Polymers & biopolymers

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Flexible metal-free hybrid hydrogel thermoelectric fibers

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ABSTRACT

Highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) fiber has been developed as a more promising candidate compared with bulk and film to achieve wearable thermoelectric energy harvesting. Single-walled carbon nanotubes (SWCNTs) with nanostructures are considered as an effective conductive filter for the further improvement in the thermoelectric (TE) performance of PEDOT:PSS fibers. However, the previous research primarily focused on PEDOT:PSS/SWCNT films instead of fibers. In this study, PEDOT:PSS/SWCNT hybrid fibers were synthesized via gelation process, which presents a 30% enhancement of the electrical conductivity with negligible changes in Seebeck coefficient. Moreover, there was a significant increase in the Young's modulus in accordance with the addition of an appropriate amount of SWCNTs. Thereafter, the as-prepared hybrid fibers were treated using ethylene glycol (EG) to further optimize the TE performance. Moreover, the influence of the treatment time and temperature was systematically investigated. The EG treatment resulted in a significant improvement in the electrical conductivity without a significant decrease in the Seebeck coefficient. Furthermore, the hybrid fibers were subject to EG treatment at elevated temperature, whose optimal power factor was approximately 30% higher than that of the EG-treated PEDOT:PSS/SWCNT fibers at 25 °C. This indicates that the solvent treatment at higher temperature improves the TE performance of hybrid fibers. The findings of this study can serve as a guide for the preparation of flexible and metal-free hybrid fiber with enhanced TE performance and Young's modulus.

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Introduction

The extensive development of wearable electronic device facilitated the progress of self-powering textiles, which involved photovoltaic [1], triboelectric [2], electrochemical [3] and thermoelectric (TE) [4] energy generation and storage techniques. Compared with thin films and bulks, fiber-shaped materials can be widely used in wearable energy supplying techniques, primarily because they can be significantly integrated into common textiles with minimal impact on comfort and breathability [5, 6]. Moreover, TE materials can utilize the temperature gradient between the human body and environment to generate power for wearable electronic devices [7–11]. The TE performance of a semiconductive material is evaluated as ZT = $\sigma S^2 T/\kappa$, where σ, S, T and κ represent the electrical conductivity, Seebeck coefficient, absolute temperature and thermal conductivity, respectively. For organic TE materials with inherently low thermal conductivity, the evaluation of their TE performance using the power factor (PF = σS^2) is widely accepted as well.

As one of the most promising organic thermoelectric materials, commercially available poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been extensively researched due to its easy processability, high electrical conductivity and nontoxicity [12–15]. Due to its simple preparation process and structural advantages, the PEDOT:PSS-based hydrogel fiber has attracted significant research attention in many fields [16–19]. In a previous study, a TE fiber was synthesized from PEDOT:PSS via a sulfuric acid-assisted gelation process. The resultant PEDOT:PSS fiber was then treated with ethylene glycol to further increase its electrical conductivity in accordance with a slight decrease in its Seebeck coefficient, whose optimized σ, S and PF values were calculated as 175 S cm^{-1}, 16 μV K^{-1} and 4.77 μW m^{-1} K^{-2}, respectively [20]. The tensile properties the abovementioned PEDOT:PSS fibers, which are critical for wearable thermoelectric energy harvesting applications, were not presented. Furthermore, the TE performance of the fibers can be further optimized by introducing nanostructured materials with excellent TE performance to the organic matrix.

In recent years, metal-free hybrid TE materials have been extensively developed due to their great potential to fulfill both merits of each component, thus leading to enhanced TE performance. Furthermore, their excellent mechanical reliability allows them to be implemented in wearable application [21–25]. As a highly conductive filler, single-walled carbon nanotubes (SWCNTs) have been extensively employed to enhance the TE performance of PEDOT:PSS based on the carrier scattering effect [26–29]. The junctions in the hybrid semiconducting materials are critical to high TE performance material. When charge carriers are transported through these junctions, charge carriers with low energy are scattered by the energy barrier in the junctions, which would benefit the Seebeck coefficient [30]. Yu et al. reported that σ of the PEDOT:PSS/CNT composite was increased to 13500 S cm^{-1} with an almost constant S ranging from 27–47 μV K^{-1} in accordance with an increase in weight content of the CNTs from 35 to 60 wt % [31]. Moreover, the introduction of SWCNTs can also increase the Young's modulus of polymer-based materials [32], which may be due to the strong π–π interaction between the PEDOT chains and SWCNTs. However, most of the previous studies were mainly focused on the PEDOT:PSS/SWCNT bulk or film. The thermoelectric and tensile properties of PEDOT:PSS/SWCNT fibers with respect to wearable thermoelectric energy harvesting applications should be considered. Moreover, EG post-treatment was verified as an effective method for the improvement in the TE performance of PEDOT:PSS-based materials due to the removal of insulating PSS chains from highly conductive PEDOT chains, thus inducing the enrichment of the conductive phase in the surface region [20, 27, 33]. The information presented above can serve as a basis for the realization of hybrid fibers with enhanced TE and tensile performance.

In this study, PEDOT:PSS/SWCNT hybrid fibers were prepared via a gelation method. The TE and tensile properties of the hybrid fibers were comprehensively characterized. EG post-treatment was then employed, and its effect on the TE performance of the as-prepared hybrid fibers was systematically investigated. Changes in the micromorphology and chemical composition of the as-prepared fibers, as induced by EG post-treatment, were detected using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The proposed hybrid fibers represent a novel scheme for the development of fiber-based TE energy harvesting system.

Experimental

Materials

The PEDOT:PSS aqueous solution (Clevios PH1000) was obtained from HC Stark. SWCNT dispersion in water (0.2 wt %, TUBALL^{TM} BATT) was purchased from OCSiAl (www.ocsial.com). Sulfuric acid (H_2SO_4) was obtained from Xilong Chemical Co. Ltd. Anhydrous ethanol (EtOH) was obtained from Sinopharm Chemical Reagent Co., Ltd. Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80%) and ethylene glycol (EG) were obtained from J&K Scientific Ltd. All the chemical agents were used as received.

Fabrication of PEDOT:PSS/SWCNT hybrid fiber

The PEDOT:PSS hybrid fibers were synthesized mainly based on a method employed in a previous study [20]. In particular, 5 mL of PEDOT:PSS and SWCNT hybrid solution which contained 0.05 M H_2SO_4 was injected into a polytetrafluoroethylene tube mold (inner diameter = 1.0 mm) that was then set in an oven at a temperature of 90 °C for 3 h. To optimize the TE performance of as-prepared hybrid fibers, they were immersed in the EG solution for a given period of time. The as-prepared hybrid fibers were denoted as EGx-PEDOT:PSS/SWCNT$_y$, where x and y represent the EG treatment temperature and weight content of the SWCNTs.

Measurement

The diameter and micromorphology of the as-prepared fibers were obtained using SEM (JSM-7500F; JEOL, Japan). The surface composition of the PEDOT:PSS fiber was detected using an Escalab 250Xi X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, USA).

The tensile properties of the as-prepared hybrid fibers were determined using a tensile testing machine (ZQ-990LB). A 5 cm fiber was fixed on the test machine, which was then stretched at 1 mm min^{-1}. A minimum of five tests were carried out for each sample. A standard four-point probe technique was employed to measure the electrical conductivity and the sheet resistance R_s of the fibers. The R_s was calculated as $R_s = 2\pi rR/L$, where L, R and r represent the length, resistance and the radius of

fibers, respectively. S is estimated as $S = -\triangle V/\triangle T$, where $\triangle V$ and $\triangle T$ represent the temperature difference-induced voltage and the in-plane temperature gradient of fibers in the axial direction, respectively. The thermopower along the axial direction under the temperature gradient was measured using a data acquisition system (Keithley 2700), which was established with a heat resistor and controlled by regulated direct current.

Results and discussion

Based on a previous report [20], PEDOT:PSS fibers can be obtained when PEDOT:PSS and sulfuric acid hybrid solution was kept at 90 °C for 3 h. To further improve the TE performance, solution-processable SWCNTs were introduced into the PEDOT:PSS matrix. First, the effect of the SWCNTs weight content on the gelation of PEDOT:PSS, with the use of sulfuric acid, was investigated. The formation of the fibers can be attributed to the introduction of sulfuric acid, which eliminates a portion of PSS, thus leading to the enhancement of the hydrophobic attraction and π–π stacking interaction between PEDOT:PSS grains [16]. Additional SWCNT hindered the formation of the cross-linking network. As shown in Fig. 1, the continuity of hybrid fibers significantly decreased in accordance with an increase in the SWCNT weight content. The PEDOT:PSS cross-linking network was unable to bear the SWCNT overload and underwent breakage when the SWCNT weight content exceeded 70 wt %. Figure 2 presents the SEM images of the as-prepared hybrid fibers. The diameters of the PEDOT:PSS/SWCNT$_{0.6}$, EG$_{25}$-PEDOT:PSS/SWCNT$_{0.6}$ and EG$_{100}$-PEDOT:PSS/SWCNT$_{0.6}$ hybrid fibers were calculated as 77.14 ± 4.81 μm, 66.11 ± 4.26 μm and 56.76 ± 2.77 μm, respectively. The diameters of hybrid fibers slightly decreased after EG treatment. Moreover, the surface of the hybrid fibers was relatively smooth. After EG treatment, more wrinkles were observed, which was in accordance with the findings of a previous study [34]. An assumption was made that the surface composite may be affected by the EG treatment.

Figure 3a, b and c presents the S2p XPS of the PEDOT:PSS/SWCNT$_{0.6}$, EG$_{25}$-PEDOT:PSS/SWCNT$_{0.6}$ and EG$_{100}$-PEDOT:PSS/SWCNT$_{0.6}$ fibers, for an accurate determination of the chemical structure. In general, the doublet at 166–170 eV can be

Figure 1 Images of PEDOT:PSS/SWCNT with different SWCNTs weight contents ranging from 0–70 wt %.
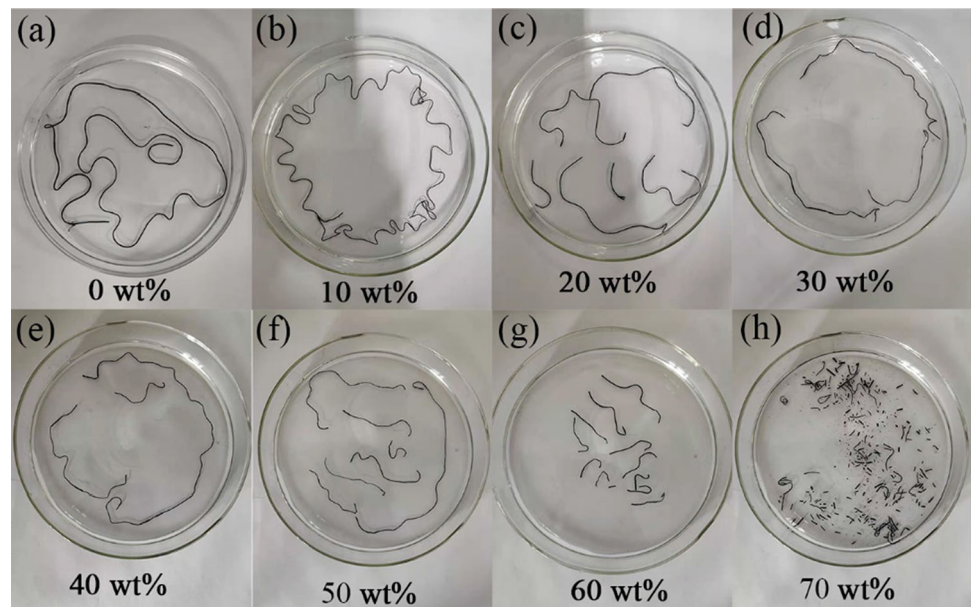
attributed to the sulfur atom from the sulfonate group in PSS, and the doublet at 162–166 eV can be attributed to the sulfur atom from the thiophene group in PEDOT [35]. The ratio between PEDOT and PSS of the PEDOT:PSS/SWCNT$_{0.6}$, EG$_{25}$-PEDOT:PSS/SWCNT$_{0.6}$ and EG$_{100}$-PEDOT:PSS/SWCNT$_{0.6}$ fiber was quantified as 1:1.77, 1:1.56 and 1:1.39, respectively. After the EG treatment, the insulative PSS molecules were readily removed from the surface region of the hybrid fibers, which can be mainly attributed to the weakening of the Coulombic force between the PEDOT and PSS chains, as induced by the EG screen effect [36]. Moreover, compared with the hybrid fibers subject to EG treatment at 25 °C, the PEDOT/PSS ratio of the EG$_{100}$-PEDOT:PSS/SWCNT$_{0.6}$ fibers decreased further. This indicates that the organic solvent treatment at an elevated temperature promotes the phase separation of PSS from PEDOT chains, thus resulting in the further enhancement of the electrical conductivity.

The representative strain–stress curves of the PEDOT:PSS/SWCNT hybrid fibers are shown in Fig. 4. All the hybrid fibers exhibited bilinear strain–stress curves, thus indicating linear strain-hardening characteristics [37]. The bilinear curves represent two sequential deformations during the stretching process. The first linear curve indicates the elastic behavior, and the second linear curve indicates plastic behavior when subject to additional stress. The bilinear behavior can be described by a simple Prandtl–Reuss elasto-plastic model, where

H ($H = (\sigma_m - \sigma_y)/D$), σ_m, σ_y and D represent the classical linear hardening parameter, final tensile stress, yield stress and plastic strain, respectively. All the tensile properties of the hybrid fibers are listed in Table 1. The introduction of SWCNT promotes the Young's modulus of the PEDOT:PSS fibers from 0.8 to 1.6 when the SWCNTs weight content reached 20 wt %, which can be attributed to the intrinsic high stiffness of the SWCNTs [38, 39]. With a further increase in the SWCNTs loading, the SWCNTs were not homogeneously dispersed in the PEDOT:PSS matrix and aggregation occurred. Consequently, the Young's modulus, fracture strain and σ_m were decreased. It should be noted that the Young's modulus of polymer-based materials is inversely proportional to the relative humidity (RH) [40]. Tensile tests were conducted on samples under 65% RH. A higher Young's modulus was obtained under a lower RH. Moreover, the Young's modulus values of the PEDOT:PSS-based materials are listed in Table 2. The hybrid fibers synthesized in this study demonstrate a relative low Young's modulus when compared with previous reports.

The TE performance characteristics of the PEDOT:PSS/SWCNT fibers are presented in Fig. 5. Hybrid fibers were obtained when the SWCNTs weight content was below 65 wt %. When SWCNTs weight content was higher than 65 wt %, the hybrid fibers were excessively weak; thus, they could not be extracted from EtOH, which was mainly because the PEDOT:PSS network lacked the strength to bear the
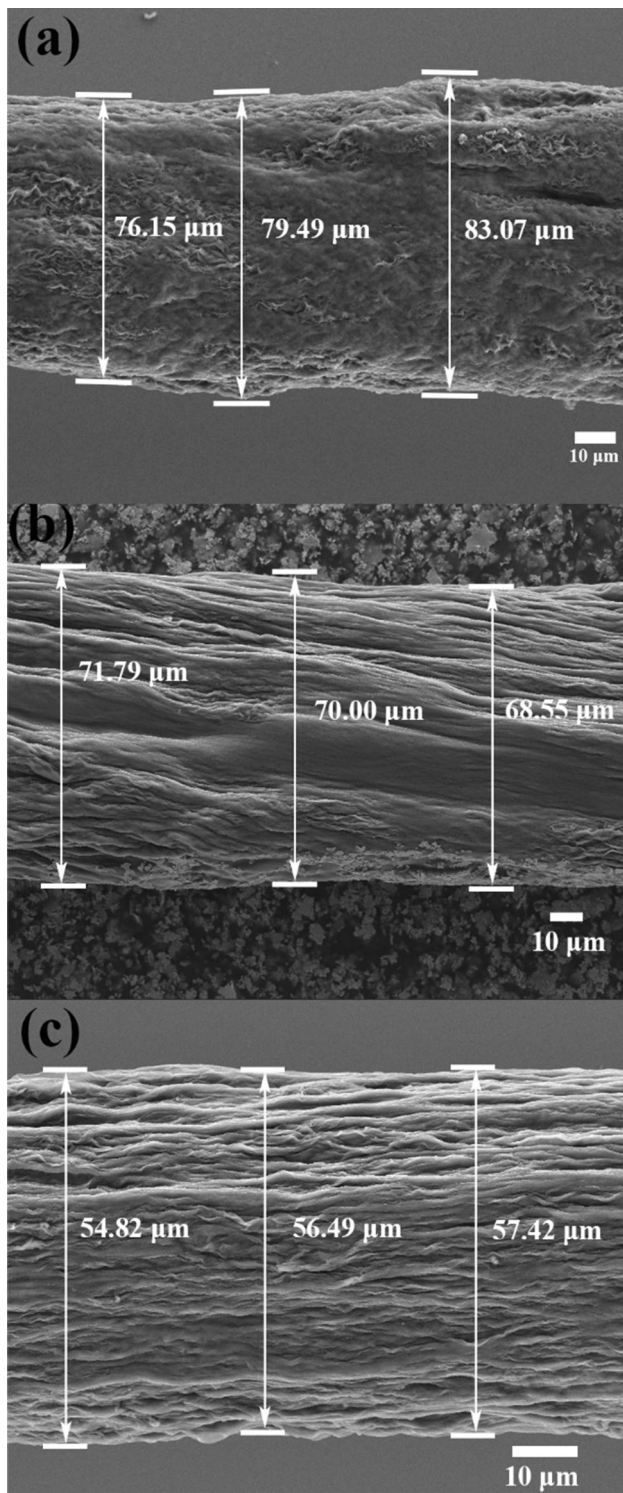
Figure 2 SEM images of PEDOT:PSS/SWCNT0.6 (**a**), EG25-PEDOT:PSS/SWCNT0.6 (**b**) and EG100-PEDOT:PSS/SWCNT0.6 (**c**).
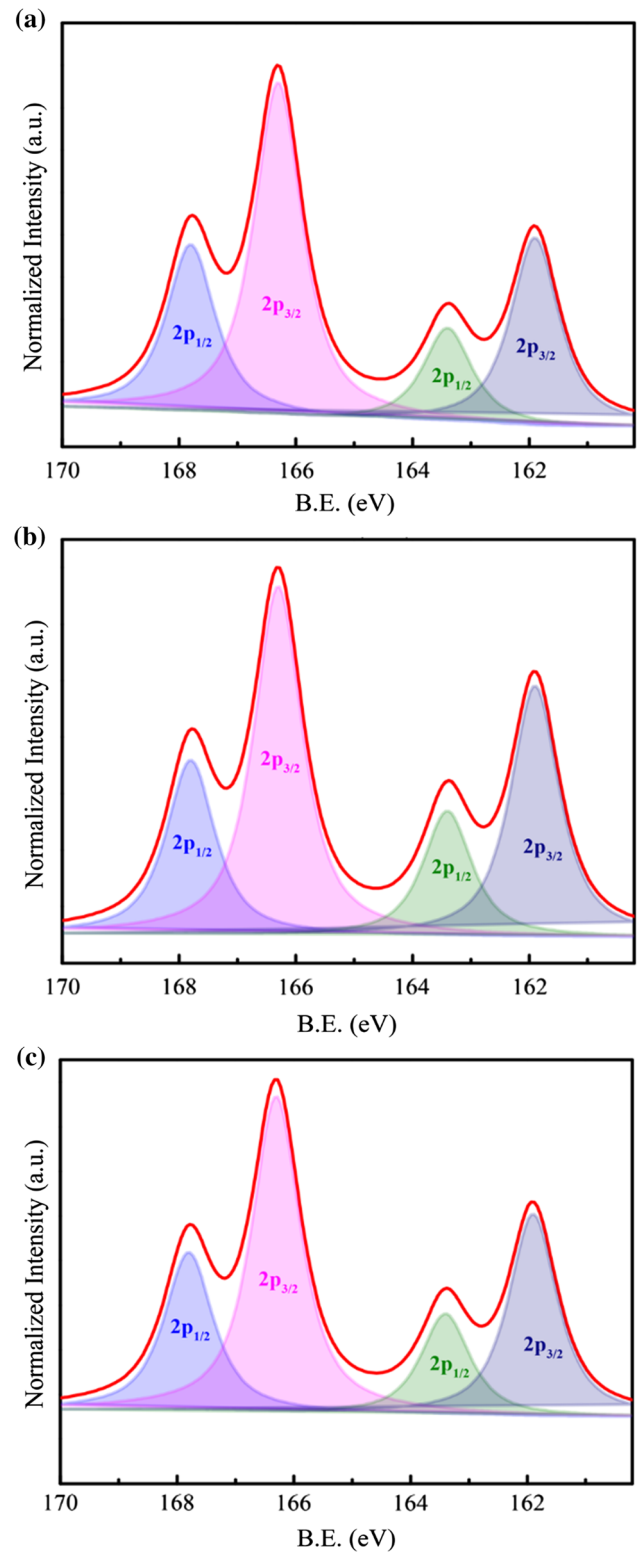

Figure 3 S2p XPS of PEDOT:PSS/SWCNT0.6 (**a**), EG25-PEDOT:PSS/SWCNT0.6 (**b**) and EG100-PEDOT:PSS/SWCNT0.6 (**c**).
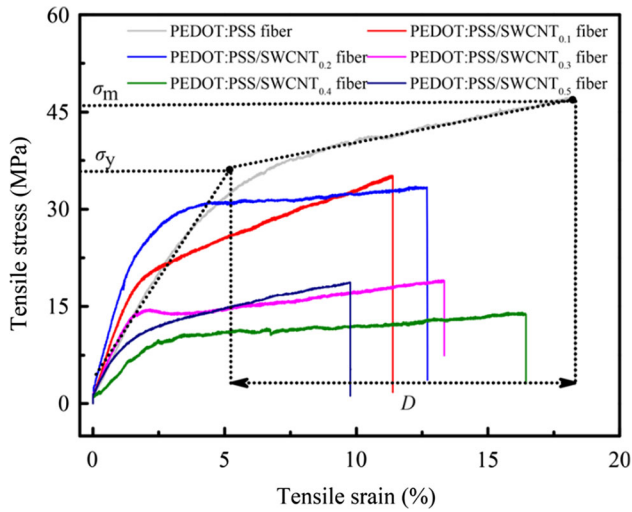
Figure 4 Representative strain–stress of PEDOT:PSS/SWCNT hybrid fibers.

excessive SWCNTs content. The TE performance of the hybrid fibers remained almost constant when the SWCNTs weight content was less than 50 wt %. With an increase in the SWCNTs weight content, σ of the hybrid fibers increased from 58.6 to 76.3 S cm^{-1} and then decreased significantly to 37.3 S cm^{-1}. The increase in electrical conductivity can be mainly attributed to (1) the intrinsic higher electrical conductivity of the SWCNTs with a highly conductive π-conjugated path for the transport of charge carriers (78.9 S cm^{-1}) [47] and the (2) filling of the junctions

between the SWCNTs by PEDOT:PSS, thus decreasing the resistance of the junctions [26, 31].

The Seebeck coefficient of the SWCNTs (13.6 µV K^{-1}) was relatively lower than that of PEDOT:PSS fibers (17.3 µV K^{-1}). Moreover, the Seebeck coefficient of the hybrid fibers did not decrease significantly upon mixture with the SWCNTs, which was possibly due to the energy filtering effect. In particular, the work functions of the PEDOT:PSS and SWCNT were different, i.e., the Fermi level that represents the average kinetic energy of the charge carriers in the two semiconducting materials was different. When the two components were in contact with each other, interfacial barriers were formed due to band bending, which could preferentially scatter low-energy carriers and allow for the passage of high-energy carrier [48–51]. The variation in the TE performance of the hybrid fibers with respect to the SWCNTs content was in agreement with the findings of previous reports [47, 52].

When the SWCNTs weight content was greater than 60 wt %, σ and S decreased simultaneously. It should be noted that the PEDOT:PSS matrix cannot contain a significant amount of SWCNTs, and an excessive amount SWCNTs severely impacts the continuity of the conductive network. In general, the optimal power factor of the hybrid fibers was 2.22 µW m^{-1} K^{-2}, which was 24 and 53% higher than those of the PEDOT:PSS fibers and SWCNTs,

**Table 1** Tensile properties of PEDOT:PSS/SWCNT hybrid fibers

SWCNT (wt %)	Young's modulus (GPa)	σ_m (MPa)	σ_y (MPa)	D (%)	H (MPa)
0	0.8	47.1	36.4	12.5	85.4
10	1.2	35.2	20.2	9.6	156.2
20	1.6	33.3	30.4	11.0	26.4
30	1.0	19.1	13.0	12.1	51.2
40	0.5	14.0	10.4	14.0	25.7
50	0.4	18.8	11.1	8.5	90.1

Table 2 Young's modulus of PEDOT:PSS-based materials

Materials	Young's modulus (GPa)	References
PEDOT/PSS fiber	8.3	[41]
PEDOT:PSS film	2.7	[40]
PEDOT:PSS-SWCNT hybrid fiber	5.2	[42]
PEDOT/PSS fiber	4.0	[43]
PEDOT/PSS film	1.0	[44]
Polyurethane/PEDOT:PSS	0.2	[45]
PEDOT:PSS/Paper	1.6	[46]
PEDOT:PSS/SWCNT fiber	1.6	This work

Figure 5 Thermoelectric performance of PEDOT:PSS/SWCNT fibers.
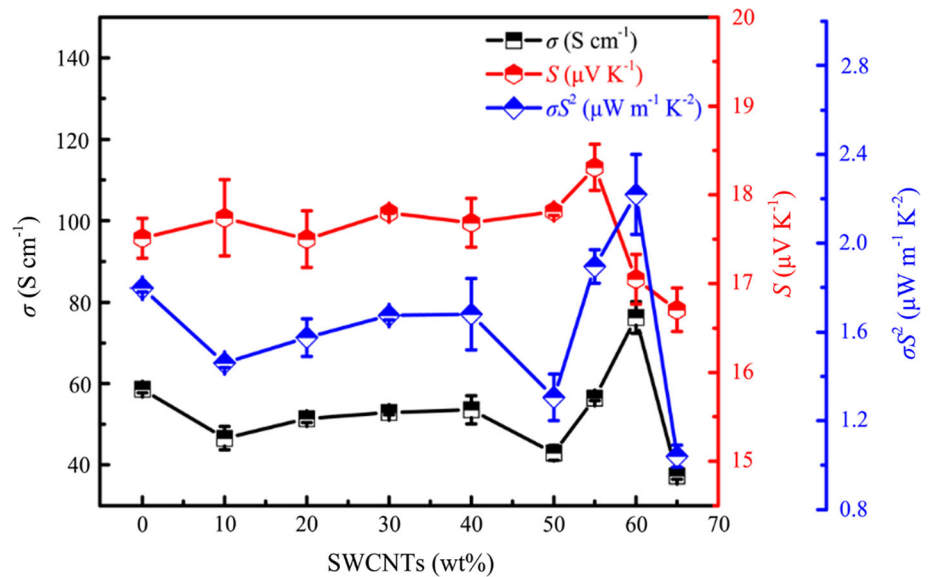
respectively, when the SWCNTs weight content was 60 wt %.

The insulating nature of the PSS chains in the hybrid fibers limits the charge carrier transport between conductive PEDOT chains. Post-treatment with polar solvents [53], such as H_2SO_4 [54], dimethyl sulfoxide (DMSO) [55–57] and EG [58], is widely considered as an efficient method for the removal of PSS and the promotion of charge carrier transport in the hybrid fibers. Figure 6 presents the TE performance of the hybrid fibers subject to EG treatment for several minutes at 25 °C. Due to the immersion treatment processing, the sheet resistance decreased, whereas the electrical conductivity significantly increased, which was mainly due to the partial removal of the insulating PSS chains in the surface region of hybrid fibers as confirmed by XPS results. This resulted in the enrichment of conductive PEDOT chains. Moreover, slight changes were observed in the Seebeck coefficient of the hybrid fiber. The optimal power factor of this hybrid fiber reached 5.57 μW m^{-1} K^{-2} after EG treatment for 45 min, which was higher than that of the untreated PEDOT:PSS/$SWCNT_{0.6}$ fibers by a factor of approximately 1.5.

The treatment temperature was assumed to have an effect on the TE performance of the PEDOT:PSS/SWCNT hybrid fibers. First, the hybrid fibers were subject to EG treatment under a series of elevated temperatures. As shown in Fig. 7a, the EG treatment at higher temperature improved the TE performance of the hybrid fiber. Thereafter, the TE performance of
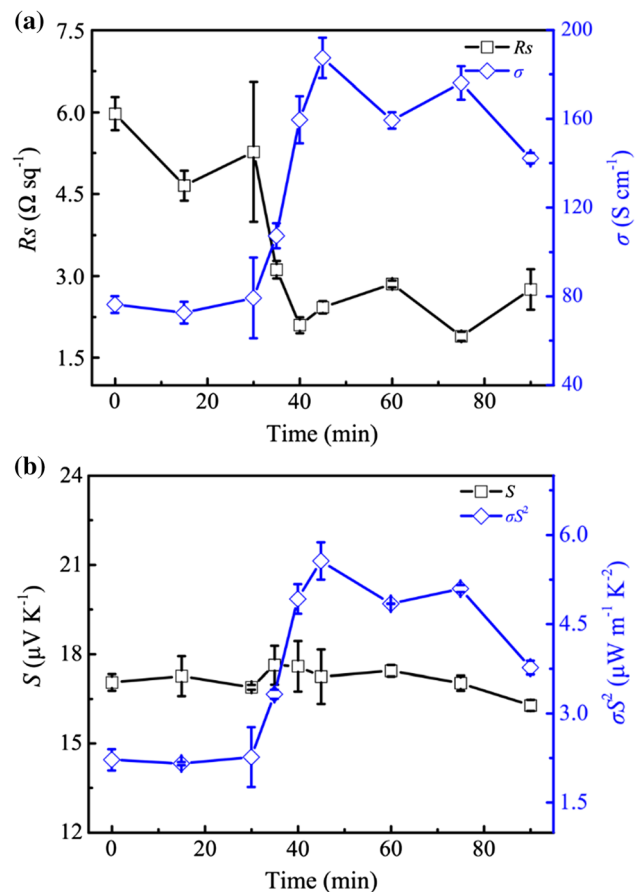

Figure 6 Sheet resistance, electrical conductivity **a**, Seebeck coefficient and power factor **b** of PEDOT:PSS/SWCNT0.6 treated with EG at 25 °C.

the hybrid fibers subject to EG treatment at 100 °C for varying durations was systematically investigated.

Figure 7 TE performance of PEDOT:PSS/SWCNT fibers subject to EG treatment for 45 min at different temperatures (**a**) and hybrid fibers subject to EG treatment at 100 °C for varying durations (**b**).
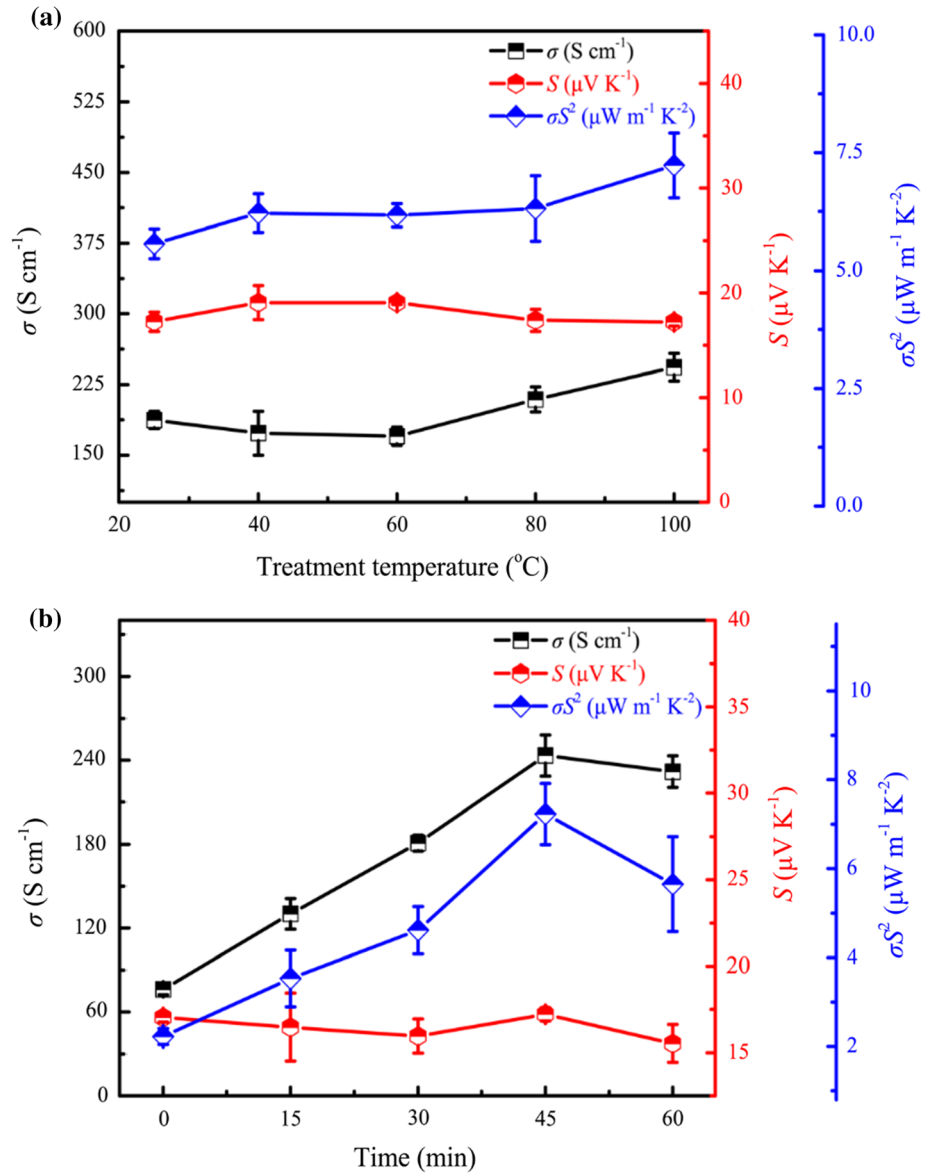

As shown in Fig. 7b, the variation trend of the electrical conductivity and Seebeck coefficient of hybrid fibers was the same as that presented in Fig. 6; thus indicating that EG treatment at an elevated temperature may further facilitate the removal of insulating PSS chains, as previously confirmed by XPS results. The optimal power factor of the hybrid fiber reached 7.23 $\mu W\ m^{-2}\ K^{-2}$ after EG treatment at 100 °C for 45 min, which was approximately 30% higher than that of EG$_{25}$-PEDOT:PSS/SWCNT$_{0.6}$.

Table 3 presents a summary of the TE performance of the PEDOT:PSS/SWCNT hybrid materials. The electrical conductivity of the pristine PEDOT:PSS fibers was found to be significantly lower than that of

the films. The significant decrease in electrical conductivity can be attributed to the abundance of insulating PSS chains within the hydrogel fibers when compared with that of the thin films. The cause for the formation of the PEDOT:PSS hydrogel is the enhanced hydrophobic interaction between PEDOT:PSS grains in addition to the π–π stacking interaction between the PEDOT chains, as induced by sulfuric acid [16]. In this self-assembly process, many insulating PSS chains may be wrapped within and on the surface regions of the fibers. Moreover, EG treatment can only remove the PSS chains in the surface regions. The remaining PSS chains within the fibers then limit the charge carrier transport. It should be noted that the electrical

Table 3 TE performance of PEDOT:PSS hybrid materials

Materials	Shape	σ (S cm^{-1})	S (µV K^{-1})	σS^2 (µW m^{-1} K^{-2})	References
PEDOT:PSS/SWCNT	Film	1000	40	160	[31]
PEDOT:PSS/SWCNT	Film	241	38.9	21.1	[61]
EG-treated PEDOT:PSS/SWCNT	Film	780 ± 51	43.7 ± 3.3	151 ± 34	[27]
DMSO-treated PEDOT:PSS/SWCNT	Film	3800	28	300	[57]
PEDOT:PSS/SWCNT	Film	533	44.3	105	[60]
PEDOT:PSS/SWCNT	Fiber	361 ± 90	16.6 ± 3.3	10.1 ± 4.5	[62]
Hydrazine-treated PEDOT:PSS/SWCNT		318 ± 33	− 33.4 ± 0.7	35.6 ± 5.2	
EG-treated PEDOT:PSS/SWCNT	Fiber	243.3	17.23	7.23	This work
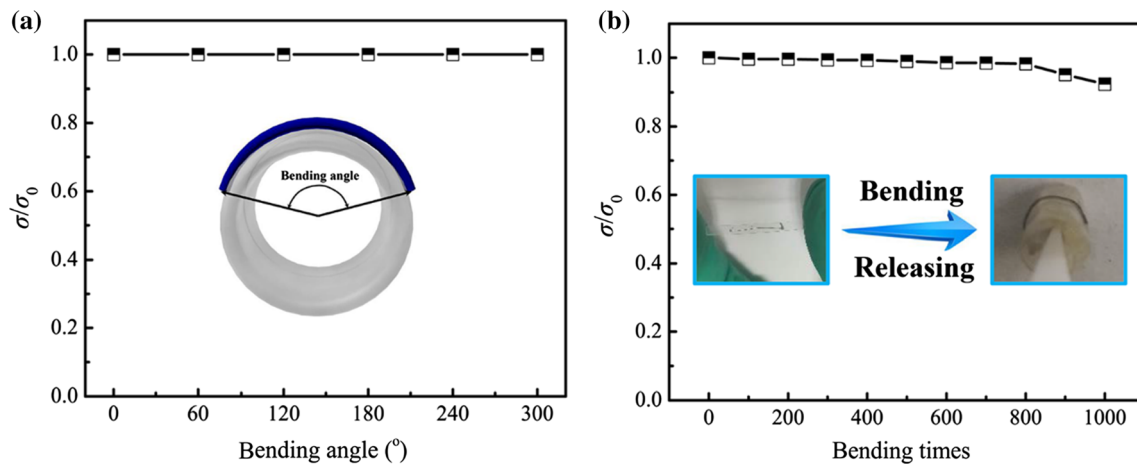
Figure 8 Electrical conductivity of EG100-PEDOT:PSS/SWCNT0.6 hybrid fibers subject to bending **a** at different angles and **b** at 300° for multiple cycles.

conductivity of the PEDOT:PSS fibers without any treatment mainly ranged from 0.4 to 74 S cm^{-1}, when prepared via a wet spinning technique [43, 59] or gelation [16, 20], which was relatively lower than that of the films. In particular, PSS chains allow for the solution to exhibit suitable processability; however, an excess of PSS chains leads to a decrease in the electrical conductivity. Hence, further research is required on the effective regulation of the amount of PSS chains necessary to balance the solution processability (also referred to as 'spinnability' for spinning dope) and electrical conductivity for the PEDOT:PSS-based fibers. Furthermore, according to the SWCNT dispersion formula, polyvinylpyrrolidone (PVP) was added to provide the SWCNTs with suitable dispersity in aqueous solutions, which severely deteriorated the charge transport between the PEDOT chains and SWCNTs [60].

The variation in electrical resistance of the optimal hybrid fibers with respect to the bending angle was investigated. As shown in Fig. 8a, there were negligible changes in the electrical conductivity after bending at an angle of 300°. Thereafter, the fiber was subject to approximately 1000 bend-and-release cycles at an angle of 300°. As shown in Fig. 8b, the fibers exhibited slight differences in electrical conductivity before and after 1000 bend-and-release cycles at an angle of 300°. The experimental results demonstrated the good mechanical reliability of the hybrid fibers.

Conclusions

In summary, the development of PEDOT:PSS/SWCNT hybrid fibers with enhanced TE and tensile performance was realized. First, the PEDOT:PSS/SWCNT hybrid fibers were fabricated via the injection of PEDOT:PSS and SWCNT homogeneous dispersion with 0.05 M H$_2$SO$_4$ into a tube mold. It should be noted that hybrid fibers were not obtained when the SWCNT weight content exceeded 65 wt %.

The Young's modulus was increased from 0.8 GPa to 1.6 GPa when the SWCNTs weight content reached 20 wt %. Compared with the power factor of the PEDOT:PSS fibers, that of the hybrid fibers was calculated as 2.22 $\mu W\ m^{-1}\ K^{-2}$, which was 24% higher than that of PEDOT:PSS fibers. Thereafter, EG post-treatment was employed to further optimize the TE performance of the hybrid fibers, thus resulting in a significant enhancement of the electrical conductivity with negligible changes in the Seebeck coefficient. This resulted in an increase in the power factor by approximately 2.5 to a value of 5.57 $\mu W\ m^{-1}\ K^{-2}$. This was primarily because the EG treatment facilitated the separation of the insulating PSS chains from the highly conductive PEDOT chains in the surface region of the hybrid fibers. Moreover, EG treatment at elevated temperature could further improve the TE performance of the hybrid fibers, whose power factor was 7.23 $\mu W\ m^{-1}\ K^{-2}$, indicating that solvent treatment under higher temperature is a more effective method for the improvement in the TE performance of hybrid fibers. The findings of this study can serve as a guide for the preparation of PEDOT:PSS-based fiber with enhanced TE performance.

Acknowledgements

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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