## **Supporting Information**

## Superassembling of Bi<sub>2</sub>Te<sub>3</sub> Hierarchical Nanostructures for Enhanced Thermoelectric Performance

Hsiu-Cheng Chang, Tsung-Han Chen, Wha-Tzong Whang, and Chun-Hua Chen\*

Department of Materials Science and Engineering, National Chiao Tung University 1001 Ta-Hsueh Rd., Hsin-Chu, 30010 Taiwan, R.O.C.

E-mail address: ChunHuaChen@mail.nctu.edu.tw



**Figure S1.** (a)-(c) The top-view SEM images indicate that the  $Bi_2Te_3$  superassemblies deposited at 350 °C are uniformly composed of spindle-like hierarchical nanostructures. (d)-(e) The cross-sectional SEM images confirm that the nanoarchitectures are vertically-aligned on the SiO<sub>2</sub>/Si substrate.



**Figure S2.** (a)-(c) The low-magnification top-view SEM images indicate that the  $Bi_2Te_3$  superassemblies prepared at 400 °C are uniformly composed of large amount of worm-like hierarchical nanostructures. The high-magnification top-view SEM images of the (d) body and (e) head of single selected worm-like hierarchical nanostructure evidence that the building blocks are 1-D nanorods. The cross-sectional SEM images shown in (f) and (h) obviously indicate that the 1-D nanorods are amazingly side-by-side aligned on the SiO<sub>2</sub>/Si substrate. The bottom epitaxial domains shown in (g) and (h) not only dominate the growth of the upper superassemblies, but provide special low-resistance channels for carriers transporting.



**Figure S3.** (a)-(d) The low-magnification top-view SEM images indicate that the  $Bi_2Te_3$  superassemblies formed at 450 °C are composed of worm-like hierarchical nanostructures. (e) The high-magnification top-view SEM image confirms that the building blocks are 2-D nanoflakes. The cross-sectional SEM images shown in (f) and (g) evidence the vertically aligned 2-D nanoflakes on the SiO<sub>2</sub>/Si substrate. (h)-(i) Only a minority of the 2-D nanoflakes are not vertically aligned.



**Figure S4.** (a)-(c) The top-view SEM images clearly show numerous nanoscopic holes periodically embedded in the  $Bi_2Te_3$  superassemblies prepared at 600 °C. (d)-(e) The corresponding cross-sectional SEM images indicate that the 2-D nanoflakes are horizontally-lying on the SiO<sub>2</sub>/Si substrate.



**Figure S5**. The low-magnification top-view SEM images of the  $Bi_2Te_3$  superassemblies fabricated at (a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 600 °C. The corresponding EDS spectra clearly show Bi, Te, Si, and O signals originated from the  $Bi_2Te_3$  superassemblies and  $SiO_2/Si$  substrate. This result is consistent with the XPS investigations.



**Figure S6.** (a) The EDS compositional analyses of the  $Bi_2Te_3$  superassemblies fabricated at various temperatures. (b) The XPS spectra of the Bi 4f and Te 3d states evidence the absence of oxidation states.