A Highly Conductive Conjugated Polyelectrolyte for Flexible Organic Thermoelectrics

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ABSTRACT

Organic thermoelectrics have attracted considerable attention owing to their remarkable advantages, including room-temperature power generation, skin-attachable/wearable applications with biocompatibility, and solution-based high-throughput fabrication. Self-doped conjugated polyelectrolytes (CPEs) constitute a promising class of conductive organic materials that are considered potential candidates for organic thermoelectrics.

However, the low power factor of CPEs derived from their low electrical conductivity (σ) has been a major drawback in CPE-based thermoelectrics. Herein, we report a strategy for enhancing the thermoelectric performance of CPEs through a post-treatment using aq. H_2SO_4 solution. The post-treatment increases σ by two orders of magnitude, originating from H_2SO_4 -induced doping accompanying a significant increase in charge carrier concentration. Consequently, a power factor of $3.0 \mu\text{W m}^{-1} \text{K}^{-2}$ is achieved at room temperature. Furthermore, using this highly conductive H_2SO_4 -doped CPE, we developed flexible thermoelectric generators that allow durable power generation under repetitive mechanical bending stresses. Our findings provide insight into developing high-performance and versatile CPEs for next-generation organic thermoelectrics.

1. INTRODUCTION

Thermoelectrics, which are capable of directly converting thermal energy into electricity, have attracted considerable attention as a promising renewable technology that enables the recovery of waste heat.¹ The energy conversion efficiency of thermoelectric materials is evaluated by a dimensionless figure of merit ($ZT = S^2\sigma T/\kappa$, where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively).²⁻³ To date, major advances in the field of thermoelectrics have been achieved using inorganic-based crystalline materials with engineered nanostructures to control their phonon and electron transport, resulting in high ZT values of more than 2.⁴⁻⁶ However, these major achievements are mainly limited to high-temperature applications, and thus the challenge remains to demonstrate efficient room-temperature thermoelectrics.⁷ Organic semiconducting and conducting materials have been

considered suitable candidates for these types of room- and low-temperature thermoelectrics, as they offer a good thermal stability of up to ≈ 200 °C.⁸ In addition, organic materials possess several tremendous advantages: (i) they are earth-abundant elements; (ii) they have low κ as compared to their inorganic counterparts;⁹⁻¹¹ (iii) they are light weight, leading to high power density;¹²⁻¹⁴ (iv) they have mechanical flexibility for use in deformable and wearable applications;¹⁵⁻¹⁹ and (v) they offer solution processability that allows for high-throughput fabrication using cost-effective printing techniques (so-called “printed thermoelectrics”).²⁰⁻²⁴

Conducting polymers (CPs) are representative and promising organic thermoelectric materials. In particular, aqueous-based CPs can be readily processed in eco-friendly ways.^{15, 25-29} The solution processability of aqueous CPs is afforded by producing a colloidal complex of π -conjugated polymers with an excess number of bifunctional counter-ions that act as soluble templates, as well as charge-balancing dopants.³⁰⁻³¹ This type of solution-processable CP complex [e.g., poly(3,4-ethylenedioxythiophene) or polyaniline doped with an insulating polyelectrolyte, poly(styrene sulfonate)] exhibits a high charge carrier density (n) of $\approx 10^{21}$ cm⁻³ with excellent doping stability.³²⁻³³ However, these heavily doped CPs have an intrinsically low $\sigma \leq 10^{-1}$ S cm⁻¹ due to the inevitable excess of insulating ionic templates, and the charge transport properties of these CPs are particularly sensitive to the microscale/nanoscale morphology of insulating and conducting binary composites.^{19, 34-35} For these reasons, considerable efforts have been made to improve the conducting network and morphology of CP films using numerous film-engineering approaches.³⁶⁻³⁸

In parallel, the aqueous solubility of CPs can also be induced by introducing ion-functionalized side chains to the conjugated backbone. The resulting structure is known as a conjugated polyelectrolyte (CPE), in which the doping charges on the polymer chains are stabilized by their own ionic groups in the side chains, yielding the so-called “self-doped”

CPs.³⁹ Mai et al. reported on the thermoelectric properties of CPEs and studied the different counter-ion effects.⁴⁰ They also proposed that the introduction of hydrophilic side chains (e.g., tetraethylene glycol) affecting the polarization of counter-ions could increase their n and, consequently, σ .⁴¹ Nonetheless, because of the weak doping efficiency of self-doped CPEs with a low n , relatively low σ (up to ca. $10^{-1} \sim 10^{-2}$ S cm⁻¹) and, thereby, low thermoelectric power efficiencies have been obtained thus far.^{40, 42} Therefore, developing efficient doping methods is required to improve the performance of CPE-based thermoelectrics.

Herein, we present an approach to increase the thermoelectric performance of a CPE, namely, poly[2,6-(4,4-bis(potassium butanysulfonate)-4H-cyclopenta-[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT-SO₃K), by boosting its σ through a solution-based post-treatment method using aq. H₂SO₄ solution. The H₂SO₄-induced σ enhancement derives from an increase in the doping level of CPE, which is determined by absorption and photoelectron spectroscopy as well as Hall measurement. In addition, X-ray photoelectron spectroscopy analysis shows that the H₂SO₄ doping process accompanies the removal of potassium counter-ions in PCPDTBT-SO₃K, which is probably through a counter-ion exchange between potassium ions and the protons of H₂SO₄. The H₂SO₄ treatment effect on the structure of PCPDTBT-SO₃K was also studied by grazing incidence wide-angle X-ray scattering (GIWAXS) analysis. The H₂SO₄-induced variations in thermoelectric parameters (i.e., σ , S , and κ) and their relationships were investigated, and a significantly increased power factor ($S^2\sigma$) was achieved based on the σ enhancement of H₂SO₄-treated CPE (i.e., 3.0 μ W m⁻¹ K⁻¹ at room temperature). Finally, by using this highly conductive as well as mechanically deformable CPE, we successfully demonstrated flexible thermoelectric generators that provide durable and reliable thermoelectric performance under repetitive mechanical bending stresses.

2. RESULTS AND DISCUSSION

In this study, a representative self-doped conducting CPE (PCPDTBT-SO₃K) was employed; the synthesis of PCPDTBT-SO₃K has been reported in previous studies.⁴² Briefly, PCPDTBT-SO₃K was synthesized through the Suzuki coupling of 2,6-dibromo-4,4-bis(potassium butanylsulfonate)-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) with a Pd(PPh₃)₄ catalyst in a mixture of dimethylformamide and H₂O at 100 °C for 24 h. Then, PCPDTBT-SO₃K was purified through dialysis against a cellulose tube (molecular weight cut-off: 7,000 g mol⁻¹) in deionized water. Figure 1a presents the structure of pristine self-doped PCPDTBT-SO₃K and H₂SO₄-treated PCPDTBT-SO₃K. We propose the H₂SO₄-doped chemical structure and a H₂SO₄ doping mechanism with a potential path for protonic acid doping (Figure S1, supporting information), on the basis of a previous research reported by Yurash et al.⁴³ The doping charges generated as a result of H₂SO₄ treatment can be coupled with sulfonate anions and hydrogen sulfate anions of H₂SO₄. These anions are energetically favorable counter ions because their delocalized structure can effectively stabilize the delocalized charges on the polymer backbone.⁴⁴ Moreover, they can be much more favorable than SO₃⁻ of PCPDTBT-SO₃K by considering the size and steric hindrance of the polymer. The sample preparation and H₂SO₄ treatment method are presented in Figure 1b. To prepare the PCPDTBT-SO₃K films with a thickness of ≈1 μm (denoted as “pristine”), a solution of PCPDTBT-SO₃K dissolved in water with a concentration of 0.7% (w/w) was drop-casted on glass or plastic substrates. The sample denoted as “H₂SO₄-treated” was fabricated through a post-treatment by dropping 10 M H₂SO₄ solution onto pristine PCPDTBT-SO₃K films. As shown in the atomic force microscopy (AFM) images in Figure S2, supporting information, the H₂SO₄ treatment resulted in a slightly increased root-mean-square (rms) roughness of 3.92 nm compared to that of the pristine films (3.73 nm), with similar film formation.

Figure 1. a) Chemical structure of self-doped PCPDTBT-SO₃K and chemical H₂SO₄ doping process and b) preparation of a PCPDTBT-SO₃K thick film and H₂SO₄ treatment process.

Figure 2a shows the ultraviolet–visible–near-infrared (UV–vis–NIR) absorbance spectra of pristine and H₂SO₄-treated PCPDTBT-SO₃K films. This absorption analysis enables a comparison of the doping-level changes of the CPE before and after H₂SO₄ treatment. The pristine film exhibits a strong absorption (*via* π – π^* transition and intramolecular charge transfer interaction) in the UV–vis range with an optical bandgap energy of 1.39 eV. The pristine film also exhibits two broad and weak absorptions in the regions of 900–1500 nm and ≥ 1600 nm, which correspond to polaronic transitions. Upon H₂SO₄ treatment, the polaronic absorption increased throughout the NIR region, whereas the π – π^* absorption clearly decreased based on the oscillator strength sum rule.⁴⁵ To further compare the n difference between pristine and H₂SO₄-treated films, we conducted Hall effect measurements. The n of pristine, $\approx 4.0 \times 10^{16}$

cm⁻³ increased remarkably to $\approx 5.0 \times 10^{18}$ cm⁻³ following H₂SO₄ treatment (Figure 2b). The both pristine and H₂SO₄-treated PCPDTBT-SO₃K films exhibit positive Hall coefficients ($\approx 3.0 \times 10^2$ and $\approx 3.0 \times 10^0$ cm³ C⁻¹, respectively), indicating that their majority carriers are holes and it is in agreement with their positive *S* values which will be discussed later. Even though the H₂SO₄ treatment increases the CPE's *n* by two orders of magnitude, the resulting *n* seems to be relatively low in highly doped organic semiconductors. The *n* estimated from Hall measurement represents Hall-effect-induced charge carriers, but not hopping charge carriers which, of course, also affect the thermoelectric properties. Recently, it has been proved that thermopower is generated from crystalline domains in highly doped polymers, while σ is limited by the localized carriers at the grain boundary.⁴⁶ Based on this, we hypothesis that H₂SO₄-induced changes in *S* and σ could be mainly attributed to the increase in coherent and incoherent *n*, respectively, although the CPE shows more highly disordered structures than polythiophene-based semi-crystalline conjugated polymers such as [poly(2, 5-bis(3-alkylthiophen-2-yl)thieno[3, 2-b]thiophene)]. Electron spin resonance (ESR) results also confirmed the H₂SO₄-induced doping level increase. The ESR signal originates from unpaired electrons (free radicals) that correspond to polaron charges on conjugated backbone. The ESR signal intensity of PCPDTBT-SO₃K was distinctly increased by H₂SO₄ treatment, with the increase in integrated area and decrease in full width at half maximum (Figure 2c).

This change in *n* altered the electronic structure of PCPDTBT-SO₃K, which was investigated using UV photoelectron spectroscopy (UPS). Figure 2d presents the secondary electron cutoff region of UPS spectra for pristine and H₂SO₄-treated films. The kinetic energy was obtained from the difference between the binding and HeI photon energies (21.22 eV). The abrupt drop in the low kinetic energy corresponds to the work function of the materials,

which was calculated by linearly extrapolating the kinetic energy onset. As shown in the inset in Figure 2d, the pristine film had a work function of 5.0 eV. As a result of the H_2SO_4 treatment, the work function increased to 5.2 eV, indicating H_2SO_4 -induced p-type chemical doping of PCPDTBT- SO_3K . Considering all of the evidence, we concluded that the H_2SO_4 treatment method is an effective means of further increasing the n of CPEs.

Figure 2. a) UV–visible–NIR absorption, b) charge carrier density (n), c) x-band ESR spectra, and d) UPS spectra of pristine PCPDTBT- SO_3K and H_2SO_4 -treated films (the corresponding work function energies are given in the inset).

To understand the effect of H_2SO_4 treatment on the morphological structure of PCPDTBT- SO_3K , an X-ray diffraction analysis was conducted on the samples before and after H_2SO_4 treatment. As shown in one-dimensional scattering q_z profiles (Figure 3a), the pristine film showed a dominant lamellar scattering at $q_z = 0.76 \text{ \AA}^{-1}$ along the out-of-plane direction, which corresponds to a lattice spacing (d) of $8.26 \text{ \AA}$. A similar GIWAXS profile for PCPDTBT- SO_3K was reported previously.⁴⁰ Upon H_2SO_4 treatment, the well-resolved out-of-plane $[h00]$

reflection appeared at $q_z = 0.45 \text{ \AA}^{-1}$ ($d = 13.96 \text{ \AA}$), suggesting an improved out-of-plane ordering. The X-ray photoelectron spectra in Figure 3b reveal that the H_2SO_4 treatment removes potassium counter-ions in PCPDTBT- SO_3K , which was probably accomplished through a counter-ion exchange between potassium ions and the protons of H_2SO_4 (as suggested in the scheme shown in Figure 1a). The potassium ions that coordinated with excess bisulfate ions of H_2SO_4 were then removed from the films during the washing process. The removal of potassium ions may also influence the morphology structure of the H_2SO_4 -treated CPE films. In contrast to the substantial changes in lamellar structures, as shown in the two-dimensional GIWAXS images (Figure 3c), the H_2SO_4 treatment causes insignificant changes in π - π stacking [010] peak along the q_z and q_{xy} directions (i.e., intensity, stacking distance, and full width at half maximum), implying that the charge transport along π - π stacking direction in PCPDTBT- SO_3K can remain intact after H_2SO_4 treatment.

Figure 3. a) GIWAXS line-cut profiles in the q_z direction. b) X-ray photoelectron spectroscopy spectra of the K(2p) regions of pristine PCPDTBT- SO_3K and H_2SO_4 -treated films. c) two-dimensional GIWAXS images for the films.

Next, the effect of H_2SO_4 treatment on the thermoelectric properties of PCPDTBT- SO_3K was evaluated. The σ was first examined as a function of temperature ranging from 300 K (i.e., near room temperature) to 380 K. The σ of the films was measured using a four-point probe method, as shown in the inset of Figure 4a. The pristine films had a relatively poor σ of 0.1 S cm^{-1} at room temperature and 0.2 S cm^{-1} at 378 K (Figure 4a). By contrast, the H_2SO_4 -treated films exhibited a remarkably increased σ of 25 S cm^{-1} at room temperature and 34 S cm^{-1} at 378 K, which are two orders of magnitude higher than those of the pristine films. Moreover, the σ is more than one order of magnitude greater than that of hydrochloric acid-treated PCPDTBT- SO_3K , which has been reported previously.⁴² It is also noteworthy that this H_2SO_4 post-treatment method is more effective to enhance the electrical conductivity of CPEs through relatively severe H_2SO_4 doping than the pre-treatment method using molar equivalent of H_2SO_4 per monomer unit of CPEs.⁴⁷ This σ enhancement must be mainly attributed to the increase in n of H_2SO_4 -treated films. The increased σ by increasing the temperature indicates that a hopping transport mechanism dominates in this CPE system.

The transport characteristics of σ , S , and κ are closely interrelated with n . Therefore, the optimization of these three parameters is the most important route to maximize the thermoelectric performance of the materials. In general, S is inversely proportional to n because an increase in n reduces entropy changes, where the density of states, already occupied by indistinguishable carriers, rises.⁴⁸ Accordingly, the S of the pristine films, that is, $129 \mu\text{V K}^{-1}$ at room temperature, was reduced to $34 \mu\text{V K}^{-1}$ after H_2SO_4 treatment (Figure 4b); this is ascribed to the increase in n of H_2SO_4 -treated films. Figure 4c plots the power factor of each sample as a function of temperature. Despite the significant decrease in S , the $S^2\sigma$ value increased by one order of magnitude (i.e., from 0.23 to $3.0 \mu\text{W m}^{-1} \text{ K}^{-2}$ at room temperature)

because of the enhancement in σ . This $S^2\sigma$ value is one of the highest reported thus far in thermoelectric CPEs without any additional highly conductive components being introduced.⁴⁰⁻

⁴¹ Additionally, we examined the $S^2\sigma$ variation with respect to the concentration of H_2SO_4 treatment solution. By increasing H_2SO_4 concentration, the $S^2\sigma$ of H_2SO_4 -treated films was increased due to the contribution of enhanced σ (Figure S3, supporting information). It is noteworthy that a maximum $S^2\sigma$ of organic thermoelectric materials tends to appear when the electronic state alters from nondegenerate to degenerate states upon charge carrier doping.⁴⁹⁻⁵⁰

As shown in Figure S4, supporting information, the σ dependence of S and $S^2\sigma$ for PCPDTBT- SO_3K treated with varied concentration of H_2SO_4 follows an empirical fit of S proportional to $\sigma^{-1/4}$ and $S^2\sigma$ proportional to $\sigma^{1/2}$, respectively, without any slope changes. Based on this, we assume that H_2SO_4 -treated PCPDTBT- SO_3K has delocalized electronic states with non-metallic conductivity although the H_2SO_4 treatment significantly increases the doping level of PCPDTBT- SO_3K ; there can be still room to reach its maximum $S^2\sigma$ by further controlling its doping level.

Figure 4. a) Electrical conductivity (σ), b) Seebeck coefficient (S), and c) power factor ($S^2\sigma$) as a function of temperature ranging from 300 K (near room temperature) to 380 K for pristine PCPDTBT- SO_3K and H_2SO_4 -treated films. The inset schematic in a) shows the four-point probe system used to measure the σ of the samples.

The in-plane κ of the films was also investigated using a chip-based 3ω method. For a more accurate evaluation, all thermoelectric parameters were measured in the lateral direction. Figure 5a shows the temperature-dependent κ values of the PCPDTBT-SO₃K film with and without H₂SO₄ post-treatments. The pristine films exhibited a fairly low κ of 0.16–0.22 W m⁻¹ K⁻¹ in this temperature range. The κ of PCPDTBT-SO₃K was increased to 0.21–0.25 W m⁻¹ K⁻¹ by the H₂SO₄ treatment. This κ of the H₂SO₄-treated film was still low in comparison to that of other typical inorganic and organic thermoelectric materials,^{11, 51-52} which is clearly advantageous for obtaining higher ZT values. Using the κ and $S^2\sigma$ which were obtained from the samples prepared in the identical condition and measured in the same in-plane direction at each temperature, we derived the ZT values from figure of merit ($ZT = S^2\sigma T/\kappa$) as shown in Figure S5, supporting information. The H₂SO₄-treated sample provides an order of magnitude higher room temperature ZT compared to that of pristine PCPDTBT-SO₃K.

The κ characteristic changes induced by H₂SO₄ treatment were further studied based on the relationship with n and σ . The total κ is composed of contributions from electrons and phonons (i.e., lattice vibrations), with $\kappa = \kappa_e + \kappa_L$ (κ_e and κ_L are electronic and lattice thermal conductivity, respectively), in which κ_e is defined based on the Wiedemann–Franz law of $\kappa_e = L\sigma T$ (where L is Lorentz factor).^{4, 53} It was assumed that L of pristine and H₂SO₄-treated samples is equal to $L_0 = 2.44 \times 10^{-8}$ V² K⁻² for a free electron gas. In short, the n increase led to an increase in both σ and κ_e , because heat could also be transported by charge carriers.¹² Accordingly, the higher κ of the H₂SO₄-treated films as compared with that of pristine films may result from an increase in κ_e , as shown in Figure 5b. Moreover, as the temperature increased, the κ_e of H₂SO₄-treated films increased, whereas its κ_L became nearly comparable to that of pristine films at higher temperatures (Figure 5c). These κ_L values for pristine and

H₂SO₄-treated films corresponded to 99.9% and 87.7% of the total κ , respectively, which implies that the ratio of κ_e to the total κ was significantly increased by H₂SO₄-induced doping.

Figure 5. a) Total thermal conductivity (κ), b) electronic thermal conductivity (κ_e), and c) lattice thermal conductivity (κ_L) as a function of temperature for pristine PCPDTBT-SO₃K and H₂SO₄-treated films. The inset picture in a) presents the sample deposited on a prepatterned chip for in-plane κ measurement.

To generate more thermoelectric power from this highly conductive CPE and to demonstrate its mechanical durability, which is a required feature for flexible device applications, we fabricated flexible thermoelectric generators (TEGs) on polyethylene naphthalate used as a polymeric substrate. In addition, the successful fabrication of this flexible TEG verified the processing applicability of the H₂SO₄ treatment on various substrates, including flexible plastics. The TEG consisted of 10 legs of H₂SO₄-treated films electrically connected in series and thermally in parallel. Detailed geometric information on the TEG module is presented in Figure S6, supporting information. First, the mechanical compliance of H₂SO₄-treated film was evaluated by monitoring resistance change as a function of bending radius (r), as shown in Figure 6a. The bending deformation of the H₂SO₄-treated film with the r down to 2.5 mm produced negligible changes in resistance, indicating that the thermoelectric performance of the films was maintained under these types of stressed conditions. With a tighter bending $r \leq 2.2$ mm applied, the resistance of the film began to increase sharply, and as

a result, the resistance was approximately doubled by the extreme bending stress with r of 1 mm.

Figure 6b shows the voltage versus current output characteristics for the H₂SO₄-doped CPE-based TEG. Under a steady-state temperature difference (ΔT) of 27 K, the TEG exhibited a short-circuit current (I_{sc}) and open-circuit thermoelectric voltage (V_{oc}) of 0.28 μ A and 8.0 mV, respectively. The V_{oc} of TEGs can be defined based on the relationship of $V_{oc} = NS\Delta T$ (where N is the number of legs).⁵⁴ The experimentally obtained V_{oc} value is nearly comparable to the calculated value, indicating that the voltage of each leg was properly built up in the series-connected circuit. The power versus current output curve of the TEG is shown in Figure 6c. The TEG provided a maximum power output (P_{max}) of 0.56 nW across an impedance-matched load resistance of ≈ 27 k Ω , which corresponds to the expected P_{max} based on the relationship of $P_{max} = I_{sc}V_{oc}/4$.⁵⁵ In addition, the bending durability of the flexible TEG was also tested by measuring the power output after a bending cycle of 100 times, with an r of 10 mm as shown in Figure 6d. Upon repeated bending stresses, the TEG still provided 79% of the initial P_{max} (i.e., 0.44 nW). The reduction in power output of the flexible TEG was mainly ascribed to the decrease in current output. The reduced current output was attributed to damage in the silver connection caused by the poor adhesion of silver paste on plastic substrates. As indicated in Figure 6a, the H₂SO₄-treated film exhibited sufficient mechanical stability upon this bending stress. Therefore, we can conclude that this H₂SO₄-doped highly conductive CPE is a promising p-type thermoelectric material for demonstrating deformable and wearable organic thermoelectrics.

Figure 6. a) Resistance change (R/R_0 = final resistance/initial resistance) versus bending radius from 10 to 1 mm for the H_2SO_4 -treated film prepared on a plastic substrate. b) Plot of voltage output, and c) power output as a function of current output for the flexible TEG before and after a bending cycle of 100 times. The inset image presents a TEG fabricated on a plastic substrate. d) Photo of a flexible TEG loaded on a bending machine with a bending radius of 10 mm.

3. CONCLUSION

We proposed a means of improving the thermoelectric performance of a self-doped CPE (PCPDTBT- SO_3K) through a solution-based post-treatment using aq. H_2SO_4 for organic thermoelectrics. The H_2SO_4 treatment enabled a significant transition in the doping state of the CPE, which was proved by UV-vis-NIR and UPS spectroscopy as well as by Hall effect analysis. With an H_2SO_4 -induced increase in charge carrier density, the electrical conductivity of the CPE increased by two orders of magnitude (i.e., from 10^{-1} to 10^1 S cm^{-1}), thus leading to an enhancement in the thermoelectric power factor of PCPDTBT- SO_3K from 0.23 to 3.0 $\mu\text{W m}^{-1} \text{K}^{-2}$ at room temperature. Using this highly conductive H_2SO_4 -doped CPE, we also fabricated flexible TEGs on plastic substrates. The developed CPE-based TEG enabled durable

and reliable power generation based on the intrinsic flexibility of polymeric CPE. Although the thermoelectric efficiency of our H₂SO₄-treated CPE is not as great as that of state-the-art-of organic thermoelectric materials, this work can provide ways to develop high-performance and versatile CPEs for next-generation organic thermoelectrics and electronics.

4. EXPERIMENTAL SECTION

Materials and preparation: To prepare pristine PCPDTBT-SO₃K films with a thickness of ≈ 1 μm , PCPDTBT-SO₃K solution with a concentration of 0.7 wt% in deionized water was drop-casted on glass, plastic, silicon, and indium–tin–oxide/glass substrates that were pre-cleaned, followed by 15 min of UV/O₃ treatment for improved wetting with the water-based solution. The samples were stored overnight at room temperature, and after the water dried out, the films were annealed at 120 °C for 10 min. To prepare the H₂SO₄-treated films, a 10 M aqueous solution of H₂SO₄ (Sigma-Aldrich Chemical Co., Inc.) was dropped onto the pristine PCPDTBT-SO₃K films and left at room temperature for 5 min; longer treatment especially using diluted H₂SO₄ solutions causes swelling and partial dissolution of the films, which can be probably due to higher water content of the solutions. The samples covered with H₂SO₄ solution were then carefully washed with deionized water, and finally, the H₂SO₄-treated films were annealed again at 120 °C for 10 min. To fabricate a flexible thermoelectric module consisting of 10 legs of H₂SO₄-treated films, the pristine PCPDTBT-SO₃K films were deposited on a polyethylene naphthalate substrate pre-masked with Kapton polyimide tapes, and then the same H₂SO₄ treatment process was applied. Finally, after the masking tapes were removed, each H₂SO₄-treated film was electrically connected in series using silver paste.

Characterization: The electrical conductivity (σ) and Seebeck coefficient (S) of the samples were measured in the in-plane direction (transport parallel to the film surface) under the dynamic flow of Ar/H₂. The σ and S measurements were performed in a temperature range of

300 to 380 K using the commercially available thermoelectric tester RZ2001i (Ozawa Science Co. Ltd., Japan). The σ at each temperature was monitored under thermal equilibrium by a linear four-point probe technique. Then, a small thermal gradient was developed by locally cooling one side of the sample, in which the local cooling was achieved by air circulation through one side of the quartz pipes holding the sample. Among the four probes, the inner two probes were thermocouple probes, which measured the differences in temperature (ΔT) and voltage (ΔV) across the sample. The S value was calculated by estimating the linear fit slope ($\Delta V/\Delta T$) from five distinct data points obtained at each temperature. To obtain an accurate S of the samples, the corresponding S of platinum at each temperature was subtracted, where the obtained S was the difference between the sample and platinum electrode, $S_{\text{measured}} = S_{\text{sample}} - S_{\text{electrode}}$. The charge carrier density of the CPE films ($1 \times 1 \text{ cm}^2$) was measured using a Hall effect measurement system (Lake Shore 7700A) with the Van der Pauw configuration at room temperature under a magnetic field of 10 kG. The thicknesses of the samples were measured using a Tencor profiler. The resistance change in the H_2SO_4 -treated films as a function of bending radius was measured by a standard two-probe method using a Keithley 2400 multimeter, while the film was bent by a customized bending machine. The electrical contact to the samples was formed using platinum wires through a liquid metal, eutectic gallium–indium. The temperature of the hot side of the thermoelectric generator was controlled using Peltier thermoelectric modules (TE-63-1.4-1.15, TE Technology, Inc.), and the cold side was maintained at room temperature. The applied temperature was monitored using a thermometer (Mastech Company). For thermal conductivity measurements, the micrometer-thick films were deposited on chips purchased from Linseis and were measured using Linseis TFA. All ESR spectra were recorded using continuous wave Bruker EMX PLUS spectrometer operating at x-band (BrukerBioSpin, Rheinstetten, Germany). The spectra were recorded by collecting using

reported parameters⁵⁶⁻⁵⁷ and Bruker Xenon software was used to collect data and for spectral processing.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: XX.XXXX/acsami.XXXXXXXX.

Doping mechanism of PCPDTBT-SO₃K by H₂SO₄ (Figure S1), AFM images for pristine PCPDTBT-SO₃K and H₂SO₄-treated films (Figure S2), variation in σ , S , and $S^2\sigma$ as a function of the concentration of H₂SO₄ treatment solution (Figure S3), σ dependence of the S and the $S^2\sigma$ (Figure S4), temperature dependent thermoelectric figure of merit ZT for pristine and H₂SO₄-treated PCPDTBT-SO₃K films (Figure S5), geometric structure of a flexible thermoelectric generator (Figure S6).

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

ZT , figure of merit; S , Seebeck coefficient; σ , electrical conductivity; $S^2\sigma$, power factor; κ , thermal conductivity; κ_e , electronic thermal conductivity; κ_L , lattice thermal conductivity; L , Lorentz factor; n , charge carrier density; T , absolute temperature; ΔT , temperature difference; CP, conducting polymer; CPE, conjugated polyelectrolyte; PCPDTBT-SO₃K, poly[2,6-(4,4-bis(potassium butanysulfonate)-4H-cyclopenta-[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]; GIWAXS, grazing incidence wide-angle X-ray scattering; d , lattice spacing; UV-vis-NIR, ultraviolet-visible-near-infrared; UPS, UV photoelectron spectroscopy; ESR, electron spin resonance; AFM, atomic force microscopy; r , bending radius; TEG, thermoelectric generator; I_{sc} , short-circuit current; V_{oc} , open-circuit thermoelectric voltage; N , number of legs in TEG; P_{max} , maximum power output.

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Table of Contents (TOC) Graphic and Synopsis

A strategy to improve thermoelectric performance of solution-processable π -conjugated polyelectrolytes (CPEs) *via* H_2SO_4 doping method is reported, and finally, CPE-based flexible thermoelectric generators that allow durable power generation under repetitive mechanical bending stresses are demonstrated.