Supplementary Information (SI)

Two-dimensional Janus X_2SSe (X=Al, Ga or In) Monolayers: A Potential Photocatalyst With Low Effective Mass

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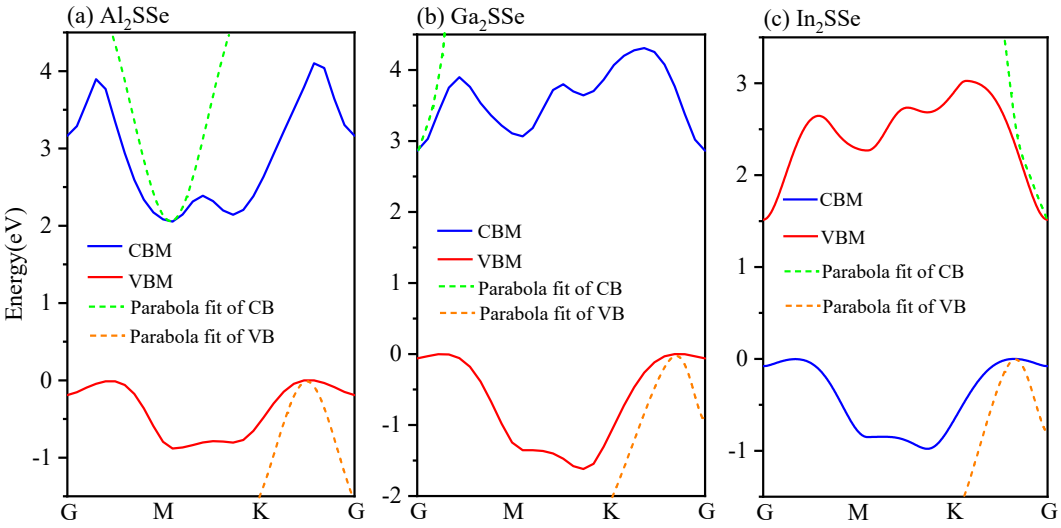


Fig. S1 The curves of VBM and CBM (solid line) for three crystal structures of X_2SSe (X=Al, Ga, or In) monolayers, and quadratic fitting curves (dash lines) at the VBM and CBM.

Table S1 Optimized lattice constants (a and b), bond lengths ($d_{Al–O}$, $d_{Al–X}$), and bond angles of the X_2SSe (X=Al, Ga, or In) monolayers after geometry optimization using PBE method with SOC effect.

Material	a (Å)	$d_{X–X}$ (Å)	$d_{X–S}$ (Å)	$d_{X–Se}$ (Å)	$\theta_{S–X–X}$ (°)	$\theta_{X–X–Se}$ (°)
Al_2SSe	3.66	2.58	2.35	2.43	115.33	119.67
Ga_2SSe	3.70	2.48	2.39	2.45	115.86	119.87
In_2SSe	4.02	2.84	2.58	2.66	115.94	119.46

Table S2 Mulliken charges and overlap populations of X_2SSe (X=Al, Ga, or In) monolayers after geometry optimization using PBE and PW91 methods.

Method	Materials	Species	Charge	Bonds	Population
PBE	Al_2SSe	Al_1	0.65	Se_1–Al_2	1.54
		Al_2	0.40	Al_2–Al_1	0.58
		S_1	–0.60	Al_1–S_1	1.46
		Se_1	–0.44		
	Ga_2SSe	Ga_1	0.31	Se_1–Ga_2	0.93
		Ga_2	0.38	Ga_2–Ga_1	0.04
		S_1	–0.40	Ga_1–S_1	1.47
		Se_1	–0.29		
	In_2SSe	In_1	0.45	Se_1–In_2	1.02
		In_2	0.44	In_2–In_1	0.18
		S_1	–0.52	In_1–S_1	1.30
		Se_1	–0.37		
PW91	Al_2SSe	Al_1	0.65	Se_1–Al_2	1.54
		Al_2	0.40	Al_2–Al_1	0.58
		S_1	–0.61	S_1–Al_1	1.45
		Se_1	–0.45		
	Ga_2SSe	Ga_1	0.30	Se_1–Ga_2	0.92
		Ga_2	0.38	Ga_1–Ga_2	0.04
		S_1	–0.40	S_1–Ga_1	1.47
		Se_1	–0.29		
	In_2SSe	In_1	0.44	Se_1–In_2	1.01
		In_2	0.44	In_2–In_1	0.17
		S_1	–0.51	In_1–S_1	1.30
		Se_1	–0.37		

Table S3 Mulliken charges and overlap populations of X_2SSe (X=Al, Ga, or In) monolayers after geometry optimization using PBE method with SOC effect.

Materials	Species	Charge	Bonds	Population
Al_2SSe	Al_1	0.92	Se_1–Al_2	1.47
	Al_2	0.62	Al_2–Al_1	0.65
	S_1	–0.83	Al_1–S_1	1.35
	Se_1	–0.70		
Ga_2SSe	Ga_1	0.58	Se_1–Ga_2	0.32
	Ga_2	0.63	Ga_2–Ga_1	–0.25
	S_1	–0.64	Ga_1–S_1	1.38
	Se_1	–0.54		
In_2SSe	In_1	0.71	Se_1–In_2	0.41
	In_2	0.81	In_2–In_1	–0.29
	S_1	–0.78	In_1–S_1	1.23
	Se_1	–0.73		

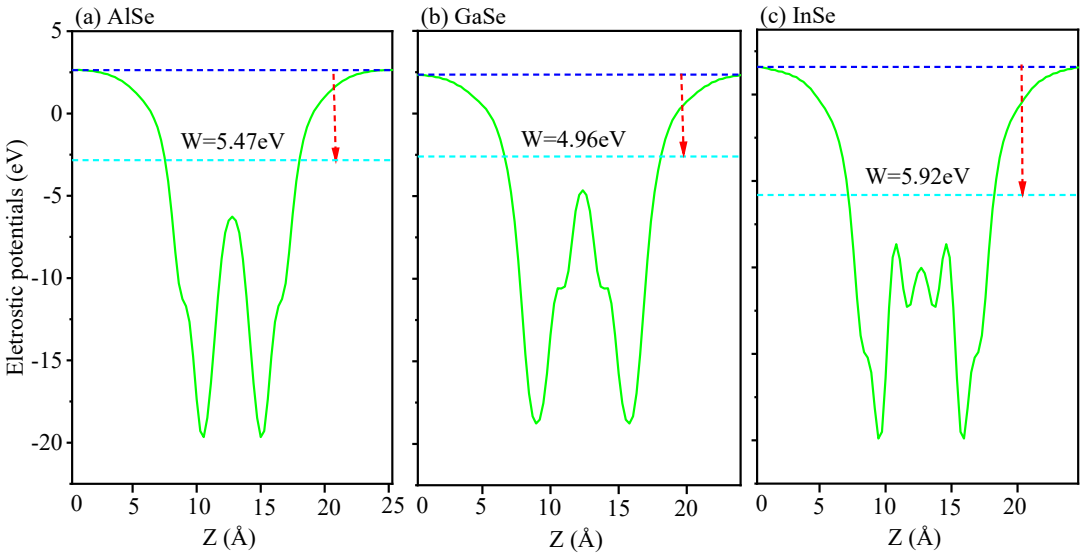


Fig. S2 The work functions of the (a) AlSe, (b) GaSe and (c) InSe monolayers are calculated.

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:

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

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

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

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

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

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

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

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

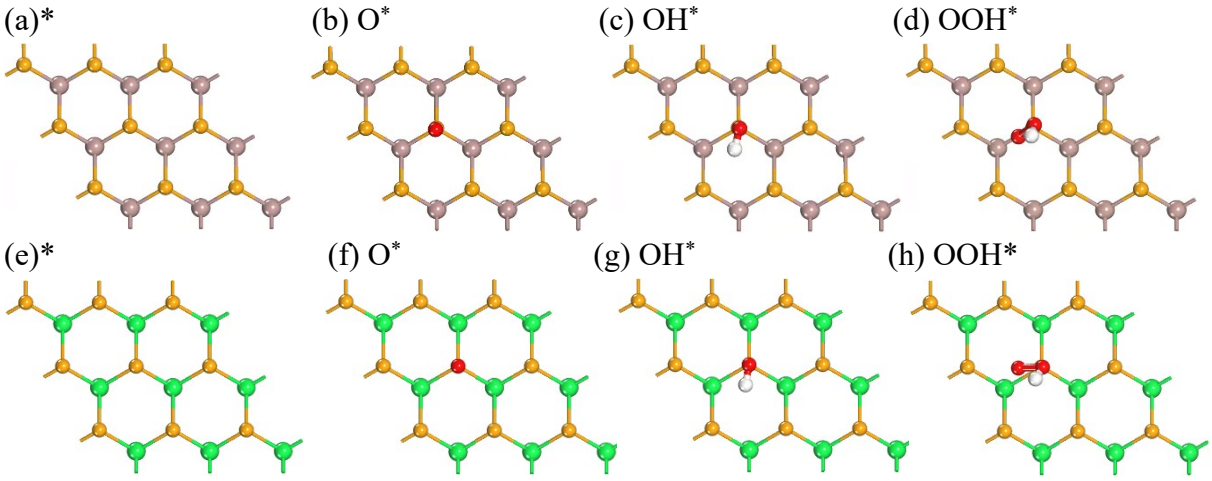
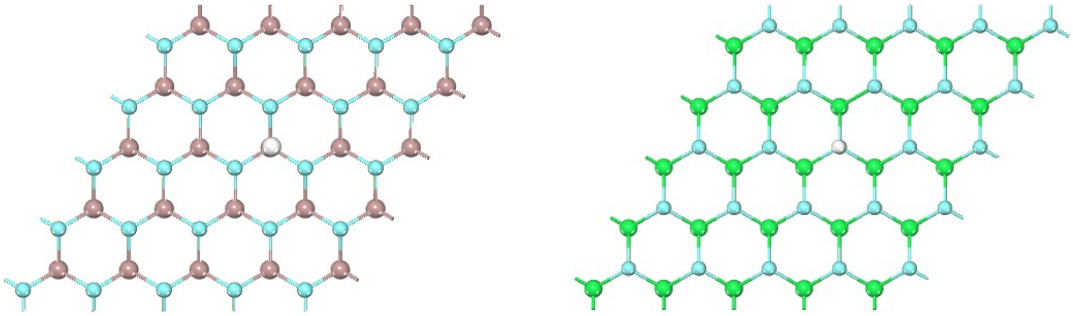


Fig. S3 The most probable intermediates absorbed on the Se–side of Janus Ga_2SSe and In_2SSe monolayers, (a) *, (b) OH^*, (c) O^* and (d) OOH^*. Here, brown, green, yellow, cyan, red and white balls represent the Ga, In, S, Se, O and H atoms, respectively.



(a) (b)

Fig. S4 The most probable intermediates absorbed on the Se–side of Janus Ga_2SSe and In_2SSe monolayers, (a) H^* in the vacancy system with a supercell of 5×5×1 of Janus Ga_2SSe monolayer, (b)H^* in the vacancy system with a supercell of 5×5×1 of Janus In_2SSe monolayer. Here, brown, green, yellow, cyan, red and white balls represent the Ga, In, S, Se, O and H atoms, respectively.