Supporting information

Room-Temperature Growth of Colloidal Bi$_2$Te$_3$ Nanosheets

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1. EXPERIMENTAL DETAILS

Materials and Stock Solutions. Bismuth triacetate (Bi(CH$_3$COO)$_3$, 99.9%, Aldrich), tellurium (Te, 99.8%, Aldrich), trioctylphosphine (TOP, technical, 90%, Aldrich), oleic acid (OlAc, technical, 90%, Aldrich), 1-octadecene (ODE, technical, 90%, Aldrich), n-hexane (dehydrated, 98%, VWR), acetone (ACS grade, VWR), and ethanol (ACS grade, VWR) were used as received without further purification.

1M trioctylphosphine telluride (TOP:Te) stock solution was prepared by dissolving 5 mmol of tellurium powder in 5 ml of trioctylphosphine at 250°C under a nitrogen flow.

Synthesis of Bi$_2$Te$_3$ Nanosheets. In a standard synthesis, 10 mL of 1-octadecene, 0.5 mmol of bismuth triacetate, and 1.5 mmol of oleic acid were mixed at room temperature and degassed for 30 minutes under vacuum in a three-neck flask equipped with a magnetic stirrer. The mixture was heated to 160°C under a dry nitrogen flow and held at that temperature until complete dissolution of bismuth salt occurred. After a clear pale-yellow solution of bismuth oleate was formed, the reaction mixture was cooled down to room temperature and turned to vacuum to remove acetic acid, and then heated to the reaction temperature varied in the range from 20°C to 170°C. Once the temperature was reached, 0.75 mL of 1M TOP:Te solution was swiftly injected into the reaction mixture initiating nanosheet growth.

Depending on the reaction temperature, the reaction time varied from 15 seconds for high-temperature syntheses to 2 hours for room-temperature growth. Finally, the reaction was quenched by rapid cooling to room temperature and Bi$_2$Te$_3$ nanosheets were precipitated by centrifugation at 3000 rpm for 20 minutes, washed several times by 20 mL of acetone-ethanol (1:1) mixture. Black precipitate was finally redispersed in 5mL of n-hexane.

2. CHARACTERISATION METHODS

X-ray Diffraction (XRD). Concentrated suspensions containing Bi$_2$Te$_3$ nanosheets were drop-cast on glass substrates. X-ray diffractograms were acquired on a Bruker D2 Phaser diffractometer equipped with the Cu source and operating in the reflection scan geometry. Diffraction patterns were collected in the range 6-65 degrees 2θ with a step size of 0.032 degrees.

Scanning Electron Microscopy (SEM). SEM imaging of the ensembles of Bi$_2$Te$_3$ nanosheets on Si/SiO$_2$ wafers was performed on a Zeiss Sigma300 field emission scanning electron microscope operated at 5 kV accelerating voltage.

Transmission Electron Microscopy (TEM). Samples for TEM analysis were prepared on carbon-coated copper grids. Preliminary low-magnification TEM imaging and elemental analysis of individual Bi$_2$Te$_3$ nanosheets were performed using a JEOL JEM-2100Plus microscope equipped with an Oxford X-Max$^N$ 80 cm$^2$ EDS detector. Standardless quantitative analysis was performed with the INCAEnergy...
software. High-resolution TEM images and selected area electron diffraction (SAED) patterns were acquired on a JEOL JEM-2100F microscope with a field-emission gun operated at 200kV accelerating voltage.

**Atomic-force microscopy (AFM).** Samples topography study was performed using an Asylum MFP-3D microscope in tapping mode, using Nanosensors PPP-NCHR tips (resonance frequency 330 kHz, tip radius <7 nm, nominal spring constant 42 N/m) tuned to a target tapping amplitude of 1 V. Typical initial scan parameters were 25 μm² scan size, 256 points per line and a scan rate of 1 Hz. Higher resolution scans were performed with 1024 points per line and scan rates of 0.5 Hz.

**Raman spectroscopy.** Raman spectroscopy was employed to study lattice vibration modes of Bi₂Te₃ nanosheets; spectra were recorded using a Renishaw inVia Qontor confocal Raman microscope at excitation wavelength of 532 nm using a 2400 lines/mm grating.

**Fourier-Transform Infrared Spectroscopy (FTIR).** FTIR spectra were collected in the range of 400-4000 cm⁻¹ using a Thermo Scientific Nicolet iS10 spectrometer with ATR (diamond) crystal, resolution 4 cm⁻¹.

### 3. BISMUTH OLEATE FORMATION

![FTIR spectra of stoichiometric bismuth oleate and oleic acid as a reference. Upon the bismuth complex formation, the C=O stretching mode of uncharged oleic acid (1710 cm⁻¹) disappears and the appearance of asymmetric (1538 cm⁻¹) and symmetric (1400 cm⁻¹) -COO⁻ stretching vibrations proves the formation of bismuth oleate. Asymmetric stretching of -COO⁻ shifts from 1556 cm⁻¹ in charged oleic acid (barely noticeable) to 1538 cm⁻¹ for bismuth oleate complex. The broad band observed at 3500-2500 cm⁻¹ in the spectrum of oleic acid is OH stretching mode. This vibration mode is absent in the spectrum of bismuth oleate that is a good indication that no free oleic or acetic acid is left in the bismuth precursor solution.](image_url)
4. SAMPLE DEGRADATION UNDER AMBIENT CONDITIONS

Although the surface oxidation of Bi$_2$Te$_3$ has been found to be negligible for bulk crystals$^1$, our results show that Bi$_2$Te$_3$ nanosheets are slowly oxidized and become partially amorphous upon prolonged exposure to moist air as was demonstrated by X-ray diffraction (Figure S2). Previous findings that surface oxidation of bulk Bi$_2$Te$_3$ crystals occurs only after simultaneous adsorption of molecular oxygen and water support our observation of difference in degradation rate for Bi$_2$Te$_3$ nanosheets in solution and in dried films since the films are exposed to both oxygen and water in moist air.$^1$

![Figure S2](image)

Figure S2. XRD patterns of Bi$_2$Te$_3$ platelets grown at 170 °C that were left for one month in air on a glass substrate (a) and in solution (b). For this experiment, an aliquot containing approximately 25 μmol of Bi$_2$Te$_3$ was taken out of the dispersions in hexane; half of the aliquot was cast onto a glass substrate and examined straight after drying and then a month later, the second half was left for a month in hexane and then examined. For the samples left on a substrate in air a significant decrease in peak intensity was observed while peak widths remained mostly unchanged, while degradation in solution was found to be slower.

5. ELEMENTAL COMPOSITION OF Bi$_2$Te$_3$ NANOSHEETS

Characteristic EDS spectrum of single Bi$_2$Te$_3$ nanosheets is shown in Figure S3. Standardless quantitative elemental analysis was achieved with the INCAEnergy software. Results of the quantitative analysis are given in Table 1. Bi:Te ratio of 2:3 was determined from the intensities of L$_{α1,2}$ lines. Carbon and Cu signals are due to the carbon coated TEM grids, while Cr signal originates from the sample holder. Intensities of Bi and Te are comparatively low due to the small amount of material.
Figure S3. EDS spectrum of an individual Bi₂Te₃ nanoplatelet suspended on a carbon coated copper TEM grid.

Table 1. Results of the quantitative elemental analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
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<tbody>
<tr>
<td>Bi</td>
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</tr>
<tr>
<td>Te</td>
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<tr>
<td>C</td>
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<tr>
<td>Cu</td>
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<td>Other</td>
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</tr>
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</table>

6. CRYSTAL STRUCTURE OF BISMUTH TELLURIDE

Bi₂Te₃ belongs to the $R3m$ space group that can be described as a rocksalt structure distorted along [111] axis with recurrent missing cation layer. Covalently bonded Te¹-Bi-Bi²-Te¹ quintuple layers, where 1 and 2 denote non-equivalent Te positions (depicted in Figure S4 as dark-blue and light-blue balls respectively). Te² has perfect octahedral coordination, Bi is bonded to three Te¹ and three Te² atoms forming a distorted octahedron, Te¹ has three covalent bonds with Bi atoms of the same layer and three van der Waals bonds with Te¹ of the adjacent quintuple layer.

Figure S4. Visualisation of crystal structure of bismuth telluride with a hexagonal unit cell.
7. SURFACE MORPHOLOGY OF Bi$_2$Te$_3$ NANOSHEETS GROWN AT 20, 70, AND 170°C

Figure S5. TEM images (a-c) and SAED patterns (d-e) acquired from the areas marked with purple circles in a-c of the branching Bi$_2$Te$_3$ nanosheets synthesised at 20 °C (a, d), 70 °C (b, e), and 170 °C (c, f) demonstrating \{011\bar{5}\} lateral termination.

References: