

Supplementary Material for
**Robustness of a Topologically Protected Surface State in a Sb₂Te₂Se
Single Crystal**

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1. Sample preparation and characterization

Single crystals of Sb₂Te₂Se were grown in a home-made resistance-heated floating-zone furnace (RHFZ). This apparatus employs a method similar to directional solidification, in which a small region of a fed rod is melted and this molten zone is moved along the crystal. The molten region moves the impurities to one end of the fed rod and leaves behind it a wake of purer material, solidified, as it moves through the ingot; the impurities concentrated in the melt have an appreciable difference of concentration between the solid and liquid phases at equilibrium. Atopological insulator (TI) crystal grown with the RHFZ method has a much more uniform crystallinity than that from a traditional vertical Bridgman technique.

Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ crystallize in the tetradymite structure with space group R_{3m} . In Sb_2Te_3 , the hexagonal cell comprises 15 layers grouped in 3 quintuple layers, $\text{Te}^2\text{-Sb-Te}^1\text{-Te}^1\text{-Sb}$, in which Te^1 and Te^2 denote the tellurium atoms at distinct Wyckoff points. In $\text{Sb}_2\text{Te}_2\text{Se}$, selenium atoms replace the Te^2 tellurium atoms and the lattice parameter along hexagonal axis c contracts. Figure S1 shows a ω -scan along the surface normal $[0\ 0\ 0\ L]$ direction of Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$. The present crystals exhibit high crystallinity and great uniformity according to X-ray diffraction (XRD). Our XRD data show that the mean value of lattice parameter c of Sb_2Te_3 is 30.428 Å and lattice parameter c of $\text{Sb}_2\text{Te}_2\text{Se}$ is 29.869 Å, consistent with the literature¹.

For further confirmation of the crystalline quality and properties, micro-Raman spectra were recorded (Horiba Jobin-Yvon T64000 triple-grating system, CCD detector)². An Ar^+ ion laser provided excitation at wavelength 514.5 nm; the beam passed through a microscope and was focused on the sample with a laser spot of micrometre size in a back-scattering geometry. A quarter-wave plate was placed in the path of the laser beam to convert the linearly polarized laser light into circularly polarized light. Stokes shifts were measured resulting from phonon emission in the inelastic scattering of the samples near 23 °C.

Figure S2 shows the Raman spectrum of a $\text{Sb}_2\text{Te}_2\text{Se}$ single crystal; the active Raman modes are observed with wavenumbers in the range 20–225 cm^{-1} . A_{1g}^1 (82.2 cm^{-1}) and A_{1g}^2 (188.9 cm^{-1}) modes are longitudinal vibrations along axis c of the crystal, at which, with neighboring atoms of groups V and VI moving in the same direction, the A^1 mode has a smaller wavenumber than the A^2 mode in which the atoms move in the opposite direction. E_g^1 (41.1 cm^{-1}) and E_g^2 (117.5 cm^{-1}) modes are lateral vibrations in the plane vertical to axis c , with the E^2 mode having a larger wavenumber shift than the E^1 mode because the group V and VI atoms move in opposite directions whereas in the same direction for the E^1 mode. An extra Raman

shift, $E^H(\text{Te})$ resulting from Te bonding, is observed at 138.3 cm^{-1} , which disappeared gradually when Se was added to the Sb-Se-Te material system replacing Te³. Concurrently, the $A^1(\text{Te})$ mode is located about the side of the E_g^2 mode and the $E^L(\text{Te})$ mode emerges on the side of the A_{1g}^1 mode of greater energy.

2. $\text{Sb}_2\text{Te}_2\text{Se}$ doped with alkali metal

Photoemission spectra were collected in a UHV chamber equipped with a hemispherical analyzer (Scienta R4000) with collecting angle $\pm 15^\circ$. The polarization vector was invariably in the angular dispersive plane. The single crystals were cleaved *in situ* and measured at sample temperature 83 K, with photon energy 24 eV and energy resolution 14 meV. The base pressure in all used chambers was less than 6.5×10^{-11} Torr. Potassium (K) and caesium atoms were deposited from a well calibrated SAES getter source at 83 K. The amount of deposited K atoms was estimated from the occupied area of the 2D Fermi surface, on mapping the area of the surface BZ in a bilayer graphene (BLG)/SiC substrate, and the core level photoemission spectra of potassium 3p. For K deposited for 5 min, the amount of charge transfer on BLG/SiC is about 0.012 electrons/per unit cell. Figure S3a displays a comparison of photoemission plots of undoped and doped $\text{Sb}_2\text{Te}_2\text{Se}$ crystals. Figure S3b shows the photoemission spectrum at normal emission with varied duration of deposition. That the peak position of the resonance surface state (RSS) moved toward increased binding energy about 83 meV after deposition for 5 min implies *n*-type doping behavior. With increasing deposition of K, no alteration of the peak position of the RSS was observed, but the energy distribution curve (EDC) became broadened because of surface pollution. Figure 3c shows MDC plots at the Fermi level for undoped and doped $\text{Sb}_2\text{Te}_2\text{Se}$ crystals. The Fermi vector $k_F \sim 0.048 \text{ \AA}^{-1}$ in doped

Sb₂Te₂Se is smaller than that, 0.065 Å⁻¹, in an undoped crystal. We observed no Dirac point because of the effect of saturated potassium doping, but the position of the Dirac point was determined at 237 meV above the Fermi level through an extrapolation of the linear dispersion of the topological surface state (TSS). The data from the experiment with caesium doping is consistent with the result of the Sb₂Te₂Se crystal doped with potassium.

3. Experiment on Sb₂Te₂Se dependent on photon energy

In the photoemission experiment, the normal component of electron wave vector $k_{\perp}$ of the initial state is based on a free-electron model in the final state⁴,

$$k_{\perp} = \sqrt{\frac{2m}{\hbar^2} (E_{kin} \cos^2 \theta + V_0)} \quad (1)$$

in which E_{kin} is the kinetic energy of the photoelectron and V_0 is the inner potential. To probe the property of a 3D bulk-valence band, we performed an ARPES experiment dependent on photon energy in a range from 12 to 50 eV. In the Bi₂Se₃ compound, the value 9.7 eV of the inner potential of Bi₂Se₃ is determined from the top of the valence band and the bottom of the conduction band observed at photon energy 19 eV. We carefully examined our data in normal emission with varied photon energy. The top of the valence band at normal emission in Sb₂Te₂Se appears at either 18 eV or 19 eV. A reasonable value of the inner potential of Sb₂Te₂Se is between 10.64 and 9.64 eV. A k -space map in the bulk Brillouin zone (BZ) plotted with varied photon energy and collecting angle $\pm 18^\circ$ of the detector was used to explore the k_z dependence of TSS, RSS and bulk bands, as shown in FS5b. A range of photon energy from 12 eV to 42 eV is expected to cover several periods of the Brillouin zone in the k_z direction. Figure S4 displays the band-mapping plots of the ARPES spectra in

Sb₂Te₂Se (0001) along direction $\bar{\Gamma} - \bar{K}$ with photon energies varied from 12 eV to 24 eV. Figure S5a displays the band-mapping plots of ARPES spectra in Sb₂Te₂Se (0001) along direction $\bar{\Gamma} - \bar{M}$ with photon energies varied from 18 eV to 42 eV. Figure S6 displays the MDC plots at the Fermi level along direction $\bar{\Gamma} - \bar{M}$ with varied photon energy. No contribution was observable from the bulk valence band in the middle of the $\bar{\Gamma} - \bar{M}$ branch. Figure S7 shows a series of EDC in the Sb₂Te₂Se crystal in direction $\bar{\Gamma} - \bar{M}$ with varied photon energy. As shown in figure S7, the edge of the valence band in the middle of $\bar{\Gamma} - \bar{M}$ labeled with a black dashed line is clearly below the Fermi level. This observed behavior shows no contribution at the Fermi level in the middle of $\bar{\Gamma} - \bar{M}$, which is consistent with the analysis of the MDC.

According to the k -space map the bulk BZ and period of k_z , the band mapping result at 18 eV and 22 eV can correspond to the result at 30 or 32 eV and 36 eV. To examine the bulk band crossing at the Γ point, EDC and MDC plots near the Fermi level at the Γ point with 18, 22, 30 and 32 eV are shown in Figs. S4b and S4c. No obvious bulk band dispersion is observed in the plots. In figure S5c, the second derivative plot of photoemission intensity mapping at 22 and 36 eV have similar band structure due to the periodic property of k_z , but no obvious bulk band dispersion was also observed in the MDC plots at 22 eV and 36 eV.

4. Fourier-transform infrared spectra (FTIR)

A commercial Fourier-transform infrared (FTIR) spectrometer (Cary 660 FTIR Spectrometer, Agilent Technology) was employed to perform temperature-dependent mid-infrared absorption measurements. Free-standing Sb₂Te₂Se samples were cleaved to be thin enough for measurements, but the actual thicknesses of the used samples are unknown. As shown in Fig. S8a, the absorption edge (2750 cm⁻¹, 341 meV) at room temperature (296 K) is higher than the theoretical prediction⁶. As the

temperature decreases, the absorption edge becomes clearer and trends to 417meV (3359 cm⁻¹) at 98 K.

5. Measurement of resistivity transport

To measure the transport properties of Sb₂Te₂Se and Sb₂Te₃ compounds, we used silver paint and gold wires to connect to the cleaved crystal. A commercial physical property measurement system (Quantum Design PPMS Model 6000) was used to measure the temperature dependence of resistivity with a conventional four-wire system. As shown in figure S9, the resistivity of Sb₂Te₂Se is clearly about ten times that of Sb₂Te₃ and the extracted carrier concentration $\sim 3.1 \times 10^{19} \text{ cm}^{-3}$ of Sb₂Te₂Se is less than that $\sim 2.2 \times 10^{20} \text{ cm}^{-3}$ of Sb₂Te₃.

References

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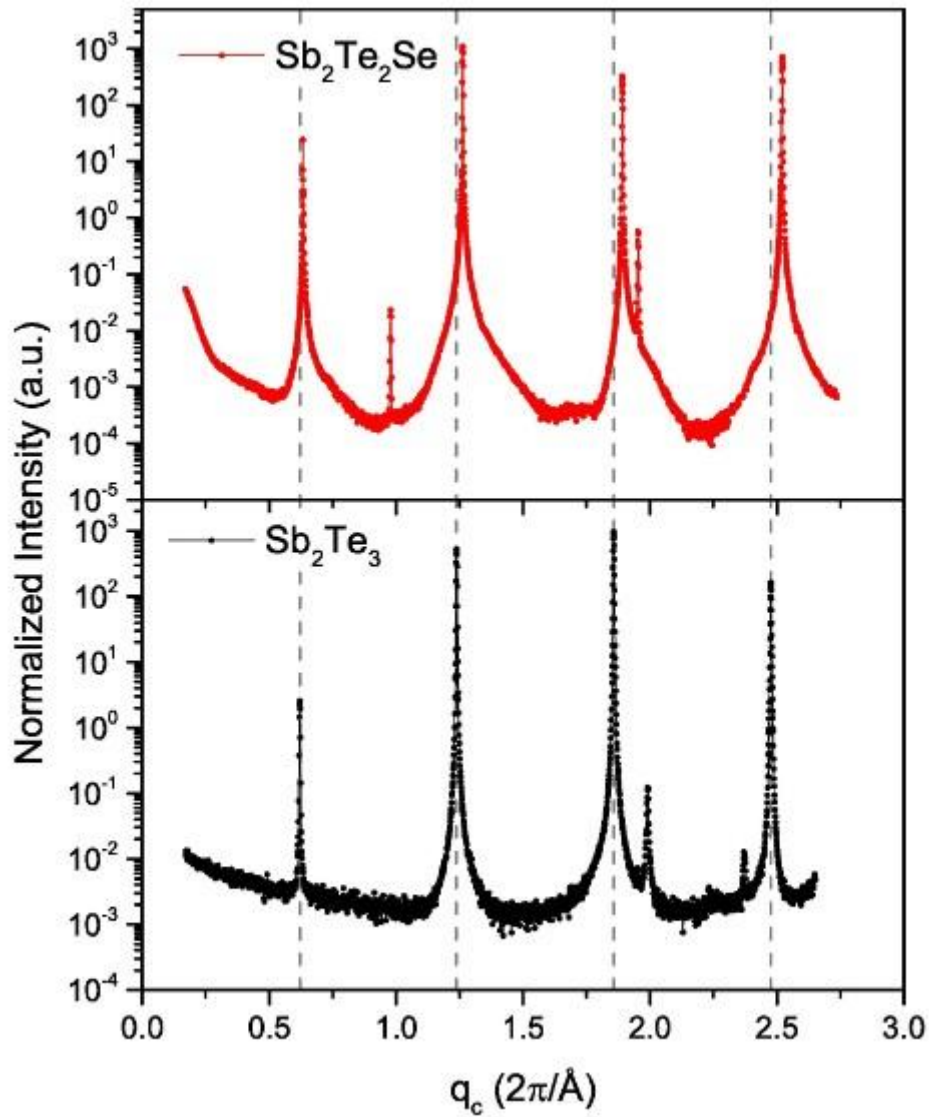


Figure S1 |*L*-scan in high-resolution X-ray diffraction measurements of Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$. Bulk crystals Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ with orientation [0001] were used for this experiment. The θ - 2θ scans along c^* of Sb_2Te_3 and $\text{Sb}_2\text{Te}_2\text{Se}$ are shown in the figure as indicated. The four major signals indicate reflections (0 0 0 3), (0 0 0 6), (0 0 0 9) and (0 0 0 12); the dashed lines show the positions of signals of Sb_2Te_3 .

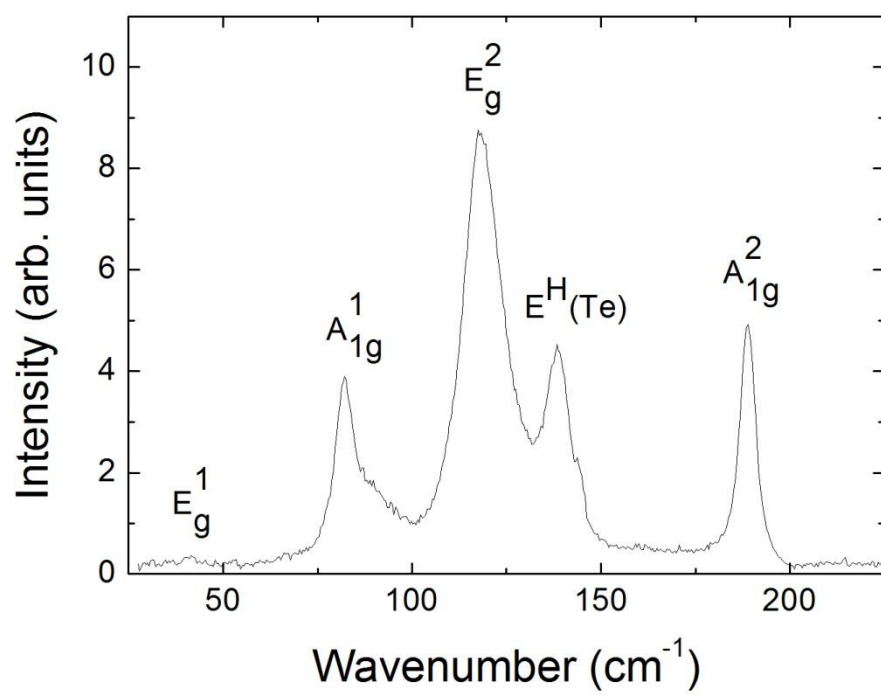


Figure S2 | Raman Stokes modes of $\text{Sb}_2\text{Te}_2\text{Se}$ near 296 K.

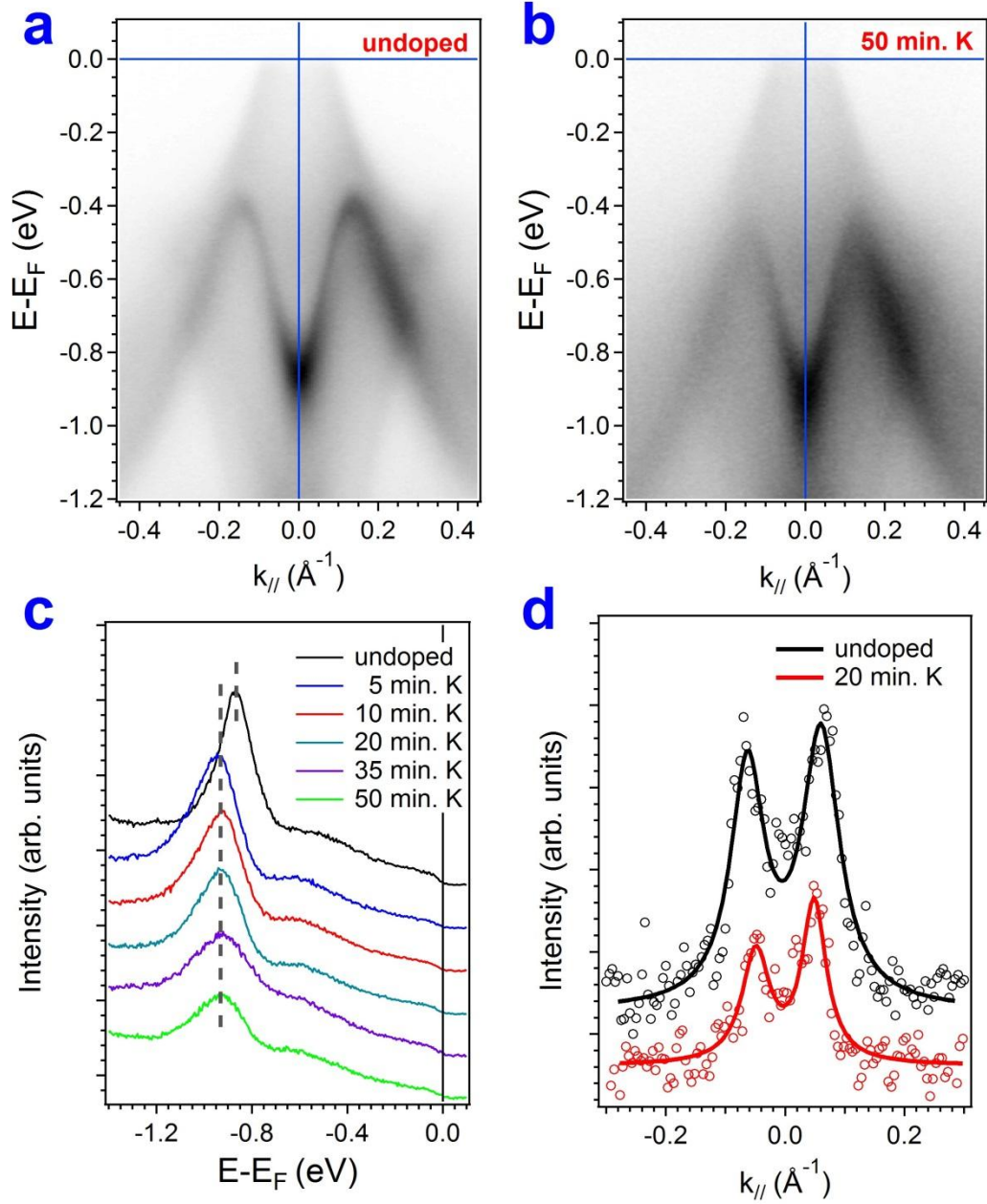


Figure S3 | Electronic structure of potassium-doped $\text{Sb}_2\text{Te}_2\text{Se}$. **a**, Image of ARPES spectra of undoped $\text{Sb}_2\text{Te}_2\text{Se}$ in direction $\bar{\Gamma} - \bar{K}$. **b**, Image of ARPES spectra of potassium-doped $\text{Sb}_2\text{Te}_2\text{Se}$ in direction $\bar{\Gamma} - \bar{K}$. **c**, Comparison of EDC in the normal emission for undoped and doped $\text{Sb}_2\text{Te}_2\text{Se}$ crystals. The position of the maximum of the RSS moves to increased binding energy after deposition for 5 min, but no further change was observed with prolonged deposition. **d**, MDC at the Fermi level for undoped and doped $\text{Sb}_2\text{Te}_2\text{Se}$ crystals. The smaller value of k_F in doped $\text{Sb}_2\text{Te}_2\text{Se}$ crystal indicates *an*-type doping behavior.

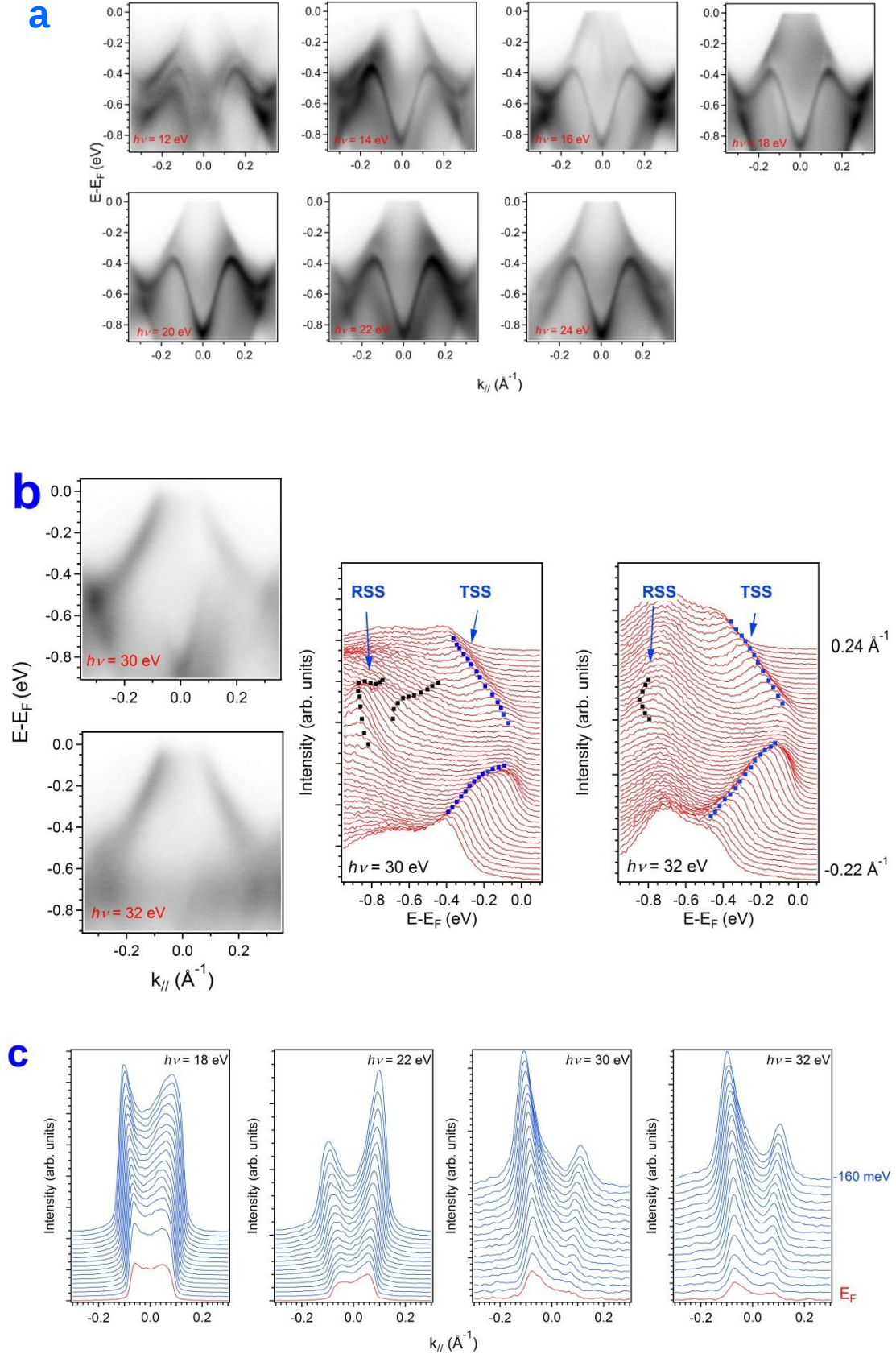


Figure S4 | Results of band mapping in a $\text{Sb}_2\text{Te}_2\text{Se}$ crystal in direction $\bar{\Gamma} - \bar{K}$ with varied photon energy. **a**, Band mapping images with varied photon energy. **b**,

Band mapping images and EDC plots with 30 and 32 eV, MDC plots around the Fermi level at the Γ point with 18, 22, 30 and 32 eV. No obvious bulk band dispersion is observed around the Γ point near the Fermi level in the EDC and MDC plots. A flat shaded area existed between -0.6 eV and -0.8 eV at 32 eV plot in **c** can be attributed as Sb 4*d* due to high order light.

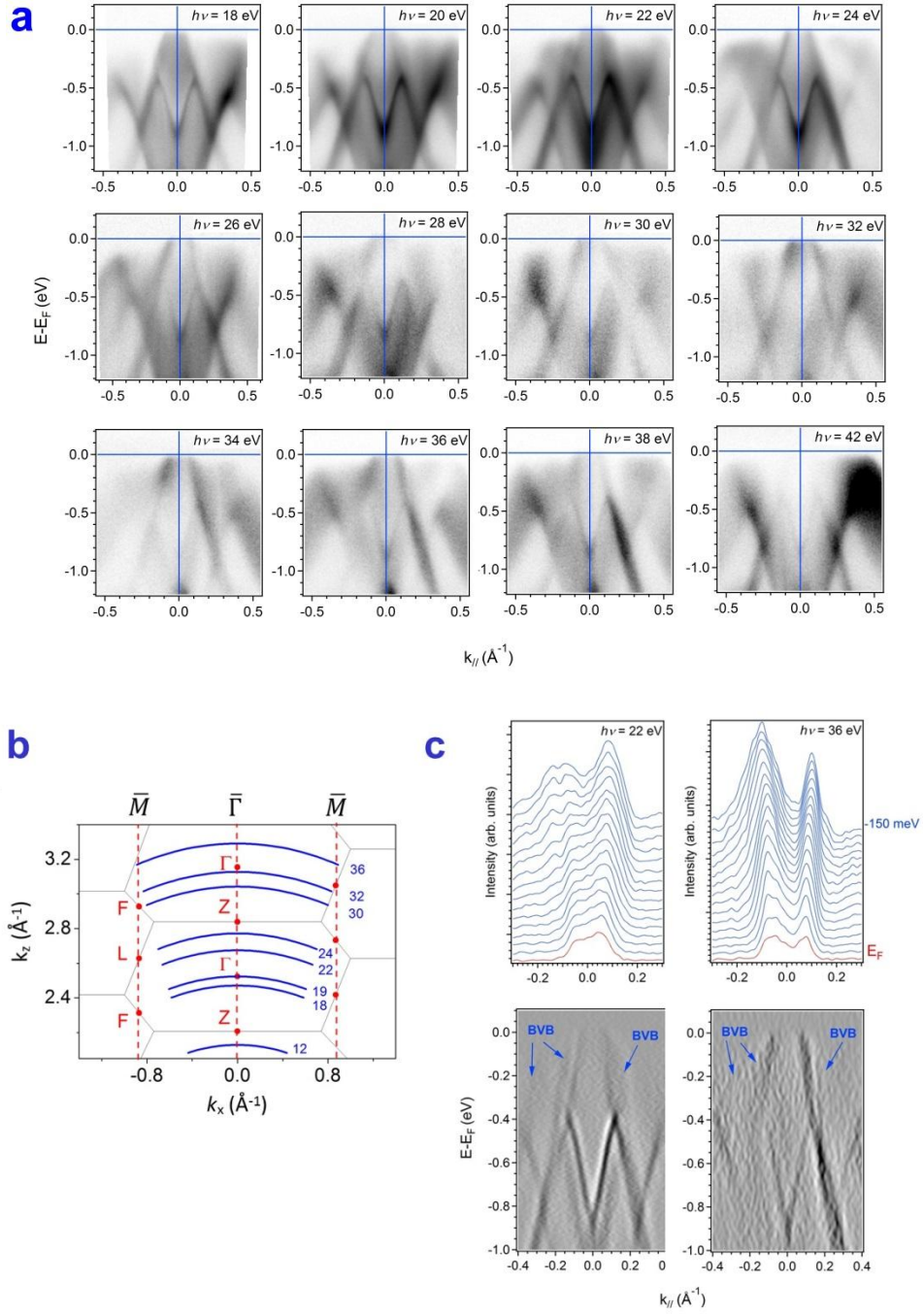


Figure S5 | Results of band mapping in a $\text{Sb}_2\text{Te}_2\text{Se}$ crystal in direction $\bar{\Gamma} - \bar{M}$ with varied photon energy. **a**, Band mapping images with varied photon energies. **b**, a k-space map in the bulk Brillouin zone (BZ) plotted with varied photon energy and collecting angle $\pm 18^\circ$ of the detector. **c**, Upper: MDC plots around the Fermi level at the $\bar{\Gamma}$ point with 18, 22, 30 and 32 eV. Bottom: Second derivative plot of photoemission intensity mapping at 22 and 36 eV.

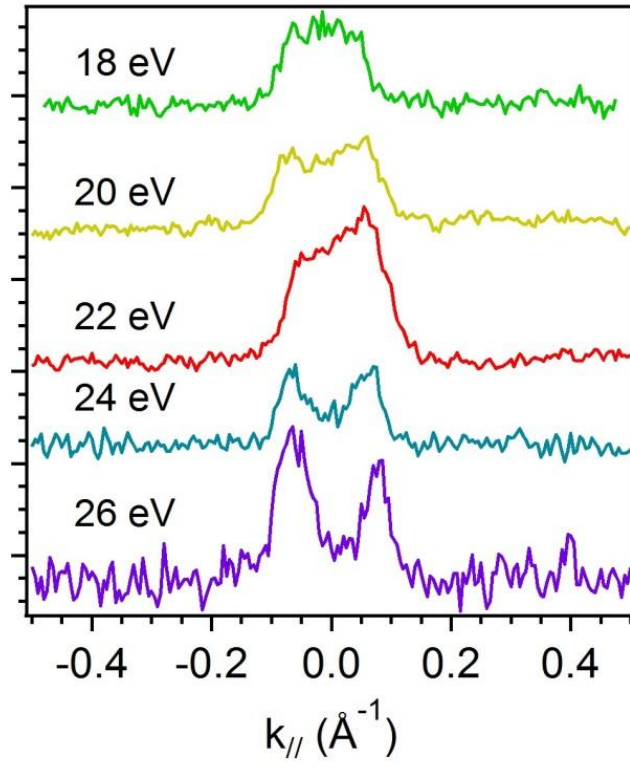


Figure S6 | MDC at the Fermi level in $\text{Sb}_2\text{Te}_2\text{Se}$ crystal in direction $\bar{\Gamma} - \bar{M}$ with varied photon energy. No contribution was observable from the bulk valence band in the middle of the $\bar{\Gamma}\bar{M}$ branch.

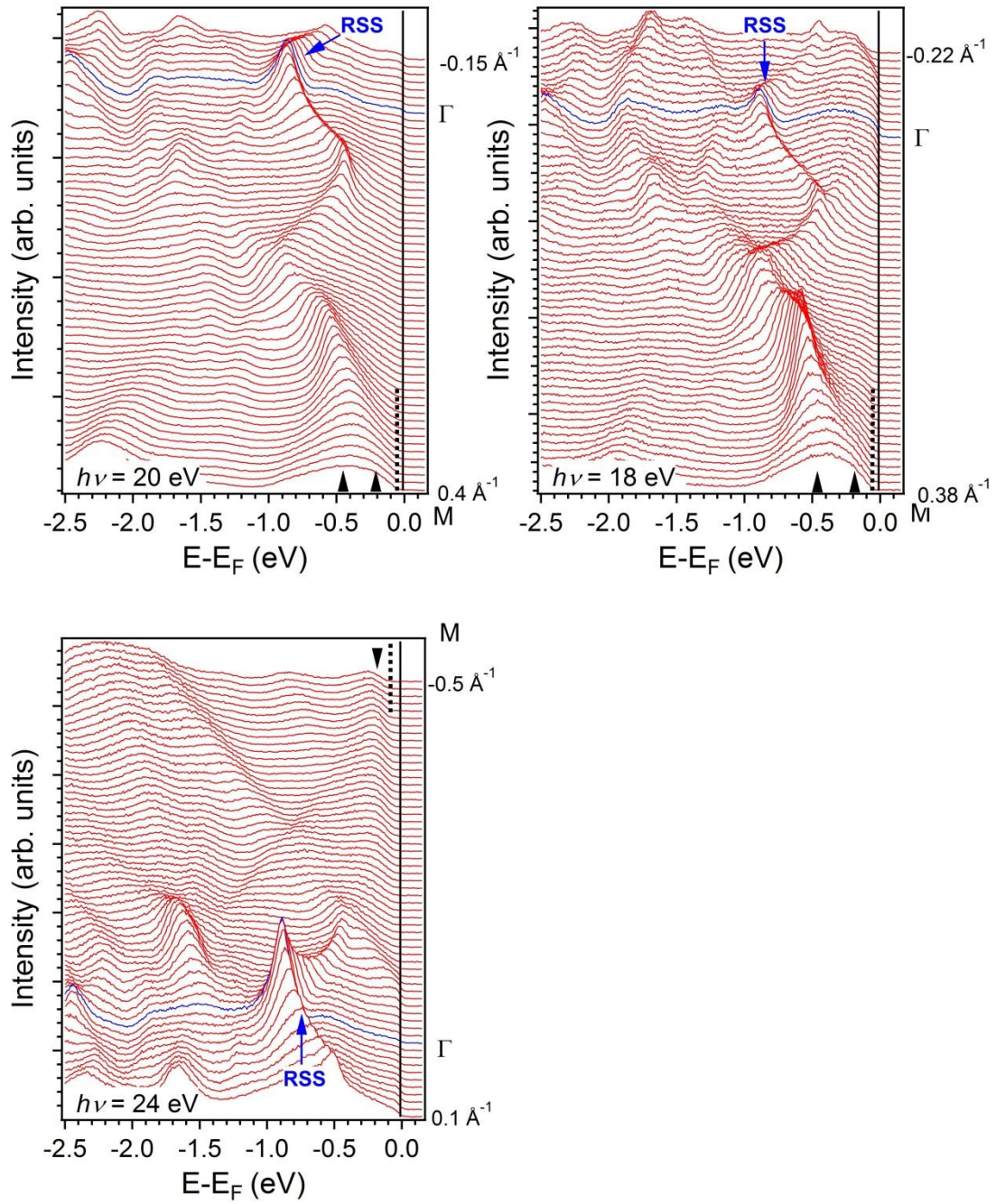


Figure S7 | EDC in $\text{Sb}_2\text{Te}_2\text{Se}$ crystal in direction $\bar{\Gamma} - \bar{M}$ with varied photon energy. As shown the dash line in each plot, no contribution was observable from the bulk valence band in the middle of the $\bar{\Gamma}\bar{M}$ branch.

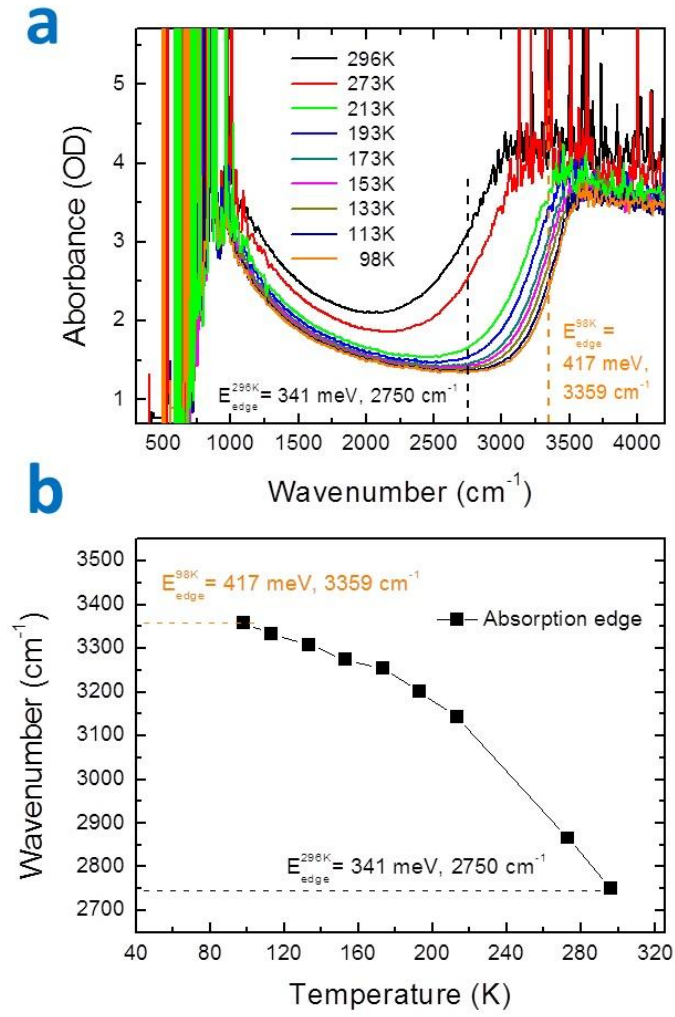


Figure S8 | FTIR spectra of free-standing $\text{Sb}_2\text{Te}_2\text{Se}$ samples at low temperature. **a**, Mid-infrared absorption spectra of free-standing $\text{Sb}_2\text{Te}_2\text{Se}$ were measured in a range 500-4200 cm^{-1} . The middle of the edges is chosen as the absorption edge. **b**, The temperature dependence of absorption edge.

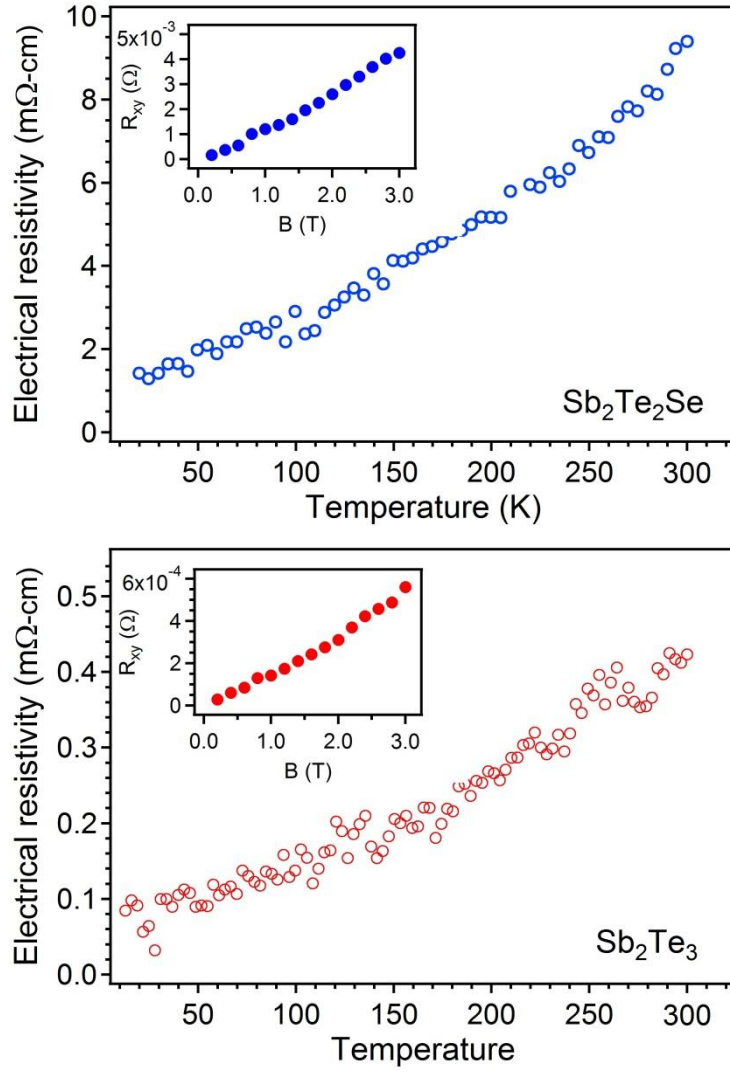


Figure S9 | The temperature dependence of resistivity and Hall measurement at RT with $\text{Sb}_2\text{Te}_2\text{Se}$ and Sb_2Te_3 single crystals. The extracted carrier number is $3.1 \times 10^{19} \text{ cm}^{-3}$ and $2.2 \times 10^{20} \text{ cm}^{-3}$ for $\text{Sb}_2\text{Te}_2\text{Se}$ and Sb_2Te_3 respectively.