Supporting Informations

Computational Studies on the Structural, Electronic and Optical Properties of Graphene-like MXenes (M_2CT_2, M = Ti, Zr, Hf; T = O, F, OH) and Their Potential Applications as Visible-Light Driven Photocatalysts.

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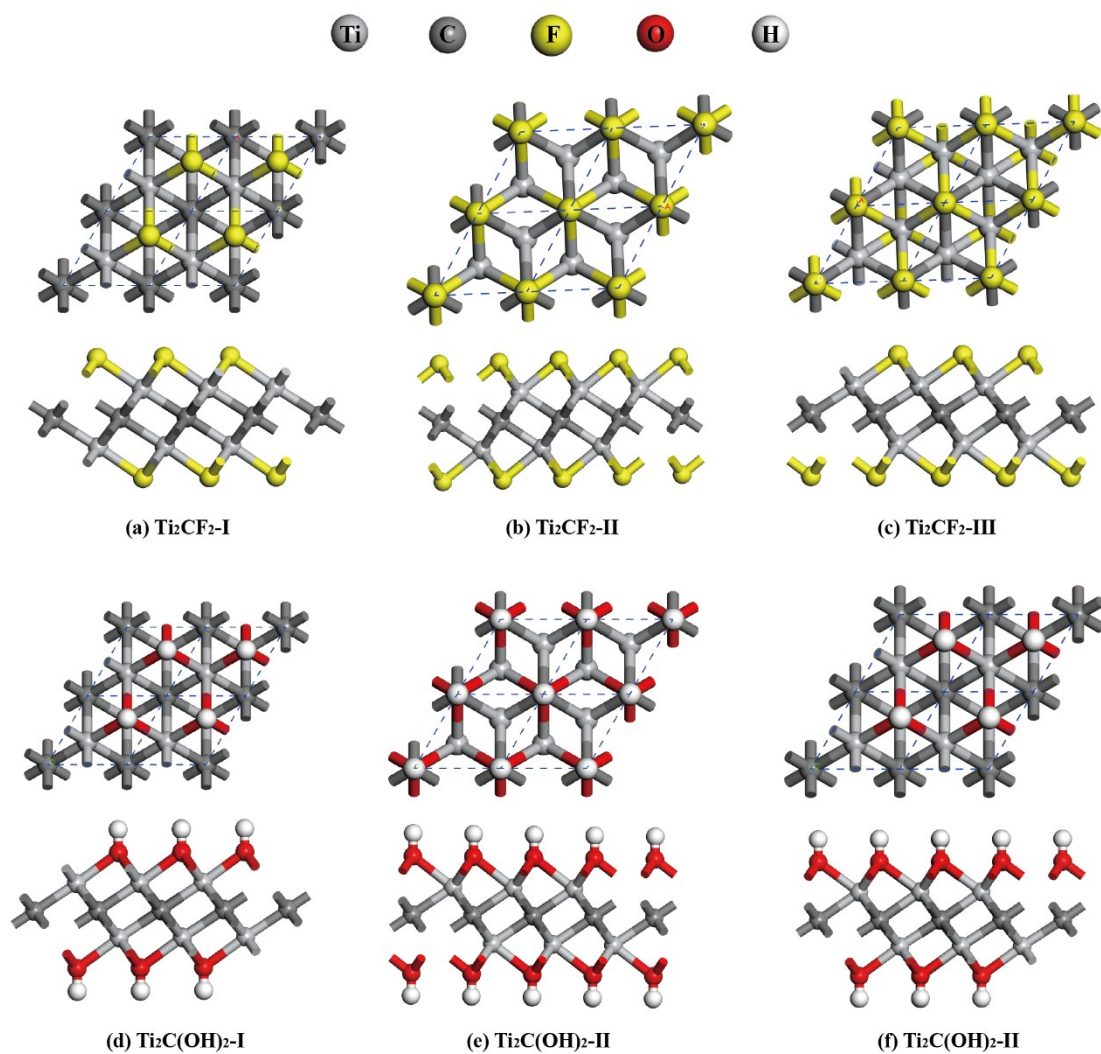
Figure S1 Top view (upper) and side view (lower) of the geometric structures for the (a) Ti$_2$CF$_2$-I, (b) Ti$_2$CF$_2$-II, (c) Ti$_2$CF$_2$-III, (d) Ti$_2$C(OH)$_2$-I, (e) Ti$_2$C(OH)$_2$-II and (f) Ti$_2$C(OH)$_2$-III.
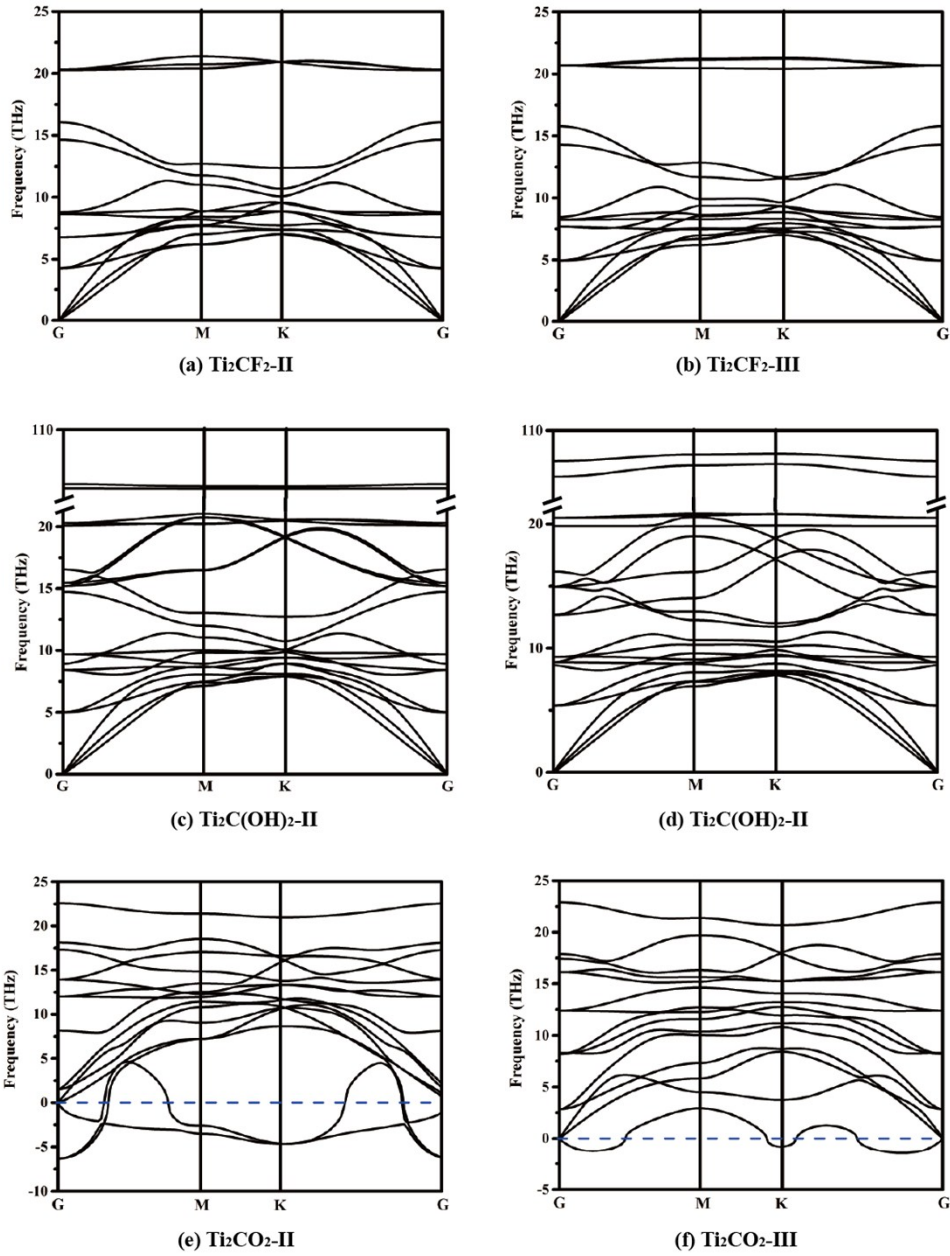
Figure S2 Phonon dispersion of the surface functionalized Ti$_2$C MXene with the Ti$_2$CT_2-II and Ti$_2$CT_2-III structures (T = O, F and OH).
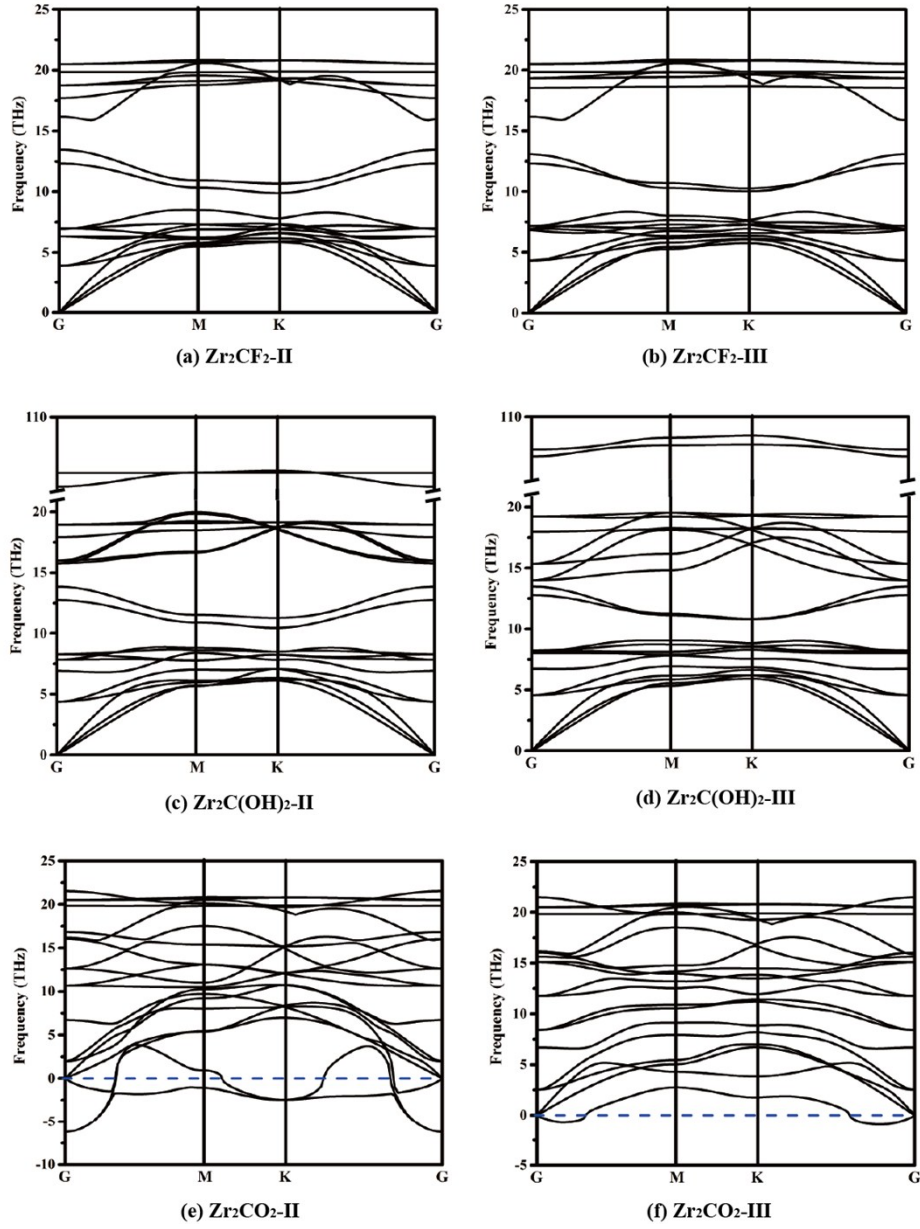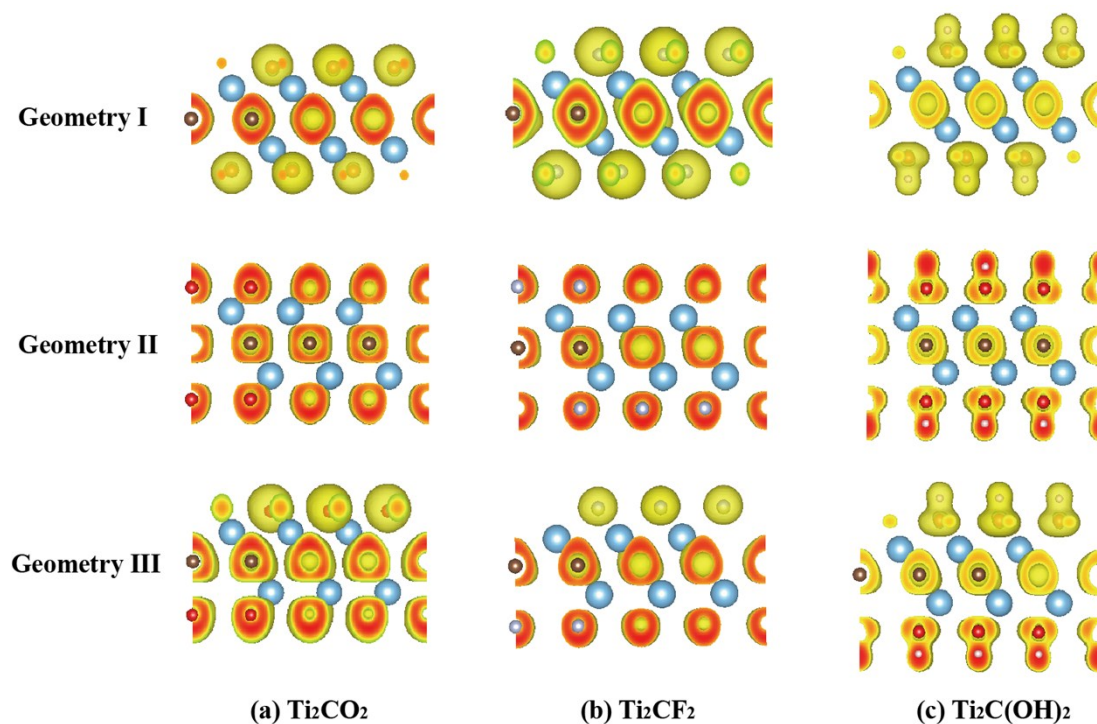
Figure S3 Phonon dispersion of the surface functionalized Zr_2C MXene with the Zr_2CT_2-II and Zr_2CT_2-III structures (T = O, F and OH).
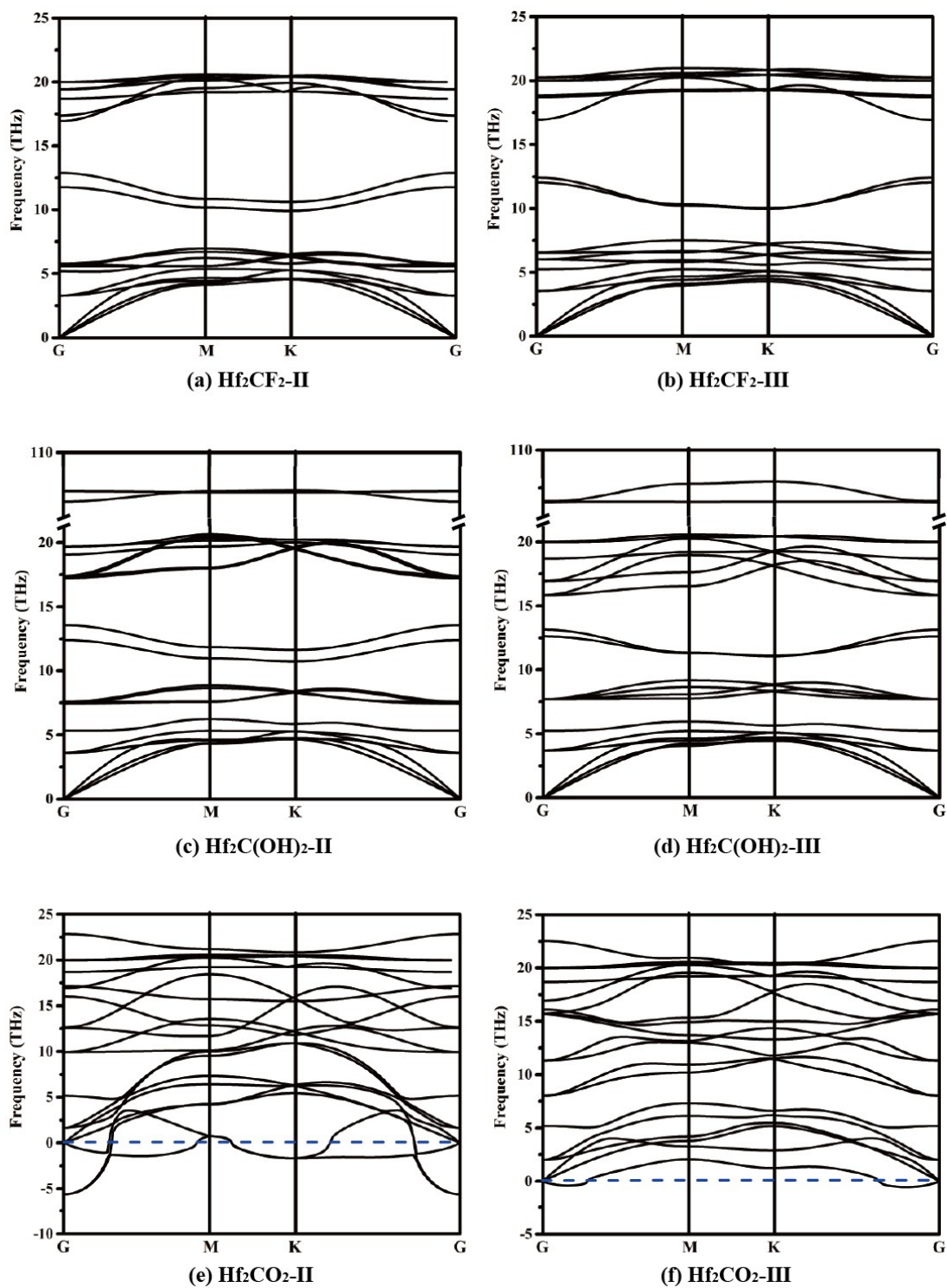
Figure S4 Phonon dispersion of the surface functionalized Hf$_2$C MXene with the Hf$_2$CT$_2$-II and Hf$_2$CT$_2$-III structures (T = O, F and OH).

| | (a) Ti₂CO₂ | (b) Ti₂CF₂ | (c) Ti₂C(OH)₂ |

Figure S5 Isosurfaces of ELF plotted with the value of 0.7 au for the (a) Ti_2CO_2, (b) Ti_2CF_2 and (c) $Ti_2C(OH)_2$ with different geometries. In view of the similar characteristics of the functionalized MXenes with different metal elements, only the isosurfaces of ELF for Ti_2CT_2 (T = O, F and OH) are presented.
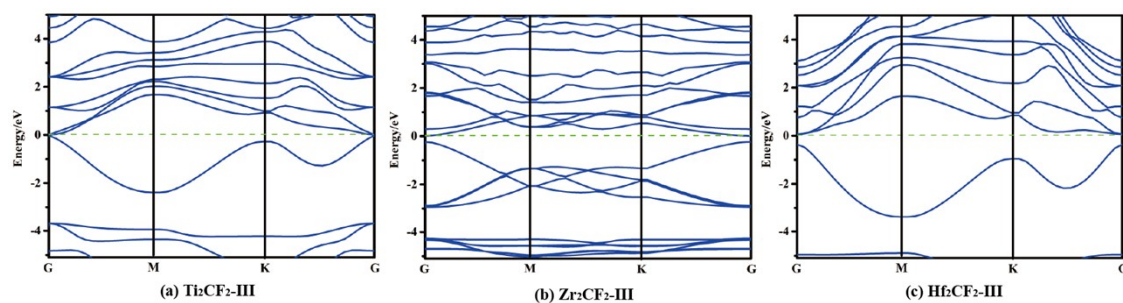
Figure S6 Band structures of the M_2CF_2-III. Green dashed lines represent the Fermi level at 0 eV.
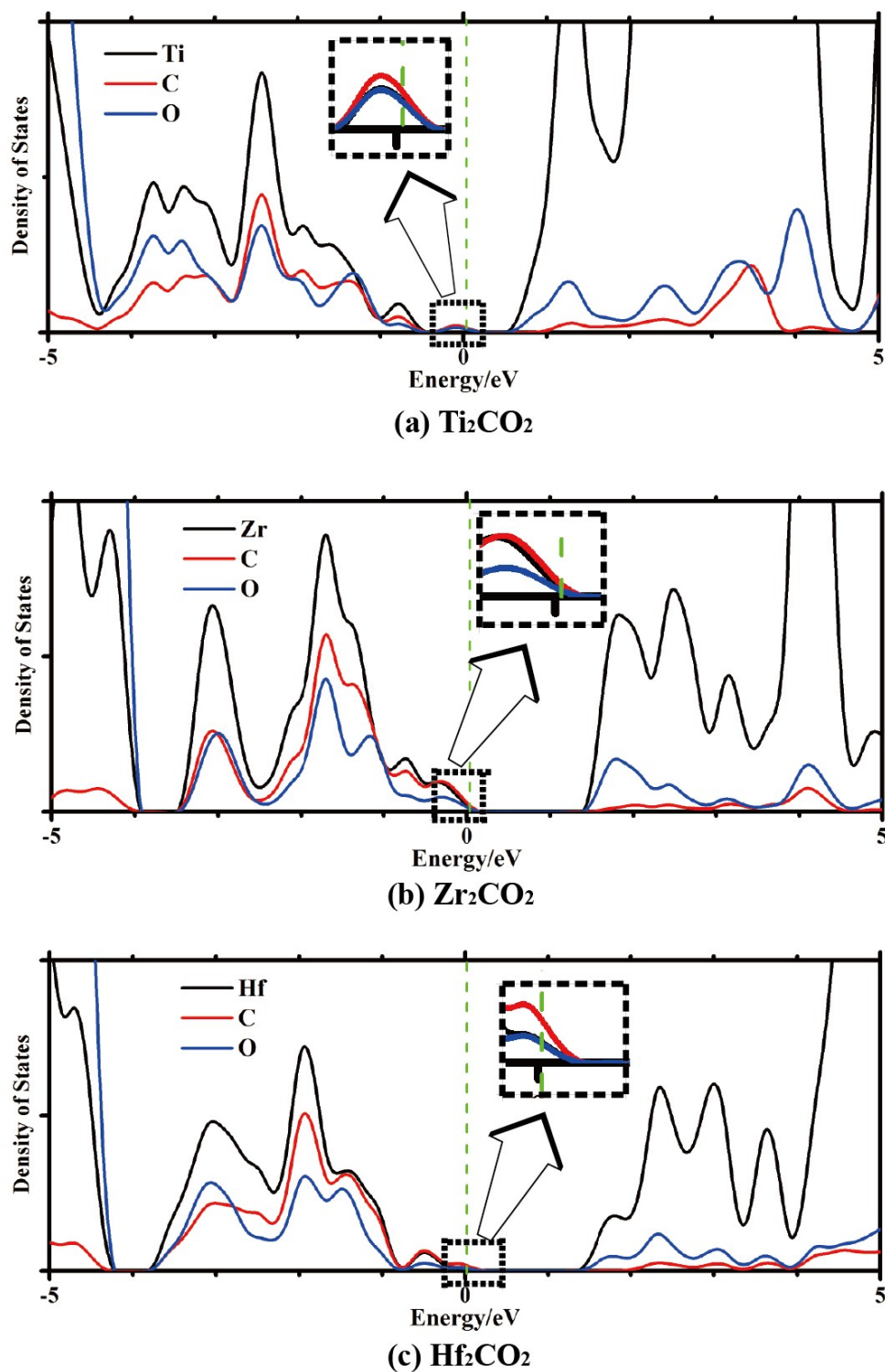
Figure S7 Density of states (DOS) and projected DOS (PDOS) of (a) Ti_2CO_2, (b) Zr_2CO_2 and (c) Hf_2CO_2. Green dashed lines represent the Fermi level at 0 eV. PDOS around the Fermi level are enlarged to clarify the VBMs contributed by different atoms (inserted images). According to the PDOS results, the VBMs are mainly composed of C-p orbitals and CBMs consist of M-d (M = Ti, Zr, Hf) states.
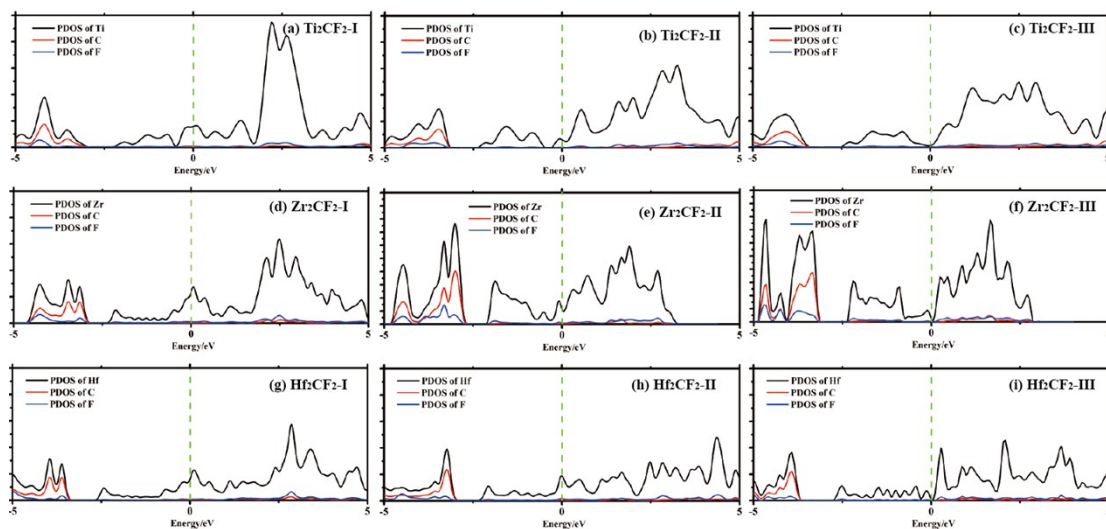
Figure S8 Projected DOS of the (a, b, c) Ti$_2$CF$_2$, (d, e, f) Zr$_2$CF$_2$ and (g, h, i) Hf$_2$CF$_2$ materials with different geometries.
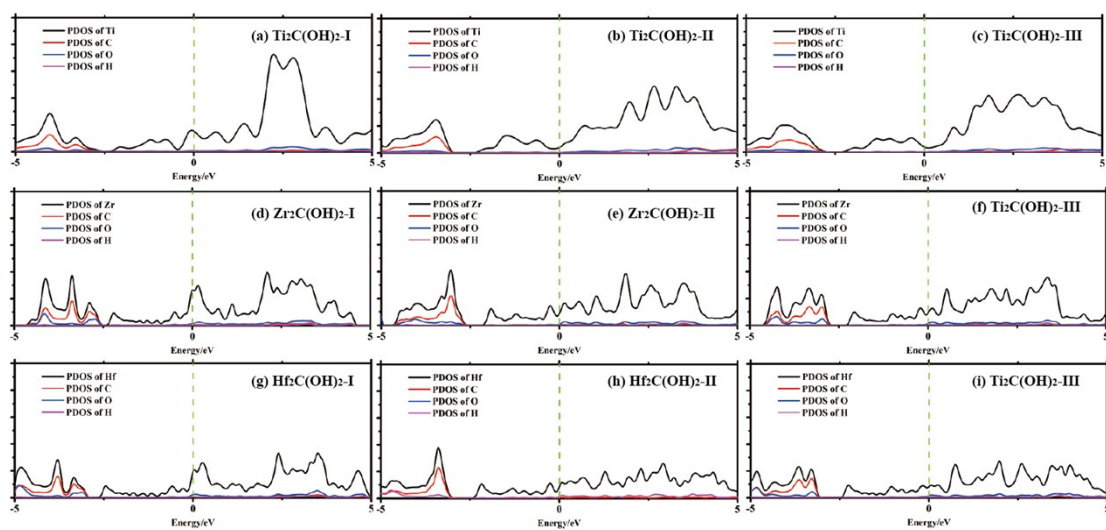
Figure S9 Projected DOS of the (a, b, c) Ti$_2$C(OH)$_2$, (d, e, f) Zr$_2$C(OH)$_2$ and (g, h, i) Hf$_2$C(OH)$_2$ materials with different geometries.
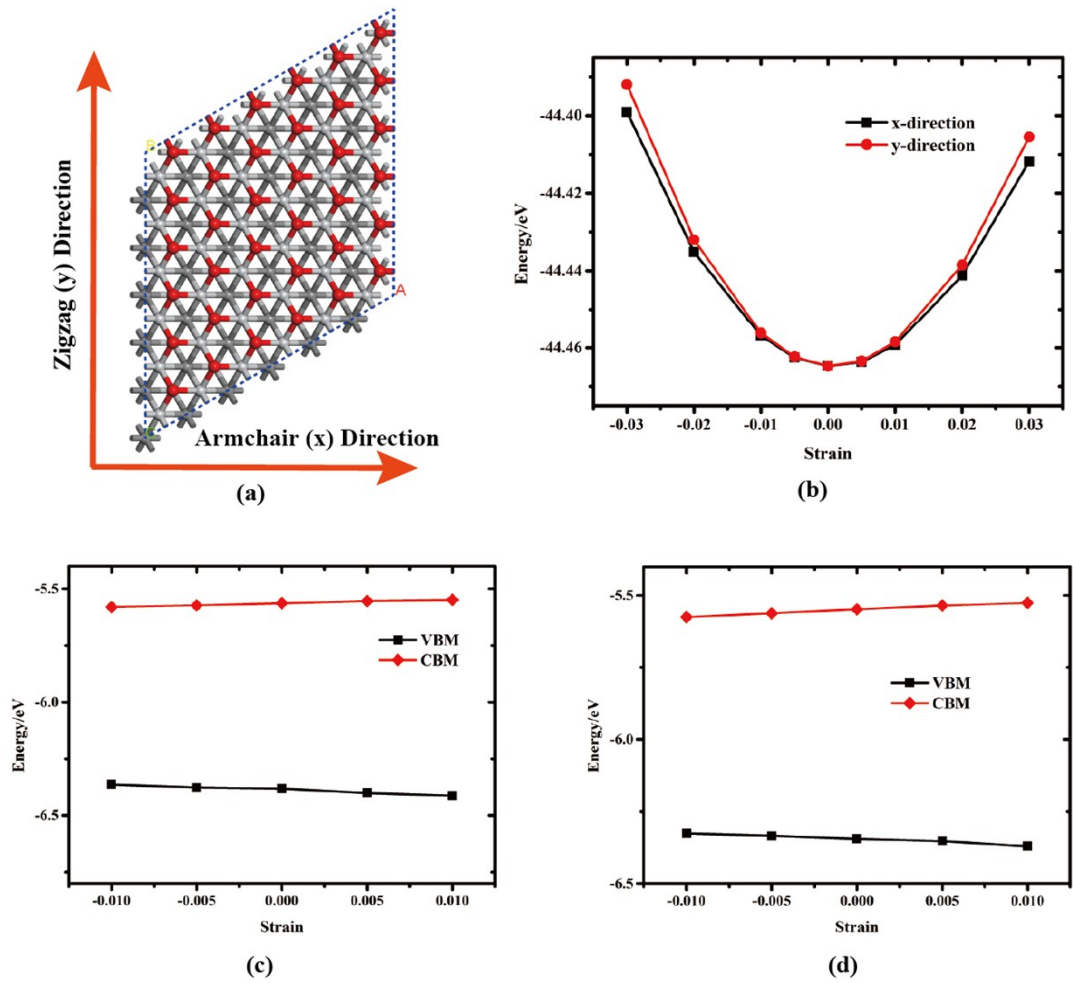
Figure S10 (a) Structure schematics of Ti_2CO_2-I monolayer in a 6×6 supercell. (b) The relationship between the total energy and strain along zigzag (y) direction and armchair (x) direction. The energy of VBM and CBM shift with respect to the lattice dilation and compression along (c) armchair and (d) zigzag directions, calculated by HSE06 method. Solid lines are guide for eyes.

Table S1 Cohesive energies (E_{coh} in eV/atom) of the functionalized MXenes

	Ti_2CT_2			Zr_2CT_2			Hf_2CT_2		
	T=O	T=F	T=OH	T=O	T=F	T=OH	T=O	T=F	T=OH
M_2CT_2-I	7.10	6.49	5.70	7.68	6.95	6.01	7.95	7.03	6.10
M_2CT_2-II	6.75	6.39	5.65	7.29	6.87	5.98	7.52	6.96	6.07
M_2CT_2-III	6.95	6.45	5.67	7.51	6.92	6.00	7.75	7.01	6.09

Table S2 Charge partitioning by Hirshfeld method for M_2CO_2 (M = Ti, Zr, Hf) with different geometries.

	Metal	Carbon	Oxygen
Ti_2CO_2-I	0.414	-0.331	-0.248
Ti_2CO_2-II	0.366	-0.291	-0.221
Ti_2CO_2-III	0.389	-0.310	-0.234
Zr_2CO_2-I	0.520	-0.402	-0.319
Zr_2CO_2-II	0.460	-0.349	-0.285
Zr_2CO_2-III	0.489	-0.370	-0.303
Hf_2CO_2-I	0.515	-0.403	-0.313
Hf_2CO_2-II	0.457	-0.355	-0.280
Hf_2CO_2-III	0.486	-0.376	-0.298

Table S3 Band gaps (E_g in eV) of the M_2CT_2 with differently functionalizing geometries. The band gaps of 0 eV denote the metallic properties of the corresponding M_2CT_2.

	Ti_2CT_2			Zr_2CT_2			Hf_2CT_2		
	T=O	T=F	T=OH	T=O	T=F	T=OH	T=O	T=F	T=OH
M_2CT_2-I	0.92	0	0	1.54	0	0	1.75	0	0
M_2CT_2-II	none	0	0	none	0	0	none	0	0
M_2CT_2-III	none	0.02	0	none	0.25	0	none	0.42	0

Computational Details of the Band Edge Positions

The band edge alignments were determined by computing the CBM/VBM energies relative to the vacuum level at 0 eV. Take the Ti_2CO_2-I for an example, the vacuum level of Ti_2CO_2-I was computed through VASP by setting the "LVTOT = TRUE". Also, under the same basic sets, we calculated the band structures and got the values of VBM and CBM level. Finally, the band edge positions can be determined by comparing the difference between the VBM (or CBM) and vacuum level. To evaluate the reduction/oxidation capability of the photocatalysts, we usually take the normal hydrogen electrode (E_{NHE}), which equals to -4.5 eV with respect to absolute vacuum scale (E_{AVS} = 0 eV), as a reference for comparing redox potentials of the band edges.

Table S4 Calculated vacuum levels (in eV), CBM and VBM energies (in eV) for M_2CO_2 (M = Ti, Zr, Hf) materials, through the HSE06 functional. V_{DFT} represents the values of CBM (or VBM) energies obtained from DFT computations, while the V_{AVS} and V_{NHE} are band edge positions relative to the absolute vacuum scale (E_{AVS} = 0 eV) and normal hydrogen electrode (E_{NHE} = -4.5 eV)

	Vacuum Level	E_{CBM}			E_{VBM}		
		V_{DFT}	V_{AVS}	V_{NHE}	V_{DFT}	V_{AVS}	V_{NHE}
Ti$_2$CO$_2$	2.70 eV	-2.90	-5.60	1.1	-3.82	-6.52	2.02
Zr$_2$CO$_2$	2.56 eV	-2.09	-4.65	0.15	-3.63	-6.19	1.69
Hf$_2$CO$_2$	2.71 eV	-1.53	-4.24	-0.26	-3.28	-5.99	1.49

Table S5 Effective mass $|m^*|$, DP constant $|E_1|$, in-plane stiffness C, and carrier mobility μ for electrons and holes along the x and y directions in 2D M_2CO_2-I (M = Ti, Zr, Hf).

		$|m^*|$ (m_e)	C (N/m)	$|E_1|$ (eV)	μ (cm^{2}V^{-1}S^{-1})
Ti$_2$CO$_2$	electrons (x)	0.42	132.59	1.62	4.07×10^3
	holes (x)	0.14	132.59	2.44	1.61×10^4
	electrons (y)	0.44	147.53	2.50	1.73×10^3
	hole (y)	0.13	147.53	2.18	2.61×10^4
Zr$_2$CO$_2$	electrons (x)	0.31	132.30	4.90	8.14×10^2
	holes (x)	0.11	132.30	1.38	8.15×10^4
	electrons (y)	0.32	148.03	11.94	1.44×10^2
	hole (y)	0.10	148.03	7.00	4.29×10^3
Hf$_2$CO$_2$	electrons (x)	0.18	146.13	5.02	2.57×10^3
	holes (x)	0.09	146.13	0.9	3.46×10^5
	electrons (y)	0.18	164.11	10.76	6.21×10^2
	hole (y)	0.09	164.11	6.98	6.18×10^3