The calculation of lattice contribution in thermal conductivity:
According to Wiedemann-Franz law (Equation S1), the thermal conductivity can be split into two parts: the lattice part ($\kappa_L$) and electron part ($\kappa_e$). $\kappa_e$ is the product of the Lorentz number (L) with electrical conductivity and temperature. For heavily degenerated semiconductors (including our materials), $2.0 \times 10^{-8} V^2 K^{-2}$ is accepted as the appropriate value of the Lorentz number L.

$$K = K_L + K_e = K_L + L\sigma T$$  \hspace{1cm} (S1)

Due to the anisotropic properties of bismuth telluride, in this work we tested the in-plane charge transport properties and cross-plane thermal transport properties. Z. Ren and co-workers have done a very detailed study on the anisotropic TE properties of Bi$_2$Te$_{2.7}$Se$_{0.3}$.\textsuperscript{1} In-plane conductivity (perpendicular to press direction) is reported to be higher for both electrical and thermal test than cross-plane (parallel to press direction) by about 10%-20%. Therefore, in this work, we applied a modified factor ~0.8 to estimate the cross-plane electrical conductivity from the experimental in-plane electrical conductivity, resulting in the modification of Equation S1 to Equation S2.

$$K_{L,\perp} = K_{\perp} - K_{e,\perp} = K_{\perp} - 0.8 \times L\sigma_{\parallel} T$$  \hspace{1cm} (S2)

Here, $K_{\perp}$, $K_{L,\perp}$ and $K_{e,\perp}$ are thermal conductivities of the total, lattice part and electron part in the cross-plane orientation respectively; and $\sigma_{\parallel}$ is the electrical conductivity in the in-plane.
orientation. The estimated lattice contributions of the three samples (BiTe_bare, BiTe_101, and BiTe_51) in cross-plane direction are shown in the inset of Fig. 3 (D).

Figure S1. HR-TEM images of the solid bismuth telluride nanospheres; the inset is the overview image.

Figure S2. TEM images of some porous bismuth telluride nanospheres.
Figure S3. (A) XRD patterns of starting materials (0 h) and the products after reacting for 3 to 6 hours. Indexing according to space group Fm\(\bar{3}\)m (0 h/nickel) and R\(\bar{3}\)m (3-6 h/bismuth telluride) are shown. (B) ICP results of Te/Bi stoichiometry and Ni contents of as-prepared powders. (C) Rietveld refinement results of the product after reacting for 4 hour. (R value is 0.126)
Figure S4. TEM images of prepared lamellas A and B. A shows polycrystalline structure and B is a single crystal.

Figure S5. Enlarged XRD pattern of BiTe_51, the marked peaks are from crystal phase of NiTe_2 (PCPDF#89-2021)
Figure S6. The selected area of EDX mapping.

Figure S7. Temperature dependence of Seebeck coefficient (A) and conductivity (B) of BiTe_21.

Figure S8. Temperature dependence of (A) mobility and (B) carrier concentrations of BiTe_bare, BiTe_101, and BiTe_51.
Figure S9. Temperature dependence of estimated figures of merit (zT) of BiTe_Bare, BiTe_101 and BiTe_51.

Reference