

Electronic Supplementary Information for
 **β -SnS/GaSe heterostructure: a
promising solar-driven photocatalyst
with low carrier recombination for
overall water splitting**

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1 Nonadiabatic Molecular Dynamics with Time-Domain Density Functional Theory

1.1 the Nonadiabatic Coupling

To begin with, the basic hamiltonian for ion-electron system can be written as

$$H = \sum_i \frac{P_i^2}{2M} + \sum_j \frac{p_j^2}{2m} + \sum_{i,i'} V_{i,i'}(|\vec{R}_i - \vec{R}_{i'}|) + \sum_{j,j'} V_{j,j'}(|\vec{r}_j - \vec{r}_{j'}|) + \sum_{i,j} V_{i,j}(|\vec{r}_j - \vec{R}_i|), \quad (1)$$

where the last three terms are ion-ion, electron-electron, and ion-electron interactions, respectively. The Born-Oppenheimer approximation begins with the assumption that the full wavefunction can be expand as

$$\Psi(\vec{R}, \vec{r}) = \sum_n \Phi_n(\vec{R}) \varphi_n(\vec{r}, \vec{R}), \quad (2)$$

in which the $\varphi_n(\vec{r}, \vec{R})$ are the solution of ion-electron problems with the fixed set of coordinates \vec{R} and the nuclear wavefunction $\Phi_n(\vec{R})$, namely, the amplitude for the ions to be found at the position \vec{R} . Letting $E_{e,n}(\vec{R})$ be the energy of the electron system with a fixed nuclear coordinates, it is easy to separate nuclear eigenvalue equation from the total hamiltonian.

$$\left\{ \sum_i \frac{P_i^2}{2M} + \sum_{i,i'} V_{i,i'}(|\vec{R}_i - \vec{R}_{i'}|) + E_{e,n}(\vec{R}) \right\} \Psi(\vec{R}, \vec{r}) = E \Psi(\vec{R}, \vec{r}). \quad (3)$$

Multiplying the nuclear eigenvalue equation by the $\varphi_m^*(\vec{r}, \vec{R})$ and integrate, it is easy to see that the $V_{i,i'}$ involving purely algebraic operators has only diagonal elements, however, the kinetic energy term has off-diagonal elements explicitly.

$$\begin{aligned} \sum_i \langle m | \frac{P_i^2}{2M} \Phi_n(\vec{R}) | n \rangle &= -\frac{\hbar^2}{2M} \sum_i \{ \langle m | \nabla_{R_i}^2 \Phi_n(\vec{R}) | n \rangle \\ &+ 2 \langle m | (\nabla_{R_i} \Phi_n(\vec{R})) \cdot \nabla_{R_i} | n \rangle + \langle m | \Phi_n(\vec{R}) \nabla_{R_i}^2 | n \rangle \}. \end{aligned} \quad (4)$$

Thus, the first term only contains the diagonal elements and the others are the n-th nonadiabatic couplings. Let the \tilde{E} denotes $V_{i,i'} + E_{e,m}(\vec{R})$ and T_n denotes $-\frac{\hbar^2}{2M} \nabla_{R_i}^2$ we rewrite equation 2 as

$$\left\{ \sum_n \{ (T_n + \tilde{E}_n) \delta_{n,m} - \frac{\hbar^2}{M} \vec{d}_{mn}^1 \cdot \nabla_{R_i} - \frac{\hbar^2}{2M} d_{mn}^2 \} \Phi_n(\vec{R}) \right\} = E \Phi_n(\vec{R}), \quad (5)$$

where the n-th order NA couplings between the electronic state n and m:

$$\begin{aligned} \vec{d}_{m,n}^1 &= \langle m | \nabla_{R_i} | n \rangle \\ d_{m,n}^2 &= \langle m | \nabla_{R_i}^2 | n \rangle. \end{aligned} \quad (6)$$

For the time-dependent (TD) Schrodinger equation,

$$i\hbar \partial_t \Psi(\vec{r}, \vec{R}, t) = \hat{H}(\vec{r}, \vec{R}, t) \Psi(\vec{r}, \vec{R}, t), \quad (7)$$

following the steps mentioned above, it is easy to obtain the equation containing n-th order NA couplings.

$$i\hbar \partial_t \Phi_i(\vec{R}(t)) = \sum_i \{ (T_i + \tilde{E}_i) \delta_{i,j} - \frac{\hbar^2}{M} \vec{d}_{i,j}^1 \cdot \nabla_{R_i} - \frac{\hbar^2}{M} d_{i,j}^2 \} \Phi_i(\vec{R}(t)). \quad (8)$$

In order to solve the time-dependent Schrodinger equation along the MD trajectory, we treat nuclear degrees of freedom classically[1]. The operator T_n and the first order of nonadiabatic coupling can be rewritten as

$$\begin{aligned} T_n &= \frac{P^2}{2M} \\ -\hbar^2 \frac{\vec{d}_{i,j}^1}{M} \nabla_R &= -i\hbar \vec{d}_{i,j}^1 \frac{P}{M}. \end{aligned} \quad (9)$$

The solution of the time-dependent Schrodinger equation is expressed on the basis of the solutions of the single-particle equations within the Kohn-Sham (KS) frame[2, 3]. The basis set is the adiabatic KS orbitals $\Phi_i(\vec{r}, \vec{R}, t) =$

$\sum_i c_i(t) \varphi_i(\vec{r}, \vec{R})$. Thus, the time-dependent Schrodinger equation transforms to an equation in the coefficients

$$i\hbar \partial_t c_i(t) = \sum_j c_j(t) \{ \varepsilon_j \delta_{i,j} - i\hbar \vec{d}_{i,j}^{\vec{1}} \dot{R} \}, \quad (10)$$

where the NA coupling

$$\vec{d}_{i,j}^{\vec{1}} \dot{R} = -i\hbar \langle i | \frac{\partial}{\partial t} | j \rangle. \quad (11)$$

The numerical evaluation of the NA coupling follow finite difference method proposed by Hammes-Schiffer and Tully [4]

$$\vec{d}_{i,j}^{\vec{1}} \dot{R} = \frac{1}{2dt} (\langle i, t | j, t + dt \rangle - \langle i, t + dt | j, t \rangle). \quad (12)$$

1.2 Fewest-switches surface hopping (FSSH)

FSSH algorithm adopts the scheme of Colleen F. Craig *et al.*[5, 1], in which the probabilities of transitions between electronic states is determined by the off-diagonal elements. For example, the electron in state $|i\rangle$ jumping into state $|j\rangle$ during the small time period dt , the probabilities of transitions is

$$P_{i,j}(t, dt) = \frac{\rho_{i,j}(t) - \rho_{i,j}(t + dt)}{\rho_{i,i}(t)}, \quad (13)$$

where the density matrix $\rho_{i,j}(t) = c_i^*(t)c_j(t)$. By using the finite difference method, the $\rho_{i,j}(t) - \rho_{i,j}(t + dt)$ is approximately equal to $-\partial_t \rho_{i,j}(t) dt$. As a result, the probabilities of transitions between the $|i\rangle$ and the rest of the state are

$$P_i(t) = 2 \sum_j \int_t^{t+dt} dt \frac{\text{Im}\{-i\hbar \vec{d}_{i,j}^{\vec{1}} c_i^*(t) c_j(t)\}}{c_i^*(t) c_i(t)}. \quad (14)$$

Noted that, if the $P_{i,j}(t) < 0$, the probabilities is reset to zero. The electron remaining in state $|i\rangle$ is given by $1 - P_i(t)$.

After we get the matrix of the probabilities, compare it to a random number between 0 and 1, then determine whether it hops to a new state or not. Moreover, the Boltzmann factor is adopted to rescale the probabilities for electron hopping to the high energy levels[1]. Thus, the state k to which the system hops is defined by the condition

$$\sum_{j=0}^{k-1} G_{i,j}(t) < \zeta \leq \sum_{j=0}^k G_{i,j}(t), \quad (15)$$

where the $G_{i,j}(t) = b_{i,j}(t) P_{i,j}(t)$ is the rescaled probabilities from state $|i\rangle$ to $|j\rangle$.

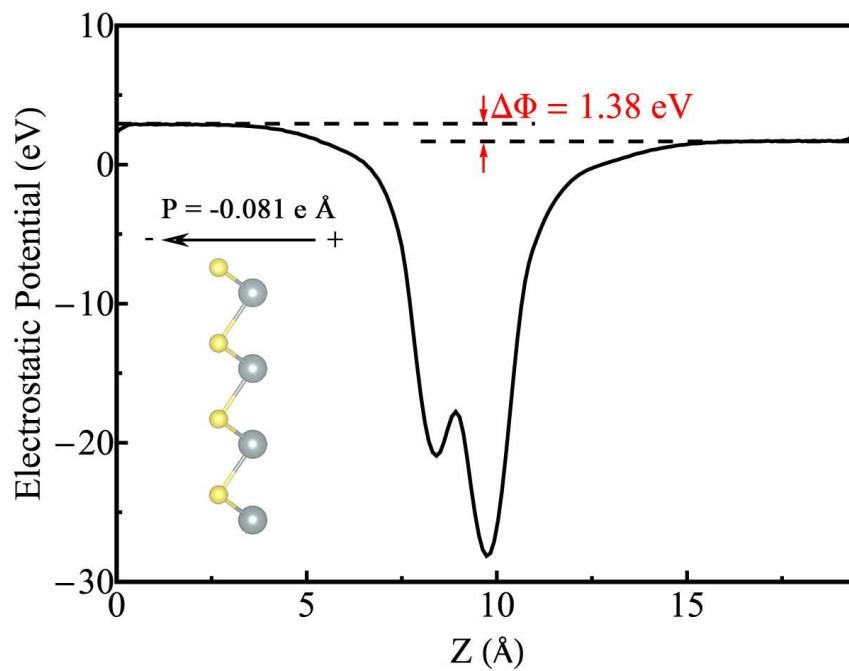


Figure S1: The averaged electrostatic potential of the β -SnS monolayer, here, the black arrow pointing from + to - stands for the intrinsic dipole of 0.081 eÅ, and the potential difference is about 1.38 eV.

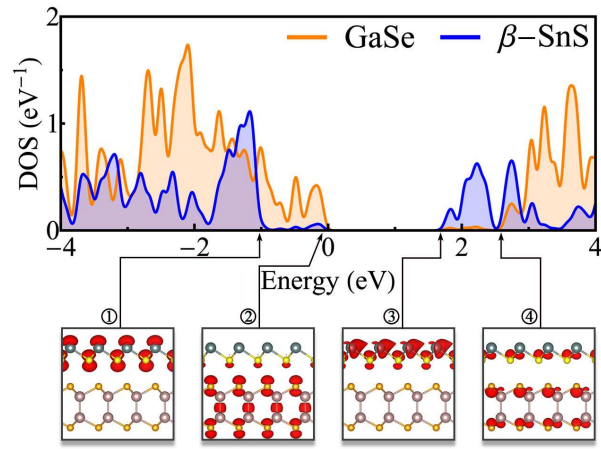


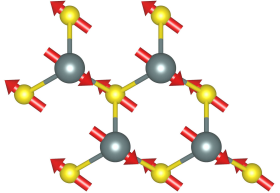
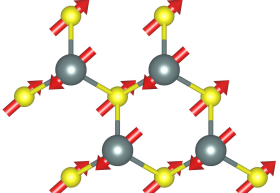
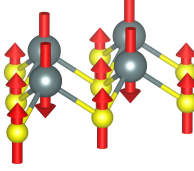
Figure S2: PDOS of GaSe and β -SnS monolayer in the β -SnS/GaSe heterostructure, and the charge densities of band edges of the β -SnS/GaSe heterostructure: ① the VBM of β -SnS monolayer, ② the VBM of GaSe monolayer, ③ the CBM of β -SnS monolayer, ④ the CBM of GaSe monolayer. The isosurface value is set to $0.01 \text{ e}/\text{bohr}^3$. The interlayer interaction delocalizes the state ④ and state ②.

Table S1: The Calculated DP constant (E_1), 2D elastic modulus (C_{2D} in the unit J/m_2), effective mass (m_* in the unit m_e), and carrier mobility (μ in the unit of $\text{cm}^2/\text{V}\cdot\text{s}$) for electron (e) and hole (h) at 300 K for GaSe and β -SnS monolayer.

		E_1	C_{2D}	m_*	μ
GaSe	e(x)	-8.73	55.64	0.19	609
	e(y)	-8.85	55.64	0.16	595
	h(x)	1.72	55.96	-1.82	166
	h(x)	2.24	55.96	-1.54	98
β -SnS	e(x)	1.84	21.48	0.58	319
	e(y)	-0.84	21.48	1.54	1516
	h(x)	0.75	21.57	-1.83	364
	h(x)	2.61	21.57	-1.37	105

We calculate the carrier mobility of the free GaSe and β -SnS monolayers at the room temperature in the framework of the deformation potential (DP)[6]. Due to the presence of heavy holes, in experiments, the measured hole mobility of few layered GaSe has small value in the range of 0.1 to 0.6 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [7], while the predicted electron mobility of GaSe monolayer by using the Boltzmann transport equation (BTE) is about 500 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [8]. It is clear that the electron mobility (600) of the GaSe monolayer is close to the reported value via solving the BTE. The hole mobilities of two different monolayers have the similar values due to the relatively large hole effective masses, which are less than the values of the electron mobility. Note that the electron mobility along y direction of the β -SnS monolayer is about 1500 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, which is obviously larger than the value (300) along the x direction, originating from the relative small DP constant in y direction.

Table S2: The Phonon modes and frequency of the β -SnS monolayer

E : 207 cm^{-1}	E : 207 cm^{-1}	A_1 : 317 cm^{-1}
		

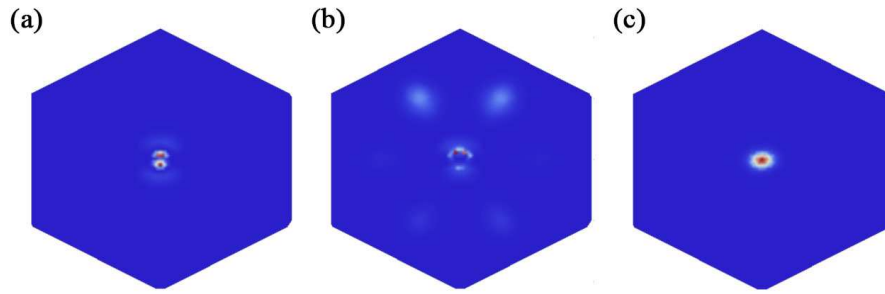


Figure S3: The bright bound excitons wave function in reciprocal space, corresponding to the sharp peaks labeled I, II, and III in Fig. 5(b). Note that the mixed type excitons does not locate exactly at the Γ point but near the degenerated saddle points.

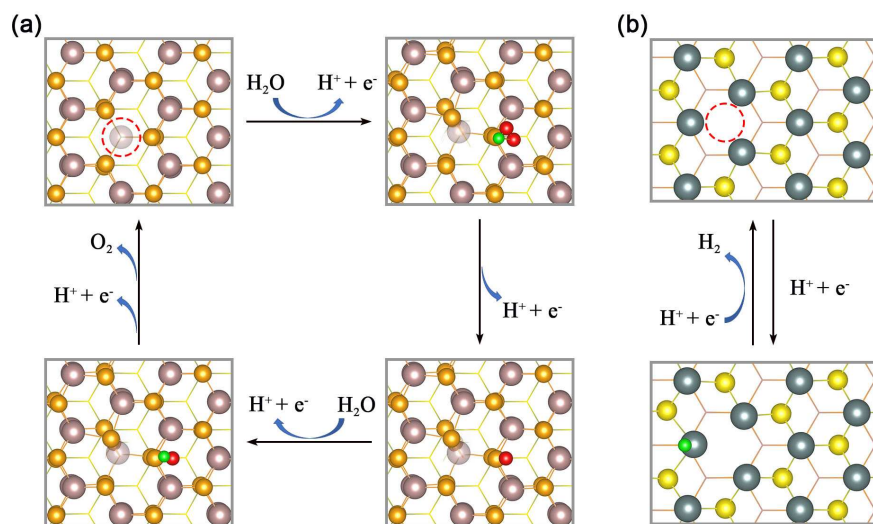
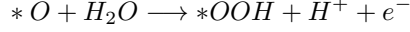
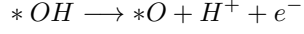
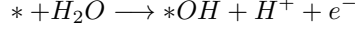


Figure S4: The adsorption configurations of intermediate species involved in the OER processes around the Ga vacancy (The virtual Ga atom circled with a red dotted line) (a) and in HER processes around the S vacancy (circled with a red dotted line) (b). Here, the green ball stands for H atom, red ball denotes O atom.

1.3 The description of OER and HER

OER process could be decomposed into four elementary oxidation steps, as follow:



where the * is the absorption site on the surface, and *OH, *OOH, and *O correspond to the radical adsorbed on the surface. The Gibbs free energy changes (ΔG) can be calculated through the following equations :

$$\Delta G_1 = 0.5G(H_2) + G(*OH) - G(*) - G(H_2O) - \Delta pH - U_h$$

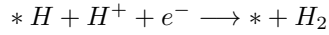
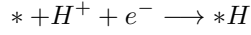
$$\Delta G_2 = 0.5G(H_2) + G(*O) - G(*OH) - \Delta pH - U_h$$

$$\Delta G_3 = 0.5G(H_2) + G(*OOH) - G(*O) - G(H_2O) - \Delta pH - U_h$$

$$\Delta G_4 = 0.5G(H_2) + G(*) + G(O_2) - G(*OOH) - \Delta pH - U_h$$

where $G(*H+e^-)$ is replaced by $0.5G(H_2)$. Noted that the effect of pH value of solvent and external potential U_h have been considered.

Meanwhile, HER process could be decomposed into two one-electron steps with each step consuming a proton and an electron:



which the corresponding Gibbs free energy changes can be written as:

$$\Delta G_1 = G(*H) - G(*) - 0.5G(H_2) + \Delta pH + U_e$$

$$\Delta G_2 = G(*) + 0.5G(H_2) - G(*H) + \Delta pH + U_e$$

where the U_e is the external potential for photogenerated electrons.

To simulate the OER(HER) processes occurring around the Ga(S) vacancy, we adopte $4 \times 4 \times 1$ supercell with single-Ga(S) vacancy. We also examine if the two atoms (Ga-S) vacancy in the heterojunction affecting the the electronic structure or not. We calculate the PDOS of pristine heterojunction and double atomic vacancy defects in the $7 \times 7 \times 1$, where the distance between the Ga vacancy and S vacancy is larger than 12 Å. The PDOS of pristine and Ga-S vacancy heterojunction shown in Fig. S5, we find that the Ga-S vacancy gives a tiny changes of electronic structure, which shall not be effect the photocatalytic water splitting.

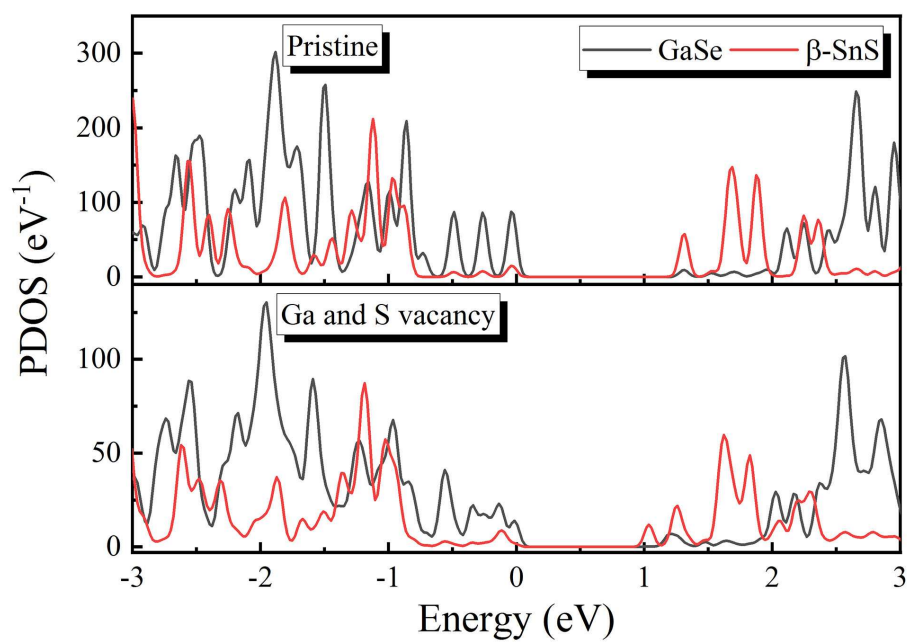


Figure S5: The PDOS of pristine and Ga-S double atomic vacancy defects in heterojunction at PBE level

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