

Electronic Supplementary Information

Two-dimensional IV-VA₃ monolayers with enhanced charge mobility for high-performance solar cells

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Fig. S9 2D elastic constant evaluation for the SiP_3 (a), SiAs_3 (b), GeP_3 (c) and GeAs_3 (d) monolayers. Total energy with respect to the lattice dilation $\Delta l/l_0$. The polynomial fit of the data gives the 2D elastic constant.

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Table S1 Structural parameters and electronic properties for relaxed AX₃ monolayers.

Table S2. Calculated cohesive energy differences (ΔE_{coh}) are given in units of eV. ΔE_{coh} is based on the ABC stacking AX₃ monolayer calculated with PBE functional.

Table S3 Effective mass m_i^*/m_0 , DP constant E_{li} in eV, elastic constant C_{2D} in Jm⁻², and carrier mobility μ in cm²V⁻¹s⁻¹, at 300 K for electrons and holes in monolayer AX₃ (A=Si, Ge; X=P, As).
(x=zigzag, y=armchair)

Table S4 Confirmed existing SCs and the PCE measured under the global AM1.5 spectrum (1000 Wm⁻²).

S1. Cohesive energy

$$E_{Coh} = \frac{nE_A + 3nE_X - E_{total}}{4n} \quad (S1)$$

E_{total} , E_A and E_X represent the total energies of AX_3 (A=Si, Ge; X=P, As, Sb) monolayers, single atoms A and X, respectively.

S2. Optical absorption coefficient and details of GW+BSE calculation

The calculated optical absorption properties rely on the complex dielectric function.

The imaginary part ($\varepsilon_2(\omega)$) of the dielectric matrix can be obtained as¹

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \times \langle u_{ck+e_{\alpha q}} | u_{vk} \rangle \langle u_{ck+e_{\beta q}} | u_{vk} \rangle^* \quad (S2)$$

where Ω is the primitive cell volume, and w_k is the k-point weight. The indices c and v denote the conduction and valence band states, respectively. ϵ is the band energy, and u is the cell periodic part of the orbitals at the k-point k . The vectors e_α and e_β stand for unit vectors for the three Cartesian directions. The real part of dielectric function $\varepsilon_1(\omega)$ is obtained from the imaginary part $\varepsilon_2(\omega)$ using the Kramers-Kronig transformation¹

$$\varepsilon_1(\omega) = 1 + \frac{4}{\pi} P \int_0^\infty \frac{\varepsilon_2(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega' \quad (S3)$$

where P is the principle value. Then, the optical absorption coefficient $\alpha(\omega)$ is calculated based on both imaginary and real parts as following²

$$\alpha(\omega) = \sqrt{2} \omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2} \quad (S4)$$

The optical absorption and excitonic effect concerned properties were carried out by the GW plus Bethe-Salpeter equation calculation (GW+BSE)³⁻⁵. Due to the interaction in periodic boundary conditions of AX_3 monolayers, the Wigner-Seitz cell truncation was adopted.⁶ The total number of bands set to 600 while calculating the dielectric function and quasi-particle (QP) energy, which guaranteed the QP bandgaps converged to 0.05 eV. The exciton wave functions and coupled electron-hole excitation energies were contained by solving BSE method. The 10 occupied and 16 unoccupied

bands were performed in constructing the electron-hole interaction kernel.

S3. Carrier mobility

In inorganic semiconductors, the coherent wavelength of thermally activated electrons or holes at room temperature is much longer than the lattice constant and is close to the acoustic phonon wavelength. The electron-acoustic phonon coupling, leading to scattering in the low energy region, can be obtained based on deformation potential (DP) theory, which is first proposed by Bardeen and Shockley.⁷ By means of the effective mass approximation, the DP theory has been widely used to investigate carrier mobility μ in 2D materials:

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{K_B T m_e^* m_d (E_1^i)^2} \quad (S5)$$

where, m_e^* is the effective mass in the transport direction; m_d is the average effective mass determined by $m_d = (m_x^* m_y^*)^{1/2}$. T is the temperature. C_{2D} is the DP constant which characterizes the shift of the band edges (the bottom of conduction band for electrons and the top of valence for holes) induced by the strain and is defined as $E_{1i} = \Delta E_i / (\Delta l / l_0)$. C_{2D} is the elastic modulus of x (zigzag) and y (armchair) uniformly deformed crystal for emulating the lattice distortion activated by the strain. For the 2D models the in-plane stiffness can be determined as $C_{2D} = [\partial^2 E / \partial \delta^2] / S_0$, here E is the total energy of the supercell, δ is the applied uniaxial strain, and S_0 is the area of the equilibrium supercell.

S4. Power conversion efficiency

The power conversion efficiency PCE (η) of such a AX_3 and B (ZnO, MoTe₂ and WS₂) described as⁸

$$\eta = \frac{J_{sc} V_{OC} \beta_{FF}}{p_{solar}} = \frac{0.65(E_g^d - \Delta E_c - 0.3) \int_{E_g^d}^{\infty} \frac{P(\hbar\omega)}{\hbar\omega} d(\hbar\omega)}{\int_0^{\infty} P(\hbar\omega) d(\hbar\omega)}$$

(S6)

where 0.65 is the fill factor β_{FF} , $P(\hbar\omega)$ is AM1.5 solar energy flux (stated in $\text{Wm}^{-2}\text{eV}^{-1}$)⁹ at the photon energy ($\hbar\omega$), and E_g^d is the band gap of the donor (AX_3). ΔE_c is the conduction band offset between donor (SiP_3 , SiAs_3 , GeAs_3) and acceptor (ZnO , MoTe_2 , WS_2). The $E_g^d - \Delta E_c - 0.3$ term is an estimation of the maximum open circuit voltage (V_{oc}).^{8,10} The integral in the numerator is the short circuit current (EQE) of 100%,¹¹ and the integral in the denominator is the incident solar radiation ($P_{solar}=1000 \text{ Wm}^{-2}$).¹²

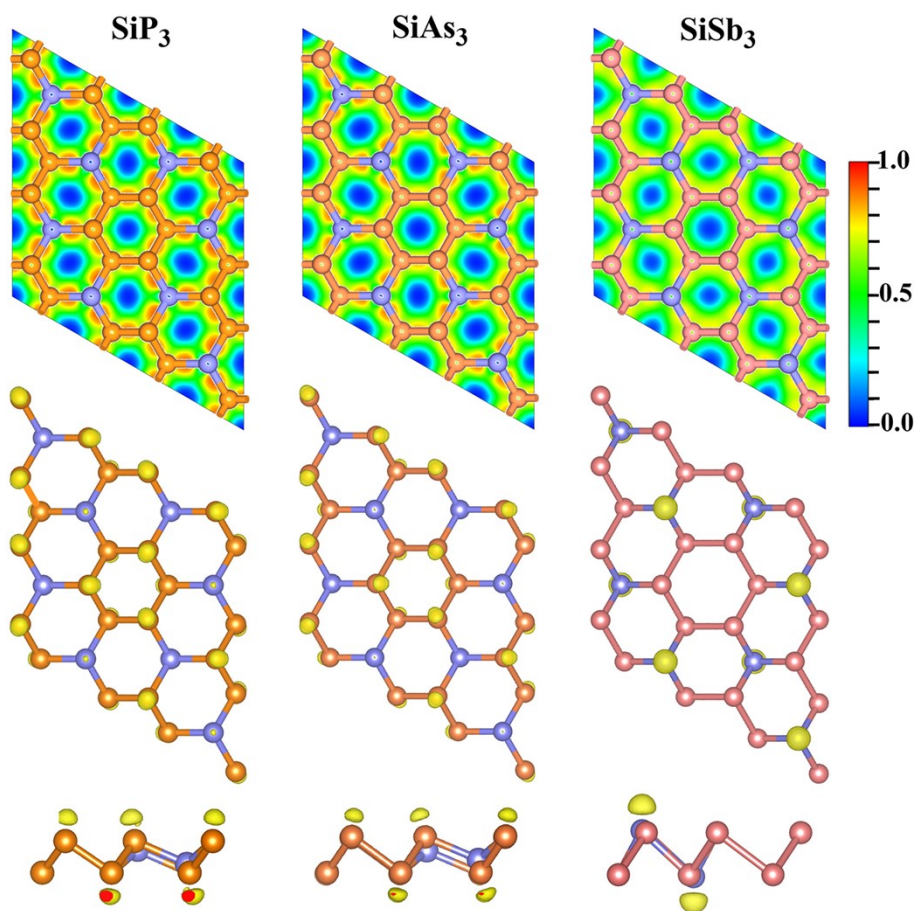


Fig. S1 The 2D and 3D ELFs of monolayer SiX_3 ($X = \text{P}, \text{As}, \text{Sb}$) are presented.

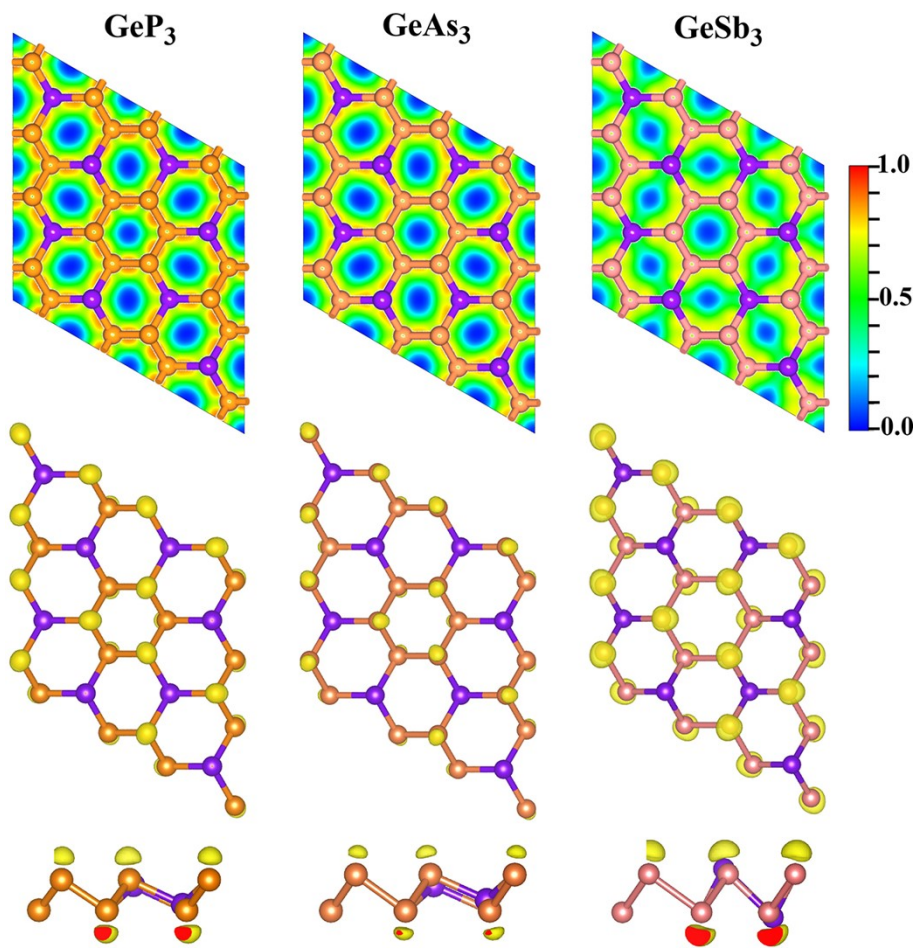


Fig. S2 The 2D and 3D ELFs of monolayer GeX_3 ($X = \text{P}, \text{As}, \text{Sb}$) are presented.

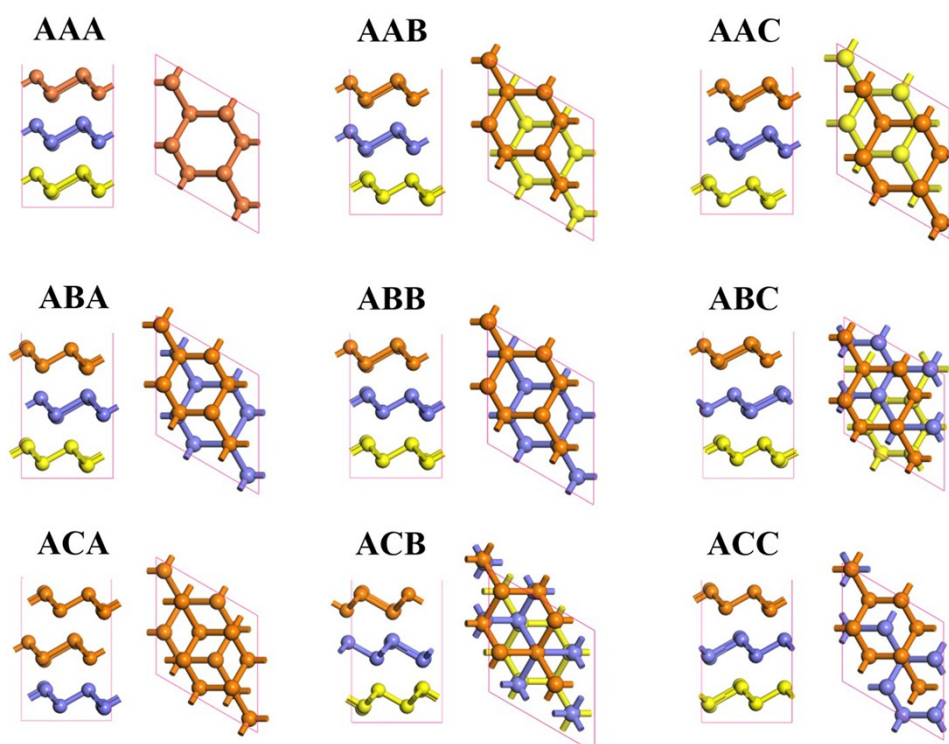


Fig. S3 Side and top views of nine stacked (AAA, AAB, AAC, ABA, ABB, ABC, ACA and ACB) bulk AX_3 ($X=P, As, Sb$). The pink lines in the bottom panels of every stacked structure stand for the rhombus primitive cell.

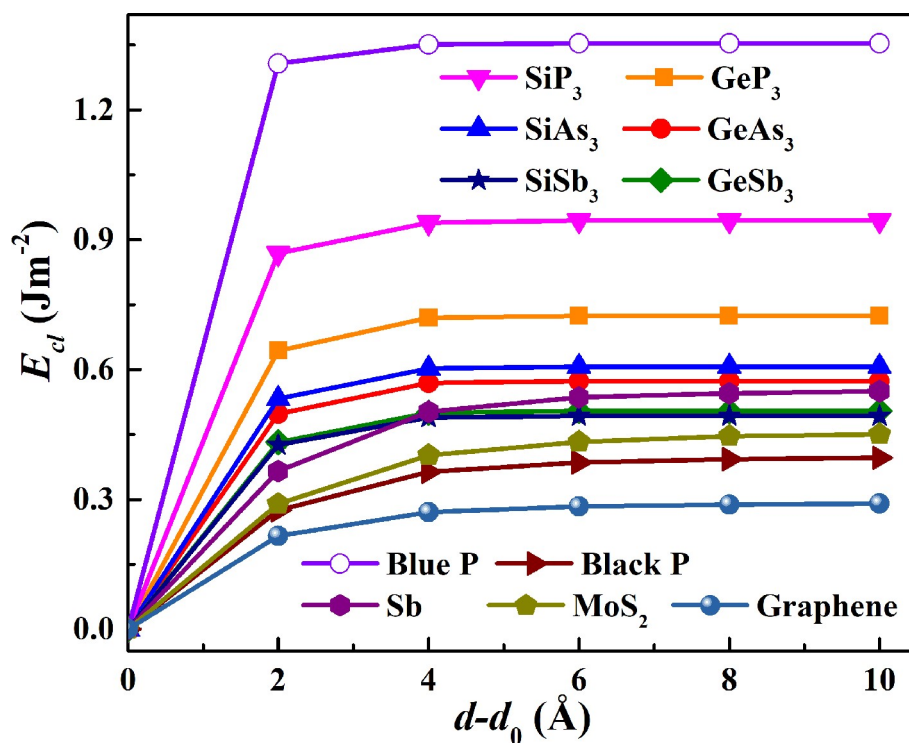


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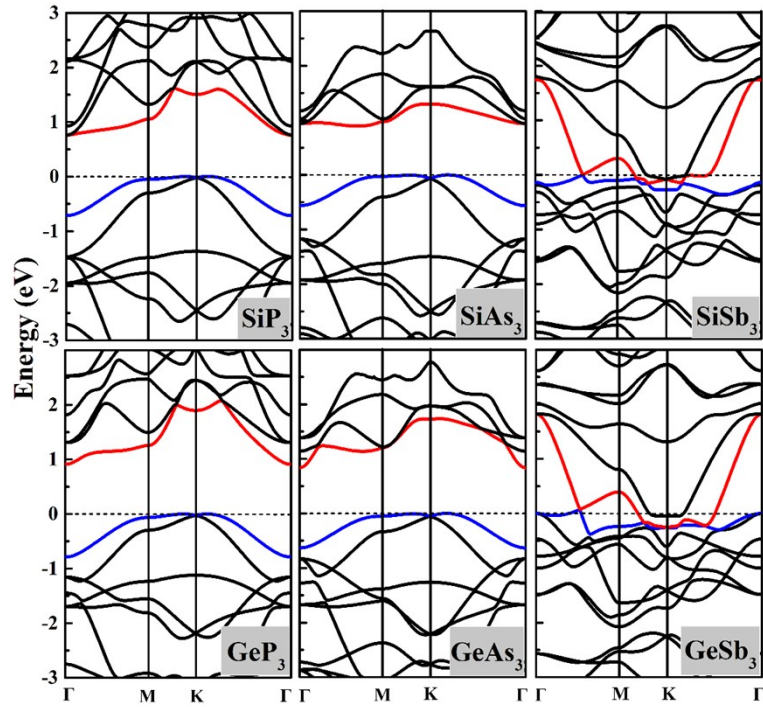


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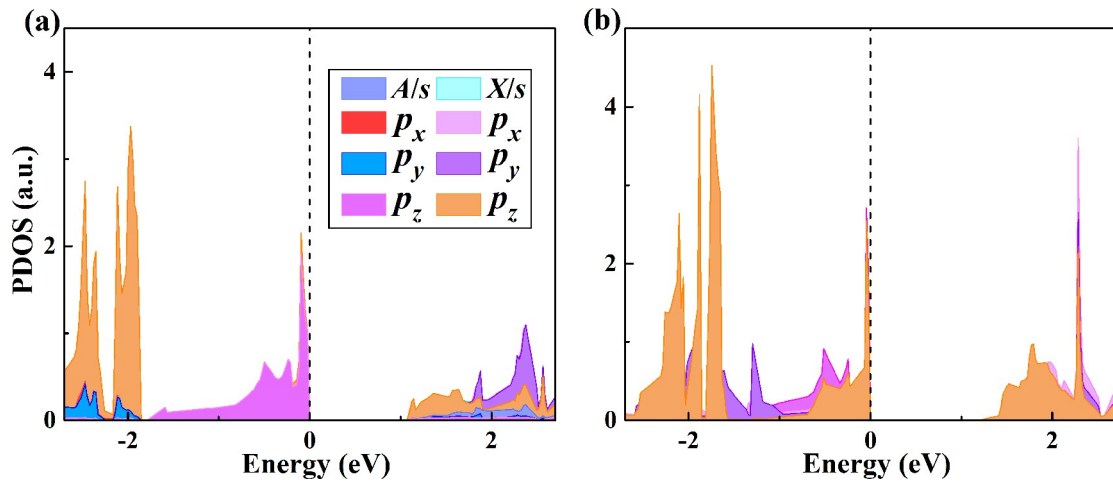


Fig. S6 The projected density of states of monolayer SiX_3 (a) and GeX_3 (b) ($X=P, As$).

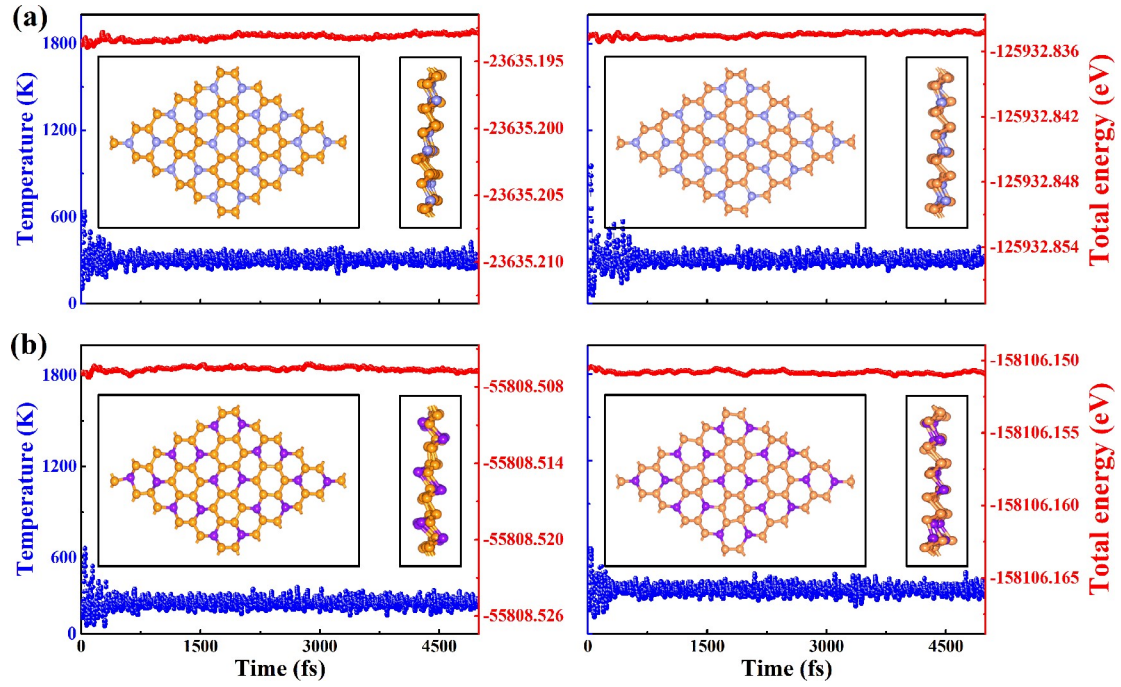


Fig. S7 Temperature and total energy during an ab initio molecular dynamics (AIMD) simulation of monolayer SiX_3 (a) and GeX_3 (b) ($X=\text{P, As}$) at 300 K. Inset: atomic structure after 5.0 ps.

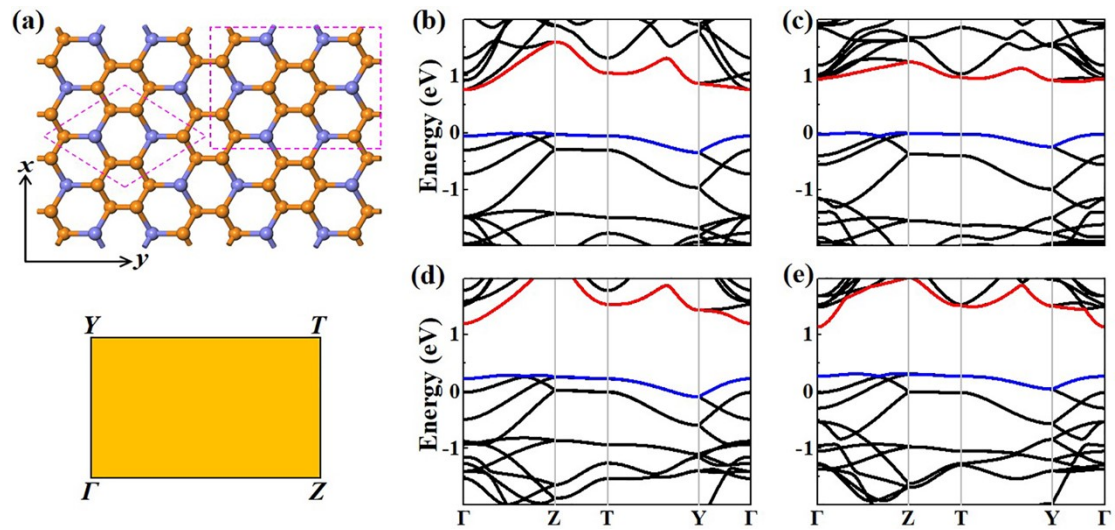


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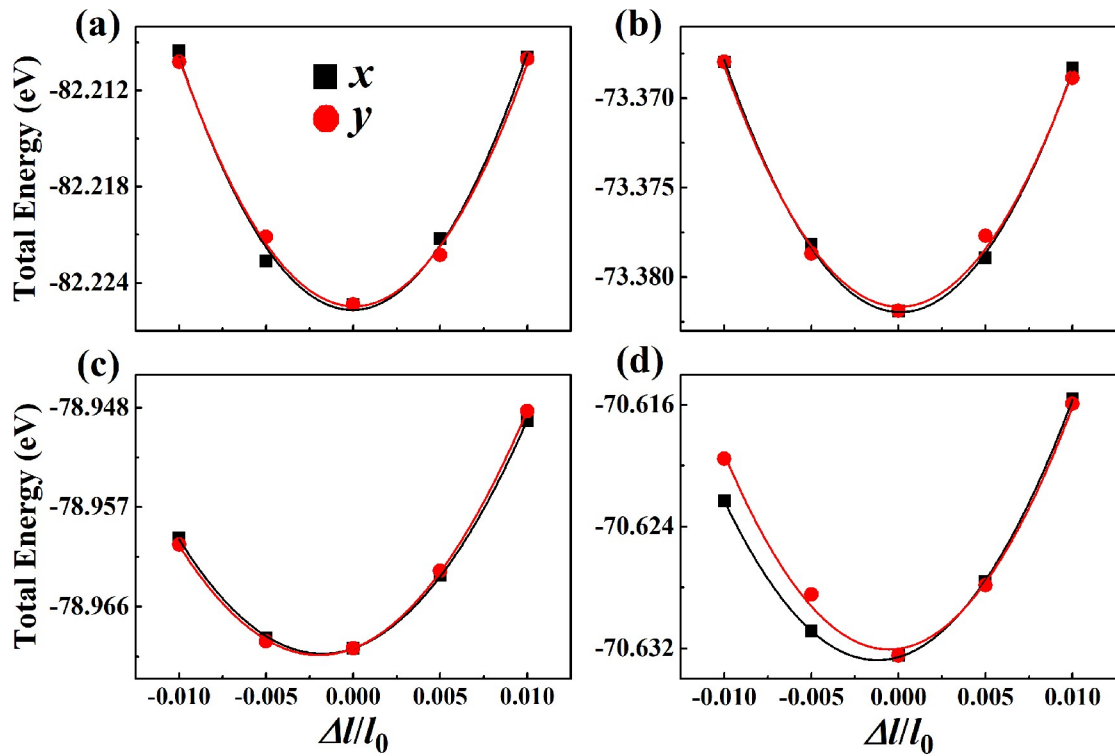


Fig. S9 2D elastic constant evaluation for the SiP₃ (a), SiAs₃ (b), GeP₃ (c) and GeAs₃ (d) monolayers. Total energy with respect to the lattice dilation Δ/l_0 . The polynomial fit of the data gives the 2D elastic constant.

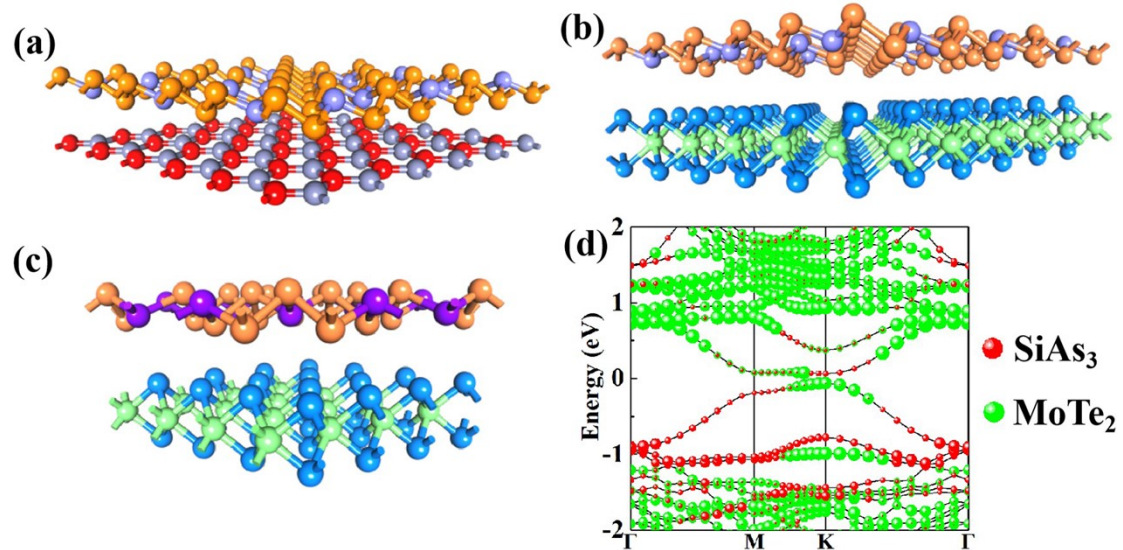


Fig. S10 SiP₃/ZnO (a), SiAs₃/MoTe₂ (b) and GeAs₃/WS₂ (c) type-II semiconductor heterojunctions. (d) Projected electronic structure of SiAs₃/MoTe₂ heterojunction calculated using HSE06 functional.

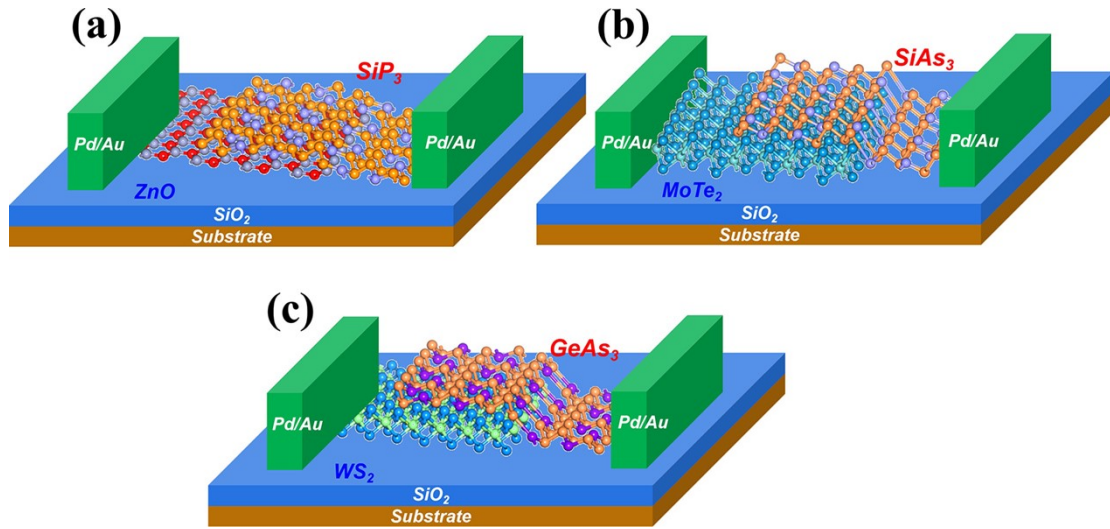


Fig. S11 The devices structures of SiP₃- (a), SiAs₃- (b) and GeAs₃-based (c) single-junction SCs.

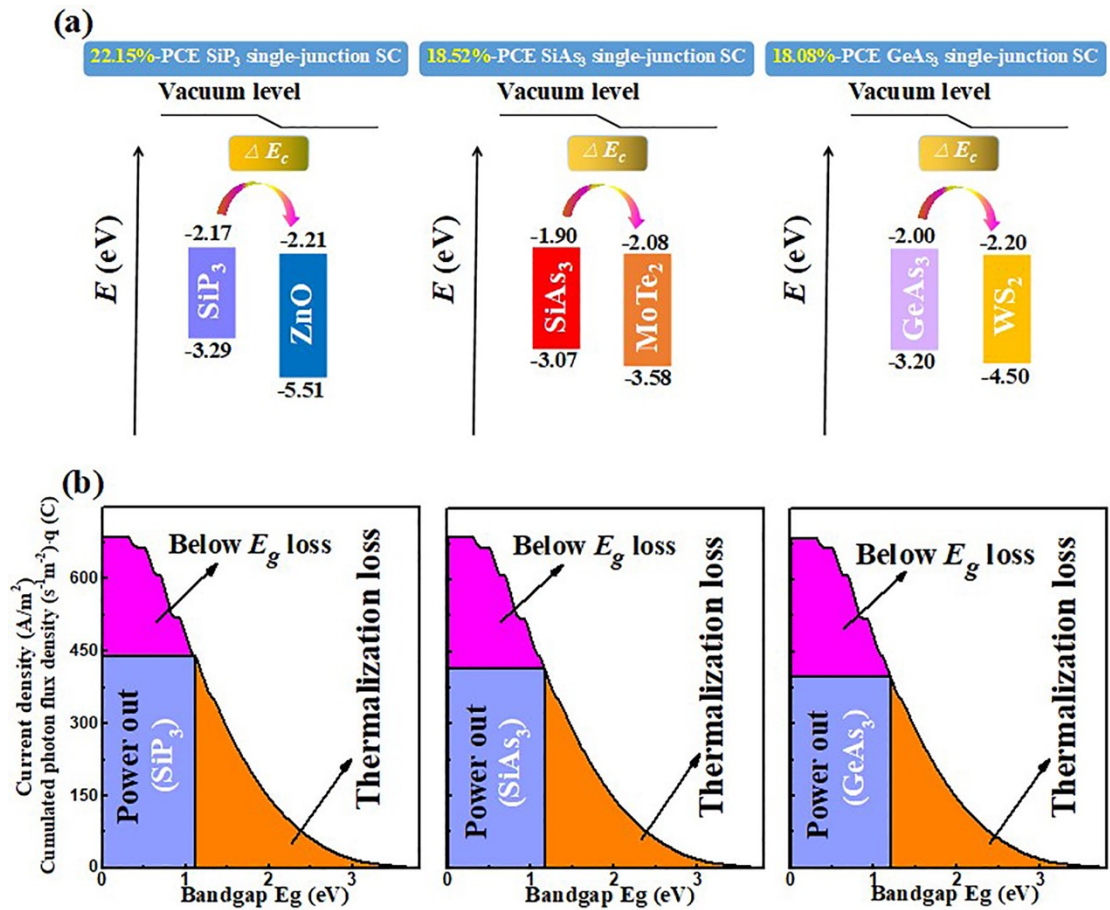


Fig. S12 (a) Energy diagram of the band alignment (HSE06 functional) for SiP₃-, SiAs₃- and GeAs₃-based single-junction SCs with 22.15%, 18.52% and 18.08% efficiency, respectively. (b) Thermalization loss and below- E_g loss in the SiP₃-, SiAs₃- and GeAs₃-based single-junction SCs.

Table S1 Structural parameters and electronic properties for relaxed AX₃ monolayers.

AX₃ (A=Si, Ge; X=P, As, Sb) monolayers											
	<i>a</i>	<i>h</i>	<i>l_{A-X}</i>	<i>l_{X-X}</i>	<i>E_{coh}</i>	<i>Eⁱ_{PBE}</i>	<i>Eⁱ_{HSE}</i>	<i>E^d_{HSE}</i>	<i>E_I</i>	<i>E_b</i>	<i>Q</i>
<i>SiP₃</i>	6.84	1.27	2.28	2.25	4.96	0.76	1.11	1.42	1.50	0.28	2.18
<i>SiAs₃</i>	7.33	1.49	2.40	2.51	4.41	0.89	1.17	1.22	1.64	0.59	1.14
<i>SiSb₃</i>	7.47	1.93	2.71	2.92	3.86	0	0	0	-	-	2.25
<i>GeP₃</i>	6.99	1.25	2.40	2.24	4.76	0.92	1.27	1.67	1.60	0.65	0.97
<i>GeAs₃</i>	7.46	1.47	2.51	2.50	4.19	0.84	1.20	1.50	2.02	0.42	0.55
<i>GeSb₃</i>	7.55	2.16	2.78	2.92	3.76	0	0	0	-	-	0.03

Lattice parameters *a*, bond lengths *l_{A-X}*, *l_{X-X}* in units of Å. Calculated indirect PBE bandgap *Eⁱ_{PBE}* and HSE06 bandgap *Eⁱ_{HSE}* associate with direct HSE06 bandgap *E^d_{HSE}* (in units of eV). The first bright excitonic energies (optical gap, *E_I* in units of eV) based on GW+BSE calculation. The cohesive energies *E_{coh}* (in units of eV/atom) are computed in reference to the spin-polarized A and X atoms. The exciton binding energies *E_b* in units of eV. Bader charges *Q* in units of e transformed from A to X atoms, while Sb to Si atom in monolayer SiSb₃.

Table S2. Calculated cohesive energy differences (ΔE_{coh}) are given in units of eV. ΔE_{coh} is based on the ABC stacking AX₃ monolayer calculated with PBE functional.

	<i>AAA</i>	<i>AAB</i>	<i>AAC</i>	<i>ABA</i>	<i>ABB</i>	<i>ABC</i>	<i>ACA</i>	<i>ACB</i>	<i>ACC</i>
<i>SiP₃</i>	0.007	0.097	0.097	0.097	0.097	0	0.097	0.114	0.097
<i>SiAs₃</i>	0.059	0.051	0.051	0.051	0.051	0	0.051	0.047	0.051
<i>SiSb₃</i>	0.056	0.060	0.060	0.060	0.060	0	0.060	0.067	0.060
<i>GeP₃</i>	0.029	0.088	0.088	0.088	0.088	0	0.088	0.118	0.088
<i>GeAs₃</i>	0.127	0.065	0.065	0.065	0.235	0	0.065	0.087	0.065
<i>GeSb₃</i>	0.071	0.065	0.065	0.065	0.065	0	0.065	0.104	0.065

Table S3 Effective mass *m_i^{*}/m₀*, DP constant *E_{li}* in eV, elastic constant *C_{2D}* in Jm⁻², and carrier mobility μ in cm²V⁻¹s⁻¹, at 300 K for electrons and holes in monolayer AX₃ (A=Si, Ge; X=P, As). (x=zigzag, y=armchair)

<i>Models</i>		<i>m_x[*]/m₀</i>	<i>m_y[*]/m₀</i>	<i>E_{Ix}</i>	<i>E_{Iy}</i>	<i>C_{x/2D}</i>	<i>C_{y/2D}</i>	$\mu_{x/2D}$	$\mu_{y/2D}$
<i>SiP₃</i>	<i>e</i>	0.46	0.18	12.24	8.66	61.86	60.25	66.71	334.05
	<i>h</i>	0.40	0.54	1.98	2.18	61.86	60.25	1798.31	1079.79
<i>SiAs₃</i>	<i>e</i>	1.40	0.03	8.05	2.09	47.18	46.28	51.30	31447.40
	<i>h</i>	0.62	0.93	1.49	0.84	47.18	46.28	955.00	1967.00
<i>GeP₃</i>	<i>e</i>	0.26	0.26	5.99	5.70	57.72	58.30	519.11	578.83

$GeAs_3$	h	0.56	1.03	2.45	2.23	57.72	58.30	488.15	322.01
	e	0.08	0.08	13.22	13.12	44.91	48.99	813.40	900.70
Si^{13}	h	0.68	0.91	0.56	0.54	44.91	48.99	5768.00	5036.00
	e								1,450
	h								450

Table S4 Confirmed existing SCs and the PCE measured under the global AM1.5 spectrum (1000 Wm^{-2}).

No.	Cell Structure	PCE (%)	References	Year
1	SiP_3/ZnO , $SiAs_3/MoTe_2$ and $GeAs_3/WS_2$ -based PV cells	22.15/18.52/18.08	This work	
2	BTPV-4F/PTB7-Th tandem SC	16.4	14	2021
3	n-CdS/p-Si heterojunction SC	18.72	15	2021
4	α -AsP/GaN SC	22.1	16	2016
5	$CH_3NH_3PbI_3$ SC	21	17	2014
6	$MoSe_2/\Psi$ -phosphorene SC	20.26	18	2017
7	TiNF/TiNCl SC	22	19	2018
8	$Ti_3C_2T_x$ -based silicon heterojunction SCs	20	20	2022
9	functionalized silicene/graphene SC	23.34	21	2021
10	Te/WTe ₂ , Te/MoTe ₂ heterojunction SCs	22.5/20.1	22	2019
11	α -Sb ₂ TeSe ₂ /HfSe ₂ , β -Sb ₂ TeSe ₂ /BiOI SCs	22.5/20.3	23	2021

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