Electronic Supplementary Information

Two-dimensional Pd₃P₂S₈ Semiconductors as Photocatalysts for Solar Oxygen Evolution Reaction: A Theoretical Investigation

Yu Jing,^{*a,b,**} Thomas Heine^{*a,b,c,**}

- ^a Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Linnéstr. 2, 04103 Leipzig, Germany;
- ^b TU Dresden, Fakultät Chemie und Lebensmittelchemie, Bergstraße 66c, 01062 Dresden, Germany.
- ^c Helmholtz-Zentrum Dresden-Rossendorf, Forschungsstelle Leipzig, Permoserstraße 15, 04318 Leipzig, Germany

*Correspondence and requests for materials should be addressed to Y. J. (email: yu.jing@mailbox.tu-dresden.de) and T. H. (email: thomas.heine@tu-dresden.de)



Fig. S1. Schematic from top and side views and band structure of bulk Pd₃P₂S₈.

Table S1. Calculated lattice parameters and band gap of bulk $Pd_3P_2S_8$ in comparison with that obtained by previous experiments.

method	a/Å	c/Å	Band gap /eV
experiment ^[1]	6.84	7.24	2.54 (indirect)
			2.89 (direct)
DFT+PBE	6.93	7.31	1.95
HSE06			2.67 (indirect)
			2.86 (direct)



Fig. S2. Top and side views of $Pd_3P_2S_8$ snapshot after BOMD simulations for 10 ps at 500 (a), 1000 (b) and 1500 K (c), respectively; (d) Side view of $Pd_3P_2S_8$ snapshot in water after stabilizing at 300 K for 5ps.

The effective masses of the electrons and holes along *a* and *b* directions (Fig. S4a) are first calculated according to m*= $\hbar^2[\partial^2 \epsilon(k)/\partial k^2]^{-1}$. As illustrated in Table S2, the monolayer shows isotropic effective masses for holes and electrons along different directions. The in-plane stiffness (C_{2D}) can be obtained by simulating the total energy (*E*) change of the 2D material motivated by the applied strain (δ), as shown in Fig. S4

b. According to $C_{2D} = [\partial^2 E / \partial \delta^2] / S_0$, we calculated the C_{2D} along a and b directions, where S_0 is the surface area of the optimized unitcell. As exhibited in Table 1, the C_{2D} of Pd₃P₂S₈ monolayer are 24.92 and 25.21 N m⁻¹ along *a* and *b* directions, respectively.



Fig. S3. (a) band structure of $Pd_3P_2S_8$ monolayer in a rectangular supercell lattice. (b) Total energy difference between strained and unstrained monolayer along a and b directions. Energy shift of VBM and CBM for the monolayer with respect to the lattice dilation and compression along x (c) and y (d) directions.

By fitting the liner relationship of the band edge (E_{edge}) for VBM and CBM with the strain exertion (δ), we further calculated the DP constants ($|E_1|$) along *a* and *b* directions (Fig. S4 c and d). As shown in Table 1, the DP constants along the *zigzag* direction are 3.72 eV for electrons and 4.70 eV for holes, while the DP constants along the *armchair* direction are 3.10 eV and 4.10 eV for electrons and holes, respectively.



Fig. S4. Schematics for the examined surface sites of $Pd_3P_2S_8$ monolayer and the corresponding adsorption energy (E_{OH^*}) for OH^{*}.



Fig. S5. Charge distribution of VBM and CBM for $Pd_3P_2S_8$ monolayer from top and side views. The isosurface is set to be 0.004 eÅ⁻³.

Reference

1 T. A. Bither, P. C. Donohue, H. S. Young, J. Solid State Chem., 1971, 3, 300–307;