

Supporting Information for

Synthesis of Thinly N-Doped Carbon-Coated MoS₂ for High-Rate Na-ion Storage

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1. Experimental Section

1.1 Chemicals and Reagents

Molybdenum trioxide (MoO_3 , A.R. grade) and zinc chloride (ZnCl_2 , A.R. grade) were purchased from Shanghai McLean Biochemical Technology Co., LTD. Formamide (CH_3NO , purity > 99%) was from Tianjin Damao Chemical Factory. Sublimed Sulfur and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., LTD. Polyvinylidene fluoride (PVDF) was purchased from Aladdin Scientific. Polypropylene (PP) separator (TOB-PP-25, 25 μm thickness, 42% porosity) was purchased from Shenzhen TOB New Energy Technology Co., LTD. Carbon black (BP2000) was purchased from Nanjing Pioneer Nanomaterials Technology Co., LTD. Coin cell case model CR2032 was purchased from Whatman Company. All reagents were used as received without further purification.

1.2 Preparation of thinly N-doped carbon-coated MoS_2 nanoparticles ($\text{MoS}_2@\text{NC}$)

$\text{MoS}_2@\text{NC}$ was prepared using a stepwise method consisting of (1) solvothermal treatment of MoO_3 nanomaterial in formamide under the assistance of ZnCl_2 , (2) annealing of the formamide-derived highly dispersed Mo/Zn-nitrogen-carbon materials at 900 $^\circ\text{C}$ in N_2 , and (3) vulcanization of the as-annealed sample at 600 $^\circ\text{C}$ in S vapor. Typically, 0.09 mmol MoO_3 and 0.01 mmol ZnCl_2 were first suspended/dissolved in 30.0 mL formamide, and the mixture was ultrasonicated for 30 min to form a homogeneous suspension, obtaining a total metal concentration of 0.003 mol L^{-1} . The suspension was then transferred to a Teflon-lined 50.0 mL-packed autoclave reactor, heated at 180 $^\circ\text{C}$ for 12 h, and allowed to cool naturally to room temperature. The slurry-like product was washed 2–3 times with water and dried at 80 $^\circ\text{C}$ overnight. The dried product was named f-Mo/Zn-NC and finely milled for further use.

f-Mo/Zn-NC precursor was then placed in a quartz tube, and heated at 900 $^\circ\text{C}$ for 1 hour at a ramp of 5 $^\circ\text{C min}^{-1}$. The as-obtained product was named $\text{Mo}_2\text{N}@\text{NC}$ due to the formation of finely sized Mo_2N nanoparticles being wrapped by N-doped carbon shells. Next, 0.10 g $\text{Mo}_2\text{N}@\text{NC}$ was placed at the center of a quartz tube. Sulfur powder (~ 1.0 g) was placed upstream of the quartz tube at 10 cm from the $\text{Mo}_2\text{N}@\text{NC}$ precursor. The system was heated at 600 $^\circ\text{C}$ for 1 hour at a ramp of 5 $^\circ\text{C min}^{-1}$. The as-obtained sample was named $\text{MoS}_2@\text{NC}$. Meanwhile, a control sample of MoS_2 was prepared via vulcanization of commercial MoO_3 material to obtain homemade MoS_2 .

1.3 Electrochemical Measurements

Electrodes were prepared by mixing active material ($\text{MoS}_2@\text{NC}$ or homemade MoS_2), conductive carbon black, and PVDF binder at a weight ratio of 7:2:1 in an appropriate amount of N-methyl-2-pyrrolidone (NMP), and ball-milled for 4 hours to obtain a homogeneous slurry. Then the slurry was blade-coated on the Al foil (15 μm thick) and then dried in a vacuum oven at 60 $^\circ\text{C}$ for over 12 h. The dried electrode was punched into 14 mm diameter disks and assembled into coin-type cells in a glove box filled with Ar gas (O_2 content <0.01 ppm, H_2O

content <0.01 ppm). The electrode material loaded on a 14 mm-disk Al foil was controlled at about 1.0 mg cm⁻². Sodium foil was used as the reference and counter electrodes, PP membrane as the separator, and commercially available 1.0 mol L⁻¹ NaClO₄ in DEC:EC (1:1 v/v, with 2% FEC, DuoDuo Chemical Company) as the electrolyte.

Constant current charge/discharge measurements were carried out using a multi-channel battery test system (LAND-CT2001A) in a potential window of 0.1–3.0 V (vs Na⁺/Na). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed at an electrochemical workstation (Bio-logic, France, VMP-3). Galvanostatic intermittent titration technique (GITT) measurements were conducted at a current density of 0.3 A g⁻¹ with a discharging/charging pulse of 5 min followed by a rest of over 20 min. Discharge titration was performed first with a cutoff voltage of 0.01 V, and then charge titration was performed in the same manner until a cutoff potential of 3 V was reached. The diffusion coefficient (D_{Li^+}) can be obtained according to the following Equation[16, 17]:

$$D = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad (1)$$

where τ is the current pulse duration, n_m is the mole of the active substance, V_m is the molar volume of the active substance, S is the contact area between the electrode and electrolyte, ΔE_s is the voltage change in steady-state processes, and ΔE_τ is part of the voltage change caused by the applied current.

1.4 Characterizations

Powder X-ray diffraction (XRD) was performed with Cu K α radiation ($\lambda = 0.15406$ nm) on a Br ker D8 Advance diffractometer at 40 kV and 40 mA. Raman spectra were obtained by a DXR2 Raman microscope (Thermo Fisher) using a 532 nm argon laser line as the excitation source. Scanning electron microscopy (SEM) images were measured on an Apreo S Hivac scanning electron microscope with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM), high-resolution TEM(HRTEM), and high-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on an FEI Talos 200S high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The surface chemical composition and valence state of the samples were studied by X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific, USA) with monochromatic Al K α radiation (1486.6 eV). An automatic gas sorption analyzer, Tristar 3000 (Micromeritics Instrument Corporation), was used to determine the porous structure of the samples. The specific surface area (SSA) and pore-size distribution were calculated from nitrogen adsorption isotherms using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

2. Supplementary Figures

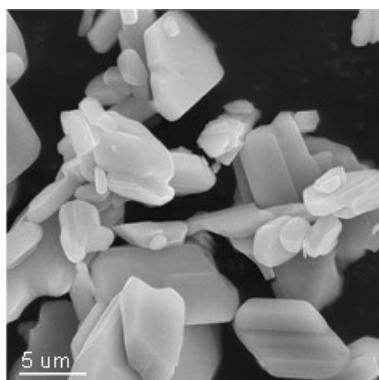


Figure S1. SEM image of commercial MoO₃.

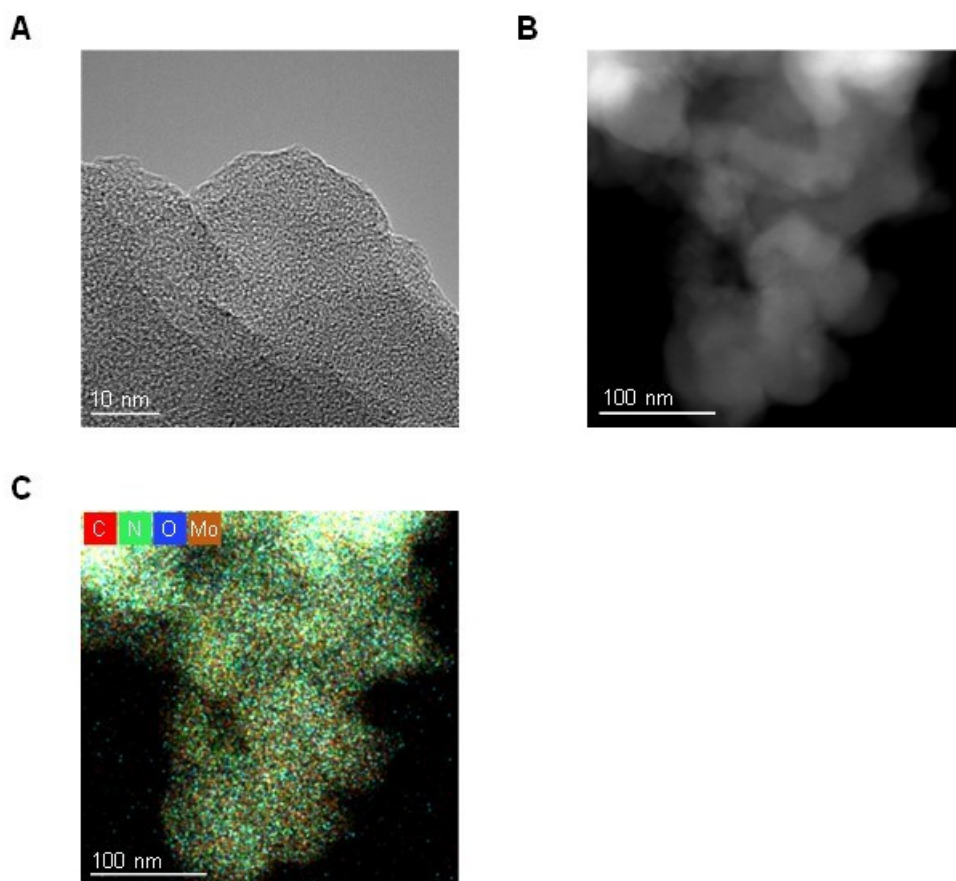


Figure S2. (A) HRTEM image, (B) HAADF-STEM image, and (C) corresponding EDS element mapping images of f-Mo-NC precursor.

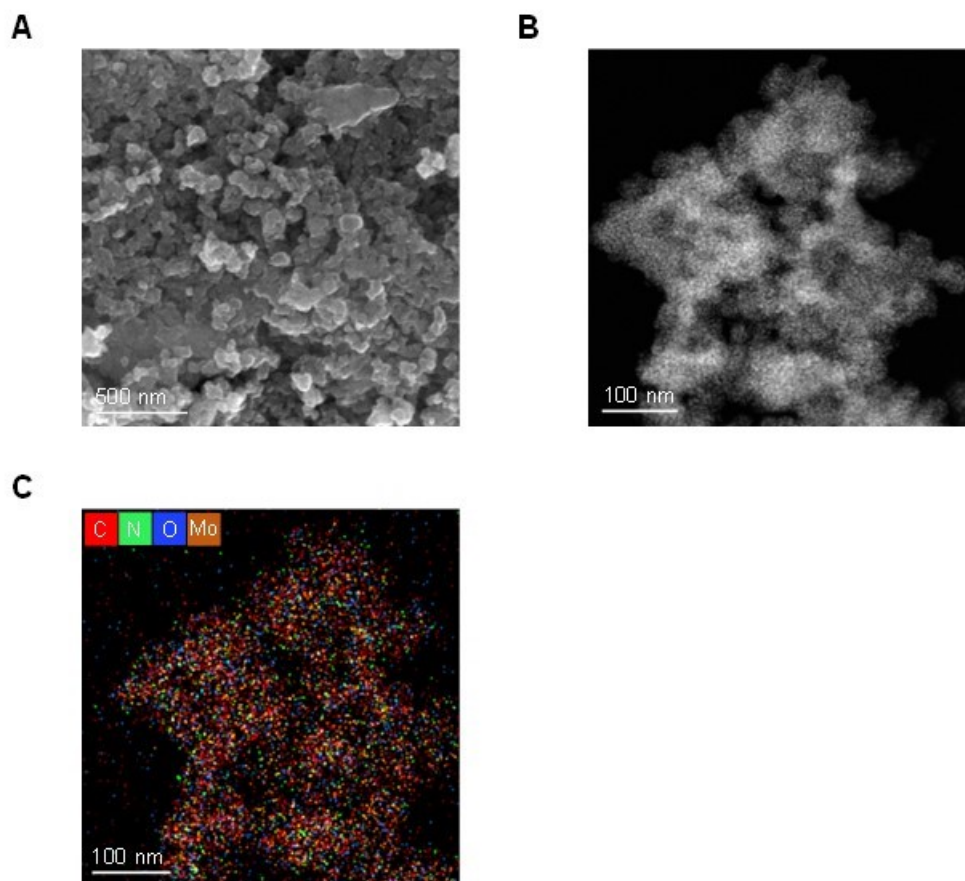


Figure S3. (A) SEM image, (B) HAADF-STEM image, and (C) corresponding EDS element mapping images of Mo₂N@NC precursor.

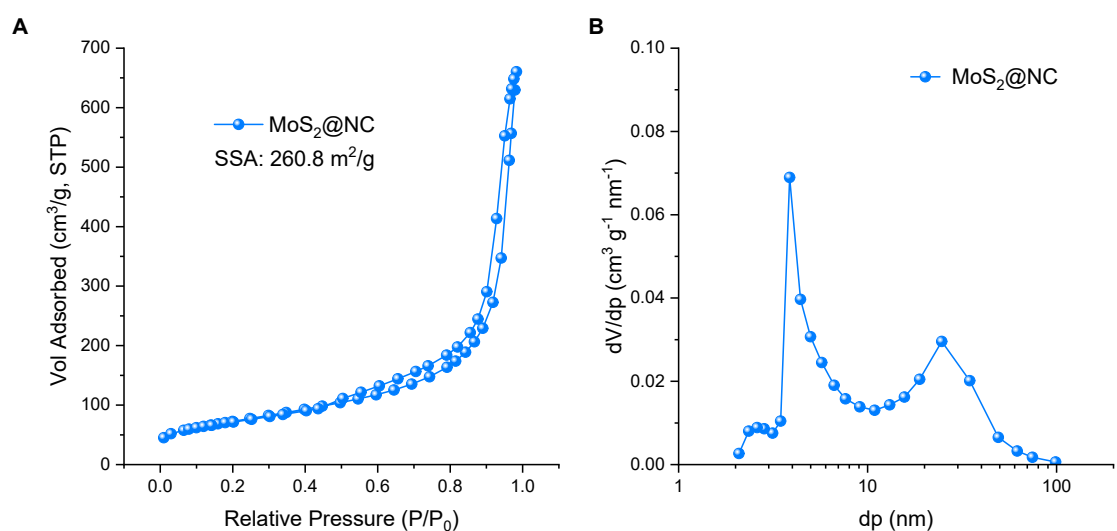


Figure S4. BET measurement of MoS₂@NC: (A) N₂ absorption/desorption isotherm curves and (B) pore distribution curves.

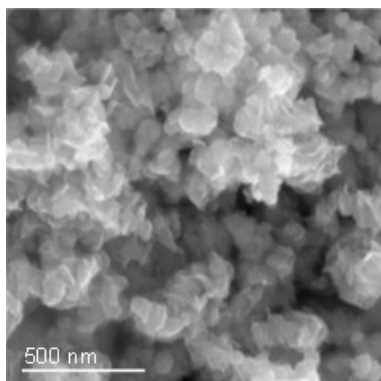


Figure S5. SEM image of MoS₂@NC.

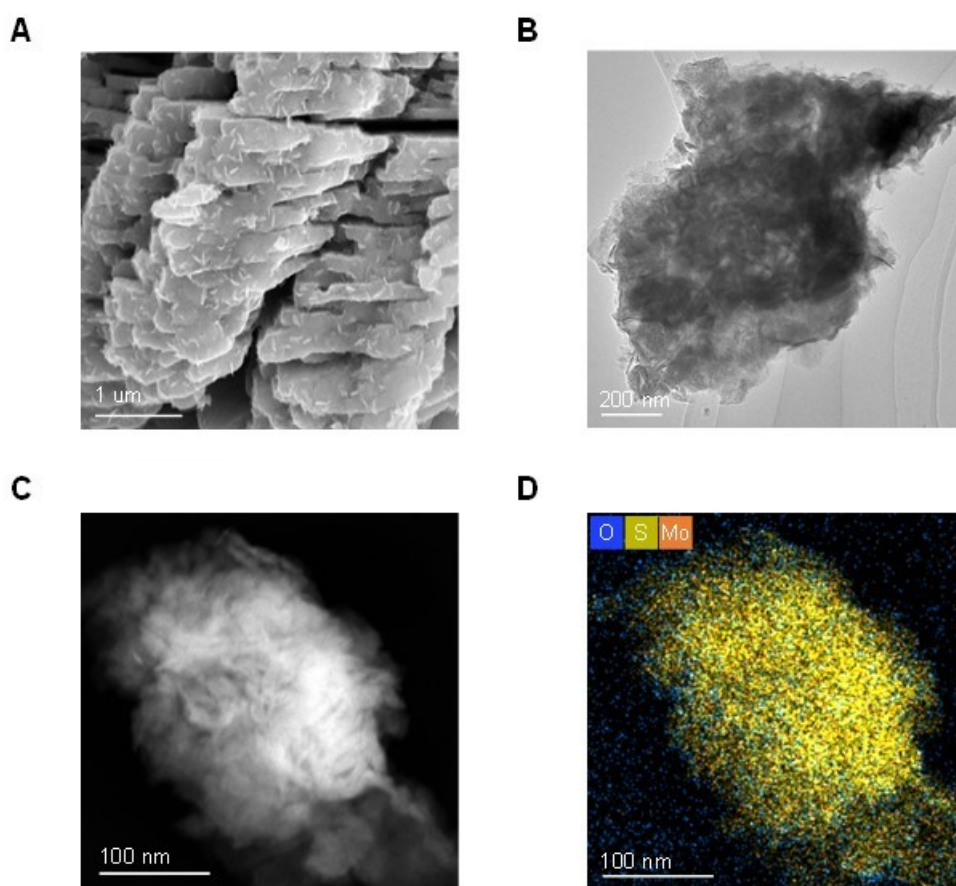


Figure S6. (A) SEM image, (B) TEM, (C) HAADF-STEM image, and (D) corresponding EDS element mapping images of home-made MoS₂.

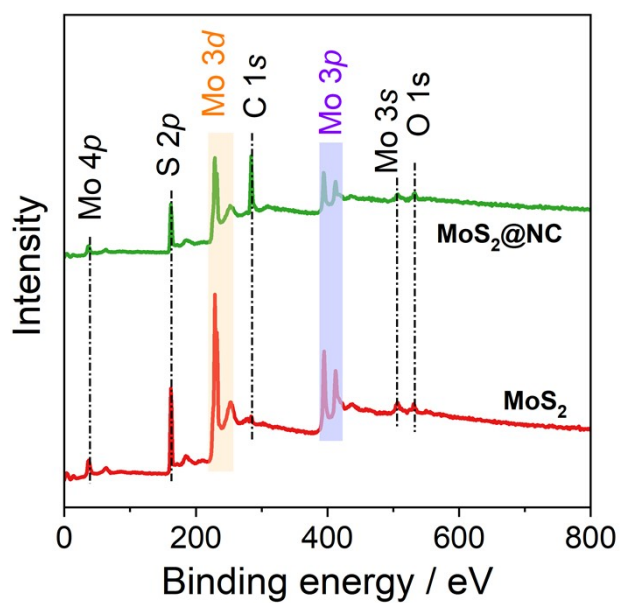


Figure S7. XPS full-spectra survey of home-made MoS_2 and $\text{MoS}_2@\text{NC}$.

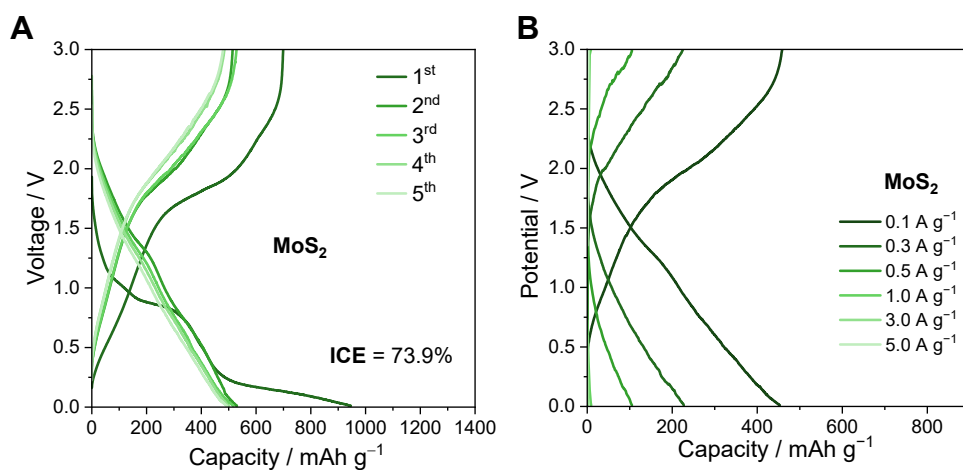


Figure S8. (A) First five cycles of charge/discharge curves of homemade MoS_2 . (B) Charge/discharge curves of homemade MoS_2 at different current rates.

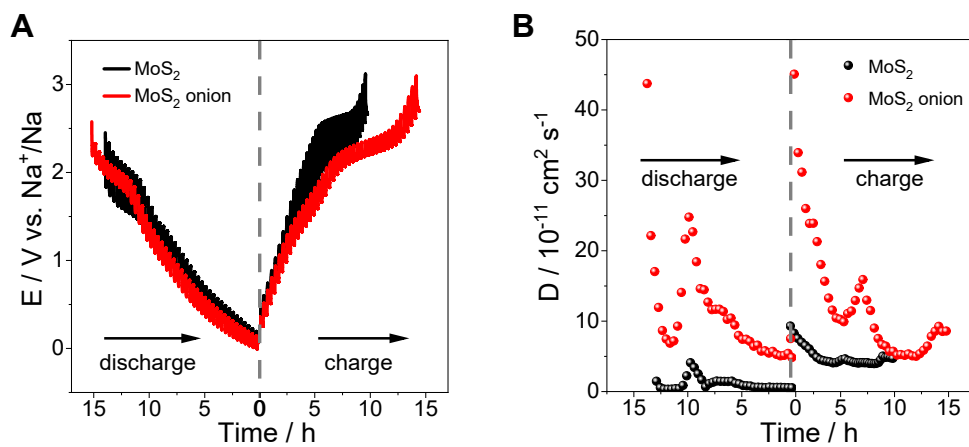


Figure S9. (A) GITT curves and (B) Na⁺ diffusion coefficient of MoS₂@NC and homemade MoS₂ from MoO₃.

3. Supplementary Table

Table S1. Comparison of Na-ion storage performance of MoS₂-based materials.

Name	Morphology	Cs (mAh/g @j)	Cs (mAh/g @j)	Cycle Life (Retention@j@cycle No.)	Source
MoS ₂ @NC	0D onion	806@0.1A/g	586@5A/g	84%@0.5A/g@300	This work
FeMoS ₂ /C-II	2D layered	700@0.1C	420@5C	83.8%@10C@3000	Adv Funct Mater, 2024, DOI: 10.1002/adfm.202404263
MoS ₂ @NCSAMn/CNTs	2D MoS ₂ with 1D CNT backbone	564.5@0.1A/g	293@1A/g	89.4%@1A/g@2000	Angew, 2024, DOI: 10.1002/anie.202411255
rGO@MoS ₂ /NAC	3D flower-like	458@0.2A/g	300@5A/g	89.7%@5A/g@3500	EcoMat, 2024, 6(8) e12479
Re-doped IF-MoS ₂	0D onion	175@0.02A/g	88@2A/g	78%@0.02A/g@30	Isr J Chem 2015, 55, 599–603
1T-rich MoS ₂ /m-C	3D flower-like	557@0.1A/g	495@5A/g	98.4@0.5A/g@300	ACS Nano 2022, 16, 12425–12436
HMF-MoS ₂	Hollow nanobox	412@0.1A/g	226@5A/g	93.7%@1A/g@130	ACS Nano 2019, 13, 5533–5540
MHPC-0.1	3D mesoporous	948@0.1A/g	579@5A/g	>100%@1A/g@300	ACS Appl Mater & Interf, 2016, 8(30), 19456–19465
BD-MoS ₂	3D flower-like	410@0.1A/g	262@5A/g	>100%@0.5A/g@100	Small, 2019, 15(12), 1805405
Note: Cs = specific capacity, j = current density, No. = number.					