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Anisotropic Conductivity of Cellulose-PEDOT:PSS Composite Materials Studied with A Generic 3D Four-Point Probe Tool

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Graphic abstract:

Keywords:
Cellulose; PEDOT:PSS; composite material; anisotropic conductivity; four-point probe

Abstract
The conductive polymer poly(3,4-ethylenedioxythiphene):poly(styrenesulfonate) (PEDOT:PSS) is widely used in organic electronics and printed electronics due to its excellent electronic and ionic conductivity. PEDOT:PSS films exhibit anisotropic conductivities originating from the interplay of film deposition processes and chemical structure. The previous studies found that high boiling point solvent treated PEDOT:PSS exhibits an anisotropy of 3 to 4 orders magnitude. Even though both the in-plane and out-of-plane conductivities are important for the device performance, the out-of-plane conductivity is rarely studied due to the complexity with the experiment procedure. Cellulose-based paper or films can also exhibit anisotropic behavior due to the combination of their intrinsic fibril structure and film formation process. We have previously developed a conductive paper based on PEDOT:PSS and cellulose which could be used as the electrodes in energy storage devices. In this
work we developed a novel measurement set-up for studying the anisotropy of the charge transport in such composite materials. A tool with two parallel plates mounted with spring loaded probes was constructed enabling probing both lateral and vertical directions and resistances from in-plane and out-of-plane directions to be obtained. The measurement results were then input and analyzed with a model based on a transformation method developed by Montgomery, and thus the in-plane and out-of-plane conductivities could be detangled and derived. We also investigated how the conductivity anisotropy depends on the microstructure of the cellulose template onto which the conductive polymer self-organizes. We show that there is a relatively small difference between the in-plane and out-of-plane conductivities which is attributed to the unique 3D-structure of the composites. This new knowledge gives a better understanding of the possibilities and limitations for using the material in electronic and electrochemical devices.

1. Introduction

Cellulose is the most abundant biopolymer on Earth, it is widely used in hand-writing, drawing, and printed media in the form of paper, it is also heavily used in carboards for packaging, and as hygienic products due to its water absorbing ability. Thanks to its fibrillar structure, mechanical strength, flexibility, hydrophilicity, and chemical and temperature robustness, recently cellulose has begun to find more and more applications in the area of flexible electronics and sensors [1-3]. Numerous sorts of cellulose based composites have been made. Besides the ordinary pulp fibers, cellulose nanofibrils (CNF), which are the separated form of pulp fibers to nanometer level fibrils, has increasingly been used due to its improved uniformity, controllability, and its compatibility with other nano scale electrical conducting materials like conductive polymers, nanocarbons(CNT and graphene) and metals [4-7].

In the last decades, novel conducting polymer materials have found applications in different kinds of organic electronic devices such as organic light emitting diodes (OLED), solar cells, supercapacitors, etc [8-9]. Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate (PEDOT:PSS) is an extensively studied and widely used highly conducting polymer material. It is currently used in different organic electronic devices such as OLED, organic solar cells, and electrochromic displays [10-12]. Research on PEDOT:PSS has been continuously conducted since its invention, and the material, process, and performance has been improved with time. PEDOT:PSS is usually used in a thin film form deposited by spin coating. Besides its high conductivity, PEDOT:PSS is also pseudocapacitive, which makes it an interesting candidate for supercapacitor applications [13-15]. However, PEDOT:PSS films typically require a supporting substrate, and although freestanding films can be produced, they are typically fragile. Cellulose materials, on the other hand, can be formed into relatively thick films/sheets that sustain their structural and mechanical integrity during bending. By combining the mechanical properties of cellulose with the electrical properties of PEDOT:PSS it is possible to achieve freestanding and flexible conductive papers. In the last few years, such papers have found applications in, e.g., reconfigurable sticker labels for organic electronic devices and in supercapacitors (power paper) [6,16,17].

When measuring the electrical conductivity of a polymer film, it is at first hand assumed to be isotropic and the conductivity is measured laterally. However, due to the intrinsic structure of these polymer materials and to the film deposition process kinetics, and the interplay of the two factors, the obtained conducting polymer film often exhibits anisotropic characteristics. It is important to understand this behavior since both the in-plane and out-of-plane conductivities will influence the device performance and often the devices are built up vertically, e.g., solar cells, electrochromic displays, and supercapacitors. Thicker cellulose-PEDOT:PSS film electrodes will give rise to higher values of capacitance, but they will also have a higher vertical resistance. In a supercapacitor, the
charge/discharge performance is dependent on the equivalent series resistance (ESR), which in turn depends on the electrode vertical resistance but also on the resistance of other parts and interfaces. This makes it important to know the vertical resistance, in order to pinpoint where the limiting resistive factors lie. Previously there has been some work on the anisotropic conductivity of PEDOT:PSS thin films [18-23]. It has been shown that spin coated PEDOT:PSS thin films are highly anisotropic. Nardes et al. studied a commercial and an in-house synthetized PEDOT:PSS, both with a PEDOT to PSS ratio of 1:6. The films thicknesses were of 65-90 nm. 4-point probe method was used for in-plane conductivity measurement while two-probe method was used for out-of-plane case. The conductivities were around $10^{-3}$ S/cm for the in-plane and $3 \times 10^{-6}$ S/cm for the out-of-plane cases, respectively. The anisotropy (numerically defined here by the ratio between the lateral and vertical conductivity) is between 2 to 3 orders of magnitude (up to 500). The relatively much lower out-of-plane conductivity is attributed to the long quasi continuous PSS chains/lamellas that are aligned parallel to the substrate and separate the flattened PEDOT-rich clusters vertically [18]. In another paper by Nardes et al. the effect of high boiling point solvent treatment on the conductivities of PEDOT:PSS thin films was studied and correlated to the film morphology. Temperature dependent conductivity was measured for both original and high boiling point solvent treated PEDOT:PSS thin films. Thinner PSS barrier upon using high boiling point solvent was considered to be the reason for the enhanced conductivity. No anisotropic conductivity data was reported for the high boiling point solvent treated samples [19]. Na et al. studied the influence of the amount DMSO on the conductivity [20]. Clevios PH510 was used. Both the in-plane and out-of-plane conductivities were measured, it was shown that conductivities increased in both directions when adding DMSO, but the anisotropy decreased from about 100 to around 10 when the DMSO was increased to 11 wt% in the mixture. In another paper by Yeo et al. [21], PH1000 was modified with high boiling point solvent DMSO, were used to modify the conductivity of the PEDOT. It was found that the lateral conductivity is 4 to 5 orders higher than the vertical one for the DMSO modified one. The anisotropy for the pristine sample is around two orders of magnitude. The conductivity improvement is more evident in the lateral direction than in the vertical one. In a paper by van de Ruit et al. [22], two sorts PEDOT:PSS, both with a PEDOT:PSS ratio of 1:2.5 but one without and another one with high boiling point solvent from AGFA were used. PEDOT:PSS ratios of 1:2.5, 1:6, 1:12, and 1:20 were prepared using the stock solution. By studying temperature dependency of the conductivity for the PEDOT:PSS films with different PEDOT and PSS ratios, they could show that the in-plane charge transport is governed by percolation of quasi 1-D filaments with variable range hopping behavior. In the consecutive work by van de Ruit et al. [23], the anisotropy was found to depend on PEDOT:PSS layer thickness and PEDOT and PSS ratio. The in-plane versus out-of-plane anisotropic conductivity ratio was found to lie between 2 to 4 orders of magnitudes, depending on the thickness and PEDOT:PSS ratio. The percolating cluster model together with the inherent anisotropy of PEDOT filaments and its in-plane aligning preference were used to explain the observations.

To the best of our knowledge, in all the previous work on PEDOT:PSS films, the out-of-plane conductivity was measured with two-point probe method, either thanks to partially overlapping electrodes [18, 23] or to via-hole junctions [20, 21]. In these cases, the effect of an unknown contact resistance may influence the results and make them non-conclusive which gave some uncertainty due to contact resistance. Moreover, no work has been done on relatively thick films up to millimeter level.

Four-point probe resistance measurement technique has been used for more than 100 years [24], and it consists in injecting a constant current from two probes and measuring the consequent voltage drop using the other two probes. Provided that the impedance of the voltage probes is near infinite, the measurement of the sample resistance can be made more accurately than the two-probe
method by removing the influence of contact resistance. When a material conducts anisotropically, the resistivity is no longer a scalar value but a second-rank tensor, and the resistance values measured along one direction depend on every resistivity component. One way to derive the different resistivity tensor components is to make four-point probe measurements along different orientations, and mathematically deduce the different resistivity components [24-27]. It should be noted that for the previous work on PEDOT:PSS, the resistivity was not considered to be a tensor and thus the values obtained are not strictly correct.

In this work we prepared thick free-standing cellulose-PEDOT:PSS films using CNF or pulp as matrix materials, respectively. Films of different thickness for each matrix material were prepared. The resistances of the films were measured in both the lateral (in-plane) and vertical (out-of-plane) directions. To facilitate the measurements, we designed and built an experimental set-up that can conduct four-point probe measurements both laterally and vertically, and that can be used generically to characterize the anisotropic conductivities of self-standing thick films. Additionally, a method to detangle the conductivity from the in-plane and out-of-plane resistance measurements using a resistivity transformation method developed by Montgomery was implemented in a MATLAB® routine to extract the in-plane and out-of-plane conductivity based on the measurements in the two perpendicular directions. The work provides a useful generic tool and method to characterize thick anisotropically conducting films. The results will help to understand the anisotropic conductivity of the thick cellulose-PEDOT:PSS films, and the information will consequently benefit future device development.

2. Experimental

2.1. Materials, mixture and thick film sample preparation

The cellulose-PEDOT:PSS composites are prepared by drying a wet mixture of aqueous cellulose dispersion in a petri dish. Both the CNF and pulp were carboxymethyl functionalized to a degree of substitution of 0.1. The CNF was then high pressure homogenized at 1700 bars [28], providing a heterogenous material consisting of fibers having widths ranging from ones to hundreds of nanometer and length from hundreds to tens of thousands of nanometer. The carboxymethylated CNF used had a solid content of 0.52 wt% and pulp 18.7 wt% The PEDOT:PSS dispersion used was PH1000 from HC-stark, the glycerol and the ethylene glycol used were purchased from Sigma Aldrich.

For preparation of the thick film, first the different ingredients, PEDOT:PSS (PH1000), ethylene glycol, glycerol and CNF/pulp with a dry (water excluding) weight ratio of 16.2:68.2: 9.5:6.1 were mixed together. The recipe is identical to the one used by Malti et al. except that ethylene glycol had replaced dimethyl sulfoxide (DMSO) [16]. The mixture was then thoroughly homogenized together with Turrex high shear rate mixer at a speed of 1000 rpm for one hour. To make Cellulose-PEDOT:PSS films, the wet mixture was cast into a petri dish with a diameter of 5.5 cm. The samples were dried at room temperature. The dried CNF-PEDOT:PSS samples have thicknesses between 46 to 1016 µm by varying the amount of cast material. The thickness was measured with a micrometer screw. For pulp-PEDOT:PSS films, the same formula was used and the dry amount of CNF and pulp is the same.

Drying of the pulp-PEDOT:PSS mixture was faster than CNF-PEDOT:PSS since the amount of water is much less in the pulp than in the CNF dispersion. Samples with different thicknesses between 44 to 2028 µm were prepared by varying the amount of cast material. Fig.1 shows photos for a typical self-standing flexible CNF-PEDOT:PSS film. The pulp-PEDOT:PSS samples look similar except a relatively rougher texture on the surfaces.
Fig. 1. Photos showing a typical CNF-PEDOT:PSS film. After casting and drying, the film is self-standing (Fig. 1a); besides the film is flexible as shown in Fig. 1b.

2.2 Probe fixture tool construction and conductivity measurement set-up
Four-point probe measurements were done with a custom made specifically designed set-up, allowing both lateral and vertical measurements to be done in a convenient way. Fig. 2 is a schematic representation of the fixture and probe build-up arrangement. The set-up consists of two identical and symmetrical probe fixtures set face to face. Spring loaded probes were inserted in the drilled through holes on a transparent polyacrylate holder. The probes were carefully aligned and fixed in place with the help of epoxy adhesive. The probes were arranged in a square pattern configuration with a spacing of 2 mm. Two precise through holes were drilled near the edge of the holder plate for two M6 screw-bolt sets, the facing holes on the two plates are positioned identically with respect to the probes on the two sides, respectively. The screws in the through holes serve two purposes simultaneously, the first is to tighten up the sample placed in between the plates and probes and to allow the probes to come into intimate contact with the sample surface; and secondly, the precise positioning of the screws enable linear alignment for the probes on the two sides. The probe tip is hemispherical in shape with a diameter of 0.33 mm (Pogo Receptacle P2662A-3ED). The rounded shaped of the probe heads in combination with the spring load on the probe minimizes damage to the sample surface, which is ideal for the flexible/soft polymer materials. The tool enables probing on both thin and relatively thick samples and eliminates the need for depositing metallic electrodes. The probes stick out from holder surface about 0.2 mm at the resting state. Upon usage, the free-standing conductive paper film is placed in between the two holders and the intimate contacts with the probes are achieved by tightening the two screws located on the edge of the holder keeping the two polyacrylate plates together. The outer diameter for the plate is 78 mm. The transparent polyacrylate plates have polished surfaces, and each plate is around 7 mm thick. Fig. 3 shows the measurement configuration for in-plane and out-of-plane resistances. In Supplementary Information sections SI 1&2, further detailed details for the setup and comparison to the two-point probe method are described.
Fig. 2. The probe fixture for measuring the conductivities of thick films. There are four probes on each plate holder, which are linearly aligned to each other by the screws going through both plates when tightened. When measuring, the sample is placed in between the two plates, and the intimate contacts between the sample surface and the probes are achieved by pressing from the two parallel plates via the tightening of the screws and bolts.

Fig. 3. Resistance measurement configuration. For in-plane measurement the four probes arranged at corners of a 2 mm square are used (left); for out-of-plane measurement two oppositely facing probes from each plate are used (right), as shown in the schematic.

During the measurement, constant current level of 10 mA is supplied with a Keithley 2602B sourcemeter, and the voltage drop was measured with a Keithley 2182A nanovoltmeter.
2.3 Data extraction

A mathematic routine was developed to extract the resistivities for both in-plane and out-of-plane orientations, based on the method developed by Montgomery [26]. Fig. 4 shows a schematic for the data extraction method. The in-plane directions are defined as the ones lying on the $x,y$ plane; vertical directions are parallel to the $z$ axis. Distances and resistances between probes are known. The in-plane resistivity is assumed to be isotropic ($\rho_x = \rho_y$) and different from that of the out-of-plane one ($\rho_z$).

The method proceeds by changing the probe distances according to the following transformations:

$$s_i' = \frac{\rho_i}{\rho} s_i$$  \hspace{1cm} (eq. 1)

where $\rho = \sqrt[3]{\rho_x \cdot \rho_y \cdot \rho_z}$ for $i = x, y, z$ being $s$ the distance between two probes. This step transforms a cubic volume with anisotropic conductivities to a parallelepiped one of isotropic resistivity $\rho$, while it preserves voltage and current, and hence resistances.

Fig. 4. Mapping of an anisotropic cubic sample into an equivalent isotropic parallelepiped.

Since $V$ and $I$ are preserved and the transformed sample is isotropic, the resistivity is given by

$$\rho = 2\pi \frac{\rho_x}{\rho} s_x \frac{V_x}{I_x} = 2\pi \frac{\rho_x}{\rho} s_x \cdot R_x$$  \hspace{1cm} (eq. 2)

but also
\[ \rho = 2\pi \frac{\rho_z s_z V_z}{\rho} = 2\pi \frac{\rho_z}{\rho} s_z \cdot R_z \] (eq. 3)

Considering the definition of \( \rho \) and eq 2,3, the following set of three equations in three variables is obtained:

\[
\begin{align*}
\rho &= \sqrt[3]{\rho_x \cdot \rho_y \cdot \rho_z} \\
\rho &= 2\pi \sqrt[3]{\frac{\rho_z}{\rho} s_z \cdot R_x} \\
\rho &= 2\pi \sqrt[3]{\frac{\rho_z}{\rho} s_z \cdot R_z}
\end{align*}
\]

It is easy to solve the system in a graphical way by looking at the intersection of the three surfaces defined by \( \rho \) on a \( \rho_x \) and \( \rho_z \) space. A MATLAB® script was written to do so. The method described so far works for samples of infinite thickness. To consider the samples finite thickness, a correction factor was introduced when deriving \( \rho(R_z) \) and \( \rho(R_x) \) by introducing a large number of image sources of current as suggested by L.B. Valdes [25].

2.4 Microstructure characterization

To correlate material structure and process to the electrical measurement results, some of the sample surfaces and cross sections for the thick films were characterized with scanning electron microscopy (SEM). The SEM used was a Zeiss Sigma 500 Gemini. The cross section was prepared by cooling the sample with liquid nitrogen and then breaking the frozen film.

3. Results and Discussion

3.1 Validation of the method

In order to verify the validity of the four-point-probe measurement set-up, a commercial graphite foil about 200 \( \mu \)m thick (Sigraflex F0513TH) with known in- and out-of-plane conductivity was characterized. By evaluating results from different combinations of probes, the deduced values from our measurements gave an average of 1004.3 and 15.8 S/cm, for the in-plane and out-of-plane conductivity, respectively. The specification for electrical resistivity at 20 °C is 1111 S/cm and 14.3-15.4 S/cm, respectively for in-plane (parallel to surface) out-of-plane (perpendicular to the surface). So the accuracy of our measurement is estimated to be within ±10%. The reasonable quantitative agreement found confirms the goodness of set-up and method.

3.2 Conductivity measurements on Cellulose-PEDOT:PSS films

The two series of CNF-PEDOT:PSS and pulp-PEDOT:PSS samples with varying thicknesses, respectively, were measured with our set-up, and the conductivities were then derived. The results are shown in Fig. 5 and Fig. 6. The figures show that all the films exhibit anisotropic conductivity with the in-plane conductivity higher than the out-of-plane one as found in literature. However, the degree of anisotropy (the ratio between in-plane and out-of-plane conductivities) ranges between only one or two orders of magnitude, which was much less than what has been reported for thin PEDOT:PSS films without any cellulose component, for which the degree of anisotropy reached up to four orders of magnitude in some studies [18, 22].
For the CNF-PEDOT:PSS films (Fig. 5), most of the in-plane conductivity values are around 200 S/cm and the out-of-plane one is usually lower than 10 S/cm, indicating at least an order of magnitude difference. The relative thickness independency of the in-plane and out-of-plane conductivities indicates that the film structure is consistent throughout the film and not influenced by the amount of cast material. It is well known that CNF films have a strong preference to align in-plane with the fibers oriented parallel to the substrate surface. In composite films, PEDOT:PSS has been found previously to orient itself around the fiber and CNF is believed to promote self-organization of the PEDOT:PSS [16]. It is plausible that the PEDOT:PSS utilizes the continuously formed CNF lamella network planar template when it dries during the film formation process. Thus, even though the film thickness is far thicker than a spin coated film which usually has sub micrometer thickness, our PEDOT:PSS films still have highly ordered anisotropic structure.

For pulp-PEDOT:PSS films the results that are shown in Fig. 6, the in-plane conductivity is also higher than the out-of-plane one. The in-plane conductivity shows similar tendency as the CNF ones. However, the out-of-plane conductivity is higher than 10 S/cm when the film is thicker than 250 µm, which is higher than in the CNF-based material. The evidence that the pulp-PEDOT:PSS became less anisotropic increasing film thickness implies that the structure is a less organized one. The difference in anisotropy vs. thickness trends of CNF and pulp samples could be due to a number of differences related to the pulp and CNF systems. For example, the physical particle size differs with a factor 1000, the aspect ratio with a factor 1-50, the surface area with a factor 5, the surface charge with a factor 5 and porosity with a factor 1000, to name a few. To deduce the cause of the difference, a more extensive study must be performed, varying the different parameters independently. However, since the difference in conductivity is of order 2-10 when comparing the Pulp-PEDOT:PSS and CNF-PEDOT:PSS, it may be a good idea to start investigating the properties that are differing the same amount.
Some complimentary insights and background to the material and measurement methods are provided in Supplementary Information sections SI3&4. In section SI 3, conductivity measurement results on reference films of pure PEDOT:PSS and PEDOT:PSS-ethylene glycol are presented. Also, drawbacks with practical two-point probe vertical resistance measurements were discussed in section SI 4.

3.3 SEM analysis

To further support and explain the electrical measurement results and their interpretation, SEM analyses were made on one CNF-PEDOT:PSS and one pulp-PEDOT:PSS film, with images of the top and bottom surfaces as well as cross sections (Fig.7). CNF-PEDOT:PSS film exhibits smooth surfaces for both the top surface (Fig. 7a) and the bottom surface (Fig. 7b), as well as its cross section (Fig. 7c). The high smoothness of the CNF films is due to the small dimensions of the CNF nanofiber and highly oriented structure that is formed during the drying, where the CNF forms sheet like structures aligning the long axis of the nanofibers perpendicular to the thickness direction (z-direction) of the films [29]. The larger pulp fiber orients in a similar way but due to their larger size (1000 to 10,000x) a much rougher structure is observed at these length scales. Evidently there is a preference for the fibers to lay parallel to the surface, though cross entangling of the fibers can be seen at some places, which probably also occurs for the nanofibers at a different length scale. The cross section for the pulp-PEDOT:PSS in Fig. 7f shows the complex structure of PEDOT:PSS (presumably) filling inside the large voids between the pulp fibers. For the nanofibers voids are smaller and the network is more compact. The results show that a weaker structural anisotropy is in agreement with the weaker electrical anisotropy measured for these films.
3.4 Summary of results

To summarize, our results show that the parallel plate tool with spring loaded probes works well with the thick films, as shown by measurement with Sigraflex graphite films. All the measured CNF-PEDOT:PSS and pulp-PEDOT:PSS films exhibit anisotropic electrical conductivities. For CNF-PEDOT:PSS films, the thickness dependency is less pronounced. For pulp-PEDOT:PSS films, the
thinner film show more anisotropical behaviour than the thicker ones. There is no big difference between CNF and pulp samples for thinner samples. For CNF-PEDOT:PSS films, SEM images show that the films are aligned in plane with lamellar structure. For pulp-PEDOT:PSS films, the structure is less defined. The electrical and structure analyses agree well.

Conclusions:
We have developed a new tool for studying the 3D-conductivity of free-standing samples and used this tool to study the in-plane and out-of-plane conductivity in conductive paper composites. This method allows to study the out-of-plane conductivity with reasonable accuracy. The flexible spring-loaded probes are also especially suitable for probing soft organic materials. We verified the validity of the measurement technique by characterizing commercial materials with known conductivity values. Besides the previously reported conductive papers made from PEDOT:PSS and nanofibrillated cellulose (CNF-PEDOT:PSS), we also manufactured similar papers using pulp-cellulose fibers (pulp-PEDOT:PSS). The results indicate a relatively small degree of anisotropy in the composite materials as compared to previous studies of PEDOT:PSS thin films, with roughly two orders of magnitude difference in the CNF-PEDOT:PSS samples and less than one order of magnitude difference in the pulp-PEDOT:PSS samples between in-plane and out-of-plane conductivities. These results are attributed to PEDOT:PSS self-organizing on the fibers/fibrils instead of being templated by the substrate onto which the films were cast. The lower degree of anisotropy in the pulp-PEDOT:PSS samples compared to the CNF-PEDOT:PSS samples is believed to result from the difference in the arrangement of fibers and fibrils. The smaller diameter and higher aspect ratio of CNF leads to a larger degree of alignment in the xy-plane, resulting in poorer charge transport in the z-direction. Another important result is that the in-plane and out-of-plane conductivities of both types of samples stay relatively constant for thicknesses higher than 100 µm. This means that there will be no added loss due to the worsened conductivity in performance when scaling up the thickness of the material in applications such as electrodes for energy storage devices. Furthermore, the increase in out-of-plane conductivity for pulp-PEDOT:PSS may be beneficial. In such devices, it is mainly the out-of-plane conductivity that will define the performance, since a metal current collector is typically used for the transport of current in the in-plane direction. The relatively high conductivity in the out-of-plane direction of the Cellulose-PEDOT:PSS materials is therefore a good result. The new insights into how the fiber structure affects the 3D-conductivity could lead to even more efficient conductors by engineering the cellulose microstructure.

Acknowledgements
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References:


Supplementary information for:
Anisotropic Conductivity of Cellulose-PEDOT:PSS Composite Materials Studied with A Generic 3D Four-Point Probe Tool

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SI 1. Photograph of the setup

Fig. S1  Experimental set-up, Keithley 2602B that supplies constant current and Keithley 2182A nanovoltmeter is used for voltage measurement. The probe kit is shown in the middle of the photo.

SI 2. 3-D four-point probe measurements, clarifications

Usually four-point probe measurements are performed laterally, which can be done with or without deposited top electrodes. For the vertical resistance measurement, usually a two-point-probe set up is used, as shown in Fig. S2a. For our case however both the in-plane and out-of-plane conductivity measurement can be done with four-point-probe methods, with one set of tools by selecting different probe combinations. The same probes can be either used for lateral or vertical measurements. Basically only 6 probes are needed, as shown in the supplementary Fig. S2b. However, by having four probes on each side, numerous combinations of lateral and vertical measurement configurations are allowed.
Fig. S2a Earlier work on the anisotropic conductivity of PEDOT:PSS thin films have been done with the combination of in-plane four-point-probe measurement and out-of-plane two-point-probe measurement.

Fig. S2b A sketch showing the set-up used in this article, where four-point probe measurements can be performed both for in-plane and out-of-plane configurations.

SI 3. Reference films of pure PEDOT:PSS and PEDOT:PSS-ethylene glycol
Reference films were made with pure PEDOT:PSS solution (PH1000) and with PH1000 and ethylene glycol (EG) mixture, respectively. The weight ratio for the PH1000 and ethylene glycol was kept the same as for cases of CNF-PEDOT:PSS and pulp-PEDOT:PSS films.

And the anisotropic conductivities were measured on one pure PEDOT:PSS film and one PEDOT:PSS-ethylene glycol film, respectively. A 100 µm thick PEDOT:PSS film made from casting method was measured, its in-plane and out-of-plane conductivity were found to be 0.0196 and 0.00125 S/cm, respectively. The in-plane conductivity data is similar to the result measured on the similar type of PEDOT:PSS material by Crispin et al. [S1].

A 231 µm thick PEDOT:PSS film that was made from a PEDOT:PSS and ethylene glycol mixture was measured and its in-plane and out-of-plane were found to be 120.8 and 30.9 S/cm, respectively.

The results are further summarized in Table SI. Besides Fig. S3 shows a collected display for CNF-PEDOT:PSS, pulp-PEDOT:PSS, pure PEDOT:PSS, and PEDOT:PSS-ethylene glycol films. That the pure PEDOT:PSS exhibits much lower conductivities and the PEDOT:PSS-ethylene glycol shows similar
conductivity levels as the CNF-PEDOT:PSS and pulp-PEDOT:PSS ones are not surprising, since it is the ethylene glycol that makes the conductivity leap for the PEDOT:PSS.

Table SI

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<thead>
<tr>
<th></th>
<th>PH1000</th>
<th>EG+PH1000</th>
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<tr>
<td>Film Thickness (µm)</td>
<td>100</td>
<td>231</td>
</tr>
<tr>
<td>In-plane conductivity (S/cm)</td>
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<td>120.8</td>
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<tr>
<td>Out-of-plane conductivity (S/cm)</td>
<td>0.00125</td>
<td>30.9</td>
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</table>

Fig. S3 A plot with films made of CNF-PEDOT:PSS, pulp-PEDOT:PSS, pure PEDOT:PSS, and PEDOT:PSS with addition of ethylene glycol.

SI 4. Two-point-probe versus four-point-probe measurements

One CNF-PEDOT:PSS with a thickness of 255 µm was used to exemplify the advantage of four-point-probe compared to two-point measurements. From our 3D four-point measurement, this sample shows an in-plane conductivity of 177.8 S/cm, and an out-of-plane conductivity of 4.50 S/cm.

While doing four-point probe measurement, Keithley SMU that is used to supply constant current source of 10 mA gives a voltage readout of 87.08 mV, which results a direct resistance of 8.708 Ω. Assuming that the probe is in contact with the sample surface with a radius of 165 µm, this will give rise to a resistance of 6.6467 Ω using the measured vertical resistivity value mentioned above. For this case, the ideal comparison would be to use only a small portion of material that corresponds to the small contact area of the probe. Nevertheless, with material present around the probe it should only be beneficial for current conduction. The apparent deviation, with the measured value from the probes higher than the value from calculation indicates that the existence of the contact resistance between PEDOT and the probe. Extracting the lead resistance 0.2 Ω for the Keithley SMU, the contact resistance is around 1.86 Ω for this rough estimation.

Another vertical measurement was done with two gold coated metal plates facing each other having an overlapping area of 8x8 mm². Using 10 mA source current, an average resistance of 1.098 Ω was
obtained. Taking away the lead resistance of 0.245 Ω for this case, a net resistance of 0.853 Ω is obtained, which is way higher than the value calculated using the vertical resistivity value derived from the 3D four-point-probe method which gives a vertical resistance value of 0.0089 Ω, indicating the total dominance of contact resistance for this case.

Reference: