Using Layer-by-Layer Self-Assembly in the Fabrication of Thin Films

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

ABSTRACT

Aims: The LBL technique is leveraged in this study to perform thin film fabrication using (diallyl dimethylammonium chloride) (PDDA) and copper phthalocyanine-tetrasulfonic acid (CuTsPc). The deposition of PDDA/CuTsPc films over a glass substrate through alternate adsorption is studied in this research. Both manual and automated methods are examined to evaluate the efficiency of the LBL technique.

Study Design: Analysis.

Place and Duration of Study: Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology-Bombay (IIT Bombay), between July 2019 and December 2019.

Methodology: A clean glass substrate is used to perform the Layer by Layer assembly technique for fabricating three thin films of PDDA/CuTsPc. The first sample is prepared manually by immersing the glass substrate in an aqueous solution of PDDA for eight minutes, which is followed by washing in deionized water and drying using nitrogen gas. This process is repeated until five bilayers are formed. UV-Vis spectroscopic measurements are used to analyze the absorbance trends. For the second sample, the same process is repeated but with an automated apparatus. An aqueous polyion solution and an automated apparatus is used for the third sample with the remaining steps being identical to that of the previous samples.

Results: For manually prepared samples, UV-Vis absorption spectra of glass covered with about one to five bilayers of PDDA/CuTsPc for showed that the increase in peaks are directly
proportional to increase in the number of bilayers. A similar linear behavior is seen for the samples prepared by automated fabrication. The linear growth of the samples is fairly alike for the monolayers of PDDA and CuTsPc.

**Conclusion:** An orderly deposition process is observed upon performing Atomic Force Microscopy and UV-Vis spectroscopy. The research findings show a linear behavior in the absorbance curve, which demonstrates the fact that monolayers form at every stage of the film fabrication process. It is also observed that the materials were being absorbed at the same rate for both the automated and manual methods.

**Keywords:** Layer-by-Layer self-assembly; PDDA; CuTsPc; atomic force microscopy; UV-Vis spectroscopy; nanoscience; nanotechnology.

1. **INTRODUCTION**

Nanoscale is a magical point on the dimensional scale; structures in nanoscale (called nanostructures) are considered at the borderline of the smallest of human-made devices and the largest molecules of living systems [1]. According to literature, the nanoworld has emerged from the combination of science and technology. A substantial number of new materials with nano elements such as ceramics, glass, polymers and fibers are making their way onto the market and are present in all shapes and forms in everyday life, from washing machines to architecture [2].

The latest areas of innovation in nanoscience and nanotechnology savor integration the Layer-by-Layer (LBL) technique with nano architectonics. Recent advances in LbL assembly technologies have explored different driving forces for the assembly process when compared with the diffusion-driven kinetics of classical LBL assembly, where a substrate is immersed in a polymer solution [3].

The LBL is a novel method for preparing charged thin films by alternate adsorption. These films are fabricated by forming alternate layers of oppositely charged materials that are infused with washing procedures. The principle of this technique is the charge reversal of the film layer during each dip which makes the surface alternate charge reversal. The film is deposited on glass/gold or quartz substrate by dipping the slide into a beaker containing polycation, manually or by automated device, and there by making the substrate positively charged (i.e. the slide positive) and then multilayered films are formed by the adsorption of polyanion and polycation successively [4].

This research paper serves as an analytical lens for the LBL technique, involving the deposition of three films of PDDA/CuTsPc over a glass substrate. A comparison is drawn between manual and automated fabrication to study the technique without exercising control over parameters such as pH, conductivity, turbidity, and temperature.

2. **METHODOLOGY**

A clean glass substrate is used to perform the Layer by Layer assembly technique for fabricating three thin films of PDDA/CuTsPc. The

![Scheme of sample preparation by LBL](image)
first sample is prepared manually by immersing the glass substrate in an aqueous solution of polycation for eight minutes, which is followed by washing in deionized water and drying using nitrogen gas. This process is repeated until five bilayers are formed. After 8 minutes of deposition the absorption gets saturated [5] and the films formed during this period are uniform.

UV-Vis spectroscopic measurements are used to analyze the absorbance trends. For the second sample, the same process is repeated but with an automated apparatus. An aqueous polyanion solution and an automated apparatus is used for the third sample with the remaining steps being identical to that of the previous samples.

The poly (diallyldimethylammonium chloride) 2 (PDDA) was used as the polycation and copper phthalocyanine-tetrasulfonic acid (CuTsPc) as the polyanion for depositing the thin films.

**Fig. 2. Structural formulas of PDDA and CuTsPc**

**Fig. 3.** (a) UV-Vis absorption spectra of glass with PDDA/CuTsPc film for various bilayers. (b) Linear graph of the absorbance at 618 and 678 nm observed as a function of bilayers of PDDA/CuTsPc

**3. RESULTS AND DISCUSSION**

**3.1 UV-VIS Spectroscopy Results**

UV-Vis spectroscopy is applied to analyze the absorption trends. Fig. 3(a) demonstrates UV-Vis absorption spectra of glass covered with about one to five bilayers of PDDA/CuTsPc for the manually prepared samples. It is seen that the increase in peaks are directly proportional to increase in the number of bilayers. This shows that adsorption of PDDA or CuTsPc occurs at every step of film deposition. The linear behavior of the absorption spectra in Fig. 3(b) indicates the orderly nature of the film fabrication process.
Fig. 4 demonstrates the linear behavior for the samples prepared by automated fabrication. The linear growth of the samples is fairly alike for the monolayers of PDDA and CuTsPc. Such a similarity validates the reproducibility of the films through the methods used in this study without having to exercise control over any of the parameters.

3.2 Atomic Force Microscopy Results

Fig. 5 demonstrates AFM images of the glass prior to film fabrication for various scan sizes. To ensure that the materials are being adsorbed, the images of the substrate before and after film deposition are compared.

The roughness Root Mean Square (RMS) values calculated from Fig. 5(a) is (479 ± 24)pm and from Fig. 5(b) is (413 ± 20)pm.

Fig. 6 shows AFM images of the substrate after it is coated with 15 bilayers of PDDA/CuTsPc. The difference in the surface images can be easily observed by comparing Fig. 6 with Fig. 5. Fig. 6 contains images of the surface topography of PDDA/CuTsPc films with an area 20 x 20 µm for Fig. 6(a) and 2 x 2 µm for Fig. 6(b).

The roughness RMS values obtained from Fig. 6(a) is (5.0 ± 0.3)nm and form Fig. 6(b) is (3.4 ± 0.2)nm.

Upon analyzing the differences between Fig. 5(b) and 6(b), it is observed that the LBL films are formed on the substrate as a consequence of the change in topography. RMS values also savor changes in roughness values which increase substantially after film deposition that is (413 ± 20)pm to (3.4 ± 0.2)nm.
Fig. 6. AFM images of the surface of the glass substrate after PDDA/CuTsPc film deposition. Scale bar: (a) 1µm and (b) 500nm

Fig. 7. (a) AFM images showing a stage of PDDA/CuTsPc film deposition. Scale bar: 10 µm (b) Height profile of this step

In Fig. 7(a), an AFM image of one of the film fabrication steps is shown. This topography image helped in determining the film thickness which can be seen in Fig. 7(b). The curves shown in Fig. 7(b) have an average thickness \( t = (33±2) \text{nm} \). The thickness of PDDA monolayer is estimated to be 1.72 nm [6] and the thickness of CuTsPc monolayer is \( \sim 0.6 \text{ nm} \) [7]. This data is not analogous to the thickness measured for the 15 PDDA/CuTsPc bilayer thickness, \( (33±2) \text{ nm} \). It demonstrates that this method is genuinely depositing monolayers at every stage of the film fabrication process.

4. CONCLUSION

The Layer-by-Layer (LBL) technique is widely regarded as one of the best thin film fabrication techniques. It enables the fabrication of ultra-thin films that can embed materials on the nanoscale, which finds substantial applications in nanoscience and nanotechnology. The most important advantages of the LBL self-assembly is the quite accurately controlled electrical, mechanical, optical, electrooptical, and magnetic properties of the nanostructured films used in electro-chemical biosensors and microelectronics [8]. Recent years have seen the rapid progress of the construction of nanoscopically ordered membranes using the LBL technique of self-assembly [9]. In this research, two methods for thin film fabrication are presented using the LBL technique. Glass substrate is used for the experiments which are coated with PDDA/CuTsPc films to study absorbance. An orderly deposition process is observed upon performing Atomic Force Microscopy and UV-Vis spectroscopy. The research findings show a linear behavior in the absorbance curve, which demonstrates the fact that monolayers form at every stage of the film fabrication process. It is also observed that the materials were being absorbed at the same rate for both the automated and manual methods savoring that
LBL is both an affordable and reproducible technique for thin film fabrication.

**COMPETING INTERESTS**

Author has declared that no competing interests exist.

**REFERENCES**