Supporting Information

Two-dimensional β−PdSeO$_3$ monolayer as a high-efficiency photocatalyst for

solar-to-hydrogen conversion

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Table S1. Structural properties of β-PdSeO$_3$ bulk and monolayer.

	a	b	c	$d_{\text{Pd-OI}}$	$d_{\text{Pd-OII}}$	$d_{\text{Se-OI}}$	$d_{\text{Se-OII}}$
Bulk	6.85	7.03	6.96	2.01	2.03	1.71	1.84
Bulk-Exp[a]	6.79	7.03	7.01	2.02	2.01	1.69	1.76
Monolayer	6.78	7.02	/	2.03	2.02	1.71	1.83

[a] Arndt,A.; Wickleder, M. S. Pd(SeO$_3$), Pd(SeO$_4$), and Pd(Se$_2$O$_5$): The First Palladium Oxoselenates. *Eur. J. Inorg. Chem*. **2007**, *27*, 4335–4339.
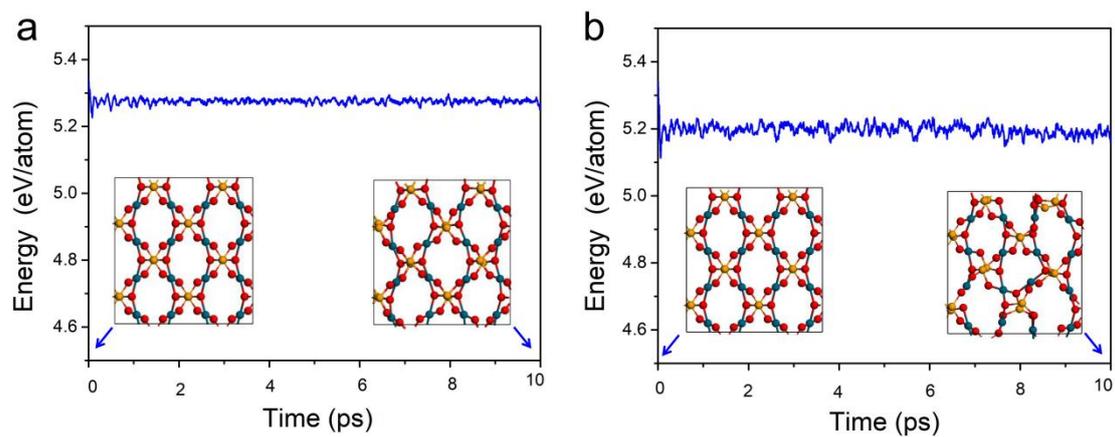
Figure S1. The evolution of the total energy of first principles molecular dynamics (FPMD) simulations for β-PdSeO$_3$ monolayer at (a) 500 K and (b) 1000 K. The insets are snapshot structures of β-PdSeO$_3$ monolayer at 0 ps and 10 ps.

Solar driven water splitting processes on 2D β-PdSeO$_3$ monolayer

The thermodynamics pathways of hydrogen reduction and water oxidation were examined to estimate the catalytic activity of 2D β-PdSeO$_3$ monolayer for water splitting.

The two electron reaction pathway of hydrogen evolution reaction (HER) can be written as:

$$* + H^+ + e^- \rightarrow H^* \qquad\qquad (1)$$

$$H^* + H^+ + e^- \rightarrow * + H_2 \qquad\qquad (2)$$
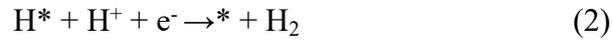
Meanwhile, the four electron reaction pathway of oxygen evolution reaction (OER) can be written as:

$$* + H_2O \rightarrow OH^* + H^+ + e^- \qquad\qquad (3)$$

$$OH^* \rightarrow O^* + H^+ + e^- \qquad\qquad (4)$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^- \qquad\qquad (5)$$

$$OOH^* \rightarrow * + O_2 + H^+ + e^- \qquad\qquad (6)$$
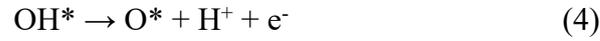
where * denotes the adsorption site, H*, OH*, O* and OOH* denote the adsorbed intermediates.

The Gibbs free energy difference (ΔG) of HER and OER is calculated by computational hydrogen electrode (CHE) method proposed by Nørskov et al. ΔG can be computed as below:

$$\Delta G = \Delta E + \Delta E\text{zpe} - T\Delta S + \Delta G_{pH} + \Delta G_U$$

where ΔE is the DFT computed adsorption energy, ΔE_{ZPE} and ΔS are the zero point energy and the entropy difference between the adsorbed state and the gas phase at 298.15 K, respectively. ΔG_{pH} refers to the free energy contribution in different pH. In

this work, the pH of the solution is assumed to be acid medium (pH = 0). ΔG_{u} denotes the light-induced potential bias (U) and equals to -eU. Thus, the free energy difference of elementary steps of HER and OER can be written as:

$$\Delta G_1 = G_{H*} - G* - 1/2G_{H2} - \Delta G_U + \Delta G_{pH} \tag{7}$$

$$\Delta G_2 = G* - G_{H*} + 1/2G_{H2} - \Delta G_U + \Delta G_{pH} \tag{8}$$

$$\Delta G_3 = G_{OH*} + 1/2G_{H2} - G_{H2O} - G* - \Delta G_U - \Delta G_{pH} \tag{9}$$

$$\Delta G_4 = G_{O*} + 1/2G_{H2} - G_{OH*} - \Delta G_U - \Delta G_{pH} \tag{10}$$

$$\Delta G_5 = G_{OOH*} + 1/2G_{H2} - G_{H2O} - G_{O*} - \Delta G_U - \Delta G_{pH} \tag{11}$$

$$\Delta G_6 = G* + 1/2G_{H2} + G_{O2} - G_{OOH*} - \Delta G_U - \Delta G_{pH} \tag{12}$$

Computation details of formation energy and cleavage energy of PdSeO3