Materials Research. 2024; 27(suppl. 2):e20240204
DOI: https://doi.org/10.1590/1980-5373-MR-2024-0204

Manufacture and Photoelectrical Characterization of Poly(3-decylthiophene) Thin Films by Drop Casting Technique

Luiz A. Riga Junior*[a]**, ***Maria V. Riga*[a]**, ***Amanda M. P. Santos*[a]**, ***Maria E. R. S. Medina*[a]**,
***Marcelo S. Borro*[a]**, ***André V. S. Simõis*[a]**, ***Clarissa A. Olivati*[a]**

[a]*Universidade Estadual Paulista (UNESP), Faculdade de Ciências e Tecnologia, Presidente Prudente, SP, Brasil.*

Received: April 30, 2024; Revised: July 11, 2024; Accepted: July 23, 2024

Poly(3-decylthiophene) is a polymer with conductive characteristics due to its conjugated polymeric chain. With the search for new applications and improvements of these materials, in sensors, and OPVs, there is a great demand for deeper knowledge about them. This work aims to characterize the P3DT, through analysis of optoelectrical measurements. Using the drop casting technique, thin films were made onto solid substrates. The films were subjected to optical characterization by UV-Vis and optical microscopy. The electrical characterization was obtained by IxV curves and then measuring the photoconductivity through Ixt curves, with a solar simulator. With UV-Vis measurements, it was observed that the absorption of light in the visible spectrum reached a peak of 520 nm in the film, blue-shifted in the solution attributed to the differences in the organization of the polymer chains. The optical microscopy measurements indicate the formation of aggregates with a higher concentration of aggregates observed for the film obtained with a more concentrated solution. Finally, the photoconductivity measurements carried out obtained a positive response to the photo-excitation of the material due to exposure to light, with an increase in current in the film as the photo-exposure cycles were repeated.

Keywords: *Drop casting, Chloroform, Optoelectronic properties.*

1. Introduction

Since the discovery of the high conductivity of doped polyacetylene made by Heeger, MacDiarmid, and Shirakawa in the 70s, the door was opened for the synthesis and study of the characteristics of a wide variety of materials identified by the π-conjugated polymeric chain that is responsible for their electrical and optical properties[1]. Most conducting polymers are generally structured by alternating single and double bonds throughout their main chain, with a delocalized electron structure[2]. Due to this structure, the π electrons can be delocalized along the polymer's backbone chain, leading to one unpaired π electron per carbon atom[3] creating the possibility of charge transport along the polymer chain, culminating in the polymer's conductive behavior and semiconductor characteristics[4,5].

The unique properties of these conjugated polymers draw attention based on their relative ease of processing, making it possible for such materials for a wide range of applications as technologically superior and more cost-effective alternatives[6]. The applications of these materials include areas such as the development of batteries[7], transistors[8], supercapacitors[9], organic light emitting diodes (OLEDs)[10], sensors[11-14], solar cells[15], and others.

Representing the most classic type of conjugated polymers we can emphasize the polythiophene and its derivatives, which have been widely studied in recent decades[16]. This class of polymers is attractive for device applications[17] due to their high stability in undoped states, can be structurally modified, and are easy to process in solution form[18].

With advancements in polymer synthesis techniques, the first synthesis route for polythiophene was developed in 1980[19]. Due to their excellent stability, polythiophenes can be processed into various types of devices. As a conjugated polymer, the polythiophenes show strong π-*stacking* interactions between its thiophenic rings, which leads to low solubility. Attaching side chains to the main chain of the polymer promotes the increase in solubility[20]. The first poly(3-alkyl thiophene) was synthesized in 1985, obtaining a material with good solubility, with regioregularities varying from 50 to 80%. Studies demonstrate that cyclic polythiophene oligomers present unique properties concerning their derivatives[21] which highlight the interest in proposing new polythiophene derivatives. Furthermore, the asymmetry of the polythiophenes' backbone chain results in varying regioregularity, culminating in the possibility of several isomeric materials[22].

Moreover, the optoelectronic properties of the polythiophenes and their derivatives create the opportunity for a plurality of studies revolving around their applicability as photodetectors, as demonstrated by an extensive number of works based on the optical and electrical characterization of such materials[1,23]. The high values of conductivity shown by these materials when suffering photo-excitation bring the possibility of fabrication of organic solar cells with increasing efficiency[18,24].

---

*e-mail: luiz.riga@unesp.br

In this work, we study the optical and electrical characterization of drop casting films of poly(3-decylthiophene-2,5-diyl) (P3DT). The measurements were taken using glass laminae as substrates for the optical and morphological characterizations and using a gold interdigitated electrode for measurements of the current versus time with applied voltage at room temperature. The effect of different concentrations on the electrical conductivity of P3DT is investigated, indicating the potential for its application as a photosensor.

2. Methodology

2.1. Materials

In this work, a regioregular polythiophene poly(3-decylthiophene-2,5-diyl) (P3DT), acquired commercially from Sigma-Aldrich, CAS number 110851-65-5, product number 495344, was used in the study of its optoelectrical properties. Figure 1 presents the condensed chemical structure of P3DT.

Glass laminae substrates were used for the optical and morphological characterizations. The conductivity and optoelectrical measurements were possible using gold interdigitated electrodes (IDE), fabricated with photolithography onto glass substrates. Au-IDEs consist of electrodes containing 50 digits with dimensions of 110 nm in height, 8 mm in length, 100 µm wide for each digit, and spacing of 100 µm between each digit.

The Au-IDE electrodes are a vital part of this study since each pair of digits amplifies the total current measured[25], facilitating the electrical characterization of the active layers deposited as films over the IDEs, which may present too low conductivity otherwise. To prepare the solutions used in the confection of the drop casting films, the solvent $CHCl_3$ (99.9%), obtained from Synth, was selected due to the good solubilization of polythiophenes derivatives in such solvent.

2.2. Drop casting films

The drop casting technique is one of the simplest processing methods for obtaining polymeric films from solution[26]. It consists of the dropping of the solution over the horizontally stable substrate, using an electronic pipette. Then, after all the solvent has evaporated, the thin film of the material is formed on the substrate, its molecules remaining linked by Van der Waals forces[27]. Although this is a quick way of obtaining a thin film of a polymer such as polythiophenes, It does not allow for fine control over the film formation, concerning the film's organization. During the evaporation of the solvent, the formation of aggregates is facilitated, resulting in films with a heterogeneous surface.

Also limited by this technique is the control over the thickness of the films. Moreover, the evaporation of the solvent is a really important part of the film formation, for the film may be dried out naturally or by some kind of thermal process, which accelerates the evaporation. This, however, may cause too much disturbance in the system during evaporation culminating in a direct impact on the film morphology[28,29].

For the confection of the films, a volume of 200 µL of the solution of P3DT (1.5 mg/mL and 2.0 mg/mL) was dropped onto the substrates (glass laminae and Au-IDE electrode), positioned over a horizontally stabilized support. The films then were left to dry out naturally at room temperature, with air humidity of approximately 30%, for 24 hours. This time was chosen to ensure the complete evaporation of the solvent.

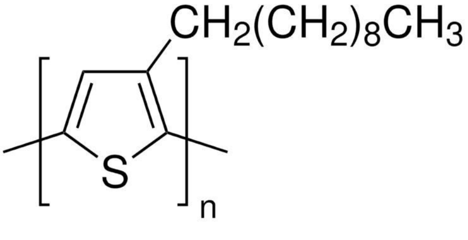

Figure 1. Chemical structure of the P3DT.

2.3. UV-vis spectroscopy

In studying the electronic transitions that happen in the UV-Visible range, it is possible to assert a wide variety of characteristics presented by the materials, like the internal structural organization of a film[30], and the orientation of the molecules of the material on an organized thin film[31,32]. The UV-Vis spectroscopy measurements were realized using the Agilent Technologies model Cary 100 UV-Vis spectrophotometer, utilizing incident light comprehending a range of 900 to 350 nm. Wavelengths lower than 350 nm are avoided since the glass of the substrates is opaque in ultraviolet light. The intensity of light absorbed by wavelength is measured by a sensor located just behind the samples.

2.4. Electrical characterization in direct current

Curves of Current *versus* Voltage (I *vs* V) were measured utilizing a Keithley Instruments model 238 Source Measure Unit, gauged in a range from -10 V to 10 V, in a controlled temperature at 23 °C. The electrical conductivity was calculated by applying Ohm's law equations in addition to the employment of the geometric factor of the Au-IDE electrode (cell constant), which was determined in previous works from the research group, following Olthuis' method[33,34]. The cell constant has a value of 5.1 m^{-1}.

2.5. Optoelectronical characterization

In order to investigate the photoconductivity of the P3DT drop casting film, the Current *versus* time curve (I *vs* t) was obtained, utilizing a voltage font Keysight B2912A Precision Source Measure Unit (SMU), in addition to the Oriel VERASOL solar simulator. The measurements were made with illumination calibrated in 199 $mW.cm^{-2}$ (AM 1.5), applying intervals of 5 minutes of illumination and 5 minutes with the sample in the dark.

3. Results and Discussion

Figure 2 exhibits the absorbance spectra per wavelength obtained via UV-Vis absorption measurements for P3DT drop casting film (2.0 mg/mL), with 200 µL deposited over the glass substrate, as well as the P3DT solution (2.0 mg/mL).

It can be noted that the absorption for both is in the visible spectra. For the drop casting film, the absorption peak at 450 nm, is related to π - π* interactions[34]. The spectra of the drop casting film are redshifted with a peak at 520 nm, this difference is attributed to the higher organization in the films in comparison to the solution. It is also possible to see two additional peaks in the film spectra, at 557 nm and 605 nm. The peaks at 520 nm and 557 nm are attributed to intrachain excitation, while the peak at 605 nm can be related to the interchain absorption[35,36]. Moreover, the difference in the intensity between drop casting film and solution is directly proportional to the amount of material.

Figure 3 shows the surface morphology of the P3DT drop casting films, produced by the deposition of 200 µL of poly(3-decylthiophene-2,5-diyl) in solution with concentrations of 1.5mg/mL and 2.0 mg/mL, and with different amplifications.

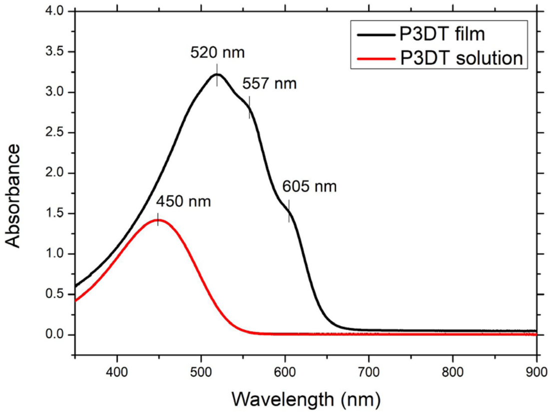

Figure 2. UV-Vis spectra obtained from P3DT solutions and drop casting films.

It is possible to note the presence of aggregates in the first two magnifications for the optical microscopy images of the drop casting film produced using the 1.5 mg/mL solution, represented by dark dots along the surface of the film, in the third amplification, however, it is virtually impossible to distinguish any aggregates on the film. In the drop casting film produced using the 2.0 mg/mL solution, however, several aggregates can be noted in the three magnifications. The formation of various aggregates is a direct consequence of the usage of the drop casting technique since this technique doesn´t offer the possibility of morphology control during the film formation[26,37]. Additionally, the higher concentration of the P3DT solution employed resulted in a film with high thickness, and difficulting the obtention of a good focus during the OM measurements.

Figure 4 shows the electrical characteristic curve (Current *versus* Voltage) carried out for the P3DT drop casting films deposited on the Au-IDE electrode, with the solutions of 1.5 mg/mL (black) and 2.0 mg/mL (red).

The linearity of the results shows the ohmic behavior of the P3DT drop casting film, which is a typical characteristic of such a configuration of its contacts (Au/active layer/Au)[38,39]. The ohmic pattern shown in the I *vs* V curve allows the applicability of Ohm's laws to calculate the electrical conductivity of the films. The value of conductivity calculated was 3.50 x 10^{-6} S/m for the drop casting film obtained using the 1.5 mg/mL solution, while the one manufactured using the 2.0 mg/mL solution reached a value of 2.57 x 10^{-6} S/m, indicating a slight lower conductivity for the higher concentration solution, which might be a consequence of the difference in organizations achieved in both films.

The curve of Current versus time for the photoconductivity response of the P3DT drop casting films with 1.5 mg/mL (red) and 2.0 mg/mL (black) is exhibited in Figure 5.

It is possible to observe in the photoconductive curve of the P3DT drop casting films, that the films respond to light in

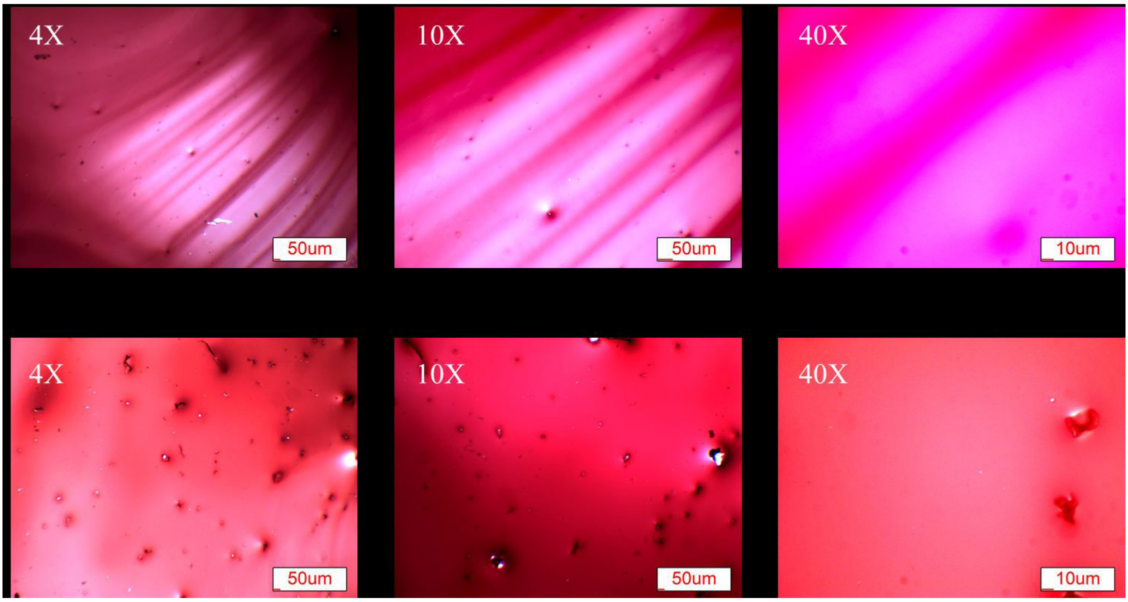

Figure 3. Optical microscopy images of P3DT drop casting film with different amplifications.

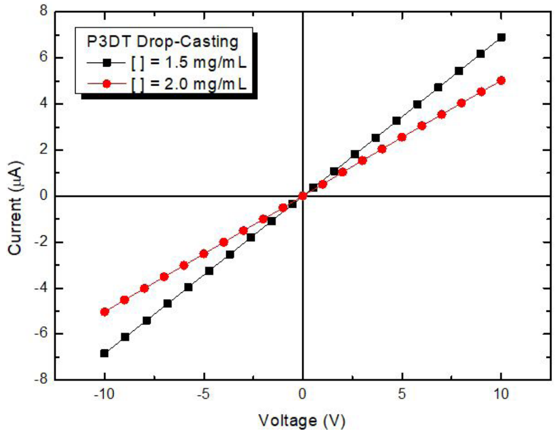

Figure 4. Electrical characteristic curves (I vs. V) of the P3DT drop casting film.

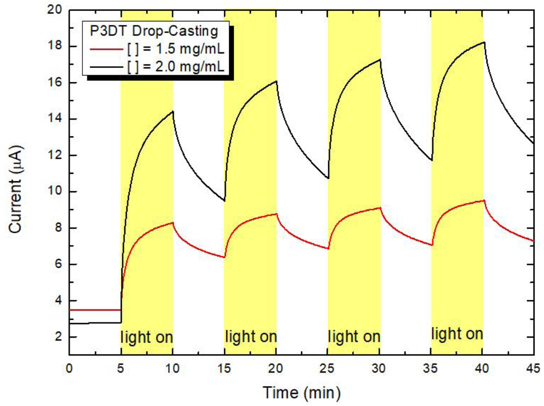

Figure 5. Photoconductivity response of the P3DT drop casting film.

such a manner that the current measured always rises when the material is exposed to light. This indicates the formation of charge carriers, originating from the photoexcitation of the polymer, promoting the decrease of the drop casting film's resistance, as it is already expected for polythiophene derivatives when exposed to light in similar conditions[34,40]. It is also possible to note that for each repetition of the photoexcitation cycle, the current assumes a higher value, for both concentrations, which may indicate the possibility of the trapping of charge carriers in structural defects along the morphology of the film. Furthermore, the concentration of the solution used in the drop casting processing technique, seems to have influenced the overall increase in current when comparing both films, since the drop casting film made using a solution of 2.0 mg/mL reached higher values in current compared to the 1.5 mg/mL film.

4. Conclusions

Through this study, it was possible to carry out characterizations of P3DT thin films made using the drop casting technique and deposited on glass laminae and gold interdigitated substrate (Au-IDE electrode) for two different concentrations, 1.5 mg/mL and 2.0 mg/mL. By carrying out UV-Vis absorption measurements, an absorption band with peaks of 520 nm and 450 nm was obtained, for the casting film and the solution, in that due order, exposing a red-shift that indicated in the thin film the presence of a better molecular organization compared to the solution. Concerning optical microscopy, an indication of the material's tendency to form polymeric agglomerates in the film during the evaporation of the solvent was observed, with an apparent higher density of agglomerates obtained for the higher concentration of the P3DT solution. The ohmic character of the P3DT drop casting film was shown in the Current *vs* Voltage measurements presented, making possible the calculation of the conductivity of the thin films at 3.50 x 10^{-6} S/m for the film produced using the 1.5 mg/mL solution and 2.57 x 10^{-6} S/m for the film made with the 2.0 mg/mL solution. Finally, the photoconductivity measurements that were carried out obtained a positive response of the material to light exposure, showing higher values of photocurrent obtained for the film made with the higher concentration solution and with the photocurrent presented by the drop casting films rising at each exposition cycle.

5. Acknowledgments

This research was funded by São Paulo Research Foundation (FAPESP), and National Council for Scientific and Technological Development (CNPq, INEO). The authors are grateful to the Brazilian Nanotechnology National Laboratory (LNNano/CNPEM, LMF project 2023090) for supplying the gold interdigitated electrodes. This study was financed by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES - Finance cod. 001).

6. References

1. Kaloni TP, Giesbrecht PK, Schreckenbach G, Freund MS. Polythiophene: from fundamental perspectives to applications. Chem Mater. 2017;29(24):10248-83.
2. Bobade RS. Polythiophene composites: a review of selected applications. J Polym Eng. 2011;31(2-3):209-15.
3. Kadac K, Nowaczyk J. Polythiophene nanoparticles in aqueous media. J Appl Polym Sci. 2016;133(23):app.43495.
4. Heeger AJ. Semiconducting and metallic polymers: the fourth generation of polymeric materials (Nobel lecture). Angew Chem Int Ed. 2001;40(14):2591-611.
5. Noriega R, Salleo A, Spakowitz AJ. Chain conformations dictate multiscale charge transport phenomena in disordered semiconducting polymers. Proc Natl Acad Sci USA. 2013;110(41):16315-20.
6. Inzelt G. Recent advances in the field of conducting polymers. J Solid State Electrochem. 2017;21(7):1965-75.
7. Gao L, Cao Y, Wang J, Ren H, Wang J, Huang J. Construction of polypyrrole coated hollow cobalt manganate nanocages as an effective sulfur host for lithium-sulfur batteries. Ceram Int. 2020;46(11):18224-33.
8. Yu Y-Y, Yang C-H. Preparation and application of organic-inorganic nanocomposite materials in stretched organic thin film transistors. Polymers. 2020;12(5):1058.
9. Viswanathan A, Gururaj Acharya M, Nityananda Shetty A. High rate capable and high energy supercapacitor performance of reduced graphene oxide/Al$(OH)_3$/polyaniline nanocomposite. J Colloid Interface Sci. 2020;575:377-87.
10. Yoon C, Yang KP, Kim J, Shin K, Lee K. Fabrication of highly transparent and luminescent quantum dot/polymer nanocomposite

for light emitting diode using amphiphilic polymer-modified quantum dots. Chem Eng J. 2020;382:122792.

11. Zhang D, Wang D, Li P, Zhou X, Zong X, Dong G. Facile fabrication of high-performance QCM humidity sensor based on layer-by-layer self-assembled polyaniline/graphene oxide nanocomposite film. Sens Actuators B Chem. 2018;255:1869-77.
12. AL-Refai HH, Ganash AA, Hussein MA. Polythiophene and its derivatives –Based nanocomposites in electrochemical sensing: a mini review. Mater Today Commun. 2021;26:101935.
13. Oliveira VJR, Borro MS, Jesus LRM, Braunger ML, Olivati CA. Using Langmuir-Schaefer deposition technique to improve the gas sensing performance of regiorandom polythiophene films. Sensors and Actuators Reports. 2022;4:100094.
14. Mohd Nurazzi N, Harussani MM, Demon SZN, Halim NA, Mohamad IS, Bahruji H, et al. Research progress on polythiophene and its application as chemical sensor. Zulfaqar J Def Sci Eng Tech. 2022 [cited 2024 Apr 30];5(1):48-68. https://zulfaqarjdset.upnm.edu.my/index.php/zjdset/article/view/65
15. Mozer AJ, Panda DK, Gambhir S, Romeo TC, Winther-Jensen B, Wallace GG. Flexible and compressible Goretex−PEDOt membrane electrodes for solid-state dye-sensitized solar cells. Langmuir. 2010;26(3):1452-5.
16. Lin Y-C, Huang Y-W, Wu Y-S, Li J-S, Yang Y-F, Chen W-C, et al. Improving mobility-stretchability properties of polythiophene derivatives through ester-substituted, biaxially extended conjugated side chains. ACS Appl Polym Mater. 2021;3(3):1628-37.
17. Ramírez-Solís A, Kirtman B, Bernal-Jáquez R, Zicovich-Wilson CM. Periodic density functional theory studies of Li-doped polythiophene: dependence of electronic and structural properties on dopant concentration. J Chem Phys. 2009;130(16):164904.
18. Mehmood U, Al-Ahmed A, Hussein IA. Review on recent advances in polythiophene based photovoltaic devices. Renew Sustain Energy Rev. 2016;57:550-61.
19. Lin JW, Dudek LP. Synthesis and properties of poly(2,5-thienylene). J Polym Sc Polym Chem Ed. 1980;18:2869-73.
20. Reynolds JR, Thompson BC, Skotheim TA, editors. Handbook of conducting polymers. Boca Raton: CRC Press; 2019. 2 volume set.
21. Sajid H, Ayub K, Mahmood T. A comprehensive DFT study on the sensing abilities of cyclic oligothiophenes (*n* CTs). New J Chem. 2019;43(35):14120-33.
22. Silva EA. Efeito da adição de moléculas anfifílicas na formação de filmes Langmuir e Langmuir-Blodgett de derivados alquilados do politiofeno: aplicação em sensores [dissertação]. Presidente Prudente: Universidade Estadual Paulista "Júlio de Mesquita Filho"; 2014.
23. Li C, Shi G. Polythiophene-based optical sensors for small molecules. ACS Appl Mater Interfaces. 2013;5(11):4503-10.
24. Ye L, Ke H, Liu Y. The renaissance of polythiophene organic solar cells. Trends Chem. 2021;3(12):1074-87.
25. Sheppard NF, Tucker RC, Wu C. Electrical conductivity measurements using microfabricated interdigitated electrodes. Anal Chem. 1993;65(9):1199-202.
26. Almeida LCP. Filmes finos multicamadas de polímeros condutores, nanotubos de carbono e fulerenos modificados para aplicação na conversão de energia solar [dissertação]. Campinas: Universidade Estadual de Campinas; 2012.
27. Castro SVF. Sensor voltamétrico para detecção de trinitrotolueno baseado em nanocompósito de óxido de grafeno reduzido e nanotubos de carbono [dissertação]. Uberlândia: Universidade Federal de Uberlândia; 2018.
28. Simõis AVS, Roncaselli LKM, de Oliveira VJR, Medina MERS, Ramanitra HH, Stephen M, et al. Polyfullerene thin films applied as NH_3 sensors. Mater Res. 2021;24(Suppl 1):e20210435.
29. Kaliyaraj Selva Kumar A, Zhang Y, Li D, Compton RG. A mini-review: how reliable is the drop casting technique? Electrochem Commun. 2020;121:106867.
30. Cea P, Martín S, Villares A, Möbius D, López MC. Use of UV−vis Reflection spectroscopy for determining the organization of viologen and viologen tetracyanoquinodimethanide monolayers. J Phys Chem B. 2006;110(2):963-70.
31. Bolognesi A, Bajo G, Comoretto D, Elmino P, Luzzati S. Characterization of poly(3-decylmethoxythiophene) multilayers. Thin Solid Films. 1997;299(1-2):169-72.
32. Rikukawa M, Rubner MF. Fabrication of Langmuir-Blodgett films of poly(3-hexylthiophene) and metal-substituted phthalocyanines. Langmuir. 1994;10(2):519-24.
33. Olthuis W, Streekstra W, Bergveld P. Theoretical and experimental determination of cell constants of planar-interdigitated electrolyte conductivity sensors. Sens Actuators B Chem. 1995;24(1-3):252-6.
34. Dicker G, Savenije TJ, Huisman B-H, de Leeuw DM, de Haas MP, Warman JM. Photoconductivity enhancement of poly(3-hexylthiophene) by increasing inter- and intra-chain order. Synth Met. 2003;137(1-3):863-4.
35. Hiorns RC, de Bettignies R, Leroy J, Bailly S, Firon M, Sentein C, et al. High Molecular weights, polydispersities, and annealing temperatures in the optimization of bulk-heterojunction photovoltaic cells based on poly(3-hexylthiophene) or poly(3-butylthiophene). Adv Funct Mater. 2006;16(17):2263-73.
36. Brown PJ, Thomas DS, Köhler A, Wilson JS, Kim J-S, Ramsdale CM, et al. Effect of interchain interactions on the absorption and emission of poly(3-hexylthiophene). Phys Rev B Condens Matter. 2003;67(6):064203.
37. Kanoun O, Müller C, Benchirouf A, Sanli A, Dinh T, Al-Hamry A, et al. Flexible carbon nanotube films for high performance strain sensors. Sensors. 2014;14(6):10042-71.
38. Iwai H, Sze SM, Taur Y, Wong H. Guide to state-of-the-art electron devices. New York: Wiley; 2013. p. 21-36.
39. Tomozawa H, Braun D, Phillips SD, Worland R, Heeger AJ, Kroemer H. Metal-polymer Schottky barriers on processible polymers. Synth Met. 1989;28(1-2):687-90.
40. Olivati CA, Gonçalves VC, Balogh DT. Optically anisotropic and photoconducting Langmuir–Blodgett films of neat poly(3-hexylthiophene). Thin Solid Films. 2012;520(6):2208-10.