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Intercorrelated in-plane and out-of-plane ferroelectricity in ultrathin two-dimensional layered semiconductor In_2Se_3

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ABSTRACT: Enriching the functionality of ferroelectric materials with visible-light sensitivity and multiaxial switching capability would open up new opportunities for their applications in advanced information storage with diverse signal manipulation functions. We report experimental observations of robust intra-layer ferroelectricity in two-dimensional (2D) van der Waals layered α -In₂Se₃ ultrathin flakes at room temperature. Distinct from other 2D and conventional ferroelectrics, In₂Se₃ exhibits intrinsically intercorrelated out-of-plane and in-plane polarization, where the reversal of the out-of-plane polarization by a vertical electric field also induces the rotation of the in-plane polarization. Based on the in-plane switchable diode effect and the narrow bandgap (~ 1.3 eV) of ferroelectric In₂Se₃, a prototypical non-volatile memory device, which can be manipulated both by electric field and visible light illumination, is demonstrated for advancing data storage technologies.

Conventional ferroelectrics such as barium titanate¹ and lead zirconate titanate (PZT)² are large bandgap insulators; hence, their information storage is based predominantly on the capacitor charging and discharging, limiting their applications. Ferroelectrics with a narrow bandgap in visible-light regimes are more desirable because additional operation with light and

convenient read-out with semiconductor features can be incorporated for advanced information storage. Two-dimensional (2D) materials exhibit various functionalities such as high on-off electronic switching, superconductivity³, ferromagnetism⁴, and piezoelectricity⁵. However, 2D ferroelectricity with a narrow bandgap has been rarely reported and its origin still remained unclear. Chang *et al.* demonstrated in-plane (IP) ferroelectricity in a three-dimensional SnTe crystal down to a 1-unit cell thickness⁶. Another known wide-bandgap ferroelectric CuInP₂S₆ crystal has been thinned down to 4 nm and demonstrated workable for out-of-plane (OOP) switching⁷. Recently, 2D layered semiconductor α -In₂Se₃ has been predicted to have both IP and OOP ferroelectric polarization at a monolayer level⁸. Here we report the experimental observations of robust IP and OOP intra-layer ferroelectricity in 2D layered α -In₂Se₃ at room temperature and fundamental understanding of their antiparallel interlayer polarization. Importantly, the field-induced switching of OOP and IP polarization for α -In₂Se₃ is proved to be intrinsically intercorrelated. Owing to its ferroelectric nature and the suitable bandgap of ~ 1.3 eV, a lateral two-terminal device based on α -In₂Se₃ shows a switchable diode effect, where the current can be modulated by electric field and visible light illumination, promising for advancing versatile 2D data storage technologies.

As illustrated in **Fig. 1a**, the In₂Se₃ layers were grown on mica substrates by chemical vapor deposition⁹. The In₂Se₃ flakes range from few hundred nanometers to several micrometers laterally, with different thicknesses exhibiting different optical contrasts (**Fig. S1**). The atomic force microscopy (AFM) in **Fig. 1b** shows that when the thickness ≥ 2 nm the In₂Se₃ layers exhibit regular shapes and straight edges, indicating good crystallinity, while those with an apparent thickness < 1.3 nm, usually display irregular shapes. From the atomic-resolution scanning transmission electron microscopy (STEM) in **Fig. S2**, we can see it is a mixture of

amorphous and mis-oriented polycrystalline phases, likely resulting from its interaction with underlying mica substrates. Note that various substrates including graphite, silicon and sapphire have been tested for the growth, and mica substrates allow the better growth for In_2Se_3 . This layer acts as a seed layer for inducing subsequent In_2Se_3 growth. Here we consider the layer grown on top of the seed layer as the monolayer. It is known that bulk In_2Se_3 exists in various crystalline phases including α and β , and there is a phase transformation between α and β phases occurring at $\sim 200^\circ\text{C}$ ^{10, 11}. Thus, the cooling rate after the growth (at 660°C) is critical for obtaining α phase (see **Methods**), which is predicted to be ferroelectric.⁸ Fig. 1c shows the Raman spectra of the as-grown In_2Se_3 flakes, where the three peaks at ~ 103 , 170 , 204 cm^{-1} observed in the sample with slow cooling ($0.1^\circ\text{C}/\text{min}$) are attributed to A_1 (LO + TO), A_1 (TO) and A_1 (LO) phonon modes of In_2Se_3 .^{9, 11} It is reported that there would be a blue shift in lattice phonon modes for β - In_2Se_3 compared with that of α - In_2Se_3 due to the smaller lattice constant of β - In_2Se_3 , and the relative peak intensity of A_1 (TO) phonon mode for β - In_2Se_3 is much weaker than that of α - In_2Se_3 .^{11, 12} In our case, we don't see obvious Raman shift between the quick cooling and slow cooling samples, because both samples are the mixtures of α - and β - In_2Se_3 . The minor peak at $\sim 170\text{ cm}^{-1}$ for the quick cooling sample indicates that it is dominated by β phase^{11, 12}, while the strong intensity of this peak for the slow cooling sample suggests that the portion of α - In_2Se_3 flakes significantly increases in the slow cooling process.

Fig. 1d displays the selected area electron diffraction (SAED) patterns from two regions of the In_2Se_3 sample obtained with slow cooling. The left SAED was acquired from a monolayer as shown in the low-magnification TEM image in the inset, which matches with α - In_2Se_3 along the $[0001]$ axis. The right SAED from another thicker flake (12 nm thick) is assigned to β - In_2Se_3 , where the additional diffraction spots along the $[1\bar{1}00]$ direction indicates the existence of

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3 superstructures^{11, 13, 14}. We note that α -In₂Se₃ is typically observed in thin flakes (e.g. less than
4 around 10L) but rarely found in thicker flakes. **Fig. 1e** shows the atomic-resolution STEM image
5 of a monolayer α -In₂Se₃, confirming the success in growing α -In₂Se₃ flakes. Because four
6 different atomic configurations have been proposed for α -phase^{8, 14}, We simulated diffraction
7 patterns based on kinematic diffraction for these various configurations (**Fig. S3**). The
8 comparison of experimental and simulated patterns allows us to conclude that α -In₂Se₃ exists in
9 the FE-ZB' configuration, agreeable with the theoretical prediction⁸.
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20 To study the spontaneous ferroelectric polarization, we investigated the as-grown α - and β -
21 In₂Se₃ thin flakes on mica substrates by piezoresponse force microscopy (PFM) (see **Methods**).
22 The PFM amplitude reflects the magnitude of the local piezoelectric response, and the phase
23 indicates the direction of the ferroelectric polarization. As expected, no phase contrast difference
24 is observed for β -In₂Se₃ in both the IP and OOP directions since it is not a ferroelectric phase
25 (**Fig. S4**). **Fig. 2a** shows the topographic image of the randomly selected triangle α -In₂Se₃ flakes
26 with the thickness from 2 nm to 6 nm. The OOP PFM images for these flakes are shown in **Fig.**
27 **S5a** (amplitude) and **S5b** (phase) and the corresponding IP PFM images are shown in **Figs. 2b**
28 (amplitude) and **2c** (phase). We observe from **Figs. 2b** and **2c** that the single ferroelectric domain
29 is formed within each terrace. Although single domain state is rarely achieved for traditional
30 ferroelectric without applying an electric field, it is favorable when the depolarizing field is small
31 and fully compensated, which is likely the case of α -In₂Se₃ because the IP polarization is larger
32 than OOP polarization. The high carrier concentration of α -In₂Se₃ could also neutralize the
33 boundary polarization charges, making it possible for the formation of single domain state¹⁵.
34 This is different from CuInP₂S₆, where OOP polarization dominates and thus the domain walls
35 easily form even for ultrathin films⁷.
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Fig. 2c also indicates that there exist two IP polarization directions with opposite phase contrasts in α -In₂Se₃ and such a phase contrast is thickness-dependent. Specifically, the phase of a 2 nm flake is $\sim 120^\circ$, while it is $\sim -60^\circ$ for a 3 nm flake, and it reverts to $\sim 120^\circ$ for a 4 nm flake. The analysis for the IP phase contrast dependency on layer number is detailed in **Fig. S6** and the results are summarized in **Fig. 2d**. Since the seed layer is poorly crystallized, we only study the ferroelectricity for the flakes ≥ 2 nm (1L). In brief, the obvious odd-even effect is observed for the flakes ranging from 1L to 6L. The anti-aligned IP polarization should generally result in zero polarization for the flakes with an even layer number (cancellation of opposite polarizations). However, PFM measurement is most sensitive to surface polarization, and a working depth of several nanometers has been reported for PZT films^{16, 17}. The working depth could be even smaller for 2D In₂Se₃ partially due to the weak van der Waals interactions between each layer. Hence, the odd-even effect could still be observed. In addition, the OOP phase mapping also shows the similar behaviors although the OOP polarization is several tens of times smaller than the IP polarization⁸. Such a layer-dependent odd-even ferroelectric effect has been predicted for monolayer Group-IV monochalcogenides¹⁸, and our results have proved the validity for the first time in 2D materials. Our density functional theory calculations for α -In₂Se₃ bilayer also indicate that both the IP and OOP polarizations favor the anti-parallel stacking (**Fig. S7**). The scanning electron diffraction (SED) is further used to study the interlayer antiparallel-polarization phenomenon in α -In₂Se₃. When the electron probe scan through the sample, it can be shifted by the local electric field or diffracted by the local atomic structure¹⁹, allowing to map the local projected electric field. **Fig. 2e** shows the high-angle annular dark field (HAADF) STEM image of the region probed with SED. Based on the image intensity from the z-contrast in **Fig. 2f** and low-mag STEM image in **Fig. S8**, a 2L to 3L boundary of α -In₂Se₃ could be identified. The map

of electric field projected along the $[0001]$ zone axis of In_2Se_3 is shown in **Fig. 2g**, where each vector shows the direction of the local electric field, with its magnitude indicating the field strength. We identified a clear electric field switching from the $[\bar{1}010]$ to the $[10\bar{1}0]$ direction within the In_2Se_3 basal plane from 2L to 3L. The line profile of mean electric field projected along the X direction in **Fig. 2h** manifests that the electric field is clearly reversed in X direction and has a small reversal in Y direction.

Ferroelectric materials should be able to respond to the applied electric field; *i.e.*, the polarization can be manipulated by the electric field. To explore the polarization switching, α - In_2Se_3 flakes were transferred onto the Au (or Pt)-coated Si substrate. The OOP (**Fig. 3b**) and IP (**Fig. 3c**) phase images acquired after writing two square patterns with opposite tip voltages (-7 V and +6 V) demonstrate that polarization direction can be controlled by the external bias. More importantly, the IP phase changes simultaneously with the OOP phase, indicating that the IP polarization is intercorrelated with the OOP polarization. According to the theoretical calculations,⁸ this unique IP and OOP intercorrelation could intrinsically originate from electric field-induced lateral movement of the central Se atomic layer in the FE-ZB' configuration (Fig. 3a). Other 2D ferroelectrics only exhibit one polarization component (e.g. IP for SnTe, and OOP for CuInP_2S_6). The intercorrelated polarization is beneficial for new memory devices switchable by a perpendicular or horizontal electric field. Meanwhile, the phase contrast of the written domains fades with time but is still identifiable after 2 h (**Fig. S9**), suggesting the good stability of the written domains. The maximum time period of the identifiable phase contrast is ~ 10 h. Together with the domain writing, the local piezoelectric loops of this 6 nm thick flake in **Fig. 3d** display a butterfly-like voltage dependent amplitude loop and the sharp change in phase up to 180° , typical for ferroelectrics. Note that similar hysteresis loops could also be observed in some

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3 non-ferroelectrics, due to the surface electrostatic effect between the tip and surface charges or
4 ion movement under high external electric field²⁰. The deposition of a top conducting electrode
5 will produce a homogeneous electric field to avoid local charge/ion accumulation, largely
6 alleviate these effects. Fig. 3e shows that butterfly-like amplitude loop and sharp phase
7 hysteresis loop were still obtained for an α -In₂Se₃ flake with a top Au electrode (see methods).
8 Thus, these possible artifacts are excluded. Compared with that of the bare In₂Se₃ flake, the
9 amplitude/phase loop acquired on In₂Se₃ flake with a top Au pad is more asymmetric and show
10 larger coercivity, which could be attributed to the dead layer between In₂Se₃ and the top gate
11 electrode induced during the Au deposition. The switchable polarization for more flakes is
12 included in **Fig. S10**.
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27 To show the possible application of ferroelectric In₂Se₃ as non-volatile memory element, we
28 investigated the transport properties of thin In₂Se₃ flakes in the OOP direction by performing
29 conducting atomic force microscope (CAFM). **Fig. 4a** is the current mapping of a 6 nm thick
30 In₂Se₃ flake after writing with -6V and +6V stripes respectively, which clearly shows high and
31 low current states corresponding to opposite polarization states. The typical local I - V curves in
32 **Fig. 4b** demonstrates that for the -6V written region the current changes by more than four
33 orders upon the polarization reversal, comparable with the resistive switching observed for other
34 traditional ferroelectric oxides²⁰. The non-linear feature of the I - V curves especially for the high
35 current state suggests that the transport is dominated by the interfacial barriers between the α -
36 In₂Se₃ and the two electrodes, where the metal/ferroelectric/metal sandwiched structure could be
37 considered as back-to-back Schottky diodes with the Schottky barrier height varied with the
38 polarization direction^{20,21}.
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Leveraging on the concurrent ferroelectric and semiconductor properties of α -In₂Se₃, a lateral resistive memory device (Au/ α -In₂Se₃/Au as illustrated in **Fig. 4c** and **Fig. S11**) based on the IP polarization is further constructed. **Fig. 4e** shows the typical I - V curves for the device performed in the range of ± 10 V. The arrows in the figure denote the voltage sweep directions. The I - V curve with distinct hysteresis behaviors shows a resistive switching (on/off ratio of ~ 10). Two I - V segments in the range of ± 4 V are replotted by red and blue solid lines, respectively, demonstrating obvious opposite rectifying features. This switchable diode effect upon the IP polarization reversal totally differs from that of the common ferroelectric capacitors which rely on the OOP polarization reversal²¹. **Fig. 4d** displays the schematic band alignment of the lateral device. Due to the built-in electric field of the ferroelectric layer, the ferroelectric polarization can enhance the Schottky barrier of one interface while reducing the barrier of the opposite interface, leading to an asymmetric transport behavior as shown in **Fig. 4e**. Detailed I - V curves with various biases are discussed in **Fig. S11**. In addition to the electric field, **Fig. 4e** shows that the α -In₂Se₃ planar device is also sensitive to the visible light due to the semiconducting nature of α -In₂Se₃, which remains semiconducting with a measured bandgap of ~ 1.3 eV even as thin as a bilayer (**Fig. S12**). A multi-functional memory device with four resistive memory states switchable with electric field and light illumination is then realized, showing potential for advanced data storage technologies. Whereas for β -In₂Se₃ based device (**Fig. S13**), we do not observe resistive switching behavior but only the light response.

In summary, robust layer dependent intra-layer ferroelectricity has been experimentally demonstrated in 2D semiconducting α -In₂Se₃. The tangled switching behavior of the IP and OOP polarization in α -In₂Se₃ distinguishes it from other 2D and conventional ferroelectrics. A simple

device taking the advantage of both the switchable polarization and the visible light absorption exhibits memristive behavior, promising for applications in 2D nanoelectronics for data storage. Our results broaden the functionalities of 2D materials and suggest new opportunities for van der Waals heterostructures.

Notes: When preparing the manuscript, we notice a recent paper by Zhou, Y., *et al*²² showing the experimental observation of OOP piezoelectricity and ferroelectricity of thick In_2Se_3 . Here, we show a fundamentally important layer dependent ferroelectricity, and intercorrelated OP and IP polarization switching of ultrathin $\alpha\text{-In}_2\text{Se}_3$. Furthermore, a switchable diode effect that can be controlled by both the electric field and visible light illumination on a two terminal device has been confirmed, which promises potential applications such as memory and optical sensors.

Methods

Growth of 2D layered In_2Se_3 . The 2D layered In_2Se_3 was synthesized on mica substrates by chemical vapor deposition method using Se and In_2O_3 powders as the precursors and the H_2/Ar mixture as the carrier gas.⁹ The boat filled with 0.1 g In_2O_3 was placed in the center of the furnace and the boat full of Se was in the upstream. The mica without any special treatment was placed in the downstream about 15 cm away from the boat of In_2O_3 . The temperature of Se and In_2O_3 were heated to 330 and 660 °C respectively in 30 min and were kept for 30 min for the growth of 2D layered In_2Se_3 under a pressure of 500 torrs in the atmosphere of 30 ml/min H_2 and 90 ml/min Ar. After synthesis, the system was cooled down to room temperature in about 20 min for fast cooling process or 3 days for the slow cooling process, respectively.

Transfer of In_2Se_3 from mica to target substrates. The transfer of In_2Se_3 was assisted with a poly(methyl methacrylate) (PMMA) transfer supporting layer. The PMMA was spin-coated on

the surface of the In_2Se_3 samples grown on mica and then baked at 180 °C for 2 min. After ultrasonic in water for 2 min, the PMMA/ In_2Se_3 film was peeled off from the mica with the assistance of water. Then the PMMA/ In_2Se_3 film was fished by the target substrates, such as silicon wafer or TEM grid.

Raman and AFM measurement. The Raman measurement was performed using an excitation laser of 532 nm (WITec alpha 300 confocal Raman microscopy). The AFM measurement was performed by Cypher ES - Asylum Research Oxford Instruments.

Electron Microscopy observation and analysis. TEM and SAED were carried out using a JEOL JEM-2100F TEM at the accelerating voltage of 200 kV. High resolution STEM imaging was acquired using the Nion UltraSTEM 200 at University of California - Irvine, equipped with C3/C5 corrector and high-energy resolution monochromated EELS system (HERMES). The instrument was operated at 60kV to avoid knock-on damage. The semi-angle of the probe-forming aperture was about 30 mrad and the beam current was about 30 pA. The inner and outer cut-off semi-angles of the HAADF detector were about 70 and 200 mrad, respectively, and the acquisition time was chosen to be 32 μs per pixel. Scanning electron diffraction was carried out on a JEOL JEM-300CF S/TEM equipped with both imaging and probe forming aberration correctors. An electron probe of the size of ~ 1 Å was formed by converging the electron beam at a convergence semi-angle of ~ 18 mrad. The electron accelerating voltage was 80 kV. Convergent beam electron diffraction patterns (CBED) were taken at each scanning point using Gatan OneView camera at the speed of 200 frames per second. The penetrating electron beam will be shifted by the local electric field along its path through the sample¹⁹. By measuring the shift of the center of weight (CoW) of the intensity in each CBED pattern, the electric field can

be quantified. The detailed description of scanning electron diffraction can be found in supplementary materials.

Ferroelectric characterization. Piezoresponse force microscopy and conducting atomic force microscopy measurements were performed using a commercial atomic force microscope (Asylum Research MFP-3D) with Pt/Ir-coated Si cantilever tips and diamond-coated Si cantilever tips, respectively. In typical PFM measurements, an ac voltage of amplitude of 1000 mV was applied on the tip. The OOP and IP piezoelectric signals are acquired at a contact resonance frequency of ~ 56 kHz and ~ 172 kHz respectively in DART (dual a.c. resonance tracking) mode²³. PFM were also performed on transferred In₂Se₃ flakes with top Au electrodes (2 μ m in diameter and 20 nm in thickness), which were fabricated by standard E-beam lithography writing, followed by Au film deposition through E-beam evaporation at a growth rate of 0.1 nm/s, and finally by standard lift-off process. For the local electric measurements, the bias voltage was applied on the sample. For CAFM mapping, a dc bias voltage of 0.5 V was applied.

Electric characterizations. *I-V* curves of planar devices were investigated by a Keithley 4200 semiconductor analyzer connected to a probe station at room temperature. A visible light LED with an intensity of ~ 8 mW/cm² was used for the light response test.

Density functional theory calculation. First principles calculations based on density functional theory (DFT) were performed using the Vienna Ab Initio Simulation Package²⁴. The exchange and correlation functionals were treated using the PBE²⁵ parametrization of GGA with the kinetic energy cutoff set to 550 eV. A $12 \times 12 \times 1$ k-meshes were used for the Brillouin zone sampling. For the band structure calculations, the hybrid functional of Hye-Scuseria-Ernzerhof

(HSE06)²⁶ was employed. A vacuum thickness of 20 Å is adopted to ensure that the interactions between the layers are negligible. The van der Waals interaction (optB88-vdW, Ref 27) was adopted in the structure relaxation steps. Optimized atomic structures were achieved when forces on all the atoms have declined to less than 0.005 eV/Å.

ASSOCIATED CONTENT

Supporting Information. The optical images, the STEM images and diffraction patterns, other PFM images, density functional calculations, and detailed electric characterizations of devices are given in this section. This material is available free of charge via the internet.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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Figure 1. Synthesis & structure characterization of 2D In_2Se_3 . **a.** Schematic illustration of the growth process of 2D In_2Se_3 with Se and In_2O_3 as the precursors and mica as the substrate. **b.** AFM image and the corresponding height profiles of In_2Se_3 sheets with the thicknesses ~ 1.3 - 4.3 nm. The scale bar is 1 μm . **c.** Raman spectra of In_2Se_3 and mica respectively with the 532 nm laser excitation. **d.** SAED patterns of α - and β - In_2Se_3 taken in the regions indicated in the TEM image in the inset, where the scale bar for SAED and TEM is 2 nm^{-1} and 500 nm respectively. **e.** Atomic-resolution STEM image of a monolayer α - In_2Se_3 . The scale bar is 2 nm.

Figure 2. PFM investigation of the as-grown In_2Se_3 on mica. **a.** AFM image of typical thin flakes with the thicknesses from 2 to 6 nm. The scale bar is 1 μm . **b and c,** The corresponding IP PFM images (b. amplitude; c. phase). **d.** Statistics of the thickness-dependent IP phase (1L-6L) from different locations. **e.** STEM-HAADF image showing the region from 2L (lower) to 3L (upper), where scanning electron diffraction was performed. The X-Y axes are indicated in bottom left, where X is along the $[2\bar{1}\bar{1}0]$ direction and Y is along the $[01\bar{1}0]$ direction of α - In_2Se_3 . The scale bar is 1 nm. **f.** Average intensity profile of HAADF image along the Y

direction in e. **g.** Projected electric field mapping in the same region as f. The major direction of electric field in upper and lower regions are close to $[10\bar{1}0]$ and $[\bar{1}010]$ directions, respectively.

h. Line profiles of the X- and Y- components of the mean projected electric field strength along X-direction and Y-direction, as indicated by E_x and E_y , respectively.

Figure 3. Ferroelectric switching of a 6 nm thin In₂Se₃ flake transferred onto the Au/Si substrate. a. schematic model of IP and OOP switching coupling. **b.** OOP phase image and **c.** the corresponding IP phase image of a 6 nm thick In₂Se₃ flake acquired immediately after writing two square patterns with a size of 2 μm and 1 μm by applying -7 V and +6 V voltages consecutively. The scale bar is 1 μm . **d and e.** Local ferroelectric switching loops without and with an Au top electrode, respectively.

Figure 4. Electrically controlled conducting behavior of In_2Se_3 . **a.** CAFM mapping for a 6 nm thick flake of $\alpha\text{-In}_2\text{Se}_3$ transferred onto a Pt/Si substrate. The mapping was collected after writing with +6 V/-6 V stripes ($1\ \mu\text{m} \times 0.5\ \mu\text{m}$). The scale bar is $1\ \mu\text{m}$. **b.** Local I - V curves measured in +6 V and -6 V switched regions. Inset, same data in log scale. **c and d.** Schematic planar device structure and the polarization direction dependent band alignment. The planar device on mica was built with an as-grown $\alpha\text{-In}_2\text{Se}_3$ thin flake ($\sim 13\ \text{nm}$) bridged by two Au electrodes. **e.** I - V curve of the planar In_2Se_3 device. The red and blue solid lines are used to guide the eyes.

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