Thin polyphenylene vinylene electrophoretically and spin-coated films – photoelectrical properties

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Abstract. Electrophoretic deposition (EPD) and spin coating (SC) techniques were compared on poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) used as a model material. Absorption spectra measured in a toluene solution and a toluene/ acetonitrile suspension with the same MDMO-PPV concentration of 0.0033 g.l\textsuperscript{-1} were analysed. An observed broadening of the characteristic absorption peak could be related to the formation of tightly-folded polymer chains in the suspension. Thin films of about 300 nm thickness were prepared by EPD from suspension and SC from solution with a concentration of 0.0033 g.l\textsuperscript{-1} and 8.95 g.l\textsuperscript{-1}, respectively. The ITO/MDMO-PPV/Al structures with EPD MDMO-PPV films behave as a photovoltaic cell, while the same sample configuration with SC MDMO-PPV films acts more like a photoresistor. EPD and SC films exhibit the same charge-carrier photogeneration mechanism. It was clearly demonstrated that the EPD method uses the deposited material more efficiently, producing films with better photoelectrical properties.

1. Introduction

Conjugated polymers are a class of organic semiconductors that have attracted much interest in recent decades from both fundamental and practical points of view.[1] The \(\pi\)-electron system on their main chain provides unique electronic and optical properties that could not be predicted by conventional solid state theories.

Much effort has been devoted to developing electronic devices that use conjugated polymers as electroluminescent diodes, photovoltaic cells[2], gas sensors, and field-effect transistors.[3] In contrast to traditional inorganic semiconductors, which require high processing temperatures, conjugated polymers are synthesized at near room-temperature conditions. Their solubility might be significantly improved to deposit wet-process films under atmospheric pressure. As a result, large-area films could be obtained by relatively inexpensive (compared to vacuum-based methods) coating technologies – spin and dip coating, spray and Langmuir Blodgett (LB) deposition, ink-jet printing, electrophoretic deposition, etc.

The spin-coating (SC) technique is a widely used method to prepare high quality polymer films for electronic devices. However, this is one of the most uneconomical methods, because most of the solution dropped on the substrate is blown away during the spinning.[4]
Electrophoretic deposition (EPD) allows the preparation of films of several hundred nanometers from a low suspension concentration.[5] The particle size in the EPD suspension can be controlled by changing the ratio of solvent and non-solvent.[6] Deposition from a suspension with a high non-solvent concentration results in a rougher film structure. This effect seems to improve the performance of gas sensor devices,[7], as the film porosity may enable the fast absorption/desorption of dopants and target molecules. In contrast, deposition from a suspension with a high solvent concentration results in smooth and uniform films, applicable as active layers in polymer electroluminescent devices or solar cells.[8]

EPD enables quick patterned deposition, because the covered area can be specified by the electrification of selected electrodes.[9]

The application of the EPD method in the development of thin layer based organic devices needs further investigation of the mechanism, kinetics of the electrophoretic process, and structure and properties of the films.

This paper presents a comparative study of the properties of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) films deposited electrophoretically and cast by SC. MDMO-PPV is a widely investigated organic semiconductor (HOMO and LUMO orbital positions at 5.4 and 3.2 eV, respectively)[10] with a potential application as a photoconductive or electroluminescent layers. The study seeks potential applications for these films in solar energy conversion technology and other branches of organic electronics.

2. Material and methods

A stock solution (concentration of 0.165 g.l\(^{-1}\)) was prepared by dissolving 3.3 mg MDMO-PPV (Sigma-Aldrich, catalogue number: 546461) in 20 ml toluene (Sigma-Aldrich Toluene, catalogue number: PLC22C11X), then heating for 5 min at 60°C, followed by ultrasonic treatment for 10 min. A homogeneous solution without clearly visible undissolved particles was obtained.

An EPD suspension with MDMO-PPV concentration of 0.0033 g.l\(^{-1}\) and toluene/ acetonitrile ratio of 50 % v/v (Sigma-Aldrich Acetonitrile, catalogue number: 34851) was prepared. For a 20 ml suspension with a concentration of 0.0033 g.l\(^{-1}\) and toluene/ acetonitrile ratio of 50 % v/v, 0.4 ml from the stock solution was diluted in 9.6 ml pure toluene, then 10 ml of acetonitrile was added. The suspension obtained clearly changes color[1], which could be related to the formation of (micro) nano-sized solid particles. The prepared suspension was immediately used for film deposition or measurement to prevent further particle coagulation.

A solution (0% v/v acetonitrile) with the same MDMO-PPV concentration of 0.0033 g.l\(^{-1}\) was prepared for optical absorption measurements. The optical absorption spectra of the prepared suspension and solution were measured by a Varian Cary 50 UV-VIS dual beam spectrophotometer. The measurement was carried out in a quartz cuvette with an optical path of 10 mm. The baseline was taken from the cuvette, filled with pure toluene or toluene/ acetonitrile mixture in a 1:1 ratio (toluene/ acetonitrile). Then the spectra in the 650-270 nm range were measured.

The electrical parameters (voltage and current) of the EPD process were controlled by the Keithley 2410 SourceMeter (voltage range of 0-1100 V and current measurement from 10 pA to 1 A).

After applying voltage between the electrodes, the current continuously decreases. A deposition on the positive electrode starts when the current reaches about 80-40 μA. The film, about 300 nm thick, completely grows within 3-4 min.

A solution with a concentration of 8.95 g.l\(^{-1}\) was prepared and SC was done on the KW-4A Spin Coater (Chemat Technology, Inc.). Spinning was applied at 1000 rpm for 3 sec. and 2600 rpm for 60 sec. to obtain about 300 nm-thick films.

The film thickness was determined by the chromatic distance method on the MicroProf® FRT optical surface measuring system.
Samples for electrical measurements of $25 \times 15 \text{ mm}$ were cut from commercial ITO-coated glass slides (Sigma-Aldrich, catalogue number: 636916). The top Al electrodes of about 100 nm thickness were deposited in a vacuum; copper wires were then bonded to the electrodes by a silver paste (Dotite® Silver Paint D-550).

Photoelectrical measurements were carried out in an oil-free vacuum of $2.2 \times 10^{-5}$ Pa with a Keithley 6517A Electrometer. Monochromatic light was produced by a LOT-Oriel halogen lamp LSH502 and a LOT-Oriel monochromator MSH101. Light power was controlled by an iris diaphragm and measured by the Gigahertz-Optik - X97 Irradiance Radiometer. Photoelectrical measurements start with spectral dependence of the photocurrent at zero applied voltage; $I$-$V$ characteristics were then measured in both directions of the voltage scale in dark and exposed to light. Finally, the dependence of the photocurrent on the incidental light power (irradiance) was measured. The sample was exposed to monochromatic light at a wavelength of 560 nm.

3. Results and Discussion

3.1. UV-VIS spectra

The optical absorption spectra of the solution and the 50% v/v toluene/ acetonitrile suspension with the same MDMO-PPV concentration of 0.0033 g.l$^{-1}$ are presented in figure 1. The solution spectrum (figure 1, curve 2) consists of the characteristic MDMO-PPV absorption peak.[11] The peak is slightly broad and asymmetric due to the "red" shift with respect to the main peak position. This effect could be related to a slight interaction of the MDMO-PPV molecules.

![Figure 1. Optical absorption spectra of MDMO-PPV suspension (curve 1) and solution (curve 2).](image1.png)

In the suspension spectrum (figure 1, curve 1), the "red" shoulder strength increases, which leads to a greater broadening of the peak. This effect could be related to the appearance of a precipitated solid phase during the suspension formation, caused by the polar precipitating acetonitrile. It is known that for more crystalline organic materials (e. g. poly(3-octylthiophene)), such precipitation can even lead to a "red" shift of the whole characteristic absorption peak.[12] The effect of the peak broadening could be used for a qualitative estimation of the suspension properties.
3.2. Electrical measurements

Spectral dependences of the photocurrent, measured at zero applied voltage between the electrodes for structures with EPD and SC MDMO-PPV films are presented in figure 2, curve 1, and figure 2, curve 2, respectively.

Comparing figures 1 and 2, it could be concluded that generally the MDMO-PPV photocurrent spectrum is similar to the absorption spectrum. There is a clear characteristic peak in the photocurrent spectrum at 560 nm. The peak position is "red" shifted (about 50 nm) with respect to the maximum of the absorption spectrum. This effect of energy gap reduction could be related to the formation of a solid state. The photocurrent peak obtained from EPD film (figure 2, curve 1) is slightly broader than the peak obtained from SC film (figure 2, curve 2). This result is similar to that obtained from absorption spectra measurement (Sec. 3.1). The photocurrent measured from structures with SC films is 3 times higher than that obtained from EPD films.

$I-V$ characteristics measured in the dark on the ITO|MDMO-PPV|Al structure with EPD and SC MDMO-PPV films of about 300 nm thickness are presented in figure 3. To estimate the electrical parameters of the samples, the data are plotted in a semilogarithmic scale (negative values of the current are multiplied by -1).

![Figure 3. $I-V$ characteristics measured in the dark (curve 1) and under illumination (curve 2) with monochromatic light ($\lambda=560$ nm, irradiance 0.59 mW.cm$^{-2}$) on ITO|MDMO-PPV|Al structures with a) EPD and b) SC MDMO-PPV film with about 300 nm thicknesses.](image-url)

From the dark current measurements on a sample with EPD film (figure 3a, curve 1), a diode contact barrier could be observed at 0.16 V. Overcoming this barrier changes the sign but does not lead to a considerable increase of the current. Therefore this effect more probably results from the influence of charged defects in the depletion region of the diode. A similar but smaller contact barrier was observed on some of samples with SC films. Therefore it is probably not only connected with the EPD process, but more probably related to the metal (oxide)/organic interface.

Overcoming the second contact barrier at 0.6 V leads to an exponential increase of the current. Therefore, this value could be considered as the diode forward voltage drop ($U_d$). Applying reverse bias, the electrical current slightly grows. Comparing the $I-V$ characteristics (figure 3a, curve 1) in forward and reverse directions (at ±1.1 V), a rectification ratio of 1.6×10$^4$ is determined. It could be concluded from the dark current measurements that the ITO|MDMO-PPV|Al structures with EPD MDMO-PPV films exhibit a clear diode behavior.

$I-V$ characteristics were measured on the same sample under illumination (figure 3a, curve 2) with monochromatic light ($\lambda=560$ nm, irradiance 0.59 mW.cm$^{-2}$). For positive voltages applied
to a sample with EPD film, the I-V characteristics measured are similar to those measured in dark (figure 3a, curve 1). For negative applied voltages, the photocurrent measured is more than 2 orders of magnitude higher than the dark current. This effect combined with the strongly asymmetric dark I-V characteristic (figure 3 curve 1) and the ability of photogeneration (figure 2) express a clear photovoltaic (PV) cell behaviour.

I-V characteristics measured on samples with SC MDMO-PPV films are nonlinear and symmetrical (figure 3b).

Processing the data for the EPD MDMO-PPV PV cell (figure 3a, curve 2) determined short circuit current J_{sc}=8.1 \times 10^{-10} \text{ A.cm}^{-2} and open circuit voltage U_{oc}=0.5 \text{ V}. From the area confined by J_{sc} and U_{oc}, the dependence of the electrical power on the voltage is plotted on figure 4, right Y axis. The maximum electrical power found were P_{max}=7.6 \times 10^{-8} \text{ mW.cm}^{-2} at voltage U_{mp}=0.2 \text{ V} and current J_{mp}=3.6 \times 10^{-10} \text{ A.cm}^{-2}.

The power conversion efficiency \eta=1.3 \times 10^{-5}\% is calculated. The low value of the power conversion efficiency measured for organic semiconductors is not exceptional. A similar value of 4.2 \times 10^{-4}\% was reported in the literature for MEH-PPV/C_{60} donor-acceptor composite, where acceptor doping is used to improve the efficiency.[13]

![Figure 4](image1.png)

**Figure 4.** Dependence of the power (right Y axis) and current (left Y axis) on the voltage applied, as calculated from figure 3a, curve 2.

![Figure 5](image2.png)

**Figure 5.** Dependence of the photocurrent on the light intensity measured at a fixed wavelength of \lambda=560 \text{ nm} on samples with EPD (curve 1) and SC (curve 2) MDMO-PPV films.

The power conversion efficiency could be considerably increased in some of the following ways: decreasing the film thickness; using donor-acceptor composite; and preparing multilayer structures to reduce the electrode/semiconductor contact barrier. Such investigations are beyond the scope of this work. It should be noted here that our previous work demonstrated the advantage of the EPD method for constructing a multilayer structure from films generally dissolved in the same solvent.[14] Similar multilayer structures could be used further for improving the PV properties.

The dependences of the photocurrent on the incidental light power (irradiance) for EPD and SC MDMO-PPV films are plotted on figure 5. In both cases, the photocurrent is proportional to G^\gamma, where G is the photogeneration rate and \gamma is the slope in the presented graphs. For the EPD and SC devices, a slope of 0.96 and 1.03 is found, respectively. This result agrees with the literature data[15] and represents a monomolecular photogeneration mechanism. It might
be concluded that the EPD process of film preparation compared to the SC method does not change the photogeneration mechanism.

The short circuit photocurrent measured from samples with SC films (figure 5, curve 2) follows the tendency observed in figure 2 and is about 1.5 times higher than EPD films (figure 5, curve 1). This result demonstrates the good photoconductive properties of the MDMO-PPV films, which could be observed at low contact barrier. It confirms that the key point for increasing the MDMO-PPV power efficiency is the optimization of the PV cell, thus increasing the Uoc. This could be achieved better with EPD (compared to SC) technique.

4. Conclusion

Absorption spectra of solution and suspension with the same MDMO-PPV concentration of 0.0033 g.l$^{-1}$ were measured. An observed broadening of the characteristic peak could be related to the formation of a solid phase in the suspension.

Thin films of about 300 nm thicknesses were prepared by EPD from a suspension and SC from a solution with a concentration of 0.0033 g.l$^{-1}$ and 8.95 g.l$^{-1}$, respectively. The EPD method produces films with the same film thickness as SC method from more than 2500 times lower concentrations.

ITO|MDMO-PPV|Al structures with EPD MDMO-PPV films behave as photovoltaic devices; the same sample configuration with SC MDMO-PPV films acts more like a photoresistor. EPD and SC films exhibit the same mechanism of charge-carrier photogeneration.

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