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,[4,5] multibeam interference lithography,[6–8] 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 ($Pm\bar{3}m$), 1.9 for G ($I4_132$), and 1.8 for D ($Fd\bar{3}m$).[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,[13] cadmium–selenium,[13] amorphous silicon,[14,15] 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]

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The D ($Fd\bar{3}m$), P ($Pm\bar{3}m$), and G ($I4_132$) structures can be described by the level surfaces as[21]

$$F_D = \sin(x+y+z) + \sin(x-y+z) + \sin(x+y-z)$$
$$+ \sin(-x+y+z) = t_1 \qquad (1)$$

$$F_P = \sin(x) + \sin(y) + \sin(z) = t_1 \qquad (2)$$

$$F_G = \sin(x+y) + \sin(x-y) + \sin(y+z) + \sin(y-z)$$
$$+ \sin(z+x) + \sin(z-x) = t_1 \qquad (3)$$

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.[2] 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,[23] a closer look of modeled 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
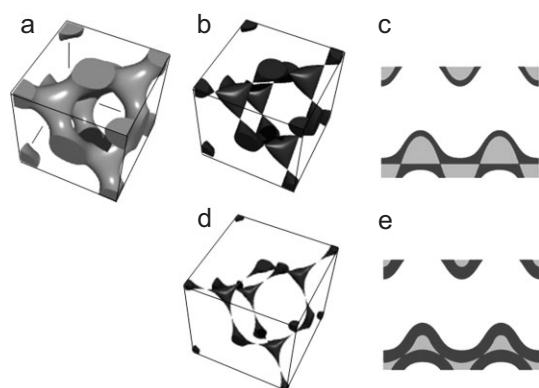
Figure 1. a) Level surface of a diamond (D) structure with $t_1 = 1.24$ in Eq. 1. The enclosed volume represents air networks inside the template. b,d) The pinch-off level surface with $t_1 = 2.0$ in Eq. 1, and $c = 0.125$ and $t_2 = 2.375$ in Eq. 4, respectively, which represents unfilled air voids. c,e) ($1\bar{1}0$) cross-sectional images of two level surfaces in (a,b) and (a,d), respectively. The black and grey regions represent the deposited layers and unfilled air voids, respectively.
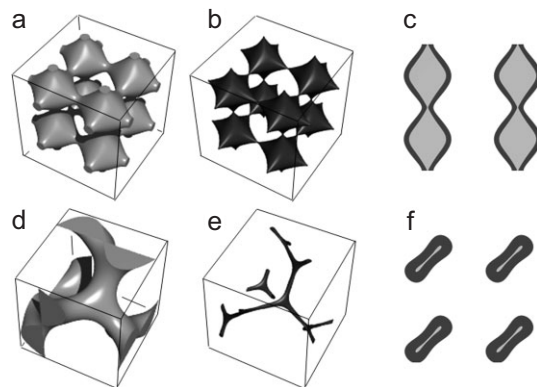
Figure 2. a) Level surface of a simple cubic (P) structure with $t_1 = 0.84$ in Eq. 2. The enclosed volume represents air networks inside the template. b) Combination level surface with $c = 0.35$ and $t_2 = 1.35$ at the pinch-off in Eq. 5, which represents unfilled air voids. c) ($1\bar{1}0$) cross-sectional images of two level surfaces of the P structure shown in (a,b). d) Level surface of a gyroid G structure with $t_1 = 2.0$ at the pinch-off in Eq. 3. The enclosed volume represents air networks inside the template. e) Combination level surface of G with $c = 0.15$ and $t_2 = 2.97$ in Eq. 6, which represents unfilled air voids. f) (210) cross-sectional images of two level surfaces of G structure shown in (d) and (e). The black and gray regions in (c) and (f) represent the deposited layers and unfilled air voids, respectively.

increased to a maximum.[24] 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.[21]

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.[25] 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 ($Im\bar{3}m$), controls pinch-off behavior of triply periodic minimal surfaces while maintaining the structure symmetry.[20] Here, we adapted this approach by using combination level surfaces[26] of D, P, and G, which were modified by the addition of P, I-WP, and I-WP, respectively,[20] to closely model the parallel grown layer shown in the back infiltration experiment as

$$G_D = F_D - c(\cos(4x) + \cos(4y) + \cos(4z)) = t_2 \qquad (4)$$

$$G_P = F_P - c(\sin(x)\sin(y) + \sin(y)\sin(z) + \sin(z)\sin(x)) = t_2 \qquad (5)$$

$$G_G = F_G - c(\cos(2x)\cos(2y) + \cos(2y)\cos(2z)$$
$$+ \cos(2z)\cos(2x)) = t_2 \qquad (6)$$

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 $(1\bar{1}0)$ 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 2π. 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).
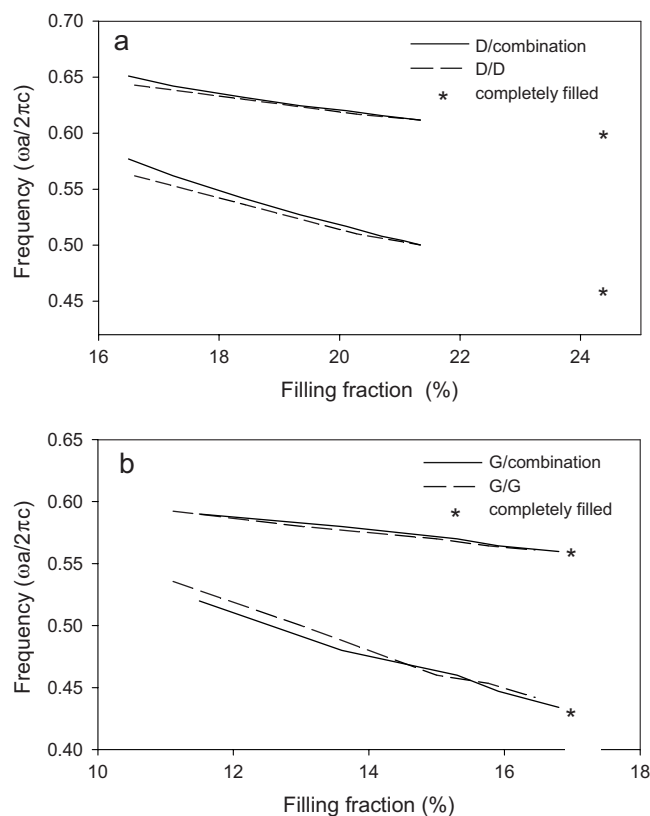
Likewise, t_2 and c at the pinch-off were examined for P (Fig. 2b) and G (Fig. 2e). Figure 2b shows the combination level surface of P (Eq. 5) with $c = 0.35$ and $t_2 = 1.35$. In the cross-sectional $(1\bar{1}0)$ plane of the P structure (Fig. 2c) the shell structure (black layer) is defined by two 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.

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.

Table 1. Parameters c, t_2, the standard deviation from template surfaces, and the volume fraction at the pinch-off.

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

[a] Lattice distance, 2π.

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 $\Delta\omega/\omega_o = 0.19$, which was 77 % of the maximum achievable bandgap ($\Delta\omega/\omega_o = 0.25$, 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 ($n = 3.6$) 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 $\Delta\omega/\omega_o = 0.24$ 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-

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,[12] in 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.[12] 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 electrophoretic deposition of titania nanoparticles into the three-termed diamondlike template. This approach has been applied to deposit a variety of materials, including metals, semiconductors, and oxides,[27–29] on 1D and 2D templates. During the deposition, the positively charged TiO_2 nanoparticles were attracted to the negatively charged indium tin oxide (ITO) glass and gelled gradually from the substrate and filled the template.[30] As shown in cross-sectional scanning electron microscopy (SEM) image of the inverse titania structure, it is noticeable that the interstitial pores were nearly completely filled (see Fig. 4 versus Fig. S1)

In summary, we have analyzed the achievable deposition fraction from triply periodic templates due to the pinch-off

problem. To closely approximate the deposited layer on P, G, and D templates, we improved the uniformity of the level surface by using combination level surfaces. The pinch-off of the level surface was estimated and applied to calculate the PBG of the deposited structure. The achievable filling fractions at the pinch-off are 84% for D, 98% for G, and 54% for P templates, resulting in 77% for D and 98% for G of the corresponding maximum PBGs, respectively, while the bandgap does not open for P at the pinch-off filling fraction. In contrast to volume fraction, the bandgap frequencies are found less sensitive to the subtle morphology difference when using different level-set approaches to approximate the level surface of the deposited layer on template. This study provides a quantitative understanding of the PBG properties regarding the template-based fabrication of triply periodic photonic crystals. To validate the theoretical study, we showed the pinch-off of an inverse three-term diamondlike silica structure and approximated the achievable filling fraction. To address the pinch-off problem, we suggested a bottom-up approach using electrodeposition, which holds great promise to completely fill the interstitial voids in templates in comparison with the top-down conformal coating.

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 PBGs using the MPB software package. We also calculated the PBGs of the shell structure defined by the same level surfaces with different t_1 values in Equations 1–3.

Electrodeposition of Titania: We fabricated a 3D polymer template from SU8 resist [12] 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_2SO_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.
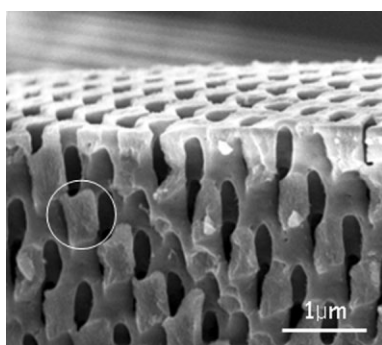
Figure 4. SEM image of an inverse diamondlike titania structure from electrodeposition on a polymer template, which was fabricated by holographic lithography. The circle highlights nearly completely filled air voids.

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