Electronic Transport and Anisotropic Conductivity Behavior on PEDOT:PSS Nanoribbons and Nanostructuring Modification by Atomic Force Microscope Nanoshaving

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Abstract
Nanoribbons of organic semiconductor salts, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS), were deposited on silicon dioxide (SiO2) by the electrospinning technique. It is possible to “shave” or mechanically displace small regions of the polymer nanoribbon by using atomic force microscopy (AFM) nanolithography techniques such as nanoshaving, leaving swaths of the surface cut to the depth of thickness of the nanoribbon. By placing the nanoribbon between two electrode pads with a 10 μm gap, for the first time was performed nanoshaving on the nanoribbon by removing portions of PEDOT-PSS and simultaneously in-situ transport measurement properties of the nanoribbon’s dependence on the remaining cross section, showed evidence of anisotropic nature of the conductivity of PEDOT-PSS nanoribbons.

Keywords: Dip-pen; Nanolithography; Nanoshaving; Atomic Force Microscopy (AFM); Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS)

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Introduction
The field of conjugated polymer semiconductors developed from a fundamental laboratory discovery into a manufacturing technological material for a range of thin-film nanostructures for electronics applications [1-3], which benefits from the compatibility of polymers with large-area, low-cost, room temperature solution processing, structural flexibility and direct-write printing. Since their discovery [4-5], polymer semiconductor applications now include emissive light-emitting diodes, flat panel displays, and low-cost thin film transistor circuits on flexible substrates [6]. Recently, it has become clear that some general manufacturing methodologies of polymer electronics, which have been successfully applied to develop conventional, thin-film electronic devices, might also open up a new pathway for functional nanostructures and devices. Fabrication methods like electro spinning provide these advantages of fabricating nanostructures like nanofibers and nanoribbons [7-10]. Utilizing nanofabrication methods of AFM Nanolithography, Nanoshaving, on Nanoribbons of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS) by nanoshaving, an atomic force microscopy nanolithography technique [11-13], we will explore the limits and flexibility of this material. This process involves an AFM tip under a relatively high force load to shave away or displace material. The fabrication of nanostructure methods of lithography has typically been achieved on materials by more standard methods like electron beam lithography, X-ray and UV photolithography, self-assembly and recently nano- and micro-imprint (“stamped”) lithography[14-17]. Other methods for fabrication are available, e-beam lithography,
But due to the aggressive beams and high photon energy they may severely damage our material on the surface and deteriorate the performance of our organic semiconductor [18-21]. Self-assembly methods, on the other hand, enable high fabrication output, but suffer from poor or limited control over feature size. Pervious nano, micro fabrication and lithography on poly(3,4-ethylenedioxythiophene) polystyrene sulfonate have demonstrated high-density arrays of organic semiconductors, showing a large throughput and high control of the features size [22-25]. On the other hand, self-assembly methods, enable high fabrication output, but suffer from poor or limited control over feature size.

Nanoribbons of organic semiconductor salts, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS), have been deposited on silicon dioxide (SiO$_2$) by the electrospinning technique. It is possible to “shave” or mechanically displace small regions of the polymer nanoribbon by using atomic force microscopy (AFM) nanolithography techniques such as nanoshaving, leaving swaths of the surface cut to the depth of thickness of the nanoribbon. By placing the nanoribbon between two electrode pads with a 10 μm gap, for the first time we performed nanoshaving on the nanoribbon by removing portions of the PEDOT-PSS nanoribbon: Figure 1a. An in-situ transport measurement was performed of the nanoribbons’ dependence on the remaining cross section.

Nanoribbon Preparation

Utilizing basic elements of electro spinning apparatus, a hypodermic syringe (0.5 cm$^3$ tuberculin syringe) a high voltage power supply (Gamma Research) and a syringe pump (Cole Parmer) as shown in Figure 1b. The needle of this syringe was connected to the power supply, with the cathode (Al foil) grounded at about 20cm. The PEDOT-PSS poly(3,4-ethylenedioxythiophene) polystyrene sulfonate was purchased from Bayer Corp and used as-received and the solution and a 1 wt.% of polyethylene oxide (PEO-plasticizer) was prepared and it was used to produce the nanoribbons via electrospinning [7-10,26]. This solution was placed in the syringe (about 0.5 mL) once the power supply was turned on the syringe pump was set at one drop per 10s. Once the power supply reached a 10kV value, the polymer droplet surpassed the surface tension it starts to jet towards the cathode in short bursts. In Figure 1a we can observe the nanoribbons deposited on the Si/SiO$_2$ substrate. In this low magnification image, we can see that some of the ribbons appear to be flattened; this may be due to the incomplete solvent evaporation prior to it striking the cathode. These nanoribbons where isolated by intercepting the jet flow of the polymer with the passing of the Si/SiO$_2$ between the syringe and the Al cathode. Electrospinning PEDOT-PSS without PEO did not yield any ribbons.

Atomic Force Microscopy (AFM) Characterization and Nanoshaving

Nanostructuring and imaging were both carried out using a NanoInk Inc. DPN 5000 System. The process of nanoshaving has been described extensively elsewhere [11-13,27-29]. Briefly, an AFM tip is used, at low force, to image the surface morphology and to select a region for nanolithography. Mechanical scratching or nanoshaving, Figure 2, may be the most straightforward way of performing nanolithography with AFM; in this process, the tip is employed to displace materials from the sample surface, creating pits or trenches surrounded by walls consisting of the initial substrate material. It has been successfully applied to surfaces of metals, semiconductors and polymers. A necessary consideration in creating reproducible patterns is the durability of the tip itself, which is prone to deformation and contamination after repeated scanning. To avoid excessive wear, it has been proposed that tips composed of, or coated with, hard materials (e.g. diamond) or dynamic mode AFM should be used for such experiments. Nanoshaving was performed under ambient conditions in an acoustic isolation box at 50% ambient humidity. AFM imaging was performed in contact mode, in which the tip is placed in contact with the surface. During the contact mode
imaging, the load force of the tip on the surface was controlled to be less than 1 nN during imaging unless otherwise specified; while for nanoshaving, loads as large as 100 nN were used. Typical scan rates for nanoshaving were 2 and 0.5 Hz, respectively. Finally, the cross-sectional height and amplitude analyses were carried out on the acquired topographical data. The software used for the data processing was Scanning Probe Image Processor (SPIP 5.0.5).

**Transport Measurements**

Transport characterization of the PEDOT-PSS nanoribbon (I-V) properties was measured with a Keithley 6517A electrometer in an environmental chamber with 50% humidity in air [7-10,30]. The ohmic contact to the nanoribbon was accomplished by thermally evaporating an Au pad by shadow mask of 100 µm x 100 µm area and 100 nm thicknesses on the nanoribbons (Figure 3). The square gold pads are separated by 10 µm for the electronic transport channel. The (I-V) stage was carefully mounted under the Atomic Force Microscope for in-situ measurements while measuring their (I-V).

**Results and Discussion**

**AFM characterization: Nanoribbon thickness and aspect ratio**

Nanoribbons of PEDOT-PSS poly(3,4-ethylenedioxythiophene) polystyrene sulfonate were fabricated by electrospinning...
methods on silicon dioxide (SiO$_2$) substrate. Due to the random nature of the electrospinning process and the lack of precise nanoribbon dimension's control, a large number of nanoribbons and nanofibers deposited as above were sought individually by means of Atomic Force Microscope contact and non-contact methods. AFM images were undertaken at a normal applied force by the AFM probe controlled to remain below 1 nN, at ambient conditions. On clean substrates of SiO$_2$, the surface is atomically flat with only a few atomic steps.

Measuring the height “thickness” and the width of the nanoribbon (Figure 4), if carried out to sufficient precision, is useful for determining the configuration of the molecules. The height “thickness” in particular has been a useful tool to determine molecular or structural information [11-13,27-28]. The cross-sectional analysis indicates the thickness of the nanoribbon and its width, as shown in Figure 4b. As a comparison tool, we measure the width vs. height plot or aspect ratio equivalent of the nanoribbon shown in Figure 5. As shown in Figure 5, the width vs. height plot exhibits a decrease in width when the height increases between 0-7.9 nm. Around 7.9 nm height, the plot undergoes a change in the relationship, in which the width and height both increase proportionally, showing evident width minima at 1.1 nm. As shown in Figure 5 inset, two-line fitting was used to calculate the intercept at 7.92 nm height at a minimal width of 1.1 nm, which defines the transition from a negative slope relationship to a positive slope. From this experimental relationship, it is possible from the electrospinning fabrication method to obtain two fibers with the same width, but with two distinct heights (“thicknesses”) of the nanoribbons.

The polymer interlayer spacing reported from crystallographic data [31-34], Figure 6, shows that the unit cell for PEDOT is ~1.4 nm along the a-axis (100) direction. The b-axis or (010) direction shows a face-to-face repetitive unit of 0.68 nm, the direction in which the plane of the thiophene ring faces each other in parallel. The c-axis 0.78 nm (001) is along the polymer chain’s main molecular axis. The polymer interlayer spacing from the nanoribbons can be estimated using Atomic Force Microscopy by defining one monolayer (1 ML) as the minimum height measured on Figure 5 to be 4.88 nm, obtained from electrospinning fabrication. This minimum value in height shown in Figure 5 to be 4.88 nm is in agreement with the literature value of crystal size reported values between 3 nm to 5 nm [33,35,36]. A monolayer (ML) is defined by an integer number of molecular monolayers. The interlaying spacing results are shown in Table 1, with a range of values between 1.37-1.63 nm. The following range of interlaying spacing agrees with the 1.4 nm interlaying spacing along the (100) or a-axis [31,32] reported from crystallographic data. The range values obtained from the results of electrospinning (Table 1), 1.37–1.63 nm (average 1.46 nm) are also in agreement with the counter-ion chemistry and d (100) spacing correlation established by Martin [31]. As shown in Table 2, the d(100) spacing reported by Martin [31], the counter-ion PSS- shows a d(100) distance of 1.46 nm.

Electronic transport properties and cross-sectional dependence

Transport measurements were performed on the nanoribbons. The nanoribbons, as described in the experimental section, were connected by thermal evaporating gold pads separated by a 10 μm gap; see Figure 4. The chosen nanoribbon of Figure 4 has an average height of 66 nm and average width of 27 μm. To study the nanoribbon’s cross-sectional dependence on the electronic transport, we used nanoshaving by Atomic Force Microscopy. As described above, nanoshaving is an Atomic Force Microscopy Nanolithography technique, in which a large normal force is applied on the tip to penetrate the material and to remove or displace materials, leaving behind the exposed original substrate. Cuts as shown in Figure 7 were purposely made to change the

![Figure 4](image_url) (a) AFM image of topography or height and crossection measurement (b) showing a nanoribbon with an average height of 66 nm and 27 um wide.
Height and width cross-sectional analysis of a diverse group of nanoribbons. Inset figure contain linear and nonlinear fitting for visual guide in order to determine a minimum width value of 1 nm for a height of 8 nm.

Interlayer spacing reported from crystallographic data\textsuperscript{31–34} shows unit cell for PEDOT is \(~1.4\) nm along the a-axis (100) direction. The b-axis or (010) direction shows a face-to-face repetitive unit of 0.68 nm, the direction in which the plane of the thiophene ring faces each other in parallel. The c-axis 0.78 nm (001) is along the polymer chain’s main molecular axis.
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Table 1: Atomic force microscopy measurements of Nanoribbon height and fitted integer of molecular monolayers with resulting polymer interlaying spacing \( d(100) \).

<table>
<thead>
<tr>
<th>Nanoribbon Height (nm)</th>
<th>Molecular Monolayer Integer</th>
<th>( d(100) ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.88</td>
<td>3</td>
<td>1.62</td>
</tr>
<tr>
<td>6.05</td>
<td>4</td>
<td>1.51</td>
</tr>
<tr>
<td>7.53</td>
<td>5</td>
<td>1.51</td>
</tr>
<tr>
<td>8.62</td>
<td>6</td>
<td>1.44</td>
</tr>
<tr>
<td>14.3</td>
<td>10</td>
<td>1.43</td>
</tr>
<tr>
<td>16.8</td>
<td>12</td>
<td>1.4</td>
</tr>
<tr>
<td>19.2</td>
<td>14</td>
<td>1.37</td>
</tr>
<tr>
<td>24.5</td>
<td>17</td>
<td>1.44</td>
</tr>
<tr>
<td>27.1</td>
<td>19</td>
<td>1.43</td>
</tr>
<tr>
<td>28.2</td>
<td>20</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Average value \( d(100) \) 1.46

Table 2: \( d(100) \) Spacing of PEDOT as a function of counter-ion chemistry as reported by Martin [31]. Abbreviations: PAA-: Poly(acrylic acid), PSS-: Polystyrene Sulfonate, PTS: p-Toluene Sulfonate, EBS: 4-Ethylbenzenesulfonate, CSA: Camphorsulfonic Acid.

<table>
<thead>
<tr>
<th>Counter-ion</th>
<th>( d(100) ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA-</td>
<td>1.52</td>
</tr>
<tr>
<td>PSS-</td>
<td>1.46</td>
</tr>
<tr>
<td>PTS</td>
<td>1.39</td>
</tr>
<tr>
<td>Cl-(NaCl)</td>
<td>1.39</td>
</tr>
<tr>
<td>Cl4SO3</td>
<td>1.37</td>
</tr>
<tr>
<td>Cl-(CaCl2)</td>
<td>1.33</td>
</tr>
<tr>
<td>EBS</td>
<td>1.32</td>
</tr>
<tr>
<td>CSA</td>
<td>1.29</td>
</tr>
<tr>
<td>F-</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Conclusions

We have shown that PEDOT-PSS nanoribbons fabricated by electrospinning can produce two types of nanoribbons, which have a very low height on the order of 5 nm, and two different widths. It is possible for thin nanoribbons of PEDOTS-PSS for their height to be correlated to the reported crystal structure and orientation and reported nanocrystal dimensions of 4.8 nm for PEDOS-PSS [33]. AFM nanolithography methods were used to study the nanoribbon’s transport behavior. The transport properties do exhibit a non-classical behavior and strong anisotropic conductivity for nanoribbons of 66 nm height. For nanoribbons of 5 nm height, on the other hand, classical behavior is shown in the conductivity of the PEDOT-PSS.
Acknowledgments

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References


