Fractal structures in casting films from chlorophyll

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Abstract. Chlorophyll (Chl) molecules are important because they can act as natural light-harvesting devices during the photosynthesis. In addition, they have potential for application as component of solar cell. In this work, we have prepared casting films from chlorophyll (Chl) and demonstrated the occurrence of fractal structures when the films were submitted to different concentrations. By using optical microscopy and the box-count method, we have found that the fractal dimension is $D_f = 1.55$. This value is close to predicted by the diffusion-limited aggregation (DLA) model. This suggests that the major mechanism – which determines the growth of the fractal structures from Chl molecules – is the molecular diffusion. Since the efficiencies of solar cells depend on the morphology of their interfaces, these finds can be useful to improve this kind of device.

1. Introduction
Chlorophyll molecules (Chls) are important because they can act as a natural light-harvesting devices occurring during the photosynthesis [1], and also as component of dye-sensitized solar cells - DSSCs [2]. There has been shown that the efficiency of solar cell depends on their surface morphologies [3]. Therefore, fractal structures – which determine different morphological structures of surfaces – can play an important role on conversion efficiency. A fractal structure is that that exhibits a fractal dimension, which exceeds its topological dimension assuming noninteger values [4]. Fractal structures are well described by the so-called Diffusion Limited Aggregation (DLA) model [5]. The DLA model account for that each immobile cluster grows by diffusion of particles with a unitary probability of sticking. A lot of experimental systems have been successfully described by using this model [6]. Fractal structures in organic films are usually studied by using analyzes of optical microscopy [7], scanning electron microscopy - SEM [8], and atomic force microscopy – AFM [6]. In particular, films from Chl were already prepared by using techniques including Langmuir-Blodgett [9], self-assembly monolayer [10], and casting [11]. In these systems, properties such as electrical, photoelectrical, as well as photogeneration of charges were examined. However, while properties of Chl films have been widely investigated, studies of surface morphology focused on fractal structures are lacking for this kind of films.

In this work, we report on investigation of the formation of fractal structures in Chl films prepared by casting technique. Two different concentrations of Chl solution were used and the fractal dimension of the structures was determined by using box count method. The results obtained were discussed on basis of DLA model.

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2. Materials and methods
Chlorophyll (Chl) was purchased from MP Biomedicals, LLC, and used as receipted. Chl solutions with different concentrations (0.50 and 0.12 g/L) have been prepared by dissolving Chl in purified water as a solvent. The solution pH was adjusted to 8 by adding appropriate amounts of ammonium hydroxide. Thin films were obtained by casting the solutions onto BK7 slices and drying in an air atmosphere at room temperature (23 °C). Surface morphologies of films were examined by using an optical microscope (Nikon, Eclipse Ci/L, USA). The fractal analyzes were performed by the box counting method [4] using the freeware software ImageJ [12]. In this method, the fractal dimension, \( D_f \), is determined as the slope of the regression line for log–log plots of the scale \( r \) and count \( N(r) \), i.e. \( D_f = -\lim(\log N(r)/\log (r)) \).

3. Results and discussion
It is well known that several systems in Nature exhibit fractal structures and they present a dependence on the temperature and concentration of solution used [13]. In order to examine the possibility of occurrence of fractal structures in Chl films, we have performed a study of dependence of film topography on the concentration. Figure 1 shows images of optical microscopy for Chl films as a function of concentration at room temperature. We can note a well-known fractal form of aggregates, as showed in Figures 1A and 1B.

![Figure 1. Optical microscopy images of Chlorophyll films at concentrations of (A) 0.50 g/L and (B) 0.12 g/L. Two selected fractal structures are indicated.](image1)

Figures 2 and 3 exhibits the processed images obtained from Figure 1 by using outline approach implemented in ImageJ software. Here, we can see clearly the fractal structure formed by
Chl molecules. The fractal form observed in Figures 2C and 3C is also found in several kinds of materials, including DNA [14], germanium nanoparticles and nanowires [15], as well as poly(ethylene oxide) crystals [16].

Figure 3. Enlarged image of the selected area in Figure 1A before (A) and after application of binarization (B), outline and noise reduction methods (C), respectively.

Figure 4. Box counting analysis for the fractal structures showed in Figure 2C and Figure 3C. \( r \) is the scale (box size/image size) and \( N(r) \) is the count of boxes of size \( r \) containing foreground pixels.

In order to gain an insight in formation mechanism of the fractal structures, we have determined the fractal dimension of the structures showed in Figures 2C and 3C using the box count method [17]. Figure 4 displays a log-log plot of number of boxes as a function of scale for fractal structures. As expect due to similar form of the fractals in Figures 2C and 3C, the value found is similar, \( D_f = 1.55 \). This value is close to \( D_f = 1.71 \), predicted for a typical case of diffusion-limited aggregation (DLA) model [18]. According to this model, the lower value found in our study suggests a faster aggregation of Chl molecules. Interestingly, the concentration did not affect the fractal dimension. This can be caused by the variation of concentrations used, which may not have been enough to change the dynamics of the formation of the fractal.

4. Conclusion
In summary, we have prepared casting films from chlorophyll molecules and investigated the formation of fractal structures at two different concentrations. The fractal dimension value of the structures was found be \( D_f = 1.55 \), which is close to that predicted by DLA model. These finds can provide insight into the understanding and improvement of devices which use Chl such as photovoltaic
cells. In addition, future works can be focused on relationships between the surface morphological structure and the photovoltaic efficiency.

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