Supporting Information

Superassembling of Bi$_2$Te$_3$ Hierarchical Nanostructures for Enhanced Thermoelectric Performance

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**Figure S1.** (a)-(c) The top-view SEM images indicate that the Bi$_2$Te$_3$ 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$_2$/Si substrate.
**Figure S2.** (a)-(c) The low-magnification top-view SEM images indicate that the Bi$_2$Te$_3$ 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$_2$/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$_2$Te$_3$ 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$_2$/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$_2$Te$_3$ 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$_2$/Si substrate.
Figure S5. The low-magnification top-view SEM images of the Bi$_2$Te$_3$ 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$_2$Te$_3$ superassemblies and SiO$_2$/Si substrate. This result is consistent with the XPS investigations.
Figure S6. (a) The EDS compositional analyses of the Bi$_2$Te$_3$ superassemblies fabricated at various temperatures. (b) The XPS spectra of the Bi 4f and Te 3d states evidence the absence of oxidation states.