Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S1 Effective carrier masses (m^*), deformation potential constants (E_d), elastic moduli (C), and carrier mobility (μ) of As_2X_3 monolayers.

Materials	Carrier Type	m^*/m_0	C (N/m)	E_d (eV)	μ ($cm^2V^{-1}s^{-1}$)
As_2O_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_2S_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_2Se_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
	Hole (y)	0.25		3.79	0.16×10^3
As_2Te_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

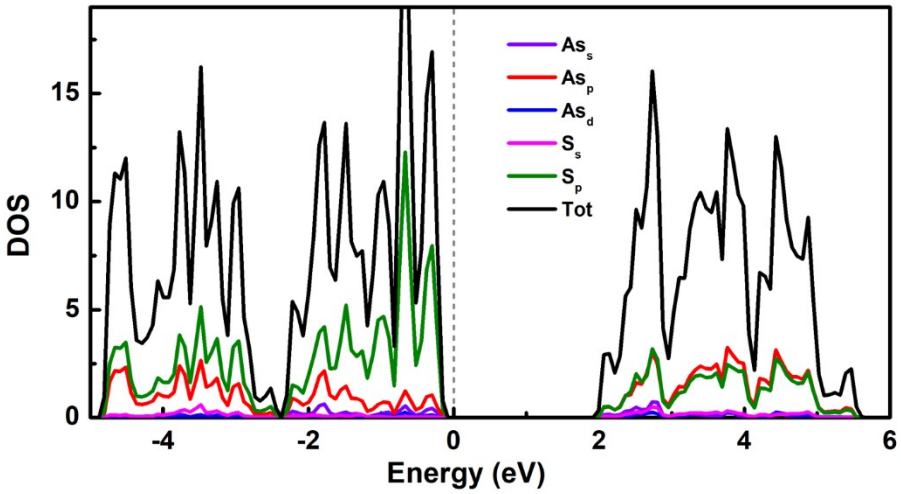

Figure S1 The calculated total and atom projected DOS of As_2S_3. The Fermi energy is set to zero.

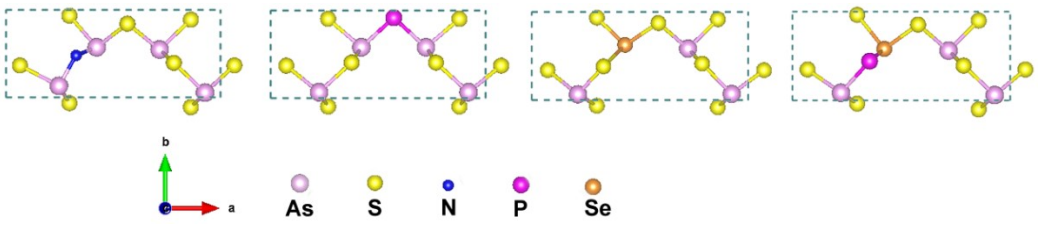

Figure S2 The crystal structures of N-doped, P-doped, and P-Se-codoped As_2S_3 monolayers.

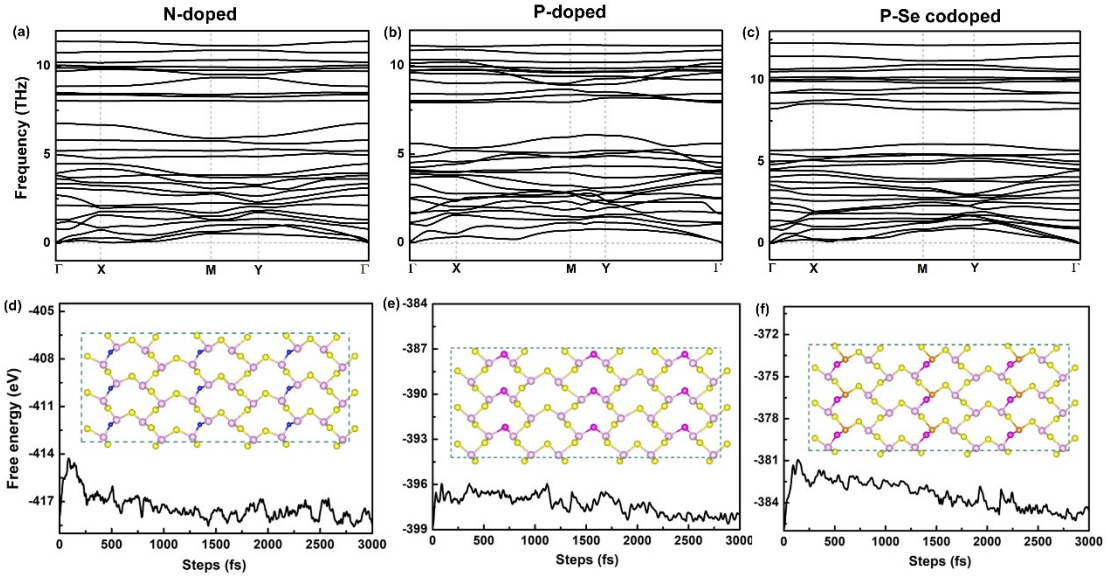

Figure S3 Phonon dispersion spectra of (a) N-doped, (b) P-doped and (c) P-Se codoped As_2S_3 monolayers. (d)-(f) The corresponding AIMD energy fluctuations at 300 K. The insets of (d)-(f) are the snapshots of equilibrium structure after 3ps.

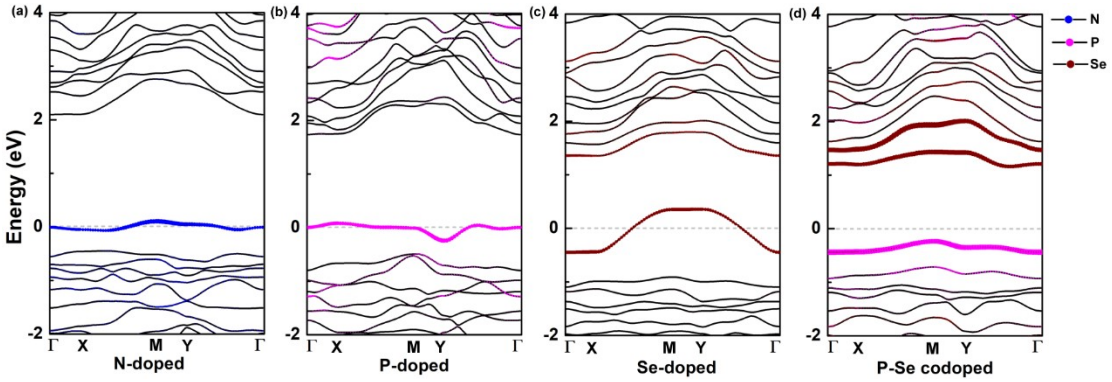

Figure S4 The projected band structures of N-, P-, Se- and P-Se doped As_2S_3 monolayers.

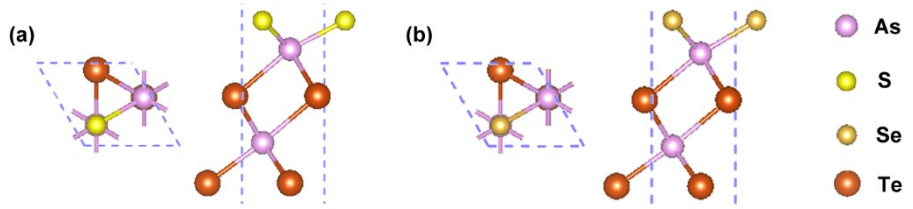

Figure S5 Top and side views of the crystal structures for (a) As_2STe_2 and (b) As_2SeTe_2 monolayers.

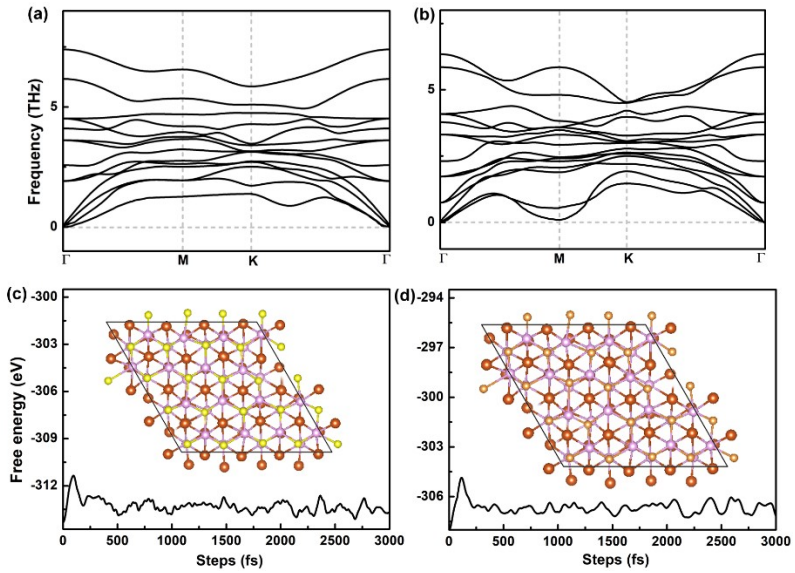

Figure S6 Phonon dispersion spectra of (a) As_2STe_2 and (b) As_2SeTe_2 monolayers. (c)-(d) The corresponding AIMD energy fluctuations at 300 K. The insets of (c)-(d) are the snapshots of equilibrium structure after 3ps.

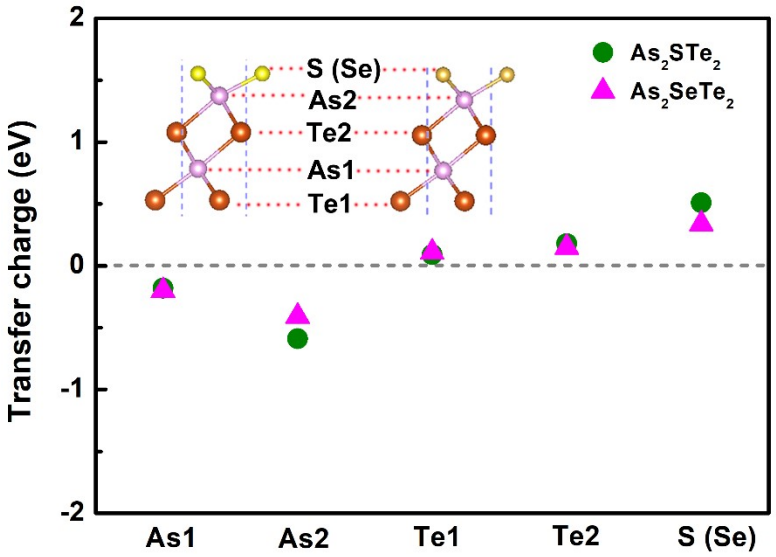

Figure S7 The transfer charges of As_2STe_2 (As_2SeTe_2) monolayers.

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_2STe_2	0.33	0.51	1.10	84.67	64.21	36.19
As_2SeTe_2	0.19	0.13	1.45	87.19	43.61	29.36