Supplementary Information (SI) for Nanoscale.

Supporting Information

Heteroatom (N, Co) Doped MXene with Tunable Doping for Enhanced Hydrogen Evolution Reaction and Energy Storage

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#equal contribution

1. MXene synthesis

$Ti_3C_2T_x$ MXene was synthesized by selectively removing the Al layer from Ti_3AlC_2 (Carbon Ukraine Ltd.) using an etchant generated in situ. Initially, 1.6 g of LiF was dissolved in 30 mL of 12 M HCl and stirred for 10 min to activate the solution. Ti_3AlC_2 powder (1.6 g) was then slowly introduced and allowed to react at 40 °C for 48 h under continuous stirring. After the etching step, the suspension was repeatedly washed with deionized water and centrifuged at 3500 rpm until the pH reached approximately 6. The obtained dark-green MXene sediment was dispersed in DI water, subjected to mild sonication for 30 min to promote layer separation, and subsequently centrifuged at 2000 rpm for 30 min to collect the delaminated nanosheets.

2. Characterizations

Structural and morphological features of the samples were examined using a Hitachi SU8010 field-emission scanning electron microscope (FESEM), while elemental composition was identified through energy-dispersive X-ray spectroscopy (EDX). The crystalline arrangement of the MXene nanogroove structures was characterized using a PANalytical X'pert PRO X-ray diffractometer. Transmission electron microscopy (TEM), elemental mapping, selected area electron diffraction (SAED), and high-resolution TEM (HRTEM) were performed on a JEOL JEM-ARM200F (JEOL

Ltd., Japan) to analyze nanoscale morphology and lattice features. Pore size distribution was assessed using a BELSORP-max adsorption analyzer (BEL Japan Inc.). Raman spectra were collected with a Renishaw InVia system (UK) to evaluate vibrational signatures. Electrochemical behavior of the symmetric supercapacitors was studied via cyclic voltammetry (CV), galvanostatic charge–discharge (CD), and impedance spectroscopy using a Bio-Logic SP-200 workstation. Interatomic bonding environments and electronic states were explored through X-ray photoelectron spectroscopy (XPS) using a PHI 5000 Versa Probe III (ULVAC PHI, Japan). Hydrogen evolution reaction (HER) tests were carried out with a Bio-Logic SP-200 in a three-electrode setup containing 1.0 M KOH as the electrolyte. The active catalyst supported on nickel foam (0.5 × 0.5 cm^2) served as the working electrode, Hg/HgO in 1 M NaOH was used as the reference, and a graphite rod functioned as the counter electrode.

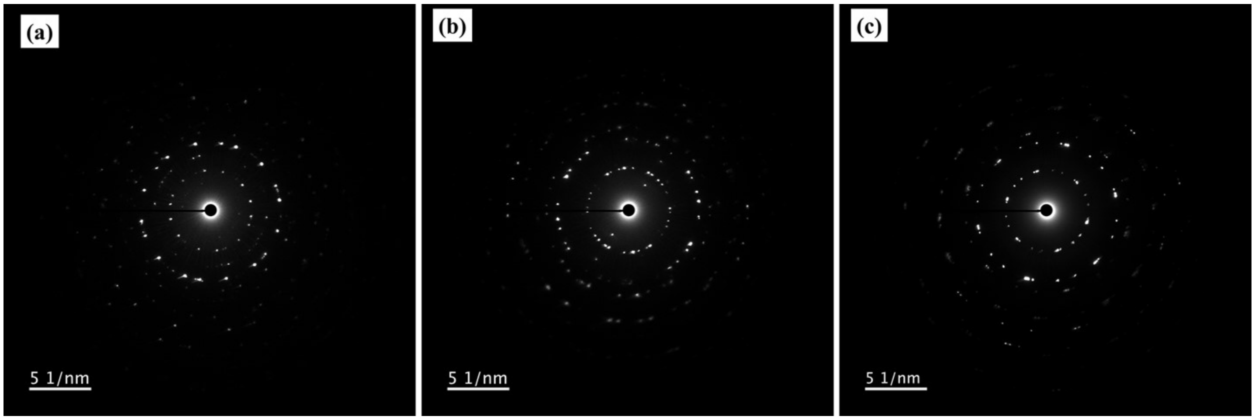

Fig. S1. SAED patterns of (a) MXene, (b) MXene/N/Co-5, and (c) MXene/N/Co-10 samples.

3. HER

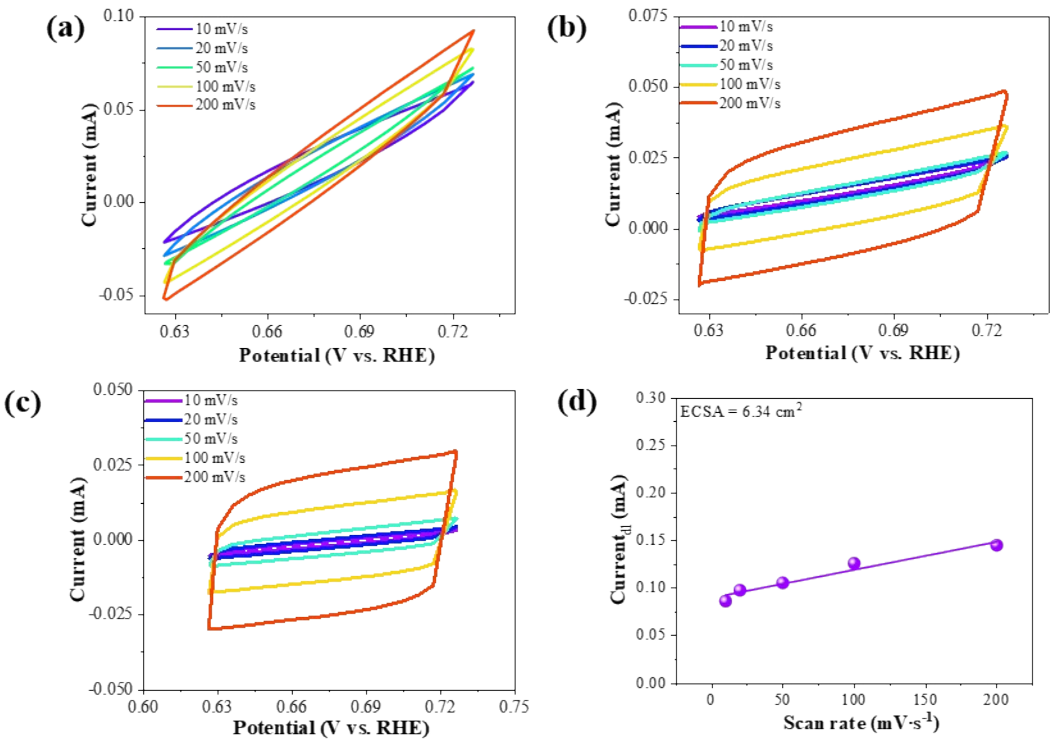

Fig. S2. Double-layer capacitance (C_{dl}) obtained from cycling voltammograms (0.627-0.727 V *vs*. RHE) of (a) MXene, (b) MXene/N/Co-5, and (c) MXene/N/Co-10 at various scan rates (10, 20, 50, 100, 200 $mV \cdot s^{-1}$). (d) ECSA of MXene electrode calculated using double-layer current (C_{dl}) as a function of scan rate (10, 20, 50, 100, and 200 $mV \cdot s^{-1}$).

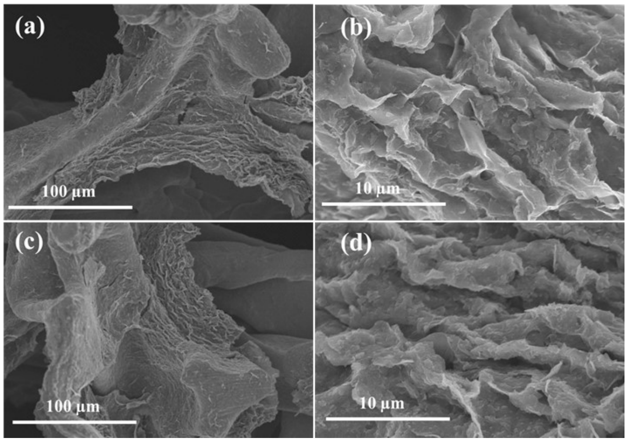

Fig. S3. SEM images of the MX/N/Co-5 catalyst on Ni-foam at low and high magnifications before (a-b) and after (c-d) the HER test.

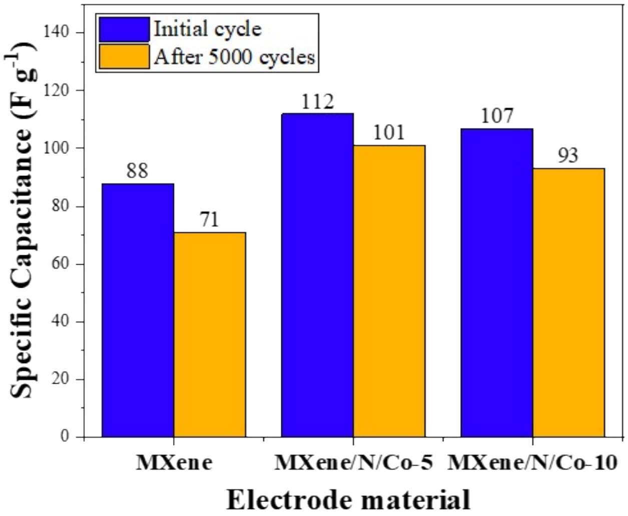

Fig. S4. Stability studies for all electrodes before and after 5000 CV cycles, investigated at a 500 mV s^{-1} scan rate.