Triply Periodic Bicontinuous Structures as Templates for Photonic Crystals: A Pinch-off Problem**

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Triply periodic bicontinuous structures, such as simple cubic (P), gyroid (G), and diamond (D), are of great interest as 3D photonic crystals because they possess wide, complete photonic bandgaps (PBGs).[1–3] To fabricate these 3D microstructures various methods, including microphase separation by block copolymers,[4–6] multibeam interference lithography,[6–9] and phase-mask lithography,[9] have been studied. However, the low refractive index of the patterned materials has limited their application as photonic crystals with complete PBGs. The minimum required refractive-index contrast to open a bandgap is 2.8 for P (Pm3m), 1.9 for G (I4132), and 1.8 for D (Fd3m).[2] One possible solution is to use the bicontinuous structures above as templates, and backfill one of the continuous networks with high-refractive-index materials[10] followed by removal of the template to obtain inverted replicas.[11,12] High-index materials, such as titania,[10] selenium,[11] cadmium–selenium,[11] amorphous silicon,[11,12] and germanium,[16,17] have been deposited through dry processes, including chemical vapor deposition (CVD)[14–17] and melting,[13] and wet chemistry, for example, liquid-phase sol–gel reaction and precipitation.[18,19] Typically, a conformal shell is formed and fills the interstitial voids by continuously growing normal to the initial surface (see Fig. S1 in the Supporting Information).[11,12]

However, previous studies on templating holographically patterned structures, including silica and silicon replicas of a diamondlike structure through CVD[12] and an inverse titania structure by atomic layer deposition (ALD).[11] suggest that it is challenging to completely fill the triply periodic templates. This is because the pore sizes are not uniform within the structure, where the “atoms” at lattice points of the corresponding structure are connected by “bridges” to their nearest neighbors. As the inorganic layer grows conformally and continuously over the template surface, the surface of the pore network pinches off (i.e., disconnects) at the narrowest pore channels before the interstitial voids are completely filled (see Fig. S1), resulting in the loss of PBGs.[12] The question remains whether or not pinch-off is a general behavior in the backfilling of triply periodic bicontinuous structures. If so, obtaining a quantitative expression for the pinch-off problem and establishing how it may impact the achievable PBGs are essential for optimizing the fabrication process.

To this end, two level surfaces were used to approximate the surfaces of D, P, or G templates and the grown layer, respectively. Specifically, we constructed a combined level surface by using tubular level surfaces,[20] which provided a simple and explicit expression of the parallel surfaces from the template, and much-improved coating uniformity in comparison with the two-parameter, level-set approach we developed earlier.[12] By searching for the pinch-off level surfaces for the grown layers, we calculated the achievable volume fraction and the PBGs at the pinch-off. It was shown that D and G templates could not be completely filled through a conformal coating approach (e.g., CVD process), resulting in narrower PBG values compared with the ideal value while in the P structure the achievable filling fraction was too low to open the bandgap. To solve this pinch-off problem, resulting from conformal growth of the shell layer, we suggest a bottom-up approach by using electrophoretic deposition. We experimentally demonstrate the fabrication of a nearly completely filled, inverse titania, diamondlike photonic crystal.

The intermaterial dividing surfaces in self-organizing systems have been approximated by the level surfaces of trigonometric functions.[21] In interference or phase-mask lithography, the intensity distribution of exposed light is directly expressed by the superposition of trigonometric functions.[22]
The D (Fd3m), P (Pm3m), and G (I4132) structures can be described by the level surfaces as: 

\[
F_D = \sin(x + y + z) + \sin(x - y + z) + \sin(x + y - z) + \sin(-x + y + z) = t_1
\]  

(1)

\[
F_P = \sin(x) + \sin(y) + \sin(z) = t_1
\]  

(2)

\[
F_G = \sin(x + y) + \sin(x - y) + \sin(y + z) + \sin(y - z) + \sin(z + x) + \sin(z - x) = t_1
\]  

(3)

where \(t_1\) is the threshold intensity. Figure 1a and Figure 2a and d show the level surfaces of D, P, and G at \(t_1\) values of 1.24, 0.84, and 2.0, respectively. These correspond to inside-volume fractions of 0.25, 0.26, and 0.17, respectively. At these values, D and G possess the maximum PBG width between the 2nd and 3rd bands, and P between the 5th and 6th bands. These volume fractions at the maximum PBG width are in agreement with previous calculations. To fabricate these structures, templates with air networks were generated (see Fig. 1a and Fig. 2a and d), followed by backfilling with high-index materials.

In general, the volume enclosed by a level surface decreases with an increase of the threshold intensity. At a sufficiently large \(t_1\), the level surface begins to form isolated domains (“pinches off”) at symmetry points. In case of a D structure, the level surface pinched off at \(t_1 = 2.0\) (Fig. 1b). Although we showed promise in predicting the PBG properties of incompletely filled structures by varying the threshold value \(t_1\) using a two-parameter level surface, a closer look of molded surfaces at different \(t_1\) values suggested that they were indeed not parallel to the original level surface of the template (Fig. 1c). The pinch-off region showed a thicker layer than the other regions. Specifically, the region where the magnitude of Gaussian curvature was minimal showed the thickest layer, and the layer thickness decreased as the curvature magnitude increased to a maximum. This deviation may be attributable to the characteristics of the level surface, because the threshold value is not related to the constant distance from a template but to the volume fraction.

Meanwhile, the real morphology of the deposited layer can be affected by various factors, including surface diffusion, the surface tension of the deposited materials, and the surface curvature. Because the formation of a solid phase occurs rather quickly during deposition, we assume that restructuring of the deposited shell to a lower surface energy might be restricted. Therefore, constructing a parallel surface would give a reasonable approximation of the grown layer. It has been demonstrated that the superposition of two simple level surfaces, including P, G, D, and I-WP (Im3m), controls pinch-off behavior of triply periodic minimal surfaces while maintaining the structure symmetry. Here, we adapted this approach by using combination level surfaces of D, P, and G, which were modified by the addition of P, I-WP, and I-WP, respectively, to closely model the parallel grown layer shown in the back infiltration experiment as

\[
G_D = F_D - c(\cos(4x) + \cos(4y) + \cos(4z)) = t_2
\]  

(4)

\[
G_P = F_P - c(\sin(x) \sin(y) + \sin(y) \sin(z) + \sin(z) \sin(x)) = t_2
\]  

(5)

\[
G_G = F_G - c(\cos(2x) \cos(2y) + \cos(2y) \cos(2z) + \cos(2z) \cos(2x)) = t_2
\]  

(6)

where the threshold value \(t_2\) changes the volume (or roughly the distance from the template) enclosed by these level surfaces, and the coefficient \(c\) determines the morphology. Increasing \(c\) leads to more tubular networks. To find \(t_2\) and \(c\) for...
each level surface, we varied \( t_2 \) and optimized \( c \) until reaching the lowest standard deviation in average distance from the template surface. For the D structure, the level surface was estimated as \( c = 0.125 \) and \( t_2 = 2.375 \) at the pinch-off (Fig. 1d). The cross section of the (11\bar{0}) plane that combines the level surfaces shown in Figure 1a and d appeared to be more uniform (Fig. 1e) compared with that shown in Figure 1c. The uniformity was quantitatively evaluated by calculating the standard deviation of the distance from the template surface of a thousand points on each level surface, and was substantially lowered from 0.404 (Fig. 1c) to 0.028 (Fig. 1e) based on a lattice distance of \( 2\pi \). At the pinch-off, the shell structure enclosed by the level surface in Figure 1a and d (black layer) possessed a volume fraction of 0.21. This value is higher than 0.18, which was obtained from using two \( t_1 \) values to construct the level surface (Fig. 1a and c).

Likewise, \( t_2 \) and \( c \) at the pinch-off were examined for P (Fig. 2b) and G (Fig. 2e). Figure 2b shows the combination level surface of P (Eq. 5) with \( c = 0.35 \) and \( t_2 = 1.35 \). In the cross-sectional (11\bar{0}) plane of the P structure (Fig. 2c) the shell structure (black layer) is defined by two level surfaces in Figure 2a and b. The volume fraction of this shell structure was estimated as ca. 0.14, which was half of the maximum filling fraction, 0.26. Meanwhile, the combination level surface of G is shown in Figure 2e, and the parameters of Equation 6 were calculated to be \( c = 0.15 \) and \( t_2 = 2.97 \) at the pinch-off. Figure 2f shows a cross section of the (210) plane of G, and the shell structure is defined by two level surfaces shown in Figure 2d and e. The volume fraction of this shell structure was found to be 0.17, close to the maximum filling fraction. The parameters \( c \) and \( t_2 \), the standard deviation from parallel surfaces, and the possible filling fractions for the D, P, and G structures are summarized in Table 1.

<table>
<thead>
<tr>
<th>Level surface</th>
<th>( c, t_2 )</th>
<th>Standard deviation [a]</th>
<th>Volume fraction at the pinch-off (c.f., complete filling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>0.125, 2.375</td>
<td>0.028</td>
<td>0.21 (0.25)</td>
</tr>
<tr>
<td>P</td>
<td>0.350, 1.350</td>
<td>0.035</td>
<td>0.14 (0.26)</td>
</tr>
<tr>
<td>G</td>
<td>0.150, 2.970</td>
<td>0.034</td>
<td>ca. 0.17 (0.17)</td>
</tr>
</tbody>
</table>

[a] Lattice distance, \( 2\pi \).

Finally, the PBG of such a constructed triply periodic dielectric shell with a refractive index of 3.6 was calculated by using the Massachusetts Institute of Technology’s photonic bands (MPB) software package. As exemplified in the diamond (D) structures, the dielectric shell defined by Equations 1 and 4 were employed for calculations. Figure 3a shows the normalized frequency range of complete PBGs between the 2nd and 3rd bands at different filling fraction. The volume fraction of the shell with uniform thickness was controlled by the threshold parameter \( t_2 \) with optimized coefficient \( c \). The calculation was achieved up to the filling volume fraction at the pinch-off. The width of the bandgap increased with the filling fraction. At the pinch-off point, the PBG was in the range 0.50–0.61, with a gap/mid-gap ratio \( \Delta\omega/\omega_0 = 0.19 \), which was 77 % of the maximum achievable bandgap (\( \Delta\omega/\omega_0 = 0.25 \), marked with an asterisk in Fig. 3a). In parallel, we investigated the band frequencies of the dielectric shell using the same level surface with different \( t_1 \) values. The ranges of the frequencies and the band diagram were found to be similar to each other at the same filling fraction. This implies that the PBG property is less sensitive to the morphology of the dielectric shell than the volume fraction. When we applied the same approach to calculate PBGs of the deposited dielectric \( \mu = 3.6 \) on a P template, no complete bandgap between the 5th and 6th bands was observed owing to the low filling fraction. Whereas in the case of a G template, the PBG was found in the range 0.43–0.56 with a gap/mid-gap ratio \( \Delta\omega/\omega_0 = 0.24 \) at the pinch-off, which was 98 % of the maximum value of the complete PBG (marked by an asterisk in Fig. 3b).

To validate the model that approximates the grown layers using a parallel surface and investigate the effect of incomplete filling on the photonic bandgap properties, we chose a three-term diamondlike structure, which has a similar symme-

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**Figure 3.** The normalized maximum and minimum frequencies of complete PBGs between 2nd and 3rd bands for a) D and b) G structures. Solid and dotted lines represent the frequencies obtained by using either the same level surfaces or the combination level surface for the grown layer, respectively. The frequencies of complete PBGs for completely filled structure are indicated by asterisks.
try to the four-term diamond D structure. More importantly, both the polymer template and its inorganic replica of the three-term diamondlike structures can be fabricated rather conveniently by holographic patterning. By contrast to the fabrication of P, G, and D structures. As seen in Figure S1, a conformal growth of silica parallel to the polymer template led to pinch-off of the network. By using the previously developed two-parameter level surface we found that the pinch-off occurred at a filling fraction of 20%, resulting in no complete photonic bandgap between the 2nd and 3rd bands (Fig. S2). While searching for an appropriate parallel level surface of the diamondlike structure to more accurately study the pinch-off characteristics, we found that a simple combination of a diamondlike level surface with a P level surface, in the same manner as we did with D structure, did not represent a parallel surface of the diamondlike structure. Thus, we constructed the surface at the pinch-off by the points with the same distance from the template surface. By analyzing the cross-sectional image, the volume fraction of the shell at the pinch-off was approximated as 30%, corresponding to ca. 75% of the complete filling and half of maximum achievable bandgap width (ca. 5.3%) considering that the bandgap was mainly determined by the volume fraction.

Clearly, the investigated triply periodic bicontinuous template cannot be completely filled by conformal coating, resulting in the loss of PBG properties. To solve the pinch-off problem, here, we attempted a bottom-up approach by electrostatic controls the volume fraction, we increased $t_2$ to have the smallest deviation from the parallel surface. In general, the increase of $t_2$ enhanced the pinching-off and, by contrast, the increase of $c$ released it. Therefore, we evaluated the deviation as increasing $c$ at a certain $t_2$ value. Meanwhile, because the combination level surface passed the pinch-off point, we used this condition to find the $c$ value at the pinching-off. For the PBG calculation, we constructed a dielectric shell having a refractive index of 3.6 by using these two level surfaces and directly applied them to calculate the PBG using the MPB software package. We also calculated the PBGs of the shell structure defined by the same level surfaces with different $t_2$ values in Equations 1–3.

**Experimental**

**Combination Level Surface and Photonic Bandgap Calculation:**

The shell structure during the conformal deposition was constructed by the level surface (Eqs. 1–3) and the combination level surface (Eqs. 4–6). Because the threshold value $t_2$ in the level surface monotonically controls the volume fraction, we increased $t_2$ and optimized $c$ to have the smallest deviation from the parallel surface. In general, the increase of $t_2$ enhanced the pinching-off and, by contrast, the increase of $c$ released it. Therefore, we evaluated the deviation as increasing $c$ at a certain $t_2$ value. Meanwhile, because the combination level surface passed the pinch-off point, we used this condition to find the $c$ value at the pinching-off. For the PBG calculation, we constructed a dielectric shell having a refractive index of 3.6 by using these two level surfaces and directly applied them to calculate the PBGs using the MPB software package. We also calculated the PBGs of the shell structure defined by the same level surfaces with different $t_2$ values in Equations 1–3.

**Electrodeposition of Titania:**

We fabricated a 3D polymer template from SU8 resist (D) on ITO glass, followed by the deposition of titania nanoparticles. A conventional three-electrode cell was used for the cathodic electrodeposition of titania [30,31]. Briefly, the titania precursor was prepared by dissolving hydrolyzed titania in 2 M H$_2$SO$_4$ solution, and the pH of the solution was adjusted to 2–3. The potentiostatic conditions were controlled with potential range from –1.0 to –1.3 V. After deposition, the sample was annealed at 500 °C to form anatase titania, which was verified by XRD.

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