

# Different approaches for fabrication of thin films by Layer-by-Layer self-assembly

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In this paper, layer-by-layer (PDDA/CuTsPc) films assembled by alternate adsorption of poly(diallyldimethylammonium chloride) (PDDA) as polycation and copper phthalocyanine-tetrasulfonic acid (CuTsPc) as polyanion on to a clean glass substrate. UV-vis spectroscopy measurements indicated that peak absorbance increased linearly with the increasing adsorption cycles. The film thickness measured by AFM was  $(33 \pm 2)\text{nm}$ , this value is consistent with the thickness of monolayers of PDDA and CuTsPc individually – showing our method is efficient for deposition of monolayers by LBL.

## I. INTRODUCTION

Nanostructured materials have emerged with the development of nanoscience and nanotechnology as new and promising materials, they have attracted much attention as their properties and functionalities can be tuned and tailored by their nanoscale compositions[1]. Nanoscale building blocks have been designed and used to fabricate nanostructured materials that feature structural control from the molecular to the micron scale.

The layer by layer (LBL) assembly, as an innovative technique, has been object of study of big interest in the scientific community. This technique presents elevated molecular organization and distinct properties of volumetric materials, allowing various types of applications. The LBL also presents other advantages, as low cost and simplicity of the experimental equipment, besides using a wide range of materials, like clays, nanoparticles, semiconductors polymers.

The LBL is a rich versatile technique for making thin films, particularly of oppositely charged layers can be prepared. In general, the LBL process is achieved by alternately exposing a substrate to positively and negatively charged polymers or particles (Figure 1). In LBL, steps are repeated continuously until the desired numbers of bilayers are achieved. Each individual layer thickness and LBL growth rate depends upon various factors including the chemistry used, charge density, molecular weight, temperature, deposition time, and concentration and pH of the species being deposited.<sup>14</sup> The ability of LBL to control the coating thickness, properties of the nanocomponents and economic use of raw materials make the assembly tool greatly superior to other techniques[2].

In this work, we investigate the reproducibility of LBL technique, due to its simplicity. We fabricated three thin films of PDDA/CuTsPc over glass. One sample was done manually (dipping and time control), the other two was done with an automated apparatus that controls the whole process (dipping and time control). Our fabrica-

tion process had no control over pH, temperature, or any other parameters.

## II. MATERIALS AND METHODS

Layer by layer assembly was performed by sequential dipping of a clean glass, for three samples. For the first sample, it was made manually dipping in a aqueous solutions of polycation for 8 minutes, washed in deionized water and dried using a very gentle  $N_2$  gas line, dipping in a aqueous solution of polianion for 8 minutes, washed and dry again, this process are repeated for 5 bilayers, the schematic of process is shown in Figure 1. For each bilayer was made a measure of UV-visible spectroscopy. For the other two samples it was made by an automated apparatus, dipping in a aqueous solutions of polication for 8 minutes, washed in deionized water and dried naturally in air, dipping in a aqueous solution of polianion for 8 minutes, washed and dry again, this process are repeated for 15 bilayers. For each layer was made a measure of UV-visible spectroscopy (for layers of PDDA and CuTsPc).

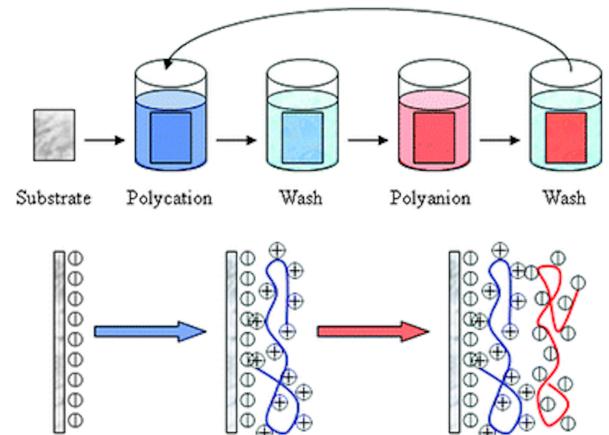


FIG. 1. Scheme of sample preparation by LBL[3].

For the fabrication of the films LBL was using as polication the poly(diallyldimethylammonium chloride)

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(PDDA), and copper phthalocyanine-tetrasulfonic acid (CuTsPc) as polyanion. The PPDA, is a polyelectrolyte with low molar mass, strongly charged, because it is strongly charged, in the formation of the LBL film occurs high repulsion between the layers, generating extremely thin layers, approximately 1.7 nm. The phthalocyanines generally have two central hydrogen atoms that can be replaced by metal ion, where the chosen metal ion was  $Cu^{2+}$ , and also as the phthalocyanines are not soluble in water, sulfonic groups  $SO_3^{-}$  are added to the benzene rings to allow their processing in water, obtaining copper phthalocyanine-tetrasulfonic acid, the phthalocyanine produces thin films, in order of 0.6 nm. The molecular structure of each polymer are show in Figure 2

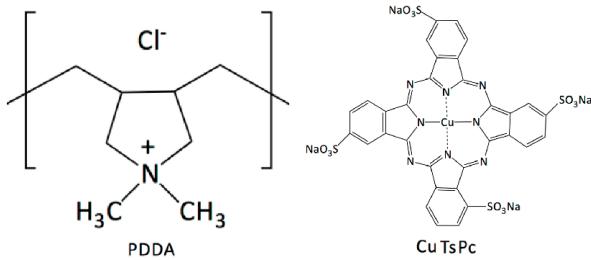


FIG. 2. Structural formulas of PDDA and CuTsPc.

AFM images were taken using the Nanosurf EasyScan2 FlexAFM. We used AFM to investigate the thin film surface (and measure surace roughness) and its thickness. The bilayers formation was monitored at each deposition step by UV-vis spectroscopy (Biochrom Libra S60 spectrometer).

### III. RESULTS AND DISCUSSION

#### A. Absorption spectra

UV-vis was used to monitor the film fabrication process. Figure 3(a) shows UV-vis absorption spectra of glass substrate coated with PDDA/CuTsPc films (where the numbers of bilayers varies from 1 to 5), for the sample that was manually prepared. Two bands can be observed in the absorption spectra at 618 and 678nm, they correspond to the  $\pi - \pi^*$  transition centered on the macrocycle of CuTsPc [6]. As can be seen by the absorbance curves, both peaks increase as the number of bilayers increases, this indicates that the PDDA or CuTsPc are being adsorbed in each step of film fabrication. In order to analyze the behavior of the growth of the bilayers during film fabrication we used the two bands that appear in figure 3(a). Figure 3(b) shows a linear behavior of the absorbance in function of number of bilayers, this linear growth implies a uniform fabrication process for the LBL films.

Figure 4 shows the linear growth of the absorbance at 618 nm as a function of layers of PDDA and CuTsPc - for

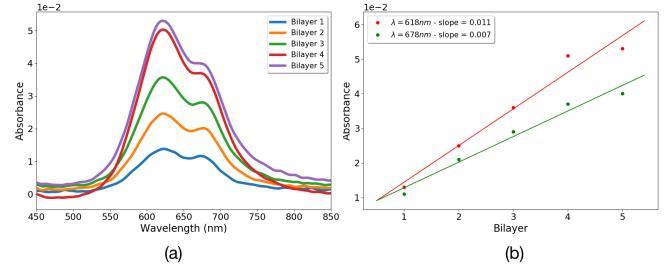


FIG. 3. (a) UV-visible absorption spectra of glass covered with PDDA/CuTsPc thin film for different number of bilayers. (b) Linear growth of the absorbance at 618 and 678 nm as a function of bilayers of PDDA/CuTsPc.

two different samples that was prepared by the apparatus. The linear behavior for both samples are very similar for each monolayer of PDDA and CuTsPc, this proximity in the curves show us the efficient reproducibility of the growth films by LBL. The slope values also indicates that our method has good reproducibility even without so much control over all the possible parameters. The two samples that were prepared with the apparatus has similar slopes for all the four curves ( $\sim 0.02$ ) and for the sample done manually we had slopes  $\sim 0.01$ , this shows the material being adsorbed in approximately the same rate in both methods making LBL a easy, cheap and reproducible technique for thin films fabrication.

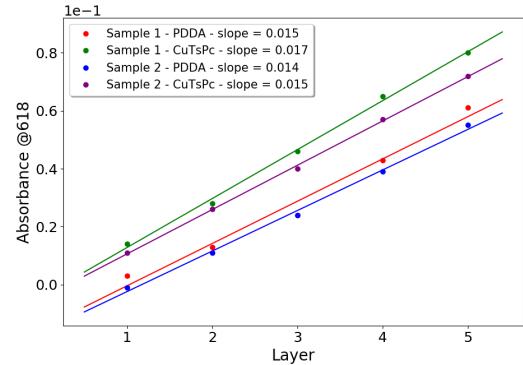


FIG. 4. UV-visible absorption spectra of glass covered with PDDA/CuTsPc thin film for different number of bilayers.

#### B. Atomic force microscopy

Figure 5 shows AFM images of the substrate before film deposition, for different scan sizes. Since the deposited film is very thin, we can compare AFM images of the substrate before and after film fabrication to verify the material are being adsorbed. We can also observe the surface is not completely flat from the images of figure 5, the roughness RMS (root mean square) values calculated from figure 5(a) and (b) are  $(479 \pm 24)$ pm and  $(413 \pm$

20)pm, respectively.

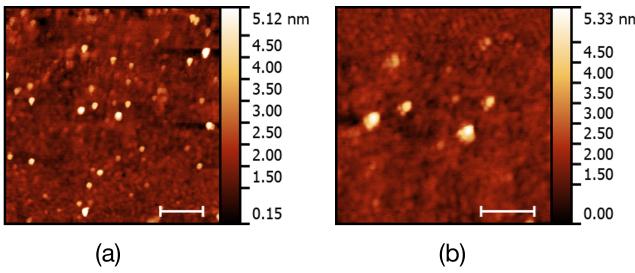


FIG. 5. Atomic force microscopy images (topography) of the surface of the substrate (hydrophilized glass) before film deposition. Scale bar: (a)  $1\mu\text{m}$  and (b)  $500\text{nm}$ .

Figure 6 shows AFM images of the substrate after the a thin film fabrication containing 15 bilayers of PDDA/CuTsPc. We can observe the surface is different from the topography image of the substrate (figure 5). Figure 6(a) and (b) present the surface topography of the LBL film of an area  $20 \times 20 \mu\text{m}$  and  $2 \times 2 \mu\text{m}$  in dimension, respectively.

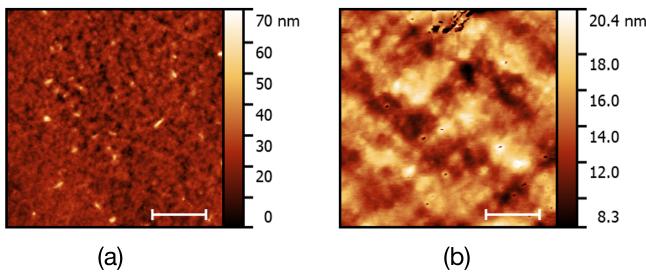


FIG. 6. Atomic force microscopy images (topography) of the surface of the film (PDDA/CuTsPc) deposited by LBL. Scale bar: (a)  $5\mu\text{m}$  and (b)  $500\text{nm}$ .

This morphologic investigation shows a very uniform surface, the roughness RMS values calculated from figure 6(a) and (b) are  $(5.0 \pm 0.3)\text{nm}$  and  $(3.4 \pm 0.2)\text{nm}$ , respectively. Comparing figure 5(b) and 6(b), the topography indicates that the film is being deposited due to the change in topography, RMS values also shows changes for both cases – roughness values increases significantly after film fabrication  $(413 \pm 20)\text{pm}$  to  $(3.4 \pm 0.2)\text{nm}$ , comparing roughness values for images of same scan size.

Figure 7(a) shows an AFM image of a step in the deposited film. Using the topography image we were able to measure the film thickness, as shown in figure 7(b). The average thickness measured for the curves shown in figure 7(b) is  $\bar{T}=(33\pm2)\text{nm}$ . According to the literature, a monolayer of PDDA film has  $\sim 1.7\text{ nm}$  thickness [4], and a monolayer of CuTsPc has  $\sim 0.6\text{ nm}$  [5]. It is consistent to the thickness measured for our 15 PDDA/CuTsPc bilayer thickness,  $(33\pm2)\text{nm}$ . This indicates our method

is actually forming monolayers in each part of the LBL process.

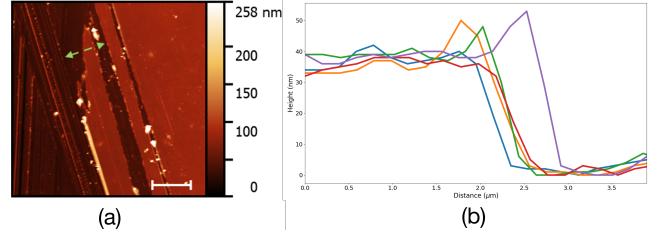


FIG. 7. (a) Atomic force microscopy image (topography) showing a step in the film deposited (PDDA/CuTsPc). Scale bar:  $10\mu\text{m}$ . (b) Height profile of the step measured with the AFM.

#### IV. CONCLUSION

In conclusion, we have presented two methods for fabrication of thin films by using a layer-by-layer technique. UVvis spectroscopy and AFM topographic images measurements show a uniform deposition process. The thin film thickness measured by AFM shows that our film fabrication is actually creating monolayers at each step of the process. UV-vis shows a linear growth in the absorbance curve, which indicates material are being absorbed at each step. We also showed that the LBL method is very efficient even without much control over the experiment by comparing a sample that was fabricated manually with one that was fabricated using an automated apparatus.

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