Electronic supplementary information (ESI)

Simultaneous observation of surface- and edge-states of a 2D topological insulator through scanning tunneling spectroscopy and differential conductance imaging

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Experimental section

Materials

Sodium selenite (Na_2SeO_3), bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), hydroxylamine solution (50 wt. % in H_2O), and poly(vinylpyrrolidone) (PVP, M_W = 55000 g/mol Da) were purchased from Sigma-Aldrich. In addition, acetic acid glacial and ethylene glycol procured from Merck chemicals were also used.

Synthesis of the Bi_2Se_3 nanoplates

The nanoplates were grown following a reported article.[S1] A 10 mL solution of PVP in ethylene glycol (20 mg/mL) was first formed in a 50 mL reaction flask. 10 mL of Na_2SeO_3 (6.1 mg/mL) and 5 mL of $Bi(NO_3)_3{\cdot}5H_2O$ (22.6 mg/mL) solutions of ethylene glycol and 6 mL of acetic acid were added to the flask under continuous stirring condition under nitrogen atmosphere. Temperature of the reaction flask was then raised to 165 °C at which the transparent solution turned light yellow. 0.6 mL of hydroxylamine diluted in ethylene glycol was injected rapidly in the flask; the solution immediately turned dark purple indicating formation of selenobismuthite Bi_2Se_3 nanoplates. After a certain time, the reaction was stopped by a rapid cooling down to room temperature. We varied the reaction time to obtain different thickness of the nanoplates.

Characterization of the nanoplates

The nanoplates were characterized with X-ray diffraction (XRD) studies, energy-dispersive X-ray (EDX) analyses, transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images, and X-ray photoelectron spectroscopy (XPS). The measurements were performed with a Rigaku MiniFlex X-ray diffractometer, and JEM 2100F Jeol TEM, and an XPS instrument (Omicron: Serial no. 0571), respectively.

More importantly, the nanoplates were characterized in a Pan-style ultrahigh vacuum scanning tunneling microscope (UHV-STM) of M/s RHK Technology at 80 K. To do so, drop-cast films of the nanoplates from an ultra-dilute solution formed on a Highly Ordered Pyrolytic Graphite (HOPG) were placed in the STM chamber. The pressure of the microscope was 1.2×10^{-10} Torr; temperature of the substrate and the tip both was 80 K. Pt/Ir (80%:20%) tips, which were formed through a mechanical cut of a wire having a diameter of 0.25 mm, were used to measure tunneling current. As set-points for approach of the tip, a range of set-currents was used by applying 1.0 V as the sample bias. Tunneling current versus sample voltage (I-V) characteristics were recorded after disabling the feed-back loop. dI/dV spectra that have correspondence to the density of states (DOS) were recorded using a lock-in amplifier (20 mV rms, 997 Hz). Since bias was applied to the sample, electrons could be injected to the conduction band (CB) at positive voltages; DOS peaks at positive voltage hence corresponded to the location of CB band-edges. The peaks at negative voltages similarly represented valence band (VB) edges. d*I*/d*V* images of the nanoplates were also recorded at different sample biases.

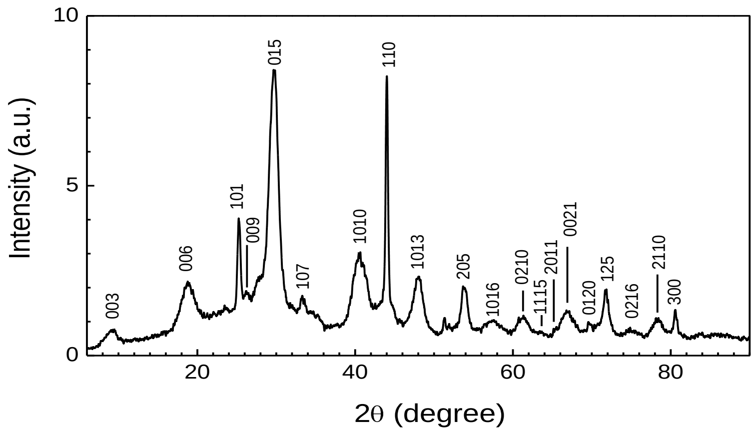

Fig. S1 XRD pattern of Bi_2Se_3 nanoplates. Lattice planes of Bi_2Se_3, as available in JCPDS Card Number #33-0214, are shown on the peaks of the spectrum.

XPS analysis

In the XPS spectrum, peaks only for Bi, Se, C, and O could be observed implying high purity of the nanoplates. The binding energies of Bi4f and Se3p could be found to overlap near 160 eV. High-resolution spectrum for Bi4f state showed that the $4f_{7/2}$ and $4f_{5/2}$ appeared at 158.0 and 162.3 eV, respectively. Similarly, the Bi4d state could be assigned to $4d_{5/2}$ and $4d_{3/2}$ with a separation of 23.85 eV, which agrees very well with the reported value of 23.5 eV. Se3d and Se3s states could be seen to appear at 53.5 and 229.2 eV, respectively. All the energies agree with the NIST X-ray Photoelectron Spectroscopy Database.

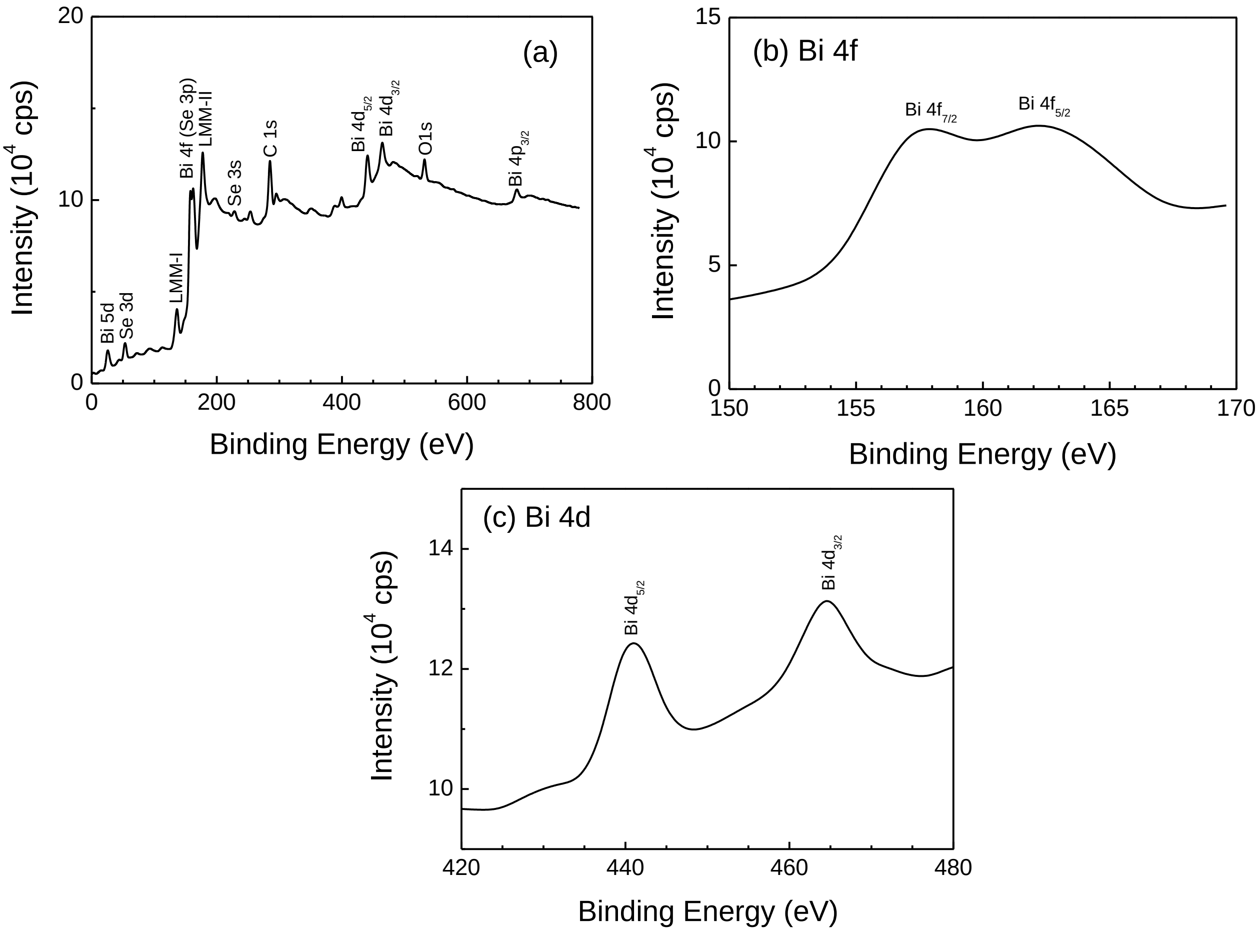

Fig. S2 (a) XPS analysis of Bi_2Se_3 nanoplates. (b) and (c) represent high-resolution spectrum to observe the splitting of Bi4f and Bi4d states, respectively.

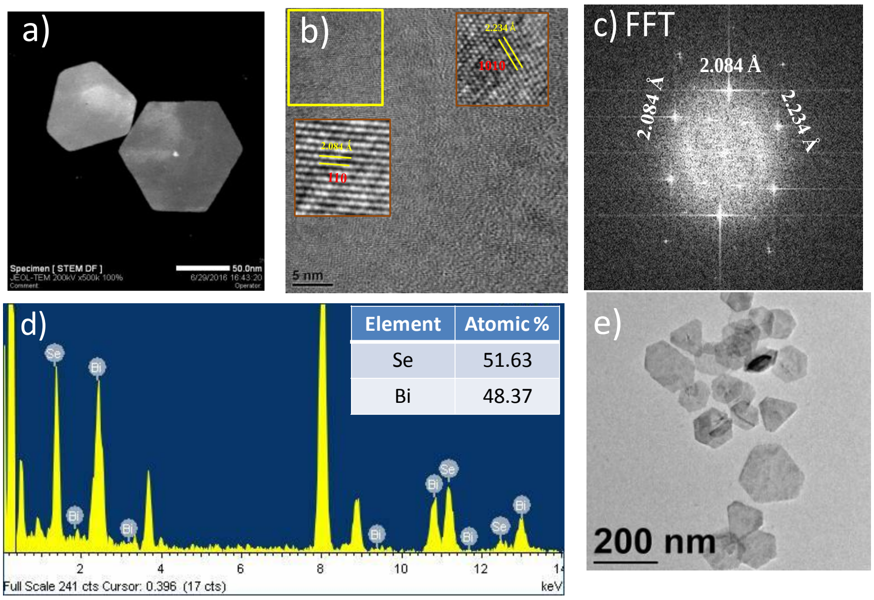

Fig. S3 (a) Dark-field TEM image of Bi_2Se_3 nanoplates. (b) HR-TEM image showing the planes of the nanocrystals; the yellow square indicates the region where FFT was performed to determine inter-planner spacing. (c) Fast-Fourier Transform (FFT) of a HR-TEM image and (d) EDX analysis of Bi_2Se_3. (e) An additional TEM image of Bi_2Se_3 nanoplates.

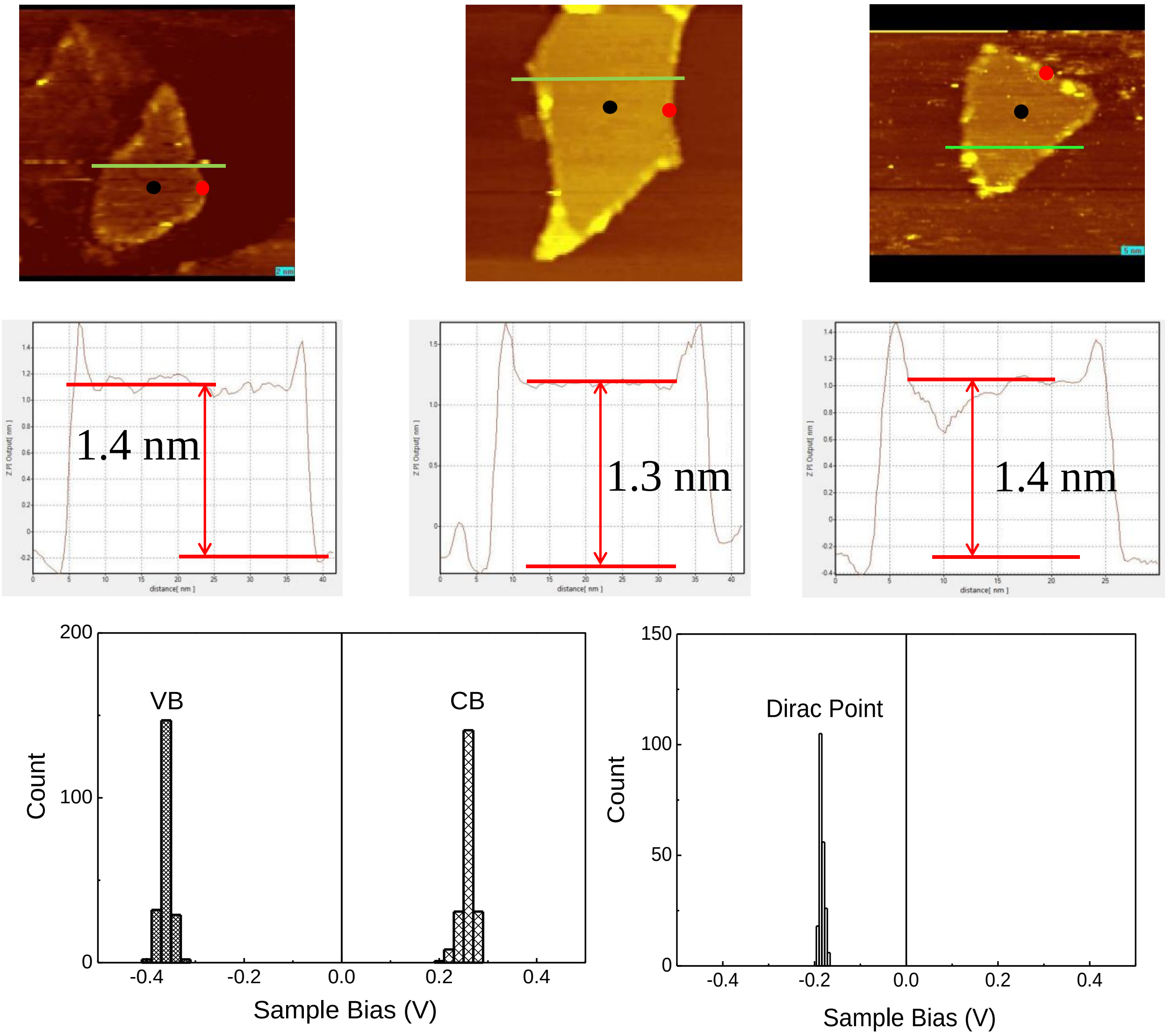

Fig. S4 STM topographies of various shapes and sizes of Bi_2Se_3 nanoplates having a thickness of around 1.4 nm. The individual height-profile indicates the thickness of the respective nanoplate. The histogram plots manifest the invariance of CB and VB band-edges as well as the Dirac point on the planar size and shape of Bi_2Se_3 nanoplates of same thickness.

S1 Y. Min, G. Park, B. Kim, A. Giri, J. Zeng, J. W. Roh, S. I. Kim, K. H. Lee, U. Jeong, *ACS Nano*, 2015, **9**, 6843-6853.