Supporting Information: Directional Electron and Hole Transfer Driven by Distinct Pd Sites in CdS Photocatalysts Revealed by Nonadiabatic Dynamics Simulations

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Section I: Theoretical Methods

Nonadiabatic Dynamics Methods

Nonadiabatic carrier transfer dynamics simulations are carried out using Tully's fewest-switches surface-hopping methods based on density functional theory. [1-4] Time-dependent density functional theory in Kohn-Sham framework maps an interacting many-body system onto a system of noninteracting particles in which their electron densities equal to each other. As a result, time-dependent charge density $\rho(r,t)$ of an interacting system is obtained from a set of time-dependent Kohn–Sham orbitals $\psi_p(r,t)$[5-9]

$$\rho(r,t) = \sum_{p=1}^{N_e} \left|\psi_p(r,t)\right|^2$$

Electron density evolution finally leads to a set of single-electron equations for evolution of Kohn–Sham orbitals $\psi_p(r,t)$[10-14]

$$i\hbar \frac{\partial \psi_p(r,t)}{\partial t} = \hat{H}(r;R)\psi_p(r,t) \quad p = 1,2,\dots,N_e$$

If expanding time-dependent electron or hole wavefunction $\psi_p(r,t)$ in terms of interested unoccupied or occupied adiabatic Kohn–Sham orbitals $\phi_k(r,t)$ calculated from density functional theory calculations along adiabatic molecular dynamics trajectories

$$\psi_p(r,t) = \sum_k c_k(t)\phi_k(r;R)$$

one can obtain a set of equations of motion for expanding coefficients $c_j(t)$

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t)\left(\varepsilon_k \delta_{jk} - i\hbar d_{jk}\right)$$

where ε_k is energy of kth adiabatic state and d_{jk} is nonadiabatic coupling between adiabatic states j and k. The former is directly obtained from density functional theory calculations and the latter is calculated numerically through finite

difference methods as overlaps of adiabatic states at times t and $t + \Delta t$:

$$d_{jk} = \left\langle \phi_j(r;R) \middle| \frac{\partial \phi_k(r;R)}{\partial t} \right\rangle \approx \frac{\langle \phi_j(t) | \phi_k(t+\Delta t) \rangle - \langle \phi_j(t+\Delta t) | \phi_k(t) \rangle}{2\Delta t}$$

in which $\phi_j(t)$ and $\phi_k(t + \Delta t)$ are wave functions of adiabatic states j and k at times t and $t + \Delta t$, respectively. We have recently implemented this nonadiabatic electron or hole dynamics method with Gaussian basis sets with CP2K [15, 16] and have successfully applied to studying many materials.[17-21]

Carrier Transfer Analysis

To estimate electron or hole transfer from one to another fragment in nonadiabatic dynamics simulations, we have developed an efficient density-matrix based method. First, we can define a density matrix D in terms of atomic orbitals χ_μ

$$D_{\mu\nu i}(t) = p_i(t)\chi_{\mu i}\chi^*_{\nu i}$$

in which $p_i(t)$ is time-dependent occupation number of the ith adiabatic state calculated on the basis of above expanding coefficients $c_i(t)$; $\chi_{\mu i}$ is the μth atomic orbital coefficient of the ith adiabatic state. Similar to Mulliken charge analysis, [22] we have then defined a population matrix P using density matrix D and atomic overlap matrix S

$$P_{\mu\nu i} = D_{\mu\nu i}S_{\mu\nu}$$

Finally, we can obtain the ath atomic charge through summing all basis functions μ belonging to that atom and all involved adiabatic states i

$$P_a = \sum_i \left(\sum_{\mu\in a, \nu\in a} P_{\mu\nu i} + \frac{1}{2}\left(\sum_{\mu\in a, \nu\notin a} P_{\mu\nu i} + \sum_{\mu\notin a, \nu\in a} P_{\mu\nu i} \right) \right)$$

It should be noted that if only an atomic orbital belongs to the ath atom, just half of $P_{\mu\nu i}$ is used, as done by Mulliken charge analysis method. Accordingly, total electron on a fragment A is done by summing all atomic charges belonging to that fragment

$$P_A = \sum_i p_i(t)P_{Ai}$$

in which

$$P_{Ai} = \sum_{a\in A}\left(\sum_{\mu\in a,\nu\in a}\chi_{\mu i}\chi_{\nu i}^{*}S_{\mu\nu} + \frac{1}{2}\left(\sum_{\mu\in a,\nu\notin a}\chi_{\mu i}\chi_{\nu i}^{*}S_{\mu\nu} + \sum_{\mu\notin a,\nu\in a}\chi_{\mu i}\chi_{\nu i}^{*}S_{\mu\nu}\right)\right)$$

In such a case, the differentiation of P_A is then derived as

$$\mathrm{d}P_A = d\left(\sum_i c_i^{*}c_i P_{Ai}\right) = \sum_i (d(c_i^{*}c_i)P_A + c_i^{*}c_i dP_{Ai})$$

in which the first term has variational occupations for adiabatic states i and the second term has constant adiabatic state occupations but changeable electron population. These two terms correspond to nonadiabatic and adiabatic electron transfer contributions. The former is mainly caused by state hoppings between different adiabatic states and the latter is primarily originated from changes of adiabatic states induced by atomic motions. Finally, it should be noted that Gaussian basis sets are used in our simulations, so molecular coefficients $\chi_{\mu i}$ are real numbers. Adiabatic states' expanding coefficients $c_i(t)$ are complex numbers, but they are not directly used; instead, their $c_i(t)c_i^{*}(t)$ products are used for calculating time-dependent occupation number $p_i(t)$ of the ith adiabatic state, which is a real number.

Marcus Theory

Marcus theory has been proved to be applicable to the electron transfer (ET) in a range of systems,[23-25] such as organic molecules,[26] quantum dots,[27] and periodic semiconductors.[28] According to the Marcus theory, the rate of ET is calculated using the following formula:

$$k_{\mathrm{Marcus}} = \frac{2\pi}{\hbar}\left|V_{if}\right|^2 \frac{1}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}} \exp\left[-\frac{(\Delta E + \lambda)^2}{4\lambda k_{\mathrm{B}}T}\right]$$

where λ is the reorganization energy, k_{B} is the Boltzmann constant, T is the temperature, ΔE and V_{if} are the energy difference and electronic coupling between initial and final states, respectively. It is worth noting that for electron-hole recombination process, V_{if} is the electronic coupling constant between the

VBM and CBM of dual Pd-modified CdS calculated by Projection-Operator Diabatization (POD) method at the excited-state minima. The reorganization energy is calculated according to the following method:

$$\lambda = (E_{ES|GS} - E_{ES|ES}) + (E_{GS|ES} - E_{GS|GS})$$

in which the $E_{ES|GS}$ and $E_{GS|GS}$ represent the excited-state and ground state energies at the optimized ground state structure, while $E_{ES|ES}$ and $E_{GS|ES}$ represent the excited-state and ground state energies at the optimized excited state structure.

Projection-Operator Diabatization (POD) Method

POD method is employed in this work to calculate the electronic couplings in electron transfer processes.[29, 30] This approach is proposed based on standard Kohn-Sham density functional theory (DFT) calculations, i.e.

$$\widehat{H}|\Psi_i\rangle = \epsilon_i|\Psi_i\rangle$$

in which $|\Psi_i\rangle$ is the adiabatic states calculated by DFT. $|\Psi_i\rangle$ can be expanded by a linear combination of atomic-centered orbitals $|\phi_j\rangle$, which can be expressed as

$$|\Psi_i\rangle = \sum_j c_{ij}|\phi_j\rangle$$

in which c_{ij} is the expansion coefficient.

In POD method, the Kohn-Sham matrix (H) of a periodic system can be represented by atomic-centered orbitals

$$H_{ij}(\mathbf{k}) = \sum_n e^{i\mathbf{k}\mathbf{R}_n}\langle\phi_i(\mathbf{r})|H|\phi_j(\mathbf{r}-\mathbf{R}_n)\rangle$$

in which $\mathbf{k}$ is a given crystal momentum, $\mathbf{R}_n$ represents a translation vector of crystal in real space, and ϕ_i corresponds to an atomic orbital. The initial non-orthogonal basis $\{\widetilde{\phi}_\iota\}$ can be converted to a new orthogonal basis $\{\phi_i\}$ using the Löwdin transform[31, 32] by the following formula

$$|\widetilde{\phi_i}\rangle = \sum_j S_{ji}^{1/2} |\phi_j\rangle$$

where S_{ij} represents the overlap of atomic orbitals through matrix elements $\langle\phi_i|\phi_j\rangle$. one can maintain the localization characteristic of the newly constructed basis function via the Löwdin transform procedure. Likewise, the Kohn-Sham matrix is also orthogonalized according to the Löwdin procedure

$$\widetilde{H} = S^{-1/2} H S^{-1/2}$$

To calculate the electronic coupling of electron transfer procedure, the system can be categorized into the electron donor (D) and the electron acceptor (A) fragments. Assuming that the atomic-centered orbitals ϕ_j are localized over nucleus, they can be divided accordingly into the donor and acceptor regions. Therefore, orthogonalized Kohn-Sham matrix can be constructed as the following donor-acceptor block structure

$$\widetilde{H} = \begin{bmatrix} \widetilde{H}_{\mathrm{DD}} & \widetilde{H}_{\mathrm{DA}} \\ \widetilde{H}_{\mathrm{AD}} & \widetilde{H}_{\mathrm{AA}} \end{bmatrix}$$

in which the diagonal blocks of the matrix represent the sub-Hamiltonians for the donor and acceptor regions, respectively. On the other hand, the interaction of donor and acceptor is described by the off-diagonal blocks. By uniformly diagonalizing the $\widetilde{H}_{\alpha\alpha}$ ($\alpha = \mathrm{D}\ or\ \mathrm{A}$) blocks, we obtain the required adiabatic charge transfer states, i.e.

$$\overline{H}_{\alpha\alpha} = D_\alpha^\dagger \widetilde{H}_{\alpha\alpha} D_\alpha$$

and the off-diagonal blocks can be transformed by unitary matrices

$$\overline{H}_{\alpha\beta} = D_\alpha^\dagger \widetilde{H}_{\alpha\beta} D_\beta$$

Therefore, through the transformation process, the original Hamiltonian can be converted into the following form

$$\overline{H} = \begin{bmatrix} \epsilon_{\mathrm{D},1} & \cdots & 0 & & & \\ \vdots & \ddots & \vdots & & \overline{H}_{DA} & \\ 0 & \cdots & \epsilon_{\mathrm{D},N} & & & \\ & & & \epsilon_{\mathrm{A},1} & \cdots & 0 \\ & \overline{H}_{AD} & & \vdots & \ddots & \vdots \\ & & & 0 & \cdots & \epsilon_{\mathrm{A},M} \end{bmatrix}$$

in which $\epsilon_{\alpha,1}$ corresponds to the one-electron energy associated with each diabatic state of donor and acceptor. The off-diagonal blocks $\overline{H}_{\alpha\beta}$ represent the electronic couplings between the diabatic states of the donor and acceptor of electron transfer processes. In this work, the POD method is applied to calculate electronic couplings between the excited- and ground state of dual Pd-modified CdS.

Section II: Supplementary Figures

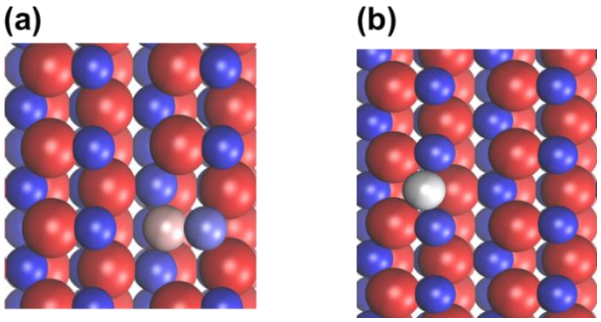

Fig S1: Bader charge distributions for CdS with (a) Pd-S_3 and (b) Pd-S_2; blue and red denote electron accumulation and depletion, respectively.

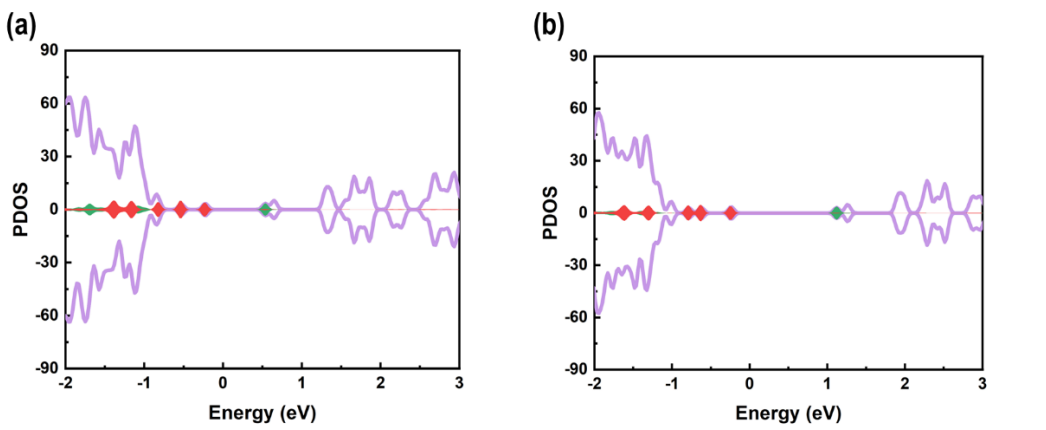

Fig S2: PDOS of the total and individual Pd atoms calculated using HSE06 with 15% and 35% Hartree–Fock exchange.

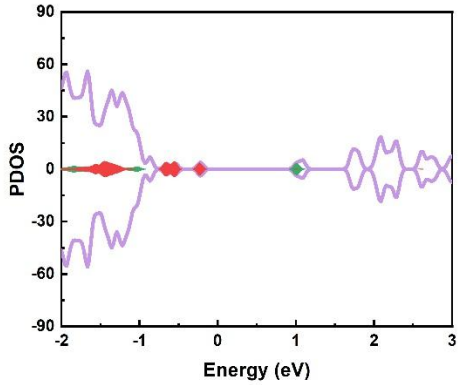

Fig S3: PDOS of a representative snapshot randomly selected from the 300 K trajectory.

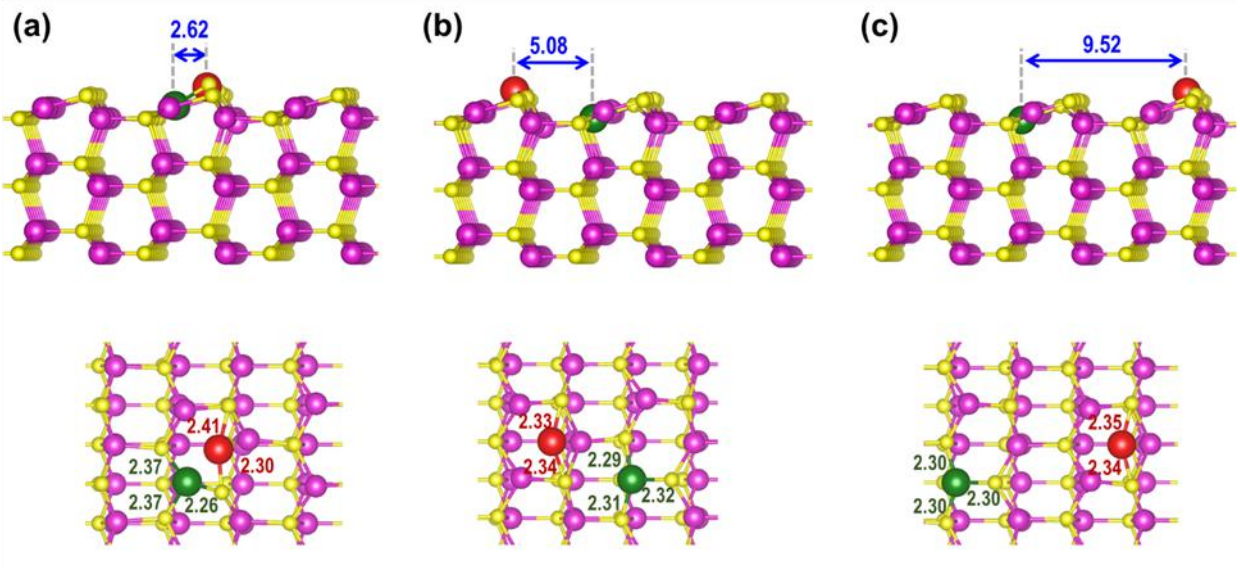

Fig S4: The side and top views of optimized dual Pd-modified CdS with a Pd–Pd distance of (a) 2.62 Å, (b) 5.08 Å, and (c) 9.52 Å.

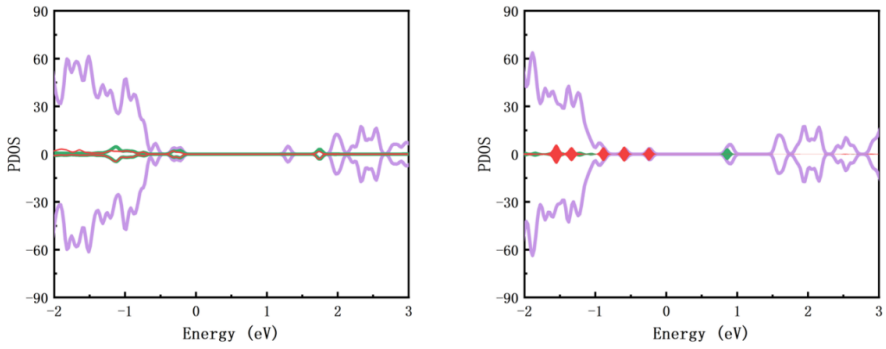

Fig S5: The PDOS of dual Pd-modified CdS with a Pd–Pd distance of (left) 2.62 Å and (right) 9.52 Å.

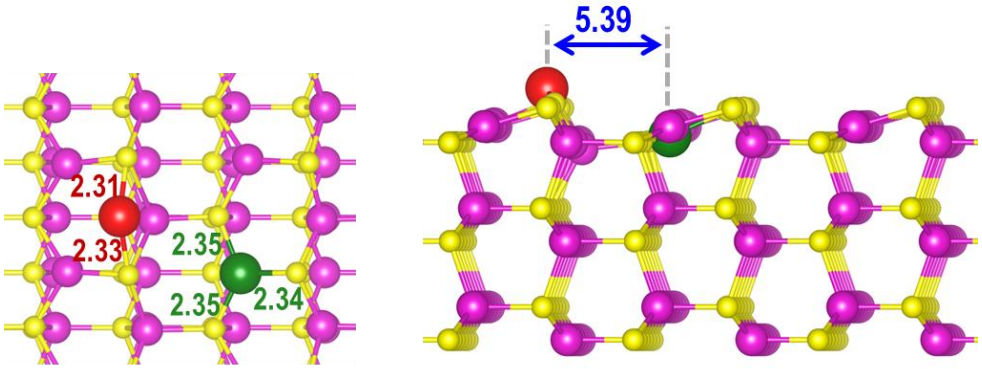

Fig S6: The top and side views of optimized excited-state structure of dual Pd-modified CdS.

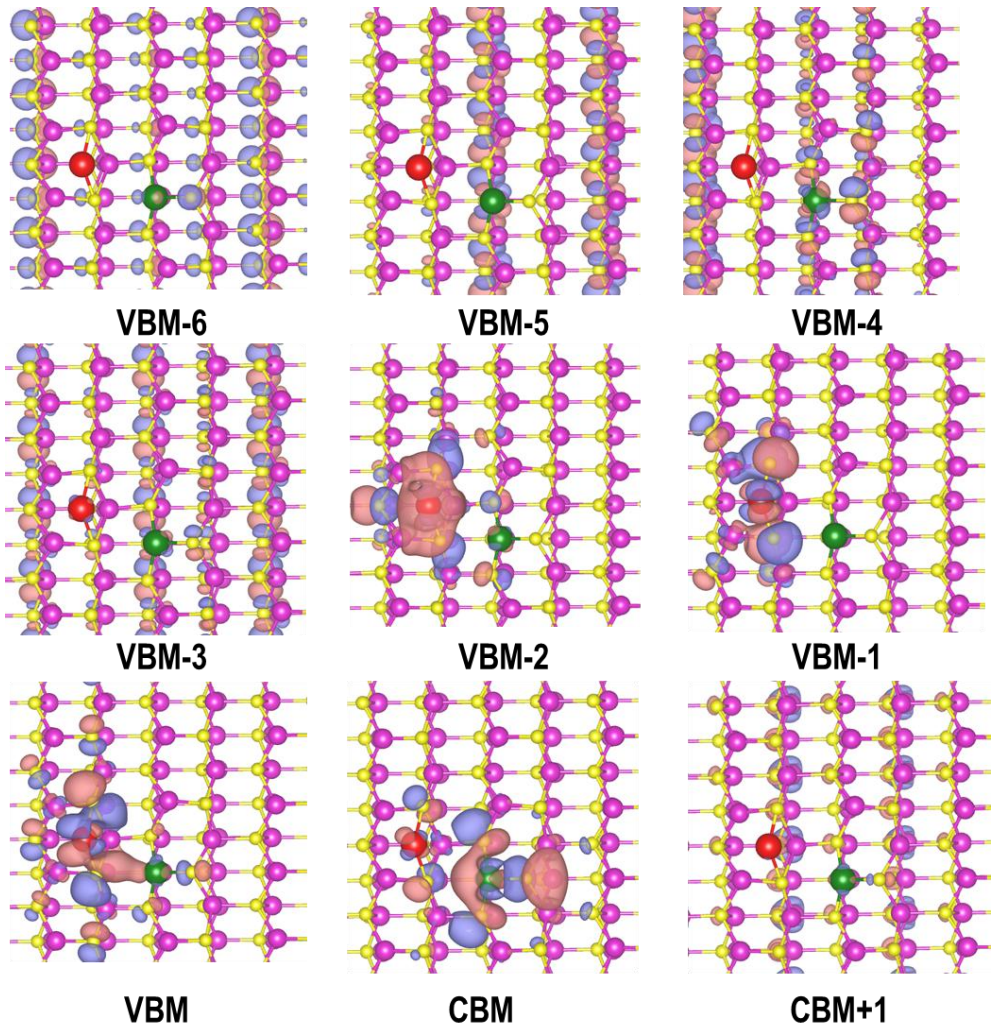

Fig S7: Spatial distributions of adiabatic states involved in the electron and hole transfer dynamics of dual Pd-modified CdS.

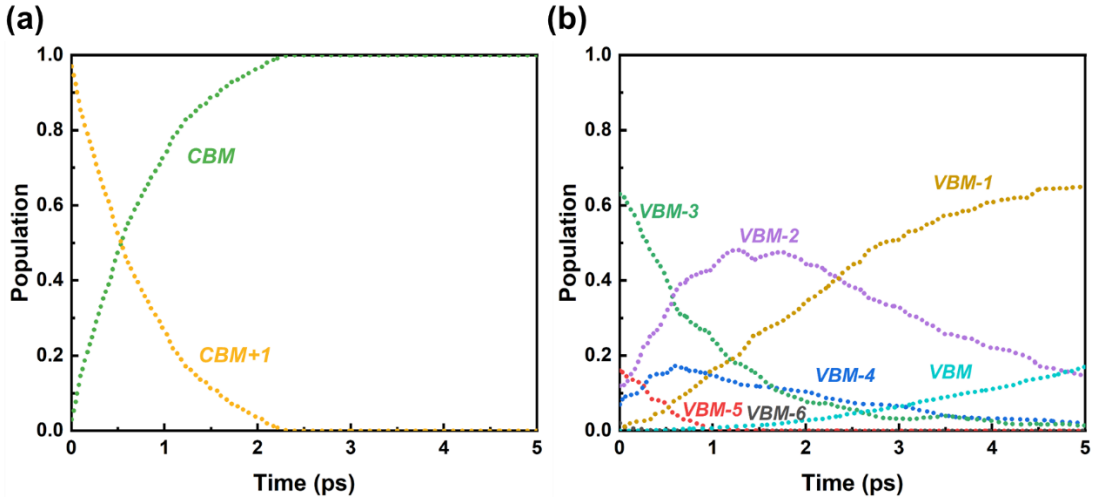

Fig S8: Time-dependent state populations in (a) electron and (b) hole transfer in the nonadiabatic dynamics simulations.

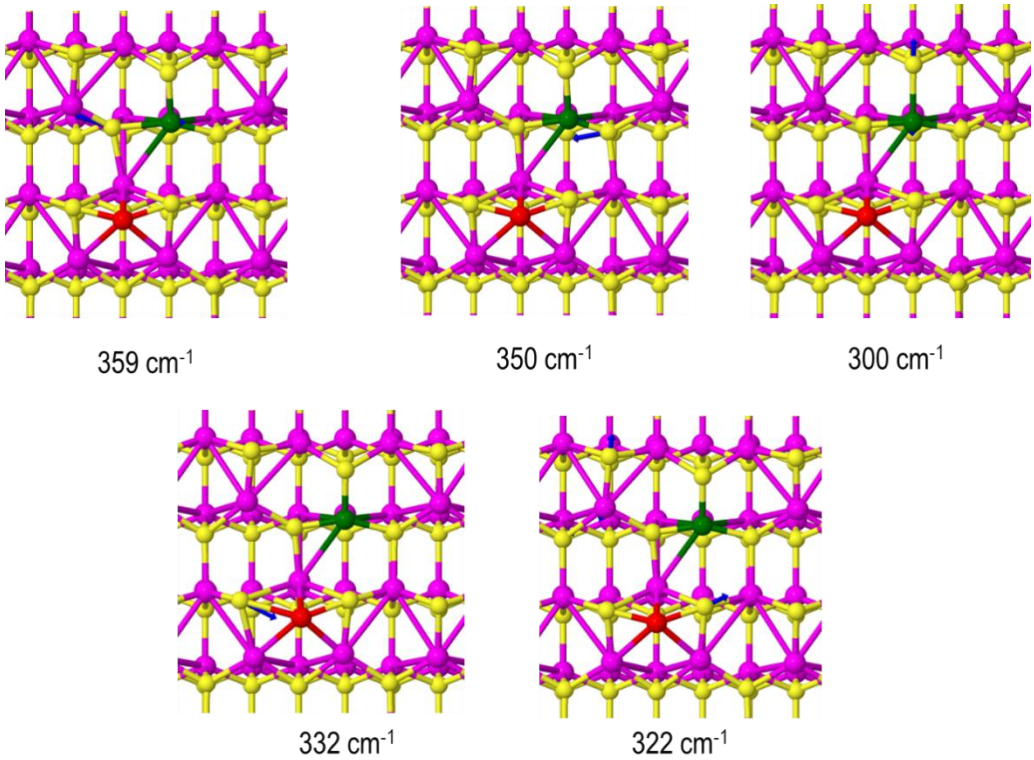

Fig S9: Pd–S vibrations of (top) Pd–S_3 and (b) Pd–S_2 motifs.

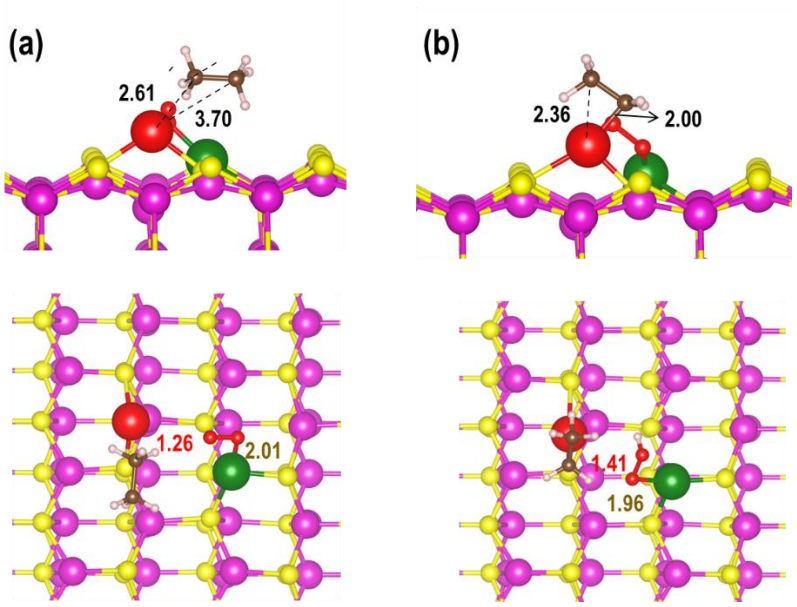

Fig S10: Optimized structures of (a) O_2 and C_2H_6 co-adsorbed on the catalyst surface and (b) the C_2H_5· and ·OOH species formed after proton transfer.

To further evaluate the reaction activity of the photocatalyst, we investigated a representative oxidative dehydrogenation reaction of ethane. The results show that O_2 can be adsorbed at the Pd-S_3 site and become activated, as evidenced by the elongation of the O–O bond length from 1.21 Å in free O_2 to 1.26 Å after adsorption. The corresponding adsorption energy is calculated to be 0.46 eV, indicating that O_2 can be stably adsorbed and activated on the catalyst surface. In addition, the photogenerated electron is transferred from the Pd site to the adsorbed O_2 molecule, leading to the formation of a superoxide-like O_2^- species, as reflected by the decrease in the spin value of Pd from 0.61 to 0.15. This result indicates that the transferred electron can directly participate in the chemical activation of O_2. We further examined the subsequent elementary step, in which one proton is transferred from C_2H_6 to the adsorbed O_2, producing C_2H_5· and ·OOH species. This step is exothermic by 0.29 eV, suggesting that the activated oxygen species can effectively promote the C–H bond activation process. Moreover, the reduced spin value at the Pd site suggests that this process is better described as proton transfer rather than hydrogen-atom transfer.

The favorable Coulomb interaction between H^+ and O_2^- is expected to further facilitate the formation of ·OOH. These results demonstrate that the catalyst not only promotes charge separation, but also possesses promising potential for driving chemically relevant oxidation reactions.

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