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MXene Supported Transitional Metal Nanoparticles Accelerate Sulfur Reduction Reaction Kinetics

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Experimental section

Synthesis of MXene Sheets, TMNPs@MXene, and TMNPs@MXene/S Composites

In a typical synthesis of MXene sheets, 0.3 g 1,4-Naphthalenedicarboxylic acid was dissolved in 30 mL deionized (DI) water. Then, 0.08 g Ti_3AlC_2 powder and 1.5 mL 40 wt% HF were added to the above solution to form a homogeneous suspension under magnetic stirring. The homogeneous suspension was transferred into a 50 ml Teflon-lined autoclave and heated at 160 °C for 6 h. The obtained sediment was washed with N, N-Dimethylformamide, and deionized (DI) water till the pH was neutral, and dried under vacuum at 60 °C for 24 h.

The TMNPs@MXene composites were also prepared by a hydrothermal method. 80 mg MXene ($Ti_3C_2T_x$) powder was dispersed in 50 ml DI water. After that, 0.4 mmol Cobalt acetate and 5mL Ammonia solution were added into the MXene suspension under vigorous stirring. The solution was immediately transferred to a 100 mL Teflon-lined autoclave and heated at 160 °C for 12 h. After the hydrothermal treatment, the resulting products were collected, washed, and dried. The as-prepared black precursors were then reduced at 600°C for 30 min under H_2/Ar atmosphere (H_2/Ar =1:9 by volume) to form CoNPs@MXene composite. FeNPs@MXene and NiNPs@MXene composites were synthesized using a similar method.

The TMNPs@MXene/S composites were synthesized via a typical meltingdiffusion route. 0.14 g TMNPs@MXene composite was ground with 0.26 g S_8 powders and the mixture was subsequently heated at 155°C for 12 h under an argon atmosphere to obtain the final products.

Soluble Lithium Polysulfide Adsorption Tests

Li_2S_6 solution was synthesized by dissolving S and Li_2S with a molar ratio of 5:1 in a mixture of 1,2-dimethoxyethane and 1,3-dioxolane (DOL) (v:v =1:1) under stirring for 12 h. 20 mg TMNPs@MXene composites were soaked with 2 mL 0.25 mM Li_2S_6 solution in an Ar-filled glovebox. The suspension was separated by filtration and the sediments were dried naturally in the Ar-filled glovebox to form Li_2S_6 coated TMNPs@MXene for the further X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi) characterizations using monochromatic Al Kα radiation.

Structural Characterizations

X-ray diffraction patterns of the samples were measured by the Rigaku X-ray diffractometer (XRD, Miniflex600, Rigaku Corporation) using Kα radiation operated at 40 kV and 15 mA. The morphologies of as-prepared samples were characterized by the field-emission scanning electron microscopy (FESEM, MAIA3, TESCAN, with an accessory EDX spectrometer). Fourier transform infrared (FT-IR) spectrum of MXene sheets was collected on a Thermo Fisher Scientific Nicolet iS50 spectrometer. The nitrogen adsorption-desorption isotherms were obtained at 77 K in N_2 atmosphere on a JW-BK200C system. The chemical composition of PB-based composites was examined using the inductively coupled plasma-mass spectrometry (ICP-MS, Spectro Blue SOP).

Electrocatalytic SRR Activity Evaluation

The Li_2S_6 symmetric cells were assembled using two identical electrodes that consist of TMNPs@MXene composites and PVDF binder with a mass ratio of 8:2. The electrolyte was 0.5 M Li_2S_6 and 1.0 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) dissolved in dioxolane (DOL)/dimethoxyethane (DME) solution (1:1/v:v) with 2.0 wt% $LiNO_3$. Cyclic voltammetry (CV) tests of Li_2S_6 symmetric cells were performed between -1.0 V and 1.0 V at a scan rate of 50 mV s^{-1}.

To test the nucleation and deposition of Li_2S, the 0.5 M Li_2S_8 solution was employed as the electrolyte. This electrolyte was prepared by dissolving sulfur and Li_2S at a molar ratio of 7:1 in DME/DOL (1:1, v/v) solution containing 1 M LiTFSI. TMNPs@MXene electrodes were used as cathodes and Li metal foil was used as anode. All the assembled cells were galvanostatically discharged to 2.09 V at 112 μA and then potentiostatically discharged at 2.08 V until the current was lower than 10^{-5} A. The final capacities of Li_2S deposition were calculated based on Faraday's law.

Linear sweep voltammetry (LSV) tests were measured on a CHI 760E electrochemical workstation coupled with the RRDE technique (Pine Research Instrument) in an argon-filled glovebox. A two-electrode H-type cell was adopted to perform these tests. 16 µl of 5 mg mL^{-1} catalyst ink that were prepared by sonicating 5 mg TMNPs@MXene catalysts in 980 µL isopropanol and 20 µL 5 wt.% Nafion solution was loaded onto a freshly polished glassy carbon electrode (0.196 cm^2) with an area mass loading of 0.2 mg cm^{-2}. This RRDE functions as the working electrode, and lithium foil as the counter and reference electrode. The electrolyte for LSV tests was 4 mM S_8 dissolved in the 1 M LiTFSI DME/DOL (1:1, v/v) solution. Before the LSV measurements, the glassy carbon electrodes should be activated in a blank electrolyte by CV scanning in the voltage range of 3.1-3 V at 10 mV s^{-1} for 30 cycles. LSV was then measured in the same cell at the sweep rate of 20 mV s^{-1} in the range of 3.3 V to 1.0 V. The LSV curve in the blank electrolyte without S_8 should also be collected to eliminate the background.

Electrochemical Measurements of Li-S Cell

The sulfur cathode was fabricated by mixing as-prepared TMNPs@MXene/S composites, KJ-black (EC600J), and polyvinylidene difluoride (PVDF) binder in N-methyl-2-pyrrolidinone with a weight ratio of 80:10:10. And then the slurry was cast onto carbon paper with a diameter of 12 mm, and subsequently vacuum-dried at 60 °C for 12 h. The CR-2032 coin cells were assembled in an argon-filled glovebox. The electrolyte was 1.0 M LiTFS dissolved in DOL/DME (1:1/v:v) with 2.0 wt% of $LiNO_3$. The typical area sulfur mass loading of the cathode is 3.0 mg cm^{-2}. The free-standing thick sulfur cathodes with a sulfur mass loading of 7.4 mg cm^{-2} were prepared using a vacuum filtration method. Galvanostatic discharge/charge measurements were performed on a LAND system in a voltage window of 1.7-2.8 V (vs. Li^+/Li). CV and electrochemical impedance spectra (EIS) were performed on a CHI760E electrochemical workstation. EIS analysis was performed with the frequency range from 100 kHz to 100 mHz. All the electrochemical data were measured at the stationary temperature of 25 °C.

Computational Methods

A first-principles approach based on density functional theory (DFT) was employed to understand the interaction between LiPS and metal sites. All simulations were performed using the Vienna Ab-initio Simulation Package (VASP). Electron–ion interactions were described by the projector augmented wave (PAW) method; the electron exchange-correlation was described using the PBE functional. The cut-off energy for the plane-wave basis was set at 400 eV. The force convergence criteria for optimizing atom positions were set to -0.02 eV/Å. The hexagonal metal clusters that have 7 metal atoms and are positioned on the single-layered Ti_3C_2 slab were used for modeling the adsorption behavior of LiPS. The adsorption energy is calculated by

$$E_{ads} = E(PS + surf) - E(PS) - E(surf),$$

where E(PS+surf) is the total energy of the entire system, E(PS) is the energy of an isolated Li_2S_4 molecule, and E(surf) is the energy of the clean surface. A more negative adsorption energy indicates a stronger binding force.

The computational hydrogen electrode (CHE) approach based on DFT was utilized to draw the full diagram of SRR. For the reduction reaction of Li_2S_2 to Li_2S, the elementary steps considered in this work are:

Li_2S_2 + TM cluster@MXene → Li_2S_2-TM cluster@MXene (1)
Li_2S_2-TM cluster@MXene + Li^+ + e^- → $Li_3S_2\cdot$-TM cluster@MXene (2)
$Li_3S_2\cdot$-TM cluster@MXene + Li^+ + e^- → $2Li_2S$-TM cluster@MXene (3)
$2Li_2S$-TM cluster@MXene → $2Li_2S$ + TM cluster@MXene (4)

The Gibbs free energy (ΔG) of the first step is the adsorption energy of one Li_2S_2 by the TM cluster@MXene substrate and the ΔG of the first step is the desorption energy of two Li_2S molecules on the TM cluster@MXene substrate. The ΔG of step 2 and step 3 can be written as follows:

$\Delta G(2)$ = G($Li_3S_2\cdot$-TM cluster@MXene)-G(Li_2S_2-TM cluster@MXene)-G(Li)
$\Delta G(3)$ = G($Li_3S_2\cdot$-TM cluster@MXene)-G(Li_2S_2-TM cluster@MXene)-G(Li)

The G(Li^+) + G(e^-) are written in the form of G(Li), which are usually used in the CHE method.

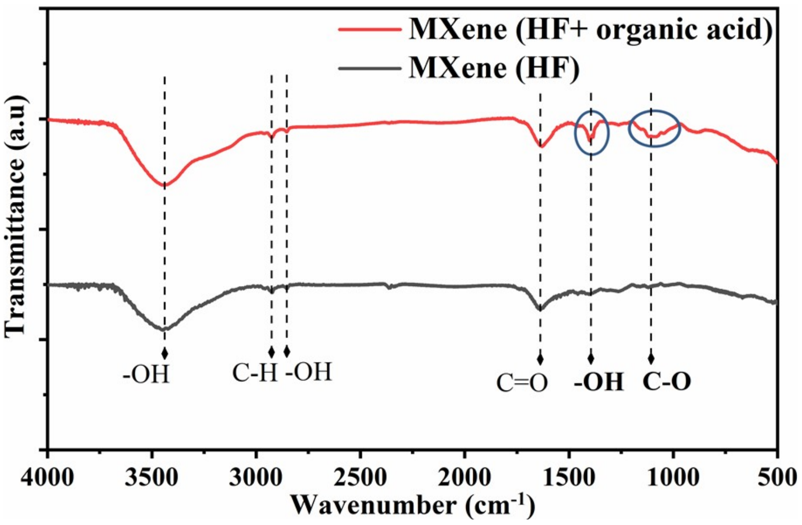


Figure S1. FT-IR spectra of MXene sheets prepared by HF-etching and HF + organic acid etching.

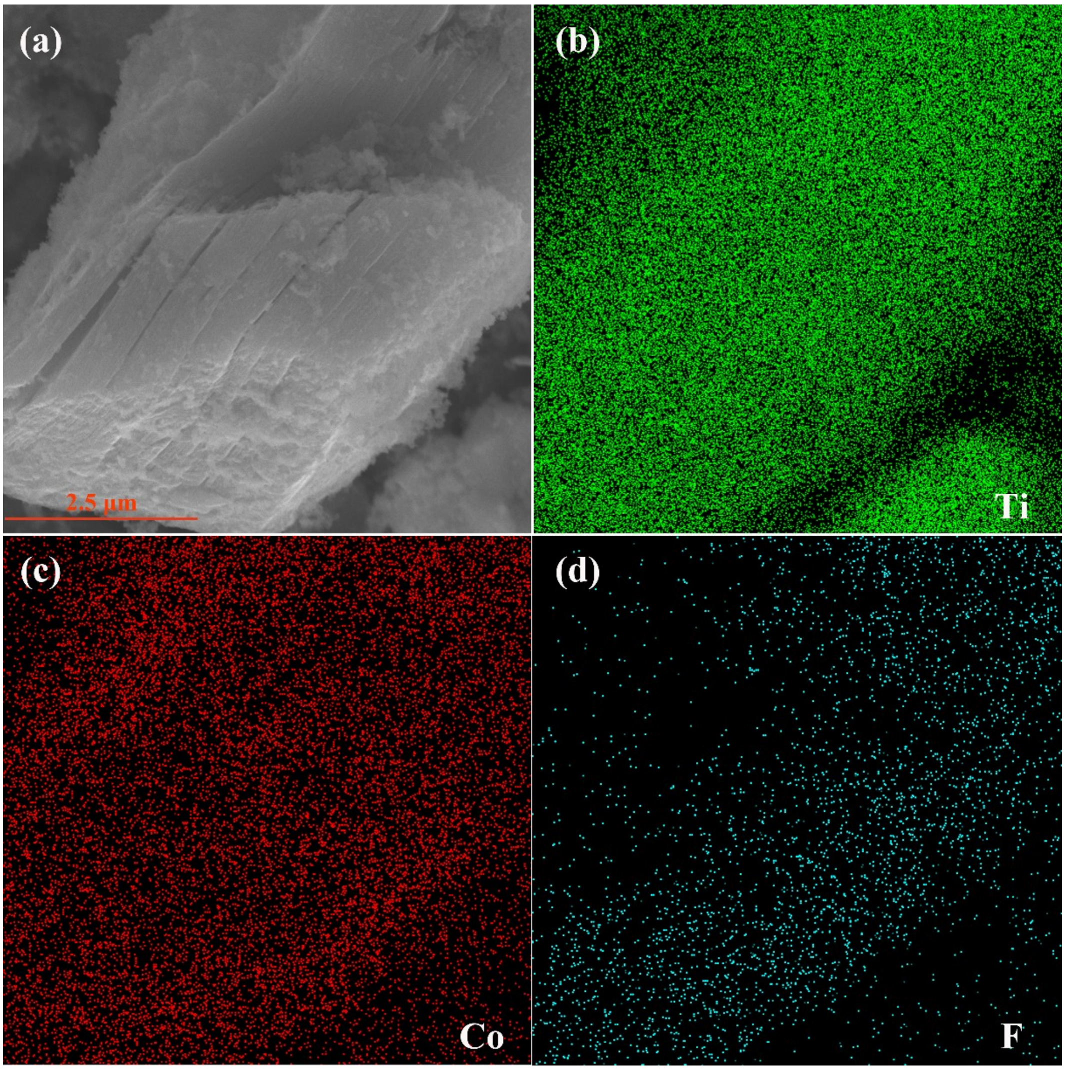


Figure S2. (a) SEM images of CoNPs@MXene composite and corresponding elemental X-ray mappings of (b) titanium, (c) cobalt, and (d) fluorine.

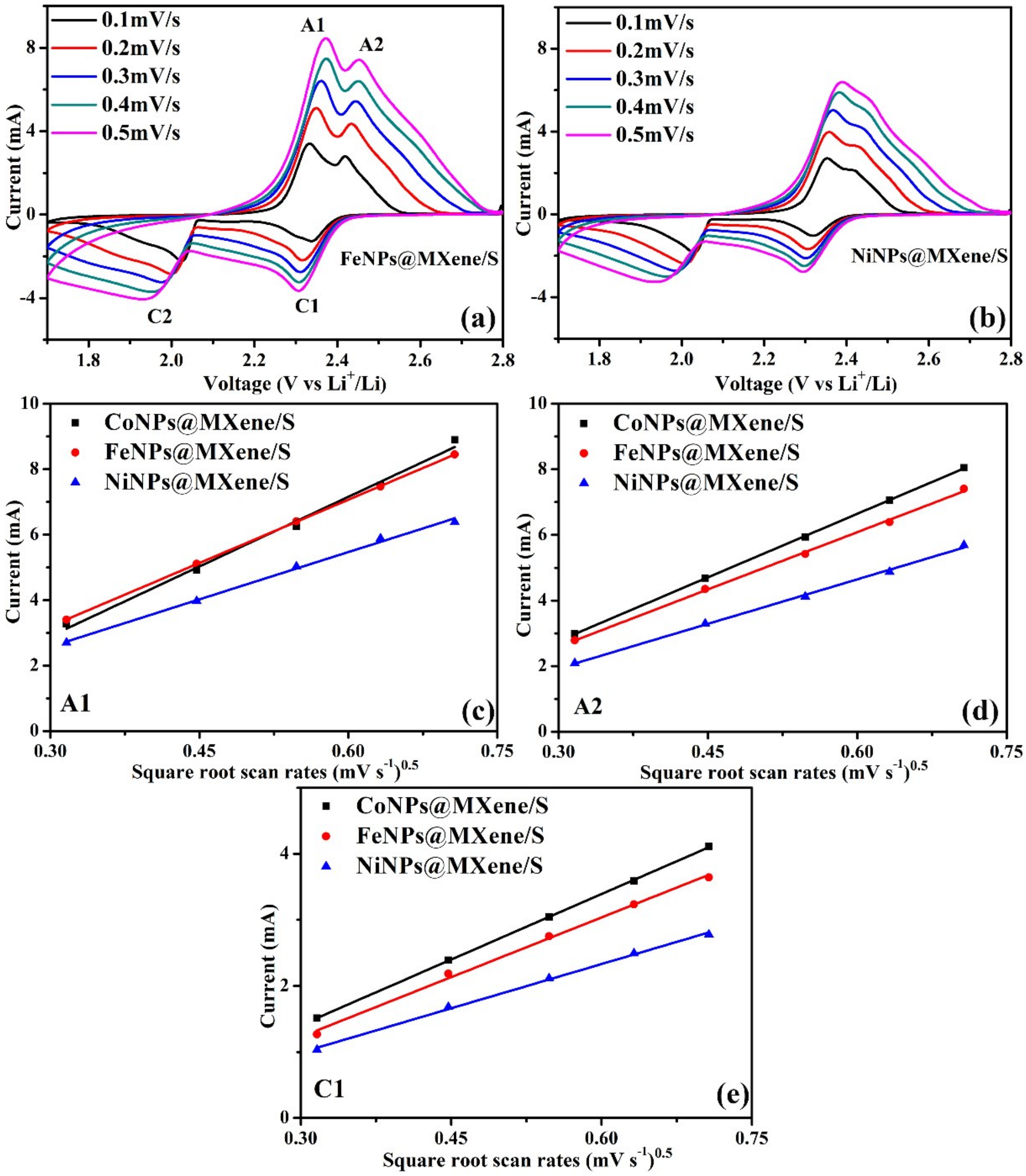


Figure S3. CV curves of the (a) FeNPs@MXene/S and (b) NiNPs@MXene/S cathode-based Li-S cell at various scan rates from 0.1 to 0.5 mV s^{-1}; Fitted plots of values of (c) A1, (d) A2 and (e) C1 peak current versus the square root of scan rates for TMNPs@MXene electrodes

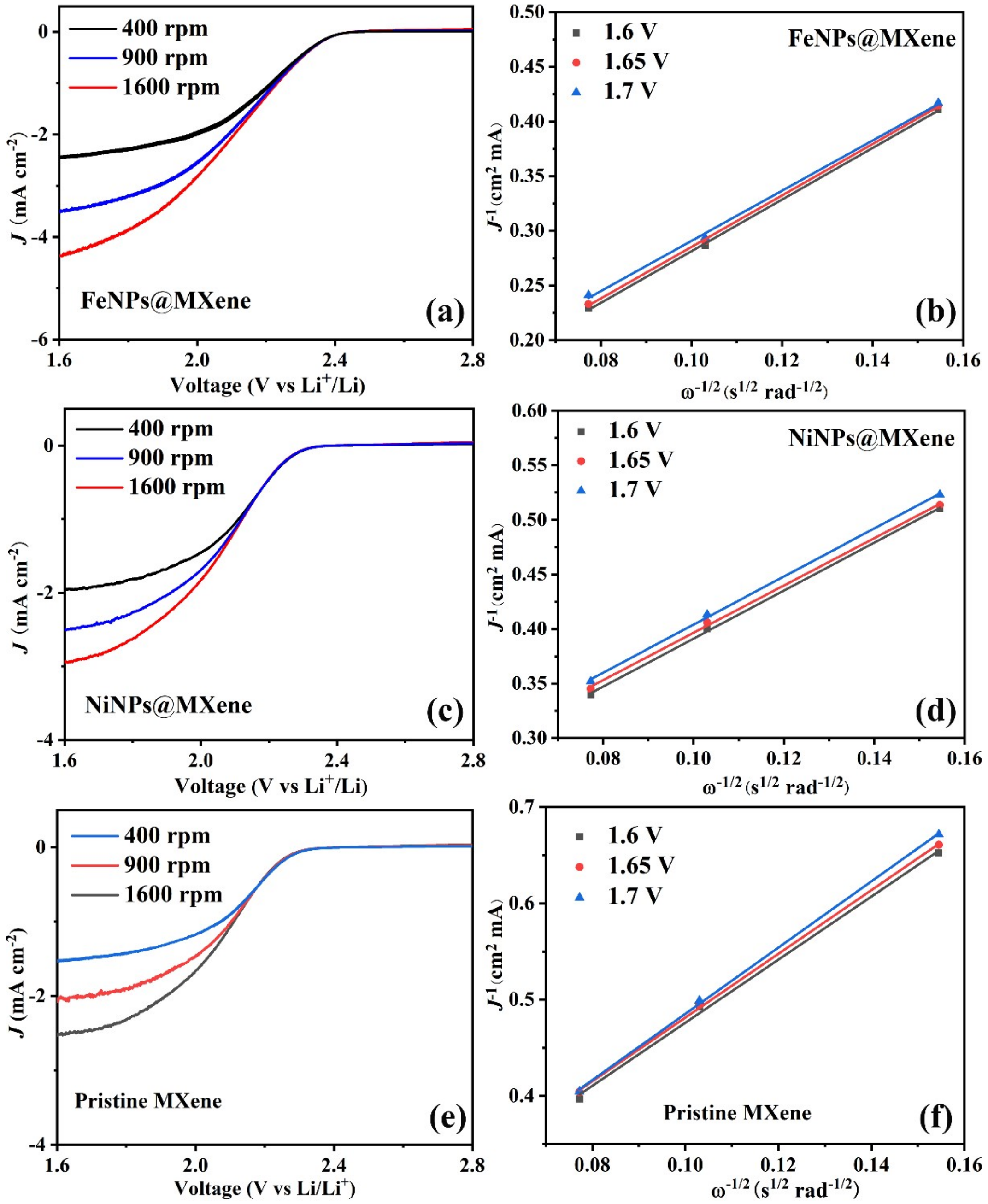
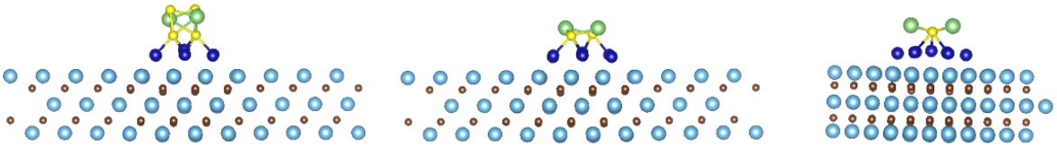


Figure S4. LSV curvess of (a) FeNPs@MXene, (c) NiNPs@MXene catalysts, and (e) MXene sheets with optimized mass loading (0.15 mg cm^{-2}) under different rotation rates; (b, d, f) Koutecky-Levich plots corresponding to part (a, c, e) at different potentials.



Li_2S_4 Li_2S_2 Li_2S

Figure S5. Side view of the optimized geometrics of Li_2S_4, Li_2S_2, and Li_2S clusters adsorbed on the TMNPs@MXene substrates.

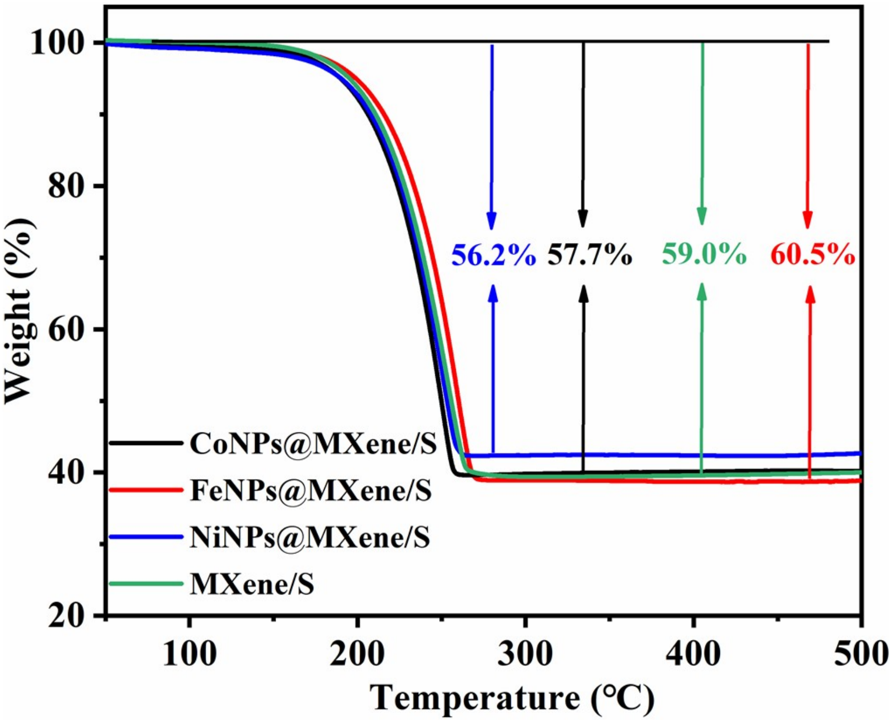


Figure S6. TGA curves of TMNPs@MXene/S and MXene/S composites.

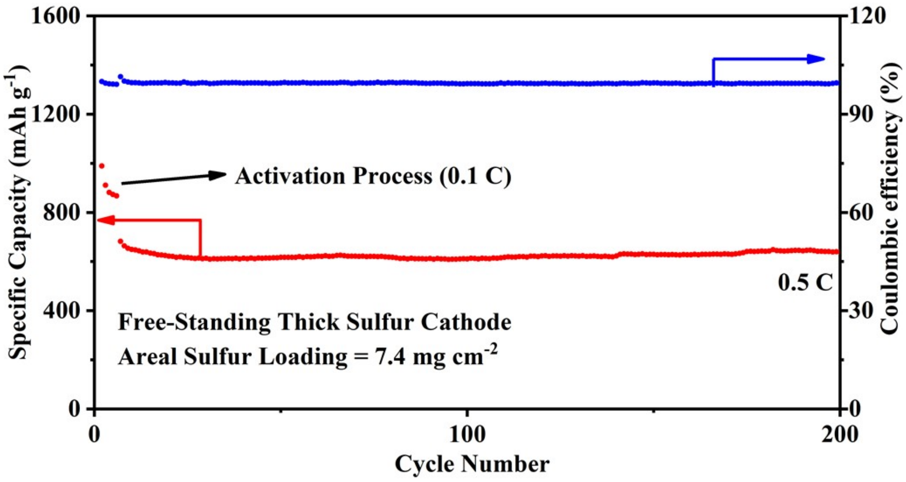


Figure S7 Cycling performance of CoNPs@MXene/S cathodes with a sulfur loading of 7.4 mg cm^{-2} at 0.5 C.

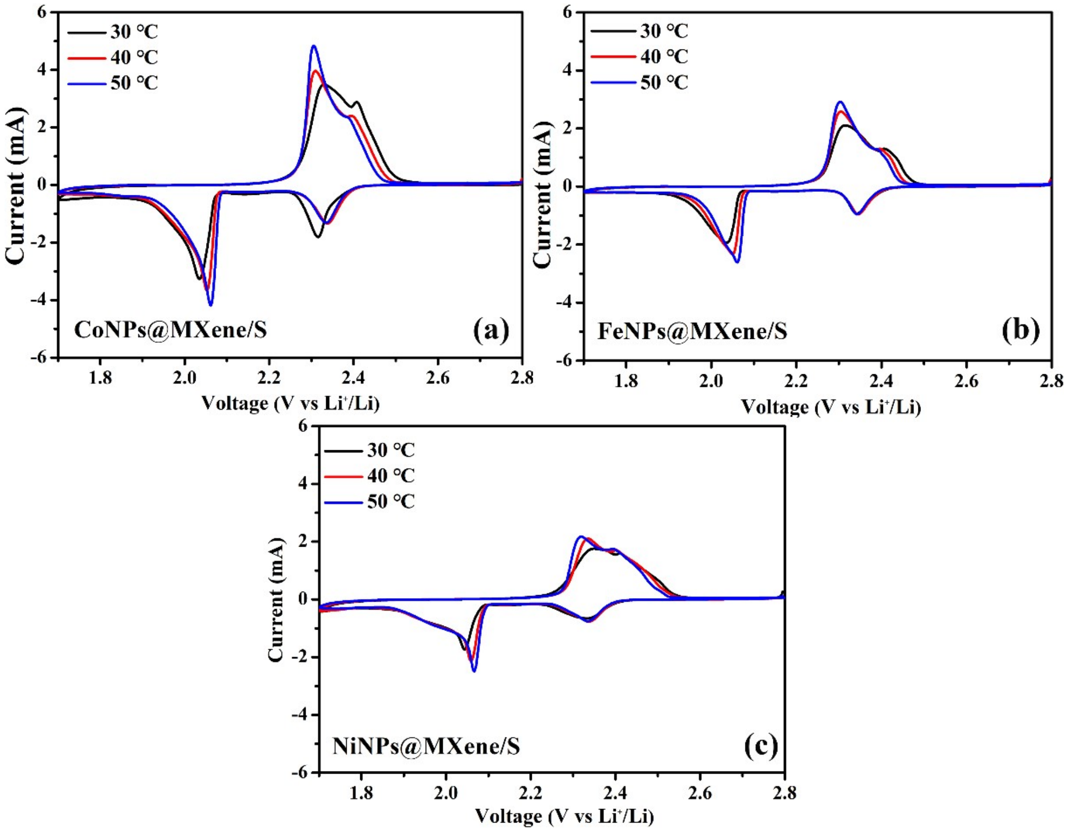


Figure S8 CV curves of (a) CoNPs@MXene/S, (b) FeNPs@MXene/S, and (c) NiNPs@MXene/S cathodes at various temperatures.

Table. S1 Comparison of performance of thick with different catalytic materials.

Catalysts	**Mass loading (mg cm^{-2})**	**Current Density (C)**	**nth Capacity (mAh g^{-1})**	**Capacity decay rate (%)**	**Ref.**
CoNPs@MXene	7.4	0.5	200th 638	0.032	**This work**
N, S-codoped graphene	8.5	0.5	200th 670	0.138	[26]
CNTs/Co	6.2	0.1	100th 570	0.405	[39]
Co@N-C/CNTs	5.1	0.2	100th 880	0.210	[40]
Co-GNTs	4.5	1	500th 452	0.076	[41]
Co–N-GC	2.5	0.2	200th 850	0.205	[42]
Co_4N@NC	4.5	2	400th 516	0.068	[43]
Mo@N-G	5	1	500th 615	0.084	[44]
Ni@C/graphene	2	0.5	1000th 518	0.061	[45]
CNT@$TiO_{2\text{-}x}$	5.5	0.05	60th 698	0.374	[46]
KB/Fe_2O_{3-x}	12.3	0.05	60th 612	0.213	[47]
TiC@G	3.5	0.2	100th 670	0.300	[48]
VN/G	3	1	200th 917	0.093	[49]
MoN-G	7	0.5	500th 678	0.072	[50]
MoN-C	3.4	0.5	500th 604	0.033	[51]
CoP-CNT	3	1	200th 835	0.021	[52]