Supporting Information for

First-principles studies on electronic and photocatalytic water splitting properties of surface functionalized Y_2C-based MXenes

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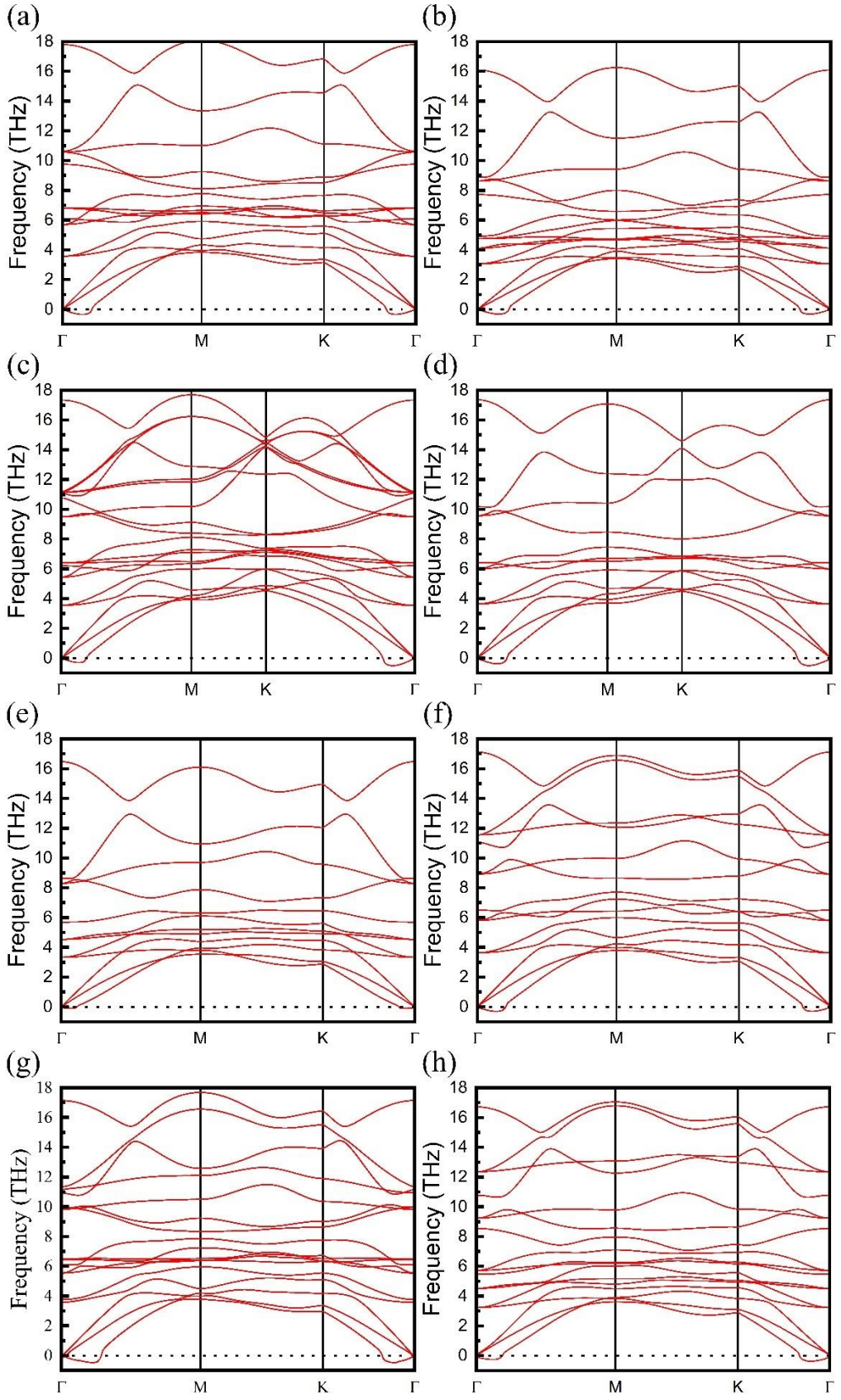


Figure S1. The calculated phono dispersion of (a) Y_2CF_2, (b) Y_2CCl_2, (c) $Y_2C(OH)_2$, (d) Y_2CHF, (e) Y_2CHCl, (f) $Y_2C(OH)H$, (g) $Y_2C(OH)F$, and (h) $Y_2C(OH)Cl$.

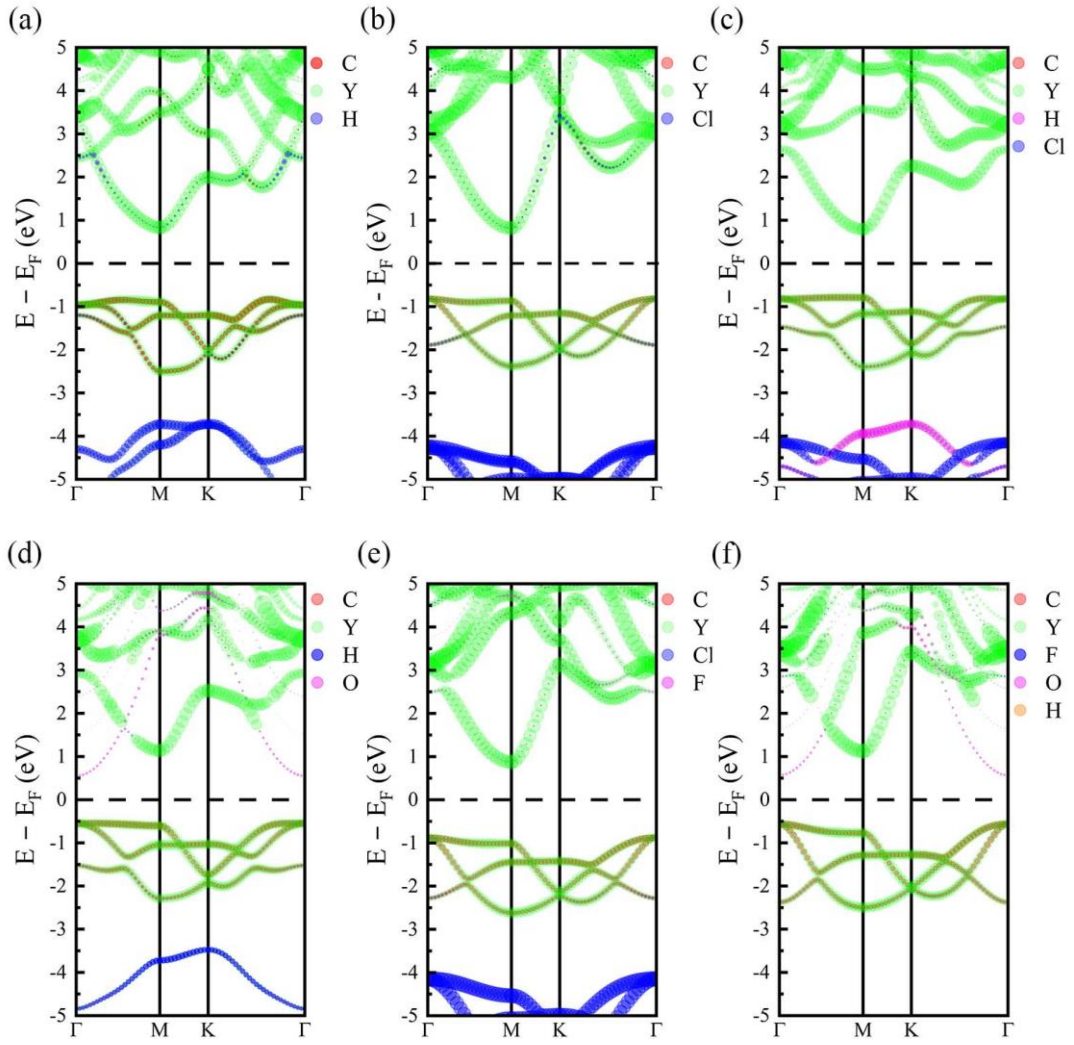
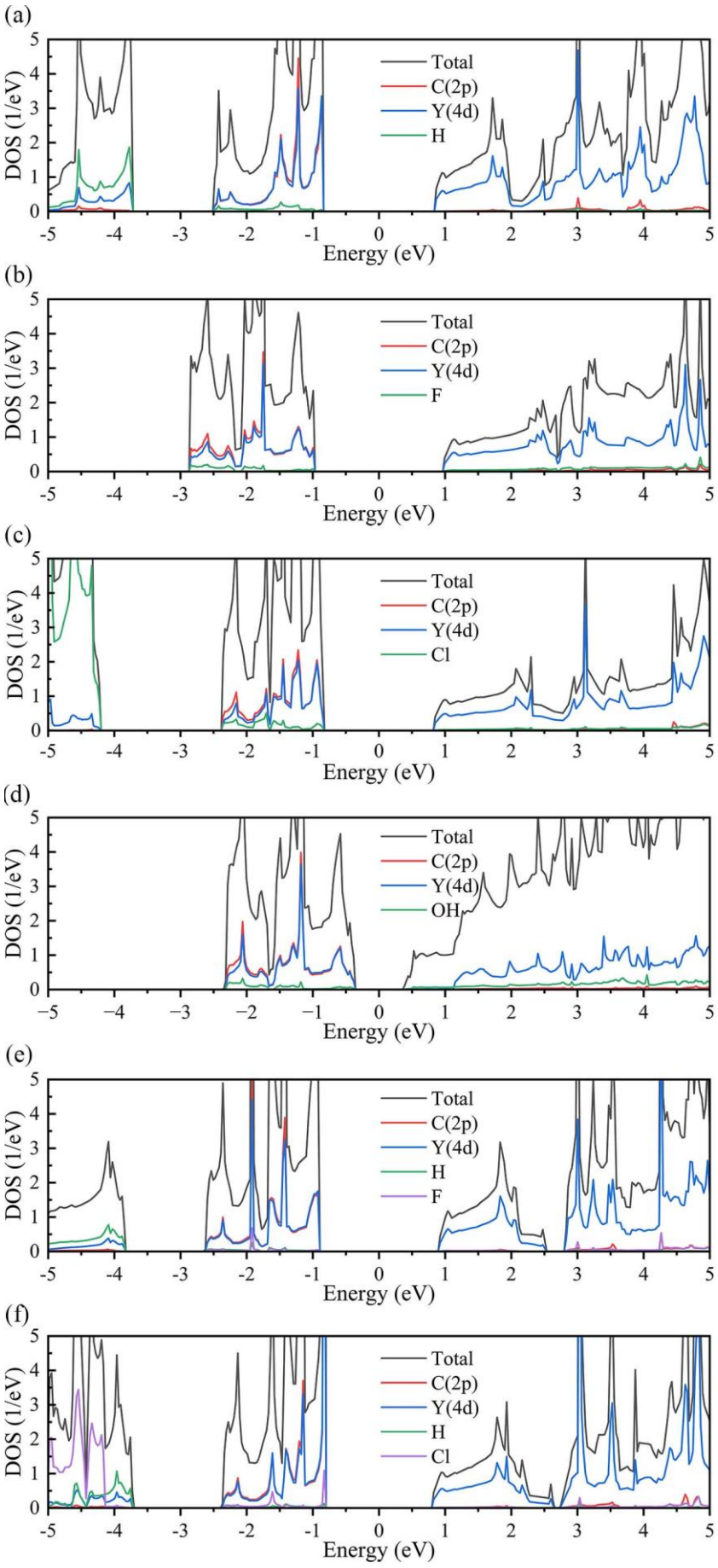


Figure S2. The calculated band structures of (a) Y_2CH_2, (b) Y_2CCl_2, (c) Y_2CHCl, (d) $Y_2C(OH)H$, (e) Y_2CFCl, and (f) $Y_2C(OH)F$. The Fermi level is put at the middle of the band gap and is set to zero.


(a)
DOS (1/eV)
Energy (eV)
Total
C(2p)
Y(4d)
H
(b)
DOS (1/eV)
Energy (eV)
Total
C(2p)
Y(4d)
F
(c)
DOS (1/eV)
Energy (eV)
Total
C(2p)
Y(4d)
Cl
(d)
DOS (1/eV)
Energy (eV)
Total
C(2p)
Y(4d)
OH
(e)
DOS (1/eV)
Energy (eV)
Total
C(2p)
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Energy (eV)
Total
C(2p)
Y(4d)
H
Cl

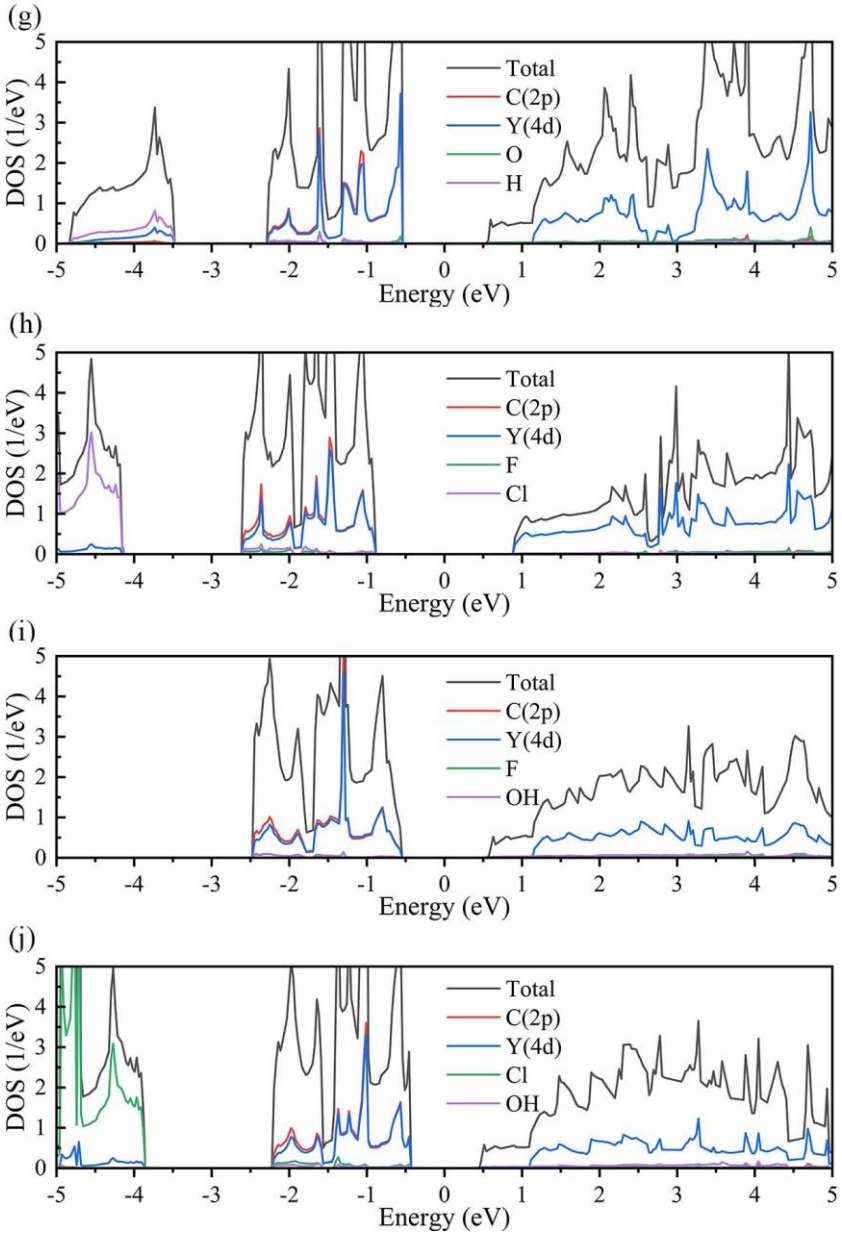

Figure S3. The density of states (DOS) of (a) Y_2CH_2, (b) Y_2CF_2, (c) Y_2CCl_2, (d) $Y_2C(OH)_2$, (e) Y_2CHF, (f) Y_2CHCl, (g) $Y_2C(OH)H$, (h) Y_2CFCl, (i) $Y_2C(OH)F$, and (j) $Y_2C(OH)Cl$. The Fermi level is put at the middle of the band gap and is set to zero.

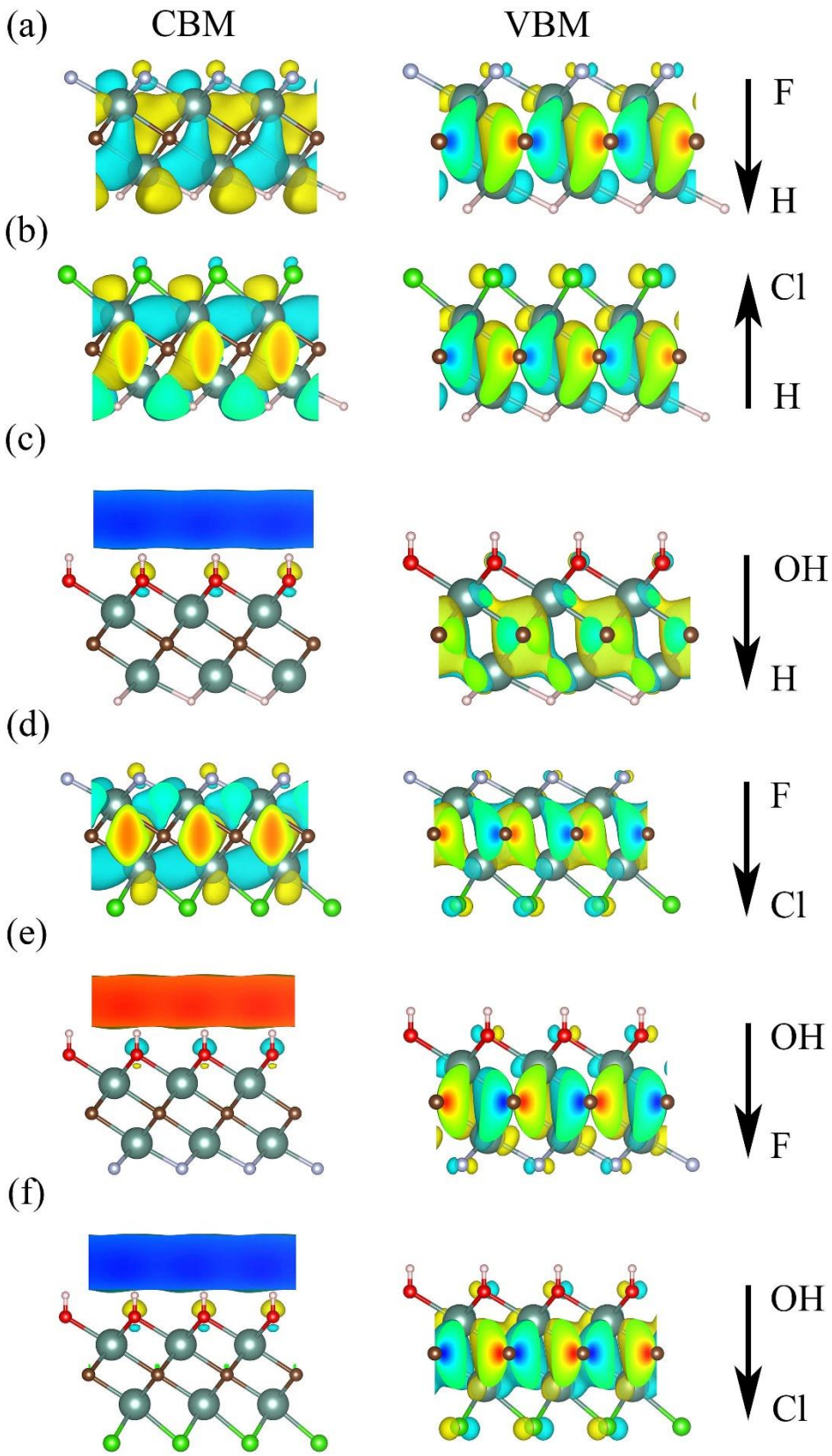

Figure S4. The spatial distributions of the wavefunctions for the conduction band minimum (CBM) and valence band maximum (VBM) for (a) Y_2CHF, (b) Y_2CHCl, (c) $Y_2C(OH)H$, (d) Y_2CFCl, (e) $Y_2C(OH)F$, and (f) $Y_2C(OH)Cl$. The black arrow represents the direction of the intrinsic electric field E_{IEF}.

Calculation method for solar to hydrogen efficiency

Based on the work reported previously,[1] assuming the 100% efficiency of catalytic reactions, the upper limits of light absorption, carrier utilization and solar to hydrogen (STH) efficiency can be predicted. The light absorption efficiency is defined as:

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

where $P(\hbar\omega)$ is the AM1.5G solar energy flux at photon energy $\hbar\omega$, E_g is the band gap of the material. The integral from 0 to infinity in the denominator is the total power density of incident simulative sunlight (Air Mass 1.5G), while the integral from E_g to infinity in the numerator represents the power density which can be absorbed by materials. 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 ΔG is the water redox potential difference of 1.23 eV, E is the photon energy that can be actually utilized for water splitting. The integral from E to infinity in the numerator is the effective photocurrent density. Considering that there are barriers for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), extra energy is demanded to overcome those barriers, which should be added in E. According to the previous reports, considering the over-potentials of OER and HER co-catalysts and the energy loss during carriers migration between materials, a suitable over-potentials for HER and OER are assumed to be 0.2 V and 0.6 V, respectively.[2-4] The value of E can be expressed as:

$$E = \begin{cases} E_g, (\chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.2 - \chi(H_2), (\chi(H_2) < 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.6 - \chi(O_2), (\chi(H_2) \geq 0.2, \chi(O_2) < 0.6) \\ E_g + 0.8 - \chi(O_2) - \chi(H_2), (\chi(H_2) < 0.2, \chi(O_2) < 0.6) \end{cases}$$

where the $\chi(H_2)$ and $\chi(O_2)$ represent over-potential of HER and OER, respectively. Then, the STH efficiency is defined as:

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

As for Janus structures, the intrinsic electric field does positive work for the separation of photon excited electrons and holes during the processing of photocatalytic water splitting, which should be added into the total energy. Therefore, the corrected STH efficiency of photocatalytic water splitting for 2D materials with vertical intrinsic electric field 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 $\Delta\Phi$ is the difference between vacuum levels of two surface, the second term in denominator is the work done by the vertical intrinsic electric field.

Table S1. The calculated light absorption, carrier utilization, STH and the corrected STH efficiency for Janus systems at pH = 7.

System	$\chi(H_2)$	$\chi(O_2)$	E	η_{abs}	η_{cu}	η_{STH}	η'_{STH}
Y_2CHF	0.61	0.03	2.3626	46.2	22.3	10.3	10.1
Y_2CHCl	0.42	1.48	1.5775	58.6	53.9	31.6	22.6
$Y_2C(OH)H$	2.72	0.07	1.6297	80.6	37.5	30.2	12.2
Y_2CFCl	0.74	1.62	1.7470	48.7	53.2	25.9	18.7
$Y_2C(OH)F$	2.47	-0.29	-	-	-	-	-
$Y_2C(OH)Cl$	2.75	1.32	0.8957	88.4	71.7	63.4	19.4

Table S2. The calculated light absorption, carrier utilization, STH and the corrected STH efficiency for Janus systems at pH = 14.

System	$\chi(H_2)$	$\chi(O_2)$	E	η_{abs}	η_{cu}	η_{STH}	η'_{STH}
Y_2CHF	0.19	0.44	1.9626	46.2	44.7	20.7	20.4
Y_2CHCl	0.01	1.89	1.7675	58.6	44.2	25.9	18.5
$Y_2C(OH)H$	2.31	0.48	1.2197	80.6	56.9	45.9	18.5
Y_2CFCl	0.32	2.03	1.7470	48.7	53.2	25.9	18.7
$Y_2C(OH)F$	2.06	0.12	1.6072	77.1	52.9	40.8	20.6
$Y_2C(OH)Cl$	2.34	1.74	0.8957	88.4	71.7	63.4	19.4

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