Development of Hybrid Solar Cells based on TiO_2 or ZnO- Graphene Oxide Heterojunctions

D. Carreira[1], P. A. Ribeiro[2][a], M. Raposo[2][b] and S. Sério[2][c]
[1]Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[2]CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa,
2829-516 Caparica, Portugal

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Abstract: Nowadays it is becoming increasingly necessary to find alternatives to fossil fuels in order to produce energy from renewable sources that do not have a negative impact on the environment. In this work, two types of hybrid solar cells devices were produced, in which the photoactive layer is made of poly (allylamine chloride) (PAH) and graphene oxide (GO) organic films and titanium dioxide (TiO_2) or zinc oxide (ZnO) inorganic films. These films were deposited on fluoride-doped tin oxide (FTO) glass substrates, being the organic layer deposited by the layer-by-layer (LbL) technique and the inorganic layer by DC-reactive magnetron sputtering. The aluminum electrodes were deposited by thermal evaporation. The final device configuration was $FTO/(PAH/GO)_x/TiO_2/Al$ and $FTO/(PAH/GO)_x/ZnO/Al$, where x is the number of bilayers deposited. $(PAH/GO)_x$ films were characterized by ultraviolet-visible spectrophotometry, which revealed a linearity in the growth of the films with the number of bilayers. Scanning electron microscopy (SEM) showed that the morphology of the inorganic layer is homogeneous and is dependent on the number of layers of the organic layer. The SEM cross section images further revealed the desired architecture. The electrical properties were characterized by constructing current-voltage curves. The $FTO/(PAH/GO)_{50}$ $/TiO_2/Al$, $FTO/(PAH/GO)_{30}/ZnO/Al$ and $FTO/(PAH/GO)_{50}/ZnO/Al$ devices were the only ones to exhibit a diode behavior, although they did not show any reaction when exposed to light. The FTO/ $(PAH/GO)_{50}/ZnO/Al$ cell experienced a decrease in current when characterized in a low humidity environment, revealing that humidity is a key factor in the conduction of the organic films.

1 INTRODUCTION

Today we live in a world completely dependent on the use of fossil fuels such as coal, oil and natural gas. This dependence manifests itself in the most diverse sectors of society, especially in the energy sector. The use of these fuels leads to a number of inherent problems, because these resources are limited and therefore there is an increasing difficulty in satisfy the energy demands of a constantly growing population. In addition, they can contribute significantly to the increase of greenhouse gases in the planet, which inevitably leads to the global warming. These implications undoubtedly represent a dangerous threat to the development of a sustainable global society.

In this sense, it is imperative to find mechanisms to produce and store energy efficiently, which present a reduced environmental impact. The first strategy to achieve this goal is to obtain energy from renewable sources such as the sun, wind and water and effectively converted into electricity or fuel. In this context there has been an increasing research on alternative materials and/or solutions such as solar cells and photoelectrochemical cells (Hu 2015). The area of solar cells has been constantly changing since the discovery of the photovoltaic effect in 1839 and considers the existence of four distinct generations of such devices, ranging from silicon-based solar cells to hybrid solar cells.

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[a] https://orcid.org/0000-0001-9665-7610
[b] https://orcid.org/0000-0003-4710-0693
[c] https://orcid.org/0000-0002-8086-7792

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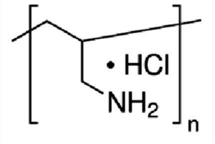
One of the materials that has attracted a huge interest in the scientific comunity is graphene and its derivatives (graphene oxide (GO) and reduced graphene oxide (rGO)). These materials have been extensively studied due to their electrical, mechanical, optical and thermodynamic properties and are presently used in several applications such as: solar cells, solar fuels, lithium ion batteries, supercapacitors, among others. In the particular case of solar cells, these compounds have been used as transparent and non-transparent electrodes, in photoactive layers and also in electron transport layers and gaps (Yin 2014).

Considering the technological progress made in this area during the last decades solar cells with hybrid heterostructures have emerged in order to overcome some drawbacks of organic solar cells such as low optical absorption and degradation of the compounds used (Roland 2015 and Wright 2012).

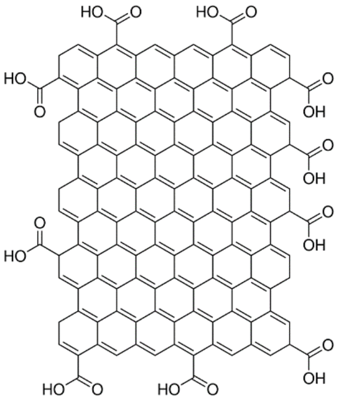
In this sense and within the scope of the knowledge and work carried out in the last two decades under organic conductive polymers, photoluminescent and photochromic (Ferreira 2013, Ferreira 2007 and Ferreira 2007) and also on semiconductors oxides films, such as TiO_2 and ZnO (Sério 2011, Sério 2011 and Siopa 2016), the present work was undertaken in order to find solutions to capture and convert the solar energy.

2 EXPERIMENTAL DETAILS

The layer-by-layer films were prepared from aqueous solutions of poly-(allylamine hydrochloride) (PAH) (Mw) 50 000-65 000 g/mol g/mol) and graphene oxide (GO) 2 mg/mL, dispersion in H_2O, with concentrations of 10^{-2} M and 0.5×10^{-2} M, respectively, using the LbL technique. The ultrapure water with a resistivity of 18 MΩ cm was supplied by a Millipore system (Milli-Q, Millipore GmbH). The chemicals were obtained from Aldrich and the corresponding molecular structures are depicted in Figure 1.



(a)



(b)

Figure 1: (a) poly-(allylamine hydrochloride) (PAH) (b) graphene oxide (GO).

Accordingly, thin films of PAH/GO that were deposited onto Fluorine- doped tin oxide (FTO) coated glass substrates (TEC15, 12-14 Ω/☐) were obtained by adsorbing alternate layers of electrically charged polyelectrolytes at solid/liquid interface, carefully washing with water the already adsorbed layers after immersion in the polyelectrolyte solution to remove the polyelectrolyte molecules that were not completely adsorbed. The adsorption time period of each layer (immersion time in each polyelectrolyte solution) was 60 s and the thin film was dried, using a nitrogen flow after the adsorption of each layer. After this sequence, the first bilayer was formed and the steps aforementioned were repeated until obtain the desired number of bilayers.

After, the inorganic layer (TiO_2 or ZnO) was deposited by DC-magnetron sputtering. Titanium and zinc discs (Goodfellow, 99.99% purity) with 64.5 mm of diameter and 4 mm of thickness each were used as the sputtering targets. A turbomolecular pump (Pfeiffer TMH 1001) was used to achieve a base pressure of 10^{-4}-10^{-5} Pa (before introducing the sputtering gas). Before the sputter-deposition step of the films, a movable shutter was interposed between the target and the substrates. The target was pre-sputtered in the Ar atmosphere for 2 min to clean the target surface. The target-to-substrate distance was kept constant at 100 mm. Gases in the system were pure Ar and O_2 and needle valves separately controlled their pressures. TiO_2 and ZnO depositions were both carried out in 100% O_2 atmosphere. For the TiO_2 film the total pressure was kept constant at 2 Pa, the sputtering power was 530 W, and the deposition time was 25 min. In the case of ZnO film, the total pressure was fixed at 4.8 Pa, the sputtering power was 300 W, and the deposition time was 30 min. The target-to-substrate distance was kept constant at 100 mm. No external substrate heating was used during the depositions. The substrate temperature was measured by a thermocouple passing through a small hole in a copper piece, which was placed in contact with the substrate. During the deposition process the sample temperature increased up to 60 °C due to the plasma particle‘s bombardment of the substrate. Finally, to obtain the desired solar cell device an aluminium (*Advent Research Materials*, 99.5%) electrode was deposited by thermal evaporation, in a vacuum chamber at a pressure between 10^{-6} and 10^{-5} mbar, over an area of approximately 0.95 cm^2.

The characterization of the thin films thickness and morphology was performed by a field emission scanning electron microscope (FEG-SEM JEOL 7001F) operating at 15 keV. A gold thin film was coated on the films surface before SEM analysis to charge build-up prevention. The images of the cross section allowed for the estimation of the films' thickness. The UV-vis spectroscopy for the films was carried out with a Shimadzu UV b - 2101PC UV/VIS spectrophotometer at room temperature within the wavelength range 200-900 nm. The electric measurements (I-V characteristic curve) of the final devices were carried out using a programmable DC power supply model Rigol DP811A (programmable DC power supply, LX1) in absence of light, at ambient light and with light from a 250 watts halogen lamp positioned at a distance of 40 cm from the device. All the I-V measurements were performed by changing the voltage between 0V and ~1.5 V, with an increment of 50 mV at room temperature, which was guaranteed by a vent placed in the measurement system.

3 RESULTS AND DISCUSSION

3.1 UV-vis Spectrophotometry

In order to study the growth of a PAH/GO film and the variation of its absorbance with the number of adsorbed bilayers, films with 20, 30 and 50 bilayers were produced using the LbL technique. In figure 2 and 3 is shown a representative ultraviolet-visible absorbance spectra of different number of bilayers of PAH/GO LBL films and the absorbance intensity at 380 nm as a function of the number of bilayers, N, respectively.

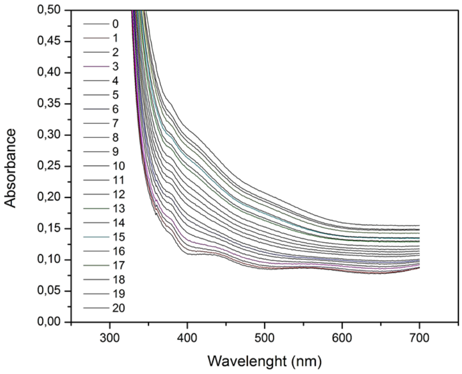


Figure 2: Absorbance spectra of PAH/GO LBL films as a function of the number of bilayers, N.

It can be observed that the absorbance at maximum increases with the number of bilayers indicating a linear film growth (see figure 3). This behaviour was detected for all the developed devices.

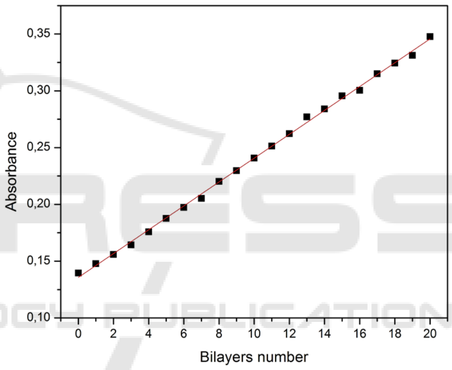


Figure 3: Absorbance intensity at 380 nm as a function of the number of bilayers, N.

3.2 Morphological Characterization

The SEM images reveal for all samples a uniform surface with no apparent defects, such as the presence of cracks. However for TiO$_2$ it can be noticed the formation of aggregates, ranging from 260 nm to 400 nm for the devices with 20 bilayers and from 200 nm to 340 nm for the 30 bilayers devices. The same is not true for the device with 50 bilayers, which are much smaller in the order of 20-30 nm (figure 4). The surface of the alumimum electrodes also were analysed and the surface was also homogeneous with no sign of cracks. The morphology was similar to the one detected for the TiO$_2$ films (images not shown).

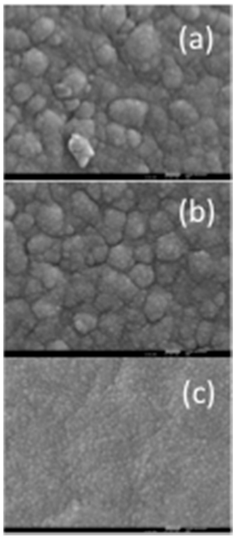


Figure 4: SEM images for three devices with the architecture (FTO/PAH/GO/TiO_2/Al)$_x$ a) x= 20 bilayers b) x= 30 bilayers and c) x= 50 bilayers. The surface corresponds to the TiO_2 film.

In the case of the devices with ZnO, for all samples an uniform is observed with no cracks (figure 5) as well for the aluminium electrode. Also for these devices the SEM images reveal that these films are formed by aggregates, which do not present significant differences in their dimensions between the analyzed devices, being their dimensions between approximately 50 nm and 200 nm. These values are considerably lower than those observed for TiO_2 films.

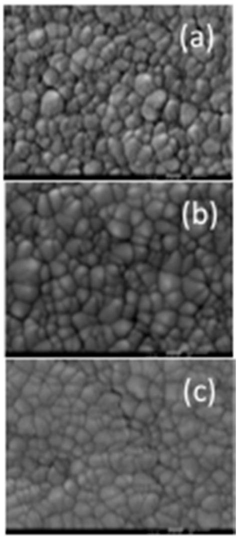


Figure 5: SEM images for three devices with the architecture (FTO/PAH/GO/ZnO/Al)$_x$ a) x= 20 bilayers b) x= 30 bilayers and c) x= 50 bilayers. The surface corresponds to the ZnO film.

3.3 Electric Characterization of FTO/(PAH/GO)$_x$/TiO_2/Al for x = 20, 30 and 50 Bilayers

The analyzed devices correspond to samples with the architectures: FTO/(PAH/GO)$_{20}$/TiO_2/Al and FTO/(PAH/GO)$_{30}$/TiO_2/Al.

It is important to point out, that the samples with 20 and 30 PAH/GO bilayers were analyzed at room temperature, at a temperature ranging from 20°C to 25°C, with a relative humidity between 50% and 60%. The samples were characterized only at ambient light and in an environment without light interaction. Figure 6 shows the current-voltage curves obtained for the FTO/(PAH/GO)x/TiO_2/Al samples, where x indicates the number of bilayers.

Analyzing the figure, it is verified that these samples do not present the expected behavior, that is, they do not show a typical semiconductor behavior, but rather a linear dependence of the current with the applied voltage- a resistive behavior. This may be due to several reasons, such as the high resistance at the photoactive electrode layer interface, which will block a large portion of the charge carriers, and the existence of a donor-acceptor junction not efficient, which may lead to an inefficient transport of charges to the electrodes. For these reasons, and since they did not exhibit the desired behavior, these samples were not analyzed when exposed to a light spot. It should be noted that in the sample with 30 PAH/GO bilayers (Figure 6 (b)) there were no measurable and significant changes with respect to exposure to ambient light. Furthermore, this device did not show any hysteresis in consecutive measurements.

On the other hand, the device with 20 bilayers shows a decrease in its conduction when it is deprived of ambient light. Given its resistive behavior, it cannot be said to be a photovoltaic phenomenon, and must rather be interpreted as a consequence of the degradation of its constituent films.

In an attempt to understand why the previously presented devices exhibited a poor performance, a device with the following architecture was developed: FTO/(PAH/GO)$_{50}$/TiO_2/Al. The number of bilayers of the organic part was increased in order to increase its thickness and to prevent the aluminum migration inside the device, as occurred in previous works carried out by the group (Magalhães-Mota 2018). Since parameters such as temperature and humidity could also influence the characterization of the sample, it was analyzed inside a desiccator, where the temperature ranged from 20°C to 23°C, with a very low relative humidity, ranging from 10%. and 15%. Although this experimental setup allowed a more accurate control of temperature and humidity, it was impossible to characterize the device under the action of a light spot. The current-voltage curve of this device is shown in Figure 6 c). Contrary to the previously analyzed devices, the sample consisting of 50 PAH/GO bilayers has a curve I (V) similar to the characteristic curve of a diode, also revealing a hysteresis effect. This phenomenon is quite noticeable from the first to the second measurement, which suggests that there may have been a degradation of the organic films, making the device less conductive. Moreover, from the analysis of Figure 6 c) it is visible that this sample is more conductive when positively polarized.

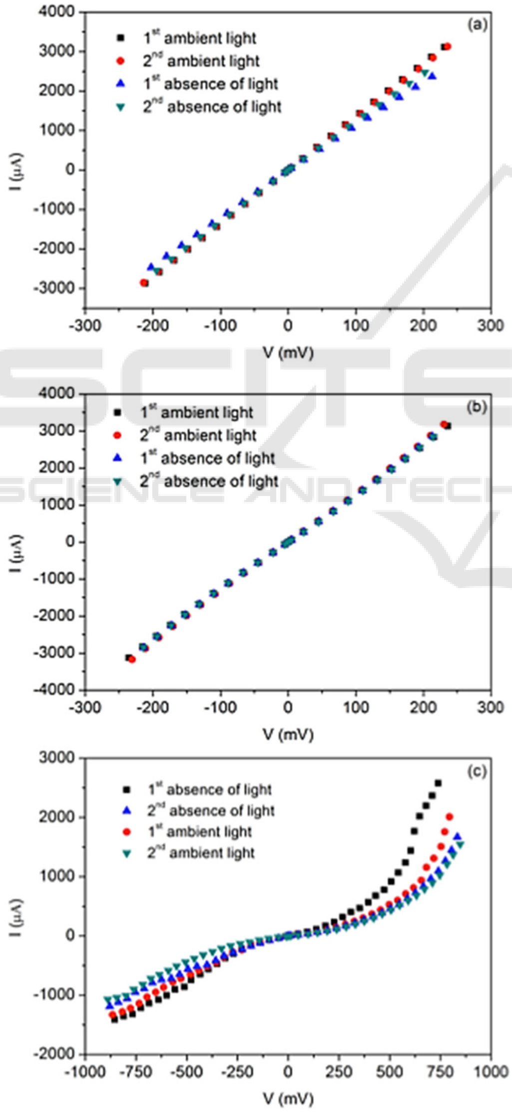


Figure 6: Electrical characterization for three devices with the architecture (FTO/PAH/GO/TiO$_2$/Al)$_x$ a) x= 20 bilayers b) x= 30 bilayers and c) x= 50 bilayers, for different light conditions.

3.4 Electric characterization of FTO/(PAH/GO)$_x$/ZnO/Al for x = 20, 30 and 50 Bilayers

The analyzed devices correspond to the samples FTO/(PAH/GO)$_x$/ZnO/Al, where the x correspond to the number of bilayers. This study was not performed under the same conditions for all samples. The analysis of the first two samples was carried out under ambient atmosphere, at a temperature ranging from 20°C to 25°C, with a relative humidity between 50% and 60%. The latter was analyzed inside a desiccator, where the temperature ranged from 20° C to 23° C, with a relative humidity ranging from 10% to 15%.

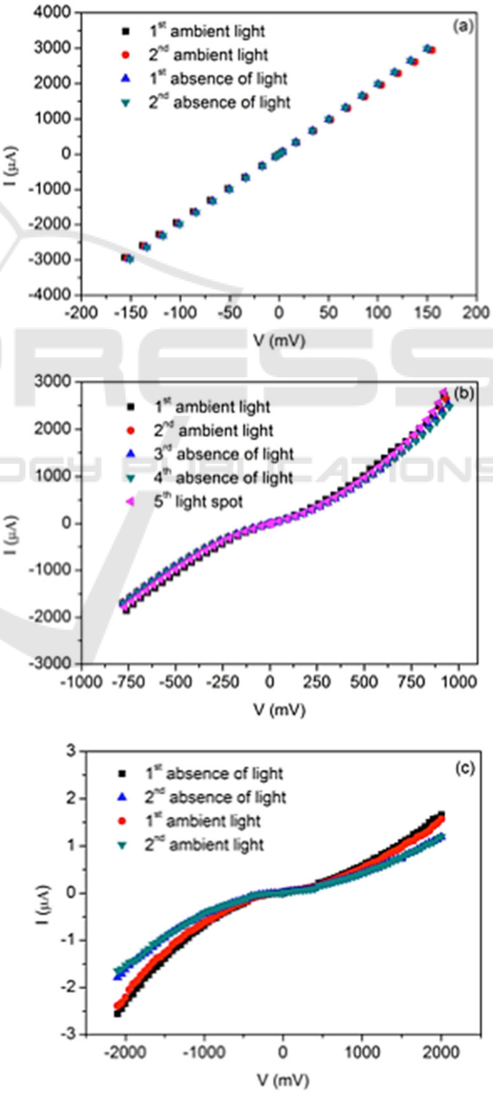


Figure 7: Electrical characterization for three devices with the architecture (FTO/PAH/GO/ZnO/Al)$_x$ a) x= 20 bilayers b) x= 30 bilayers and c) x= 50 bilayers, for different light conditions.

All samples were characterized at ambient light and in an environment without interaction with light. The sample FTO/(PAH/GO)$_{30}$/ZnO/Al was also exposed to a light spot from a halogen lamp.

The sample corresponding to Figure 7 (a) shows a typical resistance behavior where the current depends linearly on the voltage applied to the device terminals. Four measurements were performed, the first two at ambient light and the next without light, with no significant hysteresis effect noticeable. This sample also does not reveal any change in its electrical behavior when exposed to ambient light. In turn, the sample with 30 PAH/GO bilayers - Figure 7 (b) - presents a behavior very close to what would be expected for a diode. Unlike the other devices studied so far, the behavior of this latter device seemed to change when exposed to the light spot from a halogen lamp. However, when constructing its current-voltage characteristic curve, it was concluded that the slight increase in current in the presence of light was not significant enough to be considered a photosensitivity phenomenon. FTO/(PAH/GO)$_{50}$/ZnO/Al device was analyzed inside a desiccator, where the relative humidity value was considerably lower than that recorded for the devices analyzed in this subsection. Its curve I (V) is shown in Figure 7 c). For this device, four consecutive measurements were performed, in environments without light and in the presence of ambient light, alternately. In this sample, it is possible to observe a current behavior against the applied voltage similar to what would be expected for a diode type device. Between the first and second measurements and between the third and fourth, the hysteresis effect is reduced, with no significant current decreases between them. However, between the second and third measurements, this effect is quite noticeable. Again, although this device has the desired behavior, no current increase has been recorded in the presence of light and is therefore not photosensitive. Looking at the quotient between the applied voltage values and the obtained current values, it is apparent that this device proved to be much less conductive than the others. It is important to remember that this device was analyzed in an environment with 10% relative humidity, and this parameter can play a key role in the conduction of the fabricated solar cells. In fact, according to the literature (Raposo 1999), the presence of moisture and / or oxygen is a major factor in the conduction of organic films, making them more conductive.

4 CONCLUSIONS

This work reports the development of two types of solar cells devices: FTO/(PAH/GO)x/TiO$_2$/Al and FTO/(PAH/GO)x/ZnO/Al, where x, corresponds to the number of bilayers. The organic films were deposited by layer-by-layer technique, while inorganic films were deposited by DC-reactive magnetron sputtering. The aluminum electrode was deposited by thermal evaporation.

The characterization of the organic films was carried out by ultraviolet-visible spectrophotometry, which revealed a linear film growth with the number of bilayers. This means that the same amount of PAH/GO per unit area was adsorbed in each bilayer, so their number is proportional to the thickness of the films.

Scanning electron microscopy (SEM) was used to study the surface morphology of the samples, as well as to estimate the thickness of each layer which constitutes the developed devices. In the case of TiO$_2$ samples, larger aggregates were detected for the devices with 20 and 30 PAH/GO bilayers, with sizes ranging between 260 nm and 400 nm and between 200 nm and 340 nm, respectively while for the devices with 50 bilayers the aggregates were significantly smaller (20-30 nm). In the case of the samples with ZnO, the observed aggregates were smaller in size than those observed for TiO$_2$ (between 50 nm and 200 nm), with no change in size with varying number of bilayers, unlike for devices with TiO$_2$, where SEM measurements showed that the size of the aggregates decreased with increasing number of bilayers of the organic layer. None of the SEM images analyzed revealed cracks in the samples, so it is excluded that aluminum migration may have occurred at the time of electrode deposition.

The electrical characterization of the FTO/(PAH/GO)x/TiO$_2$/Al and FTO/(PAH/GO)x/ZnO/Al samples was performed based on the construction of their current-voltage characteristic curves. The samples with TiO$_2$ and in which 20 and 30 PAH/GO bilayers were deposited were analysed in air, with ambient light, showing a resistive behavior, without photosensitivity. This may be due to high resistance between the photoactive layer and the electrode or to an inefficient donor-acceptor interface. For the TiO$_2$-based device with 50 bilayers of PAH/GO (analysed inside a desiccator to reduce moisture) presented a characteristic I (V) curve of a diode, which is more conductive when positively polarized. In the case of the devices with ZnO for the device with 20 bilayers of PAH / GO an ohmic behavior was detected and for the device with 30 bilayers a semiconductor behaviour was revealed. The latter sample was exposed to a spotlight from a halogen lamp and a slight increase in current was recorded. However, it was not a significant enough increase to consider it to be photosensitive. In the device with 50 bilayers, a typical diode behavior was detected, although it was much less conductive than all the other samples analyzed. In fact, it was studied inside a desiccator, with relative humidity close to 10%, so it is concluded that humidity is a major factor in the conduction of organic films. This work further evidenced that the use of zinc oxide as an electron acceptor material in a solar cell, appears to be more suitable for the performance of such devices than titanium dioxide.

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