Supplementary Information for “Diameter dependent thermoelectric properties of individual SnTe nanowires”

1. Energy-dispersive X-ray spectroscopy study of NWs

Energy-dispersive X-ray spectroscopy (EDX) was employed to characterize the chemical composition of SnTe nanowires. Figure S1 (b) shows a typical EDX spectrum taken on a nanowire device (Figure S1 (a)) under scanning electron microscopy (SEM). The Sn: Te ratio determined by EDX analysis is ~ 1:1. It is worth noting that EDX does not have sufficiently high sensitivity to determine a few percent of Sn vacancies. Nevertheless, we would like to emphasize that our electrical resistivity data (i.e. ferroelectric phase transition at around 100 K) provides strong evidence that our NWs have a carrier concentration of ~2 × 10^{20} cm^{-3}.

![Figure S1 (a) An SEM image of a SnTe NW in a thermoelectric device. The cross denotes the position where the EDX was taken. (b) The corresponding EDX spectrum. The Au signal is likely from the nearby electrodes.](image-url)
2. 2-probe and 4-probe electrical resistance measurement

We performed 2-probe and 4-probe measurements to characterize the electrical resistances of the contacts and nanowires. The 2-probe I-V measurement was taken in a probe station system by sweeping a dc bias voltage and measuring dc current. As shown in Figure S2 (a), the I-V curve is linear in the whole bias range from -0.1 V to 0.1 V, suggesting that the contact is Ohmic. The 4-probe resistance was determined in an AC measurement, where an AC current was applied and a voltage was measured. Figure S2 (b) shows a typical AC current versus voltage curve, which is also linear. Note that the 2-probe resistance includes the resistance of the metal electrodes/pads (~225 Ω), contact resistance and nanowire resistance. After the subtraction of electrode resistance and nanowire resistance, the total resistance of the two contacts is only ~5% of the nanowire resistance, conforming a transparent Ohmic contact.

Figure S2 (a) A typical 2-probe I-V curve, which includes the nanowire resistance, contact resistance and the resistance of metal electrodes/pads. (b) The corresponding 4-probe I-V curve.
3. Determination/Calibration of temperature difference $\Delta T$ in thermopower measurement

In the thermopower $S = \frac{dV}{dT}$ measurement, an electrical current was flowed through the heater and the temperature difference $\Delta T$ between the two electrodes B and C (Figure S3 (a)) was determined by characterizing the resistance of each electrode via a four-probe measurement. Both electrodes B and C have four leads (B₁, B₂, B₃, B₄; C₁, C₂, C₃, C₄) connecting to the outside pads, allowing for four-probe resistance measurement (Figure S 3 (a)). As an example, to measure the resistance of electrode B, we applied a small AC current between B₁ and B₃, and measured the voltage drop between B₂ and B₄ (this resistance is only part of the electrode resistance in the 2-probe measurement in section 2). To determine $\Delta T$, the resistances of electrodes B and C were firstly measured as a function of measurement temperature (i.e. the cryostat temperature) without applying electric current to the heater. As shown in Figure S3 (b), the resistance is linear with temperature for both electrodes. We then fixed the measurement temperature (e.g. at 300 K) and applied electric current to the heater. The resistances of electrodes B and C were then measured again using the four-probe method mentioned above. From the linear temperature corresponding resistance, we determined the temperature of each electrode and their difference $\Delta T$. To avoid device failure (i.e. burning of device which occurs easily in such nanowire devices), the temperature calibration was first performed on blank thermoelectric platform without nanowire in a temperature range of 25-300 K, and was then verified by performing the same measurement on the actual device with nanowire at certain temperatures. The thermoelectric platform of the actual device was fabricated through exactly the same process as the blank platform. The variation of temperature difference $\Delta T$ between the blank platform and the actual device was confirmed to be minimal (only a few percent), and it was included as error bar /uncertainty in the thermopower data.

Figure S3 (a) An SEM image of a thermoelectric device. (b) A typical temperature corresponding resistance of electrodes B and C (i.e. thermometers 1 and 2, respectively)
4. Density functional theory calculation of vacancy-induced strain

We performed density functional theory (DFT) calculations to calculate the strain induced by Sn vacancies. Corresponding to a vacancy concentration of $10^{20} \text{cm}^{-3}$, the simulation cell contains 27 unit cells (108 Te and 107 Sn) which has one Sn vacancy in a 7 nm$^3$ cube. The coordinate system adopts <100>, <010>, and <001>. Periodic boundary conditions are applied for the three directions. The calculations were carried out based on DFT using the Vienna Ab initio Simulation Package (VASP)$^1$. The electronic structure calculations were performed using the projector augmented wave (PAW) method $^2$, the Perdew, Burke and Ernzerhof (PBE)$^3$ functional is adopted to describe the exchange-correlation potential. Figure S4 shows atomic structure of one {100} plane and the displacements associated with Sn vacancy. The blue rectangle outlines the 2D dimensions and the red rectangle outlines the region (half of the simulation cell) where the average volume strain is -0.016. Therefore, such high Sn vacancy concentration will result in an average volume strain of -0.008 in an infinite bulk sample.

5. Calculation of thermal conductivity

The thermal conductivity was calculated based on the one-dimensional heat-transport equation that includes Joule heating and Thomson heating $^4$.$^5$:
\[
\frac{d}{dx}[q_xA] = \frac{i^2 \rho}{A} - T \frac{dS}{dT} \frac{dT}{dx}
\]
(S1)

\[ q_x = -\kappa \frac{dT}{dx} \]  
(S2)

with the boundary condition: \( T = T_0 \) at \( x = 0, L \). Here \( A \) is the cross-sectional area of NW, \( I \) is the applied electric current, \( \rho \) is the electrical resistivity of NW, \( L \) is the channel length of NW (between electrodes B and C), and \( T_0 \) is the cryostat temperature. The last term of Eq. (S1) is the Thomson heat \(^4\) which is negligible in our NW because of the small \( S \) (calculation including this term renders a difference of < 0.1%). Equation S1 can thus be solved analytically and the mean temperature increase \( \Delta T_M \) of the NW is \(^6\):

\[
\Delta T_M = \frac{i^2 R}{12 \kappa (A/I)}
\]
(S3)

So

\[
\kappa = \frac{i^2 R}{12 \Delta T_M (A/I)}
\]
(S4)

Where \( i^2 R \) is the electrical heating power. The mean temperature increase \( \Delta T_M \) of the NW during self-heating was determined based on the increase of nanowire resistance\(^6\). In brief, we first measured the resistance (R) of the nanowires with negligible Joule heating at each stabilized temperature. We did this measurement every 5 or 10 K from 25 K to 315 K and obtained the R vs T curves (Figure S5 (a)). We then applied Joule heating in the NWs and measured the new resistance R. From the R vs T curves and the new resistance, we deduced the temperature and \( \Delta T_M \) of the NW. The thermal conductivity \( \kappa \) was then calculated based on the slope of the \( i^2 R \) versus \( \Delta T_M \) curve (an example is shown in Figure S5 (b)). The highest current density we used, for example, for NW-2 at 300K, was \( 1.95 \times 10^5 \) A/cm\(^2\) (The highest current density of other NWs is on the same order of magnitude), which is lower than the current in reference 3 (i.e. \( 8.9 \times 10^5 \) A/cm\(^2\)).

The above calculation is based on the boundary condition \( T = T_0 \) at \( x = 0, L \) (i.e. the two ends of the nanowire channel is at a constant temperature \( T_0 \)). We further performed calculation for the case that \( T = T'_0 \) at \( x = 0, L \), where \( T'_0 > T_0 \). Figure S5 (c) shows the calculated \( \kappa \) as a function of \( T \) for different \( \Delta T_0/\Delta T_M \), where \( \Delta T_0 = T'_0 - T_0 \). The calculated thermal conductivity value \( \kappa \) increases with the increase of \( \Delta T_0/\Delta T_M \). For a large increase of temperature at the boundary of
\( \Delta T_0/\Delta T_M = 30\% \), the calculated \( \kappa \) increases by \( \sim 40\% \), i.e. its room temperature value reaches \( \sim 6.05 \text{ W m}^{-1}\text{K}^{-1} \) which is still lower than thermal conductivity in bulk SnTe (7–8 W m\(^{-1}\text{K}^{-1}\)) \(^{7,8}\).

Figure S5 (a) Resistance versus temperature data for all three SnTe nanowires whose thermal conductivity was measured. (b) A linear fitting to a typical \( I^2R \) versus \( \Delta T_M \) curve. (c) Thermal conductivity as a function of temperature for different \( \Delta T_0/\Delta T_M \).
6. **Calculation of error bar for ZT**

The thermal conductivity $\kappa = G(l/A)$, where $G$ is the thermal conductance, $l$ and $A$ are the length and cross-sectional area of the nanowire, respectively. The electrical conductivity $\sigma = \frac{1}{R}(l/A)$, where $R$ is the electrical resistance of the nanowire. So $ZT = S^2 \sigma T / \kappa = S^2 T / GR$, i.e. the nanowire length $l$ and cross-sectional area $A$ are cancelled in the expression of the ZT. As a result, their corresponding errors are not considered in the calculation of the error bar of ZT.

**References**