Supporting information for

Prediction of 2D heterostructure GaSe/$YGaS_3$ 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]:

$$\eta_{abs} = \frac{\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)} \quad (1)$$

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

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

$$\eta'_{STH} = \eta_{STH} \times \frac{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)}{\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega) + \Delta\Phi \int_{E_g}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)} \quad (4)$$

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 H_2O/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, $\chi(H_2)$) and oxygen evolution reaction (OER, $\chi(O_2)$), 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:

$$2H^+ + 2e^- = H_2 \quad (6)$$

and anode conductive OER as follow:

$$H_2O + {}^* = OH^* + H^+ + e^- \quad (7)$$

$$OH^* + H^+ + e^- = O^* + 2(H^+ + e^-) \quad (8)$$

$$O^* + 2(H^+ + e^-) + H_2O = OOH^* + 3(H^+ + e^-) \quad (9)$$

$$OOH^* + 3(H^+ + e^-) = O_2 + 4(H^+ + e^-) + {}^* \quad (10)$$

Where * represents the $GaSe/YGaS_3$ 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]:

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

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

$$TS = k_bT\left[\sum_K \ln\left(\frac{1}{1-e^{h\nu/k_bT}}\right) + \sum_K \frac{h\nu}{k_bT}\left(\frac{1}{e^{h\nu/k_bT}-1}\right) + 1\right] \quad (12)$$

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

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

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

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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