Highly dispersed β-NiS nanoparticles in porous carbon matrices by a template metal-organic framework method for lithium-ion cathode

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Experimental

MOF-74(Ni). MOF-74(Ni) was synthesized following the procedure reported elsewhere.[41] Typically, a mixture of 1.12 g $Ni(CH_3COO)_2\cdot 4H_2O$, 0.45 g 2,5-dihydroxyterephthalic acid (H_2DOBDC), 30 ml H_2O and 30 ml tetrahydrofuran (THF) was loaded into a 100 ml autoclave with a Teflon cup and heated at 110 ℃ for 3 d. Upon cooling down, the yellow suspension of MOF-74(Ni) was filtered and washed with MeOH (30 ml) for 3 times. The as-synthesized MOF-74(Ni) was activated by heating at 150 ℃ for 12 h under vacuum to remove the solvent molecules.

C⊃Ni. The activated MOF-74(Ni) was heated to 400 ℃ at a speed of 10 Kmin^{-1} and kept at that temperature for 5 h under continuous reducing gas (10% H_2 in Ar) flow. Upon naturally cooling down, black powder of C⊃Ni was immediately transferred into an Ar-glovebox (H_2O, O_2 < 1 ppm).

C⊃NiS-L and C⊃NiS-H. 0.5 g C⊃Ni and 0.61 g thiourea (molar ratio, Ni:S=1:1.1) was mixed in Ar-glovebox and loaded in a 20 ml autoclave with a Teflon cup. After tightly sealed, the autoclave was transferred into an oven and heated at 160 ℃ or 180 ℃ for 24 h. Then the mixture was washed with EtOH and collected by centrifuging. The samples heated at 160 ℃ and 180 ℃ were remarked as C⊃NiS-L and C⊃NiS-H, respectively.

Battery assembling. Bare NiS, C⊃NiS-L and C⊃NiS-H were mixed with 10% acetylene black and 15% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) separately. The slurry was coated on aluminum foil as cathode. 2025 batteries are assembled with electrolyte of 1 M $LiPF_6$ in 1,3-dioxolan-2-one/dimethylcarbonate (EC/DMC, v:v=1:1), Celgard 2400 membrane and lithium foil reference anode.

Characterizations. Powder X-ray diffraction (PXRD) data were recorded on a PANalytical X'Pert PRO diffractometer at 40 kV, 25 mA for Cu Kα, (λ=1.541 Å). Thermo gravimetric analysis (TGA) was measured in a N_2 atmosphere at a scan speed of 10 K/min on a Netzsch TG209 F3 system. Scanning electron microscopy (SEM) morphologies and energy dispersive spectrometer (EDS) mappings were investigated using a Hitachi S4800 field-emission scanning electron microscopy with a HORIBA EMAX energy dispersive spectrometer. Transmission electron microscopy (TEM) morphologies were taken on a Hitachi HT7700 transmission electron microscopy. N_2 sorption properties were studied with a Quantachrome 20-E high speed gas sorption analyzer. The cyclic voltammetry (CV) data were collected with an Arbin electrochemical workstation at a scan rate of 0.1 mVs^{-1} between 0.5 and 3.0 V. The charge–discharge profiles, cyclability, with Coulombic efficiency were recorded with a LAND battery cycler between 0.5 and 3.0 V.

Carbon matrices

0.5g C⊃Ni is dispersed in 15 ml H_2O with 2 ml HCl (37%) and stirred for 3 h. Ni is dissolved and carbon matrices are collected by centrifuging and washing with H_2O. The electrochemical test conditions are the same as those of C⊃NiS with a charge/discharge rate of 20 mAg^{-1}, and the charge/discharge profiles and cycle performance are displayed in Fig. S4.

C⊃NiO

C⊃NiO was prepared by heating C⊃Ni at 400 ℃ in flowing air for 10 h at a speed of 5 $Kmin^{-1}$. The face purity was confirmed by PXRD patterns as shown in **Fig. S6a**, JCPDS NO. 47-1049. The resulting C⊃NiO features a high BET surface area of 108 m^3g^{-1} which is determined by N_2 isothermal study (**Fig. S6b**). SEM morphologies in **Fig. S7a** indicating that it has also successfully managed to maintain the basic facetted shapes of MOF-74(Ni) precursor. The highly distributed system was further proved by EDS mappings as displayed in **Fig. S7c-f**

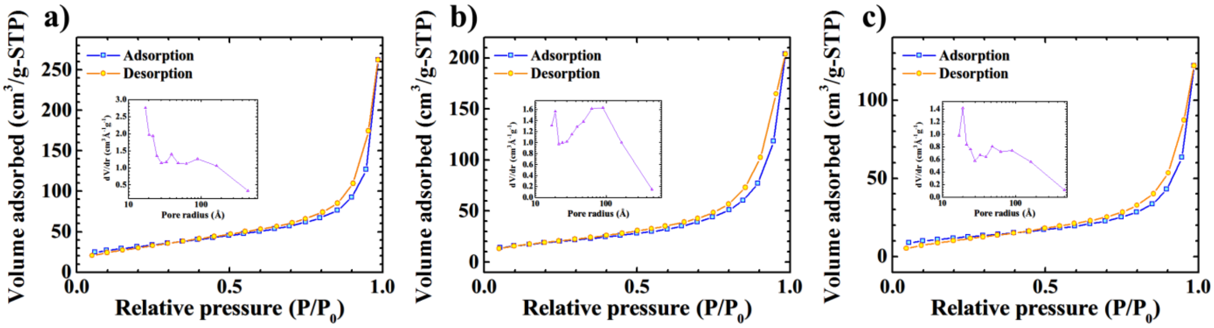

Fig. S1. Nitrogen adsorption-desorption isotherm at 77 K of (a) C⊃Ni, (b) C⊃NiS-L and (c) C⊃NiS with an inset of BJH desorption branch poresize distribution.

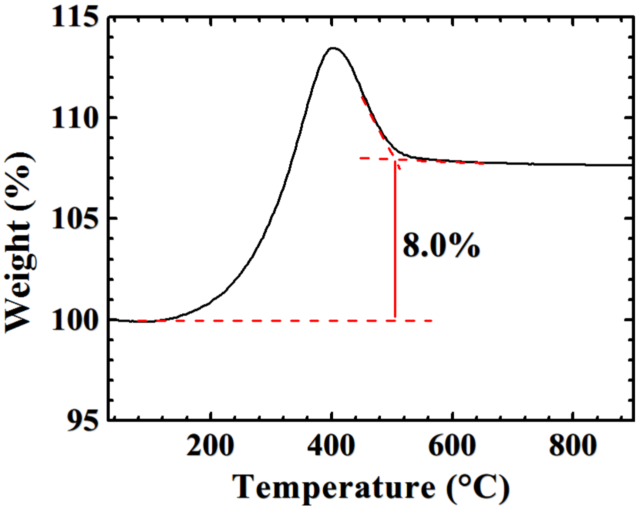

Fig. S2. TG curves of C⊃Ni under air atmosphere at a heating speed of 10 Kmin^{-1}.

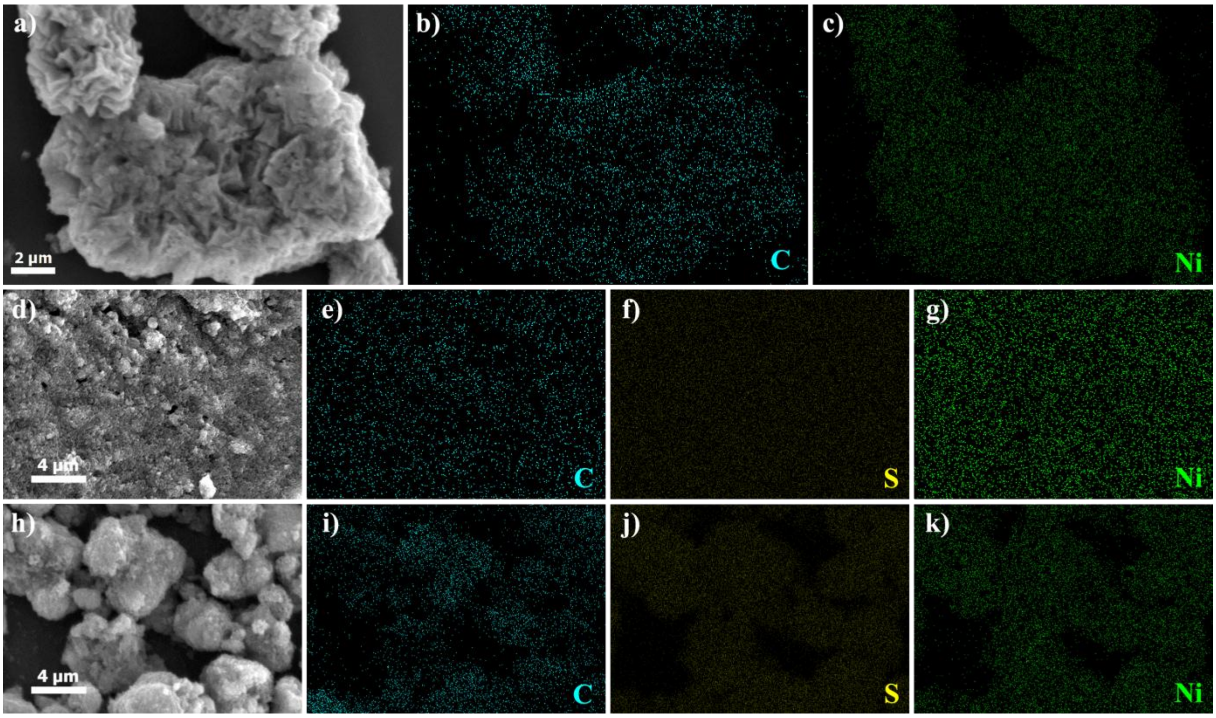

Fig. S3. EDS mappings of (a-c) C⊃Ni, (d-g) C⊃NiS-L and (h-k) C⊃NiS-H.

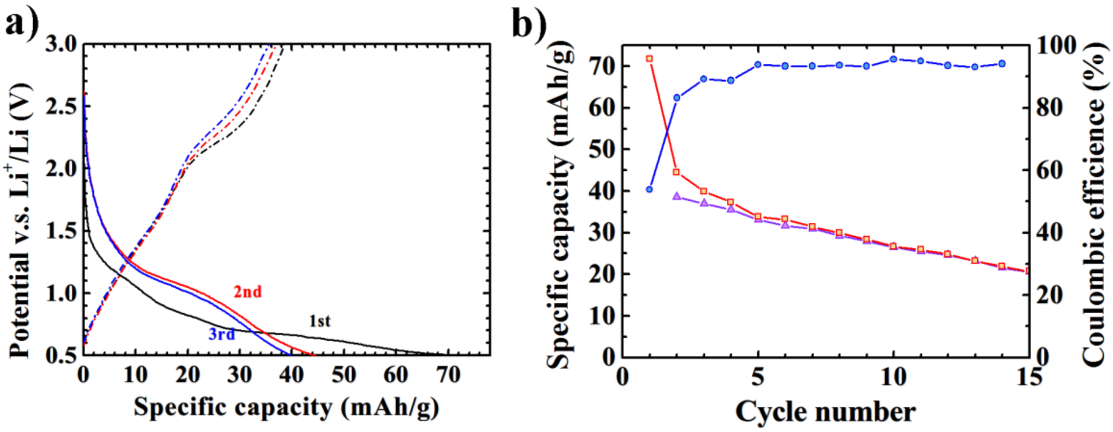

Fig. S4. (a) Charge/discharge profiles and (b) cycle performance of carbon matrices.

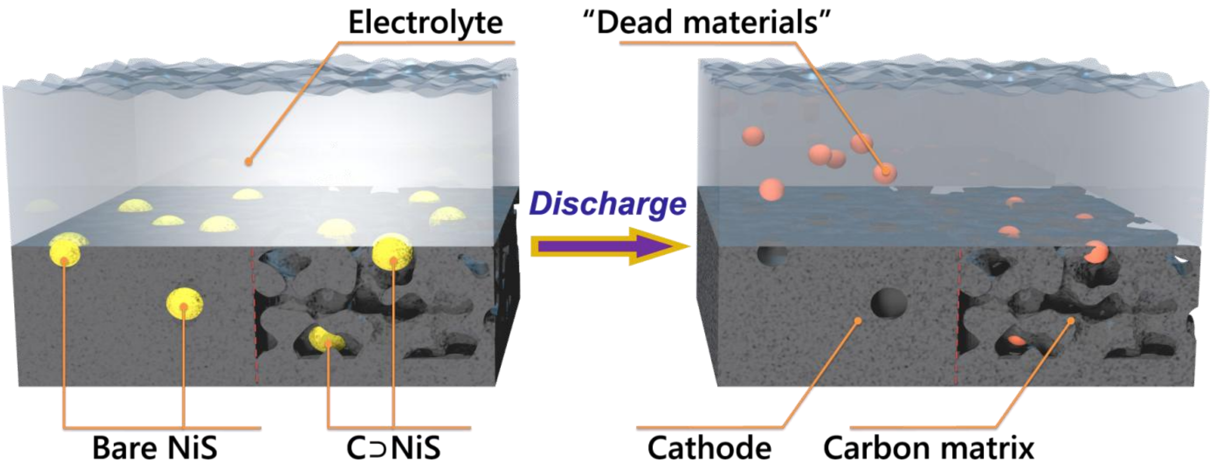

Fig. S5. Schematic illustration for the comparison of bare NiS and C⊃NiS cathodes during discharge process.

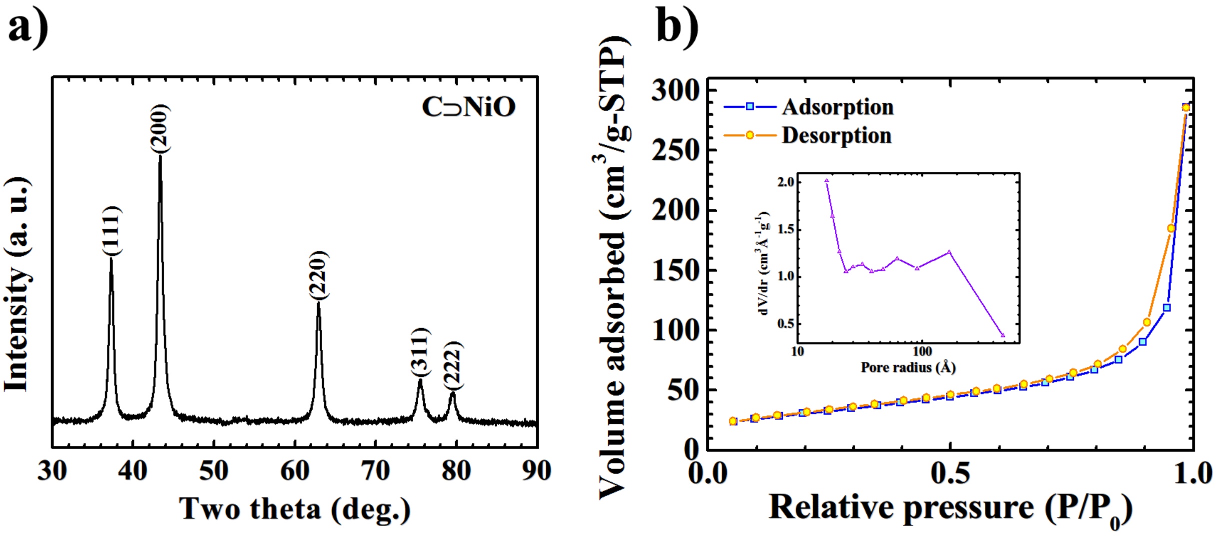

Fig. S6. PXRD patterns and N_2 isothermal of C⊃NiO with an inset of BJH poresize distribution.

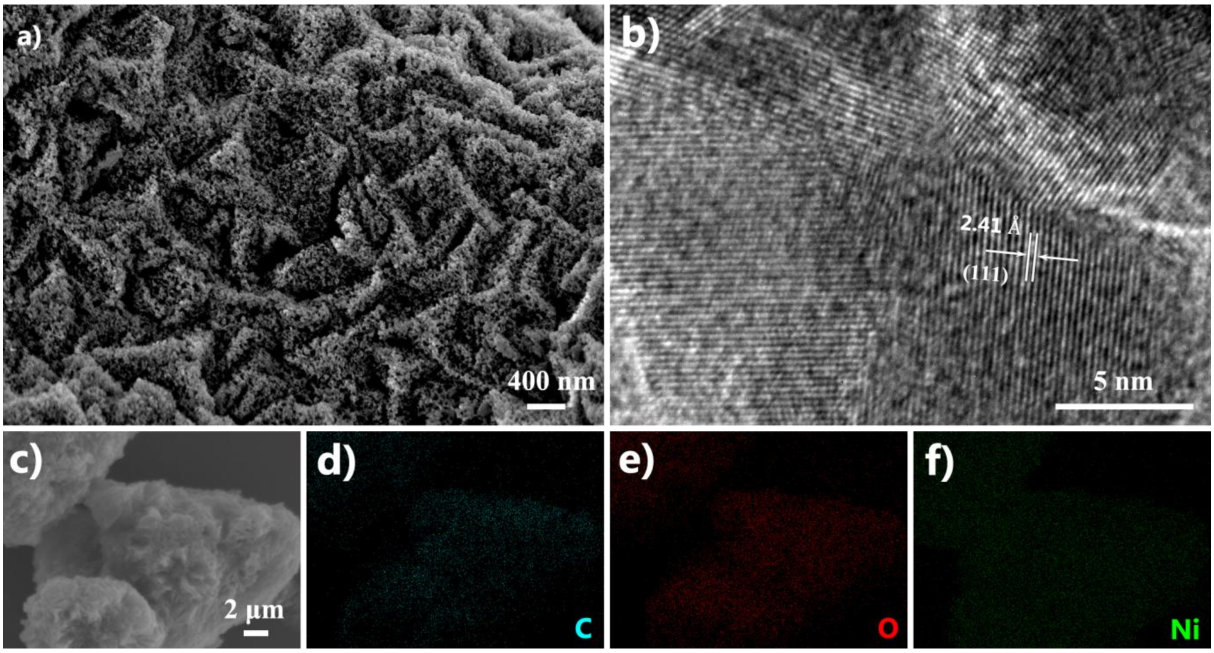

Fig. S7. (a) SEM, (b) HRTEM morphologies and (c-f) EDS mappings of C⊃NiO.