Fabrication and Control of Porous Structures Via Layer-By-Layer Assembly on PAH/PAA Polyelectrolyte Coatings

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ABSTRACT

Utilizing Layer-by-Layer (LbL) assembly, a fabrication method for the controlled creation of porous structures on Polyallylamine Hydrochloride (PAH) and Polyacrylic Acid (PAA) coatings was developed. These LbL coatings, generated through an acid corrosion process, resulted in the formation of distinctive porous structures. Experimental parameters, specifically temperature gradients from ambient to 60°C, and immersion time were systematically manipulated, enabling the successful generation of porous structures with sizes of 300 nm, 800 nm, 1200 nm, 1600 nm, and 2000 nm. Empirical evidence indicates the effective enlargement of pore sizes with increased temperature and prolonged immersion time. This research enhances the understanding of LbL assembly techniques and the size control of porous structures, paving the way for a wide range of applications, notably in biosensing and environmental monitoring.

Keywords: Layer-by-Layer (LbL) assembly; Porous Structure; Polyelectrolyte Coatings; Polyallylamine Hydrochloride (PAH); Polyacrylic Acid (PAA)

Abbreviations: LPFG: Long-Period Fiber Gratings; LbL: Layer-by-Layer; PAA: Polyacrylic Acid; PAH: Polyallylamine Hydrochloride

Introduction

The Layer-by-Layer (LbL) assembly process is an uncomplicated method for fabricating multilayers of polyelectrolytes. This is achieved through the sequential deposition of polymers bearing opposing charges (or mutually interacting species) [1]. The overall thickness of the film, spanning from nanoscale to microscale, can be easily regulated through the adjustment of deposition cycles or assembly conditions, such as pH, reaction timing, and ionic intensity. Porous polymers are currently being intensively explored to address contemporary issues in many areas such as energy technology [2], sustainable progress [3] and water sanitation [4]. Employing the LbL assembly method enables the creation of porous polyelectrolyte coatings with controlled pore designs and enhanced surface areas, which are beneficial for environmental energy and biomedical utilizations [5]. The process of inducing porosity in the LbL film involves post-assembly immersion in either acidic or basic solutions. When LbL films composed of weak polyelectrolytes, such as poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA), are submerged in an acidic solution followed by a rinse in deionized water, the formation of nano- or micropores can be observed [6]. In this study, we introduce a method to rapid fabricate a series of porous structures with diverse dimensions in PAH/PAA LbL coated Long-Period Fiber Gratings (LPFG). We selected LPFG as our substrate due to its proven efficacy in label-free biosensor applications [7], which provides a low-cost, simplistic, yet efficient detection technique [8]. This modality facilitates quick and trustworthy detections, even in challenging environments. Our approach commenced with the deposition of functional polyelectrolyte coatings on the LPFG surface via the LbL assembly process. Following this, nano-structured pores were integrated into these coatings via a post-assembly treatment under varying conditions, such as submersion time and experimental temperature. By meticulously controlling diverse experimental parameters, we successfully generated nanoporous structures with sizes ranging from 300 nm to 2000 nm. The methodology presented in this paper broadens the scope of knowledge in the realm of porous polymer creation and its versatile applicability.

Method

Chemical Reagents and Materials

Sodium hydroxide standard solution (0.1 M, NaOH), sodium chloride (NaCl), potassium chloride (KCl), sodium dihydrogen phosphate (NaH_2PO_4), disodium phosphate (Na_2HPO_4), poly(allylamine hydrochloride) (PAH, Mw~17.5 kDa), poly(acrylic acid) (PAA, Mw~450 kDa) were purchased from Sigma-Aldrich. Hydrochloric acid (1N standard solution, HCl) was obtained from Acros Organics. All chemicals were used without further purification steps. All solutions were prepared using Milli-Q ultrapure water (no less than 18.2 MΩ).

Preparation of PAH/PAA LbL Coatings

The lab-on LPFG was placed in a straight orientation between two sturdy holders affixed to a motorized arm [1]. It was then subjected to a cleaning process by immersion in a 0.1 M NaOH standard solution for a duration of 20 minutes. Following this, it was alternately dipped into containers filled with different polymer solutions and then in a rinsing phosphate-buffered saline (PBS) solution, as part of the Layer-by-Layer self-assembly cycles conducted at ambient temperature. Throughout the entire deposition procedure, the pH of the PAH solution was adjusted to 7.5, while the PAA solution was regulated to a pH of 3.5. The rinsing PBS buffer solution was maintained at a pH of 7.4. More specifically, the LPFG was immersed into a 0.2 mg/mL concentration of the PAH solution for 10 minutes. This was followed by a rinsing step in 0.1 M PBS buffer solution that lasted for 5 minutes. Subsequently, it was dipped into the 0.2 mg/mL PAA solution for 10 minutes, followed by an identical rinsing procedure. This deposition sequence was repeated 10 times to fabricate 10 bilayers of PAH/PAA. The concluding step was the addition of a PAH layer to generate the PAH/PAA-PAH polyelectrolyte coating on the surface of LPFG. (Figure 1) shows the preparation process of PAH/PAA LbL coatings.
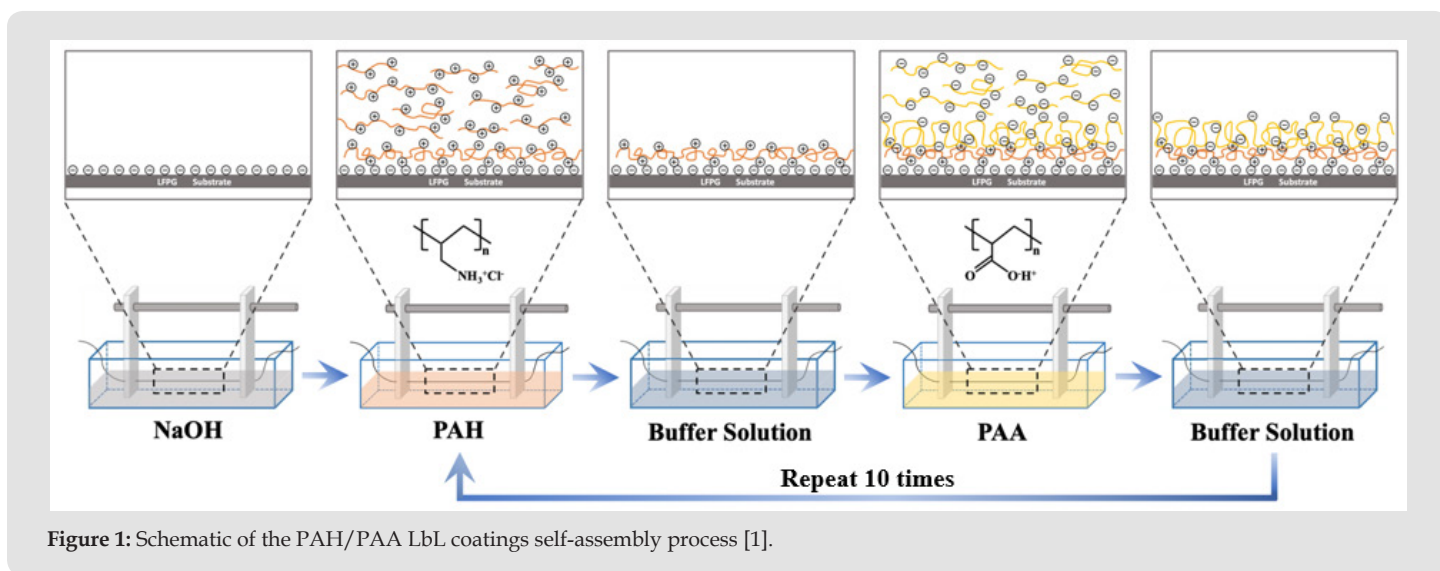

Figure 1: Schematic of the PAH/PAA LbL coatings self-assembly process [1].

Preparation of Porous PAH/PAA LbL Coatings

The preparation process for the 300 nm porous structure, which was detailed in our previous study [1], involved the following steps conducted at room temperature (20 °C): The PAH/PAA LbL coating was initially submerged in a 0.01 M NaH_2PO_4 solution for 5 s (pH adjusted to 5.0). This was followed by three successive submersion steps in a NaH_2PO_4 buffer solution at pH 4.0 for 5 s, at pH 3.3 for 1 min, and finally at pH 2.5 for 5 min. A similar process was employed to fabricate the 800 nm structure. At room temperature, the coating was submerged sequentially into a NaH_2PO_4 solution adjusted to pH 5.0 for 15 s, at pH 4.0 for 15 s, at pH 3.3 for 3 min, and at pH 2.5 for 15 min. To construct the 1200 nm structure, at room temperature, the coating was submerged successively into a NaH_2PO_4 solution of pH 5.0 for 20 s, at pH 4.0 for 20 s, at pH 3.3 for 4 min, and at pH 2.5 for 20 min. For the 1600 nm structure, all solutions were kept in a water bath at 40°C. The coating was submerged into a NaH_2PO_4 solution at pH 5.0 for 5 s, at pH 4.0 for 5 s, at pH 3.3 for 1 min, and at pH 2.5 for 5 min. For the largest structure at 2000 nm, we used a 60°C water bath for all solutions. The coating was submerged in the same sequence as for the 1600 nm structure: a NaH2PO4 solution at pH 5.0 for 5 s, at pH 4.0 for 5 s, at pH 3.3 for 1 min, and at pH 2.5 for 5 min. Each fabrication process concluded with a rinse in PBS buffer adjusted to pH 7.4 for 10 min, followed by air-drying.

### Characterization and Analysis

The characterization of the porous structures remained consistent with our previous analysis methodology by Scanning Electron Microscope (SEM), Auriga Modular Cross Beam Workstation (Carl Zeiss, Inc.), at 3kV accelerating voltage with a working distance or 7.5 mm [9-22]. The SEM images were analyzed using ImageJ 1.52 software from National Institutes of Health.

Results and Discussion

The LbL films were fabricated by using PAH and PAA. The process involved the preparation of 10 bilayers of PAH/PAA, topped off with an additional PAH layer. The incorporation of the porous structure into the LbL coatings of PAH/PAA was achieved via acid corrosion. This transformative process, being substantial and irreversible, altered the topography of the PAH/PAA coatings, leading to the formation of porous structures. The underlying mechanism for this transformation is the reduction in the ionic cross-linking within the films, subsequently followed by spinodal decomposition, thus generating thin films exhibiting a porous morphology. The detailed mechanism was reported in our previous study [1]. (Figure 2) presents a series of SEM images depicting five different PAH/PAA coatings following continuous immersion in various pH aqueous solutions at distinct time intervals and temperatures. Upon examination of these images, it becomes apparent that the surface structures of all the coatings undergo physical alterations following immersion in successively decreasing pH aqueous solutions.

(Figure 2a) showcases a porous structure with a size of 311.26±60.69 nm, while (Figure 2b) presents a structure with a size of 781.83±173.32 nm. Meanwhile, (Figure 2c) depicts a larger porous structure measuring 1219.25±123.86 nm in size. All three porous structures were prepared under room temperature conditions, with submersion time being the sole experimental variable.

This suggests that an increase in submersion duration corresponds to an enlargement in pore size. This is probably because an increase in submersion time leads to a greater number of hydrogen cations protonating some of the COO– groups. This results in a higher degree of interchain ion pair breakage within the LbL, thus enhancing the mobility of the polymer chains. This increased mobility facilitates the creation of larger pores. (Figure 2d) shows a porous structure with a size of 1557.42±211.05 nm, and (Figure 2e) displays a structure measuring 1998.01±285.06 nm in size. Comparatively, while (Figures 2) share the same experiment duration as (Figure 1), they differ in the temperature conditions of the experiments, which were conducted at 40°C and 60°C, respectively. As the temperature escalates, the increased kinetic energy causes the particles to move more rapidly and disperse more widely, accelerating the rate at which ionic bonds break. This acceleration induces a higher degree of interchain ion pair breakage within the LbL structure, thereby enhancing the mobility of the polymer chains. This enhanced mobility, in turn, expedites the formation of larger pores. As demonstrated by our experimental results, prolonging the submersion time can effectively increase the size of the porous structures. In addition, an appropriate increase in temperature aids in enhancing the pores size within a shorter timeframe. With further development and refinement, these findings – the control of pore size by manipulation of experimental conditions – will become a fundamental method for the modification of these coatings.
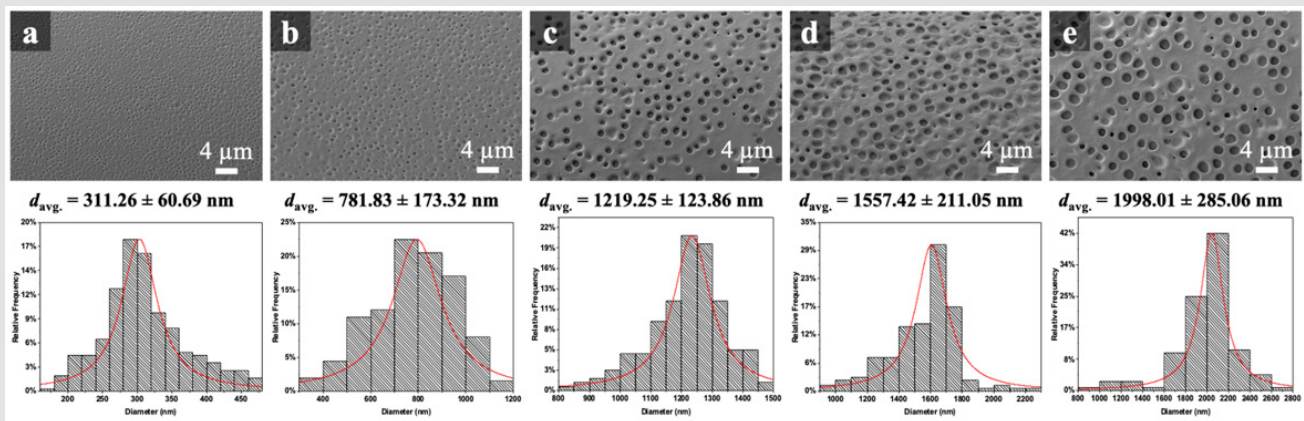
Figure 2: SEM images of porous coatings on LPFG with an average size of
a.   300 nm
b.   800 nm
c.   1200 nm
d.   1600 nm
e.   2000 nm.
The SEM images exhibit the average diameter of porous structures can be effectively manipulated from small to large scale under an elaborate time and temperature control as further shown from the nanopores diameter distribution analysis. Top row: SEM images; mid row: average diameters; bottom row: statistical size histograms.

Conclusion

In this study, the LbL assembly technique was efficiently used to fabricate PAH/PAA polyelectrolyte coatings on LPFG. We strategically utilized the protonation ability of hydrogen ions in low pH environments to break the ionic bonds between the LbL layers, ultimately forming porous structures. The size of these pores can be finely tuned by extending the immersion time and increasing the experimental temperature to achieve the desired size. These empirical findings contribute to the overall understanding of LbL assembly kinetics and fine control of porous structures. Looking forward, future research efforts will focus on optimizing this breakthrough technology for a wider range of applications, including but not limited to biosensing and environmental monitoring.

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