Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Highly Anisotropic Two-dimensional Bi_2Se_3 Crystals Synthesized by Solution-based Control of Nucleation Environment

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Experimental Section

Synthesis of large hexagonal and circular disc

Seed mediated growth

A typical synthesis starts with the preparation of small circular disc as a seed in the presence of chloride ion, followed by an *in situ* gradual addition of the complexed precursor for the overgrowth of the seed. The reaction was carried out in anhydrous ethylene glycol (EG) with poly(vinylpyrrolidone) (PVP) at 195^{o}C under Ar atmosphere in the presence of ammonium chloride and EDTA. The reaction started by the drop wise addition of EG solution (20 mL) containing 450 mg PVP and 50 mg Na_2SeO_3 in a 25 ml round bottom flux 1 (RB1) to a 50 ml round bottom flux 2 (RB2) containing Bi_2Se_3 seed in 40 mL EG. Bi_2Se_3 seed was formed when 40 mL EG, 85 mg $Bi(CH_3COO)_3$, 85 mg EDTA, 75 mg NH_4Cl and 900 mg PVP were refluxed at 195 ^{o}C for 1 hr in RB2.The drop wise addition of the complexed Bi and Se procures from RB1 to RB2 for 1.5 hr was done by using a glass tube connected with two RB through septum. Drop wise transfer through the glass tube is very important (Figure 1a). Initially we were trying to transfer through cannula composed of stainless steel. We observe that it reacts with the reaction mixture during high temperature addition. Hence a suitably bent glass tube solves the problem. Two RB (three necked) was connected with the two reflux condenser and with an Ar line. Among the other two necks of RB1, one is closed with a septum and the other is connected to RB2 through a suitably bent glass tube. The slow transfer is possible due to the excess pressure which was controlled by placing needles into the septum on the top of the reflux condenser. Then the reaction temperature was increased to 195 ^{o}C for additional 6 hr. After 6 hr, the color of the solution had changed to gray, which indicates the formation of products.

By keeping all other reaction conditions same but using 60 mg EDTA in RB2 we obtained spiral growth of the Bi_2Se_3 nanoplate.

One pot synthesis

The reaction was carried out in anhydrous EG with PVP at 195 ^oC under Ar atmosphere in the presence of ammonium chloride and EDTA. Bi_2Se_3 nanodisk having 15-20 μm lateral diameter was formed when 60 mL EG, 85 mg $Bi(CH_3COO)_3$, 85 mg EDTA, 75 mg NH_4Cl and 1350 mg PVP were refluxed together at 195 ^oC for 8 hr.

Supplementary Figures

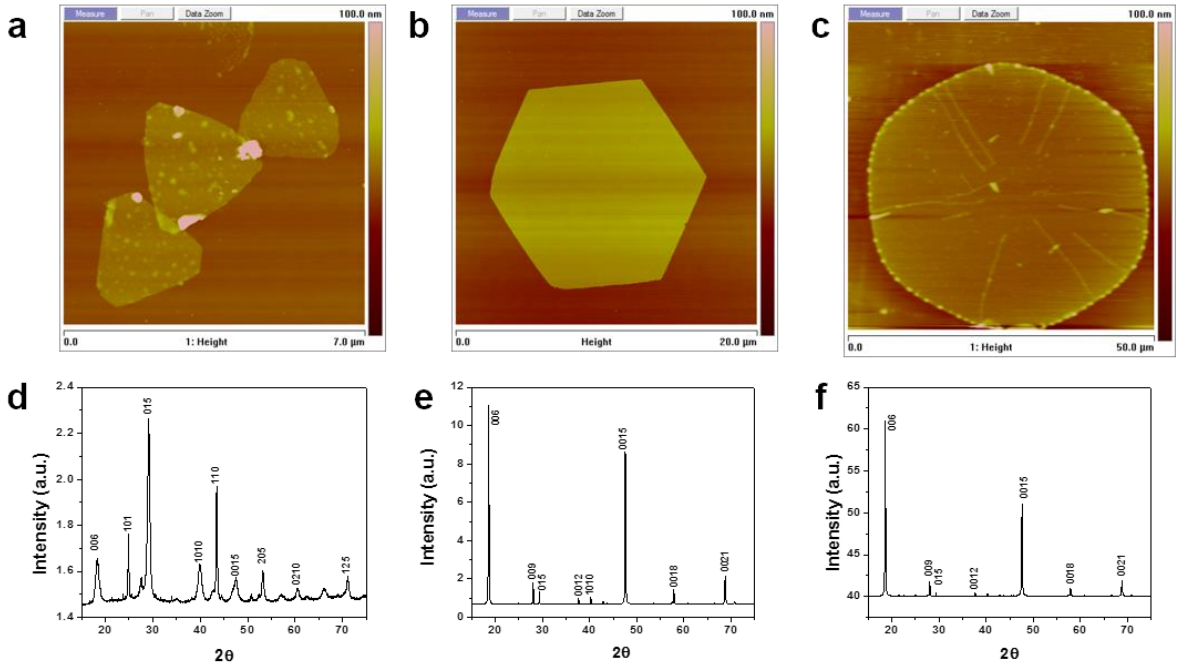

Figure S1 XRD pattern and AFM image of the as prepared Bi_2Se_3 (a) without complexing agents, (b) one pot reaction in predence of complexing agent EDTA and Cl^- , and (c) seed mediated growth in presence of EDTA and Cl^-

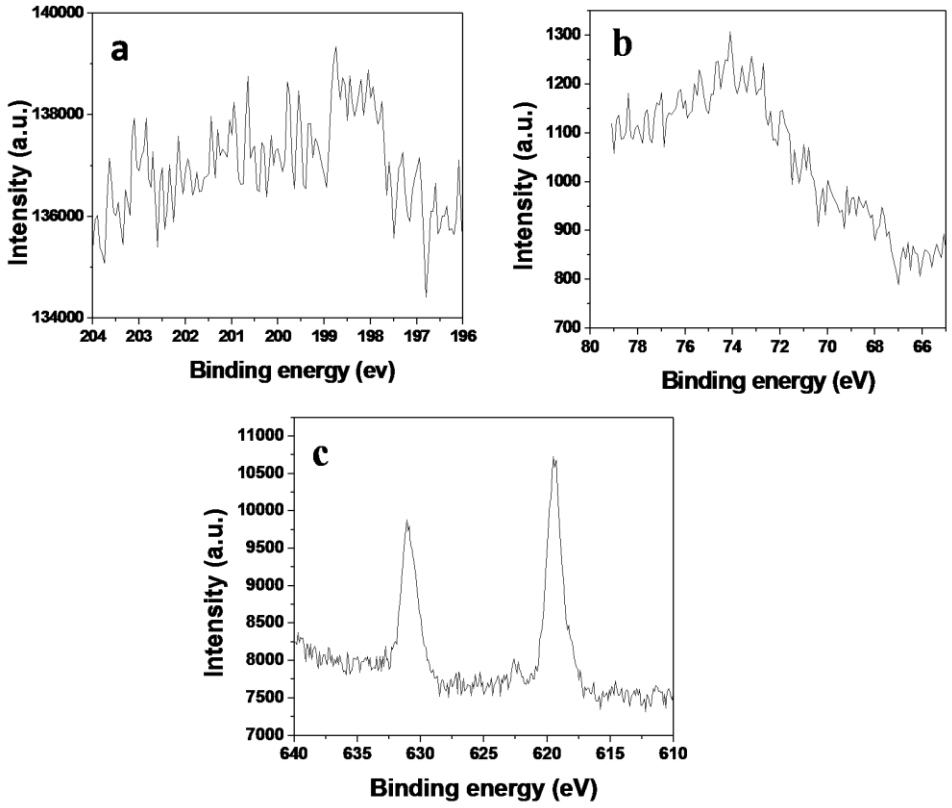

Figure S2 XPS spectra of halide ions, (a) Cl2p, (b) Br3d and (c) I3d adsorbed on the pristine Bi_2Se_3 prepared in presence of different halide ion separately.

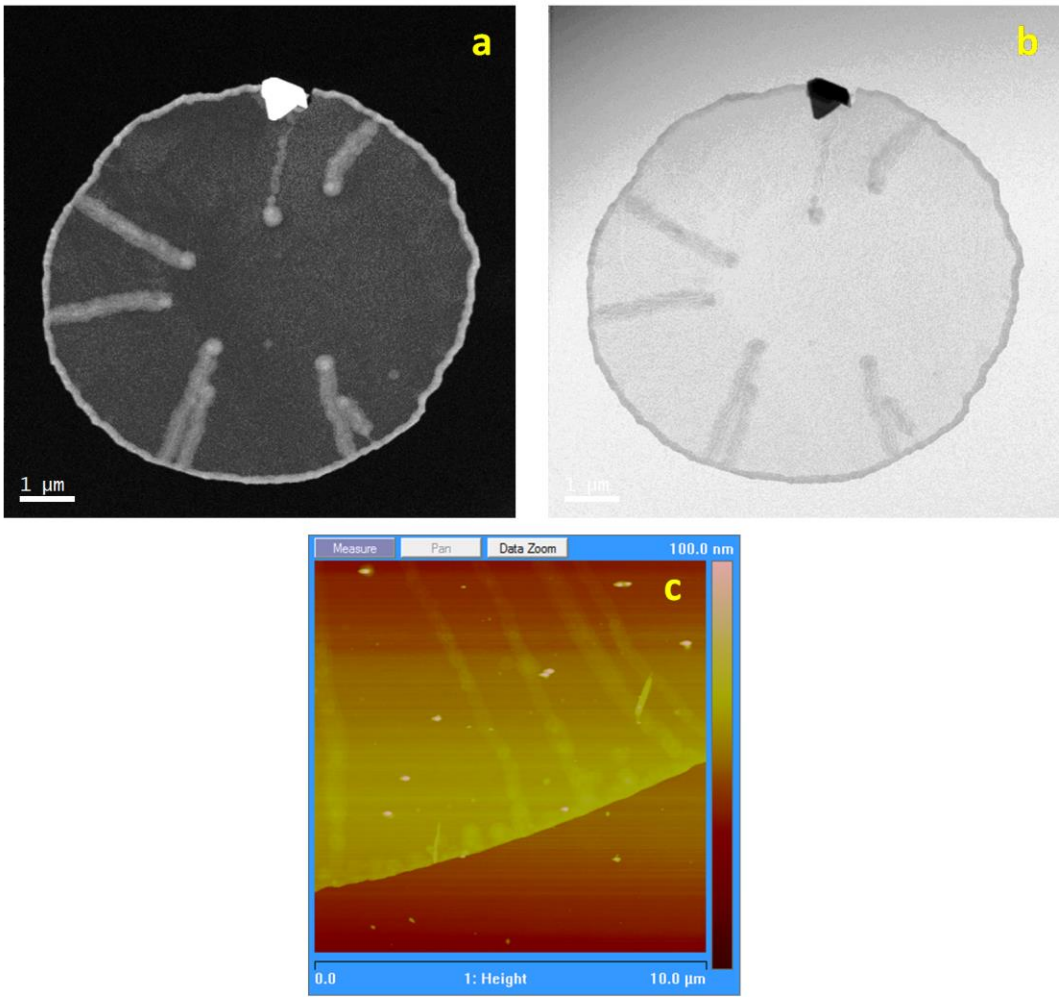

Figure S3 (a,b) HAADF-STEM and (c) AFM images of the synthesized Bi_2Se_3 disk shows the multi grained nature of the crystals.

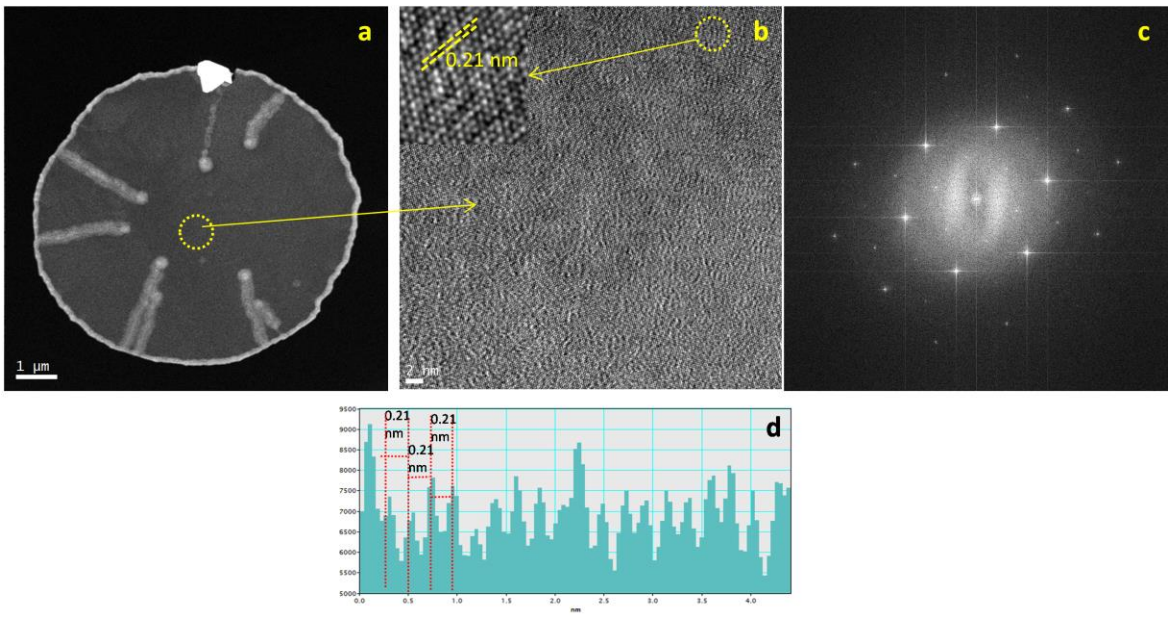

Figure S4 (a) HAADF-STEM and (b) HRTEM images of the encircled portion in figure A of the synthesized Bi_2Se_3 disk. (c) Corresponding sharp FFT pattern and (d) uniform lattice spacing of 0.21 nm between (110) planes speaks for the less defect in that region.

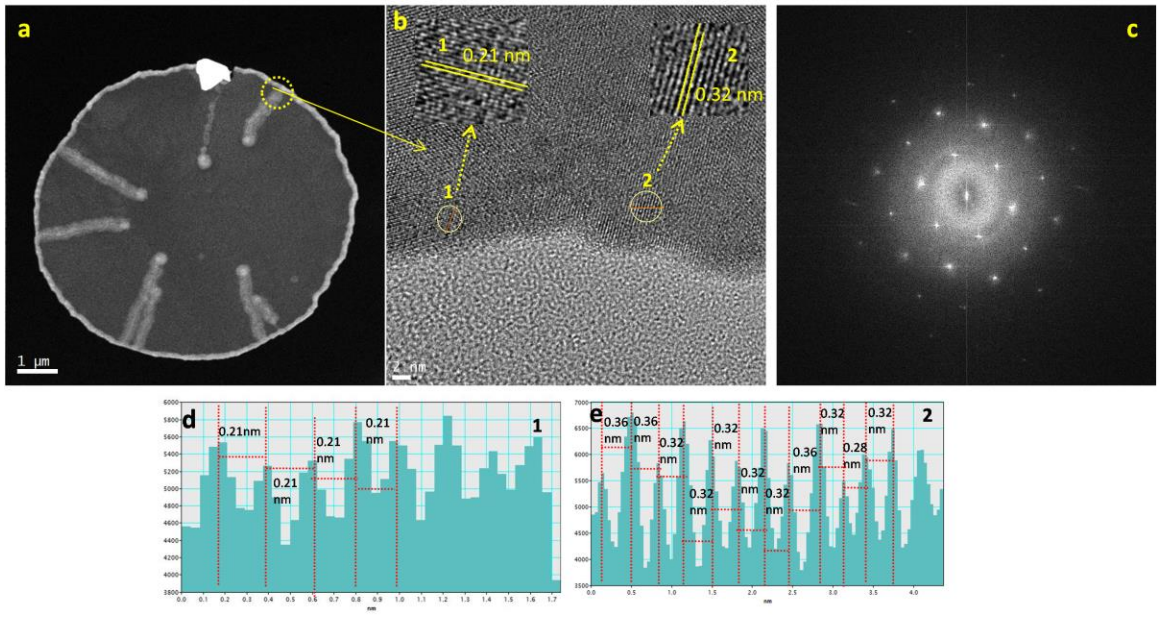

Figure S5 (a) HAADF-STEM and (b) HRTEM images of the encircled portion in figure a of the synthesized Bi_2Se_3 disk. (c) Corresponding scattered FFT pattern speaks for the more no of defect compare to the smooth region. (d, e) Shows two different lattice spacing, 0.21 nm between (110) planes and 0.32 nm for (104).

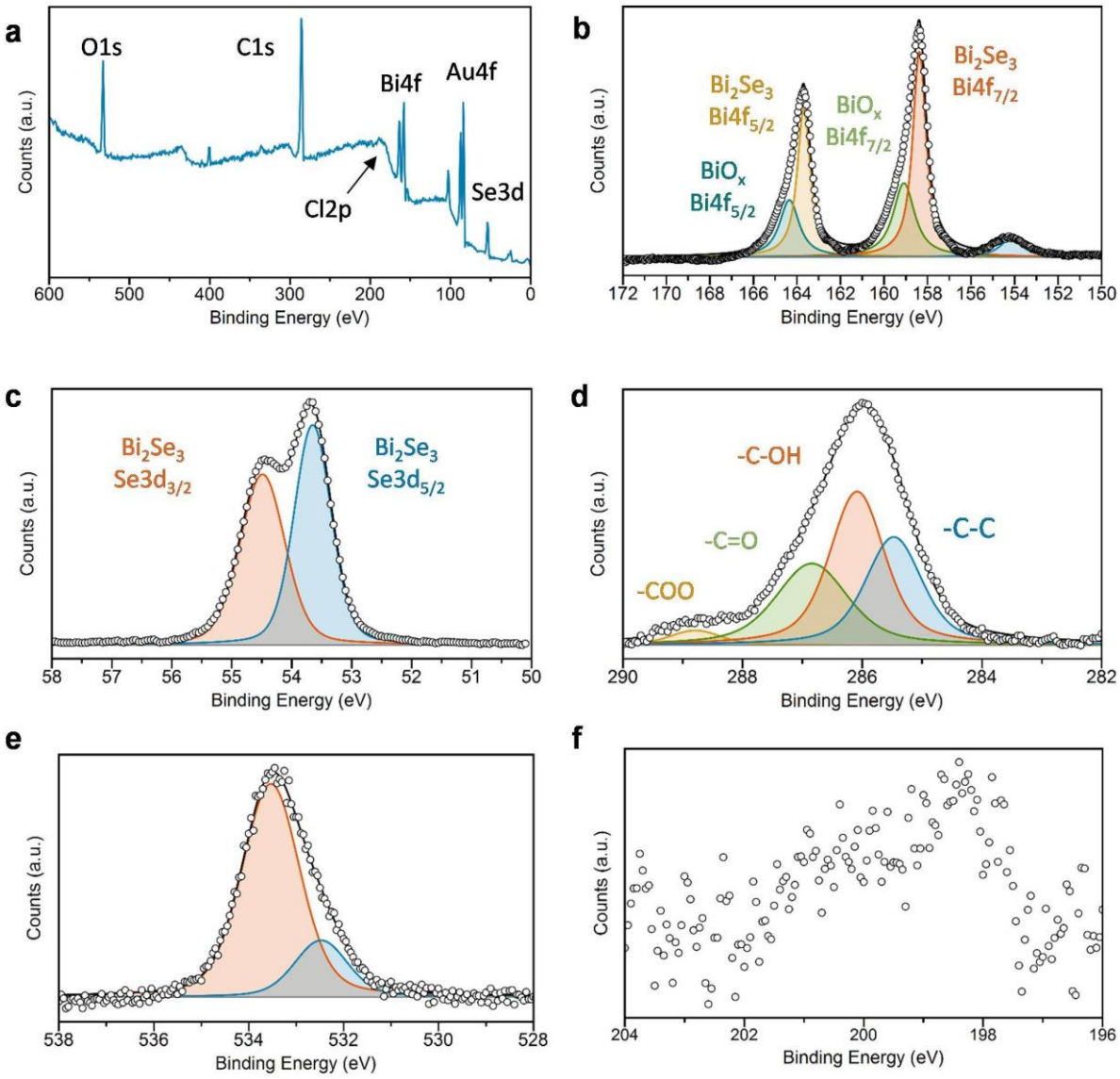

Figure S6 XPS spectrum of pristine Bi_2Se_3. (a) Survey spectrum, (b) Bi4f, (c) Se3d, (d) C1s, (e) O1s, and (f) Cl2p.

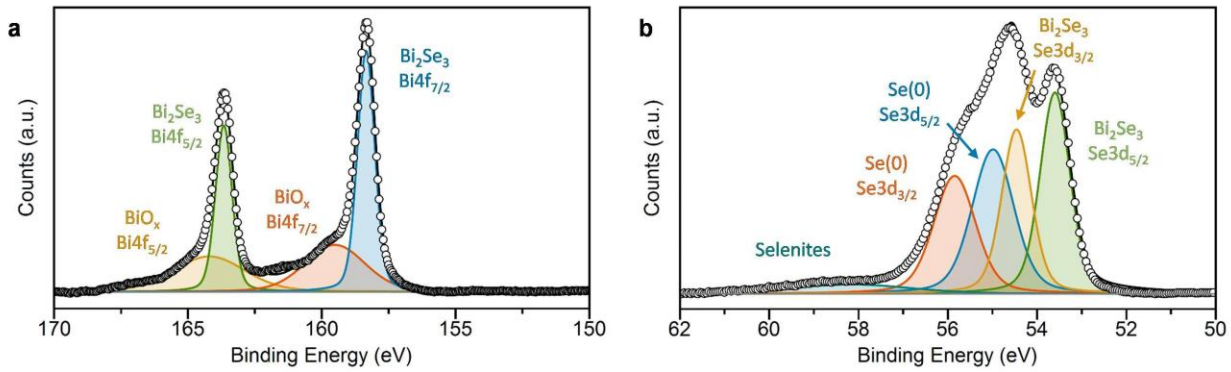

Figure S7 XPS spectra of the seeding process (a: Bi4f, b: Se3d).

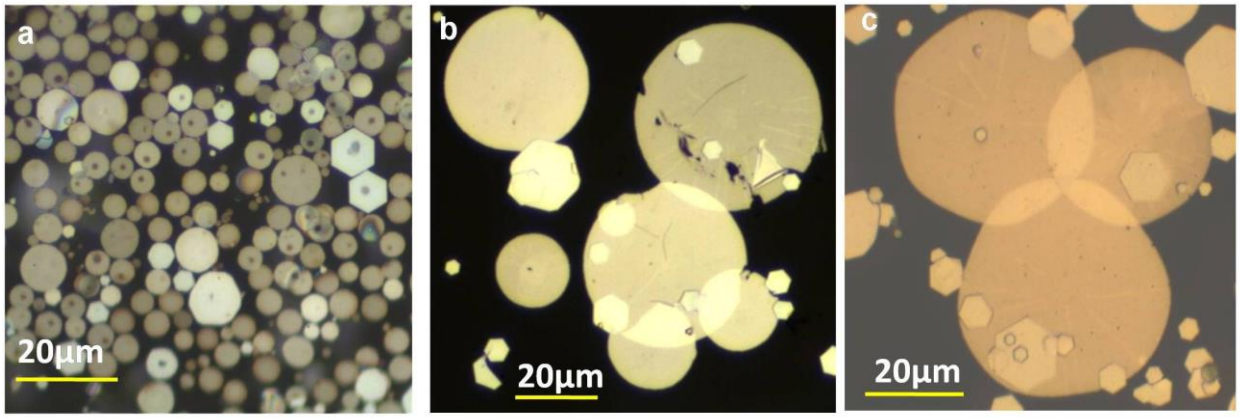

Figure S8 Time dependent growth for the seed mediated synthesis of Bi_2Se_3 at low precursor concentration: Optical imaging study at different time interval (a: After 1.5 hr, b: After 4 hr and c: After 8 hr).

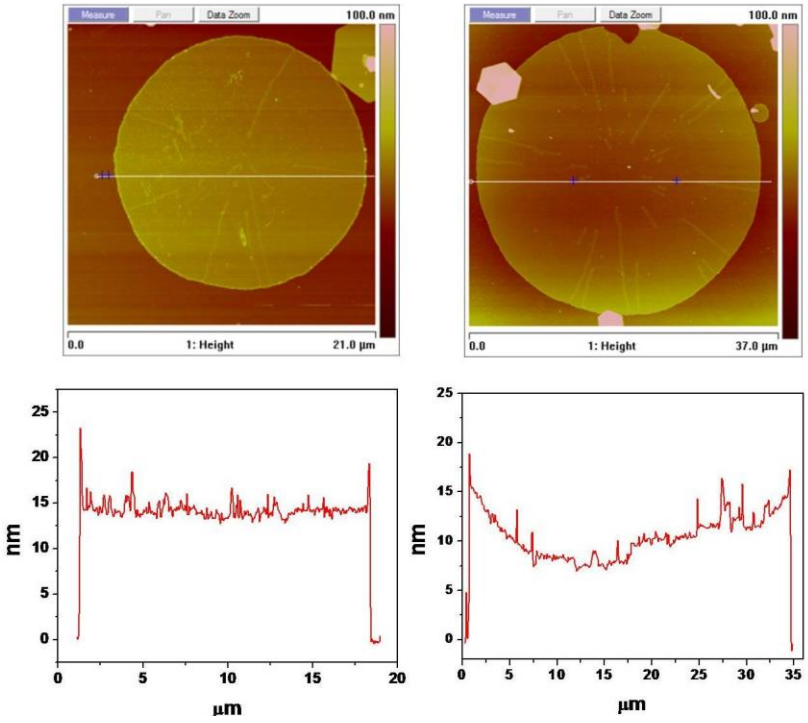

Figure S9 AFM images and corresponding height profile of circular intermediates of Bi_2Se_3 crystals obtained at different reaction time.

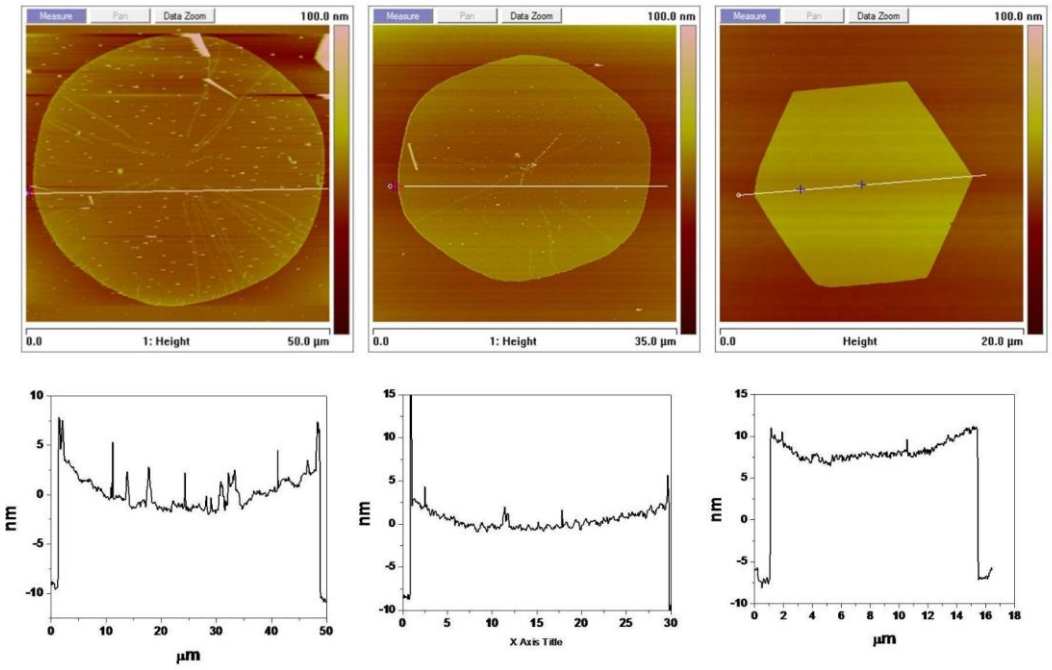

Figure S10 AFM images and corresponding height profile of hexagonal Bi_2Se_3 nanoplates.

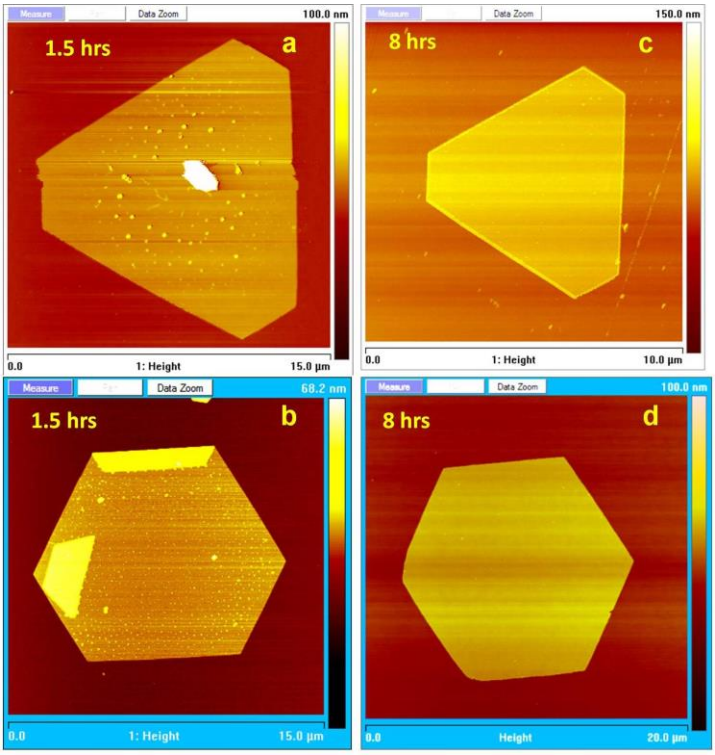

Figure S11 AFM images of (a,b) intermediate and (c,d) final product (Bi_2Se_3) prepared at high precursor concentration.

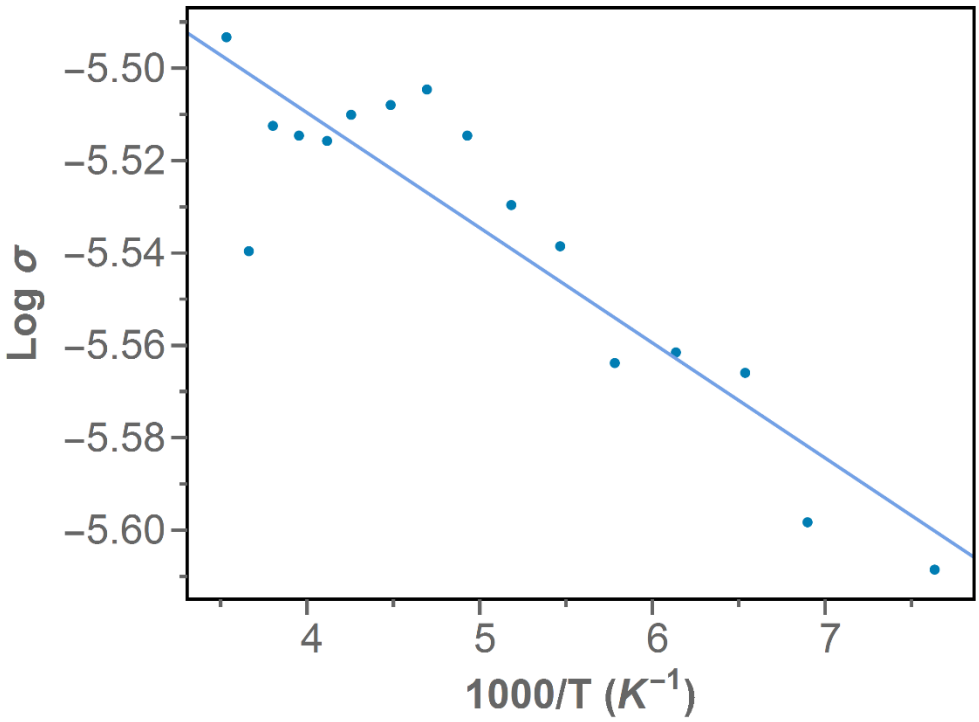

Figure S12 Temperature-dependent conductivity plot of a Bi_2Se_3 electric device. From this Arrhenius plot we found that the energy gap is 4.3 meV, which is much smaller than the band gap of typical Bi_2Se_3 crystals. We attribute this small gap to high doping; when a semiconductor is highly n-doped, the donor level is formed, and the energy gap between the conduction band and the donor level is much smaller than that of the energy gap (or the band gap) between the conduction band and the valence band. We assume that reagents such as chelating ligands or chloride anions may remain in the crystal, as discussed in the manuscript, and it may result in high doping.