



One-Dimensional Nanostructure Engineering of Conducting Polymers for Thermoelectric Applications

Kwok Wei Shah ^{1,*,†}, Su-Xi Wang ^{2,†}, Debbie Xiang Yun Soo ² and Jianwei Xu ^{2,3,*}

- ¹ Department of Building, School of Design and Environment, National University of Singapore, 4 Architecture Drive, Singapore 117566, Singapore
- ² Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634, Singapore; wangs@imre.a-star.edu.sg (S.-X.W.); debbie-soo@imre.a-star.edu.sg (D.X.Y.S.)
- ³ Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
- * Correspondence: bdgskw@nus.edu.sg (K.W.S.); jw-xu@imre.a-star.edu.sg (J.X.)
- + Both authors contribute equally to this manuscript.

Received: 2 March 2019; Accepted: 25 March 2019; Published: 4 April 2019



Abstract: The past few decades have witnessed considerable progress of conducting polymer-based organic thermoelectric materials due to their significant advantages over the traditional inorganic materials. The nanostructure engineering and performance investigation of these conducting polymers for thermoelectric applications have received considerable interest but have not been well documented. This review gives an outline of the synthesis of various one-dimensional (1D) structured conducting polymers as well as the strategies for hybridization with other nanomaterials or polymers. The thermoelectric performance enhancement of these materials in association with the unique morphologies and structures are discussed. Finally, perspectives and suggestions for the future research based on these interesting nanostructuring methodologies for improvement of thermoelectric materials are also presented.

Keywords: thermoelectric; conducting polymer; one dimensional; nanostructure; nanocomposites

1. Introduction

Development of eco-friendly and sustainable approaches for energy generation is a major global challenge faced by the world today. Thermoelectric materials that allow generation of electricity from heat and vice versa to provide a green and economic way for power generation and refrigeration have drawn tremendous interest from both industrial and scientific communities over the centuries [1–5]. The energy conversion efficiency of a thermoelectric material can be evaluated by the temperature difference and a unitless figure of merit (*ZT*), which is defined as $S^2 \sigma T/\kappa$, where *S* (V K⁻¹) is Seebeck coefficient, σ (S m⁻¹) is electrical conductivity, κ (W m⁻¹ K⁻¹) is thermal conductivity and *T* (K) is absolute temperature. The power factor (*PF*) is the product of S² and σ , which is in general used to determine the thermoelectric performance of a thermoelectric material. The traditional high performing thermoelectric materials are mainly inorganic semiconductors or semimetals which possess moderate electrical conductivity and high Seebeck coefficient [6,7]. However, most of these materials are facing significant challenges in large- scale manufacturing and practical utilization due to their heavy weight, high cost, scarcity, toxicity, poor processability, brittleness and non-flexibility, particularly for applications in wearable sensors and electronic devices.

Given the limitations of the inorganic thermoelectric materials, the organic counterparts mainly based on conducting polymers and their nanocomposites, have gained tremendous research interest and clinched considerable achievements over the past two decades [8–15]. Conducting polymers have



been considered to be the next promising thermoelectric materials owing to their unique advantages including low cost, high mechanical flexibility, light weight, low or no toxicity, and intrinsically low thermal conductivity. In addition, the electronic structures of these organic semiconductors are fairly tunable via molecular chemistry and doping treatments. Polymer-based thermoelectric materials have intrinsically low thermal conductivity (0.1–0.5 Wm⁻¹ K⁻¹), and therefore, enhancement in Seebeck coefficient and electrical conductivity is more important. Currently, the-state-of-art conducting polymers for thermoelectric applications include poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) derivatives etc. The thermoelectric performance of these conducting polymers can be further enhanced through incorporation of various inorganic nanofillers (such as Te nanowires, Bi_2Te_3 nanowires, carbon nanotubes (CNTs), graphene, etc.), which give rise to the improvement in Seebeck coefficient and/or electrical conductivity while maintaining the low thermal conductivity.

It has been acknowledged that polymer's properties are highly related to the morphologies and structures. Nanoscaled conducting polymers, especially those with one-dimensional (1D) nanostructures (such as polymer nanowires, nanotubes, nanofibers, nanorods, etc.) have their own special set of advantages over their corresponding bulk materials due to the highly ordered structure, large surface area and superior carrier transport [9,16–19]. Various methods for synthesizing 1D conducting polymers have been developed, including hard or soft template-based methods and template-free methods, such as inverse microemulsion polymerization, electrospinning method, etc. [20]. To date, significant progress has been achieved in the 1D engineering of conducting polymers for a wide variety of applications, such as batteries, supercapacitors, sensors, transistors, electrochromic displays, photovoltaics etc. [21–24]. Unfortunately, the development and performance investigation of 1D structured conducting polymers and their composites for thermoelectric applications are still limited so far, compared to the extensive research on the nanostructured inorganic thermoelectric semiconductors or semimetals [25–31]. In this review, we present the recent examples of the "bottom-up" preparation of different kinds of 1D conducting polymers for thermoelectric applications. The enhanced properties associated with the unique morphologies, structures, dopants and doping levels of these materials are also discussed. Following this discussion, we introduce the reported strategies to construct 1D nanocomposite thermoelectric materials based on these conducting polymers with further performance improvement. Finally, we will end off with an outlook on the challenges and future exploration directions for this new class of organic-based thermoelectric materials.

2. D-Conducting Polymers and Their Thermoelectric Properties

Recently, considerable progress has been achieved in the construction of 1D nanostructures (such as nano/microfibers, nanowires, nanotubes, nanorods, etc.) with polymer-based materials for thermoelectric applications. In this section, we mainly introduce the synthetic approaches towards various 1D nanoscaled conducting polymers (including PEDOT, PPy, PANI and PTh derivatives) as well as their thermoelectric performance enhancement resulted from the unique structures.

2.1. *PEDOT*

PEDOT is the most widely investigated conducting polymer for thermoelectric application due to a high electrical conductivity when mixed with the respective additives or dopants, low thermal conductivity and a relatively large Seebeck coefficient upon appropriate treatment and optimization [21–23]. Moreover, PEDOT-based materials possess significant advantages, such as material abundance, superior optical transparency, solution processability, good physical and chemical stability, providing an opportunity for large-scale fabrication of flexible and printed thermoelectric devices.

In the past few years, the synthesis and investigation of nanostructured PEDOT for different applications are gaining increasing research interest [32–39]. In 2011, Taggart et al. first investigated the thermoelectric properties of PEDOT nanowires, which were synthesized by oxidative electropolymerization of 3,4-ethylenedioxythiophene (EDOT) monomer in aqueous LiClO₄ solution

via a hard template through a lithographically patterned nanowire electrodeposition (LPNE) approach with non-dependent control over the thickness and width of the nanowire (Figure 1) [34]. These PEDOT nanowire arrays (40–90 nm thick, 150–580 nm wide and 200 μ m long) exhibit much higher Seebeck coefficient (-122μ V K⁻¹ at 310 K) compared to bulk PEDOT films (-57μ V K⁻¹ at 310 K). Moreover, the electron mobility of the prepared PEDOT nanowires is two times higher than that of the films, which is in accordance with the better electrical conductivity of the nanowires (40.5 S cm⁻¹ versus 18.3 S cm⁻¹ (films) at 310 K). The greatly enhanced thermoelectric properties are attributed to the orderly arrangement of the PEDOT chains and the crystalline structure of PEDOT within the nanowires.



Figure 1. (a) Schematic synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowire arrays using the lithographically patterned nanowire electrodeposition (LPNE) process. (b) Bright field optical micrograph of PEDOT nanowire pattered on glass. (c) Atomic force microscope (AFM) image of an array of 40×200 nm PEDOT nanowires on glass. A height versus distance trace across these nanowires is shown at bottom. (d) Measured Seebeck coefficient versus nanowire height for PEDOT nanowires and films at 310 K. (e) Electron mobilities versus the film or nanowire height, showing also (horizontal line) the mean mobility value. Readapted with permission from American Chemical Society [34].

Using the hard-template method, Zhang et al. recently reported a three-dimensional (3D) assembly of PEDOT nanowires synthesized by electrochemical polymerization in 3D-alumina templates [39]. A free-standing network was attained after removal of the template. Two types of PEDOT nanowires (C-PEDOT and T-PEDOT) were generated by using different oxidants, FeCl₃ and Fe(Tos)₃, respectively. These two types of nanowires possess a similar average diameter of 12 nm, but with different lengths (0.5–5 µm for C-PEDOT and 0.2–0.7 nm for T-PEDOT), as shown in the TEM images (Figure 2a,b). The C-PEDOT nanowires, which consist of much longer polymer chains and higher molecular weights, exhibit an extremely high electrical conductivity of 540 S cm⁻¹ and an enhanced Seebeck coefficient, which is 2.6 times that of the PEDOT: poly(styrenesulfonate) (PSS) films. After hydrazine treatment, the 3D network can reach an optimum power factor of 35.8 µW m⁻¹ K⁻², which is the highest ever reported amongst all of the reported 1D conducing polymers based films.



Figure 2. Transmission electron microscopy (TEM) images of (**a**) T-PEDOT nanowires and (**b**) C-PEDOT nanowires. Scanning electron microscopy (SEM) images of (**c**) T-PEDOT nanowires and (**d**) C-PEDOT nanowire-based films. The scale bar is 500 nm for all images. (**e**) S, σ , and (**f**) power factor of C-PEDOT nanowire-based film with respect to the hydrazine treatment duration. Readapted with permission from Elsevier Ltd. [39].

In 2015, Hu et al. reported the thermoelectric performance of nanostructured PEDOT with various morphologies (Figure 3a-e) by chemical oxidation polymerization in reverse microemulsions with sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as the surfactant [35]. Tuning the quantity of oxidizing agent added and the rate of polymerization gave rise to PEDOT with different nanostructures, which were proved to have great effects on the thermoelectric properties (Figure 3f–h). The improvement in thermoelectric properties in terms of electrical conductivity, Seebeck coefficient and power factor follows the order of bulk PEDOT < globular nanoparticle < nanorod < nanotube < nanofiber. The PEDOT nanofibers exhibit the best electrical conductivity of 71.4 S cm⁻¹ and Seebeck coefficient of 48.0 μ V K⁻¹, which is considerably higher than those of the bulk powder samples (0.032 S cm⁻¹; S = 10.7 μ V K⁻¹). The mechanism study shows the oxidation/doping level of PEDOT, the carrier concentration and mobility and the orderly arrangement of the polymer chains all have close relationship with the thermoelectric performance enhancement of the PEDOT nanostructures. Later in 2017, the same research group also reported the relation of thermoelectric performance with post-treatment conditions (acid treatment with H₂SO₄ and chemical reduction using Na₂SO₃) for PEDOT nanorods synthesized by reverse microemulsion polymerization. Through varying the acid concentration and reduction treatment time, the intensity of doping and oxidation, the carrier type transition and orderliness of polymer chain interaction is adjustable. Therefore, the thermoelectric properties of PEDOT nanorods can be modified easily and efficiently [40].



Figure 3. SEM images of (**a**) bulk PEDOT power; (**b**) globular nanoparticles; (**c**) nanorods or ellipsoidal nanoparticles; (**d**) nanotubes; (**e**) nanofibers; (**f**) Seebeck coefficient and (**g**) power factor of bulk PEDOT and PEDOT nanostructures; (**h**) Carrier mobilities and carrier concentrations of bulk PEDOT and PEDOT nanostructures. Readapted with permission from The Royal Society of Chemistry [35].

Flexible fiber-based thermoelectric generators which are lightweight and 3D deformable are receiving increasing research interest for applications in wearable energy harvesting and mobile electronic systems [41]. Very recently, Liu et al. fabricated a p-type PEDOT:PSS fiber that is highly conductive with via a gelation methodology with the assistance of sulfuric acid in a capillary at an elevated temperature of 90 °C (Figure 4a) [42]. The hydrogel was then released to a solvent bath to yield a free-standing fiber with the average diameter of 142.5 ± 42.2 µm and a length of more than 20 cm (Figure 4b–d). Post-treatment of the fibers with ethylene glycol or dimethyl sulfoxide successfully improved the electrical conductivity by three times (up to 172.5 S cm⁻¹) with only 5% decrease in Seebeck coefficient (14.8 µV K⁻¹), giving rise to an optimum power factor of 4.77 µW m⁻¹ K⁻². Furthermore, a p–n-type thermoelectric generator was assembled with five p-n-type units where the p-type materials were made of PEDOT:PSS hydrogel fibers while n-type material is made of CNT fibers (Figure 4e,f). This fiber-based device showed a satisfactory output voltage of 20.7 mV and a power density of 481.2 µW cm⁻² when the difference in temperature between the two junctions is ~60 K. This is a good example of using organic thermoelectric fibers to harness energy via a wearable device.



Figure 4. (a) The effect of the H_2SO_4 concentration on the gelation process of PEDOT:PSS. Shaded regions present that PEDOT:PSS is able (green) and unable (gray) to gel with various H_2SO_4 contents. (b) Digital photographs of as-fabricated PEDOT:PSS fiber. SEM images of PEDOT:PSS fibers (c) before and (d) after ethylene glycol post-treatment. (e) Schematic diagram for thermoelectric device and (f) the output voltage and power density of five couples of legs at various temperature differences ranging from 5 to 60 K. Readapted with permission from American Chemical Society [42].

2.2. Poly (3-alkylthiophene)

Polythiophene and its derivatives are regarded as the most promising conducting polymers for thermoelectric applications [43–45]. Coupled on the good environmental stability of the polymer, a significant overlap among the π electron orbitals delocalized throughout the polymer chains and highly orientated semicrystalline structure give rise to a high carrier transport [46]. Among the various polythiophenes, poly(3-alkylthiophene) (P3AT) is a noteworthy family which is extensively investigated for their electrical transport mechanisms, processing methods and device applications in solar cells, sensors, optoelectronics and so on [44,47–50]. A variety of 1D nanostructured materials based on P3AT have been prepared by different kinds of approaches. It has been reported that continuous long nanofibers from P3AT can be produced by electrospinning method, [24,51,52] while the shorter P3AT nanofibers are mostly formed via self-assembly in solution with good crystallinity owing to strong interactions along their longitudinal axis [53–56]. Other approaches, such as vapor-assisted imprinting [57], electrochemical synthesis [58,59] and solution casting method [60,61] using sacrificial templates have also been employed to prepare P3AT nanowires or nanotubes for diverse applications.

Samitsu et al. developed high-aspect-ratio P3AT nanofibers by the Whisker method utilizing anisole as a solvent [46]. The formation and properties of the fibers largely depend on the length of the alkyl chain and molecular weight of the polymer. In a typical experiment, a P3AT polymer is well dissolved in anisole under heating and stirring. Then, during a quick cooling process to room temperature, nanofibers can grow in the solution. Using the Whisker method, Endrodi et al. prepared poly(3-hexylthiophene) (P3HT) nanofibers (50–60 nm in width and several microns in length), which further self-assembled to form networks via drop casting and subsequent doping by silver perchlorate to adjust the level of oxidation (Figure 5a–d) [62]. The nanonet structure exhibits a ZT value (0.0026) that is six times greater than its bulk polymer counterpart, owing to the highly

regularly spaced, crystalline supramolecular structure, the 1D nanofiber morphology and the close electrical contact between each nanofibers inside the nanonet structure. Hiura et al. also prepared P3HT nanofiber mats with high crystallinity using the similar method (Figure 5e,f) [63]. They found the thermal conductivity of the nanofiber mat was two times lower than the non-fibrous P3HT polymer despite having comparable electrical conductivity, which is due to presence of a more efficient electron transport route and a large void fraction in the fibrous mats.



Figure 5. TEM images of (**a**) neutral and (**b**) Ag doped P3HT nanonet (the inset shows a SEM image of the silver particles. (**c**) Comparison of the power factors measured for the bulk and nanonet structured P3HT, doped with 1 mM AgClO₄ solution. (**d**) Maximum power factor of the P3HT nanonet at different oxidant concentrations. (**e**) Scanning force microscopy (SFM) image of a P3HT nanofiber mat ($10 \times 10 \text{ m}$) and (**f**) corresponding binarized image. Readapted with permission from The Royal Society of Chemistry [62] and MDPI [63].

2.3. PPy

PPy is amongst the family of conducting polymers that is widely used in broad applications such as anti-electrostatic coatings, biosensors, solid electrolytic capacitors, polymer batteries, etc. [64–66]. It possesses a wide variety of advantages such as simple synthetic methods, commendable electrical conductivity, low thermal conductivity, good environmental stability and low toxicity, and proved to be a potential thermoelectric material to yield great thermoelectric properties [66–70]. In 2014, Wu et al. first reported the fabrication of free-standing PPy nanotube films for thermoelectric applications [71]. Two kinds of PPy nanotubes (Ppy-1 and Ppy-2) were prepared via similar self-degraded template methods which involves the oxidation of pyrrole monomers in the presence of methyl orange as the soft templates. The as-prepared PPy nanotube suspensions were dried in petri dishes to afford free-standing flexible films through self-assembly (Figure 6a,b). As shown in the SEM and TEM images (Figure 6c–f), PPy-2 nanotubes exhibit longer length and smaller diameters (~40 nm), leading to higher electrical conductivity and Seebeck coefficient at different temperatures (Figure 6g,h). At 310 K, the PPy-2 films exhibit a power factor of 0.31 μ W m⁻¹ K⁻² and a ZT value of 5.71 × 10⁻⁴. The ZT_{max} of PPy-2 film can reach 7.84 × 10⁻⁴ at 370 K, which is triple that of PPy-1 film. The developed free-standing PPy nanotube films can be applied to fabricate flexible thermoelectric devices.

In 2018, Du et al. successfully prepared PPy of different texture and topography (nanoparticles, nanotubes and nanowires) with or without various surfactants (methyl orange (MO), cetyltrimethyl ammonium bromide (CTAB)) and using different oxidants (ammonium peroxydisulfate (APS), FeCl₃) through a chemical oxidative polymerization approach (Figure 7) [72]. The effects of different

morphologies on their thermoelectric properties have been studied, and PPy nanowires with a diameter of 30–60 nm were found to exhibit the highest electrical conductivity and Seebeck coefficient, leading to an optimal power factor of $0.3 \ \mu W \ m^{-1} \ K^{-2}$ at 380 K. Using the similar approach, Liang et al. also studied the controlled synthesis of 1D nanostructured PPy with various morphologies (straight wires, curly wires, necklace-like structure, etc.) by adjusting the experimental conditions, including type of oxidizing agent, concentration of oxidizing agent, duration of polymerization and the solvent used for the reaction mixture [73]. It was found that the electrical conductivity and power factor were more easily affected than the Seebeck coefficient, by the morphology of PPy.



Figure 6. (**a**,**b**) Photographs of the flexible free-standing PPy nanotube film. SEM images of the free-standing (**c**) PPy-1 films and (**d**) Ppy-2 films. TEM images of (**e**) PPy-1 nanotubes and (**f**) PPy-2 nanotubes. The temperature dependence of (**g**) electrical conductivity and (**h**) Seebeck coefficient of PPy-1 and PPy-2 films. Readapted with permission from Elsevier B.V. [71].



Figure 7. (a) Schematic illustration of the formation procedure of PPy nanoparticles (PTs), nanotubes (NTs) and nanowires (NWs). TEM images of (b) PPy-PTs, (c) PPy-NTs and (d) PPy-NWs. (e) Thermoelectric power factor of PPy-PTs, PPy-NTs and PPy-NWs. Readapted with permission from MDPI [72].

2.4. PANI

PANI is another important conducting polymer due to its low cost, good stability, simple synthetic method and adjustable electronic properties for a wide range of applications [74–78]. In order to enhance the transport properties, various protonic acids (such as H₂SO₄, HCl, HClO₄, polyacrylic acid,

sulfosalicylic acid, p-toluenesulfonic, etc.) have been used as dopants for PANI and the conductivities are greatly influenced by the doping level and dopants. In 2010, Sun et al. prepared β -naphthalene sulfonic acid (β -NSA) doped PANI nanotubes using a template-free method through oxidation polymerization of aniline monomer using APS as the oxidizing agent with β -NSA as dopant and soft template [79]. The length of the tubes ranges from 5 to 8 µm with an average diameter of 200 nm (Figure 8a,b). The β -NSA doped PANI without nanostructure was also synthesized and used as reference to study the thermoelectric properties (Figure 8c,d). Different doping levels were investigated, and the PANI nanotubes synthesized with an aniline/NSA ratio of 4:1 exhibit an optimum Seebeck coefficient of 212.4 μ V K⁻¹ at 300 K, which is greater than the reference sample by seven folds. Additionally, electrical conductivity increased by almost two folds from 0.0045 to 0.0077 S cm⁻¹, while thermal conductivity decreased from 0.29 to 0.21 W m⁻¹ K⁻¹. The PANI nanotubes structures are strongly twisted and entangled, thereby increasing the phonon scattering at the boundary during heat transfer. As a consequence, the phonons mean free path significantly decreases then nanostructures are introduced into the system.



Figure 8. (**a**,**b**) SEM images of PANI-NSA nanotubes. (**c**) Electrical conductivities (\Box) and Seebeck coefficients (Δ) of PANI nanotubes with different doping ratio. (**d**) Thermal conductivities (\Box) and ZT value (Δ) of PANI nanotubes changed with the doping ratio. Readapted with permission from Elsevier B.V. [79].

In 2014, Wu et al. also reported the synthesis and thermoelectric performance study of PANI nanowires or nanorods doped with different acids (Figure 9) [80]. The 1D nanostructured PANI was synthesized using the soft template method with APS as oxidizing agent, CTAB as soft template and different acids (HCl, acetic acid and p-toluenesulfonic (p-TSA)) as dopants. The effects of doping agents and doping levels on the thermoelectric properties were systematically studied. The p-TSA was found to be the best dopant between the three acids as the bulky p-toluenesulfonic anions helps to orientate the polymer chains better. Also with the same doping concentration, p-TSA-doped nanowires with reduced diameters and more consistent nanostructures (70 nm in diameter and 1–2 m in length) produced a higher Seebeck coefficient and lower thermal conductivity compared to p-TSA-doped nanorods (150 nm in diameter and 0.2 to 1 m in length), which is due to the improved charge carrier mobility as a result of more ordered arrangement of the polymer chains.





Figure 9. SEM images of (**a**) PANI nanorods prepared in an ice bath; (**b**) PANI nanowires prepared at room temperature. (**c**) The temperature (T) dependence of figure-of-merit ZT of different acid doped PANI nanowires. (**d**) The temperature (T) dependence of figure-of-merit ZT of p-TSA doped PANI nanowires and nanorods. Readapted with permission from Elsevier B.V. [80].

3. Strategies to form 1D Conducting Polymer Nanocomposite Thermoelectric Materials

3.1. In Situ Polymerization of Conducting Polymers on 1D Nanofillers

Currently, surface coating of conducting polymers via in situ polymerization on inorganic or carbon nanomaterials is the most commonly used strategy to fabricate composite thermoelectric materials. To attain high thermoelectric performance, it is essential to construct the coating polymer with ordered orientation and extended chain conformation, which can reduce the energy needed for inter-chain and intra-chain hopping, offering improved carrier mobility of the polymer. The in situ polymerization method can make monomer molecules polymerize and extend in a systematic mode on the surface of the nanofillers as a result of the interfacial interactions (conjugation, hydrogen-bonding, van der Waals forces, etc.) between polymer and nanofillers. Moreover, the thickness of the polymer coating can be easily altered by varying the weight ratios of the monomers to nanofillers. A series of 1D nanocomposite materials with enhanced thermoelectric performance have been successfully developed, such as PEDOT/Te nanowires [81–83], PEDOT/CNTs [84,85], PANI/Bi₂Te₃ nanowires [86], PANI/CNTs [87–94], PANI/ZnO nanorods [95], PPy/CNTs [96–98], etc.

To obtain highly aligned polymer chains at molecular level, Wang et al. prepared PANI/CNT composite nanofibers by in situ polymerization combined with electrospinning process [87]. As shown in Figure 10b, PANI was coated on multi-walled CNTs via in situ polymerization of aniline using APS as oxidant. The prepared composite powders were then re-dispersed in chloroform and subjected to electrospinning using rotating drum collector to generate aligned nanofibers with diameters around 150–200 nm, which were finally pressed into compacted pellets for thermoelectric performance measurement. Electrospun fibers from directly mixed CNTs and PANI composite (DM-CNT/PANI) were also prepared as a comparison. It was found highly ordered polymer chains were grown on the CNTs via in situ polymerization as a result of strong conjugation interactions between PANI and CNTs. Furthermore, during the electrospinning process, the high voltage electrical field is also effective for aligning both CNTs and PANI polymer chains due to their anisotropic electric dipole moment. As shown in the SEM and TEM images (Figure 10c,d), all the nanotubes were evenly enclosed by PANI and oriented along the fiber axis in the CNT/PANI samples. The DM-CNT/PANI fibers have a similar structure but less homogeneity due to the existence of isolated PANI particles and bare parts of PANI coating layer. The CNT/PANI composite fibers were found to with significantly greater electrical conductivity and power factor (75% improvement compared to DM-CNT/PANI samples) in the polymer chain oriented direction.



Figure 10. Schematic representations of the formation mechanism of DM-CNT/PANI (**a**) and CNT/PANI (**b**) nanofibers. The enlarged part shows the highly ordered arrangement of the PANI backbone chains on the surface of the CNTs. SEM images of the fiber mats of DM-CNT/PANI (40 wt%) (**c**) and CNT/PANI (40 wt%) (**d**). The inserts are the TEM images of a single fiber. Arrows denote the alignment direction of fibers. Readapted with permission from The Royal Society of Chemistry [87].

Flexible, stretchable and mechanically stable thermoelectric materials are most promising for next-generation wearable electronic devices [99]. In 2016, Liang et al. reported the facile preparation of a super flexible and mechanically stretchable thermoelectric films with tunable thickness via in situ polymerization of PPy on single-walled CNTs (SWCNTs) followed by a vacuum filtration process (Figure 11a,b) [96]. The CNTs were fully exfoliated by using sodium dodecyl sulfate (SDS) in water with or without ethanol, and then pyrrole monomers were added and polymerized on the surface of CNTs using iron sulfate as oxidant. The thickness of the PPy coating layers are easily altered by tuning the SWCNT: Py mass ratios. After vacuum filtration, these composite fibers can self-assemble to free-standing films of different size and thickness (20–150 mm). With a CNT: Py ratio of 60 wt% and aqueous ethanol as solvent, the nanocomposite films exhibit a remarkably high thermoelectric performance. The electrical conductivity, Seebeck coefficient and power factor can reach up to 399 \pm 14 S cm⁻¹, 22.2 \pm 0.1 μ V K⁻¹ and 19.7 \pm 0.8 μ W m⁻¹ K⁻², respectively. Furthermore, the reported composite films exhibit excellent mechanical stability upon various deformations. As shown in Figure 11c-e, no obvious reduction is observed with thermoelectric properties after bending for as many as 1000 times and the performance maintained after being stretched to a strain of 2.6%, demonstrating great promise of this thermoelectric material to be applied in wearable devices for energy harvesting.



Figure 11. (a) Schematic illustration showing the preparation procedure for the PPy/SWCNT nanocomposites via a template-directed in situ polymerization approach with water or aqueous ethanol as reaction medium. (b) SEM image of the composites with a SWCNT: Py ratio of 20 wt%, prepared in the medium of aqueous ethanol. Inset is a photo of the PPy/SWCNT nanocomposite thermoelectric film. (c) Bending measurement of the flexible film with a bending radius of 2 mm. (d) thermoelectric performance of the PPy/SWCNT nanocomposite film (40 wt%, aqueous ethanol) before and after bending up to 1000 times. (e) Dependence of mechanical stretching on the thermoelectric performance of the PPy/SWCNT nanocomposite film (40 wt%, aqueous ethanol). Insets are SEM images showing no cracks after bending or stretching. Readapted with permission from The Royal Society of Chemistry [96].

3.2. Covalent Grafting of Conducting Polymers on 1D Nanofillers

For preparation of polymer nanocomposite thermoelectric materials, the conventional physical mixing or in situ polymerization method still cannot effectively prevent agglomeration of the nanofillers, especially at high loading levels. Therefore, it poses as great challenge to achieve intimate interfacial connections between the conducting polymers and inorganic/carbon nanofillers to avoid aggregation and also assist carrier transport without scattering the carriers at the boundary. In 2017, An et al. developed a P3HT-based nanocomposite thermoelectric material through chemically grafting P3HT onto the surface of double-walled CNTs (DWCNTs) [100]. As shown in Figure 12, amino-terminated P3HT (P3HT-NH₂) was prepared via a Grignard metathesis polymerization process, which is a general methodology for preparing polythiophenes with small molecular weight distribution and large regularity. Then P3HT-NH₂ was covalently grafted onto DWCNTs through an amidation reaction with the acyl moieties on the exterior of the acid-treated DWCNTs. The as-prepared P3HT grafted DWCNTs (P3HT-g-DWCNT) nanocomposites exhibit excellent dispersibility in organic solvents; hence, resulting in smaller aggregate sizes.





Figure 12. (a) Schematic comparison of preparation of P3HT/DWCNT nanocomposites through simple blending and covalent grafting. Reaction route for the synthesis of (b) P3HT-NH₂ and (c) P3HT-g-DWCNT. (d) Seebeck coefficient (red column), electrical conductivity (blue column), and corresponding power factor (green column); (e) thermal conductivity, and (f) figure of merit of pristine DWCNT, P3HT-g-DWCNT, and physically mixed P3HT/DWCNT nanocomposites. Readapted with permission from Elsevier Ltd. [100].

The thermoelectric performance of the P3HT-g-DWCNT films was investigated in comparison with the physically mixed P3HT/DWCNT composite and pristine DWCNTs (Figure 12d–f). The chemically anchored P3HT-g-DWCNT composite films exhibit a greatly improved Seebeck coefficient of 116. 6 μ V K⁻¹, while the P3HT/DWCNT composite by physical blending only yielded a Seebeck coefficient of 69.2 μ V K⁻¹. It is believed that the intimate and large contact interface resulted from covalent bonding can facilitate the carrier transport by decreasing the carrier scattering at the boundary. Moreover, due to the reduced diameter of CNT bundles, the P3HT-g-DWCNT composites also exhibit reduced thermal conductivity. The in-plane ZT value of the P3HT-g-DWCNT films can reach up to 0.0069, which is about two-fold superior to the pristine DWCNT and the physically mixed P3HT/DWCNT composites, demonstrating the effectiveness of this approach for fabrication of high performance thermoelectric nanocomposite materials.

3.3. Self-Assembly of 1D Conducting Polymer with Nanofillers

Very recently, Hu et al. reported a new type of thermoelectric composite film by self-assembly of PEDOT naonwires with tellurium nanowires (Figure 13) [101]. The PEDOT nanowires (with an average diameter of 12.2 nm and length of 1.2 μ m) were synthesized by oxidation polymerization of ethylenedioxythiophene (EDOT) monomer using SDS as cylindrical soft template and FeCl₃ as oxidant and further doped with 5% dimethyl sulfoxide to improve the dispensability. The PEDOT nanowire suspensions were physically mixed with various fractions of Te nanowires (with average diameter of 40 nm and length of 3 μ m) and subjected to vacuum filtering to afford the PEDOT nanowire/Te nanowire composite films. When Te nanowires were added, the thermoelectric power factor of the composites improved by ~40%. When increasing the Te nanowire content from 0 to 95 wt%, the Seebeck coefficient rose from 20.18 to 28.46 μ V K⁻¹, and the electrical conductivity dropped from 541 to 38.76 S cm⁻¹. The maximum PF of 29.05 μ W m⁻¹ K⁻² was achieved with 30 wt% Te nanowire content, which is significantly greater than the respective components (22 μ W m⁻¹ K⁻² for PEDOT nanowires, 1.28 μ W m⁻¹ K⁻² for Te nanowires). The thermoelectric performance enhancement could be attributed to the large carrier mobility in nanowire composites and proper energy barrier at polymer/inorganic boundary.



Figure 13. (a) Schematic illustration of the fabrication process of the Te nanowire/PEDOT nanowire composite films. (b) Measured thermoelectric properties including S, σ and PF of the composites relative to the mass fraction of Te nanowires. (c) SEM image of the surface morphology of 70 wt% Te nanowire/PEDOT nanowire composite films. Readapted with permission from American Chemical Society [101].

In addition to PEDOT, 1D nanostructured PPy has also been reported to form self-assembled hyrid themoelectric materials with carbonaceous nanofillers. Xin et al. have prepared free-standing PPy nanotube/reduced graphene oxide (rGO) composite films with good mechanical strength and flexibility through vacuum filtration of a blend of GO nanosheets and solution-prepared PPy nanotubes, followed by hydrogen iodide (HI) reduction (Figure 14a,b) [102]. The PPy naontubes were homogeneously intercalated into the rGO nanolayers, which effectively prevent the agglomeration of rGO nanosheets and provide sufficient conducting pathways for charge transfer. The power factor of the PPy/rGO composite film can reach up to 7.28 μ W m⁻¹ K⁻² at room temperature, which is 135 times that of the pure PPy film. Liang et al. also reported self-assembled composite films from PPy nanowires and SWCNTs (Figure 14c,d) [103]. The PPy nanowires prepared by chemical oxidative polymerization were physically mixed with CNTs and subjected to vacuum filtration to afford the free-standing hybrid films. A classic layered structure made up of parallel CNT nanosheets in between PPy nanowires with a diameter of 55–75 nm was obtained. The hybrid films exhibit outstanding thermoelectric performance with optimum power factor up to 21.7 \pm 0.8 μ W m⁻¹ K⁻², which outperforms other PPy-based composites reported thus far.





Figure 14. (a) Schematic of the synthesis procedure of PPy/rGO hybrid film. (b) Cross-sectional SEM image of the PPy/rGO hybrid film with a mass ratio of PPy:GO 1:0.6. (c) Schematic illustration of the preparation process for the PPy-nanowire/SWCNT nanocomposite free-standing films by solution mixing and subsequent vacuum filtration. (d) SEM image of the S/S-PPy nanowire/SWCNT composite films with SWCNT:PPy-nanowire mass ratio of 60 wt%. The arrows in blue point to the PPy nanowires, while the red arrows point toward the SWCNTs. Readapted with permission from Elsevier Ltd. [102,103].

3.4. Incorporation of 1D Conducting Polymer into Polymer Matrix by Physical Mixing

Besides organic-inorganic hybrid materials, 1D nanostructured conducting polymers can also be incorporated into polymer matrix to generate polymer/polymer composites. Recently, Zhang et al. integrated the in situ polymerized PEDOT nanowires into PSS-doped and tosylate-doped PEDOT hosts via physical mixing to afford a novel free-standing composite thermoelectric films [104]. As revealed in the AFM image, the PEDOT nanowires are homogenouly dispersed in the polymer matrix (Figure 15a). The best themoelectric performance was achieved with addition of only 0.2 wt% PEDOT nanowires. The power factor of the hybrids with tosylate-doped PEDOT host can reach a high of 446.6 μ W m⁻¹ K⁻² and the corresponding figure of merit can reach 0.44 at room temperature. Furthermore, these free-standing PEDOT nanowire/PEDOT composite films were employed as p-type legs for fabrication of a thermoelectric power generator, which delivered a normalized power output of ~0.5 mW m⁻² at Δ T = 10.1 K. These promising outcomes demonstrate the effectiveness of this new strategy for the design and preparation of high performance organic thermoelectric materials.



Figure 15. (a) The AFM image of 1 wt% PEDOT nanowire/PEDOT:PSS nanocomposites showing the random distribution of PEDOT nanowires in the PEDOT:PSS matrix and percolated networks. (b) Thermoelectric power factor of PEDOT nanowire/PEDOT:PSS hybrids. (c) Power factors of (from left to right) the as-prepared 5 vol% DMSO/PEDOT:PSS, nominal 0.2 wt% PEDOT nanowire/PEDOT:PSS with ethylene glocyl treatment, the as-synthesized PEDOT:Tos, and nominal 0.2 wt% PEDOT nanowire/PEDOT:PSS nanowire/PEDOT:Tos nanocomposites. Readapted with permission from The Royal Society of Chemistry [104].

4. Conclusions and Outlook

Nanostructure engineering of conducting polymers and their composites to realize significant performance enhancement is an attractive new direction in the thermoelectric materials research, especially for the development of next-generation flexible and light weight organic thermoelectric devices, such as wearable self-powered sensors, health monitors, electronic devices, etc. This review provides an overview of the construction and thermoelectric performance study of various conducting polymers and polymer nanocomposites with 1D morphology (nanowires, nanotubes, nanorods, nano-/microfibers, etc.). The thermoelectric properties and preparation methods of these 1D structured polymers and hybrid materials are summarized in Tables 1 and 2. Compared to their bulk counterparts, considerable enhancements in both electrical conductivity and Seebeck coefficient have been achieved with these nanoscaled conducting polymers due to the highly orientated order of the polymer chains and enhanced carrier mobility within the 1D nanostructrues. Their thermoelectric performance can be readily tuned and further enhanced by using different kinds of dopants, varying the doping levels and post-treatment methods. Through hybridization with inorganic/carbonaceous nanofillers via covalent bonding, in situ polymerization, physical mixing and self-assembly, the obtained 1D polymer nanocomposite materials with higher power factors can be generated and most of them can be obtained as free-standing flexible (even stretchable) films, providing great potential for thermoelectric device fabrication.

Preparation Method	σ (S cm ⁻¹)	S (μV K ⁻¹)	PFmax (μW m ⁻¹ K ⁻²)	$(W m^{-1} K^{-1})$	ZT	Ref
Hard template	43 ± 5	28 ± 2	3.4	_	_	[33]
Hard template	12	-85	8.7	-	-	[34]
Reverse microemulsion	71.4	48	16.4	-	-	[35]
Hard template + post-treatment	541	20.78	23.4	-	-	[39]
Reverse microemulsion + post-treatment	16.9	23.3	0.91	-	-	[40]
Acid gelation + post-treatment	172.5	14.8	4.77	-	-	[42]
Whisker method + silver doping	18.3	61.1	6.84	0.80	$2.6 imes10^{-3}$	[62]
Whisker method	12.6	48.8	3.7	0.0708	$1.6 imes10^{-2}$	[63]
Soft template	9.81	17.68	0.31	0.17	$5.71 imes 10^{-4}$	[71]
Soft template	22.5	11.5	0.3	-	-	[72]
Soft template	2.217	10.1	0.023	-	-	[73]
Soft template $+$ acid doping	0.0077	212.4	0.035	0.21	$4.86 imes 10^{-5}$	[79]
Soft template + acid doping	1.24	15	0.028	0.32	$2.75 imes 10^{-5}$	[80]
	Preparation Method Hard template Hard template Reverse microemulsion Hard template + post-treatment Reverse microemulsion + post-treatment Acid gelation + post-treatment Whisker method + silver doping Whisker method Soft template Soft template Soft template Soft template + acid doping Soft template + acid doping	Preparation Method σ (S cm ⁻¹)Hard template43 ± 5Hard template12Reverse microemulsion71.4Hard template + post-treatment541Reverse microemulsion + post-treatment16.9Acid gelation + post-treatment172.5Whisker method + silver doping18.3Whisker method12.6Soft template9.81Soft template22.5Soft template2.217Soft template + acid doping0.0077Soft template + acid doping1.24	$\begin{array}{c c} \hline Preparation Method & \sigma & S \\ (S \ cm^{-1}) & (\mu V \ K^{-1}) \end{array} \\ \hline Hard template & 43 \pm 5 & 28 \pm 2 \\ Hard template & 12 & -85 \\ Reverse microemulsion & 71.4 & 48 \\ Hard template + post-treatment & 541 & 20.78 \\ Reverse microemulsion + post-treatment & 16.9 & 23.3 \\ Acid gelation + post-treatment & 172.5 & 14.8 \\ Whisker method + silver doping & 18.3 & 61.1 \\ Whisker method + silver doping & 18.3 & 61.1 \\ Whisker method & 12.6 & 48.8 \\ Soft template & 9.81 & 17.68 \\ Soft template & 22.5 & 11.5 \\ Soft template + acid doping & 0.0077 & 212.4 \\ Soft template + acid doping & 1.24 & 15 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

Table 1. Summary of the thermoelectric properties of 1D structured conducting polymers.

Table 2. Summary of the thermoelectric properties of 1D conducting polymer nanocomposite materials.

Polymer Composites	Preparation Method	σ (S cm ⁻¹)	S (μV K ⁻¹)	PFmax (μW m ⁻¹ K ⁻²)	$(W m^{-1} K^{-1})$	ZT	Ref
PEDOT/CNTs	In situ polymerization	586	18	19.00 ± 1.43	_	_	[84]
PEDOT/CNTs	In situ polymerization	15	12	0.229 ± 0.014	-	-	[85]
PANI/Bi ₂ Te ₃ nanowires	In situ polymerization	12	35	1.57	0.1096	0.0043	[86]
PANI/CNTs	In situ polymerization	17	10	0.18	-	-	[87]
PANI/SWCNTs	In situ polymerization	125	40	20	-	-	[88]
PANI/ZnO nanorods	In situ polymerization	28.15	41.55	4.86	0.87	0.0017	[95]
PPy/SWCNTs	In situ polymerization	399 ± 14	22.2 ± 0.1	19.7 ± 0.8	-	-	[96]
P3HT/DWCNTs	Covalent grafting	115	35	46	2.0	0.0069	[100]
Te/PEDOT nanowires	Self-assembly	500	24	29.05	-	-	[101]
PPy nanotubes/rGO	Self-assembly	80	28	7.28	-	-	[102]
PPy nanowires/CNTs	Self-assembly	300	27	21.7		-	[103]
PEDOT nanowires/PEDOT	Physical mixing	1270	59.3	446.6	0.26	0.44	[104]

Future breakthroughs in this exciting new area may reside in the molecular design and preparation of novel monomers or polymers and the incorporation of other functional inorganic nanofillers. In spite of the significant performance enhancement achieved with these 1D materials, the in-depth mechanism understanding of the structure-property relationships and interfacial interactions in the composites are still needed for future design and engineering of high performance polymer-based thermoelectric materials and devices.

Author Contributions: Conceptualization, J.X. and K.W.S.; writing—original draft preparation, S.-X.W. and D.X.Y.S.; writing—review and editing, K.W.S.; supervision, J.X.; funding acquisition, K.W.S. and J.X.

Funding: This research was funded by A*STAR, SERC, Thermoelectric Materials Programmer. Grant number: 1527200019.

Acknowledgments: This work was also supported by National University of Singapore, Department of Building.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. DiSalvo, F.J. Thermoelectric cooling and power generation. Science 1999, 285, 703–706. [CrossRef]
- 2. Bell, L.E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. *Science* **2008**, *321*, 1457–1461. [CrossRef] [PubMed]
- 3. Tritt, T.M. Thermoelectric phenomena, materials, and applications. In *Annual Review of Materials Research;* Clarke, D.R., Fratzl, P., Eds.; Annual Reviews: Palo Alto, CA, USA, 2011; Volume 41, pp. 433–448.
- 4. Zhang, X.; Zhao, L.-D. Thermoelectric materials: Energy conversion between heat and electricity. *J. Materiomics* **2015**, *1*, 92–105. [CrossRef]
- 5. Zhao, D.L.; Tan, G. A review of thermoelectric cooling: Materials, modeling and applications. *Appl. Therm. Eng.* **2014**, *66*, 15–24. [CrossRef]
- 6. Ren, P.; Liu, Y.; He, J.; Lv, T.; Gao, J.; Xu, G. Recent advances in inorganic material thermoelectrics. *Inorg. Chem. Front.* **2018**, *5*, 2380–2398. [CrossRef]
- Fergus, J.W. Oxide materials for high temperature thermoelectric energy conversion. J. Eur. Ceram. Soc. 2012, 32, 525–540. [CrossRef]
- 8. Culebras, M.; Gomez, C.M.; Cantarero, A. Review on polymers for thermoelectric applications. *Materials* **2014**, *7*, 6701–6732. [CrossRef]
- 9. Du, Y.; Shen, S.Z.; Cai, K.F.; Casey, P.S. Research progress on polymer-inorganic thermoelectric nanocomposite materials. *Prog. Polym. Sci.* 2012, *37*, 820–841. [CrossRef]
- 10. Yao, H.; Fan, Z.; Cheng, H.; Guan, X.; Wang, C.; Sun, K.; Ouyang, J. Recent development of thermoelectric polymers and composites. *Macromol. Rapid Commun.* **2018**, *39*, 1700727. [CrossRef] [PubMed]
- 11. Zhang, Q.; Sun, Y.M.; Xu, W.; Zhu, D.B. Organic thermoelectric materials: Emerging green energy materials converting heat to electricity directly and efficiently. *Adv. Mater.* **2014**, *26*, 6829–6851. [CrossRef]
- 12. Russ, B.; Glaudell, A.; Urban, J.J.; Chabinyc, M.L.; Segalman, R.A. Organic thermoelectric materials for energy harvesting and temperature control. *Nat. Rev. Mater.* **2016**, *1*, 14. [CrossRef]
- Dubey, N.; Leclerc, M. Conducting polymers: Efficient thermoelectric materials. J. Polym. Sci. B-Polym. Phys. 2011, 49, 467–475. [CrossRef]
- 14. Chen, G.M.; Xu, W.; Zhu, D.B. Recent advances in organic polymer thermoelectric composites. *J. Mater. Chem. C* 2017, *5*, 4350–4360. [CrossRef]
- 15. He, M.; Qiu, F.; Lin, Z.Q. Towards high-performance polymer-based thermoelectric materials. *Energy Environ. Sci.* **2013**, *6*, 1352–1361. [CrossRef]
- 16. Ghosh, S.; Maiyalagan, T.; Basu, R.N. Nanostructured conducting polymers for energy applications: Towards a sustainable platform. *Nanoscale* **2016**, *8*, 6921–6947. [CrossRef] [PubMed]
- 17. Li, C.; Bai, H.; Shi, G.Q. Conducting polymer nanomaterials: Electrosynthesis and applications. *Chem. Soc. Rev.* **2009**, *38*, 2397–2409. [CrossRef] [PubMed]
- 18. Nguyen, D.N.; Yoon, H. Recent advances in nanostructured conducting polymers: From synthesis to practical applications. *Polymers* **2016**, *8*, 38. [CrossRef]
- 19. Yoon, H. Current trends in sensors based on conducting polymer nanomaterials. *Nanomaterials* **2013**, *3*, 524–549. [CrossRef]

- 20. Zhang, L.; Du, W.; Nautiyal, A.; Liu, Z.; Zhang, X. Recent progress on nanostructured conducting polymers and composites: Synthesis, application and future aspects. *Sci. China Mater.* **2018**, *61*, 303–352. [CrossRef]
- Aleshin, A.N. Polymer nanofibers and nanotubes: Charge transport and device applications. *Adv. Mater.* 2006, 18, 17–27. [CrossRef]
- 22. Chen, C.; Fan, Y.Q.; Gu, J.H.; Wu, L.M.; Passerini, S.; Mai, L.Q. One-dimensional nanomaterials for energy storage. *J. Phys. D-Appl. Phys.* **2018**, *51*, 14. [CrossRef]
- 23. Tran, H.D.; Li, D.; Kaner, R.B. One-dimensional conducting polymer nanostructures: Bulk synthesis and applications. *Adv. Mater.* **2009**, *21*, 1487–1499. [CrossRef]
- 24. Yu, H.; Kim, D.Y.; Lee, K.J.; Oh, J.H. Fabrication of one-dimensional organic nanomaterials and their optoelectronic. *J. Nanosci. Nanotechnol.* **2014**, *14*, 1282–1302. [CrossRef] [PubMed]
- 25. Dresselhaus, M.S.; Chen, G.; Tang, M.Y.; Yang, R.G.; Lee, H.; Wang, D.Z.; Ren, Z.F.; Fleurial, J.P.; Gogna, P. New directions for low-dimensional thermoelectric materials. *Adv. Mater.* **2007**, *19*, 1043–1053. [CrossRef]
- 26. Kanatzidis, M.G. Nanostructured thermoelectrics: The new paradigm? *Chem. Mater.* **2010**, 22, 648–659. [CrossRef]
- 27. Vineis, C.J.; Shakouri, A.; Majumdar, A.; Kanatzidis, M.G. Nanostructured thermoelectrics: Big efficiency gains from small features. *Adv. Mater.* **2010**, *22*, 3970–3980. [CrossRef] [PubMed]
- 28. Pichanusakorn, P.; Bandaru, P. Nanostructured thermoelectrics. *Mater. Sci. Eng. R-Rep.* **2010**, *67*, 19–63. [CrossRef]
- 29. Li, J.F.; Liu, W.S.; Zhao, L.D.; Zhou, M. High-performance nanostructured thermoelectric materials. *NPG Asia Mater.* **2010**, *2*, 152–158. [CrossRef]
- 30. Lan, Y.C.; Minnich, A.J.; Chen, G.; Ren, Z.F. Enhancement of thermoelectric figure-of-merit by a bulk nanostructuring approach. *Adv. Funct. Mater.* **2010**, *20*, 357–376. [CrossRef]
- 31. Minnich, A.J.; Dresselhaus, M.S.; Ren, Z.F.; Chen, G. Bulk nanostructured thermoelectric materials: Current research and future prospects. *Energy Environ. Sci.* **2009**, *2*, 466–479. [CrossRef]
- Liu, R.; Lee, S.B. MnO₂/poly (3, 4-ethylenedioxythiophene) coaxial nanowires by one-step coelectrodeposition for electrochemical energy storage. *J. Am. Chem. Soc.* 2008, 130, 2942–2943. [CrossRef] [PubMed]
- 33. García-Barberá, A.; Culebras, M.; Roig-Sánchez, S.; Gómez, C.M.; Cantarero, A. Three dimensional PEDOT nanowires network. *Synth. Met.* **2016**, *220*, 208–212. [CrossRef]
- 34. Taggart, D.K.; Yang, Y.; Kung, S.-C.; McIntire, T.M.; Penner, R.M. Enhanced thermoelectric metrics in ultra-long electrodeposited PEDOT nanowires. *Nano Lett.* **2010**, *11*, 125–131. [CrossRef] [PubMed]
- 35. Hu, X.; Chen, G.; Wang, X.; Wang, H. Tuning thermoelectric performance by nanostructure evolution of a conducting polymer. *J. Mater. Chem. A* **2015**, *3*, 20896–20902. [CrossRef]
- 36. Liu, R.; Cho, S.I.; Lee, S.B. Poly (3, 4-ethylenedioxythiophene) nanotubes as electrode materials for a high-powered supercapacitor. *Nanotechnology* **2008**, *19*, 215710. [CrossRef] [PubMed]
- 37. Yao, B.; Wang, H.; Zhou, Q.; Wu, M.; Zhang, M.; Li, C.; Shi, G. Ultrahigh-conductivity polymer hydrogels with arbitrary structures. *Adv. Mater.* **2017**, *29*, 1700974. [CrossRef]
- 38. Yoon, H.; Chang, M.; Jang, J. Formation of 1D poly (3, 4-ethylenedioxythiophene) nanomaterials in reverse microemulsions and their application to chemical sensors. *Adv. Funct. Mater.* **2007**, *17*, 431–436. [CrossRef]
- 39. Zhang, J.; Zhang, K.; Xu, F.; Wang, S.; Qiu, Y. Thermoelectric transport in ultrathin poly (3, 4-ethylenedioxythiophene) nanowire assembly. *Compos. Part B-Eng.* **2018**, *136*, 234–240. [CrossRef]
- 40. Zhao, J.; Tan, D.; Chen, G. A strategy to improve the thermoelectric performance of conducting polymer nanostructures. *J. Mater. Chem. C* 2017, *5*, 47–53. [CrossRef]
- 41. Zhang, L.; Lin, S.; Hua, T.; Huang, B.; Liu, S.; Tao, X. Fiber-based thermoelectric generators: Materials, device structures, fabrication, characterization, and applications. *Adv. Energy Mater.* **2018**, *8*, 1700524. [CrossRef]
- Liu, J.; Jia, Y.; Jiang, Q.; Jiang, F.; Li, C.; Wang, X.; Liu, P.; Liu, P.; Hu, F.; Du, Y. Highly conductive hydrogel polymer fibers toward promising wearable thermoelectric energy harvesting. *ACS Appl. Mater. Interfaces* 2018, 10, 44033–44040. [CrossRef] [PubMed]
- 43. Zhang, J.; Song, G.; Qiu, L.; Feng, Y.; Chen, J.; Yan, J.; Liu, Y.; Huang, X.; Cui, Y.; Sun, Y.; et al. Highly conducting polythiophene thin films with less ordered microstructure displaying excellent thermoelectric performance. *Macromol. Rapid Commun.* **2018**, *39*, 1800283. [CrossRef] [PubMed]
- 44. Kaloni, T.P.; Giesbrecht, P.K.; Schreckenbach, G.; Freund, M.S. Polythiophene: From fundamental perspectives to applications. *Chem. Mater.* **2017**, *29*, 10248–10283. [CrossRef]

- 45. Imae, I.; Koumoto, T.; Harima, Y. Thermoelectric properties of polythiophenes partially substituted by ethylenedioxy groups. *Polymer* **2018**, *144*, 43–50. [CrossRef]
- Steyrluthner, R.; Zhang, Y.; Zhang, L.; Kraffert, F.; Cherniawski, B.P.; Bittl, R.; Briseno, A.L.; Bredas, J.-L.; Behrends, J. Impact of morphology on polaron delocalization in a semicrystalline conjugate polymer. *Phys. Chem. Chem. Phys.* 2017, *19*, 3627–3639. [CrossRef] [PubMed]
- 47. Zhang, Q.; Sun, Y.; Xu, W.; Zhu, D. Thermoelectric energy from flexible P3HT films doped with a ferric salt of triflimide anions. *Energy Environ. Sci.* **2012**, *5*, 9639–9644. [CrossRef]
- Hong, C.T.; Lee, W.; Kang, Y.H.; Yoo, Y.; Ryu, J.; Cho, S.Y.; Jang, K.-S. Effective doping by spin-coating and enhanced thermoelectric power factors in SWCNT/P3HT hybrid films. *J. Mater. Chem. A* 2015, *3*, 12314–12319. [CrossRef]
- 49. Xuan, Y.; Liu, X.; Desbief, S.; Leclère, P.; Fahlman, M.; Lazzaroni, R.; Berggren, M.; Cornil, J.; Emin, D.; Crispin, X. Thermoelectric properties of conducting polymers: The case of poly (3-hexylthiophene). *Phys. Rev. B* **2010**, *82*, 115454. [CrossRef]
- Bhatt, M.P.; Magurudeniya, H.D.; Rainbolt, E.A.; Huang, P.; Dissanayake, D.S.; Biewer, M.C.; Stefan, M.C. Poly(3-hexylthiophene) nanostructured materials for organic electronics applications. *J. Nanosci. Nanotechnol.* 2014, 14, 1033–1050. [CrossRef]
- 51. Laforgue, A.; Robitaille, L. Fabrication of poly-3-hexylthiophene/polyethylene oxide nanofibers using electrospinning. *Synth. Met.* 2008, 158, 577–584. [CrossRef]
- Pierini, F.; Lanzi, M.; Nakielski, P.; Pawłowska, S.; Urbanek, O.; Zembrzycki, K.; Kowalewski, T.A. Single-material organic solar cells based on electrospun fullerene-grafted polythiophene nanofibers. *Macromolecules* 2017, 50, 4972–4981. [CrossRef]
- Samitsu, S.; Shimomura, T.; Heike, S.; Hashizume, T.; Ito, K. Effective production of poly(3-alkylthiophene) nanofibers by means of whisker method using anisole solvent: Structural, optical, and electrical properties. *Macromolecules* 2008, 41, 8000–8010. [CrossRef]
- 54. Sun, S.; Salim, T.; Wong, L.H.; Foo, Y.L.; Boey, F.; Lam, Y.M. A new insight into controlling poly (3-hexylthiophene) nanofiber growth through a mixed-solvent approach for organic photovoltaics applications. *J. Mater. Chem.* **2011**, *21*, 377–386. [CrossRef]
- 55. Byun, M.; Laskowski, R.L.; He, M.; Qiu, F.; Jeffries-El, M.; Lin, Z. Controlled evaporative self-assembly of hierarchically structured regioregular conjugated polymers. *Soft Matter* **2009**, *5*, 1583–1586. [CrossRef]
- 56. Liu, J.; Sun, Y.; Gao, X.; Xing, R.; Zheng, L.; Wu, S.; Geng, Y.; Han, Y. Oriented poly (3-hexylthiophene) nanofibril with the π–π stacking growth direction by solvent directional evaporation. *Langmuir* 2011, 27, 4212–4219. [CrossRef] [PubMed]
- 57. Liu, J.; Sun, Y.; Zheng, L.; Geng, Y.; Han, Y. Vapor-assisted imprinting to pattern poly (3-hexylthiophene)(P3HT) film with oriented arrangement of nanofibrils and flat-on conformation of P3HT chains. *Polymer* **2013**, *54*, 423–430. [CrossRef]
- 58. Park, D.; Kim, B.; Jang, M.; Bae, K.; Lee, S.; Joo, J. Synthesis and characterization of polythiophene and poly (3-methylthiophene) nanotubes and nanowires. *Synth. Met.* **2005**, *153*, 341–344. [CrossRef]
- Park, D.H.; Kim, M.; Kim, M.S.; Kim, D.-C.; Song, H.; Kim, J.; Joo, J. Electrochemical synthesis and nanoscale photoluminescence of poly (3-butylthiophene) nanowire. *Electrochem. Solid State Lett.* 2008, 11, K69–K72. [CrossRef]
- 60. Byun, J.; Kim, Y.; Jeon, G.; Kim, J.K. Ultrahigh density array of free-standing poly (3-hexylthiophene) nanotubes on conducting substrates via solution wetting. *Macromolecules* **2011**, *44*, 8558–8562. [CrossRef]
- 61. Smith, M.K.; Singh, V.; Kalaitzidou, K.; Cola, B.A. Poly (3-hexylthiophene) nanotube array surfaces with tunable wetting and contact thermal energy transport. *ACS Nano* **2015**, *9*, 1080–1088. [CrossRef]
- 62. Endrődi, B.; Mellar, J.; Gingl, Z.; Visy, C.; Janáky, C. Reasons behind the improved thermoelectric properties of poly (3-hexylthiophene) nanofiber networks. *RSC Adv.* **2014**, *4*, 55328–55333. [CrossRef]
- 63. Hiura, S.; Okada, N.; Wakui, J.; Narita, H.; Kanehashi, S.; Shimomura, T. Thermoelectric properties of poly (3-hexylthiophene) nanofiber mat with a large void fraction. *Materials* **2017**, *10*, 468. [CrossRef] [PubMed]
- Wang, L.X.; Li, X.G.; Yang, Y.L. Preparation, properties and applications of polypyrroles. *React. Funct. Polym.* 2001, 47, 125–139. [CrossRef]
- 65. Zhao, C.E.; Wu, J.; Kjelleberg, S.; Loo, J.S.C.; Zhang, Q. Employing a flexible and low-cost polypyrrole nanotube membrane as an anode to enhance current generation in microbial fuel cells. *Small* **2015**, *11*, 3440–3443. [CrossRef] [PubMed]

- 66. Mateeva, N.; Niculescu, H.; Schlenoff, J.; Testardi, L.R. Correlation of seebeck coefficient and electric conductivity in polyaniline and polypyrrole. *J. Appl. Phys.* **1998**, *83*, 3111–3117. [CrossRef]
- 67. Maddison, D.S.; Roberts, R.B.; Unsworth, J. Thermoelectric-power of polypyrrole. *Synth. Met.* **1989**, *33*, 281–287. [CrossRef]
- Kemp, N.T.; Kaiser, A.B.; Liu, C.-J.; Chapman, B.; Mercier, O.; Carr, A.M.; Trodahl, H.J.; Buckley, R.G.; Partridge, A.C.; Lee, J.Y.; et al. Thermoelectric power and conductivity of different types of polypyrrole. *J. Polym. Sci. B-Polym. Phys.* 1999, 37, 953–960. [CrossRef]
- 69. Maddison, D.S.; Unsworth, J.; Roberts, R.B. Electrical-conductivity and thermoelectric-power of polypyrrole with different doping levels. *Synth. Met.* **1988**, *26*, 99–108. [CrossRef]
- 70. Culebras, M.; Uriol, B.; Gomez, C.M.; Cantarero, A. Controlling the thermoelectric properties of polymers: Application to pedot and polypyrrole. *Phys. Chem. Chem. Phys.* **2015**, *17*, 15140–15145. [CrossRef]
- 71. Wu, J.; Sun, Y.; Pei, W.-B.; Huang, L.; Xu, W.; Zhang, Q. Polypyrrole nanotube film for flexible thermoelectric application. *Synth. Met.* **2014**, *196*, 173–177. [CrossRef]
- 72. Du, Y.; Niu, H.; Li, J.; Dou, Y.; Shen, S.; Jia, R.; Xu, J. Morphologies tuning of polypyrrole and thermoelectric properties of polypyrrole nanowire/graphene composites. *Polymers* **2018**, *10*, 1143. [CrossRef]
- 73. Liang, L.; Chen, G.; Guo, C.-Y. Polypyrrole nanostructures and their thermoelectric performance. *Mater. Chem. Front.* 2017, *1*, 380–386. [CrossRef]
- 74. Ćirić-Marjanović, G. Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications. *Synth. Met.* **2013**, *177*, 1–47. [CrossRef]
- Dhand, C.; Das, M.; Datta, M.; Malhotra, B. Recent advances in polyaniline based biosensors. *Biosens. Bioelectron*. 2011, 26, 2811–2821. [CrossRef] [PubMed]
- 76. Bhadra, S.; Khastgir, D.; Singha, N.K.; Lee, J.H. Progress in preparation, processing and applications of polyaniline. *Prog. Polym. Sci.* **2009**, *34*, 783–810. [CrossRef]
- 77. Li, D.; Huang, J.; Kaner, R.B. Polyaniline nanofibers: A unique polymer nanostructure for versatile applications. *Acc. Chem. Res.* 2008, 42, 135–145. [CrossRef] [PubMed]
- 78. Liao, G.F.; Li, Q.; Xu, Z.S. The chemical modification of polyaniline with enhanced properties: A review. *Prog. Org. Coat.* **2019**, *126*, 35–43. [CrossRef]
- 79. Sun, Y.; Wei, Z.; Xu, W.; Zhu, D. A three-in-one improvement in thermoelectric properties of polyaniline brought by nanostructures. *Synth. Met.* **2010**, *160*, 2371–2376. [CrossRef]
- 80. Wu, J.; Sun, Y.; Xu, W.; Zhang, Q. Investigating thermoelectric properties of doped polyaniline nanowires. *Synth. Met.* **2014**, *189*, 177–182. [CrossRef]
- 81. Bae, E.J.; Kang, Y.H.; Jang, K.-S.; Cho, S.Y. Enhancement of thermoelectric properties of PEDOT: PSS and tellurium-PESOT: PSS hybrid composites by simple chemical treatment. *Sci. Rep.* **2016**, *6*, 18805.
- 82. See, K.C.; Feser, J.P.; Chen, C.E.; Majumdar, A.; Urban, J.J.; Segalman, R.A. Water-processable polymernanocrystal hybrids for thermoelectrics. *Nano Lett.* **2010**, *10*, 4664–4667. [CrossRef] [PubMed]
- Coates, N.E.; Yee, S.K.; McCulloch, B.; See, K.C.; Majumdar, A.; Segalman, R.A.; Urban, J.J. Effect of interfacial properties on polymer–nanocrystal thermoelectric transport. *Adv. Mater.* 2013, 25, 1629–1633. [CrossRef] [PubMed]
- Hu, X.; Chen, G.; Wang, X. An unusual coral-like morphology for composites of poly (3, 4-ethylenedioxythiophene)/carbon nanotube and the enhanced thermoelectric performance. *Compos. Sci. Technol.* 2017, 144, 43–50. [CrossRef]
- Zhang, Z.; Chen, G.; Wang, H.; Li, X. Template-directed in situ polymerization preparation of nanocomposites of PEDOT: PSS-coated multi-walled carbon nanotubes with enhanced thermoelectric property. *Chem. Asian J.* 2015, 10, 149–153. [CrossRef] [PubMed]
- 86. Chatterjee, K.; Mitra, M.; Kargupta, K.; Ganguly, S.; Banerjee, D. Synthesis, characterization and enhanced thermoelectric performance of structurally ordered cable-like novel polyaniline–bismuth telluride nanocomposite. *Nanotechnology* **2013**, *24*, 215703. [CrossRef] [PubMed]
- Wang, Q.; Yao, Q.; Chang, J.; Chen, L. Enhanced thermoelectric properties of CNT/PANI composite nanofibers by highly orienting the arrangement of polymer chains. *J. Mater. Chem.* 2012, 22, 17612–17618. [CrossRef]
- 88. Yao, Q.; Chen, L.; Zhang, W.; Liufu, S.; Chen, X. Enhanced thermoelectric performance of single-walled carbon nanotubes/polyaniline hybrid nanocomposites. *ACS Nano* **2010**, *4*, 2445–2451. [CrossRef]

- 89. Chen, J.; Wang, L.; Ren, D.; Chu, Y.; Wu, Y.; Meng, K.; Miao, J.; Xu, X.; Jiang, Y. Revealing the anisotropy in thermoelectric transport performances in CNT/PANI composites. *Synth. Met.* **2018**, 239, 13–21. [CrossRef]
- 90. Chatterjee, M.J.; Banerjee, D.; Chatterjee, K. Composite of single walled carbon nanotube and sulfosalicylic acid doped polyaniline: A thermoelectric material. *Mater. Res. Express* **2016**, *3*, 12. [CrossRef]
- Wang, Y.; Zhang, S.; Deng, Y. Semiconductor to metallic behavior transition in multi-wall carbon nanotubes/polyaniline composites with improved thermoelectric properties. *Mater. Lett.* 2016, 164, 132–135. [CrossRef]
- Sobha, A.P.; Narayanankutty, S.K. Electrical and thermoelectric properties of functionalized multiwalled carbon nanotube/polyaniline composites prepared by different methods. *IEEE Trans. Nanotechnol.* 2014, 13, 835–841. [CrossRef]
- 93. Yan, H.Y.; Kou, K.C. Enhanced thermoelectric properties in polyaniline composites with polyaniline-coated carbon nanotubes. *J. Mater. Sci.* **2014**, *49*, 1222–1228. [CrossRef]
- 94. Zhang, K.; Davis, M.; Qiu, J.J.; Hope-Weeks, L.; Wang, S.R. Thermoelectric properties of porous multi-walled carbon nanotube/polyaniline core/shell nanocomposites. *Nanotechnology* **2012**, *23*, 8. [CrossRef] [PubMed]
- 95. Mitra, M.; Kargupta, K.; Ganguly, S.; Goswami, S.; Banerjee, D. Facile synthesis and thermoelectric properties of aluminum doped zinc oxide/polyaniline (AZO/PANI) hybrid. *Synth. Met.* **2017**, *228*, 25–31. [CrossRef]
- 96. Liang, L.; Gao, C.; Chen, G.; Guo, C.-Y. Large-area, stretchable, super flexible and mechanically stable thermoelectric films of polymer/carbon nanotube composites. *J. Mater. Chem. C* 2016, *4*, 526–532. [CrossRef]
- 97. Song, H.; Cai, K.; Wang, J.; Shen, S. Influence of polymerization method on the thermoelectric properties of multi-walled carbon nanotubes/polypyrrole composites. *Synth. Met.* **2016**, *211*, 58–65. [CrossRef]
- 98. Liu, J.; Yu, H.Q. Thermoelectric enhancement in polyaniline composites with polypyrrole-functionalized multiwall carbon nanotubes. *J. Electron. Mater.* **2014**, *43*, 1181–1187. [CrossRef]
- 99. Culebras, M.; Choi, K.; Cho, C. Recent progress in flexible organic thermoelectrics. *Micromachines* **2018**, *9*, 638.4. [CrossRef]
- 100. An, C.J.; Lee, Y.C.; Kang, Y.H.; Cho, S.Y. Improved interaction between semiconducting polymer and carbon nanotubes in thermoelectric composites through covalent grafting. *Carbon* **2017**, *124*, 662–668. [CrossRef]
- 101. Hu, X.; Zhang, K.; Zhang, J.; Wang, S.; Qiu, Y. Thermoelectric properties of conducting polymer nanowire-tellurium nanowire composites. *ACS Appl. Energy Mater.* **2018**, *1*, 4883–4890. [CrossRef]
- Xin, S.; Yang, N.; Gao, F.; Zhao, J.; Li, L.; Teng, C. Free-standing and flexible polypyrrole nanotube/reduced graphene oxide hybrid film with promising thermoelectric performance. *Mater. Chem. Phys.* 2018, 212, 440–445. [CrossRef]
- Liang, L.; Chen, G.; Guo, C.-Y. Enhanced thermoelectric performance by self-assembled layered morphology of polypyrrole nanowire/single-walled carbon nanotube composites. *Compos. Sci. Technol.* 2016, 129, 130–136. [CrossRef]
- Zhang, K.; Qiu, J.; Wang, S. Thermoelectric properties of PEDOT nanowire/pedot hybrids. *Nanoscale* 2016, *8*, 8033–8041. [CrossRef] [PubMed]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).