

## Electronic Supporting Information (ESI)

### Ultrathin Septuple Layered $\text{PbBi}_2\text{Se}_4$ Nanosheets

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#### Detailed Experimental Section

**Reagents.** Lead (II) acetate trihydrate (ACS, 99.0-103.0% Alfa Aesar), Bismuth (III) acetate (90%, Alfa Aesar), Selenourea (99%, Alfa Aesar), Oleic Acid (tech. 90%, Sigma Aldrich), 1-Octadecene (tech. 90%, Sigma Aldrich) were used for synthesis without further purification.

**Synthesis of  $\text{PbBi}_2\text{Se}_4$  nanosheets.** In a typical synthesis, 50.8 mg (0.131 mmol) of  $\text{Bi}(\text{OAc})_3$ , 25mg (0.065 mmol)  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  and 8 ml oleic acid were taken in a 50 mL three neck round bottom flask and heated at 100 °C for 2 hours under vacuum to obtain a homogeneous clear metal precursor. The resulting clear precursor transferred in a 50 mL Teflon lined stainless steel autoclave inside an  $\text{N}_2$ -filled glove box and 31.9 mg (0.26 mmol) selenourea and ~12 ml of 1-octadecene were added. The reaction mixture was then kept in a pre-heated oven at 200 °C for 2 hours and then immediately quenched by immersing the hot autoclave in ice-water. Black coloured precipitates of  $\text{PbBi}_2\text{Se}_4$  nanosheets were washed several times with 1:1; hexane: ethanol. Finally the product was dried in vacuum at 60 °C.

**Capping agent removal.** In order to remove the organic capping ligand, as prepared nanosheets were treated with chloroform (~6 ml), methanol (~2 ml) and hydrazine (~8 ml) under vigorous stirring. Stirring was continued until the nanosheets were precipitated. The supernatant solution was decanted, and the surfactant free nanosheets were washed several times with ethanol and dried in vacuum at 60 °C for 6 h.

**Densification.** In order to measure electrical transport properties, surface cleaned nanosheets were hot pressed in vacuum ( $10^{-5}$  torr) by a graphite die, by applying pressure of 20 MPa at 673 K for 30 min. Density of the hot pressed pellet was ~94% of theoretical density.

**Powder X-ray diffraction.** Powder X-ray diffraction for all the samples were recorded using a Cu K $_{\alpha}$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation on a Bruker D8 diffractometer.

**Band gap measurements.** To probe optical energy gap of these compounds, optical diffuse reflectance measurements were performed on finely ground powders at room temperature. The spectra were recorded at the range of 200 nm to 3000 nm using a Perkin Elmer Lambda 900, UV/Vis/NIR spectrometer. Absorption ( $\alpha/\Lambda$ ) data were calculated from reflectance data using Kubelka-Munk equations:  $\alpha/\Lambda = (1 - R)^2/(2R)$ , where  $R$  is the reflectance and  $\alpha$  and  $\Lambda$  are the absorption and scattering coefficients, respectively. The energy band gaps were derived from  $\alpha/\Lambda$  vs.  $E$  (eV) plots.

**X-ray photoelectron spectroscopy.** XPS measurement has been performed with Mg-K $_{\alpha}$  (1253.6 eV) X-ray source with a relative composition detection better than 0.1% on an Omicron Nano-technology spectrometer.

**Field emission scanning electron microscopy.** FESEM experiments were performed using NOVA NANO SEM 600 (FEI, Germany) operated at 15 KV. Energy dispersive spectroscopy (EDS) analysis was performed with an EDAX Genesis instrument attached to the SEM column. Actual compositions were estimated by EDX analysis, which is nearly same as the nominal composition of the nanosheets.

**Transmission electron microscopy.** TEM experiments were performed using a JEOL (JEM3010) transmission electron microscope (TEM) fitted with a Gatan CCD camera operating at a 300 KV accelerating voltage. In a holey carbon coated Cu grid, one drop of nanosheets dispersed in toluene solution was taken for TEM imaging.

**Atomic force microscopy.** AFM was carried out on a Bruker Innova Microscope in tapping mode with an antimony doped Silicon tip with 10 nm resolution.

**Transport properties.**  $\sigma$  and  $S$  were measured in similar directions for a particular sample.  $\sigma$  and  $S$  were measured simultaneously on a sample of the dimension, 2 mm  $\times$  3 mm  $\times$  8 mm, under a He atmosphere from room temperature to 710 K by ULVAC-RIKO ZEM-3 instrument. Heating and cooling cycles give repeatable electrical properties for a given sample.

**Hall measurement.** Carrier concentrations were determined using Hall coefficient measurements at room temperature with a PPMS system. Four-contact Hall-bar geometry was used for the measurement. Assuming parabolic bands and a single band conduction process at 300 K, we estimated the carrier concentration,  $n$ , from the formula:  $n=1/eR_H$ , where  $e$  is the electronic charge.

**Table S1** Nominal composition, EDX composition, band gap and lattice parameters of  $\text{PbBi}_2\text{Se}_4$ ,  $\text{Pb}_{1.1}\text{Bi}_2\text{Se}_4$  and  $\text{Pb}_{1.2}\text{Bi}_2\text{Se}_4$ . Slight increase in band gap and lattice parameter is observed with increasing lead concentration.

Nominal composition	EDX composition	Band gap (eV)	Lattice parameter
$\text{PbBi}_2\text{Se}_4$	$\text{Pb}_{0.84}\text{Bi}_{2.37}\text{Se}_{3.41}$	0.62	$a = b = 4.1538 \text{ \AA}$ , $c = 40.3967 \text{ \AA}$ , $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$
$\text{Pb}_{1.1}\text{Bi}_2\text{Se}_4$	$\text{Pb}_{0.92}\text{Bi}_{2.35}\text{Se}_{3.50}$	0.66	$a = b = 4.1603 \text{ \AA}$ , $c = 40.5145 \text{ \AA}$ , $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$
$\text{Pb}_{1.2}\text{Bi}_2\text{Se}_4$	$\text{Pb}_{0.95}\text{Bi}_{2.35}\text{Se}_{3.69}$	0.77	$a = b = 4.2447 \text{ \AA}$ , $c = 40.9879 \text{ \AA}$ , $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$

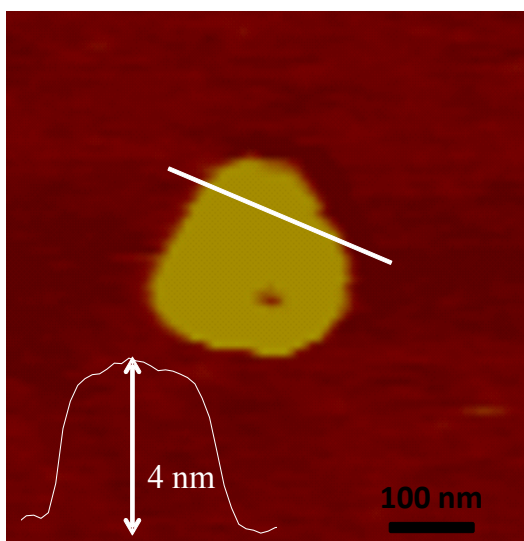
**Table S2:** Comparison of the electrical transport properties of present  $\text{PbBi}_2\text{Se}_4$  nanosheets with bulk homologous layered counterpart part compounds such as  $\text{Pb}_5\text{Bi}_6\text{Se}_4$ ,  $\text{Pb}_5\text{Bi}_{12}\text{Se}_{23}$  and  $\text{Pb}_5\text{Bi}_{18}\text{Se}_{32}$  and also with bulk  $\text{PbBi}_2\text{Te}_4$  and  $\text{Bi}_2\text{Se}_3$  nanosheets at 300K.

Compound	$n \text{ (cm}^{-3}\text{)}$	$S \text{ (}\mu\text{V/K)}$	$\sigma \text{ (S/cm)}$	$\mu \text{ (cm}^2\text{/Vs)}$
<b><math>\text{PbBi}_2\text{Se}_4</math> nanosheets-present work</b>	<b><math>2.05 \times 10^{19}</math></b>	<b>-56</b>	<b>500</b>	<b>153</b>
$\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ [1]	$8.6 \times 10^{19}$	-28	454	33
$\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ [1]	$1.15 \times 10^{20}$	-27	375	20
$\text{Pb}_5\text{Bi}_{18}\text{Se}_{32}$ [1]	$1.19 \times 10^{20}$	-52	256	14
$\text{PbBi}_2\text{Te}_4$ [1]	$2 \times 10^{20}$	-56	775	24
$\text{Bi}_2\text{Se}_3$ nanosheets [2]	-	-75	223	-
$\text{Bi}_2\text{Se}_3$ nanosheets [3]	-	-90	175	-

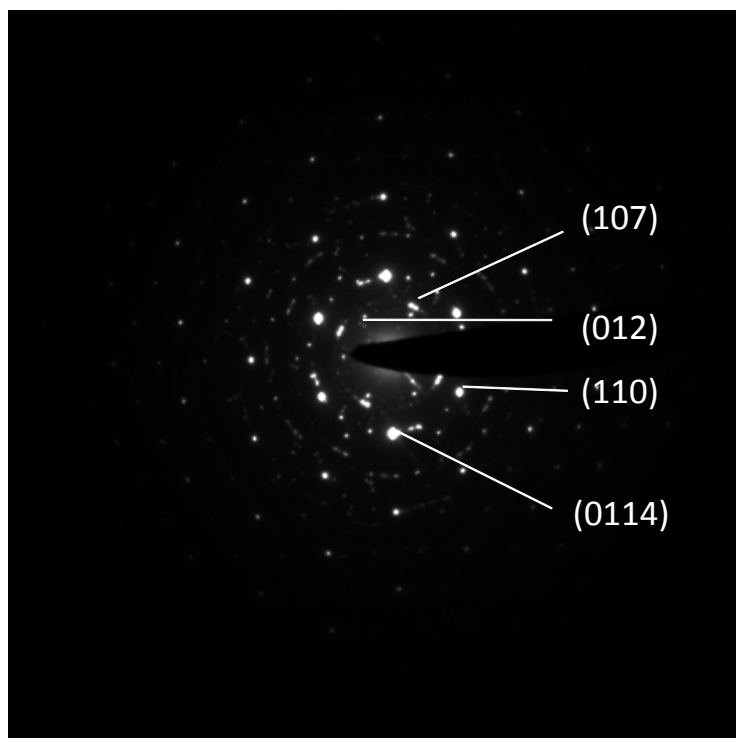
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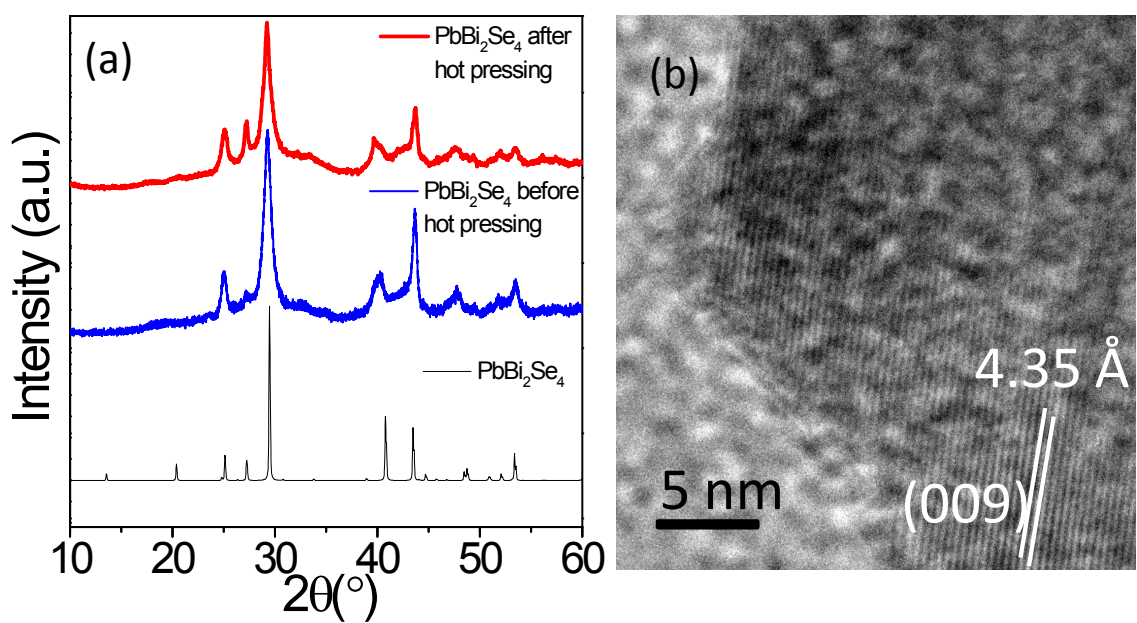
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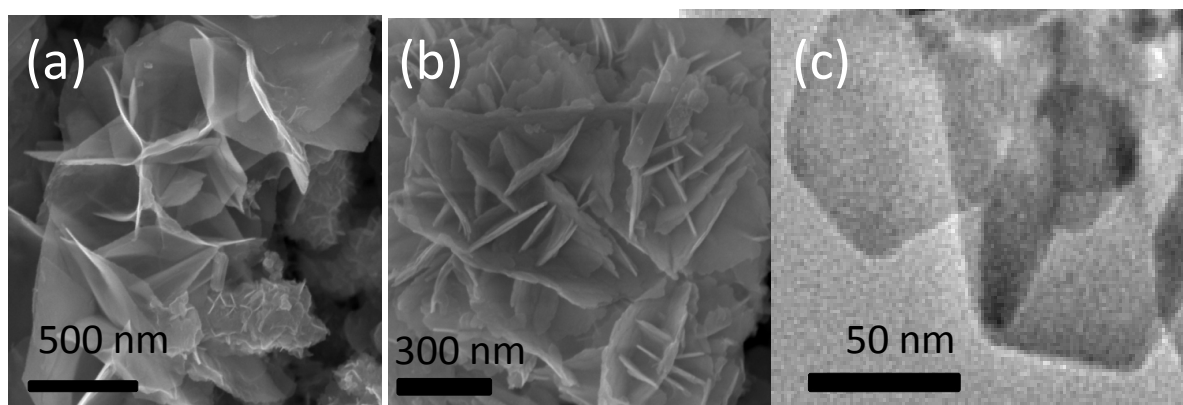
**Fig. S1** AFM image of PbBi<sub>2</sub>Se<sub>4</sub> nanosheet. Height profile shows that the nanosheet is 3SL (~4 nm) thick.



**Fig. S2** SAED pattern of  $\text{PbBi}_2\text{Se}_4$  nanosheet.



**Fig. S3** (a) PXRD pattern of  $\text{PbBi}_2\text{Se}_4$  nanosheets (before and after hot pressing). (b) HRTEM image of  $\text{PbBi}_2\text{Se}_4$  after hot pressing.



**Fig. S4** FESEM image of  $\text{PbBi}_2\text{Se}_4$  (a) before and (b) after hot pressing; and (c) low magnification TEM image of  $\text{PbBi}_2\text{Se}_4$  after hot pressing.