

Morphological Structure Characterization of PAH/NiTsPc Multilayer Nanostructured Films

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ABSTRACT

Morphological structure and growth process of LbL nanostructured films from nickel tetrasulfonated phthalocyanine (NiTsPc) alternated with polyallylamine hydrochloride (PAH) were investigated. The experimental results of UV-visible adsorption kinetics (modeled by Johnson-Mehl-Avrami functions) and AFM images analyzes suggested that the surface morphology structure of films is formed by rod-shaped aggregates produced by a two-step growth process: nucleation and diffusion-limited growth.

Keywords: Phthalocyanine, Layer-by-Layer Films, Growth Processes, Adsorption Kinetics

1. Introduction

Phthalocyanines are interesting due to their properties and possible applications [1-3]. As this type of compound is highly conjugated [4], it has interesting electric and photoelectric properties. Neutral phthalocyanines are insoluble in polar solvents; however, this can be changed by substituting the benzene rings with polar compounds. Several techniques have been used to produce phthalocyanine films, such as evaporation deposition [5-7], molecular beam deposition [8], Langmuir-Blodgett [9-13], and self-assembly layer-by-layer (LbL) [14-18]. The latter one is possible because the sulfonation of the ring of phthalocyanine resulting in tetrasulfonated phthalocyanines, which are more soluble in polar solvents, such as water, and thus allows their application in the production of films by the LbL technique.

The research on LbL films has been performed focusing on the effects from charge density of the molecules in solution [16-20], drying procedure, solution ionic strength, solvent nature, and dipping time on the growth characteristics of the multilayers [17]. With regard to the structure of the films, important findings were the interpenetration of successive polyelectrolyte layers [21], and the preferential orientation of polymer chains perpendicularly to the interfaces [22]. In particular, the dc conduction processes in LbL films from phthalocyanines was investigated in the early days due to its important role in technological applications, such as light emission diode.

For instance, Promnimit *et al.* [19] investigated the current-voltage characteristics in the forward and reverse bias conditions demonstrated rectifying behaviors in the onset of conduction voltage, which makes these films attractive for future electronic devices. The surface morphology of films is another interesting property to be investigated because the film/electrode interfaces are found in all devices and play an important role in their operation [20]. The surface morphology structure of LbL films is determined by the processes responsible for the growth of the layers and is strongly dependent on the preparation conditions [21].

Although there are several studies on LbL films from NiTsPc [22-25], only a few reports on the surface morphology structure have been carried out [26-28]. In this work, we have prepared LbL films from NiTsPc alternated with PAH and investigated their surface morphology structure and the mechanisms of the adsorption process associated to it. From adsorption kinetics experiments and AFM analyses, we have found that films are formed by rod-shaped aggregates promoted by nucleation and diffusion-limited growth.

2. Materials and Methods

Nickel tetrasulfonated phthalocyanine (NiTsPc) and poly(allylamine hydrochloride) (PAH) were acquired from Aldrich and used as supplied. NiTsPc and PAH solutions were prepared as follows: 0.05 g of NiTsPc or PAH were

diluted in 100 mL of ultrapure Milli-Q water (resistivity of 18 M Ω .cm). The mixtures were stirred for 1 h and the solutions were completely clear. The pH was adjusted to 7.5 by adding appropriate amounts of 1 M NH₄OH. The experimental procedures for film fabrication were essentially the same as those described by Decher *et al.* [29]. To build multilayers, PAH (cationic solution) was alternated with NiTsPc (anionic solution). The films were rinsed with an aqueous solution with pH adjusted to 7.5 with 1 M NH₄OH. After that, they were adsorbed onto BK7 optical glass (36 mm $\times$ 14 mm $\times$ 1 mm) rendered hydrophilic in 3:7 hydrogen peroxide (H₂O₂)/concentrated sulfuric acid (H₂SO₄). The slides were then rinsed with pure water and further cleaned in a solution containing 5:1:1 (v:v:v) ultrapure water, H₂O₂, and ammonium hydroxide (NH₄OH). BK7 glass was chosen due to its negligible absorbance in the visible region and its nicely polished surface. NiTsPc adsorption was monitored by measuring the UV-Vis spectra with a double-beam spectrophotometer (Hitachi U2001). Surface morphology was investigated using an atomic force microscope (AFM) from Topometrix. 512 $\times$ 512-pixel images were obtained in tapping mode in ambient conditions.

3. Results and Discussion

In order to investigate the morphological structure of surface and the growth processes of self-assembled PAH/NiTsPc films, we have performed adsorption kinetics experiments with bilayers, which use distinct substrates. It is well known that any study of adsorption kinetics by UV-Vis spectroscopy requires the knowledge of the absorbance peak of material. As reported else-where [30] NiTsPc in solution displays two bands in its UV-Vis spectrum, peaking at 620 nm (Q-band) and 330 nm (Soret band) [30]. The peak around 620 nm is associated with dimers and the shoulder in the 620 - 645 nm region is associated with the NiTsPc monomers [31]. Both adsorptions are attributed to π - π^* electronic transitions. These bands are also observed in our LbL films from PAH/NiTsPc with absorbance maximum shifts to higher energy values. In our work, the absorbance at 615 nm ($\lambda_{\max}$) was used to monitor the building of multilayers, since PAH does not adsorb in this wavelength [32]. The experimental procedures to obtain the films are essentially the same as those found in our latest work [32].

The amount of mass adsorbed per area unit can be estimated using the Beer-Lambert law from the absorbances and taking into consideration the two faces of the substrate [32]. The immersion time of the substrate in the NiTsPc solution varied during the films growth from 5 to 100 s on PAH layers (3 minutes for all film layers). **Figure 1** displays the adsorbed mass amount of NiTsPc per bi-layer

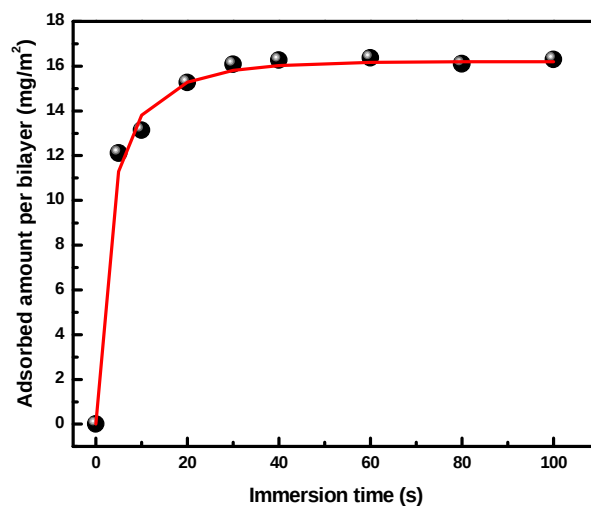


Figure 1. Adsorbed mass amount of NiTsPc per bilayer as a function of the immersion time. The points were obtained from the growth curve slope of the films for variable immersion times. The full curve is the fitting with the JMA equation.

versus the accumulated immersion time. It is noted that the adsorbed amount of mass increases with the increase in time and exhibited a saturation plateau.

The experimental curve showed in **Figure 1** was fitted by using the Johnson-Mehl-Avrami-type (JMA) second-order function:

$$A = K_1 \left(1 - e^{-t/\tau_1}\right) + K_2 \left(1 - e^{-(t/\tau_2)^n}\right), \quad (1)$$

where A is the absorbance (taken as proportional to the amount of adsorbed material) [33], K_1 , K_2 , τ_1 , and τ_2 are constants, and n is the Avrami exponent. This model gives a phenomenological description of the adsorption kinetics without revealing molecular details; it has been used to explain growth processes due to its mathematical simplicity and proper description of the experimental data of polymeric systems [34]. The results of the phenomenological analysis of the growth of the PAH/NiTsPc LbL films employing the JMA model were summarized in **Table 1**. The proportionality constants K_1 and K_2 correspond to the adsorbed mass amount of NiTsPc per area unit ($K_1 + K_2$).

From the JMA analysis, we can say that the process of formation of the films (growth) results from two mechanisms: one first extremely fast, with constant time τ_1 , that

Table 1. Parameters obtained from the JMA fitting of adsorbed mass amount per bilayer.

	K_1	τ_1 (s)	K_2	τ_2 (s)	n
PAH/NiTsPc	11 ± 3	5 ± 2	5 ± 1	31 ± 3	1

may be associated with a nucleation, and a slow one with time constant τ_2 , associated with a diffusion-controlled growth. A two-stage adsorption process was also proposed by Raposo [34] and Tsukruk [35]. It is possible to use the Avrami parameter n to distinguish between growth on the interface or by diffusion. The parameter value of Avrami, $n = 1$, indicates needle-shaped or rod-shaped structures (1D adsorption) produced by diffusion controlled growth and without the formation of new nuclei during adsorption [21,36,37].

Due to the sensibility of the parameter n , it is difficult to identify the process without additional information on the film growth [33], which can be obtained from AFM image analysis. To corroborate the adsorption kinetics results, morphological investigation of the 10-bilayer PAH/NiTsPc films were carried out with layers of NiTsPc adsorbed for 3 min. **Figure 2** shows the image of the surface of PAH/NiTsPc film (NiTsPc on top), which exhibits rod-shaped aggregates and a schematic model proposed to its structure. This finding is consistent with the previous adsorption kinetics results [38,39]. We can see the film forming units, which initially seem small “lying” rods that can be due to aggregation of adjacent NiTsPc rings in the films, which are driving by intermolecular forces [40,41].

Figure 3 (log-log) shows that the heights of aggregates increases when their diameters decreases. The data were taken at distinct cross sections of the images and the error bars included in the inset are average values of several scans. The inset shows three different height

profile. As noted, there is a preferential vertical growth, unlike from films prepared with the polydisperse POMA [21] and PANI [42], which show globular aggregates with no preferential growth direction. This kind of structure had already been identified by Nishida *et al.* [43] for phthalocyanine films onto gold surfaces by STM data. In fact, our result corroborates the aggregate growth as columns suggested by the previous results of adsorption kinetics and parameters of Avrami.

The growth process of NiTsPc in LbL films starts with nuclei formed in the beginning of the adsorption. The adsorption process is the result of compromise between the energy factors, such as electrostatic forces, Van der Waals forces, hydrogen bonds, solvent quality, and entropic factors. The adsorption of polyelectrolytes on charged surface can be described by a rapid adsorption followed by a relatively long period in which the chains are being rearranged. In the first stage, the molecules adsorb on the surface while keeping its conformation in solution. When substrates are immersed in the solution of NiTsPc, immediately some molecules are adsorbed (according to the results of kinetics). The interaction of chains by hydrogen bonds favors the formation of aggregates. These aggregates tend to carry their connection with the surface increasing the number of segments attached to the substrate, *i.e.* a rearrangement of molecules.

4. Conclusions

Nickel tetrasulfonated phthalocyanine has been used together with PAH to produce LbL films. The morpho-

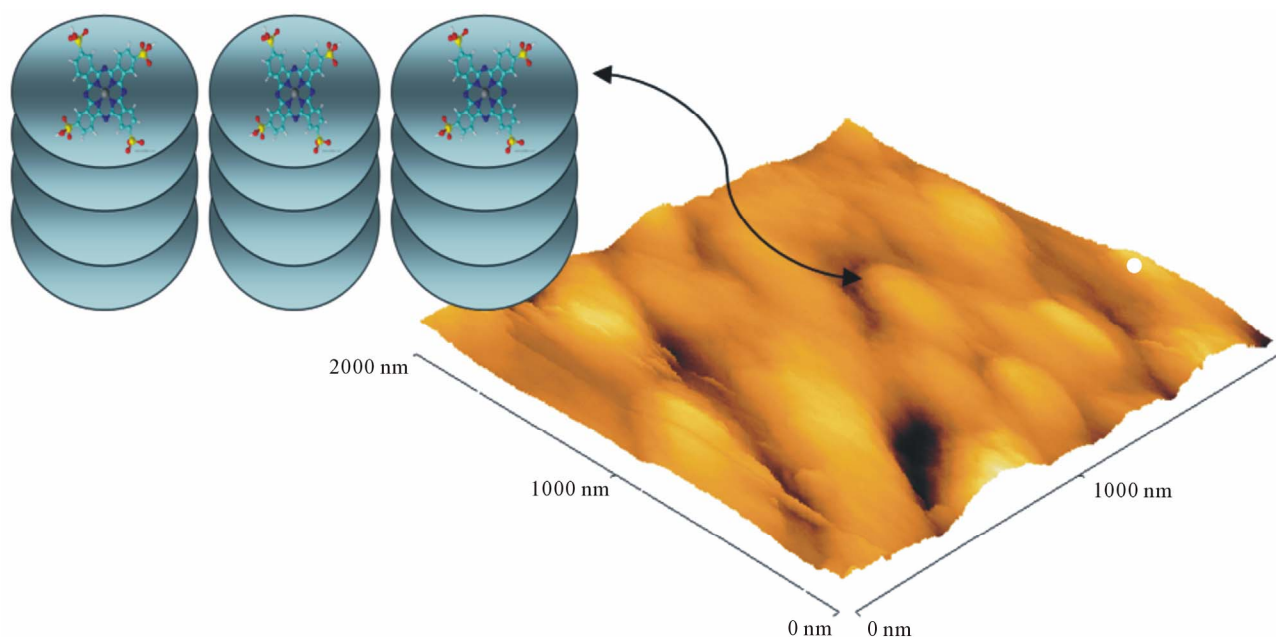


Figure 2. AFM image of a 10-bilayer PAH/NiTsPc film whose layers were adsorbed for 3 min using a NiTsPc solution. The scanning window size is $2\ \mu\text{m} \times 2\ \mu\text{m}$. The scheme shows the NiTsPc molecule which forms the aggregates.

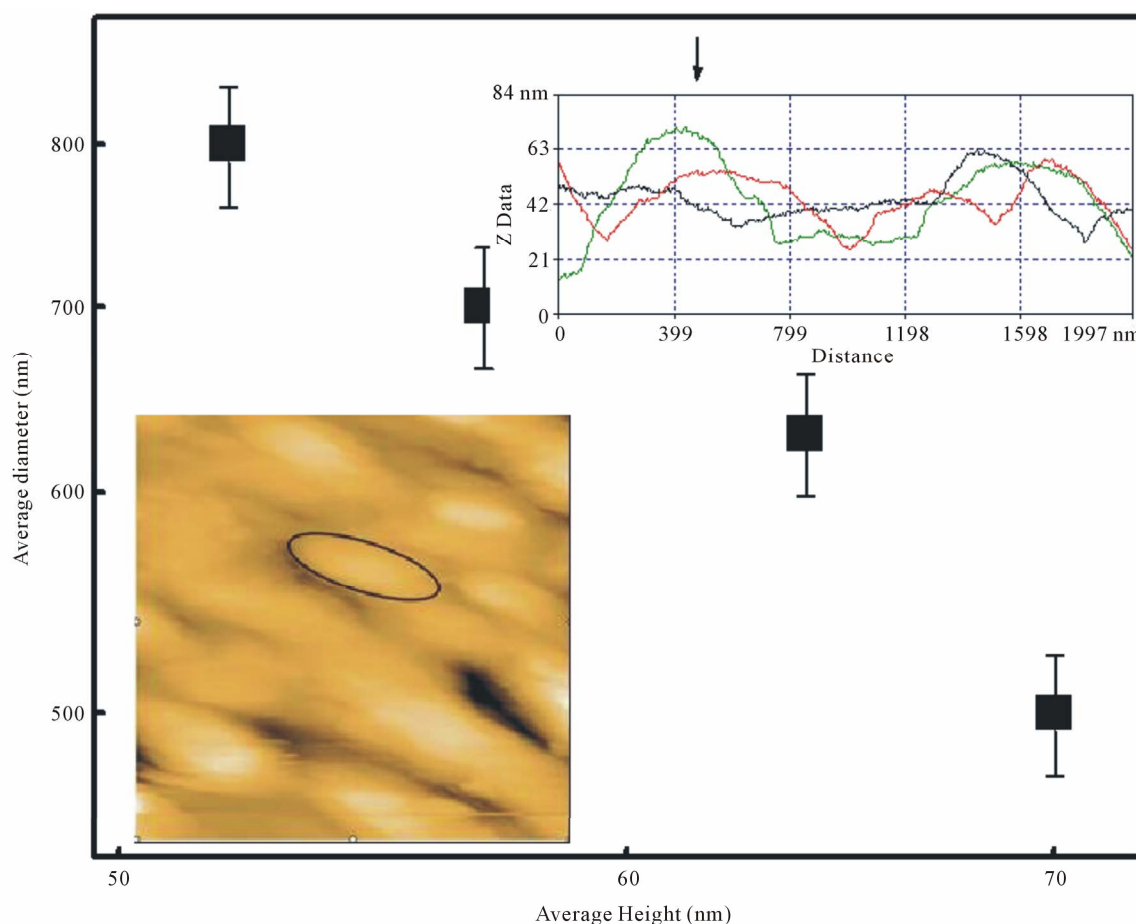


Figure 3. Diameter versus height of aggregates of the PAH/NiTsPc film. The insets show the full curve drawn on the image of the surface of the film, which identifies the rod-shaped structures and the height profile of the films in three distinct cross-sections of the image (the arrow indicates a column corresponding to a surface forming unit).

logical structure of the films was investigated by using a combined method of the adsorption kinetics curves, modeled with JMA functions, and the behavior of diameter versus height of aggregates obtained from AFM images. This approach indicated that the aggregates are rod-shaped, which are produced by an adsorption process with two mechanisms: nucleation in the first stage ($\tau_1 \approx 5 - 10$ s) and diffusion-limited growth in another. Since NiTsPc is a semiconductor organic with applications in sensors, our results may be used as a starting point to future research on devices and bring out new insights on the nanostructured films from this kind of material.

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