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Supplementary material of "Janus PtXO (X=S,Se) monolayers: the visible light driven water splitting photocatalysts with high carrier mobilities"

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Outline

Fig. S1: The relaxed crystal structures of Janus PtSeO and PtTeO. The Pt, Se, Te and O atoms are respectively marked by grey, green, blue and red. The solid lines denote the hexagonal primitive cell, and the rectangle cell used for the carrier mobility calculations.

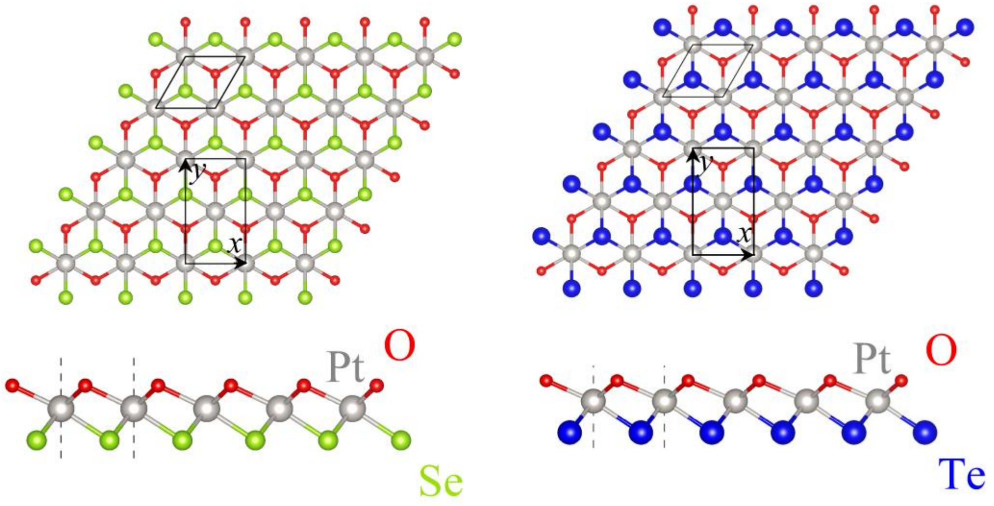


Table S1 The structural parameters of PtXO obtained by PBE and HSE06.

PtXO	structural parameters			
	a_0 (Å)	$d_{\text{Pt-X}}$ (Å)	$d_{\text{Pt-O}}$ (Å)	$\theta_{\text{X-Pt-O}}$ (degree)
PtSO (PBE)	3.37	2.28	2.18	81.4
PtSO (HSE06)	3.31	2.26	2.13	81.83
PtSeO (PBE)	3.47	2.4	2.22	81.88
PtSeO (HSE06)	3.4	2.37	2.17	82.09
PtTeO (PBE)	3.64	2.53	2.29	80.9
PtTeO (HSE06)	3.57	2.51	2.24	80.9

Table S2 The HSE06 calculated bandgaps (E_g), potential drop ($\Delta\phi$), overpotentials ($\chi(H_2)$, $\chi(O_2)$) using the PBE and HSE06 relaxed structures.

PtXO	E_g (eV)	$\Delta\phi$ (eV)	$\chi(H_2)$ (eV)	$\chi(O_2)$ (eV)
PtSO	2.5	2.51	0.43	3.26
PtSO	2.47	2.48	0.51	3.21
PtSeO	1.85	3.22	0.63	3.12
PtSeO	1.8	3.17	0.66	3.08

Table S3 The influence of density functional on the formation energy (E_f).

relaxed structures	E_f (meV/atom) using HSE06		
	PtSO	PtSeO	PtTeO
PBE	141.67	275.73	474.63
HSE06	133.17	252.73	458.17
	E_f (meV/atom) using PBE		
PBE	89.5	218.5	374

Fig. S2: Angular-dependent Young’s modulus and Possion’s ratio of Janus PtSO (marked by red). The value of each isoline is marked by green. We can see that the Young’s modulus and Possion’s ratio of Janus PtSO are mechanically isotropic, which are also found in Janus PtSeO and PtTeO (not shown here).

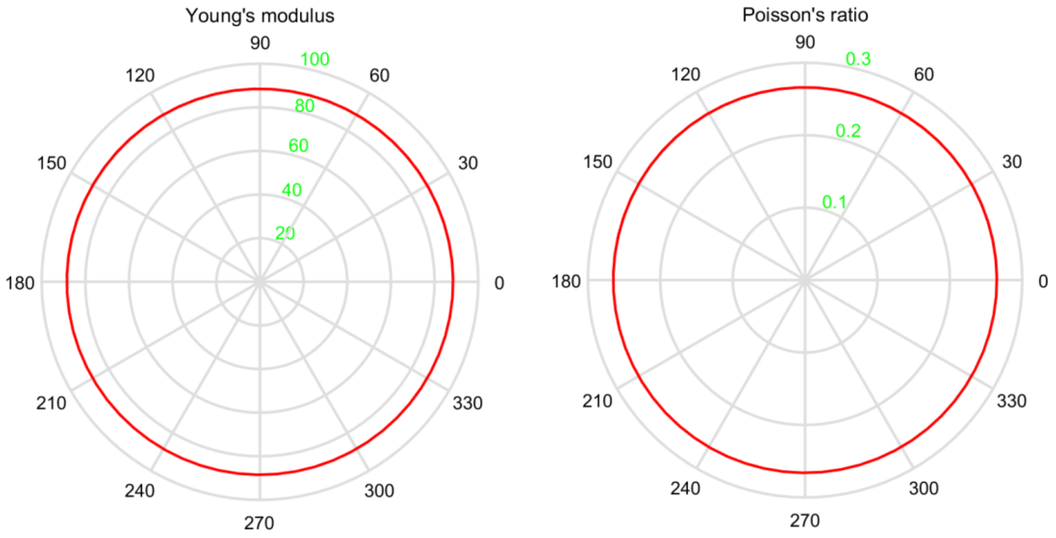


Fig. S3 AIMD simulations of Janus PtSO and Janus PtSeO 1000 K. Insets are the structures at 10 ps..

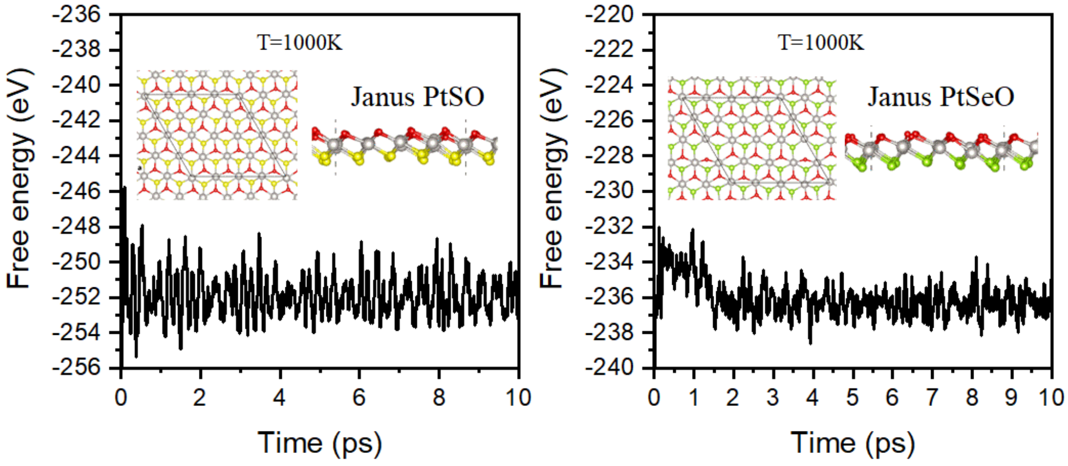


Fig. S4 The formation energies of PtX$_n$O$_{2-n}$ with different concentrations. For each PtX$_n$O$_{2-n}$, we manually create 30 crystal structures with different concentrations. Insets are the relaxed favorable structures at n=1. Some structures are not shown since their E_fs are out of the ordinate scale.

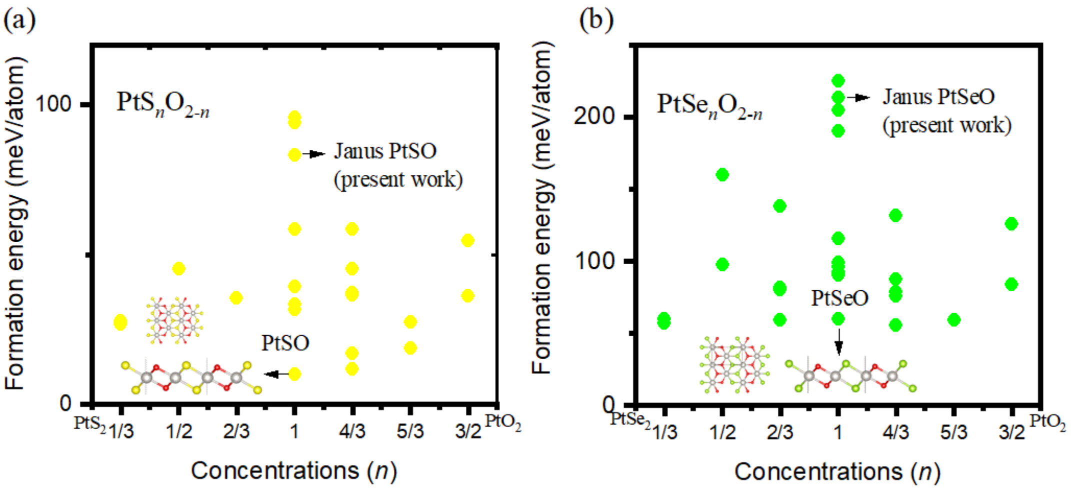


Fig. S5 The relation between vacuum level and normal hydrogen electrode (NHE). In the main text, the vacuum level is taken as reference. The dashed lines denote the standard redox potentials of water at pH=0.

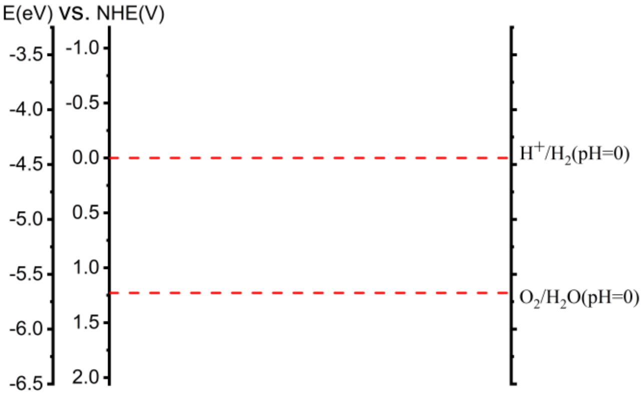


Fig. S6: Band alignments of pristine monolayer PtS_2 and $PtSe_2$.

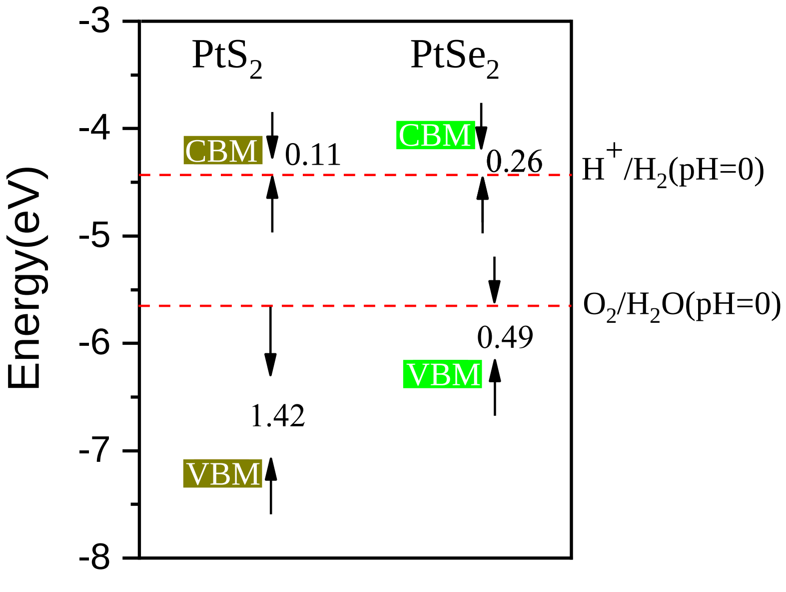


Fig. S7 The planar-average electrostatic potentials of the favorable PtXO along the *z* directions.

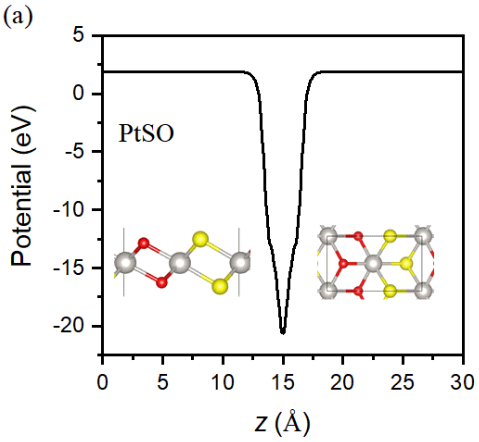
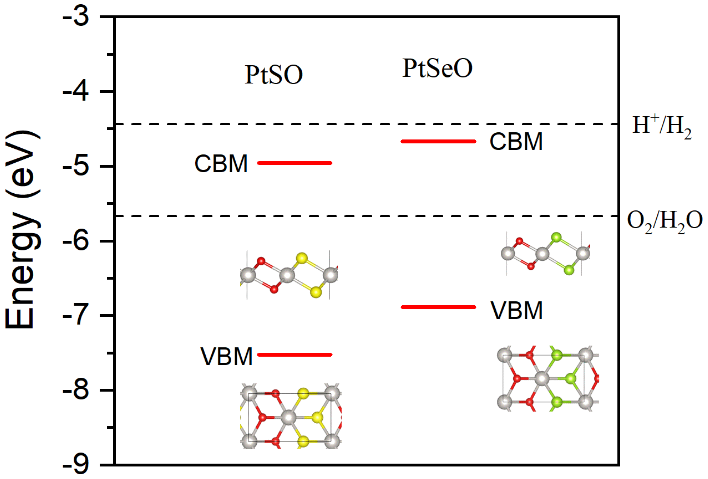


Fig. S8 The band alignments of the favorable PtSO(PtSeO). The water redox levels at pH=0 are marked by dashed lines.



Text S1 Calculation details of the free energy difference (ΔG).

As mentioned in the main text, the strategy proposed by Norskov et *al*. is used to calculate the ΔG. The ΔG at pH = 0 without solar irradiation is defined as: $\Delta G = \Delta E + \Delta E_{zpe} - T\Delta S$. ΔE is the adsorption energy, ΔE_{zpe} and ΔS are respectively the difference in zero point energy and entropy difference between the adsorbed state and the gas phase.

In the oxidation half reaction, there are four steps to transform H_2O into O_2 molecule:

$$* + H_2O \rightarrow OH* + H^+ + e^- \quad (1)$$

$$OH* \rightarrow O* + H^+ + e^- \quad (2)$$

$$O* + H_2O \rightarrow OOH* + H^+ + e^- \quad (3)$$

$$OOH* \rightarrow * + O_2 + H^+ + e^- \quad (4)$$

Simultaneously, the hydrogen production half reaction equation can be written as :

$$* + H^+ + e^- \rightarrow H* \quad (5)$$

$$*H + H^+ + e^- \rightarrow * + H_2 \quad (6)$$

where * denotes the adsorbed materials, OH*, O*, OOH* and H* are the adsorbed intermediates.

For each reaction of both oxidation and hydrogen production, the free energy difference under the effect of pH and an extra potential bias can be written as:

$$\Delta G(1) = G(OH*) + \frac{1}{2}G(H_2) - G* - G(H_2O) + \Delta G(U) - \Delta G(pH)$$

$$\Delta G(2) = G(O*) + \frac{1}{2}G(H_2) - G(OH*) + \Delta G(U) - \Delta G(pH)$$

$$\Delta G(3) = G(OOH*) + \frac{1}{2}G(H_2) - G(O*) - G(H_2O) + \Delta G(U) - \Delta G(pH)$$

$$\Delta G(4) = G* + \frac{1}{2}G(H_2) + G(O_2) - G(OOH*) + \Delta G(U) - \Delta G(pH)$$

$$\Delta G(5) = G(H*) - \frac{1}{2}G(H_2) - G* + \Delta G(U) + \Delta G(pH)$$

$$\Delta G(6) = G* + \frac{1}{2}G(H_2) - G(H*) + \Delta G(U) + \Delta G(pH)$$

Where ΔG(pH) ($\Delta G(pH) = k_B T \times \ln 10 \times pH$) is the free energy contributed at different pH concentration. ΔG(U) ($\Delta G(U) = -eU$) represents the extra potential bias provided by an electron in the electrode, where U is the electrode potential relative to the standard hydrogen electrode (SHE).

Fig. S9: Top and side views of the optimized geometries of (a) *H, (b) *OH, (c) *O, and (d) *OOH intermediates for PtSO; (e) *H, (f) *OH, (g) *O, and (h) *OOH intermediates for PtSeO; (i) and (j) are optimized geometries of *H intermediates for S-defected PtSO and Se-defected PtSeO, respectively.

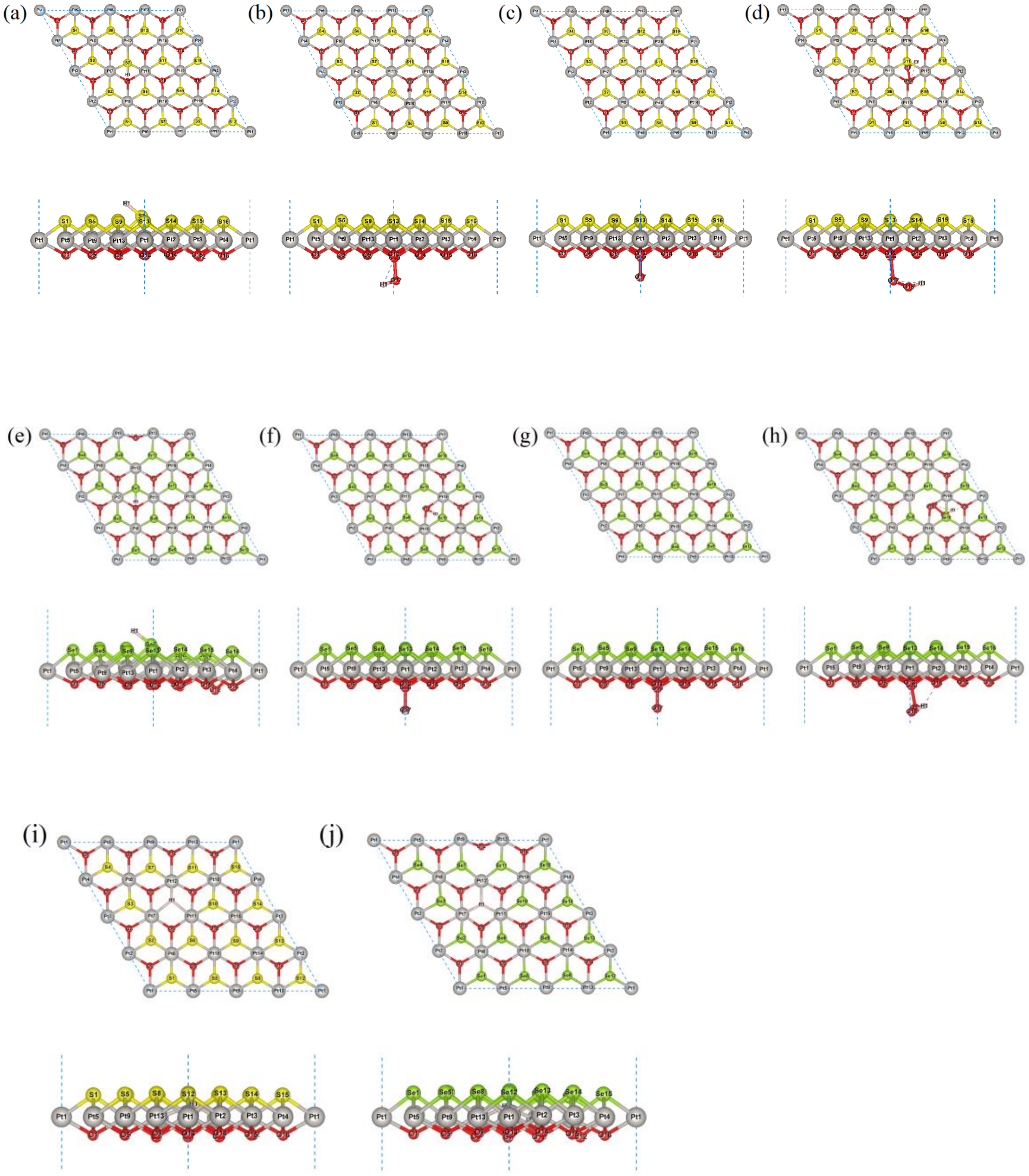


Fig. S10: Band alignment of Janus PtSO at biaxial strain (σ) of 3%. We can see below that the band edges still straddle the water redox levels.

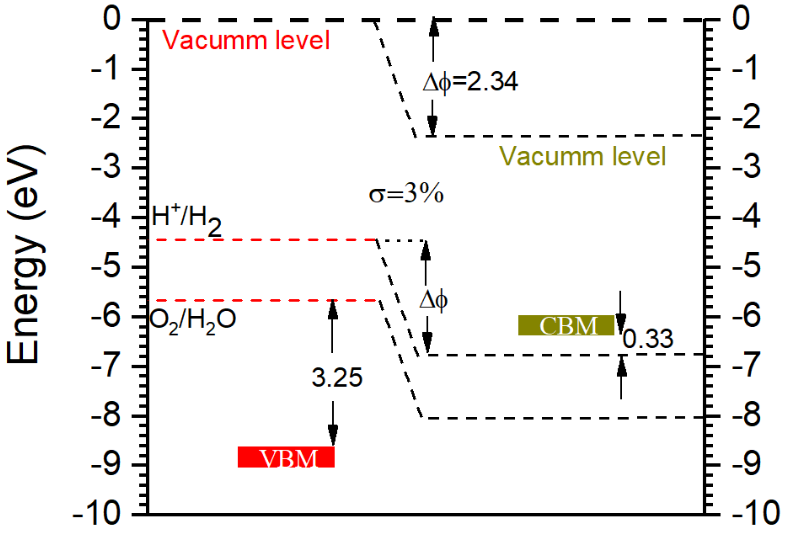
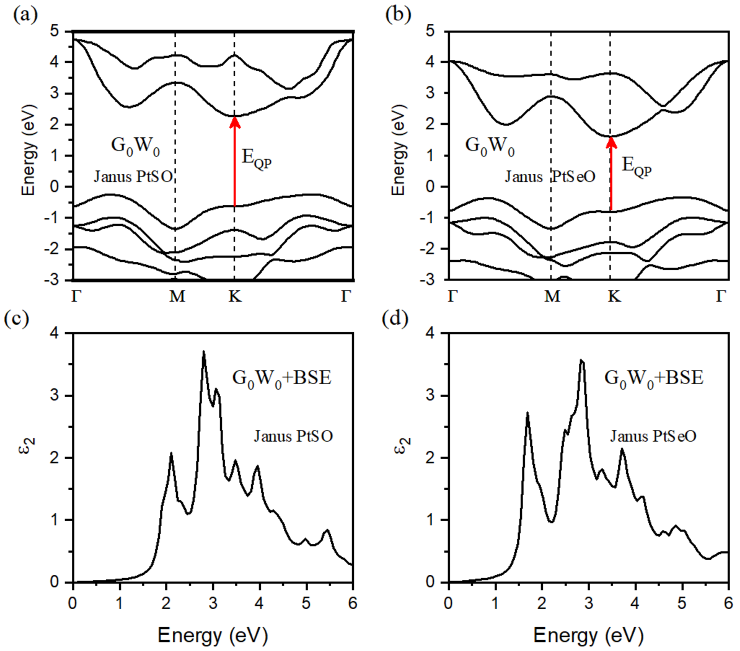


Fig. S11 (a)-(b) G_0W_0 calculated quasi-particle (QP) band structures and (c)-(d) G_0W_0+BSE calculated imaginary part (ε_2) of the dielectric function of Janus PtXO. The E_{QP}s are respectively 2.9 and 2.41 eV for Janus PtSO and PtSeO.



Text S2 Calculation details of solar to hydrogen (STH) efficiency.

The STH is calculated by $\eta_{STH} = \eta_{cu} \times \eta_{abs}$, where $\eta_{cu} = \frac{\Delta G_0 \int_E^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_{E_g}^{\infty} P(\hbar\omega) d(\hbar\omega)}$, $\eta_{\mathrm{abs}} = \frac{\int_{E_g}^{\infty} P(\hbar\omega) d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega) d(\hbar\omega)}$. η_{cu} and η_{abs} are respectively the energy conversion efficiency of carrier utilization and light absorption. ΔG_0 is the free energy of water splitting (1.23 eV). E_g is the bandgap. E represents the photon energy that can be actually utilized in the process of water splitting:

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

The η_{cu}, η_{abs} are given in Table S4.

Table S4 The calculated energy conversion efficiency of carrier utilization (η_{cu}) and light absorption (η_{abs}). η_{STH} is the STH efficiency. $\chi(H_2)$ and $\chi(O_2)$ are the overpotentials. E_g is the bandgaps.

Materials	$\chi(H_2)$ (eV)	$\chi(O_2)$ (eV)	E_g	η_{abs}	η_{cu}	η_{STH}
PtSO	0.43	3.26	2.5	17.93	42.53	7.62
PtSeO	0.63	3.12	1.85	43.65	51.46	22.46