Electronic Supplementary Information (ESI)

Spray-printed CNT/P3HT organic thermoelectric film and power generator

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Experimental Section

Fabrication of CNT/P3HT nanocomposite films

Purified carbon nanotubes (CNTs, catalog number: XNM-UP-11050, purity >98%) were purchased from XinNano Materials (www.xinnanomaterials.com). Regioregular poly(3-hexylthiophene) (P3HT, M_w 37,685 g mol^{-1}, regioregularity 98.5%) and anhydrous chloroform were purchased from Sigma-Aldrich. All chemicals in this study were used as received. After dissolving the P3HT in chloroform, the CNTs were then added to this solution. The total solid concentration of inks was fixed at 2 mg mL^{-1}. The mixture was sonicated in an ice bath using a probe sonicator (VCX-750 Vibra-Cell, Sonics & Materials) at 10 W for 1 hr. The as-prepared inks were then drop-cast or spray-printed onto glass substrates (76 mm × 26 mm).

Fabrication of CNT films

The purified HiPco single-walled CNTs were obtained from Unidym. The mixture of single-walled or few-walled CNTs (30 mg) and chloroform (30 mL) was sonicated in an ice bath using a probe sonicator at 10 W for 1 hr. The as-prepared mixture was then vacuum-filtrated with a nylon membrane filter (pore size: 0.2μm, diameter: 47 mm). The thicknesses of the single-walled and few-walled CNT films were 24.9 and 28.0 μm, respectively.

Fabrication of spray-printed CNT/P3HT organic thermoelectric generator (OTEG)

For spray-printing, a commercially available spray gun (Iwata, Plus HP-SB Plus), with a nozzle diameter of 200 μm, was used. The as-prepared ink was spray-printed onto a polyimide substrate in air with a shadow mask. We used air with 30 psi as a carrier gas, and the ink was successfully sprayed without clogging the nozzle. The nozzle-to-substrate distance, the spray time, and the substrate temperature were 10 cm, 2 min, and room temperature, respectively. The spray-printed 41 p-type active lines, with a width of 1 mm and a length of 15 mm, were connected in series by silver electrodes that were dispenser-printed using a Musashi Shotmaster 200DS-s (Fig. S6).

Characterizations

The Seebeck coefficients of the nanocomposite films were measured under dark ambient conditions utilizing a custom-built system. Before the measurement, silver paste was printed onto the CNT/P3HT nanocomposite films through a screen mask. Two silver electrodes, 5 mm in width, were separated by a distance of 40 mm. The temperature gradient between the two electrodes was varied from 1 to 10 ºC. The Seebeck voltage generated by the temperature difference was measured with a Keithley 2182A Nanovoltmeter. The Seebeck coefficient was estimated from the slope of the straight line fit of $\Delta V/\Delta T$.[S1] The electrical conductivity of the CNT/P3HT nanocomposite films was measured with the standard van der Pauwe direct current four-probe method.[S2] All the measurements were conducted at room temperature using a Keithley 195A digital multimeter and a Keithley 220 programmable current source.

The thickness of the films was determined by an alpha-step surface profiler (α-step DC50, KLA Tencor). The surface morphologies of the films were observed with a field-emission scanning electron microscope (SEM, MIRA3, TESCAN) operating at 20 kV, and a tapping-mode atomic force microscope (AFM, Nanoscope IV, Digital Instruments). The fracture surface morphology of the CNT/P3HT nanocomposite film was observed with a field-emission high resolution SEM (Magellan 400, FEI) operating at 3 kV. The cross-section TEM sample was prepared using the *ex situ* lift-out technique using the focused ion beam (FIB, FB-2100, Hitachi) and imaged with a field-emission transmission electron microscope (TEM, Tecnai F30 S-Twin, FEI).

The power-generation characteristics of the spray-printed CNT/P3HT OTEG were measured under dark ambient conditions utilizing a custom-built system. We set the temperature difference between the two sides of the spray-printed CNT/P3HT lines to 10 ºC by using two Peltier plates (Fig. S7). The voltage-current and power-current curves of the thermoelectric generator were obtained with a Keithley 2450 Sourcemeter by varying the load resistance.

Figures

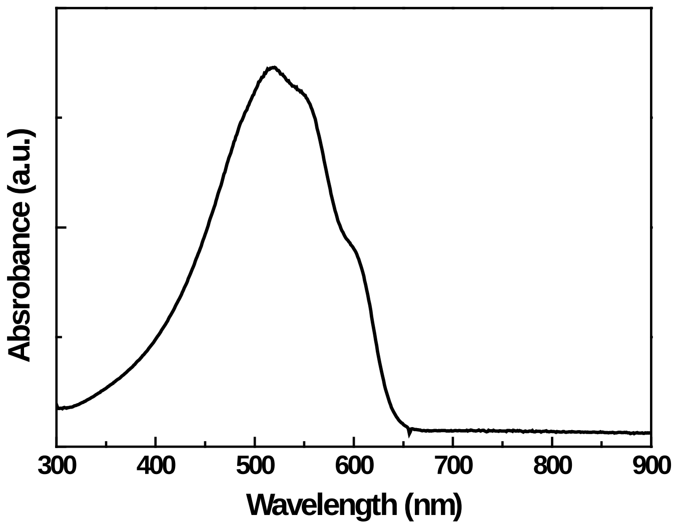

Fig. S1 UV-vis spectrum of the P3HT film.

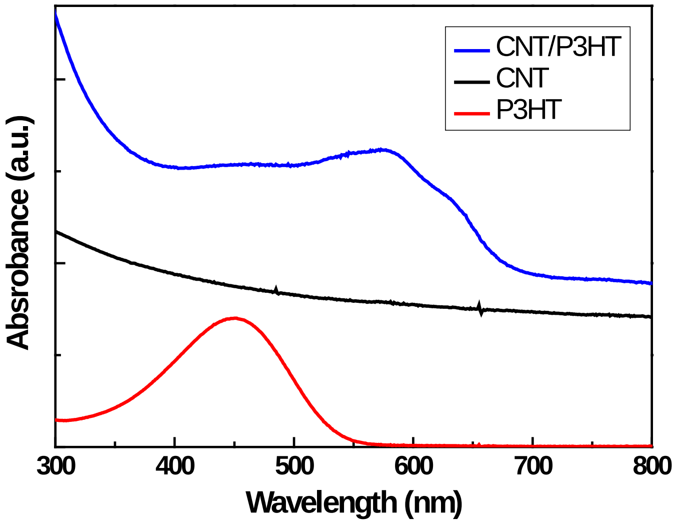

Fig. S2 UV-vis spectra of the CNT/P3HT ink with 50 wt% CNTs, CNT dispersion in chloroform, and P3HT solution in chloroform.

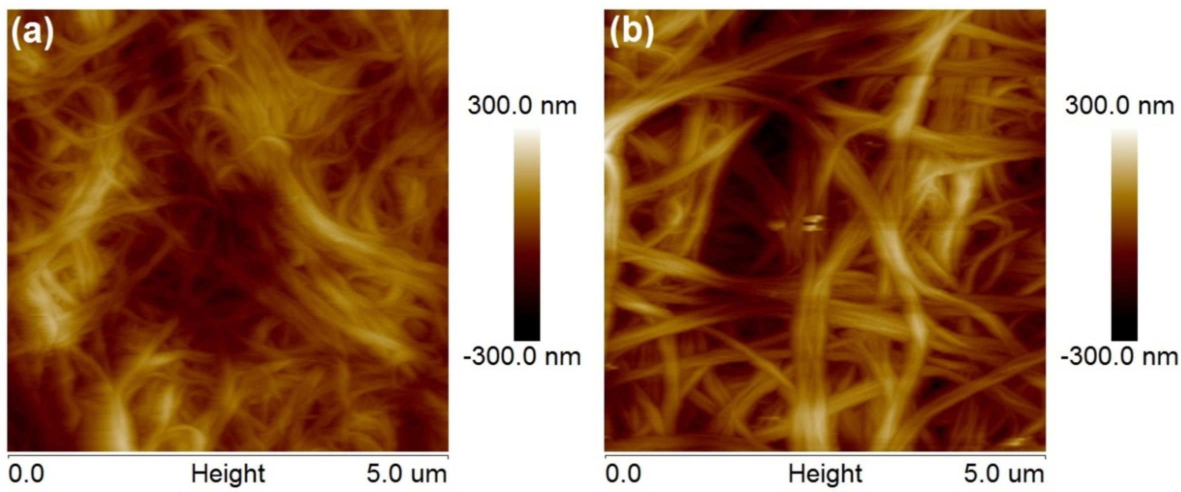

Fig. S3 AFM images of the vacuum-filtrated (a) single-walled and (b) few-walled CNT films.

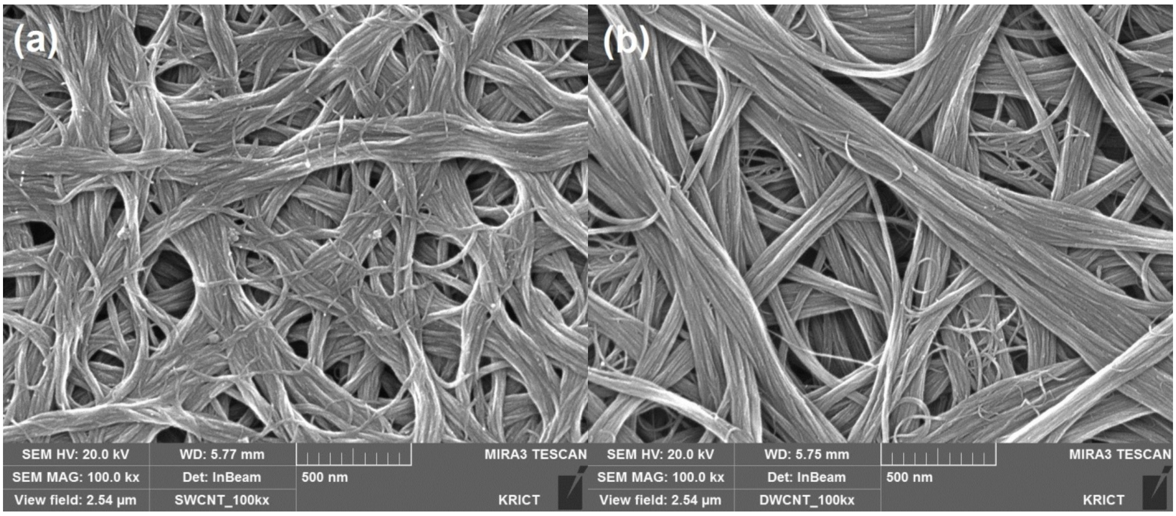

Fig. S4 SEM images of the vacuum-filtrated (a) single-walled and (b) few-walled CNT films.

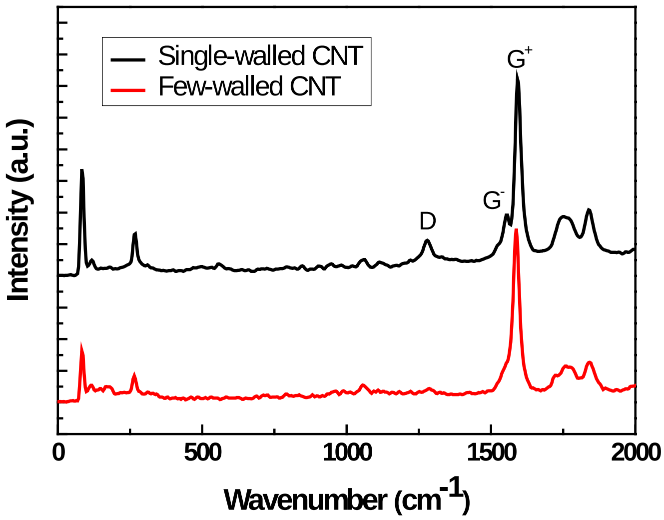

Fig. S5 Raman spectra of single-walled and few-walled CNTs.

Fig. S6 Schematic drawing and photograph of the spray-printed CNT/P3HT organic thermoelectric generator.

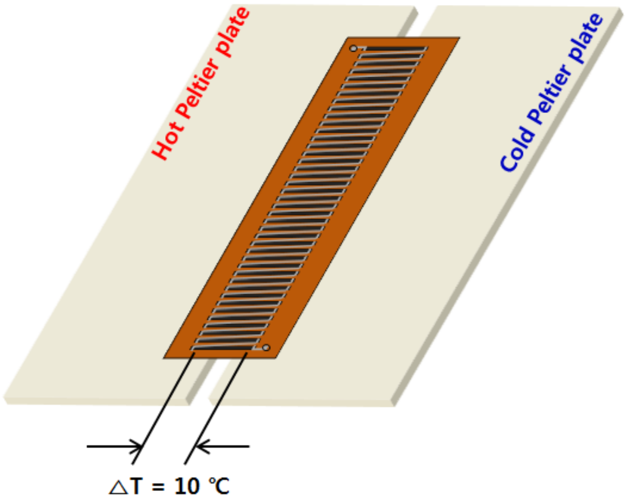

Fig. S7 Schematic drawing of setting the temperature difference between the two sides of the spray-printed CNT/P3HT lines to 10 ºC with two Peltier plates.

References

S1 C. T. Hong, W. Lee, Y. H. Kang, Y. Yoo, J. Ryu, S. Y. Cho and K.-S. Jang, *J. Mater. Chem. A*, 2015, **3**, 12314.

S2 L. T. van der Pauwe, *Philips Res. Rep.*, 1958, **13**, 1.