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Properties of customized PEDOT:PSS inks for applications in organic electronics

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Abstract

Poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is considerate one of the most popular conductive polymer. Generally, the properties of PEDOT:PSS films are tuned by the use of additives or post-treatments. However, the modification of their properties via chemical synthesis is still missing in literature. Here we propose the use of a modified PEDOT:PSS synthesis to obtain inks with different charge carrier density. The charge density of the synthesized inks was evaluated by optical and Raman spectroscopy. On the other hand, the monomer to polymer conversion was determinate by X-ray photoelectron spectroscopy (XPS). The measurements revealing that the amount of oxidizing agent in the synthesis route is directly correlated with the PEDOT:PSS conductivity.

Keywords: *PEDOT:PSS; chemical synthesis; carrier density; conductivity.*

Introduction

The discovery of conducting polymers by Shirakawa, MacDiarmid, and Heeger in 1977, paved the way for the development of materials that are known today as polymers of fourth generation. One of these polymers is the Poly(3,4–ethylenedioxythiophene) (PEDOT) a polythiophene developed by Bayer in 1988.[1] PEDOT has become one of the most important conducting polymers due to its high ionic- electronic conduction, transparency in visible range, and air stability.[2] These properties make PEDOT a promising candidate for several applications in the field of organic electronic. PEDOT is obtained by oxidative polymerization of EDOT, beginning with oxidation of EDOT monomers, to create positive charged chains which are compensated by coupling with negatives species or counter-ions.[3] The typical material reported in literature which is used as counterion is polystyrene sulfonate (PSS). The PSS is negatively charged due to the deprotonatonation of sulfonic groups in water. The combination of PEDOT and PSS results in the commercially available conducting polymer, known as PEDOT:PSS. For instance, the company Heraeus markets several grades of PEDOT:PSS for different application necessities, from Hole transport layer (HTL) to conductive polymer electrodes.

Even with the technological importance of PEDOT:PSS, their chemical synthesis is not fully understood.[4] The mechanism of polymerization does not explain how to achieve inks with different properties. The traditional mechanism consist in three steps: oxidative polymerization, oxidative doping and counter balancing and coupling to form PEDOT:PSS. In this study we look for gaining deeper insights about the mechanism behind the PEDOT:PSS synthesis, for determining the impact of synthetic parameters on final material, and optimizing synthetic routine for desired application. In here, we specifically studied the impact of the oxidant agent concentration (OAC).

Experimental Procedure

Synthesis of doping-controlled inks

The synthesized PEDOT:PSS inks are in the following referred to as 0.5P, 1P, 3P, and 5P, according to their pre-synthetic molar ratio between the oxidizing agent potassium persulfate ($K_2S_2O_8$) and the EDOT monomer (see Table 1).

Table 1. P-series inks pre-synthesis $K_2S_2O_8$/EDOT molar ratio.

Code	**$K_2S_2O_8$/EDOT molar ratio**
0.5P	0.26 mmol/0.52 mmol = 0.5
1P	0.52 mmol/0.52 mmol = 1
3P	1.56 mmol/0.52 mmol = 3
5P	2.60 mmol/0.52 mmol = 5

The synthetic route of PEDOT:PSS used throughout this work was based on the work reported by Louwet et al.,[5] where the water dispersion of PEDOT:PSS is obtained by mixing EDOT, PSS, the oxidizing agent $Na_2S_2O_8$ and the catalyzer $Fe_2(SO_4)_3$ followed by a purification of the resultant mixture .

Here, we modified the Louwet-route by varying the quantity of the oxidant agent. Moreover, $Na_2S_2O_8$ was substituted for $K_2S_2O_8$, maintaining, however, the same oxidative molecule, the persulfate anion.

Results and Discussion

We investigate the composition ratio between PEDOT and PSS of the P-Series inks using X-ray photoelectron spectroscopy (XPS). Here, the XPS spectra were analyzed looking for the S(2p) electron signal in the region of 160 to 175 eV for films of each individual ink. The composition ratio was assumed to be equal to the areas below the deconvoluted signals in the ranges 162 to 167 eV (Sulphur atoms in PEDOT), and 167 to 173 eV (Sulphur atoms in PSS).[6] The obtained $PSS/PEDOT_{XPS}$ ratios follow a decreasing trend with increasing OAC (Table 2). Considering that the amount of PSS remains unchanged during the synthesis and the dialysis, an EDOT-to-PEDOT conversion can also be calculated by dividing the pre-synthesis PSS/EDOT molar ratio by the post-synthesis PSS/PEDOT ratio obtained via XPS. The corresponding EDOT-to-PEDOT conversions were determined to be 37.70 %, 58.40 %, 72.12 % and 76.15 % for 0.5P, 1P, 3P, and 5P, respectively (Table 2), confirming that the quantity of oxidizing agent is a key factor for increasing the EDOT-to-PEDOT conversion.

Table 2. P-series inks with post-synthesis characteristics, such as PSS/PEDOT ratio according to XPS analysis, EDOT-to-PEDOT conversion rate and film conductivities.

Code	Post-synthesis PSS/PEDOT $_{XPS}$ ratio	EDOT-to-PEDOT conversion rate (%)	Conductivity (S/cm)
0.5P	5.05	37.70	24.3 ± 2.7
1P	3.26	58.40	37.6 ± 0.7
3P	2.64	72.12	17.8 ± 2.9
5P	2.50	76.15	12.4± 1.3

Fourier-transform infrared (FTIR) spectroscopy measurements were performed for 100 nm-thick films of the synthesized inks. The ratio between the signal's intensities at 831 cm^{-1} and at 685 cm^{-1} is a measure of the average PEDOT chain length. Hence it allows to compare the different samples.[7] As shown in Figure 1, the obtained ratios are quite similar (~1.10), meaning that the PEDOT chains have all similar average sizes. Hence, we conclude that higher OAC promote the formation of more but not of larger PEDOT chains.

Table 2 also presents the conductivities of the P-series inks as obtained using the 4-point probe method. It is found that the sample 1P gives the highest conductivity value, followed by 0.5P and 3P. 5P possesses the lowest conductivity. This means that the higher values of EDOT-to-PEDOT conversion rate do not result in higher conductivities.

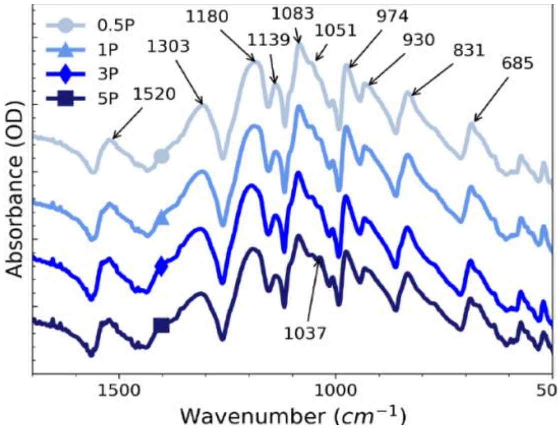

Figure 1. FTIR spectra of PEDOT:PSS P-series inks

The charge density was studied by means of UV-Vis-NIR spectroscopy. **Figure 2** presents the obtained spectra for films of 100 nm thickness. The absorbance at about 900 nm is normally associated to the polaronic transition, whereas >1200 nm corresponds to the bipolaronic transition.[8] The absorbance of the 0.5P is more intense than the other P-Series samples, indicating that the density of polarons and bipolarons are lower in inks with higher OAC.

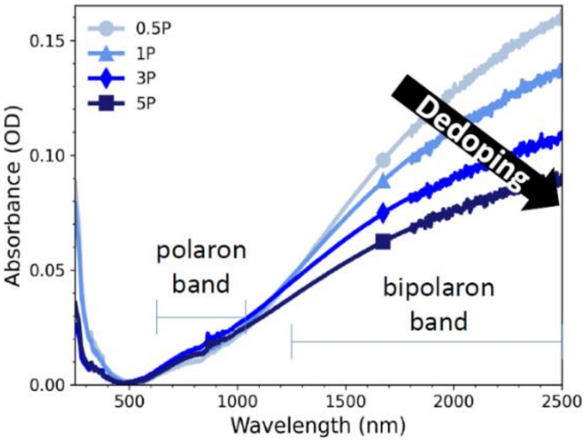

Figure 2. UV-Vis-NIR spectra of PEDOT:PSS P-series inks in the wavelength interval of 250 nm to 2500 nm.

Given that the conductivity is proportional to the product of charge density and electronic mobility, a relative mobility can be estimated. According to the Beer-Lambert law the absorbance intensity is proportional to the concentration of the absorbing species. Accordingly, Figure 2 provides an effective way to estimate relative charge densities in the different inks. We use 0.5P as the reference ink and: the absorbance intensity at 2500 nm. . Assuming that the absorbance is dominated by the bipolarons, we are able to estimate the relative charge densities $n_{x}/ n_{0.5P}$. The obtained values are: 1.00, 0.88, 0.69 and 0.56 for 0.5P, 1P, 3P and 5P, respectively. These values and the measured film conductivities allows concluding on the relative mobilities of the P-series inks. Using the conductivity (σ) equation $\sigma = e\, n\, \mu,$ where e is the elementary charge, n is the charge density, and μ is the charge carrier mobility, the obtained relative mobilities (μ_{x} / $\mu_{0.5P}$) are 1.00, 1.77, 1.07 and 0.91 for inks 0.5P, 1P, 3P and 5P, respectively. According to this estimation, 1P yields the highest and 5P the lowest electronic mobility following a trend that resembles that of the conductivity.

To quantify the doping level, films of P-Series inks was evaluated by Raman spectroscopy. As show in Figure 3, the increase of OAC cause a shift in the region of $C_{\alpha}=C_{\beta}$ stretching, indicating a decrease in the conjugation length, which is related to the transformation of PEDOT chains from quinoid to benzenoid structure.[9] Thereby, the increase of the OAC level tends to create more PEDOT segment with less charge carriers.

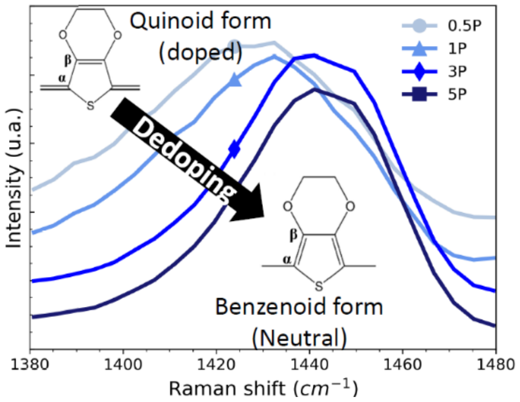

Figure 3. Raman spectra of P-series inks in the region of $C_{\alpha}=C_{\beta}$ stretching

Conclusions

Upon varying the concentration of the oxidizing agent during the oxidative synthesis we were able to tune the charge carrier density and consequently altering the material conductivity.

The aforementioned results confirm the success of our facile protocol to control the charge density in PEDOT:PSS inks through oxidative polymerization, resulting in inks with great applicability. Our easy-to-implement synthetic approach unlocks new strategies for producing stable and tunable charge-density materials.

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