

Supporting Information

Metal–Organic Framework-Derived NiSe Embedded into a Porous Multi-Heteroatom Self-Doped Carbon Matrix as a Promising Anode for Sodium-Ion Battery

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1. Materials and Methods

Preparation of NiSe@MC composites

The Ni-MOFs was synthesized by a typical hydrothermal method. First, the CTP-COOH (399 mg) ligand and $\text{C}_4\text{H}_6\text{O}_4\text{Ni}\cdot 4\text{H}_2\text{O}$ (320 mg) were dissolved in 35 mL of DMF, and the mixture was stirred at room temperature for five minutes, and then the light-green precipitate was isolated from the solution by centrifugation and further washed with DMF and THF several times, and it was further dried at 70 °C overnight.

To obtain the Ni@MC, 1 g Ni-MOFs was annealed at 600 °C for 2 h in Ar atmosphere with a rate of 1 °C·min⁻¹.

To prepare the NiSe@MC, 0.316 g Se power was dissolved in 10 mL 80% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and stirred for 10 min, then 0.18 g Ni@MC and 50 mL H_2O were added into the solution and stirred for another 30 min. Then, the mixture was transferred into 100 mL Teflon-lined autoclave and maintained at 200 °C for 12 h. The synthesized products were washed with distilled water and ethanol three times. Then, the products were dried at 80 °C for 10 h in a vacuum oven and then annealed at 600 °C for 2 h under Ar atmosphere.

2. Materials characterization

The X-ray diffraction (XRD) patterns, morphologies and the elemental mapping were test on a X-ray diffractometer (Bruker D8 ADVANCE, Cu $\text{K}\alpha$ radiation), field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, FEI Thermo Talos F200S), respectively. Energy dispersive X-ray (EDX) measurements were performed on an FEI Quanta 250 FEG SEM. X-ray photoelectron spectroscopy (XPS) spectra were performed on an X-ray photoelectron spectrometer (Thermo Fisher ESCALAB 250Xi). Thermogravimetric analyzer (Mettler, 3+/1600HT) were used to determine NiSe@MC in the composite. N_2 adsorption/desorption was conducted by using a Micromeritics ASAP2460 instrument. The specific surface area was collected using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated from the adsorption branch of the isotherm.

3. Electrochemical measurements

The active material, acetylene black and CMC (7:2:1, w/w/w) were mixed with distilled water.) to form a slurry. Then the mixture was uniformly applied onto an Cu foil and vacuum-dried at 60 °C for 12 h. The mass loading of active material was 0.85-1.1 mg cm⁻². A glass fiber membrane and Na-metal foil were used as separator and counter electrode. The electrolyte was

NaPF₆ soluble in Diglyme, The cell were galvanostatically charged/discharged at battery testing system (Shenzhen Neware Battery Co., China). Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested by an electrochemical workstation (CHI760e, China) with a scanning speed of 0.1 mV s⁻¹ at 0.01 V~3 V, and in a frequency ranging from 10⁻² Hz to 10⁵ Hz.

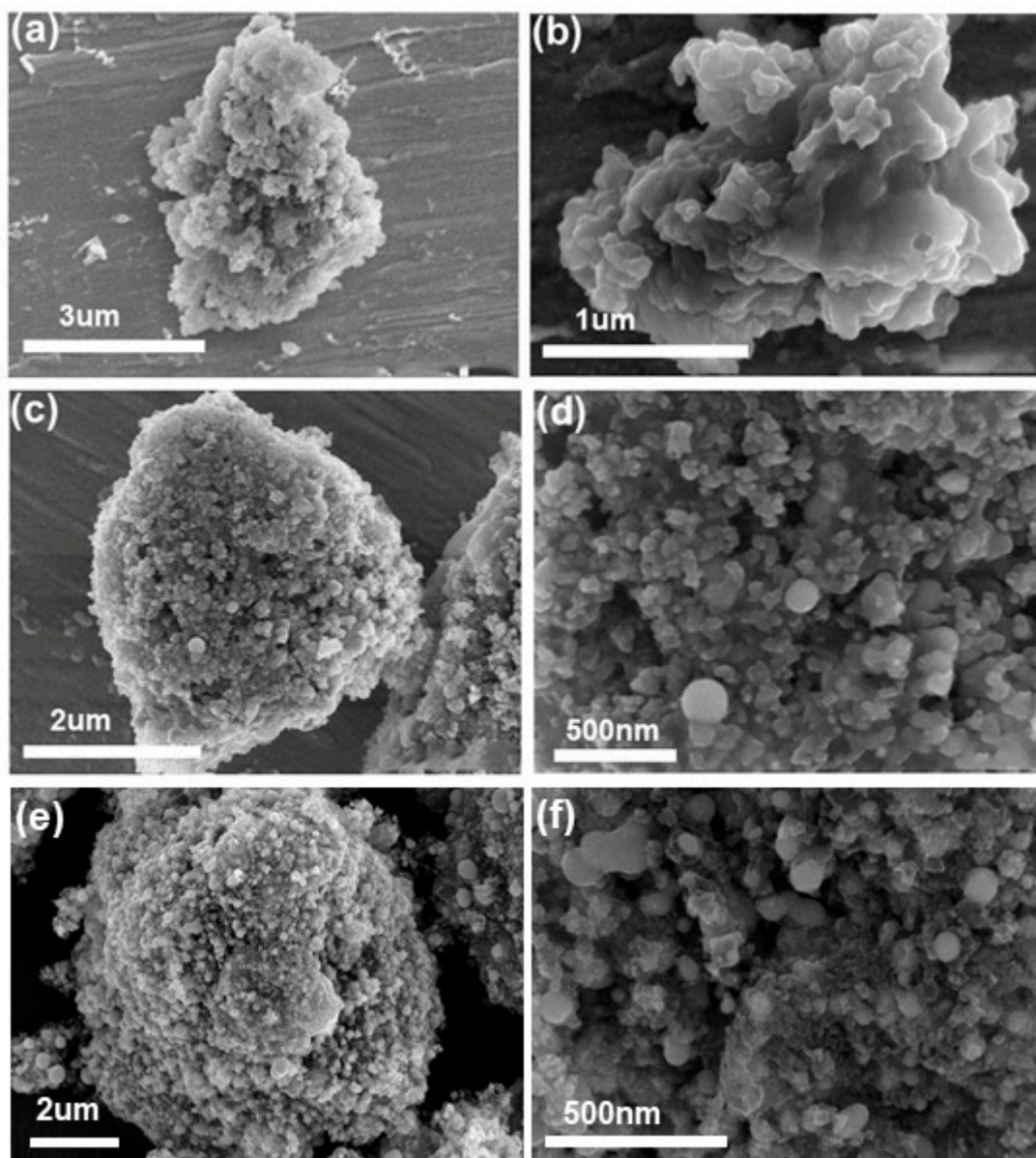


Figure S1. SEM images of Ni-MOFs (a,b), Ni@MC (c,d), and NiSe@MC (e,f).

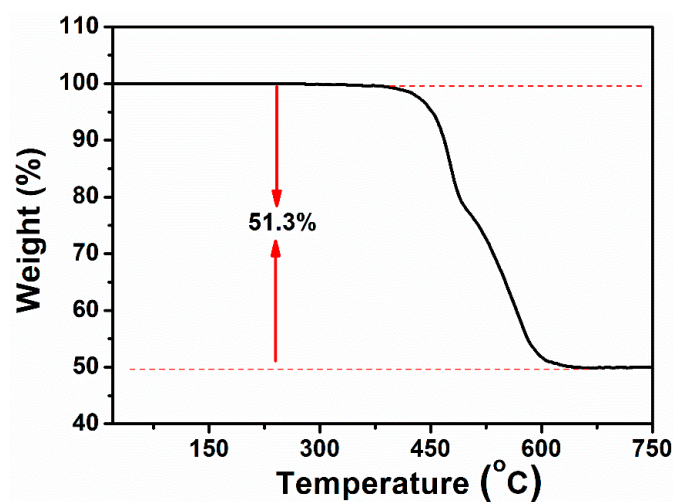


Figure S2. TGA curve of NiSe@MC.

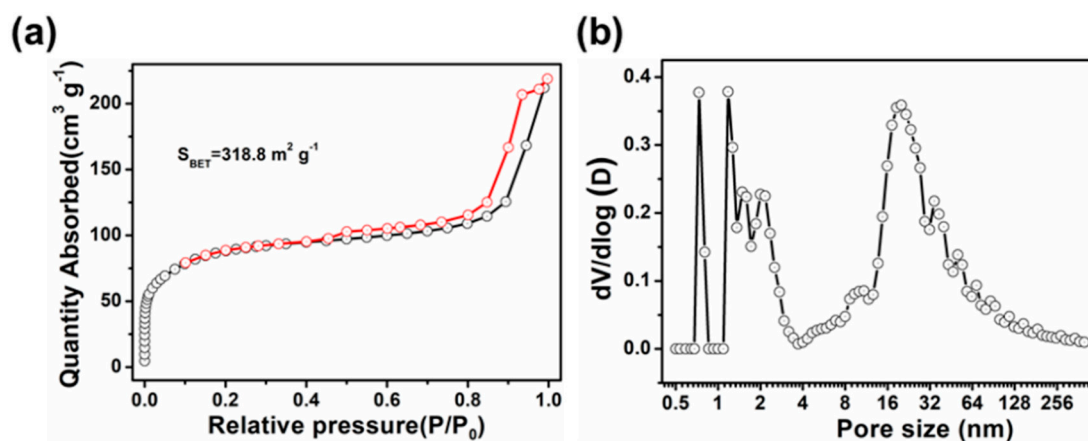


Figure S3. Nitrogen adsorption-desorption isotherms (a) and pore size distribution curves (b) of NiSe@MC.

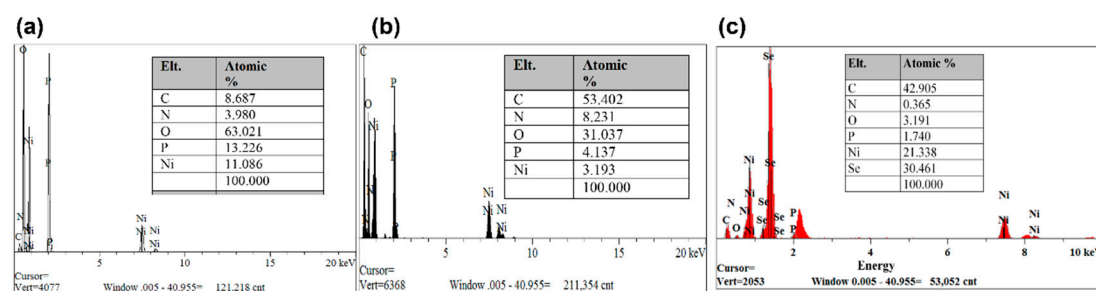


Figure S4. EDS analysis spectrum of Ni-MOF (a), Ni@MC (b), and NiSe@MC (c).

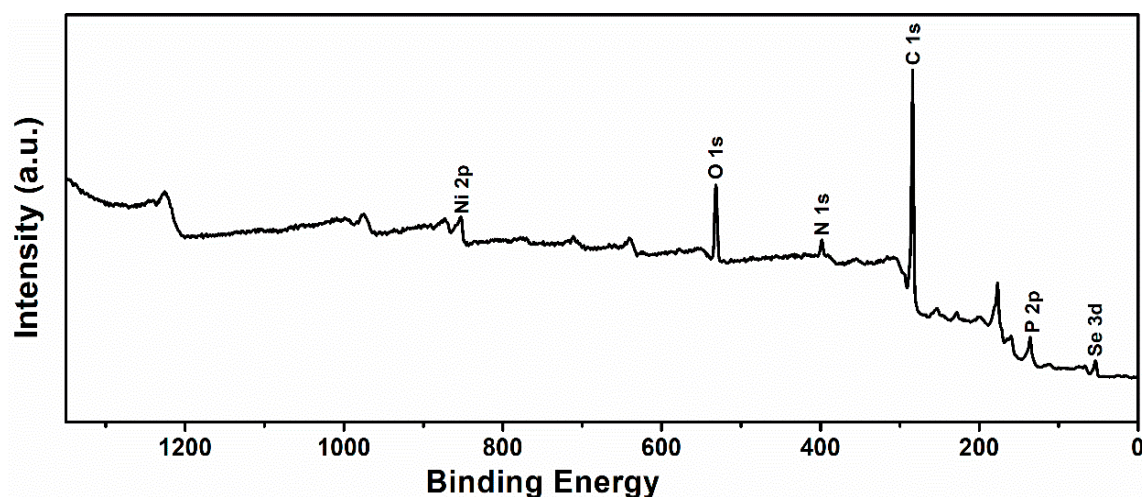


Figure S5. XPS survey spectrum of NiSe@MC.

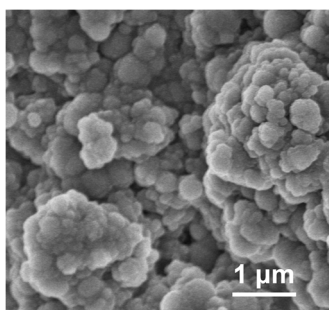


Figure S6. SEM image of NiSe@MC electrode after 200 cycling tests at 1 A g⁻¹.

Table S1. Previously reported NiSe-based analogues and their application in SIBs.

Materials.	Morphology	Voltage window (V vs. Na/Na ⁺)	Voltage of discharge platforms (V vs. Na/Na ⁺)	Cycle number	Capacity (mAh g ⁻¹) (A g ⁻¹)	Ref.
NiSe/rGO	Nanoparticles and nanosheets	0-3	1.0, 1.35	50	378 (0.05)	35
NiSe@C	hollow microspheres	0.5-3.0	1.11, 1.44	100 2000	276.4 (0.3) 160 (3)	21
NiSe@C@NCNFs	nanofibers	0.01-3.0	0.96	100 1000	374 (0.1) 164 (2)	36
P-NiSe@C	Particles on the	0.01-3.0	0.99, 1.25	100	598.2	16

	cole pollen				(0.2)	
NiSe/C	core-shell like	0.01–3.0	1.1, 1.2	50	280 (0.1)	37
	Multi-heteroatom				568.9	
NiSe@MC	doped	0.01-3.0	1.46, 1.12, 0.63	1000 1200	(1) 227.8	this work
	carbonaceous NiSe particles				(5)	

References

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3. Zhang, Z.; Shi, X.; Yang, X. Synthesis of core-shell NiSe/C nanospheres as anodes for lithium and sodium storage. *Electrochim. Acta* **2016**, *208*, 238–243.