Robust Control over Morphologies and Grain Interfaces of Three-Dimensional Well-Ordered Superstructures Programmed by Hybrid Topographical-Chemical Templates

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It is an extremely challenging task to construct three-dimensional (3D) well-ordered superstructures with controllable morphologies and predictable internal components. Using computational modeling, we conceive and demonstrate a novel class of templates with topographically and chemically patterned surfaces for directing the self-assembly of symmetric block copolymers. Large-cell simulations of self-consistent field theory corroborate that the 3D sophisticated structures of vertical lamellae with different in-plane orientations are achieved and the placements of grain interfaces are regulated by the post height and the commensurability conditions. Notably, non-orthogonally crossed structures are created by simply modulating the periodicities of post arrays. This work may provide a novel route for experimentalists to fabricate the 3D long-range ordered structures with tunable local characteristics.

Introduction

True potential of block copolymers in the semiconductor industry is likely to come from the inherently three-dimensional (3D) characteristics of microphase-separated nanostructures,[1,2] which allow researchers to construct 3D ordered superstructures in single self-assembly step. The directed self-assembly structures with 3D sophisticated features provides an enabling platform for nanofabrication of electronic, magnetic or photonic devices.[3,4] However, creating the 3D ordered nanostructures that simultaneously possess the controllable morphologies as well as the precisely arranged internal components (such as interconnections and grain interfaces) still remains challenging.[5,6]

Recent efforts of experiments and simulations have shown that guiding templates for the directed self-assembly play a critical role in building up the 3D well-ordered structures of block copolymers.[7,8,9,10] For example, Ross and co-workers designed a rectangular array of topographical posts to program the 3D superstructures of cylinder-forming block copolymer bilayer films.[11,12,13,14] Unlike the cases of bulk, the orientations of cylinders in the top and bottom layers are regulated simultaneously and independently. Nevertheless, the vertical interconnections between the crossing cylinders, which play an important role in improving performance and power of 3D integrated-circuit systems,[15] are formed in the limited range of design elements of guiding templates, such as film thickness, post height and wetting properties of surfaces.[14,16]

Another approach to achieve the 3D highly ordered architectures is based on utilization of chemical stripes.[17,18] Since the top surfaces cannot eliminate possible orientations, the block copolymers guided by the mismatch chemical stripes self-assemble into the non-bulk structures containing many degenerate states.[8,19,20,21] In the group of de Pablo, the 3D twisted structures with continuity of lamellae and interconnections are elaborately realized through the self-assembly of symmetric block copolymers directed by the templates with two orthogonally oriented chemically patterned surfaces.[22,23] Unfortunately, as the films become thick, the interfaces separating the grains of lamellae are randomly distributed inside the 3D structures due to the short-range guiding characteristics of chemical stripes. This poses a significant stumbling block to achieve the controllable morphologies of 3D structures with precise placements of grain interface, which foreshadow the potential to fabricate 3D integrated-circuit elements, photovoltaic devices and energy storage devices.[23]

In this contribution, we theoretically engineer novel templates, which combine the top chemically and bottom topographically patterned surfaces, to direct the self-assembly of lamella-forming block copolymers. In comparison with the templates mentioned above, the key advantage of the hybrid templates is that the morphologies of complex 3D structures could be robustly and flexibly controlled by the post height

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and the commensurability conditions, and the grain interfaces in the 3D long-range ordered nanostructures could be restricted to the narrow zones of films. In addition, the hybrid templates facilitate the formation of non-orthogonally crossed architectures through simply tuning the periodicities of topographical posts.

Computational Modeling

Full technical details of the model can be found in Part A of Electronic Supplementary Information (ESI) and Figure S1 of ESI. In brief, the AB block copolymers are confined between the top and bottom surfaces as schematically illustrated in Figure 1. Two types of templates are explored in the simulations. Figure 1a displays the templates consisting of two chemically patterned surfaces with orthogonal orientations. In the hybrid templates, the bottom chemical stripes are replaced by topographical posts (Figure 1b). We utilize self-consistent filed theory (SCFT) of polymers to probe into the directed self-assembly behaviors of block copolymers.[24,25] The Flory-Huggins interaction parameter between the A and B blocks is set as χN=14.0. In the bulk, the symmetric block copolymers self-assemble into the lamellae with natural periodicity L_0~3.6R_g, where R_g is the ideal gyration radius. The interaction parameters between the blocks and the surfaces are fixed at λN =10.0. For the posts modeled by external fields, the changes at the well edge for the A and B blocks are respectively set as 0.10R_g and 0.20R_g, implying that the posts are weakly attractive to the A blocks.

Results and Discussion

We first observe the ordered superstructures of block copolymer films in the chemical templates. Figures 2a and 2b show the morphologies of 3D structures of block copolymer films with thicknesses H=4.0R_g and H=6.5R_g, respectively. The two chemical stripes on the top and bottom surfaces direct the block copolymers to self-assemble into grains of lamellae perpendicular to the surfaces. Due to the orthogonally oriented stripes, the two lamellar grains are twisted inside the films (inset of Figure 2a), producing the 3D structures with continuity of nanodomains. The grains of lamellae with different in-plane orientations are separated by interfaces (the positions are marked by the planes enclosed in the white boxes as shown in Figure 2b). From the 3D views of superstructures, one can identify that the film thickness has a significant effect on the positions of grain interfaces. In the cases of thin films, the locations of interfaces are restricted to the center of films (Figure 2a). However, the interfaces are delocalized away from the middle of thick films (Figure 2b).

To quantitatively measure the localizations of interfaces in the 3D structures, we introduce position parameters m to characterize the positions of interfaces separating the lamellar grains in the unit cells V_0,[26] which have different domains on the top and bottom surfaces as shown in Figure 2b. The grain interfaces located at the center of cells V_0 will result in m=0. As the position parameters m are larger than zero, the interfaces will move towards the top surfaces. Histograms of position parameters are obtained via analyzing a large number of 3D structures in the cell V_0 collected from different samples. More details about the position parameters can further refer to Part A of ESI.

Figure 2c displays the probability distributions of position parameters for different film thicknesses H=4.0R_g and H=6.5R_g.

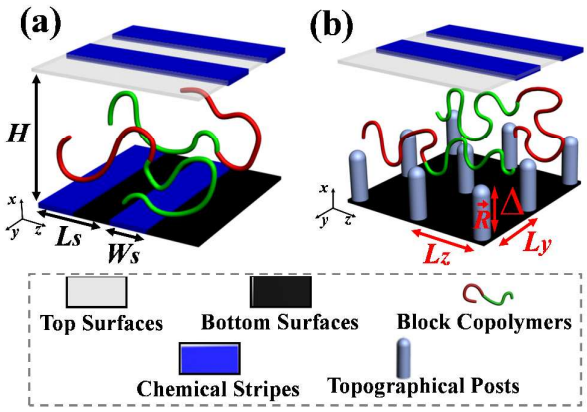

Fig. 1 Simulation setups. (a) Block copolymers confined between two orthogonally oriented chemically patterned surfaces. The patterns comprise periodic stripes with width W_s and periodicity L_s. H represents the film thickness. (b) Block copolymers directed by hybrid templates with chemically and topographically patterned surfaces. An array of posts with height Δ and radius R is located on the bottom surfaces. The periodicities of post lattice in the y and z directions are specified by L_y and L_z, respectively.

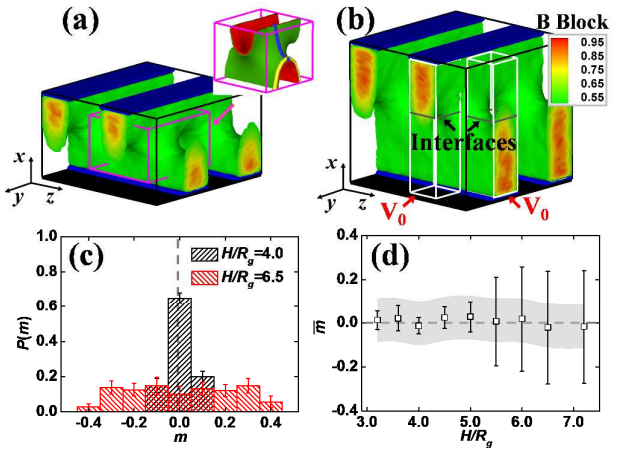

Fig. 2 (a and b) Three-dimensional ordered structures of block copolymers guided by chemical templates with stripe width W_s=1.8R_g and periodicity L_s=3.6R_g for various film thicknesses (a) H=4.0R_g and (b) H=6.5R_g. The A-rich domains and top surfaces are removed for visualization purpose. In the color bar, red and green colors indicate B-rich domains and internal interfaces between the A-rich and B-rich domains, respectively. Inset of panel (a) displays the zoomed-in image of internal surface at the orientation transition of lamellae, and the blue and yellow curves show two representative curves across the saddle points of Scherk's surfaces. In image (b), the planes enclosed in the unit cells V_0 represent the positions of grain interfaces. (c) Probability distributions $P(m)$ of position parameter m at different film thicknesses H=4.0R_g and H=6.5R_g. (d) Averaged position parameters $\bar{m}$ of three-dimensional structures as a function of film thickness. The error bars represent the standard deviations. The dashed lines at m=0.0 indicate the grain interfaces located at the center of films. The filled area in image (d) indicates that the standard deviations from the averaged position parameters are less than 0.1.

The position parameter histogram for the film thickness H~1.0L_0 exhibits a narrow distribution with a single peak at m=0.0, indicating that the grain interfaces are restricted to the narrow zones at the center of thin films. When the film thickness H is larger than 1.5L_0, the probability distributions $P(m)$ are approximately uniform, implying that the grain interfaces fluctuate over a wide range of block copolymer films. We also examine the effects of various parameters, such as the width W_s and periodicity L_s of chemical stripes, and the interactions λN between the blocks and chemical stripes, on the positions of grain interfaces (Figure S2 of ESI). It is found that the histograms of position parameters maintain at an approximately uniform distribution in the case of the thick films of block copolymers.

Figure 2d depicts the averaged position parameters $\bar{m} \equiv \sum_j P(m_j) m_j$ as a function of the film thickness. The averaged position parameters $\bar{m}$ of 3D structures approach zero. However, the film thickness has a remarkable effect on the standard deviations SD(m) represented by error bars, which are calculated by $\mathrm{SD}(m) \equiv \left(\sum_j P(m_j)(m_j - \bar{m})^2\right)^{1/2}$. We define the standard deviations SD(m)<0.1 as 'the narrow zone', which is represented by the filled area in Figures 2d. In the thin films, there is little room for variation of position parameters, indicating that the grain interfaces are restricted to the narrow zones of films. The statistical spreads in the amount of position parameters increase dramatically in the range of film thickness $H \geq 5.5R_g$. The main reason is that the difference of free energies of 3D structures in the thick films is slight as the position parameters are fluctuated in the range of $-0.30 \leq \bar{m} \leq 0.30$ (Figure S3 of ESI).

In the recent experiments and simulations of de Pablo group, the morphologies of block copolymers confined between two chemically patterned surfaces were explored.[22,23] The lamellae of symmetric block copolymers are continuously connected by the interfaces resembling the Scherk's first minimal surfaces. Inset of Figure 2a displays two representative curves across the saddle points of Scherk surfaces given by the expression $e^{cx}cos(cy) - cos(cz) = 0$ with c=1.9R_g. The good agreement between the simulation data and the analytical expression suggests that our SCFT calculations reproduce the surface topologies reported by the de Pablo group. In addition, Monte Carlo simulations of a coarse-grained model corroborate the random distribution behaviors of grain interfaces, which are consistent with the findings of SCFT simulations (Figure 2c).

It should be pointed out that the single templates only consisting of topographical posts on the bottom surfaces cannot guide the symmetric block copolymers to self-assemble into the 3D well-ordered superstructures with internal components. Figure S4 of ESI shows the self-assembled nanostructures of block copolymers directed by the topographical posts. When the post spacing is commensurate with the natural periodicity of block copolymer nanostructures, the symmetric block copolymers form the well-ordered lamellae perpendicular to the surfaces. Meanwhile, the in-plane orientations of the vertical lamellae are programmed by the designed parameters of post arrays.

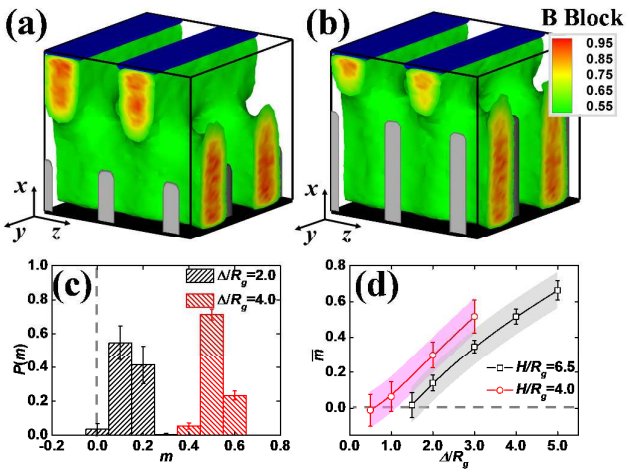

Fig. 3 (a and b) Three-dimensional ordered structures of block copolymers directed by hybrid templates for various post heights (a) Δ=2.0R_g and (b) Δ=4.0R_g. The other model parameters are L_y=3.6R_g, L_z=3.0R_g and H=6.5R_g. In the color bar, the red and green colors represent the B-rich domains and internal interfaces, respectively. The posts are specified by the gray color. Note that only 1/30 part of the simulation box is shown. (c) Probability distributions $P(m)$ of position parameter m for various post heights Δ. (d) Averaged position parameters $\bar{m}$ of three-dimensional ordered structures as a function of post height Δ under various film thicknesses H. The representations of colors, error bars, dashed lines and filled areas are the same as those of Figure 2.

Next, inspired by recent works of Ross *et al.*,[11,13] we seek to theoretically engineer hybrid templates containing an array of topographical posts on the bottom surfaces and chemical stripes on the top surfaces (Figure 1b), which provide strong thermodynamic deriving force for modulating the placements of grain interfaces in the 3D structures. To elucidate the unique directed self-assembly behaviors and expand on the strategy to achieve the controllable morphologies of 3D ordered superstructures over a wide area, the large-cell simulations of SCFT for the novel templates are performed.[25] Figure 3 shows the directed self-assembly behaviors of block copolymers confined between the top chemically and bottom topographically patterned surfaces. It should be noted that the bottom surfaces are neutral. The periodicities L_y and L_z of post lattice in the y and z directions are fixed at L_y=3.6R_g and L_z=3.0R_g, respectively. Since the post spacing L_y satisfies the commensurability conditions of block copolymer domains, the vertical lamellae in the bottom part of films are oriented along the z-axis to minimize the strain energy. In the top part of films, the vertical orientation of lamellae is preserved and the in-plane orientation of lamellae is consistent with the y direction of the B-wetting stripes with width W_s=1.8R_g and periodicity L_s=3.6R_g. As a result, the lamellae with different in-plane orientations meet inside the films and the 3D structures with the interconnections are also realized in the hybrid topographical-chemical templates (Figures 3a and 3b).

Remarkably, the complex 3D architectures in the hybrid templates reveal a new structural feature. As the topographical posts become tall, the grain interfaces are shifted towards the top surfaces of templates and the

corresponding morphologies of 3D ordered structures are reshaped, as depicted in Figures 3a and 3b. To reinforce the impressions from examining the morphologies, the histograms of position parameters for various post heights are presented in Figure 3c. Compared with the uniform distributions of position parameters in the cases of chemical templates, the distributions of position parameters of 3D structures registered by the hybrid templates show a single peak at $m \geq 0$. The observations manifest the fact that the grain interfaces are restricted to the narrow zones in the top part of thick films. Furthermore, the peak locations of distributions are tuned by the post height.

To further evaluate the effects of post height on the positions of grain interfaces, the averaged position parameters are calculated (Figure 3d). Since the guiding behaviors of short posts are very similar with the cases of chemical stripes, the volume fractions of lamellae with various orientations are roughly equal and therefore the averaged position parameters of 3D structures registered by the hybrid templates are close to zero. As the height of topographical posts increases, the bottom part of block copolymer films remains, but the polymer chains in the top part reassemble in response to the tall posts. Since the dimension L_z of post lattice is not commensurate with the periodicity of block copolymer domains, the increased strain energy of system triggers the rearrangement of block copolymer domains in the top part of films, which leads to a decrease of volume fraction of lamellae registered by the chemical stripes. Correspondingly, the grain interfaces show a shift towards the top surfaces. As a result, an increase of the post height raises the averaged position parameters of 3D ordered structures. The same behaviors of averaged position parameters as a function of the post height are inspected in the cases of thin films with thickness H=4.0R_g. Another important outcome of Figure 3d is that the standard deviations from the averaged position parameters are less than 0.1, suggesting that the grain interfaces can be localized in the narrow zones of films. Given these observations, the robust control over the morphologies of 3D sophisticated structures and the placements of grain interfaces is properly achieved through integrating the chemically and topographically patterned surfaces.

It is also important to comprehend the roles of other parameters of templates, such as the periodicities (L_y and L_z) of topographical posts and the dimension (W_s and L_s) of chemical stripes, on the directed self-assembly behaviors of block copolymer films. To clarify these issues, the averaged position parameters of 3D ordered structures as functions of L_y and L_s are shown in Figures 4a and 4b, respectively. As the periodicity L_y of post lattice is not satisfied with the commensurability conditions, the domains of block copolymers directed by the posts possess a higher free energy due to a tensile or compressive strain to fit within the post array. To relieve the deformation of lamellae, the grain interfaces move towards the bottom surfaces. This leads to a decrease of averaged position parameters as the commensurability conditions are not satisfied (Figure 4a). Similarly, as the periodicity L_s of chemical stripes deviates from the commensurability conditions, the grain interfaces move towards the top chemically patterned surfaces to alleviate the energy contributions from the compressed or elongated lamellae (Figure 4b). It should be mentioned that the interface positions are also tuned by the stripe width. These results suggest that the commensurability conditions could be exploited to manipulate the placements of grain interfaces and the corresponding morphologies of 3D superstructures. The findings provide significant guidance for experimentalists to select the geometry parameters of hybrid templates to engineer the 3D ordered structures with tunable internal components.

It should be noted that the chemical selectivity of the bottom surfaces has effects on the morphologies and orientations of self-assembled structures programmed by the topographical templates and the hybrid templates (Figures S5 and S6 of ESI). When the bottom surfaces strongly repel the B blocks, A-rich flat layers are produced in the bottom part of films and destabilize the 3D well-ordered structures of vertical lamellae.

On the basis of the tunable in-plane orientations of lamellae registered by the rectangular lattice of topographical posts (Figure S4 of ESI), the hybrid topographical-chemical templates provide a new route to construct the non-orthogonally crossed lamellar structures without additional

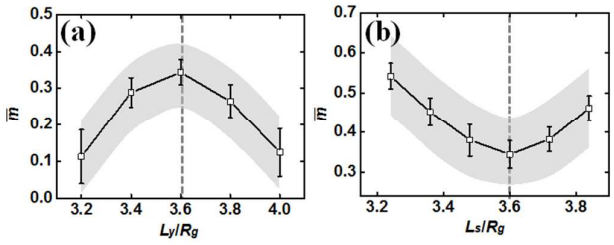

Fig. 4 (a) Averaged position parameters $\bar{m}$ of three-dimensional ordered structures as a function of periodicity L_y of post lattice in the y direction. Note that the dimension of chemical stripes satisfies the commensurability conditions. (b) Averaged position parameters $\bar{m}$ of three-dimensional ordered structures as a function of periodicity L_s of stripes. The periodicities of post lattice are L_y=3.6R_g and L_z=3.0R_g. The dashed lines indicate the cases where the periodicities of post lattices or stripes satisfy the commensurability conditions of block copolymer domains. The filled areas represent the standard deviations SD(m)<0.1.

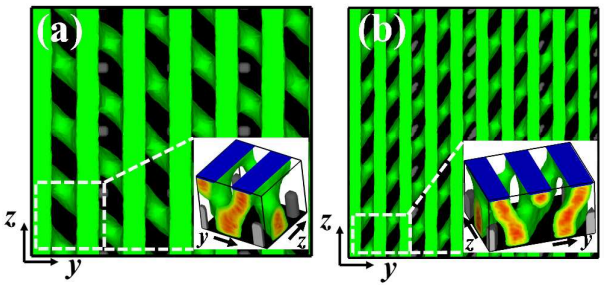

Fig. 5 Top-down views of three-dimensional structures of lamellae with tunable orientations through changing periodicities L_y and L_z of post lattice. (a) L_y=5.4R_g and L_z=4.8R_g, and (b) L_y=9.0R_g and L_z=6.0R_g. Note that the topographical posts in image (b) have the elliptical shape. Insets are the three-dimensional views of local structures enclosed in the dashed boxes. Only 1/16 and 1/24 portions of the simulation cells are shown in insets (a) and (b), respectively.

treatments on the chemically patterned surfaces. In order to demonstrate this ability, the simulations for the hybrid templates with a series of periodicities of post lattice are carried out. As predicted from the commensurability conditions, the vertical lamellae near the bottom surfaces align diagonally with respect to the post lattice when the post spacing is set as L_y=5.4R_g and L_z=4.8R_g. Combining the lamellae in registration with the chemically patterned surfaces, one obtains the non-orthogonally crossed structures (Figure 5a). When the spacing of posts further increases, the block copolymers self-assemble into the poorly ordered patterns. As shown in Figure S7 of ESI, the lamellae with degenerate orientations appear due to the isotropic characteristics of circular posts. To achieve the highly ordered superstructures, one promising strategy is the introduction of anisotropic posts with elliptical shape,[25] which provide additional in-plane orientation guidance. As demonstrated in Figure 5b, the bock copolymers guided by the hybrid templates with elliptical posts self-assemble into the crossed superstructures with single in-plane orientation in the bottom part of films.

Finally, we would like to emphasize that the local structures of grain interfaces are highly degenerate and have different possible morphologies or geometries due to the frustrated features of 3D superstructures with distinct lamellar orientations.[22,27,28] For example, Gido *et al.* experimentally found that both the morphologies of Scherk's surfaces and helicoid sections exist in the intersecting lamellar nanodomains at low twist angles, and theoretically demonstrated that the energies of both morphologies are comparable in this twist range.[29, 30,31] These findings provide a valuable clue for exploring the interfacial structures of lamellar grains (*i.e.*, besides the Scherk's surfaces, the helicoid section morphologies of grain interfaces possibly emerge in the non-orthogonally crossed structures as shown in Figure 5). It should be mentioned that in comparison with the approach proposed by Gido and co-workers, the SCFT used here provides a powerful tool for screening the novel local morphologies of complex superstructures such as helicoid section,[31] connected tubes,[22] and Schwarz *P* phases.[32] Future studies based on SCFT will be devoted to elucidating in more detail the structural characteristics of grain interfaces in the frustrated superstructures including vertical interconnections between the top and bottom lamellae as well as mean and Gaussian curvatures of local structures.

Conclusions

In summary, we theoretically propose and demonstrate a new category of templates to guide the self-assembly of block copolymers. Our large-cell simulations of SCFT predict that by collaborating with the top chemically patterned surfaces, the topographical posts in the bottom surfaces direct the symmetric block copolymers to self-assemble into the 3D long-range ordered superstructures with controllable morphologies and predictable placements of grain interfaces. The positions of grain interfaces are strongly dependent on the post height and flexibly adjusted by the commensurability conditions. Additionally, the 3D structures of lamellae with non-orthogonal orientations are successfully constructed by simply modulating the periodicities of post arrays. The above findings indicate that incorporating the topographical posts into the template design significantly enhances the regulation of 3D well-ordered structures, which gains access to novel materials with tunable properties via the rational self-assembly of smart block copolymers.

Acknowledgements

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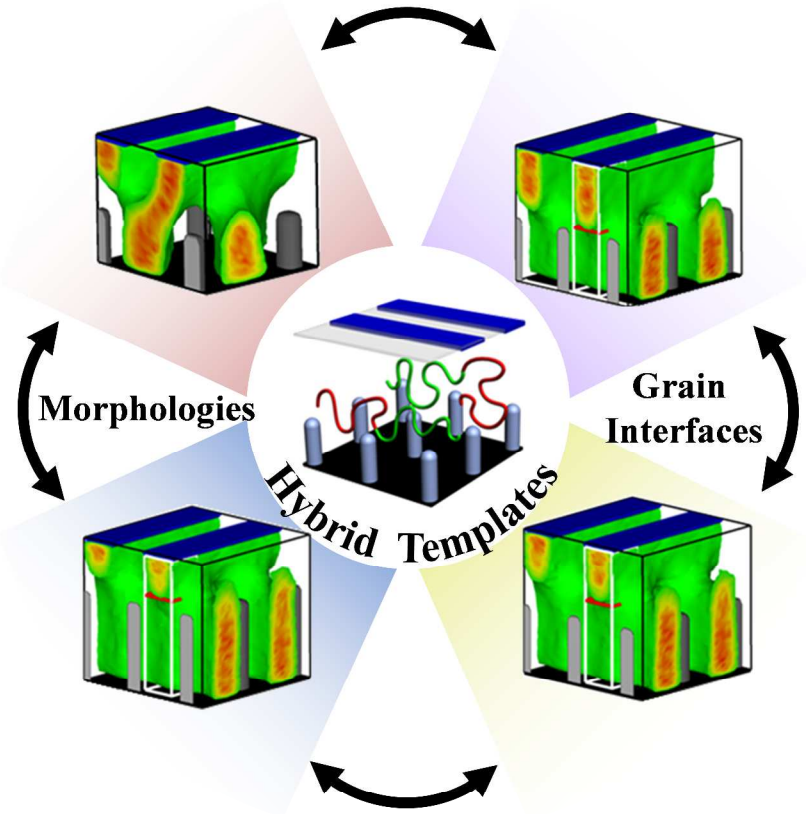
Graphical abstract



Template Design for 3D Superstructures

We theoretically engineer and demonstrate a novel class of hybrid templates for directing self-assembly of block copolymers into three-dimensional defect-free nanostructures with controllable morphologies and predictable internal components.