June 2007

Triply periodic bicontinuous structures as templates for photonic crystals: a pinch-off problem

Jun Hyuk Moon
University of Pennsylvania

Yongan Xu
University of Pennsylvania

Yaping Dan
University of Pennsylvania

Seung-Man Yang
Korea Advanced Institute of Science and Technology

Alan T. Johnson
University of Pennsylvania, cjohnson@physics.upenn.edu

See next page for additional authors

Postprint version. Published in *Advanced Materials*, Volume 19, Issue 11, June 2007, pages 1510-1514.
Publisher URL: http://dx.doi.org/10.1002/adma.200700147

Triply periodic bicontinuous structures as templates for photonic crystals: a pinch-off problem

Keywords
holography, network structures, photonic crystals, templates

Comments
Postprint version. Published in *Advanced Materials*, Volume 19, Issue 11, June 2007, pages 1510-1514.
Publisher URL: http://dx.doi.org/10.1002/adma.200700147

Author(s)
Jun Hyuk Moon, Yongan Xu, Yaping Dan, Seung-Man Yang, Alan T. Johnson, and Shu Yang

DOI: 10.1002/adma.200((Please insert last 6 DOI digits))

Triply periodic bicontinuous structures as templates for photonic crystals: a pinch-off problem **

*By Jun Hyuk Moon, Yongan Xu, Yaping Dan, Seung-Man Yang, Alan. T. Johnson, and Shu Yang**

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], multi-beam interference lithography[6-8], and phase-mask lithography[9] have been studied. The low refractive index of the patterned materials, however, 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($Pm\overline{3}m$), 1.9 for G($I4_132$), and 1.8 for D($Fd\overline{3}m$), respectively.[2] One possible solution is to use the above bicontinuous structures as templates and backfill with high refractive index materials,[10] followed by removal of the template to obtain inverted replica.[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 process, including chemical vapor deposition (CVD)[14-17] and melting,[13] and wet chemistry through liquid phase sol-gel reaction and precipitation.[18,19] Typically, a conformal shell is formed and grows continuously normal to the initial surface to fill the interstitial voids (Fig. S1).[11, 12]

Previous studies on templating holographically patterned structures, including silica and silicon replicas of a diamond-like structure through sequential CVD process[12] and an inversed titania structure by atomic layer deposition (ALD)[11], however, suggest that it is challenging to completely fill the triply periodic templates (see Fig. S2). It is because that 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 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. The question remains whether or not the pinch-off is a general behavior in backfilling of a triply periodic bicontinuous structures. If so, how to quantitatively express the pinching-off problem and how it may impact the achievable PBGs will be essential to the optimization of the fabrication process.

To this end, two level surfaces were used to approximate the surface of D, P, and G templates and the grown layer, respectively. Specifically, we constructed the combined level surface using tubular level surfaces,[20] which provided simple and explicit expression of the parallel surfaces from the template, and much improved coating uniformity in comparison to 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 conformal coating approach (e.g. CVD process), resulting in narrower PBG compared to the ideal value, while the achievable filling fraction was too low in P structure to open the bandgap. To solve this pinch-off problem as a result of conformal growth of the shell layer, we suggested a bottom-up approach using electrophoretic deposition. We experimentally demonstrated the fabrication of a nearly completely filled, inversed titania diamond-like photonic crystal.

The intermaterial dividing surfaces in self-organizing system has been approximated by the level surfaces of trigonometric functions.[21] In the interference lithography or phase-mask lithography, the intensity distribution of exposed light is directly expressed by the superposition of trigonometric functions.[22] The diamond D ($Fd\overline{3}m$), simple cubic P ($Pm\overline{3}m$) and gyroid G($I4_132$) structures can be described by the level surface as the following:[21]

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

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

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

Fig. 1a, 2a, and 2d shows the level surface of D, P, and G at t_1 = 1.24, 0.84 and 2.0, respectively, corresponding to inside volume fraction of 0.25, 0.26 and 0.17, respectively. At these values, D and G possess the maximum PBG width between 2nd and 3rd bands, and 5th and 6th bands for P, respectively. These volume fractions at the maximum PBG width are in agreement with the previous calculation.[2] Considering the fabrication of

[*] Dr. J. H. Moon, Y. Xu, Prof. S. Yang
Department of Materials Science and Engineering
University of Pennsylvania
Philadelphia, PA 19104 (USA)
Phone: +1-215-284-6235
E-mail: shuyang@seas.upenn.edu
Y. Dan
Department of Electrical and Systems Engineering
Prof. A. T. Johnson
Department of Physics and Astronomy
University of Pennsylvania (USA)
Prof. S.-M. Yang
National Creative Research Initiative Center for Integrated Optofluidic Systems and Department of Chemical and Biomolecular Engineering
Korea Advanced Institute of Science and Technology
Yuseong-gu, Daejeon (Korea)

[**] This research is supported by the Office of Naval Research (ONR), Grant # N00014-05-0303 and NSF NIRT ECS-0303981. SY is thankful for the 3M Nontenured Faculty Grant. JHM acknowledges the Korea Research Foundation postdoc fellowship (# KRF-2005-000-10299). SMY is supported by the Creative Research Initiative Program of MOST/KOSEF. Supporting information is available online from Wiley

these structures, the templates with air networks in Fig. 1a, 2a, and 2d are generated, followed by the backfilling of high-index materials.

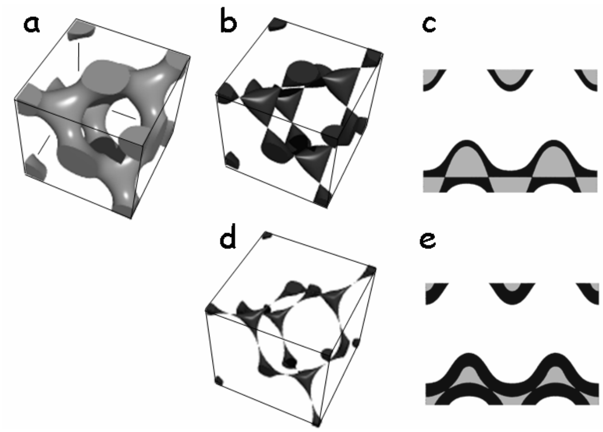


Figure 1. (**a**) Level surface of a diamond D structure with t_1 = 1.24. The enclosed represents air networks inside the template. (**b** and **d**) The pinch-off level surface with t_1 = 2.0 in Eq. 1 and with c = 0.125 and t_2 = 2.375 in Eq. 4, respectively, which represents unfilled air void. (**c** and ***e***) $(1\bar{1}0)$ cross-sectional images of two level surfaces in **a** and **b**, and **a** and **d**, respectively. The black and grey regions represent the deposited layers and unfilled air voids, respectively.

In general, the enclosed volume by a level surface decreases with the increase of the threshold intensity, t_1. At a sufficiently large t_1, the level surface begins to form isolated domains (or pinched-off) at symmetry points. In the case of a diamond 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 modelled surfaces at different t_1 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 the maximum.[24] We believe that this deviation could be attribute to characteristics of 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 deposited layer can be affected by various factors, including surface diffusion, surface tension of deposited materials, and the surface curvature.[25] Since the formation of a solid phase during deposition is rather fast, 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 superposition of two simple level surfaces, including P, G, D, and I-WP, 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 was 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:

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

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

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

The threshold value t_2 changes the volume (or roughly the distance from the template) enclosed by these level surface and the coefficient c determines morphology. Increasing c leads to more tubular networks. In order to find t_2 and c of each level surface, we varied t_2 value and optimized c until reaching the lowest standard deviation in average distance from the template surface. In the case of 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 $(1\bar{1}0)$ plane that combines the level surfaces shown in Figs. 1a and 1d appeared to be more uniform (Fig. 1e) compared to that shown in Fig. 1c. The uniformity was quantitatively evaluated by calculating the standard deviation of the distance of thousand points on each level surface from the template surface, which was substantially lowered from 0.404 (Fig. 1c) to 0.028 (Fig. 1e) based on the lattice distance of 2 π. At the pinch-off, the shell structure enclosed by the level surface in Fig. 1a and 1d (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 Fig. 1c).

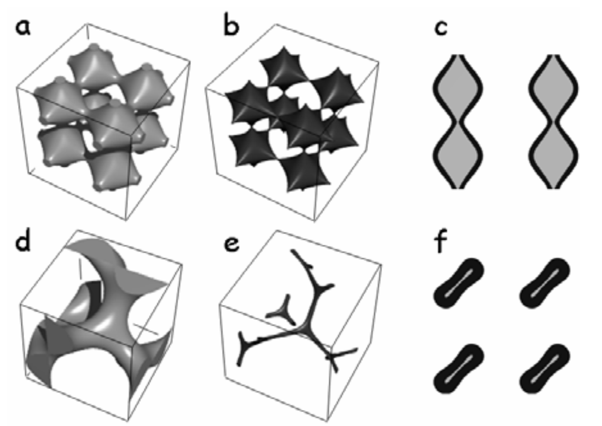


Figure 2. (**a**) Level surface of a simple cubic P structure with t_1 = 0.84 in Eq. 2. The enclosed represents air networks inside the template. (**b**) Combination level surface with c = 0.35 and t_2 = 1.35 in Eq. 5, which represents unfilled air cavities. (**c**) $(1\bar{1}0)$ cross-sectional images of two level surfaces of P structure shown in **a** and **b**. (**d**) Level-surface of gyroid G structure with t_1 = 2.0 in Eq. 3. The enclosed represents air networks inside the template. (**e**) Combination level surface with c = 0.15 and t_2 = 2.97 in Eq. 6, which represents unfilled air void. (**f**) (210) cross-sectioned images of two level surfaces of G structure shown in **d** and **e**. The black and grey regions represent the deposited layers and unfilled air voids, respectively.

Likewise, t_2 and c at the pinch-off was examined for P (Fig. 2b) and G (Fig. 2e), respectively. Fig. 2b shows the combination level surface of P (Eq. 5) with c = 0.55 and t_2 = 1.55. In the cross-sectional $(1\bar{1}0)$ plane of P structure (Fig. 2c), the shell structure (black layer) is defined by two level surfaces in Figs. 2a and 2b. The volume fraction of this shell structure was estimated as ~ 0.14, which was half of the maximum filling fraction, 0.26. Meanwhile, the combination level surface of G was shown in Fig. 2e and the parameters of Eq. 6 was calculated to be c = 0.15 and t_2 = 2.97 at the pinch-off. Fig. 2f shows the cross-section of (210) plane of G and the shell structure is defined by two level surfaces shown in

Figs. 2d and 2e. The volume fraction of this shell structure was found 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 D, P and G structure are summarized in Table 1.

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	~ 0.17 (0.17)

[a] Lattice distance, 2π

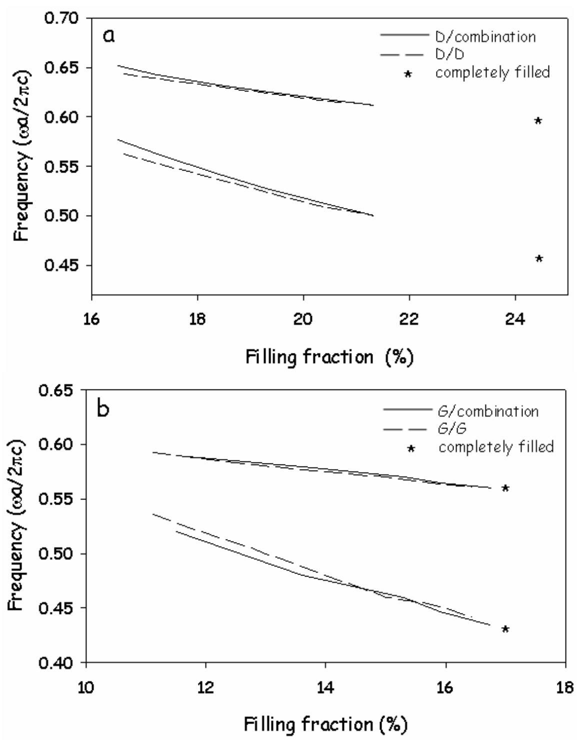


Figure 3. The normalized maximum and minimum frequencies of complete PBGs between 2nd and 3rd bands for (**a**) D and **(b**) G structures, respectively. Solid and dotted lines represent the frequencies using either the same level surfaces or the combination level surface for the grown layer, respectively. The frequencies of complete PBGs for completely filled structure are indicated by *.

Finally, the PBG was calculated on such constructed triply periodic dielectric shell with a refractive index, n = 3.6 using the MIT photonic bands (MPB) software package. As exemplified in the diamond D structures, the dielectric shell defined by Eq. 1 and 4 were employed for calculations. Fig. 3a shows the normalized frequency range of complete PBGs between 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) (* 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 frequencies and band diagram were found similar to each other at the same filling fraction. This implies that PBG property is less sensitive to the morphology of dielectric shell than the volume fraction. When we applied the same approach to calculate PBGs of the deposited dielectric (n = 3.6) on P template, no complete bandgap between 5th and 6th bands was observed due to the low filling fraction. Whereas in the case of G template, the PBG was found in the range 0.43 - 0.56 with 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 (* in Fig. 3b).

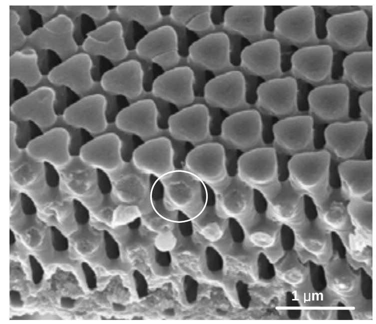


Figure 4. SEM image of an inverse diamond-like titania structure from electrodeposition on a polymer template, which was fabricated by holographic lithography. The circle highlights nearly completely filled air voids.

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 diamond-like structure, which has similar symmetry to the four-term diamond D structure. More importantly, both the polymer template and its inorganic replica of the three-term diamond-like structures can be fabricated rather conveniently[12], in contrast to the fabrication of P, G, and D structures by holographic patterning. As seen in Fig. S1 and S2, a conformal growth of silica in parallel to the polymer template led to pinch-off of the network.[12] Using the previously developed two-parameter level surface we found that the pinch-off occurred at filling fraction of 20%, resulting in no complete photonic bandgap between 2nd and 3rd bands.[12] While searching for an appropriate parallel level surface of the diamond-like structure to more accurately study the pinch-off characteristics, we found that a simple combination a diamond-like level surface with a P level surface, in the same way as we did with D structure, did not represent a parallel surface of the diamond-like 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, we found that the volume fraction of the shell at the pinch-off was ~ 30%, corresponding to ~ 75% of the complete filling and half of maximum achievable bandgap width (~ 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 diamond-like template. This approach has been applied to deposit a variety of materials, including metals, semiconductors and oxides[28-30] on 1D and 2D templates. During the deposition, the positively charged TiO_2 nanoparticles were attracted to the negatively charged ITO glass and gelled gradually from the substrate and filled the template.[27] As shown in cross-sectional SEM image of the inversed titania structure, it is noticeable that the interstitial pores were nearly completely filled (see Fig. 4 vs. Fig S2)

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 PBG of the deposited structure. The practically achievable filling fractions at the pinch-off are 84% for D, 98% for G, and 54% for P templates, respectively, 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 diamond-like 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 to the top-down conformal coating.

Experimental

Finding combination level surface and photonic bandgap calculation: The shell structure during the conformal deposition was constructed by the level surface (Eq. 1-3) and the combination level surface (Eq. 4-6). Since the threshold value t_2 in the level surface monotonically controls the volume fraction, we increased t_2 and optimized c to have smallest deviation from the parallel surface. In general, the increase of t_2 enhances the pinching-off and on the contrary, the increase of c releases it. Therefore, we evaluated the deviation as increasing c at a certain t_2 value. Meanwhile, since the combination level surface passes the pinch off point, we used this condition to find the c at the pinching-off. In terms of PBG calculation, we constructed the dielectric shell having the refractive index of 3.6 by using these two level surfaces and directly applied to calculate PBGs using the MIT photonic bands (MPB) software package. We also calculated the PBGs of the shell structure defined by the same level surfaces with different t_1 in Eq. 1-3.

Electrodeposition of titania: We fabricated 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.[27, 31] Briefly, the titania precursor was prepared by dissolving hydrolyzed titania in 2M 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.

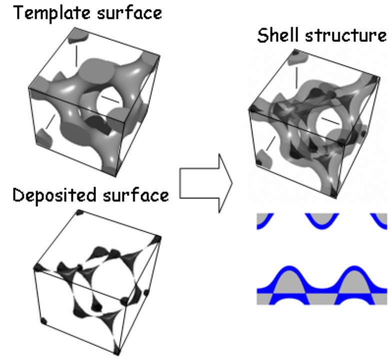
[1] L. Martin-Moreno, F. J. Garcia-Vidal and A. M. Somoza. *Phys. Rev. Lett.* **1999**, *83*, 73.
[2] M. Maldovan, A. M. Urbas, N. Yufa, W. C. Carter and E. L. Thomas. *Phys. Rev. B* **2002**, *65*, 165123.
[3] V. Babin, P. Garstecki and R. Holyst. *Phys. Rev. B* **2002**, *66*, 235120.
[4] R. G. H. Lammertink, M. A. Hempenius, E. L. Thomas and G. J. Vancso. *J. Polym. Sci. B-Polym. Phys.* **1999**, *37*, 1009.
[5] A. C. Finnefrock, R. Ulrich, A. Du Chesne, C. C. Honeker, K. Schumacher, K. K. Unger, S. M. Gruner and U. Wiesner. *Angew. Chem. Inter. Ed.* **2001**, *40*, 1207.
[6] O. Toader, T. Y. M. Chan and S. John. *Appl. Phys. Lett.* **2006**, *89*, 101117.
[7] M. Campbell, D. N. Sharp, M. T. Harrison, R. G. Denning and A. J. Turberfield. *Nature* **2000**, *404*, 53.
[8] O. Toader, T. Y. M. Chan and S. John. *Phys. Rev. Lett.* **2004**, *92*, 043905.
[9] T. Y. M. Chan, O. Toader and S. John. *Phys. Rev. E* **2006**, *73*, 046610.
[10] J. Wijnhoven and W. L. Vos. *Science* **1998**, *281*, 802.
[11] J. S. King, E. Graugnard, O. M. Roche, D. N. Sharp, J. Scrimgeour, R. G. Denning, A. J. Turberfield and C. J. Summers. *Adv. Mater.* **2006**, *18*, 1561.
[12] J. H. Moon, S. Yang, W. T. Dong, J. W. Perry, A. Adibi and S. M. Yang. *Opt. Express* **2006**, *14*, 6297.
[13] P. V. Braun, R. W. Zehner, C. A. White, M. K. Weldon, C. Kloc, S. S. Patel and P. Wiltzius. *Adv. Mater.* **2001**, *13*, 721.
[14] Y. A. Vlasov, X. Z. Bo, J. C. Sturm and D. J. Norris. *Nature* **2001**, *414*, 289.
[15] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader and H. M. van Driel. *Nature* **2000**, *405*, 437.
[16] H. Miguez, E. Chomski, F. Garcia-Santamaria, M. Ibisate, S. John, C. Lopez, F. Meseguer, J. P. Mondia, G. A. Ozin, O. Toader and H. M. van Driel. *Adv. Mater.* **2001**, *13*, 1634.
[17] H. Miguez, F. Meseguer, C. Lopez, M. Holgado, G. Andreasen, A. Mifsud and V. Fornes. *Langmuir* **2000**, *16*, 4405.
[18] N. B. J. Hetherington, A. N. Kulak, K. Sheard and F. C. Meldrum. *Langmuir* **2006**, *22*, 1955.
[19] W. B. Yue, A. N. Kulak and F. C. Meldrum. *J. Mater. Chem.* **2006**, *16*, 408.
[20] K. Michielsen and J. S. Kole. *Phys. Rev. B* **2003**, *68*, 115107.
[21] C. A. Lambert, L. H. Radzilowski and E. L. Thomas. *Phil.Trans. Roy.Soc. Lond. Ser. A-Math. Phys. Eng. Sci.* **1996**, *354*, 2009.
[22] C. K. Ullal, M. Maldovan, M. Wohlgemuth and E. L. Thomas. *J. Opt. Soc. Am. A* **2003**, *20*, 948.
[23] J. H. Moon, S. Yang and S. M. Yang. *Appl. Phys. Lett.* **2006**, *88*, 121101.
[24] P. E. Harper and S. M. Gruner. *Europ. Phys. J. E* **2000**, *2*, 217.
[25] J. A. Sethian and D. Adalsteinsson. *IEE Trans. Semi. Manufact.* **1997**, *10*, 167.
[26] M. Wohlgemuth, N. Yufa, J. Hoffman and L. E. Thomas. *Macromolecules* **2001**, *34*, 6083.
[27] Z. Miao, D. S. Xu, J. H. Ouyang, G. L. Guo, X. S. Zhao and Y. Q. Tang. *Nano Lett.* **2002**, *2*, 717.
[28] H. W. Yan, Y. L. Yang, Z. P. Fu, B. F. Yang, L. S. Xia, S. Q. Fu and F. Q. Li. *Electrochem. Comm.* **2005**, *7*, 1117.
[29] P. Braun and P. Wiltzius. *Adv. Mater.* **2001**, *13*, 482.
[30] Y. C. Lee, T. J. Kuo, C. J. Hsu, Y. W. Su and C. C. Chen. *Langmuir* **2002**, *18*, 9942.
[31] C. Natarajan and G. Nogami. *J. Electrochem. Soc.* **1996**, *143*, 1547.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents

COMMUNICATION

Triply periodic D, P, and G structures were studied as templates for fabrication of 3D photonic crystals. The achievable backfilling volume fraction and bandgap properties were analyzed by considering the pinch-off of level surface. We found conformal coating on such templates resulted in incomplete filling and loss of PBG. To solve this problem, we attempted electrophoretic deposition, which showed nearly completely filled titania 3D structure.



Photonic Crystals

J. H. Moon, Y. Xu, Y. Dan, S.-M. Yang, A. T. Johnson, S. Yang*

Triply periodic bicontinuous structures as templates for photonic crystals: a pinch-off problem

Supporting Information

Triply periodic bicontinuous structures as templates for photonic crystals: a pinch-off problem

By Jun Hyuk Moon, Yongan Xu, Yaping Dan, Seung-Man Yang, Alan. T. Johnson, and Shu Yang,*

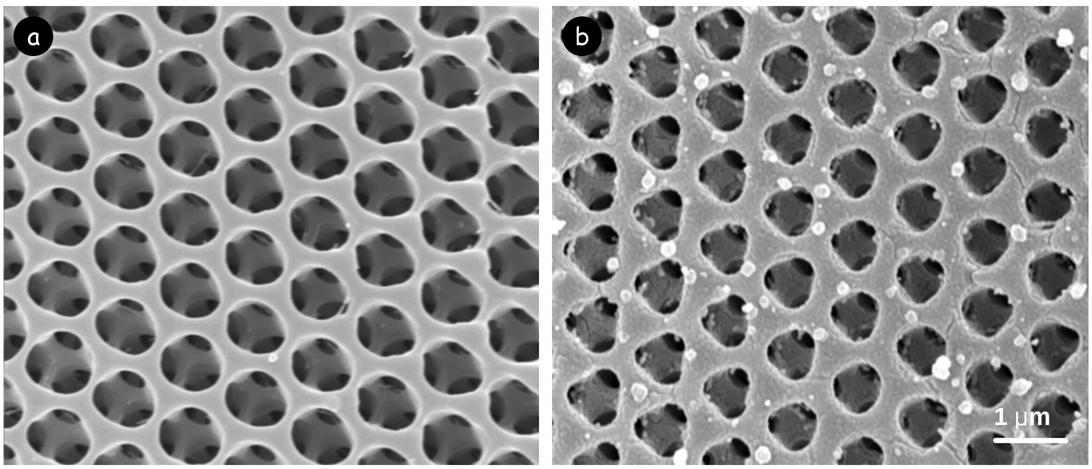


Figure S1. SEM images of the (111) planes of the diamond-like structure. (**a**) Polymer template. (**b**) ~100 nm silica deposited on polymer template shown in (**a**). To form the diamond-like structure, we used four-beam umbrella-like beam assembly and exposed the interference pattern onto SU8 photoresist.[1] The deposition of silica was achieved in a batch reactor under atmospheric pressure and at room temperature. The polymer template was treated with consecutive exposures to $SiCl_4$ vapor and water vapor using atmospheric pressure at room temperature.

[1] J. H. Moon, S. Yang, W. T. Dong, J. W. Perry, A. Adibi and S. M. Yang. *Opt. Express* **2006**, *14*, 6297

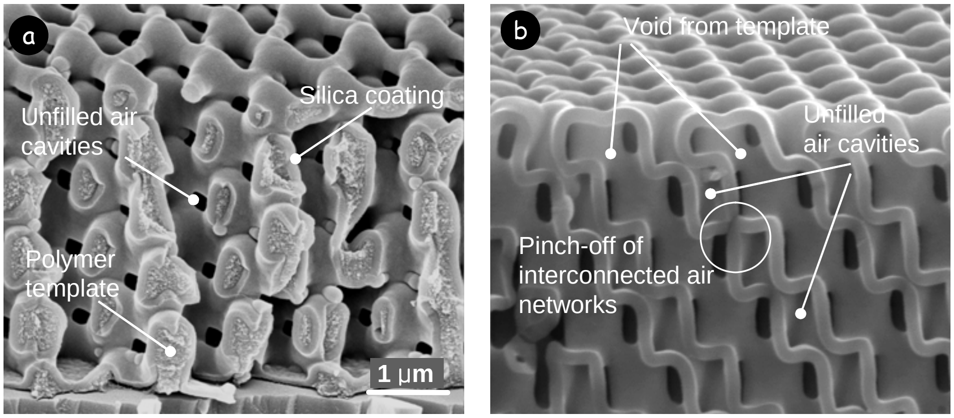


Figure S2. Cross-sectional SEM images of back-filled silica structures from the diamond-like polymer template before (**a**) and after (**b**) sintering at 500°C. The pinch-off of interstitial void networks left unfilled air cavities.