Electronic supplementary information

for

A Nitrogenous Pre-Intercalation Strategy for the Synthesis of Nitrogen-Doped $Ti_3C_2T_x$ MXene with Enhanced Electrochemical Capacitance

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Fabrication of MXene electrode

A glassy carbon electrode (GCE) (3 mm in diameter) was firstly polished, rinsed with deionized water. and then dried under a stream of nitrogen gas. MXene powder was sonicated for 30 minutes in deionized water to obtain a homogeneous MXene dispersion. The MXene dispersion (4 uL, 2 mg mL^{-1}) was dropped on the GCE and dried in vacuum for 30 min at room temperature. Then 3 uL of nafion solution (5 wt % in ethanol) was dropped on the MXene/GCE and dried in vacuum at room temperature to ensure a good adhesion.

Characterization

The interlayer space *d* was calculated from the **Bragg's Law**

$$n\lambda = 2dsin\theta$$

Where, n=1 with Cu Kα radiation (λ = 0.15406 nm)

From the CV curve, the gravimetric capacitance (C, F g^{-1}) of the electrode can be calculated as the following equation,

$$C = \frac{\int I_m \, dU}{V\Delta E}$$

Where I_m is the charge/discharge mass current density, V is the potential scan rate (V s^{-1}) and ΔE is the potential window (V) of the initial and final potential either on charging or discharging process.

From the galvanostatic charge discharge curve, the capacitance can be calculated from the following formula,

$$C = Q/\Delta E$$

Where Q = I*Δt, Q is the total charge stored or released by the supercapacitor, I is the applied current and Δt is the charge/discharge duration, ΔE is the voltage difference between the initial and final potential either on charging or discharging process.

The formula for formation energy in manuscript.

In general, the formation energy, E_{form}, of a compound is defined as,

$$E_{form} = E_{comp} - \sum_{i=1}^{n} N_i E_i \quad , \qquad (1)$$

Where E_{comp} is the total energy of the compound, n is the number of elements in the compound, N_i is the number of atoms of ith element, and E_i is the total energy per atom of the most stable elemental of ith element. And the formation energy per atom, E_{form,per_atom}, can be obtained by $\frac{E_{form}}{\sum_{i=1}^{n} N_i}$. Here, to reflect the formation energy variation of MXene during nitrogen adsorption or substitution, we define ΔE_{form} as,

$$\Delta E_{form} = \begin{cases} E_{form}(MXene + N) - E_{form}(MXene + N) & initial \\ E_{form}(vacancy\_MXene + N + replaced\_group) - E_{form}(MXene + N) & for\ transitional\ states \\ E_{form}(N\_MXene + replaced\_group) - E_{form}(MXene + N) & final \end{cases} \qquad (2)$$

where E_{form}(MXene+N) indicates the formation energy of the system containing pure MXene and a dissociative nitrogen atom, E_{form}(vacancy-MXene+N+replaced_group) means that containing MXene with vacancy, dissociative nitrogen atom and the replaced group (such as C, F, OH and Ti), and E_{form}(N-MXene +replaced group) represents that containing nitrogen doped MXene and the dissociative replaced group, as shown in the following Fig.S1.

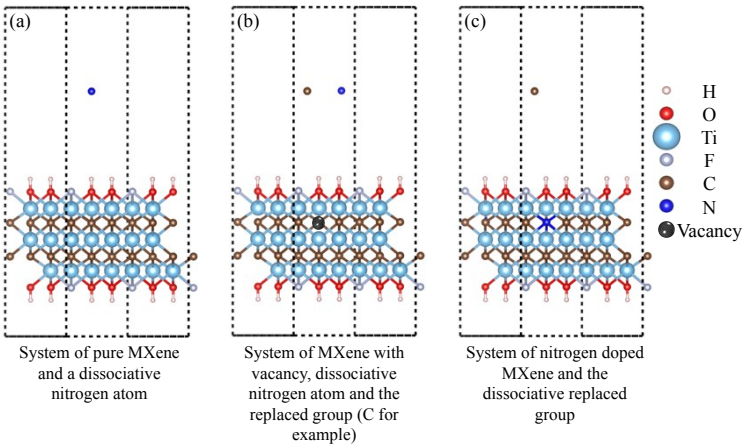

Fig.S1 Models of the systems for the calculation of ΔE_{form}.

Characterisation

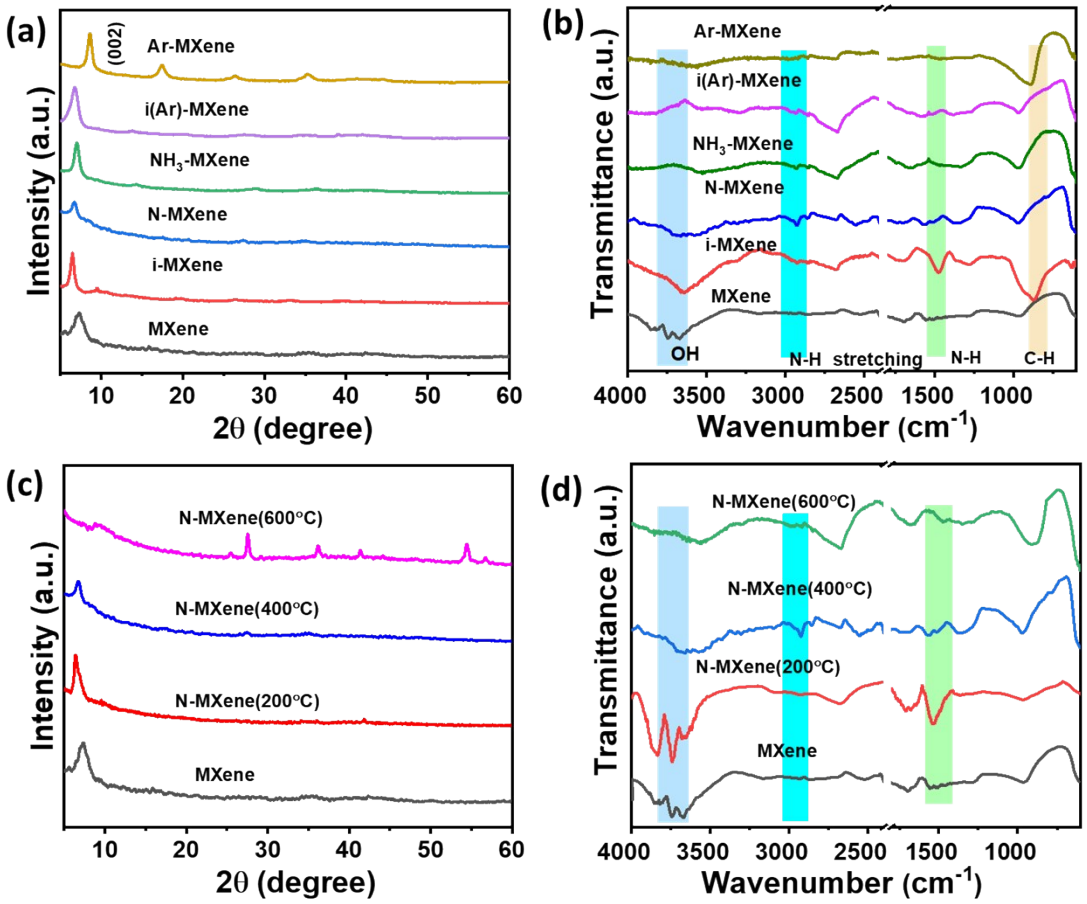

Fig. S2. (a–b) The XRD and FTIR profiles of different samples. (c–d) The XRD and FTIR of N-MXene at different temperature obtained in 1M H_2SO_4.

Table S1. The interlayer spacing (d) of MXene samples with different treatment methods calculated from XRD.

Parameters / Sample	(002) position (2θ degree)	d (nm)
MXene	7.2	1.23
i-MXene	6.6	1.36
N-MXene	6.7	1.32
NH_3-MXene	7.0	1.26
i(Ar)-MXene	6.9	1.28
Ar-MXene	8.4	1.05

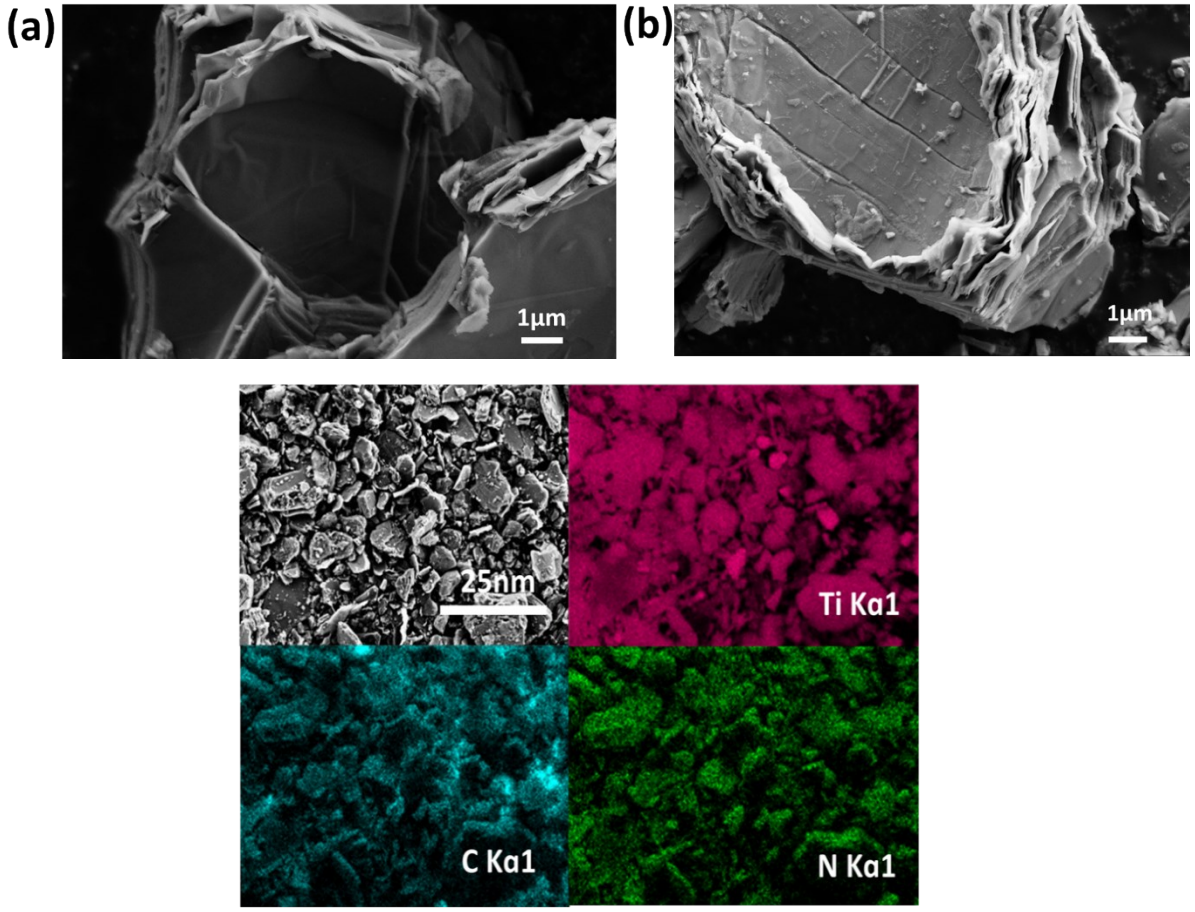

Fig. S3. SEM of MXene and N-MXene. (c) EDS images showing the morphology of N-MXene.

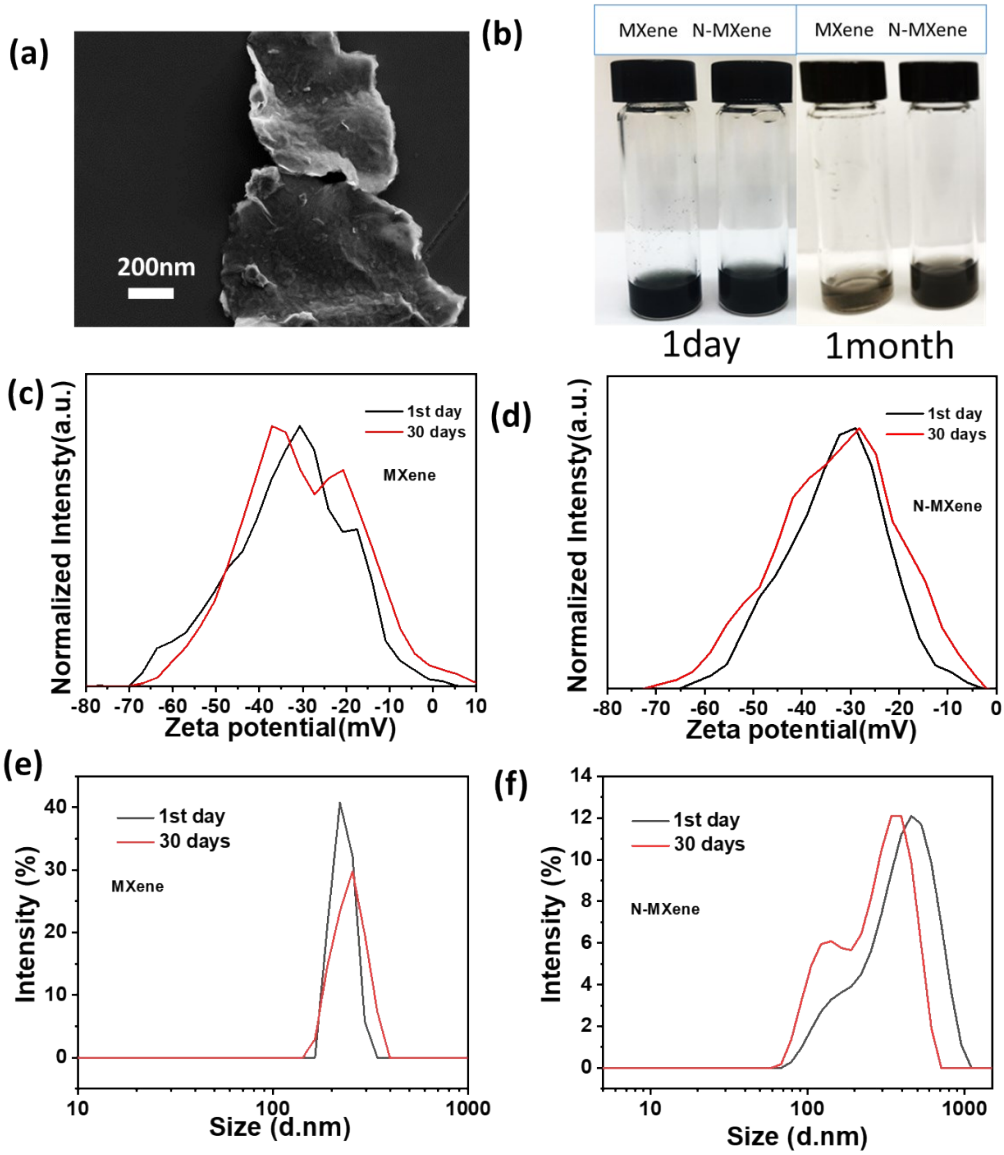

Fig. S4 (a) SEM of N-MXene. (b)The color change and (c, d) zeta potential of MXene and N-MXene before and after storage for 30 days in air at room temperature. (e, f) The particle size distribution of MXene and N-MXene from DLS.

The MXenes were aged to test shelf stability and resistance to oxidation, after being stored for 30 days under ambient conditions. Unlike MXene, N-MXene retained a near black hue (Fig. 3c)

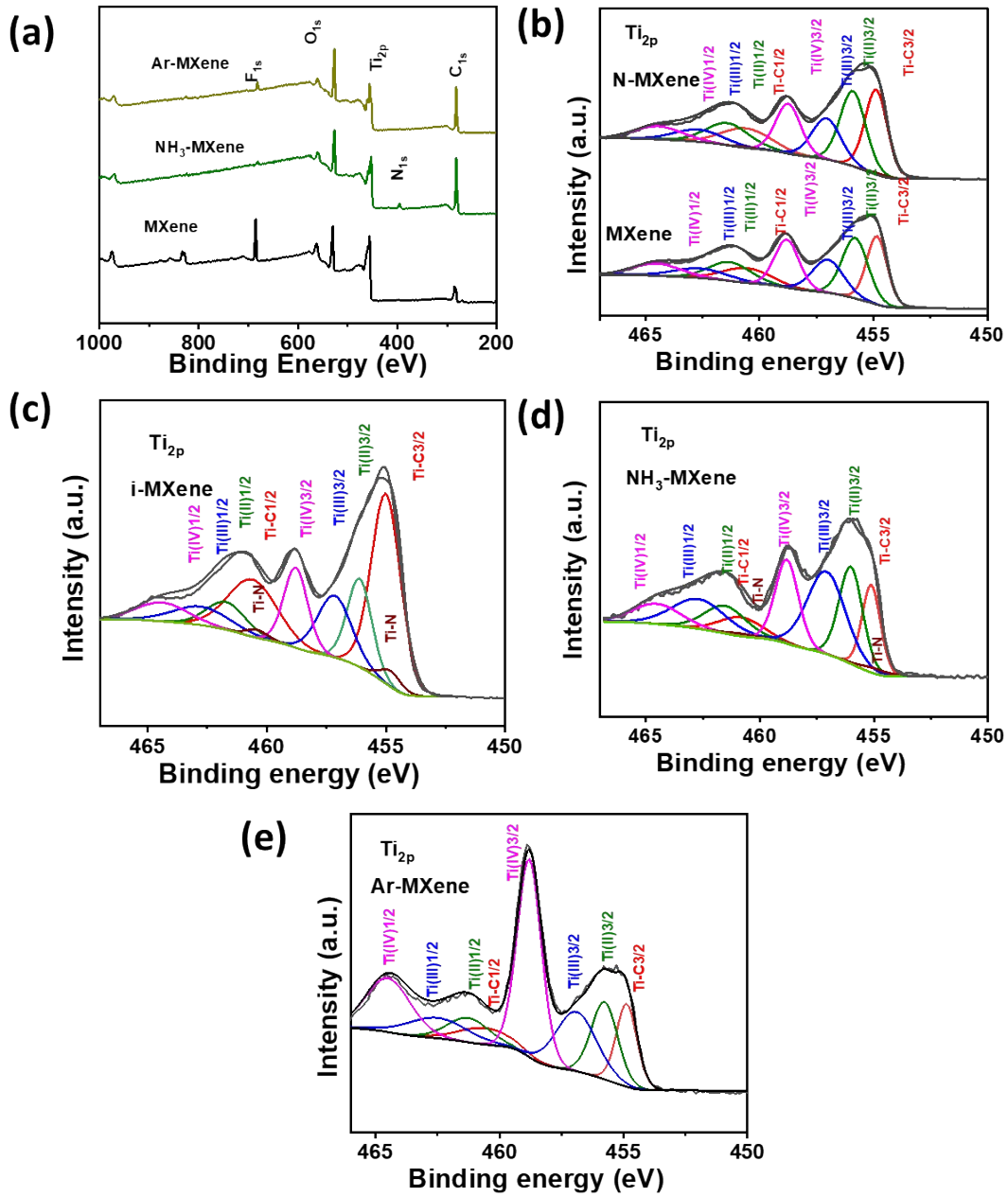

Fig. S5. (a) XPS spectra of Ar-MXene and NH_3-MXene, (b-e) Ti_{2p} spectra of MXene, N-MXene. i-MXene NH_3-MXene and Ar-MXene.

Table S2. Elemental Nitrogen content of all MXenes.

Samples	MXene	i-MXene	N-MXene	NH_3-MXene	Ar-MXene
N content (at %)	-	3.2%	6.3%	3.6%	-

Table S3. The Nitrogen element content the N-MXene characterisation by XPS.

N content (at %)	SA nitrogen (401.7 eV, at %)	SF nitrogen (399. eV, at %)	LS nitrogen (396.1 eV, at %)
6.31 %	80.35 %	8.68 %	10.97%

Table S4. Peak fitting results of high-resolution XPS spectra in the Ti_{2p} region for as-synthesised MXene and N doped MXene samples.

Sample	Binging energy (eV)	FWHM	Assignment	Percent (%)
MXene Ti $2p_{3/2}$	455.8	1.35	Ti(II)	30.4
	454.8	1.06	Ti-C	27.1
	458.8	1.26	Ti(IV)	22.6
	457.0	1.61	Ti(III)	19.9
N-MXene Ti $2p_{3/2}$	454.8	1.15	Ti-C	30
	455.9	1.31	Ti(II)	30.6
	457.1	1.49	Ti(III)	18.9
	458.7	1.29	Ti(IV)	19.8
	454.8	0.99	Ti-N	0.6

Electrochemical Data

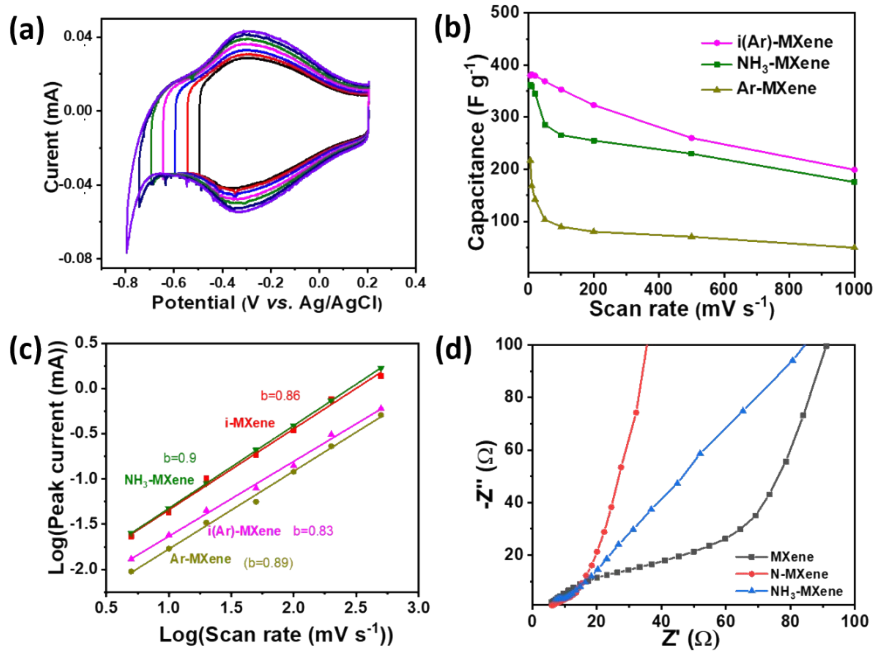

Fig. S6. (a) CV plots of N-MXene in 1 M H_2SO_4 electrolyte at different potentials. (b) Specific capacitances of different MXene samples in H_2SO_4 electrolyte at different scan rate. (c) Logarithmic dependence of discharge peak current (i_p) versus scan rate of different MXene samples. (d) The EIS results o MXene, N-MXene and NH_3-MXene obtained in 1 M H_2SO_4.

Table S5. The capacitance of samples with different treatment methods calculated from CV at 5mV s^{-1}.

Capacitance / Sample	Capacitance (F g^{-1})
MXene	321
i-MXene	351
N-MXene	475
NH_3-MXene	362
i(Ar)-MXene	380
Ar-MXene	217

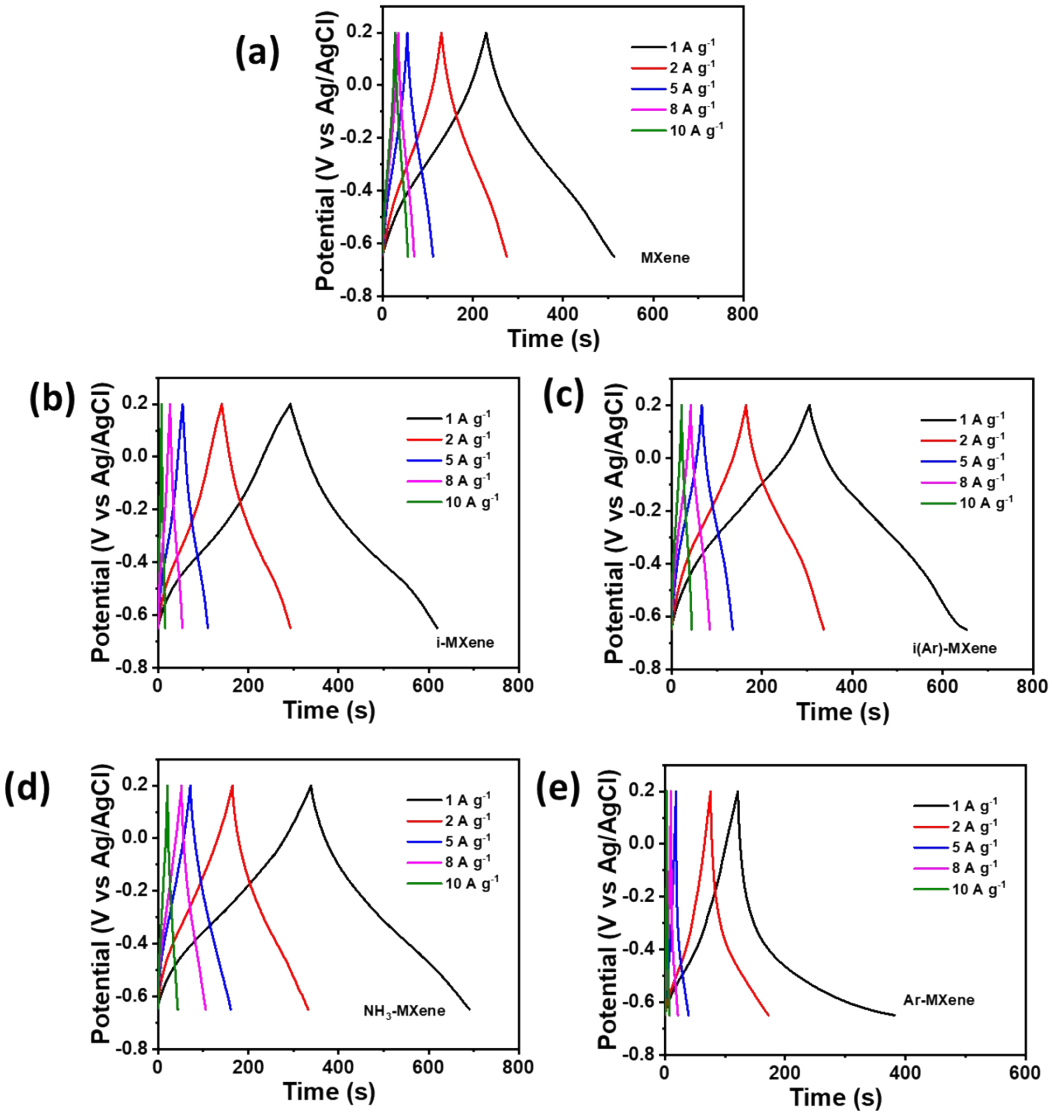

Fig. S7. Galvanostatic charging-discharging curve of MXene samples at different current density (1 A g^{-1} to 10 A g^{-1}).

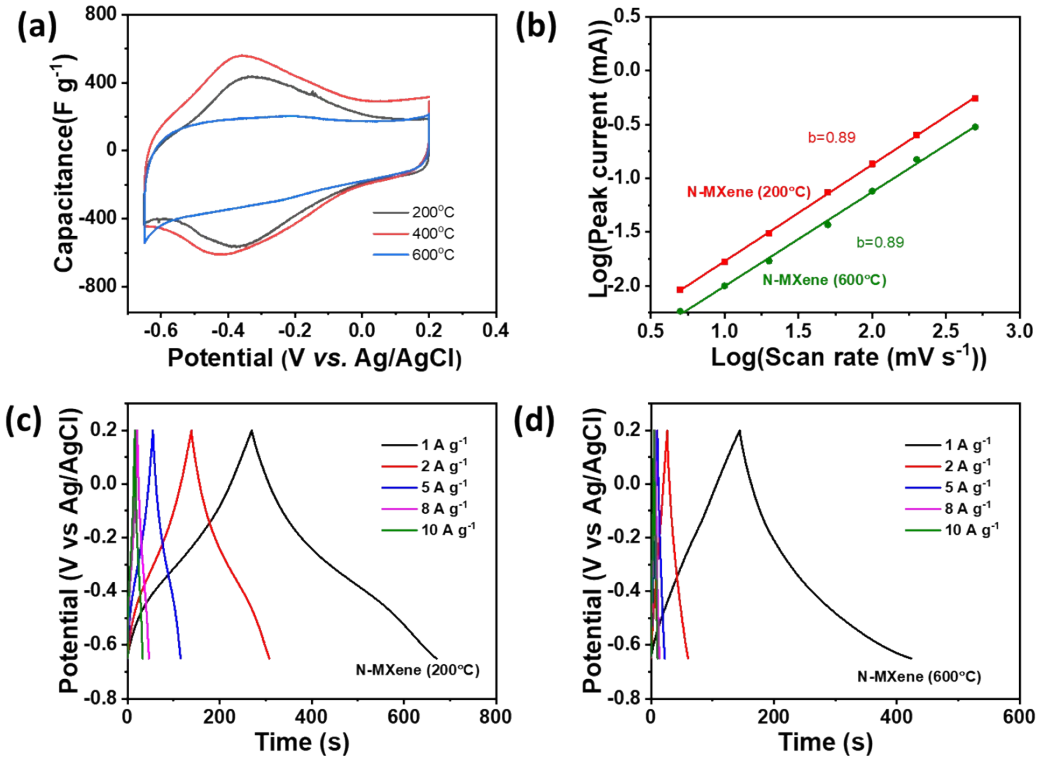

Fig. S8. (a) The CV curves of N-MXene at different temperatures at 5mv s^{-1}obtained in 1M H_2SO_4. (b) Galvanostatic charging-discharging curve of N-MXene (200 °C and 600 °C) samples at different current density (1 A g^{-1} to 10 A g^{-1}). (c) and (d) Galvanostatic charging-discharging curve of N-MXene (200 °C and 600 °C) samples at different current density (1 A g^{-1} to 10 A g^{-1}).

Simulation Data

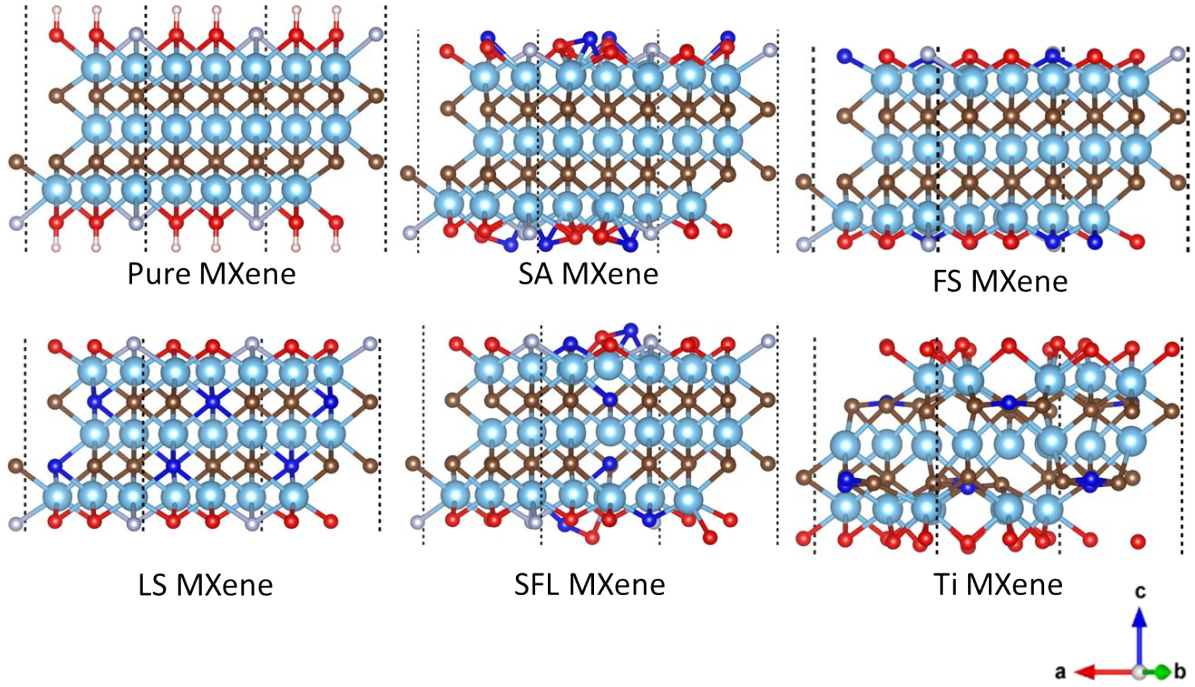

Fig. S9. DFT Simulation. Atomic schemes of MXene with all possible sites for nitrogen dopants.

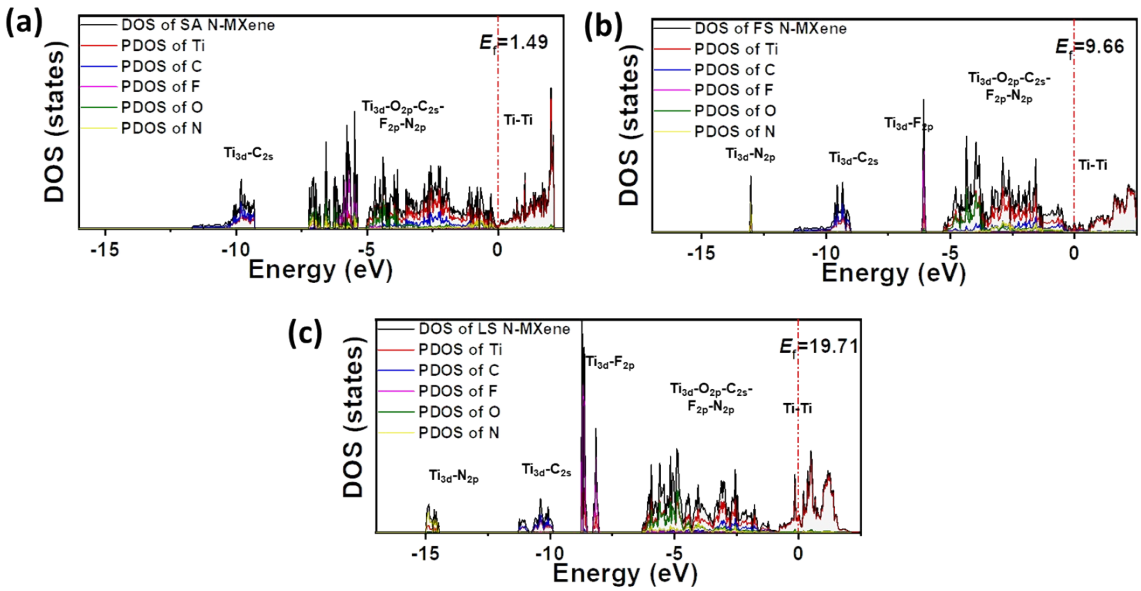

Fig. S10. The computed electron density of states (DOS) of (a) SA, (b) FS, (c) LS-N-MXene.

Table S6. Number of atoms of each different element used in MXene model

Elements	Pristine-MXene	SA N-MXene	FS N-MXene	LS N-MXene	SFL N-MXene
Ti	27	27	27	27	27
C	18	18	18	12	16
F	6	6	2	6	5
O	12	12	10	12	11
H	12	0	0	0	0
N	--	6	6	6	6

Table S7. The average valance of the elements in MXene

Elements	Pristine-MXene	SA N-MXene	FS N-MXene	LS N-MXene	SFL N-MXene
Ti	1.527	1.60	1.63	1.63	1.61
C	-1.61	-1.52	-1.45	-1.55	-1.55
F	-0.75	-0.68	-0.69	-0.67	-0.67
O	-1.26	-0.83	-0.99	-1.05	-0.87
H	0.61	--			--
N	--	-0.30	-1.10	-1.48	-0.97

Table S8. The increments of available orbits of O and Ti

Element	Pure-MXene	SA N-MXene	FS N-MXene	LS N-MXene	SFL N-MXene
O	0.00	0.58	0.36	0.28	0.53
Ti	0.000	0.046	0.065	0.065	0.052

Table S9. Collection of the properties of N-MXene in the experiment and simulations comparing to pristine MXene.

Property	Experiment	SA-N-MXene	FS-N-MXene	LS-N-MXene	SFL-N-MXene
Conductivity					
Capacitive part					
Diffusion-controlled part					

* Note: Colour green indicates significant enhancements for the capacitances, yellow means moderate enhancements for the capacitances, and red represents poor enhancement.

** Effect on the conductivity was based on DOS results.