Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary material

Benchmark characterization of thermoelectric properties of individual single-crystalline CdS nanowire by H-type sensor

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1. Synthesis method of CdS nanowires

The single-crystalline CdS nanowires were synthesized via a solid-source catalytic chemical vapor deposition (CVD) method. CdS powder was first placed onto a ceramic boat at the center of a quartz tube. The silicon substrate coated with 1 nm thick of Au catalyst was placed at the downstream of the carrier gas flow. After that, the quartz tube was pumped down to a pressure of 1×10^{-3} mbar, a mixture gas (argon/hydrogen = 100:20) was then introduced into the quartz tube at a flow rate of 50 sccm (standardstate cubic centimeter per minute). The CdS powder was heated to 700°C and maintained for about 60 min at a pressure of 100 mbar. Finally, the system was cooled down to room temperature, a large amount of CdS nanowires was found on the surface of the silicon substrate.

2. More SEM images of CdS nanowires and Pt deposition process

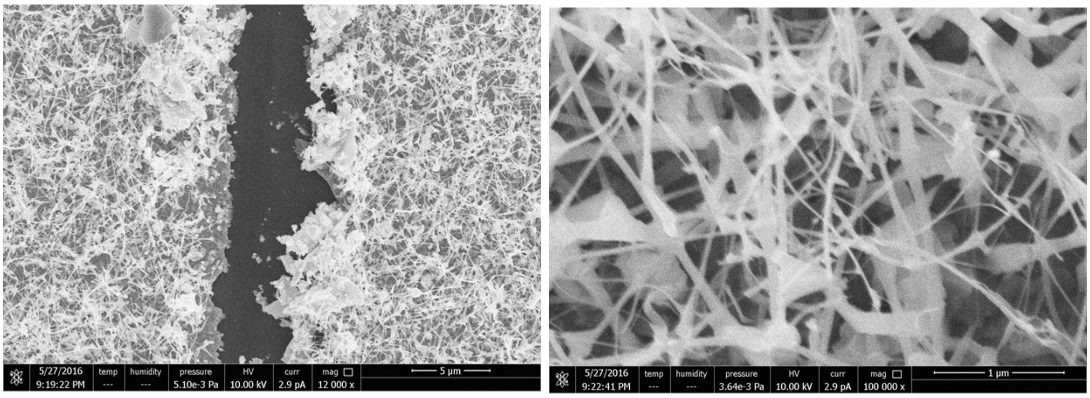

Fig. S1 SEM images of CdS nanowire arrays observed from top.

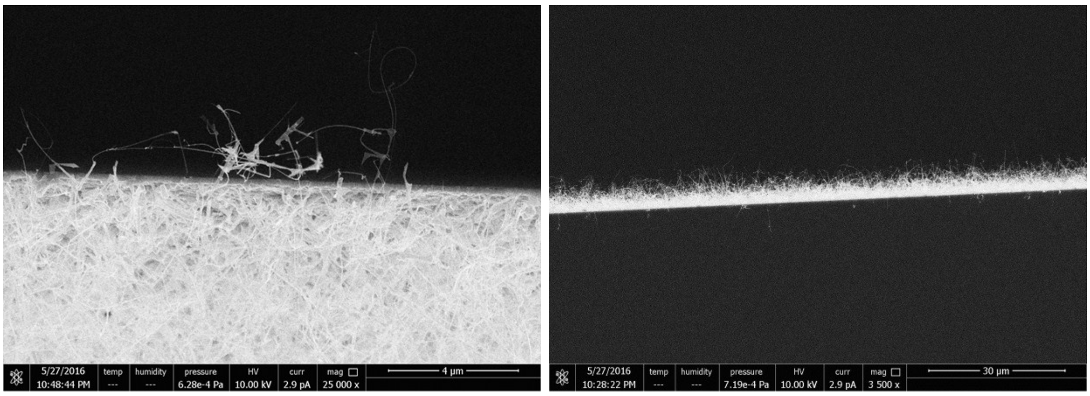

Fig. S2 SEM images of CdS nanowire arrays observed from a titled angle.

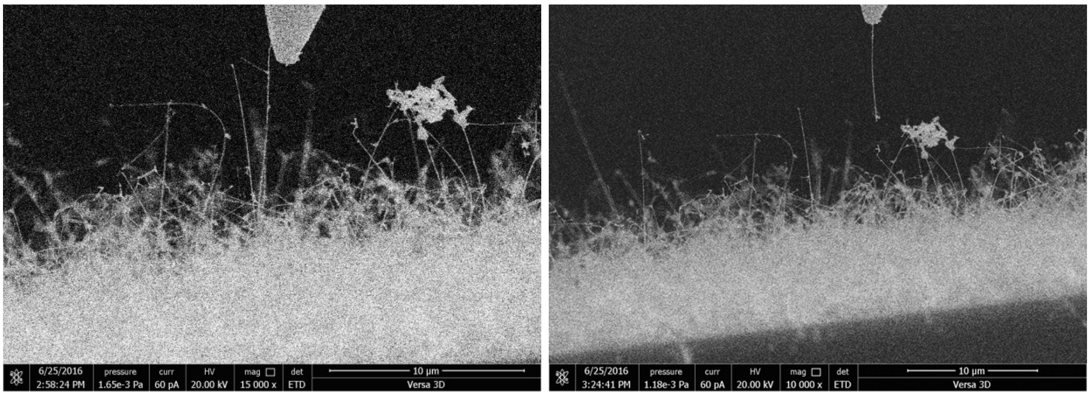

Fig. S3 SEM images of individual CdS nanowire picked up by nanomanipulation probe.

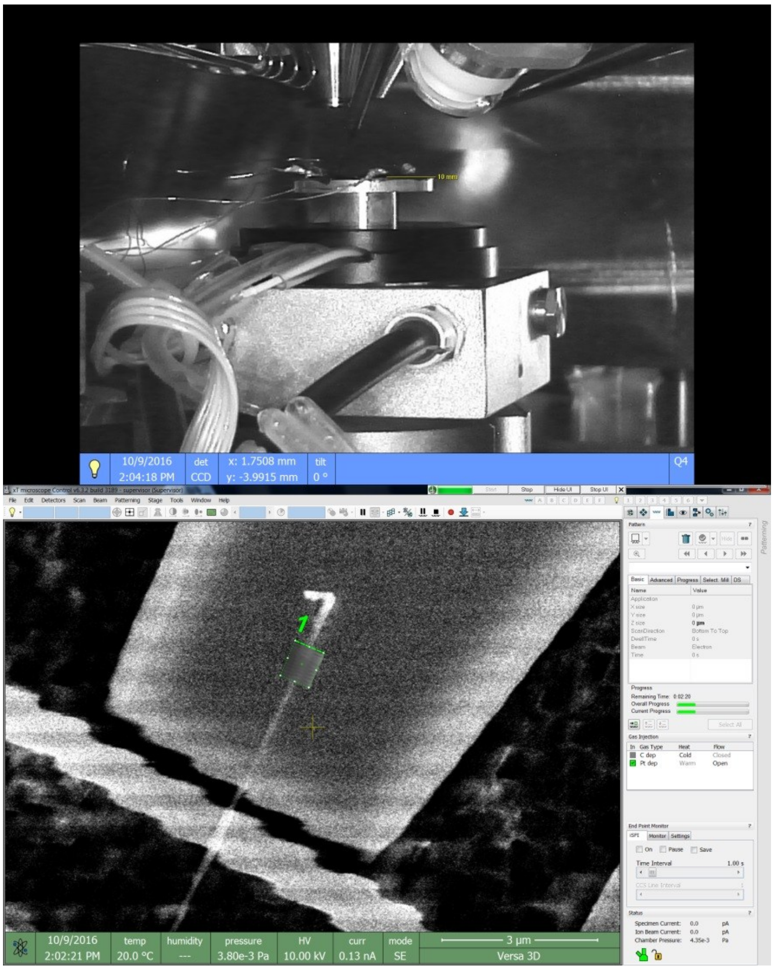

Fig. S4 Pt deposition on the CdS nanowire by using an EBID (electron beam induced deposition) method.

The fabrication process of H-type sensor connected with an individual CdS nanowire is illustrated from Fig. S1 to Fig. S4. Fig. S1 shows the top view of CdS nanowire array under SEM. A large amount of nanowires were grown on the silicon substrate with random orientations. Then, the substrate was tilted by 90˚ under the electron beam gun. As shown in Fig. S2, the nanowire array looks like a forest on the substrate. The tip of a nanomanipulation probe was adjusted to be vertical to the substrate and carefully moved into the nanowire array. The CdS nanowire was attached to the probe tip by Coulomb force, which was close to the adhesion force between the nanowire and substrate quantitatively. After several trials, an individual nanowire could be directly picked up from the array as shown in Fig. S3. Then, the nanowire was placed on the prepared H-type sensor by using the manipulation probe. In order to reduce the electrical and thermal contact resistances between the nanowire and Pt sensor, EBID (electron beam induced deposition) was employed to deposit Pt on the nanowire as shown in Fig. S4.

3. Temperature response of H-type sensor

In the H-type method, two nanofilm sensors were used as a Joule heater and a precise thermometer, respectively. The H-type sensor has higher thermal sensitivity than our previous T-type sensor, because the temperature response of one sensor can be measured simultaneously as the other sensor is electrically heated. The suspended nanowire is the only heat conduction channel between two sensors. The thermal conductivity of nanowire is decided by the temperature difference between two sensors.

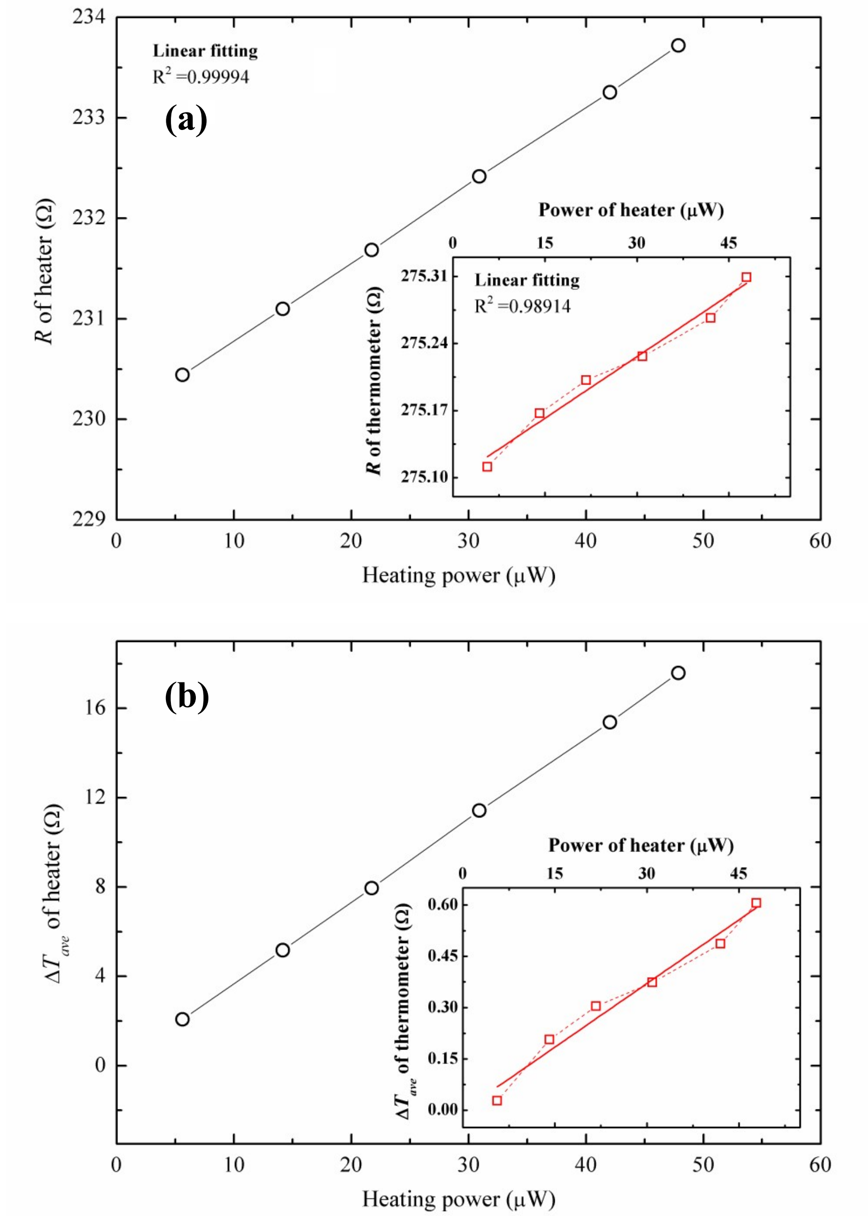

Fig. S5 Resistance/temperature changes of two sensors serving as heater and thermometer, respectively. (a) Black circles are the measured resistance change of heater and the inset is the resistance change of thermometer at the same time. (b) The temperature change of each sensor was calculated through the calibrated temperature-resistance coefficient of

the Pt nanofilm.

Figure S5 shows the resistance/temperature changes of two sensors during the experiment. The inset shows the resistance or temperature change of one sensor as a thermometer while the other sensor is electrically heated. The temperature-resistance coefficient of sensor was calibrated beforehand. The maximum average temperature rise of thermometer was about 0.6 K, while the average temperature rise of heater was about 18 K. The temperature resolution of H-type sensor was estimated to be 0.01 K [1]. Considering the uncertainties caused by the geometric size of sample and thermal analysis, the uncertainty of measured thermal conductivity of nanowire was about 5%. The nanoscale size of suspended sensor and H-type sensing scheme ensure a high thermal sensitivity, making it a promising method for measuring the thermoelectric nanowires with low thermal conductivity.

4. Measurement uncertainty analysis

The uncertainties of electrical conductivity, thermal conductivity and Seebeck coefficient are analyzed as following.

[Electrical conductivity] The electrical conductivity of nanowire σ is calculated as:

$$\sigma = \frac{1}{R}\frac{l}{A}, \tag{R1}$$

where R is the electrical resistance, l is the length of nanowire, $A = 0.25\pi d^2$ is the cross-sectional area of nanowire, d is the diameter. According to the error propagation rule, the uncertainty of electrical conductivity is given as:

$$\frac{\delta\sigma}{\sigma} = \left[\left(\frac{\delta R}{R}\right)^2 + \left(\frac{\delta l}{l}\right)^2 + \left(\frac{\delta A}{A}\right)^2\right]^{1/2}. \tag{R2}$$

The resistance was measured by using a four-probe method, where two high-precision digital multimeters Keithley 2002 were used and the uncertainty was calculated as:

$$\frac{\delta R_h}{R_h} = \sqrt{\left(\frac{\delta V_h}{V_h}\right)^2 + \left(\frac{\delta I_h}{I_h}\right)^2} < 0.01\%. \tag{R3}$$

The length and diameter of nanowire were determined by the high-resolution scanning electron microscope (SEM) image and the uncertainties were $\delta l/l$ = 0.1% and $\delta d/d$ = 3.0%, respectively. Because the diameter of nanowire is only 125 nm, much smaller than the length, the uncertainty of diameter is relatively higher. The final uncertainty of electrical conductivity is 4.2% from the Eq. (R2), where the largest part comes from the uncertainty of diameter.

[Thermal conductivity] The thermal conductivity of nanowire was measured by using two nanofilm sensors in a letter "H" form. Based on a one-dimensional heat conduction model, the thermal conductivity of nanowire can be estimated as:

$$\lambda = \frac{Ql}{\left(\Delta T_h - \Delta T_t\right)} \frac{1}{A}, \tag{S4}$$

where Q is the heating power, ΔT_h and ΔT_t are the average temperature rises of heater and thermometer, respectively. According to the error propagation rule, the uncertainty of thermal conductivity is given as:

$$\frac{\delta\lambda}{\lambda} = \left[\left(\frac{\delta Q}{Q}\right)^2 + \left(\frac{\delta\left(\Delta T_h - \Delta T_t\right)}{\Delta T_h - \Delta T_t}\right)^2 + \left(\frac{\delta l}{l}\right)^2 + \left(\frac{\delta A}{A}\right)^2\right]^{1/2}. \tag{S5}$$

In the experiment, the Pt nanofilm was used as Joule heater and precise resistance thermometer. After careful calibration, the temperature resolution of sensor could reach 0.01K. Fig. S5 in the supplementary material shows the temperature response of H-type sensor, where the maximum temperature rise of thermometer sensor is 0.6K while the temperature rise of heater is 18K. Hence, the temperature uncertainty of Pt nanofilm sensor is 1.7%. Based on Eq. (S5), the total uncertainty of thermal conductivity is 4.6%, where the uncertainties of diameter and temperature are important.

[Seebeck coefficient] The Seebeck coefficient was determined as $S = |V_{tp} / \Delta T|$, where V_{tp} is the thermoelectric potential of nanowire and ΔT is the temperature difference along the sample. The uncertainty of Seebeck coefficient is given as:

$$\frac{\delta S}{S} = \left[\left(\frac{\delta V_{tp}}{V_{tp}}\right)^2 + \left(\frac{\delta \Delta T}{\Delta T}\right)^2\right]^{1/2}. \tag{S6}$$

$\Delta T = 16\text{K}$ was measured by using the Pt sensor. The temperature uncertainty was 0.1%.

V_{tp} was measured by using the precise digital multimeter. Because the amplitude of V_{tp} is only 300μV, much smaller than the amplitude of voltage along the Pt sensor, the uncertainty of V_{tp} is relatively large, about 5%. Besides, there is a small distance between the heating Pt sensor and the electrode for measuring the thermoelectric potential. Thus, there will be a small voltage drop between the heating sensor and electrode. From the SEM image, this distance is about 7% of the total length of CdS nanowire and it may cause uncertainty of V_{tp} measurement. Hence, the total uncertainty of Seebeck coefficient is about 12%.

5. 2D thermal analysis model

In our method, both sensor and nanowire sample were suspended from the substrate. A part of the electrode pad was also suspended, which is shown as the overhang area in the SEM image of Fig. 3 in the main article. Thus, the temperature at the join-point between the sensor and electrode pad is higher than the substrate temperature T_0. In order to consider the effect of this temperature rise, we carried out 2D thermal analysis using COMSOL Multiphysics™ software.

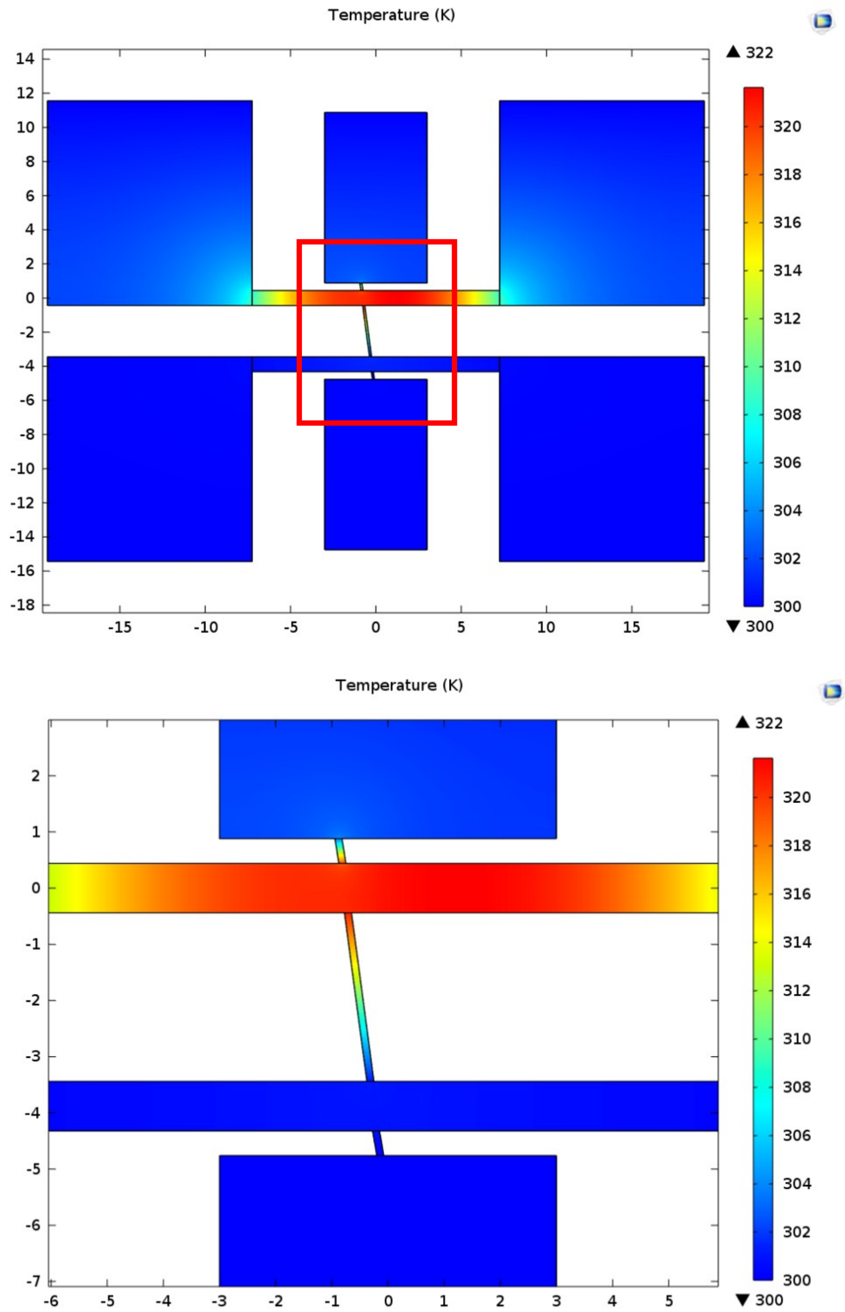

Fig. S6 Temperature distribution of H-type sensor. The central area of nanowire sample in a red dashed box is enlarged and shown in the second figure.

Figure S6 shows the calculated temperature distribution of the H-type sensor with an individual CdS nanowire connected in between. The geometric sizes of Pt sensor and nanowire were decided based on the SEM images. The Joule heating power and thermal conductivity of Pt sensor were measured in the experiment as input parameters. The thermal conductivity of CdS nanowire was the only unknown parameter. The result shows an obvious temperature rise at the end of sensor due to the overhang effect. The nanowire conducts heat from the heater to the thermometer, causing a detectable resistance change of the sensor. Later in the measurement of Seebeck coefficient, the thermal conductivity of nanowire was already known. We measured the electrical power of sensor and then accurately obtained the temperatures at both ends of nanowire. The thermoelectric potential across the nanowire was measured by using another digital multimeter.

References

[1] H. D. Wang, S. Q. Hu, K. Takahashi, X. Zhang, H. Takamatsu and J. Chen, Experimental study of thermal rectification in suspended monolayer graphene, Nature Commun., currently under review.