

Two-dimensional nonlayered CuInSe₂ flakes with in-plane polarization for self-powered broadband Schottky photodetectors

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ABSTRACT: Ultrathin nonlayered chalcopyrite semiconductors provide a unique platform for integrating strong light-matter interactions, asymmetric crystal fields, and intrinsic defect engineering into high-performance optoelectronic devices. However, the device implementation has been hindered by controlled materials synthesis and reliable contact engineering. Herein, we demonstrate a molecular sieve-assisted chemical vapor deposition (CVD) strategy for the bottom-up growth of highly-crystalline two-dimensional (2D) CuInSe₂ flakes with well-defined (112) facet orientation and periodic Cu vacancy ordering. Comprehensive structural and spectroscopic characterizations reveal that the ordered cation sublattice breaks inversion symmetry, producing spontaneous in-plane polarization that can be electrically modulated via Cu⁺ ion migration. Coupled with a selected Au/CuInSe₂ Schottky contact, the intrinsic p-type conduction of 2D CuInSe₂ is verified, and the combined effects of polarization and junction fields enable efficient photocarrier separation and extraction under zero bias. The resulting self-powered photodetectors exhibit broadband operation across 450–1064 nm, with high responsivity of 0.6 A/W, detectivity of 2.97×10^{10} Jones, and external quantum efficiency of 119% under 637 nm illumination. Furthermore, the devices deliver a peak power conversion efficiency of 10.4% and a rapid photoresponse time of 85–103 ms. These results establish 2D chalcopyrite semiconductors as a versatile platform for next-generation energy-efficient optoelectronic technologies.

KEYWORDS: two-dimensional (2D) nonlayered materials, copper indium selenide, self-powered photodetection, in-plane polarization, Cu vacancies

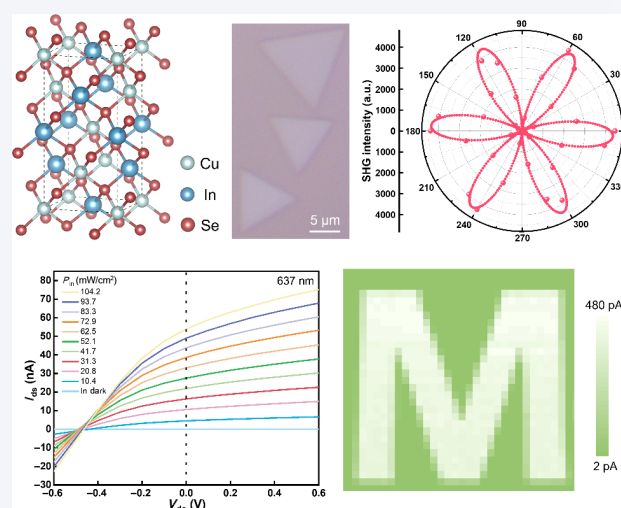
1 Introduction

Self-powered photodetectors, capable of operating without external power sources, have attracted significant interest for energy-efficient and autonomous applications such as wearable electronics, environmental monitoring, and the Internet of Things (IoT) [1–3].

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Unlike conventional photodetectors that require an applied voltage to separate photogenerated carriers, self-powered devices exploit built-in electric fields to drive charge separation and extraction under illumination. These internal fields can originate from band offsets at p-n or Schottky junctions [4–10], or from intrinsic spontaneous polarization in noncentrosymmetric materials [11, 12]. By leveraging such fields, self-powered photodetectors effectively suppress dark currents, enhance signal-to-noise ratios, and accelerate carrier transport, leading to high sensitivity and fast temporal response.

Two-dimensional (2D) semiconductors are particularly attractive for self-powered photodetection owing to their atomic thickness,

tunable band structures, and excellent compatibility with flexible substrates [13–15]. While considerable progress has been achieved with 2D layered van der Waals (vdW) semiconductors such as MoS_2 and WSe_2 , their absence of intrinsic polarization and moderate absorption coefficients limit the strength of built-in fields and ultimately constrain self-powered device performance [11, 12, 16]. These limitations have spurred growing interest in nonlayered ternary semiconductors, which often exhibit stronger optical absorption, richer defect chemistry, and intrinsic polar lattice structures [17–19]. Among them, semiconductors with chalcopyrite structure are especially promising since their asymmetric cation arrangements can break inversion symmetry and produce spontaneous polarization fields or enhanced piezoelectric responses that are absent in conventional vdW systems [20, 21]. In addition, the greater compositional diversity of chalcopyrites enables systematic bandgap and defect-state engineering across a broad spectral range, offering an effective pathway to tailor the performance of self-powered photodetectors. For example, copper indium selenide (CuInSe_2) is of particular interest due to its direct bandgap of ~ 1.2 eV, exceptionally high absorption coefficient, and long carrier diffusion length, all of which have established its success as a thin-film solar absorber [20, 22–25]. Extending these desired bulk properties into the 2D limit is expected not only to preserve strong optical absorption but also to unlock new functionalities, such as in-plane spontaneous polarization on the (112) facets that are weak or inaccessible in bulk crystals [26]. Despite these opportunities, realizing ultrathin single-crystalline CuInSe_2 remains challenging. Its strong three-dimensional bonding and lack of a natural cleavage plane make mechanical exfoliation impractical, while solution-based approaches often yield polycrystalline or defect-rich films with poorly defined facets [25, 27]. As a result, key aspects of 2D CuInSe_2 , including its band structure, intrinsic polarization, and Schottky contact, remain largely unexplored.

Here, we address these challenges by developing a molecular sieve-assisted chemical vapor deposition (CVD) approach to synthesize ultrathin and highly crystalline 2D CuInSe_2 flakes with well-defined (112) facet orientation and periodic Cu vacancy ordering. The use of molecular sieves effectively suppresses premature halide sublimation and promotes lateral rather than vertical growth, yielding uniform nonlayered flakes suitable for device integration. Detailed structural and spectroscopic analyses reveal broken inversion symmetry and spontaneous in-plane polarization, which in combination with an optimized Au/ CuInSe_2 Schottky interface, enable efficient broadband self-powered photodetection across 450–1064 nm. The resulting devices exhibit high responsivity and detectivity, as well as rapid response without external bias. These results establish polar nonlayered 2D chalcopyrite semiconductors as an appealing candidate for realizing high-performance and energy-efficient optoelectronic functionalities beyond the reach of conventional layered semiconductors.

2 Experimental

2.1 Molecular sieve-assisted CVD growth and transfer of CuInSe_2 flakes

2D CuInSe_2 flakes were synthesized using a dual-zone CVD process. An aqueous solution containing 2.5 mg/mL of CuCl and

7.5 mg/mL of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ was prepared, and 400 μL of the solution was drop-cast onto a clean silicon substrate (1 cm $\times$ 1.2 cm). After complete drying, an uniform layer of 3 Å molecular sieve powder (20 mg) was spread over the precursor film. Freshly cleaved mica substrate was positioned 5 mm above the precursor layer. 30 mg of selenium powder was placed in the upstream zone of the furnace. During growth, the selenium and metal precursor zones were gradually heated to 300 and 670 $^\circ\text{C}$ over 40 min, respectively. Argon was used as the carrier gas at a constant flow of 50 sccm, while 10 sccm H_2 was only introduced during the growth stage to assist chalcogenide formation. The growth was maintained for 20 min at the target temperatures, followed by natural cooling under Ar flow. For transfer, the as-grown CuInSe_2 flakes on mica were sequentially spin-coated with a poly(methyl methacrylate) (PMMA) layer (2500 rpm, 60 s) and a poly(propylene carbonate) (PPC) layer (2000 rpm, 45 s), with each layer baked at 90 $^\circ\text{C}$ for 10 min to remove residual solvent and solidify the film. The polymer/ CuInSe_2 stack was then gently detached from the mica substrate in deionized water. The floating stack was picked up by polydimethylsiloxane (PDMS) stamp and subsequently transferred onto the target substrate under an optical microscope. To improve adhesion, the transferred film was annealed at 90 $^\circ\text{C}$ for 1 h. Finally, the PPC and PMMA supporting layers were dissolved in acetone for 2 h, yielding clean and well-adhered CuInSe_2 flakes on the desired substrates.

2.2 Material characterizations

The morphology and thickness of the CuInSe_2 flakes and devices were examined by optical microscopy (OM), scanning electron microscopy (SEM, JSM-IT800, JEOL), and atomic force microscopy (AFM, Cypher ES, Oxford Instruments). The piezoresponse force microscopy (PFM) phase and amplitude curves were acquired from commercial scanning probe microscope (Dimension Icon, Bruker). Crystallographic structure was analyzed via X-ray diffraction (XRD, APEXII, Bruker), and atomic-scale lattice information and elemental composition were obtained from high-resolution transmission electron microscopy (HRTEM, Talos F200X G2, Thermo Fisher) coupled with energy-dispersive X-ray spectroscopy (EDS). The chemical composition and oxidation states were probed by X-ray photoelectron spectroscopy (XPS, SHIMADZU AXIS SUPRA). Optical properties were characterized using ultraviolet–visible–near infrared (UV–Vis–NIR) microspectrophotometry (CRAIC 20/30PV), as well as Raman and photoluminescence (PL) spectroscopy with a 532 nm excitation source (inVia confocal, Renishaw). SHG measurements were performed by an optical system (ScanPro Advance, Metatest) with a 1064 nm femtosecond laser (pulse width of 6 ps) as the excitation source.

2.3 Device fabrication and measurement

The patterned electrodes were fabricated by photolithography, metal deposition, and lift-off processes on the SiO_2/Si substrate. The 2D CuInSe_2 flakes were transferred onto the pre-patterned Au electrodes to construct the FET devices. Electrical and optoelectronic measurements were carried out under ambient conditions using a probe station (CRX-6.5K, Lake Shore). Electrical transport characteristics were recorded using a semiconductor parameter analyzer (Keithley 4200-SCS). For photoresponse studies, lasers with different wavelengths and tunable power densities were coupled into the device through optical fibers,

enabling systematic evaluation of broadband responsivity, detectivity, and temporal response.

3 Results and discussion

3.1 CVD growth and characterization of 2D nonlayered CuInSe₂ flakes

CuInSe₂ crystallizes in the chalcopyrite structure (space group *I*42*d*), belonging to the tetragonal crystal system. As shown in Fig. 1(a), the unit cell parameters are $a = b = 5.8$ Å and $c = 11.6$ Å, with copper and indium cations occupying distinct tetrahedral sites coordinated by selenium anions. The ordered cation sublattices not only ensure charge neutrality but also define the intrinsic bandgap of CuInSe₂ [28]. Thermodynamically favored copper vacancies (V_{Cu}) are frequently present in chalcopyrite CuInSe₂, acting as shallow acceptors and thereby imparting p-type conductivity [29, 30]. Beyond hole donation, such vacancies can also alter the dielectric screening, introduce localized states near the band edges, and broaden the absorption spectrum [31, 32], collectively influencing carrier dynamics and the optoelectronic response. 2D nonlayered CuInSe₂ flakes were synthesized by a molecular sieve-assisted CVD method (see Experimental section). In this process, CuCl and InCl₃·4H₂O serve as metal precursors and Se powder as the chalcogen source. The 3 Å molecular sieves suppress premature sublimation and provide a steady release of the halide precursors at the growth temperature, which promotes anisotropic lateral expansion over vertical thickening [33, 34]. OM images of the triangular flakes (Fig. 1(b)) show uniform color contrast across large lateral dimensions, implying high phase purity and the 2D nature of the synthesized samples. Such uniformity is consistent with homogeneous nucleation and near-steady-state growth

kinetics, rather than island-like growth [35]. A statistical analysis reveals that most of the flakes fall within a lateral size range of 6–20 μm (Fig. S1 in the Electronic Supplementary Material (ESM)). AFM (Fig. 1(c)) reveals smooth surfaces with a representative thickness of ~20.7 nm and a root mean square (RMS) roughness of ~1.2 nm. Notably, flakes with thicknesses below 10 nm are also obtained (Fig. S2 in the ESM), underscoring the robustness of the molecular sieve strategy for producing ultrathin nonlayered semiconductors. For comparison, the growth without molecular sieves, with SiO₂/Al₂O₃ powders, and with 5 Å molecular sieve powders was also conducted (Fig. S3 in the ESM). The results show that although CuInSe₂ could still be formed, the overall 2D yield dropped markedly and the flakes were thicker. More importantly, due to the distinct chemical component of the molecular sieves (K_nNa_{12-n}[(AlO₂)₁₂(SiO₂)₁₂]) from the SiO₂/Al₂O₃ powders, the alkali Na element released from the molecular sieves during high-temperature CVD growth was supposed to assist in the formation of 2D CuInSe₂ flakes with consistently exposed (112) surfaces. The growth substrate after CVD process was characterized by XPS, where the Na signal is clearly detected (Fig. S4 in the ESM). Previous studies showed that Na incorporation into CuInSe₂, typically via substitution at Cu sites, can modify the electronic structure and lead to bandgap widening [36, 37]. However, for our synthesized flakes, the bandgap values extracted from optical absorption and PL measurements are in excellent agreement with those of pristine CuInSe₂ (1.24 eV, shown later), suggesting that significant Na substitution into the lattice is unlikely. Therefore, the Na species primarily act as a surface-active species to promote 2D growth rather than as a dopant [38]. Raman spectroscopy was used to probe lattice vibrations of the 2D CuInSe₂ flakes using a 532 nm excitation laser. As shown in Fig. 1(d), five distinct Raman peaks are observed, corresponding to the characteristic phonon modes of

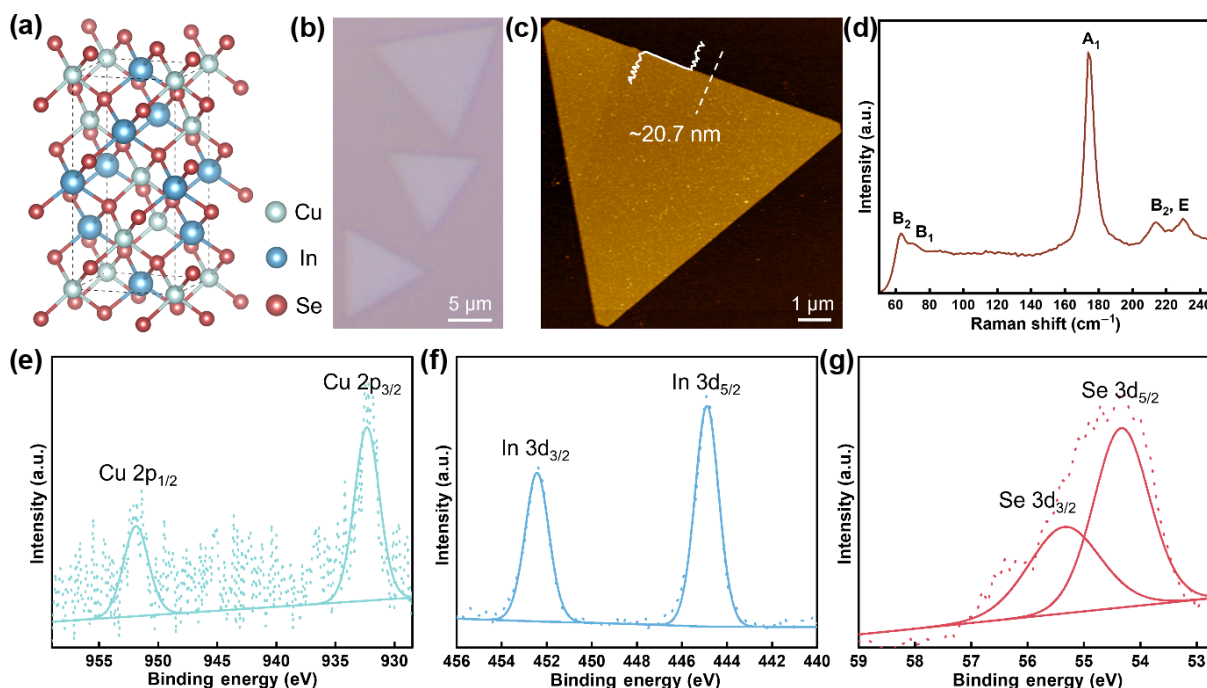


Figure 1 Structural and chemical characterization of CuInSe₂ flakes. (a) Crystal structure of tetragonal CuInSe₂, showing ordered distribution of Cu⁺ and In³⁺ cations within Se²⁻ tetrahedral coordination. The lattice constants are $a = b = 5.8$ Å and $c = 11.6$ Å. (b) OM image of the CVD-grown CuInSe₂ flakes. (c) AFM height image of a representative CuInSe₂ flake with a thickness of ~20.7 nm. (d) Raman spectrum of one CuInSe₂ flake, showing the dominant A₁ mode at 174 cm⁻¹ and additional B and E modes at 63, 70, 214, and 230 cm⁻¹. (e)–(g) High-resolution XPS spectra of Cu 2p, In 3d, and Se 3d core levels, confirming the presence of Cu⁺, In³⁺, and Se²⁻ chemical states.

the chalcopyrite lattice [39]. The dominant A_1 mode at $\sim 174\text{ cm}^{-1}$ is assigned to the symmetric axial Se vibrations along the c -axis and serves as a fingerprint for phase identification. Additional peaks at ~ 63 , 70 , 214 , and 230 cm^{-1} arise from B and E modes involving coupled cation-anion vibrations. The clear presence of these weaker peaks indicates that the long-range order of the chalcopyrite lattice is preserved in the ultrathin thickness, with no evidence of amorphization or surface reconstruction that is typically seen in defective thin films. A highly consistent Raman spectrum was also obtained from the hexagonal flakes (Fig. S5 in the ESM), verifying that the triangular and hexagonal morphological variation is not associated with differences in chemical composition. The chemical composition and oxidation states of the 2D CuInSe_2 flakes were clarified using high-resolution XPS. As presented in Fig. 1(e), the Cu 2p core-level spectrum reveals two peaks located at ~ 932.4 and $\sim 952.2\text{ eV}$, corresponding to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ components with a spin-orbit splitting of 19.8 eV . The In 3d spectrum (Fig. 1(f)) exhibits two peaks at 444.6 and 452.2 eV , corresponding to In $3d_{5/2}$ and In $3d_{3/2}$ levels, respectively, characteristic of trivalent indium. The Se 3d spectrum (Fig. 1(g)) displays two deconvoluted peaks at ~ 54.3 and $\sim 55.3\text{ eV}$, attributed to the Se $3d_{5/2}$ and Se $3d_{3/2}$ spin-orbit components, respectively. Quantification of the integrated peak areas indicates a slightly Cu-deficient composition, consistent with a comparatively weaker Cu signal and the formation of V_{Cu} . Such Cu deficiency typically yields shallow acceptors rather than deep traps and therefore beneficially supports p-type transport [28–30, 32].

XRD was performed on flakes transferred to indium tin oxide (ITO) substrates to determine the crystallographic orientation. As shown in Fig. 2(a), a strong diffraction peak at $2\theta \sim 26.7^\circ$ is revealed, indexed to the (112) plane of chalcopyrite CuInSe_2 (JCPDS No. 40-1487), indicating preferential exposure of the (112) facet. The rocking curve exhibits a narrow full-width at half maximum (FWHM) of 0.35° (Fig. S6 in the ESM), which provides strong evidence for the high crystalline across the sampled region. The densely packed (112) plane is also anticipated to exhibit pronounced in-plane polarization due to alternating cation ordering. A minor peak at $\sim 30.7^\circ$, attributed to the (200) plane, likely originates from secondary deposition of CuInSe_2 particles or nanowires (Figs. S1 and S7 in the ESM). No signatures of secondary phases such as Cu_2Se or In_2Se_3 are detected, confirming the high chemical purity of the sample. The atomic-scale features of the flakes were further revealed by TEM. As shown in Fig. 2(b), HRTEM image displays well-ordered lattice fringes with an interplanar spacing of 0.21 nm , corresponding to the $(2\bar{2}0)$ planes. The selected area electron diffraction (SAED) pattern in Fig. 2(c) exhibits sharp and hexagonally arranged diffraction spots, further confirming the single-crystalline nature of the CuInSe_2 flakes. The primary diffraction spots (outlined by red dashed hexagon) are indexed to the $(2\bar{2}0)$ planes, while notably additional weak diffraction spots, as outlined by green dashed hexagon (Fig. 2(c)), suggest the presence of ordered V_{Cu} with a doubled superlattice periodicity of $\sim 0.42\text{ nm}$ [20]. This structure is also corroborated by the fast Fourier transform (FFT) and inverse FFT (iFFT) filtered image analyses (Fig. S8 in the ESM). Such ordered cationic vacancies are commonly observed in vacancy-rich metal chalcogenides [40, 41]. EDS analysis (Fig. 2(d)) confirms the presence of Cu, In, and Se elements, with an approximate atomic ratio of $0.8:1:2$, suggesting a 20% Cu deficiency in the lattice. Elemental mapping (Figs. 2(e)–2(h)) reveals an uniform spatial

distribution of all three elements, with no signs of phase segregation or compositional clustering. Such homogeneity is crucial for reproducible device performance and indicates that V_{Cu} are evenly distributed rather than agglomerated, thereby minimizing potential scattering centers.

3.2 Schottky-type contact and p-type carrier transport

The verification of the intrinsic p-type transport in 2D CuInSe_2 has been hindered by the lack of large single-crystalline flakes and by difficulties in selecting contact metals that can probe the intrinsic electronic behavior without introducing uncontrolled barriers. The availability of high-quality 2D single-crystal CuInSe_2 flakes with ordered V_{Cu} here enables a direct study of carrier transport with a field-effect transistor (FET) configuration. Because contact energy barriers profoundly influence the measured conductivity and photoresponse, the band structure of the synthesized flakes was first determined to guide the selection of metal contacts. UV–Vis–NIR absorption spectroscopy (Fig. 3(a)) reveals a clear absorption edge near 1000 nm , corresponding to a bandgap of $\sim 1.24\text{ eV}$, which is also supported by the density functional theory (DFT) calculations (Fig. S9 in the ESM). This value is consistent with that of CuInSe_2 bulk materials and polycrystalline films [22–25], indicating that negligible quantum confinement effects occur at the thicknesses examined. An extended absorption tail into the NIR region reflects defect-assisted transitions associated with V_{Cu} , which introduce shallow acceptor levels [31]. Room-temperature PL (inset of Fig. 3(a)) under 532 nm excitation shows an emission peak at 1.24 eV , indicative of direct band-to-band recombination that is in accordance with the absorption edge. Ultraviolet photoelectron spectroscopy (UPS) was conducted on flakes transferred to ITO to determine energy-level alignment. The secondary electron cutoff energy is $\sim 16.7\text{ eV}$ (Fig. 3(b)), yielding a work function (Φ_s) of $\sim 4.52\text{ eV}$. The valence band maximum (VBM) lies 0.35 eV below the Fermi level (Fig. 3(c)), placing the VBM at $\sim 4.87\text{ eV}$ and the conduction band minimum (CBM) at $\sim 3.63\text{ eV}$, consistent with p-typed band structures. This band energy level suggests that a high work-function metal should be chosen to minimize hole injection barriers and reveal majority-carrier transport. Accordingly, Au ($\Phi_M \sim 5.1\text{ eV}$) was selected to align with the VBM and minimize the Schottky barrier. To further suppress Fermi-level pinning commonly induced by high-energy metal deposition process, the CuInSe_2 flakes were dry-transferred onto pre-patterned Au electrodes, producing cleaner interfaces and better preserving channel properties [42]. The estimated hole barrier height is $\sim 0.23\text{ eV}$ according to the Schottky–Mott law [42]. The band alignment before and after Au-2D CuInSe_2 contact is schematized in Fig. 3(d). A small Schottky barrier forms due to slight energy mismatch, yet remains sufficiently low to allow efficient hole injection and rapid separation of photogenerated carriers under illumination. Figures 3(e) and 3(f) display the output and transfer characteristics of the FET device (OM image shown in the inset of Fig. 3(e)), respectively. A pronounced rectification behavior in the source-drain current–voltage ($I_{\text{ds}}-V_{\text{ds}}$) curves indicates a Schottky-dominated transport regime (Fig. 3(e)). Increasingly negative gate voltages (V_g) enhance I_{ds} , confirming p-type transport behavior (Figs. 3(e) and 3(f)). The hole mobility and current on/off ratio were calculated to be $2.6 \times 10^{-5}\text{ cm}^2/(\text{V}\cdot\text{s})$ and 8.13 , respectively. These relatively low metrics were examined by checking the device with SEM and AFM (Fig. S10 in the ESM). The results show that an interfacial air gap with a low dielectric constant is present between

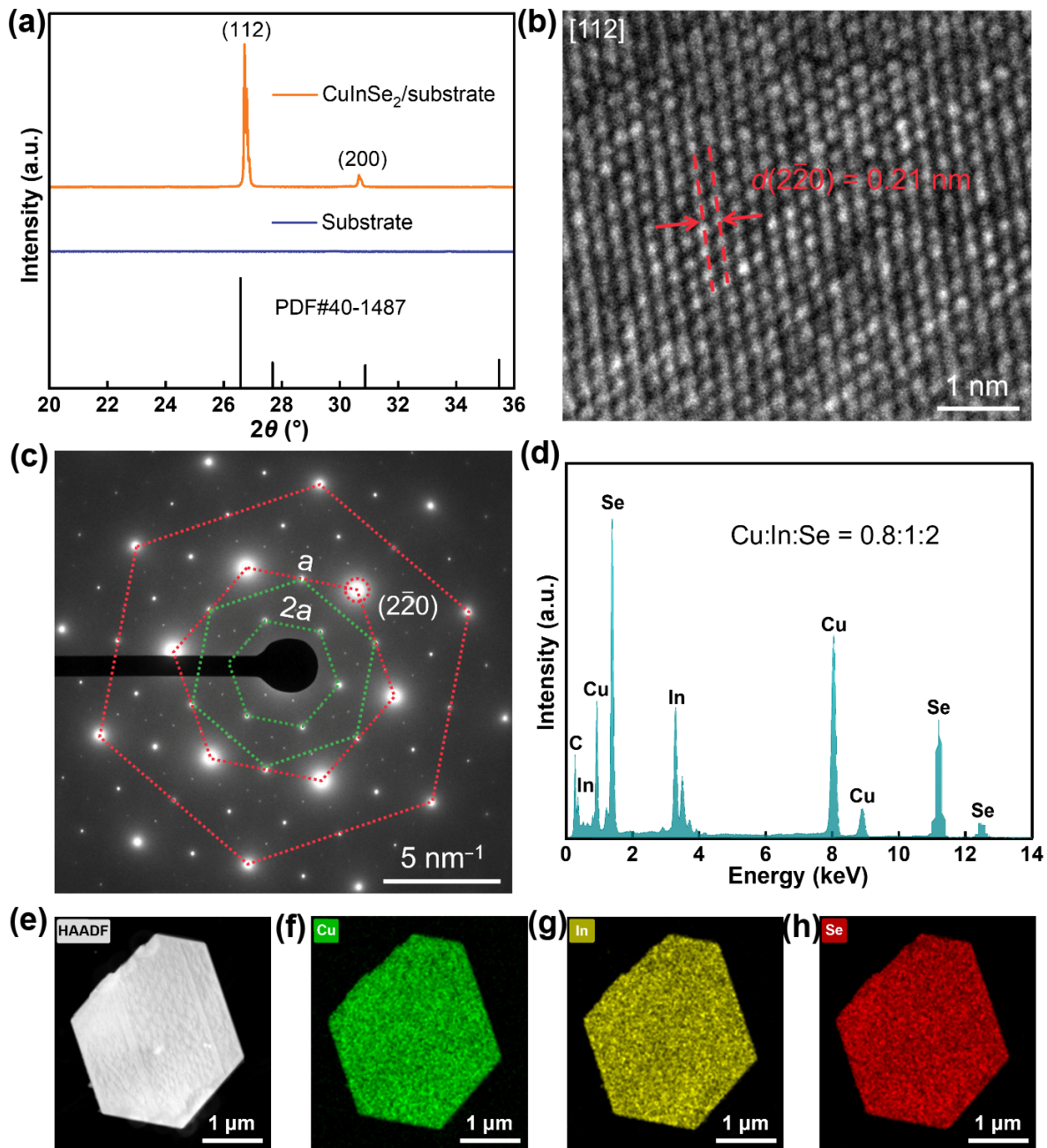


Figure 2 Microstructural and compositional analysis of CuInSe₂ flakes. (a) XRD pattern of CuInSe₂ flakes transferred onto an ITO substrate. (b) HRTEM image showing atomically resolved lattice fringes. (c) SAED pattern with indexed (220) reflections and additional superlattice spots ascribing to V_{Cr}. (d) EDS spectrum confirming the presence of Cu, In, and Se. (e)–(h) EDS elemental mapping images of Cu, In, and Se, demonstrating uniform distribution of all elements and ruling out significant phase segregation or non-stoichiometry.

the CuInSe₂ flake and the dielectric layer (SiO₂), which significantly weakens the electrostatic coupling between the gate electrode and the channel and thus suppress the gate-voltage tunability. As such, we also fabricated FET devices in which the metal electrodes were transferred onto the CuInSe₂ flakes that were already lying on the SiO₂/Si substrate, ensuring close contact between the flakes and the dielectric layer (Fig. S11 in the ESM). In this device configuration, we observed a significantly improved hole mobility of ~ 0.06 cm²/(V·s), which is increased by over three orders of magnitude. Despite this improvement, the metrics remain lower than those of many reported 2D semiconductors. This can be attributed to the theoretically lower value restricted by the heavy hole mass [43], as

well as the abundant defects within the flakes and Schottky contact resistance, which can be further improved by optimizing the metal-semiconductor contact to form an Ohmic contact, employing a high-*k* dielectric layer with an atomically smooth interface, and by reducing defect density through material growth optimization or surface passivation strategies. Collectively, these results validate the combined strategy of CVD-grown 2D CuInSe₂ and optimized Au contacts to achieve majority carrier-dominated transport, a prerequisite for efficient self-powered photodetection.

3.3 Broken in-plane inversion symmetry

The chalcopyrite lattice is derived from zinc blende structure but

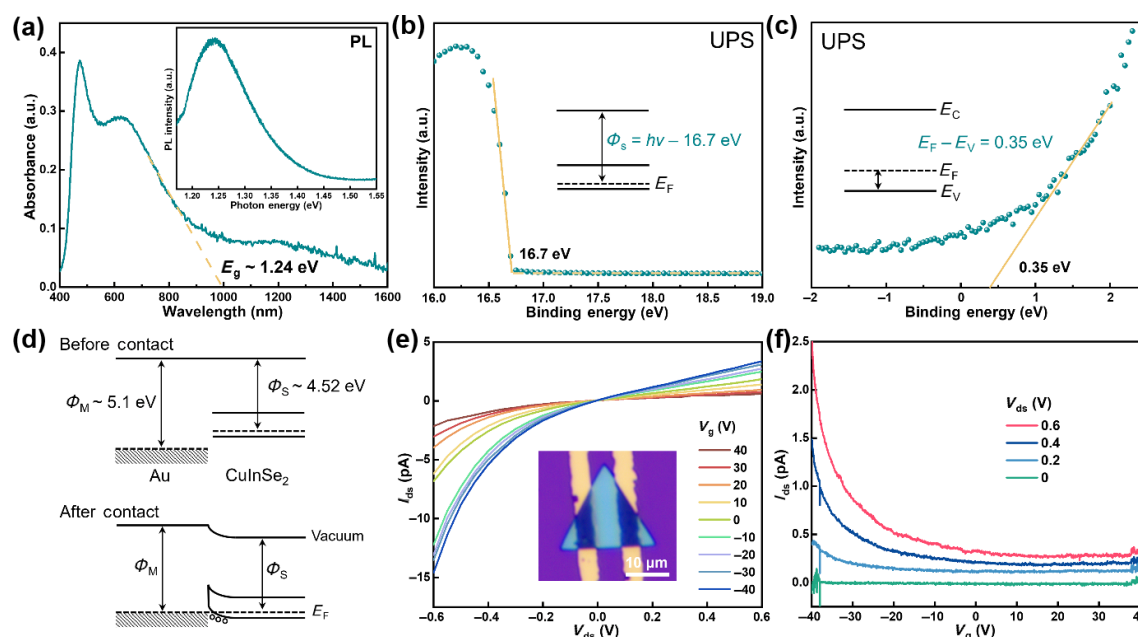


Figure 3 Band structure and electrical transport properties of CuInSe₂-based devices. (a) The micro-zone absorbance curve of the 2D CuInSe₂ flake. Inset shows the room-temperature PL spectrum of the 2D CuInSe₂ flake. (b) Secondary electron cutoff region in the UPS spectrum of CuInSe₂. (c) Valence band spectrum from UPS. (d) Band alignment at the Au/CuInSe₂ interface before and after contact. (e) Output characteristics (I_{ds} - V_{ds}) of a back-gated FET based on a triangular 2D CuInSe₂ flake, exhibiting diode-like rectification and gate-tunable asymmetry due to Schottky contact behavior. Inset shows the OM image of the measured device. (f) Transfer characteristics of the device under different V_{ds} values, displaying strong p-type gate modulation.

exhibits cation ordering, with Cu⁺ and In³⁺ occupying distinct tetrahedral sites. This ordering breaks inversion symmetry at the atomic level and generates the possibility of spontaneous polarization, particularly on the (112) planes predominantly exposed by the CVD-grown flakes [26]. Figure 4(a) depicts the atomic arrangement within the (112) plane, highlighting the absence of centrosymmetry both in-plane and along the [112] direction. Such symmetry breaking underlies second-order nonlinear optical responses and can potentially enable the bulk photovoltaic effect (BPVE), wherein carriers are driven by asymmetric internal potentials without an external bias [11, 12, 44, 45]. SHG measurements were performed on the CuInSe₂ flake shown in the inset of Fig. 4(b) under 1064 nm excitation. A clear SHG peak is observed at 532 nm (Fig. 4(b)), characteristic of frequency doubling in a noncentrosymmetric crystal. The SHG intensity scales quadratically with excitation power that can be well-fitted by $I \propto P^\theta$ (Fig. 4(c)), yielding an exponent θ value of ~ 2 , as expected for a second-order process. The SHG intensity mapping (inset of Fig. 4(c)) reveals a spatially uniform signal across the flake, indicating homogeneous nonlinear susceptibility and thickness. The polarization-resolved SHG was conducted in both parallel (//) and perpendicular (⊥) detection configurations (Figs. 4(d) and 4(e)), revealing six-lobed polar patterns that are rotated by 30°, consistent with the expected in-plane anisotropy of the chalcopyrite (112) surface. The angular dependence of SHG intensity is well described by Eq. (1) [46]

$$I(2\omega) = |E(2\omega)|^2 = C^2 \chi^{(2)}(\omega)^2 \cos^2(3\Phi + \Phi_0) \quad (1)$$

where C is a proportionality factor accounting for local-field effects, Φ is the incident polarization angle, and Φ_0 defines the initial crystallographic orientation. The noncentrosymmetric lattice implies the presence of in-plane spontaneous polarization, and the magnitude of this polarization is closely related to the asymmetry of

the local electric fields and the degree of dipole moment imbalance in the crystal lattice. The presence of in-plane polarization could be further supported by the clear hysteresis and butterfly-shaped loops in the PFM phase and amplitude tests (Fig. S12 in the ESM). A clear 180° phase switching and consistent butterfly-shaped curves are always observed when the tested temperature is decreased, which is a hallmark of polarization switching and is distinct from electrostatic artifacts or ionic migration effects. Apart from SHG and PFM, the presence of a macroscopic in-plane polarization could be further supported by characterizing the devices with symmetric contacts (Fig. 4(f)). These devices are characterized by a symmetric I_{ds} - V_{ds} curve passing through the origin in dark. When the device is illuminated, a measurable photocurrent is still generated, which increases with increasing light intensity at $V_{ds} = 0$ V. In this case, the photocurrent in the absence of external bias can only originate from the intrinsic in-plane polarization field of the CuInSe₂ channel. This behavior is analogous to the BPVE observed in noncentrosymmetric crystals, where photocurrent arises from the asymmetric crystal field rather than from p-n junctions or metal-semiconductor interfaces. To examine its tunability by Cu⁺ migration, voltage pulses were applied to the drain terminal of the CuInSe₂ FETs. As shown in Fig. 4(g), as the pulse magnitude increased from 0.6 to 4.5 V, the linear I_{ds} - V_{ds} curves shifted progressively away from the initial one, evidencing electric field-induced enhancement of in-plane polarization, plausibly mediated by Cu⁺ ion migration [30, 32]. The reversible migration of Cu⁺ ions under an electric field in such 2D CuInSe₂ flakes was further supported by bidirectional I_{ds} - V_{ds} sweeps. As shown in Fig. S13 in the ESM, a clear hysteresis loop was observed during the positive and negative V_{ds} sweeps, further supporting the reversible ionic-electronic coupling characteristic in CuInSe₂-based chalcopyrites [19]. To quantitatively evaluate the timescale, reversibility, and stability of this ionic process, we applied voltage pulses of gradually increasing amplitude to the device (Fig. S14 in

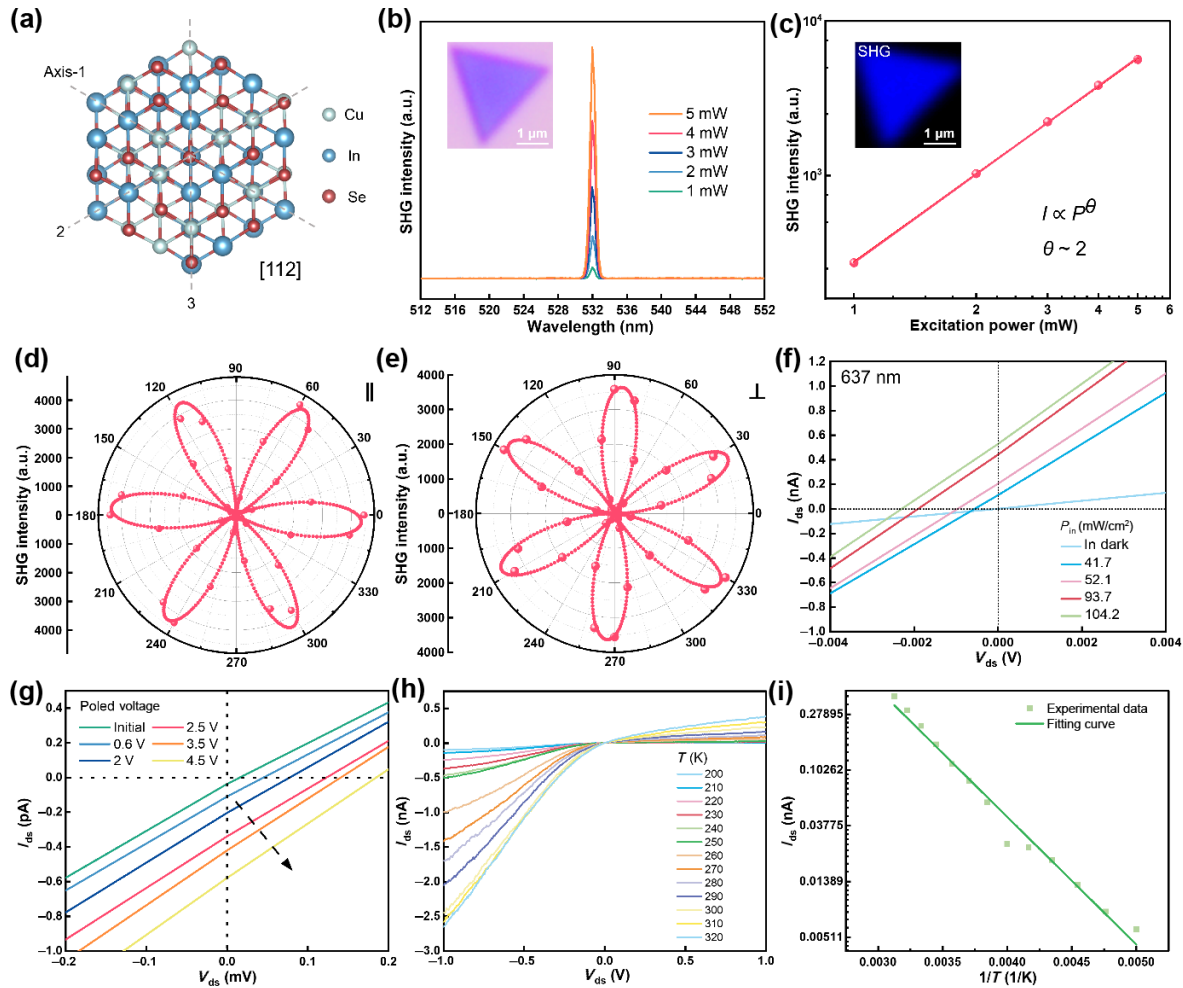


Figure 4 In-plane polarization of 2D CuInSe₂ flake. (a) Atomic structure of the CuInSe₂ lattice viewed along the [112] direction, showing the noncentrosymmetric in-plane atomic arrangement. (b) and (c) Power-dependent SHG intensity evolution under 1064 nm excitation. The inset in (b) shows the OM image of the CuInSe₂ flake for SHG test and the inset in (c) shows the SHG intensity mapping of this flake. Polarization-resolved SHG patterns under (d) parallel and (e) perpendicular configurations, both exhibiting six-lobed symmetry, consistent with the chalcopyrite structure and confirming anisotropic nonlinear optical response from the (112) surface. (f) I_{ds} - V_{ds} curves of one symmetrically-contacted device measured in dark and under different light intensities. (g) I_{ds} - V_{ds} characteristics of CuInSe₂ devices after applying increased poling bias, showing asymmetric polarization behavior that gradually deviates from the initial one, indicative of internal dipole alignment and field-induced Cu⁺ ion migration. (h) Temperature-dependent I_{ds} - V_{ds} characteristics of the device measured from 200 to 320 K. (i) Arrhenius plot of I_{ds} versus $1/T$ extracted at $V_{ds} = 1$ V, and the linear fitting curve used to determine the effective activation energy E_a .

the ESM), with both pulse width and interval fixed at 100 ms. For pulse amplitudes ranging from 1 to 4 V, the current rapidly reached a stable value upon application of each pulse, indicating that Cu⁺ migration occurs within a timescale comparable to the device response time. Repeated pulses at the same voltage produced nearly identical current level, suggesting that the redistributed Cu⁺ configuration is stable after each pulse, while recovery to the initial state requires an opposite bias. Furthermore, we observed that Cu⁺ migration contributes to enhanced channel conductivity: The current increases from 0.02 nA at 1 V (0.02 nA/V) to 0.055 nA at 2 V (0.0275 nA/V), 0.12 nA at 3 V (0.04 nA/V), and 0.22 nA at 4 V (0.055 nA/V). The progressive increase in normalized conductance with higher pulse voltage supports the conclusion that additional Cu⁺ ion migration contributes to the observed electrical tunability. Cu⁺ migration in CuInSe₂ can proceed through two well-established pathways: (i) a V_{Cu} -mediated mechanism, and (ii) an interstitial mechanism, with an activation energy (E_a) of 1.0–1.3 and 0.2 eV, respectively [47–51]. We determined the E_a of our devices by measuring and analyzing the temperature-dependent output

characteristics (Fig. 4(h)). The I_{ds} obtained at various temperatures could be well-fitted using an Arrhenius-type relation, given by

$$I(T) = I_0 e^{\left(-\frac{E_a}{k_B T}\right)} \quad (2)$$

where $I(T)$ denote I_{ds} at temperature T , I_0 is the pre-exponential factor, and k_B is the Boltzmann constant (Fig. 4(i)). The extracted E_a of 0.194 eV lies within the range expected for thermally activated Cu⁺ migration and is in good agreement with the reported migration barrier for interstitial Cu transport. Combined with the observed hysteresis behavior and its dependence on poled voltages, these results indicate that Cu⁺ migration contributes to the electrically tunable polarization, while electronic transport remains the dominant conduction pathway.

3.4 Self-powered photodetection

The coexistence of strong light absorption, an internal polarization field, and a clean Au-CuInSe₂ Schottky interface enables 2D CuInSe₂ flakes to function as both photovoltaic devices and self-

powered photodetectors. As shown in Fig. 5(a), the $I_{\text{ds}}-V_{\text{ds}}$ characteristics under 637 nm laser illumination display an obvious photovoltaic effect at all tested light power densities. The nearly linear increase in short-circuit current (I_{sc}) with incident light power densities confirms efficient photocarrier generation and separation, free from trap-mediated recombination (Fig. 5(b)). In contrast to biased phototransistors, the built-in fields from the Schottky barrier and spontaneous polarization suffice to drive carriers to the contacts without external bias, reducing power consumption and dark noise current. The open-circuit voltage (V_{oc}) and fill factor (FF) remain stable at ~ 0.48 V and 35%, respectively, as the light power densities increase (Fig. 5(c)). The calculated maximum power conversion efficiency (PCE) reaches 10.4% at an incident power density of 41.7 mW/cm^2 (Fig. S15 in the ESM), superior to most reported 2D semiconductors in planar device configurations [2, 4, 6, 13, 52–55]. This underscores that ultrathin CuInSe₂ retains its classical photovoltaic properties even at reduced thickness. Importantly, measurable photocurrent is observed under zero bias, confirming self-powered operation. The key figures of merit, responsivity (R), specific detectivity (D^*), and external quantum efficiency (EQE) are calculated using $R = I_{\text{ph}}/(P_{\text{in}}A)$, $D^* = R \cdot A^{1/2}/(2eI_{\text{dark}})^{1/2}$, and $\text{EQE} = Rhc/e\lambda$, respectively, where I_{ph} is the photocurrent, P_{in} is the incident light power density, A is the effective illumination area, and I_{dark} is the dark current. As shown in Fig. 5(d), the device delivers a stable R of $\sim 0.6 \text{ A/W}$, D^* of 2.97×10^{10} Jones, and EQE of $\sim 119\%$ across a broad light intensity range.

The relatively constant R , D^* , and EQE as a function of light intensity are ascribed to the photovoltaic-typed nature of the devices. The EQE value above unity arises from asymmetric carrier dynamics and multiple transits before recombination, frequently associated with strong built-in fields and extended carrier lifetimes [56]. Multiple devices were also fabricated under similar conditions (Fig. S16 in the ESM), which exhibit comparable performance, indicating the reproducibility of the materials growth and device fabrication processes. The photodetection metrics are comparable with the reported self-powered photodetectors based on 2D semiconductor channels (Table 1) [54, 57–63], owing to the strong optical absorption of CuInSe₂ and the defect-assisted photoconductive gain mechanism associated with Cu vacancies and related defect states. Broadband response is observed from 450 to 1064 nm (Fig. 5(e) and Figs. S17 and S18 in the ESM), enabled by the wide absorption spectrum of 2D CuInSe₂ flakes (Fig. 3(a)). Under repeated 637 nm on/off illumination cycling, the device retains stable self-powered performance (Fig. S19 in the ESM), with rise and decay time of ~ 85 and ~ 97 ms, respectively (Fig. 5(f)). Comparable response time is recorded for 450, 785, and 1064 nm excitation (Fig. S20 in the ESM), indicating a bias-free and rapid photoresponse over the visible-NIR range. The fast switching highlights the role of Schottky and polarization fields in suppressing trapping and enabling efficient carrier extraction without external bias. Note that a trade-off between R , D^* , EQE, and response speed exists in these devices, i.e., the photogain that enables efficient

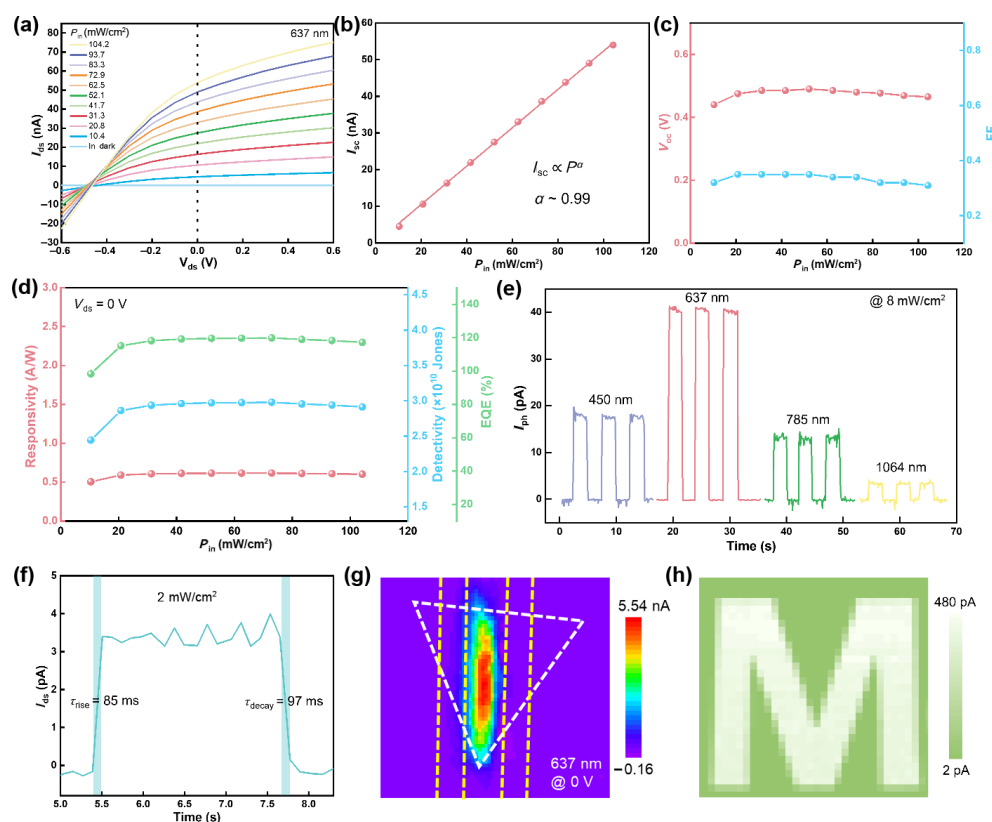


Figure 5 Self-powered broadband photodetector based on Au/CuInSe₂ Schottky junction. (a) The $I_{\text{ds}}-V_{\text{ds}}$ curves under 637 nm laser illumination with increasing power densities, showing a photovoltaic response behavior. (b) I_{sc} as a function of incident laser power density under 637 nm illumination. The linear fitting yields an ideal power exponent of ~ 0.99 . (c) V_{oc} and FF as a function of incident laser power density under 637 nm illumination. (d) The calculated R , D , and EQE at zero bias ($V_{\text{ds}} = 0$ V). (e) Spectral response of the device across 450–1064 nm under $V_{\text{ds}} = 0$ V, confirming a self-powered broadband photodetection capability. (f) Temporal response curve under 637 nm light at 2 mW/cm^2 , showing a fast rise time of ~ 85 ms and decay time of ~ 97 ms. (g) Photocurrent mapping of the device under 637 nm laser illumination at $P_{\text{in}} = 6.37 \text{ W/cm}^2$ and $V_{\text{ds}} = 0$ V. The 2D CuInSe₂ flake and a pair of Au electrodes are outlined by white and yellow dashed lines, respectively. (h) Demonstration of a letter “M” imaging under spatially modulated laser excitation using a shallow mask, showcasing a potential self-powered imaging application.

Table 1 The key self-powered photodetection performance metrics comparison between this work and other reported 2D photodetectors with a single active channel material

2D channel	λ (nm)	R (mA/W)	D' (Jones)	Response time (ms)	Mechanism	Ref.
MoS ₂	532	280	7.6×10^{10}	0.224	Plasma treatment and asymmetric electrodes	[57]
MoS ₂	1310	680	1.89×10^{12}	—	Internal photoemission	[58]
MoSe ₂	470	3.4	4.75×10^{10}	—	Asymmetric electrodes	[59]
MoSe ₂	830	280	6.93×10^{10}	0.034	p-n homojunction	[60]
MoSe ₂	650	89.5	2.24×10^{10}	9.6	Asymmetric electrodes	[61]
NiPS ₃	515	2.3	6.2×10^9	40	Schottky barriers	[62]
Bi ₂ O ₂ Se	1310	1.32	9.8×10^7	4	Asymmetric electrodes	[54]
MAPbBr ₃	White light	2	1.4×10^{10}	0.07	Vertical asymmetric electrodes	[63]
CuInSe ₂	637	600	2.97×10^{10}	85	Schottky contact and in-plane polarization	This work

carrier separation, suppressed dark current, and high sensitivity under self-powered conditions inherently constrains the achievable response speed. Consequently, the present device is particularly well suited for low-power, high-sensitivity applications such as weak-light sensing and environmental monitoring. The self-powered working principles were further revealed by photocurrent mapping. Under 637 nm illumination without applying V_{ds} , an asymmetric photocurrent intensity is observed between the two Au-CuInSe₂ contacts (Fig. 5(g)), indicating the formation of distinct Schottky barriers during the device construction process. More importantly, in contrast to the typical situation of photocurrent being spatially confined in the vicinity of a Schottky interface for a Schottky-typed photodetector, the most prominent photocurrent is generated nearly in the center of the CuInSe₂ channel between the Au electrodes, evidencing the contribution of photocarriers generation and extraction with the assistance of in-plane polarization field [64]. When the device is illuminated near the center of the flake, electrons and holes travel nearly equal distances toward their respective electrodes (Fig. S21 in the ESM). This balanced transport minimizes trapping and recombination probabilities, yielding the highest photocurrent intensity at the channel center. As the excitation spot moves closer to either electrode, one carrier species must traverse a much longer path to reach its collecting contact, increasing its likelihood of encountering traps or undergoing recombination (Fig. S21 in the ESM). As such, the observed photocurrent distribution can be explained as follow: The in-plane polarization field facilitates carrier separation and directional transport within the channel, while the contact-related fields contribute to local carrier separation near the electrodes. The symmetric transport pathways then lead to the maximal photocurrent at the channel center rather than at the contact interfaces. These effects together account for the observed spatial photocurrent profile. A similar photocurrent mapping was observed under 1064 nm laser illumination (Fig. S22 in the ESM). Finally, passive imaging using a patterned “M” mask under 637 nm illumination (Fig. 5(h)) demonstrates that the self-powered CuInSe₂ detector faithfully reproduces spatial features, supporting its applicability in low-power imaging systems.

4 Conclusions

In summary, we have developed a reliable molecular sieve-assisted CVD route to synthesize ultrathin nonlayered 2D CuInSe₂ flakes with well-defined (112) facet orientation and periodic Cu vacancy ordering. Correlated structural and optical measurements

demonstrate that the broken inversion symmetry in the chalcopyrite lattice gives rise to in-plane spontaneous polarization, which is electrically tunable via field-driven Cu⁺ ion migration. When interfaced with high work-function Au electrodes, a Schottky junction is formed, whose built-in fields, combined with the intrinsic polarization field, drive rapid and efficient photocarrier separation without the need for an external bias. The resulting self-powered photodetectors display broadband response across the 450–1064 nm spectral range, high responsivity and detectivity, fast rise/decay time, and excellent cycling stability. A peak PCE of $\sim 10.4\%$ under 637 nm illumination further underscores the efficient generation and extraction of photocarriers enabled by the synergistic effects of vacancy modulation, symmetry breaking, and contact engineering. Beyond photodetection, the combination of broadband absorption, tunable polarization, and Schottky contacts provides a versatile foundation for polarization-controlled photovoltaics, nonlinear optics, and compact self-powered imaging, underscoring the broader potential of 2D chalcopyrite semiconductors in next-generation optoelectronics.

Electronic Supplementary Material: Supplementary material (additional AFM and OM images, Raman spectrum, XRD rocking curve, PFM loops, band structure calculations, electrical output and transfer data, as well as I_{ds} – V_{ds} and I_{ds} – t curves under varying illumination powers at different wavelengths) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908739>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. Y. W.: Data curation, project administration, validation, writing manuscript, experimental design. Y. W.: Data curation, project administration, validation, experimental design. Q. C. X.: Project administration, writing manuscript. G. Y. L.: Writing manuscript. Y. L.: Project administration. W. T. Y.: Writing manuscript. C. Y. Y.: Project administration. Y. C. S.: Project administration, funding acquisition. T. L.: Project administration, funding acquisition, writing manuscript. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] Tang, W.; Sun, Q. J.; Wang, Z. L. Self-powered sensing in wearable electronics-a paradigm shift technology. *Chem. Rev.* **2023**, *123*, 12105–12134.
- [2] Wang, J. Y.; Ling, C. C.; Xue, X.; Ji, H. G.; Rong, C.; Xue, Q. Z.; Zhou, P. H.; Wang, C. K.; Lu, H. P.; Liu, W. P. Self-powered and broadband photodetectors based on high-performance mixed dimensional $\text{Sb}_2\text{O}_3/\text{PdTe}_2/\text{Si}$ heterojunction for multiplex environmental monitoring. *Small* **2024**, *20*, 2310107.
- [3] Xiao, H.; Liang, T.; Xu, J.; Xu, M. S. Solution-processed monolithic $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PbI}_2$ vertical heterostructure for high-performance flexible and broadband photodetector. *Adv. Opt. Mater.* **2021**, *9*, 2100664.
- [4] Lee, C. H.; Lee, G. H.; van der Zande, A. M.; Chen, W. C.; Li, Y. L.; Han, M. Y.; Cui, X.; Arefe, G.; Nuckolls, C.; Heinz, T. F. et al. Atomically thin p-n junctions with van der Waals heterointerfaces. *Nat. Nanotechnol.* **2014**, *9*, 676–681.
- [5] Zhang, Q.; Ni, S.; Zhang, D. H.; Wang, Y.; Xue, Q. C.; Wang, Y. Y.; Zhang, J. Z.; Zhu, F. Y.; Pan, C. Y.; Shao, Y. C. et al. Multicolor and polarization-sensitive photodetection of $\alpha\text{-In}_2\text{Se}_3/2\text{H-MoTe}_2$ vdW heterostructure for imaging and optical communication. *ACS Appl. Mater. Interfaces* **2025**, *17*, 31248–31256.
- [6] Zhou, C. J.; Raju, S.; Li, B.; Chan, M. S.; Chai, Y.; Yang, C. Y. Self-driven metal-semiconductor-metal WSe_2 photodetector with asymmetric contact geometries. *Adv. Funct. Mater.* **2018**, *28*, 1802954.
- [7] Liu, F. J.; Zhuang, X. M.; Wang, M. X.; Qi, D. Q.; Dong, S. P.; Yip, S.; Yin, Y. X.; Zhang, J.; Sa, Z.; Song, K. P. et al. Lattice-mismatch-free construction of III-V/chalcogenide core-shell heterostructure nanowires. *Nat. Commun.* **2023**, *14*, 7480.
- [8] Wang, M. X.; Zhuang, X. M.; Liu, F. J.; Chen, Y.; Sa, Z.; Yin, Y. X.; Lv, Z. T.; Wei, H. M.; Song, K. P.; Cao, B. Q. et al. New approach to low-power-consumption, high-performance photodetectors enabled by nanowire source-gated transistors. *Nano Lett.* **2022**, *22*, 9707–9713.
- [9] Liu, D.; Liu, F. J.; Liu, Y.; Pang, Z. Y.; Zhuang, X. M.; Yin, Y. X.; Dong, S. P.; He, L. B.; Tan, Y.; Liao, L. et al. Schottky-contacted high-performance GaSb nanowires photodetectors enabled by lead-free all-inorganic perovskites decoration. *Small* **2022**, *18*, 2200415.
- [10] Wang, M. X.; Liu, F. J.; Zhang, T. Y.; Wang, G. C.; Sa, Z.; Zang, Z. Q.; Qi, D. Q.; Song, K. P.; Cui, P.; Yang, Z. X. Toward low-power-consumption source-gated phototransistor. *Appl. Phys. Lett.* **2024**, *124*, 203504.
- [11] Zhang, Y. J.; Ideue, T.; Onga, M.; Qin, F.; Suzuki, R.; Zak, A.; Tenne, R.; Smet, J. H.; Iwasa, Y. Enhanced intrinsic photovoltaic effect in tungsten disulfide nanotubes. *Nature* **2019**, *570*, 349–353.
- [12] Akamatsu, T.; Ideue, T.; Zhou, L.; Dong, Y.; Kitamura, S.; Yoshii, M.; Yang, D. Y.; Onga, M.; Nakagawa, Y.; Watanabe, K. et al. A van der Waals interface that creates in-plane polarization and a spontaneous photovoltaic effect. *Science* **2021**, *372*, 68–72.
- [13] Qiao, H.; Huang, Z. Y.; Ren, X. H.; Liu, S. H.; Zhang, Y. P.; Qi, X.; Zhang, H. Self-powered photodetectors based on 2D materials. *Adv. Opt. Mater.* **2020**, *8*, 1900765.
- [14] Xiao, H.; Liang, T.; Xu, M. S. Growth of ultraflat PbI_2 nanoflakes by solvent evaporation suppression for high-performance UV photodetectors. *Small* **2019**, *15*, 1901767.
- [15] He, T.; Ma, H.; Wang, Z.; Li, Q.; Liu, S. N.; Duan, S. K.; Xu, T. F.; Wang, J. C.; Wu, H. T.; Zhong, F. et al. On-chip optoelectronic logic gates operating in the telecom band. *Nat. Photonics* **2024**, *18*, 60–67.
- [16] Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically thin MoS_2 : A new direct-gap semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- [17] Xing, J. B.; Tang, Y.; Li, J. X.; Wu, C. W.; Gu, Y. R.; Li, X. B.; Zhang, H.; Zhang, M. W.; Wang, X.; Zhou, X. et al. Intrinsic out-of-plane and in-plane ferroelectricity in 2D AgCrS_2 with high Curie temperature. *Adv. Mater.* **2024**, *36*, 2407655.
- [18] Zuo, N.; Nie, A. M.; Hu, C. G.; Shen, W. F.; Jin, B.; Hu, X. Z.; Liu, Z. Y.; Zhou, X.; Zhai, T. Y. Synergistic additive-assisted growth of 2D ternary In_2SnS_4 with giant gate-tunable polarization-sensitive photoresponse. *Small* **2021**, *17*, 2008078.
- [19] Xu, X.; Chen, Y. X.; Liu, P. B.; Luo, H.; Li, Z. X.; Li, D. Y.; Wang, H. Y.; Song, X. Y.; Wu, J. S.; Zhou, X. et al. General synthesis of ionic-electronic coupled two-dimensional materials. *Nat. Commun.* **2024**, *15*, 4368.
- [20] Wang, Y. Y.; Xue, Q. C.; Zhang, J. C.; Wang, Y.; Wang, J. Y.; Li, G. Y.; Yang, C. Y.; Shao, Y. C.; Liang, T. Chemical vapor deposition growth of 2D nonlayered CuInSe_2 for vacancy-assisted broadband photodetection. *Small* **2025**, *21*, 2409137.
- [21] Malyshev, R.; Brekke, B.; Svenum, I. H.; Selbach, S. M.; Brüne, C.; Brataas, A.; Tybell, T. Shear strain-induced multiferroic response in the altermagnetic semiconductor CuFeS_2 . 2025, arXiv: 2503.21637v2. <https://doi.org/10.48550/arXiv.2503.21637> (Apr 1, 2025).
- [22] Keller, J.; Kiselman, K.; Donzel-Gargand, O.; Martin, N. M.; Babucci, M.; Lundberg, O.; Wallin, E.; Stolt, L.; Edoff, M. High-concentration silver alloying and steep back-contact gallium grading enabling copper indium gallium selenide solar cell with 23.6% efficiency. *Nat. Energy* **2024**, *9*, 467–478.
- [23] Ramanujam, J.; Singh, U. P. Copper indium gallium selenide based solar cells-a review. *Energy Environ. Sci.* **2017**, *10*, 1306–1319.
- [24] Liu, H.; Yu, M. M.; Qin, F. L.; Feng, W.; Hu, P. G. Two-dimensional nonlayered CuInSe_2 nanosheets for high-performance photodetectors. *ACS Appl. Nano Mater.* **2018**, *1*, 5414–5418.
- [25] Pang, C.; Hu, S. B.; Guo, C.; Wang, J. T.; Zou, S. H.; Pan, Z. X.; Liu, J. C.; Shen, L. M.; Bao, N. Z.; Ning, H. L. et al. High-performance inorganically connected CuInSe_2 nanocrystal thin-film transistors and integrated circuits based on the solution process of colloidal synthesis, ligand exchange, and surface treatment. *Chem. Mater.* **2021**, *33*, 8775–8785.
- [26] Hinuma, Y.; Oba, F.; Kumagai, Y.; Tanaka, I. Ionization potentials of (112) and (11 $\bar{2}$) facet surfaces of CuInSe_2 and CuGaSe_2 . *Phys. Rev. B* **2012**, *86*, 245433.
- [27] Wooten, A. J.; Werder, D. J.; Williams, D. J.; Casson, J. L.; Hollingsworth, J. A. Solution-liquid-solid growth of ternary Cu-In-Se semiconductor nanowires from multiple- and single-source precursors. *J. Am. Chem. Soc.* **2009**, *131*, 16177–16188.
- [28] Wada, T. CuInSe_2 and related I-III-V $_2$ chalcopyrite compounds for photovoltaic application. *Jpn. J. Appl. Phys.* **2021**, *60*, 080101.
- [29] Zhang, S. B.; Wei, S. H.; Zunger, A.; Katayama-Yoshida, H. Defect physics of the CuInSe_2 chalcopyrite semiconductor. *Phys. Rev. B* **1998**, *57*, 9642–9656.
- [30] Oikonen, L. E.; Ganchenkova, M. G.; Seitsonen, A. P.; Nieminen, R. M. Formation, migration, and clustering of point defects in CuInSe_2 from first principles. *J. Phys.: Condens. Matter* **2014**, *26*, 345501.
- [31] Jyothirmai, M. V.; Thapa, R. Role of intrinsic defects in enhancing the

- photoabsorption capability of $\text{CuZn}_2\text{AlSe}_4$. *ACS Omega* **2022**, *7*, 31098–31105.
- [32] Nádaždy, V.; Yakushev, M.; Djebbar, E. H.; Hill, A. E.; Tomlinson, R. D. Switching of deep levels in CuInSe_2 due to electric field-induced Cu ion migration. *J. Appl. Phys.* **1998**, *84*, 4322–4326.
- [33] Zhou, L.; Xu, K.; Zubair, A.; Zhang, X.; Ouyang, F. P.; Palacios, T.; Dresselhaus, M. S.; Li, Y. F.; Kong, J. Role of molecular sieves in the CVD synthesis of large-area 2D MoTe_2 . *Adv. Funct. Mater.* **2017**, *27*, 1603491.
- [34] Wang, Y.; Xue, Q. C.; Zhang, J. C.; Wang, Y. Y.; Ma, H.; Zhong, F.; Zhou, N.; Yang, C. Y.; Shao, Y. C.; Liang, T. Anisotropic growth of 2D nonlayered $\alpha\text{-Fe}_2\text{O}_3$ for artificial optoelectronic synapse. *Adv. Opt. Mater.* **2025**, *13*, 2403424.
- [35] Zhou, J. D.; Lin, J. H.; Huang, X. W.; Zhou, Y.; Chen, Y.; Xia, J.; Wang, H.; Xie, Y.; Yu, H. M.; Lei, J. C. et al. A library of atomically thin metal chalcogenides. *Nature* **2018**, *556*, 355–359.
- [36] Wei, S. H.; Zhang, S. B.; Zunger, A. Effects of Na on the electrical and structural properties of CuInSe_2 . *J. Appl. Phys.* **1999**, *85*, 7214–7218.
- [37] Timmo, K.; Altosaar, M.; Raudoja, J.; Mellikov, E.; Varema, T.; Danilson, M.; Grossberg, M. The effect of sodium doping to CuInSe_2 monograin powder properties. *Thin Solid Films* **2007**, *515*, 5887–5890.
- [38] Kronik, L.; Cahen, D.; Schock, H. W. Effects of sodium on polycrystalline Cu(In, Ga)Se_2 and its solar cell performance. *Adv. Mater.* **1998**, *10*, 31–36.
- [39] Rincón, C.; Ramírez, F. J. Lattice vibrations of CuInSe_2 and CuGaSe_2 by Raman microspectrometry. *J. Appl. Phys.* **1992**, *72*, 4321–4324.
- [40] Tan, J. Y.; Zhang, Z. T.; Zeng, S. F.; Li, S. N.; Wang, J. W.; Zheng, R. X.; Hou, F. C.; Wei, Y. P.; Sun, Y. J.; Zhang, R. J. et al. Dual-metal precursors for the universal growth of non-layered 2D transition metal chalcogenides with ordered cation vacancies. *Sci. Bull.* **2022**, *67*, 1649–1658.
- [41] Wang, H.; Wen, Y.; Zhang, X. L.; Zhai, B. X.; Cheng, R. Q.; Yin, L.; Yu, Y. L.; Li, Y. S.; Jiang, J.; Zhu, H. et al. Revealing enhanced optical nonlinearity and robust ferromagnetism in atomically sharp stacking binary-ternary magnetic heterostructures. *ACS Nano* **2024**, *18*, 22978–22988.
- [42] Liu, Y.; Guo, J.; Zhu, E. B.; Liao, L.; Lee, S. J.; Ding, M. N.; Shakir, I.; Gambin, V.; Huang, Y.; Duan, X. F. Approaching the Schottky-Mott limit in van der Waals metal-semiconductor junctions. *Nature* **2018**, *557*, 696–700.
- [43] Gorley, P. M.; Khomyak, V. V.; Vorobiev, Y. V.; González-Hernández, J.; Horley, P. P.; Galochkina, O. O. Electron properties of n- and p- CuInSe_2 . *Sol. Energy* **2008**, *82*, 100–105.
- [44] Gong, Y.; Duan, R. H.; Hu, Y.; Wu, Y.; Zhu, S.; Wang, X. L.; Wang, Q. J.; Lau, S. P.; Liu, Z.; Tay, B. K. Reconfigurable and nonvolatile ferroelectric bulk photovoltaics based on 3R- WS_2 for machine vision. *Nat. Commun.* **2025**, *16*, 230.
- [45] Sangwan, V. K.; Chica, D. G.; Chu, T. C.; Cheng, M.; Quintero, M. A.; Hao, S. Q.; Mead, C. E.; Choi, H.; Zu, R.; Sheoran, J. et al. Bulk photovoltaic effect and high mobility in the polar 2D semiconductor SnP_2Se_6 . *Sci. Adv.* **2024**, *10*, eado8272.
- [46] Zhao, M.; Ye, Z. L.; Suzuki, R.; Ye, Y.; Zhu, H. Y.; Xiao, J.; Wang, Y.; Iwasa, Y.; Zhang, X. Atomically phase-matched second-harmonic generation in a 2D crystal. *Light: Sci. Appl.* **2016**, *5*, e16131.
- [47] Malitckaya, M.; Komsa, H. P.; Havu, V.; Puska, M. J. Effect of alkali metal atom doping on the CuInSe_2 -based solar cell absorber. *J. Phys. Chem. C* **2017**, *121*, 15516–15528.
- [48] Chernyak, L.; Gartsman, K.; Cahen, D.; Stafsudd, O. M. Electronic effects of ion mobility in semiconductors: Semionic behaviour of CuInSe_2 . *J. Phys. Chem. Solids* **1995**, *56*, 1165–1191.
- [49] Oikkonen, L. E.; Ganchenkova, M. G.; Seitsonen, A. P.; Nieminen, R. M. Mass transport in CuInSe_2 from first principles. *J. Appl. Phys.* **2013**, *113*, 133510.
- [50] Dagan, G.; Cizek, T. F.; Cahen, D. Ion migration in chalcopyrite semiconductors. *J. Phys. Chem.* **1992**, *96*, 11009–11017.
- [51] Pohl, J.; Klein, A.; Albe, K. Role of copper interstitials in CuInSe_2 : First-principles calculations. *Phys. Rev. B* **2011**, *84*, 121201.
- [52] Gong, F.; Fang, H. H.; Wang, P.; Su, M.; Li, Q.; Ho, J. C.; Chen, X. S.; Lu, W.; Liao, L.; Wang, J. et al. Visible to near-infrared photodetectors based on MoS_2 vertical Schottky junctions. *Nanotechnology* **2017**, *28*, 484002.
- [53] Liu, W. J.; Wu, Y. F.; Bao, X. Z. D.; Sun, L.; Xie, Y. E.; Chen, Y. P. High-performance infrared self-powered photodetector based on 2D van der Waals heterostructures. *Adv. Funct. Mater.* **2025**, *35*, 2421525.
- [54] Wang, G. C.; Liu, F. J.; Chen, R. C.; Wang, M. X.; Yin, Y. X.; Zhang, J.; Sa, Z.; Li, P. S.; Wan, J. C.; Sun, L. et al. Tunable contacts of $\text{Bi}_2\text{O}_3\text{Se}$ nanosheets MSM photodetectors by metal-assisted transfer approach for self-powered near-infrared photodetection. *Small* **2024**, *20*, 2306363.
- [55] Wang, H. Y.; Wang, W.; Zhong, Y. L.; Li, D. Y.; Li, Z. X.; Xu, X.; Song, X. Y.; Chen, Y. X.; Huang, P.; Mei, A. Y. et al. Approaching the external quantum efficiency limit in 2D photovoltaic devices. *Adv. Mater.* **2022**, *34*, 2206122.
- [56] Garin, M.; Heinonen, J.; Werner, L.; Pasanen, T. P.; Vähänissi, V.; Haarahiltunen, A.; Juntunen, M. A.; Savin, H. Black-silicon ultraviolet photodiodes achieve external quantum efficiency above 130%. *Phys. Rev. Lett.* **2020**, *125*, 117702.
- [57] Zhou, C. J.; Liu, Q. L.; Fu, X.; Niu, W. C.; Wang, J. L.; Liu, X. Q.; Zou, X. M.; Miao, J. S.; Shan, F. K.; Yang, Z. Y. Self-powered and reconfigurable double-terminal MoS_2 photodetector for image recognition. *Nano Lett.* **2025**, *25*, 3515–3523.
- [58] Mao, Y. C.; Xu, P. P.; Wu, Q.; Xiong, J.; Peng, R. M.; Huang, W.; Chen, S. Y.; Wu, Z. Y.; Li, C. Self-powered high-detectivity lateral MoS_2 Schottky photodetectors for near-infrared operation. *Adv. Electron. Mater.* **2021**, *7*, 2001138.
- [59] Ghanbari, H.; Abnavi, A.; Ahmadi, R.; Mohammadzadeh, M. R.; Fawzy, M.; Hasani, A.; Adachi, M. M. 2D MoSe_2 geometrically asymmetric Schottky photodiodes. *Adv. Opt. Mater.* **2024**, *12*, 2401682.
- [60] Zhong, F.; Ye, J. F.; He, T.; Zhang, L. L.; Wang, Z.; Li, Q.; Han, B.; Wang, P.; Wu, P. S.; Yu, Y. Y. et al. Substitutionally doped MoSe_2 for high-performance electronics and optoelectronics. *Small* **2021**, *17*, 2102855.
- [61] Liu, B. Y.; Zhao, C.; Chen, X. Q.; Zhang, L. R.; Li, Y. F.; Yan, H.; Zhang, Y. Z. Self-powered and fast photodetector based on graphene/ MoSe_2 /Au heterojunction. *Superlattices Microstruct.* **2019**, *130*, 87–92.
- [62] Zong, L. H.; Song, J. M.; Wang, S. X.; Chen, W. H.; Yang, J. J.; Li, B. D.; Hu, P.; Fan, H. B.; Teng, F.; Zhao, X. A broadband self-powered photodetector based on NiPS_2 . *J. Mater. Chem. C* **2024**, *12*, 593–599.
- [63] Shaikh, P. A.; Shi, D.; Retamal, J. R. D.; Sheikh, A. D.; Haque, M. A.; Kang, C. F.; He, J. H.; Bakr, O. M.; Wu, T. Schottky junctions on perovskite single crystals: Light-modulated dielectric constant and self-biased photodetection. *J. Mater. Chem. C* **2016**, *4*, 8304–8312.
- [64] Feng, P.; Gong, Z. H.; Wang, B. Y.; Wang, Z. Y.; Xu, H. R.; Zou, L. R.; Liu, C.; Han, X.; Cheng, Y. C.; Yu, B. et al. High-efficiency bulk photovoltaic effect with ferroelectric-increased shift current. *Nat. Commun.* **2025**, *16*, 9839.



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