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Hierarchically Ordered Polymer Films by Templated Organization of Aqueous Droplets**

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Hierarchically ordered structures facilitate the incorporation of diverse functions simultaneously. The present report introduces a simple and novel strategy for producing hierarchically ordered polymeric films. Hierarchical ordering of aqueous droplets on a polymer solution is realized by the imposition of physical confinement via various shaped gratings. After drying of the solution, well-ordered hierarchical structures were fabricated in the remaining polymer film. The size of the grating structure and the lattice size of spontaneous hexagonally packed aqueous pores comprise two different length scales, thereby offering multiscale ordering. Interfacial wetting of the polymer solution to the grating surface was crucial in terms of obtaining a highly ordered structure that can be tuned by dissolving a small amount of surfactant in the polymer solution. The present novel approach provides a new opportunity for lithography-free fabrication of complex hierarchical structures.

1. Introduction

Hierarchically ordered structures have attracted a great deal of attention because they hold promise for numerous applications such as photonic devices,[1,2] micro-structured electrode surfaces,[3] biosensor arrays,[4] membranes for separation, catalysts,[5] and lithographic masks for complex structures.[6] The multilevel ordering of a hierarchical structure facilitates incorporation of diverse functions simultaneously. It is well known that a considerable portion of complex functionalities of living systems relies on their hierarchical structures.[7–9]

Polymeric materials have particular advantages for preparing ordered structures.[10–15] Simple solution or melt processing is applicable to a variety of chemical structures, providing diversity in their functionalities. They can be used as template materials for functional structures and are easily removed without a severe calcination process. For hierarchically ordered polymeric structures, various fabrication methods have been exploited. A top-down approach such as two photon laser fabrication has been applied to fabricate well-ordered hierarchical structures.[16,17] However, this technique requires a complicated process with expensive equipment. Moreover, as it is an intrinsically serial process, application to a high throughput process is limited.

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A hybrid technology combining top-down and bottom-up approaches ensures better productivity and lower cost. Various bottom-up fabrication methods utilizing self-assembling materials have been combined with top-down fabrication approaches to yield hierarchically ordered structures.[1,2,18–25] In these approaches, a length scale in the finally prepared structure is practically determined by the choice of self-assembling material, thus prohibiting dynamic control over characteristic length scales. Moreover, complex chemistry including highly toxic agents is frequently involved in the fabrication process, which limits application towards diverse polymeric materials.

Here we introduce templated organization of aqueous droplets as a simple strategy to prepare various hierarchically ordered polymeric structures. The spontaneous ordering of liquid droplets has been frequently applied to prepare a variety of porous structures.[26–28] However, the finally obtained structure consists of the multi-grains of ordered domains accompanying a high density of defects at grain boundary. We applied various shapes of gratings to induce template assisted organization of aqueous droplets on polymer solution surfaces. After the complete evaporation of solvents, well-ordered hierarchical porous structures whose lattice direction was perfectly registered by the physical confinement from gratings were fabricated in the remaining polymer films. To the best of our knowledge, it is the first demonstration that templated organization of liquid droplets was readily achieved and applied to fabricate hierarchical structures. This novel approach provides a new opportunity for fabricating diverse hierarchical structures from liquid emulsion.

2. Results and Discussion

Two- or three-dimensionally ordered porous polymer structures can be simply fabricated by applying humid air to a polymer solution; this is known as a 'breath figure'.[29,30] Water droplets condensed from humid air spontaneously pack into a hexagonal array. The size of the fabricated pores is easily controllable by adjusting various processing parameters such as the polymer concentration,[31] molecular weight or chemical structure of used polymer,[32–35] humidity or flow rate of applied air stream,[36] solvent evaporation rate,[37] solution casting temperature,[38] film thickness,[39] etc. Encapsulation of aqueous droplets by a thin polymer stratum induced by thermocapillary or Marangoni convection has been suggested as a mechanism for a hard colloid-like interaction between aqueous droplets without the use of colloid stabilizer.[28] However, the length scale for long range ordering is limited, and thus breath figure morphology usually consists of multi-grains. Figure 1a shows a typical SEM image of breath figure morphology prepared from a benzene solution of monocarboxy terminated polystyrene. Moiré fringes caused by interaction between the scanning line pattern of the electron microscope and the hexagonal lattice of the bubble arrays reflects multi-grain morphology as well as highly ordered surface packing in each grain. A Fourier transform of the SEM image shown in Figure 1b reveals a circular pattern, confirming the multi-grain morphology. The detailed structure around the grain boundary is demonstrated in the magnified image shown in Figure 1c. Defects involved with five or seven neighbors are arrayed to constitute the grain boundary. Because hexagonal close packing occurred at the growth stage of pores, the trajectory of the grain boundary exhibits considerable roughness.[35]

A hierarchically ordered porous structure could be prepared simply by applying a grating structure as a physical confinement to induce templated organization of aqueous droplets. The procedure for templated organization process is schematically summarized in Figure 2. First, a polymer solution was prepared by dissolving a polymer in an organic solvent. A monocarboxy terminated PS (M_w: 50 kg mol^{-1}) was used as the polymer and its concentration in benzene solution was fixed at 4 wt %. The prepared solution was dropped on an organically modified silicon wafer under humid air and ambient temperature. A copper grating was placed over the polymer solution to facilitate templated organization of the aqueous droplets (Fig. 2a). As the solvent evaporated, aqueous droplets condensed on the polymer solution surface and spontaneously organized into hexagonally packed arrays in the mesh spaces (Fig. 2b and c). After the complete evaporation of solvent and water, a hierarchically ordered polymer thin film was obtained (Fig. 2d). Note that applying a disposable grating was crucial to induce a highly ordered hierarchical structure. When the grating was placed before depositing polymer solution, well-ordered structure was not obtained.[27] Topographic grating has

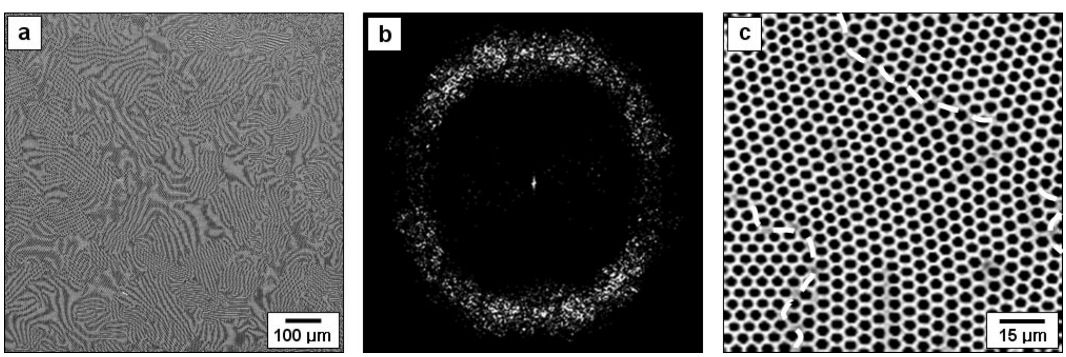

Figure 1. a) SEM image of typical breath figure morphology of monocarboxy terminated PS over a broad area of 920 µm by 920 µm. b) A Fourier transform of the SEM image in the porous region. c) A magnified SEM image showing the detailed structure around the grain boundary; the white line indicates grain boundary involving defects surrounded by five or seven neighbors.

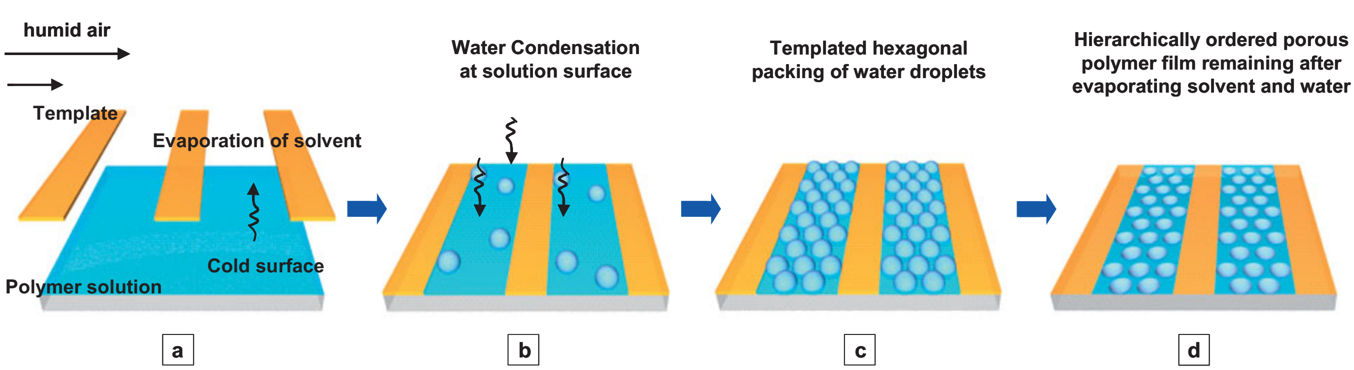

Figure 2. Experimental procedure for fabricating a hierarchically ordered polymeric film by templated organization of aqueous droplets. In step a, the polymer solution is dropped on an organically modified silicon wafer under humid conditions and a grating is applied over the solution drop. In steps b and c, as the solvent evaporates, water droplets condense on the polymer solution surface and undergo template assisted organization. In step d, complete evaporation of the solvent and water leads to a hierarchically ordered porous polymer film.

to be floated on the liquid surface to effectively guide the ordering of aqueous droplets.

Figure 3a shows a SEM image of a hierarchical structure fabricated using a parallel grating. Pores are linearly arrayed along the edge of the grating, thus demonstrating the physical confinement imposed by the template structure. The pores formed away from the grating edge are subsequently ordered by spontaneous close packing of aqueous droplets during film preparation. A Fourier transform of the SEM image shows hexagonal spots of a single grain structure (Fig. 3b). As shown in Figure 3c, the SEM image of a fractured sample reveals that a single layer of pores were fabricated at the surface of films. The copper grid was peeled off before fracturing the sample. Pores was formed only in the region where polymer solution surface had been exposed to humid air. The interval between neighboring gratings and lattice size of the hexagonal packing of pores constitute two independent length scales for the hierarchical structure. Note that defect-free hierarchical structure could be prepared over a broad area of about 770 μm by 500 μm (Fig. S1b) without optimizing processing conditions. It demonstrates that the present approach does not have any intrinsic limitation for ordered area. By applying the grating after aqueous droplets were nucleated, a hierarchical structure consisting of two kinds of pore arrays could be fabricated (Fig. 3d). Large pores with a fairly low degree of ordering appeared at the region covered by the grating. The pores formed in the interval between gratings show perfectly ordered hexagonal packing.

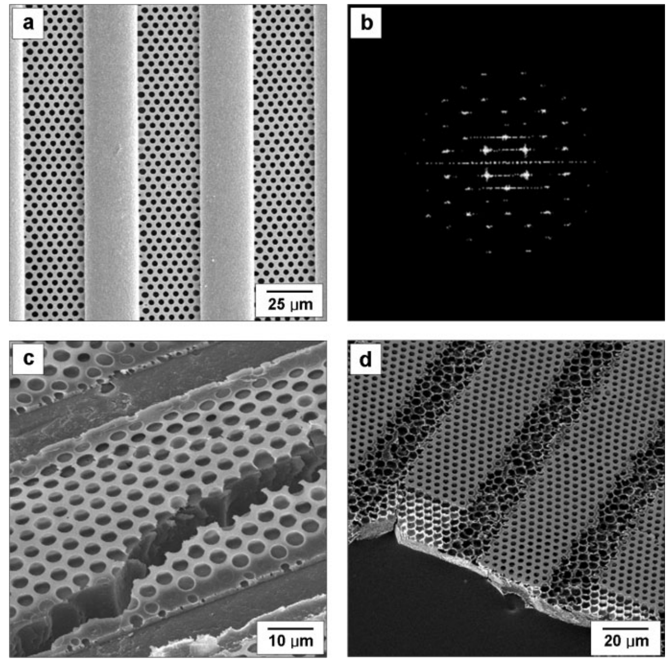

Figure 3. a) SEM image of well-ordered hierarchical structure fabricated using a parallel grating. b) A Fourier transform of the SEM image, demonstrating single grain structure. c) SEM image for a fractured sample showing a two-dimensionally ordered hierarchical structure. d) SEM image of another type of hierarchical structure having different pore sizes in each periodic length scales.

In the present approach, wetting of polymer solution onto a template material was found to play an important role in determining the degree of ordering. In order to achieve a highly ordered structure, favorable wetting is required between the polymer solution and the template. As shown in Figure 4a, the templated organization on a 'pure' polymer solution did not lead to a well-ordered structure. A principal lattice direction of hexagonal order was mostly directed by the parallel grating. However, the hexagonal packing of pores included a large amount of defects. Significantly, pores were absent in the vicinity of the grating edge. The confinement effect from the grating was substantially hampered in this morphology. The degree of ordering could be greatly improved by dissolving a small amount of polystyrene-block-poly(ethylene oxide) in the polymer solution. Adding 0.4 wt % of the polymeric surfactant markedly improved the degree of ordering (Fig. 4b). When the amount of surfactant reached 0.8 wt %, a defect-free hierarchical structure was obtained. A linear array of pores was formed along the edge of the grating and neighboring pores were subsequently well-ordered (Fig. 4c). The commercial copper grid applied as a template structure has a hydrophilic surface property. Because the pure polymer solution was rather hydrophobic, its low wettability to the copper grid led to the formation of a convex meniscus at the polymer solution/template wall interface, as depicted in Figure 4d. This gradient in solution thickness could bring about large polydispersity of the aqueous droplet size due to inhomogeneous evaporation of the solvent.[39] The ordering of polydisperse droplets led to numerous defects. Applying a small amount of polymeric surfactant to the polymer solution was found to be an effective means to promoting wetting of the polymer solution. The polymer film fabricated from a solution including 0.8 wt % of surfactant did not show thickness variation around the template wall. Stair-like terrace morphology was observed upon removal of the grating. This signifies that a flat meniscus formed at the grating/polymer solution interface during film preparation. The segregation of surfactant molecules at the interface could reduce interfacial tension (Fig. 4e). (The contact angle of the polymer solution on a flat copper plate was decreased from 23° to 16° by adding 0.8 wt % polymeric surfactant.) The physical confinement from the template effectively directed the ordering of aqueous droplets in this morphology. Additionally dissolving a small amount of surfactant in the polymer solution caused a decrease in the pore size. The mean diameter of the porous structure decreased from 5.0 μm to 2.8 μm by adding 0.8 wt % of the surfactant.

In order to investigate the influence of the surfactant upon the ordering of aqueous droplets, porous films were prepared without using a grating. As shown in Figure 5a, the mean diameter of the pores decreased linearly with the concentration of the surfactant. Nucleation of aqueous droplets is known to be promoted in a polymer solution containing a hydrophilic polymer component.[32] However, the overall condensation rate of the aqueous droplets does not significantly depend on the chemical nature of the dissolved polymer. As a result, pore size decreases with the content of hydrophilic component. Interestingly, the average grain size also decreased with the concentration of polymer surfactant. As plotted in Figure 5b, the average grain size decreased from 0.60 mm^2 to 0.03 mm^2 by adding the

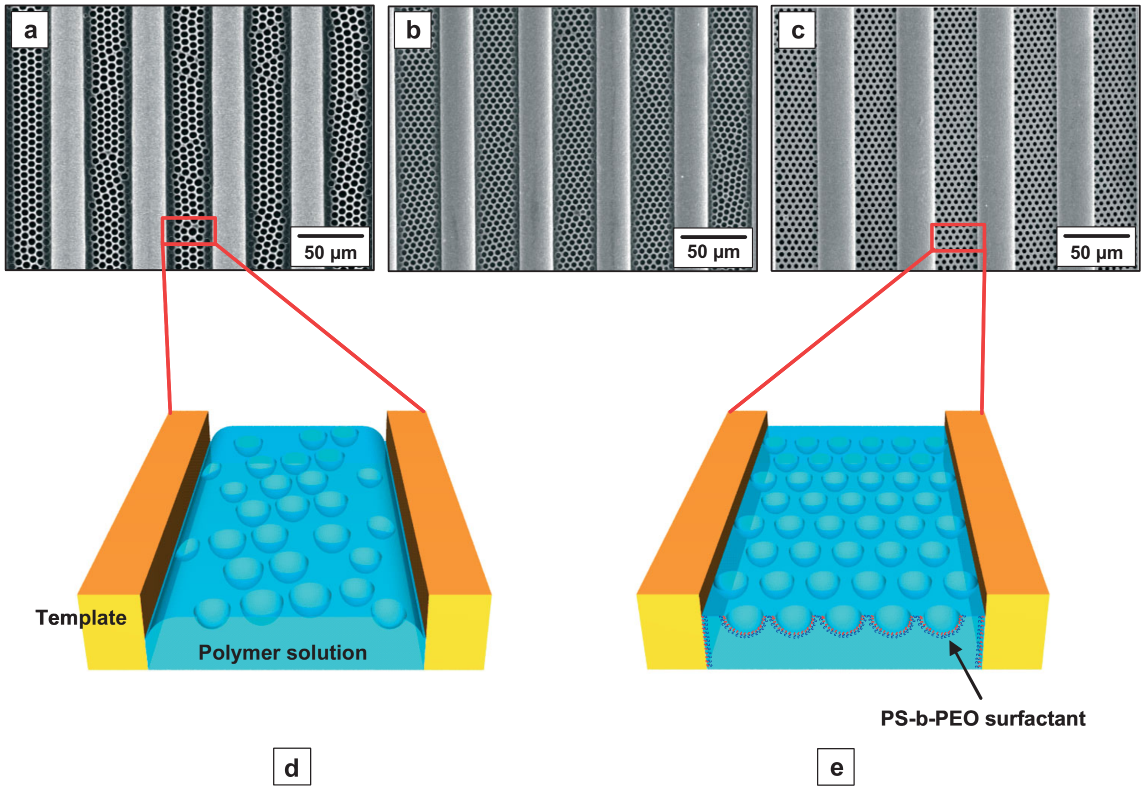

Figure 4. Surfactant effect in polymer solution to induce the highly ordered structure. SEM images of hierarchical structure formed by a) 4 wt % polymer solution without polymeric surfactant, polystyrene-block-poly(ethylene oxide). b) 4 wt % polymer solution involving 0.4 wt % polymeric surfactant. c) 4 wt % polymer solution involving 0.8 wt % polymeric surfactant. d) and e) compare the shapes of polymer solution menisci at the grating wall. In (d), convex meniscuses are formed due to poor wetting between the polymer solution and grating surface. In (e), added surfactants segregate at the grating surface and reduce the interfacial tension such that flat meniscus are formed. The red chain indicates the hydrophilic PEO blocks and the blue chain indicates the hydrophobic PS blocks.

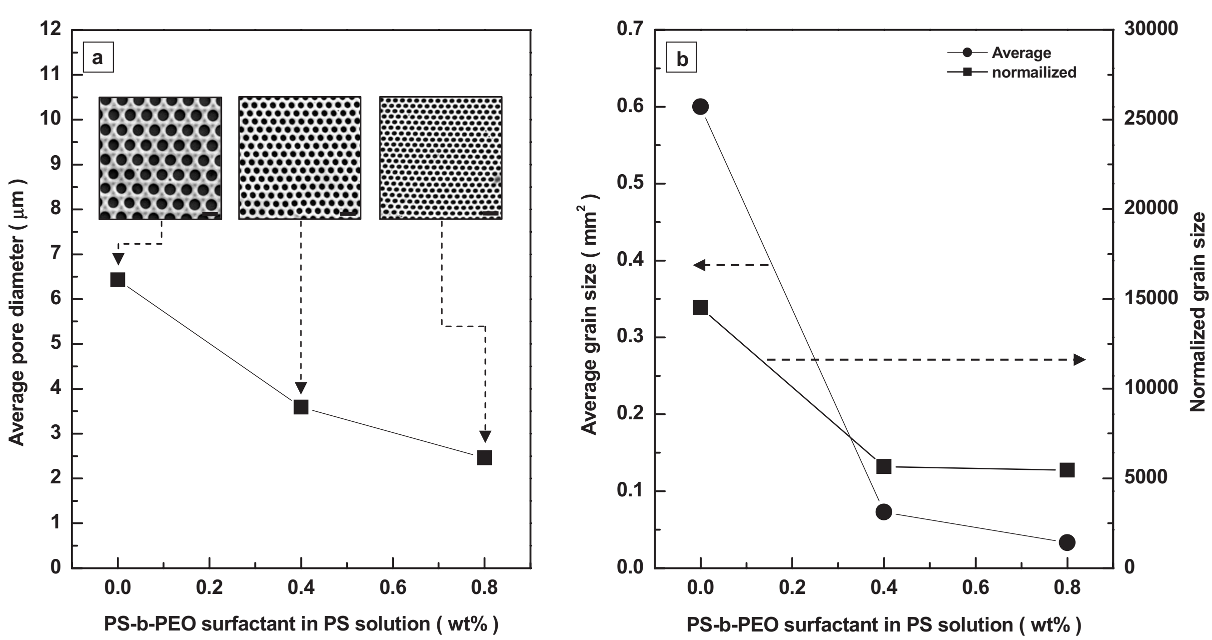

Figure 5. a) Average pore sizes in the porous PS films according to the addition of various concentrations of polymeric surfactant without a copper grating. The insets are SEM images corresponding to each concentration. Scale bar is 10 µm. b) Average grain sizes and normalized grain sizes versus various concentrations of polymeric surfactant.

same amount of surfactant. The normalized grain size given by the measured grain size divided by the square of the pore diameter also decreased. This indicates that addition of the surfactant effectively reduced the pore size but did not enhance the ordering of pores. Consequently, the highly ordered nature of the hierarchical structure fabricated by applying grating is entirely attributed to the templated organization of aqueous droplets imposed by the physical confinement.

We applied various shapes of template structures for diverse hierarchical structures. The same amount of polymeric surfactant, 0.8 wt %, was applied in all cases. Figure 6a shows a hierarchical structure fabricated using a hexagonal grating. Figure 6b and c show ordered structures fabricated using a parallel and square grating, respectively. If the applied template and hexagonal pore array shared a principal lattice in more than one direction, a well-registered hierarchical structure could be produced. Since the hexagonal grating shared all three principal lattices with the hexagonal pore array, a perfectly registered hierarchical structure was fabricated, as shown in Figure 6a. The parallel grating registered only one principal lattice but this was sufficient to induce a highly ordered two-dimensional structure through spontaneous organization of aqueous droplets (Fig. 6b). For the square grating, the morphology showed poor registration of the lattice due to a discrepancy in their lattice structures. Nevertheless, the degree of ordering was markedly improved (Fig. 6c). In all cases, physical confinement by the template successfully induced hierarchical structures with a high degree of ordering.

3. Conclusions

We presented a simple and novel strategy for producing hierarchically ordered polymeric films. Physical confinement from various shapes of gratings assisted hierarchical ordering of aqueous droplets on a polymer solution. The grating structure itself and hexagonally packing of pores constitute independent multiscale orderings in the remaining polymer film. Application of disposable grating and good wettability of the polymer solution onto the grating were crucial in terms of obtaining a highly ordered structure. Polymeric surfactant was applied to promote interfacial wetting, and defect-free hierarchical structures could be produced in polymeric films. A large spectrum of polymeric materials is anticipated to be applied in this approach to prepare diverse hierarchical structures without concerning complicated chemistry or expensive facilities.

4. Experimental

Materials: A monocarboxy terminated polystyrene [M_w: 50 kg mol^{-1}] was purchased from Scientific Polymer Products. Polystyrene-block-poly(ethylene oxide) [PS block: 19 kg mol^{-1}, PEO block: 6.4 kg mol^{-1}] was purchased from Polymer Source. Various copper grids were purchased from Gilder Grids and used as templates for templated organization of aqueous droplets. Each hexagonal, parallel and square grid consists of 460, 400, and 300 meshes.

Hierarchical Structure Fabrication: A polymer solution including 4 wt % of polystyrene and various amounts (0, 0.4, and 0.8 wt %) of polystyrene-block-poly(ethylene oxide) was dropped on organically modified silicon wafer surface under a stream of humid air (relative humidity of 80 %, air flow rate of 4 L min^{-1}) at room temperature. A copper grid was placed over the polymer solution to induce template assisted organization. The solution was left in the stream of humid air until it was completely dried.

Characterization: Surface morphologies of hierarchically ordered porous polymer films were investigated using a field emission scanning electron microscopy (FE-SEM, FEI Sirion) at an accelerating voltage of 10 kV. A Fourier transform was obtained from the SEM images using Scion image software (www.scioncorp.com). The difference of wetting for a pure polymer solution on copper and a polymer solution with PS-*b*-PEO surfactant on copper was measured using a contact angle analyzer at a static mode (Phoenix 150, SEO).

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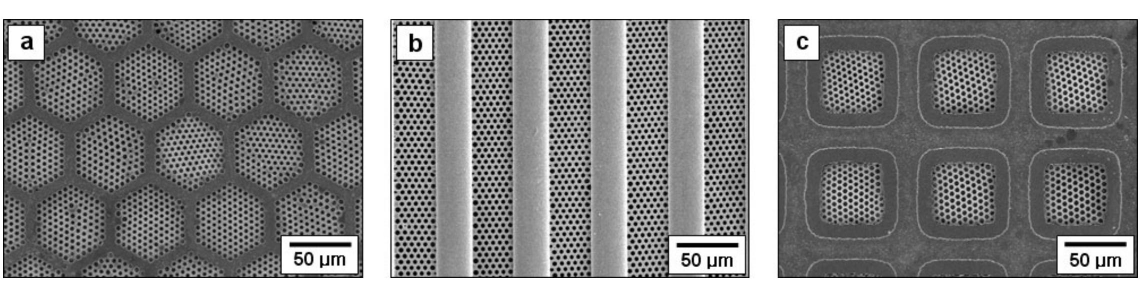

Figure 6. Diverse hierarchical porous structures induced by various shapes of gratings. a) SEM image of hierarchical structure fabricated using a hexagonal grating. b) SEM images of ordered structures fabricated using a parallel grating and c) a square grating.

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