

MOFs derived ultrasmall CoSe₂ nanoparticles encapsulated by N-doped carbon matrix and their superior lithium/sodium storage properties

Synthesis of Co-MOFs

The synthetic route for the ligand 9-(3,5-dicarboxylic acid-benzyl)-9H-indazole-3,6-dicarboxylic acid (H₄DCDC) is referred to the previous report (Inorg. Chim. Acta, 2016, 446, 198-202). 42 mg H₄DCDC and 96 mg CoCl₂·6H₂O were dispersed into a mixture solution of 4 mL dimethylacetamide and 16 mL deionized water at room temperature. Then the uniform solution was transferred to Teflon-lined stainless-steel container (25 mL) and maintained at 120 °C for 48 h. After cooling spontaneously, centrifugation by washing with ethanol and deionized water, and vacuum drying at 60 °C overnight, the purple pink products were successfully obtained and these were Co-MOFs.

Synthesis of CoSe₂@N-doped Carbon Matrix (CoSe₂@NC)

The prepared Co-MOFs precursor was ground into a powder, and the selenium powder and the Co-MOFs precursor were placed into the upstream and downstream of a corundum boat, respectively. Then the corundum boat was placed in a tube furnace and maintained at 500 °C for 2 h under Argon gas atmosphere. After the tube furnace was naturally cooled, CoSe₂@NC powders were obtained.

Characterization

The crystal phases of as-prepared samples were characterized by X-ray diffractometer (XRD) on a Rigaku MiniFlex 600 diffractometer. Thermogravimetric analysis (TGA/DSC3, Mettler-Toledo) was carried out from room temperature to 1000 °C with a temperature ramp of 10 °C min⁻¹ in air atmosphere. X-ray photoelectron spectroscopy (XPS) spectra were recorded to analyze the elemental bonding state with an Escalab250Xi spectrometer. Scanning electron microscopy (SEM, Zeiss Sigma) performed at 40 kV and transmission electron microscopy (TEM,

FEI TECNAI G20) performed at 200 kV were conducted to investigate microscopic structures and elemental distribution. Raman spectra were collected by using a Thermo Fischer DXR spectrometer.

Electrochemical Measurement

The CoSe₂@NC powders were mixed with acetylene black and polyvinylidene difluoride binder in a mass ratio of 70:20:10 and dispersed in N-methyl pyrrolidinone solution. The slurries were uniformly coated onto Cu foil and dried at 100 °C in a vacuum oven overnight. The active material of the electrode was $\sim 1.0 \text{ mg cm}^{-2}$. The electrolytes were 1 M LiPF₆ in a mixture solution of ethylene carbonate, dimethyl carbonate and ethyl-methyl carbonate (1:1:1 in volume) for LIBs and 1 M NaClO₄ in a mixture solution of diethyl carbonate and ethylene carbonate (1:1 in volume) for SIBs. The separators were Celgard 2500 membrane for LIBs and glass fiber for SIBs. The counter electrodes were lithium foil for LIBs and sodium foil for SIBs. Galvanostatic charge/discharge tests were carried out by LAND CT2001A battery test system at different current densities. Cyclic voltammetry (CV) were performed on electrochemical workstation (Bio-Logic) at different scan rates.

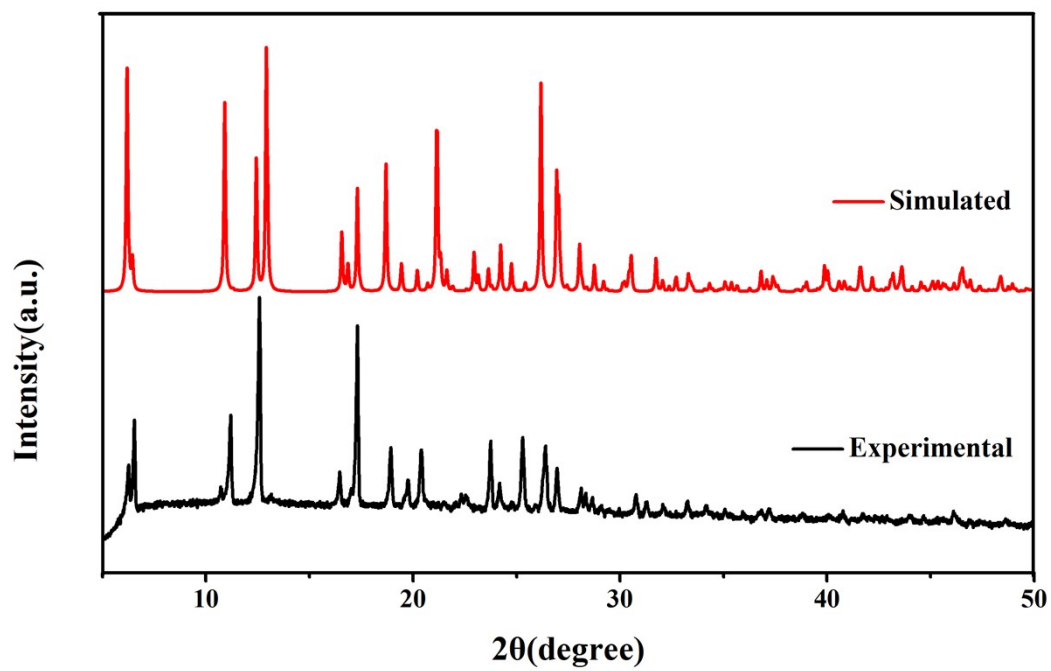


Fig. S1. XRD pattern of [Co(H₂DCDC)(H₂O)₂]_n (Co-MOFs) composite.

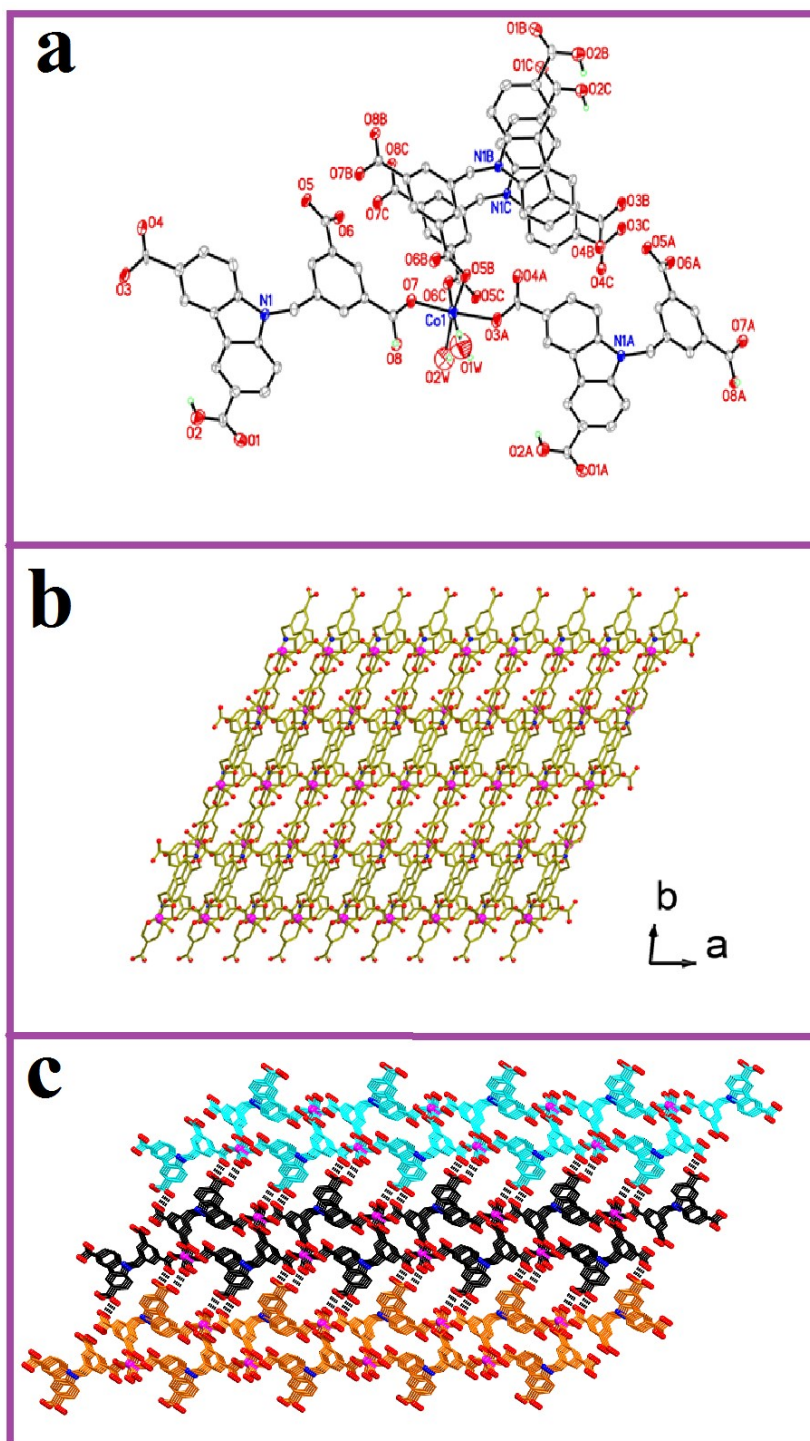


Fig. S2. (a) View of the coordination environment of the Co1 center in 1 with a labeling scheme and 30% thermal ellipsoids. All H atoms were omitted for clarity. Symmetry code: (A) $x - 1, y, z$; (B) $-x, -y, -z + 1$; (C) $-x - 1, -y, -z + 1$. (b) View of 2D layer of 1 constructed by H₂DCDC and Co (looking down the *c* axis). (c) View of 3D network of 1 connected by hydrogen-bonding interactions. The red, blue and pink balls represent O, N and Co respectively.

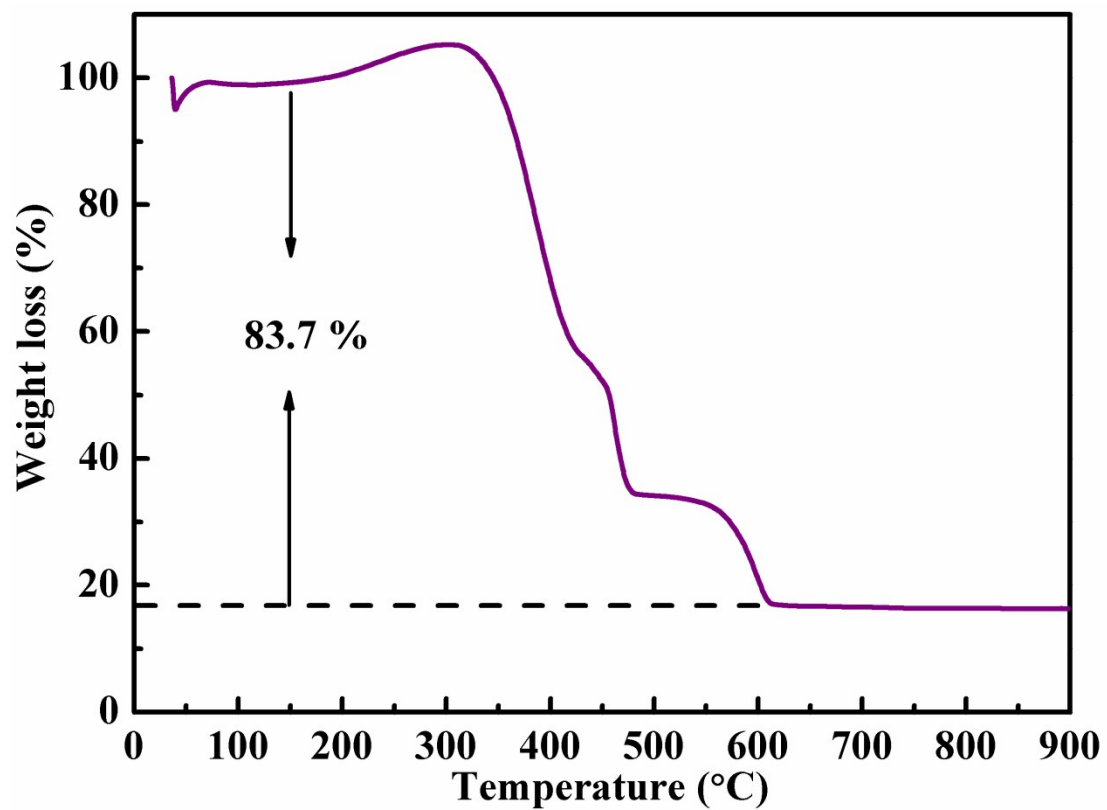


Fig. S3. TGA curves of CoSe₂@NC.

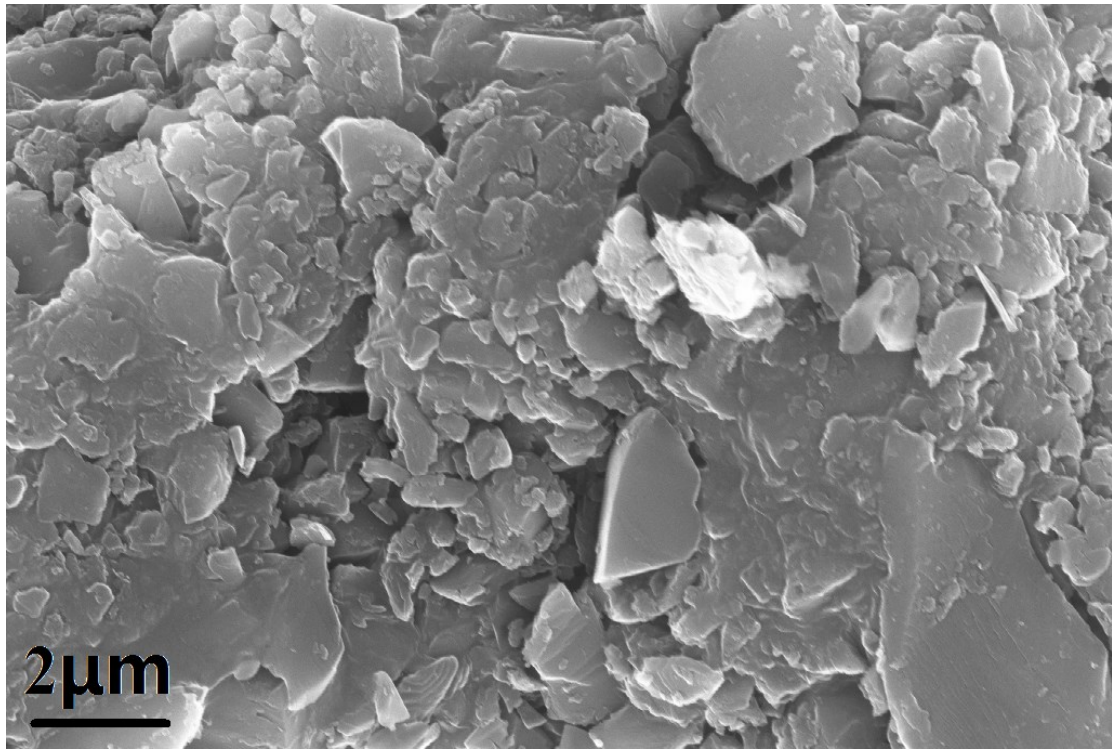


Fig. S4. SEM image of Co-MOFs template.

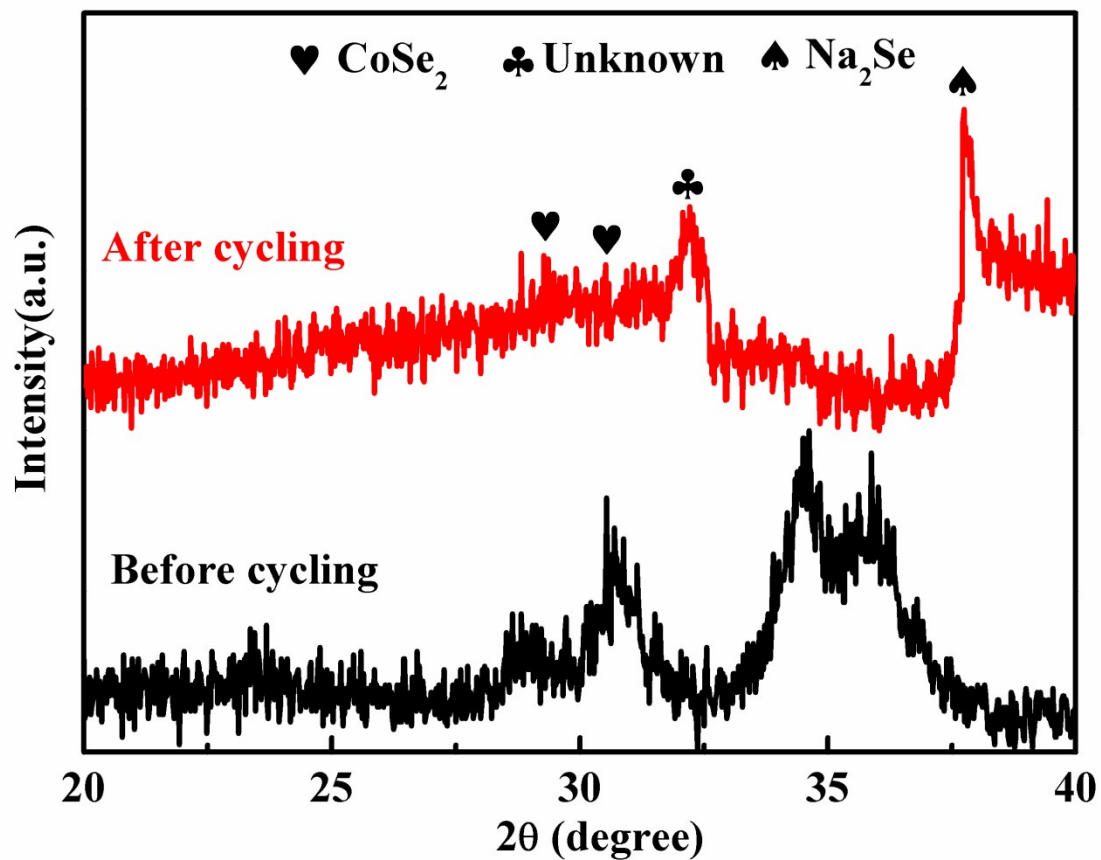


Fig. S5. XRD patterns of CoSe₂@NC before cycling and after 10 cycles.

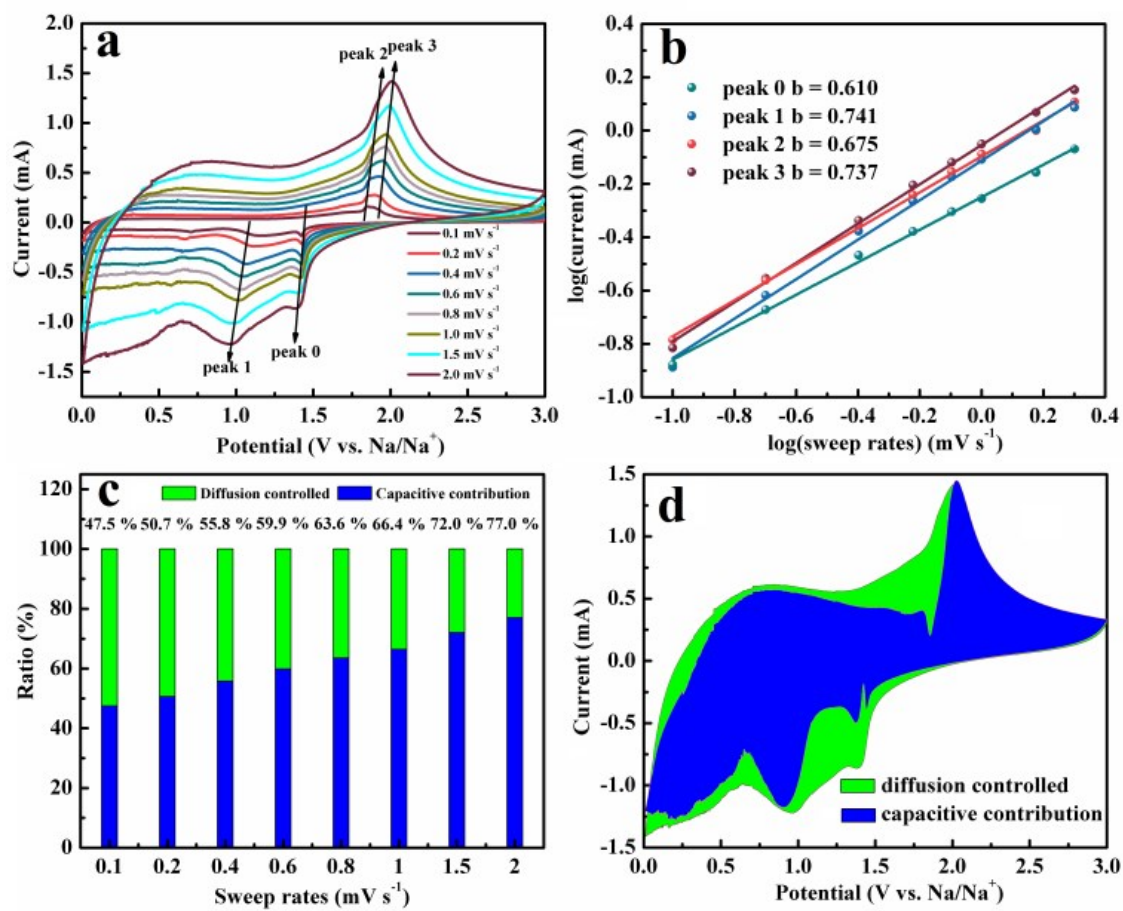


Fig. S6. Electrochemical reaction dynamics analysis of the CoSe₂@NC for Na⁺ batteries: (a) CV curves at different scan rates; (b) Functional relationship of log(i) versus log(v) at each redox peak; (c) Normalized percentage of pseudocapacitance at different scan rates; and (d) The pseudocapacitance contribution to the total current at a scan rate of 2.0 mV s⁻¹.