Thermoelectric properties of PEDOT nanocomposites with electrochemically tuned oxidation state

Daniela Gallian
PhD Student
University of Milano-Bicocca
Material Science Department
Conjugated Polymers as Thermoelectric Materials

Poly(3.4-ethylendioxythiophene) PEDOT

Interesting Features

• Low thermal conductivity
• Medium-high electrical conductivity
  • Easy processability
• Tunable electronic properties
• Adaptability to flexible substrate
• Environmental stability

An⁻ = Tos⁻, Cl⁻, PSS⁻, ecc

Performance Implementation Strategies

Nanostructuration

Inorganic Material Inspired Strategies

Conjugated Polymer Tailored Strategies

Secondary Dopants Treatment

Oxidation Level Tuning

Counterion Variation


**Oxidation Level Tuning: How to deal with PEDOT?**

<table>
<thead>
<tr>
<th>Polymerization</th>
<th>Chemical Paths</th>
<th>Electrochemical Paths</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Easy process</td>
<td>✓ Good control process</td>
<td>✓ Conductive substrate</td>
</tr>
<tr>
<td>✓ Insulant substrate</td>
<td>✓ Low control process</td>
<td>✓ Low thickness films</td>
</tr>
<tr>
<td>✓ Easy to embed nanomaterials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>✗ Low control process</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Doping</th>
<th>Chemical Paths</th>
<th>Electrochemical Paths</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ No need of conductive substrate</td>
<td>✓ High control level</td>
<td>✓ Need of properly designed set up</td>
</tr>
<tr>
<td>✗ Low control process</td>
<td>✓ Standard set up</td>
<td></td>
</tr>
<tr>
<td>✗ Need of properly designed set up</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CuO

p-type material

work function: 5.3 eV
Nanocomposite Film Making: Samples

1) Solution deposition
2) Solution spreading
3) Film drying

Kapton Substrate → Gold Evaporation → Gold Pattern → In situ polymerization → Nanocomposite Film

Oxidation Level Tuning

- 5 cycles of CV (3 mV/s)
- Linear Scan to desired potential (1 mV/s)
- Relaxation Time

5 cycles of CV (3 mV/s) → Linear Scan to desired potential (1 mV/s) → Relaxation Time

ECT 2016 Lisbon
Nanocomposite Film Making: Samples

Continuous gold pattern
Not measurable sample

Discontinuous gold pattern
Measurable sample

Modified Oxidation Level Sample

Cutting

Thermoelectric Measurements
Charge Transport Properties

Parameters
\[ \sigma_{E_0}(T) \] transport coefficient
\[ s \] transport parameter

Transport function:
\[ \sigma(E, T) = \sigma_{E_0}(T) \cdot \left( \frac{E - E_t}{k_B T} \right)^s \]
- \( E > E_t \)
- \( E < E_t \)

Electrical conductivity:
\[ \sigma = \int_{E_0} \sigma(E) \left( \frac{\partial f}{\partial E} \right) dE \]

Seebeck Coefficient:
\[ S = \frac{1}{\sigma} \left( \frac{k_B}{\epsilon} \right) \int \left( \frac{E - E_t}{k_B T} \right) \frac{\sigma(E)}{\sigma_{E_0} \left( \frac{\partial f}{\partial E} \right)} dE \]

\[ \eta = \frac{E_F - E_t}{k_B T} \ll -1 \]
non-degenerate limit
\( (E_t: \text{transport edge}) \)

Charge Transport model for conducting polymers

Stephen Dongmin Kang¹ and G. Jeffrey Snyder²
(Private communication)

¹Department of Applied Physics and Material Science, California Institute of Technology, CA 91125, USA
²Department of Materials Science and Engineering, Northwestern University, IL 60208, USA
Preliminary Results

\[
S = \frac{k_B}{e} \left[ s + 1 - \ln \left( \frac{\sigma}{\sigma_{E_0} S \Gamma(s)} \right) \right]
\]

Increasing Oxidation Level

\[ S = 1 \]
\[ \sigma_{E_0} = 70 \Omega^{-1} cm^{-1} \]

PEDOT:Tos

CuO NL 0.58 \(10^{-3}\) g/l

CuO NL 1.18 \(10^{-3}\) g/l

CuO NL 2.94 \(10^{-3}\) g/l
Conclusions

- Preparation of PEDOT based nanocomposite
- Modification of sample oxidation level
- Study of charge transport properties of novel materials

Electrochemical Path

Thermoelectric measurements
Preliminary Conclusions and Further Developments

- Chemical Polymerization
- Electrochemical Oxidation Tunining Method
- Different CuO NL concentration
- Find charge transport model limits
- Different inorganic/organic interphase interactions
- Understand interaction role

Further Developments
Thank you for your kind attention!

Acknowledgments

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Dr. Luca Bertini

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Dr. Simone Battiston

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Questions are welcome!
Charge Transport Model

**Charge Transport model for conducting polymers**

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(Private communication)

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![Graph showing the relationship between Seebeck coefficient and electrical conductivity for different values of s = 1 and s = 3, with parameters σE₀ = 75 S/cm and σE₀ = 10 S/cm.]
CV Comparison

PEDOT:Tos

PEDOT:Tos/Cu NL (2.94 × 10⁻³ g/l)
SEM images comparison

PEDOT:Tos before ECT

PEDOT:Tos after ECT
Poly(ethylene glycol)-\textit{block}-poly(propylene glycol)-
\textit{block}-poly(ethylene glycol)
Optimal oxidation level

Electrical Conductivity (Ω⁻¹ cm⁻¹)

Oxidation Level (V vs Fc⁰⁺)

Seebeck Coefficient (µVK⁻¹)

Power Factor (µWK⁻² m⁻¹)
Oxidation Level Tuning: Results

PEDOT:Tos/Cu NL \( (0.58 \times 10^{-3} g/l) \)

- Electrical Conductivity (\( \Omega^{-1} \text{cm}^{-1} \))
- Oxidation Level (V vs Fc^{0/+})
- Seebeck Coefficient (\( \mu \text{VK}^{-1} \))
- Power Factor (\( \mu \text{WK}^{-2} \text{m}^{-1} \))
PEDOT:Tos/Cu NL ($2.94 \times 10^{-3} \text{ g/l}$)

![Graph showing Electrical Conductivity, Oxidation Level, Seebeck Coefficient, and Power Factor versus Oxidation Level (V vs Fc$^{0/+}$).]
Nanostructuralisation: How to deal with PEDOT?

**NANOCOMPOSITE**

PEDOT:Tos chain

Inorganic nanolamella

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1 μm

EHT = 5.00 kV

WD = 5.0 mm

Signal A = InLens

Mag = 5.00 K X

Sample ID = CuO 1 mg
Nanostructuration:
Energy Filtering

![Diagram showing energy bands and related phenomena](diag.png)

- **Conduction Band**
- **Valence Band**
- **Localization of low velocity holes**
- **Decrease of carrier concentration** $n$
- **Increase of average carrier mobility** $\mu$

$\phi_m$, $E$, $E h^+$
Does nanostructured material modifies PEDOT charge transport properties?

### Table

<table>
<thead>
<tr>
<th>Materials</th>
<th>S (μV/K)</th>
<th>PF (μW/m·K²)</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS/SWCNT</td>
<td>30</td>
<td>25</td>
<td>0.02</td>
</tr>
<tr>
<td>PEDOT:PSS/MWCNT</td>
<td>70</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>PEDOT:PSS/Bi₂Te₃</td>
<td>60</td>
<td>130</td>
<td>0.1</td>
</tr>
<tr>
<td>PEDOT:PSS/Te</td>
<td>163</td>
<td>70.9</td>
<td>0.1</td>
</tr>
<tr>
<td>PEDOT:PSS/Au NPs</td>
<td>26.5</td>
<td>51.2</td>
<td>~0.1</td>
</tr>
<tr>
<td>PEDOT:PSS/Au nanorods</td>
<td>12</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>PEDOT:PSS/Ge</td>
<td>~50</td>
<td>165</td>
<td>0.1</td>
</tr>
</tbody>
</table>


1. Kapton Substrate
2. Gold Evaporation
3. Gold Pattern
4. In situ polymerization
5. Nanocomposite Film
6. Electrochemical Treatment
Modified Oxidation Level Sample

Cutting

Thermoelectric Measurements