Highly stretchable organic thermoelectrics with an enhanced power factor due to extended localization length

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A B S T R A C T

Wearable electronics, as a new form of ubiquitous technology, require a sustainable self-powering system with an enhanced mechanical durability. In this report, we demonstrate a conducting polymer based stretchable thermoelectric performance with a synergetic effect of an enhanced power factor due to electron delocalization. The fluorosurfactant treatment of poly(3,4-ethylenedioxythiophene):poly(styrene-sulphonate) (PEDOT:PSS) films induced a significant dedoping effect with an enhanced Seebeck coefficient and a morphological change into an elongated lamellar structure. Such structural transformation led to a reduced transport dimensionality with strongly extended electron delocalization yielding a simultaneous enhancement of the electron mobility and the Seebeck coefficient, which produced an improved thermoelectric power factor. Most notably, the mechanical durability of the PEDOT:PSS film was greatly improved tolerating up to a 60% static strain and over several hundred cycles of 50% strain. The demonstrated concomitant enhancement of the mechanical stretchability and thermoelectric performance inspires a promising approach for improving shape-adjustable self-powering devices.

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1. Introduction

Recently, the prospect of wearable electronics as a new paradigm of ubiquitous electronics has been highlighted and a variety of their new functionalities has been developed and tested [1–8]. Operation of these devices requires a continuous self-powering system in order to be functional in any environment [5,9,10]. Various self-powering schemes, such as nano-generator [11,12] and solar cell [13] have been under intense research. The thermoelectric (TE) power generation could be a promising energy source because it sustains a highly reliable power generation without complex components. In addition, a human body maintains a constant temperature regardless of the outdoor weather. The use of the TE device for the wearable electronics can be boosted when the TE materials are able to endure a mechanical strain in order to adjust dynamic motions of the human body. In this strategy, several attempts have been made to enhance mechanical durability of TE materials [4,5,9,14–19]. A flexible TE generator using inorganic bulk particles of Bi₂Te₃ and Sb₂Te₃ has been shown to be operational with a bending radius as low as 20 mm [14]. Carbon nanotube-based composites also displayed the flexible thermoelectricity with an exceptional bendable radius of 2 mm [15]. Intercalation of organic materials into a layered transition metal dichalcogenide (TMDC) also demonstrated flexible TE properties [16]. In addition to the flexible TE operation, the stretchable TE performance was also recently demonstrated by using TMDC nanosheets [9]. However, these materials have drawbacks of scarcity of materials, high temperature synthesis and processing, high production costs, and/or low power generation.

Organic TE materials [20–24], such as conducting polymers, could draw a high hope for the wearable self-powering applications [25]. They are inherently soft, lightweight, and flexible, and can even be stretchable with some chemical additives [26–28]. Besides, they offer several advantages over traditional TE materials, such as low production costs, natural abundance, and facile large-area deposition. While the applications of wearable organic TE module are still in proof-of-principle stage, various device architectures and
fabrics have been proposed and tested [22,24,29,30]. The performance of a TE material is determined by the dimensionless figure of merit $ZT = S^2\sigma T/k$, where $S$, $\sigma$, $T$, and $k$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively [31]. Fine tuning of the parameters, $S$, $\sigma$, and $k$ is essential to improve the efficiency of a thermoelectric power conversion. Unfortunately, these parameters are not independent and entangled each other mostly through trade-off relations [32]. The intrinsic low thermal conductivity of organic materials ($<0.5\ W/mK$) [33–35] is an undeniable merit for improving the $ZT$ value. Most importantly, the organic TE materials could have a complementary relation between $S$ and $\sigma$ in contrast to the conventional trade-off relation in inorganic TE materials, where increasing $S$ generally reduces $\sigma$. This complementary relation in organic TE materials is highly desirable for improving the thermoelectric power factor ($PF = S^2\sigma$) [33].

Poly(3,4-ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS), one of the representative conducting polymers, is water-soluble, air stable, restorable, highly transparent, and amenable to a solution-based coating. Above all, its conductivity can be remarkably enhanced (by 2−3 orders of magnitude) by additional solvent treatments, such as sorbitol, ethylene glycol (EG), dimethyl sulfoxide (DMSO), sulfuric acid ($\text{H}_2\text{SO}_4$), or nitric acid ($\text{HNO}_3$) [36–41]. These solvent treatments partly wash out the insulating PSS and induce a morphological rearrangement from separated coil-like grains to aggregated and elongated grains [42,43]. In the extreme case, the effect of solvents can even increase both $S$ and $\sigma$ simultaneously in contrast to the trade-off between these parameters in inorganic TE materials [32,33]. Such peculiar behavior was attributed to the minimized total dopant volume, which assists thermally activated hoppings due to reduced effective tunneling distances [33]. Recent theoretical study emphasized the doping effect on structural configuration and electronic scattering in optimizing $ZT$ [35]. But detailed microscopic understanding on the behavior of the charge transport need to be further addressed.

In this work, we report the PEDOT:PSS based stretchable thermoelectric performance with a synergetic effect of an enhanced power factor due to electron delocalization. The PEDOT:PSS film with the addition of fluorosurfactant Zonyl-FS 300 (Zonyl) displayed a significant dedoping effect, leading to an enhanced $S$ and also a morphological change into a stronger lamellar structure with elongated grains. A detailed study of the carrier transport revealed that the dimensionality of the charge transport was reduced from 2D- to 1D-like hopping with a strongly enhanced electron delocalization. As a result, a simultaneous increase of both $S$ and $\mu$ was obtained, resulting in an improved power factor. Most importantly, the PEDOT:PSS films with the addition of Zonyl exhibited a robust stretchable thermoelectric performance enduring up to 60% strain and over several hundreds of strain cycles (up to 50% strain). The demonstrated mechanical durability together with the enhanced TE performance of the conducting polymer establishes a new avenue for further advances in thermoelectric self-powering systems for wearable electronics.

2. Experimental

2.1. Sample preparation and characterization

A PEDOT:PSS solution (Clevis PH1000, Heraeus) was mixed with 5% DMSO and different amounts of Zonyl FS-300 (0%, 0.1%, 1.0%, and 10.0%) in a nitrogen ($N_2$) filled glove box, which were labeled as PDZ 0%, PDZ 0.1%, PDZ 1%, and PDZ 10%, respectively. The Zonyl FS-300 used in this study was purchased from Dupont. The solutions were stirred by a magnetic bar for more than 6 h at room temperature. $\text{SiO}_2$ (300 nm)/$p$-Si substrates were used for transport measurements and quartz glasses were used for optical spectroscopy. Prior to a spin coating, these substrates were cleaned with acetone, ethanol, and deionized water in sequence. In order to perform a stretchable performance, the PDMS (Sylgard 184) purchased from Dow Corning was used. A base and curing agent of PDMS were mixed with a ratio of 15:1. The mixed solution was spin-coated on a Si wafer at 200 rpm for 120 s. The spin-coated PDMS films were cured at 50 °C for 12 h. In order to induce a hydrophilic surface of PDMS, $\text{UV}_2\text{O}_3$ of Mercury lamp (254 nm) was irradiated for 15 min [27]. After filtering the PDZ solution through a PVDF syringe (0.45 µm), the solution was spin-coated at 1000 rpm (60 s) on the PDMS substrate and at 2000 rpm (60 s) for other substrates. Typical thicknesses of the spin-coated films were ~100 nm, determined by using a surface profiler (P-6, KLA Tencor) and atomic force microscopy (DI-3100, Veeco). Then, the prepared films were annealed on a hot plate at 120 °C for 20 min.

Raman spectra were recorded by using Alpha 300R spectrometer (WITec) with a 532 nm laser source. The laser spot on the sample was ~900 nm diameter with 0.8 numerical aperture (NA) of 50× objective lens, and the obtained spectra were all averaged for 10 repeated acquisitions. UV–Vis–NIR spectra were measured by using Cary 5000 spectrometer (Agilent). The spot size of a light source was 5 mm in diameter. The UV–Vis–NIR spectra were recorded for 1 nm step with a scan rate of 300 nm/min. A D2 lamp for the UV region and a tungsten halogen lamp for the Vis-NIR region were alternatively used for source lights. XPS was performed by utilizing a Thermo Scientific spectrometer (K-Alpha) with a monochromatic Al Ka X-ray source (1486.6 eV). The spot size used for the incident x-ray was 400 µm.

2.2. Electrical and thermoelectric measurement

All electrical measurements including temperature and electric field dependent resistance were carried out in a high vacuum (<10−6 Torr) by using a physical property measurement system (PPMS, Quantum Design). 4-terminal measurements were performed with a Keithley 2636A sourcemeter and a Keithley 2182A nano-voltmeter. For contact electrodes, thermally deposited Au (40 nm)/Cr (0.5 nm) layers were used. Prior to measurements, samples were annealed at 385 K for 1 h in the PPMS chamber in order to eliminate residual moisture.

The temperature dependent resistances were recorded from 10 K to 300 K. Typical source currents used for measurements were kept less than 1 μA to prevent thermal effect at low temperature. Temperature dependent Seebeck coefficients were measured by using a thermal transport option (TTO) of the PPMS. For the measurement, the prepared PDZ solution was spin-coated on a 7 mm × 15 mm quartz substrate. Then, 4-terminal Au/Cr electrodes (1 mm width and 3 mm separation) were thermally deposited on the prepared films. The top and bottom electrodes were connected to heater and cold-foot, respectively. The central two electrodes were used to sense thermoelectric voltages and temperature gradients. At each temperature, the Seebeck coefficient was measured with a 0.1% temperature stability. The recorded data were average values of 60 individual measurements. The typical standard deviations of measured $S$ values were less than 0.3 µV/K.

2.3. Stretchable measurement

The PDZ films were prepared on pre-strained PDMS substrates in order to enhance stretchable performances of the PDZ films. The PDMS substrates were pre-strained (5% strain) by fixing the edges of the substrates with usual clips. Then, the PDZ solution was spin-coated on the pre-strained PDMS and annealed. For a flexible electrical contact, Eutectic Gallium–Indium (EGaIn, Sigma Aldrich)
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