Supporting Information

Benchmark Study of the Length Dependent Thermal Conductivity of Individual Suspended, Pristine SWCNTs

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1. Determination of the focused laser spot size

The focused laser spot from the Raman spectroscopy served as both the local heater and the local temperature sensor. The laser spot intensity profile is one of the key parameter in determining the thermal conductivity. A laser beam profiler was used to measure the laser intensity distribution at the outlet of the Ar^+/Kr^+ gas laser and the large focused laser spot, as shown in Fig. S1(A) and (B), displaying a good correlation (~92.5%) with Gaussian laser profile.



Figure S1. (A) and (B) Laser intensity profile.

The green laser (514.5 nm) was focused by a \times 40 Olympus objective (including the correction collar) to form a laser spot smaller than several microns, which was very difficult to measure by the laser beam profiler. Thus, a new method was used to determine the laser spot diameter by fitting the Raman signal profile obtained by scanning across an individual SWCNT with very small step sizes, as shown in Fig. S1(C).



Figure S1. (C) Focused laser spot scanning across an individual suspended SWCNT.



Figure S1. (D) Raman signal intensity profile. The focused laser spot was scanned across the SWCNT along the direction perpendicular to the SWCNT axis with a 0.1 μ m step size to measure the Raman intensity profile shown as the squares in Fig. S1(D). The Gaussian peak function $I=405\exp(-(x/0.45)^2)$ and $I=405\exp(-(x/0.53)^2)$ fit well with the experimental results. Thus, the experimental results indicate that the laser spot profile is $I=405\exp(-(x/0.49)^2)$.

2. Centering of the laser spot on the SWCNT

The laser spot serves as both the heater and the temperature sensor, so the laser absorptivity must be the same when the laser spot irradiates different positions along the sample. The SWCNT is only 1~2 nanometers in diameter, which is not visible with an optical microscope. Thus, the Raman spectroscopy accurate scanning mode (Duoscan mode) was used to scan across the SWCNT sample step by step with very small step sizes in 3 dimensions to determine the best focus (corresponding to the maximum laser absorption coefficient and laser heating temperature rise).



Figure S2. Movement of the laser spot to the SWCNT center. (A) Scan along the trench to find the SWCNT with high intensity Raman G band. (B) Then, the laser was scanned along the X axis to find the middle of the suspended SWCNT. (C) The laser was then scanned in the YZ plane at the middle of SWCNT position.



Figure S2. (D) Laser heating induced G band red-shift and temperature rise change with the laser spot position. The intrinsic Raman G band frequency indicated by \bigstar was measured to be 1577.50 cm⁻¹ using a very low power laser. The laser heating induced G band frequency shift and temperature rise are indicated by the closed square \blacksquare and triangle \blacktriangle . Note that the maximum temperature rise appear at two points since the step size is very small.

3. Analytical solution for the temperature profile



Figure S3. Focused laser spot irradiating a suspended SWCNT.

The physical model for the focused Gaussian laser spot heating of an individual suspended SWCNT is shown in Fig. S3. At the laser spot edge $x=\pm r_0$, the temperature rises are θ_1 and θ_2 . L_1 , L_2 and $2r_0$ are the sample lengths at the left side, the right side and inside the laser spot. Since the focused Gaussian laser spot diameter ($d_e=0.98 \mu m$) is far larger than the SWCNT diameter, the laser power heating can be treated as a Gaussian line heat source as:

$$I = I_0 \exp\left(-x^2 / r_e^2\right) \tag{S1}$$

The maximum laser intensity I_0 (W/m) is the intensity at the laser spot center can be found from:

$$I_{0} = \frac{Q}{\int_{-r_{0}}^{r_{0}} \exp\left(-x^{2} / r_{e}^{2}\right) dx}$$
(S2)

More than 99% of the laser power was included in the range of -0.9~0.9 μ m, so the laser spot edge was set to ±0.9 μ m from the laser spot center.

$$\int_{-r_0}^{r_0} \exp\left(-x^2 / r_e^2\right) dx > 0.99 \int_{-\infty}^{\infty} \exp\left(-x^2 / r_e^2\right) dx$$
(S3)

The one-dimensional steady-state heat conduction equation and its boundary conditions of temperature rises of θ_1 and θ_2 at the laser spot edge ($x=\pm 0.9 \mu m$) are.

$$\frac{d^{2}\theta}{dx^{2}} + \frac{I_{0}}{\pi db\lambda} \exp\left(-\frac{x^{2}}{r_{e}^{2}}\right) = 0$$

$$\begin{cases} x = -r_{0}, \theta = \theta_{1} \\ x = r_{0}, \theta = \theta_{2} \end{cases}$$
(S4)

The Gaussian laser heating power is then modeled as an internal heat source, Φ (W/m³) as:

$$\Phi = \frac{I_0 \exp\left(-\frac{x^2}{r_e^2}\right)}{\pi db}$$
(S5)

The temperature rises at the left and right laser spot edges, θ_1 and θ_2 , can be derived from the energy conservation equations as:

$$\begin{cases} -\lambda A \frac{d\theta}{dx} \Big|_{x=r_0} = \frac{\theta_2}{R_2 + R_c} \\ \frac{\theta_1}{R_1 + R_c} + \frac{\theta_2}{R_2 + R_c} = Q \end{cases}$$
(S6)

Where $R_1 = L_1/(\lambda A)$, $R_2 = L_2/(\lambda A)$, and R_c is the thermal contact resistance between the SWCNT and the substrate.

The temperature distribution inside the Gaussian laser spot is then given by:

$$\theta = F\left[xerf\left(x / r_e\right) + r_e / \left(\sqrt{\pi} \exp\left(x^2 / r_e^2\right)\right)\right] + \frac{\theta_2 - \theta_1}{2r_0}x + \frac{\theta_1 + \theta_2}{2} - F\left[r_0 erf\left(r_0 / r_e\right) + r_e / \left(\sqrt{\pi} \exp\left(r_0^2 / r_e^2\right)\right)\right]$$
(S7)

Where F, θ_1 and θ_2 are given by:

$$\begin{cases} F = -\frac{I_0}{\pi db\lambda} \frac{r_e \sqrt{\pi}}{2} \\ \theta_1 = \frac{Q(R_2 + R_c) - 2R_{r_0} \lambda AFerf(r_0 / r_e)}{R + 2R_c} (R_1 + R_c) \\ \theta_2 = \left(Q - \frac{Q(R_2 + R_c) - 2R_{r_0} \lambda AFerf(r_0 / r_e)}{R + 2R_c}\right) (R_2 + R_c) \\ Q = \alpha P \end{cases}$$
(S8)

The Raman spectroscopy system then measures the laser intensity weighed average temperature rise inside the focused laser spot as:

$$\theta_{m} = \frac{\int_{-r_{0}}^{r_{0}} I(x)\theta(x)dx}{\int_{-r_{0}}^{r_{0}} I(x)dx} = F \frac{\int_{-r_{0}}^{r_{0}} xerf\left(\frac{x}{r_{e}}\right) \exp\left(\frac{-x^{2}}{r_{e}^{2}}\right)dx + \frac{r_{e}}{\sqrt{\pi}}\int_{-r_{0}}^{r_{0}} \exp\left(\frac{-2x^{2}}{r_{e}^{2}}\right)dx}{\int_{-r_{0}}^{r_{0}} \exp\left(\frac{-x^{2}}{r_{e}^{2}}\right)dx} + \frac{\theta_{1} + \theta_{2}}{2} - F\left[r_{0}erf\left(\frac{r_{0}}{r_{e}}\right) + \frac{r_{e}}{\sqrt{\pi}}\exp\left(\frac{-r_{0}^{2}}{r_{e}^{2}}\right)\right]$$
(S9)

4. Fabrication of the silicon substrate



Figure S4. (A) Fabrication of the silicon substrates. The substrate fabrication has 5 key steps: (1) Preparation of a cleaned silicon wafer, (2) Fabrication of a 300 nm thick SiO_2 layer on the silicon wafer as electrical insulating layer using the thermal oxidation method, (3) Spinning of the photoresist, (4) Electron beam lithography, (5) Reactive ion beam etching of the wafer, (6) Removal of the photoresist.



Figure S4. (B) Optical and SEM images of the fabricated silicon substrate. The trenches were all $\sim 6 \mu m$ deep with the silicon substrate between two neighbouring trenches serving as the CNTs' heat sink. The sharp trench edge provides more accurate determination of the suspended sample length.

5. CNT Synthesis

All the substrates were cut into small pads and then cleaned with acetone, alcohol, and deionized water and then dried in a N_2 gas flow. A catalyst was transferred onto the cleaned substrates that were then put into a quartz tube. The air in the quartz tube was replaced by an Ar gas flow. After the quartz tube was heated to 950°C, the Ar gas flow was stopped. Then, the carbon feedstock (absolute ethyl alcohol) was carried into the high temperature quartz tube by an H_2 carrier gas.



Figure S5. Ultra-long CNTs grown across the silicon trench, the catalyst adheres to the head of the CNT, just like "flying a kite". The CNTs fall onto the substrate when the gas flow is stopped after finishing the synthesis.



6. Searching for a SWCNT with a high intensity Raman signal

Figure S6. Raman laser spot scan along the trench. Normally, the excited Raman signal intensity for an individual SWCNT is too low to be detected by the Raman spectroscopy system. The Raman signal will only be high enough if the SWCNT had strong resonance Raman scattering^{31,32}, however, very few CNTs can resonant with the laser. Since the individual CNT are not visible in an optical microscope, the Raman system was used to scan a long distance of several millimeters along the trench with a scanning step size of 1.0 μ m to find SWCNTs with high intensity Raman signals.

7. Laser absorption coefficient

The focused laser spot diameter is far larger than the diameter of a SWCNT, which means most laser power went missing. For SWCNT, the laser absorption coefficient was measured using the stead state Raman method developed by our research group, detailed in the first reference. This method consisting of two main steps, the first is to measure the thermal conductivity using Raman spectroscopy. As shown in Fig.S7 (A), the focused laser spot irradiate at the center of suspended sample. Electrical power change $((IU)_1-(IU)_2)$ induced temperature rise $\theta_{L/2}$ is measured by Raman spectroscopy. We can determine the thermal conductivity using

$$\lambda = \frac{L(I_1U_1 - I_2U_2)}{8A\theta_{L/2}}$$
(S10)

Where, $\theta_{L/2}$ is electrical heating induced temperature rise at the middle of suspended segment.



Figure S7. (A) Determination of thermal conductivity

Then, after the thermal conductivity is determined, two different powers (P_1 and P_2) focused laser spot irradiate on the sample, as shown in Fig.S7 (B). Laser heating induced G band frequency shift (ΔG) was recorded by Raman spectroscopy, and the local temperature rise at irradiation point is $\theta = k\Delta G$, SWCNT absorbed laser power and laser absorption coefficient η can be determined by Eq.(S11) and Eq.(S12), respectively.

$$\eta \left(P_1 - P_2 \right) = 2\theta / \left[\frac{L}{2(\lambda A)} \right]$$
(S11)

$$\eta = \frac{2\theta}{P_1 - P_2} / \left[\frac{L}{2(\lambda A)} \right]$$
(S12)



Figure S7. (B) Determination of laser absorption coefficient

The thermal conductivity and laser (514.5nm) absorption coefficient of a 1.3 nm diameter SWCNT is experimentally determined to be 2760 W/($m\cdot K$) and 1.4×10^{-4} at the temperature of 360 K. The diameters of two SWCNT samples used in this paper are 1.28 nm and 1.61 nm, so we use the same laser absorption coefficient as that of 1.3 nm diameter SWCNT. The uncertainty of laser absorption coefficient does not change the length dependent thermal conductivity.

8. Uncertainty analysis

Raman spectroscopy is widely used to measure the local temperature. The temperature resolution is determined by its spectral resolution and the slope of the temperature response G band frequencies. A Horiba T64000 Raman system triple additive model (focus length was 1.92 m and the grating density was 1800 gr/mm) had a spectral resolution of 0.15 cm⁻¹ found by measuring the full width half maximum (FWHM) of a neon lamp 585 nm peak. The temperature change was determined from the Raman G band shift, with the temperature resolution determined from the spectrum shift resolution, which is very different from the usually defined Raman spectral resolution.

Since the excited signal intensity from the SWCNT is much lower than that of the bulk material, the single mode (focus length 0.64 m, grate density 1800 gr/mm) was used to obtain a high intensity Raman signal. In the temperature range of 298~338 K, the silicon Raman peak was determined to shift linearly with a slope of 50.7 K/cm⁻¹, which fits well with the reference value^{33,34}. In the temperature range of 308~348 K, the single mode Raman G band of SWCNT shifted linearly with temperature as shown in Fig. S8(A). Repeated measurements at the ambient temperature $T_0=295$ K indicated that the G band frequencies were in the range of 1581.86±0.07 cm⁻¹, indicating that the uncertainty in the G band frequency measurement was 0.07 cm⁻¹.



Figure S8. Uncertainty analysis. (A) SWCNT G band shift with temperature, (B) Uncertainty in the G band frequency measurement.

Use of the same sample and maintaining the same laser absorptivity at different measurement positions excluded the largest uncertainty. According to Eq. S7, the uncertainties are the laser power measurement, sample length measurement, cross-sectional area and temperature rise measurement. The other factors can be neglected compared with the uncertainty induced by the temperature rise measurement. The uncertainty of temperature change induced G band frequency shift is ~0.1 cm⁻¹ as given by:

$$\delta\left(G_{P_2} - G_{P_1}\right) = \sqrt{\left(\delta G_{P_1}\right)^2 + \left(\delta G_{P_2}\right)^2}$$
(S13)

In these experiments, the typical temperature rise induced G band frequency shift ranged from

1.8 to 2.4 cm⁻¹, so the corresponding relative uncertainty was less than $4.2\% \sim 5.6\%$ according to the error propagation equation³⁵.

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