattern of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.
21. **Figure S20.** The electrochemical performances of the C-MSC// $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Na-ion full cell material for SIBs. Cycling performance at $0.5 \text{ A g}^{-1}_{\text{anode}}$ (the capacity is calculated by the mass of anode).
22. **Table S1.** SIB performance summary of MoSe_2 -based hybrids and their analogues.

Experimental Section

Synthesis of 3DOM $\text{MoO}_2@\text{C}$ framework

The 3DOM $\text{MoO}_2@\text{C}$ framework was synthesized via a template route using silica spheres as the template obtained by Stober's method (Figure S1). First, The SiO_2 nanospheres, polyvinylidene fluoride (PVDF) and Bis(acetylacetonato)-dioxomolybdenum(VI) ($\text{MoO}_2(\text{acac})_2$) were dispersed in NMP solution at appropriate proportion, and then, dried at $80 \text{ }^\circ\text{C}$ overnight to get a well-mixed mixture. The mixture calcined at $500 \text{ }^\circ\text{C}$ for 2 h in N_2 atmosphere to convert PVDF into carbon materials, $\text{MoO}_2(\text{acac})_2$ into MoO_2 . Afterwards, the resultant product was immersed in HF solution for 24 h to remove SiO_2 template, resulting in 3DOM $\text{MoO}_2@\text{C}$ framework formation.

Synthesis of 3DOM $\text{MoSe}_2@\text{C}$

In a typical procedure for 3DOM $\text{MoSe}_2@\text{C}$, Selenium (0.316 g) was dissolved in 10 ml hydrazine hydrate followed by adding the $\text{MoO}_2@\text{C}$ (0.472 g) and 50 ml deionized water to form a black suspension under intensively magnetic stirring at room temperature. The as-prepared suspension transferred into Teflon-lined stainless-steel autoclave with 80 mL and kept at $200 \text{ }^\circ\text{C}$ for 24 h. After cooling naturally, the powder was collected by filtered and washed with deionized water and

absolute ethyl alcohol several times, and subsequently dried at 80 °C overnight, forming 3DOM MoSe₂@C (MSC). The obtained MSC was further calcined in N₂ atmosphere at 600 °C for 5 hours to combine carbon and molybdenum selenide more tightly, producing calcined MSC (C-MSC). The pristine MoSe₂ (MS) was prepared by Na₂MoO₄ rather than MoO₂@C via the same hydrothermal process of MSC.

Synthesis of 3DOM MoP@C:

In this general phosphating process, the MoO₂@C and NaH₂PO₂ were put into a tube furnace for calcination at a weight ratio of 1: 10, among that, the NaH₂PO₂ at upstream under H₂ (5%)/Ar₂ atmosphere keeping 2 h at 800 °C with the heating rate of 5 °C/min. After cooling down to room temperature, the MoP@C was obtained.

Synthesis of 3DOM MoS₂@C

The synthetic procedure of 3DOM MoS₂@C is the same as 3DOM MoSe₂@C except change selenium into sulfur.

Synthesis of 3DOM Mo₂C@C

The synthesis of 3DOM Mo₂C@C is also very similar to that of 3DOM MoS₂@C. The difference is calcination of 3DOM MoO₂@C in hydrogen at 500 °C for 2 h. After naturally cooling down to room temperature, the black powder is 3DOM Mo₂C@C.

Synthesis of Na₃V₂(PO₄)₃/C:

The Na₃V₂(PO₄)₃/C (NVP/C) was synthesized according to the work by Yang et al.⁶⁰ The NH₄VO₃: NaH₂PO₄: C₆H₁₂O₆ were added into 20 mL of ethyl alcohol at the weight ratio of 1.37: 2.106: 0.613. And then, the solution was milling at 600 rpm for 24 h in a planetary ball mill. And then, the slurry was dried for 12 h in a vacuum oven and heated at 800 °C for 4 h under flowing Ar₂/H₂ (5%) atmosphere to form the NVP/C.

Material Characterization

The crystalline structure and morphology of the products were examined by transmission electron microscope (TEM, JEOL JEM 1011, Japan), high-resolution transmission electron microscopy (HRTEM, JEOL 2100, Japan) and scanning electron microscopy (SEM, JEOL JSM-7100F). The composition and crystalline structure of the synthesized samples were characterized by X-ray diffraction (XRD, Bruker D8 Advanced, Germany). Raman spectra were acquired on a Raman spectrometer (NEXUS 670, Nicolet), and thermal gravimetric analysis (TGA) was

measured on a thermal analyzer (Mettler Toledo TGA/SDTA 851) in the air from room temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Scientific K-Alpha using an Al K α X-ray source.

Electrochemical measurements

The anode electrode material, MoSe₂@C (C-MSC) composites, acetylene black and polyvinylidene fluoride (PVDF) at the proportion of 7:2:1 was adequately milled with the solvent of N-methyl-2-pyrrolidinone (NMP) solution. Then, copper foil was pasted by the forming slurry, dried at 60 °C overnight under vacuum and punched into the round slices (12 mm diameter) with mass loading about 1.0 mg cm⁻¹. As the anode electrode in sodium ion battery, the obtained disc was assembled with the counter electrode (fresh sodium foil) and separator (Whatman GF/F) in an argon-filled glove box. Additionally, 1 M NaPF₆ in diglyme became the electrolyte transporting ions. Finally, all cyclic voltammetry (CV) curves were measured in a CHI760E electrochemistry workstation at a scan rate of 0.1 mV s⁻¹ under the voltage range from 0.01-3.0 V. Galvanostatic discharge/charge tests were carried out on a LAND battery-test instrument (CT2001A) within the potential window of 0.01-3.0 V. Electrochemical impedance spectroscopy (EIS) was tested at a CHI-760E electrochemical workstation in 0.01-100 kHz frequency range.

The homemade Na₃V₂(PO₄)₃/C (NVP/C) (80 wt %) as the cathode material in full cell, the acetylene black (10 wt %) and PVDF (10 wt %) were dispersed in NMP solution to form a wilt slurry film adhering to the aluminum foil. After dried at 60 °C under vacuum overnight, the aluminum foil was punched into round slice with the diameter of 16 mm. As the cathode materials, the rate and cycling performance of NVP/C were examined under the potential range of 2.5-3.8 V. With the proportion of capacity for anode MoSe₂@C and cathode NVP/C was 1:1.2-1.4 in the full cell, the Galvanostatic measurements were respectively conducted on LAND CT2001A battery test system from 3.8 V to 1.0 V.

Details of DFT calculations

We model contact between MoSe₂ and Graphene (Gr) by using a 6×4 MoSe₂ flake interacting with the Graphene substrate which is a (8×8) periodic layer. All the DFT calculations were conducted with the Vienna Ab initio Simulation Package (VASP).⁵⁰ The typical GGA-PBE

functional is used to obtain the total energy, together with DFT-D3 method to count dispersion correction. $3 \times 3 \times 1$ k-points were sampled in the calculations.^{51,52} The cutoff energy for the planewave basis is 400 eV and the electronic smearing was chosen as gaussian type with width of 0.03 eV. All the structures are relaxed until the maximum force is smaller than 0.01 eV/Å.

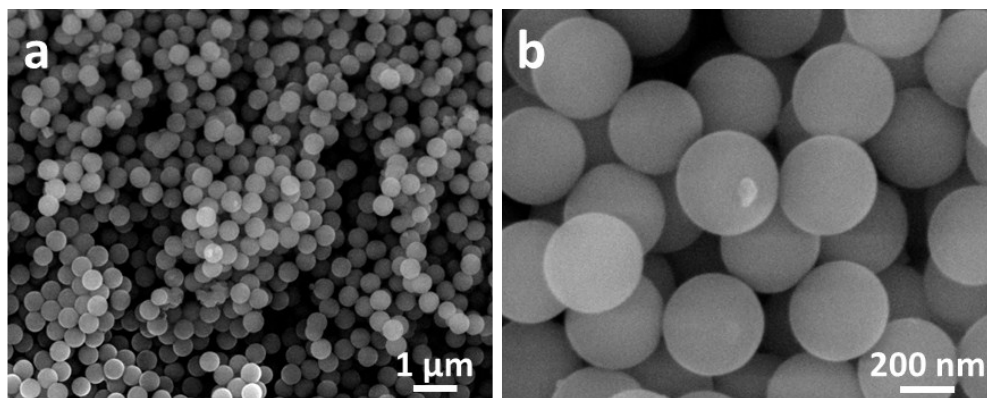


Figure S1. SEM images of SiO₂.

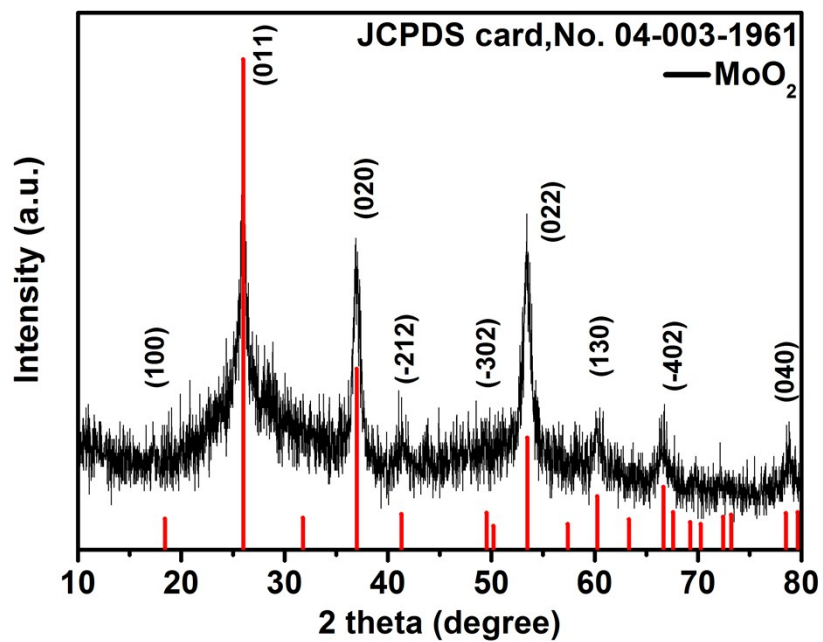


Figure S2. XRD pattern of the MoO₂@C.

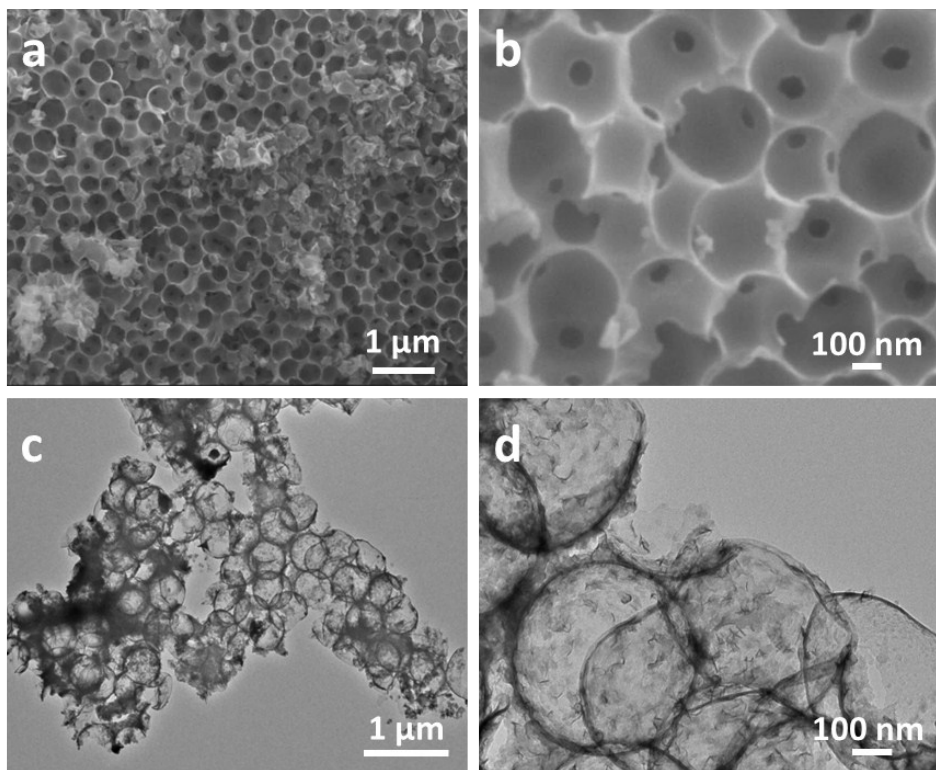


Figure S3. a, b) SEM images 3DOM MoO₂@C. c, d) TEM images.

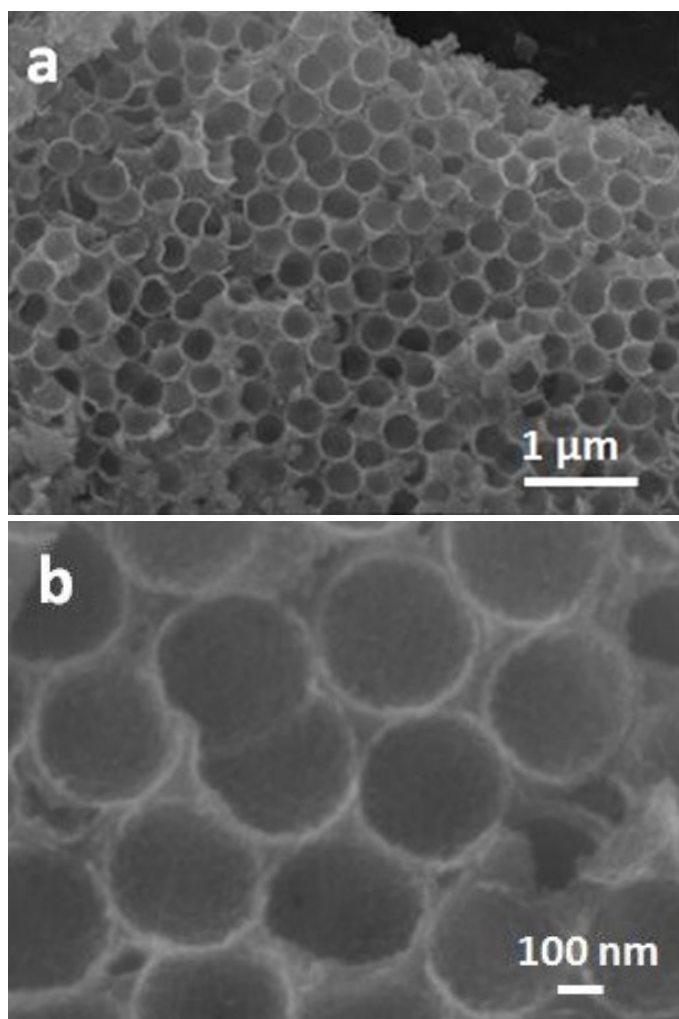


Figure S4. SEM images of 3DOM MSC.

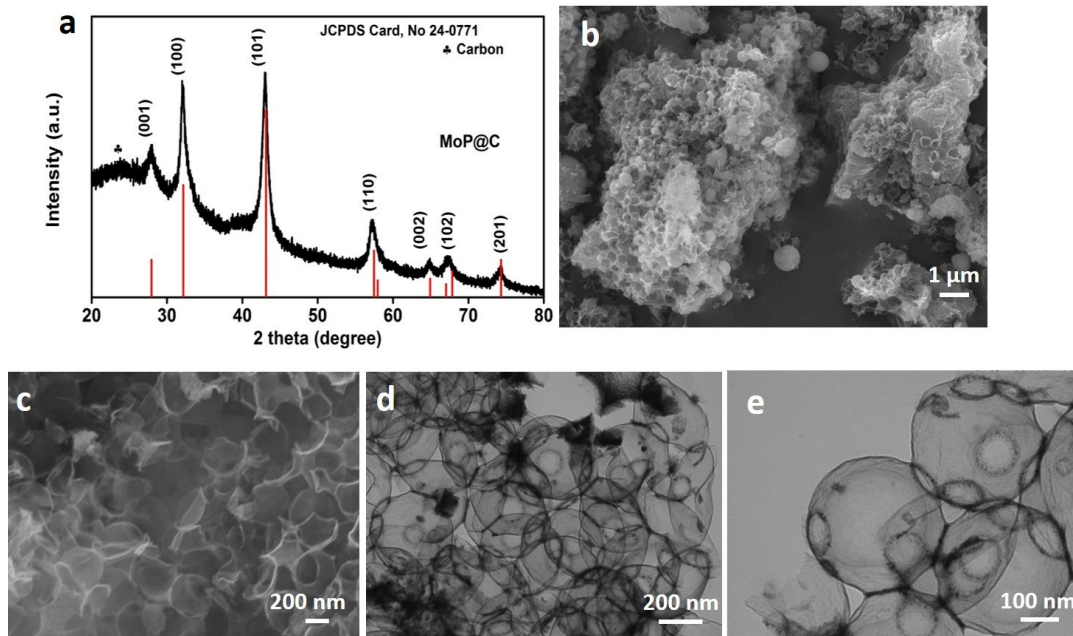


Figure S5. a,) XRD pattern. b, c) SEM images and d, e) TEM images of MoP@C.

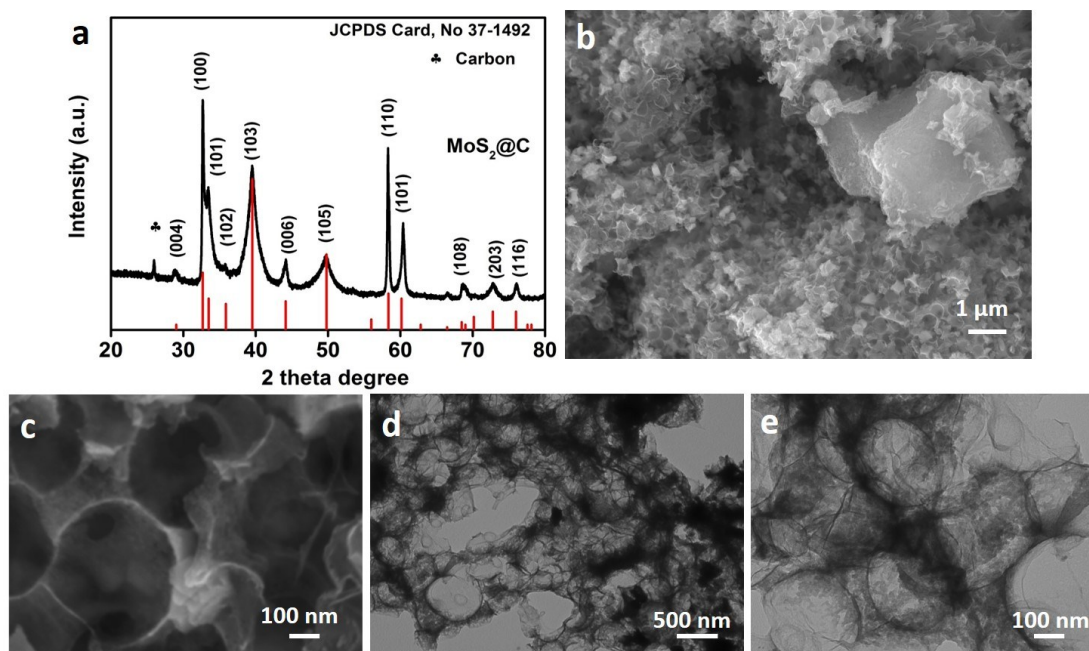


Figure S6. a) XRD pattern. b, c) SEM images and d, e) TEM images of MoS₂@C.

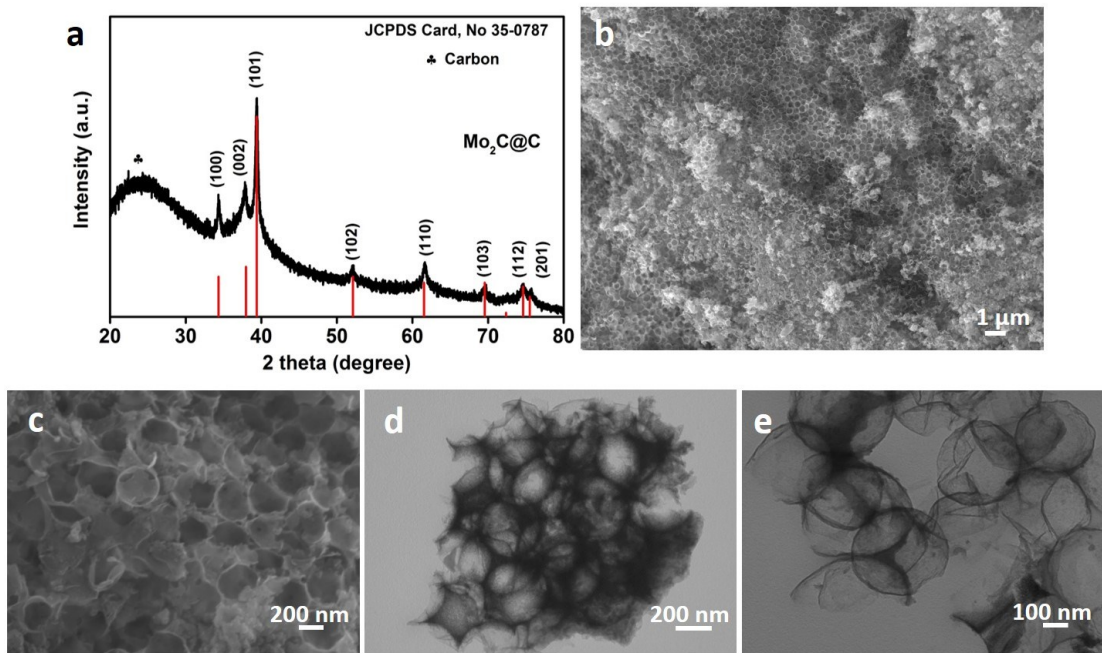


Figure S7. a.) XRD pattern. b, c) SEM images and d, e) TEM images of Mo₂C@C.

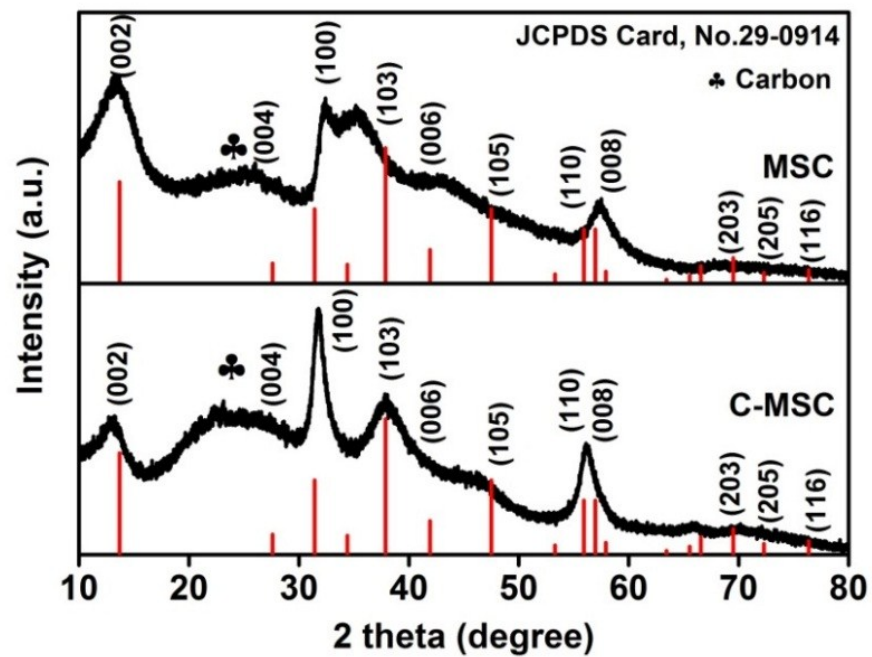


Figure S8. XRD patterns of MSC and C-MSC.

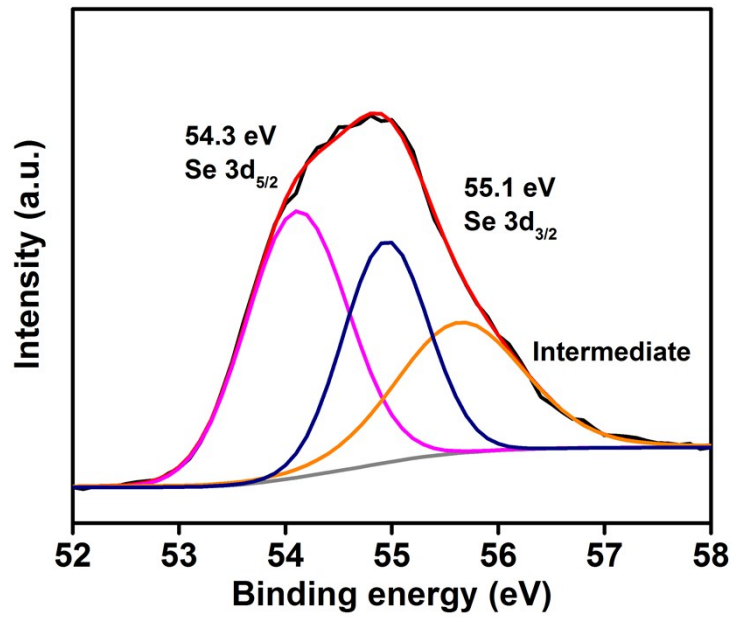


Figure S9. XPS spectra of MSC: Se 3d.

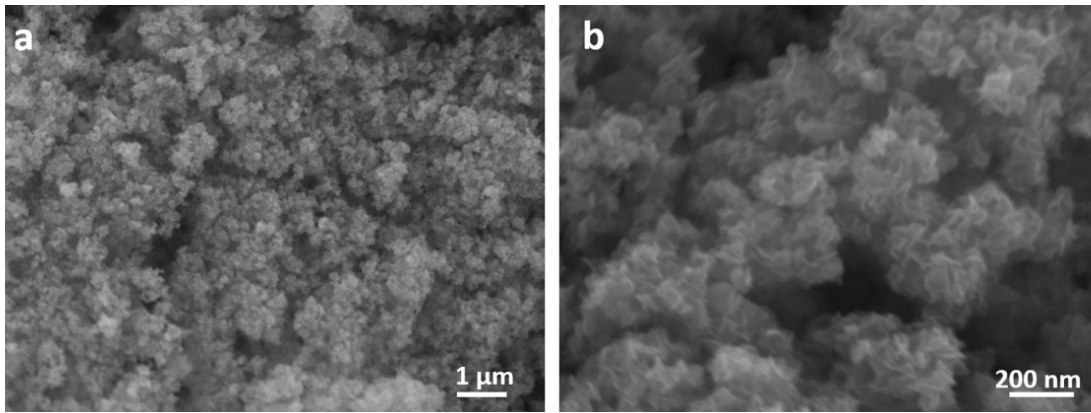


Figure S10. SEM images of pure MoSe₂.

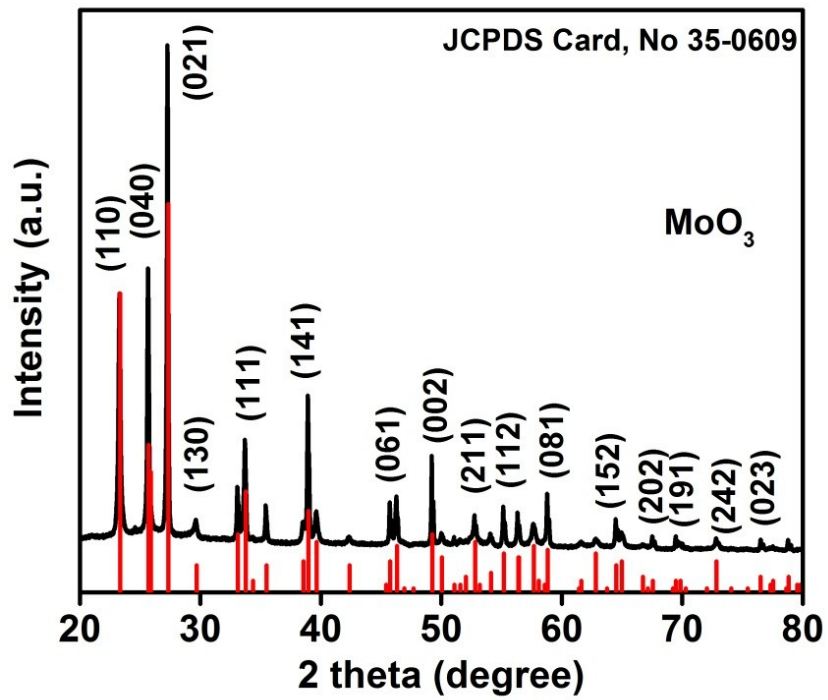


Figure S11. XRD pattern of the C-MSC nanocomposite after full oxidation into MoO₃ at 600 °C in air.

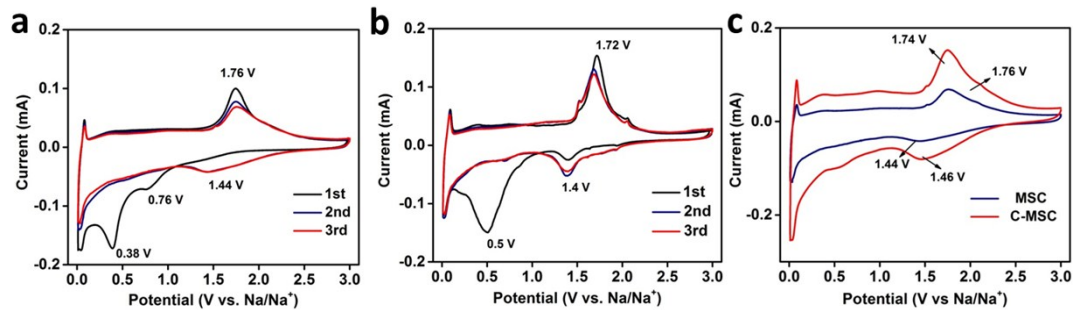


Figure S12. The electrochemical performance of MSC and MS as anode materials for SIBs. a) CV curves of MSC at a scan rate of 0.1 mV s^{-1} for the first three cycles. b) MS at a scan rate of 0.1 mV s^{-1} for the first three cycles. c) CV curves of C-MSC and MSC at third cycle.

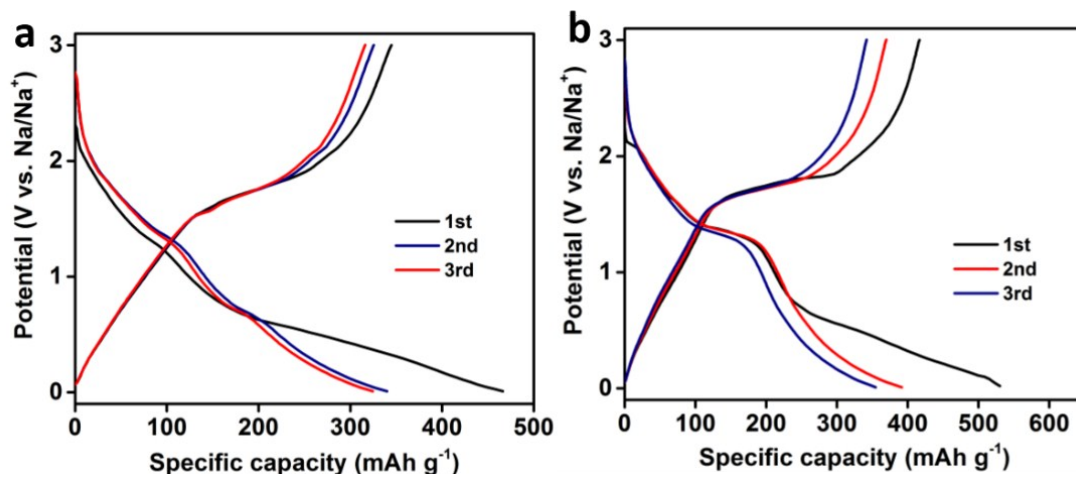


Figure S13. a) Discharge/charge curves of MSC at 0.5 A g⁻¹. b) Discharge/charge curves of MS at 0.5 A g⁻¹.

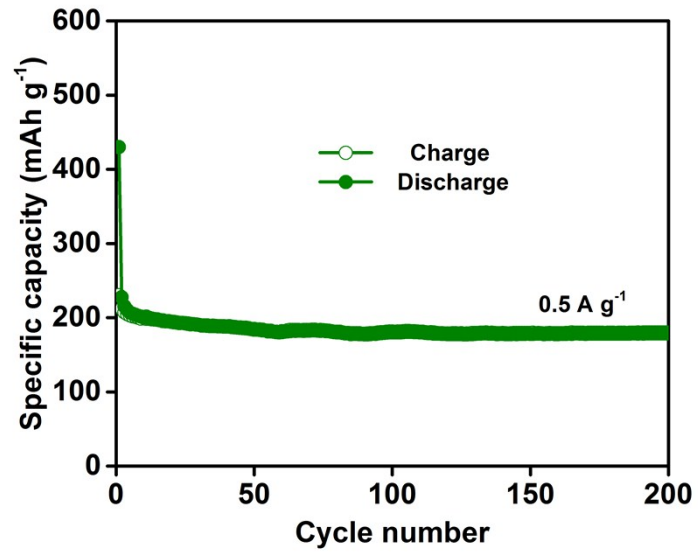


Figure S14. Charge-discharge curves of 3D-C at a current density of 0.5 A g⁻¹.

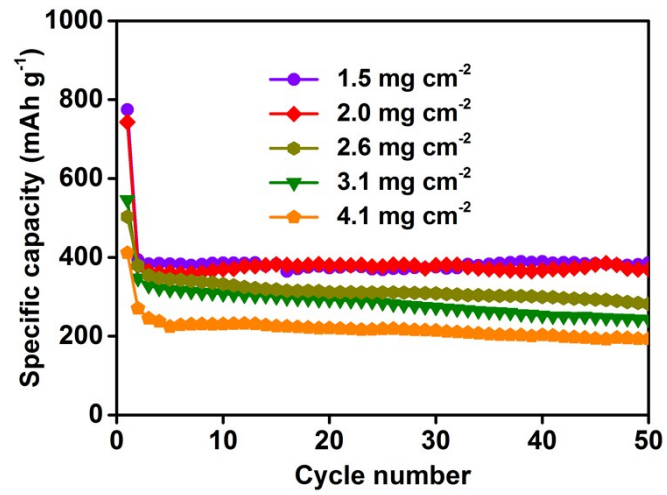


Figure S15. a) Discharge capacities of C-MSC with different areal loadings.

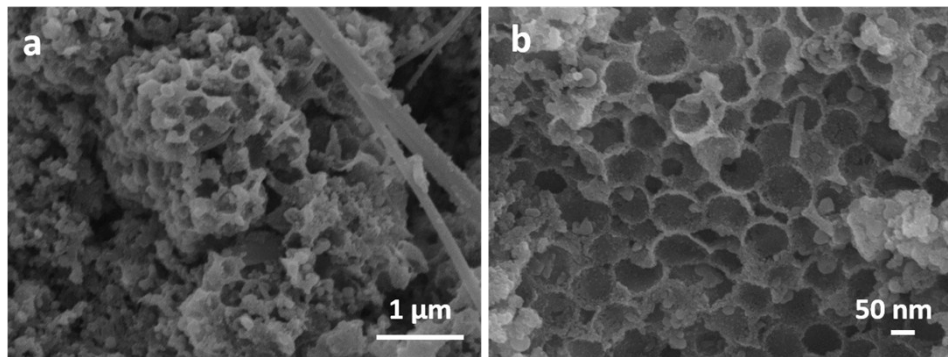


Figure S16. SEM images of C-MSC composite as anode materials for SIBs. a,b) after 100 cycles at the current density of 0.5 A g^{-1} .

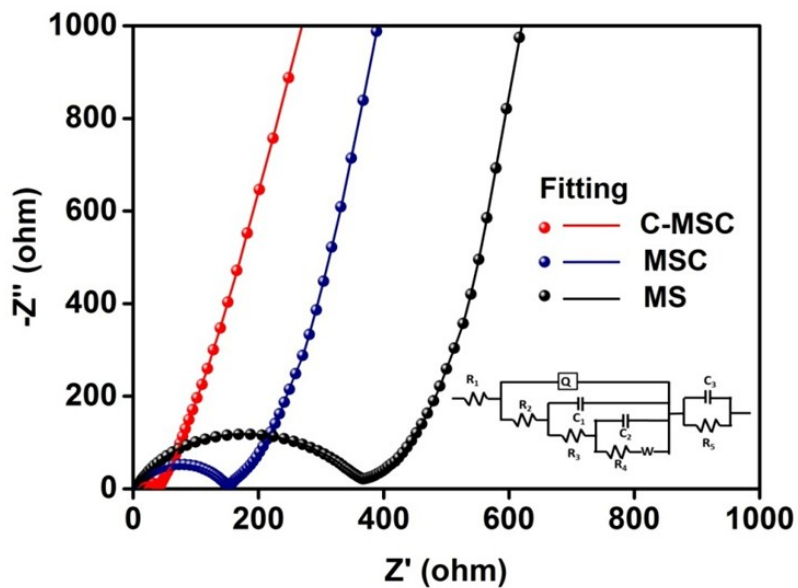


Figure S17. a) Nyquist plots for the electrodes made of C-MSC, MSC, and MS.

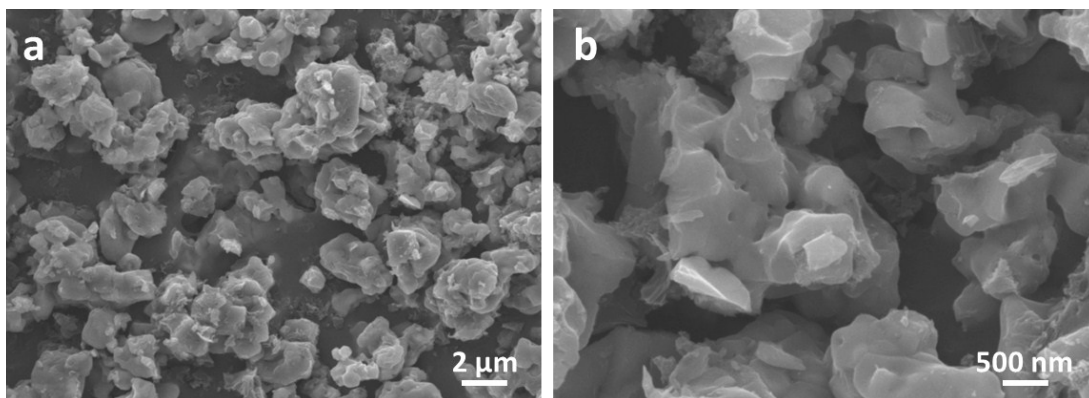


Figure S18. SEM images of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$.

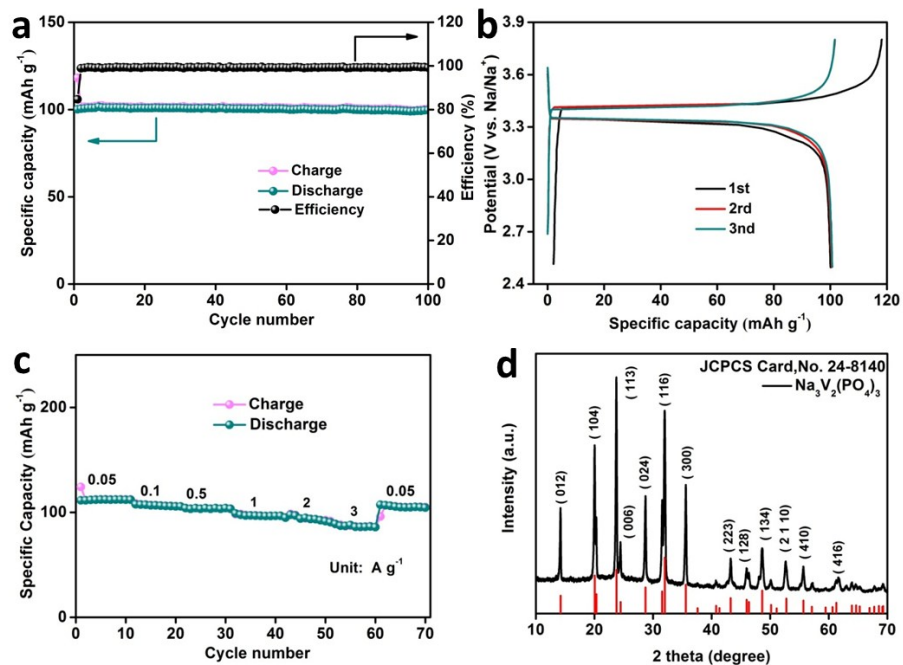


Figure S19. The electrochemical performances of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material for SIBs. a) Cycling stability at 0.1 A g^{-1} . b) Discharge/charge profiles at different cycles under a current density of 0.1 A g^{-1} . c) Rate performance and d) XRD pattern of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.

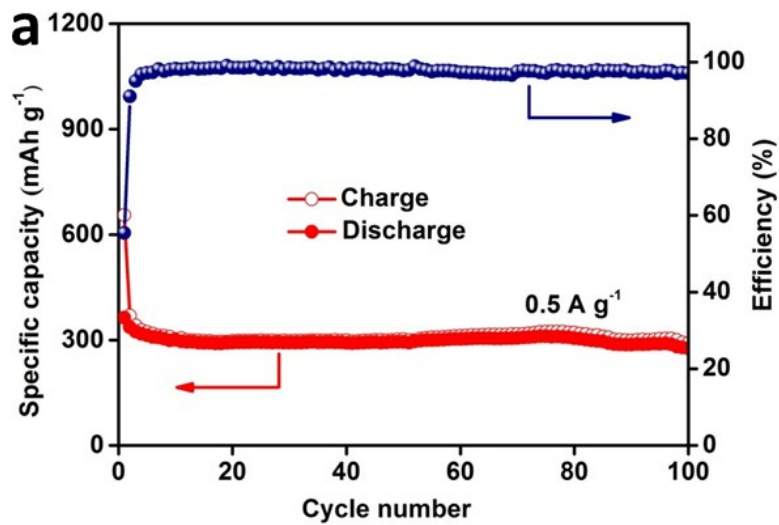


Figure S20. The electrochemical performances of the C-MSC//Na₃V₂(PO₄)₃/C Na-ion full cell material for SIBs. Cycling performance at 0.5 A g⁻¹_{anode} (the capacity is calculated by the mass of anode).

Table S1. SIB performance summary of MoSe₂-based hybrids and their analogues.

Sample	Capacity/current (considering total weight of composite electrodes)	Reference
MoSe ₂ @3DOM	382 mAh g ⁻¹ at 5 A g ⁻¹ (2000 cycles)	This work
MoSe ₂ /N,P-rGO	276 mAh g ⁻¹ at 5 A g ⁻¹ (1000 cycles)	Adv. Funt. Mater. 2017, 27, 1700522.
C- MoSe ₂ /rGO	225 mAh g ⁻¹ at 1 A g ⁻¹ (1500 cycles)	Nano Res. 2016, 9, 1618.
MoSe ₂ /HPCFS	234.1 mAh g ⁻¹ at 1 A g ⁻¹ (1500 cycles)	Chem. Eng. J. 2018, 233, 2190.
VG/MoSe ₂ /N-C	298 mAh g ⁻¹ at 2 A g ⁻¹ (1000 cycles)	Adv. Energy. Mater. 2017, 7, 1061804.
MoSe ₂ /G	368 mAh g ⁻¹ at 3.2 A g ⁻¹ (1500 cycles)	Nano Energy, 2018, 47, 224.
MoSe ₂ nanotube	228 mAh g ⁻¹ at 1 A g ⁻¹ (1500 cycles)	J. Mater. Chem. A 2017, 5, 24859.
MoSe ₂ /P-C@TiO ₂	214 mAh g ⁻¹ at 5 A g ⁻¹ (8000 cycles)	Adv. Sci. 2019, 6,1081222.
MoSe ₂ @CoSe/N-C	347 mAh g ⁻¹ at 2 A g ⁻¹ (300 cycles)	Energy Storage Mater. 2018, 21, 97.
MoSe ₂ -rGO-CNT	335 mAh g ⁻¹ at 1 A g ⁻¹ (400 cycles)	ACS Appl. Mater. Inter. 2017, 9, 10673.
Mo(Se _{0.85} S _{0.15}) ₂	312 mAh g ⁻¹ at 1A g ⁻¹ (100 cycles)	Small 2015, 11, 5667.
O- MoSe ₂ /SnO ₂	298 mAh g ⁻¹ at 1 A g ⁻¹ (100 cycles)	Chem. Eng. J. 2018, 354, 1164.