# Formation of Branched Fractal CdS Patterns in Oligomer LB Monolayers: A Study Using Transmission Electron Microscopy

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Transmission electron microscopy images of the treelike fractal aggregates of CdS nanoparticles in amphiphilic oligomer (polymaleic acid with octadecanol ester) LB matrix were observed. The features of these aggregates were developed into the micrometer regime. By changing the ratio between carboxylic groups and hydrocarbon chains, as well as the surface pressure, different fractal CdS patterns could be obtained. These results lead us to propose the mechanism of the formation of branchlike patterns, very much analogous to two-dimensional irreversible fractal-growth models such as diffusion-limited aggregates (DLA). Weak hydrophobic and hydrophilic interaction for interfacial molecular recognition at the organic/inorganic interface had been proposed as providing a possible elucidation for the formation of some aspects of a self-similar fractal-like pattern. At a ratio of 7:1, the fractal dimension was calculated by the box-counting method, and the dominant value was  $1.69 \pm 0.03$ , which was in good agreement with two-dimensional DLA.

## Introduction

It has been demonstrated that amphiphilic molecules containing a hydrophobic chain and a hydrophilic headgroup can form organized assemblies of various shapes. For example, micelles, vesicles, bilayers, monolayers, and liquid crystalline structures have all been observed. It has frequently been used in schemes to prepare inorganic nanoparticles where the organic structure serves as either a template or a reaction vessel of limited size.<sup>1,2</sup> The Langmuir-Blodgett (LB) technique, as a kind of molecularscale technology for the creation of new materials, has been the object of increasing technological and scientific interesting over the past decades.<sup>3-5</sup> The films deposited by the LB technique have potential applications in the areas of molecularbased electronics, photonics, optoelectronics, and bioelectronics. Most of these applications rely upon the self-organization of amphiphilic molecules to form very thin and essentially perfect films. However, the uniform, constant thickness monolayer and multilayer films are unstable due to bilayer step defects and quickly spread to cover the entire film.<sup>6,7</sup> The molecular relaxation and reorientation in the uniform film after deposition exactly happens on a microscopic scale.<sup>6,8,9</sup> The driving force for the reorganization can be attributed to the strength of the headgroup-headgroup interface relative to the headgroupsubstrate and headgroup-water interfaces. Because the defects originally appear random and meandering, it will affect the macroscopic physical properties. So it will be important and magnificent if the films still keep ordered and reordered after reorganization.

Here we introduce a kind of amphiphilic oligomer as a Langmuir–Blodgett (LB) matrix used for the synthesis of CdS nanoparticles. CdS nanoparticles are grown and reorganized in this LB matrix and formed two-dimensional irreversible

## SCHEME 1

COOH  

$$-[(-CH-)_{X} - (-CH-)_{y}]_{N} - N \sim 20, X > Y$$
  
 $c = 0$   
 $0 - C_{18}H_{37}$ 

treelike fractal aggregates. The amphiphilic oligomer's molecular structure is shown in Scheme 1. A hydrophobic chain was induced by chemically linking the amphiphilic molecules through a hydrophilic space of adjustable length by octadecyl polymaleicate (PMAO) that we synthesized.<sup>10,11</sup> In the preliminary reports, we just described the reaction of cadmium and lead PMAO LB films with gaseous H<sub>2</sub>S to form CdS and PbS nanoparticles within a layered PMAO matrix.<sup>11,12</sup> Due to the sulfide aggregation being restricted within one PMAO molecule, PbS as well as CdS within PMAO LB films showed a blue shift of the optical absorption edge that formed within the stearic acid LB films. It also indicated a larger blue shift of the optical absorption edge with the decreasing of the ratio between the carboxylic groups and the hydrocarbon chains. In this paper we present a complete report of the images of CdS aggregates by transmission electron microscopy (TEM) and transmission electron diffraction (TED). We will analyze the structural properties of this kind of amphiphilic oligomer monolayers and present an explanation on understanding the formation of fractal patterns.

### **Experimental Section**

The synthesis of the PMAO has been described elsewhere.<sup>10</sup> Stearic acid (SA) was A.R. grade and recrystallized from ethanol, and chloroform (A.R. grade) was redistilled twice before use. Cadmium chloride was analytical grade and was recrystallized before use. Water, with a conductivity of 18 M $\Omega$  cm, was used to prepare the subphase. The PMAOs with a concentration of approximately 5 × 10<sup>-4</sup> mol/L (lateral chain

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**Figure 1.**  $\pi$ -A isotherms of (a) SA, (b) PMAO1, (c) PMAO2, and (d) PMAO3 on the surface of CdCl<sub>2</sub> solution. The isotherms were all recorded at 20 ± 1 °C, and the compression speed was 3 cm<sup>2</sup>/min.

concentration) and stearic acid with a concentration of  $1 \times 10^{-3}$ mol/L dissolved in a chloroform solvent were spread on the subphase containing CdCl<sub>2</sub> (3  $\times$  10<sup>-4</sup> mol/L) + NaHCO<sub>3</sub> (2  $\times$  $10^{-4}$  mol/L). The pH value of the subphase was 5.8. An appropriate amount of the spreading solutions (50  $\mu$ L) was carefully injected onto the cleaned, thermostatic, air/water interface. After the solvent evaporated, the monolayer was compressed at a speed of 3 cm<sup>2</sup> min<sup>-1</sup>, and the surface pressure was recorded versus the area at 20 °C on a LB trough with a multicompartmental round trough from Mayer-Fein technic (Germany). The monolayers were built up on the copper grid substrates (200 mesh) by the vertical dipping method under a constant pressure. The prepared samples were examined in the bright-field mode and by electron diffraction using a transmission electron microscope operating at 200 kV (H-8100IV transmission electron microscope, Japan). The deposition speed was well controlled at 10 cm/min. The surface pressure for transfer was chosen by the detailed experimental condition. The transfer ratios were nearly 1.0. In a saturated water steam system (20 °C), monolayers were reacted with H<sub>2</sub>S, which was produced from the hydrolysis of thioacetamide. After reacting with H<sub>2</sub>S, CdS nanoparticles were grown and reorganized in the LB matrix and formed a two-dimensional irreversible morphological multibifurcation. The observed growth patterns for different PMAO LB templates could be reproduced and kept for a long time.

### **Results and Discussion**

**Monolayers at the Air/Water Interface.** Figure 1 shows surface pressure—surface area ( $\pi$ –A) isotherms for the samples of PMAOs with three different ratios between carboxylic groups and hydrocarbon chains (3:1, 5:1, and 7:1) and stearic acid, respectively. From the isotherm, it can be seen that the area per molecule increase with increasing ratios between carboxylic groups and hydrocarbon chains. Monolayers, compressed at a controlled rate up to the surface pressure with 15 and 30 mN/m, respectively, are transferred onto electron microscope copper grids sandwiched between a Formvar film and a glass slide under two different phase regions. Two different regions corresponding to different phases can be distinguished in the  $\pi$ –A curves: (i) a liquid-expanded (LE) phase and (ii) a liquid-condensed (LC) phase.

Morphological Structures Analysis. Transmission electron microscopy (TEM), as a direct imaging method, is widely used

to observe nanostructured materials. In our previous reports, the oligomer we introduced could be used for the ordered synthesis and ordered assembly of the inorganic nanoparticles.<sup>11,12</sup> But little is known about the growing process of the inorganic nanoparticles in the LB matrix. A question arise whether the size and shape of the nanoparticles vary with the PMAOs chemical ratios between carboxylic groups and hydrocarbon chains of the monolayers. In particular, transition pressures can alter molecular orientation, which thereby really can change the morphological structure of the nanoparticles. Here we take advantage of transmission electron microscopy to investigate the morphological structure of nanoparticles that were produced through the reaction of CdPMAO monolayer with H<sub>2</sub>S. The morphologies of CdS nanoparticles are different from that of the epitaxial growth or oriented growth of inorganic crystals under Langmuir monolayers or on Langmuir-Blodgett films.<sup>4,13–17</sup> Among these, Fendler et al. reported that rodlike CdS and equilateral triangular PbS nanocrystallites were grown under arachidic acid monolayers, respectively.13,14

Cadmium stearate (CdSt) monolayer is prepared at the dipping speed of 10 cm/min and the surface pressure of 30 mN/m. After being exposed to H<sub>2</sub>S, distinct particles begin to form and appear as darker regions. It exhibits domains with less uniform shape (Figure 2a). After being exposed to H<sub>2</sub>S over a period of 24 h, the particles have an average size of about 2-5 nm in diameter. These particles are close to each other and tend to form more bigger domains (10-20 nm). That is to say, in the CdSt monolayer matrix, the CdS particles are apt to aggregate into large domains which are composed of several small particles. Moreover, the size of domains increases with increasing reaction time. When the reaction time lasted for 48 h, the bigger domains with an average size of 30 nm and a relatively close-packed arrangement can be observed (Figure 2b). Electron diffraction from a 1.0 mm diameter area of the film shows the formation of hexagonal CdS arising from the randomly oriented particles (Figure 2c).

The CdPMAO monolayers with a ratio of 3:1 between carboxylate groups and hydrocarbon chains are transferred in LC region at the surface pressure of  $\pi = 30$  mN/m. After the CdPMAO LB film was exposed to H<sub>2</sub>S, its TEM images display a branchlike morphology up to several micrometers (Figure 3a,b). The morphology of this sample is different from that of the domain structure of CdS/St LB films. The observed particles have an average size of about 15 nm with well-defined edges. Electron diffraction of the film can also be assigned to hexagonal CdS arising from a randomly oriented particles (Figure 3c). The intriguing observation is that the morphology depends strongly on the ratios between carboxylic groups and hydrocarbon chains. When the CdPMAO with a ratio of 5:1 monolayer was exposed to H<sub>2</sub>S, its image is changed. It shows a short branchlike morphology range with the length from 500 nm up to 2  $\mu$ m. The isolated large particles possess featureless morphologies with a length of 100-250 nm and width of 10-40 nm (image not shown here). When the surface pressure decreases from 30 to 15 mN/m, the morphology is changed to a less welldefined shape. The average size of the particles is about tens of nanometers. The TED pattern is the same as that of CdS/ PAMO with a ratio of 3:1.

As the ratio increased to 7:1, multibifurcate morphology becomes visible and develops into the scale of micrometers (Figure 4a, b). The observed particles range in size from 10 to 30 nm. When the surface pressure decreases from 30 to 15 mN/m, we cannot obtain the clear fine bifurcation structures again. Meanwhile, the isolated particles ranging from 100 to



**Figure 2.** TEM image of CdS particles formed in a cadmium stearate LB monolayer after reaction with H<sub>2</sub>S: (a) reaction time lasted 24 h; (b) reaction time lasted 48 h; (c) 200 kV TED pattern from a 1  $\mu$ m diameter area in (b).  $\pi = 30$  mN/m, dipping speed = 10 cm/min, and scale bars = 100 nm.

300 nm in size can be obviously observed (Figure 5a,b). The particles are formed with less well-defined edges. This indicates that the fine bifurcations formed at the higher surface pressure involve the fractal growth processes; i.e., it is possible to form bifurcations or branchlike patterns easily at higher surface pressure. Electron diffraction patterns of selected areas are Fractal CdS Patterns in LB Monolayers







**Figure 4.** TEM of PMAO/CdS LB monolayer (X:Y = 7): (a) 10 000× magnification; (b) 80 000× magnification; (c) 200 kV TED pattern from a 1  $\mu$ m diameter area in (a).  $\pi$  =30 mN/m, dipping speed = 10 cm/min, reaction time lasted 48 h, and scale bars = 100 nm.

taken using a 1  $\mu$ m aperture of the area as the micrograph for Figure 4a. The result also shows the formation of a hexagonal crystal. However, the corresponding electron diffraction pattern has more dispersed spots to form an electron diffraction ring (Figure 4c), indicating a disordered nanocrystallite alignment.





**Figure 5.** TEM of PMAO/CdS LB monolayer (X:Y = 7): (a) 10 000× magnification; (b) 80 000× magnification.  $\pi$  =15 mN/m, dipping speed = 10 cm/min, reaction time lasted 48 h, and scale bars = 100 nm.

The above results of morphological multibifurcations lead us to propose a mechanism for the formation of branchlike patterns, very much analogous to two-dimensional irreversible fractal-growth models such as diffusion-limited aggregates (DLA). In this model, the formation of a stable aggregation nucleus is required, which can then exhibit a one-dimensional growth, so as to optimize the lateral nucleus—nucleus contacts.<sup>18,19</sup> In our work, the fractal dimensions are calculated by dividing the patterns into a concentric box with various lengths and counting the occupied and calculated by the boxcounting method. At the ratio of 7:1, the dominant value is  $1.69 \pm 0.03$ , which is in good agreement with two-dimensional DLA.<sup>20</sup>

Fractal geometry, which repeats on smaller and smaller scales, can provide a new perspective on nature and allows us to consider irregularities as intrinsic entities. The property of self-similarity implies irregularities at all scales.<sup>18,19</sup> This model is applied to elucidate the formation of bifurcations of CdS nanoparticles in the PMAO matrixes. There are several steps:

(1) These kinds of oligomers interact with each other at the air/water interface. Because the adjacent -COOH groups within one oligomer molecules are only separated by no more than 0.3 nm and the distance of each individual oligomer molecule separation exceeds 0.5 nm, the hydrophilic part of

each molecule of oligomer that aggregates by forming the sideways hydrogen bonding should be limited within itself. The size of aggregates should be in the nanometer range because the average degree of the polymerization is approximately 20.<sup>12</sup> And it is possible to make every PMAO molecule form a stable aggregation nucleus at the air/water interface.

(2) The orientation of alkyl side chains at the air/water interface is a function of the surface pressure, indicating that a disorder orientation at lower surface pressure changes to an order orientation at higher surface pressure. The tails of alkyl chains tilt in the LE state. As the monolayer enters the LC state, the tilt angle tends to decrease and the alkyl chains are more upright. This will affect the weak hydrophobic and hydrophilic interaction forces between the aggregates. And it will also affect the formation of the fractal CdS nanoparticles in the next step.

(3) The molecular relaxation and reorientation in the uniform monolayer happen during the formation of CdS nanoparticles in a saturated water steam system. In fact, the homogeneous and uniformly constant thickness monolayer and multilayer films are unstable to bilayer step defects and quickly spread to cover the entire film (a form of "dewetting").<sup>6</sup> Due to the sulfide aggregate being restricted within one PMAO molecule,<sup>11,12</sup> the formation process of nanoparticulate CdS two-dimensional domains should be governed by the diffusion of oligomeric PMAO molecules and their sticking to a cluster. After reacting with H<sub>2</sub>S, CdS nanoparticles are produced and reorganized in the LB matrix and form a two-dimensional irreversible morphological multibifurcation. That is, the uniformly thick LB film departs from the substrate and reorganizes to form an orderly structure. So it effectively weakens the CdS crystalline anisotropy. The total processes lead to an irregular fractal-like crystal growth of CdS nanoparticles. So the morphologies of CdS nanoparticles are different from the reports about the rodlike CdS and equilateral triangular PbS nanocrystallites grown under arachidic acid Langmuir monolayers.<sup>13,14</sup> Moreover, the same bifurcations or branchlike patterns still can be observed after half a year. It shows that the films keep relatively stable after the fractal-like growth structure is reorganized.

#### Conclusions

An amphiphilic oligomer as LB matrix used in the synthesis of CdS nanoparticles was introduced. CdS nanoparticles were grown and reorganized in this LB matrix and formed a twodimensional irreversible morphological multibifurcation. We analyzed the structural images of CdS nanoparticles in the oligomer matrixes by TEM and proposed an explanation on understanding the relationship between morphological structures and the formation of fractal patterns.

These kinds of amphiphilic oligomers could be used to build different fractal patterns directly through changing the ratio between carboxylic groups and hydrocarbon chains, the degree of oligomer's polymerization, and the surface pressure. The wide variety of possible patterns presents an opportunity for future molecular design of synthesis of organized organic/ inorganic heterostructured materials.

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