




# Optimization of Graphene Oxide Layer-by-Layer Films to Be Used as an Enhancer Coating of Optical Fibers Sensors

Carlota Xavier <sup>a</sup>, Paulo Zagalo, Paulo A. Ribeiro <sup>b</sup> and Maria Raposo <sup>c</sup>  
CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, UNL, Campus de Caparica,  
2829-516, Caparica, Portugal  
{c.xavier, p.zagalo}@campus.fct.unl.pt, {pfr, mfr}@fct.unl.pt

**Keywords:** Optical Fiber Sensors, Graphene Oxide, Layer-by-Layer Films, Adsorption, Desorption.

**Abstract:** The stability of Graphene oxide (GO) layers obtained by the layer-by-layer (LbL) films was investigated having in view the development of tunnable surfaces for optical fibre sensors in aqueous environments. For this purpose layer-by-layer (LbL) films based polyethylenimine (PEI) and GO, were prepared and characterized. The kinetics of adsorption of PEI/GO LBL films revealed that the adsorbed amount per bilayer increases linearly with the number of bilayers as expected. Furthermore adsorbed amount per bilayer for short adsorption times tends to a constant value revealing that GO layer growth also follows the adsorption behaviour expected polyelectrolytes in which electrostatic interaction is ruling the process. Finally desorption studies carried out to infer about GO layer stability revealed that GO layers are more stable at higher solutions pHs and if the adsorption time for each layer is short. These results/conclusions allowed to infer on the possible range of applications of PEI/GO LbL films.

## 1 INTRODUCTION


Graphene oxide thin films, prepared by the layer-by-layer (LbL) technique (Oliveira, 2001), have been used as sensing layers for different kind of sensors namely for detection of triclosan in water (Marques, 2017) and wastewater (Magro, 2019) using the electronic tongue concept (Magro et al, 2019a), (Magro et al, 2019b) and by measuring the impedance spectra. However, studies on the contribution of pH of wastewater matrices for the stability of the GO thin films revealed to be strongly influenced by pH (Magro et al, 2019a; Magro et al, 2019b). Recently, it was demonstrated the possibility of using GO as a coating material for enhancing sensing properties of fiber sensors (Monteiro, 2019). Moreover, GO LbL deposited on optical fibers revealed to work as temperature sensors of aqueous solutions (Costa, 2018). It should be also referred that the optical fiber devices are widely explored in literature for hydrostatic pressure (Xu, 1993), lateral load (Novais, 2017), and strain (Liu, 2015; Monteiro,


2017) sensing, having therefore general application as optical sensing devices.


In this work, LbL films prepared from polyethylenimine (PEI) and GO, were prepared and characterized in order to optimize its stability on different pHs.

## 2 MATERIALS AND METHODS

Thin films were prepared by the LbL technique (Oliveira et al., 2001) using the polyelectrolyte polyethyleneimine (PEI) and graphene oxide (GO). These compounds were acquired from Sigma-Aldrich (St Louis, MO, USA). These films were adsorbed onto quartz supports by adsorbing alternate layers of PEI and GO at solid/liquid interface. PEI aqueous solutions with a monomeric concentration of  $2 \times 10^{-2}$  M and GO solution with a concentration of 2mg/mL were prepared by diluting these compounds in ultra-pure water, produced with a Millipore system (Bedford, MA, USA). The adsorption times for each layer were of 5, 15 and 30 s, and after adsorption of

<sup>a</sup>  <https://orcid.org/0000-0003-3970-4155>

<sup>b</sup>  <https://orcid.org/0000-0001-9665-7610>

<sup>c</sup>  <https://orcid.org/0000-0003-4710-0693>

each layer the solid support was washed with ultrapure water to remove the molecules which are not completely adsorbed on the adsorbed layer. After the adsorption of each layer, the thin-film was dried using a flux of nitrogen gas. Films of PEI/GO were prepared with different number of bilayers. To analyse the effect of pH of PEI/GO LbL films prepared with 12 bilayers, (PEI/GO)<sub>12</sub> were immersed in aqueous solutions with different pHs to characterize the desorption as a function of time. The adsorbed/desorbed amounts were characterized by ultra-violet spectroscopy using a double beam spectrophotometer UV-2101PC (Shimadzu).

### 3 RESULTS AND DISCUSSION

#### 3.1 Buildup of PEI/GO LbL Films

Figures 1 a), b), and c) show the obtained UV-Vis spectra of PEI/GO LbL films, prepared with 5, 15 and 30s adsorption times.

The obtained spectra bands shown in figure 1 are essentially associated to the electronic transitions of GO, namely, the peak located at 230 nm is associated with  $\pi$ - $\pi^*$  transitions of the aromatic ring (phenol) and to  $n$ - $\pi^*$  transition of the group carboxylic acid. The maximum absorption band located at 247 nm can be associated with transitions of  $\pi$ - $\pi^*$  type of the benzene aromatic ring. The band at 299 nm correspond to  $n$ - $\pi^*$  transitions of the carbonyl group (Silverstein et al, 1991). These curves also reveal that the PEI/GO layers grow linearly with the number of bilayers as demonstrated in graph of Figure 2 where the absorbance at 230 nm is plotted versus the number of bilayers. The slopes of obtained from these curves, displayed in table 1, reveal that the adsorbed amount per unit of area and per bilayer increases with adsorption time up to a constant value. This indicates that the adsorption kinetics curve of GO onto PEI layer at lower adsorption times presents a first short characteristic time, in accordance with what is normally observed in polyelectrolyte adsorption, followed of a second adsorption process associated to diffusion process (Raposo, 1997; Ferreira, 2013), as observed in the adsorption of GO onto optical fibers measured by reflectance (Monteiro, 2019).

The decrease of adsorption time also lead to increased films the uniformity as observed by optical microscopy, data not shown here, result which is crucial for optical applications.

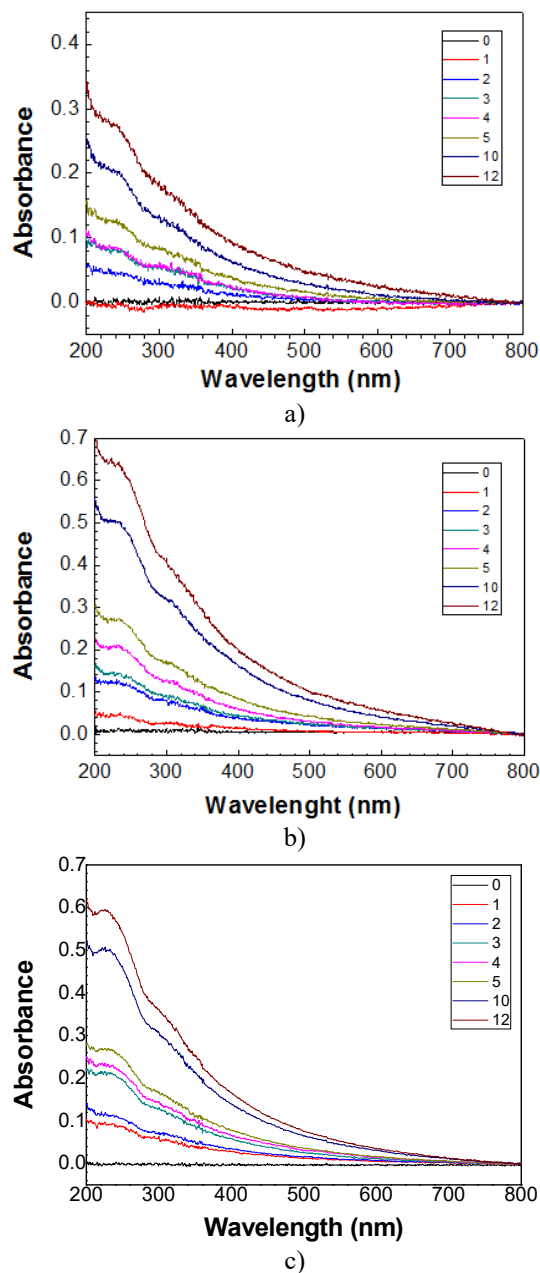


Figure 1: Absorbance spectra of PEI/GO LbL films with different number of bilayers prepared with: a) 5s, b) 15 and c) 30s of adsorption of each layer.

Table 1: Calculated values of absorbance at 230 nm per bilayer, i.e, the slope of data of figure 2.

Adsorption Time per Layer (s)	Absorbance @ 230 nm per Bilayer
5	0.0226 $\pm$ 0.0009
15	0.0510 $\pm$ 0.0008
30	0.052 $\pm$ 0.002

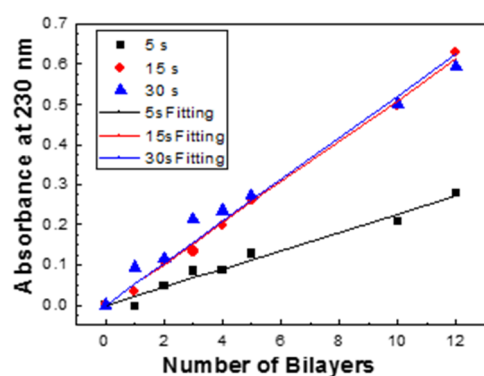


Figure 2: Absorbance at 230 nm as a function of the number of bilayers of PEI/GO LbL films prepared at different adsorption period of time, namely, 5, 15 and 30 s.

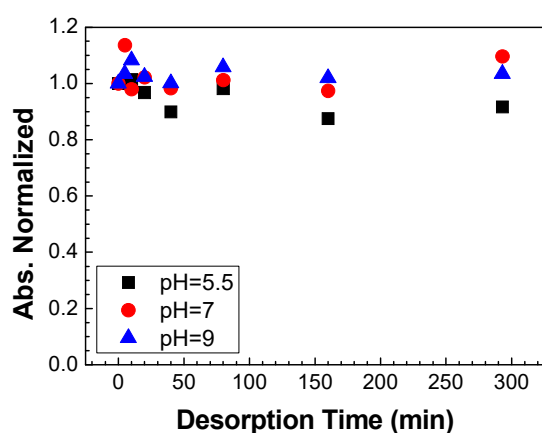


Figure 3: Evolution of the normalized absorbance at 230 nm of the (PEI/GO)<sub>12</sub> LbL films prepared with an adsorption time of each layer 30s as a function of immersion in aqueous solutions with different pHs.

### 3.2 GO Desorption Kinetics

To analyse the stability of the PEI/PSS LbL films, films with 12 bilayers were immersed in aqueous solutions with different pH, namely, 5.5, 7 and 9, and the UV–visible spectra were measured after different immersion times. The obtained desorption kinetics obtained for films prepared with an adsorption period of time of 30s are shown in Figure 3. These adsorption kinetics were obtained by plotting the absorbance at 230 nm after normalization with respect to the value of this absorbance before immersing the films in the aqueous solutions a different pHs. Similar curves are obtained for short adsorption times. Although the obtained curves reveal that pH does not have a strong effect in the GO desorption, when films are prepared with short adsorption times, a small desorption takes place at smaller pHs.

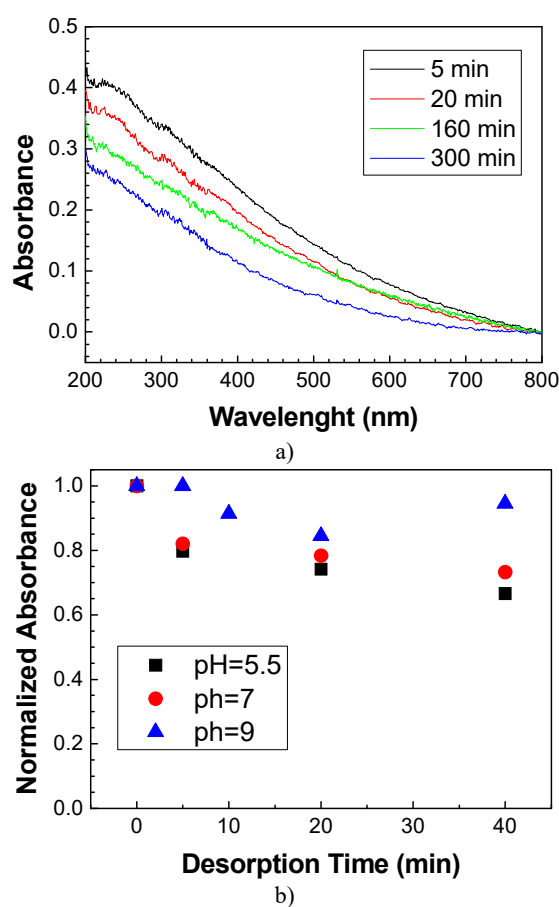


Figure 4: a) Absorbance spectra of a (PEI/GO)<sub>12</sub> LbL film prepared with 60s of adsorption of each layer after to be immersed in an pH=7 aqueous solution. b) Evolution of the normalized absorbance at 230 nm of the (PEI/GO)<sub>12</sub> LbL films prepared with an adsorption time of each layer 60s as a function of immersion in aqueous solutions with different pHs.

However, films prepared with higher adsorption times revealed to desorb in a large amount as demonstrated in Figure 4 a) in which the normalized absorbance of a (PEI/GO)<sub>12</sub> LbL film, prepared with 60s of adsorption of each layer after to be immersed in an pH=7 aqueous solution during several periods of time is seen to decrease. In fact a similar trend but more intense to that observed in desorption kinetics of Figure 3, is attained, when the normalized absorbance at 230 nm of the (PEI/GO)<sub>12</sub> LbL films, prepared with 60s adsorption time of each layer, are plotted as a function of immersion time in aqueous solutions with different pHs. This result demonstrates that the molecules which are strongly adsorbed by ionic interactions are less affected than the ones adsorbed as a result of the process.

## 4 CONCLUSIONS

This study allowed to conclude that the adsorption of a GO layer on PEI/GO LbL films follows the general two stages adsorption processes found polyelectrolytes. The first adsorption stage takes place within the first seconds, the adsorption is dominated by the adsorption of molecules which are bound to the last layer of polyelectrolyte by ionic interactions. At a given adsorption time these adsorbed molecules somehow prevent more molecules to be adsorbed and for larger adsorption times, the presence of counterions and diffusion process enable that more GO molecules to be adsorbed. As a results these last molecules are not so strongly bound to the last polyelectrolyte layer and can be removed more easily by desorption. Therefore the layers with smaller adsorption times are more stable than for higher adsorption times. This study also revealed that these films are more stable at higher pHs allowing choose the adequate solutions for sensor applications where these LbL films are stable.

## ACKNOWLEDGEMENTS

The authors acknowledge the financial support from FEDER, through Programa Operacional Factores de Competitividade COMPETE and Fundação to Fundação para a Ciência e Tecnologia, Portugal, through projects “Development of Nanostructures for Detection of Triclosan Traces on Aquatic Environments” (PTDC/FIS-NAN/0909/2014) and the UID/FIS/00068/2019. PM Zagalo acknowledges to Fundação para a Ciência e a Tecnologia for his PhD fellowship (PD/BD/142768/2018) from RABBIT Doctoral Programme.

## REFERENCES

- Costa, H.F.C. 2018. Desenvolvimento de dispositivos sensores de fibras ópticas revestidas de filmes finos de óxido de grafeno, Master Degree Thesis, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal.
- Ferreira, Q., Ribeiro, P.A., Raposo, M. 2013. Villain's fractal growth of poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] J-aggregates onto layer-by-layer films and its effect on film absorbance spectrum *Journal of Applied Physics*, 113, 243508.
- Liu, S.; Yang, K.; Wang, Y.; Qu, J.; Liao, C.; He, J.; Li, Z.; Yin, G.; Sun, B.; Zhou, J.; Wang, G.; Tang, J.; Zhao, J. 2015. High-sensitivity strain sensor based on in-fiber rectangular air bubble. *Sci. Rep.*, 5, 7624.
- Magro, C., 2019. Advances in applied electrokinetics: Treatment, by-products reuse and sensors' system, PhD Thesis, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal.
- Magro, C., Mateus, E., Raposo, M., Ribeiro, A. B., 2019 Overview of electronic tongue sensing in environmental aqueous matrices: Potential for monitoring emerging organic contaminants”, *Environmental Reviews*, 27(2), 202-214
- Magro, C., Zagalo, P.M., Pereira-da-Silva, J., Mateus, E.P., Ribeiro, A.B., Ribeiro, P.A., Raposo, M. 2019b. Triclosan detection in aqueous environmental matrices by thin-films sensors: impedantometric electronic tongue. *Proceedings 2019*, 15, 24, 2019, <https://doi.org/10.3390/proceedings2019015024> .
- Marques, I., Magalhães-Mota, G., Pires, F., Sério, S., Ribeiro, P.A., Raposo, M. 2017. Detection of Traces of Triclosan in Water”, *Applied Surface Science*, 421, 142–147.
- Monteiro, C. S., Raposo, M., Ribeiro, P.A., Silva, S., Frazão, O. 2019. Graphene oxide as a tunable platform for microsphere-based optical fiber sensors, *Proc. SPIE 11207*, Fourth International Conference on Applications of Optics and Photonics, 112070X; <https://doi.org/10.1117/12.2527267>.
- Monteiro, C.; Silva, S.; Frazao, O. 2017. Hollow Microsphere Fabry–Perot Cavity for Sensing Applications. *IEEE Photonics Technol. Lett.* 29, 1229–1232
- Novais, S., Ferreira, M. S., Pinto, J. L. 2017. Lateral Load Sensing with an Optical Fiber Inline Microcavity. *IEEE Photonics Technol. Lett.*, 29, 1502–1505.
- Oliveira, O.N., Raposo, M., Dhanabalan, A., 2001. In Langmuir-Blodgett (LB) and Self-assembled (SA) polymeric films, in: Nalwa, H.S.B.T.-H. of S. and I. of M. (Ed.), *Handbook of Surfaces and Interfaces of Materials*. Academic Press, Burlington, pp. 1–63.
- Raposo, M., Pontes, R. S., Mattoso L. H. C., Oliveira Jr., O. N. 1997. Kinetics of Adsorption of Poly (o-methoxyaniline) Self-assembled films, *Macromolecules*, 30, 6095-6101.
- Silverstein, R. M., Bassler, G. C. & Morrill, T. C. 1991. *Spectrometric Identification of Organic Compounds*.
- Xu, M. G., Dakin, J. P. 1993. Novel hollow-glass microsphere sensor for monitoring high hydrostatic pressure. In *Fiber Optic and Laser Sensors X*, Vol. 1795, pp. 2–7.
- Zagalo, P.M., Magro, C., Pereira-da-Silva, J., Bouchikhi, B., el Bari, N., Ribeiro, P.A., Raposo, M. (2019). Detection of Triclosan in tuned solutions by pH and ionic strength using PAH/PAZO thin films. *Proceedings 2019*, 15, 25, <https://doi.org/10.3390/proceedings2019015025> .