# Large *n*- and *p*-type thermoelectric power factors from doped semiconducting single-walled carbon nanotube thin films

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# **Supporting Information**

- 1. Relationship between thermopower and electrical conductivity
- 2. Maximum electrical conductivity vs. Electrical conductivity at peak TE Power factor
- 3. Stability of *n*-type doping in air and at elevated temperatures
  - a. Unprotected *n*-type PT:PFPD samples
  - b. Alumina-protected n-type HiPCO:SMP samples at elevated temperatures
- 4. Comparison of *n*-type performance metrics and theoretical power density
- 5. Temperature-dependent thermal conductance in polymer-free s-SWCNT networks
- 6. Comparison of the TE power factor for s-SWCNTs enriched by two cleavable polymers

#### Relationship between thermopower and electrical conductivity

The trendlines in Figure 2A–D of the main manuscript, as well as those in Figure S2 below, are constructed using an empirical modified Mott-Heike formula for thermopower in semiconductors:<sup>1,2</sup>

$$\alpha = \frac{k_B}{e} \frac{1}{\beta} \ln \left( \frac{\sigma}{\sigma_{\text{max}}} \right)$$
(S1)

where  $\alpha$  and  $\sigma$  are the experimentally measured thermopower and electrical conductivity, respectively;  $k_B$  is the Boltzmann constant; e is the elementary charge; and  $\beta$  and  $\sigma_{max}$  are fitting parameters that primarily determine the thermopower limit at low electrical conductivities and the electrical conductivity at which the thermopower is zero (i.e., the intercept on the x-axis), respectively. Figure S1 illustrates the impact that (a)  $\beta$  and (b)  $\sigma_{max}$  have on the curve of  $\alpha$  vs.  $\sigma$ .



**Figure S1.** The impact of the parameters (a)  $\beta$  and (b)  $\sigma_{max}$  on the thermopower vs. electrical conductivity curves described by the modified Mott-Heike relationship for thermopower in semiconductors.

This relationship has been employed to analyze the dependence of the thermopower on the electrical conductivity in various doped polymers, where the values of  $\beta$  and  $\sigma_{max}$  are dependent on the polymer morphology and "the chemical nature of the dopant".<sup>1</sup> It is interesting to note that  $\sigma_{max}$  is qualitatively similar to the transport coefficient ( $\sigma_{E0}$ ) described by Kang et al.,<sup>3</sup> which was introduced in a recent paper describing a model for charge carrier transport in conjugated polymers. In that model,  $\sigma_{E0}$  functions as a weighted charge carrier mobility. An increase in either coefficient,  $\sigma_{max}$  or  $\sigma_{E0}$ , shifts the electrical conductivity-dependent thermopower curve to the right (as shown for  $\sigma_{max}$  in Figure S1a), resulting in an increased maximum TE power factor.

Figure S2 illustrates the improvement in the TE performance for enriched s-SWCNT prepared by the (top) arc discharge (AD) and (bottom) pulsed laser vaporization (LV) synthetic processes. As described above, the lines are calculated using Equation S1.



**Figure S2.** Improvement of TE performance for AD (a and b panels) and LV (c and d panels) SWCNTs for cleavable polymer (SMP) versus non-cleavable polymer (PFO-BPy).

#### Maximum electrical conductivity vs. Electrical conductivity at peak TE Power factor

In order to justify our use of the maximum electrical conductivity (fully doped network) as a predictor for the peak TE power factor (optimally doped network; Figure S3a and Figure 2e), we explore the correlation between the peak TE power factor and the electrical conductivity for the optimally doped network (Figure S3b). This figure shows demonstrates that similar observations can be made for Figure 3a and 3b: (1) the linear correlation between the electrical conductivity and peak TE power factor is strong and (2) the networks prepared using cleavable polymers consistently outperform those containing residual wrapping polymer. In addition, as would be expected given the observations described above, Figure S3c illustrates the strong linear correlation between the electrical conductivity for the optimally doped network and the maximum electrical conductivity, once again showing that electrical transport is enhanced in the polymer-free networks.



**Figure S3.** Dependence of the peak TE power factor (optimally doped network) on (a) the maximum electrical conductivity (fully doped network) and (b) the electrical conductivity at the peak TE power factor (optimally doped network). (c) Correlation between the electrical conductivity at the peak TE power factor (optimally doped network) and the maximum electrical conductivity (fully doped network). In all panels, the electrical transport of all networks utilizing cleavable polymers (blue oval) exceeds the values for networks containing residual wrapping polymer (orange oval).

#### Stability of *n*-type doping in air and at elevated temperatures

#### **Unprotected** *n***-type PT:PFPD** samples

A small number of studies have reported that mixed (containing both metallic and semiconducting nanotubes) SWCNT films can be doped *n*-type in air and retain some degree of *n*-type conductivity for long periods of time in air with no encapsulation or protection.<sup>4-7</sup> Our studies on s-SWCNT films stand in marked contrast to these results, as exemplified by Figure S4 and discussed in more detail below. None of the *n*-type dopants that we have utilized – crown ether/salt complexes, viologens, indoles, metallocenes, phosphine ligands, and ethyleneimines - have enabled the large, air-stable carrier densities within our s-SWCNT networks that we are able to achieve with a variety of *p*-type dopants. Figure S4 provides exemplary data for our attempts to obtain *n*-type doping that is stable in air without an Al<sub>2</sub>O<sub>3</sub> over-coat. Figure S4a demonstrates our attempt to dope a PT:PFPD film with benzo-18-crown-6 ether and KOH. When immersing the film in the dopant in ambient conditions, we see no quenching of the  $S_{11}$  or  $S_{22}$  transitions, indicating little or no doping of the thin film. In contrast, when the same film is immersed in the dopant solution in a  $N_2$  glovebox, the  $S_{11}$  transitions are completely doped and the  $S_{22}$ transitions are partially doped, indicating strong *n*-type doping. The *n*-type doping of this film is also stable indefinitely if stored in the  $N_2$  glovebox. We note that since the film is not coated with  $Al_2O_3$ , the absorbance measurement must be performed in an air-tight cell (see yellow traces in panels (a) and (b)). Figure S4b demonstrates that when the same unprotected *n*-type doped PT:PFPD film is brought out from the glovebox (or air-free holder into which it was loaded in the glovebox), the absorption rapidly changes. The bleached  $S_{11}$  excitonic transitions quickly regain some of their initial oscillator strength, indicating that the electron density that quenched these transitions is reduced by exposure to air. This loss of electron density can be easily observed by a rapid change of the Seebeck coefficient (Figure S4c). Figure S4c demonstrates that once an *n*-type film with relatively high power factor (i.e. Seebeck coefficient near that needed to produce maximum power factor) is exposed to air, the Seebeck magnitude increases quickly and dramatically to a high negative value. Without knowing the full characteristics of the power factor curve, this high value of thermopower – which is fairly stable with time - would potentially look attractive. However, when comparing these thermopower values to the values found in Figure 2 of the main manuscript, it is clear that this rapid change in thermopower corresponds to an immediate and sharp reduction in carrier density (and associated electrical conductivity), which reduces the power factor by approximately a factor of three.

At this point, it is unclear which experimental and/or sample parameters contribute most prominently to a number of these differences. First, all of these previous studies are performed on SWCNTs that contain metallic SWCNTs, so the presence of metallic SWCNTs could play a role. Second, most of these studies are performed on SWCNT samples that have relatively large average diameters, i.e. d > 1.3 nm. The smallest diameter SWCNTs studied by Nonoguchi et al.<sup>7</sup> for benzo-crown ether doping (d ≈1.3 nm) is larger than the HiPCO SWCNTs probed in the current study, and is roughly equivalent to the LV SWCNTs studied here. In that study, the authors found that the stability of *n*-type conductivity was dramatically compromised relative to the larger diameter SWCNTs when studied over a relatively short time period (ca. 25 hours), although these experiments were performed at 150 °C.<sup>7</sup> Through exhaustive literature search, we have found no studies that display air-stability of large *n*-type conductivities of un-encapsulated semiconducting SWCNTs with diameters <1.7nm. Our process of encapsulating these *n*-doped s-SWCNTs therefore represents a step forward for the TE community, enabling us to take advantage of the high conductivities, large thermopowers, and highly tunable properties of smaller-diameter (1.0 - 1.5 nm), enriched s-SWCNTs on the *n*-type leg of thermoelectric generators.



**Figure S4.** Instability of *n*-type doping for unprotected s-SWCNT films when doping in air or exposing to air after doping in a glovebox. (a) Comparison of absorption spectra for PT:PFPD films doped either in air or in a glovebox with the benzo-18-crow-6 dopant. (b) Absorption comparison demonstrating de-doping of an *n*-type PT:PFPD film upon removal of the film (originally doped in N<sub>2</sub> glovebox) to an ambient environment. (c) Time-dependent Seebeck coefficient for an *n*-type PT:PFPD film upon exposure of the sample to air. In this experiment, the sample is first doped in the glovebox and sealed in an air-tight container within the glovebox. The sample is removed from this air-tight container in the immediate vicinity of the Seebeck system and is quickly placed on the system. After placement on the Seebeck system, the system is sealed and is evacuated to approximately 100 mTorr using a diaphragm pump. We estimate that the sample sees about 30 seconds of air exposure during this loading

process. The Seebeck coefficient of this sample under active vacuum is  $-40 \mu$ V/K. At t = 10 minutes (arrow in figure), the vacuum is stopped and vented, exposing the sample to ambient environment.

#### Alumina-protected *n*-type HiPCO:SMP samples at elevated temperatures

To explore the impact that exposure to elevated temperatures, such as might be experienced during operation in low-grade waste heat recovery applications, has on the TE performance, we measured the TE properties on a *n*-type doped,  $Al_2O_3$ -overcoated HiPCO:SMP sample after heating for ca. 21 hours at 35 °C, followed by 24 hours at 50 °C (Figure S5).



Figure S5. Dependence of the thermoelectric properties of an  $Al_2O_3$ -encapsulated, polymer-free HiPCO s-SWCNT network after being held at elevated temperatures for almost two days.

### Comparison of *n*-type performance metrics and theoretical power density

A comparison of the *n*-type performance of the s-SWCNT networks demonstrated here to recent literature results on conducting polymers and SWCNTs is given in Table S1. Our s-SWCNT *n*-type power factor is nearly thirty times higher than the best *n*-type performance for a solution-processable semiconducting polymer, the BDPPV polymer demonstrated by Shi et al.,<sup>8</sup> and a factor of two to ten times higher than for the difficult-to-process n-type transition metal coordination polymers demonstrated by the research group of Daoben Zhu.<sup>9,10</sup> This demonstrates a clear advantage for s-SWCNTs over semiconducting polymers as the sole material in all-organic TE modules. The high power factors demonstrated here would not only enable significantly higher ultimate power densities than previously demonstrated semiconducting polymers, but would also enable straightforward balance of electron and hole transport in *n*- and *p*-type legs that is needed for full TE generators.<sup>11</sup>

**Table S1.** Comparison of conductivity, thermopower, and power factor for the best demonstrations of *n*-type organic semiconductors in the literature.

					Power
			Conductivity	Seebeck	Factor
Reference	Year	Semiconductor/Dopant	(S m <sup>-1</sup> )	(μV K <sup>-1</sup> )	(µW m <sup>-1</sup> K <sup>-2</sup> )
Current	2017	PT s-SWCNTs/BV <sup>a</sup>	119,000	-78.5	730
Nonoguchi <sup>7</sup>	2016	eDIPS mixed SWCNT/18-crown- 6-ether:KOH <sup>b</sup>	205,000	-33	223
Wang <sup>12</sup>	2016	BBL/TDAE <sup>c</sup>	100	-60	0.43
Sun <sup>10</sup>	2016	poly(Ni-ett) <sup>d</sup>	22,750	-126	361
Mai <sup>13</sup>	2015	CPE–PyrBIm <sub>4</sub> -wrapped mixed AD SWNTs <sup>e</sup>	10,500	-41	17.8
Shi <sup>8</sup>	2015	FBDPPV/N-DMBI <sup>f</sup>	1,400	-140	28
Fukumaru <sup>6</sup>	2015	cobaltocene@SWCNTs <sup>g</sup>	43,000	-40.4	70.7
Schlitz <sup>14</sup>	2014	P(NDIOD-T2)/N-DMBI <sup>h</sup>	0.8	-850	0.6
Russ <sup>15</sup>	2014	PDI-3	50	-170	1.4
Nonoguchi <sup>5</sup>	2013	sCVD mixed SWCNT/dppp <sup>j</sup>	9,800	-52	26.5
Yu <sup>16</sup>	2012	CVD mixed SWCNT/PEI:NaBH <sub>4</sub> <sup>k</sup>	6,000	-80	38
Sun <sup>9</sup>	2012	poly[K <sub>x</sub> (Ni-ett)] <sup>1</sup>	4,500	-121	66

<sup>a</sup> PT = plasma torch, BV = benzyl viologen; <sup>b</sup> KOH = potassium hydroxide (with 18-crown-6-ether); <sup>c</sup> BBL =

polybenzimidazobenzophenanthroline, TDAE = tetrakis(dimethylamino)ethylene; <sup>d</sup> poly(Ni-ett) = poly(nickelethylenetetrathiolate) coordination polymer; <sup>e</sup> AD = arc discharge, CPE–PyrBIm<sub>4</sub> = poly(cyclopenta-[2,1-*b*;3,4-*b*']-dithiophene*alt*-4,7-(2,1,3-benzothiadiazole)) with tethered pyridinium groups, CPE–PyrBIm<sub>4</sub> also acts as the *n*-type dopant; <sup>f</sup> FBDPPV = fluorinated benzodifurandione-based poly(*p*-phenylene vinylene), N-DMBI = ((4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazol-2yl)phenyl)dimethylamine); <sup>g</sup> cobaltocene dopant is encapsulated inside the endohedral volume of mixed Meijo-SO SWCNTs; <sup>h</sup> P(NDIOD-T2) = poly{N,N'-bis(2-octyl-dodecyl)-1,4,5,8-napthalenedicarboximide-2,6-diyl]-alt- 5,5'-(2,2'-bithiophene)}; <sup>i</sup> PDI-3 = perylene diimide with tethered quaternary ammonium cations; <sup>j</sup> sCVD = "supergrowth" chemical vapor deposition, dppp = 1,3bis(diphenyl- phosphino)propane; <sup>k</sup> PEI = polyethyleneimine, NaBH<sub>4</sub> = sodium borohydride; <sup>l</sup> poly[ $K_x$ (Ni-ett)] = potassium poly(nickel-ethylenetetrathiolate) coordination polymer.

As a point of comparison, one can calculate the maximum potential power density ( $PD_{max}$ ) delivered by a TE generator consisting of *p*- and *n*-type legs with particular values of power factor, using Equation S2:<sup>11</sup>

$$PD_{\max} = \frac{\left(\alpha_p - \alpha_n\right)^2}{\left(\sqrt{L_p \rho_p} + \sqrt{L_n \rho_n}\right)^2} \frac{\Delta T^2}{4}$$
(S2)

In Equation S2,  $\alpha$ , L, and  $\rho$  are the Seebeck coefficient, length, and resistivity (the inverse of conductivity:  $\rho = \sigma^{-1}$ ), respectively, of TE generator leg, with the  $\rho$  or n subscript denoting the  $\rho$ - or n-type leg, respectively. Note that Equation S2 assumes that  $\alpha$  and  $\rho$  are temperature independent, which is a reasonable assumption when the operating temperature difference ( $\Delta T$ ) is small.<sup>11</sup> Integrating over the temperature-dependent thermopower and resistivity provides a more accurate calculation of power density.<sup>11</sup> However, since the references given in Table S1 do not provide any data for  $\alpha(T)$  or  $\rho(T)$ , Equation S2 must be used to provide relative values of  $PD_{max}$ .

Using the metrics shown in Table S1 and this simplified estimation of  $PD_{max}$  (Eqn. S2),<sup>11</sup> the maximum theoretical power density achievable for p/n pairs of s-SWCNTs or semiconducting polymers can be calculated. This comparison is shown in Figure S6 for the two best SWCNT cases besides the current study,<sup>7,13</sup> along with the three solution-processable polymer<sup>8,12,14</sup> and two transition-metal coordination polymer<sup>9,10</sup> cases shown in Table 1. In contrast to semiconducting polymers, where the same material system cannot easily be employed for both the *p*- and *n*-type legs, s-SWCNTs can be easily doped so that either holes or electrons are the majority carrier. As such, we only present values in Figure S6 for studies where both *p*- and *n*-type TE properties are reported. We note that the other three *n*-type SWCNT cases shown in Table S1<sup>5,6,16</sup> produce  $PD_{max}$  values in the range of 1.2 – 1.9, but are omitted from Figure S6 for clarity. For each of the polymer calculations, the best published results for PEDOT:PSS (Kim et al.)<sup>17</sup> were used as the theoretical *p*-type leg. For these two SWCNT cases,<sup>7,13</sup> both the *p*- and *n*-type values for conductivity, thermopower, and power factor reported in each of these studies were used to calculate  $PD_{max}$  and the average power factor:

$$PF_{avg} = \frac{PF_p + PF_n}{2}$$
(S3)

Importantly, Figure S6 demonstrates that the *p*- and *n*-type s-SWCNT pairs demonstrated here provide a theoretical  $PD_{max}$  that is an order of magnitude higher than can be achieved for the highest performance solution-processed polymer pair in Table S1, i.e. consisting of *p*-type PEDOT:PSS (best results published by Kim et al.)<sup>17</sup> and *n*-type BDPPV (Shi et al.).<sup>8</sup>



**Figure S6.** Comparison of the relative maximum power density ( $PD_{max}$ ) that can be achieved for a theoretical TE generator composed of a particular pair of *p*- and *n*- legs, using Equation S2. The particular *p*/*n* legs are labeled beside each point; Polymer *p*/*n* pairs are shown as blue points and SWCNT *p*/*n* pairs are shown as orange points, with the current study highlighted by the green circle. The values for *n*-type performance metrics can be found in Table S1, and *p*-type metrics can be found in the given references. The y-axis can be converted into an absolute value for  $PD_{max}$  if the following values are used in Equation S2 for the leg length (*L*) and the temperature difference ( $\Delta T$ ): *L* = 10 mm,  $\Delta T$  = 50 K. Note that the asterisks beside the polymer data points corresponding to the *n*-type coordination polymers are meant to draw attention to the fact that, unlike the other *p*/*n* pairs in the figure, these polymers are not solution-processed.



#### **Temperature-dependent thermal conductance in polymer-free s-SWCNT networks**

**Figure S7.** Raw data for thermal conductance measurements as a function of temperature. The black points represent the measured thermal conductance of the Si-N bridge with no s-SWCNT film deposited on top of the bridge. The blue, red, and purple data points represent the thermal conductance of the bridge and s-SWCNT film, where the s-SWCNT film has been doped with OA to produce the electrical conductivity values displayed in the legend.

#### Comparison of the TE power factor for s-SWCNTs enriched by two cleavable polymers



Figure S8. Comparison of TE performance for AD (top panel) and LV (bottom panel) SWCNTs for the two cleavable polymers, SMP and PFPD.

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