Supplementary Information for

Ferroelectric polarization promotes efficient Overall Water splitting of CdS/In_2Se_3 heterostructures

Minglei Jia,[a,] * Chao Jin,[b] Baoshan Wang,[c] Bing Wang [b,] *

[a] *School of Electro-Mechanical Engineering, Zhongyuan Institute of Science and Technology, Xuchang 461000, China.*

[b] *Institute for Computational Materials Science, Joint Center for Theoretical Physics (JCTP), School of Physics and Electronics, Henan University, Kaifeng, 475004, China.*

[c] *Zibo Huatian Rubber Plastic Technology CO.LTD, Zibo, 256410, China.*

†email: jiaminglei@zykj.edu.cn

††email: wb@henu.edu.cn

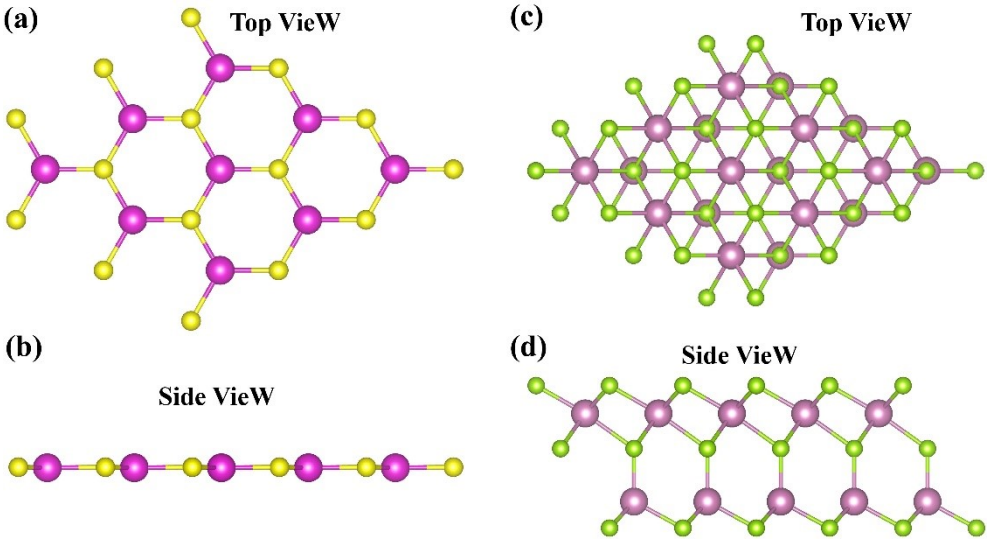

Figure S1 Structures of (a) and (b) CdS, (c) and (d) In_2Se_3.

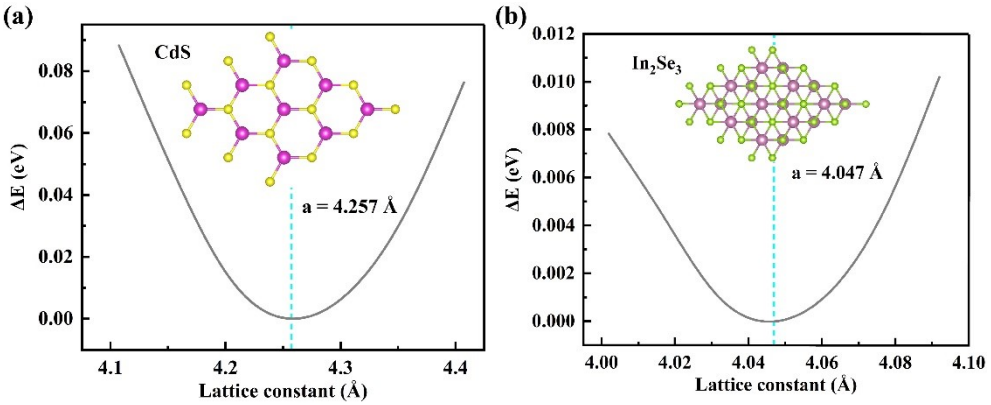

Figure S2 (a) (b) Testing the lattice constants of CdS and In_2Se_3, respectively.

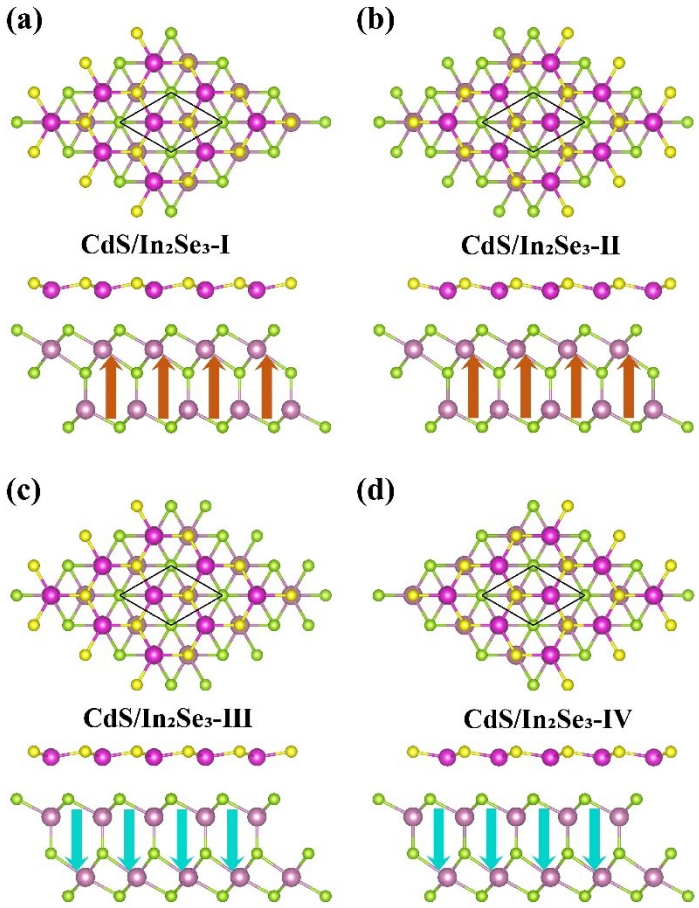

Figure S3 (a-d) Top and side views of the optimized structure for the CdS/In_2Se_3-(I-IV) heterostructures.

The binding energies of heterojunctions with different stacking configurations are calculated, and the binding energies of CdS/In_2Se_3-(I-IV) heterostructures are -0.495, -0.510, -0.456 and -0.470 eV, respectively.

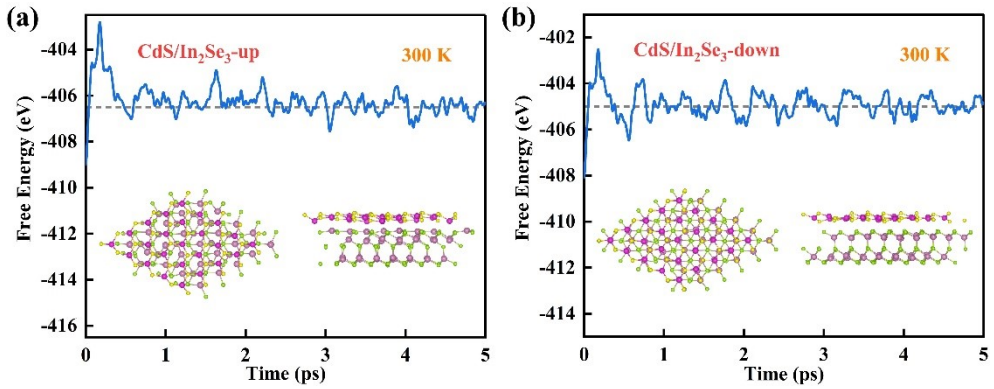

Figure S4 Total potential energies and the corresponding snapshots of (a) CdS/In_2Se_3-up and (b) CdS/In_2Se_3-down in the AIMD simulations after stabilizing at 300 K for 5 ps.

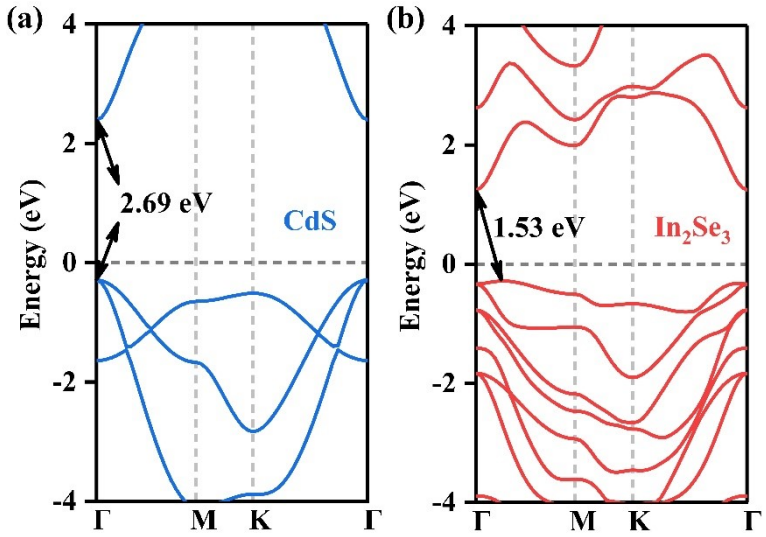

Figure S5 Band structures for (a) CdS and (b) In_2Se_3, respectively, on the basis of the HSE06 functional.

The HER includes the following steps:[1]

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

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

The process of the OER mechanism is demonstrated by eqn (8)-(11):[1]

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

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

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

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

To compute the free energy change (ΔG) in the hydrogen reduction and water oxidation reactions, we adopted the method developed by Nørskov et al.,[2, 3] according to which the ΔG of an electrochemical reaction is computed as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U \# (S7)$$

where ΔE is the DFT computed reaction (electronic) energy, ΔE_{ZPE} and ΔS are the zero-point energy difference and the entropy difference between the adsorbed state and the gas phase, respectively, and T is the system temperature (298.15 K, in our work). The $\Delta G_{pH} = 0.059 \times \text{pH}$ represents the free-energy contribution due to the variations in H concentration.

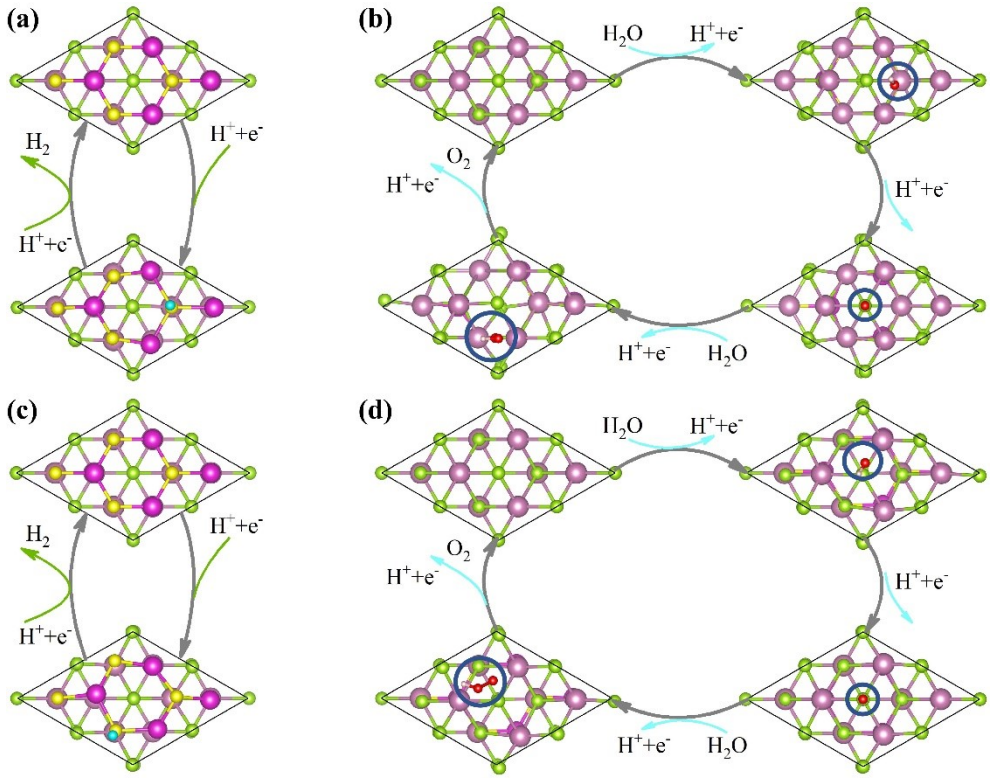

Figure S6 (a) (c) The optimized structures for different hydrogen coverage on the CdS monolayer in CdS/In_2Se_3-up and CdS/In_2Se_3-down heterostructures, respectively. (b) (d) The optimized structures for OH*, O* and OOH* intermediates for CdS/In_2Se_3-up and CdS/In_2Se_3-down heterostructures, respectively.

The optical absorption properties are essential for efficient solar energy harvesting materials. As for the calculation of optical absorption, the absorption coefficient is defined by:[4]

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c}\left\{\left[{\varepsilon_1}^2(\omega) + {\varepsilon_2}^2(\omega)\right]^{1/2} - \varepsilon_1(\omega)\right\}^{1/2} \#(S8)$$

in which ${\varepsilon_1}^2(\omega)$ and ${\varepsilon_2}^2(\omega)$ are the real and imaginary parts of the dielectric constant, ω and c are the angular frequency and the speed of light in a vacuum, respectively.

According to the calculation approach of η_{STH} proposed by Li et al.,[5] the η_{STH} of the layered materials in this work was obtained as:

$$\eta_{STH} = \eta_{abs} \times \eta_{cu} \#(S9)$$

where the η_{abs} and η_{cu} are the efficiency of light absorption and carrier utilization, respectively.

The efficiency of light absorption (η_{abs}) is defined as

$$\eta_{abs} = \frac{\int_{\infty}^{E_g} P(h\omega)d(h\omega)}{\int_{0}^{\infty} P(h\omega)d(h\omega)} \#(S10)$$

where $P(h\omega)$ is the AM1.5G solar energy flux at the photon energy $h\omega$ and E_g is the band gap of materials.

The efficiency of carrier utilization (η_{cu}) is defined as

$$\eta_{cu} = \frac{\Delta G \int_{E}^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)}{\int_{E_g}^{\infty} P(h\omega)d(h\omega)} \#(S11)$$

where ΔG is the potential difference of 1.23 eV for water splitting and E is the energy of photons that can actually be utilized for water splitting. The integral from E to ∞ in the numerator is the effective photocurrent density.

Considering the energy loss during carrier migration between different materials, the required overpotentials for HER and OER are assumed to be 0.2 and 0.6 eV, respectively. Then, E is determined by

$$E = \begin{cases} E_g, (\chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.2 - \chi(H_2), (\chi(H_2) < 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.6 - \chi(O_2), (\chi(H_2) \geq 0.2, \chi(O_2) < 0.6) \\ E_g + 0.8 - \chi(H_2) - \chi(O_2), (\chi(H_2) < 0.2, \chi(O_2) < 0.6) \end{cases} \#(S12)$$

The intrinsic E_p does positive work for the electron-hole separation during the process of photocatalytic water splitting. Therefore, this part of work should be added into the total energy, and then the corrected STH efficiency of photocatalytic water splitting for 2D material with vertical intrinsic E_p is calculated as:

$$\eta_{STH}^{'} = \eta_{STH} \times \frac{\int_{0}^{\infty} P(h\omega)d(h\omega)}{\int_{0}^{\infty} P(h\omega)d(h\omega) + \Delta V \int_{E_g}^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)} \#(S13)$$

where ΔV is electrostatic potential difference.

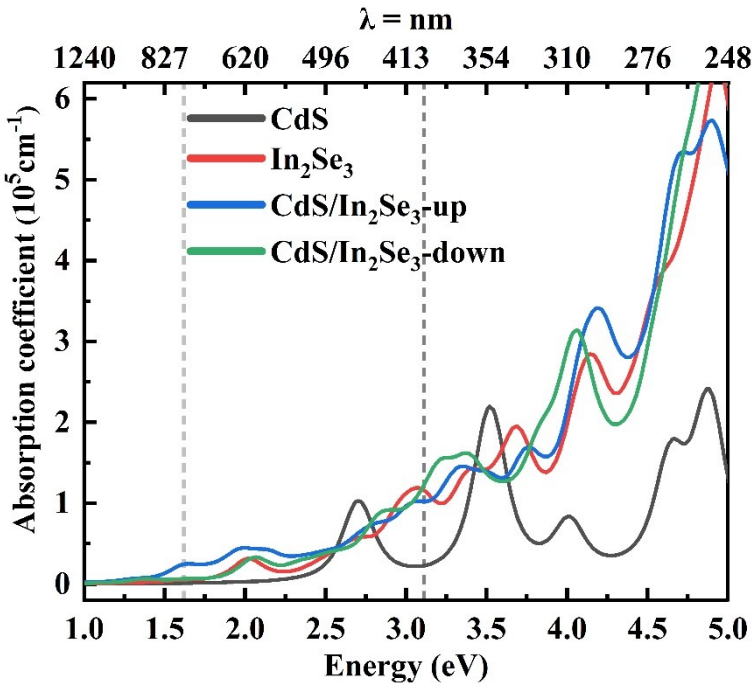

Figure S7 Calculated optical absorption spectra of CdS, In2Se3, CdS/In_2Se_3-up and CdS/In_2Se_3-down heterostructures using TDHF.

References

1 M. Jia, F. Ren, X. Chen, W. Han, C. Jin, C. Peng and B. Wang, *International Journal of Hydrogen Energy* **2023**, *48*, 19554-19563.

2 Nørskov, Jens Kehlet, Jan Rossmeisl, Ashildur Logadottir, L. R. K. J. Lindqvist, John R. Kitchin, Thomas Bligaard, and Hannes Jonsson, *The Journal of Physical Chemistry B* **2004** 108(46), 17886-17892.

3 Qiao, Man, Jie Liu, Yu Wang, Yafei Li, and Zhongfang Chen, *Journal of the American Chemical Society* **2018**, 140(38), 12256-12262.

4 C. Xuefeng, H. Wenna, J. Minglei, R. Fengzhu, P. Chengxiao, G. Qinfen, W. Bing and Y. Huabing, *Journal of Physics D: Applied Physics* **2022**, *55*, 215502.

5 C.-F. Fu, J. Sun, Q. Luo, X. Li, W. Hu and J. Yang, *Nano letters* **2018**, *18*, 6312-6317.