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Highly electrical and thermoelectric properties of PEDOT:PSS thin-film via direct dilution-filtration†

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Jinhua Xiong,‡ Fengxing Jiang,‡ Weiqiang Zhou, Congcong Liu and Jingkun Xu*

Herein, a rapid and robust method for highly conductive PEDOT:PSS thin-film has been developed by direct dilution-filtration with common organic solvents. A large electrical conductivity of 1500 S cm^{-1} has been achieved and a high thermoelectric figure of merit (*ZT*~0.1) makes it a promising organic thermoelectric candidate.

Highly conductive organic thin-film material design are of immense scientific interest and have created opportunities for the development of organic electronic materials with the ease, low cost, and scalability of process.[1-3] Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been regarded as an excellent organic electronic material due to its flexibility, lightweight, transparence, and highly conductive properties.[4-7] An essential post-treatment with common organic solvents for pristine PEDOT:PSS is required especially to allow for thin-film fabrication and improvement in electrical conductivity. However, these treatment processes are liable to induce film damage leading to a nonuniform thin-film.

The highly conductive PEDOT:PSS have been respected as one of the most promising organic thermoelectric (TE) materials available today. Recent years have witnessed a great increase of TE property with two orders in magnitude from 10^{-3} to 10^{-1} for PEDOT:PSS.[4, 8, 9] The TE property is determined by the dimensionless figure of merit:

$$ZT = \frac{\sigma S^2}{\kappa} T \quad (1)$$

where σ, S, T, and κ are the electrical conductivity, Seebeck coefficient, absolute temperature, and thermal conductivity, respectively. The enhanced σ inspired by thin-film fabrication and post treatment makes a great contribution to the high TE performance of PEDOT:PSS. It has been accepted widely that the addition of high boil point polar solvents such as dimethylsulfoxide (DMSO) and ethylene glycol (EG) can lead to a high σ (~800 S cm^{-1}) of PEDOT:PSS.[10, 11] Further, the drop-treatment and dip-treatment methods were developed to enhance the σ (800~1400 S cm^{-1}) of PEDOT:PSS films by depletion of insulating PSS in a DMSO or EG bath, as well as their combination.[12-15] Actually, the enhancement of σ is attributed to the agglomerate of PEDOT-rich nanoparticles with respect to the segregation or removal of PSS from PEDOT:PSS solid films.[11] However, these treatments involve in a complex process including the time consuming and delicate steps. Moreover, the positive effect subjects to a solvent limitations only for high boil organic solvents.

Presently, the limited technologies such as spin-coating and printing have been employed to fabricate a highly conductive PEDOT:PSS thin-film with an extra treatment.[5, 18] Here, we integrate the PEDOT:PSS thin-film fabrication and solvent treatment by a simple, rapid, robust method using one-step direct dilution-filtration with common organic solvents without any further post-treatment. The PEDOT:PSS film on PVDF was so thin and flexible that it can be cut any desired forms and pasted on a transparent PET substratum (Fig. 1). The thickness of thin-film can be controlled by changing the amount of pristine PEDOT:PSS aqueoucus in common solvents such as methanol (MeOH), ethanol (EtOH), isopropanol (IPA), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethylene glycol (EG) and N-methyl-2-pyrrolidone (NMP). This approach, avoiding the waste of pristine PEDOT:PSS, sophisticated instruments, the limitation of solvent types, and the complex processes, is

Fig. 1 Schematic illustration of suction filtration for PEDOT:PSS thin-film on PVDF.

[a] Address here. Department of Physics, Jiangxi Science and Technology Normal University, Nanchang 330013, China. Email: xujingkun@tsinghua.org.cn
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‡ These authors contributed equally.

Table 1 The corresponding parameters of P100 samples.

Solvent	PSS:PEDOT Ratio / %	Carrier concentration /×10^{22} # cm^{-3}	Mobility / $cm^2 V^{-1} s^{-1}$	σ^b /S cm^{-1}	σ^c /S cm^{-1}	$T_0{}^d$ /K
Pristine[a]	2.55:1	-	-	-	0.05	-
Water (H_2O)	2.03:1	-	-	-	1.2	-
Methanol (MeOH)	1.64:1	7.33	0.11	1290	1220	43.8
Ethanol (EtOH)	1.62:1	5.54	0.14	1241	1369	66.3
Iso Propyle Alcohol (IPA)	1.91:1	6.54	0.08	837	838	125.8
Dimethyl Formamide (DMF)	1.29:1	5.73	0.15	1375	1470	42.8
DMF drop-treatment	1.86:1	1.78	0.22	627	1011	-
Dimethylsulfoxide (DMSO)	1.18:1	3.11	0.30	1492	1399	41.9
Ethylene glycol (EG)	1.33:1	5.0	0.17	1360	1411	38.3
N-methyl-2-pyrrolidone (NMP)	1.35:1	3.6	0.08	461	538	173.2

[a] Provided by Heraeus Co; [b] The calculated values based on $\sigma = ne\mu$; [c] The measured results; [d] T_0 is the characteristic temperature based on VRH model.

expected to produce the positive effects on the electrical and TE properties.

It is difficult to prepare a thin-film by the direct filter of pristine PEDOT:PSS aqueous solution (Clevios PH1000) owing to its narrow particle size distribution of 20~30 nm. The buildup of large nanoparticles is the necessary requirement to achieve filtration separation of PEDOT:PSS from solution. The common organic solvents (Table S1, ESI†) were chosen to dilute the pristine PEDOT:PSS. This process led to the agglomeration of PEDOT:PSS nanoparticles over 250 nm due to the partial dissolution of PSS in diluent (Table S2, ESI†). Therefore, the operation of dilution-filtration succeeded in separation of PEDOT:PSS nanoparticles from solvents. The as-prepared PEDOT:PSS film has an average thickness of about 233 nm (Fig. S1 and Table S2, ESI†) and denotes as P100.

To obtain the structure and composition information, the XPS was performed and showed in Fig. S2. An evident change can be observed for the intensity of S(2p) peaks, assigned to the sulfur signals from the sulfonate of PSS (166-170 eV) and the thiophene of PEDOT (162-166 eV) between pristine and diluted PEDOT:PSS thin-films.[5, 19] The PSS ratio in PEDOT:PSS thin-films markedly decrease based on the area of S(2p) peaks (Table 1). The largest drop of PSS with 53.7% can be observed for the DMSO-diluted PEDOT:PSS thin-film, which is lower than the result (36%) reported by Kim and co-workers.[15] The similar phenomenon was observed also by Pipe *et al.*[5] using dip-treatment in EG bath and by Ouyang *et al.*[12, 13] using drop-treatment method with acids. The drop-treatment with DMF on P100-H_2O yielded a decline of PSS about 8.37% from XPS (Fig. S2, ESI†). This slight decrease probably originates from the conformation change of PEDOT:PSS since the PSS cannot be removed from the solid thin-film during the DMF drop-treatment. Also, it indicates that the diluent-treatment with solvent is a more effective strategy for depletion of PSS from PEDOT:PSS compared to other treatments. Furthermore, the removal of PSS was confirmed by Raman spectroscopy (Fig. S3, ESI†) and UV-Vis-NIR absorption spectroscopy (Fig. S4, ESI†).

Fig. 2 and Fig. S5 (ESI†) show the atomic force microscopy (AFM) images of P100. One can see that the striking difference is the bright phase on the morphology images which corresponds to PEDOT-rich grains.[15, 20] It implies that the diluent-treatment process can induce the phase separation between conductive PEDOT and insulating PSS, since the pristine PEDOT:PSS thin-film exhibits a weak phase separation.[15, 21] The phase separation allows for the aggregation of PEDOT chains and the formation of crystallinity of

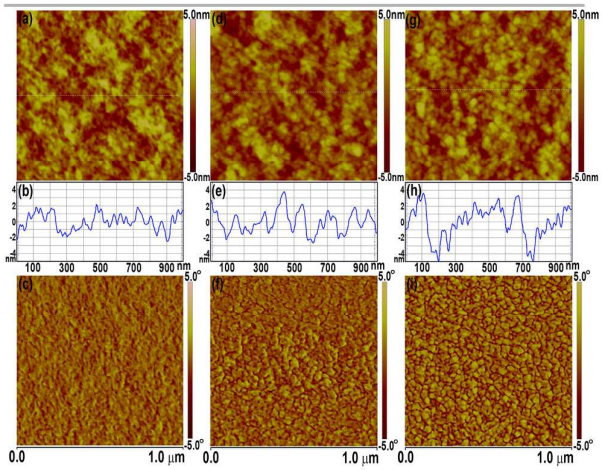

Fig. 2 AFM images of PEDOT:PSS thin-films obtained by suction filtration with H_2O (a-c), EtOH (d-f), and DMSO (g-i) as dilution. The upper layer (a, d, and g) is topography image, the middle one (b, e, and h) is the curve of surface roughness, and the bottom one (c, f, and i) is phase image.

PEDOT surrounded by the hydrophilic PSS shell. Note that the aggregated nanoparticles on P100-DMSO and P100-EtOH are more visible compared with P100-H_2O in the bright regions, indicating a more distinct phase boundaries between the conductive PEDOT and insulating PSS. The AFM images display that the surface roughness of films with a root-mean-square (RMS) are 1.039, 1.373, and 2.048 nm for the P100-H_2O, P100-EtOH, and P100-DMSO, respectively, which are closed to the previous values reported by Mengistie *et al.* with formic acid treatment (RMS= 1.31~1.89 nm).[22] A larger RMS value is associated with a more removal of PSS.[23] Takano *et al.*[10] found that the EG is a more effective solvent for improving the PEDOT crystallinity than water and ethanol. However, we found that the ethanol as diluent can also induce the aggregation of PEDOT. Unlike them, it is due to a large quantity depletion of PSS by dilution-filtration, leading to the aggregation of PEDOT with a increasing crystallinity in PEDOT:PSS solid thin-film, which is likely to accelerate the charge hopping eventually.[22]

Fig. 3a shows the in-plane σ of P100 with different organic diluents at room temperature. The σ has no remarkable change for P100-H_2O (1.2 S cm^{-1}) compared with that of pristine PEDOT:PSS thin-film by spin-coating (0.2 S cm^{-1}). When the diluent of water is replaced by organic solvents, the σ of P100 experience dramatic changes with four orders of magnitude enhancement from 10^{-1} to 10^{3} S cm^{-1}. DMF, DMSO, and EtOH as diluent show a more positive effect on the σ of PEDOT:PSS close to 1500 S cm^{-1}. It can be found, based on the results of AFM, that the PEDOT-rich particles with a larger size (40~60 nm) agglomerate randomly on the surface of P100-DMSO and P100-EtOH solid thin-films. It due to the fact that the PSS depletion leads to a thinner thickness of PSS layer separating PEDOT-rich grains and consequents alignment of the PEDOT grains inevitably.[24] The temperature dependent σ can be described by the quasi one dimensional variable range hopping (VRH) model (Fig. S6, ESI†),

$$\sigma = \sigma_0 \exp[-(\frac{T_0}{T})^{1/2}] \quad (2)$$

The T_0 values (Table 1) suggest that P100 thin-films have different energy barrier between localized states for charge transport. A lower T_0 value implies that the charge hopping among the PEDOT chains is easier and the degree of disorder in disordered regions of PEDOT:PSS is smaller due to improved intrachain and interchain packing of PEDOT-rich nanoparticles.[25-27]

For comparison, the dip-treatment for P100-H_2O were performed in different organic solvents. Unfortunately, the as-prepared P100-H_2O film is so thin that it broke up in the organic solvent bath. After that, we tried to use the drop-treatment method with pure organic solvents on the surface of solid P100-H_2O thin films. We found that the pure low boiling point solvent had little effect on the electrical conductivity of P100-H_2O film. These results are consistent to that reported by Ouyang *et al.*[28] They also found that a co-solvent of common low boiling point organic solvent (EtOH, IPA, *etc.*) and water slightly enhanced the σ of PEDOT:PSS thin-film by drop-treatment (72.7 S cm^{-1}), but no striking effects could be observed for pure organic solvent. Our experimental results found only the co-solvent of EtOH and H_2O (80%:20%, *vol*:*vol*) shows a positive effect (122 S cm^{-1}), since no obvious enhancement is obtained by drop-treatment with pure low boiling point organic solvent which cannot effectively solvate PSS after the conformational changes of PEDOT:PSS and the phase separation of PSS from PEDOT:PSS.

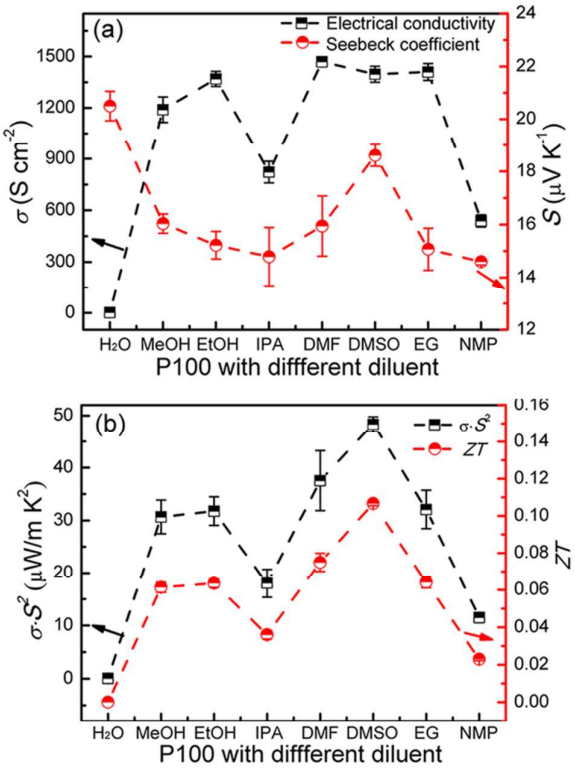

Fig. 3 (a) σ and S, and (b) the thermoelectric σS^2 and ZT values of PEDOT:PSS thin-films.

Therefore, the low boiling point organic solvents cannot give rise to a significant enhancement for the σ of PEDOT:PSS thin-film. In contrast, the striking changes are achieved just with the high boiling point solvents such as DMF, DMSO, EG, and NMP (Fig. S7, ESI†). However, the σ is still lower than that of the diluted P100 with the corresponding organic solvents, which is further confirmed by the $\sigma=ne\mu$ with the tested carrier concentration (n) and mobility (μ) in Table 1 and Table S3 (ESI†). Furthermore, the P100 thin-films were immersed in different organic solvents, yet the films is too thin to suffer from destroy. Note that the strategy by diluent-treatment for increasing σ is not limited to high boiling point solvents. Surprisingly, the low boiling point solvents (MeOH, EtOH, and IPA) show the similar effects, especially for EtOH (1369 S cm^{-1}).

On the other hand, Fig. 3a presents a little difference of S among P100 samples (14.6~18.6 μV K^{-1}), similar to the value of pristine spin-coated PEDOT:PSS film (15.2 μV K^{-1}). A slightly higher S was observed for the P100-H_2O (20.5 μV K^{-1}) and P100-DMSO (18.6 μV K^{-1}) as diluent. During the diluent process, the oxidation state of PEDOT:PSS thin-films do not change according to the UV-Vis-NIR spectroscopy (Fig. S4, ESI†), indicating that the slight change of S cannot be attributed to doping levels of P100 based on Mott relation.[29, 30] However, an enhanced S is not observed for P100 with the depletion of PSS, which is in agreement with the results Stöcker *et al.*[31] Importantly, the significant increase of σ does not lead to the striking decrease of S. Moreover, both σ (Fig. S7, ESI†) and S (Fig. S8, ESI†) of P100 still achieved 90% of initial value after 30 days

in ambient atmosphere, indicating a good environment stability. TE performance of P100 were accessed using power factor (σS^2) and *ZT* value in Fig. 3b and Fig. S9 (ESI†). The highest σS^2 is achieved to be 48.3 μW m^{-1} K^{-2}, and the largest *ZT* value is 0.1 for the P100-DMSO thin-film (κ = 0.18 W m^{-1} K^{-1}, ESI†) which is higher than those reported by Yoo et al. $(1.37\times10^{-3})^3$ and Liu et al. $(0.065)^2$. Greater enhancement for the TE property of PEDOT:PSS can thus be expected if the Seebeck coefficient is enhanced further without sacrificing its highly electrical conductivity.

Conclusions

In conclusion, a highly flexible and conductive PEDOT:PSS TE thin-film has been fabricated using a direct dilution-filtration technology with common organic solvents. The diluting process leads to a significant aggregation of PEDOT-rich nanoparticles due to the partial dissolution of PSS in organic solvents. The resulting PEDOT:PSS thin-films show the high σ of about 1500 S cm^{-1} not only for high boiling point solvents, but also for low boiling point ones. This facile treatment method simplifies the operation and combines the positive effects of drop-treatment and dip-treatment with organic solvents on the enhancement of σ. The *S* of PEDOT:PSS thin-films remains fairly constant between 14.5 and 20.5 μV K^{-1} in despite of the depletion of PSS. Both σ and *S* of PEDOT:PSS thin-films have the good long-term stability in ambient atmosphere. The large power factor (48.3 μW m^{-1} K^{-2}) and *ZT* value (0.1) have been achieved with a facile treatment, which is a great progress compared to previous most reports (~10^{-2}) as a prospective organic TE material . The enhancement of *S* will be explored to further obtain a high *ZT* value for organic TE devices. This technology and experimental studies also can give new insights into the design of organic electronic thin-film devices.

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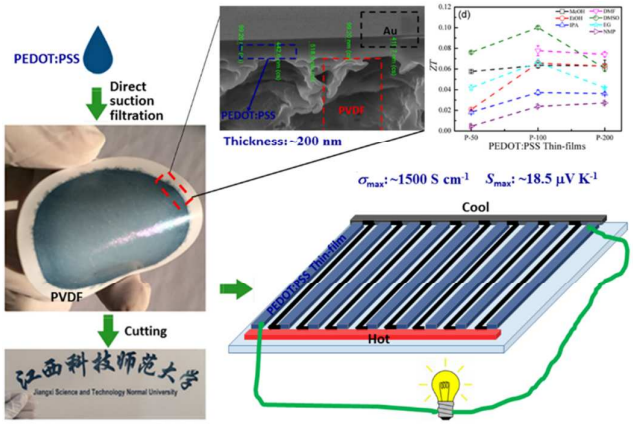
Graphical Abstract



A flexible PEDOT:PSS thin-film achieves the high electrical conductivity (1500 S cm^{-1}) and the high thermoelectric figure of merits (ZT~0.1) by a rapid direct dilution-filtration with common organic solvents.