## Supporting Information

## Enhanced Electrocatalytic Activity by Chemical Nitridation of Two-Dimensional Titanium Carbide MXene for Hydrogen Evolution

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In this supplement, we provide the following data and description, which support to our

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Figure S12. The Calculated formation energies  $(E_f)$  for each surfaces to analyze the possible active sites.

# **1.** Description to calculate turn over frequency (TOF) for H<sub>2</sub> of pristine and nitrided sample:

The structural data of  $Ti_2CT_x$  as follows:

Density of  $Ti_2CT_x = 4$  g cm<sup>-3</sup>. Average size of nanoparticle (determined from the Scherrer equation) = 300 nm. The shapes of the nanoparticles are approximated to spherical.

Total volume of  $Ti_2CT_x$  particles present on the electrode

$$= (1 \times 10^{-5}) / 4 = 2.5 \times 10^{-6} \text{ cm}^{3}$$

Total number of  $Ti_2CT_x$  nanoparticles present on the electrode

$$= (2.5 \times 10^{-6}) / [(4/3) (\pi) (r^3)]$$
$$= (2.5 \times 10^{-6}) / [4.18 \times (150 \times 10^{-7})^3]$$
$$= 1.70 \times 10^8 \text{ particles}$$

Surface area of one  $Ti_2CT_x$  nanoparticle

$$= (4) (\pi) (r^2)$$
$$= 7.07 \times 10^{-16} \text{ m}^2$$

Total surface area of all  $Ti_2CT_x$  the nanoparticles present

$$= (1.4 \times 10^{12}) \times (7.07 \times 10^{-16}) = 9.9 \times 10^{-4} \text{ m}^2$$

The area of per unit cells of  $Ti_2CT_x = 1.10 \times 10^{-19} \text{ m}^2$ 

After dividing effective atoms by total number of particles, we can get turn over frequency at particular potentials.

#### 2. Computational Details

To perform the first-principle calculations, we used the Vienna Ab initio Simulation Package (VASP) source code. The atomic pseudopotentials were modeled using the Projector Augmented Wave (PAW) method, as provided with the aforementioned package. A plane-wave basis set with an energy cutoff of 400 eV and the Perdew-Burke-Ernzerhof (PBE) type gradient-correlated functional was employed to describe the exchange-correlation potential. All of the model structures were free to optimize until the self-consistent energy and forces reached  $1 \times 10^{-5}$  eV and 0.05 eV/A, respectively, and non-spin polarized calculation was

performed for geometry optimization. The k-point grids for each structure were sampled 9x9x1 by using the scheme of the Monkhorst-Pack.

For the calculation structure modeling, we prepared the 3x3x1 supercell of surface terminated single layer MXene with hydroxide group  $(Ti_{18}C_9(OH)_{18})$ . From the XPS survey spectra, we selected 6 species, vacancy  $(V_x)$ , Al, O, N, F, and OH, and substituted one OH group for one of these species.

The formation energies for each surfaces were defined by

$$E_{f} = E_{Ti_{18}C_{9}(OH)_{17}X} - E_{Ti_{18}C_{9}(OH)_{18}} - E_{OH} + E_{X}$$

, where  $E_{Ti_{18}C_9(OH)_{17}X}$ ,  $E_{Ti_{18}C_9(OH)_{18}}$ ,  $E_{OH}$ , and  $E_X$  are the total energy of structure of  $Ti_{18}C_9(OH)_{17}X$ ,  $Ti_{18}C_9(OH)_{18}$ , OH(aq), and X, respectively. The Gibbs free energies for hydrogen adsorption were defined by

$$\Delta G_{\rm H} = \Delta E_{\rm H} + \Delta E_{\rm ZPE} - T\Delta S_{\rm H}$$

, where  $\Delta E_{ZPE}$  and  $\Delta S_H$  are the zero-point energy and entropy difference, respectively, between the phase for gas state and phase for adsorbed state on the active site.  $\Delta E_H$ , hydrogen adsorption energy, was calculated by

$$\Delta E_{\rm H} = E_{\rm H*} - E_* - \frac{1}{2} E_{\rm H_2}(g)$$

, where  $E_{H*}$  is the total energy of hydrogen adsorbed state,  $E_*$  is the total energy of state for catalyst surface without hydrogen atom, and  $E_{H_2}(g)$  is the energy of a gas phase hydrogen molecule. Shortly, the overall correction is

$$\Delta G_{\rm H} = \Delta E_{\rm H} + 0.24 \text{ eV}$$



**Figure S1.** XRD pattern of the  $Ti_2CT_x$  MXene after nitridation with excess NaNH2 (ratio of 1.0).



Figure S2. Nitrogen adsorption and desorption isotherms of all synthesized materials.

Samples	BET (m <sub>2</sub> g <sup>-1</sup> )	Total pore volume $(cm_3 g^{-1})$	Ave. pore diameter (nm)
<i>Pristine</i> -Ti <sub>2</sub> CT <sub><math>x</math></sub>	2.8575	0.0152	21.2830
2%-Ti <sub>2</sub> CNT <sub>x</sub>	5.5083	0.0258	18.7738
3%-Ti <sub>2</sub> CNT <sub>x</sub>	10.8671	0.0635	23.4015
5%-Ti <sub>2</sub> CNT <sub>x</sub>	17.1498	0.0679	15.3077
11%-Ti <sub>2</sub> CNT <sub>x</sub>	24.3891	0.1527	25.0593

**Table S1.** BET surface areas and the pore volume structures of the all-synthesized materials after nitridation reaction by NaNH<sub>2</sub>



**Figure S3.** TEM images of all nitrided samples (a)  $2N-Ti_2CT_x$ , (b)  $3N-Ti_2CT_x$  and (c)  $5N-Ti_2CT_x$ .



**Figure S4.** Elemental mapping of all  $N-Ti_2CT_x$  samples for characterizing the distribution of Ti, C, O and N.



**Figure S5.** Control experiments for proving oxidation behavior of *pristine*-Ti<sub>2</sub>CT<sub>x</sub> under high temperature without NaNH<sub>2</sub>



**Figure S6.** SEM images of Control experiments for proving oxidation behavior of *pristine*- $Ti_2CT_x$  under high temperature without NaNH<sub>2</sub>. (a and b) SEM images of *pristine*- $Ti_2CT_x$  under high temperature without NaNH<sub>2</sub> and (c-d) SEM images of *N*- $Ti_2CT_x$  with NaNH<sub>2</sub>.

Samples	Ti (at.%)	C (at.%)	O (at.%)	N (at.%)	F (at.%)	Al (at.%)
Pristine- Ti <sub>2</sub> CT <sub>x</sub>	38.50	22.52	24.34	-	11.95	2.65
2%-Ti <sub>2</sub> CNT <sub>x</sub>	41.34	29.58	22.14	1.98	2.37	2.54
3%-Ti <sub>2</sub> CNT <sub>x</sub>	42.52	29.37	20.83	3.12	1.21	2.81
5%-Ti <sub>2</sub> CNT <sub>x</sub>	45.65	28.92	17.64	4.81	0.62	2.31
11%-Ti <sub>2</sub> CNT <sub>x</sub>	41.51	28.13	15.68	12.22	-	2.34

**Table S2.** The element percentages in all the samples are calculated from the XPS survey spectra and their values are listed.



**Figure S7.** Raman results show that changes of chemical structures as a function of nitridation degrees



**Figure S8.** Linear sweep voltammetry (LSV curves) without iR correction of the samples after nitridation with excess NaNH<sub>2</sub> shows a tendency for increasing the overpotential.



**Figure S9.** (a) LSV curves for  $11N-Ti_2CT_x$  before and after 24 h cycling at a scan rate of 50 mV s<sup>-1</sup>. (b) Chronoamperometry measurement for  $11\%-Ti_2CNT_x$  electrocatalysts, showing the good cyclic stability.



**Figure S10.** Chemical stability of  $11N-Ti_2CT_x$  is characterized by XPS. Ti 2p core level spectra shows that  $11N-Ti_2CT_x$  has good electrochemical inertness in both acidic and basic conditions.



**Figure 11.** Dispersion of  $11N-Ti_2CT_x$  in water and after standing for 12 days later. The color of dispersion is changed from black to white, indicating *pristine*-Ti<sub>2</sub>CT<sub>x</sub> is oxidized. On the other hand,  $11N-Ti_2CT_x$  is stable even after 12 days later



**Figure S12.** The Calculated formation energies  $(E_f)$  for each surfaces to analyze the possible active sites. (a) Vacancy, (b) Al, (C) O, (d) N, (e) F, and (f) OH.