Supplementary material of “Janus PtXO (X=S,Se) monolayers: the visible light driven water splitting photocatalysts with high carrier mobilities”

Haonan Shen\textsuperscript{a}, Yang Zhang\textsuperscript{a}, Guangzhao Wang\textsuperscript{c}, Weixiao Ji\textsuperscript{d}, Xiaoming Xue\textsuperscript{a}, Wei Zhang\textsuperscript{a,b,*}

\textsuperscript{a)Physicochemical Group of College of Criminal Science and Technology & Forensic Center of Public Security of National Forestry Bureau, Nanjing Forest Police College, Nanjing, 210023, China
\textsuperscript{b)NNU-SULI Thermal Energy Research Center (NSTER) & Center for Quantum Transport and Thermal Energy Science (CQTES), School of Physics and Technology, Nanjing Normal University, Nanjing 210023, China
\textsuperscript{c)Key Laboratory of Extraordinary Bond Engineering and Advanced Materials Technology of Chongqing, School of Electronic Information Engineering, Yangtze Normal University, Chongqing 408100, China.
\textsuperscript{d)Spintronics Institute, School of Physics and Technology, University of Jinan, Jinan 250022, China

*E-mail: zhangw@nfpc.edu.cn; zhangw@njnu.edu.cn
Phone: +86 025-85878792

Outline

Fig. S1: The relaxed crystal structures of PtSeO and PtTeO .........................................................2
Table S1: The structural parameters of PtXO obtained by PBE and HSE06 ..................................2
Table S2: The bandgaps, potential drop, overpotentials using PBE and HSE06 relaxed structures ...2
Table S3: The influence of density functional on the formation energy .....................................3
Fig. S2: Angular-dependent Young’s modulus and Possion’s ratio of PtSO ..................................3
Fig. S3: AIMD simulations of Janus PtSO and PtSeO at 1000 K. .............................................4
Fig. S4: The formation energies of PtX\textsubscript{n}O\textsubscript{2-n} with different concentrations ..........4
Fig. S5: The relation between vacuum level and normal hydrogen electrode (NHE) .................5
Fig. S6: Band alignments of pristine monolayer PtS\textsubscript{2} and PtSe\textsubscript{2} ..........................5
Fig. S7: The planar-average electrostatic potentials of the favorable PtSO(PtSeO) ..................6
Fig. S8: The band alignments of the favorable PtSO(PtSeO) ..................................................6
Text S1: Calculation details of the free energy difference (\Delta G) ...........................................7
Fig. S9: Top and side views of the optimized geometries in the \Delta G calculations ......................8
Fig. S10: Band alignment of PtSO at biaxial strain (\sigma) of 3% ................................................9
Fig. S11: G\textsubscript{0W0} calculated quasi-particle band structures and G\textsubscript{0W0+BSE calculated dielectric function of Janus PtXO .................................................................9
Text S2: Calculation details of STH efficiency ..................................................................10
Table S4 The calculated STH efficiency of Janus PtXO .......................................................10
Fig. S1: The relaxed crystal structures of Janus PtSeO and PtTeO. The Pt, Se, Te and O atoms are respectively marked by grey, green, blue and red. The solid lines denote the hexagonal primitive cell, and the rectangle cell used for the carrier mobility calculations.

Table S1 The structural parameters of PtXO obtained by PBE and HSE06.

<table>
<thead>
<tr>
<th>PtXO</th>
<th>$a_0$ (Å)</th>
<th>$d_{Pt,X}$ (Å)</th>
<th>$d_{Pt,O}$ (Å)</th>
<th>$\theta_{X-Pt-O}$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSO (PBE)</td>
<td>3.37</td>
<td>2.28</td>
<td>2.18</td>
<td>81.4</td>
</tr>
<tr>
<td>PtSO (HSE06)</td>
<td>3.31</td>
<td>2.26</td>
<td>2.13</td>
<td>81.83</td>
</tr>
<tr>
<td>PtSeO (PBE)</td>
<td>3.47</td>
<td>2.4</td>
<td>2.22</td>
<td>81.88</td>
</tr>
<tr>
<td>PtSeO (HSE06)</td>
<td>3.4</td>
<td>2.37</td>
<td>2.17</td>
<td>82.09</td>
</tr>
<tr>
<td>PtTeO (PBE)</td>
<td>3.64</td>
<td>2.53</td>
<td>2.29</td>
<td>80.9</td>
</tr>
<tr>
<td>PtTeO (HSE06)</td>
<td>3.57</td>
<td>2.51</td>
<td>2.24</td>
<td>80.9</td>
</tr>
</tbody>
</table>

Table S2 The HSE06 calculated bandgaps ($E_g$), potential drop ($\Delta \phi$), overpotentials ($\chi(H_2)$, $\chi(O_2)$) using the PBE and HSE06 relaxed structures.

<table>
<thead>
<tr>
<th>PtXO</th>
<th>$E_g$ (eV)</th>
<th>$\Delta \phi$ (eV)</th>
<th>$\chi(H_2)$ (eV)</th>
<th>$\chi(O_2)$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSO</td>
<td>2.5</td>
<td>2.51</td>
<td>0.43</td>
<td>3.26</td>
</tr>
<tr>
<td>PtSO</td>
<td>2.47</td>
<td>2.48</td>
<td>0.51</td>
<td>3.21</td>
</tr>
<tr>
<td>PtSeO</td>
<td>1.85</td>
<td>3.22</td>
<td>0.63</td>
<td>3.12</td>
</tr>
<tr>
<td>PtSeO</td>
<td>1.8</td>
<td>3.17</td>
<td>0.66</td>
<td>3.08</td>
</tr>
</tbody>
</table>
Table S3 The influence of density functional on the formation energy ($E_f$).

<table>
<thead>
<tr>
<th>relaxed structures</th>
<th>$E_f$ (meV/atom) using HSE06</th>
<th>$E_f$ (meV/atom) using PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PtSO</td>
<td>PtSeO</td>
</tr>
<tr>
<td>PBE</td>
<td>141.67</td>
<td>275.73</td>
</tr>
<tr>
<td>HSE06</td>
<td>133.17</td>
<td>252.73</td>
</tr>
</tbody>
</table>

Fig. S2: Angular-dependent Young’s modulus and Possion’s ratio of Janus PtSO (marked by red). The value of each isoline is marked by green. We can see that the Young’s modulus and Possion’s ratio of Janus PtSO are mechanically isotropic, which are also found in Janus PtSeO and PtTeO (not shown here).
Fig. S3 AIMD simulations of Janus PtSO and Janus PtSeO 1000 K. Insets are the structures at 10 ps.

![Graph showing free energy vs. time for Janus PtSO and PtSeO](image1)

Fig. S4 The formation energies of Pt$X_nO_{2-n}$ with different concentrations. For each Pt$X_nO_{2-n}$, we manually create 30 crystal structures with different concentrations. Insets are the relaxed favorable structures at $n=1$. Some structures are not shown since their $E_f$s are out of the ordinate scale.

![Graph showing formation energy vs. concentrations for Pt$X_nO_{2-n}$](image2)
Fig. S5 The relation between vacuum level and normal hydrogen electrode (NHE). In the main text, the vacuum level is taken as reference. The dashed lines denote the standard redox potentials of water at pH=0.

Fig. S6: Band alignments of pristine monolayer PtS$_2$ and PtSe$_2$. 

![Band alignments of pristine monolayer PtS$_2$ and PtSe$_2$.](image)
Fig. S7 The planar-average electrostatic potentials of the favorable PtXO along the $z$ directions.

Fig. S8 The band alignments of the favorable PtSO(PtSeO). The water redox levels at pH=0 are marked by dashed lines.
As mentioned in the main text, the strategy proposed by Norskov et al. is used to calculate the ΔG. The ΔG at pH = 0 without solar irradiation is defined as: ΔG =ΔE+ΔE_{zpe} -TΔS. ΔE is the adsorption energy, ΔE_{zpe} and ΔS are respectively the difference in zero point energy and entropy difference between the adsorbed state and the gas phase.

In the oxidation half reaction, there are four steps to transform H₂O into O₂ molecule:

\[
\begin{align*}
* + H₂O & \rightarrow OH^* + H^+ + e^- \quad (1) \\
OH^* & \rightarrow O^* + H^+ + e^- \quad (2) \\
O^* + H₂O & \rightarrow OOH^* + H^+ + e^- \quad (3) \\
OOH^* & \rightarrow * + O₂ + H^+ + e^- \quad (4)
\end{align*}
\]

Simultaneously, the hydrogen production half reaction equation can be written as :

\[
\begin{align*}
* + H^+ + e^- & \rightarrow H* \quad (5) \\
*H + H^+ + e^- & \rightarrow * + H₂ \quad (6)
\end{align*}
\]

where * denotes the adsorbed materials, OH*, O*, OOH* and H* are the adsorbed intermediates.

For each reaction of both oxidation and hydrogen production, the free energy difference under the effect of pH and an extra potential bias can be written as:

\[
\begin{align*}
ΔG(1) &= G(OH^*) + \frac{1}{2}G(H₂) - G(\text{H}_2\text{O}) + ΔG(U) - ΔG(pH) \\
ΔG(2) &= G(O^*) + \frac{1}{2}G(H₂) - G(OH^*) + ΔG(U) - ΔG(pH) \\
ΔG(3) &= G(\text{OOH}^*) + \frac{1}{2}G(H₂) - G(O^*) - G(\text{H}_2\text{O}) + ΔG(U) - ΔG(pH) \\
ΔG(4) &= G^* + \frac{1}{2}G(H₂) + G(\text{O}_2) - G(\text{OOH}^*) + ΔG(U) - ΔG(pH) \\
ΔG(5) &= G(H^*) - \frac{1}{2}G(H₂) - G^* + ΔG(U) + ΔG(pH) \\
ΔG(6) &= G^* + \frac{1}{2}G(H₂) - G(H^*) + ΔG(U) + ΔG(pH)
\end{align*}
\]

Where ΔG(pH) (ΔG(pH)=k_B T × ln10 × pH) is the free energy contributed at different pH concentration. ΔG(U) (ΔG(U)=−eU) represents the extra potential bias provided by an electron in the electrode, where U is the electrode potential relative to the standard hydrogen electrode (SHE).
Fig. S9: Top and side views of the optimized geometries of (a) *H, (b) *OH, (c) *O, and (d) *OOH intermediates for PtSO; (e) *H, (f) *OH, (g) *O, and (h) *OOH intermediates for PtSeO; (i) and (j) are optimized geometries of *H intermediates for S-defected PtSO and Se-defected PtSeO, respectively.
Fig. S10: Band alignment of Janus PtSO at biaxial strain ($\sigma$) of 3%. We can see below that the band edges still straddle the water redox levels.

Fig. S11 (a)-(b) $G_0W_0$ calculated quasi-particle (QP) band structures and (c)-(d) $G_0W_0+BSE$ calculated imaginary part ($\varepsilon_2$) of the dielectric function of Janus PtXO. The $E_{QP}$s are respectively 2.9 and 2.41 eV for Janus PtSO and PtSeO.
Text S2 Calculation details of solar to hydrogen (STH) efficiency.

The STH is calculated by $\eta_{\text{STH}} = \eta_{\text{cu}} \times \eta_{\text{abs}}$, where $\eta_{\text{cu}} = \frac{\Delta G_0}{E_g \int_0^\infty P(\hbar \omega) d(\hbar \omega)}$, $\eta_{\text{abs}} = \frac{\int_0^\infty P(\hbar \omega) d(\hbar \omega)}{\int_0^\infty P(\hbar \omega) d(\hbar \omega)}$.

$\eta_{\text{cu}}$ and $\eta_{\text{abs}}$ are respectively the energy conversion efficiency of carrier utilization and light absorption. $\Delta G_0$ is the free energy of water splitting (1.23 eV). $E_g$ is the bandgap. $E$ represents the photon energy that can be actually utilized in the process of water splitting:

$$E = \begin{cases} E_g, & (\chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.2 - \chi(H_2), & (\chi(H_2) < 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.6 - \chi(O_2), & (\chi(H_2) \geq 0.2, \chi(O_2) < 0.6) \\ E_g + 0.8 - \chi(H_2) - \chi(O_2), & (\chi(H_2) < 0.2, \chi(O_2) < 0.6) \end{cases}$$

The $\eta_{\text{cu}}$, $\eta_{\text{abs}}$ are given in Table S4.

<table>
<thead>
<tr>
<th>Materials, Materials</th>
<th>$\chi(H_2)$ (eV)</th>
<th>$\chi(O_2)$ (eV)</th>
<th>$E_g$</th>
<th>$\eta_{\text{abs}}$</th>
<th>$\eta_{\text{cu}}$</th>
<th>$\eta_{\text{STH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSO</td>
<td>0.43</td>
<td>3.26</td>
<td>2.5</td>
<td>17.93</td>
<td>42.53</td>
<td>7.62</td>
</tr>
<tr>
<td>PtSeO</td>
<td>0.63</td>
<td>3.12</td>
<td>1.85</td>
<td>43.65</td>
<td>51.46</td>
<td>22.46</td>
</tr>
</tbody>
</table>