MECHANISMS FOR PERFORMANCE ENHANCEMENT OF Bi2Te3 IN POLYMER COMPOSITES

By

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A thesis submitted to Johns Hopkins University in conformity with the requirements for the degree of Master of Science

Baltimore, Maryland

May, 2018
Abstract

We demonstrated the use of the as-received conjugated polymer P3HT (poly (3-hexylthiophene-2,5 diyl) doped with F4TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) as a matrix for forming a composite with as-received, commercially available p-type Bi$_2$Te$_3$ powder. The optimized formulation, containing no small inorganic ions, exhibits a power factor of up to 5.3 uW K$^{-2}$ m$^{-1}$, about nine times higher than the highest power factor we achieved from mixtures of only P3HT and F4TCNQ. The Bi$_2$Te$_3$ was responsible for increases in both Seebeck coefficient and electrical conductivity. P3HT, with higher hole mobility, was superior to PQT12 (poly(bisdodecylquaterthiophene), and F4TCNQ was superior to FeCl$_3$, for matrix and dopant, respectively, for this purpose. The power factor obtained is about 40% of that reportedly obtained from synthesized Bi$_2$Te$_3$ nanowires in FeCl$_3$-doped P3HT. Thus, a doped conjugated polymer system made only from commercial-grade components was shown to support the extraction of thermoelectric performance by a commonly used inorganic semiconductor.

Advisor: Howard E. Katz
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1. Introduction

The relationship of energy conversion for thermoelectric performance is

\[ ZT = S^2 \sigma T / \kappa \]

where \( S \) is the Seebeck coefficient (also known as thermopower, the change in voltage with the change in temperature), \( \sigma \) is the electrical conductivity, \( T \) is the temperature in Kelvin and \( \kappa \) is the thermal conductivity.\(^1\) The power factor \( P \) incorporates Seebeck coefficient and electrical conductivity; the exactly relation is \( P = S^2 \sigma \). While the original thermoelectric materials, such as \( \text{Bi}_2\text{Te}_3 \), are inorganic, organic materials have recently been considered because of their potential printability, mechanical flexibility, and use of earth-abundant elements.\(^2\) Many of the latter materials are conjugated thiophene polymers, including the prototypes poly (3-hexylthiophene-2,5 diyl) (P3HT) and poly(3,3''-didodecyl quarter thiophene) (PQT-12). While in special cases, power factors of about 10 \( \text{uW K}^{-2} \text{ m}^{-1} \) can be obtained from all-organic systems,\(^3\) values of 1 \( \text{uW K}^{-2} \text{ m}^{-1} \) are more typical.\(^4\) Thus, it is attractive to use polymers as matrices in which the higher performance characteristics of the inorganic materials can be captured.

\( \text{Bi}_2\text{Te}_3 \) has been used in composites with the conducting polymer composition known as PEDOT-PSS (poly(ethylenedioxythiophene) polystyrenesulfonate).\(^5\)
While strictly speaking, this is a doped thiophene polymer, result on such composites, including from our own group, did not take into account the more recently appreciated complication that some of the thermoelectric response could be due to mobile ions, such as protons, in the formulation. Thus, it is desirable to characterize Bi$_2$Te$_3$ composites in conducting polymer matrices that do not incorporate mobile ions such as the sulfonic acid protons of PSS. Several years ago, there was a report of achieving a high power of about 13.6 uW K$^{-2}$ m$^{-1}$ by mixing synthesized Bi$_2$Te$_3$ nanowires into synthesized P3HT doped with FeCl$_3$. Neither the polymer or the inorganic semiconductor are generally available from commercial sources, and the dopant is not soluble in solvents compatible with the polymer, decreasing some of the cost and processing advantages of the organic composites and making it difficult to quantify the introduced dopant. Thus, we were motivated to characterize related systems using a solvent-compatible dopant and all-commercial material sources. In this work, we used commercial P3HT, commercial Bi$_2$Te$_3$ powder, and the organic dopant F4TCNQ. With this material set, we observe the pronounced contribution of the Bi$_2$Te$_3$. The highest power factor we obtained, about 5.3 uW K$^{-2}$ m$^{-1}$, is 40% of the value that was reported by He et al. for the specifically synthesized nanowire-polymer combination. The influence of charge carrier mobility of the matrix polymer on the composite performance was also shown.
2. Experimental Section

2.1 Materials
Commercial P3HT (poly (3-hexylthiophene-2,5 diyl)), typical Mw=50-70KDa, PD=1.4-1.6, was purchased from Solaris Chem Inc. Commercial PQT12 (poly(3,3′-didodecylquaterthiophene)) was purchased from Solaris Chem Inc. Commercial F4TCNQ (2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane), was purchased from Ossila. Commercial Bi$_2$Te$_3$, powder, 99.99% trace metals basis, was purchased from Sigma Aldrich.

2.2 Sample Preparation

The P3HT powder was dissolved into chlorobenzene with a concentration of 10 mg (P3HT)/ml (chlorobenzene). F4TCNQ was dissolved into chlorobenzene with a concentration of 2 mg (F4TCNQ)/ml (chlorobenzene). The P3HT solution was heated on a hot plate at 45 °C for 30 minutes. The F4TCNQ solution was heated on a hot plate at 60 °C for 30 minutes. The two solutions were combined, with further heating at 60 °C for 30 minutes. Bi$_2$Te$_3$ powder was added directly into the mixed solution, which was then heated at 60°C for 1h.

The solution was dropcast onto a glass substrate with 2 gold electrodes on it. The glass substrate was pre-cleaned with deionized water, acetone and 2-propoal. The gold electrodes were made by thermal evaporation and their thickness was 50 nm. The effective sample area was 0.7 cm long, 0.9 cm wide. The width of gold electrodes and that of the space between the 2 electrodes was 0.3 cm. After most of the solvent was
evaporated from the dropcast films, they were baked at 60 °C in a nitrogen filled glove box. Above that temperature, we found significant electronic property degradation.

2.3 Characterization

Film thickness was measured using a laser microscope. Surface roughness was characterized using scanning electron microscopy (SEM). S and σ were measured using techniques previously described.8

3. Results and Discussion

We first checked the thermoelectric performance of pure commercial P3HT, which was very poor. The typical conductivity was $10^{-4}$ S/cm and S was about 800 µV/K, for a power factor of about 0.01 W K$^{-2}$ m$^{-1}$. We then characterized P3HT with F4TCNQ with a weight ratio of 2:1, (66.6%(P3HT):33.3%(F4TCNQ)) (Table 1).

Table 1. P3HT/F4TCNQ: average power factor: 0.56 $uW/mK^2$, standard deviation: 0.39, highest :0.93

<table>
<thead>
<tr>
<th>Weight ratio</th>
<th>Seebeck coefficient (uV/K)</th>
<th>Conductivity (S/cm)</th>
<th>power factor ( $uW/mK^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>2:1</td>
<td>48.6</td>
<td>3.95</td>
</tr>
<tr>
<td>#2</td>
<td>2:1</td>
<td>22.3</td>
<td>3.3</td>
</tr>
<tr>
<td>#3</td>
<td>2:1</td>
<td>43.8</td>
<td>3.04</td>
</tr>
</tbody>
</table>

This is the best ratio we have found to achieve the highest thermoelectric performance. The conductivity was 3 S/cm and S was 44 µV/K, for a power factor of
0.6 W K\(^{-2}\) m\(^{-1}\), typical for a doped polymer with moderate charge carrier mobility.\(^9\)

The correspondence of the two measurements is shown in Figure 1.

![Figure 1](image)

Figure 1. Position of doped P3HT, with (red) and without (blue) Bi\(_2\)Se\(_3\), on the S-\(\sigma\) plot of Chabinyc (ref. 8).

We added Bi\(_2\)Te\(_3\) at different weight ratios into the P3HT-F4TCNQ solution. Thermoelectric parameters are listed for these ratios in Table 2. The evolution is also shown graphically in Figure 2.
Figure 2. Evolution of power factor with increasing addition of Bi$_2$Te$_3$ to polymer and F4TCNQ in 2:1 ratio. The multiples along the x-axis refer to the relative amounts of Bi$_2$Te$_3$ to the combined organics.

Table 2. P3HT-F4TCNQ-Bi$_2$Te$_3$ Composite Properties

<table>
<thead>
<tr>
<th>Weight ratio</th>
<th>Seebeck coefficient (μV/K)</th>
<th>Conductivity (S/cm)</th>
<th>power factor (μW/m K$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1:5</td>
<td>58.3</td>
<td>3.57</td>
<td>1.21</td>
</tr>
<tr>
<td>2:1:10</td>
<td>86.7</td>
<td>7</td>
<td>5.35</td>
</tr>
<tr>
<td>2:1:14</td>
<td>62</td>
<td>6.25</td>
<td>2.4</td>
</tr>
<tr>
<td>2:1:20</td>
<td>44</td>
<td>1.17</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The order of the weight ratio is P3HT:F4TCNQ:Bi$_2$Te$_3$.

We found that the best ratio for the 3 materials is 2:1:10 (weight ratio, P3HT:F4TCNQ:Bi$_2$Te$_3$) or 15% polymer, 8% dopant and 77% Bi$_2$Te$_3$, where we achieved a power factor of 5.3 μW/m K$^2$. This was about 9 times higher than the
P3HT/F4TCNQ device. This conclusion is based on three P3HT/F4TCNQ devices and three P3HT/F4TCNQ/Bi$_2$Te$_3$ devices (Table 3). As the ratio of Bi$_2$Te$_3$ to P3HT goes over 5:1, the thermoelectric performance of the composite starts to decrease. This seems to be because too much Bi$_2$Te$_3$ powder will compromise the integrity and continuity of the composite, creating highly resistive interruptions. This deleterious effect was visualized by SEM images shown in Figure 3.

Figure 3a:
PQT12-F4TCNQ-Bi$_2$Te$_3$

Figure 3b:
P3HT-F4TCNQ-Bi$_2$Te$_3$
From the scanned pictures we can see that the white dots uniformly distributed on the film should be the $\text{Bi}_2\text{Te}_3$ particles.

Table 3. P3HT/F4TCNQ/$\text{Bi}_2\text{Te}_3$: average power factor: $4.2 \, \mu W/m\,K^2$, standard deviation: 1.02, highest: 5.35

<table>
<thead>
<tr>
<th>Weight ratio</th>
<th>Seebeck coefficient (uV/K)</th>
<th>Conductivity (S/cm)</th>
<th>power factor ($\mu W/m,K^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>2:1:10</td>
<td>66.3</td>
<td>7.69</td>
</tr>
<tr>
<td>#2</td>
<td>2:1:10</td>
<td>86.8</td>
<td>7</td>
</tr>
<tr>
<td>#3</td>
<td>2:1:10</td>
<td>80.3</td>
<td>6.03</td>
</tr>
</tbody>
</table>
Figure 4. Graphical comparison of composite power factor and polymer hole mobility of P3HT and PQT12.

When we used PQT-12 in these doped composite formulations instead, we achieved a power factor of 0.96 \( \mu W/m K^2 \). This is also ~9 times higher than what we obtained from PQT-12 and F4TCNQ composite, but not quite as high as for the P3HT samples, as shown graphically in Figure 4.

We spincoated coat pure P3HT/PQT-12 onto 300 nm SiO\(_2\) wafers and vapor-deposited gold electrodes to form field-effect transistors. Mobilities measured from these devices are shown in Table 4.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Unit ((cm^2 * V^{-1} * s^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT #1</td>
<td>0.0011</td>
</tr>
<tr>
<td>P3HT #2</td>
<td>0.00097</td>
</tr>
<tr>
<td>P3HT #3</td>
<td>0.00085</td>
</tr>
</tbody>
</table>

Sample average: 0.000973, standard deviation: 0.000125
We also performed the experiment analogous to the study that used FeCl₃ and Bi₂Te₃ nanowires in P3HT. We doped P3HT with FeCl₃, with a weight ratio of 30-33% FeCl₃ to P3HT. Because FeCl₃ is only slightly soluble in chlorobenzene, we also made a comparison experiment to check if there is difference between adding FeCl₃ powder directly into the P3HT solution and adding FeCl₃ solution (in ethanol) into the P3HT solution. We also added Bi₂Te₃ powder into the solution. The highest thermoelectric performance we obtained from FeCl₃ doped P3HT is 24 uV/K for Seebeck coefficient and 27 S/cm for electrical conductivity. A power factor of 1.56 uW/mK² was achieved from these data. The highest thermoelectric performance we obtained from FeCl₃ doped P3HT with Bi₂Te₃ powder is 43 uV/K for Seebeck coefficient and 21 S/cm for electrical conductivity (Table 5). A power factor of 3.81 uW/mK² was achieved from these data. SEM of this sample is shown in Figure 5.

Table 5. Thermoelectric performance of FeCl₃ dope P3HT with Bi₂Te₃ powder.

<table>
<thead>
<tr>
<th>Type</th>
<th>Seebeck coefficient (uV/K)</th>
<th>Conductivity (S/cm)</th>
<th>power factor (u W/m K²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>powder</td>
<td>34</td>
<td>16</td>
<td>1.9</td>
</tr>
<tr>
<td>solution</td>
<td>43</td>
<td>21</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Figure 5:
P3HT-FeCl₃-Bi₂Te₃
4. Conclusion

We demonstrated that thermoelectric contributions of as-received Bi$_2$Te$_3$ powders are obtainable in mixtures of commercially available conjugated polymers and dopants. Compared with reference 5 published in Energy & Environmental Science, the major differences are the dopant and the Bi$_2$Te$_3$ powder we used. The dopant F4TCNQ results in lower conductivity than FeCl$_3$, and our results show that the highest conductivity of P3HT/F4TCNQ composite is 3.95 S/cm, compared to 21 S/cm from P3HT/FeCl$_3$ composite, consistent with expectations. We believe that the major enhancement in the prior work is due to the Bi$_2$Te$_3$ nanowires. Compared with powder, nanowire has a more crystalline and interconnected structure. This usually results in better alignment and better conductivity. From the combined results from our work and reference 5, we found
out that our Seebeck coefficient value are similar, ~80-100 uV/K, which is reasonable because we both used the same material. But our conductivity only reached 7 S/cm while theirs reached 18 S/cm. Additionally, our results offer a new combination of organic/inorganic campsites which can show very good thermoelectric performance without using the nanowire effects. We have shown that with more generally available and commercialized materials, we can still achieve the results that agree with the Chabinyc Model in Figure 1 of general thermoelectric performance distribution.
Bibliography


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University of Illinois at Urbana-Champaign, 08/2011-12/2014  
Major: Bachelor’s degree of Science in Physics  
Minor: Mathematics

Johns Hopkins University, 08/2016-present  
Major: Master in Material Science & Engineering

Research interests
Photovoltaics  semiconductors  super-conductors  
thermoelectric materials  electronic material processing  
renewable energy technologies  Nano materials  thin film technologies

Research Experience
Undergraduate School
Undergraduate Researcher in Department of Physics, Summer 2012
Use C programming to create a code to solve the differential equations

Undergraduate Researcher in Department of MSE, Fall 2014

- Learn the method purification of aligned arrays of single-walled carbon nanotubes (SWNTs) by using nanoscale thermocapillary flows
- Process optimization and design to look for an ideal condition that can completely eliminate metallic single-walled carbon nanotubes (m-SWNTs).
- Used micro-probe station to characterize SWNT devices

Research assistant, Spring 2015-Summer 2016

- Use the method of microwave to look for an ideal condition that can completely eliminate metallic single-walled carbon nanotubes (m-SWNTs).
- Use e-beam evaporator to deposit materials on carbon-nanotube samples for purification
- Sample characterization via AFM and SEM
- Use photolithography to create two terminal SWNT devices

Graduate School
Graduate Research Assistant in Department of MSE, Fall 2016-present

- Doping thiophene based polymers with inorganic semiconductors to achieve ultra-high thermoelectric performance (mostly p-type materials, several n-type ones).
- Mixing thiophene based polymers with carbon nano-structures to make devices, and observe their thermoelectric performance.
- Looking for new combinations of organic and inorganic materials to make devices with good thermoelectric performance
- Looking for techniques to improve the thermoelectric performance of existed devices
- Testing the influence of annealing process on thermoelectric performance of different materials.

Publications

"Mechanisms for Performance Enhancement of Bi2Te3 in Polymer Composites" In progress

Technical Skills
Programming
Microsoft Programs (i.e. Excel, Word, etc.) C Programming
Deposition
Thermal evaporator  Atomic Layer Deposition (ALD)
E-beam evaporator  Spin coating  Drop casting

**Measurement & characterization**
Atomic Force Microscope (AFM)  Scanning Electron Microscope (SEM)

**Probe station**

**Surface fabrication**
Photolithography  Reactive Ion Etch

**Other Special**
Brush deposition

(self-developed method to make films with sticky solution with very little solvent or with materials that cannot be dissolved in solvent)