

Supplementary Information

Investigation of superior sodium storage and reversible Na₂S conversion reaction in porous NiS₂@C composite using *In Operando* X-ray diffraction

Trang Thi Vu,^{†,‡} Sohyun Park,^{†,‡} Jimin Park,^{†,‡} Seokhun Kim,[†] Vinod Mathew,[†] Muhammad H. Alfaruqi,^{†,‡} Kwang-Ho Kim,[§] Yang-Kook Sun,^{||} Jang-Yeon Hwang,^{†,*} Jaekook Kim^{†,*}

[†] Department of Materials Science and Engineering, Chonnam National University, Gwangju 61186, Republic of Korea

[‡] Department of Teknik Metalurgi, Universitas Sumbawa, Jl. Raya Olat Maras, Sumbawa, Nusa Tenggara Barat, 84371, Indonesia

[§] School of Materials Science and Engineering, Pusan National University, Busan, 46241, Republic of Korea

^{||} Department of Energy Engineering, Hanyang University, Seoul 04763, Republic of Korea

Author Information

[‡] These authors contribute equally to this work.

Corresponding Author

*E-mail: hjy@jnu.ac.kr; jaekook@chonnam.ac.kr

Experimental Section

Material preparation:

Synthesis of Ni-based MOFs: In a typical procedure, 1.274 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.512 g trimesic acid, and PVP were mixed and dissolved in a 1:1:1 (water : ethanol : dimethylformamide) mixture. After vigorous stirring for 1 h, the obtained homogeneous solution was transferred to a 40 mL Teflon-lined bomb and pyrolyzed at 150 °C for 16 h. A light green powder of Ni-MOFs was obtained after several times of washing with ethanol followed by drying at 80 °C overnight.

Fabrication of the p-NiS₂@C nanoparticles and s-NiS₂@C spheres: The Ni-MOFs and sulfur powder were placed together in a tube furnace and pyrolyzed at 450 °C for 2 h under an Ar atmosphere with a ramp rate of 5 °C/min to obtain porous NiS₂@C(p-NiS₂@C) nanoparticles. In the comparison, one reference sample of solid NiS₂@C(s-NiS₂@C) was prepared using the same procedure while adjusting the annealing conditions of Ni-MOFs to those of the oxidation route (500 °C for 2 h with a ramp rate of 5 °C/min) before the sulfurization stage.

Material Characterization: The structural characteristics of the obtained powder were examined by XRD (powder X-ray diffractometer, CCRF, Chonnam National University) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at a voltage of 60 kV in the 2 θ range of 10–80° with 0.01° steps. The structural morphology and lattice fringes were examined by FE-SEM (S4700, Hitachi) and HRTEM at a voltage of 200 kV (Philips Tecnai F20, at KBSI, Gwangju Center), respectively. XPS (Thermo VG Scientific, Multilab 2000) analysis was performed using Al K α as the X-ray source to determine the oxidation states of the electrode. The utilized spectrometer was calibrated for the binding energy of the C 1s peak (284.8 eV). The structural evolution of p-NiS₂@C nanospheres in the sodium half-cell was examined by conducting in operando XRD measurements using an X-ray diffractometer (PANalytical, Empyrean) with Mo K α radiation ($\lambda = 0.70926 \text{ \AA}$) under conditions : 60kV - 30mA, the 2 θ range of 4.6° to 34.5°, and step-width 0.0064°. The cell was cycled to the fully discharged and charged states using a portable potentiostat at a constant current density of 0.05 A g⁻¹.

Electrochemical Measurements: A CR 2032-type half-cell was assembled using the NiS₂ electrode and sodium metal as the counter and reference electrodes, respectively. A 1.0 M solution of

sodium hexafluorophosphate (NaPF_6 , 99%, Alfa Aesar) in Dimethylglyoxime (DEGDME) was used as the electrolyte for NIBs. The working electrodes were prepared by mixing the active material (80%), Super P (10%), and polyacrylic acid (10%) utilized as a functional binder for transition metal compounds. Distilled water was optimized and added to the resulting powder mixture and transferred to a Spex ball mill for 10 min to obtain a homogeneous slurry, which was subsequently coated onto the copper foil surface using a doctor blade. The coin cell was assembled in an argon-filled glove box using sodium foil and $\Phi 16$ mm Whatman glass fiber as the separator and 1.0 M NaPF_6 in DEGDME as the ether-based electrolyte. The NiS_2 half-cell was operated in a window of 0–2.5 V (vs. Na^+/Na) at room temperature and various applied current densities. A programmable battery tester (BTS-2004H, Nagano, Japan) and potentiostat/galvanostat (Bio-Logic Science Instruments) were employed for galvanostatic, CV, and PEIS analyses.

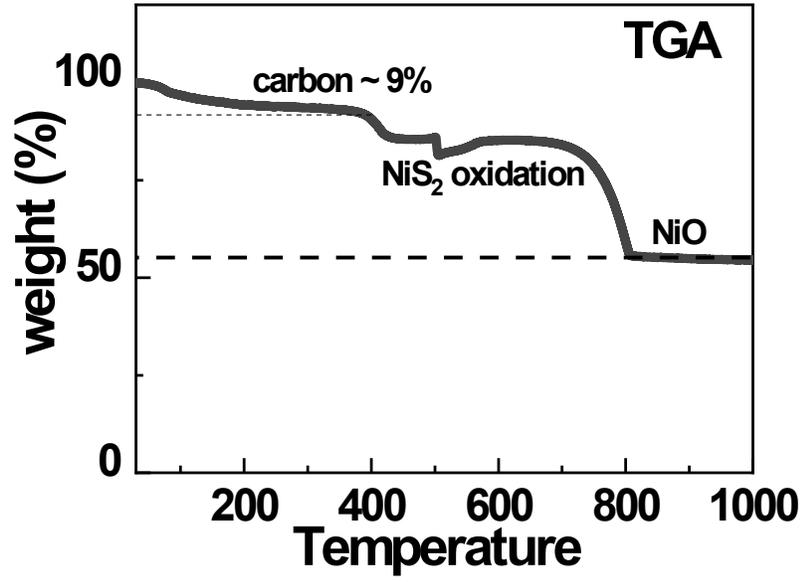


Fig.S1 TGA curve of p-NiS₂@C.

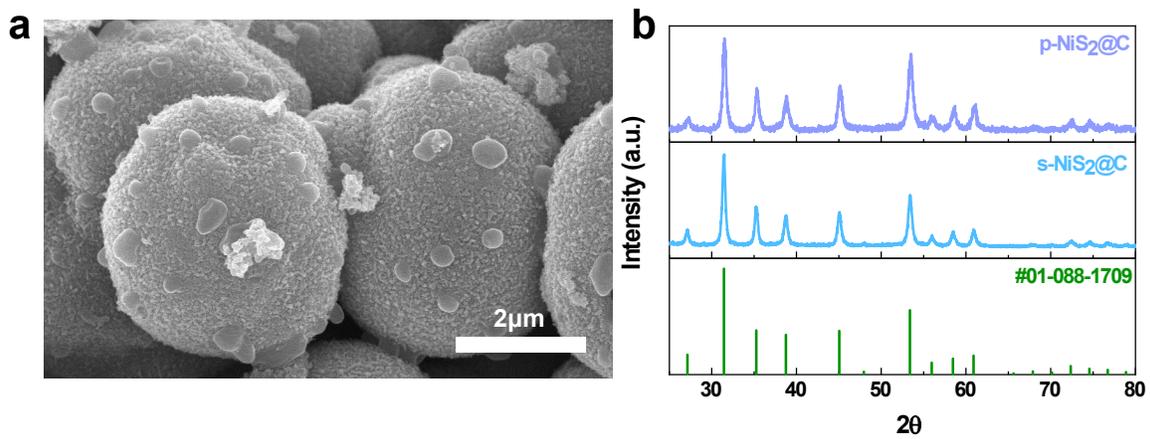


Fig.S2 (a) SEM image and (b) X-ray diffraction pattern of s-NiS₂@C, and p-NiS₂@C (inset is XRD of NiO)

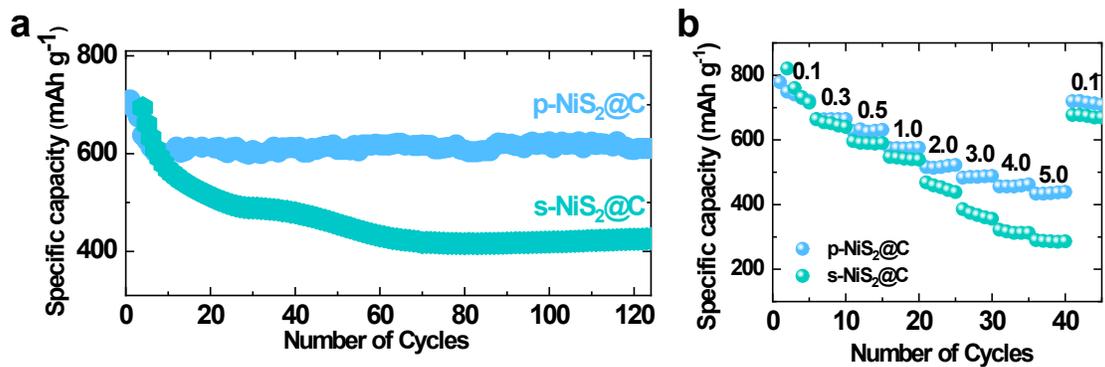


Fig. S3 (a) Cycle stability performance and (b) Rate performance of solid p-NiS₂@C and s-NiS₂@C

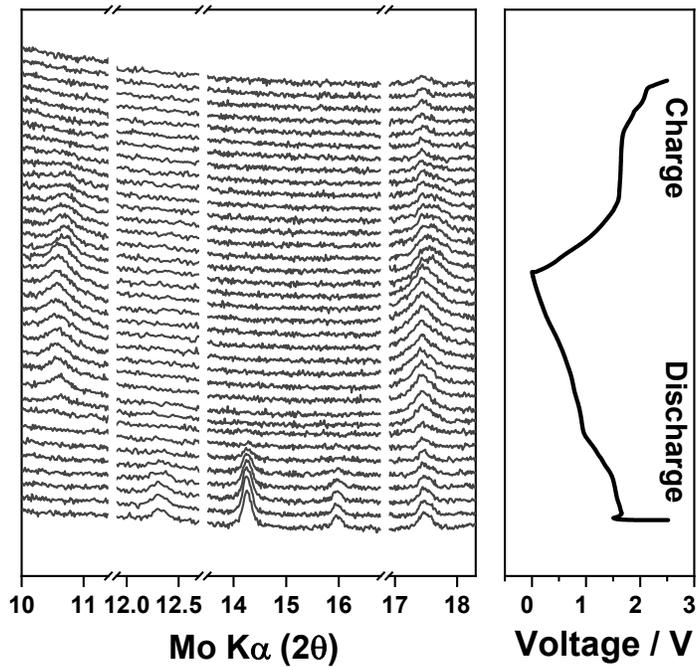


Fig. S4 In Operando XRD patterns of p-NiS₂@C

Table S1. Comparison of the proposed composite with that of previous studies on NiS₂

Materials	Carbon content (%)	Voltage range (V)	Electrolyte	Rate performance		Cycling performance		Ref
				Capacity (mAh g ⁻¹)	Current (Ag ⁻¹)	Low current	High current	
porous NiS ₂ @C	8.5	0 – 2.5	1M NaPF ₆ in DGM	782, 659, 623, 574, 519, 486, 459 and 437	0.1, 0.3, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0	848 mAh g ⁻¹ after 50 cycles at 0.1A g ⁻¹	Over 700 mAh g ⁻¹ after 500 cycles at 1.0 a g ⁻¹	This work
Ultrasmall NiS ₂	43.6	0 – 3.0	1M NaPF ₆ in EC/PC (1:1) + 5% FEC	540, 505, 475, 450, 370 and 300	0.05, 0.1, 0.2, 0.5, 1.0 and 2.0	371 mAh g ⁻¹ after 200 cycles at 0.1 A g ⁻¹	Below 200 mAh g ⁻¹ after 1000 cycles at 2 A g ⁻¹	Nanoscale 2019 ¹
NiS ₂ /C	17	0.005 – 3.0	1M NaPF ₆ in DGM	634.2, 585.4, 569.4, 549.5 and 527.8	0.1, 0.2, 0.5, 1.0 and 2.0	848 mAh g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	530mAh g ⁻¹ at 2.0 Ag ⁻¹ after 300 cycles	JMCA 2018 ²
NiS ₂ /PCF	61.7	0.01 – 3.0	1M NaClO ₄ in EC/PC (1:1) + 2 % FEC	580, 516, 450, 391, 347, 302 and 245	0.087, 0.16, 0.43, 0.87, 1.6, 4.3 and 8.7	561 mAh g ⁻¹ after 300 cycles at 0.087 A g ⁻¹	275 mAh g ⁻¹ after 5000 cycles at 4.3 A g ⁻¹	Adv. Energy.Mater 2018 ³
Pomegranate NiS ₂ /NC	25.7	0.005 – 3.0	1M NaClO ₄ in EC/PC (1:1) + 5 % FEC	528.3, 513.4, 452.2, 410.1, 343.5 and 294.4	0.1, 0.5, 1.0, 1.5, 2.0 and 3.0	505.7 mAh g ⁻¹ after 100 cycles at 0.1A g ⁻¹	356.2 mAh g ⁻¹ after 300 cycles at 0.5A g ⁻¹	JMCA 2018 ⁴
Nickel sulfide-embedded carbon matrix	51.3	0 – 3.0	1M NaClO ₄ in EC/PC (1:1) + 5 % FEC	680, 630, 580, 520, 410, 310 and 230	0.2, 0.5, 1,2, 5, 10 and 15	650 mAh g ⁻¹ after 200 cycles at 0.5 A g ⁻¹	300 mAh g ⁻¹ after 800 cycles at 1 A g ⁻¹	ESM 2020 ⁵
NiS ₂ decorated withCarbon	50.6	0.01 – 3.0	1M NaClO ₄ in PC + 5 % FEC	694, 671, 670, 631, 555 and 448	0.1, 0.2, 0.4, 0.8 and 1.6	580.8 mAh g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	-	Adv.Funt.Mater 2018 ⁶
Mesoporous NiS ₂	-	0.4 – 2.9	1M NaClO ₄ in DGM	681, 490, 420 and 253	0.3, 1.0, 2.0 and 5.0	692 mAh g ⁻¹ after 100 cycles at 0.1 A g ⁻¹	319 mAh g ⁻¹ after 1000 cycles at 0.5 A g ⁻¹	Small 2017 ⁷

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