

Supporting information for

Prediction of 2D heterostructure GaSe/YGaS₃ for highly efficient photocatalytic water splitting

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Note 1. Details for solar-to-hydrogen (STH) efficiency calculation.

The STH efficiency is evaluated using the following equation[1]:

$$\eta_{\text{abs}} = \frac{\int_{E_g}^{\infty} P(\hbar\omega) d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega) d(\hbar\omega)} \quad (1)$$

$$\eta_{\text{cu}} = \frac{\Delta G \int_E^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_{E_g}^{\infty} P(\hbar\omega) d(\hbar\omega)} \quad (2)$$

$$\eta_{\text{STH}} = \eta_{\text{abs}} \times \eta_{\text{cu}} \quad (3)$$

$$\eta'_{\text{STH}} = \eta_{\text{STH}} \times \frac{\int_0^{\infty} P(\hbar\omega) d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega) d(\hbar\omega) + \Delta\Phi \int_{E_g}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)} \quad (4)$$

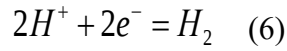
where $P(\hbar\omega)$ represents the solar energy flux (AM1.5G) at a given photon energy ($\hbar\omega$), with adjustments made to align with the band gap of the targeted photocatalyst. ΔG denotes the 1.23 eV redox potential difference between H^+/H_2 and $\text{H}_2\text{O}/\text{O}_2$ during the water splitting reaction. The efficiency parameters η_{abs} , η_{cu} , and η_{STH} correspond to the conversion efficiency of incident light into absorbed energy, carrier utilization efficiency, and overall STH efficiency, respectively, thereby providing a comprehensive theoretical framework for evaluating the photocatalyst's solar-to-hydrogen conversion capability.

Notably, for systems with an intrinsic electric field, it is essential to incorporate the interfacial potential difference ($\Delta\Phi$) as a correction factor, leading to the modified STH efficiency η'_{STH} . This potential difference is determined by the CBM, VBM, and the redox potentials of the hydrogen evolution reaction (HER, $\chi(\text{H}_2)$) and oxygen evolution reaction (OER, $\chi(\text{O}_2)$), and can be further expressed as:

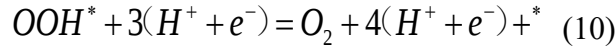
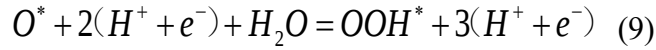
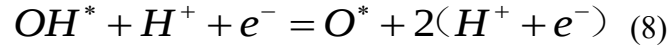
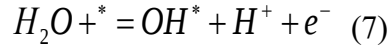
$$E = \begin{cases} E_g, \chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6 \\ E_g + 0.2 - \chi(H_2), \chi(H_2) < 0.2, \chi(O_2) \geq 0.6 \\ E_g + 0.6 - \chi(H_2), \chi(H_2) \geq 0.2, \chi(O_2) < 0.6 \\ E_g + 0.8 - \chi(H_2) - \chi(H_2), \chi(H_2) < 0.2, \chi(O_2) < 0.6 \end{cases} \quad (5)$$

Note 2. Details for the Gibbs free energy calculation of HER and OER.

Upon adsorption, the water splitting reaction bifurcates into two half-reactions: HER and OER, with the cathode promoting HER as follow:



and anode conductive OER as follow:



Where * represents the GaSe/YGaS₃ heterostructure, while H_2O^* , OH^* , O^* , and OOH^* denote small molecules adsorbed on the heterostructure. The change in Gibbs free energy (ΔG) for each reaction equation is calculated using the following equation[2]:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S - \Delta G_U - \Delta G_{pH} \quad (11)$$

$$ZPE = \frac{1}{2} \sum hv_i \quad (14)$$

$$TS = k_b T \left[\sum_K \ln \left(\frac{1}{1 - e^{hv/K_b T}} \right) + \sum_K \frac{hv}{K_b T} \left(\frac{1}{e^{hv/K_b T} - 1} \right) + 1 \right] \quad (12)$$

$$\Delta G_U = -eU \quad (13)$$

$$\Delta G_{pH} = -k_b T \ln 10 \times pH \quad (14)$$

$$\Delta G_{pH} = k_b T \ln 10 \times pH \quad (15)$$

where G , E , ZPE , TS , ΔG_U and ΔG_{pH} represent the free energy, total energy, zero-point energy, entropy contribution, potential bias effect, and pH effect, respectively.

Note 3. Details for optical properties calculation.

The transverse dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is used to describe the optical properties of materials[3,4], where ω is the photon frequency, $\varepsilon_1(\omega)$ is the real part and $\varepsilon_2(\omega)$ is the imaginary part of the dielectric function, respectively. The absorption coefficient can be evaluated according to the expression[3]:

$$\alpha(\omega) = \frac{\sqrt{2\omega}}{c} \left\{ \left[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) \right]^{\frac{1}{2}} - \varepsilon_1(\omega) \right\}^{\frac{1}{2}} \quad (16).$$

References

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