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High-performance n-type thermoelectric composites of acridones with tethered tertiary amines and carbon nanotubes

Chunmei Gao,^a Yijia Liu,^b Yuan Gao,^{a, *} Yan Zhou,^a Xiaoyan Zhou,^b Xiaojun Yin,^b Chengjun Pan,^b Chuluo Yang,^b Hanfu Wang,^d Guangming Chen,^{b,c*} and Lei Wang^{b,*}

Very recently, amino-substituted perylene diimides (PDINE) and naphthalene diimides (NDINE) have been reported as good n-type thermoelectric (TE) materials, rational design of their derivatives is strongly desired to further enhance their TE performance. In this study, based on the molecular structure of PDINE and NDINE, a series of acridones with different terminal tertiary amine groups (ADTA) at the C2 and/or C7 positions of the acridone ring was designed and synthesised as potential n-type TE materials. Then, single-walled carbon nanotubes (SWCNT) were combined with the acridones to form flexible SWCNT/ADTA composite films. The composites exhibited excellent n-type TE performance. Furthermore, the terminal tertiary amine and the number of side chains greatly affected the TE properties of the composites. The composite containing an acridone with two terminal diethyl amine groups displayed the highest power factor of 289.4 \pm 2.8 μ W m⁻¹ K⁻² at 430 K, which is perhaps one of the highest values for a composite containing n-type TE behaviour with a high power factor of 211.6 \pm 9.9 μ W m⁻¹ K⁻² at room temperature. Our results demonstrate that SWCNT/acridone composites with appropriate substituents show promise as TE materials, which opens a new avenue for TE material design.

Introduction

Thermoelectric (TE) devices can achieve direct energy conversion between heat and electricity, which are quiet because they do not contain mechanically moving parts or bulk fluids.1-3 TE devices are attractive to harvest waste heat generated from industrial processes or daily life, which can not only improve fuel utilization, but also lower exhaust emissions and protect the environment. Therefore, TE devices have important application prospects in sustainable energy development. The performance of TE devices depends on the figure of merit (ZT) of their TE materials, $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. Recently, organic TE materials have been widely developed because of their low κ , non-toxicity, easy processability, and abundant resources.^{1, 4} Because the κ values of organic TE materials are generally below 1 W m⁻¹ K⁻¹, their performance is evaluated by /-- -- · . .

An integrated TE device consists of both p- and n-type materials. The major carries of p-type materials are holes, while those of n-types are electrons. In the past decades, p-type organic TE materials have been developed extensively and their performance has reached and even surpassed that of p-type inorganic TE materials.⁵⁻⁷

However, the development of n-type organic TE materials is still lagging behind because of the issue of electron trapping.^{1-4, 8-11} Because the electrical conductivity of organic materials is very low, their TE performance is often improved by chemical doping or hybridization with inorganic materials. Recently, the performance of n-type TE materials has been greatly improved using organic polymer semiconductors.5, 12-18 Compared with polymers, organic small molecules (OSMs; here, OSMs refer to materials with molecular weight of around or below 1000) possess the merits of exact structure and easy synthesis and derivatisation, which aids exploration of their structure-activity relationship. These features make OSMs more attractive than polymers as TE materials. However, only small families of OSMs have been developed as n-type TEMs, including fullerenes, perylene diimides (PDIs). and diketopyrrolopyrrole-based quinoidal molecules. Fullerene and its derivatives can be doped with alkaline metals, metal complexes and salts,19 or (4-(1,3-dimethyl-2,3-di-hydro-1Hbenzoimidazol-2-yl) phenyl)dimethylamine (N-DMBI) and its derivatives²⁰⁻²³ to provide n-type TE materials. For example, PTEG-1/ TEG-DMBI systems displayed a PF of 19.1 µW m⁻¹ K^{-2,21} Kemerink's group reported that [6,6]-phenyl-C61-butyric

^{a.}College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China. *E-mail: szgaoy311@163.com

^{b.} Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China. *E-mail: chengm@szu.edu.cn, wl@szu.edu.cn.

^{c.} Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^d CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology of China, Beijing 100190, China.

⁺ Electronic Supplementary Information (ESI) available: Measurements of in-plane thermal conductivities, Synthesis schematic, Carrier concentration and mobility, TE performance, Temperature dependence of electrical conductivity, and SEM images. See DOI: 10.1039/x0xx00000x

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acid methyl ester doped with the N-DMBI achieved a high PF of 35 μ W m⁻¹ K⁻².²³ Segalman et al. found that PDIs had large negative *S* values, and a highest PF of 1.4 μ W m⁻¹ K⁻² was achieved.^{24, 25} Recently, Zhu and co-workers reported that the diketopyrrolopyrrole-based quinoidal molecule TDPPQ and its derivatives are good n-type TE materials.^{26, 27} In addition, they found that chemically doped DPPTT derivatives are promising n-type TE materials.²⁷ In particular, A-DCV-DPPTT had the highest PF of 236 μ W m⁻¹ K⁻² at 373 K and a *ZT* value of 0.23, which is the highest value reported to date for a TE material based on an OSM.

Although OSMs have made a great progress in TE materials, there are also obvious and potential limitations. Compared to conjugated polymers, the films of OSMs generally cannot be formed by drop-casting because of their good crystallization property. They might also have lower mechanical property and electrical conductivity at the same conditions due to their smaller molecular weights and lower conjugated degrees compared with those of the polymers. The composition of OSMs with single-walled carbon nanotubes (SWCNTs) is one of the effective ways to solve these problems.

SWCNTs are highly electrically conductive, flexible, nontoxic, and lightweight, making them attractive in TE materials.²⁸⁻³¹ SWCNTs have been combined with polymers by different methods to obtain n-type composites with moderate to excellent performance;^{5,12,32} however, few n-type OSM/SWCNT composite TE materials have been reported. SWCNTs with n-type conductivity have been obtained by doping with reduced viologen³³⁻³⁴, malachite green,^{35,36} tetraalkylammonium cations or cationic crown ether complexes,37 small peptides containing electron-donor substituents,³⁸ PEI (molecular weight 600)²⁸ and phosphinecontaining aromatic molecules.³⁹ Recently, PDINE/SWCNT and NDINE/SWCNT composites (1:1 mass ratio; PDINE and NDINE are amino-substituted perylene diimide and naphthalene diimide, respectively) with maximum PF of 112 and 135 μ W m⁻¹ K⁻² were reported.⁴⁰

Our group has been focusing on the development of organic and organic/inorganic composites for use as TE



Figure 1. a) The scaffolds of NDINE, PDINE and ADTA (from left to right), and their calculated energy levels and orbital distribution, respectively; b) Chemical structures of the ADTA(a-g), and ADTAb1.

materials, some of which have displayed good performance; for example, the maximum PF of $DOUPO_PRE/CU/SWCNT$ composite was 200.2 μ W m⁻¹ K⁻².⁴⁰⁻⁴⁸ Herein, based on our previous results and the structures of PDINE and NDINE, we design a series of acridones with different tertiary amine groups at the C2 and C7 positions on the acridone ring (denoted as ADTAa–g) as potential n-type TE materials (Figure 1a and 1b). Although acridone derivatives have been used in many fields, they have seldom been investigated as TE materials ^{49,50} Our design is based on the following three

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1a and 1b). Although acridone derivatives have been used in many fields, they have seldom been investigated as TE materials.49,50 Our design is based on the following three factors. First, the acridone scaffold not only can form π - π interactions with SWCNTs, like perylene and naphthalene, but also has a higher highest occupied molecular orbital (HOMO) energy than those of perylene and naphthalene (Figure 1c), which favours electron transfer from the scaffold to SWCNTs.³⁸ Second, the weakly electron-donating 3,5-dimethyoxybenzyl group is introduced to adjust the electronic properties and strengthen the π - π interactions. Third, the side chains of PDINE and NDINE are retained to provide electron charge carriers. We also synthesize ADTAb1 (Figure 1b) to determine the effect of the number of terminal amine groups on the TE properties of the materials. Composites of ADTA(a-g) and b1 with SWCNTs are then formed to improve electron conductivity. The TE properties of the composite films are evaluated and their structure-activity relationships are also studied. Our results demonstrate that the TE performance of the composite thin films can be dramatically enhanced through rational modification of the side chains to achieve a highest PF of 289.4 μW m⁻¹ K⁻² at 430 K.

Experimental Section

2.1. Chemicals and Materials. All chemical reagents were purchased from Energy Chemical, and used without further purification. The SWCNTs (diameter: 1–2 nm, purity: >95.0%) were provided by Nanjing XFNANO Materials Tech Co., Ltd, China.

2.2. Preparation of ADTAa-g and ADTAb1. ADTAb1 was synthesized according to the method reported in the literature.⁵¹ ADTA(a-g) were prepared using the references' methods with a little modification,^{52,53} which was shown in Scheme 1s. Acridone (2.34 g, 12 mM) was stirred vigorously in 12 ml 36% acetic acid and then glacial acetic acid (6 ml) and nitric acid (65%, 3 mL) were added. The reaction was stirred for 4 h at about 50-60 $^{\circ}$ C, which was cooled and slowly poured into ice-water. Yellow precipitates were formed, which were then filtered and dried. The precipitates were dissolved in sulphuric acid (24 ml) by stirring. A solution of nitric acid fuming (640 µl) in sulphuric acid (8 ml) was added drop-wisely with rapid stirring under ice-water bath. Stirring was maintained for a further 0.5 hours, and then poured on to crushed ice. The yellow precipitates 2 (impurity) were collected, washed with water and then they were refluxed in 8% Na₂CO₃ to remove the trinitroacridones. The solids were obtained, washed with water and dried, which were then suspended in dry DMF (60 mL), and NaH (576 mg, 14.4 mmol).

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The mixture was stirred vigorously under Ar for 1 h at room temperature. The 3, 5-dimethoxyl benzyl bromide (4.16 g, 18 mmol) and KI (400 mg, 2.4 mmol) were added. The mixture was stirred overnight at room temperature. 80 ml water and 20 mL ethanol were added with rapid stirring at room temperature. Yellow solids (impurity) were obtained after filtration, which were then washed with water for 3 times. The solids 3 were then stirred in 10 mL CH₂Cl₂, filtered and washed with CH_2Cl_2 for 3 times, which were then added to 15 $\ensuremath{\,\text{mL}}$ ethanol containing sodium sulfide nonahydrate aqueous solution (30%, 30 mL). The mixture was heated at reflux under nitrogen for 12 h. After cooling to room temperature, water was added with rapid stirring. The resulting yellow solids were filtered off, washed with water and ethanol. The yellow solids 4 were obtained, which was then reacted with the corresponding secondary amines to achieve the desired ADTA(a-g).

2.3. Preparation of SWCNT/ADTA Composite Films. The SWCNT/ADTA composites were prepared based on a previously published procedure.⁴⁰ All the films were prepared in air. 7.5 mg of SWCNT was added into 15 mL of DMSO solution containing a desire amount of ADTA. The mixture was ultrasonically treated until it was well-distributed. After that, the mixture was vacuum filtered by nylon membrane (pore diameter: 0.45 μ m) to achieve the composite film. Finally, the obtained film was dried under vacuum at 60 °C for 4 h. The composite films were about 5 μ m thickness.

2.4. Structural and Morphological Characterization. The morphology of the composite films was examined by scanning electron microscopy (SEM; SU-70). Raman spectra were recorded within the wavenumber range of 100–3200 cm⁻¹ using a Raman spectrometer (Renishaw invia Raman Microscope) with an excitation wavelength of 514.5 nm. Thermogravimetric analyses (TGA) of the composites were performed under nitrogen atmosphere by a synchronous thermal analyser (Q50) at a heating rate of 10 K min⁻¹.

2.5. Thermoelectric Performance Measurements. The σ and S values of the films were measured using a thermoelectric parameter test system (MRS-3, JiaYiTong Company) from 300 to 460 K in a vacuum environment. The S value of Ni at room temperature was measured as a reference sample; the measured value of $-16 \pm 0.3 \ \mu V \ K^{-1}$ was in good agreement with the literature value of $-15 \ \mu V \ K^{-1}.^{45}$

2.6. Hall effect measurements. Hall effect measurements were conducted in a Quantum Design, physical properties measurement system (PPMS) with good ohm contact established using Au electrodes.

2.7. In-plane thermal conductivity measurements. The in-plane thermal conductivities of the composite films were measured by the parallel thermal conductance method. The detailed information is described in ESI[†].

2.8. X-ray photoelectron spectra measurements. The electron binding energy were performed on an X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher).



Figure 2. TGA curves of SWCNT/ADTA(a-g, b1) composites and pure SWCNTs.

Results and Discussion

3.1 Thermal stability characterization

Composite films of SWCNT/ADTA(a–g, b1) with a 1:1 mass ratio were firstly fabricated because this ratio displayed the best performance in our previous work.⁴⁰ The thermal properties of the composite films were evaluated by TGA. Figure 2 reveals that all the films were stable below 240 °C, which indicated that the SWCNT/ADTA(a–g, b1) composites had excellent thermal stability.

3.2 TE properties

The S values of the films were determined to see whether the structure of the terminal amines affected their TE performance. S of the SWCNTs was 41.5 μ V K⁻¹ at room temperature (298 K), which was consistent with the literature.^{39, 40} The positive S of the SWCNTs indicates they are a p-type TE material. The S values of the SWCNT/ADTA(a-g) composite films were measured, and the data are listed in Table 1. To our surprise, the S values of the composite films varied considerably. S of SWCNT/ADTAf and SWCNT/ADTAg were even more positive than that of the SWCNTs at 298 K, indicating that invalid n-doping of ADTAf and ADTAg occurred within the SWCNT matrix. In contrast, SWCNT/ADTA(b-e) showed negative S values at 298 K, revealing that the majority carriers of the SWCNTs were successfully switched from p- to n-type via effective n-doping. The SWCNT/ADTAa film displayed a positive S value that was lower than that of the pristine SWCNTs, indicating that the holes were partly annihilated by electron transfer from ADTAa to the SWCNTs.

Although we lack a complete theory to explain the observed behaviour, we can rationalise the results by considering the structures of the materials. The structure of ADTA contains a diphenylamine group in the acridone ring and the side chain has a terminal amino moiety. Aromatic amines and alkyl amines are well-known hole transport moieties with electron-donating ability, which leads to their n-type doping

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characteristics.^{17,24,54} Compounds with strong electron- donating ability are preferred to induce n-type doping at the online

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films	S [μV Κ-1]		σ [S cm ⁻¹]		PF [μW m ⁻¹ K ⁻²]	
	298 K	Max.	298 K	Max.	298 K	Max.
SWCNT/ADTAa	12.1 ± 1.2	-63.1 ± 1.0	424.2 ± 22.4	441.5 ± 10.3	6.2 ± 2.1	175.7 ± 3.3
SWCNT/ ADTAb	-44.5 ± 5.0	-64.6 ± 1.1	642.4 ± 39.2	715.0 ± 7.2	124.4 ± 10.5	289.4 ± 2.8
SWCNT/ ADTAc	-7.5 ± 3.2	-55.4 ± 0.9	286.0 ± 25.1	343.1 ± 5.1	1.6 ± 1.1	101.9 ± 1.6
SWCNT/ ADTAd	-27.5 ± 2.4	-59.2 ± 2.1	528.0 ± 44.5	1193.3 ± 13.7	39.8 ± 9.8	265.7 ± 7.3
SWCNT/ ADTAe	-46.8 ± 4.6	-60.5 ±0.2	454.0 ± 23.4	580.9 ± 6.4	96.1 ± 9.6	184.7 ± 13.4
SWCNT/ ADTAf	55.1 ± 5.2	-56.9 ± 0.8	478.4 ± 29.2	478.4 ± 29.2	150.5 ± 10.3	89.9 ^a ± 1.2
SWCNT/ ADTAg	47.8 ± 3.9	-53.6 ± 2.4	924.1 ± 45.3	924.1 ± 45.3	211.6 ± 9.9	192.4ª ± 1.3
SWCNT	41.5 ± 2.5	١	601.4 ± 32.2	١	103.4 ± 5.6	\

^a Maximum PF of the composite films with n-type feature.

Table 2. pKa values, HOMO energies and orbital distributions of the terminal amine groups of ADTA(a-g).



electron-donating abilities of amines are related to their pKa values. As pKa rises, the Lewis basicity increases, which enhances the electron-donating ability of a compound. The pKa values of various terminal amines reported in a chemical handbook⁵⁵ are summarized in Table 2. Considering both Table 1 and 2, if the pKa value of the ADTA in the composite is larger than 11, it can convert the majority carriers of SWCNTs from holes to electrons; otherwise, the composites still displayed p-type characteristics, except for ADTAc. Although *S* of SWCNT/ADTAa was positive, it was only 12.1 ± 1.2 μ V K⁻¹, indicating that some of the SWCNTs had been n-doped.

The pKa value of 4-hydroxypiperidine was predicted using ACD/Labs software, a powerful commercial software to predict pKa,⁵⁶ because it was not listed in the chemical handbook. Table 2 shows that the predicted pKa values were similar to those from the chemical handbook except for ADTAc. The predicted pKa of the terminal amine of ADTAg was between those of ADTAa and ADTAf; therefore, *S* of SWCNT/ADTAg was positive. The results suggested that the pKa values of the tertiary amines of the ADTAs influenced the *S* values of the composites. In addition, density functional theory calculations were also performed to see whether the different *S* values

were caused by the different frontier molecular orbital (FMO) distributions and energy levels of ADTA(a–g). The calculation results, which are also shown in Table 2, revealed ADTA(a–g) displayed similar FMO distributions and HOMO energies.

The electrical conductivity of the composite films was then evaluated. Of the composites, SWCNT/ADTAg displayed the highest electrical conductivity at room temperature. SWCNT/ADTAg displayed a high PF of 211.6 \pm 9.9 μ W m⁻¹ K⁻² at 298 K, which is one of the highest values reported for a ptype SWCNT/OSM composite to date. Although the S of SWCNT/ADTAf was larger than that of SWCNT/ADTAg, its electrical conductivity was only about half that of SWCNT/ADTAg, which led to a lower PF of 150.5 \pm 10.3 μW m⁻¹ K⁻². Among the composite films, SWCNT/ADTAc displayed the lowest S and σ values, rendering the lowest PF of 1.6 ± 1.1 μ W m⁻¹ K⁻² at room temperature. The carrier concentration and carrier mobility of the SWCNT/ADTA(b-e) composite films with n-type properties at room temperature were obtained by Hall effect measurement (Table S1). The equation σ = neµ (where *n*, *e* and μ are the carrier concentration, the electron charge and the carrier mobility) indicated that the electrical conductivity is proportional to n and μ . Notably, the favourable

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n and μ of the SWCNT/ADTAb contributed to the large σ . These data illustrate that the structure of the tertiary amine strongly affected the TE performance of the composites.

The temperature dependence of S of the SWCNT/ADTA composites was evaluated because thermal activation promotes electron transfer from the dopants to the host,^{20, 57} which might affect the S values of the SWCNT/ADTA composites. Since the SWCNTs are p-doped with oxygen, thermal activation can promote the electron injection from ADTA to SWCNTs, which could compensate the holes in SWCNTs and thus decrease the S values of p-type composites (SWCNT/ADTAa, f and g). When the temperature further increased, more electron transfer could induce n-type charge carriers in SWNTs and then increase S. As shown in Figure 3a, S of SWCNT/ADTAa, f and g with positive S values at 298 K decreased and then became negative with increasing temperature, indicating that the ADTAs can convert the SWCNTs from p- to n-type at elevated temperature. S of SWCNT/ADTA(b-e) with negative S values at 298 K became more negative as the temperature increased. SWCNT/ADTAb, SWCNT/ADTAd and SWCNT/ADTAe with relatively large negative S values at room temperature exhibited small changes of S, whereas SWCNT/ADTAf and SWCNT/ADTAg with large positive S values at room temperature showed large S changes. All the composite films displayed similar maximum S values (-59 \pm 5 μ W m⁻¹ K⁻²), among which SWCNT/ADTAb had the largest S value (-64.6 \pm 1.1 μ W m⁻¹ K⁻²). As temperature increased, most of the composite films displayed low conductivity at first, which then increased and finally decreased (Figure 3b). The conductivity of SWCNT/ADTAd and SWCNT/ADTAe increased with rising temperature. The maximum conductivities of the composite films are summarized in Table 1.

The PFs of the composites were calculated using the determined values of S and σ . Figure 3c and Table 1 indicate that SWCNT/ADTAb had the highest PF of up to 289.4 \pm 2.8 μ W m^{-1} K⁻² at 430 K, which is one of the highest values obtained to date for an n-type composite of an OSM and SWCNTs. The performance of SWCNT/ADTAd was slightly lower than that of SWCNT/ADTAb, with a maximum PF of 265.7 \pm 7.3 $\mu W~m^{-1}~K^{-2}$ at 395 K. SWCNT/ADTAg, which was a good p-type TE material at 298 K (211.6 \pm 9.9 μ W m⁻¹ K⁻²), displayed good n-type performance at 444 K (192.4 \pm 1.3 μ W m⁻¹ K⁻²). Since SWCNT/ADTAb and SWCNT/ADTAd displayed the best n-type performance, the κ values of them were evaluated. As shown in Table S2, the two composites almost displayed similar κ values to that of the SWCNTs, which indicated that the structure of ADTAs had a little effect on the κ values of SWCNTs. All the results indicated that SWCNT/ADTA composites are promising as TE materials.

Because SWCNT/ADTAb displayed the highest whether of the composites, SWCNT/ADTAb1 was prepared to see whether the number of side chains on the acridone ring affected on the TE performance of the composites. As shown in Figure 3d, SWCNT/ADTAb1 under the same conditions, which indicated that acridones with two terminal amine substituents had a greater influence on the TE performance than the corresponding acridone derivatives with one terminal amine substituent. These results suggest that more electron-donating groups introduced on the side chains might further improve the TE properties of the SWCNT/ADTA composites.

In addition, TE performance of SWCNT/ADTAb films with different mass ratios was also evaluated. Figure 3e indicated that *S* increased with the mass ratio increased, and SWCNT/ADTAb with 2:1 and 3:1 ratio displayed the similar S values at room temperature. With temperature increased, the *S* of Figure 3e displayed a similar trend to those of Figure 3a. At 430 K, SWCNT/ADTAb with a 1:1 mass ratio had the highest *S* value. With *S* and σ (Figure S2) of SWCNT/ADTAb films with different mass ratios, PF were calculated (Figure 3f), and SWCNT/ADTAb with 1:1 mass ratio displayed the highest PF at 430 K (Table 3).

3.3 SEM analysis

The morphology of the SWCNT/ADTA composite films was observed by SEM. As shown in Figure 4, compared with the morphology of SWCNTs, ADTA crystals were observed in the films of the SWCNT/ADTA composites. The ADTA crystals did not change the morphology of the SWCNT bundles (Figure S3). These results indicate that ADTA(a–g) were well dispersed in the SWCNT networks and formed strong π – π interactions with the SWCNTs.

3.4 Photophysical properties

Raman spectroscopy has been widely used to study the interaction between SWCNTs and organic compounds. Raman spectra of the SWCNT/ADTA(a–g) composites were measured (Figure 5). The characteristic Raman bands of the SWCNT-doped composite films involve the G band related to carbon atom vibrations along the nanotube plane, and D band indicating structural defects in continuous graphitic sheets of the nanotubes.⁵⁸ The Raman spectra of SWCNT/ADTA(a–e) contained a blue-shifted G-band near 1591.8 cm⁻¹ compared with that of the SWCNTs. The blue shift indicates that electron transfer occurred from ADTA(a–e) to the SWCNTs, which is consistent with n-type doping of the SWCNTs.^{12,31} (Although S of SWCNT/ADTAa was positive, it was lower than that of the SWCNTs, suggesting that some of the SWCNTs had been n-doped.) In contrast, ADTAf and g induced a red shift of the

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Figure 3. Temperature (*T*) dependence of the Seebeck coefficient *S* and conductivity σ of SWCNT/ADTA(a–g) composites. a) *S versus T*, b) σ versus *T* and c) PF versus *T*. d) TE performance of SWCNT/ADTAb and SWCNT/ADTAb1. e) *S versus T* and f) PF versus *T* for SWCNT/ADTAb films with different mass ratios.

Table 3. A comparison of thermoelectric performance of composites of OSMs with SWC	NTs.
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Sample	S [μV Κ ⁻¹]	σ [S cm ⁻¹]	PF _{max} [μW m ⁻¹ K ⁻²]	Ref.
SWCNT/ ADTAb	-64.6 ± 1.1	715.0 ± 7.2	289.4 ± 2.8	this work
SWCNT/dppp	∽-52	~100	∽27.0	39
SWCNT/TPM-CB(PH 12)	-59	497	172	35
SWCNT/PEI	-32.5 ± 1.6	12.70	1.47	28
SWCNT/MGH(solvent: CHP)	-43	1097	200	36
SWCNT/KOH/18-Crown-6	-33	2050	230	37
SWCNT / NDINE	_	400 ± 17	135 ± 14	40

G-band of SWCNTs, suggesting p-type doping.³⁸ These results were consistent with the *S* values and SEM images of the composites. The D/G ratios of the SWCNT/ADTA composites were comparable to that of SWCNTs, suggesting that the ADTAs did not induce structural defects in the SWCNTs.

X-ray photoelectron spectroscopy (XPS) of the composite with the best n-type performance (SWCNT/ADTAb) was conducted, along with that of SWCNTs and ADTAb for reference. As shown in Figure 6, no N1s peak was detected for the SWCNT film, whereas it was present in the spectrum of the SWCNT/ADTAb composite film, indicating that ADTAb formed a composite with the SWCNTs. The N 1s peak of SWCNT/ADTAb was centred at 399.7 eV, which was at higher binding energy than that of ADTAb (399.3 eV). The N 1s electrons in the SWCNT/ADTAb film had a higher binding energy than those in ADTAb owing to the oxidative quaternary ammonium, indicating the electron transfer had been occurred from the amine of ADTAb to SWCNTs. Journal of Materials Chemistry A

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Figure 4. SEM images of the surfaces of a) SWCNT/ADTAa, b) SWCNT/ADTAb, c) SWCNT/ADTAc, d) SWCNT/ADTAd, e) SWCNT/ADTAe, f) SWCNT/ADTAf, g) SWCNT/ADTAg and h) pure SWCNT films.



Figure 5. Raman spectra of SWCNT/ADTA composites. From the top to the bottom, the Raman spectra are of SWCNT/ADTAa, SWCNT/ADTAb, SWCNT/ADTAc, SWCNT/ADTAd, SWCNT/ADTAe, SWCNT/ADTAf, SWCNT/ADTAg and pure SWCNTs.

Conclusion

In conclusion, a series of composite films of SWCNT/ADTA(a-g) were investigated as TE materials, all of which displayed n-type properties at the appropriate temperatures. The number and pKa of the terminal amine groups of the ADTA greatly affected the σ and S values of the composite films. Among thesecomposites, SWCNT/ADTAb with a 1:1 mass ratio displayed the best TE properties with the highest PF of 289.4 \pm 2.8 μ W m⁻¹ K⁻² at 430 K, which is one of the highest values



Figure 6. XPS analysis of ADTAb, SWCNT/ADTAb and SWCNTs.

reported for an n-type SWCNT/OSM hybrid to date. Our results indicated that the structure of the OSMs is very important to the TE performance. More OSMs with different scaffolds are needed to be explored and the relationship between the structure and performance should be further studied.

Conflicts of interest

There are no conflicts to declare.

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High-performance n-type thermoelectric composites of acridones with tethered tertiary amines and carbon nanotubes

Chunmei Gao, Yijia Liu, Yuan Gao, Xiaoyan Zhou, Xiaojun Yin, Chengjun Pan, Chuluo Yang, Hanfu Wang, Guangming Chen, and Lei Wang

Acridone derivatives with different terminal tertiary amine groups were firstly developed as good n-type thermoelectric composites, and a high-power factor of 289.4 μ W m⁻¹ K⁻² at 430 K was achieved.

