

## Explaining the effects of processing on the electrical properties of PEDOT:PSS.

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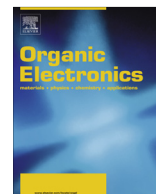
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# Explaining the effects of processing on the electrical properties of PEDOT:PSS



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## ABSTRACT

By simultaneously measuring the Seebeck coefficient and the conductivity in differently processed PEDOT:PSS films, fundamental understanding is gained on how commonly used processing methods improve the conductivity of PEDOT:PSS. Use of a high boiling solvent (HBS) enhances the conductivity by 3 orders of magnitude, as is well-known. Simultaneously, the Seebeck coefficient  $S$  remains largely unaffected, which is shown to imply that the conductivity is improved by enhanced connectivity between PEDOT-rich filaments within the film, rather than by improved conductivity of the separate PEDOT filaments. Post-treatment of PEDOT:PSS films by washing with  $H_2SO_4$  leads to a similarly enhanced conductivity and a significant reduction in the layer thickness. This reduction strikingly corresponds to the initial PSS ratio in the PEDOT:PSS films, which suggests removal and replacement of PSS in PEDOT:PSS by  $HSO_4^-$  or  $SO_4^{2-}$  after washing. Like for the HBS treatment, this improves the connectivity between PEDOT filaments. Depending on whether the  $H_2SO_4$  treatment is or is not preceded by an HBS treatment also the intra-filament transport is affected. We show that by characterization of  $S$  and  $\sigma$  it is possible to obtain more fundamental understanding of the effects of processing on the (thermo)electrical characteristics of PEDOT:PSS.

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## 1. Introduction

The doped semiconductor poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), shown in Fig. 1, finds use in solution-processable electrode layers [1,2] and potentially in novel devices like thermoelectric generators [3–6] because of its relatively high conductivity and Seebeck coefficient. Several approaches exist to improve the conductivity of PEDOT:PSS. Most commonly used are the addition of high boiling solvents (HBS) like ethylene glycol (EG) [1,7], dimethyl sulfoxide (DMSO) [4,8], or other [9] to the PEDOT:PSS aqueous solution and

the post-treatment of the PEDOT:PSS film by washing with sulfuric acid ( $H_2SO_4$ ) [2] or ethylene glycol (EG) [3]. In spite of extensive investigation it is still hard to pinpoint the physical reason(s) for such changes beyond the level of ‘general morphological changes’. Even if evident changes to the morphology are readily observed by AFM or TEM [10–12], it can be problematic to tell which exactly are the changes that are responsible for the observed conductivity increase. E.g. changes in aggregation and phase separation may lead to improved inter-grain [13] or inter-filament [9] transport. Also more microscopic changes [14] may lead to both improved inter- and intra-chain transport. In the hierarchical morphology that is typical for PEDOT:PSS both may, in turn, be reflected in improved intra-grain or intra-filament transport.

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As a typical example, in Ref. [9] the addition of a HBS into the PEDOT:PSS solution, prior to deposition, was shown to significantly enhance the conductivity and also change the temperature dependence of the conductivity. Without HBS the conductivity of the PEDOT:PSS can be described by a quasi-1-dimensional variable range hopping model. In addition a super-linear dependence of the conductivity on the weight fraction of PEDOT in the PEDOT:PSS was found, suggesting that transport takes place via a critical percolating network of quasi-1D filaments [15]. These filaments consist of conductive PEDOT chains, surrounded by PSS which stabilizes the doping of the PEDOT segments. The PSS itself is an electrical insulator. With HBS, the conductivity of the PEDOT:PSS thin film was found to be significantly enhanced and became linearly dependent on the PEDOT weight fraction, indicating that conduction is no longer limited by a percolation through a critical network of filaments [9]. The differences between the PEDOT:PSS with and without HBS could not be explained by major changes in the morphology as proven by TEM showing very similar filamentary structures in both films [9]. Therefore the different conductivity of PEDOT:PSS films with and without HBS could either be due to a change in the microscopic intrachain transport, i.e. easier transport along the filaments, or to an improved connectivity between the filaments resulting in more, but otherwise unchanged filaments contributing to the conductive network. Measurements of the conductivity did not give a definite answer. This impossibility to determine the fundamental origin behind conductivity changes on basis dc conductivity measurements alone is a general problem for research on PEDOT:PSS.

Here we combine an investigation of the conductivity with a study of the thermoelectric properties via the Seebeck effect to determine the microscopic origin of the conductivity changes in differently processed films of PEDOT:PSS. The basic idea is that the Seebeck coefficient reflects the average energy a charge carrier takes along when it moves through a material [16], whereas, in percolating systems, the conductivity is determined by the most difficult steps, being relatively rare events. Hence, improving the conductivity by adding more, but similar filaments to the percolating network is not expected to

lead to significant changes in  $S$ . In contrast, when the transport within the filaments is improved, the Seebeck coefficient is expected to change as well. Hence, the Seebeck coefficient is a probe of (the energetics of) the constituent conductive pathways inside the percolating network.

The investigated PEDOT:PSS films were deposited from solution with or without HBS. Both were characterized before and after washing the deposited films with a 1 M  $\text{H}_2\text{SO}_4$  solution. The addition of HBS prior to spin-coating leads to an enhanced conductivity in the resultant PEDOT:PSS films while the Seebeck coefficient only slightly decreases. This supports the microscopic picture of improvement of the (inter-filament) connectivity in the PEDOT:PSS film. Post-treatment of the PEDOT:PSS with  $\text{H}_2\text{SO}_4$  reduced the thickness by a factor similar to the weight ratio of PSS in PEDOT:PSS. This indicates that the insulating PSS is removed and replaced by  $\text{HSO}_4^-$  or  $\text{SO}_4^{2-}$ . The Seebeck coefficient is increased in case no HBS was previously used, which indicates that the spread in conductivities between the filaments is modified.

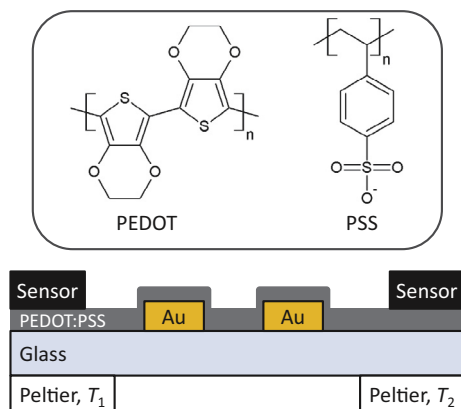
## 2. Experiment

### 2.1. Sample preparation

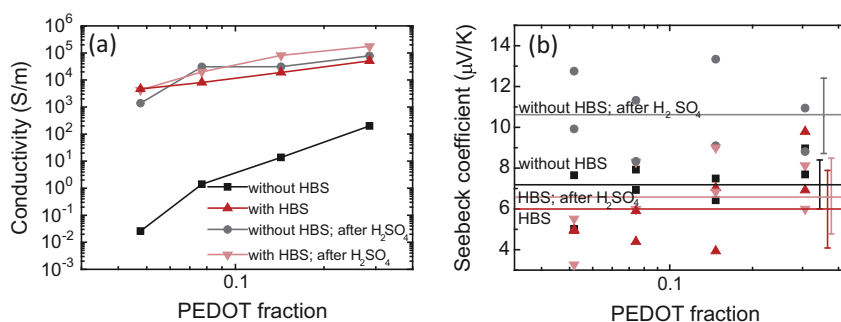
Samples were prepared similarly as reported in Ref. [9]. PEDOT:PSS dispersions were obtained from AGFA-Gevaert N.V. The stock dispersion to prepare the other dispersions had a PEDOT:PSS ratio of 1:2.5, and is commercially available with HBS as Orgacon HIL-1005 and without HBS as Orgacon ICP-1050. PEDOT:PSS dispersions with ratios 1:2.5, 1:6, 1:12, 1:20, with and without HBS, were prepared by mixing with the stock PSS dispersion, followed by the optional addition of water to obtain a PEDOT:PSS solid content of  $0.90 \pm 0.05$  wt%. Subsequently these dispersions were sonicated to improve the homogeneity of the dispersion. Samples were prepared on  $3 \times 3$  cm<sup>2</sup> pre-cleaned glass substrates. Four electrodes (1 mm by 8 mm, 1 mm apart from each other) of 100 nm gold were evaporated on top of each substrate. Then the filtered (0.5  $\mu\text{m}$  filter) PEDOT:PSS dispersions were deposited on the substrates in air by spin coating at 1000 RPM for 1 min, followed by 3000 RPM for 1 min to dry the layer. This resulted in layer thicknesses of roughly 40–60 nm, as indicated per dispersion in the [Supplemental Information](#). After spin coating, the samples were transferred into a glovebox ( $\text{H}_2\text{O} < 1$  ppm and  $\text{O}_2 < 1$  ppm), where they were annealed on a hot plate at 200 °C for 5 min to remove residual water. The optional  $\text{H}_2\text{SO}_4$  treatment was performed outside the glovebox similarly as described in Ref. [2]. A 1 M  $\text{H}_2\text{SO}_4$  solution was prepared in water. The substrates were placed on top of a hot plate at 160 °C. Droplets of the  $\text{H}_2\text{SO}_4$  solution were then deposited on top of the sample. After five minutes the sample was rinsed with demineralized water for three times and transported into the glovebox. There the sample was dried on a hot plate for another 5 min at 200 °C.

### 2.2. Electrical characterization

Conductivity measurements were performed using a Keithley 2636a source-measure unit. To do so, the bias



**Fig. 1.** Chemical structure of PEDOT:PSS and schematic layout of the experimental setup for conductivity and Seebeck coefficient measurements on thin films of PEDOT:PSS.



**Fig. 2.** (a) Conductivity and (b) Seebeck coefficient in thin films of PEDOT:PSS from different processing conditions. The legend in (a) specifies whether HBS or  $\text{H}_2\text{SO}_4$  treatment was used for processing of PEDOT:PSS. The horizontal lines in (b) represent average values for PEDOT:PSS films from different compositions, processed under identical conditions. The vertical lines represent the error margins defined by the standard deviation in the data points. PEDOT fraction is defined as the weight ratio of PEDOT/(PEDOT + PSS).

voltage was swept from  $-2$  V to  $2$  V with steps of  $50$  mV, while measuring the current. Four probes were used, two to apply the voltage sweeps and two additional probes to measure the actual voltage drop between the two gold electrodes contacting the PEDOT:PSS films. The obtained linear graphs were fitted to obtain  $\sigma$  per sample.

The Seebeck coefficient was also measured by the Keithley 2636a source measure unit [17]. A schematic of the experimental setup is shown in Fig. 1. The substrate was positioned on two Peltier elements in such a way that a temperature gradient can be established across the substrate. Since the thermal conductance of the approximately  $100$  nm thick electrodes is negligible compared to the thermal conductance of the  $1.5$  mm thick glass substrate, a linear temperature profile can be assumed across the glass substrate between the Peltier elements. Two silicon diodes were used to measure the temperature on each side of the sample. The electrodes were contacted by Au probe needles. The thermovoltage  $\Delta V$  at a given temperature gradient  $\Delta T$  was determined by measurement of the zero crossing of the  $I$ - $V$  characteristic.  $S$  was then determined by fitting the measured  $\Delta V$  over a range of  $\Delta T$  with  $S = \Delta V/\Delta T$ . The device geometry used in our experiments is expected to give rise to an overestimation of  $S$  by a factor  $1.3$  according to Ref. [17]. The Seebeck coefficients reported here are corrected by this factor.

### 3. Results and discussion

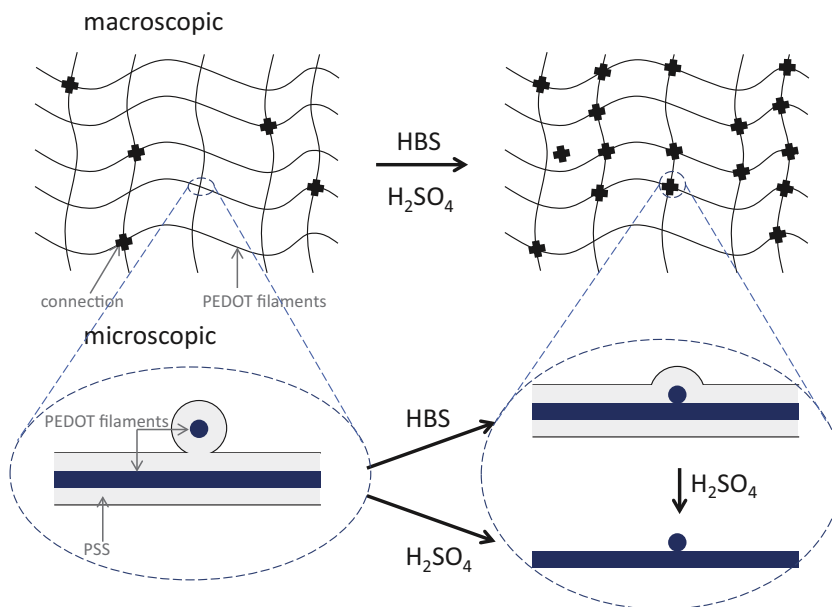
To determine the effect of the two different processing methods, i.e. the use of HBS in the PEDOT:PSS solution prior to spin-coating or post-treatment with  $\text{H}_2\text{SO}_4$ , four series of devices were prepared. For each series, four different PEDOT:PSS ratios were used. These devices were characterized as outlined above to determine  $\sigma$  and  $S$ . The results are shown in Fig. 2a and b, respectively.

In case of the pristine PEDOT:PSS film, a relatively low conductivity (see black squares in Fig. 2a) is obtained which is strongly dependent on the PEDOT:PSS ratio. In Ref. [9] this behavior was attributed to the structure of the PEDOT:PSS, where conductive PEDOT filaments are formed and connect to each other, forming a critical percolating network. Reduction of the PEDOT weight fraction in

PEDOT:PSS results therefore in a strong reduction of the number of conductive paths that are formed and gives rise to the strong, super-linear dependence of the conductivity on the PEDOT:PSS ratio in Fig. 2a. The Seebeck coefficient was found to be roughly independent of the PEDOT:PSS ratio as shown in Fig. 2b (black squares). An average Seebeck coefficient of  $7.2 \pm 1.2$   $\mu\text{V}/\text{K}$  was obtained. This independence is in line with the rationalization of the composition dependence of the conductivity: although the number of percolating pathways increases for increasing PEDOT:PSS ratio, the transport characteristics through each pathway remain unchanged. More percolating pathways lead to a better overall conductivity, but to the same Seebeck coefficient which reflects that the transport energetics of the constituent pathways remained largely unchanged.

The addition of HBS to the PEDOT:PSS solutions prior to spin coating results in a significantly improved conductivity as shown in Fig. 2a (red<sup>1</sup> triangles). Furthermore, the conductivity is no longer super-linearly dependent on the PEDOT:PSS ratio, which is in line with the explanation given in Ref. [9] that the percolating filamentary network is no longer critical, i.e. the film conductivity is no longer determined by a limited number of percolating pathways. TEM images reported in Ref. [9] furthermore show no difference in morphology between films processed with and without HBS. Both show a large number of very similar filamentary structures. Since  $S$  of the HBS processed film (red triangles in Fig. 2) is only slightly reduced compared to  $S$  of the pristine film (black squares in Fig. 2), the origin of the strongly enhanced conductivity after use of HBS can be attributed to an improved filament connectivity, i.e. to improved inter-rather than intra-filament transport. This improved connectivity enables more filaments, with the same average conductivity, to contribute to the overall conductivity of the PEDOT:PSS. Microscopically this means that the HBS creates connections between overlapping PEDOT chains, as shown in Fig. 3. Most likely HBS results in removal of PSS between the PEDOT chains which would otherwise isolate them from each other.

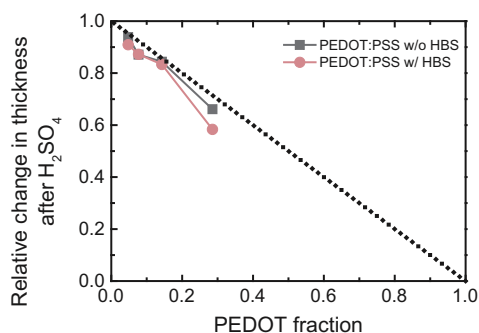
<sup>1</sup> For interpretation of color in Fig. 2, the reader is referred to the web version of this article.



**Fig. 3.** Schematic of the proposed mechanism for enhanced connectivity between PEDOT filaments by processing PEDOT:PSS with HBS or  $\text{H}_2\text{SO}_4$ . Top: macroscopic conducting network. Black crosses indicate electrical connections, enabling filaments to contribute to the network's conductivity. Bottom: proposed microscopic realizations of processing-induced electrical connection between two crossing filaments.

Treatment with  $\text{H}_2\text{SO}_4$  followed by rinsing with water results in a reduced layer thickness. For the PEDOT:PSS films processed with and without HBS the relative reduction of the layer thickness is plotted in Fig. 4 versus the PEDOT weight ratio. The dotted line indicates the PSS weight ratio in the PEDOT:PSS. The change in layer thicknesses of the PEDOT:PSS films after  $\text{H}_2\text{SO}_4$  treatment is strikingly similar to the dotted line. This may indicate that most of the PSS is washed away and replaced by  $\text{HSO}_4^-$  or  $\text{SO}_4^{2-}$  to maintain the PEDOT doping [2].

Post-treatment by  $\text{H}_2\text{SO}_4$  of the PEDOT:PSS film processed with HBS does not result in significant changes in  $\sigma$  and  $S$  as shown in Fig. 2. This means that the conductive PEDOT network remains unchanged, despite the removal of PSS. This indicates that the previous HBS treatment had already connected the vast majority of PEDOT filaments, as indicated in Fig. 3.



**Fig. 4.** Relative thickness after post-treatment of the PEDOT:PSS films with  $\text{H}_2\text{SO}_4$ . The dotted line indicates the PSS weight fraction of the PEDOT:PSS films and corresponds to a full removal of PSS from the film. PEDOT fraction is defined as the weight ratio of PEDOT/(PEDOT + PSS).

In view of the above, post-treatment by  $\text{H}_2\text{SO}_4$  of the PEDOT:PSS film processed without HBS should lead to a similar connectivity and hence a similar conductivity as for the HBS-treated film. This is indeed observed, see gray circles in Fig. 2a. The improved  $\sigma$  can be attributed to the removal of PSS which enhances the connectivity between the PEDOT filaments.  $S$  is observed to be increased as well in Fig. 2b (gray circles). Note that this was not observed after  $\text{H}_2\text{SO}_4$  treatment of PEDOT:PSS films that were previously processed with HBS. Apparently the charge transport within the filaments is modified as well in this case. Likely the use of HBS results in stronger phase separation, which subsequently enables a removal of PSS by  $\text{H}_2\text{SO}_4$  without perturbing the intra-filament transport.

The reduced thickness and the relatively high conductivity after treatment of PEDOT:PSS films by  $\text{H}_2\text{SO}_4$  indicates that insulating PSS is removed, improving the connections between PEDOT filaments. This effect is shown schematically in Fig. 3. In a recent paper Oostra et al. [15] reported a reduced conductivity of a similar PEDOT:PSS material after treatment with hypochlorite. This reduction was attributed to the loss of material due to reaction between the PEDOT and the hypochlorite, which reduced the number of contributing pathways in the percolating network.

When considering the use of PEDOT:PSS for efficient thermoelectric power generators, large values of  $S$  are required in combination with large values of  $\sigma$ . The values of  $S$  for the PEDOT:PSS formulations studied here (between 4 and  $9 \mu\text{V}/\text{K}$ ) are, however, relatively low compared to  $S$  values around  $30 \mu\text{V}/\text{K}$  reported for similar, high-conductivity PEDOT:PSS formulations [3]. We believe that these relatively large values have, apart from lab-to-lab and batch-to-batch variations, to do with the used contact geometry as discussed in detail in Ref. [17].

#### 4. Summary and conclusion

By characterization of the Seebeck coefficient and the conductivity in differently processed films of PEDOT:PSS, the microscopic origin of the improved conductivity due to these processing methods is understood. Addition of a HBS to the PEDOT:PSS solution before spin coating improves the conductivity but leaves the Seebeck coefficient and the morphology of the PEDOT:PSS film largely unchanged. The unaffected Seebeck coefficient indicates that the microscopic structure within the PEDOT filaments remains unchanged. The improved conductivity can therefore be attributed to an enhancement of the connectivity between PEDOT filaments. Post-treatment of PEDOT:PSS by  $H_2SO_4$  is found to lead a reduction of the active layer thickness by a factor that equals the PSS weight ratio in the PEDOT:PSS. This indicates that PSS is removed which explains the observation of a relatively high conductivity by improved connectivity between the remaining PEDOT filaments.

We show that by the combined measurement of  $S$  and  $\sigma$  it is possible to obtain more fundamental and more complete understanding of the effects of processing methods on the electrical characteristics of PEDOT:PSS than is possible on basis of  $\sigma$  alone.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orgel.2014.10.029>.

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