Multiple Strategies of Improving Photocatalytic Water Splitting Efficiency in 2D Arsenic Sesquichalcogenides

Xiaoteng Li¹*, Chuanlu Yang¹*, Yuliang Liu¹, Endao Han², Wenkai Zhao¹, Xinxin Jiang³, Dongqing Zou¹, Yuqing Xu¹

Carrier Mobility

The carrier mobility at room temperature is obtained based on deformation potential (DP) approach, the formula as follows:

$$
\mu_{2D} = \frac{2e\hbar^3 C}{3K_B T|m^*|^2 E_d^2}
$$

(S1)

$$
C = \frac{(\partial^2 E/\partial \epsilon^2)/S_0} is the elastic modulus, where E is the whole energy and S₀ is the area of monolayers. \(E_d\) denotes the deformation potential constant, defined as

$$
E_d = \partial E_{edge}/\partial \epsilon
$$

Effective mass \((m^*)\) is determined as

$$
m^* = \pm \frac{\hbar^2\left(\frac{d^2E_k}{dk^2}\right)^{-1}}{4}
$$

Table S1 Effective carrier masses \((m^*)\), deformation potential constants \((E_d)\), elastic moduli \((C)\), and carrier mobility \((\mu)\) of \(\text{As}_2\text{X}_3\) monolayers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Carrier Type</th>
<th>(m^*/m_0)</th>
<th>(C) (N/m)</th>
<th>(E_d) (eV)</th>
<th>(\mu) (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{As}_2\text{O}_3)</td>
<td>Electrons (x)</td>
<td>0.92</td>
<td>26.95</td>
<td>3.80</td>
<td>0.31 × 10²</td>
</tr>
<tr>
<td></td>
<td>Hole (x)</td>
<td>0.91</td>
<td></td>
<td>2.96</td>
<td>0.53 × 10²</td>
</tr>
<tr>
<td></td>
<td>Electrons (y)</td>
<td>0.84</td>
<td>50.98</td>
<td>2.2</td>
<td>0.21 × 10³</td>
</tr>
<tr>
<td></td>
<td>Hole (y)</td>
<td>0.79</td>
<td></td>
<td>4.2</td>
<td>0.66 × 10²</td>
</tr>
<tr>
<td>(\text{As}_2\text{S}_3)</td>
<td>Electrons (x)</td>
<td>0.52</td>
<td>40.74</td>
<td>2.53</td>
<td>0.33 × 10³</td>
</tr>
<tr>
<td></td>
<td>Hole (x)</td>
<td>0.49</td>
<td></td>
<td>3.69</td>
<td>0.18 × 10³</td>
</tr>
<tr>
<td></td>
<td>Electrons (y)</td>
<td>0.58</td>
<td>13.11</td>
<td>1.85</td>
<td>0.16 × 10³</td>
</tr>
<tr>
<td></td>
<td>Hole (y)</td>
<td>0.49</td>
<td></td>
<td>3.87</td>
<td>0.25 × 10²</td>
</tr>
<tr>
<td>(\text{As}_2\text{Se}_3)</td>
<td>Electrons (x)</td>
<td>0.47</td>
<td>52.6</td>
<td>1.82</td>
<td>1.01 × 10³</td>
</tr>
<tr>
<td></td>
<td>Hole (x)</td>
<td>0.43</td>
<td></td>
<td>3.42</td>
<td>0.35 × 10³</td>
</tr>
<tr>
<td></td>
<td>Electrons (y)</td>
<td>0.51</td>
<td></td>
<td>0.99</td>
<td>0.57 × 10³</td>
</tr>
</tbody>
</table>

¹ College of physics and optoelectronic engineering, Ludong University, Yantai 264000, People’s Republic of China
² School of Physical and Mathematical Sciences, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
³ School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People’s Republic of China
<table>
<thead>
<tr>
<th></th>
<th>Hole (y)</th>
<th>Electrons (x)</th>
<th>Hole (x)</th>
<th>Electrons (y)</th>
<th>Hole (y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂Te₃</td>
<td>0.25</td>
<td>0.12</td>
<td>0.18</td>
<td>0.09</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>3.79</td>
<td>65.09</td>
<td>2.02</td>
<td>10.11</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>0.16 × 10³</td>
<td>1.58 × 10⁴</td>
<td>7.46 × 10³</td>
<td>1.13 × 10³</td>
<td>0.96 × 10³</td>
</tr>
</tbody>
</table>

Figure S1 The calculated total and atom projected DOS of As₂S₃. The Fermi energy is set to zero.

Figure S2 The crystal structures of N-doped, P-doped, and P-Se-codoped As₂S₃ monolayers.

Figure S3 Phonon dispersion spectra of (a) N-doped, (b) P-doped and (c) P-Se codoped As₂S₃
monolayers. (d)-(f) The corresponding AIMD energy fluctuations at 300 K. The insets of (d)-(f) are the snapshots of equilibrium structure after 3ps.

Figure S4 The projected band structures of N-, P-, Se- and P-Se doped As$_2$S$_3$ monolayers.

Figure S5 Top and side views of the crystal structures for (a) As$_2$STe$_2$ and (b) As$_2$SeTe$_2$ monolayers.

Figure S6 Phonon dispersion spectra of (a) As$_2$STe$_2$ and (b) As$_2$SeTe$_2$ monolayers. (c)-(d) The corresponding AIMD energy fluctuations at 300 K. The insets of (c)-(d) are the snapshots of equilibrium structure after 3ps.
The Gibbs free energy

The free energy of the absorbed states is calculated according to the formula:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T \Delta S$$

(S2)

where $\Delta E$ is the adsorption energy, $\Delta E_{ZPE}$ and $\Delta S$ represent the variations of the zero-point energy and vibrational entropy between the adsorbed states and corresponding free-standing states, respectively. $\Delta E_{ZPE}$ is defined as:

$$E_{ZPE} = \frac{1}{2} \sum \nu$$

(S3)

where $\nu$ stands for the vibrational frequency. TS is defined as:

$$TS = k_b T \left[ \sum_k \ln \left( \frac{1}{1 - e^{-\frac{\nu}{k_b T}}} \right) + \sum_k \frac{\nu}{k_b T} \left( \frac{1}{e^{\frac{-\nu}{k_b T}} - 1} + 1 \right) \right]$$

(S4)

Wherein, $e$, $h$ and $k_b$ represents the electron charge, Planck’s constant and Boltzmann’s constant. The value of $T$ is 298.15K.

Here we take external potential and pH into account to evaluate the OER and HER activities. The HER process include two steps and the corresponding $\Delta G_{\text{H}^+}$ can be
expressed as:

1) $^* + \text{H}^+ + e^- \rightarrow \text{H}^*$  \hspace{1cm} (S5)

$$
\Delta G_1 = G_{^*} - \frac{1}{2}G_{\text{H}_2} - G_{^*} + \Delta G_U + \Delta G_{pH}
= \Delta E_{H} + \Delta E_{ZPE(U)} - T\Delta S_{H} + \Delta G_{U} + \Delta G_{pH}
= \Delta G_H
$$

(\text{S6})

While the OER contains four elementary steps and the $\Delta G$ can be derived as follows:

2) $\text{H}_2\text{O}(l) + ^* \rightarrow \text{OH}^* + \text{H}^+ + e^-$  \hspace{1cm} (S7)

$$
\Delta G_2 = G_{\text{OH}^*} - \frac{1}{2}G_{\text{H}_2} - G_{^*} - G_{\text{H}_2\text{O}} + \Delta G_U - \Delta G_{pH}
= \Delta E_{\text{OH}} + \Delta E_{ZPE(\text{OH})} - T\Delta S_{\text{OH}} + \Delta G_{U} - \Delta G_{pH}
= \Delta G_{\text{OH}}
$$

(\text{S8})

3) $\text{OH}^* \rightarrow \text{O}^* + \text{H}^+ + e^-$  \hspace{1cm} (S9)

$$
\Delta G_3 = G_{\text{O}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{OH}^*} + \Delta G_U - \Delta G_{pH}
= (\Delta E_{O} + \Delta E_{ZPE(O)} - T\Delta S_{O} + 2\Delta G_{U} - 2\Delta G_{pH}) - (\Delta E_{\text{OH}} + \Delta E_{ZPE(\text{OH})})
= \Delta G_{\text{O}} - \Delta G_{\text{OH}}
$$

(\text{S10})

4) $\text{H}_2\text{O}(l) + \text{O}^* \rightarrow \text{OOH}^* + \text{H}^+ + e^-$  \hspace{1cm} (S11)

$$
\Delta G_4 = G_{\text{OOH}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{O}^*} - G_{\text{H}_2\text{O}} + \Delta G_U - \Delta G_{pH}
= (\Delta E_{\text{OOH}} + \Delta E_{ZPE(\text{OOH})} - T\Delta S_{\text{OOH}} + 3\Delta G_{U} - 3\Delta G_{pH}) - (\Delta E_{O} + \Delta E_{ZPE(O)})
= \Delta G_{\text{OOH}} - \Delta G_{O}
$$

(\text{S12})

5) $\text{OOH}^* \rightarrow \text{O}_2(g) + \text{H}^+ + e^-$  \hspace{1cm} (S13)

$$
\Delta G_5 = G_{^*} + \frac{1}{2}G_{\text{H}_2} + G_{\text{O}_2} - G_{\text{OOH}^*} + \Delta G_U - \Delta G_{pH}
$$
\[
(4.92 + 4\Delta G_U - 4\Delta G_{pH}) - (\Delta E_{OOH} + \Delta E_{ZPE(OOH)} - T\Delta S_{OOH} + 3\Delta G_U -
\]

\[
= (4.92 + 4\Delta G_U - 4\Delta G_{pH}) - \Delta G_{OOH}
\]

(S14)

wherein, \( \Delta G_U = -eU \), denotes extra potential bias provided by an electron in the electrode, where \( U \) represents the potential difference from the standard hydrogen electrode potential. \( \Delta G_{pH} \) is the pH-dependent \( \Delta G \), and the corresponding formula is \( \Delta G_{pH} = k_b T \times \ln 10 \times \text{pH} \).

**Solar-to-hydrogen (STH) efficiency**

The efficiency of light absorption (\( \eta_{abs} \)) is defined as:

\[
\eta_{abs} = \frac{\int_{E_g}^{\infty} P(h\omega)d(h\omega)}{\int_0^\infty P(h\omega)d(h\omega)}
\]

(S17)

where \( E_g \) is the band gap of semiconductors and \( P(h\omega) \) is the AM1.5 solar energy flux at the photon energy \( h\omega \). The efficiency of carrier utilization (\( \eta_{cu} \)) is calculated by the formula:

\[
\eta_{cu} = \frac{\int_{E}^{\Delta G_{H_2O}} \int_{E_g}^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)}{\int_{E_g}^{\infty} P(h\omega)d(h\omega)}
\]

(S18)

where \( \Delta G_{H_2O} \) is the redox potential difference of H2O (1.23 eV) and \( E \) is the photons energy which can be fully used for water splitting. \( E \) can be defined as:
\[ E = \begin{cases} E_g, & (\chi(H_2) \geq 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.2 - \chi(H_2), & (\chi(H_2) < 0.2, \chi(O_2) \geq 0.6) \\ E_g + 0.6 - \chi(O_2), & (\chi(H_2) \geq 0.2, \chi(O_2) < 0.6) \\ E_g + 0.8 - \chi(H_2) - \chi(O_2), & (\chi(H_2) < 0.2, \chi(O_2) < 0.6) \end{cases} \] (S19)

where \( \chi(H_2) \) and \( \chi(O_2) \) represent the overpotentials of HER and OER, respectively.

Then the STH efficiency is defined as:

\[ \eta_{STH} = \eta_{abs} \times \eta_{cu} \] (S20)

When the photocatalysts possess internal electric filed, the STH efficiency will be corrected to:

\[ \eta'_{STH} = \eta_{STH} \times \frac{\int_0^\infty P(h\omega)d(h\omega)}{\Delta\Phi \int_{E_g}^\infty \frac{P(h\omega)}{h\omega}d(h\omega) + \int_0^\infty P(h\omega)d(h\omega)} \] (S21)

where \( \Delta\Phi \) is the vacuum level difference between the two respective surfaces.

**Table S2** The overpotentials for HER (\( \chi(H_2) \)) and OER (\( \chi(O_2) \)), the photons energy \( (E) \), the efficiency of light absorption (\( \eta_{abs} \)) and carrier utilization (\( \eta_{cu} \)), and corrected STH (\( \eta'_{STH} \)).

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \chi(H_2) ) (eV)</th>
<th>( \chi(O_2) ) (eV)</th>
<th>( E ) (eV)</th>
<th>( \eta_{abs} ) (%)</th>
<th>( \eta_{cu} ) (%)</th>
<th>( \eta'_{STH} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂S₇e₂</td>
<td>0.33</td>
<td>0.51</td>
<td>1.10</td>
<td>84.67</td>
<td>64.21</td>
<td>36.19</td>
</tr>
<tr>
<td>As₂S₄e₂</td>
<td>0.19</td>
<td>0.13</td>
<td>1.45</td>
<td>87.19</td>
<td>43.61</td>
<td>29.36</td>
</tr>
</tbody>
</table>

**References**