Ultralight conducting PEDOT:PSS/carbon nanotube aerogels doped with silver for thermoelectric materials

Xijing Sun, Yanhong Wei, Juanjuan Li, Jinghong Zhao, Lijuan Zhao* and Quan Li*

ABSTRACT A significant enhancement in the thermoelectric performance was observed for three-dimensional conducting aerogels, which were obtained from poly(3,4-ethylenedioxythiophene) : poly(4-styrenesulfonic) (PEDOT:PSS) and multiwalled carbon nanotubes (MWCNTs) suspensions by adding different concentrations of metallic silver (Ag). It was found that the electrical conductivity and Seebeck coefficient could be simultaneously increased with the unique structure. Moreover, the conducting aerogels have an ultralow thermal conductivity ($0.06 \text{ W m}^{-1} \text{ K}^{-1}$) and a large Brunauer-Emmett-Teller surface area ($228 \text{ m}^2 \text{ g}^{-1}$). The highest figure of merit (zT) value in this study was 7.56×10^{-3} at room temperature upon the addition of 33.32 wt.% Ag. Although the zT value was too low, our work may provide new insights into the design and development of the thermoelectric material for applications. Further investigation with PEDOT:PSS aerogels will be continued to get an economical, lightweight, and efficient polymer thermoelectric material.

Keywords: PEDOT:PSS, thermoelectric, carbon nanotube, silver, aerogel

INTRODUCTION

Most countries are now seeking new energy conversion materials, and one promising candidate is thermoelectric (TE) materials, which can convert waste heat into electricity [1]. Traditional TE materials are mainly based on inorganic materials such as bismuth-telluride (Bi-Te) and metal oxides [2,3]. However, commercially available inorganic TE materials have limited applications due to their instability, high cost, potential toxicity, and scarcity of some key elements. Meanwhile, most inorganic TE materials show their optimum performance at high temperatures, but a huge amount of waste heat is of low grade, i.e., the temperature below 200°C , and these materials have a low

energy conversion efficiency due to the small temperature difference [4,5]. In order to recover the low-temperature waste heat by the use of TE materials, conducting organic TE materials have become the ideal choice because of their low cost and processing convenience. Furthermore, organic TE materials have many other advantages such as a low energy consumption, stability in air, wide sources, environmental friendliness, and easy synthesis and processing [6,7].

For TE materials, the ability to convert energy between heat and electricity depends on the figure of merit, $zT = S^2\sigma T/\kappa$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. A combination of a high σ and S with a low κ is a key factor to obtain a high zT value. The conducting polymer has a low thermal conductivity, which is about 1–3 orders of magnitude lower than those of inorganic materials [8–11]. Organic TE materials including polyaniline, polyacetylene, polythiophene, and polypyrrole have been intensively evaluated, and the past years have also witnessed their remarkable developments [12–15]. However, it is found that the zT values of organic TE materials are still too low to be satisfactory, which imposes a great challenge for conducting polymers to be used as TE materials. Nevertheless, a breakthrough was achieved by controlling the doping and oxidation level of poly(3,4-ethylenedioxythiophene) (PEDOT). For example, PEDOT composites generate $zT = 0.42$ at room temperature, which is comparable to those of some traditional inorganic materials [6,16–20]. Organic/inorganic hybridization is another promising way to improve the thermoelectric performance of polymers [21–23]. Zhang *et al.* [24] reported that the template-directed *in situ* polymerization preparation of nanocomposites of

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PEDOT:poly(4-styrenesulfonic) (PSS) coated with multiwalled carbon nanotubes (MWCNTs) can enhance the thermoelectric properties. There is a strong interaction between PEDOT:PSS and MWCNTs, which can lead to the formation of interconnected electrical conducting channels to improve the electrical conductivity. Zhang *et al.* found that a post-treatment can remove part of the insulating PSS from the surface of the PEDOT:PSS/reduced graphene oxide (r-GO) composite film, resulting in a significant conductivity enhancement of the composites because the addition of r-GO can trigger a change in the PEDOT main chain from a benzene structure to a quinoid structure, which can achieve the transfer of electric charge [25]. Compared with traditional inorganic TE materials, the electrical conductivity and Seebeck coefficients of PEDOT:PSS composites are not very high, and the zT values are still low (10^{-3} to 10^{-1}) [26–28]. However, the thermal conductivity is in the range of $0.1\text{--}0.4\text{ W m}^{-1}\text{ K}^{-1}$, which is much lower than those of traditional inorganic TE materials [7,29,30]. Therefore, the main challenge for organic polymer TE materials is to obtain a large Seebeck coefficient and electrical conductivity simultaneously while keeping a low thermal conductivity.

Aerogels are ultralight nanoporous materials with large surface areas and a high porosity, which allow them to have potential applications in electronic devices, catalysis, and detectors [31–33]. In this work, we report a new nanocomposite aerogel based on PEDOT:PSS, MWCNTs, and Ag (PCA). The choice of the latter two components is motivated by the fact that MWCNTs are expected to construct a three-dimensional (3D) solid skeleton, and the excellent bulk electrical conductivity of Ag is introduced into PEDOT:PSS system to enhance the electrical conductivity [34]. The results show that PCA aerogels possess a large specific surface area, electrical conductivity, and Seebeck coefficient simultaneously, while the thermal conductivity is nearly one order of magnitude lower compared with that of pure PEDOT:PSS ($0.348 \pm 0.01\text{ W m}^{-1}\text{ K}^{-1}$) [7], and the zT value is greatly enhanced with various Ag contents.

EXPERIMENTAL SECTION

Materials

A PEDOT:PSS aqueous solution (Clevios PH 1000) was purchased from H. C. Stark (Germany). The concentration of PEDOT:PSS is about 1.3 wt.%, and the weight ratio of PSS to PEDOT is 2.5. MWCNTs were offered by SkySpring Nanomaterials, Inc. (Belgium). All experimental chemicals were used without further purification, and

other chemicals were purchased from Chengdu Kelong Company (China).

Preparation of PCA aerogels

Different amounts of Ag with 0.065 g of MWCNTs were mixed in 5 g of the PEDOT:PSS solution by ultrasonication ($20\text{--}30^\circ\text{C}$, 100 W, and 2 h). The resulting PCA suspensions were quenched with liquid nitrogen and then freeze-dried for 24 h to obtain the PCA aerogels. The relative Ag contents would be 8.89, 16.67, 20.87, 25.93, 28.81, 33.32, and 37.28 wt.% in the PCA aerogels. Moreover, a PEDOT:PSS/MWCNTs (PC) aerogel was also prepared for comparison. The preparation process of the PCA aerogels is illustrated in Fig. 1.

Characterization

The microstructures of the PCA and PC aerogels were examined by scanning electron microscopy (SEM, Quanta250). Nitrogen sorption measurements were performed with a TriStar Micromeritics instrument to obtain pore properties such as the Brunauer-Emmett-Teller (BET) specific surface area.

The thermal conductivity (k) was measured by a transient plane source method using a Hot Disk 2500-OT analyzer. A standard four-probe method was used for the electrical conductivity (σ) measurement at room temperature on the RTS-8 equipment (Guangzhou Four-probe Technology Company, China). The current transmitted through the sample during measurement was 10 mA. The Seebeck coefficient (S) was measured by placing the sample between two copper cylinders attached to two Peltier modules, with one for heating and another for cooling. It would generate the temperature gradient (DT) across the sample and induce a thermal voltage. DT was accurately measured by two miniature thermocouples, and the induced voltage gradient (DV) was measured using the voltage probes. Thus, the Seebeck coefficient (S) was determined from the slope of the linear relationship between the thermoelectric motive force and the temperature difference between two points on the aerogels, which was expressed as $S = DV/DT$. The figure of merit at room temperature was calculated by $zT = S^2T\sigma/k$.

RESULTS AND DISCUSSION

The microstructures of the PC and PCA aerogels were examined with SEM. The PC aerogel has a 3D porous network with interconnected particles and continuously open macropores (as shown in Fig. 2a). More interestingly, most MWCNTs are embedded in PEDOT, showing a strong interaction between the MWCNTs and PEDOT, as indicated

Figure 1 Illustration of the process for the preparation of the PCA aerogels.

Figure 2 SEM images of the PC aerogel (a, b) and the PCA aerogels with Ag contents of 20.87 wt.% (c, d) and 37.28 wt.% (e, f).

Figure 3 Energy dispersive X-ray analysis and the mapping images (insets) for the samples with Ag contents of 20.87 wt.% (a) and 37.28 wt.% (b).

in Fig. 2b. Meanwhile, the compacted connection would lead to the carrier mobility and generate the electrical conductivity. As illustrated in Fig. 2c–f, the PCA aerogels also have porous network structures that are similar to that of the PC aerogel, and the network structures become denser with the presence of Ag, which is over 20.87 wt.% in the matrix. The interconnected structures can benefit the improvement in the electrical conductivity and result in a reduction in the thermal conductivity. However, normally defects exist in the large porous structure, which easily lead to a discontinuous phase and decrease the electrical conductivity in PCA aerogels. Moreover, the network structure becomes agglomerated when the Ag contents are overloaded, as demonstrated in Fig. 2e, which may result in an enhancement in the thermal conductivity because the more compacted connection would reduce the phonon scattering and improve the heat conduction. The mapping images of samples with 20.87 and 37.28 wt.% Ag contents are shown in Fig. 3a, b. It is demonstrated that the actual Ag contents in the composites are 21.16 and 37.09 wt.%, respectively, which are consistent with our experiments.

A large specific surface area and a low weight are two typical characteristics of aerogels [35,36]. The evolution of the BET surface area of PCA aerogels with different Ag contents is shown in Fig. 4. After introducing MWCNTs to the PEDOT:PSS solution, the MWCNTs disperse in the solution as a certain molecular precursor, and this precursor builds up a 3D porous structure, where the MWCNTs will be finally immobilized by a cross-linked organic binder of polymer, which forms the junctions between the adjacent MWCNT bundles. As presented in Fig. 4, the pure PC aerogel has a BET surface area of 143 m² g^{−1}. With the incorporation of 25.93 wt.% Ag in the PCA aerogels, the BET surface area increases significantly to 228 m² g^{−1}, suggesting that the hybridized structures composed of Ag flakes are

Figure 4 BET surface area of the PCA aerogels with different weight fractions of Ag.

beneficial to the porous structure. However, further additions of Ag flakes to the PCA aerogels lead to a decreased BET surface area due to the denser porous structure, as shown in the SEM images. In the PCA aerogels with 37.28 wt.% Ag, the BET surface area shows a remarkable decrease from 228 to 169 m² g^{−1}. The reason is that the Ag flakes cannot be effectively dispersed between the organic binder at a higher Ag weight fraction, which prevents the formation of micropores in aerogels and results in a decrease in the BET surface area.

According to $zT = S^2\sigma T/\kappa$, excellent TE materials depend on a high Seebeck coefficient and electrical conductivity. Meanwhile, in order to build up a high temperature difference, it is necessary for TE materials to have a low thermal conductivity.

Fig. 5a shows the electrical conductivity values of PCA aerogels with different weight fractions of Ag at room temperature, and the electrical conductivity of the aerogels effectively improved after adding Ag flakes. Particularly, the

Figure 5 Electrical conductivity (a), Seebeck coefficient (b), thermal conductivity (c) and the zT values (d) of the PCA aerogels with different weight fractions of Ag at room temperature.

electrical conductivity of the PC aerogel is 38.1 S m^{-1} because the PEDOT and MWCNT sheets form an intact 3D network with tight junctions, which is more effective for electron transport than a physically-bonded network [37]. Upon the addition of 25.93 wt.% Ag, the electrical conductivity of the PCA aerogel increases to 377.4 S m^{-1} , which is nearly 10 times higher than that of the PC aerogel. The reason for the improvement is that Ag flakes and MWCNTs create better electrically contacted bridges between nanoparticles. A conductivity of 671.1 S m^{-1} is achieved with 33.32 wt.% Ag loading, indicating that the samples with higher Ag contents exhibit a higher electrical conductivity at room temperature. However, the electrical conductivity exhibits a slight decrease with a further increase in the Ag content because it is difficult to disperse Ag flakes in a PC suspension at a high Ag weight fraction, which has a negative effect on the integrity of the network.

Despite the great increase in the electrical conductivity by adding Ag, the Seebeck coefficients of PCA aerogels as a function of the Ag content range from 30 to $70 \text{ } \mu\text{V K}^{-1}$, as shown in Fig. 5b. These Seebeck coefficient values are higher than those of pure PEDOT:PSS ($\sim 20 \text{ } \mu\text{V K}^{-1}$) and PC

composites ($15\text{--}30 \text{ } \mu\text{V K}^{-1}$) [29,35,38]. The Seebeck coefficient of the PC aerogel is measured to be $31.6 \text{ } \mu\text{V K}^{-1}$, while it is prominent that the Seebeck coefficient increases upon the addition of Ag. A significant enhancement of $61.3 \text{ } \mu\text{V K}^{-1}$ is achieved when the Ag content is 28.81 wt.%, but the further addition of Ag oppositely suppresses the Seebeck coefficient slightly. Therefore, the PCA aerogels are more efficient in converting the temperature gradient into a voltage than the PC aerogels, which maybe originates probably from an energy-filtering effect [39]. It is very difficult to understand the simultaneous increases in the Seebeck coefficient and electrical conductivity in the porous structure. However, it is interesting that the results of our experiments show that the electrical conductivity and Seebeck coefficient increase simultaneously in the porous structure. This is because there are abundant interfaces among the MWCNTs, Ag flakes, and PEDOT:PSS, and the work functions of these three components are different. Low-energy carriers can be strongly scattered by an appropriately engineered potential barrier at the interface, which allows carriers with a higher energy to pass through, thereby increasing the mean carrier energy in the flow, i.e., the Seebeck

coefficient. However, the interface in the PCA aerogel decreases with the further addition of Ag, so the energy-filtering effect is weakened and accompanied by a reduction in the Seebeck coefficient simultaneously. Actually, the energy-filtering effect has already been successfully used to interpret the increased Seebeck coefficient in many other hybrid composites [40,41].

Besides the large electrical conductivity and Seebeck coefficients, a low thermal conductivity is also crucial for TE materials. It is well-known that the thermal conductivity is mainly divided into the electrical thermal conductivity (κ_e) and the lattice thermal conductivity (κ_l): $\kappa = \kappa_e + \kappa_l$ [23]. Reducing κ_l is one of the effective ways to improve the zT value. Although MWCNTs have an ultrahigh thermal conductivity ($3075 \text{ W m}^{-1} \text{ K}^{-1}$) at room temperature due to efficient heat transfer by lattice vibrations [42], the PC aerogel keeps a low thermal conductivity of around $0.05 \text{ W m}^{-1} \text{ K}^{-1}$ in Fig. 5c because the unique network structure can effectively scatter phonons, resulting in a reduction in the lattice thermal conductivity without having to compromise the carrier mobility values. However, with the addition of Ag, the thermal conductivity increases slightly. It is exciting that the thermal conductivity of the PCA aerogels is in the range of 0.06 to $0.11 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, which is much smaller than the thermal conductivity of many reported organic polymer TE materials [43–45]. The gaseous, radiative, and convective thermal conductivities also play important parts in the thermal conductivity of aerogel materials [46,47], which results in the ultralow thermal conductivity of the PCA aerogels.

With the combined effects of the Seebeck coefficient, electrical conductivity, and thermal conductivity, the highest zT value of 7.56×10^{-3} is generated at room temperature upon the addition of a Ag content of 33.32 wt.%, as it is displayed in Fig. 5d. Compared with that of the pure PC aerogel, the zT value is nearly one order of magnitude higher. Although the zT value is still low for practical applications, this work explores the basic TE properties of PCA aerogels.

CONCLUSIONS

In this work, a series of conducting aerogels based on PEDOT:PSS, MWCNTs, and Ag flakes were successfully prepared; meanwhile, the relationships between their thermoelectric properties (Seebeck coefficient, electrical conductivity, and thermal conductivity) and microstructure were investigated. This type of conducting aerogel possesses a large specific surface area with a BET surface area up to $228 \text{ m}^2 \text{ g}^{-1}$. The incorporation of MWCNTs and Ag flakes si-

multaneously benefits in building the 3D porous network structure and increases the electrical conductivity and Seebeck coefficient simultaneously, while the thermal conductivity of the conducting aerogels remains at a very low level of 0.06 to $0.11 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. Therefore, the results of this study demonstrate that the three TE parameters are successfully decoupled in the new conducting aerogels, which significantly improves the zT value at room temperature. Furthermore, by taking advantage of its easy processing and environmentally friendly nature, the conducting PC aerogels doped with Ag have potential applications in thermoelectric refrigeration and microgeneration areas.

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Author contributions Zhao L conceived the post-fabrication tuning of random modes and contributed to the theoretical analysis; Sun X designed and engineered the samples; Sun X, Wei Y, Li J and Zhao L performed the experiments; Sun X and Zhao L performed the data analysis; Sun X wrote the paper with support from Zhao L and Li Q. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

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银掺杂PEDOT: PSS/碳纳米管超轻导电气凝胶热电材料

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摘要 本文以导电高分子PEDOT:PSS、多壁碳纳米管(MWCNTs)、银纳米片(Ag)为原料制备了导电复合气凝胶。研究发现, 该材料具有特殊的3D网络结构, 并且该结构的存在有利于复合材料电导率和Seebeck系数同时提高, 而热导率保持较低水平。室温下复合材料热导率低至 $0.06 \text{ W m}^{-1} \text{ K}^{-1}$, 比表面积高达 $228 \text{ m}^2 \text{ g}^{-1}$ 。当Ag含量为33.32%时, 该气凝胶热电材料室温下 zT 值最高为 7.56×10^{-3} 。虽然该 zT 值仍较低, 尚不能用于实际生产, 但本研究为热电材料的设计和开发利用提供了新的设计方法。下一步工作将立足于PEDOT:PSS气凝胶制备经济、轻质、高效的聚合物热电材料。