

Electronic Supplementary Information (ESI)

**Confinement of ZIF-67 derived N, Co-Doped C@Si on
2D Mxene for Enhanced Lithium Storage**

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EXPERIMENTS

Chemicals. All of the reagents and solvents, including cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, Aladdin), Si nanoparticles (~30nm, AR, Aladdin), Polyvinylpyrrolidone (PVP, AR, Heowns Biochem Technologies, LLC, Tianjin), 2-Methylimidazole (AR, Aladdin), Ti_3AlC_2 (Aladdin), HF solution (Sigma-Aldrich), HCL solution (Sigma-Aldrich), LiCl (Heowns), H_2SO_4 (Sigma-Aldrich), ethanol (EtOH, 99.5%, Tianjin Concord), were commercially obtained and used without further purification. Distilled water was used in experiments.

Synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was prepared by selectively etching the Ti_3AlC_2 precursor using the HF/HCl mixture as the etchant. Generally, 3 ml deionized water (DIW), 1ml HF and 5 ml HCl under stirring to form a homogeneous solution, and 1 g of Ti_3AlC_2 was gradually added to the $\text{H}_2\text{O}/\text{HF}/\text{HCl}$ mixture and stirred for 24 h at 41 °C to realize the etching of Al atoms in Ti_3AlC_2 . After that, the product was centrifugated at 3500 rpm for 1 min to remove the etchant and byproducts and washed with deionized water (DIW) several times until the pH of the supernatant exceeded 6. The black precipitate are collected by centrifugation. Then, 1.5 g LiCl and 25 ml deionized water (DIW) under stirring to form a homogeneous solution, and the black precipitate was gradually added to the LiCl solution mixture and stirred for 2 h at 41 °C. Finally, the black precipitate was separated by centrifugation at 3500 rpm for 5 minutes, washed with deionized water (DIW) for 3 times, and then collect the suspension into a glass bottle, the collection was repeated for 7 times. The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nano-layer suspension was obtained.

Synthesis of N, Co-Doped C@Si@MXene and N-Doped C@Si@MXene. 0.2 g (3 mmol) of Si NPs and 1.0 g (4 mmol) PVP were uniformly dispersed into ethanol (60 ml) through stirring for 12 h at room temperature. The obtained Si@PVP nanoparticles (NPs) was washed three times with ethanol to remove excess PVP and collected by Vacuum filtration. The collected Si@PVP NPs and 1.642g (10 mmol) of

2-Methylimidazole were redispersed into 100 mL ethanol stirring for 30min at room temperature, labeled as solution A. 1.456 g (4.4 mmol) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved into 100 mL ethanol, followed by addition of 50 ml (2 mg/ml) $\text{Ti}_3\text{C}_2\text{T}_x$ solution under stirring, labeled as solution B. Poured solution B into solution A and stir for 24 hours at room temperature obtained the ZIF-67@Si@MXene suspension. The ZIF-67@Si@MXene was obtained by Vacuum filtration and washed three times with ethanol to remove excess Cobalt ion, dried under vacuum at 60 °C for 12 h. To prepare N, Co-doped C@Si@MXene, the ZIF-67@Si@MXene powder was calcined at 800 °C for 3 h with a heating rate of 5 °C /min under Ar atmosphere. For comparison, N-doped C@Si@MXene was prepared by soaking N, Co-doped C@Si@MXene in diluted H_2SO_4 solution (2mol/L) to remove the doped Co. Finally, N-Doped C@Si@MXene was prepared by Vacuum filtration, washed with ethanol and dried under vacuum at 60 °C for 12 h.

Material Characterization. The morphologies and micro-structures of the samples were analyzed using a scanning electron microscope (SEM, Hitachi S4800), Thermogravimetric (TG) analysis was performed on a Rigaku TG-DTA 8122 instrument under an Ar atmosphere with a heating rate of 5 °C min^{-1} from room temperature (25 °C) to 800 °C. X-ray powder diffraction (XRD) was carried out on a X'Pert-Pro MPD diffractometer (PANalytical) with monochromatic Cu $K\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$, 5°C min^{-1}). The surface chemical properties of samples were investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 220i-XL, Thermo Scientific, USA). The elemental contents of Co, Si and Ti were measured on an inductively coupled plasma-optical emission spectroscopy (ICP-OES) Agilent720ES equipment. Fourier transformed infrared (FT-IR) spectra were measured on a Bruker ALPHA FT-IR spectrometer.

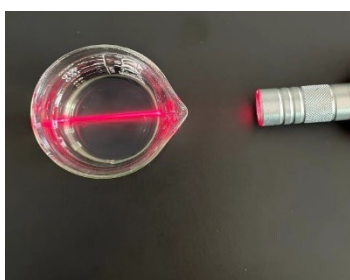
Electrochemical Measurements. The working electrodes were prepared by mixing active materials, conducting agent (acetylene black), and PVDF in a weight ratio of

8:1:1 in N-methyl-2-pyrrolidone (NMP) to form the slurry. After being coated on a copper foil, the electrode was dried at 80 °C for 12 h. The CR2032 coin cells were used to evaluate electrochemical performance of half-cells. A polypropylene (PP) microporous membrane served as a separator, and the electrolyte was the mixture of ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1 containing 1 M LiPF₆. The anodes were punched from copper sheet using a punch die, and the final surface area of each sheet was ~1.13 cm², the thickness of the electrode was ~9 μm. Lithium metal foil, Celgard 2400 microporous membrane, and gaskets were used as counter electrode, separator, and fixture, respectively. A LAND multichannel battery tester (CT3002A) was used to perform a constant current charge and discharge test between 0.01 and 3.0 V at various current densities from 0.2 to 4.0 A g⁻¹. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in the electrochemical workstation (CHI 660D). EIS was performed with ±5 mV amplitude and within the frequency range of 100 kHz–10 mHz.

Table S1. Weight ratio of Co, Si, and Ti in N, Co-Doped C@Si@MXene.

Element	Content (W%)
Co	24.3537%
Si	24.0851%
Ti	8.0043%

(a)



(b)



Fig. S1. (a,b) Tyndall effect of the MXene solution.

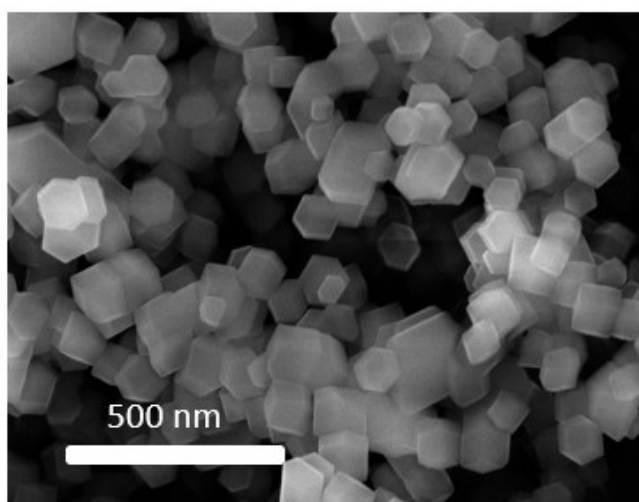


Fig. S2. SEM image of ZIF-67.

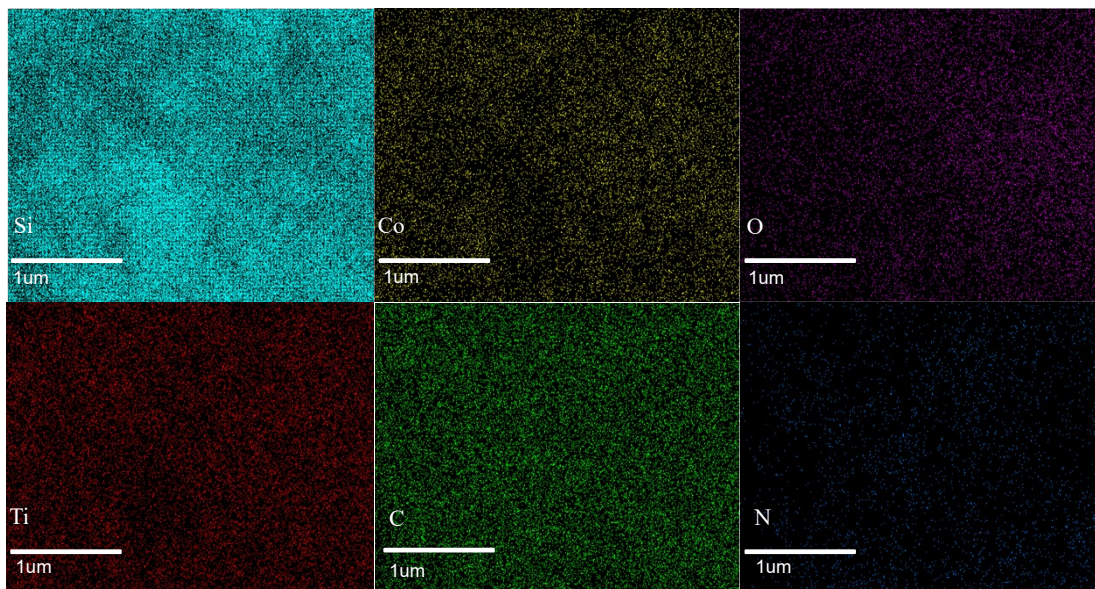


Fig. S3. EDS elemental mapping images N, Co-Doped C@Si@MXene.

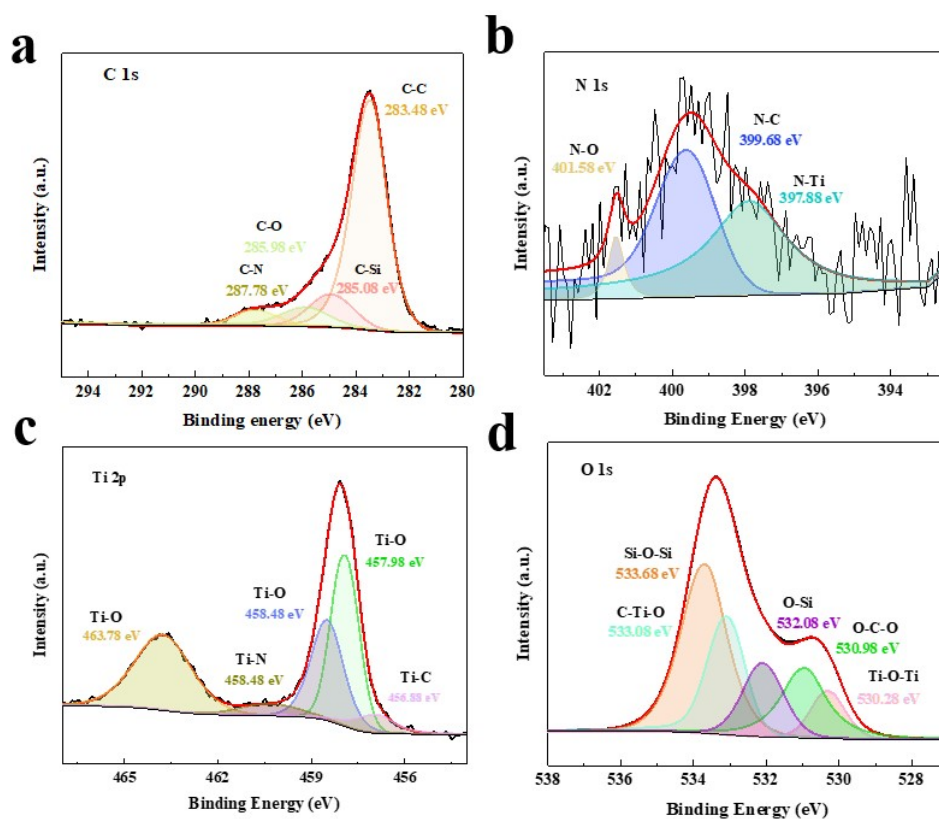


Fig. S4. XPS spectra of N, Co-Doped C@Si@MXene (a) C 1s XPS spectra (b) O 1s XPS spectra (c) Ti 2p XPS spectra (d) N 1s XPS spectra.

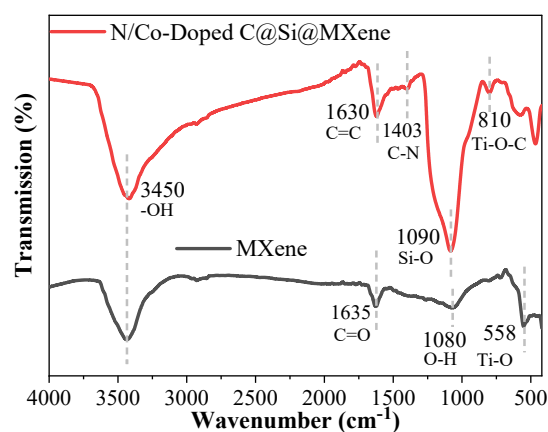


Fig. S5. FT-IR of N, Co-Doped C@Si@MXene and MXene.

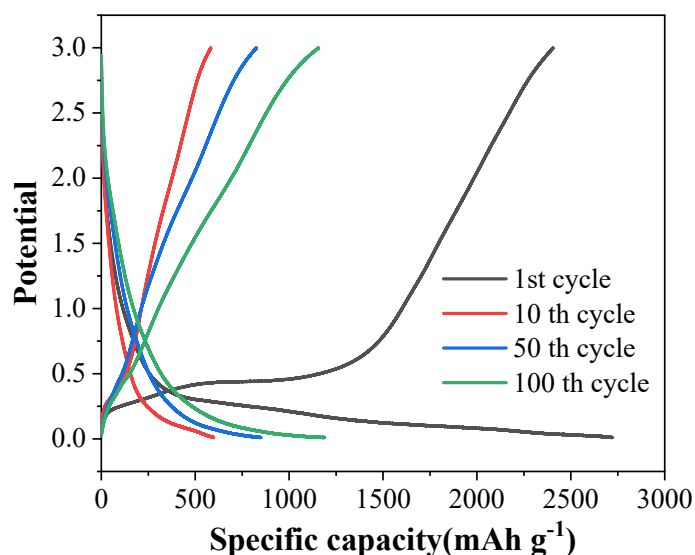


Fig. S6. Galvanostatic charge-discharge curves of N-doped C@Si@MXene at 0.2 A g^{-1} .

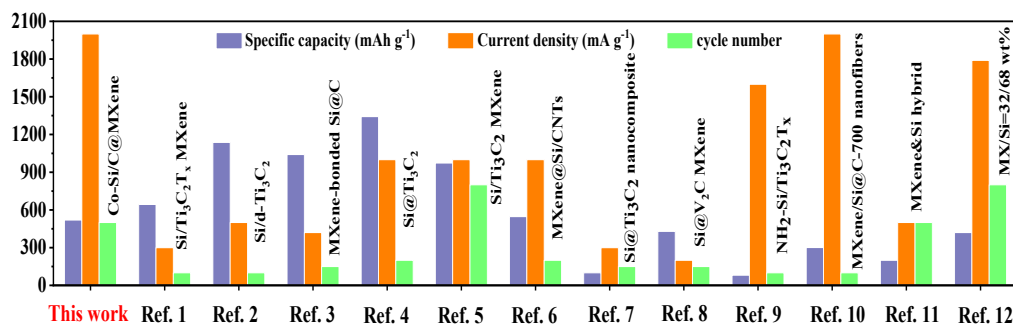


Fig. S7. Performance comparison of N, Co-doped C@Si@MXene with other reported Si- and MXene-based anodes.

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