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Optimization of PEDOT:PSS layers for hole transporting layers of organic photodetectors

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Short abstract

The study focuses on the optimization of PEDOT:PSS ink for the preparation of a hole transport layer. The ink was developed for the spiral bar coating technique and for subsequent organic photodetector preparation. In this study, the effect of various variables such as secondary dopant, surfactant, PEDOT:PSS complex ratio, and ink composition on selected characteristics such as conductivity, work function, charge carrier mobility, etc. is demonstrated.

Keywords: PEDOT:PSS, secondary dopant, hole transport layer, organic photodetectors, conductivity

1. Introduction

Conducting polymers are one of the most commonly used materials in printed or organic electronics. They can be used in a wide range of functional structures, such as photovoltaic cells, organic electrochemical transistor (OECT), organic field effect transistors (OFET), electroluminescent displays, and others. Conducting polymers can be used where their properties – semiconductivity and transparency are beneficial as in the case of hole transport layer (HTL). This group of conductive polymers includes, the poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), which is often used in the field of organic photovoltaics (OPV) or organic photodetectors (OPD) for either HTL preparation or transparent conductive layer (TCL). In the research of PEDOT:PSS-based inks for the OPD field, our study is directed to develop an ink for the spiral bar coating technique for the preparation of PEDOT:PSS HTL and TCL layers.

OPD, similar to conventional OPV, consists of several layers – TCL, electron transport layer (ETL), photoactive layer (PAL), HTL, and top electrode (Figure 1). All layers have a significant effect on the performance of OPD. In our study, we focused specifically on optimizing and characterization of the HTL layer as one of the components of the OPD. In general, for optimal OPD performance, parameters such as high charge carrier mobility of holes are required for HTL to ensure efficient and selective hole transport into the PAL layer. Furthermore, an optimum value of the work function (WF) of the PEDOT:PSS layer is needed, which is optimized in its value with respect to the preceding and following layers. Last but not least, relatively high conductivity of the PEDOT:PSS layers is required, which will contribute positively to the low internal resistance of the OPD. In addition to the physical parameters mentioned above, high homogeneity of the layers, with no craters/pinholes present, and low thickness are also important. For the preparation of TCLs based on PEDOT:PSS, high conductivity of the layers and high transparency and homogeneity of the layers are important. The aforementioned parameters can be modified by different approaches, especially by modifying the ink composition but also by choosing specific conditions for the synthesis of the PEDOT:PSS or by selection of complex ratios, where PSS- serves as the primary doping counterion.

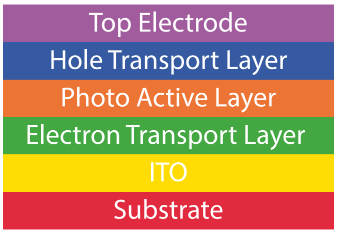

Figure 1: Schematic cross section of the layers structure of OPD, Indium Tin Oxide (ITO)

Several studies in the literature have been focused on determining the effect of secondary dopants on the conductivity of the PEDOT:PSS layer. It has been found that PEDOT:PSS layers additionally treated with ethylene glycol exhibited conductivity up to 1 418 S/cm, which has been attributed to the removal of some PSS$^-$ from PEDOT:PSS layers (Kim, et al., 2011). Ouyang (2013) published that PEDOT:PSS film can reach 3 000 S/cm when post-treated with sulfuric acid. Ouyang, et al. (2004) achieved conductivities of 200 S/cm and 143 S/cm using secondary dopants ethylene glycol and dimethyl sulfoxide, respectively, which they attributed to increased interaction between the chains. When ethylene glycol was used as a secondary dopant, a conductivity of 160 S/cm was determined by Ouyang, et al. (2005). This was attributed to conformational changes. In another study, the authors obtained a conductivity of 966 S/cm, due to the addition of dimethylsulfoxide (DMSO) (Gasiorowski, et al., 2013). Kim, et al. (2002) added tetrahydrofuran to PEDOT:PSS which gave a specific conductance of 4 S/cm, 30 S/cm using dimethylformamide, and 80 S/cm using DMSO. Increases in conductivity up to 48 S/cm attributed to morphological changes caused by various secondary solvents were published by Jönsson, et al. (2003). There are some new approaches to doping or posttreatment of PEDOT:PSS layers, where Khasim, et al. (2022) published posttreatment by camphor sulphonic acid, resulting in 1 826 S/cm. Tang, et al. (2020) used for secondary doping various oxoammonium salts (TEMPO+X−) which enhanced conductivity and allowed to tune work function of PEDOT:PSS layers. Mineral acids were used by Zhang, et al. (2020) into PEDOT:PSS ink formulations resulting to high conductivity up to 2 244 S/cm.

The aim of our study is to investigate ink for the preparation of the HTL layer for the OPD. The investigated inks were prepared from synthesized PEDOT:PSS dispersions with different ratios, ranging from the 1:1 to the 1:5 complex ratio. The composition and other properties of the inks were modified by various solvents, which served as secondary dopants and by surfactants, which enabled high-quality wetting of the printing substrate or the underlying film.

2. Materials and methods

In the study, layers of the PEDOT:PSS conductive polymer were prepared from its modified water-based dispersions. PEDOT:PSS dispersions synthesized with complex ratios of 1:1, 1:1.4, 1:2.5, 1:3.5 and 1:5 were used to prepare the layers. Spiral bar coating technique (TQC AB3120) and corona (Alhbrandt) treated PET substrates (Melinex ST506 125 µm or 175 µm) substrate were used for layers fabrication.

In the case of experiments where the effect of solvents on the electrical conductivity of PEDOT:PSS layers was studied, inks were prepared using a PEDOT:PSS 1:2.5 pristine dispersion with a dry solid content of 0.8 wt.%. Secondary dopant (5 wt.%) was added dropwise to the dispersion while stirring with a magnetic stirrer at 600 RPM. Stirring was carried out for 6 hours at 600 RPM. The prepared ink formulations were filtered through a polytetrafluoroethylene (PTFE) syringe filter (0.45 µm). The solvents used as secondary dopant included the glycol family, amides, and some other aprotic solvents with high dielectric constants up to 180 (Table 1).

Table 1: Types of solvents used as secondary dopants of PEDOT:PSS 1:2.5 layers

Secondary dopant SD #	Sample
Pristine dispersion	Pristine dispersion
SD 1	Amide I
SD 2	Amide II
SD 3	Amide III
SD 4	Amide IV
SD 5	DMSO
SD 6	Glycol I - EG
SD 7	Glycol II
SD 8	Glycol III
SD 9	Organic amine
SD 10	Sulfone I

In the case of the study of the effect of surfactants on the conductivity of layers, the formulations consisted of a pristine dispersion of PEDOT:PSS 1:2.5, 5 wt.% ethylene glycol as a secondary dopant and 0.5 wt.% surfactant (Table 2).

Table 2: Types of surfactant for the improvement of the surface tension of PEDOT:PSS 1:2.5 inks

Surfactant Surf #	Chemical type of surfactant
Pristine dispersion	Pristine dispersion
Surf 1	acetylenic diol
Surf 2	polyether siloxanecopolymer
Surf 3	polyether-modified polydimethylsiloxane
Surf 4	polyethylene glycol phenylether I
Surf 5	polyethylene glycol phenylether II
Surf 6	polyoxyethylene alkyl ether
Surf 7	polyoxyethylene sorbitan oleate
Surf 8	siloxane-based gemini surfactant
Surf 9	tetramethyl decynediol

In the study of the influence of secondary dopant on the conductivity and WF of PEDOT:PSS layers, 5 different solvents were studied (Table3). Ink based on PEDOT:PSS 1:1.4 dispersion consisted of 0.1 wt.% Surf 5, 10 wt.% 2-propanol and 5 wt.% solvents.

For all experiments, inks were coated with an automated spiral bar coater (50 µm spiral bar) at a speed of 100 mm/s. The deposited layers were dried first at 95 °C for 10 min, then at 120 °C for 30 min in a Memmert UF75 hot-air oven.

The electrical properties of PEDOT:PSS layers were measured using the four-point method (digital multimeter Rigol DMM 3068 6 ½) at laboratory temperature in an air-conditioned laboratory at 20 °C and 35 % relative humidity. Geometrical characteristics of the measured samples were determined by optical microscopy (Nikon). The thickness of the prepared layers was measured by mechanical profilometry (KLA Tencor P-7). UV-VIS spectra were measured on a Specord 210 UV-VIS spectrophotometer.

Table 3: Types of secondary doping solvents for improving work function and conductivity of PEDOT:PSS 1:2.5 layers

Secondary dopant SD #	Sample
Pristine dispersion	Pristine dispersion
SD6	Glycol I
SD1	AMIDE I
SD11	AMIDE V
SD12	AMIDE VI
SD13	organic acid

The work function was determined by ultraviolet photoemission spectroscopy (UPS) performed in an UHV apparatus (ESCA 2SR, Scienta-Omicron). XPS spectra were determined at X-ray photoelectron spectroscope (ESCA 2SR, Scienta Omicron).

3. Results and discussion

3.1 Influence of the type of secondary dopant on PEDOT:PSS conductivity

The influence of secondary doping solvents on the conductivity of layers was investigated in the first part of the study. In general, the influence of the solvents can be evaluated in terms of better/worse morphology adjustment of the PEDOT:PSS layer compared to the condition of setting the layer for pristine dispersion. The addition of given secondary dopants often improves the conductivity as well. In some cases, conductivity improvements of up to 3 orders of magnitude are observed. In the experiments, 5 wt% of secondary dopant was added to the pristine dispersion based on our previous experience. In total, 10 different solvents were compared, including a pristine PEDOT:PSS 1:2.5 dispersion.

The amide solvent group has a decreasing value in the terms of permittivity in row Amide I to Amide IV. The overall decreasing trend in the series from Amide I to Amide IV is also at the boiling point. For glycols, Glycol I is ethylene glycol, and the series Glycol I to Glycol III has an increasing trend in terms of the boiling point and molecular weight. In the series Glycol I to Glycol III, the permittivity has a decreasing trend.

Ethylene glycol is used as the standard solvent for secondary doping because of its very good compatibility with PEDOT:PSS dispersions and good secondary doping performance. It is used as a baseline, and the solvent is generally used in further development because of its relatively low toxicity, good conductivity-enhancing properties, does not cause precipitation in combination with many ink additives, and its improvement of the film forming and leveling properties of ink formulations.

From the determined conductivities (Figure 2), it can be concluded that there is a strong correlation between the conductivity of PEDOT:PSS films and the permittivity of the solvents. With increasing solvent permittivity, PEDOT:PSS films generally exhibit higher conductivity. This trend is evident for all solvents considered, but also for a number of amides or glycols. From Figure 2, it can be seen that the layers prepared from ink with SD1 – Amide I solvent (highest permittivity) show the highest conductivity of 78 S/cm. This conductivity is higher than that of the commonly used DMSO.

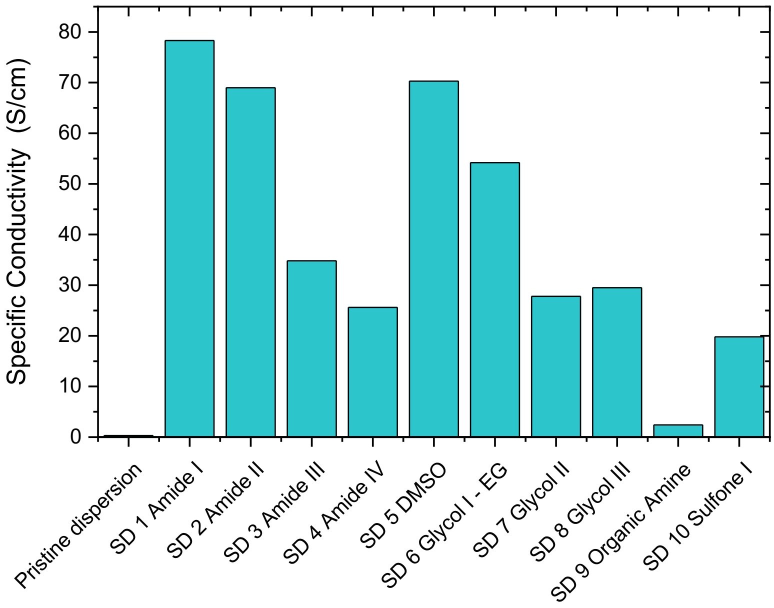

Figure 2: Dependence of conductivity of PEDOT:PSS 1:2.5 layers on the secondary dopant (solvent)

3.2 Influence of the type of surfactant on conductivity and overall layer quality

Nine non-ionic surfactants of different types were used to improve the surface tension of the PEDOT:PSS-based waterborne ink. The effect on the ink wetting capabilities of the print substrate, the appearance of the layers after application, and the conductivity of the layers themselves were investigated.

Because the composition of all of the inks was analogous, all of the layers were compared using the relative conductivity of the layers, which were normalized to the most conductive PEDOT:PSS layer. Figure 3 shows that the layers prepared from inks based on Surf 5 and Surf 7 surfactants had the highest conductivity.

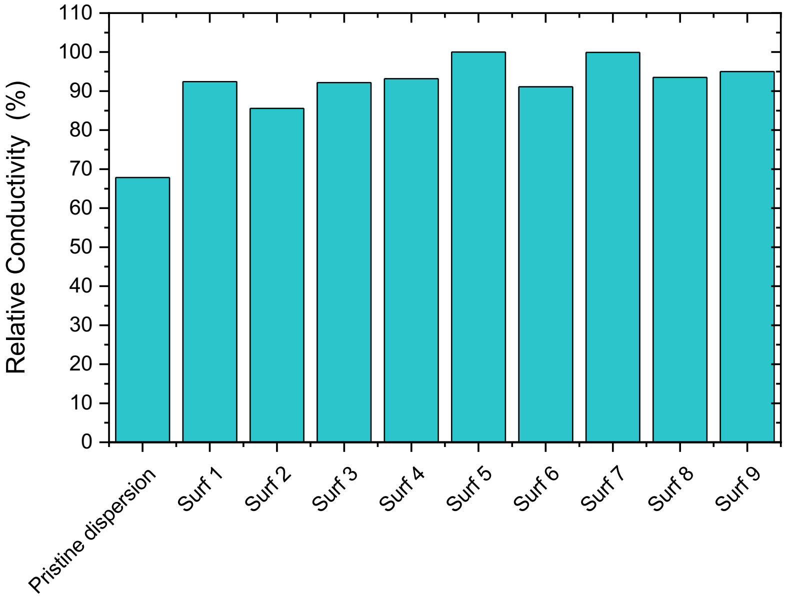

Figure 3: Dependence of relative conductivity of PEDOT:PSS layers on the surfactant

Alongside the evaluation of layer conductivity, the quality/appearance of the layer was evaluated too, because HTL requires high quality/homogeneity imperfection free surface/layer. The evaluation of appearance quality was subjective, assessing the quality of the layer both wet, immediately after coating, and the quality of the layer after drying. The homogeneity of the wet layer and the wetting quality of the PET substrate were observed. For the dry layer, the homogeneity of the layer, the gloss of the layer, the presence of craters, agglomerates, or surfactant residues on the surface of the layer were observed too. Layers with the highest quality of surface appearance had generally the smoothest surface with high surface gloss and without defects (mottling, pinholes, rough surface, etc.). A relative scale was determined from 1 to 5, where the samples with the highest surface quality having a number of 5 (Figure 4). From the given perspective, it was the PEDOT:PSS layers based on ink with Surf 5 that showed high performance - high layer quality and also the highest conductivity.

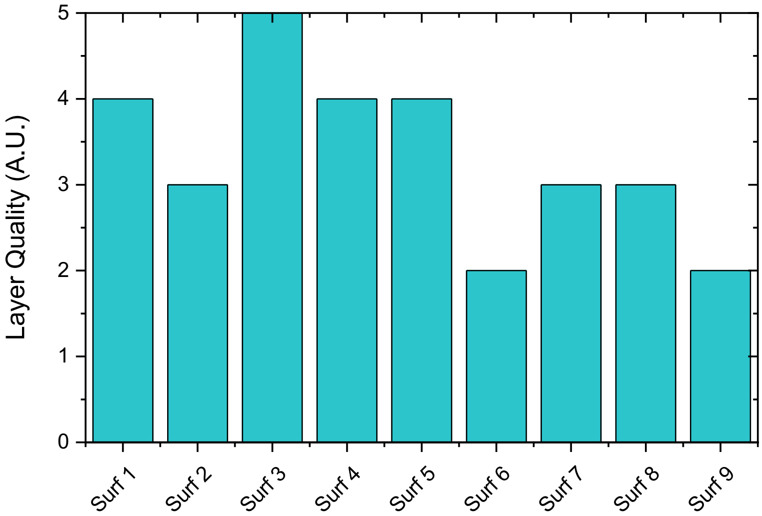

Figure 4: Dependence of layer quality of PEDOT:PSS layer on the surfactant

Based on conductivity and layer quality, Surf 5 (polyethylene glycol phenyl ether II) surfactant was used for further research of ink composition. The surfactant shows excellent film-forming behavior, achieves high film uniformity, high gloss, and no surface defects. The film-forming properties of the ink were very good for the PAL used for the OPD.

3.3 Influence of the complex ratio of PEDOT:PSS to the layer conductivity

In a study of the effect of primary dopant (PSS-) on the conductivity of PEDOT:PSS layers, 5 different complex ratios were studied. Two sets of inks were prepared, where the first set of inks did not contain secondary dopant, whereas the second set of inks contained 5 wt.% SD6 - ethylene glycol. In all inks, 0.5 % Surf 5 surfactant was used to improve the wetting behavior of the inks.

Table 4: Estimated characteristics of PEDOT:PSS films with various ratios of PEDOT:PSS complex

Conductive polymer	Ratio	Without secondary dopant	With 5 % of SD6 Ethylene glycol	Conductivity ratio
		Conductivity [S/cm]	Conductivity [S/cm]	
PEDOT:PSS	1:1	23.98	122.9	6
PEDOT:PSS	1:1.4	9.87	140.7	13
PEDOT:PSS	1:2.5	1.75	85.8	59
PEDOT:PSS	1:3.5	0.42	30.5	64
PEDOT:PSS	1:5	0.24	11.2	47

From Table 4, it can be seen that the most conductive layer is based on PEDOT:PSS with a complex ratio of 1:1.4 improved by secondary dopant SD6. Given ink also exhibited very good film-forming behavior. It is also evident that for samples without SD6, PEDOT:PSS with a ratio of 1:1 is the most conductive. Layers with PEDOT:PSS ratios of 1:3.5 and 1:5 showed the highest surface quality (smoothness, transparency, gloss), although they provide much lower conductivity than the PEDOT:PSS layer with 1:1.4 ratio. These results were confirmed for both sets of inks – with and without secondary dopant. Comparing the analogous dispersion with/without SD6, the improvement in conductivity is more pronounced for the dispersion with a higher PEDOT:PSS ratio. The effect of the secondary dopant solvent is lowest for the PEDOT:PSS complex with a 1:1 ratio.

3.4 Influence of various solvents on the conductivity and work function of PEDOT:PSS layer

Influence of various types of solvents/secondary dopants with specific properties on conductivity and WF were tested. The results in Figure 5 show the significant effect of the selected solvent types on the WF and also on the conductivity of the PEDOT:PSS layers.

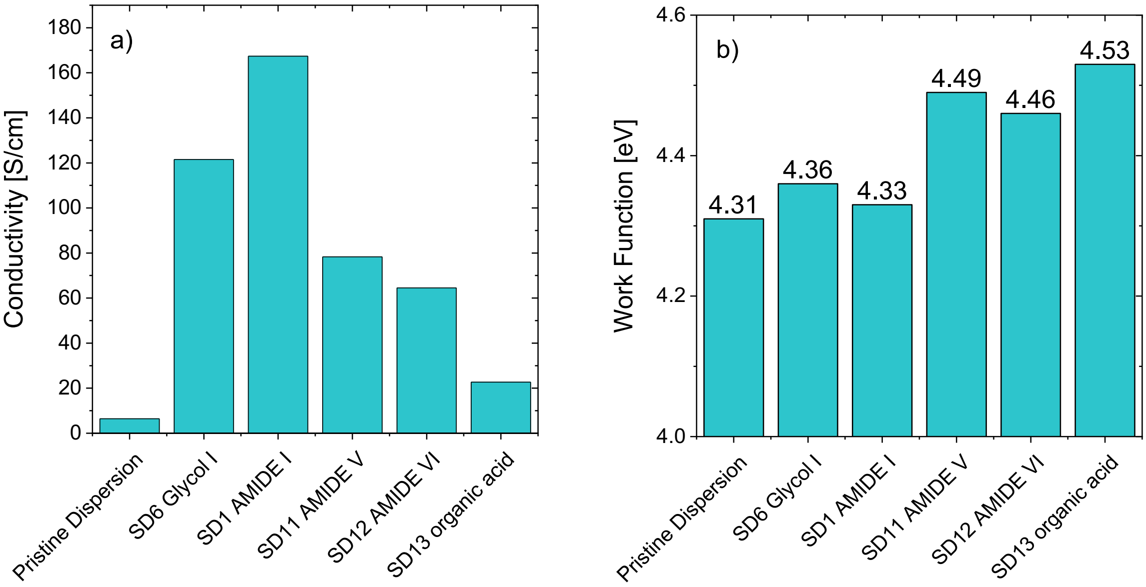

Figure 5: Dependence of conductivity (a) and WF (b) of PEDOT:PSS 1:1.4 layers on type of secondary doping solvent

The best conductivity was achieved for the layers prepared from ink containing SD1 – AMIDE I, whereas the higher WF value of PEDOT:PSS layer was achieved by the SD11 – AMIDE V solvent based ink. The effect of SD13 – organic acid on the high WF value of PEDOT:PSS layer is also interesting in terms of optimizing the energy levels in the OPD and tuning its performance.

4. Conclusion

It has been demonstrated that various characteristics of PEDOT:PSS films can be tuned by a number of the variable parameters of inks. One of the most influential is the PEDOT:PSS complex ratio. It has shown that the highest conductive films can be prepared for a 1:1.4 complex ratio, while the least conductive films are based on a 1:5 complex ratio. The conductivity of PEDOT:PSS layers can also be affected by the addition of solvents/secondary dopants with a high dielectric constant. These additives allowed us to increase the conductivity up to two orders of magnitude, where for PEDOT:PSS 1:1.4 layers a specific conductivity of 167 S/cm was achieved in the case of SD1 – AMIDE I solvent based ink. The choice of surfactant also has a significant influence on not only the conductivity but also on the quality of the prepared PEDOT:PSS layer.

In the case of HTL layer formation with a thickness of about 40 nm, the high homogeneity of the layer is essential for the preparation of high-performance multilayer structures such as OPVs or OPDs. Finally, it can be stated that the specific solvents/secondary dopants can be used to effectively influence the work function of PEDOT:PSS layers. This is a strong tool for enhancing the performance of various multilayer structures too. Further findings from our research related to PEDOT:PSS layers will be presented at the iarigai conference.

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