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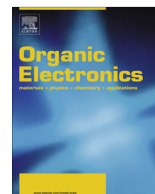
A facile dedoping approach for effectively tuning thermoelectricity and acidity of PEDOT:PSS films

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A B S T R A C T

A facile approach namely controlling the pH level of 5 wt% dimethyl sulfoxide (DMSO) doped poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) solution with sodium hydroxide (NaOH) was utilized for the first time in successfully optimizing the thermoelectric conversion efficiency of PEDOT:PSS films. The largely varied Seebeck coefficients and electrical conductivities of the pH controlled PEDOT:PSS films which could thus construct a beneficial curve for locating the optimized power factor are clearly shown from the significant changes of the carrier concentration via the dedoping of PEDOT. The correlation between pH value and carrier concentration as well as the power factor is experimentally found with numerical description covering a full pH range. The applied technique and the resulting optimized thermoelectric properties and possible bio-compatibility not only provide a fundamental understanding of the thermoelectric conducting polymers but widely disclose a variety of potential applications in the future.

1. Introduction

In recent years, thermoelectric (TE) polymers have drawn a great deal of attention and become a popular research topic not only due to their unique solubility and flexibility, which allows them to be easily processed with other TE materials [1], but also a series of exhilarating breakthroughs in inorganic [2] and organic [3] TE materials. The effectiveness of a TE material is related to the dimensionless figure-of-merit (ZT), which is defined as [1]:

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

in which: σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, T is the absolute temperature, and P is the power factor. From the definition as well as the development of conducting polymers, improvement of the electrical conductivity should be a potential and preferred strategy for better TE energy conversion. However, it is difficult to independently enhance the electrical conductivity (σ) without depressing the Seebeck coefficient (S) due to their competing relationship in the physical nature ($p = \sigma/e\mu_H = N_\mu \exp(-eS/k_B)$, where p is the carrier concentration of hole, e the unit charge, μ_H the hall mobility, N_μ the effective density of states of transport level and k_B the Boltzman constant) [4,5], meaning that there should be an optimized carrier concentration for achieving a highest power factor. Effectively tuning the carrier concentration across a very wide range is thus rather critical for optimizing the thermoelectric properties of ICPs.

Among the various organic TE materials investigated [6–9], poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [10], a water dispersion of the ionic conductive PEDOT with a relatively high and potentially improvable electrical conductivity, is considered a promising candidate for practical TE applications. However, the very high carrier concentration of pristine PEDOT:PSS and the resulting rather low Seebeck coefficient are not especially designed to have the expected optimized ZT [11].

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Controlling redox levels has been proven to be one of the most effective ways for significantly dedoping ICPs [12–15]. It has been shown that the Seebeck coefficients sensitively vary with the redox level and an optimized ZT value is thus present at a specific redox level [13]. via electrochemical dedoping [11,16], two further successful cases have demonstrated great variation in the carrier concentration of PEDOT:PSS [11,16]. In addition to these two described categories, blending ammonium formate with the pristine PEDOT:PSS, which induces an ion exchange between ammonium ions and H$^+$ of PSS, also leads to a remarkable enhancement in the Seebeck coefficient [17].

In this work, a facile approach, that is, the addition of sodium hydroxide (NaOH) for controlling pH values, is applied to dedope the pristine PEDOT:PSS, in order to obtain a desired carrier concentration. The acidity of PSS could be neutralized by NaOH as expressed below:

$$PSS^-H^+ + Na^+OH^- \rightarrow H_2O + Na^+PSS^- \tag{2}$$
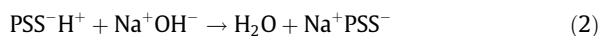
It is known that the PSS groups within the pristine PEDOT:PSS intrinsically involve both PSS-Na and PSS-H, and PSS-H exhibits better capability in generating carriers than PSS-Na. The addition of NaOH would further transform a certain amount of PSS-H into PSS-Na and the carrier concentration of the NaOH treated PEDOT:PSS films would thus accordingly decrease with the gradually increased pH value up to 14. An optimized carrier concentration, which leads the highest power factor, is expected to be found.

2. Experiment

The pH value of a 5 wt% dimethyl sulfoxide (DMSO, Tedia, 4L) doped PEDOT:PSS solution (Clevios PH 1000, Heraeus) was adjusted from the initial state of about 1.5 up to 13.42 by the stepwise addition of NaOH aqueous solution (SHOWA) with stirring and a pH meter (EUTECH instruments pH 510 with sensor form SENSOREX SG200CD). Litmus papers (Advantec universal, Toyo Roshi) are used only to visualize the acidity of the baked films wetted by D.I. water droplets.

A constant volume of 200 μl of the prepared well-blended PEDOT:PSS solution with a controlled pH value was uniformly spread onto several pieces of cleaned glass substrates (1.5 × 1.5 cm^2). The deposited films were then dried at atmosphere at 50 °C for an hour, followed by another 1 h of heating at 120 °C to completely remove the solvents. For measurement of the Seebeck coefficient, a microheater was applied to create a temperature difference between the two ends of the polymer film. Two positions along the heat flow direction were selected and their temperatures and temperature difference were measured using calibrated thermocouples. The resulting Seebeck voltages were detected using a pair of thin Cu wires that were electrically connected to the sample with silver paint at the same positions as the junctions of the thermocouples, in order to acquire the Seebeck coefficient under atmosphere. Hall measurements (ECOPIA, HMS-3000) were taken by utilizing Ag paste on four corners of the prepared film as electrodes, with an applied magnetic

field of 0.58 Tesla. To understand the dedoping condition of the NaOH treated PEDOT:PSS films, the UV–visible absorption spectra (Thermo Scientific, Evolution 300) and the Raman spectra (Horiba Jobin Yvon Labram, HR 800) equipped with a nitrogen-cooled CCD detector and a He–Ne laser (633 nm) were recorded.

3. Results and discussion

Fig. 1 shows the measured Seebeck coefficient and electrical conductivity of the NaOH treated PEDOT:PSS films with a very wide range of pH values. Obviously, the addition of NaOH, which could alternate acid PSS-H with neutralized PSS-Na, is very effective, not only for tuning the pH value but, more importantly, the Seebeck coefficient. Although the electrical conductivity also simultaneously decreases with increasing pH, we believe that such a facile approach and the resulting extensive variation in the Seebeck coefficient, as well as the electrical conductivity, are important for understanding and outlining the desired optimized power factor.

The present tendencies of the Seebeck coefficient and the electrical conductivity on the pH value are very similar to those on the carrier concentration. To qualitatively identify the physical and chemical roles of the pH variation, the carrier concentration of each film was measured as displayed in Fig. 2. The Seebeck coefficient and electrical conductivity are obviously functions of the carrier concentration.

Based on the physical functions provided in the prior section, two fitting curves respectively reproduce the numerical data of the measured Seebeck coefficient and electrical conductivity quite well, evidently showing the role of the pH tuning on changing the doping level of the PEDOT:PSS films. Through the curve fittings, two intrinsic physical parameters, that is, N_μ and μ_H, can thus be obtained as 1.74×10^{21} cm^{-3} and 20.56 cm^2/Vs, respectively, where the measured mobilities fall into the range of 19.41–21.98 cm^2/vs. It is worth noting that the experimental maximum Seebeck coefficient shown in Fig. 2 should not be the upper limitation of the present system, since the
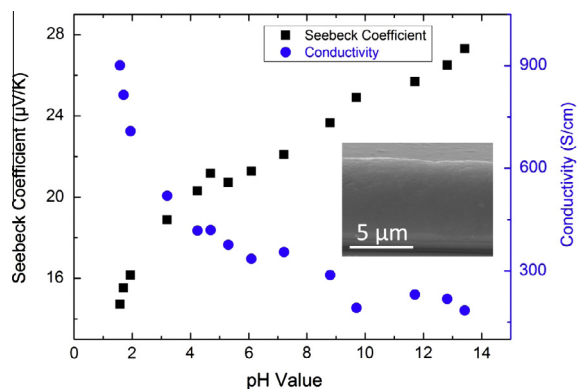

Fig. 1. Seebeck coefficient (square) and electrical conductivity (circle) of the prepared PEDOT:PSS films as functions of pH value. The cross-section SEM image indicates the thickness of the prepared films (inset).
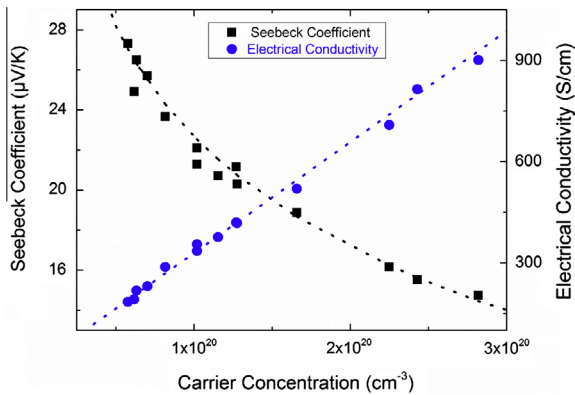
Fig. 2. Seebeck coefficient (square) and electrical conductivity (circle) of the prepared PEDOT:PSS films as functions of carrier concentration.

Seebeck coefficient may further increase when the carrier concentration is dedoped to lower than 3×10^{19} cm^{-3}.

The corresponding power factors respectively obtained from the measured raw data as presented above are shown in Fig. 3(a). The dot line presents the calculated power factor using the theoreti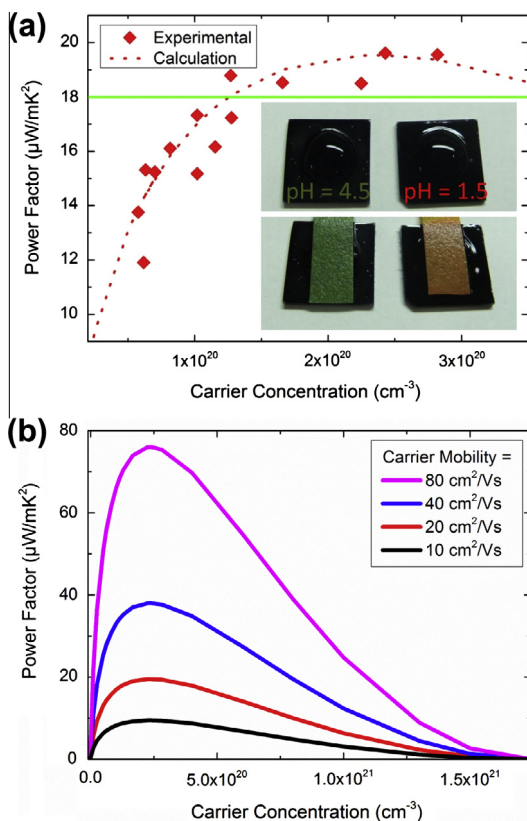cal Seebeck coefficient and electrical conductivity shown in Fig. 2. Since the measured carrier concentration covers a very wide range, the expected peak-like distribution of the power factor is clearly shown. A maximum power factor can thus be obviously found at the carrier concentration of 2.4×10^{20} cm^{-3}, which is slightly lower than 2.7×10^{20} cm^{-3} of the pristine PEDOT:PSS film, indicating the importance of the dedoping process for obtaining optimized PEDOT:PSS for thermoelectric applications. In addition, the broadened peak shown in Fig. 3(a) suggests that a relatively high power factor, *e.g.* 19 μW/mK^2, can be retained over a rather wide range of carrier concentration, roughly from 1.7×10^{20} cm^{-3} to 3.0×10^{20} cm^{-3}. In other words, carrier concentrations falling into this unresponsive region will not lead to a significant change in the power factor. It is worth noting that, as shown in the inset of Fig. 3(a), the acidity of the baked films can vary from a very high degree to a rather mild one which is more compatible to human skin or metallic components, while relatively high power factors can be retained. Furthermore, by breaking down $P = S^2\sigma$ into $P = \left(-\frac{k_B}{e} \log \frac{p}{N_\mu}\right)^2 \mu_H ep$, Fig. 3(b) shows the calculated power factors with a variety of carrier mobilities (μ_H) and constant $N_\mu = 1.74 \times 10^{21}$ cm^{-3} at a broader scale of carrier concentration. It is clear that the power factor exhibits a much sharper peak at higher carrier mobilities comparing to the broadened peak at lower carrier mobilities. This behavior on the other hand reassures the importance of carrier concentration tuning for seeking the optimized power factor of materials with higher mobilities.

In contrast to the carrier concentration, which should be determined after the film formation, the precise addition of NaOH provides a facile and effective way of preparing PEDOT:PSS films with not only improved thermoelectric properties but with planned pH values before the film formation. As can be seen in Fig. 4, the relationship between the pH value of the well-blended PEDOT:PSS solution and the carrier concentration of the formed PEDOT:PSS film can be well fitted with an exponential equation: $p = p_0 + A \exp(R_0(V_{pH}))$, where $p_0 = 6.3 \times 10^{19}$ cm^{-3}, $A = 3.6 \times 10^{20}$ cm^{-3}, $R_0 = -0.37703$ and V_{pH} is the pH value. It is clear that the carrier concentration shows

Fig. 3. (a) Power factor of the prepared PEDOT:PSS films as a function of carrier concentration, and (b) calculated power factors with various carrier mobilities as functions of carrier concentration, where $N_\mu = 1.74 \times 10^{21}$ cm^{-3}. The insets are Litmus tests on the sample surfaces wetted by D.I. water.
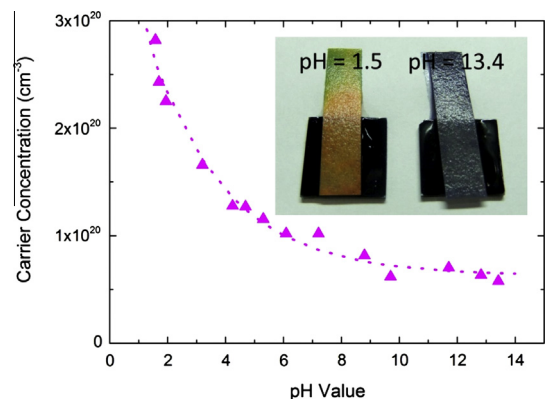

Fig. 4. Carrier concentration as a function of pH value. The insets are Litmus tests on the sample surfaces wetted by D.I. water.
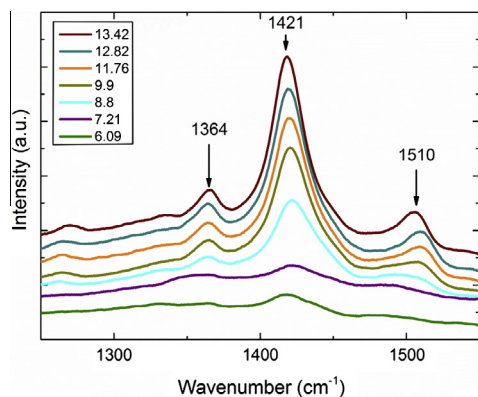
Fig. 5. Raman spectra of the prepared PEDOT:PSS films at different pH values.

a sensitive response in the acid region (pH < 7), but is unresponsive in the base region (pH > 7).

Fig. 5 shows the acquired Raman spectra of the PEDOT:PSS films prepared at different pH values. The growing peaks at 1364 cm^{-1}, 1421 cm^{-1} and 1510 cm^{-1} with the increase in pH value evidently indicate the transformation from a high conductance quinoid PEDOT to a low conductance benzoid one, supporting the dedoping of the PEDOT:PSS films [15,18–22]. The peak at 1364 cm^{-1} is assigned to C—C stretching deformation and those at 1421 cm^{-1} and 1510 cm^{-1} to the symmetric and asymmetric C=C in-plane stretch vibrations, respectively [19,20].

It is known that there are three redox states, namely, PEDOT^{2+} (bipolaron), PEDOT^{+} (polaron) and PEDOT (neutral), which might be present in PEDOT. Each of these three states exhibits distinguishable characteristic absorption bands in the UV–Vis spectra for qualitatively identifying the redox state of PEDOT. As displayed in Fig. 6, for the pristine PEDOT:PSS (pH = 1.58), a very broad absorption band found in the near infrared region indicates the dominative role of the PEDOT^{2+}. When the pH value stepwise increases from 1.58 up to 13.42, the main absorption band moves from the near infrared region to around 900 nm (polaron), and even to 600 nm (neutral) [23]. The
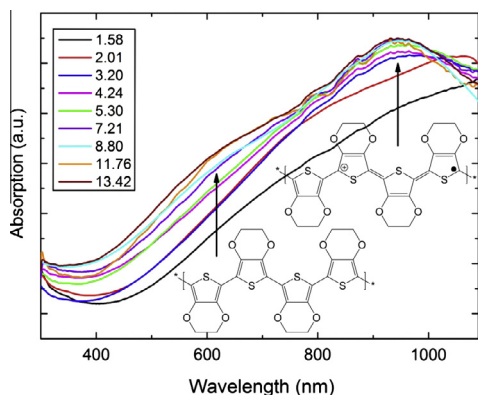
blue-shifting of the absorption bands evidently represents the transformation of the dominative redox state of the PEDOT. When the polymer solution becomes basic (pH = 7.21), the neutral PEDOT begins to appear and continuously grows with the pH value.

4. Conclusion

In conclusion, a facile dedoping approach was successfully achieved by the control of acidity by NaOH for sensitively tuning the thermoelectricity of PEDOT:PSS films. The resulting extensive variation in the Seebeck coefficient and electrical conductivity are important for optimizing the power factor. The optimized power factor of ∼19.6 μW/mK^2 was obtained at pH 1.8, which is slightly higher than pH 1.5 of the DMSO-modified PEDOT:PSS films. Interestingly, based on the present data, a relatively high power factor, *e.g.* 19.0 μW/mK^2, can be retained over a rather wide pH value, roughly from 1.5–4.5, which clearly demonstrates potential bio-compatibility in future bio-relevant applications. The dedoping of PEDOT caused by pH tuning is obviously evidenced by the Hall measurement, Raman spectra and UV-NIR spectra. With the relationship identified between the pH value of the polymer solution and the carrier concentration of the formed film, PEDOT:PSS films with not only improved thermoelectric properties but pH values planned before film formation can thus be fabricated and utilized for a variety of applications.

Fig. 6. UV–Visible absorption spectra of the prepared PEDOT:PSS films at different pH values.

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