Supporting Information

The direct Z-scheme character and roles of S vacancy in $BiOCl/Bi_2S_3$-(001) heterostructure for the superior photocatalytic activity: A hybrid density functional investigation

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Note S1. Ab into molecular dynamic (AIMD)

Ab into molecular dynamic (AIMD) simulations are performed to evaluate the thermal stabilities of the adopted models with a canonical ensemble (NVT) and a simulation temperature of 300 K [1]. In the AIMD simulations, the Anderson thermostat is employed with a time step of 1 fs, and the total AIMD time is 8 ps.

Note S2. Carrier mobility

The mobility along the x and y directions of $BiOCl/Bi_2S_3$-(001) and $BiOCl/V_S$-Bi_2S_3-(001) can be calculated on the basis of effective mass approximation with deformation potential (DP) theory using the following equation [2]:

$$\mu = \frac{e\hbar^3 C_{2D}}{k_B T m^* m_d E_d^2} \quad (1)$$

where e, $\hbar$, k_B, and T are the electron charge, simplified Planck constant, Boltzmann constant, and temperature (T = 300 K in our calculation), respectively; C_{2D} is the elastic modulus of the materials and can be obtained from $C_{2D} = 2[\partial^2 E/\partial^2 \delta]/S_0$, where E is the total energy of the material after applying the strain ($\delta = \Delta l/l_0$) along the a or b axis, and S_0 is the unstrained area. The m^* is the effective mass of the electron or hole in the x or y direction, and the average effective mass is defined as: $m_d = \sqrt{m_x^* m_y^*}$. The final parameter, DP constant E_d is calculated by $E_d = \partial E_{edge}/\partial(\Delta l/l_0)$, where E_{edge} represents the energy of the VBM or CBM under the strain.

Note S3. The hydrogen evolution reaction process

The Gibbs free energy difference (ΔG) is calculated using the following equation[3]:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (2)$$

where ΔE, ΔE_{ZPE}, and ΔS represent the differences in absorption energy, zero-point energy, and entropy between products and reactants of the reactions, respectively. $\Delta G_U = -qU$, with q being the charge of the carrier and U being the potential of the carrier, relative to the standard water reduction potential of H^+/H_2, which depends on the pH value in the solution. ΔG_{pH} ($\Delta G_{pH} = K_B T \times ln10 \times pH$) represents the free energy contributed in different pH concentrations.

The equations involved in HER can be expressed as [4, 5]:

$$* + H^+ + e^- = H^* \quad (3)$$

$$H^* + H^+ + e^- = * + H_2 \quad (4)$$

$$\Delta G_h = G(H^*) - G(*) - 0.5G(H_2) + 0.059 \times pH - eU \quad (5)$$

$$\Delta G_h' = G(*) - G(H^*) + 0.5G(H_2) + 0.059 \times pH - eU \quad (6)$$

where * represents the active adsorption sites on the $BiOCl/Bi_2S_3$-(001) and $BiOCl/V_S$-Bi_2S_3-(001) heterostructures, and H^* represents the adsorption states during the HER process.

Note S4. Optical absorption

The optical absorption coefficient $A(\omega)$ of the 2D material is calculated using the formula $A(\omega) = \omega L\varepsilon 2(\omega)/c$ [6], where L is the vacuum thickness, and c is the vacuum speed of light. This approach is used to calculate the dielectric constant in the "Linear Optical Spectra for Two Dimensional Semiconductors" module of the VASPKIT code [7].

Reference

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