Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Double Doping Approach for Unusually Stable and Large N-type Thermoelectric Voltage from P-type Multi-walled Carbon Nanotube Mats

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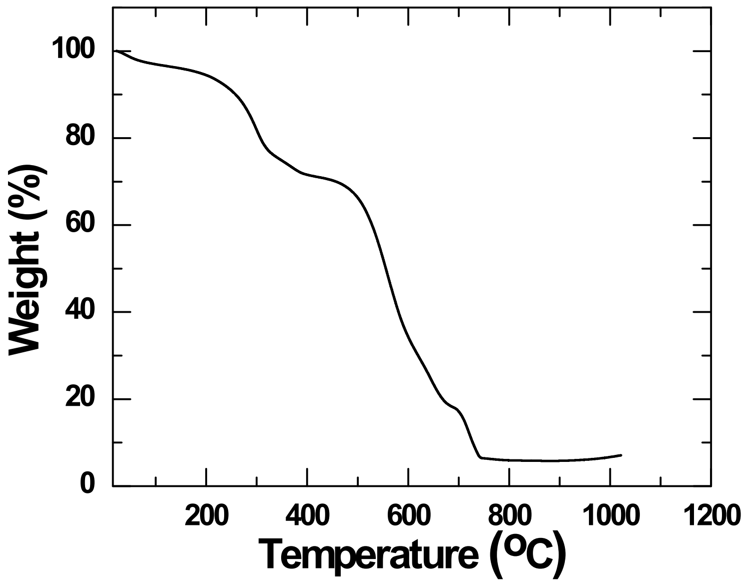

Fig. S1 TGA of pristine MWCNTs in the temperature range of 25-1025 ^oC.

As shown in Fig. S1, the weight loss of an MWCNT sample below 380 K is about 5%, which should be attributed to the evaporation of water. MWCNT mats have a porous structure as shown in Fig. 2b. They can absorb some water due to their large surface area. The absorbed water will evaporate when increasing the temperature approaching 380 K (Fig. S1)

Additional experiments have been performed to evaluate the effect of water absorption under 380 K (Table S1). A pristine MWCNT sample was tested to have an electrical conductivity (σ) of 286 S/cm and a Seebeck coefficient (S) value of 57 μV/K. Then, the sample was heated to 380 K for 20 min for three times. The annealed sample showed an average electrical conductivity of 294 S/cm and an average Seebeck coefficient of 55 μV/K. The errors between the sample before and after annealed are 2.7% (σ) and 3.5% (S), which are close to the error range of the SBA 458 testing system (5% for σ and for 7% for S).

Therefore, the weightlessness of water will not affect the electrical conductivity and Seebeck coefficient.

Table S1, Electrical conductivity and Seebeck coefficient of a pristine MWCNT sample before and after annealing at 380 K for 20 min.

Samples	**Electrical Conductivity (S/cm)**	**Seebeck coefficient (μV/K)**
Before annealed	286	57
After annealed 1	301	53
After annealed 2	283	56
After annealed 3	298	55

Table S2 Comparison of the properties of CNT-based flexible thermoelectric materials.

Material	Electrical conductivity (S/cm)	Seebeck coefficient (μV/K)	Power factor $\mu Wm^{-1}K^{-2}$	Publication year
a-CNT web/BV	2228	−116	3103	2017[1]
SWCNT/PEI	3630	−64	1500	2017[2]
TDAE–PEDOT/CNT	7.3	−1200	1050	2015[3]
CNT/KOH/18-crown-6-ether	2050	−33	230	2016[4]
DWCNT–PEI/graphene–PVP	300	−80	190	2016[5]
SWCNT/CTAB	840	−47	185.7	2018[6]
SWCNT/TPM-CB	497	−59	172	2017[7]
SWCNT/NDINE	400	−57	135	2017[8]
This work	357	-56	112	2019
SWCNT/PDINE	500	−47.5	112	2017[8]
$CoCp_2$ @SWCNT	432	−41.8	75.4	2005[9]
CNTs/PEI/DETA-$NaBH_4$	52	−86	38	2014[10]
MWCNT PEDOT:PSS	689	23.2	37.08	2015[11]
CNTs/PEI–$NaBH_4$	60	−77	35.6	2012[12]
SWCNT/DETA–CaH_2	165	−41	27.7	2016[13]
SWCNT/dppp	100	−52	27	2013[14]
MWCNT PEDOT:PSS	81	56.1	25.9	2015[3]
SWCNT/tpp	48	−72	25	2013[14]
CPE–$PyrBIm_4$ /SWCNT	106	−41	17.8	2015[15]
CNTs/PEI/DETA	39	−63	15.5	2014[10]
CNTs/PEI	30	–57	9.7	2012[16]
MWCNT P3HT	-	-	6	2013[17]
MWCNT polypyrrole	39.4	24.4	2.2	2016[18]
MWCNT polypyrrole	33	25	2.079	2014[19]
MWCNT polyvinylpyrrolidone	77	-16	1.98	2017[20]
MWCNT nafion	13	24	0.8	2011[21]
MWCNT PANI	20	15	0.5	2016[22]
As growth MWCNT	110	-5	0.275	2019[23]
MWCNT PEDOT	15.9	12	0.229	2017[20]
MWCNT polypyrrole	17	15	0.22	2015[11]
MWCNT PVAc	1.28	28	0.1	2012[24]
MWCNT Yarn +PVP	1	-14	0.02	2018[25]
MWCNT PVDF	0.199	10	0.002	2018[26]

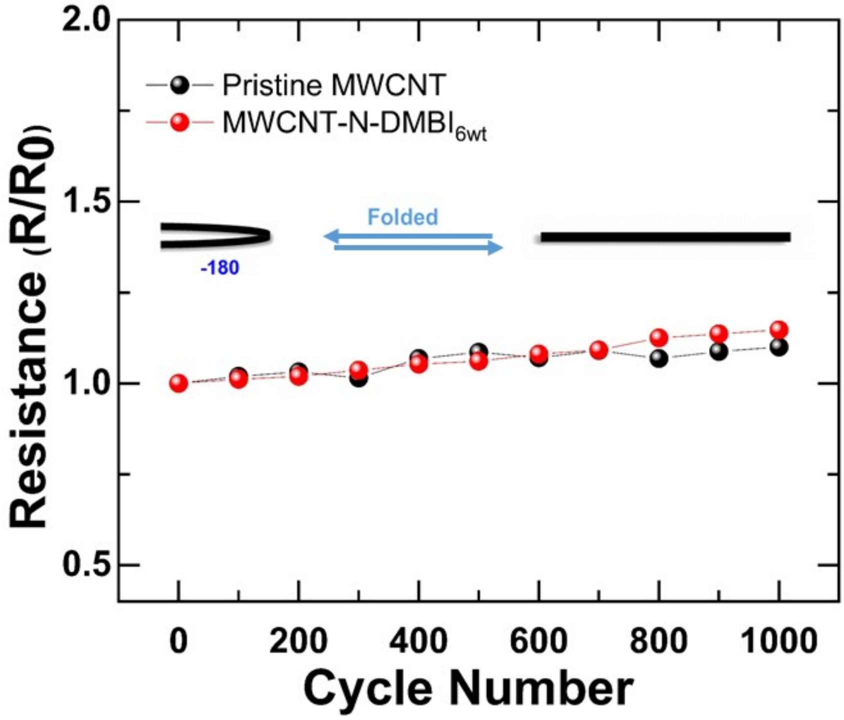

Fig. S2 Change in internal resistance (R) as a function of the number of bending cycles of a strip of pristine MWCNT mats and MWCNT-N-$DMBI_{6wt}$.

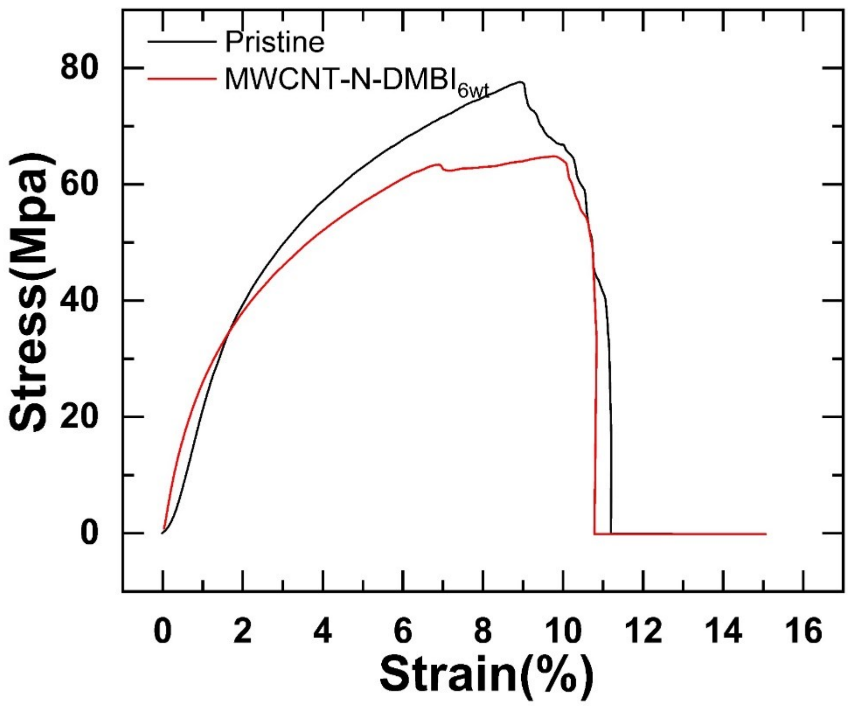

Fig. S3 Stress-strain performance of the pristine MWCNT mats and MWCNT-N-$DMBI_{6wt}$ mats.

Table S3 Hall measurement results of pristine MWCNT mats and MWCNT-N-DMBI mats.

Samples	n(cm^{-3})	μ(cm^2/V-s)
Pristine	3.75 x 10^{21}	0.34
2 Wt.%. N-DMBI	3.71 x 10^{21}	0.38
4 Wt.%. N-DMBI	3.70 x 10^{21}	0.38
6 Wt.%. N-DMBI	3.61 x 10^{21}	0.48
8 Wt.%. N-DMBI	3.70 x 10^{21}	0.41

Hall effect measurement was performed for both pristine MWCNT mats and MWCNT-N-DMBI mats (Table S2). The carrier concentration (n) of all the MWCNT mats is similar, which is around 3.7 x 10^{21} cm^{-3}. The carrier mobility (μ) of the pristine MWCNT mat is of 0.34 cm^2/V-s, which is smaller than those of MWCNT-N-DMBI mats. The peak carrier mobility of 0.48 cm^2/V-s was observed from the MWCNT-N-$DMBI_{6wt}$ mat, which is higher than 0.4 cm^2/V-s from the MWCNT-N-$DMBI_{8wt}$ mat. The results indicate that the electrical conductivity variation in Fig. 4d depends on the variation of carrier mobility.

Table S4 The output power of several typical organic TE devices is compared with the output power of this work.

Material	Number of p-n pair	Output power (μW)	ΔT(K)	Publication year
PEDOT:PSS	6	1.28	60	2019[27]
CNT yarn	240	4.2	5	2017[28]
SWCNT foam	8	1.5	13.9	2019[29]
SWCNT	9	1.8	50	2014[10]
CNT composite	5	0.0085	10	2016[5]
CNT web	7	1.7	20	2016[30]
MWCNT	5	1.48	60	2019 This work

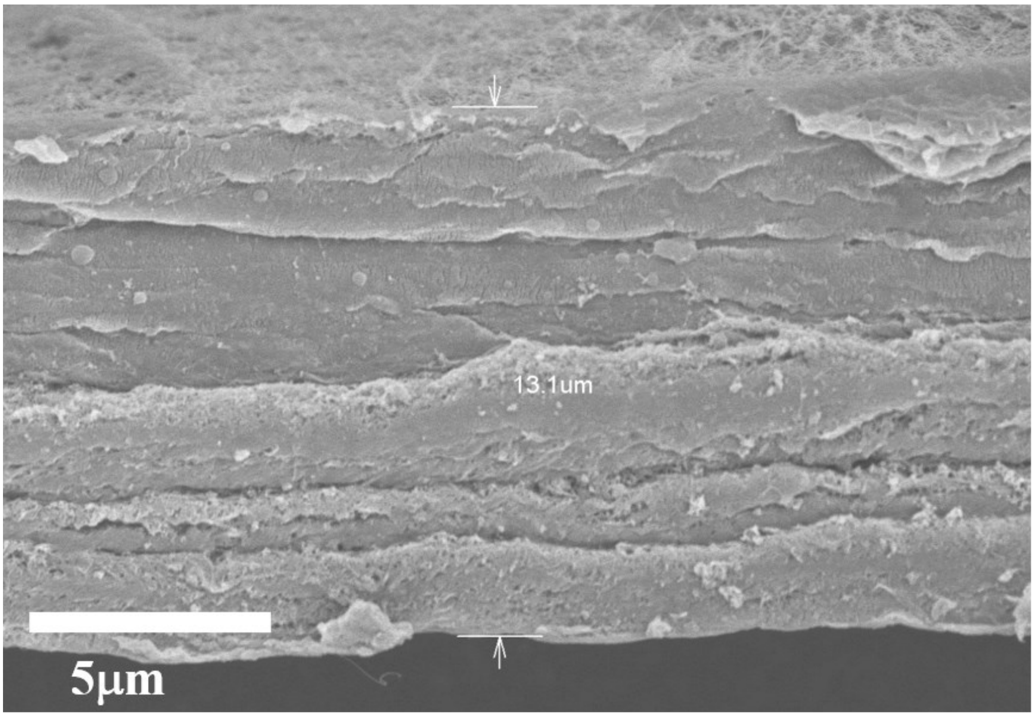

Fig. S4 SEM image of the cross-section of the pristine MWCNT mats.

Table S5. Thermal conductivity of carbon nanomaterials and other organic nanocomposites.

Sample	k (W/m-K)	Ref.
Individual CNT	35 ~ 6600	Ref[31]
Graphene	~ 5000	Ref[32]
PANi-MWCNT	0.4 ~ 0.5	Ref[33]
MWCNT:TCPP/PVAc	0.1 ~ 0.3	Ref[34]
Un-aligned SWCNT networks	~20	Ref[35]
MWCNT/epoxy	~ 1	Ref[36]
MWCNT array	0.15	Ref[37]

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