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Improving the thermoelectric power factor of PEDOT:PSS films by a simple two-step post-treatment method

Abstract: This study demonstrates a simple two-step post-treatment method for improving the thermoelectric power factor of low-cost poly(3,4-ethylenedioxythiophene):poly(4-styrene-sulfonate) (PEDOT:PSS) films. The dry re-dispersible PEDOT:PSS pellets are cost-effective, however, they exhibit extremely low thermoelectric performance. On treating with ethylene glycol followed by hydrazine, the power factor of the PEDOT:PSS films increased from 0.0632 ± 0.0097 $\mu W\ m^{-1}K^{-2}$ to 13.3 ± 1.5 $\mu W\ m^{-1}K^{-2}$. The enhancement might be attributed to the effective removal of the free, non-complexed PSS chains and fine control of the oxidation level of PEDOT by the two-step post-treatment.

1 Introduction

Thermoelectric materials have been extensively studied owing to their potential applications in energy harvesting. Thermoelectric materials can convert waste heat directly into electrical energy via the Seebeck effect. The performance of thermoelectric materials is evaluated by a dimensionless figure of merit (ZT) which is defined as $S^2\sigma T/\kappa$, where S, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity of the materials, respectively. The power factor, $S^2\sigma$, is occasionally used as an alternative

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to ZT when the measurement of thermal conductivities is difficult. Various types of thermoelectric materials have been reported. Recently, thermoelectric polymers have attracted considerable attention owing to their potential use in low-cost, printed, and flexible thermoelectric generators (1–23). Because thermoelectric polymers exhibit a much lower thermoelectric performance than inorganic thermoelectric materials, more research efforts are needed to improve their thermoelectric performance. Among various conjugated polymers, PEDOT:PSS has most widely been used as a thermoelectric polymer (9–17).

Bae et al. (9) reported that PEDOT:PSS films exhibited power factors up to 51.85 $\mu W\ m^{-1}K^{-2}$ at room temperature on treating with H_2SO_4. By immersing PEDOT:PSS films in ethylene glycol or H_2SO_4, the total volume of the PSS chains was reduced, thereby improving the thermoelectric properties. Wang et al. (10) reported that PEDOT:PSS films exhibited power factors of up to 19 $\mu W\ m^{-1}K^{-2}$ at room temperature on controlling the pH of the PEDOT:PSS inks. McCarthy et al. (11) obtained PEDOT:PSS films exhibiting power factors up to 334 $\mu W\ m^{-1}K^{-2}$ at room temperature on treating the films with H_2SO_4 and NaOH. The doping level of PEDOT:PSS films was tuned by varying the concentration of OH^- for optimizing their thermoelectric properties. Thermoelectric properties of the commercially available PEDOT:PSS can be effectively improved by employing various post-treatment methods (9–13). However, the PEDOT:PSS aqueous dispersions exhibiting excellent thermoelectric properties are expensive. Although the low cost is one of the main advantages of thermoelectric polymers, no studies on cost-effective thermoelectric polymers and their processes have been reported.

In this study, we used dry re-dispersible PEDOT:PSS pellets which are more cost-effective than the aqueous dispersions of PEDOT:PSS. However, PEDOT:PSS films prepared from the pellets exhibit poor thermoelectric properties. For thermoelectric applications, the thermoelectric properties should be improved. In this study, we report a simple two-step post-treatment method for improving the thermoelectric properties of the PEDOT:PSS films. Initially, the as-prepared PEDOT:PSS films were treated with ethylene glycol for reducing the amount of PSS. The PEDOT:PSS films were then treated with hydrazine aqueous solution

for controlling the oxidation level of PEDOT. With the ethylene glycol treatment, the power factor of the PEDOT:PSS films increased from 0.0632 ± 0.0097 μW m^{-1}K^{-2} to 6.31 ± 0.71 μW m^{-1}K^{-2}. With the two-step post-treatment, the power factor of the PEDOT:PSS films could be increased up to 13.3 ± 1.5 μW m^{-1}K^{-2}. The two-step post-treatment method is simple and effective for improving the thermoelectric power factors of the low-cost PEDOT:PSS films.

2 Experiment

PEDOT:PSS pellets, ethanol, ethylene glycol, and hydrazine aqueous solution were purchased from Sigma-Aldrich. All chemicals were used as received. The PEDOT:PSS pellets were dispersed in a mixture of distilled, deionized water and ethanol with a weight ratio of 3:1 using a mortar and pestle. The solid concentration of the inks was 1.5 wt%. The 2 ml of the as-prepared ink was drop-cast onto glass substrates (76 mm × 26 mm). For performing the ethylene glycol treatment, the PEDOT:PSS films were immersed in ethylene glycol for 1 h followed by annealing at 453 K for 60 min to remove the residual solvent. The 3 ml of the hydrazine aqueous solutions with different concentrations was then dropped onto the PEDOT:PSS films. After 20 min, the hydrazine aqueous solution was completely evaporated on a hot plate at 423 K.

Seebeck coefficients of the PEDOT:PSS films were measured under dark ambient conditions using a custom-built measurement system. For preparing the electrodes, silver paste was deposited on the PEDOT:PSS films. Two silver electrodes with a width of 5 mm were fabricated, which were separated by a distance of 35 mm. The temperature difference between both ends of the sample is controlled using Peltier devices, which are elaborately controlled by a Keithley 2200 power source and a Keithley 2460 source meter. Two pairs of T-type thermocouples with a diameter of 1 mm are employed to detect and control the temperature of the surface of sample and Peltier devices. Seebeck voltage was measured using a Keithley 2182A nanovoltmeter. The gold probe tip with a diameter of 5 μm is employed to evaluate thermoelectrical characteristics of samples. The temperature difference between the two electrodes was varied from 1°C to 8°C. The Seebeck coefficient was extracted from the slope of the straight-line fit of the ΔV vs. ΔT plot (18–23). The example of the ΔV vs. ΔT plot is given in the supplementary material file. The electrical conductivity was measured using the standard four-point probe method. All the measurements were performed at room temperature using a Keithley 195A digital multimeter and a Keithley 220 programmable current source. The

thickness of the prepared films was determined using an alpha-step surface profiler (α-step DC50, KLA Tencor).

3 Results and discussion

For fabricating of cost-effective thermoelectric polymer films, commercially available dry PEDOT:PSS pellets,
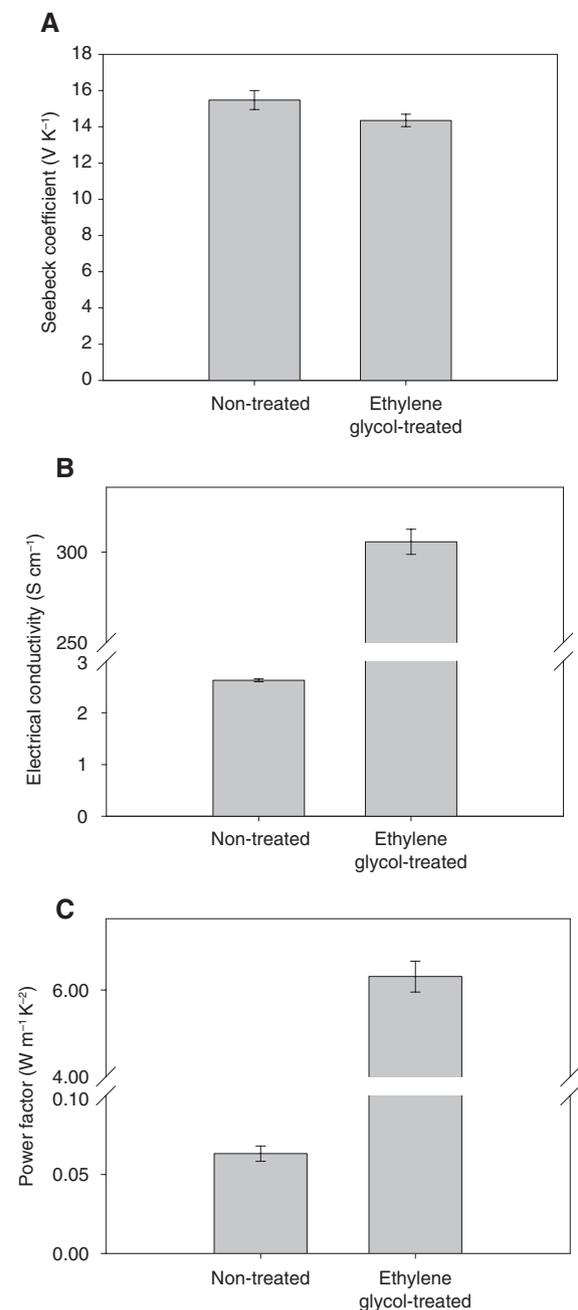

Figure 1: (A) Seebeck coefficients, (B) electrical conductivities, and (C) power factors of the non-treated and ethylene glycol-treated PEDOT:PSS films.

re-dispersible in water, were used. Uniform PEDOT:PSS films were obtained by drop-casting the ink using a mixture of distilled, deionized water and ethanol as the solvent for improving the wettability of the ink on a glass substrate. The as-prepared PEDOT:PSS films with a thickness of 7.60 ± 0.067 μm exhibit a positive Seebeck coefficient value, revealing the p-type characteristic of the PEDOT:PSS. Figure 1 shows the thermoelectric properties of the PEDOT:PSS films. The Seebeck coefficient, electrical conductivity, and power factor of the non-treated PEDOT:PSS films are 15.5 ± 1.0 μV K^{-1}, 2.63 ± 0.054 S cm^{-1}, and 0.0632 ± 0.0097 μW m^{-1}K^{-2}, respectively (Figure 1). Owing to the low electrical conductivity, the non-treated PEDOT:PSS films exhibit a poor power factor.

For improving the power factor of the as-prepared PEDOT:PSS films, we used a post-treatment method with ethylene glycol. Figure 2 shows the schematic of the morphological changes in the PEDOT:PSS film by ethylene glycol treatment. An excessive amount of PSS is generally present in PEDOT:PSS aqueous dispersions for maximizing the carrier concentration because the doping efficiency of conjugated polymers is much lower than that of inorganic materials (23–28). The free, non-complexed PSS chains occupy a volume; however, they are not electrically conductive and do not play any role in the doping of PEDOT (23–28). Thus, by effectively removing the non-complexed PSS, the electrical conductivity of the PEDOT:PSS films can be increased (Figure 2). It was reported that the non-complexed PSS chains could be effectively removed by immersing PEDOT:PSS films and microfibers in ethylene glycol (23–28). To improve the thermoelectric properties of the PEDOT:PSS films, the post-treatment method was employed. The drop-cast PEDOT:PSS films were immersed in ethylene glycol for 1 h. The films were then annealed at 453 K for 60 min for removing the residual ethylene glycol. After employing the post-treatment, the thickness of the PEDOT:PSS films decreased from 7.60 ± 0.67 μm to 4.38 ± 0.16 nm. The reduction in the thickness of the PEDOT:PSS films could

be attributed to the reduced volume owing to the removal of the non-complexed PSS (Figure 2). The Seebeck coefficient, electrical conductivity, and power factor of the ethylene glycol-treated PEDOT:PSS films are 14.4 ± 0.7 μV K^{-1}, 306 ± 14 S cm^{-1}, and 6.31 ± 0.71 μW m^{-1}K^{-2}, respectively (Figure 1). After carrying out the post-treatment with ethylene glycol, the Seebeck coefficient slightly decreased, and the electrical conductivity dramatically increased. As a result, the power factor of the PEDOT:PSS films is drastically increased. The ethylene glycol treatment is effective for enhancing the electrical conductivity and power factor of the PEDOT:PSS films. However, the power factor of the PEDOT:PSS films should be enhanced further for use in thermoelectric applications.

For further improving the thermoelectric properties, the ethylene glycol-treated PEDOT:PSS films were subjected to hydrazine treatment. The hydrazine aqueous solutions were dropped onto the PEDOT:PSS films in order to cover the whole surface of the films. The films were then annealed on a hot plate at 423 K. Because the hydrazine aqueous solutions were completely evaporated, additional rinsing was not required. With chemical reduction, the thermoelectric properties of the PEDOT:PSS films could be effectively tuned (10, 11). During the chemical dedoping process, the transition of PEDOT occurs from the bipolaron to the polaron or neutral state. As a result, the oxidation level and charge carrier concentration of PEDOT decrease. To evaluate the thermoelectric properties of the ethylene glycol- and hydrazine-treated PEDOT:PSS films, the hydrazine concentration-dependent Seebeck coefficient, electrical conductivity, and power factor were measured (Figure 3). The hydrazine concentration significantly affects the thermoelectric properties of the PEDOT:PSS films. As the hydrazine concentration increases from 0.05 wt% to 0.15 wt%, the Seebeck coefficient increases and the electrical conductivity decreases because of the decreased oxidation level of PEDOT. As the hydrazine concentration increases from 0.15 wt% to 0.25 wt%, the Seebeck coefficient and electrical
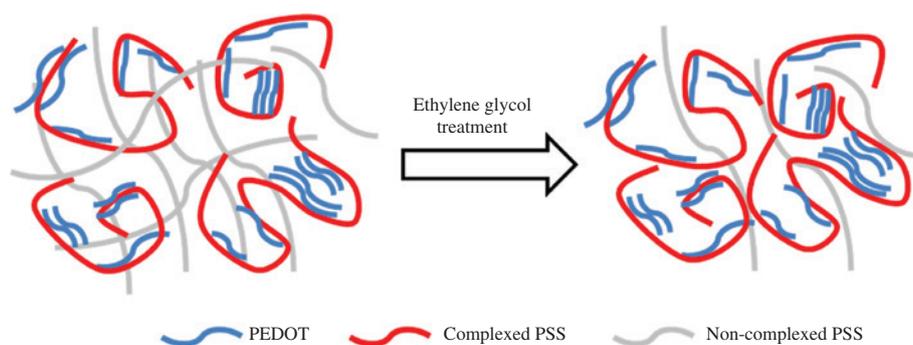

PEDOT   Complexed PSS   Non-complexed PSS

Figure 2: Schematic showing the morphological changes in the PEDOT:PSS film by ethylene glycol treatment.
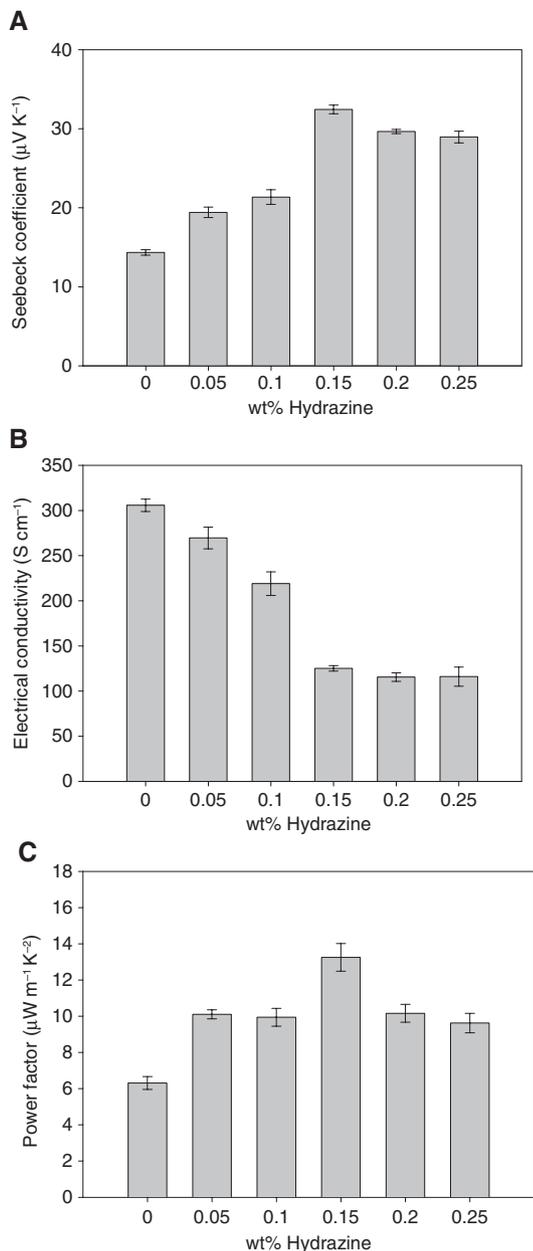
A

B

C

Figure 3: (A) Seebeck coefficients, (B) electrical conductivities, and (C) power factors of the ethylene glycol- and hydrazine-treated PEDOT:PSS films with 0.05, 0.1, 0.15, 0.2 and 25 wt% hydrazine aqueous solutions.

Table 1: Summary of the thermoelectric properties of the ethylene glycol- and hydrazine-treated PEDOT:PSS films.

Hydrazine concentration (wt%)	Seebeck coefficient ($\mu V\ K^{-1}$)	Electrical conductivity ($S\ cm^{-1}$)	Power factor ($\mu W\ m^{-1}K^{-2}$)
–	14.4 ± 0.7	306 ± 14	6.31 ± 0.71
0.05	19.4 ± 1.3	270 ± 24	10.1 ± 0.5
0.1	21.4 ± 1.9	219 ± 26	9.95 ± 0.99
0.15	32.5 ± 1.1	125 ± 6	13.3 ± 1.5
0.2	29.7 ± 0.5	116 ± 9	10.2 ± 1.0
0.25	29.0 ± 1.5	116 ± 21	9.62 ± 1.07

of 0.15 wt%. To investigate the effect of the order of the treatment, we prepared the hydrazine- and ethylene glycol-treated PEDOT:PSS films. However, with the hydrazine treatment, the as-cast PEDOT:PSS films not treated with ethylene glycol treatment were significantly damaged. This could be attributed to the degradation of PSS occurring in the present of the basic solution. Because the as-cast films have a higher PSS content than the ethylene glycol-treated films, the as-cast films might be more sensitive to the basic solution.

Figure 4 shows the thermoelectric performance stabilities of the PEDOT:PSS films. To investigate the stabilities of the thermoelectric properties, the PEDOT:PSS films were aged under an ambient environment with a relative humidity around 50% (Figure 4). It is well-known that most conjugated polymers show degradation when exposed to oxygen and moisture. In the case of the ethylene glycol-treated PEDOT:PSS film, the Seebeck coefficient gradually decreases with aging. However, the electrical conductivity steeply decreases toward zero after 2 days. As a result, the power factor is drastically decreased after 2 days. Interestingly, the electrical conductivity of the ethylene glycol- and hydrazine-treated PEDOT:PSS film gradually increases with aging. This is might be due to the re-doping of the PEDOT:PSS chemically dedoped with hydrazine. With aging, the Seebeck coefficient gradually decreases and the electrical conductivity gradually increases. As a result, the power factor of the ethylene glycol- and hydrazine-treated PEDOT:PSS film is more stable with aging. The stability of the PEDOT:PSS films might be improved by introducing a passivation layer.

On performing the simple two-step post-treatment, the power factor of the PEDOT:PSS films increases from $0.0632 \pm 0.0097\ \mu W\ m^{-1}K^{-2}$ to $13.3 \pm 1.5\ \mu W\ m^{-1}K^{-2}$. We demonstrated that the thermoelectric performance of the low-cost PEDOT:PSS films could be effectively improved using a simple two-step post-treatment process. Due to the limitation in measurement of the in-plane thermal
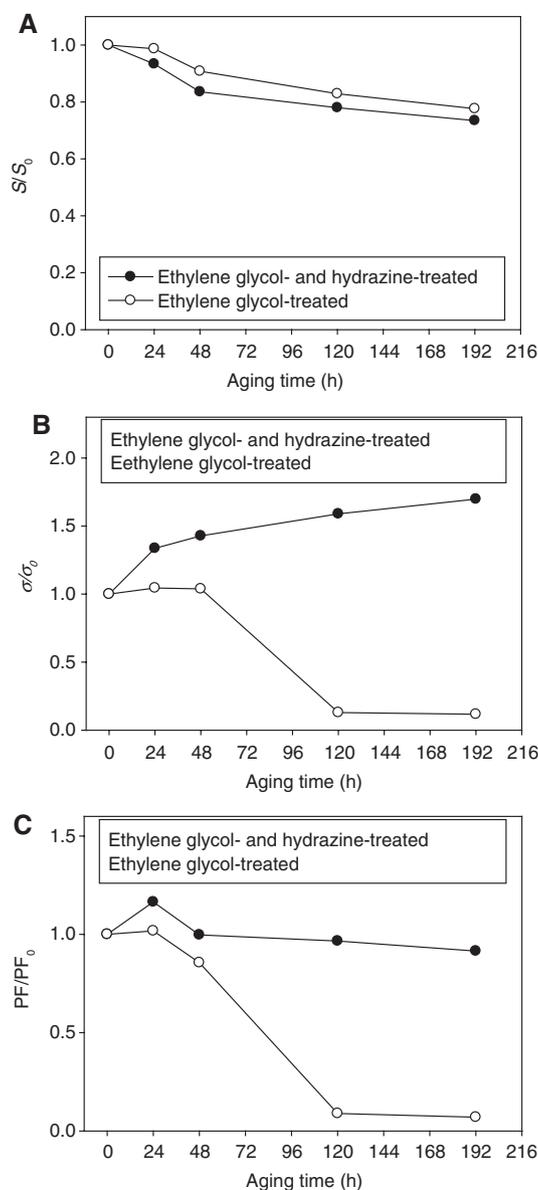
conductivity slightly decrease. The use of a hydrazine aqueous solution with a concentration of >0.2 wt% is not effective for reducing the oxidation level of PEDOT. The calculated power factors of the PEDOT:PSS films treated with hydrazine aqueous solutions with concentrations of 0.05, 0.1, 0.15, 0.2 and 0.25 wt% are 6.31 ± 0.71, 10.1 ± 0.5, 9.95 ± 0.99, 13.3 ± 1.5, 10.2 ± 1.0 and $9.62 \pm 1.07\ \mu W\ m^{-1}K^{-2}$, respectively, as summarized in Table 1. The maximum power factor is calculated to be $15.4\ \mu W\ m^{-1}K^{-2}$ with a hydrazine concentration

Figure 4: (A) Seebeck coefficient, (B) electrical conductivity, and (C) power factor stabilities of the PEDOT:PSS films.

conductivity of thin films on a substrate, the thermal conductivities of the PEDOT:PSS films could not be measured. The thermal conductivity could be expressed as a sum of the lattice thermal conductivity, κ_l, and the electronic thermal conductivity, κ_e ($\kappa = \kappa_l + \kappa_e$). Using the Weidemann-Franz relation ($\kappa_e = L_0 \sigma T$, where L_0 is Lorentz constant of 2.45×10^{-8} V^2 K^{-2}), the electronic thermal conductivity could be estimated. The estimated electronic thermal conductivities of the PEDOT:PSS film treated with ethylene glycol and 0.15 wt% hydrazine aqueous solution is 0.091 W m^{-1}K^{-1}. The estimated electronic thermal conductivity is very low and the total in-plane thermal conductivity should be measured in the future.

4 Conclusion

In summary, we report the results obtained after performing a two-step wet-chemical treatment of the PEDOT:PSS films aimed at enhancing the thermoelectric properties of the low-cost thermoelectric polymers. The thermoelectric power factor of the PEDOT:PSS films increased from 0.0632 ± 0.0097 µW m^{-1}K^{-2} to 13.3 ± 1.5 µW m^{-1}K^{-2} after performing ethylene glycol and hydrazine treatments. On treating with ethylene glycol, the non-complexed PSS chains could be removed, thereby dramatically increasing the electrical conductivity. With the subsequent treatment with a hydrazine aqueous solution, the oxidation level of PEDOT could be controlled for maximizing the power factor. Our results suggest that the two-step process is a simple and effective method for improving the thermoelectric performance of the low-cost PEDOT:PSS films.

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