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

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Carrier Mobility

The carrier mobility at room temperature is obtained based on deformation potential (DP) approach, the formula as follows[1]:

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

(S1)

$C = (\partial^2 E/\partial \varepsilon^2)/S_0$ is the elastic modulus, where E is the whole energy and S_0 is the area of monolayers. E_d denotes the deformation potential constant, defined as $E_d = \partial E_{edge}/\partial \varepsilon$. Effective mass ($m^*$) is determined as $m^* = \pm \hbar^2 (\frac{d^2 E_k}{dk^2})^{-1}$.

Table S1 Effective carrier masses (m^*), deformation potential constants (E_d), elastic moduli (C), and carrier mobility (μ) of As$_2$X$_3$ monolayers.

Materials	Carrier Type	m^*/m_0	C (N/m)	E_d (eV)	μ (cm^{2}V^{-1}s^{-1})
As$_2$O$_3$	Electrons (x)	0.92	26.95	3.80	0.31×10^2
	Hole (x)	0.91		2.96	0.53×10^2
	Electrons (y)	0.84	50.98	2.2	0.21×10^3
	Hole (y)	0.79		4.2	0.66×10^2
As$_2$S$_3$	Electrons (x)	0.52	40.74	2.53	0.33×10^3
	Hole (x)	0.49		3.69	0.18×10^3
	Electrons (y)	0.58	13.11	1.85	0.16×10^3
	Hole (y)	0.49		3.87	0.25×10^2
As$_2$Se$_3$	Electrons (x)	0.47	52.6	1.82	1.01×10^3
	Hole (x)	0.43		3.42	0.35×10^3
	Electrons (y)	0.51	10.29	0.99	0.57×10^3

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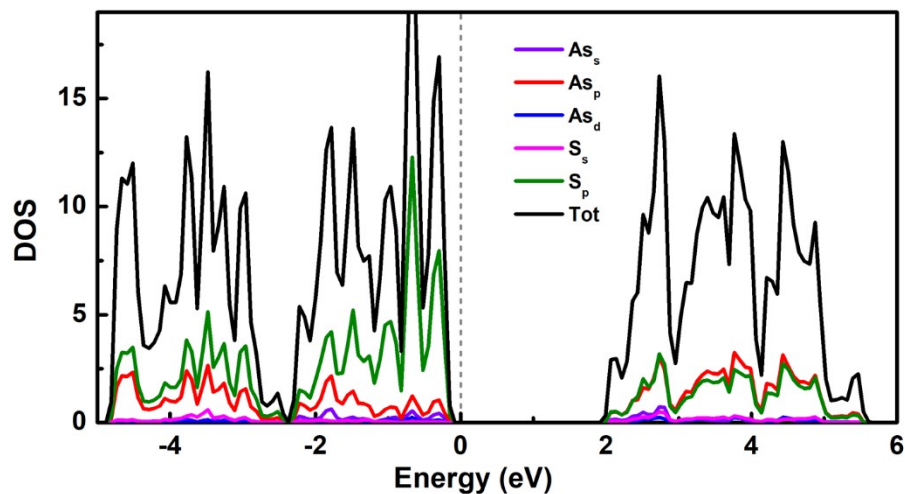|					
	Hole (y)	0.25		3.79	0.16×10^3
As$_2$Te$_3$	Electrons (x)	0.12	65.09	2.02	1.58×10^4
	Hole (x)	0.18		1.86	7.46×10^3
	Electrons (y)	0.09	65.48	10.11	1.13×10^3
	Hole (y)	0.18		5.46	0.96×10^3

Figure S1 The calculated total and atom projected DOS of As$_2$S$_3$. The Fermi energy is set to zero.
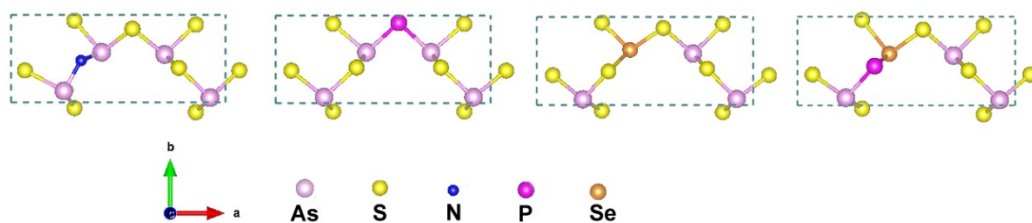

Figure S2 The crystal structures of N-doped, P-doped, and P-Se-codoped As$_2$S$_3$ monolayers.
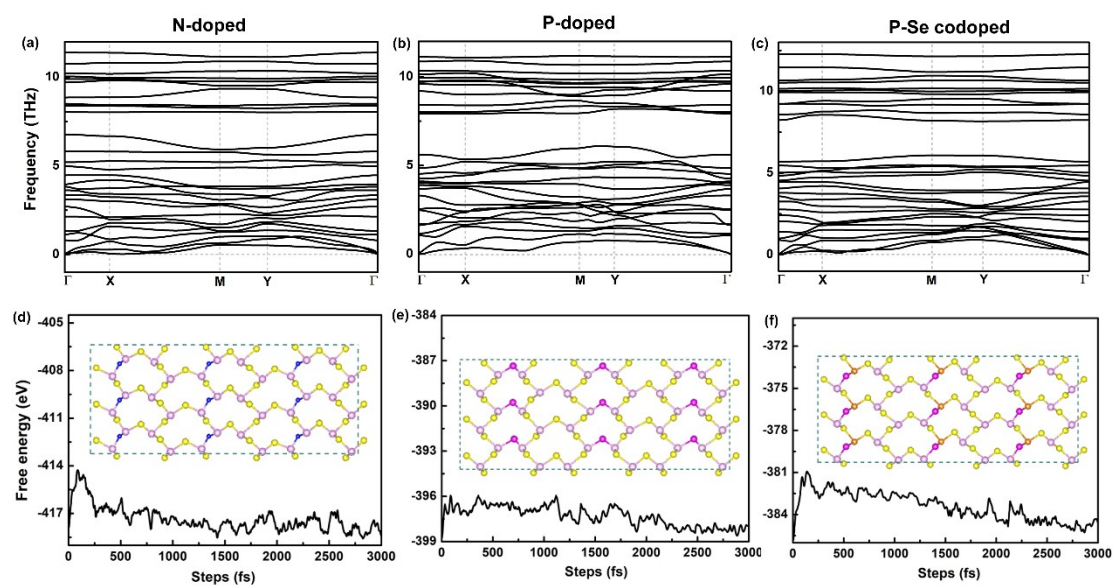

Figure S3 Phonon dispersion spectra of (a) N-doped, (b) P-doped and (c) P-Se codoped As$_2$S$_3$

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_2S_3 monolayers.

Figure S5 Top and side views of the crystal structures for (a) As_2STe_2 and (b) As_2SeTe_2 monolayers.

Figure S6 Phonon dispersion spectra of (a) As_2STe_2 and (b) As_2SeTe_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.
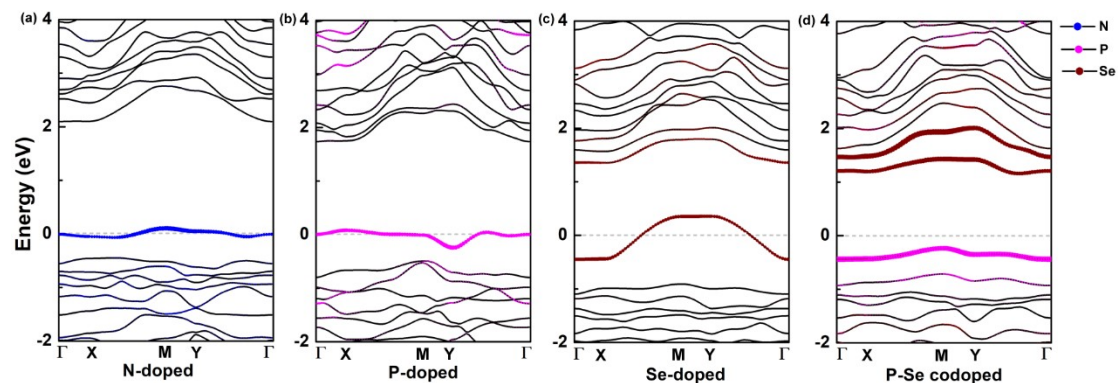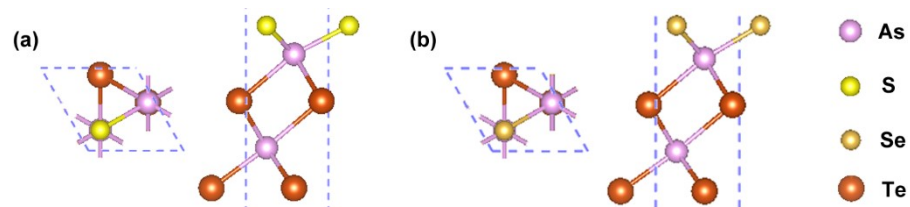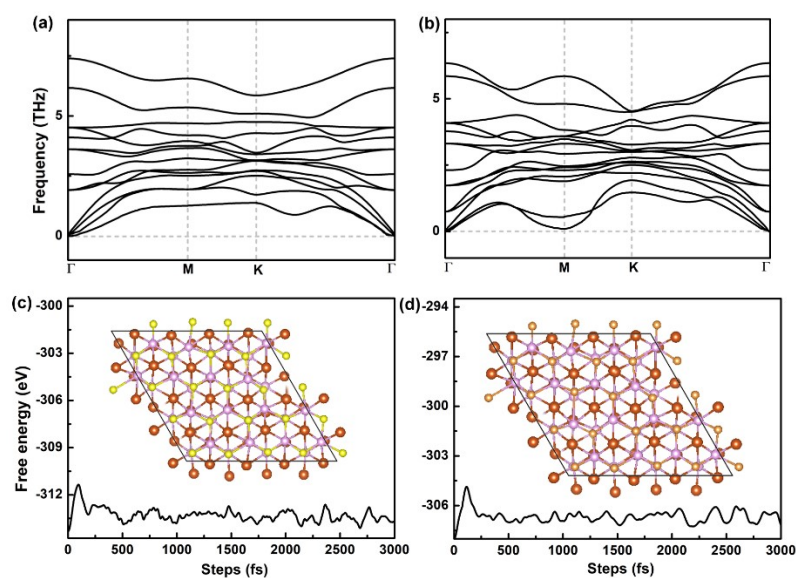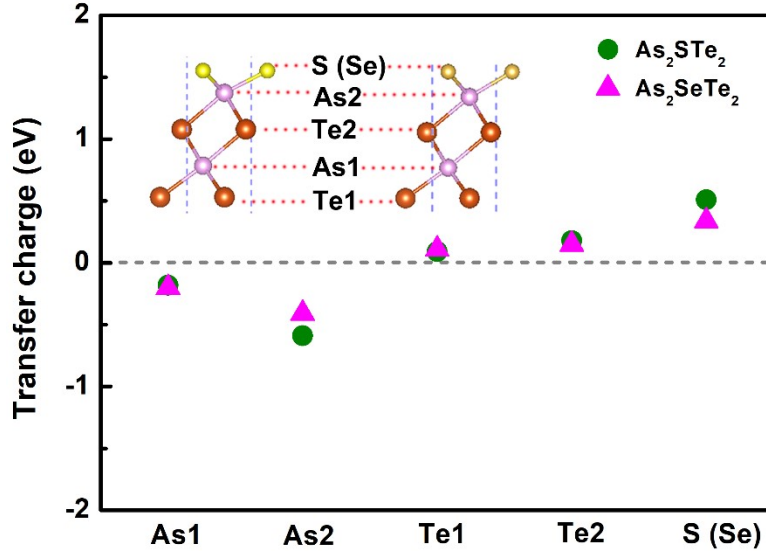
Figure S7 The transfer charges of As_2STe_2 (As_2SeTe_2) monolayers.

The Gibbs free energy

The free energy of the absorbed states is calculated according to the formula[2]:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \tag{S2}$$

where ΔE is the adsorption energy, ΔE_{ZPE} and ΔS represent the variations of the zero-point energy and vibrational entropy between the adsorbed states and corresponding free-standing states, respectively. ΔE_{ZPE} is defined as:

$$E_{ZPE} = {}^1\!/_2 \sum h\nu \tag{S3}$$

where ν stands for the vibrational frequency. TS is defined as:

$$TS = k_b T \left[\sum_K \ln\left(\frac{1}{1 - e^{-h\nu/k_b T}}\right) + \sum_K \frac{h\nu}{k_b T}\left(\frac{1}{e^{-h\nu/k_b T} - 1} + 1\right) \right] \tag{S4}$$

Wherein, e, h and k_b represents the electron charge, Planck's constant and Boltzmann's constant. The value of T is 298.15K.
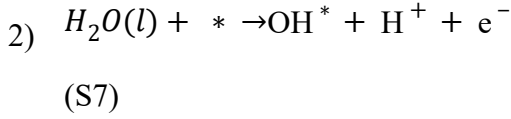
Here we take external potential and pH into account to evaluate the OER and HER activities. The HER process include two steps and the corresponding ΔG_{H*} can be

expressed as:

1) $* + H^+ + e^- \rightarrow H^*$ (S5)

$$\Delta G_1 = G_{H^*} - \frac{1}{2}G_{H_2} - G_* + \Delta G_U + \Delta G_{pH}$$
$$= \Delta E_H + \Delta E_{ZPE(H)} - T\Delta S_H + \Delta G_U + \Delta G_{pH}$$
$$= \Delta G_H \qquad\qquad\qquad\qquad\qquad\qquad (S6)$$

While the OER contains four elementary steps and the ΔG can be derived as follows:

2) $H_2O(l) + * \rightarrow OH^* + H^+ + e^-$

(S7)

$$\Delta G_2 = G_{OH^*} + \frac{1}{2}G_{H_2} - G_* - G_{H_2O} + \Delta G_U - \Delta G_{pH}$$
$$= \Delta E_{OH} + \Delta E_{ZPE(OH)} - T\Delta S_{OH} + \Delta G_U - \Delta G_{pH}$$
$$= \Delta G_{OH} \qquad\qquad\qquad\qquad\qquad\qquad (S8)$$

3) $OH^* \rightarrow O^* + H^+ + e^-$ (S9)

$$\Delta G_3 = G_{O^*} + \frac{1}{2}G_{H_2} - G_{OH^*} + \Delta G_U - \Delta G_{pH}$$
$$= (\Delta E_O + \Delta E_{ZPE(O)} - T\Delta S_O + 2\Delta G_U - 2\Delta G_{pH}) - (\Delta E_{OH} + \Delta E_{ZPE(OH)} - \Delta G_U - \Delta G_{pH})$$

$$= \Delta G_O - \Delta G_{OH} \qquad\qquad\qquad\qquad\qquad\qquad (S10)$$

4) $H_2O(l) + O^* \rightarrow OOH^* + H^+ + e^-$

(S11)

$$\Delta G_4 = G_{OOH^*} + \frac{1}{2}G_{H_2} - G_{O^*} - G_{H_2O} + \Delta G_U - \Delta G_{pH}$$
$$= (\Delta E_{OOH} + \Delta E_{ZPE(OOH)} - T\Delta S_{OOH} + 3\Delta G_U - 3\Delta G_{pH}) - (\Delta E_O +$$
$$\Delta S_O + 2\Delta G_U - 2\Delta G_{pH})$$

$$= \Delta G_{OOH} - \Delta G_O \qquad\qquad\qquad\qquad\qquad\qquad (S12)$$

5) $OOH^* \rightarrow *+ O_2(g) + H^+ + e^-$ (S13)

$$\Delta G_5 = G_* + \frac{1}{2}G_{H_2} + G_{O_2} - G_{OOH^*} + \Delta G_U - \Delta G_{pH}$$

$$= (4.92 + 4\Delta G_U - 4\Delta G_{pH}) - (\Delta E_{OOH} + \Delta E_{ZPE(OOH)} - T\Delta S_{OOH} + 3\Delta G_U -$$
$$)$$

$$= (4.92 + 4\Delta G_U - 4\Delta G_{pH}) - \Delta G_{OOH} \tag{S14}$$

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. ΔG_{pH} is the pH-dependent ΔG, and the corresponding formula is $\Delta G_{pH} = k_b T \times ln10 \times$ pH.

Solar-to-hydrogen (STH) efficiency

The efficiency of light absorption (η_{abs}) is defined as[3]:

$$\eta_{abs} = \frac{\displaystyle\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}{\displaystyle\int_{0}^{\infty} P(\hbar\omega)d(\hbar\omega)}$$

(S17)

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

$$\eta_{cu} = \frac{\Delta G_{H_2O}\displaystyle\int_{E}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega}d(\hbar\omega)}{\displaystyle\int_{E_g}^{\infty} P(\hbar\omega)d(\hbar\omega)}$$

(S18)

where ΔG_{H_2O} is the redox potential difference of H_2O (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:

$$\eta'_{STH} = \eta_{STH} \times \frac{\displaystyle\int_0^\infty P(\hbar\omega)d(\hbar\omega)}{\displaystyle\Delta\Phi \int_{E_g}^\infty \frac{P(\hbar\omega)}{\hbar\omega}d(\hbar\omega) + \int_0^\infty P(\hbar\omega)d(\hbar\omega)}$$

(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 (η_{abs}) and carrier utilization (η_{cu}), and corrected STH (η'_{STH}).

Materials	$\chi(H_2)$(eV)	$\chi(O_2)$(eV)	E (eV)	η_{abs} (%)	η_{cu} (%)	η'_{STH} (%)
As$_2$STe$_2$	0.33	0.51	1.10	84.67	64.21	36.19
As$_2$SeTe$_2$	0.19	0.13	1.45	87.19	43.61	29.36

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