

Application of Zinc Oxide in Hybrid Solar Cells Using a P3HT and P3OT Polymer Junction as Charge Carrier

Letícia Fernanda Gonçalves Larsson^{a,*}, Guilherme Arielo Rodrigues Maia^b, Gideã Taques Tractz^a,
Tatiana Lima Valério^a, Danielle Cristina Silva Oliszeski^b, Rodrigo Helleis^b, Maico Taras da Cunha^b,
Paulo Rogério Pinto Rodrigues^b, Everson do Prado Banczek^b

^aUniversidade Estadual do Centro-Oeste - UNICENTRO, Simeão Varela de Sá, 03, 85015-430, Guarapuava, PR, Brasil

^bDepartamento de Química, Universidade Estadual do Centro-Oeste - UNICENTRO, Simeão Varela de Sá, 03 85015-430, Guarapuava, PR, Brasil

Received: December 07, 2018; Revised: May 11, 2019; Accepted: May 19, 2019

Hybrid solar cells show an increasing number in researches due to its low cost and easy of production. They are composed by and organic material and a semiconductor oxide. The aim of this paper was to synthesis and characterize zinc oxide by coprecipitation and apply it in a hybrid solar cell that uses a P3HT/P3OT copolymer as charge carrier. The cell was assembled in "sandwich" form using FTO/ZnO/P3HT-P3OT as work electrode, (Pt/FTO) as counter electrode and I/I-3 redox couple as electrolyte. Through the X-ray diffractogram the formation of a single ZnO wurtzite hexagonal phase was observed. The morphology obtained for the oxide was spherical. The results of photochromoamperometry showed current density values of $j_{P3HT/P3OT} = 0.55 \text{ mA}\cdot\text{cm}^{-2}$ for the cell in the presence of the copolymer and the curve $j \times V$ showed an efficiency of 0.16% for the studied cell, demonstrating that the polymer was a satisfactory sensitizer.

Keywords: photovoltaic effect, polymeric photosensitizer, coprecipitation.

1. Introduction

The search for new devices that can convert solar energy to electricity is one of the most promising methodologies for the century, due to issues caused by the burning of fossil fuels. Many types of photovoltaic devices (PV) have been studied, even though silicone based solar cells have shown better efficiency of harvesting light, it has a higher cost, and a more complicated fabrication process, as described by Mahalingam and Andullah¹.

Third generation PV cells are devices that do not follow the Shockley Queisser limit. In this class, the perovskite solar cells (PVK), dye sensitized solar cells (DSSC), quantum dots sensitized solar cells (QDSC) and, the focus of this paper, hybrid solar cells (HSC) are found^{2,3}. The operation of the HSC system, is shown in Figure 1⁴.

When receiving light, the organic photosensitizer eject electrons to a higher energy state, and into the conduction band of a nanocrystalline oxide. The organic compound is regenerated by the use of an electrolyte, that intermediates the charges in all anodic and cathodic interfaces^{5, 6}. The oxidized molecules diffuse to a counter electrode, where they are rapidly reduced, leading to an electron flow, and consequently an electric current.

The most commonly oxide used in this system is TiO_2 , with PCBM polymer ([6,6]-phenyl-C61-butiric acid methyl ester), however, these materials present a high cost, which leads for researches of new organic/inorganic materials⁷.

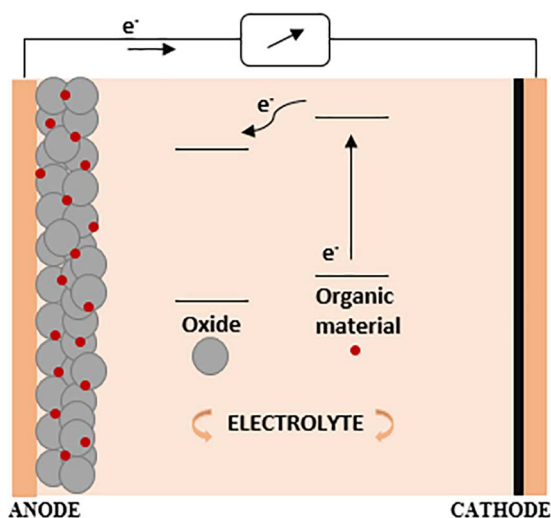


Figure 1. Hybrid solar cell assembly.

Therefore, ZnO, and thiophene derivatives polymers are promising materials to be used in HSC due to the low cost of production and remarkable redox, electronic and optic properties to be used as supramolecular compounds⁸.

ZnO has many advantages, as thermodynamic stability, good photochemical properties, great crystallinity, produce transparent films in invisible light and presents band gap in the order of 3.4 eV⁴.

*e-mail: let.larsson@gmail.com

This work aims to produce ZnO particles by the coprecipitation method and applied in on hybrid solar cells, with P3HT/P3OT copolymer.

2. Experimental

2.1 ZnO particle synthesis

The ZnO particles were synthesized by the co-precipitation method⁹ by mixing solution of 0.1 mol L⁻¹ triethanolamine (TEA) in an aqueous solution of 0.05 mol L⁻¹ of Zn(NO₃)₂·6H₂O, with magnetic stirring. The solution was left in an ultrasonic bath for 10 min. The obtained powder was centrifuged at 4000 rpm and dried in an oven at 60°C.

2.2 Scanning electron microscopy (SEM)

The scanning electronic microscopy images were collected with a TESCAN VEGA3 SEM with an SE detector and tungsten filament at 20 kV and a WD of 10 and 15 mm.

2.3 X-ray diffraction analysis (XRD)

The X-ray diffraction was performed in a Bruker XRD D2 Phaser instrument with CuKα radiation of 1.54 Å at 30 kV, 10 mA, a scan speed of 0.5 s⁻¹ and a LynxEye detector.

2.4 ZnO particle application in solar cell

The ZnO deposition (working electrode), was made with a suspension composed by 3g of zinc oxide, 4 mL of ultrapure H₂O, 0.1 mL acetylacetone (VE TEC) and 0.1 mL of Triton-X (VE TEC). The paste was coated by the Spin Coating method, in conductor glass fluorine tin oxide (FTO) at 2500 rpm. After the deposition, the film was calcinated at 450°C for 30 min. The ZnO films after calcination, were immersed in a P3OT/P3MT solution for 24 h for the adsorption⁴. The P3OT/P3MT copolymer was synthesized by electrochemical method and the solution was prepared using 0.1 g of P3OT/P3MT in 100 mL of Toluene.

The HSC was assembled in a "sandwich" form, with the photoanode and counter electrode with electrolytic solution between the plates, in active area of 0.2 cm². The electrolyte used consisted of 0.1 mol L⁻¹ LiI, 0.05 mol L⁻¹ I₂, and 0.5 mol L⁻¹ 4-tert-butyl pyridine in acetonitrile.

2.4.1 Electrochemical characterization of solar cells

The characterization of the hybrid solar cell systems was performed in a Zahner potentiostat, Zennium Electrochemical Workstation model, linked to XPot and a LOT Oriel-Quantum Design GmbH-solar simulator, with a xenon lamp and a beam diameter of 25 mm. The measurements were performed under illumination of 100 mW cm⁻², with a standard solar spectrum at AM 1.5G.

The open circuit potential was attained when the variation of Voc was ± 5 mV for 15 min and the photochronoamperometry

measurements were performed for 660 s, with the lamp being interrupted in intervals of 60 s. Current versus potential curves (j-V) were measured to obtain the photovoltaic parameters of the cells and calculate the energy conversion efficiency of the systems.

3. Results and Discussion

Figure 2 shows the X-ray diffractograms of ZnO particles.

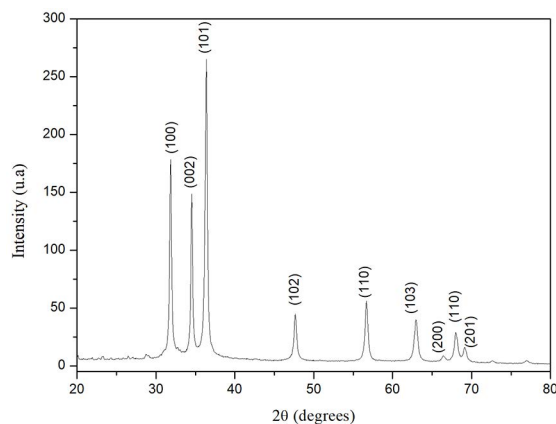


Figure 2. X-ray diffractogram of ZnO particles synthesized by coprecipitation.

The samples were investigated by XRD and the synthesized particles showed peaks identified as (100), (002), (101), (102), (110), (103), (200), (110) and (201), which correspond to the reflection planes characteristic of ZnO of hexagonal wurtzite crystalline phase. All peaks were identified characteristic to ZnO, with no peaks corresponding to other compounds or impurities¹⁰. Thus, the synthesized zinc oxide showed high purity and the peaks were narrow and intense indicating a high crystallinity of the oxide. The cataloging of the peaks was performed by comparison with the crystallographic record PDF 01-075-0576 using EVA software, referring to pure ZnO.

The morphological aspect of the powder was analyzed by scanning electron microscopy (SEM), as shown in Figure 3.

The morphology of the ZnO particles is very sensitive to factors such as the reaction time, concentration, synthesis temperature and production method¹¹ and SEM image (figure 3) present spherical morphology for the ZnO, characteristic of the coprecipitation method and precursor concentration used¹². According to Zhao (2015), ZnO is a crystal with a positive pole (Zn²⁺) and a negative pole (O²⁻), when the molar ratio is 1: 7.5 the particles seek to minimize the surface energy and rearrange on the surface of the ZnO nuclei, so that the structures are in the spherical form¹³.

It is observed that the particles have different sizes, but with uniform and defined morphology composed of agglomerates formed due to the high surface energy associated to the extensive surface area of the particles¹⁴.

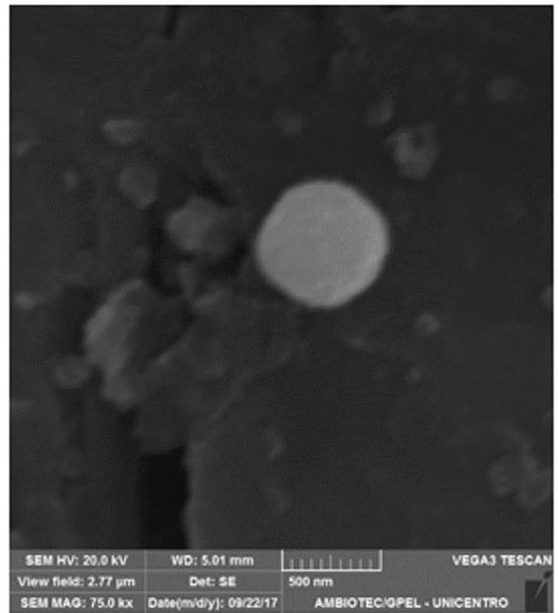
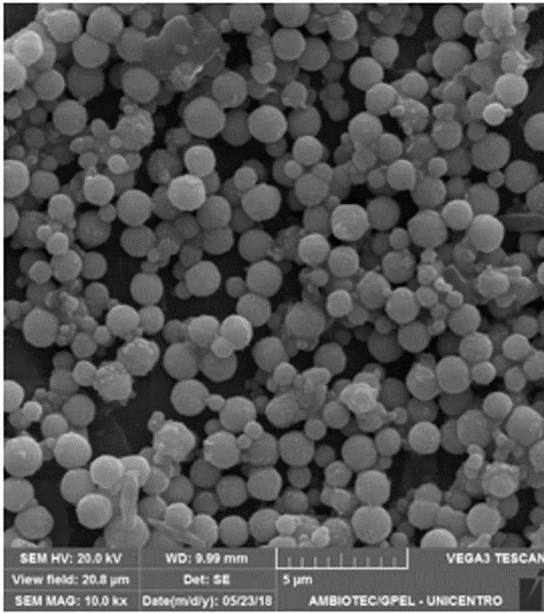


Figure 3. SEM images of ZnO particles synthesized by coprecipitation.

To evaluate the response of the cell in the presence of light, the photochromoamperometry technique was performed and the values for the cell produced only with ZnO and ZnO + P3HT / P3OT are presented in Figure 4.

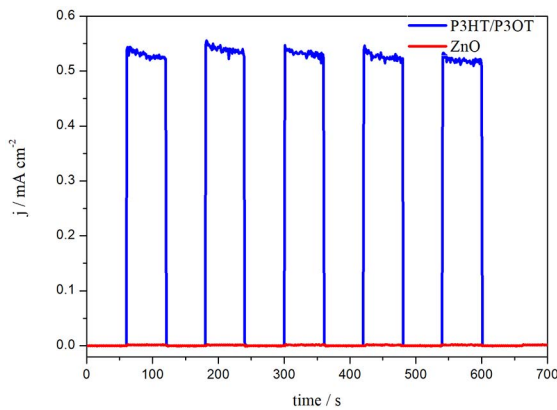


Figure 4. Photochromoamperometry measurements for samples under 100 mW cm^{-2} of illumination. The lamp was interrupted at a time interval of 60 s.

It can be seen in Figure 4 that the system ZnO+P3HT/P3OT presented a high on/off ratio and fast switching because when light struck the cell, the increase in current was instantaneous, and when the lamp was interrupted, the current for both systems was close to zero⁵. This proves that the reactions that govern the device are extremely fast. It was also verified that the cell produced only with ZnO showed a photocurrent close to zero, while the solar cell sensitized presented $j_{\text{P3OT/P3HT}} = 0.55 \pm 0.03 \text{ mA cm}^{-2}$, proving

the high electron injection capacity on the surface of the semiconductor. During the analysis period, the device did not present current density decay, indicating no tendency to degradation and consequently the diffusion processes of the recombination reaction are minimized.¹⁵

Figure 5 shows the open circuit potential curves (V_{oc}) for solar cells in the dark and presence of light.

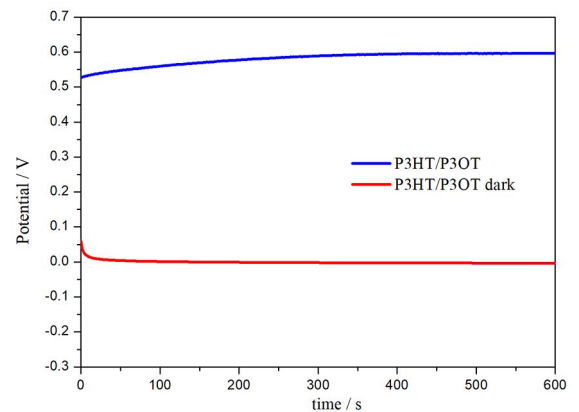


Figure 5. Open circuit potential obtained for the ZnO solar cells with P3HT/P3OT copolymer in under illumination of 100 mW cm^{-2} and without light.

It is observed that without light, the solar cell demonstrate equilibrium potential close to zero, and in the presence of light the dispositive shows cathodic equilibrium potential. This significant increase of V_{oc} characterizes a photoelectrochemical process⁴.

The open circuit potential is directly associated to electronic transfer processes that occur at the solar cell interfaces¹⁶. The recombination processes that occur at the FTO / electrolyte interface of the cells interferes in the potential and the high value of $V_{oc} = -0.597$ V indicates that the recombination processes decreased¹⁷.

Figure 6 shows the current density *versus* potential curve ($j \times V$) and from the graph the photovoltaic parameters of the cell were evaluated.

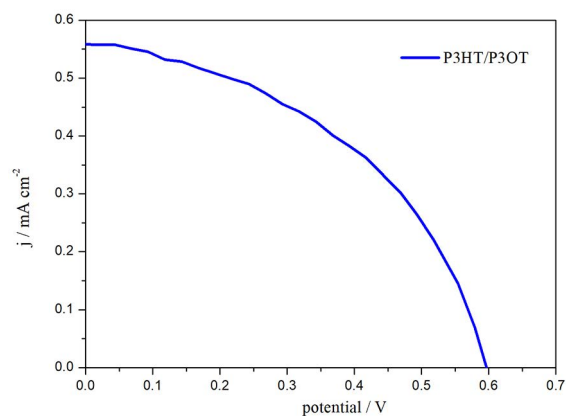


Figure 6. Typical j - V curve obtained from the cell analyzed under 100 mW cm^{-2} of simulated solar irradiation.

Using the results shown in Figure 6, it was possible to determine the photovoltaic parameters of the device listed in Table 1 and calculate the energy conversion efficiency (η) using Equation 1, being that, V_{oc} = open-circuit potential, J_{sc} = short-circuit current, FF = fill factor and P_{in} = solar irradiation, of 100 mW cm^{-2} ¹⁸.

$$\eta = \left(\frac{J_{sc} \times V_{oc} \times FF}{I_o} \right) \times 100\%$$

Table 1. Parameters obtained from the j - V curves of ZnO cell sensitized with copolymer P3HT/P3OT

Solar cell	$J_{sc} / \text{mA cm}^{-2}$	P_{max} / mW	V_{max} / V	FF	η %
ZnO + P3HT/P3OT	0.548 ± 0.06	0.032 ± 0.1	-0.605 ± 0.02	0.48 ± 0.015	0.16 ± 0.02

When the electrical voltage is zero, the current reaches its maximum and the current is associated with the electron injection mechanism and the charge transport of the carriers⁴. As the potential is applied the current decays, so there is an increase in resistance.

The ZnO cell using the polymer P3HT/P3OT showed the efficiency value, $\eta = 0.16 \pm 0.02\%$, and the current density value, $j = 0.605 \text{ mA cm}^{-2}$, demonstrating the contribution of the polymer to the sensitization of the cell.

The ZnO+P3HT/P3OT cell had a high V_{oc} value of 0.605 V, similar to the values found for cells using high performance dyes. Guimarães and coworkers reached values of 0.60 V and 0.61 V for TiO_2 cells using ruthenate dyes, that have a high production costs, when compared to *polymers* containing *thiophene* ring¹⁹.

4. Conclusion

The X-ray diffractograms showed purity and crystallinity of ZnO, which exhibited wurtzite hexagonal phase and the SEM images demonstrated the spherical morphology of ZnO.

The V_{oc} and photocurrent analysis demonstrated that the sensitized solar cell showed immediate response in the presence of light, presenting $j = 0.55 \text{ mA cm}^{-2}$ this proves that the reactions that govern the device are extremely fast.

The photovoltaic parameters analyzed by the $j \times V$ curve showed that the ZnO + P3HT/P3OT cell presented an energetic conversion efficiency of $0.16 \pm 0.02\%$ indicating an efficient sensitization of the copolymer in the cell.

5. Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The authors are also grateful to CNPq, SETI/UGF, FINEP.

References

- Mahalingam S, Abdullah H. Electron transport study of indium oxide as photoanode in DSSCs: A review. *Renewable and Sustainable Energy Reviews*. 2016;63:245-255.
- Thavasi V, Renugopalakrishnan V, Jose R, Ramakrishna S. Controlled electron injection and transport at materials interfaces in dye sensitized solar cells. *Materials Science and Engineering: R: Reports*. 2009;63(3):81-89.
- de Freitas JN, Li RWC, Nogueira AF, Gruber J. Conjugated copolymers based on poly(flurenylene vinylene) derivatives containing push-pull units: Synthesis and characterization. *Materials Chemistry and Physics*. 2011;130(1-2):223-230.
- Maia GAR, Larsson LFG, Viomar A, Matos LAC, Antunes SRM, Maia ECR, et al. Influence of zinc oxide morphology in hybrid solar cells of poly(3-octylthiophene). *Journal of Materials Science: Materials in Electronics*. 2016;27(8):8271-8278.
- Tractz GT, Maia GAR, Dias BV, Ignachewski F, Rodrigues PRP. Avaliação da adsorção e estudo eletroquímico de células solares produzidas com TiO_2 e corante extraído do *Hibiscus*. *Química Nova*. 2018;41(5):512-518.
- Beek WJE, Slooff LH, Wienk MM, Kroon JM, Janssen RAJ. Hybrid Solar Cells Using a Zinc Oxide Precursor and a Conjugated Polymer. *Advanced Functional Materials*. 2005;15(10):1703-1707.

7. Da Pian M, Maggini M, Vancso GJ, Causin V, Benetti EM. Assembly of poly-3-(hexylthiophene) nanocrystals in marginal solvent: The role of PCBM. *European Polymer Journal*. 2018;109:222-228.
8. Zhang F, Wu D, Xu Y, Feng X. Thiophene-based conjugated oligomers for organic solar cells. *Journal of Materials Chemistry*. 2011;21(44):17590-17600.
9. Kashyout AB, Soliman M, El Gamal M, Fathy M. Preparation and characterization of nano particles ZnO films for dye-sensitized solar cells. *Materials Chemistry and Physics*. 2005;90(2-3):230-233.
10. Giraldi TR, Santos GVF, de Mendonça VR, Ribeiro C, Weber IT. Effect of synthesis parameters on the structural characteristics and photocatalytic activity of ZnO. *Materials Chemistry and Physics*. 2012;136(2-3):505-511.
11. Li D, Haneda H. Morphologies of zinc oxide particles and their effects on photocatalysis. *Chemosphere*. 2003;51(2):129-137.
12. Meng F, Yin J, Duan YQ, Yuan ZH, Bie LJ. Co-precipitation synthesis and gas-sensing properties of ZnO hollow sphere with porous shell. *Sensors and Actuators B: Chemical*. 2011;156(2):703-708.
13. Zhao J, Wu J, Zheng M, Huo J, Tu Y. Improving the photovoltaic performance of dye-sensitized solar cell by graphene/titania photoanode. *Electrochimica Acta*. 2015;156:261-266.
14. Hong RY, Li JH, Chen LL, Liu DQ, Li HZ, Zheng Y, et al. Synthesis, surface modification and photocatalytic property of ZnO nanoparticles. *Powder Technology*. 2009;189(3):426-432.
15. Valerio TL, Maia GAR, Viomar A, Dias BV, Rodrigues PRP. Study of the influence of Nb₂O₅ in ZnO solar cells. *Orbital: The electronic Journal of Chemistry*. 2018;10(3):234-238.
16. Patrocínio AOT, Mizoguchi SK, Paterno LG, Garcia CG, Iha NYM. Efficient and low cost devices for solar energy conversion: Efficiency and stability of some natural-dye-sensitized solar cells. *Synthetic Metals*. 2009;159(21-22):2342-2344.
17. Viomar A, Maia GAR, Scremin FR, Khalil NM, da Cunha MT, Antunes AC, et al. Influência do Método de Obtenção de Partículas de Nb₂O₅ Empregadas em Células Solares Sensibilizadas por Corante Compostas de TiO₂/Nb₂O₅. *Revista Virtual de Química*. 2016;8(3):889-900.
18. Narayan MR. Review: Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews*. 2012;16(1):208-215.
19. Guimaraes RR, Parussulo ALA, Matias TA, Toma HE, Araki K. Electrostatic blocking barrier as an effective strategy to inhibit electron recombination in DSSCs. *Electrochimica Acta*. 2017;255:92-98.