Supporting Information (SI)

Two-dimensional tetragonal AlOX (X=Cl, Br, or I) monolayers for promising photocatalytic performance: first-principles investigations

Yijing Ren,[a] Xinguo Ma, *[ab] Gang Yuan,[a] Jiajun Liao,[a] Nan M[c], Di Li[d] and Hui Lv [a]

[a.] *school of science, Hubei University of Technology, Wuhan 430068, China.*

[b.] *State Key Laboratory of Advanced Technology for Float Glass, Bengbu Glass Industrial Design and Research Institute, Bengbu, 233030, China.*

[c.] *Key Laboratory of Inorganic Functional Materials and Devices, Chinese Academy of Sciences, Shanghai 201899, China.*

[d.] *School of Metallurgical Engineering, Xi'an University of Architecture and, Xi'an, Technology 710055, China.*

***Corresponding Authors, E-mail:** maxg@hbut.edu.cn; manan@mail.sic.ac.cn.

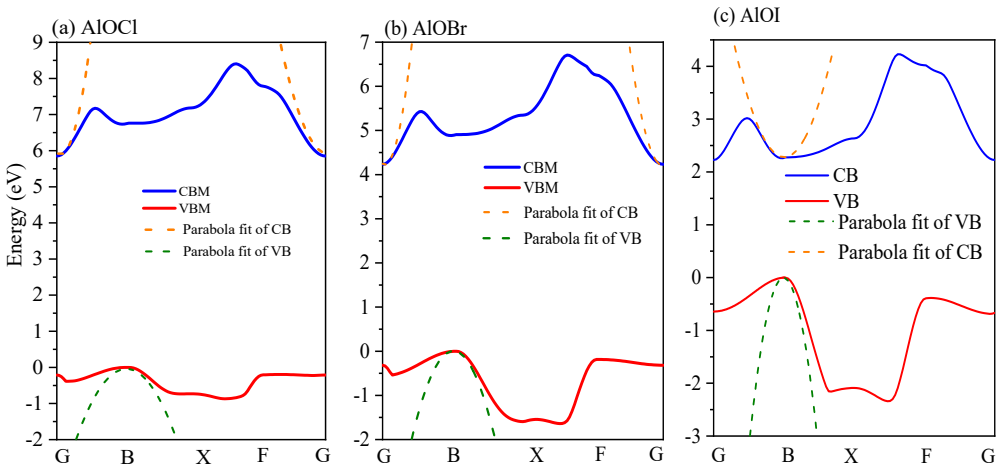

Fig. S1 The curves of VBM and CBM (solid line) for three crystal structures of AlOX (X=Cl, Br, or I) monolayers, and quadratic fitting curves (dash lines) at the VBM and CBM.

Table S1 Optimized lattice constants (a and b), bond lengths ($d_{Al–O}$, $d_{Al–X}$), and bond angles of the AlOX (X=Cl, Br, or I) monolayers after geometry optimization using PBE method with SOC effect

material	a (nm)	b (nm)	$d_{Al–O}$ (nm)	$d_{Al–X}$ (nm)	$\theta_{X–Al–O}$	$\theta_{Al–O–Al}$	$\theta_{O–Al–O}$
AlOCl	0.30	0.46	0.18, 0.19	0.23	90.94	88.27	90.81
AlOBr	0.30	0.37	0.19, 0.20	0.25	90.61	90.03	89.91
AlOI	0.33	0.46	0.18, 0.19	0.27	89.99	90.00	90.00

Table S2 Mulliken charges and overlap populations of AlOX (X=Cl, Br, or I) monolayers after geometry optimization using PBE and CAPZ methods

method	materials	species	charge	bonds	population
PBE	AlOCl	Al_1	1.66	O_1-Al_1	0.44
		Al_2	1.66	O_2-Al_2	0.44
		O_1	-1.25	O_2-Al_1	0.60
		O_2	-1.25	O_1-Al_2	0.60
		Cl_1	-0.41	Al_2-Cl_1	0.75
		Cl_2	-0.41	Al_1-Cl_2	0.75
	AlOBr	Al_1	1.36	O_1-Al_1	0.52
		Al_2	1.36	O_2-Al_2	0.52
		O_1	-1.20	O_2-Al_1	0.51
		O_2	-1.20	O_1-Al_2	0.51
		Br_1	-0.16	Al_2-Br_1	0.91
		Br_2	-0.16	Al_1-Br_2	0.91
	AlOI	Al_1	1.26	O_1-Al_1	0.67
		Al_2	1.26	O_2-Al_2	0.67
		O_1	-1.18	O_2-Al_1	0.38
		O_2	-1.18	O_1-Al_2	0.38
		I_1	-0.07	Al_2-I_1	0.78
		I_2	-0.07	Al_1-I_2	0.78
CAPZ	AlOCl	Al_1	1.48	O_1-Al_1	0.53
		Al_2	1.48	O_2-Al_2	0.53
		O_1	-1.09	O_2-Al_1	0.64
		O_2	-1.09	O_1-Al_2	0.64
		Cl_1	-0.39	Al_2-Cl_1	0.74
		Cl_2	-0.39	Al_1-Cl_2	0.74
	AlOBr	Al_1	1.34	O_1-Al_1	0.56
		Al_2	1.34	O_2-Al_2	0.56
		O_1	-1.08	O_2-Al_1	0.59
		O_2	-1.08	O_1-Al_2	0.59
		Br_1	-0.26	Al_2-Br_1	0.75
		Br_2	-0.26	Al_1-Br_2	0.75
	AlOI	Al_1	1.22	O_1-Al_1	0.59
		Al_2	1.22	O_2-Al_2	0.59
		O_1	-1.06	O_2-Al_1	0.54
		O_2	-1.06	O_1-Al_2	0.54
		I_1	-0.16	Al_2-I_1	0.78
		I_2	-0.16	Al_1-I_2	0.78

Table S3 Mulliken charges and overlap populations of AlOX (X=Cl, Br, or I) monolayers after geometry optimization using PBE method with SOC effect

materials	species	charge	bonds	population
AlOCl	Al_1	1.15	O_1-Al_1	0.60
	Al_2	1.15	O_2-Al_2	0.60
	O_1	-0.51	O_2-Al_1	0.60
	O_2	-0.51	O_1-Al_2	0.60
	Cl_1	-0.63	Al_2-Cl_1	0.10
	Cl_2	-0.63	Al_1-Cl_2	0.09
AlOBr	Al_1	0.83	O_1-Al_1	-0.03
	Al_2	0.85	O_2-Al_2	-0.02
	O_1	-0.35	O_2-Al_1	0.22
	O_2	-0.35	O_1-Al_2	0.22
	Br_1	-0.49	Al_2-Br_1	-0.52
	Br_2	-0.48	Al_1-Br_2	-0.49
AlOI	Al_1	0.46	O_1-Al_1	-0.08
	Al_2	0.46	O_2-Al_2	-0.05
	O_1	-0.48	O_2-Al_1	-0.03
	O_2	-0.48	O_1-Al_2	-0.04
	I_1	0.04	Al_2-I_1	0.08
	I_2	0.02	Al_1-I_2	0.09

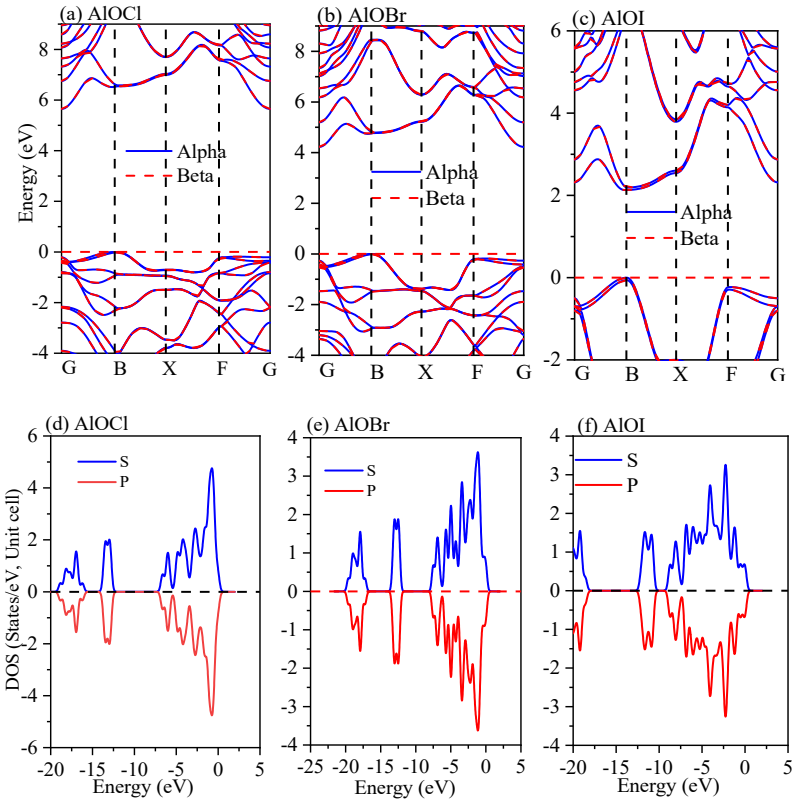

Fig.S2 (a-c) Energy band structures and (d-f) DOS of AlOCl, AlOBr, and AlOI monolayers with SOC formalism.

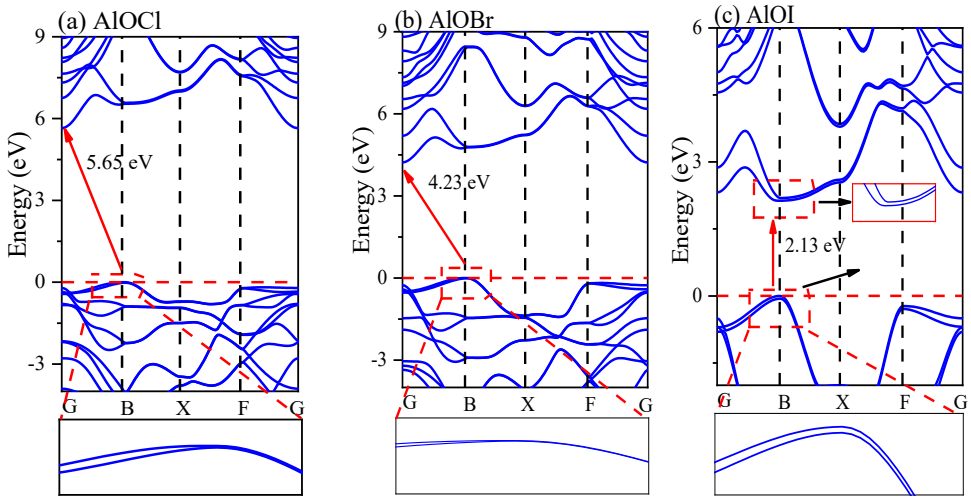

Fig.S3 Energy band structures of (a) AlOCl, (b) AlOBr, and (c) AlOI monolayers with SOC formalism.

At the acid condition, the photocatalytic reaction of water-splitting is composed of the following two half-reactions.

For HER at pH = 0, it can be described as:

$$*+e^{-}+H^{+} \rightarrow H \quad \text{(S1)}$$

$$H^{*}+H^{+}+2e^{-} \rightarrow H_2 \quad \text{(S2)}$$

In terms of OER, it follows a four-electron transferred reaction pathway:

$$^{*}+H_2O \rightarrow OH^{*}+e^{-}+H^{+} \quad \text{(S3)}$$

$$OH^{*} \rightarrow O^{*}+e^{-}+H^{+} \quad \text{(S4)}$$

$$O^{*}+H_2O \rightarrow OOH^{*}+e^{-}+H^{+} \quad \text{(S5)}$$

$$OOH^{*} \rightarrow O_2+e^{-}+H^{+} \quad \text{(S6)}$$

where * is the active site on the photocatalysts, O*, OH*, OOH* and H* are adsorbed intermediates.

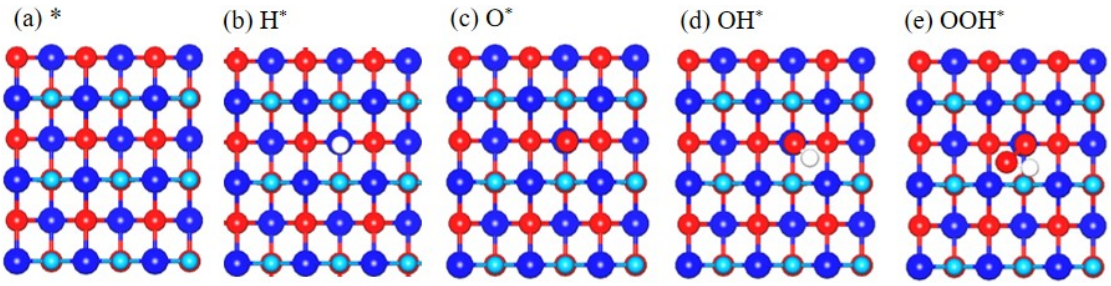

Fig. S4 The most probable intermediates absorbed on the Al of alocl monolayer, (a) * , (b) H* , (c) O* and (d) OH* and (e) OOH*. Here, blue, red, yellow, and white balls represent the Al, O, Cl and H atoms, respectively.