

EFFECT OF HYDROIODIC ACID TREATMENT ON PEDOT: PSS THIN FILMS FOR ENERGY CONVERSION

ASHIS K. SARKER*

Department of Chemistry, Mawlana Bhashani Science and Technology University,
Tangail-1902, Bangladesh

Abstract

The poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) thin films were prepared by spin coating on glass substrates and treated with different concentration of hydroiodic acid for designing thermoelectric devices. This facile approach was utilized for the first time in successfully optimizing the thermoelectric conversion efficiency of PEDOT: PSS films. The optimized power factor was found to be $14.5 \mu\text{W}/\text{mK}^2$ at 45% concentrated HI treated PEDOT PSS. The applied technique and the resulting optimized thermoelectric properties not only provide a fundamental understanding of the thermoelectric conducting polymers but also widely disclose a variety of potential application in the future.

Keywords: Hydroiodic acid, thermoelectricity, energy, thin film, efficiency

Introduction

Energy is obligatory for industrial production and daily life. Currently the majority sources of energy are produced from fossil fuels. These fuels are combusted in heat engines to generate mechanical energy, which is then transformed through electrical generators into electricity for utilization and storage. In contrast, there is a neat heat engine called thermoelectric generator (TEG) which is able to convert temperature differences directly into electrical voltages via the Seebeck effect (Bender *et al.*, 1987). Upon supply of electrical energy, TEG devices can also work as heat pumps driven by Peltier effect, which is roughly an inverse process of the Seebeck effect (Bubnova *et al.*, 2012). According to its working principles, a TEG device neither requires moving parts nor consumes liquid or gas media, implying favorable qualities, such as high reliability and eco-friendliness (Bubnova *et al.*, 2011). Moreover, TEG devices can employ low-quality heat, which is otherwise dissipated (Du *et al.*, 2012; Hiroshige *et al.*, 2006). Therefore, the research of thermoelectricity has attracted great interest from both scientific and industrial communities.

The thermodynamic limit of the energy-conversion efficiency of a TEG device is defined by reversible car not cycles. The energy-conversion efficiency, namely the output electrical energy over the input thermal energy, is a function of the materials, figure-of-

* Corresponding author: ashischemru@gmail.com

merit, average working temperature of the device, and temperature difference between the hot and cold ends (Yakuphanoglu *et al.*, 2008; Vineis *et al.*, 2010). Although efficiency can be improved via thermal engineering, it is figure-of-merit (ZT) that fundamentally predominates (Kim *et al.*, 2013). The figure-of-merit of thermoelectric materials is $ZT = S^2\sigma T/\kappa$, where, S (V/K) is Seebeck coefficient or thermopower, σ (S/cm) is electrical conductivity, κ is the thermal conductivity and T is absolute Temperature. Furthermore, it should be noted that electrical conductivity, Seebeck coefficient and thermal conductivity are not independent, namely it is hardly possible to optimize one parameter without affecting the other parameters. Typically a TEG element, which should meet the following criteria:

- a) The thermal conductivity is as low as possible to maintain larger temperature difference,
- b) A higher Seebeck coefficient is preferred to achieve higher Seebeck voltages and
- c) A higher electrical conductivity is required for larger short-circuit current.

In general, inorganic materials showed high performance for thermoelectric properties, nevertheless, they have huge drawback in processing, cost and heavy weight. Given the aforementioned obstacles met by current inorganic thermoelectric materials (Du *et al.*, 2012); Jakobsson *et al.*, 2006), organic candidates are attracting more and more attention. After all, organic materials are potentially abundant, light-weight, flexible, solution-processable and low-cost. Moreover the marvelous development of organic electronics has provided hundreds of organic semiconductors with the highest field-effect mobilities approaching that of polycrystalline silicon (Hiroshige *et al.*, 2007; Kok *et al.*, 2004). In particular, there are two features of organic solids that justify serious consideration and devoted endeavor to exploit organic thermoelectric materials (Chang *et al.*, 2009; Luo *et al.*, 2013; Garreau *et al.*, 1999). Firstly, thermal conductivity of organic materials is typically below $1 \text{ W m}^{-1}\text{K}^{-1}$ approaching the lower limit of thermal conductivity of inorganic thermoelectric materials (Ouyang *et al.*, 2005; Tsai *et al.*, 2011). Second, electronic structures of organic (semi) conductors are fairly tunable through molecular chemistry and doping treatments (Meannig *et al.*, 2001; Nollau *et al.*, 2000). Therefore, organic, thermoelectric materials hold much promise in applications at low temperatures (Ouyang *et al.*, 2004; Park *et al.*, 2013). Despite all the above advantages, further development in organic thermoelectric materials is impeded by bottleneck problems including low electrical carrier mobilities and mediocre Seebeck coefficients.

In this study, we investigate an innovative route for processing PEDOT: PSS into TE devices. We also describe a simple wet process that aims at enhancing the power factor of PEDOT: PSS layers. This straightforward method allowed us to increase the power factor of the polymer up to $14.5 \mu\text{W}/\text{mK}^2$ at 45% concentrated HI treated film. The combination of the simple deposition process and the secondary doping method (HI treatment) led to the fabrication of flexible thermoelectric devices with improved sensitivity.

Materials and Methods

Aqueous PEDOT: PSS solution (1.3 wt%, CLEVIOS™ PH1000) was purchased from Heraeus Precious Metals, GmbH & Co. KG, and the weight ratio of PSS to PEDOT was 2.5. Hydroiodic acid (HI, 55%) was purchased from Sigma-Aldrich. Ultrapure water (Water purification system, Human Power I+) was used for all experiments including the preparation of acid solutions, and cleaning steps.

Electrode preparation

Glass substrate of area $4.0 \times 4.0 \text{ cm}^2$ was cleaned successively using ultra-sonicating in acetone, isopropyl alcohol and deionized water for 30 min per each treatment, and then dried in an oven at $120 \text{ }^\circ\text{C}$ in ambient condition. The PEDOT:PSS filtered through a 1.0 mm size filter was spin-coated at 2000 rpm for 40 s on a cleaned glass substrate that was pretreated 10 min with UV/ozone plasma. The substrate coated with PEDOT: PSS was then annealed on a hot plate in the ambient condition at $120 \text{ }^\circ\text{C}$ for 10 min to remove the residual amount of water. Then, PEDOT: PSS film was immersed in HI at different concentrations for 30 min. subsequently, the PEDOT: PSS film was washed with acetone and deionized water to remove the residual HI prior to drying at $120 \text{ }^\circ\text{C}$ for 60 min. The HI treated film was highly stable during the washing step, while as-prepared film was washed away from the glass substrate.

Seebeck coefficient measurement

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 temperature and temperature difference were measured using calibrated thermocouples. The resulting Seebeck voltage 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.

Conductivity measurement

Sheet resistivity, ρ_s of the multilayer films with finite thickness, w were measured using four-point probe head (1 mm probe spacing) connected to Keithley 2400 source meter and the body resistivity, ρ were determined based on equation, $\rho = \rho_s w = (V/I)wCF$, where V is the voltage, I is the current, and both C and F are the correction factors according to the dimension of the thin films. The electrical conductivity, σ , was obtained by simply inverting the corresponding value of the body resistivity, ρ^{-1} .

Thickness Measurement

The Thickness of the multilayer films deposited onto a silicon wafer was determined using real-time spectroscopic ellipsometer (Elli-SE-F Ellipso Technology) equipped with

a Xe arc lamp (350-820 nm), a rotating polarizer, a liquid cell with optical access at an incidence angle of 60° , an analyzer, and a multichannel detection system. The experimental data including optical functions of refractive index, n and extinction coefficient, k were fitted to Lorentz model.

The transmittance and absorption spectra were recorded by a UV/visible spectrophotometer (Beckman Coulter, US/DU 7000 Series). The thickness measurement of PEDOT: PSS film was performed using atomic force microscopy (AFM) (Park Systems, XE-100).

Results and Discussion

Preparation of electrode

PEDOT: PSS solution was spin coated on glass substrates. The coated substrate was annealed at 120°C for 10 min in hot plate. After cooling, the substrate was dipped into different concentration of HI solutions for 30 min. The treated substrate was washed with acetone and deionized water and annealed at 120°C for 60 min in hot plate. The water surrounding the samples became lightly turbid during the washing after HI treatment. The chemical nature of this phenomenon was not investigated, but it is most likely due to the desorption of PSS from the layer, as stated by Ouyang *et al.* (Ouyang *et al.*, 2004). The removal of PSS from the PEDOT: PSS thin film caused by HI is obviously evidenced by the UV absorption spectroscopy. Dipping layers of PEDOT: PSS in a hydroiodic solution bath triggers several noticeable changes. After a 30 min submersion the electrical conductivity, the mechanical resistance and the stability toward water were drastically improved. Longer immersions (up to 3h) did not improve further electrical and mechanical properties of the material. The water contact angle was measured to be $(41\pm 3)^\circ$ on HI treated PEDOT:PSS films, whereas the droplet was readily absorbed by the pristine polymer layer. The effect of a water bath on a pristine polymer layer and an HI treated polymer layer were illustrates in our previous work (Sarker *et al.*, 2015). While being dipped into water, the untreated polymer rapidly dispersed in the bath, leading to an aqueous dispersion of the polymer. In contrast, the treated polymer films stayed solid and their physical and electrical properties remained unchanged, no matter the duration of the water immersion. The dipping in HI enhanced the hydrophobic behavior of the layer, thus preventing its dispersion in water.

UV/visible absorption

UV/visible absorption spectra of PEDOT: PSS film was measured after using different concentration of HI solutions (Fig. 1). After HI treatment the absorbance was decreased tremendously in all the concentration of HI solutions. Among the HI concentrations the absorbance was gradually decreased with the concentration increased. This indicates the effect of concentration of HI in the PEDOT: PSS thin film. The removal of PSS from the

PEDOT: PSS film is highly depending on the concentration of HI solution. The two peaks at 196 and 225 nm are formed from PSS. These peaks are gradually decreased with the concentration increased. The dependency of HI concentration on the removal of PSS from the PEDOT: PSS film is clearly observed from this UV/visible absorption spectra. The peak at 225 nm is split into two peaks after HI treatment. This indicates the structural changes in remaining PSS. There is no massive change in PEDOT in the PEDOT:PSS film which can be observed in higher wavelength range (250-300 nm) in the visible absorption spectra.

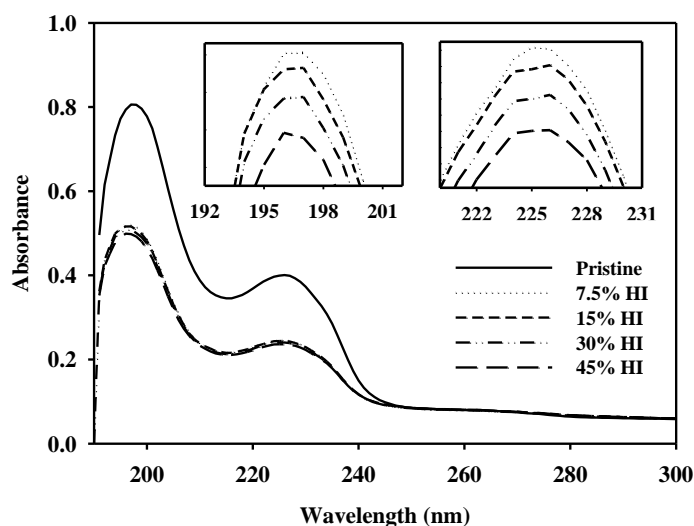


Fig. 1. UV absorption spectroscopy of pristine and different concentrated HI treated PEDOT: PSS thin films. Insets indicated the magnification of PSS peaks.

Conductivity of HI treated PEDOT: PSS thin film

The conductivity improvement resulting from such doping steps is probably due to the removal of a fraction of PSS from the layer, followed by unfolding of the macromolecular chains and an improvement of the current percolation through the PEDOT network. The increased conductivity of the PEDOT: PSS film by the acid treatment is mainly attributed to phase separation of PEDOT and PSS chains. This leads to larger grain sizes of PEDOT and excess insulate PSS on the film surface can be washed away.

Xia et al. have reported that the interaction between PEDOT and PSS chains can be lowered by the acids, resulting in the separation between PSS and PEDOT chains (Xia *et al.*, 2010). In addition, the acid anions may penetrate into the PEDOT: PSS film and replace some PSS⁻ as the counter-anions. These PSS anions can combine with protons of the acid to become hydrophilic PSSH and be removed from the PEDOT: PSS film in the presence of aqueous solution. Moreover, the hydrophobic PEDOT chains will be changed

from the coiled conformation to the linear or extended-coil conformation, which helps the inter-chain charge transport and increases the conductivity of the film. When deposited onto flexible materials like PET films, and excellent conformability of the layer was observed, with a stable electrical conductivity measured at 1200 S/cm.

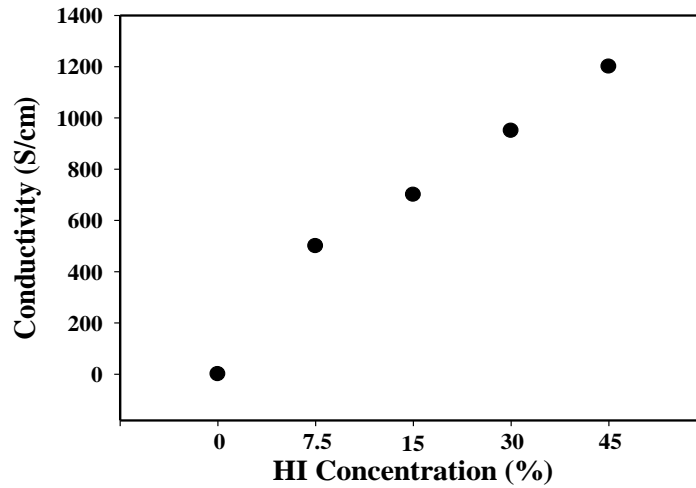


Fig. 2. Conductivity of pristine and different concentrated HI treated PEDOT: PSS thin films.

Thermoelectric power improvement through HI treatment of PEDOT: PSS layers

The pristine PEDOT: PSS thin film showed Seebeck coefficient around 14~18 $\mu\text{V}/\text{K}$, where the electrical conductivity was very poor (0.02 S/cm). Due to the lowest electrical conductivity, the power factor becomes negligible. So, it is imperative that the overall thermopower should be improved to get the highest conversion of heat to electricity.

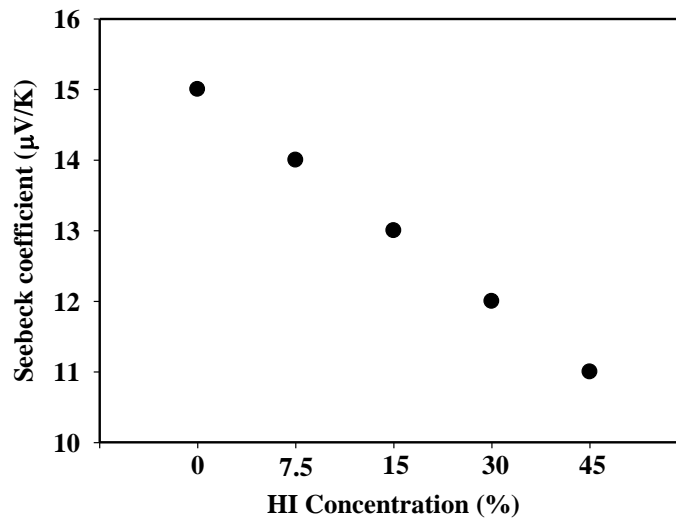


Fig. 3. Seebeck coefficient of pristine and different concentrated HI treated PEDOT: PSS thin films.

To increase the conductivity, the PEDOT: PSS thin film was treated with different concentration of HI solution, which were prepared by the dilution of concentrated (55%) HI solution. The used concentrations were gradually increased up to 45%, where the highest electrical conductivity was observed. The Seebeck coefficients were gradually decreased with the concentration of HI increased due to the rapid growing of electrical conductivity. With the enlarged electrical conductivity, the potential difference (V) of the two point of the film decreased and ultimately the Seebeck coefficient reduced to 11 $\mu\text{V/K}$.

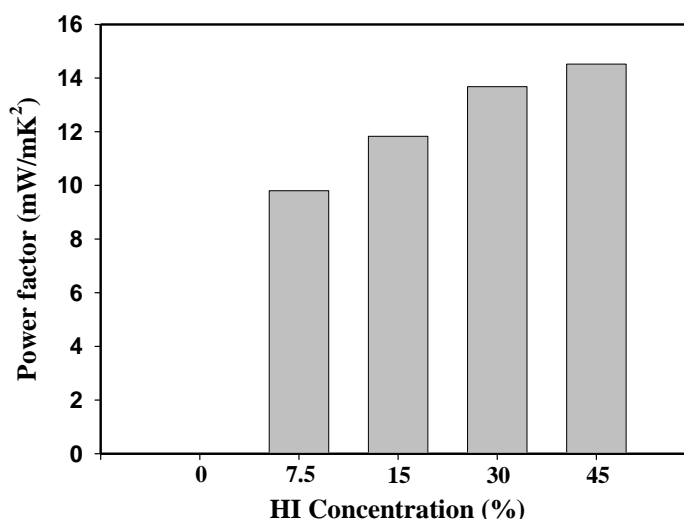


Fig. 4. Power factor of pristine and different concentrated HI treated PEDOT: PSS thin films.

To improve the power factor of the organic polymer the secondary doping is necessary which can improve the power factor throughout the electrical conductivity. The lower thermopower can be enhanced by the treatment of HI. This thermopower enhancement can be explained by the hydrophobicity of the layer, reducing the diffusion length of aqueous solutions inside the polymer layers. For the same reason, when lower concentration of HI was used onto a pristine PEDOT:PSS layer, the power factor enhancement was moderate 9.8 $\mu\text{W/mK}^2$, whereas a higher concentration of HI led to more efficient secondary doping with a power factor enhancement up to 14.5 $\mu\text{W/mK}^2$.

Conclusion

A simple HI treatment has been demonstrated to improve the thermopower of PEDOT: PSS up to 14.5 $\mu\text{W/mK}^2$. This secondary doping approach was successfully achieved by the control of concentration by water 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 14.5 $\mu\text{W/mK}^2$ was obtained at the concentration of 45% HI. This

enhancement of Seebeck coefficient for organic polymers opens the way for various applications such as heat flux sensing and more importantly heating/cooling and power generation from waste heat.

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