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Enhancement of thermoelectric properties of PEDOT:PSS thin films by addition of anionic surfactants

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Abstract

The thermoelectric properties of poly(3,4-ethylendioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) thin films were investigated following the introduction of the anionic surfactants sodium dodecyl sulfate (SDS) or sodium dodecylbenzene sulfonate (SDBS). The power factor of the PEDOT:PSS films were enhanced by approximately two orders of magnitude after the addition of either SDS or SDBS when compared with the control PEDOT:PSS film, which was a result of their improved electrical conductivity. Additionally, the wettability of the PEDOT:PSS solution towards a range of substrates was improved after the addition of SDS or SDBS. These results showed that the addition of anionic surfactants to a PEDOT:PSS solution is an effective way to improve both the thermoelectric properties of PEDOT:PSS thin films and the wettability of the solution. Importantly, this method allows for uniform film formation on a range of substrates using wet process coating.

1 Introduction

Thermoelectric energy conversion shows great promise as an environmentally friendly technology to recover energy from industrial waste heat and natural heat. The performance of thermoelectric materials depends on the thermoelectric figure of merit (*ZT*) and the power factor (*P*), which are given by equations (1) and (2):

$$ZT = \frac{S^2 \sigma T}{\kappa} \tag{1}$$

$$P = S^2 \sigma \tag{2}$$

where S, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. Research on thermoelectric materials has primarily focused on inorganic semiconductors, such as Bi_2Te_3, which exhibit high *ZT* values [1].

Recently, polymer materials have attracted significant attention for their potential for use in flexible, light weight and low cost thermoelectric generators [2–21]. PEDOT:PSS is a particularly promising thermoelectric polymer because its σ and S are greater than other polymer materials [2–18]. The thermoelectric properties of PEDOT:PSS can be improved by treatment on PEDOT:PSS solutions or films using a solvent with a high boiling point, such as ethylene glycol (EG) or dimethyl sulfoxide (DMSO) [2–7], an ionic liquid [8, 9], an acid [10–12], an alkali [13, 14] or a reducing reagent [15, 16]. These treatments increase the σ or S of PEDOT:PSS, which improves the *P* and *ZT*.

PEDOT:PSS thin films are generally formed using wet processing techniques, including spin coating and drop casting. To ensure uniform PEDOT:PSS thin films are formed via wet coating methods, high wettability of a PEDOT:PSS solution to the substrate is required. As the wettability of a PEDOT:PSS solution is usually dependent on the substrate material, improving its wettability to a range of substrates is important for the advancement of PEDOT:PSS thermoelectric thin films.

Herein, we report a method that improves both the thermoelectric properties of PEDOT:PSS and its wettability on a range of substrates. This method involved the addition of the anionic surfactants SDS or SDBS into PEDOT:PSS. The wettability of the PEDOT:PSS solution was improved because the anionic surfactant reduced the surface tension, irrespective of the substrate material. Although the addition of the anionic surfactants is reported to improve the conductivity of PEDOT:PSS [22], the details of their effects on the thermoelectric properties of PEDOT:PSS have not been clarified. We have investigated these effects and found that

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the *P* of PEDOT:PSS was enhanced by approximately two orders of magnitude.

2 Experimental details

Soda-lime glass, Pyrex glass and PET substrates were cleaned using acetone and methanol in an ultrasonic bath. The clean substrates were subsequently exposed to UV-ozone for 10 min. PEDOT:PSS (Clevious PH510) solution was mixed with an aqueous solution of either SDS or SDBS anionic surfactant (10 wt%). The PEDOT:PSS and surfactant aqueous solutions were mixed at a ratio of 20:1 (v/v). Thin films of the PEDOT:PSS/surfactant mixtures were formed on the substrates by spin coating at 1500 rpm for 30 s. After spin coating the substrates were immediately annealed at 200 °C for 5 min to evaporate water from the films. A control PEDOT:PSS sample was also prepared using the same method [PEDOT:PSS solution with water at a ratio of 20:1 (v/v)]. The thickness of the films was determined using a surface profiler (Ulvac Veeco, Dektak 150) and were all approximately 110 nm. The sheet resistance of the films was measured using the four point probe method at ambient temperature. The electrical conductivity of the films was calculated using the measured sheet resistance and the film thickness (110 nm). The Seebeck coefficients of the films were determined using a custom built system that was calibrated using the Seebeck coefficient of Pt [23]. The contact angle of the PEDOT:PSS solutions to the substrates were characterized by measuring the angle where a 3 μL droplet of the PEDOT:PSS solution met the surface of the substrates. The surface morphologies of the films were characterized using atomic force microscopy (AFM, Seiko Instruments SPI/SPA300). Raman measurements were performed using a Raman spectrometer (JASCO NRS-1500 W). The excitation line used for the Raman measurement was 532 nm.

3 Results and discussion

The *σ*, *S* and *P* at 294 K of a control PEDOT:PSS thin film and PEDOT:PSS thin films that contained either SDS or SDBS are shown in Table 1. The introduction of SDS or SDBS into PEDOT:PSS enhanced the *σ* of the PEDOT:PSS thin films by approximately two orders of magnitude. The control PEDOT:PSS had a *σ* value of 0.61 S $\mathrm{cm^{-1}}$, while the films containing SDS and SDBS had *σ* values of 70 and 224 S $\mathrm{cm^{-1}}$, respectively.

Fan et al. proposed that the observed enhancement in the *σ* of PEDOT:PSS containing an anionic surfactant was caused by changes in the conformation of the conductive PEDOT chains [22]. It has also been shown that the introduction of solvents with high boiling points into PEDOT:PSS improves their *σ* because the size of the conductive domains grows as a result of partial phase separation [24, 25]. The size of the domains on the surface of our PEDOT:PSS films was determined by examining the surface roughness using AFM, as shown in Fig. 1. The surface roughness increased following the introduction of the anionic surfactants. The root mean square (RMS) surface roughness of the control PEDOT:PSS film and the films containing SDS and SDBS were 1.22, 1.38 and 1.82 nm, respectively. The *σ* as a function of RMS surface roughness for the different films is shown in Fig. 2. The value of *σ* increased with increasing RMS surface roughness. This trend was similar to that observed following the addition of solvents with high boiling points into PEDOT:PSS [24, 25]. Raman spectroscopy measurement was carried out in order to characterize the oxidation level of PEDOT by the addition of SDS or SDBS [25, 26]. As shown in Fig. 3, the all samples exhibit the main peak at around 1440 $\mathrm{cm^{-1}}$, which corresponding to the symmetric C=C stretching vibration in PEDOT, but the significant change was not observed. Therefore, the improvement of *σ* by addition of SDS or SDBS is mainly caused by the growing size of the conductive domains.

Although the *σ* of the PEDOT:PSS films increased following the introduction of SDS or SDBS, the values of *S* decreased slightly (Table 1). However, a detailed mechanism is still unclear. Further investigations on the electrical properties of PEDOT:PSS films containing anionic surfactants are required to clarify the mechanism, which are ongoing in our laboratory.

The value of *P* is given by the square of the *S* multiplied by the *σ* as shown in Eq. (2). The addition of SDS or SDBS into PEDOT:PSS significantly enhanced the value of *P* for the PEDOT:PSS thin films, which was a result of

Table 1 Electrical conductivity (*σ*), Seebeck coefficient (*S*) and power factor (*P*) at 294K of thin films consisting of control PEDOT:PSS, PEDOT:PSS with SDS and PEDOT:PSS with SDBS on soda-lime glass substrates

Sample	Electrical conductivity (*σ*) (S $\mathrm{cm^{-1}}$)	Seebeck coefficient (*S*) (μV $\mathrm{K^{-1}}$)	Power factor (*P*) (μW $\mathrm{m^{-1}\,K^{-2}}$)
Control PEDOT:PSS	0.61	17.8	0.019
PEDOT:PSS with SDS	70	13.1	1.2
PEDOT:PSS with SDBS	224	12.5	3.5

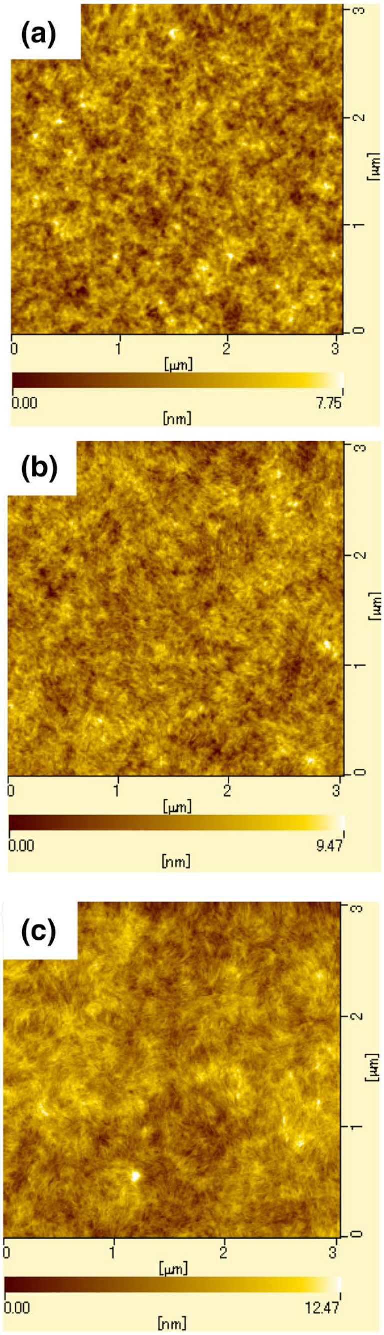

Fig. 1 AFM images of PEDOT:PSS thin films on soda-lime glass substrates. **a** Control PEDOT:PSS, **b** PEDOT:PSS containing SDS and **c** PEDOT:PSS containing SDBS

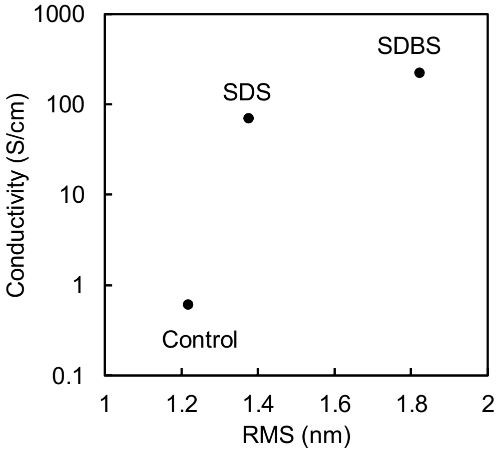

Fig. 2 Plot of the electrical conductance versus RMS surface roughness of PEDOT:PSS thin films on soda-lime glass substrates. (control PEDOT:PSS, PEDOT:PSS containing SDS and PEDOT:PSS containing SDBS)

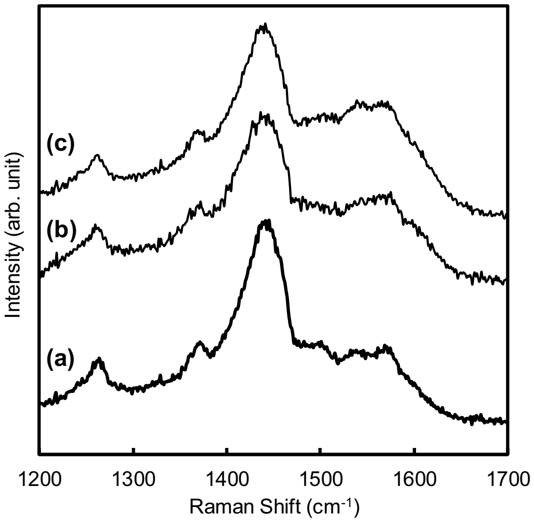

Fig. 3 Raman spectra of PEDOT:PSS thin films. *a* Control PEDOT:PSS, *b* PEDOT:PSS containing SDS and *c* PEDOT:PSS containing SDBS

their improved σ. The control PEDOT:PSS film had a P value of 0.019 $\mu W\ m^{-1}\ K^{-2}$, which increased to 1.2 and 3.5 $\mu W\ m^{-1}\ K^{-2}$ for the PEDOT:PSS films containing SDS and SDBS, respectively. Therefore, the introduction of the anionic surfactants was an effective way to improve the thermoelectric properties of the PEDOT:PSS films. In order to investigate the effect of the ratio of the surfactant to PEDOT:PSS on the thermoelectric properties, we prepared a PEDOT:PSS thin film that contained SDS by mixing 30 wt% SDS aqueous solution. We confirmed that the thermoelectric properties depend on the surfactant concentration. The PEDOT:PSS thin film prepared with 30 wt% SDS aqueous solution shows a P value of 5.6 $\mu W\ m^{-1}\ K^{-2}$, which is higher thermoelectric property than that with 10 wt% SDS solution.

High wettability of PEDOT:PSS solutions to a substrate is required to form uniform PEDOT:PSS thin films via solution process such as spin coating, otherwise the PEDOT:PSS solution will be repelled from the substrate during the coating process. The wettability of the PEDOT:PSS solutions towards a range of substrates was characterized by measuring the contact angle. PEDOT:PSS solutions containing EG and DMSO were also prepared for comparison [PEDOT:PSS solution: EG or DMSO at a ratio of 20:1 (v/v)]. The contact angle measurements of the PEDOT:PSS solutions on polyethylene terephthalate (PET), soda-lime glass and Pyrex glass substrates are shown in Fig. 4. The contact angles of the control PEDOT:PSS solution on soda-lime glass was small but large contact angles were observed on Pyrex glass and PET substrates. In fact, PEDOT:PSS thin films were not able to be formed on the Pyrex glass and PET substrates by spin coating because of the low wettability to the substrates. The PEDOT:PSS solutions that contained either DMSO or EG exhibited similar behavior to that of the control PEDOT:PSS solution. Conversely, small contact angles were observed between all substrates and the PEDOT:PSS solutions that contained either SDS or SDBS. This was attributed to a decrease in the surface tension because of the presence of the anionic surfactants, which led to improved wettability towards the substrates used in this work. Therefore, the introduction of anionic surfactants was an effective way to improve the thermoelectric properties of PEDOT:PSS thin films as well as increasing the wettability of PEDOT:PSS solution towards the substrates.

4 Summary

In summary, PEDOT:PSS that contains anionic surfactants has been successfully demonstrated as a thermoelectric material. The addition of the SDS or SDBS enhanced the power factor of the PEDOT:PSS thin films by approximately two orders of magnitude, which was a result of enhanced electrical conductivity. The wettability of the PEDOT:PSS solutions that contained either SDS or SDBS towards a range of substrates were improved significantly. These results indicated that the addition of anionic surfactants is an effective way to improve both the thermoelectric properties of PEDOT:PSS thin films and the wettability of PEDOT:PSS solutions. This led to uniform film formation on a range of substrates via wet process coating.

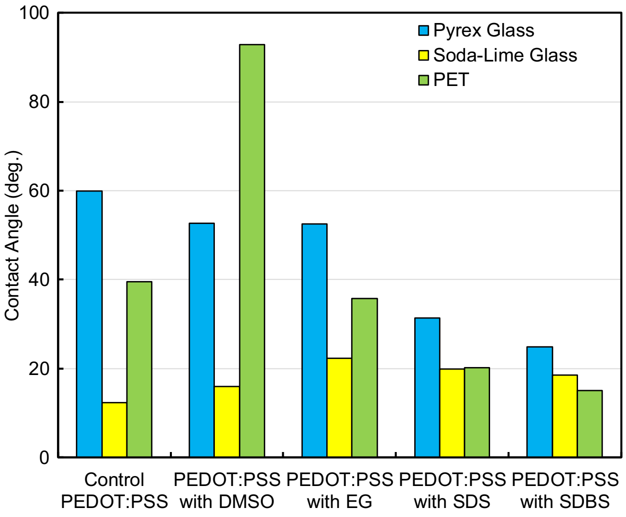

Fig. 4 Contact angles of the different PEDOT:PSS solutions (control PEDOT:PSS, PEDOT:PSS with SDS, SDBS, EG or DMSO) on PET, Pyrex glass and soda-lime glass substrates

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