

Preparation of PAH/Graphene Oxide Layer-by-Layer Films for Application on Solar Cells

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Keywords: Graphene Oxide, PAH, Hybrid Solar Cells, LBL Films.

Abstract: In this study we provide the preparation and characterization of layer-by-layer LBL films made with poly(allylamine hydrochloride) (PAH) alternated with graphene oxide. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) showed a smooth surface with a RMS roughness of 5.74 nm. The LBL films were also characterized by means of UV-vis spectroscopy. The I-V characteristic curve evidenced a typical semiconductor behaviour.

1 INTRODUCTION

Since the nineteenth century, the humanity has relied mainly on fossil fuels for energy needs. However, with the growing concern and awareness around the environmental problems caused by the increase in greenhouse gases and other pollutants responsible for the global warming, as well as the possibility of depletion of fossil fuels, increased the demand for energy sources environmentally friendly and sustainable (Choe, 2013). The challenge to obtain renewable energy sources with low-cost, led the scientific community to develop other alternatives, namely efficient photovoltaic cells (Günes, 2007).

Efforts to find alternative energy sources to fossil fuels have been recorded globally. In 2006, the US announced its "Advanced Energy Initiative", which outlined a goal of reducing oil imports from the Middle East by 75% by the year 2025 through the development of new energy sources and also renewable. The European Union (EU) approved a plan (SET-Plan) which set the target of reducing emissions of EU greenhouse gases emissions by at least 20% up to 2020 compared to emissions in 1990. The Korean government established "The second National Plan for Technology Energy Development". With this plan, South Korea aims to develop new renewable energy technologies and improve energy efficiency by increasing investment

in research and development of renewable energy up to 2020. In addition, Japan, China and Canada have also established national agendas for the development of new renewable energy technologies to reduce their dependence on fossil fuels and promote the strategic development of Green industries.

Currently, the most widely used systems for the conversion of solar energy are inorganic solar cells, including silicon solar cells which dominate 85% of photovoltaic industry market. Due to the high production costs of silicon cells, researchers in recent years have focused on research and development of alternatives for this type of cells (Sun, 2015; Rowell, 2006).

The development of organic solar cells (OSC) based on polymer materials, is a new technology that within a short period, can produce clean energy at a more reasonable cost. Since the polymeric solar cells are light and capable of becoming flexible opens up a range of new applications. Furthermore, large OSC (large area) can be manufactured easily and inexpensively by employing low-cost techniques, such as screen printing, slot-die coating, gravure and spray coating, etc. (Sun, 2015).

OSCs have emerged as a promising alternative to photovoltaic technology, due to profitable production potential of flexible devices of large surface using processing techniques with low environmental impact and also versatility in organic

material “design” (Bian, 2012). For the production of polymer thin films for application in the OSC, several techniques are used. Among them, the layer-by-layer technique (Layer-by-Layer, LBL) having several advantages such as no pollutants production and also the fact of doesn't requires highly sophisticated equipment, makes it an important technique in such applications. In this context, with the present 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).

2 EXPERIMENTAL DETAILS

The layer-by-layer films were prepared from aqueous solutions of poly(allylamine hydrochloride) (PAH) (M_w) 50 000-65 000 g/mol) and graphene oxide (GO) 2 mg/mL, dispersion in H_2O , with concentrations of 10^{-2} M. The chemicals were obtained from Aldrich, and the corresponding molecular structures are shown in Figure 1. The ultrapure water with a resistivity of 18 $M\Omega$ cm was supplied by a Millipore system (Milli-Q, Millipore GmbH). The adsorption period was 1 min for the PAH and GO layers. After adsorption of each layer, the films were washed with ultra pure water and dried with a nitrogen flux.

The films were deposited on quartz, Fluorine-doped tin oxide (FTO) coated glass and interdigitated glass substrates for the different characterizations (UV-spectroscopy, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and I-V measurements).

The quartz and interdigitated glass substrates were cleaned with a “piranha” solution containing hydrogen peroxide and a sulfuric acid (1:1) bath for 1h and then rinsed exhaustively with pure water. The substrates were after dried with nitrogen flow. The FTO coated glass substrates were ultrasonically cleaned in a concerted sequence using acetone, isopropanol, and deionized water, for 5 min each step and then dried using nitrogen gas flow to remove any adsorbed organic contamination on substrates surface.

The films were prepared at room temperature as well as all the characterizations.

The surface morphology of the films were investigated by a field-emission scanning electron microscope (JEOL 7001F) operating at 15 keV. In order to prevent charge build up, a thin chromium

film was coated on the films surfaces before the analysis.

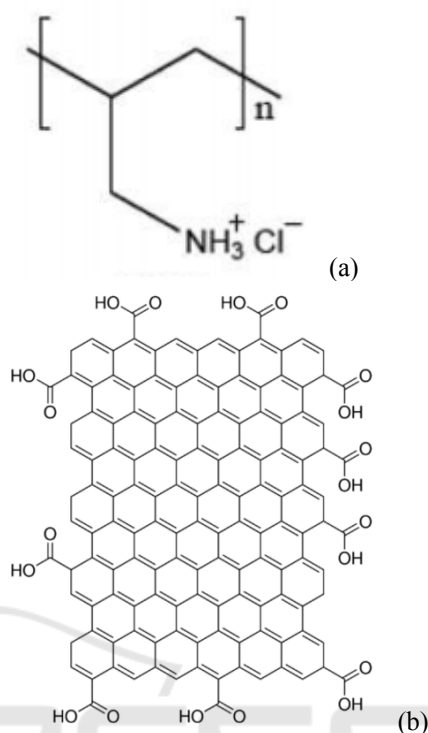


Figure 1: (a) poly-(allylamine hydrochloride) (PAH); (b) graphene oxide.

To study the films surface, Atomic Force Microscopy (AFM) images were obtained with a Scanning Tunneling Microscopy (STM), Agilent Technologies, model PicoScan. For each film, scans of $2 \mu m \times 2 \mu m$ were obtained. The films surface morphology was characterized by the root mean square roughness (RMS), which was calculated by Gwyddion software.

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) were carried out with a DC POWER SUPPLY model DF1730SB3A at room temperature and ambient light, by changing the voltage between 0V and $\sim 1V$, with an increment of 20 mV.

3 RESULTS AND DISCUSSION

In figure 2 and figure 3 are depicted some representative SEM and AFM images for the

PAH/GO LBL films with 20 bilayers. In general it can be observed from the SEM image that the films exhibit a smooth surface, which is also consistent with the RMS roughness value estimated from the AFM images, which corresponds to 5.74 nm.

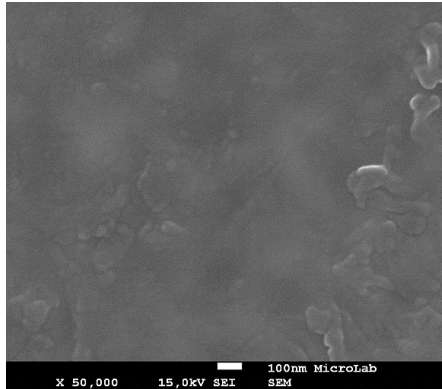


Figure 2: Representative SEM image of (PAH/GO)₂₀ LBL film deposited on FTO coated glass substrate.

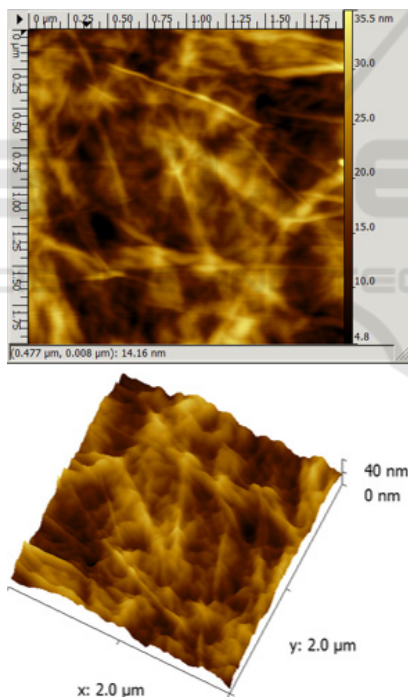


Figure 3: Representative AFM image of (PAH/GO)₂₀ LBL film deposited on FTO coated glass substrate.

In figure 4 a) and b) is shown the ultraviolet-visible absorbance spectra of different number of bilayers of PAH/GO LBL films and the absorbance intensity at 228 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 4b).

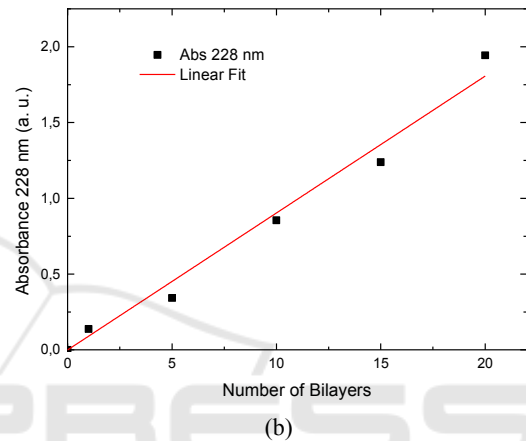
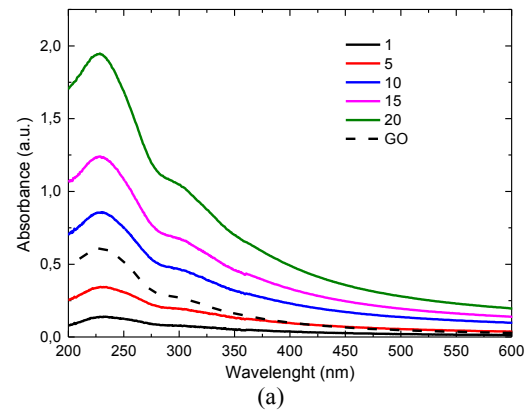


Figure 4: (a) Absorbance spectra of PAH/GO LBL films as a function of the number of bilayers, N. For comparison, the absorbance spectrum of a GO film is also present. (b) Absorbance intensity at 228 nm as a function of the number of bilayers, N.

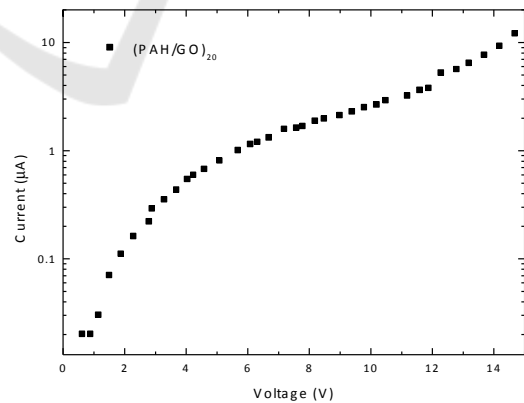


Figure 5: I-V characteristic curve for (PAH/GO)₂₀ LBL film on interdigitated glass substrate.

In order to characterize the deposited LBL film regarding the electric behaviour, it was measured the I-V characteristic curve at ambient light, which is presented in figure 5. The observed curve evidences

for the produced PAH/GO with 20 bilayers a semiconductor behaviour. More studies regarding the optimization of the PAH/GO LBL films preparation are currently under progress in order to improve the electric behaviour.

4 CONCLUSIONS

In this work we report the preparation of PAH/Graphene oxide layer-by-layer (LBL) films for application in hybrid solar cells. The surface morphology characterization carried out by scanning electron microscopy (SEM) and atomic force microscopy (AFM) evidenced that the deposited LBL films exhibit a smooth surface with a RMS roughness of 5.74 nm. The UV-vis spectroscopy showed a linear film growth and the I-V characteristic curve revealed a typical semiconductor behaviour evidencing a promising combination of films for the development of hybrid solar cells.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from FEDER, through Programa Operacional Factores de Competitividade – COMPETE and Fundação para a Ciência e a Tecnologia – FCT, for the project UID/FIS/00068/2013.

REFERENCES

- Choe, H. et al. 2013. Patent citation network analysis for the domain of organic photovoltaic cells: Country, institution, and technology field. *Renew. Sustain. Energy Rev.* 26, 492–505.
- Günes, S., Neugebauer, H. & Sariciftci, N. S., 2007. Conjugated polymer-based organic solar cells. *Chem. Rev.* 1324–1338.
- Sun, Y. et al. 2015. Recent development of graphene materials applied in polymer solar cell. *Renew.*

- Sustain. Energy Rev.* 43, 973–980.
- Rowell, M. W. et al. 2006. Organic solar cells with carbon nanotube network electrodes. *Appl. Phys. Lett.* 88, 233506.
- Bian, L. et al. 2012. Progress in Polymer Science Recent progress in the design of narrow bandgap conjugated polymers for high-efficiency organic solar cells. *Prog. Polym. Sci.* 37, 1292–1333.
- Ferreira, Q., Gomes, P. J., Ribeiro, P. A., Jones, N. C., Hoffmann, S. V., Mason, N. J., Oliveira Jr., O. N., Raposo, M., 2013. Determination of Degree of Ionization of Poly(allylamine hydrochloride) (PAH) and Poly[1-[4-(3-carboxy-4 hydroxyphenylazo) benzene sulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) in Layer-by-Layer Films using Vacuum Photoabsorption Spectroscopy”, *Langmuir*, 29 (1), 448–455.
- Ferreira, Q., Gomes, P. J., Raposo, M., Giacometti, J. A., Oliveira Jr., O. N., Ribeiro, P. A., 2007. Influence of Ionic Interactions on the Photoinduced Birefringence of Poly[1-[4-(3-Carboxy-4 Hydroxyphenylazo) Benzene Sulfonamido]-1,2-Ethanediyl, Sodium Salt] Films, *J. Nanosci. Nanotechnol.* 7, 2659–2666.
- Ferreira, Q., Gomes, P.J., Maneira, M. J. P., Ribeiro, P. A., Raposo, M., 2007. Mechanisms of Adsorption of an Azo-polyelectrolyte onto Layer-by-Layer Films. *Sensors and Actuators B: Chemical*, 126, 311-317.