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# **Novel Solution-Processable, Dedoped Semiconductors for Application in Thermoelectric Devices**

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The thermoelectric performance of poly(3,4-ethylenedioxythiophene) complexed with a poly(4-styrenesulfonic acid) (PEDOT:PSS) film was enhanced by a three-step process. First, ultrafiltration was applied to remove non-complexed PSS from PEDOT:PSS grains. The ultrafiltration treatment leads to an improvement in the power factor  $(S^2 \cdot \sigma)$  from 54.9 to 83.2  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> and a decrease in the thermal conductivity (*κ*) from 0.330 to 0.170 W m<sup>-1</sup> K<sup>-1</sup>. Second, the fully de-doped PEDOT:PSS solution was prepared by addition of hydrazine, which acted as a reducing agent. Third, the two PEDOT:PSS solutions (ultrafiltered and hydrazine-treated) were mixed in different ratios by simple ultrasonication blending without any post treatment. The optimal  $S^2 \cdot \sigma$  value of 115.5  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> (~10 times higher than that of the pristine PEDOT:PSS film) and *ZT* value of 0.2 were recorded at 33 wt% of the hydrazine-treated, ultrafiltered PEDOT:PSS in the blend.

### **Introduction**

Recently, considerable progress has been made in energy harvesting, spurred by the rising demand in global energy.<sup>1</sup> Energy harvesting is a technology that allows the capture of ambient energy (such as sunlight, wind, vibration, strain, temperature gradients, and energy associated with gas or liquid flow) and its conversion into electrical energy, which can be either stored or used directly for sensing or actuation applications. $2-4$  Among various energy harvesting strategies, thermoelectric (TE) devices are considered the most promising because they utilize waste or natural heat from diverse sources.<sup>5-7</sup> Significant efforts have been devoted to developing inorganic and organic (conducting polymer) materials for TE devices. Compared to inorganic semiconductor materials, polymeric semiconductors possess unique advantages as thermoelectric materials, such as low intrinsic thermal conductivity, high electrical conductivity, cost-effectiveness, the ability to be mass produced using straightforward synthetic methods, and the ability to be deposited over large areas.  $8-10$  In particular, poly(3,4-ethylenedioxythiophene) (PEDOT) complexed with poly(4-styrenesulfonic acid) (PSS) has been regarded as the most promising conducting polymer for TE applications.<sup>11-16</sup>

There have been numerous approaches reported for enhancing the TE performance of PEDOT:PSS; post-treatment methods based on doping & de-doping, such as over-coating<sup>15, 17, 18</sup>, dipping<sup>19</sup>, or vapour-treatment methods<sup>19</sup> have been developed because these processes affect the oxidation level and electron transport, properties strongly associated with TE performance. Among the various post-treatment methods available, the most effective is the dipping method reported by Kim et al. Recordhigh values could be obtained for the thermoelectric figure of merit  $(ZT = 0.42)$  of the polymer by selectively removing PSS molecules from the PEDOT:PSS film by using a hydrophilic solvent. PSS has enabled the dispersibility and processability of PEDOT:PSS solutions by virtue of being a polymeric surfactant.<sup>21,22</sup> Although PSS molecules play an important role in the film as the primary dopant for coulombic interaction of the deprotonated sulfonate groups with the oxidized (positively charged) PEDOT chain, $^{23}$  it is necessary to selectively remove the PSS after fabricating the films. This is because excess PSS molecules give rise to insulating properties in the PEDOT:PSS film, leading to a decrease in the electron mobility, thus decreasing the electrical conductivity  $(\sigma)$  and the Seebeck

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**Scheme 1.** Schematic illustration of the effect of ultrafiltration on PEDOT:PSS solutions. (a) Selective removal of free PSS molecules from an aqueous PEDOT:PSS pristine solution. (b) Selective removal of free PSS and non-incorporated hydrazine from main PSS in the PEDOT:PSS/hydrazine mixture.

coefficient  $(S)$  of the PEDOT:PSS film.<sup>17, 18, 24</sup> This behavior is only typical for organic semiconductors but not in inorganic semiconductors where S and sigma have an opposing behavior.<sup>19</sup> Due to such advantages that post-treatment methods offer in enhancing TE performance, PSS removal from PEDOT:PSS films has become essential. However, the current post-treatment processes have limited practical applicability because of long process times, limitations with respect to mass production, complexity, and the generation of defects on the film surface owing to polymer swelling and detaching owing to dissolution during the dipping treatment.

Herein, we report the solution processable removal of excess PSS molecules from PEDOT:PSS dispersions via ultrafiltration without post-treatment. The effects of ultrafiltration on the thermoelectric performance of PEDOT:PSS films are also reported. Moreover, in order to maximize the thermoelectric efficiency, the oxidation level of the PEDOT:PSS pristine solution after ultrafiltration (pristine-UF) should be precisely controlled because the Seebeck coefficient (*S*) depends on the oxidation level.<sup>25</sup> We successfully controlled the oxidation level

of the pristine-UF by simple blending with a solution of ultrafiltered PEDOT:PSS, de-doped with hydrazine as reducing agent. It is noteworthy that this process enhances the thermoelectric properties by only solution processing, thereby providing unique conducting polymer/polymer complexes with excellent thermoelectric performance.

### **Results and Discussion**

Scheme 1 shows a schematic illustration of the selective removal of free PSS and hydrazine from the PEDOT:PSS pristine solution (a) and PEDOT:PSS/hydrazine mixture (b) via ultrafiltration. Two types of PSS molecules exist in PEDOT:PSS solutions: (1) 'main PSS' complexed to PEDOT grains, and (2) uncomplexed 'free PSS' that act as surfactants to lower intermolecular interactions between two PEDOT grains and can be removed by ultrafiltration. The soluble free PSS and impurities such as residual oxidants, water-soluble EDOT oligomers, and excess electrolytes are smaller than the



**Figure 1**. (a) Photographic images of the PEDOT:PSS-Pristine, Pristine-UF, PHz-UF, filtrate (the waste solution being removed from PEDOT:PSS pristine solution) and pure PSS solutions. (b) FT-IR spectra of pure PSS, filtrate, and PEDOT:PSS. (c) XPS S(2p) spectra of the ultrafiltered PEDOT:PSS pristine film (blue line) and ultrafiltered PEDOT:PSS/hydrazine film (red line) compared to the PEDOT:PSS pristine film before ultrafiltration (black line). The observed PEDOT-to-PSS ratio increases after ultrafiltration. (d) Removal content (%) of impurities from the PEDOT:PSS solution via ultrafiltration.

membrane pore size, and are, therefore, flushed out of the cell through the membrane by distilled de-ionized (DDI) water, which is continuously filled into the ultrafiltration cell to maintain a stable concentration of the suspended PEDOT:PSS in the feed solution. The suspended PEDOT:PSS solutes have a larger size than the membrane pore size (100 nm), and hence, are retained above the membrane (inside the cell) during ultrafiltration (Scheme 1a). In addition, hydrazine is used as a chemical de-dopant for improving the *S* of PEDOT:PSS by decreasing the oxidation level. Excess hydrazine is added to the PEDOT:PSS solution for preparing fully de-doped PEDOT:PSS. During ultrafiltration, the hydrazine molecules that are not incorporated into the main PSS are removed along with free PSS (Scheme 1b).

The results of PSS removal using the ultrafiltration of a PEDOT:PSS solution is shown in Figures  $1(a)$ –(d). Figure  $1(a)$ shows the photographs of the PEDOT:PSS solution (Pristine), ultrafiltered PEDOT:PSS solution (Pristine-UF, PHz-UF), filtrate, and pure PSS. We confirmed that ultrafiltered PEDOT:PSS solutions were stabilized like the PEDOT:PSS pristine solution. In general, the main role of PSS in PEDOT:PSS solution is to stabilize the PEDOT grains in aqueous medium. The stability of the PEDOT:PSS solute is strongly affected by the charge density of PSS covering the PEDOT grains. The PEDOT grains in the Pristine-UF and PHz-UF solutions are stabilized because the main PSS molecules continue to cover their surface. The ultrafiltration effects on the PEDOT:PSS solution were visually identified by comparing the colour of the filtrate and the pure PSS solution. The filtrate from the PEDOT:PSS solution was darker in colour than the pure PSS solution because the filtrate contained residual oxidant and unreacted monomer or oligomer in addition to PSS; nonetheless, we confirmed that colour of both the solutions was almost identical.

The chemical structures of pure PSS, the filtrate, and pristine PEDOT:PSS were analyzed by FT-IR spectra in the range



**Table 1.** Effects of ultrafiltration and treatment with additives on the thermoelectric properties compared to those of pristine PEDOT:PSS before ultrafiltration.

<sup>a</sup> PEDOT:PSS pristine solution; <sup>b</sup> PEDOT:PSS pristine solution purified by ultrafiltration.; <sup>c</sup> PEDOT:PSS/hydrazine mixture; <sup>d</sup> PEDOT:PSS/hydrazine mixture purified by ultrafiltration

 $1800-600$  cm<sup>-1</sup>, and the result is shown in Figure 1(b). The vibration bands at  $1640 \text{ cm}^{-1}$  and between 1495 and 1412  $\text{cm}^{-1}$ in the spectrum of PSS could be assigned to the skeletal vibration of  $C=C$  in the aromatic ring.<sup>26</sup> The vibration bands between  $1250$  and  $1140$  cm<sup>-1</sup>, which usually appeared as a broad band with a shoulder, were attributed to the  $SO<sub>3</sub>$ asymmetric stretching vibration. The vibration bands at 1035 and 1000 cm<sup>-1</sup>, which appeared as two sharp bands, belonged to the  $SO_3$  symmetric stretching vibration. These abovementioned peaks could be seen in the spectra of the filtrates, pristine PEDOT:PSS, and pure PSS.

Next, we analyzed the removal of free PSS molecules by ultrafiltration of the PEDOT:PSS pristine solution using X-ray photoelectron spectroscopy (XPS). Both PEDOT and PSS contain one sulfur atom per repeating unit. The sulfur atom of PEDOT is located within the thiophene ring, whereas in PSS, it is part of the sulfonate moiety. Because of the different chemical environments, the S(2p) electrons have different binding energies. Hence, the XPS S(2p) spectra of PEDOT:PSS films allowed us to directly determine the thiophene/sulfonate ratio at the surface of PEDOT:PSS films.<sup>27, 28</sup> Figure 1(c) shows a comparison between the S(2p) XPS spectrum of the PEDOT:PSS film (blue line) after ultrafiltration (pristine-UF) and the PEDOT:PSS pristine film (black line). The sulfur signal for PSS appears at higher binding energy (168.8 eV) owing to the presence of three electronegative oxygen atoms, which withdraw electrons from the sulfur atom. The S(2p) doublet at 164.2 eV comes from PEDOT. The selective removal of the free PSS via ultrafiltration is evidenced by the increased ratio of PEDOT to PSS. Moreover, the higher-energy shift in the PSS unit of the pristine-UF film compared to the pristine film indicates that the sodium sulfonate residues  $(-SO_3 \text{Na}^+)$  are converted to sulfonic acid (-SO<sub>3</sub> H<sup>+</sup>) during ultrafiltration.<sup>29</sup> A similar higher-energy shift for the PEDOT sulfur atoms indicates that additional doped states between PEDOT and PSS units may be formed from the sulfonic acid groups  $(-SO_3H^+)$ . Figure 1(c) also shows the S(2p) peak of the ultrafiltered PEDOT:PSS/hydrazine (PHz-UF) film compared to that of the

pristine film. Contrary to the above, the selective removal of free PSS via ultrafiltration is evidenced by the increase of the intensity of PEDOT S(2p) peaks compared to that of the PSS S(2p) peaks. The lower-energy shift of the sulfur atoms in the PEDOT units after the addition of hydrazine indicates the formation of de-doped PEDOT. The electrostatic interaction between PEDOT and PSS units might be cancelled out by hydrazine molecules reacting with the sulfonic acid groups (-  $SO_3H + N_2H_4 \rightarrow SO_3^N N_2H_5^{\{1\}}$ ,<sup>15, 30</sup> leading to the neutralization of PEDOT.

As shown in figure 1(d), the amount of impurity removed from the PEDOT:PSS solution (referred to as removal content hereinafter) via ultrafiltration was calculated using the following equation:

Removal content (%) =  $\frac{1}{Solids\ of\ PEDOT: PSS\ solution\ (W_0)} \times 100\%$ Solids of filtrate  $(W_f)$ 

where  $W_0$  represents the initial solid weight in the PEDOT:PSS solution,  $W_f$  represents the accumulated solid weight of the filtrate according to filtrate volume (ml). An increase in the removal content from 0 to 3 % was observed on increasing the accumulated filtrate volume (mL). From these results, we concluded that the ultrafiltration technique effectively removed impurities from the aqueous PEDOT:PSS dispersion via solution processing, eliminating the need for additional posttreatment methods after film formation.

Pristine-UF and PHz-UF films were prepared by spin coating from an ultrafiltered PEDOT:PSS pristine solution and PEDOT:PSS/hydrazine mixture. The values for  $\sigma$ , *S*, the power factor ( $S^2 \cdot \sigma$ ), thermal conductivity (κ), and *ZT* of the pristine film and PHz film were measured to investigate the effects of ultrafiltration on the thermoelectric properties (Table 1). The value of  $\sigma$  for the pristine-UF film increased from 677 to 788 S cm-1, whereas the *S* value increased slightly from 28.5 to 32.5  $\mu$ V K<sup>-1</sup> after ultrafiltration. This was attributed to the removal of free PSS. Free PSS is an insulator and its removal increases



$$
(2) -SO_3H + [N_2H_5]^+ + OH \rightarrow -SO_3^{-}[N_2H_5]^+ + H_2O
$$

**Scheme 2.** Scheme of the de-doping of PEDOT and neutralization of the sulfonic acid groups in the PSS moiety of PEDOT:PSS solutions by the addition of  $N_2H_4$ .

electron transport for the inter-chain and inter-domain charge hopping. Increase in the charge-carrier mobility has been shown to enhance  $\sigma$  and *S* of the of PEDOT:PSS films.<sup>19, 31</sup> As expected,  $S^2 \sigma$  increases from 54.9  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> for the pristine film to 83.2  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> for the pristine-UF film, indicating that ultrafiltration efficiently improves the TE properties of PEDOT:PSS. The conductivity of the PHz film produced from the PEDOT:PSS/hydrazine mixture is 41 S cm-1and the *S* is

61.0  $\mu$ V K<sup>-1</sup>. Because the  $\sigma$  and *S* values depend on the oxidation level of PEDOT, this result indicates that the oxidation level of the PHz film can be controlled through a chemical reaction with hydrazine (de-doping).<sup>17</sup> The *S* value of the PHz-UF film decreases from 61.0 to 43.0  $\mu$ V K<sup>-1</sup> after ultrafiltration, while the conductivity increases from 46 to 416  $S \text{ cm}^{-1}$ . As shown in scheme 2, this can be attributed to the removal of some hydrazine molecules incorporated in the main PSS after an acid-base reaction with the sulfonic acids groups (-  $SO_3$ <sup>+</sup>N<sub>2</sub>H<sub>5</sub><sup>+</sup> $\leftrightarrow$ -SO<sub>3</sub><sup>-</sup>N<sub>2</sub>H<sub>5</sub><sup>+</sup>). Hence, the oxidation level of the PHz-UF film increases slightly compared to that of the PHz film. Nevertheless, the *S* of the PHz-UF film is higher than that of pristine-UF films (43.0 vs. 32.5  $\mu$ V K<sup>-1</sup>). As a result, the power factor of the PHz-UF film increases to 76.9  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> from 17.2  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> for the PHz film.

The effect of ultrafiltration on the thermal conductivity and *ZT* values of PEDOT:PSS was also investigated. The ultrafiltered PEDOT:PSS had a thermal conductivity lower than that of pristine PEDOT:PSS. The thermal conductivity of pristine PEDOT:PSS decreased dramatically from 0.311 W  $m^{-1}$  K<sup>-1</sup> (before ultrafiltration) to  $0.170 \text{ W m}^{-1} \text{ K}^{-1}$  (after ultrafiltration). The PHz sample shows an analogous, dramatic decrease from 0.366 W m<sup>-1</sup> K<sup>-1</sup> to 0.185 W m<sup>-1</sup> K<sup>-1</sup>. The total thermal conductivity of thermoelectric materials is the sum of electronic  $\kappa_e$  (charge carriers) and lattice  $\kappa_L$  (phonons) contributions. According to the literature, the thermal conductivity of conducting polymers is dominated by phonon transport and can



**Figure 2.** Schematic representations of the blending method of the Pristine/PHz-UF complex and AFM topographic 3D images  $(2\times2 \mu m^2 \text{ area})$  of (a) Pristine-UF, (b) PHz-UF, and (c) Pristine/PHz-UF complex films. .



Figure 3. Thermoelectric properties: (a) Seebeck coefficients, (b) electrical conductivities, (c) thermoelectric power factors, (d) thermal conductivities and *ZT* values, (e) carrier concentration , and (f) carrier mobility of pristine/PHz-UF complexes as a function of PHz-UF content (wt%). The electrical conductivity ( $\sigma$ ) is proportional to  $n \times \mu$ .

be affected by dopants that may alter polymer heat capacity and density.<sup>32, 33</sup> The effect of ultrafiltration on the diffusivity, specific heat capacity, and density of PEDOT:PSS is shown in Table S1 (SI). The removal of PSS from the PEDOT:PSS solution by ultrafiltration decreased all the parameters (specific heat capacity, density, and thermal diffusivity) related to thermal conductivity. The *ZT* values for the pristine-UF and PHz-UF samples were calculated to be 0.146 and 0.123, respectively by using the equation  $ZT = S^2 \sigma T / k$ , where *S* is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature.<sup>34</sup> Accordingly, the decrease in the thermal conductivity of the PEDOT:PSS films increased their energy conversion efficiency. Thus, the ultrafiltration technology offers new routes to enhance the thermoelectric efficiency.

Removal of the free PSS by ultrafiltration enhances the TE performance of both the PEDOT:PSS pristine solution and the PEDOT:PSS/hydrazine mixture. Furthermore, we investigated the TE performance of polymer-polymer blends at various PHz-UF contents relative to pristine-UF. Figure 2 shows a schematic representation of the preparation of pristine/PHz-UF complexes and AFM topographic images of (a) pristine-UF, (b) PHz-UF, and (c) pristine/PHz-UF complex films spin-coated on the glass. In particular, the Pristine/PHz-UF film was fabricated after the mixture was prepared by directly blending pristine-UF/ PHz complex solutions using ultrasonication. The PHz-UF film surface (Figure 2b) has larger PEDOT grains than the pristine-

UF film (Figure 2a). The surface RMS roughness  $(R_q)$  of the pristine-UF, PHz-UF, and pristine/PHz-UF complex films were determined to be 4.3, 7.9, and 3.4 nm, respectively. These differences in the degree of roughness arise from different stabilities of the PEDOT:PSS dispersions. The stability of the PEDOT:PSS solute is strongly affected by the charge density of PSS covering the PEDOT grains. This charge density is also affected by the number of protonated hydrazine molecules incorporated in PSS as sulfonate  $(SO<sub>3</sub>)$  salts. Accordingly, some sulfonic acid groups  $(-SO<sub>3</sub>H)$  from the main PSS molecules in PHz-UF reacted with hydrazine to form  $SO_3$ <sup>-</sup>  $N_2H_5^+$ , decreasing the negative charge density of the main PSS, thereby causing collision-induced agglomeration of the PEDOT chains in the dispersion. This aggregation explains the irregular and rough surface morphology of PHz-UF surface films (Figure 2b). In contrast, the small grains  $(R_q \text{ of } 3.6 \text{ nm})$  on the surface of the film coated by the pristine/PHz-UF complex solution indicate more dense PEDOT areas and, consequently, improved Seebeck coefficient values. This was a result of enhanced carrier mobility owing to the reduction in the charge-transport barrier.<sup>25</sup>

The effect of PHz-UF content (0 to 100 wt% PHz-UF) in the pristine/PHz-UF nanocomplexes on their TE properties is shown in Figure 3. The electrical conductivity of the pristine/PHz-UF film continuously decreases from 788 S cm-1 at 0 wt% PHz-UF to  $677$  S cm<sup>-1</sup> on increasing the PHz-UF content to the optimal 33 wt% (Figure 3a). This conductivity **Journal Name ARTICLE** 

decrease is attributed to the reduction in the oxidation level by the addition of increasing amounts of the de-doped PHz-UF. The *S* value of pristine/PHz-UF films steeply increases from 32.5 to 43  $\mu$ V K<sup>-1</sup> with increasing PHz-UF contents up to 100 wt% (Figure 3b). PHz-UF plays dual roles of enhancing the *S* value by de-doping and acting as a filler to reduce the tunnelling distance between PEDOT grains. Figure 3c shows the power factor of the pristine/PHz-UF complexed films with varying PHz-UF content. As expected, the power factor also increases with increasing PHz-UF content up to 33 wt%, where the highest power factor of 115.48  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> is observed. The optimum power factor in thermoelectric polymer complexes may also be realized by improving the carrier mobility while slightly decreasing the carrier concentration in the complexes. The variation in carrier concentration (proportional to the oxidation level) and electron mobility with PHz-UF content is shown in Figures 3(e, f). Figure 3d shows the thermal conductivity and *ZT* values of the pristine/PHz-UF films with varying PHz-UF content. Obviously, the increased carrier mobility and slightly decreased oxidation level in the pristine/PHz-UF complex are responsible for the improvement in the thermoelectric performance of *ZT* to 0.2 at 33 wt% of PHz-UF.

### **Experimental Section**

### **Materials**

The PEDOT:PSS solutions were obtained following the Baytron P synthesis procedure.<sup>35</sup> The optimum PEDOT/PSS weight ratio was confirmed to be  $1:0.8$  in our previous work.<sup>17</sup> 3,4-Ethylenedioxythiophene (EDOT; 99%), poly(4 styrenesulfonic acid) (PSS; 18 wt% in water), sodium persulfate  $(Na_2S_2O_8; \ge 98\%)$ , iron (III) sulfate hydrate  $(Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; 97%)$ , and hydrazine (Hz; 35 wt% in water) were purchased from Sigma-Aldrich (St Louis, MO, USA). Dimethyl sulfoxide (DMSO; 99%) was purchased from Samchun Pure Chemicals Co., LTD (Pyungtaek, Korea). Distilled de-ionized (DDI) water was used in all the experiments. The ultrafiltration of the PEDOT:PSS solution was conducted in a set-up assembled in-house using an ultrafiltration stirred cell (model 8400, Millipore and Amicon, USA; 400 mL maximum volume), a magnetic stirring table, and a water bath to maintain the solution volume. All ultrafiltration runs were conducted with stirring at 500 rpm. An ultrafiltration disc membrane with a pore size of 100 nm was used. In order to maintain stable concentrations of the substances in the feed solution, DDI water was continuously added to the ultrafiltration cell to compensate for the waste filtrate solution being removed.

### *Ultrafiltration of PEDOT:PSS pristine solution*

Two separate runs were conducted in order to prepare the oxidized and reduced states of the PEDOT:PSS pristine solution. Two cells were filled with the PEDOT:PSS pristine solution and PEDOT:PSS/hydrazine mixture (250 mL each). Then, ultrafiltration was initiated by applying water pressure from a water-filled feed tank. The cells were thereafter operated in the batch concentration mode. The filtrate was collected in a beaker until it reached pH 7, whereupon ultrafiltration was stopped.

### *Fabrication of pristine/PHz-UF film*

The ultrafiltered PEDOT:PSS pristine solution and ultrafiltered PEDOT:PSS/hydrazine mixture (PHz-UF) were blended in different ratios (wt%) by direct mixing under ultrasonication for 10 min. Then, DMSO (5 wt%) as a secondary dopant was added to the blended solutions. After mixing for 30 min, Pristine/PHz-UF films were prepared by spin coating (spin speed of 1000 rpm and spin time of 30 s) on a  $7 \times 7$  cm<sup>2</sup> glass substrate that was pre-treated in oxygen plasma for 30 min. The films were dried at 150 °C on a hot plate for 5 min in ambient atmosphere. The film thickness was about 150 nm (measured by surface profiler).

### **Conclusions**

In summary, we successfully enhanced the *ZT* values (0.2) of the PEDOT:PSS films by ultrafiltration and blending of pristine-UF and PHz-UF samples. Ultrafiltration removes the free PSS from the aqueous PEDOT:PSS solution, reducing the amount of PSS molecules in the PEDOT:PSS film, and thereby, resulting in a decrease in  $\kappa$  from 0.33 to 0.18 W m<sup>-1</sup> K<sup>-1</sup>. The oxidation level of the pristine-UF sample for TE performance can be optimized by tuning the wt% of fully de-doped PHz-UF in the blend, with the highest power factor of 115.5  $\mu$ W m<sup>-1</sup> K<sup>-2</sup> and room-temperature *ZT* of 0.2 obtained at an optimum oxidation level of 33 wt% PHz-UT.

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### **Notes and references**

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Electronic Supplementary Information (ESI) available: Details of the experimental method; diffusivity, specific heat capacity, and sample

density measurements; a comparison of thermal conductivity measured by our laser flash method and literature values measured by 3-omega technique of commercial material; UV-Vis-NIR absorption spectra, and stability tests. See DOI: 10.1039/b000000x/

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### **GRAPHICAL ABSTRACT**

# **Novel Solution-Processable, Dedoped Semiconductors for Application in**

## **Thermoelectric Devices**

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Ultrafilitration and polymer/polymer blending



purified by ultrafiltration (Pristine-UF)



purified by ultrafiltration (PHz-UF)



Pristine/PHz-UF nanocomplex