Development of Graphene Oxide and TiO_2 Heterojunctions for Hybrid Solar Cells

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Abstract: This work reports the development of hybrid devices composed of organic and inorganic thin films, deposited on fluorine doped tin oxide coated glass substrates (FTO). The organic layers, graphene oxide (GO) and poly (ethylenimine) (PEI) were deposited by the layer by layer technique (LbL), through the aerosol spray variant. The inorganic layer, titanium dioxide (TiO_2), was deposited by sputtering and the aluminium electrode by thermal evaporation. To characterize these devices was used UV-Visible spectrophotometry to observe the films growth and optical microscopy to analyze the surface morphology. Finally, the electrical measurements were performed by measuring the I-V characteristic curves. The final device (FTO/PEI/GO/ TiO_2/Al)$_{20}$ showed a significant change in the behaviour when interacting with light.

1 INTRODUCTION

The industrial revolution has marked the beginning of a new technological stage, which was characterized by the use of fossil fuels and minerals as the main source of energy.

Since then, several studies have shown the harmful impact of these forms of energy production have on planet Earth, causing depletion of the ozone layer and increasing of global warming. Currently, about 80% of CO_2 emissions come from the energy sector, thus demonstrating the need to develop new approaches of generating energy in a sustainable and clean way. Therefore, it is important and urgent the development of devices capable of generating energy without the need of use fossil fuels, such as solar cells, biomass, wind turbines, among others. However, this type of technology has two inherent limitations, the price of the materials used and their efficiency, leading to the prevalence of fossil fuels.

Nevertheless, great progress has been made in these technological areas, making its use more feasible, being presently around 8% of the energy generated in the United States coming from renewable sources (Serrano 2009).

This growing demand for alternative methods for energy production has led to the development of new architectures as well as research of new materials in order to increase the efficiency of these devices. One of the materials that has attracted significantly the researchers' attention 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 in electron transport layers and gaps (Yin 2014).

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

In this context, with this work it is aimed to find solutions to capture solar energy, based on the knowledge acquired 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, in particular titanium dioxide, TiO_2 (Sério 2011 and Sério 2011).

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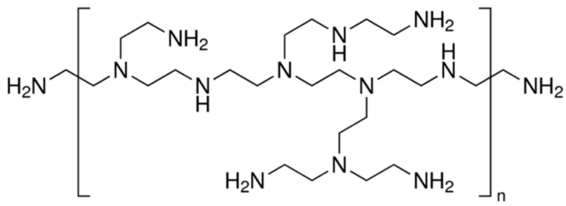
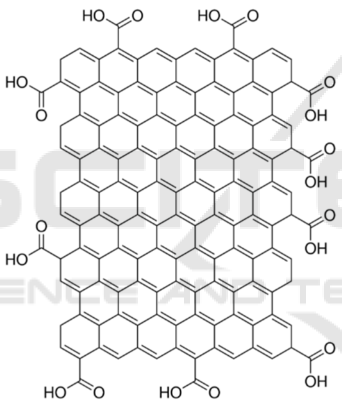
2 EXPERIMENTAL DETAILS

The layer-by-layer films were prepared from aqueous solutions of poly(ethyleneimine) (PEI) (Mw) 750 000 g/mol) and graphene oxide (GO) 2 mg/mL, dispersion in H_2O, with concentrations of 3×10^{-3} M and 10^{-2} M, respectively, using the LbL technique, implemented through aerosol spray variant, instead of adsorption from bulk solution. The chemicals were obtained from Aldrich and the corresponding molecular structures are depicted in Figure 1.



(a)



(b)

Figure 1: (a) poly(ethyleneimine) (PEI) (b) graphene oxide (GO).

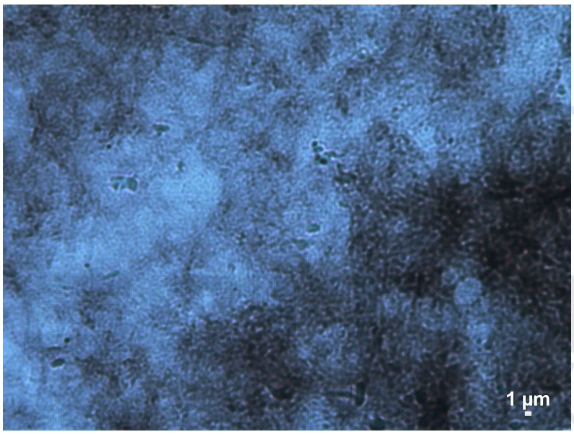
The ultrapure water with a resistivity of 18 MΩ cm was supplied by a Millipore system (Milli-Q, Millipore GmbH). Accordingly, both cationic and anionic solutions, as well as washing ultra-pure water, were placed in aerosol spray dispensers and were ordered with the following sequence: cationic solution, ultra-pure water, anionic solution and ultra-pure water. The films were sprayed onto Fluorine-doped tin oxide (FTO) coated glass substrates (TEC15, 12-14 Ω/☐). The solid supports were placed at a distance of 6 cm from the spray dispenser and the solutions were alternately sprayed following the order aforementioned. Each dispenser was pressed twice to guarantee a satisfactory amount of ejected solution towards the supports. After the adsorption of the cationic layer solution, the substrate becomes positively charged. It is then washed with water to remove the amount of cationic molecules solution that wasn't satisfactorily adsorbed on the substrate. Then the same procedure was used for the anionic layer, washed again with water and finally dried with nitrogen flow. After this sequence, the first bilayer film was formed and, the steps abovementioned were repeated until obtain the desired number of bilayers. The lag time between each solution spraying was of 10 s and all the films were produced with 20 bilayers: $(PEI/GO)_{20}$.

After, the inorganic layer (TiO_2) was deposited by DC-magnetron sputtering. The sputtering was carried out at room temperature (RT) using a titanium disc (99.99% purity, GoodFellow) with 64.5 mm of diameter and 4 mm of thickness as sputtering target. A turbomolecular pump was used to achieve a base pressure of 10^{-4}-10^{-5} Pa (before introducing the sputtering and reactive gases). Before the deposition, a movable shutter was interposed between the target and the substrates, and the target was pre-sputtered in Ar atmosphere for 5 min to clean the target surface. The deposition of TiO_2 was carried out in 100% O_2 atmosphere (99.999% purity) at constant total gas pressure of 1.2 Pa, a sputtering power of 500 W during 10 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 (FTO / PEI / GO / TiO_2 / Al), 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 films were characterized by optical microscopy using a Nikon Eclipse LV100.

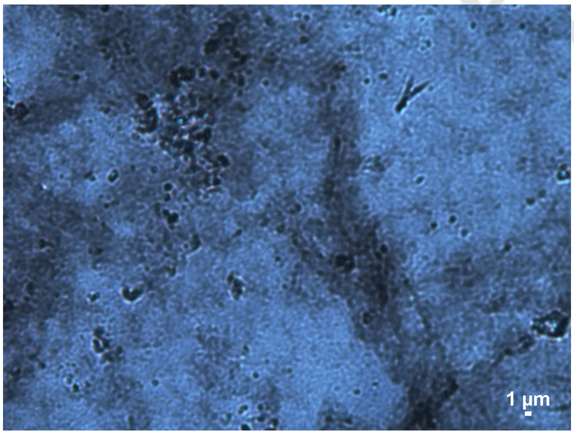
The UV-vis spectroscopy for the films was carried out with a Shimadzu UV b - 2101PC UV/VIS spectrophotometer at room temperature within the wavelength range 200-900 nm. The electric measurements (I-V characteristic curve) of the final device were carried out using a programmable DC power supply model Rigol DP811A 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

In figure 2 are depicted some representative images obtained by optical microscopy for the PEI/GO LBL films with 20 bilayers without and with TiO_2 film. In general it can be observed that the films are homogeneous in both situations, although can be detected some aggregates (with and without TiO_2). This homogeneity remains even for bigger magnifications.



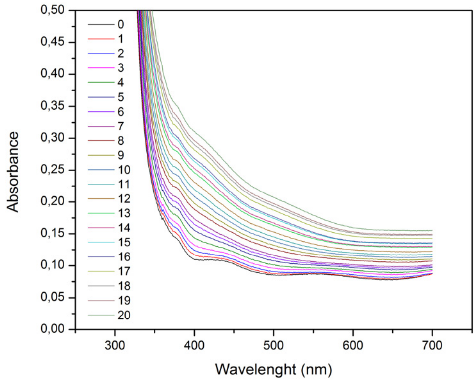
(a)



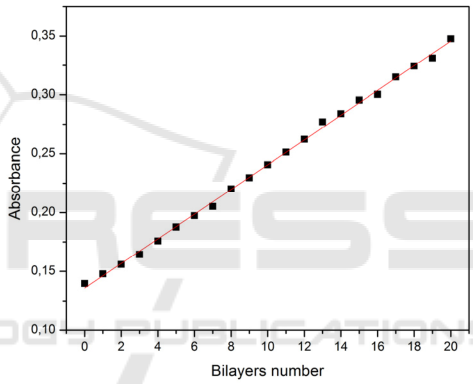
(b)

Figure 2: Optical microscopic images for (a) $(PEI/GO)_{20}$ without TiO_2 (b) $(PEI/GO)_{20}$ with TiO_2.

In figure 3 a) and b) is shown the ultraviolet-visible absorbance spectra of different number of bilayers of PEI/GO LBL films and the absorbance intensity at 380 nm as a function of the number of bilayers, N, respectively. It can be observed that the absorbance at maximum increases with the number of bilayers indicating a linear film growth (see figure 3b).



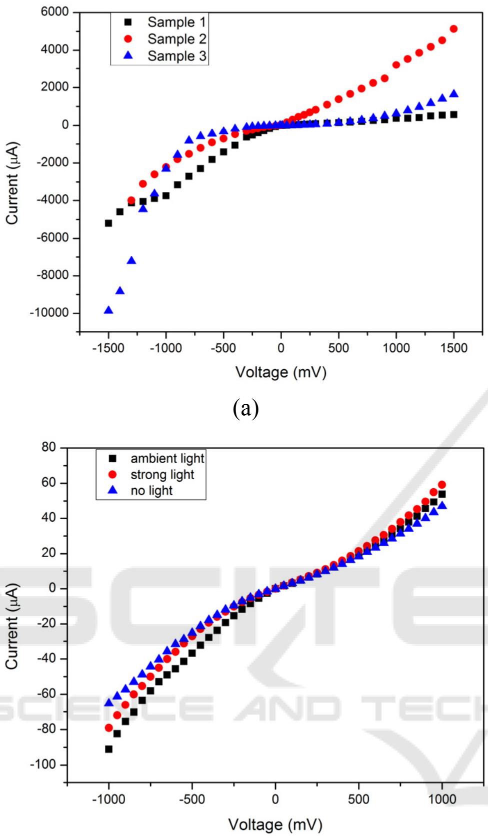
(a)



(b)

Figure 3: (a) Absorbance spectra of PEI/GO LBL films as a function of the number of bilayers, N. (b) Absorbance intensity at 380 nm as a function of the number of bilayers, N.

Figure 4 shows the I-V curves for three devices with the structure $(FTO/PEI/GO/TiO_2/Al)_{20}$ after production and without interaction with radiation. Although, it is expected that the LBL films have the same thickness, the presence of aggregates as revealed by optical microscopy may have led to regions with different thicknesses. Considering this possible difference in the thickness of the deposited films, this fact can lead to a short circuit and therefore explaining the erratic behavior of the I-V curves observed in Figure 4 a). However, with a another similar device produced using the same conditions, I-V curves were obtained for different experimental conditions (without light, strong light, ambient light), which are depicted in Figure 4 b). The analysis of the figure shows an increase of the current for positive voltages when the device is exposed to the light in comparison to the other experimental conditions. The same behavior is verified for negative voltages, however when the device interacts with ambient light there is an increase in current in the circuit, indicating an increase of the charge carriers.



(a)

(b)

Figure 4: Electrical characterization for three devices with the architecture $(FTO/PEI/GO/TiO_2/Al)_{20}$ a) without the interaction with light b) ambient light, strong light and in absence of light.

Presently, more studies are in progress in order to avoid the short circuit of the devices, increasing the number of the bilayers.

4 CONCLUSIONS

In this work we report the development of hybrid solar cells with the configuration $(FTO/PEI/GO/TiO_2/Al)_{20}$. The organic layers, PEI and GO, were deposited by layer-by-layer technique through the aerosol spray variant and it was revealed by optical microscopy that the deposited LBL films are homogeneous, although are detected some aggregates.

Considering the I-V characteristic curves for several devices developed with this architecture, it is observed a change of the behavior for the different experimental conditions, increasing the conduction in the following order: absence of light, ambient light and strong light, for positive voltages. However, for negative voltages the devices exhibit increased conduction when exposed to ambient light, indicating an increase in charge carriers. It was further observed that some devices with this architecture, the I-V curves performed without the interaction with radiation presented an erratic behavior, possibly due to differences in the thickness of the films leading to the short circuit of the devices. Moreover, this study also evidences that the inorganic layer prevents the degradation of the organic layers when exposed to the atmospheric conditions.

Therefore, this work allows to conclude that this device not only reacts to light but also that the combination of materials and techniques used for its manufacture are appropriate.

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