

Article

Preparation and Thermoelectric Properties of Graphite/poly(3,4-ethylenedioxythiophene) Nanocomposites

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Received: 12 August 2018; Accepted: 28 September 2018; Published: 22 October 2018



Abstract: Graphite/poly(3,4-ethylenedioxythiophene) (PEDOT) nanocomposites were prepared by an in-situ oxidative polymerization process. The electrical conductivity and Seebeck coefficient of the graphite/PEDOT nanocomposites with different content of graphite were measured in the temperature range from 300 K to 380 K. The results show that as the content of graphite increased from 0 to 37.2 wt %, the electrical conductivity of the nanocomposites increased sharply from 3.6 S/cm to 80.1 S/cm, while the Seebeck coefficient kept almost the same value (in the range between 12.0 $\mu\text{V/K}$ to 15.1 $\mu\text{V/K}$) at 300 K, which lead to an increased power factor. The Seebeck coefficient of the nanocomposites increased from 300 K to 380 K, while the electrical conductivity did not substantially depend on the measurement temperature. As a result, a power factor of 3.2 $\mu\text{Wm}^{-1} \text{K}^{-2}$ at 380 K was obtained for the nanocomposites with 37.2 wt % graphite.

Keywords: PEDOT; graphite; nanocomposites; thermoelectric properties

1. Introduction

Thermoelectric (TE) materials can directly convert energy from thermal to electrical and vice versa by transporting carriers [1,2]. Poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives are promising for TE applications, mainly because of its low thermal conductivity, low density, and the possibility of achieving high electrical conductivity after doping [3–10]. PEDOT and its derivatives have been synthesized primarily by chemical oxidation polymerization [11], vapor-phase polymerization [12], and electrochemical polymerization [13]. Although the ZT value (the thermoelectric figure of merit $ZT = S^2\sigma T/k$, where T , S , σ , and k are absolute temperature, Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively [5]) of PEDOT and its derivatives have been significantly enhanced [14,15], it is still much lower than that of typical inorganic TE materials.

Many researchers have used carbon materials, such as carbon nanotubes (CNTs) and graphene, as thermoelectrics in their own right [10] and as fillers for preparation of conducting polymer-based nanocomposites [10,16–25], mainly because of their high electrical conductivity and excellent thermal stability [26,27]. For instance, we fabricated carbon black (CB)/poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) composite films using a spin-coating process, and a power factor of 0.96 $\mu\text{Wm}^{-1} \text{K}^{-2}$ was obtained for the composite film with 2.52 wt % CB [16]. In contrast, for our dip-coated polyester fabric, using a mixture solution of PEDOT:PSS and water base colloidal graphite, a power factor of only 0.025 $\mu\text{Wm}^{-1} \text{K}^{-2}$ at 398 K was

determined with 15 wt % graphite content [20]. When graphene was used as filler, a power factor of $11.09 \mu\text{Wm}^{-1} \text{K}^{-2}$ was obtained for graphene/PEDOT:PSS nanocomposite films, fabricated through a solution spin coating method with 2 wt % graphene at room temperature [17]. A power factor about $5.2 \mu\text{Wm}^{-1} \text{K}^{-2}$ was achieved for PEDOT-reduced graphene oxide (rGO) nanocomposites prepared by a template-directed in-situ polymerization method with 16 wt % rGO at room temperature [18]. In contrast, higher power factors around $50 \mu\text{Wm}^{-1} \text{K}^{-2}$ have been obtained [22,23]. For example, a room-temperature power factor of $45.7 \mu\text{Wm}^{-1} \text{K}^{-2}$ was achieved for graphene/PEDOT:PSS composites prepared by in-situ polymerization with 3 wt % graphene [22], and a room-temperature power factor of $53.3 \mu\text{Wm}^{-1} \text{K}^{-2}$ was obtained for graphene/PEDOT:PSS composites fabricated by vacuum filtration with 3 wt % graphene [23]. For a PEDOT: PSS/graphene-iron oxide nanocomposite (GINC), a power factor of $51.93 \mu\text{Wm}^{-1} \text{K}^{-2}$ was achieved for the composites with 95 wt % GINC at 300 K [28]. Furthermore, CNTs can be used as fillers. For example, Wang et al. [19] fabricated multi-walled carbon nanotube (MWCNT)/PEDOT composites by in-situ oxidative polymerization, and a power factor of $25.9 \mu\text{Wm}^{-1} \text{K}^{-2}$, was obtained for the composites with 26.5 wt % MWCNTs at room temperature. Several examples of CNT-containing composites yield much higher power factors [24,25]. For example, Zhang et al. [24] fabricated a single-wall carbon nanotube (SWCNT)/PEDOT: PSS composite by mixing aqueous dispersions of SWCNT and PEDOT: PSS, and a room-temperature power factor of $300 \mu\text{Wm}^{-1} \text{K}^{-2}$ was obtained with 74 wt % SWCNTs. Wang et al. [25] prepared an n-type CNT/PEDOT composite by in-situ polymerization, and a power factor of $1050 \mu\text{Wm}^{-1} \text{K}^{-2}$ was achieved with 10.7 wt % CNTs at room temperature.

These examples from the background research show that the TE properties of PEDOT and its derivatives can be greatly improved when using carbon materials, such as carbon black, carbon nanotubes, or graphene, as fillers in composites with a PEDOT or PEDOT-derivative matrix. Compared to carbon nanotubes and graphene, graphite is much cheaper, motivating the need for studies of thermoelectric properties of graphite/PEDOT nanocomposites. In this work, graphite/PEDOT nanocomposites were prepared by an in-situ oxidative polymerization method and their composition, microstructure, and TE properties were investigated.

2. Materials and Methods

2.1. Materials

Graphite powder (APS 7–11 micron, 99%) and anhydrous ethanol were purchased from Shanghai Titan Technology Co., Ltd. (Shanghai, China). 3,4-ethylenedioxythiophene (EDOT) (purity $\geq 99.0\%$) was purchased from Adamas-beta. Chloroform (CHCl_3) and Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the materials were used without further treatment or purification.

2.2. Preparation of Graphite/PEDOT Nanocomposites

A designed amount of graphite (to obtain 8.9, 18.1, 29.8 and 37.2 wt % with respect to the sum of the weight of graphite and monomer) was added into 100 mL CHCl_3 , ultrasonicated for 1 h and then stirred for 30 min (solution A). Next, 0.85 mL EDOT monomer was dissolved in 50 mL CHCl_3 and then stirred for 30 min (solution B). Solution B was mixed with solution A, ultrasonicated for 10 min and then stirred for 30 min (solution C). 8.65 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as oxidant was dissolved in 50 mL CHCl_3 to form solution D. Solution D was dropped into solution C, stirred for 24 h, and then washed with deionized water and anhydrous ethanol for several times until the filtrate became colorless. Finally, the products were dried at 60°C under vacuum for 8 h. The prepared graphite/PEDOT nanocomposite powders were pressed into thin pellets with a diameter of 15 mm and thickness of about 1.5 mm by compacting at a room temperature under the pressure of 30 MPa for 30 min. The pure PEDOT particles and pellets were prepared using the same procedure without addition of graphite.

2.3. Sample Characterization

The graphite/PEDOT nanocomposite powders were characterized by X-ray power diffraction (XRD; TD3500, Dandong, China), and scanning electron microscopy (SEM; FEI Quanta200 FEG) and X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe (ULVAC-PHI)), using Al K α radiation from an X-ray tube operated at 15 kV and 40 W. The spot size was 200 μ m. The base pressure for the measurement was about 6×10^{-7} Pa. The samples were not plasma-etched before measurement. The electrical conductivity and Seebeck coefficient of the graphite/PEDOT nanocomposite bulk materials were measured simultaneously from 300 K to 380 K on an MRS-3L thin-film TE test instrument system in a vacuum atmosphere (Wuhan Giant Instrument Technology Co., Ltd., Wuhan, China).

3. Results and Discussion

Figure 1 is a schematic illustration of the fabrication process of the graphite/PEDOT nanocomposites and bulk materials. When the EDOT monomer was added into the graphite dispersion, the EDOT monomer was adsorbed on the surface of graphite due to electrostatic attraction [29]. After the oxidant of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dropped into the solution, the EDOT monomer was in-situ polymerized on the surface of graphite, and then formed graphite/PEDOT nanocomposites. Figure 2a shows XRD results of PEDOT, graphite and graphite/PEDOT nanocomposites with 37.2 wt % graphite. It can be seen that the as-prepared PEDOT shows an amorphous XRD feature as expected [30], while the graphite shows a strong peak at about 26.48° , which is attributed to diffraction from the (002) plane of graphite [31]. The graphite/PEDOT nanocomposite also shows this characteristic peak of graphite combined with the amorphous feature from PEDOT. Figure 2b shows XPS survey spectra of graphite and graphite/PEDOT nanocomposites with 37.2 wt % graphite. It can be seen from Figure 2b that the pure graphite mainly contains carbon, with a small amount of oxygen from surface contaminations detected. In contrast, for the graphite/PEDOT nanocomposites, S and Cl were detected. The Cl originates from the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ used in the synthesis process [32,33]. Sulphur is a characteristic element of PEDOT. The binding energy at around 164.2 eV is attributed to the S_{2p} band in PEDOT [34]. Since XPS is a highly surface-sensitive technique, this indicates that that PEDOT was coated on the surfaces of graphite.

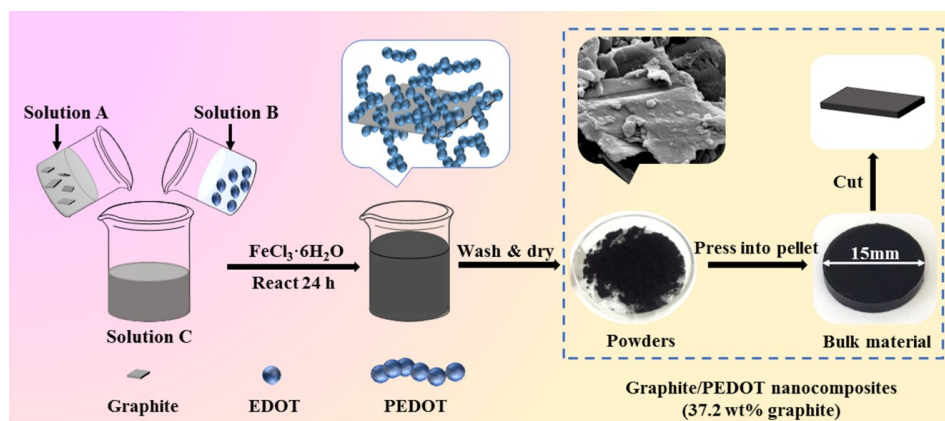


Figure 1. Schematic of the fabrication process of the graphite/poly(3,4-ethyenedioxythiophene) (PEDOT) nanocomposites and pellets.

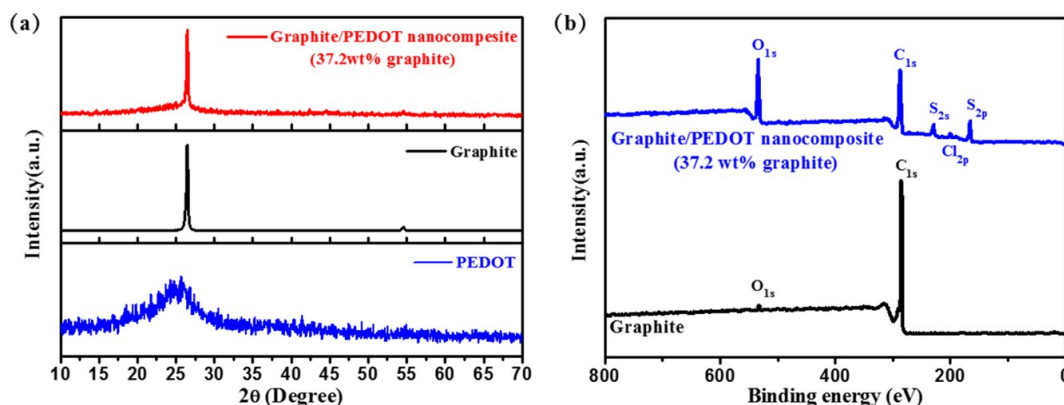


Figure 2. (a) X-ray power diffraction (XRD) patterns of PEDOT, graphite, and graphite/PEDOT nanocomposite with 37.2 wt % graphite, and (b) X-ray photoelectron spectroscopy (XPS) of graphite and graphite/PEDOT nanocomposites with 37.2 wt % graphite.

Figure 3a–f show SEM images of graphite (a & b) and graphite/PEDOT nanocomposites with 8.9 wt % (c), 18.1 wt % (d), 29.8 wt % (e), and 37.2 wt % (f) graphite. The surfaces of pure graphite are much smoother than those of graphite/PEDOT nanocomposites, indicating that PEDOT is homogeneously coated on the graphite surfaces. Figure 3g,h show an SEM image and corresponding energy dispersive spectrometer (EDS) map of sulphur for the graphite/PEDOT nanocomposites with 37.2 wt % graphite. As indicated by the EDS map, the sulphur is homogeneously dispersed in the graphite/PEDOT nanocomposites (Figure 3h).

The electrical conductivity, Seebeck coefficient, and power factor at 300 K for the graphite/PEDOT nanocomposites with graphite content from 0 to 37.2 wt % are shown in Figure 4a. The electrical conductivity and Seebeck coefficient of pure PEDOT are in the range of 3.5 S/cm–6.0 S/cm and 12.0 μ V/K–16.0 μ V/K, respectively. With increasing graphite content from 8.9 wt % to 37.2 wt %, the electrical conductivity of the composites significantly increases from 30.5 S/cm to 80.1 S/cm, in all cases an order of magnitude higher than that of pure PEDOT. The reason for this increase is in part because the electrical conductivity of graphite is much higher than that of PEDOT [35]. It may also be affected by the π – π interactions between PEDOT and graphite, which causes PEDOT to grow along the graphite surface. As a result, a more ordered PEDOT molecular chain may be formed, which is beneficial to decrease the carrier hopping barrier and enhance the carrier mobility [29,36].

The Seebeck coefficient of all the composites retains almost the same value (14.1 μ V/K–15.1 μ V/K), which is close to that of pure PEDOT. As the graphite content is increased from 8.9 wt % to 37.2 wt %, the power factor of the graphite/PEDOT composites increases from $\sim 0.7 \mu$ W/mK² to 1.6 μ W/mK² at 300 K. This was mainly due to the increased electrical conductivity and almost unchanged Seebeck coefficient of all the nanocomposites.

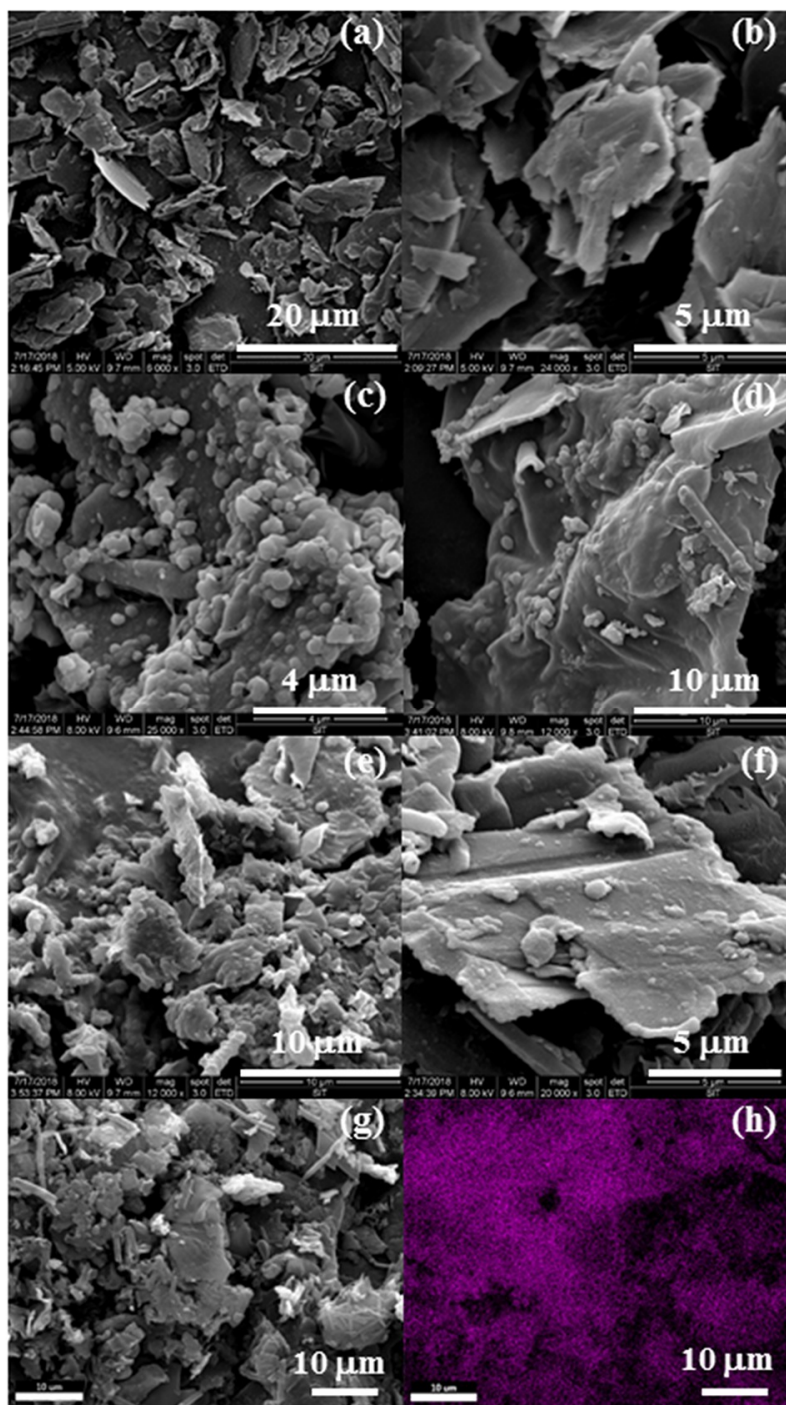


Figure 3. Scanning electron microscopy (SEM) (a) images of graphite (20 μm) and (b) images of graphite (5 μm), graphite/PEDOT nanocomposites with 8.9 wt % (c), 18.1 wt % (d), 29.8 wt % (e), and 37.2 wt % (f) graphite. SEM image (g) and corresponding energy dispersive spectrometer (EDS)-mapping of sulphur (h) for the graphite/PEDOT nanocomposites with 37.2 wt % graphite.

In order to investigate the influence of temperature on the TE properties of graphite/PEDOT composites, the electrical conductivity, Seebeck coefficient, and power factor of graphite/PEDOT, composites with different graphite content were measured in the temperature range from 300 K to 380 K (Figure 4b–d). As the measurement temperature was increased from 300 K to 380 K, the electrical conductivity of the composites was nearly constant. In contrast, the Seebeck coefficient increased, e.g., from 15.1 $\mu\text{V/K}$ to 24.7 $\mu\text{V/K}$, and from 14.1 $\mu\text{V/K}$ to 21.7 $\mu\text{V/K}$, for the nanocomposites with

8.9 wt % and 37.2 wt % graphite, respectively. As a result, the power factor also increased as the temperature increased, and a maximum power factor of $3.2 \mu\text{Wm}^{-1} \text{K}^{-2}$ at 380 K was obtained for the nanocomposites with 37.2 wt % graphite. This is about 30 times higher than that of pure PEDOT ($0.1 \mu\text{W/mK}^2$) prepared by the same procedure, and also much higher than those of a CB/PEDOT nanocomposite ($0.96 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 2.52 wt % CB at 300 K) [16] and a graphite-PEDOT: PSS coated polyester fabric ($0.025 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 15 wt % graphite content at 398 K) [20]. However, this value is lower when compared to the nanocomposites using graphene or carbon nanotube as fillers, for example, a graphene/PEDOT:PSS nanocomposite ($11.09 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 2 wt % graphene at 300 K) [17], a rGO/PEDOT composite ($5.2 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 16 wt% rGO at 300 K) [18], a MWCNT/PEDOT composite ($25.9 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 26.5 wt % MWCNT at 300 K) [19], a PEDOT:PSS/graphene-iron oxide nanocomposite ($51.93 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 95 wt % GINC at 300 K) [28], a graphene/PEDOT:PSS composite ($53.3 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 3 wt % graphene at room temperature) [23], a SWCNT/PEDOT:PSS composite ($300 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 74 wt % SWCNTs at room temperature) [24], and a CNT/PEDOT composite ($1050 \mu\text{Wm}^{-1} \text{K}^{-2}$ with 10.7 wt % CNTs at room temperature) [25]. The possible potential applications of our graphite/PEDOT nanocomposites can be used in the following aspects: wrist watches, remote wireless sensors, biomedical devices, etc. [37].

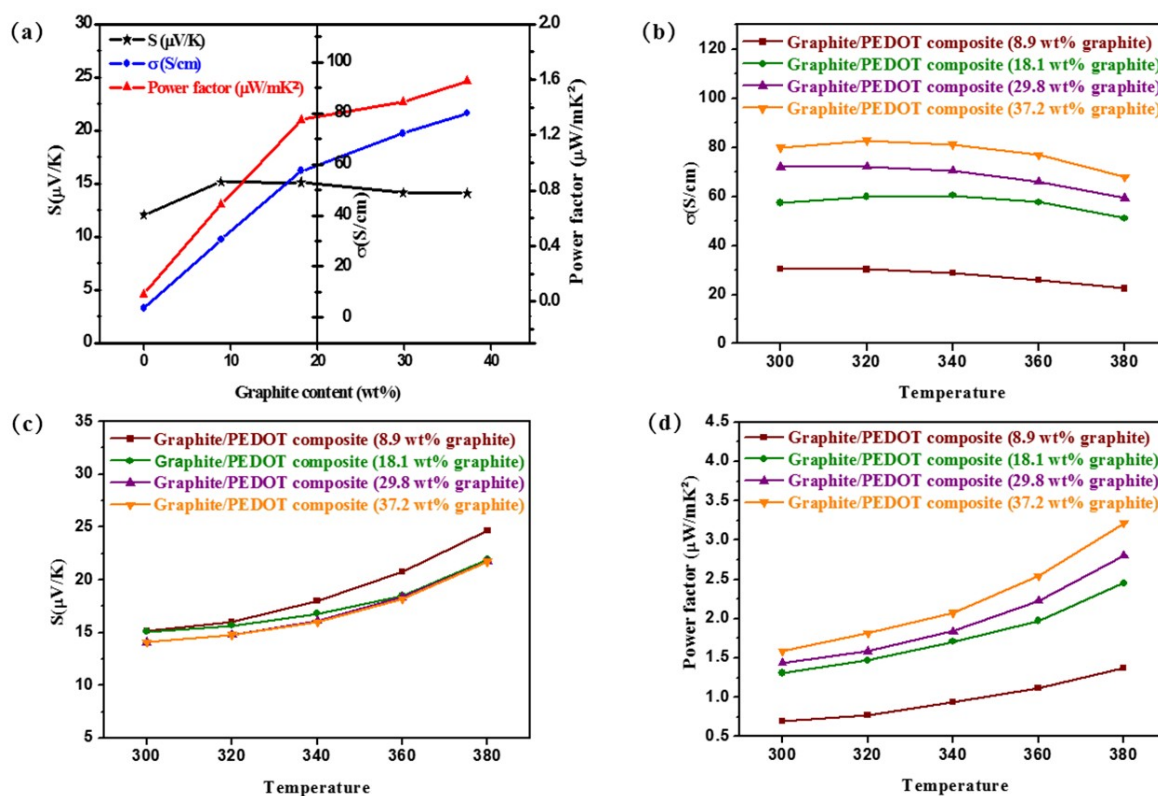


Figure 4. (a) electrical conductivity, Seebeck coefficient, and power factor of graphite/PEDOT nanocomposites with different content of graphite from 0 to 37.2 wt % at 300 K. Temperature dependency of (b) electrical conductivity, (c) Seebeck coefficient, and (d) power factor of graphite/PEDOT nanocomposites with different content of graphite from 8.9 to 37.2 wt %.

4. Conclusions

Graphite/PEDOT nanocomposites were prepared by an in-situ polymerization method with different content of graphite. The electrical conductivity of these nanocomposites was greatly enhanced with the graphite content increased from 0 to 37.2 wt %, while the Seebeck coefficient stayed nearly constant at 300 K. As the measured temperature increased from 300 K to 380 K, the power factor of the nanocomposites increased, mainly because of the similar trend in the Seebeck coefficient. A power

factor of $3.2 \mu\text{W}/\text{mK}^2$ at 380 K was obtained for the nanocomposites with 37.2 wt % graphite, which is about 30 times higher than that of the pure PEDOT, though lower than nanocomposites using graphene or carbon nanotubes as filler. Nonetheless, graphite is economically advantageous compared to carbon nanotubes and graphene. Furthermore, the present study shows that using graphite as filler is an effective method to enhance the TE properties of PEDOT, and also indicates that graphite could be used in other conducting polymer systems.

Author Contributions: Y.D. (Yong Du) designed the experiments, performed data analysis, wrote and revised the manuscript; H.L. and X.J. performed the experiments, data analysis, and wrote the manuscript; Y.D. (Yunchen Dou) performed part of data analysis; J.X. and P.E. revised the manuscript and provided additional intellectual insight; Y.D. (Yong Du) conceived the overall project.

Acknowledgments: This research was funded by the National Natural Science Foundation of China (61504081, 61611530550), the Shanghai Innovation action plan project (17090503600), and the Program for Professor of Special Appointment (Young Eastern Scholar Program) at Shanghai Institutions of Higher Learning (QD2015039). P.E. acknowledges support from the Swedish Foundation for Strategic Research (SSF) through the Future Research Leaders 5 program, the Knut and Alice Wallenberg Foundation through the Wallenberg Academy Fellows program, and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009 00971).

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

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