Effect of Terminations on the Hydrogen Evolution Reaction Mechanism on Ti_3C_2 MXene

Ling Meng,[a,b] Li-Kai Yan,[*,b] Francesc Viñes,[*,a] Francesc Illas[a]

[a] *Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1-11, 08028 Barcelona, Spain*

[b] *Institute of Functional Material Chemistry, Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China.*

[*] Corresponding authors: Francesc Viñes (francesc.vines@ub.edu), Li-Kai Yan (yanlk924@nenu.edu.cn)

Table S1. Summary of the potential determining steps, based on the calculated ΔG_H as a descriptor, on the explored Ti_3C_2 models, either pristine, or covered according to the specified terminations. The required overpotential, η, is specified, as well as the Volker-Heyrovsky (VH) or Volmer-Tafel (VT) mechanism (the preferred in shown in bold), specifying the subtype of path, either O-TER, OH-TER, or TER-TER. In the case of pristine Ti_3C_2, note that the strong H-affinity prevents any H_2 formation, regardless of η.

Model	Mechanism	Subtype	ΔG_H / eV	η / V
Pristine Ti_3C_2	—	—	-1.32	—
O	**VH**	—	-0.40	0.40
	VT[a]	—	-0.44*	—
H	**VH**	—	0.63	0.63
	VT	—	2.30*	2.30*
OH	**VH**	—	-0.48	0.48
	VT	—	0.75	0.75
F	**VH**	—	2.62	2.62
$O_{1/3}OH_{2/3}$	**VH**	OH-TER	0.08	0.08
	VH	O-TER	0.62	0.62
	VT	TER-TER	0.19	0.19
	VT	O-TER	0.74	0.74
$O_{1/2}OH_{1/2}$	**VH**	OH-TER	0.23	0.23
	VH	O-TER	0.36	0.36
	VT[a]	TER-TER	0.44*	—
	VT	O-TER	0.74	0.74
$O_{2/3}OH_{1/3}$	**VH**	O-TER	-0.01	0.01
	VH	OH-TER	0.66	0.66
	VT[a]	TER-TER	0.82*	—
	VT	O-TER	0.09	0.09
$F_{1/3}O_{1/3}OH_{1/3}$	**VT**	TER-TER	-0.01	0.01
	VH	OH-TER	0.66	0.66
	VH	O-TER	0.46	0.46
	VT	TER-TER	0.58	0.58

$F_{3/9}O_{4/9}OH_{2/9}$	**VH**	O-TER	0.01	0.01
	VH	OH-TER	0.32	0.32
	VT[a]	TER-TER	0.29*	—
	VT	O-TER	0.46	0.46

[a] Not a real Volmer-Tafel mechanism, but similar to the Tafel step, *i.e.*, the formation of H_2 from two H atoms of the –OH surface group.

* For those the main energy impediment comes from only chemical step, *i.e.*, Tafel step, where two adjacent –OH termination groups react to form two –O groups and $H_2^{(g)}$ molecule.

Fig. S1 Schematic of $Ti_3C_2T_x$ modelled by (a) full –OH and (b) $O_{2/3}OH_{1/3}$ termination, occupying H_C or H_{Ti} sites, respectively, accompanied by their total energies. Blue, brown, red, and white spheres denote Ti, C, O, and H atoms, respectively.

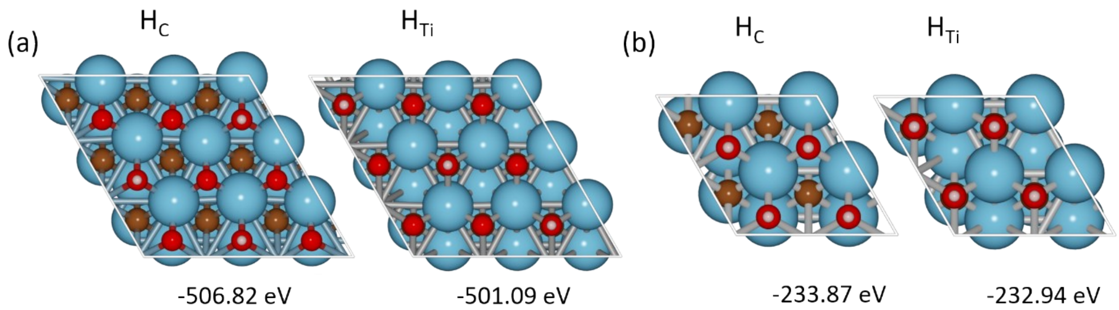

Fig. S2 Schematic arrangement of the fully –O, –OH, –H, and –F terminated Ti_3C_2 (0001) $p(2\times2)$ supercell, where moieties occupy H_{Ti} sites. The free (*) and occupied sites are colour-coded.

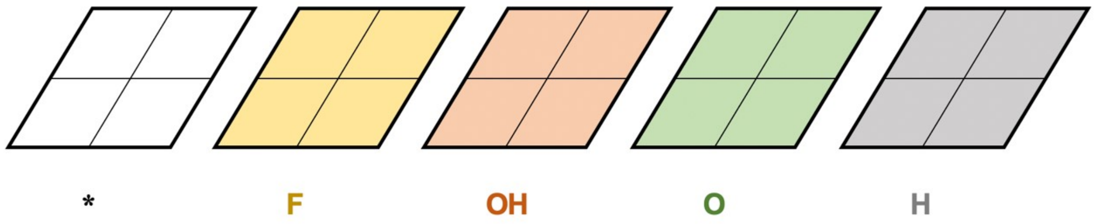

Fig. S3 Schematic arrangement of the binary ½ ML *vs.* ½ ML situations admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(2×2) supercell, exemplified on the $OH_{1/2}O_{1/2}$ case. Colour coding as in Fig. S1.

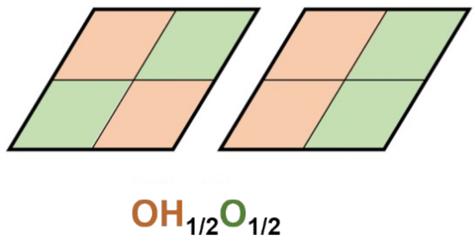

Fig. S4 Schematic arrangement of the binary $^{1}/_{4}$ ML *vs.* $^{3}/_{4}$ ML situation admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(2×2) supercell, exemplified on the $OH_{1/4}O_{3/4}$ case. Colour coding as in Fig. S1.

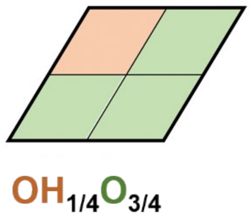

Fig. S5 Schematic arrangement of the binary $^{2}/_{3}$ ML *vs.* $^{1}/_{3}$ ML situations admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(3×3) supercell, exemplified on the $OH_{1/3}O_{2/3}$ case. Colour coding as in Fig. S1.

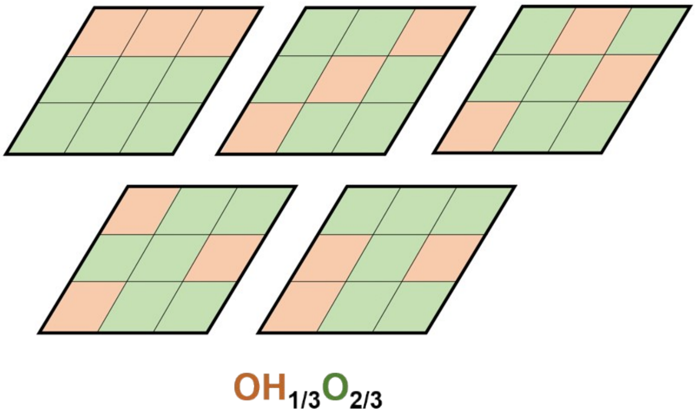

Fig. S6 Schematic arrangement of the ternary ¼, ¼, ½ ML situations admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(2×2) supercell, exemplified on the $F_{1/4}OH_{1/4}O_{1/2}$ case. Colour coding as in Fig. S1.

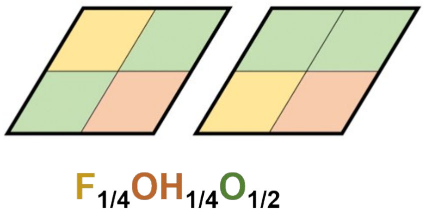

Fig. S7 Schematic arrangement of the ternary ⅓, ⅓, ⅓ ML situations admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(3×3) supercell, exemplified on the $F_{1/3}OH_{1/3}O_{1/3}$ case. Colour coding as in Fig. S1.

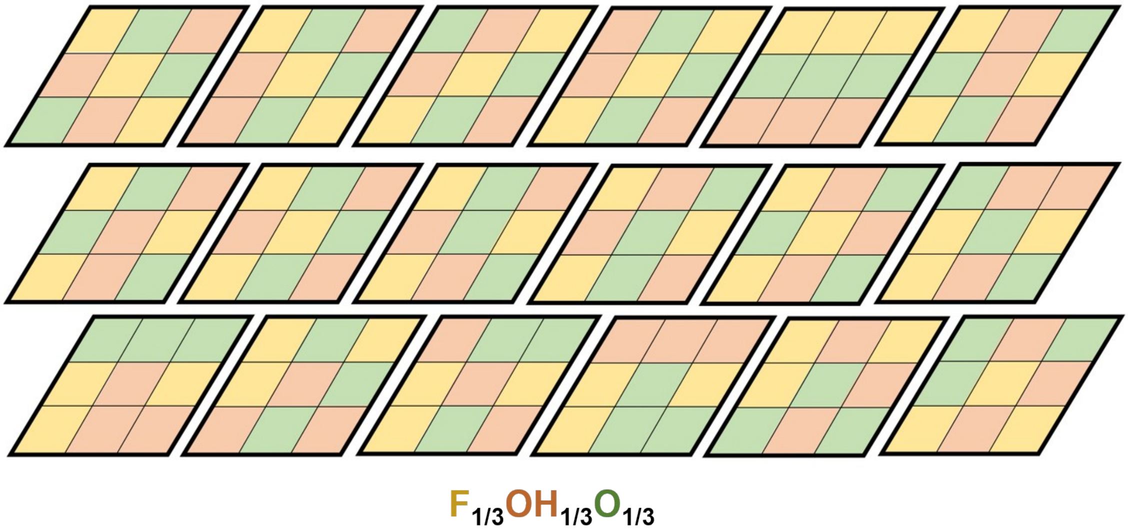

Fig. S8 Schematic arrangement of the ternary $^3/_9$, $^4/_9$, $^2/_9$ ML situations admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(3×3) supercell, exemplified on the $F_{3/9}OH_{4/9}O_{2/9}$ case. Colour coding as in Fig. S1.

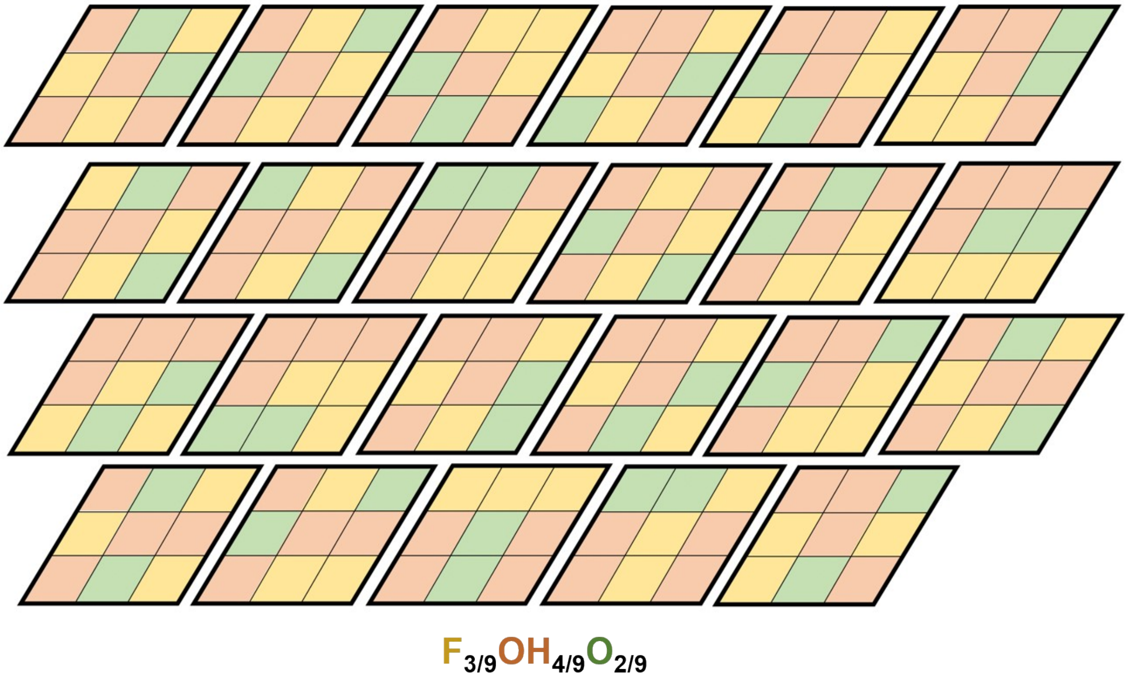

Fig. S9 Schematic arrangement of the ternary $^{3}/_{9}$, $^{5}/_{9}$, $^{1}/_{9}$ ML situations admixing –O, –OH, –H, and –F terminations, as well as * free sites, on the Ti_3C_2 (0001) *p*(3×3) supercell, exemplified on the $F_{3/9}OH_{5/9}O_{1/9}$ case. Colour coding as in Fig. S1.

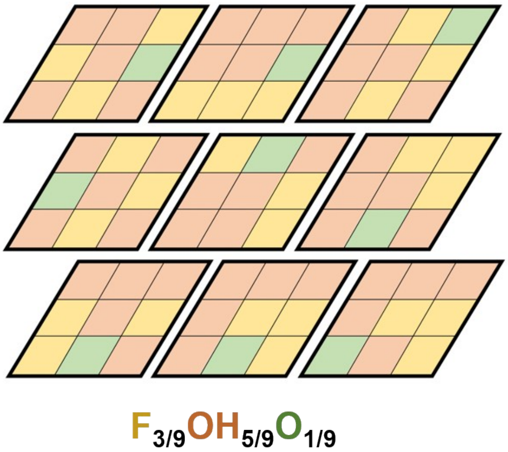

Fig. S10 Total and PDOS of the pristine Ti_3C_2 (0001) model, as those fully –O, –OH, –H, and –F terminated, and having different mixtures according to HER conditions and Pourbaix diagrams found in Figs. 2 and 3 of the main text. Energy levels are referred to the Fermi energy, E_F.

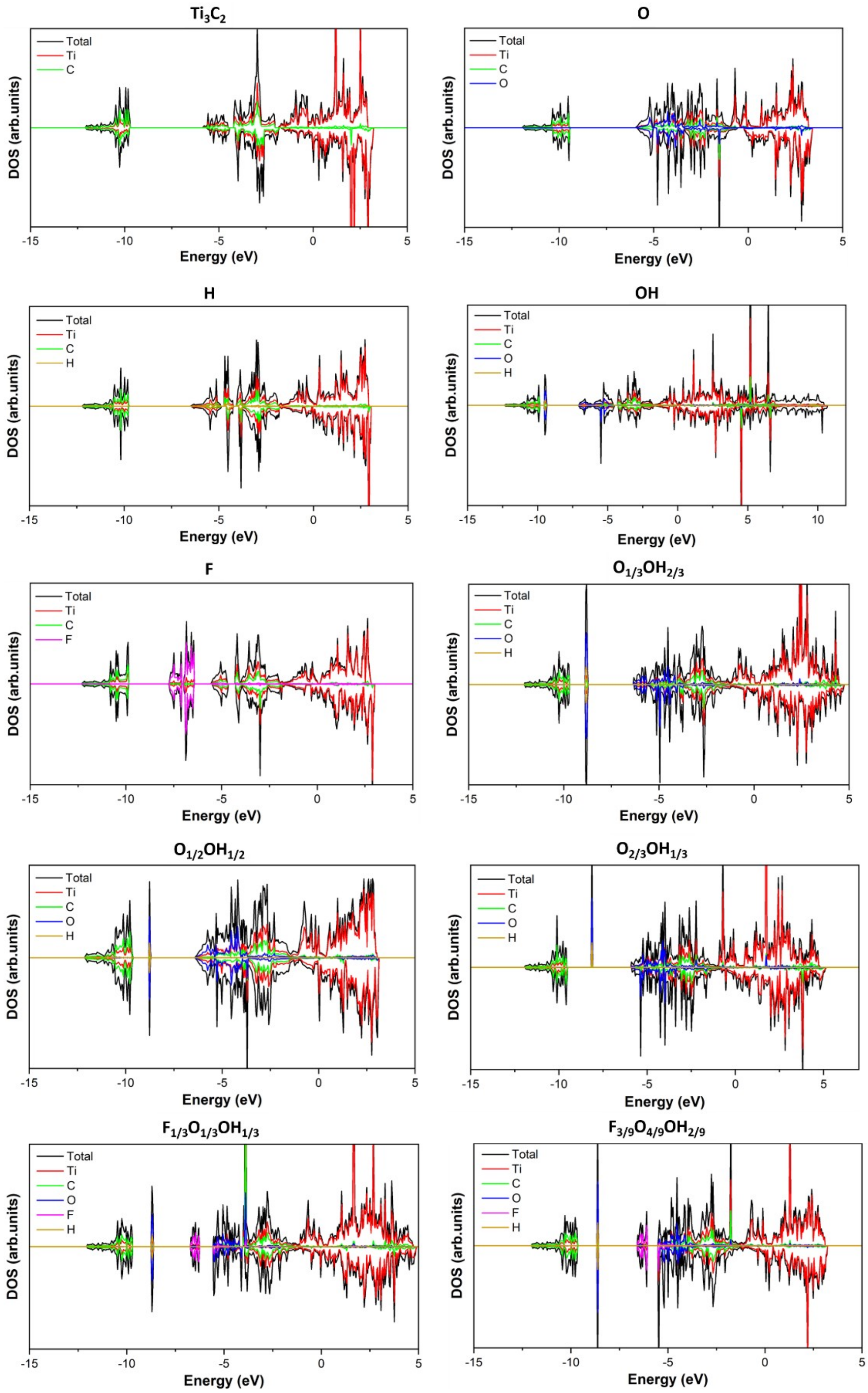

Fig. S11 Top view of the charge density difference (CDD) plots of the Ti_3C_2 (0001) fully –O, –OH, –H, and –F terminated, and having different mixtures according to HER conditions and Pourbaix diagrams found in Figs. 2 and 3 of the main text. Yellowish regions denote electron depletion, and the formation of positively charged regions, while blueish regions denote electron accumulation, and the formation of negatively charged regions. The contour intervals range up to 0.005 $e\cdot Å^{-3}$.