Electronic Supplementary Material (ESI) for Nanoscale.

Viable Method to Enhance the Electrical Conductivity of CNT Bundles: Direct In Situ TEM Evaluation

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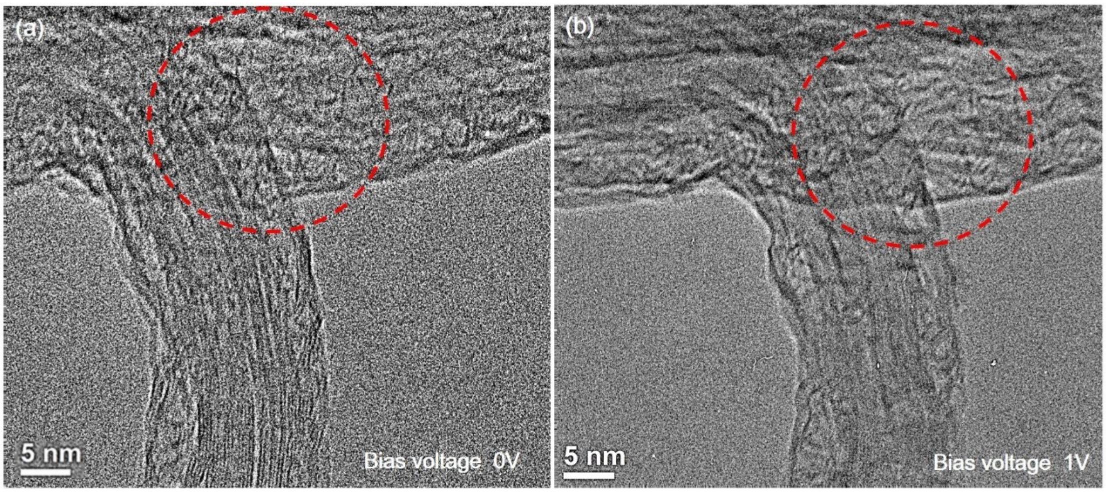
Supporting Information

1. Detailed TEM images for welded process

1.1 Boundary evolution at contacting part of neighboring cross-over CNTs

Firstly, we have focused on boundary evolution at contacting part of neighboring cross-over CNTs under different bias voltage. As shown in Figure S1, We have chosen a certain range of the CNT bundle for detailed observation. Figure S1a is initial state of two neighboring cross-over CNTs with obvious boundary (red circle). As we added the bias voltages (maintain the joule heating for 2min at each bias voltage), we can clearly see that the boundary in red circle becomes obscure, indicating welded process occurs.



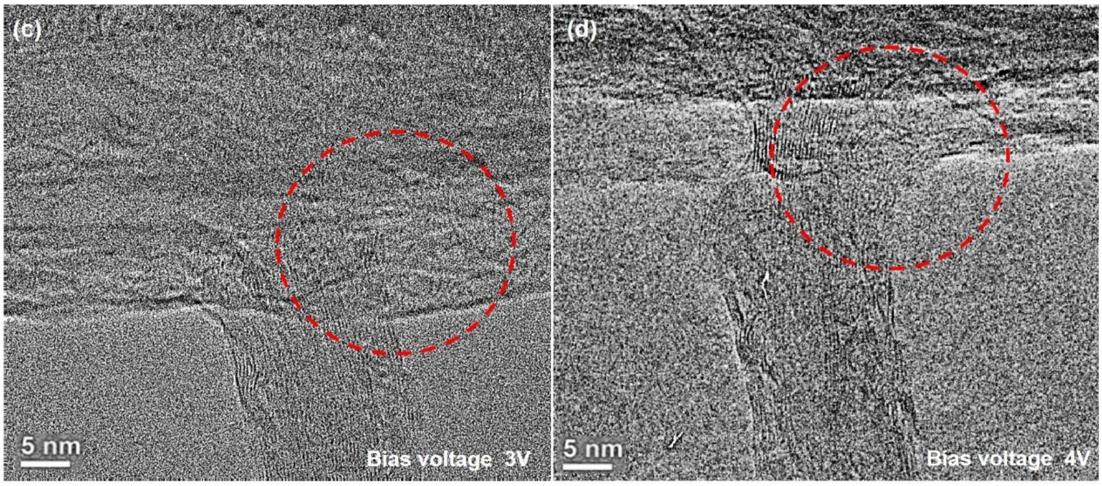


Figure S1. Detail of merged boundary between the cross-over CNT bundles during electric-induced Joule-heating process. (a) Before treatment. (b-c) Joule heating under bias voltage of 1, 3, 4 V, respectively.

1.2 Boundary evolution at contacting part of neighboring parallel CNTs

Secondly, we have focused on boundary evolution at contacting part of neighboring parallel CNTs under different bias voltage. As shown in Figure S2, We have chosen a certain range of the CNT bundle for detailed observation. Figure S2a is initial state of CNT bundles with obvious boundary. Compared with the TEM images under the bias voltage of 4 V (Figure S2b), we can clearly see that the CNT bundles become much clearer, the carbon amorphous atom layer become thinner and boundary between parallel CNTs becomes obscure. We have also observed the region marked in red circles under larger magnification (Figure S3). The observations show that the number of walls decrease (Figure S3b) and size of single CNT seems to be larger than that of pristine CNT bundle (Figure S3a). These results indicate the welding process have occurred between neighbor CNTs by utilizing the amorphous carbon atoms absorbing on the outside wall of CNTs.

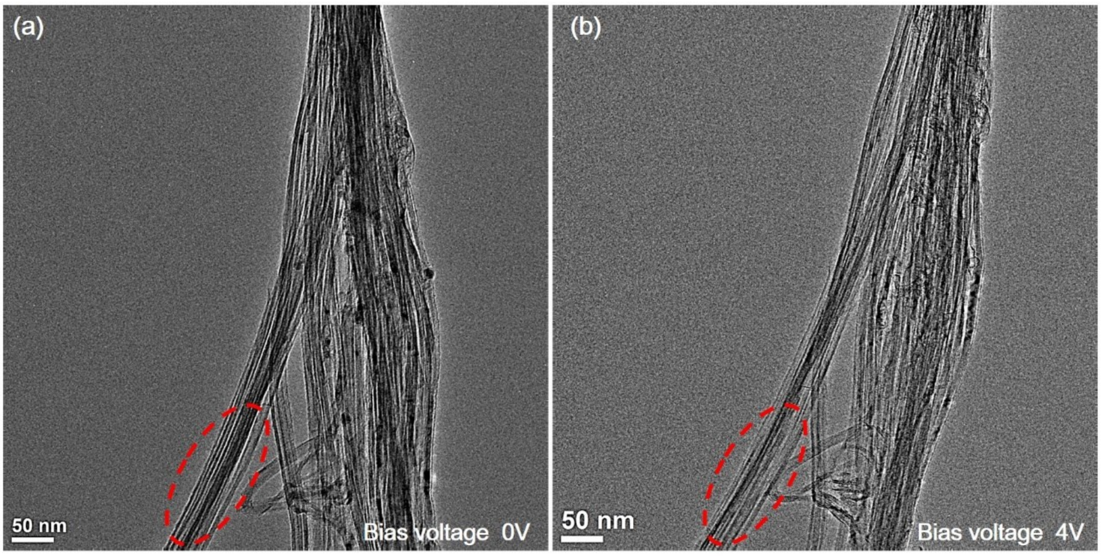


Figure S2. Detail of merged boundary between the parallel CNTs during electric-induced Joule-heating process. (a) Before treatment. (b) Joule heating under bias voltage of 4 V.

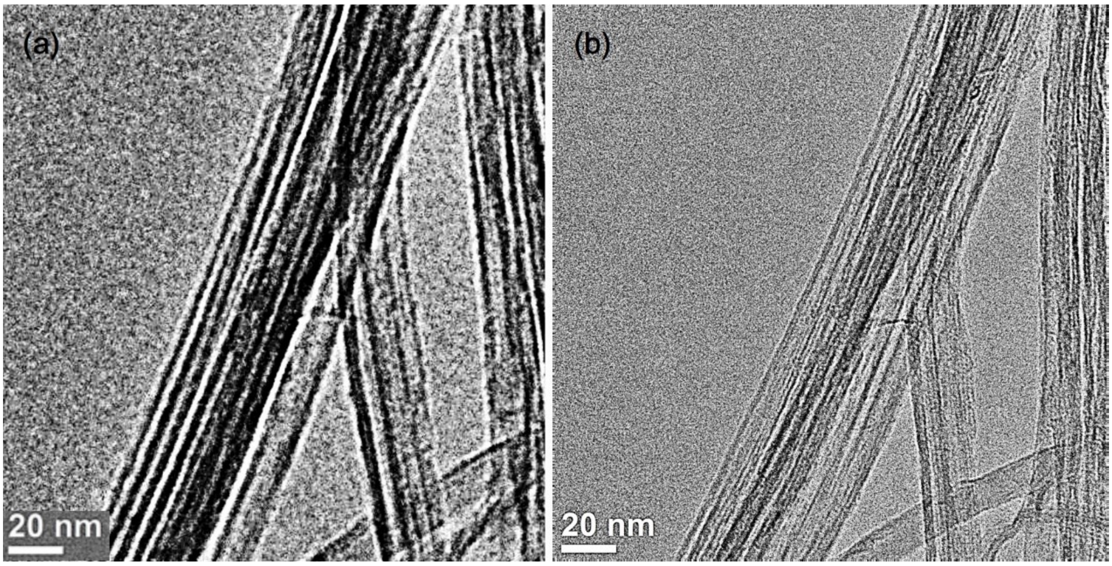


Figure S3. Larger magnification of the regions marked in red circles in Figure S2. (a) Pristine CNT bundles. (b) Joule heating under bias voltage of 4 V.

2. The electrical conductivity of CNT bundle under different bias voltage

Typically, the electrical resistivity (ρ) can be calculated as $\rho = \frac{R \cdot S}{L}$ (1).[S1] The electrical conductivity (E_c) of CNT bundle is calculated by the following formula: $E_c = \frac{1}{\rho} = \frac{L}{R \cdot S}$ (2), where R is resistance of CNT bundle, obtained from experimental measurements in Figure 1g, L is the effective length of CNT bundle between edge of the grid and W tip as shown in Figure 1a, S is average cross-section area of CNT bundle. We measured diameters of three points along CNT bundle and obtained the average value for the calculations. And we assume the sectional shape of CNT bundle as a sphere. Hence, we can obtain the value of E_c under different bias voltage, as shown in the following Table1.

Table1: The corresponding electrical conductivity of CNT bundle under different bias voltage.

Bias Voltage (V)	L (m)	D (m)	R (Ω)	E_c (S/m)
0 V	~5.0×10^{-6}	~0.24×10^{-6}	~1.0×10^{6}	~1.1×10^{2}
1 V	~5.0×10^{-6}	~0.23×10^{-6}	~3.4×10^{5}	~3.5×10^{2}
2 V	~5.0×10^{-6}	~0.21×10^{-6}	~1.80×10^{5}	~8.1×10^{2}
3 V	~5.0×10^{-6}	~0.18×10^{-6}	~1.70×10^{3}	~1.2×10^{5}
4 V	~5.0×10^{-6}	~0.15×10^{-6}	~1.28×10^{3}	~2.3×10^{5}

3. The temperature of CNT bundle under different bias voltage

For terminal-suspended CNTs, the highest temperature appears at the middle point of these suspended CNTs, which are reported ranges from 900-2000 K[S2-S4], according to different types of tubes. When a voltage is applied on the 1D conductor system, heat will be generated along the nanotubes or nanowires via Joule heating. Meanwhile, because of the vacuum environment, the heat can only be dissipated along the conductor through the two ends; and the thermal equilibrium of the system can be set up within a short time. Therefore, assuming the thermal equilibrium, we can establish the heat transport equation for a suspended nanotube, which is given by[S5]

$$-\kappa\frac{d^2T(x)}{dx^2}=j\frac{U}{L} \tag{1}$$

where κ is the thermal conductivity, T(x) is the temperature along the conductor, j is the current density, U is the voltage drop, and L is the length of the conductor. The left side is thermal conduction and the right side is the Joule heating.

Here, we just consider the simplest case when the temperature at the contact is maintained at a constant temperature T_0 and the thermal and electrical conductivity are also constant. The temperature distribution along the conductor is given by

$$T(x)=-\frac{jU}{2\kappa L}x^2+\frac{jUL}{8\kappa}+T_0 \tag{2}$$

The temperature difference between contacts and the middle point is

$$\Delta T=T_{max}-T_0=\frac{jUL}{8\kappa}=\frac{E_cU^2}{8\kappa} \tag{3}$$

Hence, the highest temperature at the middle point is estimated to be $T_{max}\sim f\ (E_c, U,\kappa\ )$

$$T_{max}=T_0+\frac{E_cU^2}{8\kappa} \tag{4}$$

where E_c is the electrical conductivity. κ is thermal conductivity, we can obtain κ from the direct electrical heating experiment[S6] (set up and measure details are shown in Figure S4). As for MWNT bundle in our case (electrically pre-treated as shown in Figure 3b, joule-heating temperature of MWNT bundle is 2480°C, with average diameter of 9 µm, length of 13 mm), κ is ~230 W/mK measured at 300K.

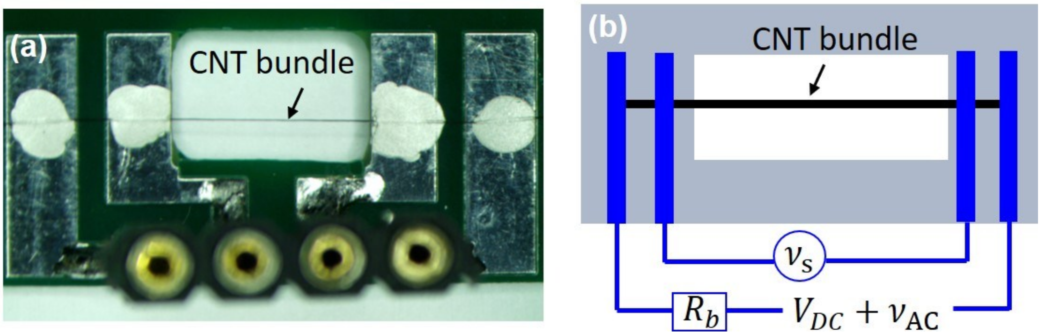


Figure S4. (a) Optical image of a 4-probe device. (b) Schematic of the measurement circuit. The contacts between the sample and the four probes were treated with silver conductive paint (SPI 05001-AB) to reduce both electrical and thermal contact resistance. A variable resistor R_b was connected with the sample in series. A DC voltage, V_{DC}, coupled with an AC voltage of 1400

Hz, v_{AC}, was applied on the circuit. We used the DC only to heat the sample and the AC to sense the electrical resistance of the sample. In our measurements, both V_{DC} and v_{AC} were supplied by a lock-in amplifier (Stanford Research Systems SR830).

Actually, it should be noted that the conductivity κ is in general temperature dependent, and it is still very hard to obtain κ of MWNT bundle at higher temperature in our case. So, here we estimate the value of T_{max} by using same value of κ measured at 300 K. Moreover, the temperature rise induced by irradiation of the electron beam can be ignored. The temperature T_0 of CNT bundle is considered to be same as the room temperature when there is no electrical current. The corresponding highest temperatures at the middle point under different bias voltage are shown in Figure S5. It is interesting to find that the relationship between measured electrical conductivity and estimated Joule-heating induced temperature on CNT bundles follows natural logarithm law, i,e, $E_c \sim A\ln T_{max}$-B. As previous reference reported[S7], when measured temperature is higher than 500 K, the value of κ of MWNT will decrease with the increasing temperature, hence if we use value of κ measured at 300 K to estimate T_{max} in equation (3), our estimated T_{max} under large bias voltage (> 3 V) will be smaller than the actual values.

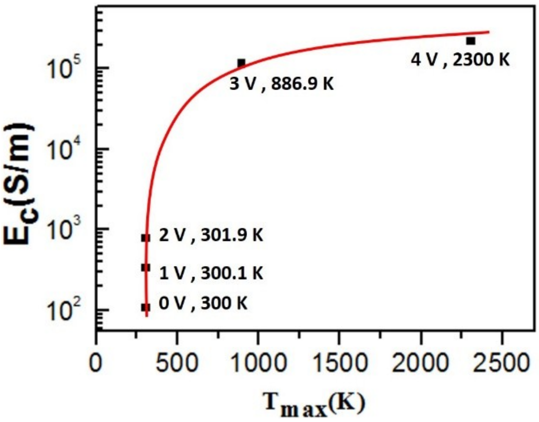


Figure S5. The relationship between estimated T_{max} and measured E_c. T_{max} under each bias voltage is shown in image.

4. TGA result of carbon nanotube fiber

The TGA curve of carbon nanotube fiber is shown in the following. The temperature region of mass loss is 500-880 °C, which is similar with the high-quality carbon nanotube fibers produced by arc discharge method (500-910 ºC), meaning that our sample has good thermal stability. From TGA curve (Figure S5), we can also see that weight loss of fiber is 82 wt.%, weight loss of fiber is residue is 18 wt.% and we can obtain that the C content of carbon nanotube fiber is 87.4 wt. %."

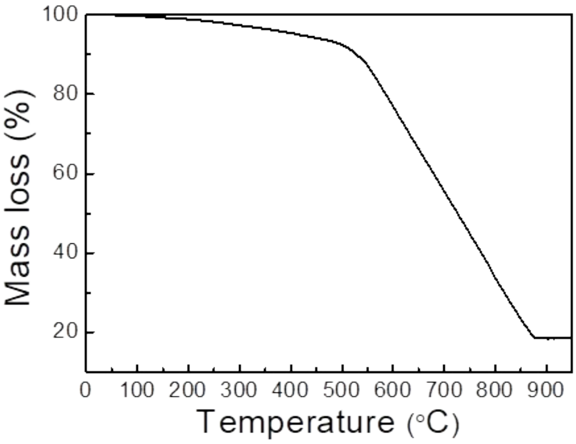


Figure S5. The TGA curve of carbon nanotube fiber.

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