Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

MXene nanoribbon as electrocatalysts for hydrogen evolution reaction with fast kinetics

Xiaowei Yang, Nan Gao, Si Zhou*, Jijun Zhao

Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Ministry of Education, Dalian 116024, China

* Corresponding author. Email: sizhou@dlut.edu.cn (S. Zhou)

Table S1. Vibrational frequencies and zero-point energies (ZPE) for H* adsorption on the edges of various O-terminated MXenes nanoribbons. The value of (ZPE – *TS*) for gaseous H_2 at T = 298 K is –0.70 eV per H atom, given by the NIST-JANAF thermodynamics table.[1] Thus, the difference of (ZPE – *TS*) between the adsorbed H* and gaseous H_2 phases ranges from 0.22 to 0.30 eV per H atom for various MXene nanoribbons.

nanoribbon	Vibrational frequencies (cm^{-1})			ZPE (eV)
Ti_2C	192.3	77.9	36.5	0.15
V_2C	214.2	86.2	57.8	0.18
(Ti, Nb)C	148.2	141.2	79.6	0.18
Nb_2C	152.7	138.8	89.8	0.19
Mo_2C	222.7	152.7	89.8	0.18
Zr_3C_2	149.6	121.0	67.4	0.17
Ti_3C_2	145.4	125.7	77.3	0.17
Hf_3C_2	151.1	129.8	77.2	0.18
Ti_3CN	150.3	140.5	69.8	0.18
Ti_4N_3	140.7	119.0	84.9	0.17
Nb_4C_3	146.6	138.9	85.5	0.18
Ta_4C_3	150.9	146.4	88.0	0.19

Table S2. Binding energy of H* species (ΔE_{H*}) on the top site of C atoms on the ribbon edge and H−C bond length ($d_{H–C}$), free energy of formation for hydrogen adsorption (ΔG_{H*}) on the hollow site of metal atoms on the ribbon edge and distance between H and metal atoms ($d_{H–M}$), and *d* band center relative to Fermi level (ε_d) for various O-terminated MXene nanoribbons with width $N = 12$.

nanoribbon	ΔE_{H*} (eV)	$d_{H–C}$ (Å)	ΔG_{H*} (eV)	$d_{H–M}$ (Å)	ε_d (eV)
Ti_2C	–0.83	1.12	0.51	1.75	–4.47
V_2C	–0.48	1.12	0.44	1.64	–4.45
Mo_2C	–0.54	1.12	0.25	1.72	–4.74
Nb_4C_3	–0.67	1.15	0.19	1.84	–4.37
(Ti, Nb)C	–0.93	1.15	0.04	1.99	–5.12
Ti_3C_2	–1.11	1.12	–0.07	1.95	–4.18
Zr_3C_2	–1.08	1.13	–0.29	2.09	–4.26
Ti_3CN	–0.75	1.12	–0.44	1.90	–4.49
Nb_2C	–0.37	1.15	–0.50	2.20	–4.74
Ti_4N_3	0	1.04	–0.44	1.94	–4.89
Ta_4C_3	–0.64	1.16	–0.56	1.97	–5.36
Hf_3C_2	–1.04	1.13	–0.59	2.06	–4.69

Table S3. Free energy of formation for hydrogen adsorption (ΔG_{H^*}) at different H* coverage (θ) for zigzag nanoribbons of O-terminated Ti_3C_2 MXene with width $N = 12$.

θ	ΔG_{H^*} (eV)
1/2	−1.11
5/8	−1.05
2/3	−1.07
7/8	−1.09
1	−1.11

Table S4. Free energy of formation for hydrogen adsorption (ΔG_{H*}) for O-terminated Ti_3C_2 and (Ti, Nb)C MXene nanoribbons with different ribbon width *N*.

N	ΔG_{H*} (eV)	
	Ti_3C_2	(Ti, Nb)C
4	0	--
5	0.04	--
6	–0.12	--
7	0	--
8	–0.09	0.02
9	0.01	–0.05
10	–0.06	0.04
11	–0.01	0.05
12	–0.07	0.04
13	–0.01	–0.12
14	–0.07	0.04
15	–0.02	–0.11
16	–0.06	0.09
17	–0.02	0.03

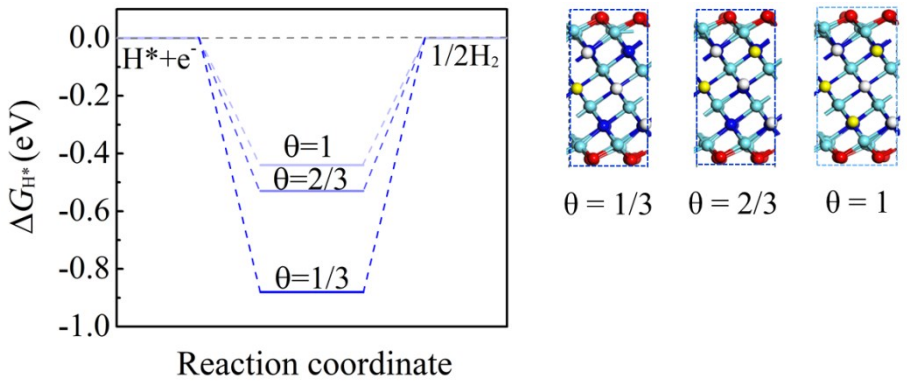

Fig. S1 Free energy diagrams for hydrogen evolution at zero potential and pH = 0 on the edges of Ti_4N_3 MXene nanoribbons at different H* coverage (θ). The black dashed line indicates the ideal ΔG_{H*} for HER catalysis. The structures of ribbon edge with H* adsorption is shown on the right panels. The H, O, Ti and N atoms are shown in white (yellow), red, cyan and blue colors, respectively. The H atoms in white and yellow colors are adsorbed on the top site of N atoms and on the hollow site between Ti atoms, respectively. All these adsorption sites exhibit too strong binding strength for HER catalysis.

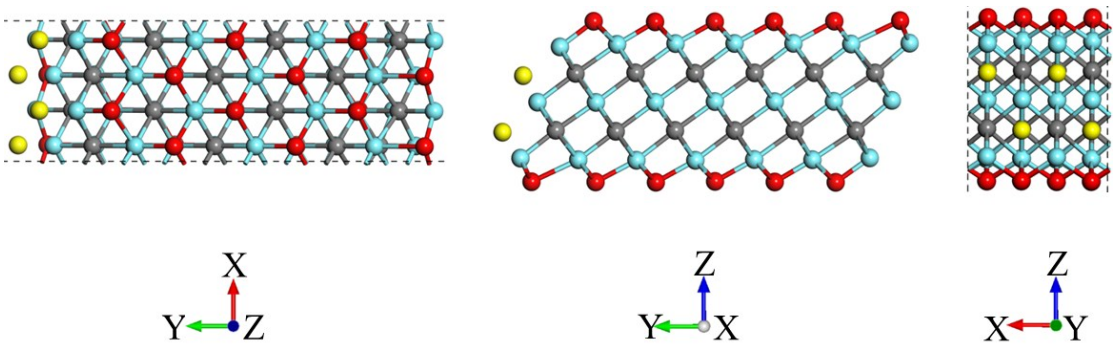

Fig. S2 Top view (left panel), side view (middle panel) and edge (right panel) of zigzag nanoribbons of O-terminated Ti_3C_2 MXene. The C, O and Ti atoms are shown in grey, red and cyan colors, respectively. The yellow balls indicate the adsorbed H* species on the ribbon edge.

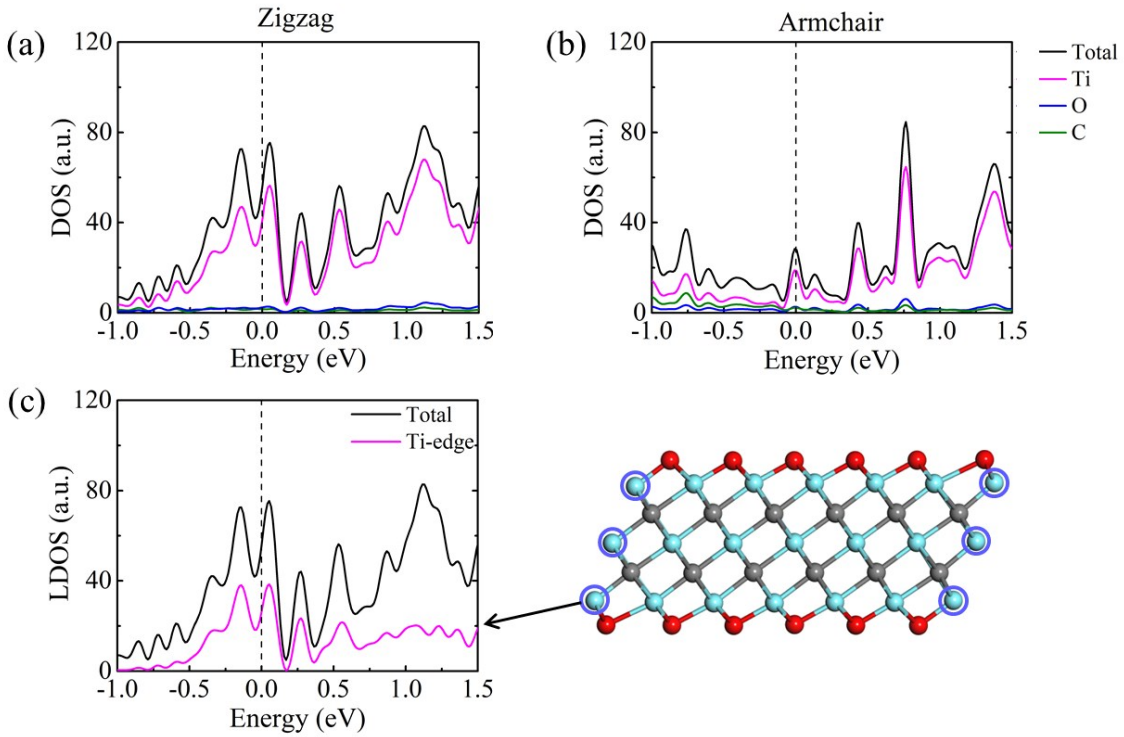

Fig. S3 Density of states (DOS) of (a) zigzag and (b) armchair nanoribbons of O-terminated Ti_3C_2 MXene with width N = 12. The color lines show the DOS from different atoms. (c) Local DOS from Ti atoms on the edge of zigzag Ti_3C_2 nanoribbon (magenta line, the corresponding atomic structure is displayed on the right panel), compared with total DOS (black line). The Fermi level is shifted to zero.

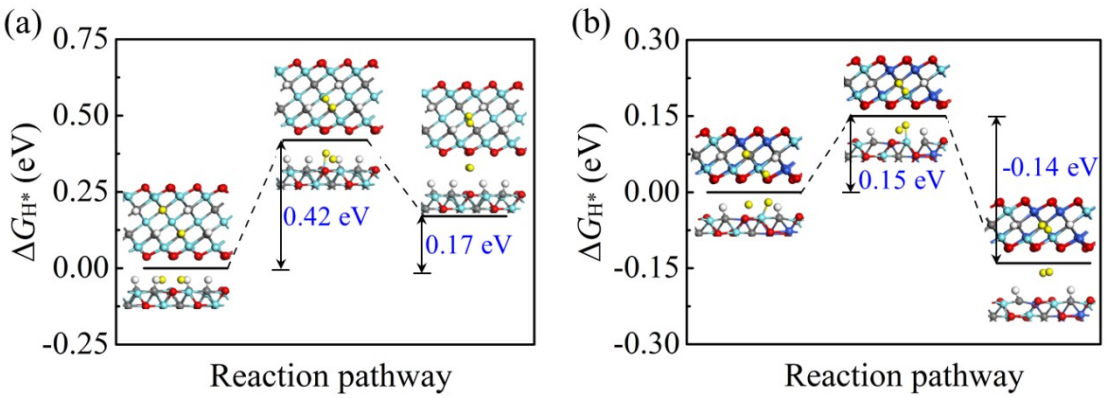

Fig. S4 Free energy profiles of Tafel reaction for H_2 formation on the edges of (a) Ti_3C_2 and (b) (Ti, Nb)C MXene nanoribbons with width N = 13 and 15, respectively. The top and side views of the ribbon edge are shown (from left to right) for the initial, transition and final states, respectively. The H, C, O, Ti and Nb atoms are shown in while (yellow for the two H* reactants), grey, red, cyan and blue colors, respectively. The blue numbers indicate the energy barrier (left) and Gibbs free energy of formation (right).

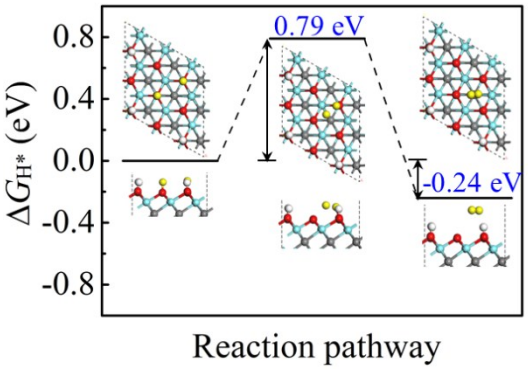

Fig. S5 Free energy profile of Tafel reaction for H_2 formation on 2D Ti_3C_2 monolayer with O-terminated surface and at optimal H* coverage (1/2). The insets (from left to right) show the top and side views of the initial, transition and final states, respectively. The H, C, O, and Ti atoms are shown in while (yellow for the two H* reactants), grey, red and cyan colors, respectively. The blue numbers indicate the energy barrier (left) and Gibbs free energy of formation (right).

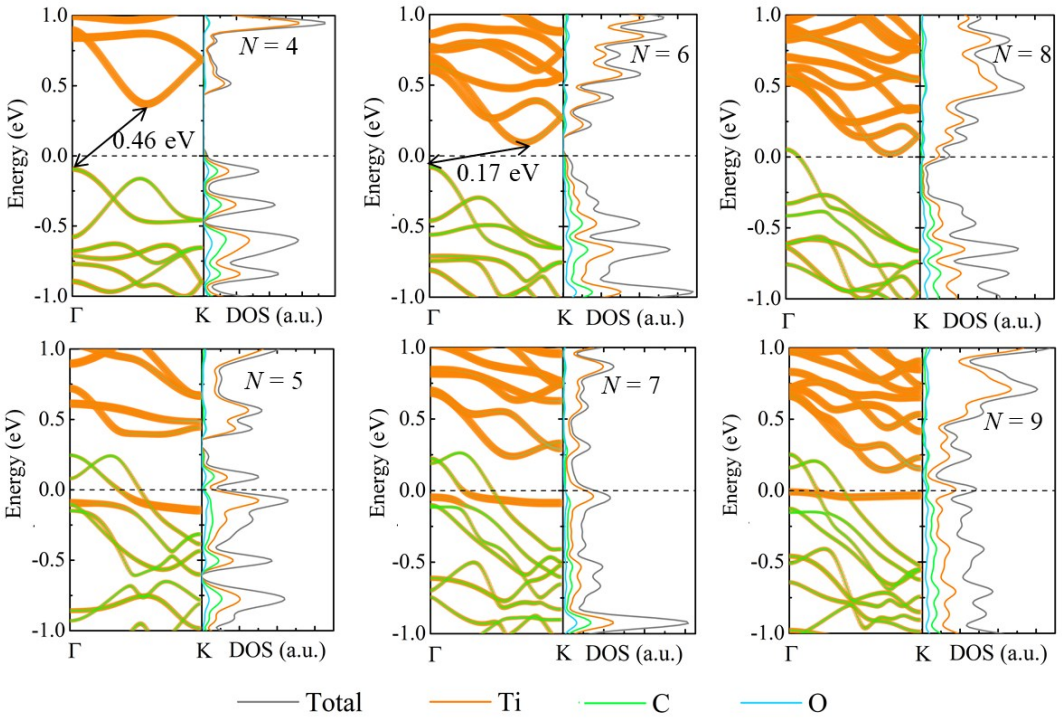

Fig. S6 Band structures (left panel) and DOS (right panel) of armchair Ti_3C_2 MXene nanoribbons with different width N = 4~9. The color indicates the contribution of the bands or DOS from C, O and Ti atoms, and the line width is proportional to weight. The Fermi energy is set to zero.

References

1 M. W. Chase, *NIST-JANAF Thermochemical Tables*, American Institute of Physics: New York, 1998.