Supporting Information

Surface Termination-Dependent Sc_2C MXenes: First-Principles study on Photocatalytic Water Splitting

Mingzhu Liu[a,b], Tengfei Wang[a], Xiaohong Li[*b], Xuehai Ju[*a]

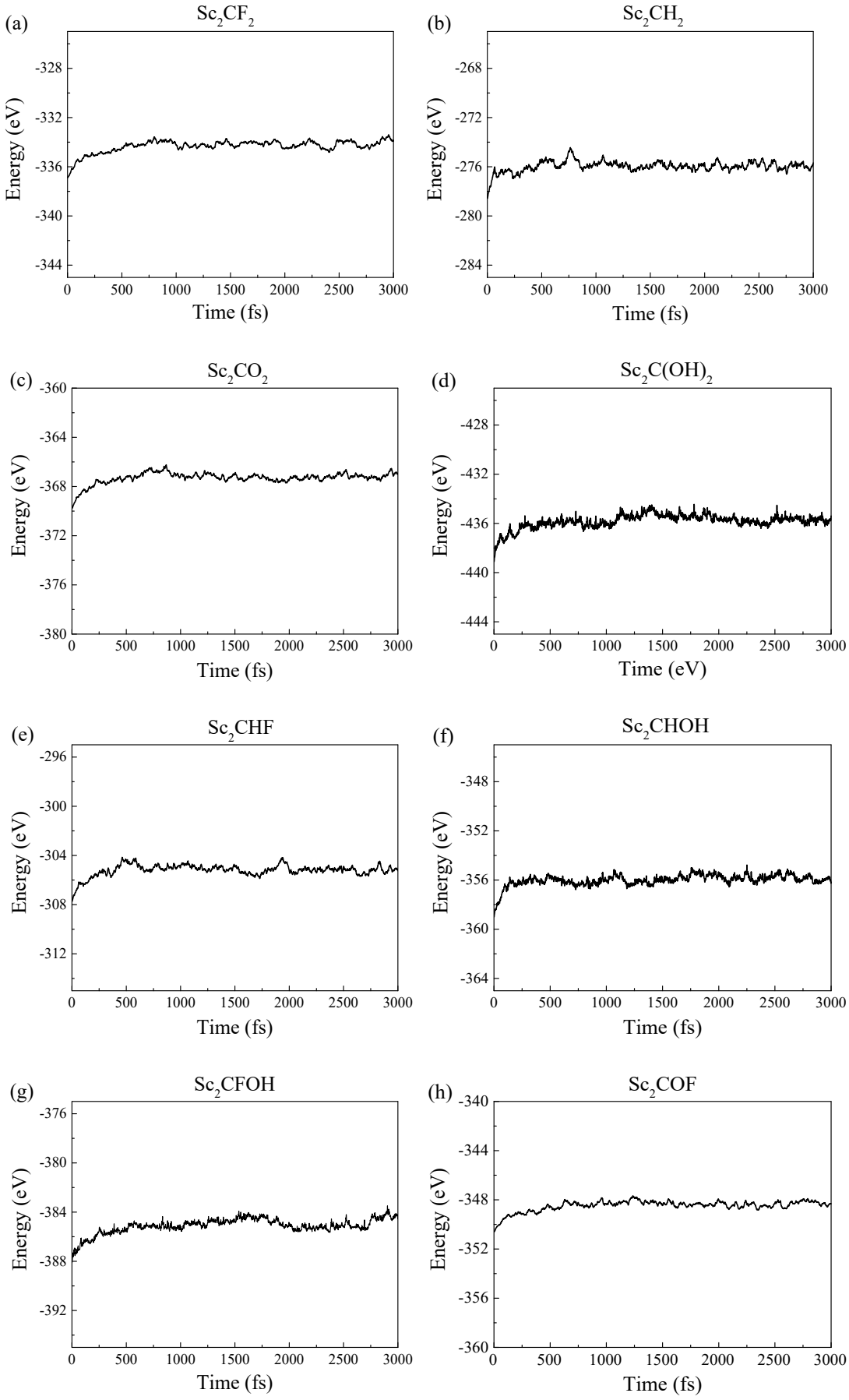
[a] Key Laboratory of Soft Chemistry and Functional Materials of MOE, School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China

[b] Longmen Laboratory, College of Physics and Engineering, Henan University of Science and Technology, Luoyang 471023, P. R. China

*Corresponding Author's Email: lorna639@126.com; xhju@njust.edu.cn

Table S1 Total energies (in eV) for Sc_2CT_2 and Sc_2CXT MXenes with different structural models and their lattice constants (Å). The energy for the Model-1 structure is chosen to be zero for each system.

system	Model-1	Model-2	Model-3	Model-4	*a (Å)*
Sc_2CF_2	0	1.21	0.58	–	3.270
Sc_2CH_2	0	1.22	0.87	–	3.277
Sc_2CO_2	0	–0.43	–0.56	–	3.425
$Sc_2C(OH)_2$	0	0.76	0.37	–	3.287
Sc_2CFOH	0	0.98	0.37	0.58	3.281
Sc_2CHF	0	4.03	0.56	6.78	3.273
Sc_2CHOH	0	0.83	0.35	0.44	3.283
Sc_2COF	0	0.92	0.66	0.39	3.247
Sc_2COH	0	0.65	0.44	0.37	3.259
Sc_2COOH	0	0.78	0.43	0.49	3.254


(a)
Sc_2CF_2
Energy (eV)
-328
-332
-336
-340
-344
0
500
1000
1500
2000
2500
3000
Time (fs)
(b)
Sc_2CH_2
Energy (eV)
-268
-272
-276
-280
-284
0
500
1000
1500
2000
2500
3000
Time (fs)
(c)
Sc_2CO_2
Energy (eV)
-360
-364
-368
-372
-376
-380
0
500
1000
1500
2000
2500
3000
Time (fs)
(d)
$Sc_2C(OH)_2$
Energy (eV)
-428
-432
-436
-440
-444
0
500
1000
1500
2000
2500
3000
Time (eV)
(e)
Sc_2CHF
Energy (eV)
-296
-300
-304
-308
-312
0
500
1000
1500
2000
2500
3000
Time (fs)
(f)
Sc_2CHOH
Energy (eV)
-348
-352
-356
-360
-364
0
500
1000
1500
2000
2500
3000
Time (fs)
(g)
Sc_2CFOH
Energy (eV)
-376
-380
-384
-388
-392
0
500
1000
1500
2000
2500
3000
Time (fs)
(h)
Sc_2COF
Energy (eV)
-340
-344
-348
-352
-356
-360
0
500
1000
1500
2000
2500
3000
Time (fs)

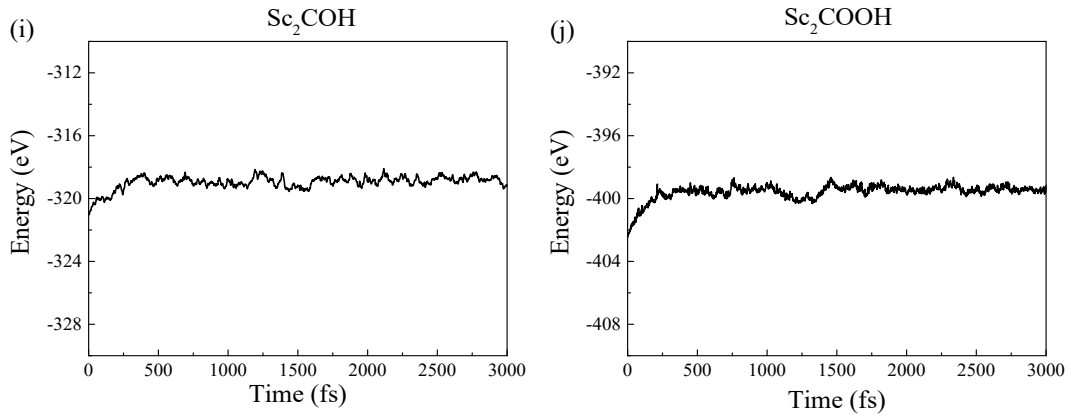


Fig. S1 The total energies of Sc_2CT_2 and Sc_2CXT (X, T= F, H, O, OH) supercells as a function of time.

Building upon prior theoretical frameworks [1] and assuming ideal catalytic reactionefficiency (100%), the upper bounds of light absorption efficiency (η_{abs}), carrier utilization efficiency (η_{cu}), and solar-to-hydrogen (STH) conversion efficiency can be quantitatively evaluated. These parameters are defined as follows:

$$\eta_{abs} = \frac{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)}$$

where P($\hbar\omega$) denotes the AM1.5G solar spectral irradiance at photon energy $\hbar\omega$, and E_g is the bandgap of the photocatalyst. The denominator represents the total incident solar power density, while the numerator quantifies the absorbed power density by the material. The carrier utilization efficiency is defined as:

$$\eta_{cu} = \frac{\Delta G \int_{E}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}$$

where $\Delta G = 1.23\ eV$ is the thermodynamic potential difference for water splitting. The integral from E to infinity represents the effective photocurrent density. Considering

the barriers present in the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), additional energy is required to overcome these barriers, and this portion of energy should be included in *E*. Based on established research progress regarding the overpotentials of OER and HER electrocatalysts as well as the energy loss of charge carrier migration between materials, typical overpotentials are assumed as $\eta_{HER} = 0.2\ V$ and $\eta_{OER} = 0.6$. The adjusted E is determined by:

$$\begin{cases} E_g, if\ \eta_{HER} \geq 0.2\ eV,\ \eta_{OER} \geq 0.6\ eV \\ E_g + 0.2 - \eta_{HER}, if\ \eta_{HER} < 0.2\ eV, \eta_{OER} \geq 0.6\ eV \\ E_g + 0.6 - \eta_{OER}, if\ \eta_{HER} \geq 0.2\ eV, \eta_{OER} < 0.6\ eV \\ E_g + 0.6 - \eta_{HER} - \eta_{OER}, if\ \eta_{HER} < 0.2\ eV, \eta_{OER} < 0.6\ eV \end{cases}$$

The theoretical STH efficiency is given by:

$$\eta_{STH} = \eta_{abs} \times \eta_{cu}$$

For Janus materials with a vertical intrinsic electric field (E_{IEFE}), the enhanced carrier separation due to the built-in potential ($\Delta\Phi$) modifies the STH efficiency which should be defined as:

$$\eta_{STH}^{'} = \eta_{STH} \times \frac{\int_0^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega)d(\hbar\omega) + \Delta\Phi \int_{E_g}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}$$

Where $\Delta\Phi$ denotes the vacuum-level offset between surfaces, the second term in the denominator represents the energy contribution of the vertically oriented intrinsic electric field.

Table S2 The calculated over-potential at pH = 0, 7 and 14 for the hydrogen evolution reaction $\chi(H_2)$ and the oxygen evolution reaction $\chi(O_2)$ in eV, the energy conversion efficiency of light absorption η_{abs}, carrier utilization η_{cu}, STH η_{STH} and corrected STH $\eta_{STH'}$ in %.

pH = 0	$\chi(O_2)$	$\chi(H_2)$	η_{abs}	η_{cu}	η_{STH}	$\eta_{STH'}$
Sc_2CF_2	-0.2541	0.9186	-	-	-	-
Sc_2CH_2	-0.3109	0.8891	-	-	-	-
Sc_2CO_2	0.4484	1.3214	6.10	25.49	1.55	1.51
Sc_2CHF	-0.1501	0.8375	-	-	-	-

pH = 7	$\chi(O_2)$	$\chi(H_2)$	η_{abs}	η_{cu}	η_{STH}	$\eta_{STH'}$
Sc_2CF_2	0.1596	0.5049	41.40	30.06	12.44	-
Sc_2CH_2	0.1028	0.4754	46.00	29.50	13.57	-
Sc_2CO_2	0.8621	0.9077	6.10	36.71	2.24	2.18
Sc_2CHF	0.2636	0.4238	40.30	33.65	13.56	13.18
pH = 14	$\chi(O_2)$	$\chi(H_2)$	η_{abs}	η_{cu}	η_{STH}	$\eta_{STH'}$
Sc_2CF_2	0.5733	0.0912	41.40	41.92	17.35	-
Sc_2CH_2	0.5165	0.0617	46.00	39.87	18.34	-
Sc_2CO_2	1.2758	0.4940	6.10	36.71	2.24	2.18
Sc_2CHF	0.6773	0.0101	40.30	39.48	15.91	15.46

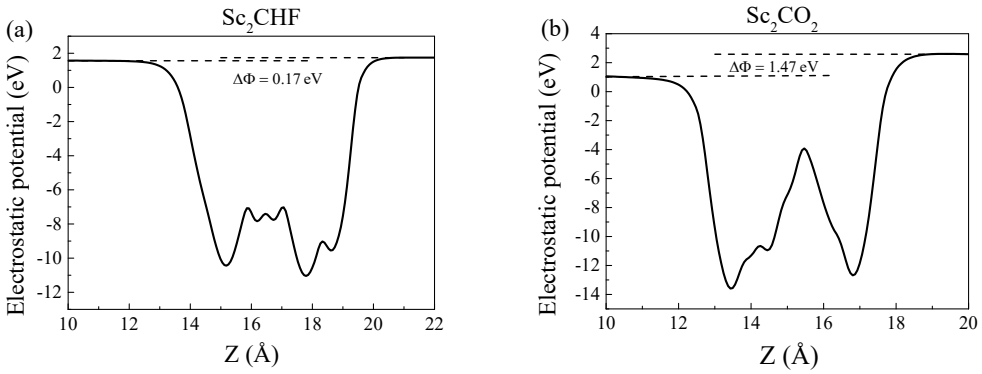
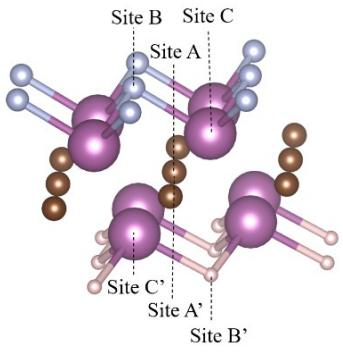


Fig. S2 The electrostatic potential energy differences (in eV) of Sc_2CHF and Sc_2CO_2.

(a)



(b)

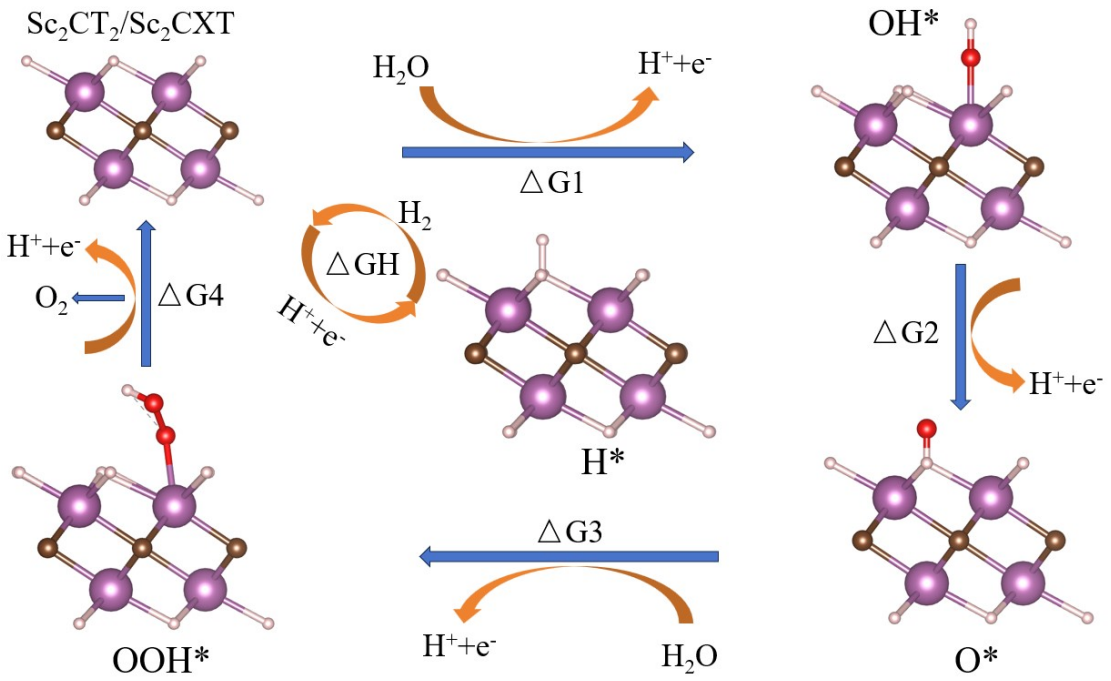


Fig. S3 The adsorbed sites and flowchart of HER and OER.

Table S3 The total energies (in eV) for adsorbed structures with different adsorbed sites, the energy for siteA is set to zero for each system.

		siteA	siteB	siteC	siteA'	siteB'	siteC'
Sc_2CH_2	H	0	-0.287	0.181	-	-	-
	O	0	-3.017	-0.317	-		
	OH	0	0.6171	-0.255			
	OOH	0	-0.042	-0.066			
Sc_2CF_2	H	0	1.154	0.070	-	-	-
	O	0	-0.471	-0.480			
	OH	0	0.071	-0.044			
	OOH	0	-0.029	-0.053			
Sc_2CHF	H	0	0.049	0.001	0	-0.049	0.003
	O	0	1.538	-0.309	0	-0.813	-0.398
	OH	0	-0.072	-0.082	0	0.074	-0.575
	OOH	0	-0.031	-0.046	0	-0.001	-0.003

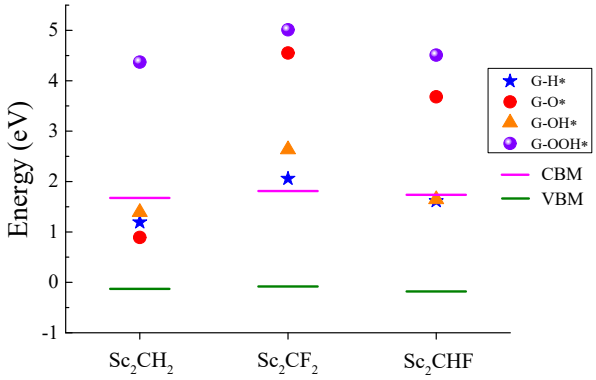
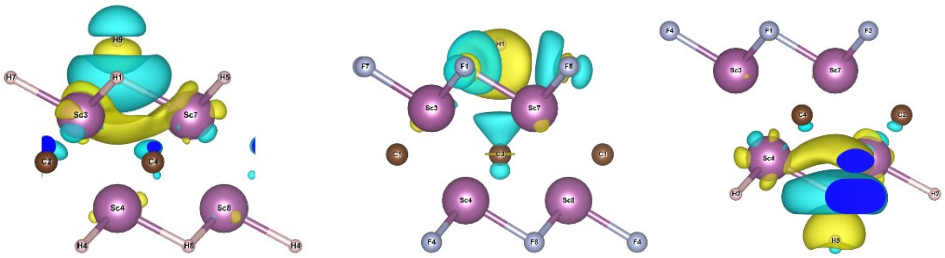
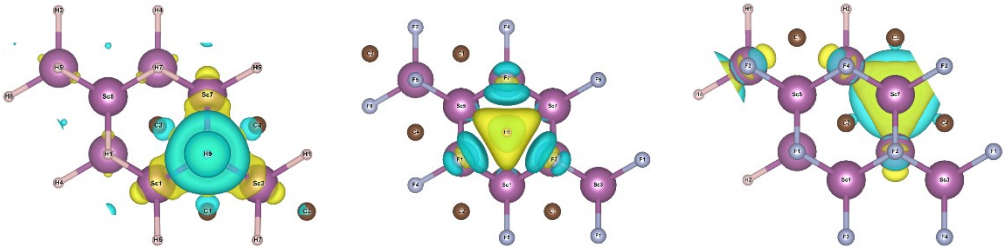


Fig. S4 The locations of CBM and VBM, ΔG of HER and OER at pH = 7 on U = 0 V of Sc_2CH_2, Sc_2CF_2 and Sc_2CHF.

sidee

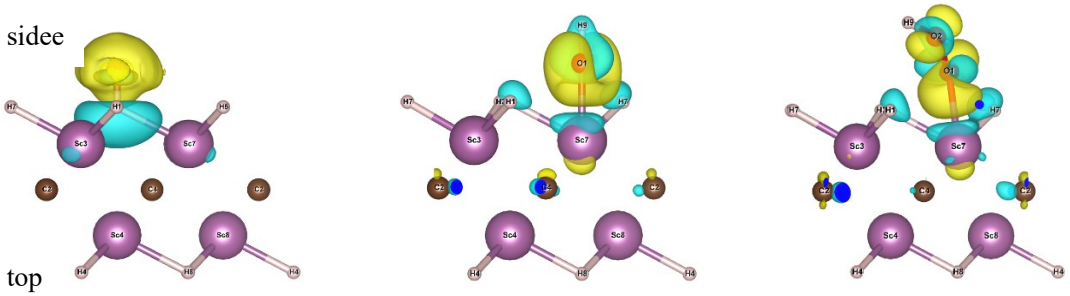


top

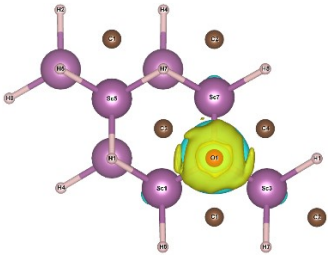


(a) Sc_2CH_2-H* (b) Sc_2CF_2-H* (c)Sc_2CHF-H*

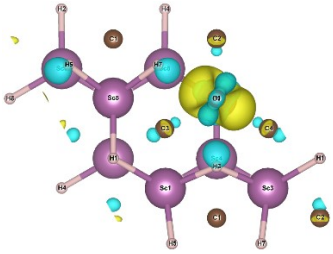
sidee



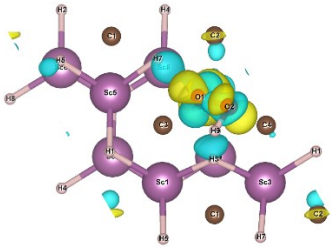
top



(d) Sc_2CH_2-O*



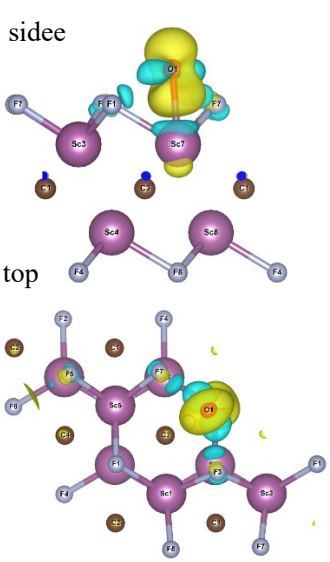
(e) Sc_2CH_2-OH*



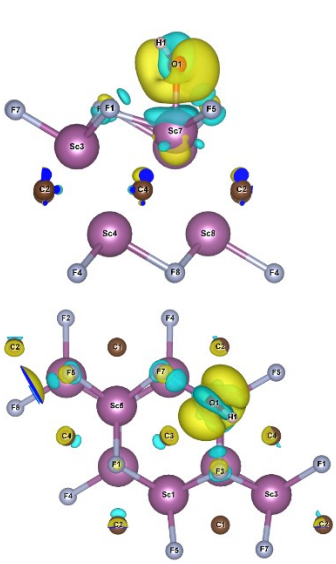
(f) Sc_2CH_2-OOH*

sidee

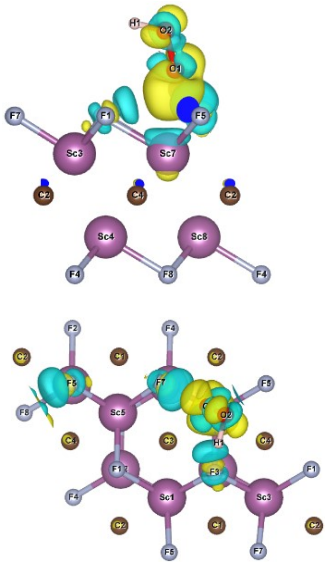
top



(g) Sc_2CF_2-O*



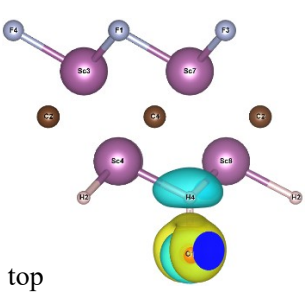
(h) Sc_2CF_2-OH*



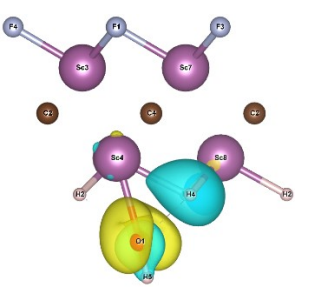
(i) Sc_2CF_2-OOH*

sidee

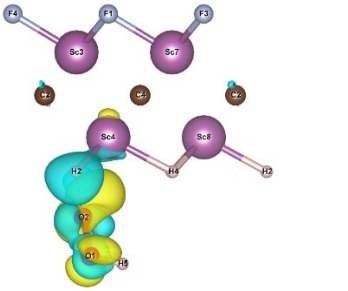
top



(j) Sc_2CHF-O*



(k) Sc_2CHF-OH*



(l) Sc_2CHF-OOH*

Fig. S5 The charge density difference of Sc_2CH_2, Sc_2CF_2 and Sc_2CHF of HER (a-c) and OER (e-l) from side and top view. The yellow and cyan indicate charge accumulation and consumption.

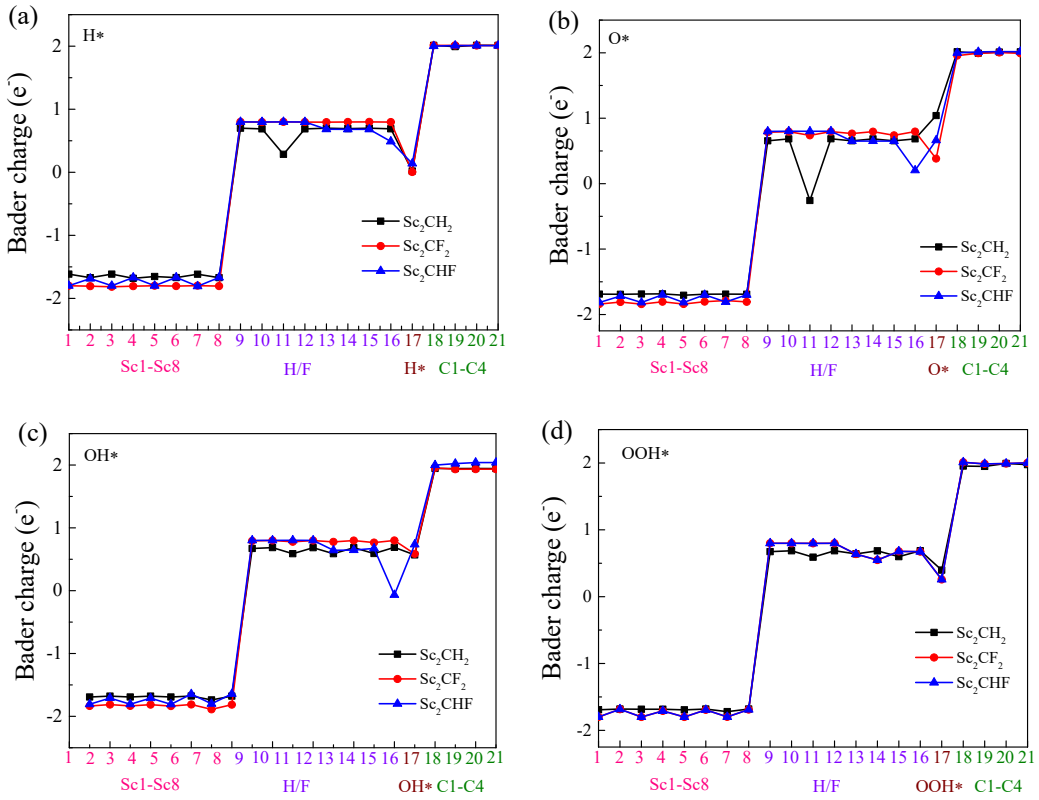


Fig. S6 Bader charge of HER and OER intermediates on Sc_2CH_2, Sc_2CF_2, and Sc_2CHF. All systems comprise 4 parts, including Sc1-Sc8, C1-C4, the adsorbed atoms, and their respective functional groups (H, F, or mixed H/F). Atom labels are consistent with Fig. S5.

References

1. C. F. Fu, J. Y. Sun, Q. Q. Luo, X. X. Li, W. Hu and J. L. Yang, *Nano Lett.*, 2018, **18**, 6312-6317.