

## Controlled Growth of Micropatterned, Oriented Calcite Films on a Self-Assembled Multilayer Film

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A micropatterned multilayer film, which was fabricated from layer-by-layer electrostatic self-assembly of nitrodiazo-resin (NDR)/poly(acrylic acid) (PAA) followed by photolithography, was utilized as a structured template for the biomimetic mineralization of calcium carbonate. Micropatterned  $\text{CaCO}_3$  films consisting of regularly aligned calcite crystals oriented in the  $\langle 104 \rangle$  direction were selectively deposited on the patterned NDR/PAA multilayer film.

### Introduction

It is well-known that biomineralization is an elaborate process that produces biominerals with complex and fascinating morphologies as well as superior mechanical properties. It has inspired materials scientists to investigate how biomineralization occurs and to exploit the basic principles to biomimetically synthesize advanced materials, which usually involve the use of appropriate organic templates and/or additives to manipulate the size, shape, polymorph, and organization of inorganic materials.<sup>1,2</sup> In particular, there have been extensive studies of the crystallization of  $\text{CaCO}_3$ , one of the most abundant biominerals, by using bioinspired methods.<sup>3</sup> For controlled  $\text{CaCO}_3$  crystallization in solution, crystal growth modifiers<sup>4</sup> and structured three-dimensional (3D) templates or reaction fields<sup>5</sup> have been widely used. On the other hand, a variety of structured two-dimensional (2D) organic surfaces, such as Langmuir monolayers,<sup>6</sup> self-assembled monolayers (SAMs),<sup>7–9</sup> fatty acid bilayer stacks,<sup>10</sup> and polysaccharide thin films,<sup>11</sup> have been used as templates for the controlled growth of  $\text{CaCO}_3$  crystals or films. Notably, patterned SAMs have been successfully used for the formation of ordered calcite crystal arrays,<sup>7a,b</sup> patterned calcite single crystals,<sup>7c</sup> patterned calcite,<sup>7d</sup> or vaterite<sup>9</sup> films. However, the structural variety of the 2D

templates previously used for  $\text{CaCO}_3$  crystallization is still limited and it remains a great challenge to develop new 2D organic templates. Herein, ordered polyelectrolyte multilayer film fabricated via layer-by-layer (LbL) self-assembly was utilized as an effective template for the patterned crystallization of calcite films.

The LbL assembly method has proved to be one promising technique for constructing ultrathin composite films with tailored structures because of the simple and convenient regulation of the architecture of the film and the introduction of functional components.<sup>12</sup> In particular, LbL polyelectrolyte multilayer films have been used as nanoreactors for the in situ preparation of metal and semiconductor nanoparticles<sup>13</sup> or as seeding layers for the controlled crystallization of  $\text{FeOOH}$  nanocrystallites.<sup>14</sup> It is noteworthy that a polyelectrolyte multilayer has been used as a preformed matrix for electrochemical deposition of gold clusters to produce a super-hydrophobic surface.<sup>15</sup> Recently, a novel technique was developed to fabricate patterned DR/PAA multilayer films via LbL electrostatic self-assembly of photosensitive polycationic diazo-resin (DR) and polyanionic poly(acrylic acid) (PAA), followed by selective photolithography through photomasks.<sup>16</sup> By using a similar strategy, we fabricated micropatterns of nitrodiazo-resin (NDR)/inorganic nanoparticles multilayer film.<sup>17</sup> In this work, micropatterned NDR/PAA multilayer film was further used as a template for the selective deposition of unique, patterned calcite films consisting of densely aligned rhombohedral crystals predominantly oriented in the  $\langle 104 \rangle$  direction. To the best of our knowledge, this is the first report of utilizing patterned polyelectrolyte multilayer film as a structured template for the controlled crystallization of inorganic minerals.

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- (1) Mann, S. *Biomaterialization: principles and concepts in bioinorganic materials chemistry*; Oxford University Press, New York, 2001.  
 (2) (a) Cölfen, H.; Mann, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2350. (b) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980.  
 (3) (a) Kato, T.; Sugawara, A.; Hosoda, N. *Adv. Mater.* **2002**, *14*, 869. (b) Cölfen, H. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 23.  
 (4) (a) Cölfen, H.; Qi, L. *Chem.—Eur. J.* **2001**, *7*, 106. (b) Estroff, L. A.; Incarvito, C. D.; Hamilton, A. D. *J. Am. Chem. Soc.* **2004**, *126*, 2.  
 (5) (a) Qi, L.; Li, J.; Ma, J. *Adv. Mater.* **2002**, *14*, 300. (b) Li, M.; Lebeau, B.; Mann, S. *Adv. Mater.* **2003**, *15*, 2032.  
 (6) Xu, G. F.; Yao, N.; Aksay, I. A.; Groves, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 11977.  
 (7) (a) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1999**, *398*, 495. (b) Aizenberg, J. *J. Cryst. Growth* **2000**, *211*, 143. (c) Aizenberg, J.; Muller, D. A.; Grazul, J. L.; Hamann, D. R. *Science* **2003**, *299*, 1205. (d) Han, Y.-J.; Aizenberg, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3668.  
 (8) Travaille, A.; Kaptijn, L.; Verwer, P.; Hulskens, B.; Elemans, J.; Nolte, R.; van Kempen, H. *J. Am. Chem. Soc.* **2003**, *125*, 11571.  
 (9) Lee, I.; Han, S. W.; Lee, S. J.; Choi, H. J.; Kim, K. *Adv. Mater.* **2002**, *14*, 1640.  
 (10) Damle, C.; Kumar, A.; Sainkar, S. R.; Bhagawat, M.; Sastry, M. *Langmuir* **2002**, *18*, 6075.  
 (11) (a) Sugawara, A.; Kato, T. *Chem. Commun.* **2000**, 487. (b) Sugawara, A.; Ishii, T.; Kato, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 5299.

- (12) Decher, G. *Science* **1997**, *277*, 1232.  
 (13) (a) Joly, S.; Kane, R.; Radzilowski, L.; Wang, T.; Cohen, R. E.; Thomas, E. L.; Rubner, M. F. *Langmuir* **2000**, *16*, 1354. (b) Wang, T. C.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2002**, *18*, 3370.  
 (14) (a) Dante, S.; Hou, Z.; Risbud, S.; Stroeve, P. *Langmuir* **1999**, *15*, 2176. (b) Dutta, A. K.; Jarero, G.; Zhang, L.; Stroeve, P. *Chem. Mater.* **2000**, *12*, 176.  
 (15) Zhang, X.; Shi, F.; Yu, X.; Liu, H.; Fu, Y.; Wang, Z.; Jiang, L.; Li, X. *J. Am. Chem. Soc.* **2004**, *126*, 3064.  
 (16) Shi, F.; Dong, B.; Qiu, D.; Sun, J. Q.; Wu, T.; Zhang, X. *Adv. Mater.* **2002**, *14*, 805.  
 (17) (a) Lu, C.; Wu, N.; Jiao, X.; Luo, C.; Cao, W. *Chem. Commun.* **2003**, 1056. (b) Lu, C.; Wu, N.; Wei, F.; Zhao, X.; Jiao, X.; Xu, J.; Luo, C.; Cao, W. *Adv. Funct. Mater.* **2003**, *13*, 548. (c) Lu, C.; Wei, F.; Wu, N.; Zhao, X.; Jiao, X.; Luo, C.; Cao, W. *Langmuir* **2004**, *20*, 974.

## Experimental Section

**Fabrication of the Micropatterned NDR/PAA Multilayer Film.** Micropatterned, six-bilayer NDR/PAA film, denoted as (NDR/PAA)<sub>6</sub>, exhibiting an outer PAA layer was generated on a modified silicon wafer substrate via LbL electrostatic self-assembly of NDR and PAA following the literature.<sup>16,17</sup> The silicon wafer substrate, pretreated in a boiling mixture of H<sub>2</sub>O<sub>2</sub> (30%)–H<sub>2</sub>SO<sub>4</sub> (98%) with a volume ratio of 3:7 for 0.5 h, was alternately dipped into aqueous solutions of NDR (0.5 mg/mL) and PAA (*M<sub>n</sub>* ~ 5100, 1 mg/mL, pH ~ 7) for 10 min, respectively, with the interruption of deionized water rinsing and cool air drying. After repetition of the procedure for *n* times in the dark, a composite multilayer film was formed with *n* bilayers of NDR/PAA on both sides of the substrate. In this work, six bilayers were selected, since relatively even films can be facily formed for such a film thickness. The resulting NDR/PAA assembled films were selectively exposed to 360 nm UV light (3 mW/cm<sup>2</sup>, 2 min) through a photomask having different resolution images. After being developed in sodium dodecyl sulfate (SDS) aqueous solution (0.25 M) for 2 h at room temperature (~25 °C) in the dark, the patterned film was sonicated in deionized water for 1 min and cleaned thoroughly by deionized water.

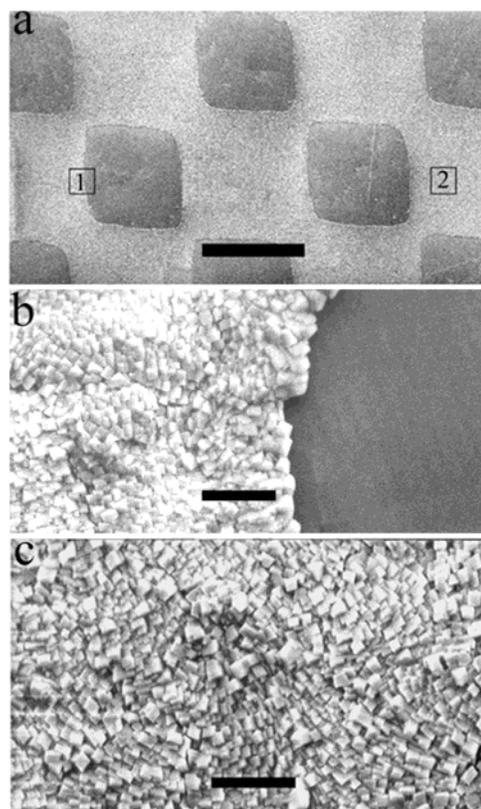
**Selective Deposition of CaCO<sub>3</sub> on the Micropatterned Film.** At room temperature, the template of the micropatterned (NDR/PAA)<sub>6</sub> film was upside-down-dipped in a mixed solution of 10 mM CaCl<sub>2</sub> and 40 μg/mL PAA (pH ~ 10) in a closed desiccator containing a vial of ammonium carbonate, with carbon dioxide from the decomposition of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> diffusing into the solution to induce the nucleation of CaCO<sub>3</sub>. The overgrown specimens were then slightly rinsed in deionized water and dried naturally.

**Characterization of CaCO<sub>3</sub> Deposited on the Micropatterned Film.** The as-prepared CaCO<sub>3</sub> on the polyelectrolyte multilayer film, supported on the silicon wafer substrate, was characterized with scanning electron microscopy (SEM, AMERY 1900, 10 kV), an X-ray diffractometer (Rigaku Dmax-2000) operating at 40 kV, and at a current of 100 mA with Cu Kα radiation. The infrared spectra of the sample were recorded on a Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer.

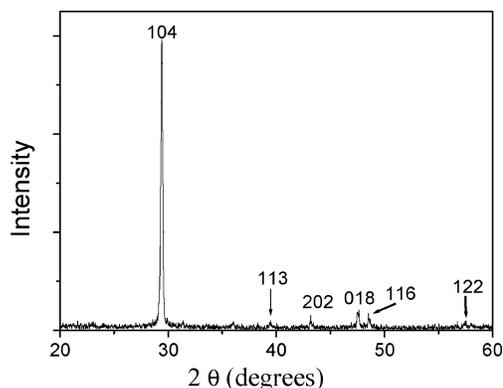
## Results and Discussion

Figure 1 shows representative scanning electron microscopy (SEM) images of as-deposited CaCO<sub>3</sub> film on the micropatterned (NDR/PAA)<sub>6</sub> film. An overview shown in Figure 1a suggests that CaCO<sub>3</sub> crystals are selectively deposited on the carboxylate-terminated NDR/PAA multilayer surface and the resultant large-area interconnected CaCO<sub>3</sub> film almost replicates the underlying micropatterned organic template. A high-magnification image showing the edge of the crystallized CaCO<sub>3</sub> film (Figure 1b) demonstrates that no CaCO<sub>3</sub> crystals are deposited on the exposed silicon substrate. Although the size and orientation of the primary crystals are not uniform for the boundary region possibly due to an edge effect, the inner region of the continuous CaCO<sub>3</sub> film consists of primary crystals with relatively uniform size and orientation. As shown in Figure 1c, the inner part of the continuous CaCO<sub>3</sub> film is rather even and consists of densely aligned primary crystals that are apparently arrayed radially from some centers, indicating the presence of some preferential nucleation sites during the formation of the film. Furthermore, the primary CaCO<sub>3</sub> crystals are relatively uniform in size (typically 0.2–0.4 μm) and exhibit a rhombohedral morphology typical for calcite, the most stable polymorph of CaCO<sub>3</sub>. Moreover, the rhombohedral crystals are predominantly oriented in the <104> crystallographic direction, indicating the formation of a <104>-oriented calcite film. The X-ray diffraction (XRD) pattern of the as-deposited CaCO<sub>3</sub> film is shown in Figure 2, which exhibits sharp peaks characteristic of calcite with the (104) reflection intensified significantly, confirming the formation of the calcite film oriented in

## Results and Discussion



**Figure 1.** SEM images of interconnected CaCO<sub>3</sub> film grown on the micropatterned (NDR/PAA)<sub>6</sub> film. Parts b and c represent enlarged images of framed areas 1 and 2, respectively, in part a. Scale bars: (a) 100 μm; (b and c) 2 μm.



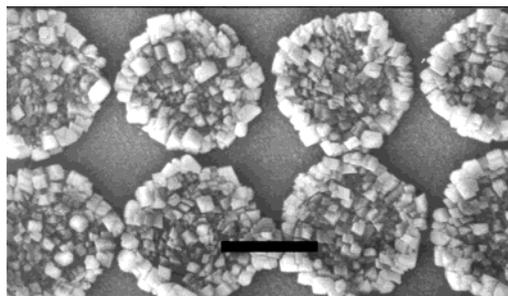
**Figure 2.** XRD pattern of interconnected CaCO<sub>3</sub> film grown on the micropatterned (NDR/PAA)<sub>6</sub> film.

the <104> direction. The related infrared (IR) spectrum of the CaCO<sub>3</sub> film shows absorption bands at 714 and 876 cm<sup>-1</sup>, providing further support for the pure calcite habit of the crystalline film.<sup>4a</sup>

It has been previously demonstrated that calcite nucleation occurs most readily on the COOH-terminated surface and localized crystallization on patterned SAMs can be realized due to diffusion-controlled nucleation.<sup>7a,b</sup> Therefore, it is reasonable that the current crystallization of CaCO<sub>3</sub> is entirely restricted to the micropatterned carboxylate-terminated NDR/PAA multilayer film exhibiting an outer PAA layer and does not occur on the region of the bare silicon substrate under the similar conditions of diffusion-controlled nucleation (Figure 1b). It is noted that patterned calcite films on micropatterned SAMs were fabricated by patterning rapidly nucleating regions (car-

boxylate-terminated SAMs) in regions that are slowly nucleating (methyl-terminated SAMs).<sup>7b</sup> However, the obtained calcite films consisted of irregularly sized calcite crystals (as large as several micrometers) and did not look very dense. Moreover, only  $\langle 012 \rangle$ - or  $\langle 015 \rangle$ -oriented calcite films were obtained, since carboxylate-terminated SAMs on Ag or Au substrate specifically induced calcite nucleation from the (012) and (015) planes, respectively.<sup>7a,b</sup> In the present case, the patterned  $\langle 104 \rangle$ -oriented calcite film could result from the enhanced structural flexibility of the LbL multilayers. It has been suggested that more fluid Langmuir monolayers have the ability to rearrange to accommodate and stabilize nucleating or growing crystals,<sup>18</sup> indicating the potential advantages of relatively flexible templates in directing inorganic mineralization compared with rigid templates. Hence, compared with SAMs showing relatively rigid architecture on metal substrates, self-assembled multilayer films may provide relatively flexible structures that can be used as effective templates for biomimetic mineralization of  $\text{CaCO}_3$  thin films. It is noted that SAMs have been used to create unique patterned calcite single crystals with a resolution below  $10 \mu\text{m}$ ; however, the structural variety of the calcite crystals/films remains to be extended. In the present work, novel micropatterned calcite films consisting of densely aligned rhombohedral crystals that predominantly oriented in the  $\langle 104 \rangle$  direction were created under the direction of patterned LbL films, indicating that the LbL films may represent a useful addition to the reported 2D organic templates.

It is noteworthy that the presence of PAA in the  $\text{CaCl}_2$  solution plays a key role in the formation of the patterned, continuous calcite film on the template. In the absence of PAA, only discrete and segregated calcite crystals were grown on the patterned multilayer surface. It may be rationalized by considering that the soluble PAA can promote preferential nucleation on the patterned template over nucleation in the solution and prevent crystal growing in the direction normal to the template, which has been previously proposed for the formation of continuous  $\text{CaCO}_3$  films at a porphyrin template/subphase interface<sup>6</sup> and for the formation of patterned  $\text{CaCO}_3$  films on a thin matrix of hydrophobically modified polysaccharide<sup>11b</sup> by using PAA as a soluble inhibitor. Interestingly, patterned  $\text{CaCO}_3$  films of vaterite polymorph have been prepared on patterned SAMs on a gold substrate by



**Figure 3.** SEM image of isolated islands of  $\text{CaCO}_3$  films grown on the micropatterned (NDR/PAA)<sub>6</sub> film produced from a photoresist mask with a higher resolution. Scale bar:  $5 \mu\text{m}$ .

employing carboxylate-terminated gold nanoparticles as nucleation initiators.<sup>9</sup> It may be also possible to induce patterned  $\text{CaCO}_3$  films of polymorphs other than calcite on self-assembled multilayer films by using suitable initiators.

Furthermore, it was found that isolated regular islands of oriented calcite films could be produced by using a discontinuously patterned NDR/PAA multilayer film. As shown in Figure 3, isolated calcite islands were produced when a patterned (NDR/PAA)<sub>6</sub> film fabricated from a photoresist mask with a higher resolution was used as the template. However, the size of the deposited calcite crystals appeared larger on average on the edge of the round features than in the center, which could also be attributed to the edge effect, leading to a considerably decreased uniformity in the size and arrangement of the primary calcite crystals of the segregated films.

### Conclusions

In summary, LbL self-assembled multilayer films with a PAA surface layer have been used, for the first time, as templates for the controlled growth of micropatterned,  $\langle 104 \rangle$ -oriented calcite films. As flexible templates with readily tailored architectures, self-assembled multilayer films may show a great potential in the study of biomineralization as well as in the biomimetic construction of advanced inorganic/composite materials with high performance.

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(18) (a) Cooper, S. J.; Sessions, R. B.; Lukbetkin, S. D. *J. Am. Chem. Soc.* **1998**, *120*, 2090. (b) Backov, R.; Lee, C. M.; Khan, S. R.; Mingotaud, C.; Fanucci, G. E.; Talham, D. R. *Langmuir* **2000**, *16*, 6013. (c) Volkmer, D.; Fricke, M.; Vollhardt, D.; Siegel, S. *J. Chem. Soc., Dalton Trans.* **2002**, *24*, 4547.