Supporting information

Theoretical investigation of 2D/2D van der Waals $SbPO_4/BiOCl_xBr_{1-x}$ heterojunctions for photocatalytic water splitting

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1 ηHER and ηOER calculations

Fig. S1 and Fig. S2 show the Gibbs free energy steps for OER and HER, respectively. OER is conducted at BiOCl layer and HER at $SbPO_4$ layer. As shown in Figures, the values of ηHER and ηOER are 1.21eV and 0.46eV, respectively.

Gibbs free energy: $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}$

Overpotential: $\eta_{OER} = \Delta G_{max} / e - 1.23$

OER:

$* + H_2O \rightarrow *OH + H^+ + e^-$

$*OH \rightarrow *O + H^+ + e^-$

$*O + H_2O \rightarrow *OOH + H^+ + e^-$

$*OOH \rightarrow * + O_2 + H^+ + e^-$

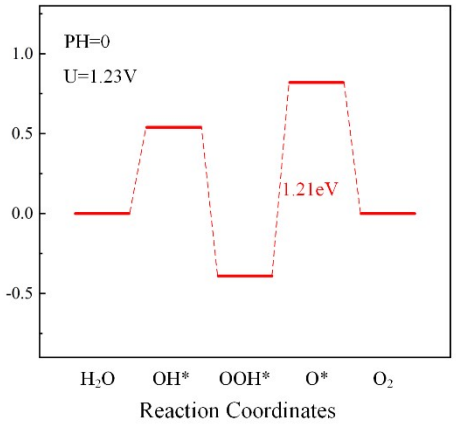

Fig. S1 Gibbs free energy steps for the Oxygen Evolution Reaction at different adsorption sites.

HER:

$*+H^{+}+e^{-} \rightarrow *H$

$*H+H^{+}+e^{-} \rightarrow *+H_2$

Overpotential: $\eta_{HER} = \Delta G_{max} / e$

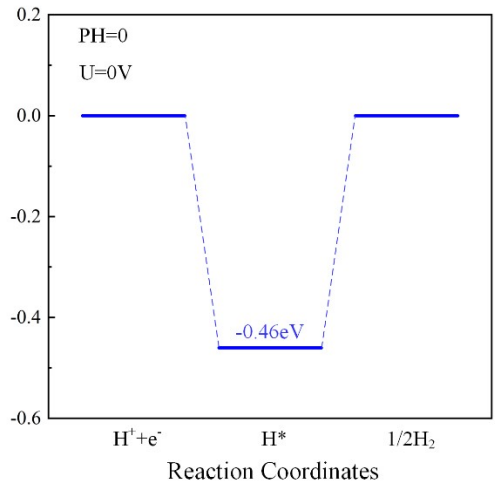

Fig. S2 Gibbs free energy steps for the Hydrogen Evolution Reaction at different adsorption sites

We attempted to apply COHP analysis to investigate the interaction strength within the $SbPO_4$/BiOCl heterojunction during hydrogen evolution reactions, particularly focusing on hydrogen atom adsorption. The result is shown in the Fig. S3.

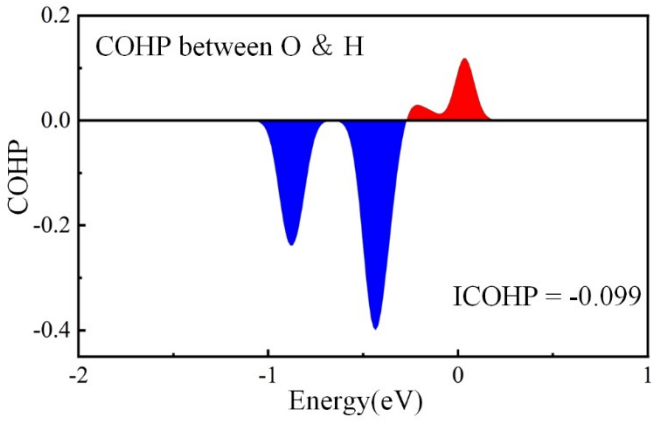

Fig. S3 crystal orbital Hamilton population of the adsorbed H on $SbPO_4$/BiOCl.

As shown in Fig. S3, most of the bonding component is present in the occupied state. Only a partial antibonding component exists near the Fermi energy level. The value of ICOHP is calculated to be -0.099, so the constructed hydrogen atom adsorption

model is bonding stable.

2 STH efficiency calculations

The ηSTH of the heterojunction can be found by the following equation:

$$\eta_{STH} = \eta_{abs} \times \eta_{cu} \#(1)$$

where η_{abs} is the light absorption efficiency and η_{cu} is the carrier utilisation efficiency. The η_{abs} can be explained by

$$\eta_{abs} = \frac{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)} \#(2)$$

where E_g is the bandgap and $P(\hbar\omega)$ is the AM1.5G solar energy flux at the photon energy $\hbar\omega$. The η_{cu} can be explained by

$$\eta_{cu} = 0.5 \times \frac{\Delta G \times \int_{E'}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)} \#(3)$$

where ΔG is the water redox potential (1.23 eV) and E' is the used photon energy for water splitting and can be expressed by

$$E' = \begin{cases} \max(E_{gA}, E_{gB}), (\chi_A(H_2) \geq \eta_{HER}, \chi_B(O_2) \geq \eta_{OER}) \\ \max(E_{gA} + \eta_{HER} - \chi_A(H_2), E_{gB}), (\chi_A(H_2) < \eta_{HER}, \chi_B(O_2) \geq \eta_{OER}) \\ \max(E_{gA}, E_{gB} + \eta_{OER} - \chi_B(O_2)), (\chi_A(H_2) < \eta_{HER}, \chi_B(O_2) < \eta_{OER}) \\ \max(E_{gA} + \eta_{HER} - \chi_A(H_2), E_{gB} + \eta_{OER} - \chi_B(O_2)), (\chi_A(H_2) < \eta_{HER}, \chi_B(O_2) < \eta_{OER}) \end{cases} \#(4)$$

where $\chi(H_2)$ and $\chi(O_2)$ are the differences between the CBM and the H^+/H_2 potential, the VBM and the O_2/H_2O potential, respectively. E_{gA}, E_{gB} are the band gaps of the two materials respectively. Considering the energy loss during carrier migration between different materials, the required overpotentials for HER and OER are assumed to be 0.5 eV and 1.3 eV, respectively. The η_{STH} of the heterojunction is calculated to be 10.68%.

Reference:

[1] Zhu H, Zhang X, Nie Y, et al. 2D/2D Janus BiTeCl/GeSe vdW heterostructure as a robust high-performance S-scheme photocatalyst for water splitting[J]. Applied Surface Science, 2023, 635: 157694.