Birefringence Creation by Solar Light
A New Approach to the Development of Solar Cells with Azobenzene Materials

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Abstract: The conversion of solar energy into electricity is one of the viable alternatives regarding energy demand and sustainability. This work shows that novel energy storage devices can be developed by using materials containing highly polarizable molecules as poly{1-(4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfonamido) -1,2-ethanediyl, sodium salt} (PAZO). In the present case, layer-by-layer (LbL) of PAZO and poly(allylamine hydrochloride) (PAH) thin films were prepared and the creation and relaxation of photoinduced birefringence were characterized. These results demonstrate that birefringence can be induced in these films by visible light with a spectrum similar to solar light. Comparing the characteristics parameters of birefringence creation and relaxation, it was seen that the writing birefringence characteristic time, with a value of 1.4 hours, is quite slower than the obtained with laser beam but the relaxation characteristic time is of the order of 7 days. In addition, the birefringence value is proportional to the amount of azo-groups in the sample. These preliminary results allows us conclude that solar devices based in that principle can be studied, namely, the conversion of the oriented dipoles stored energy in power.

1 INTRODUCTION

Exhaustion of fossil fuels reserves and greenhouse gases suppression are two main issues to be solved regarding energy demand and sustainability (Hill, 2012). As such, there is stress in spreading the use of renewable sources, such as sun, wind and water, particularly in what concerns to electrical energy production. As often renewable energies sources are not available when they are more needed it is also fundamental to develop low cost efficient energy storage systems. The conversion of solar energy into electricity is one of the viable alternatives although it is still somehow costly for large scale applications.

Sunlight hits the earth's surface intermittently and with intensity unpredictable, i.e. the production of electricity from solar radiation can change rapidly, making it difficult to distribute.

Developments in nanotechnology, biotechnology, and generally materials science may trigger new solutions for efficient and cheaper solar energy conversion-storage systems (Lewis, 2007). For example the novel electrochemical capacitors, called supercapacitors (Wang, 2014), are able to offer an alternative to the most used lithium ions which are known to lose their charging capacity with successive charge-discharge cycles, thus, not meeting the high speed requirements for high power systems. These are believed to become the next power generation storage devices, mainly due to high energy densities stored, fast charge-discharge cycles and higher service life (Hu,2014), (Wang,2011).

Another possibility to develop novel energy storage devices is the use of materials containing highly polarizable molecules, which can be easily polarized by sunlight, as is the case of azobenzene. These compounds are formed by two benzene rings linked through two double bounded nitrogen atoms. These molecules are characterized by an absorption band, low energy in the visible region, and other, high energy, in the ultraviolet region. Since in 1937, Hartley discovered photoisomerization ability of these molecules, or the ability to spatially rearrange by light of adequate wavelength. This process can give rise to a macroscopic birefringence in a bulky material containing azobenzene molecules (Hartley, 1937).

This work addresses on the energy storage capabilities of thin films of poly{1-(4-(3-carboxy-4-hydroxy-phenylazo)benzenesulfonamido)   -1,2-

ethanediyl, sodium salt} (PAZO), a main chain azobenzene containing polyeletrolyte. Particularly the optical birefringence response, induced by visible light of layer-by-layer (LbL) of PAZO and poly(allylamine hydrochloride) (PAH) thin films, deposited on a substrate glass covered with a semiconductor thin film of tin oxide doped with fluorine (FTO) will be presented.

2 EXPERIMENTAL

2.1 Materials and Methods

The polyelectrolytes PAH and PAZO, supplied by Sigma Aldrich, were used to prepare layer-by-layer (LbL) films. The chemical structures of these polyelectrolytes are shown in Figure 1. Solutions with a concentration of 10^{-2} M of PAH and PAZO were obtained by dissolving the polyelectrolytes in Milli-Q ultrapure water with resistivity of 18 MΩ·cm at 25ºC, (Millipore). Both pH were maintained constant to 5 for PAH and 7 for PAZO. The PAH/PAZO LbL films were prepared onto BK7 substrates with a layer of FTO.The LbL film preparation procedure consisted of alternated adsorption from solution of both polyelectrolytes, namely, the substrate was:1) immersed in the PAH solution, for 3 minutes; 2) washed with ultrapure water; 3) immersed layer in the PAZO solution, for 3 minutes; 4) washed with ultrapure water. If the above procedure is repeated n times, a film with n bilayers, referred as (PAH/PAZO)n, is obtained. The immersion time in the polyelectrolytes solutions of 3 minutes is a compromise between optimized time for films preparation and the time required to achieve 80% of adsorbed amount per layer, taking into account the adsorption kinetics described by (Ramsden, 1995) and (Ferreira, 2007a). The maintenance of constant adsorption times allows to control the thickness of the films.
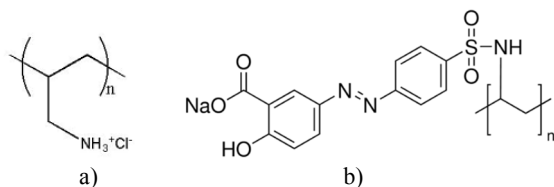

Figure 1: Chemical structures of a) PAH and b) PAZO.

2.2 Birefringence Measurements

The samples were irradiated with a halogen lamp of 250 W and 24V to simulate the solar spectrum, after this light to be polarized by a linear polarizer of adjustable angle and focused with a convex lens. The irradiated area was of 1cm². The radiation power was of 250 mW. This value was measured with a Heavy Duty Light Meter, Extech Intruments.,

The photoinduced birefringence was measured with a laser diode PASCO OS-8525A of 0.9 mW and 650 nm of wavelength. The sample was placed between crossed polarizers, in what concerns to the probe beam, with polarization set at 45º with respect to the writing beam polarization. An optical chopper modulates the probe beam and the birefringence signal was measured with a photodetector, Newport 884-UV, through a lock-in amplifier, Princeton Applied research, model 5101.

3 RESULTS AND DISCUSSION

In figure 2a) is shown the ultraviolet-visible absorbance spectra of different number of bilayers of PAH/PAZO LBL films. The absorbance peak centred near 360 nm is associated to the π - π* chromophore transition (Ferreira, 2013), and the absorbance at maximum is seen to increase with the number of bilayers indicating a linear film growth, see figure 2b). From the slope of that the fitted, one can calculate the PAZO adsorbed amount per unit of area and per bilayer which takes the value of 0.014±0.001 mg.m⁻², using the Beer-Lambert law and the PAZO absorption coefficient, at 360 nm, ε_{360nm} = 4.30±0.07 m²g⁻¹ (Ferreira, 2007b). The PAZO adsorbed amount for a film of 30 bilayers is of 0.42±0.03 mg.m⁻² a high value when compared with films prepared onto glass (Timóteo, 2016).

The birefringence creation and relaxation kinetics curves obtained for PAH/PAZO LbL films with are shown in figure 3. The birefringence creation curves correspond to the increase of transmitted light signal until the polarized light be turned off while the birefringence relaxation curves is obtained immediately the light to be turned off and correspond to decrease of the transmission signal.

he birefringence creation kinetic curves can be analysed fitting the experimental data to a bi-exponential function, containing two distinct processes in accordance with literature, see (Ferreira, 2012) and references therein. The fast process is normally assigned to the *trans−cis−trans* photoisomerization processes contributing to the birefringence, which depend on the free local volume available and on interactions between chromophores
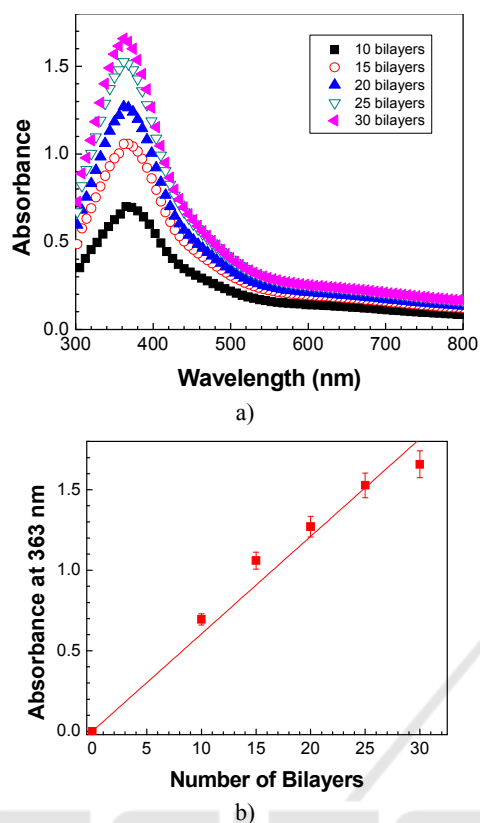
Figure 2: a) Absorption spectra of PAH/PAZO LbL films with distinct numbers of bilayers. b) Maximum absorbance (363 nm) versus the number of bilayers in the PAH/PAZO LbL film.
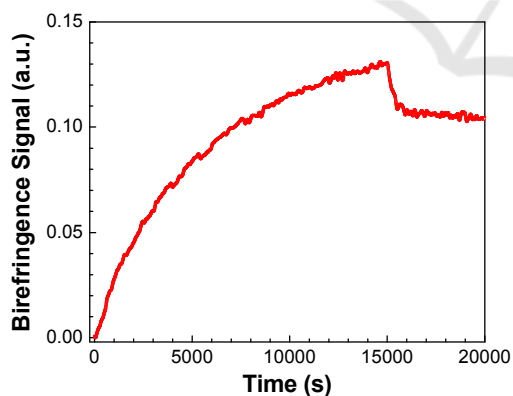

Figure 3: Birefringence creation and relaxation kinetics curve at room temperature obtained in (PAH/PAZO)$_{30}$ LbL films with polarized visible light.

and PAH. The slower process is attributed to the main chain mobility, which relies on chain size and T interactions between both polyelectrolytes. However, in the present case, the birefringence creation, $I_{writing}$, is very slow and the experimental data can be fitted only with a exponential function:

$$I_{writing} = I_{w0}\left(1 - exp\left(-\frac{t}{\tau_w}\right)\right) \qquad (1)$$

where I_{w0} is the pre-exponential factor that represent the magnitude of the process and τ_w is the characteristic time constant. In the present case, the the characteristic time takes a value of 5180±20 s a long time compared with the value of 1700±36 s obtained in PAH/PAZO films prepared onto glass and using as writing beam a 514 nm beamline of a tuneable Ar+ laser (Monteiro-Timóteo, 2016). This means that the incidence of light increase the temperature of the sample hindering the creation of birefringence. It is also observed that the induced birefringence is proportional to the amount of azo-groups present in the sample, i.e., of the number of PAZO layers.

The obtained decay curve can be fitted with two exponential Debye like processes, being the one with short characteristic associated with dipole disorientation and the one with longer characteristic time the long-term relaxation related to disorientation arising from the movement of polymer chains, as follows:

$$I_{relaxation} = I_{r1}exp\left(-\frac{t}{\tau_{r1}}\right) + I_{r2}exp\left(-\frac{t}{\tau_{r2}}\right) \qquad (2)$$

where I_{r1} and I_{r2} are the pre-exponential factors for the birefringence normalized intensity, τ_{r1} and τ_{r2} are the characteristic time constants of the processes. For the earliest moments of relaxation, process the obtained characteristic time is a value of 1970±30 s while the second characteristic time is of $(0.63\pm0.03)\times10^6$ s. These values are in accordance with the birefringence decay characteristic times of PAZO (Ferreira, 2012). However, it should be noticed that the second value correspond to a characteristic time of 7.3 days. This value promises the use of these materials as solar cells, however the conversion of orientated dipoles energy in power should be studied.

4 CONCLUSIONS

This work demonstrate that birefringence can be induced in PAH/PAZO LbL films by irradiation with visible light with a spectrum similar to solar light with a characteristic time of 1.4 hours. Although the writing birefringence characteristic time to be quite slower that the obtained with a laser beam, the

relaxation characteristic time is of the order of 7 days. Moreover, it is also observed that the induced birefringence is proportional to the amount of azo-groups present in the sample. These achievements guarantees that solar devices based in that principle can be implemented and characterized.

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REFERENCES

Ferreira, Q., P. J. Gomes, M. Raposo, J. A. Giacometti, O. N. Oliveira Jr. P. A. Ribeiro , 2007 a. 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., 2007b. Mechanisms of Adsorption of an Azo-polyelectrolyte onto Layer-by-Layer Films. *Sensors and Actuators B: Chemical*, 126, 311-317.

Ferreira, Q., Ribeiro, P.A., Oliveira Jr., O. N., Raposo, M., 2012. Long-term stability at high temperatures for birefringence in PAZO/PAH layer-by-layer films, *ACS Applied Materials and Interfaces*, 4, 1470-1477.

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.

Hartley, G. S.; 1937. The cis-form of azobenzene, Nature, 140, 281.

Hill, C. A., Such, M. C., Chen, D., Gonzalez, J., Grady, W. M., 2012. Battery energy storage for enabling integration of distributed solar power generation". *IEEE Transactions on Smart Grid*, 3(2), 850–857.

Hu, C., Song, L., Zhang, Z., Chen, N., 2014.Tailored graphene systems for unconventional applications in energy conversion and storage devices". *Energy & Environmental Science* 8, 31–54.

Lewis. N. S., 2007. Toward cost-effective solar energy use." Science 315(5813), 798–801.

Monteiro Timóteo, A.M, Ribeiro, J. H.F., Ribeiro, P.A., Raposo, M., 2016. Dynamics of creation photoinduced birefringence on (PAH/PAZO)n layer-by-layer films:

Analysis of consecutive cycles. *Optical Materials 51*, 18–23.

Ramsden, J. J., Lvov, Y., Decher, G., 1995. Determination of optical constants of molecular films assembled via alternate polyion adsorption, *Thin Solid Films* 254, 246-251.

Wang, H., Liang, Y., Mirfakhrai, T., Chen, Z., Casalongue, H. S., Dai. H., 2011. Advanced asymmetrical supercapacitors based on graphene hybrid materials. *Nano Research.* 4(8), 729–736.

Wang, K., Wu, H., Meng Y., Wei. Z., 2014. Conducting polymer nanowire arrays for high performance supercapacitors". *Small* 10(1), 14–31.