

Supporting Information

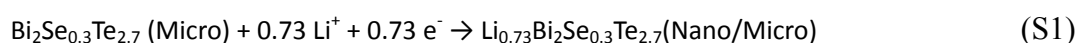
Experimental Details:

a) Preparation of Pristine Micro-scale $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ Powder

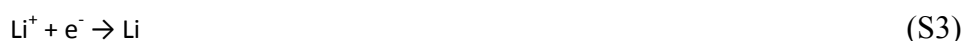
Pristine micro-powder of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ has been obtained by mechanically mashing $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ crystal rods, which were produced by melting and directional solidification of pure Bi, Se and Te with nominal compositions.

b) Lithium Intercalation / De-intercalation Process

The intercalation process has been carried out by discharging the self-designed two-electrode Swagelok-type lithium ion cells that taking microscaled $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ powder as the positive electrode according to Ref.16. The intercalation process was carried out under 0.5 mA discharging current, and the lithium intercalation amounts for all lithium ion cells were fixed to 25 mAh/g amounts of lithium, which equals to achieve $\text{Li}_{0.73}\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ nominally (See Equation S1).



After the intercalation process, as-used lithium ion cells are recharged by using 0.2 mA constant electrical currents in reversed direction, which causes a lithium deintercalation process that pulls out the originally intercalated Li atoms. Specifically, the lithium atoms between the van der Waals bonded interlayers of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ are ionized into Li^+ ions and electrons, with Li^+ ions transferred towards the Li foil electrode through the electrolyte while electrons are transferred to the Li foil electrode through the outside circuit (shown in Equation S2). The Li^+ ions from electrolyte combine with the electrons from the outside circuit to form Li metal again, and are deposited onto the surface of Li foil electrode (shown in Equation S3).



As to adjust the residual lithium content of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ samples, the recharging time was precisely controlled to achieve deintercalation amounts within 19-28 mAh/g nominally. The actual lithium content in the samples was measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

c) Sintering Process and Characterizations

After above electrochemical lithium intercalation / de-intercalation processes, the cells were disconnected and the powder in the bottom cell was taken out, rinsed in acetone, and dried in vacuum. 6 g or 1.5g of obtained powder was sintered into a bulk pellet using the spark plasma sintering (SPS) technique at 380 °C under 20MPa for 6 min in a graphite die. For measurements of thermoelectric properties in directions both along and perpendicular to the SPS direction, the samples were cut and polished according to Figure S1. The measurement of thermal diffusivity (λ) was carried out using the laser flash method in a flowing Ar atmosphere (Netzsch LFA 427), and the measurement was performed in the temperature range of 20-227 °C. Thermal conductivity (κ) was calculated from the relationship $\kappa = \rho\lambda C_p$, where λ is the thermal diffusivity coefficient, C_p is the heat capacity and ρ is the density of the material. The measurement of electrical conductivity

and Seebeck coefficient were carried out using ZEM-3 (ULVAC-RLKO) under the same temperature range. The Li content of the samples has been detected by ICP-OES. X-ray powder diffraction measurement was performed using diffractometer with Cu-K α ($\lambda = 0.15406$ nm) radiation. TEM analysis was performed on a JEM-2100F transmission electron microscope (accelerating voltage, 200kV). SEM analysis was performed on a JSM-6360LV scanning electron microscope.

Supporting Figures

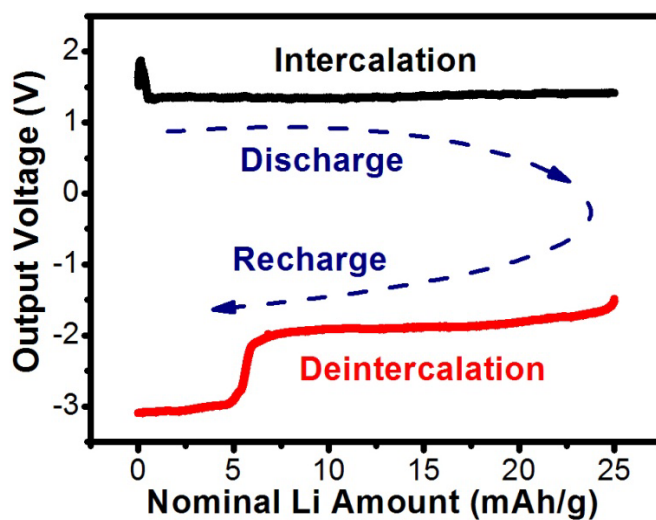


Figure S1. Discharging and recharging curve of the electrochemical lithium ion cells that were used for Li intercalation and deintercalation of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$. The discharging process was carried out under 0.5 mA while the recharging process was carried out under 0.2 mA. Lithium intercalation/deintercalation amounts were controlled through discharging/recharging time.

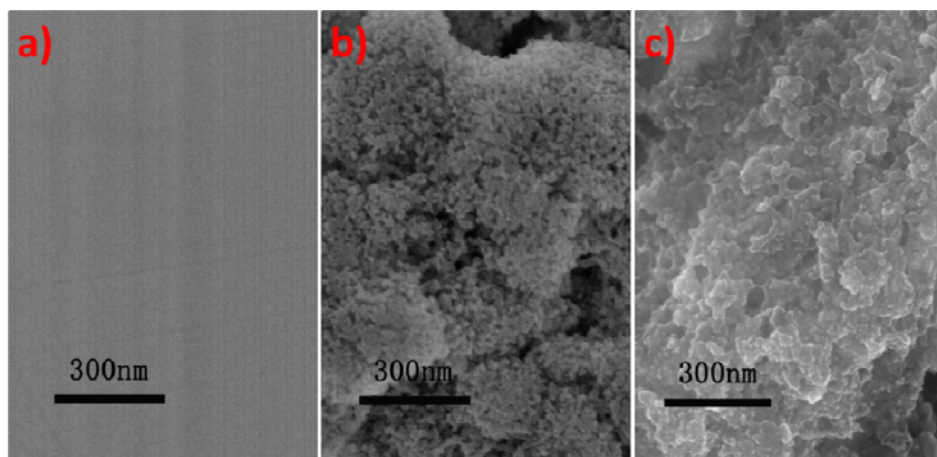


Figure S2. SEM image of $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ surface morphologies: **a)** original; **b)** after Li intercalation process (intercalation amount of 25 mAh/g); **c)** after the Li intercalation and de-intercalation processes (intercalation amount of 25 mAh/g and de-intercalation amount of 23 mAh/g).

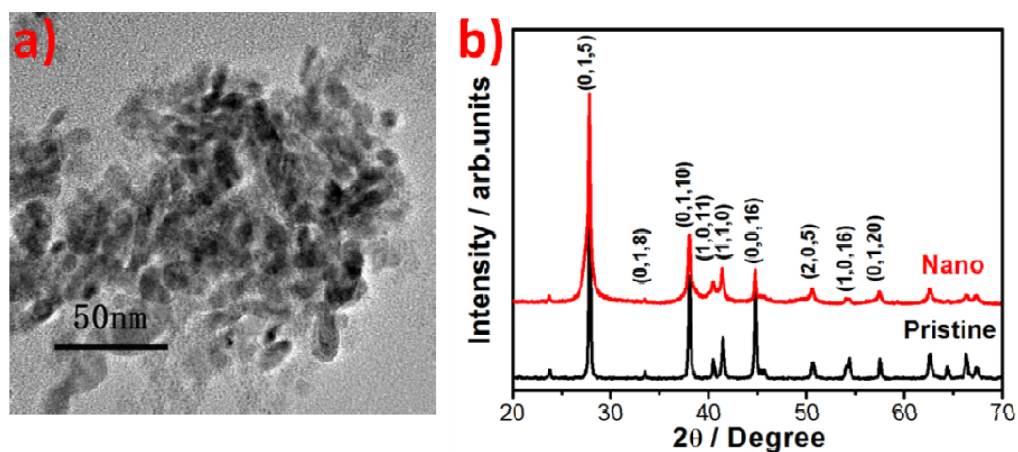


Figure S3. a) TEM image of roughly separated $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ nano-scale particles that were exfoliated by lithium intercalation and deintercalation process (with intercalation amount of 25 mAh/g and de-intercalation amount of 23 mAh/g). b) XRD pattern of the as-separated nano-particles, compared with that of pristine micro-scale $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ powder.

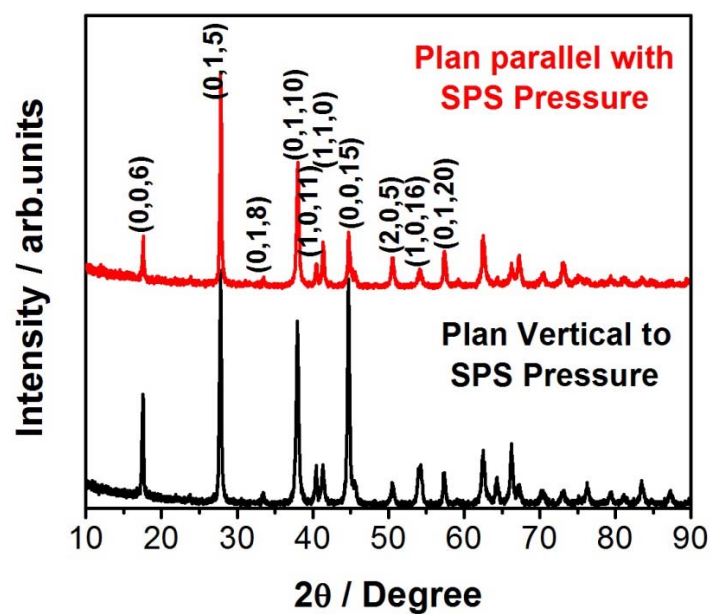


Figure S4. XRD Patterns of as-SPSed $\text{Li}_{0.11}\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ composite crystalline sample with scanning plans both parallel and vertical to the SPS pressure.

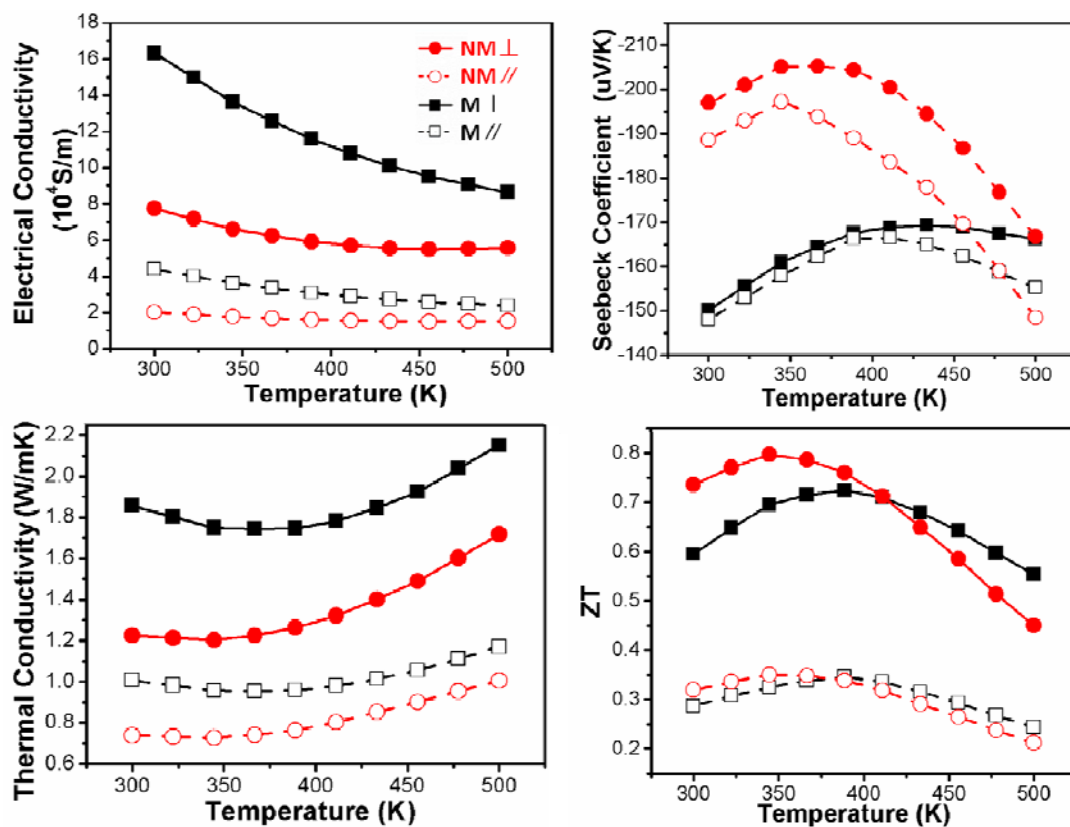


Figure S5. Temperature dependence of electrical conductivities, Seebeck coefficients, thermal conductivities and ZT values of as-fabricated nano/micro composite crystalline $\text{Li}_{0.11}\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$ (marked as: **NM**) in directions both perpendicular (marked as: \perp) and parallel (marked as: \parallel) to SPS pressure, compared with that of the samples SPSed using pristine micro-powders under same conditions (marked as: **M**).