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Full Color Stop Bands in Hybrid Organic/Inorganic Block Copolymer Photonic Gels by Swelling−Freezing

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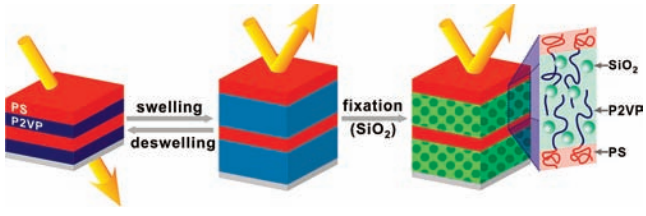
Block copolymers have been widely investigated for fabricating functional nanomaterials due to their unique properties of self-assembly.[1−4] For example, block copolymers have been used as platforms for creating various 1D, 2D, and 3D photonic crystals, periodic dielectric structures where the propagation of electromagnetic waves is prohibited over a certain range of frequencies.[5−13] Typically, block copolymer photonic crystals exhibiting stop bands in the visible region of wavelengths have employed extremely high-molecular-weight polymers ($\sim 10^6$ g/mol) with narrow molecular weight distribution. Hence, tailoring the optical properties of block copolymer photonic crystals is limited by the difficulty of synthesis and processing of such high-molecular-weight copolymers. To address this problem, Kang et al. recently reported swollen photonic gels, which demonstrated that selective swelling of the block copolymer lamellar structure allows extremely large tunability of the photonic stop band from the UV region to the IR region (λ_{peak} = 350−1600 nm).[14] In this case, lower-molecular-weight block copolymers ($<5 \times 10^4$ g/mol) can also be used as materials for creating photonic crystals by swelling, but obviously the optical properties of the swollen photonic gels disappear when the gels dry.

Herein, we report a facile way of fabricating organic/inorganic hybrid 1D photonic crystals exhibiting stop bands in the visible regime after drying by self-assembly of the modest-molecular-weight gel block copolymers and a subsequent stop band fixation process we term "swelling−freezing" (Scheme 1). The general idea

Scheme 1



is that the easily tunable photonic gels in solution phase can be used as a template for incorporation of components that will transform the soft gel to a solid. To demonstrate our idea, swollen photonic gels were first prepared by self-assembly of polystyrene-*block*-poly(2-vinylpyridine) diblock copolymer PS_{190}-*b*-$P2VP_{190}$ ($M_n \times 10^3$ = 190/190, PDI = 1.10, purchased from Polymer Source Inc., Dorval, Canada) and then subsequently fixed with SiO_2. PS_{190}-*b*-$P2VP_{190}$ photonic gel films were prepared as previously described.[14] Briefly, in-plane lamellar films were prepared by spin-casting from a 5% PS_{190}-*b*-$P2VP_{190}$ solution in propylene glycol monomethyl ether acetate and subsequently annealing the film in chloroform vapor at 50 °C for 7 days. The as-prepared, dry films were transparent since both the periodicity and the refractive index contrast were insufficient to exhibit stop bands in the visible region of wavelengths. The photonic gel films were then swollen with methanol, a selective solvent for the P2VP blocks, and displayed a uniform blue color. Spectrophotometer data show two stop bands at 465 and 928 nm (Figure S1, Supporting Information). Since the primary band is out of the visible region, the visible blue color is due to the second-order peak, positioned at 465 nm. On the basis of the UV/vis spectrum, we calculated the size of swollen P2VP microdomains using the transfer matrix method,[15] which gave t_{P2VP}(swollen) ≈ 280 nm − almost 5.5 times the original domain size (t_{P2VP} = 50 nm).[14] This suggests that the swollen P2VP domains can be filled with other materials since the content of P2VP in the layer is only 18% by volume. Infiltration of SiO_2 was carried out by sol−gel processing using tetraethoxysilane (TEOS) as a precursor for SiO_2.[16−18] TEOS was added to the methanol bath containing the swollen gel ([TEOS] = 0.45 M), and then ammonium hydroxide was gradually added with vigorous stirring ([NH_4OH] = 0.15 M), which made the solution basic with pH = 11. After 20 min of stirring at room temperature, the pH of solution was lowered to pH = 9 by adding concentrated hydrochloric acid. Upon addition of hydrochloric acid, the clear solution gradually became turbid and viscous, and eventually formed gel-like solids. The films were aged at pH = 9 for different periods of time (τ_a) to complete the fixation. The final frozen photonic gels ("*f*-photonic gels") were obtained after drying the films in air. In basic condition, TEOS is catalytically hydrolyzed, forming discrete colloidal particles, and they grow with time. These colloidal particles aggregate into a continuous network, forming a SiO_2 gel under lowered pH.[19] When the sol−gel reaction was carried out entirely either at pH = 11 or pH = 9, the fixation failed not only because of insufficient capability of infiltration but also because of formation of a thick residual coating over the film which deteriorates the optical properties by random scattering. We found that, by sequentially lowering the pH from 11 to 9, the structure of swollen photonic gels could be appropriately fixed.

After drying, the *f*-photonic gels showed strong reflective colors for months without any change. The persistent reflective color of the dry *f*-photonic gels suggests that the swollen photonic gels were successfully fixed by infiltration of SiO_2. Fixation was fully controllable and reproducible. As shown in Figure 1, the position of stop bands of the *f*-photonic gels could be easily varied with increasing aging time τ_a. For a short aging time (τ_a = 15 min), a well-defined stop band first appeared at λ_{peak} = 381 nm, gradually shifted to longer wavelengths as the aging time increased, and finally

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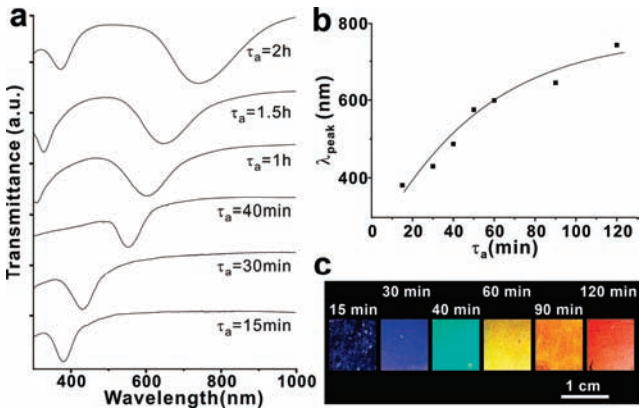

Figure 1. (a) Transmission spectra of dry *f*-photonic gels prepared at different aging times (τ_a =15 min to 2 h). (b) Variation in λ_{peak} with τ_a. The line is provided as a guide to the eye only. (c) Color variation of the *f*-photonic gel films with aging time. Photographs were taken on a black background under white light illumination.

reached λ_{peak} = 741 nm when the sample was aged for 2 h. The shift of λ_{peak} with aging time implies that the amount of SiO_2 infiltrated within the P2VP domains gradually increased, and accordingly the P2VP/SiO_2 domain size and the overall periodicity also increased. We found that the position of the stop band increased approximately logarithmically as a function of the aging time (Figure 1b). The bandwidth also gradually increased with increase of the aging time. Bandwidth broadening is mainly due to the increase of the refractive index contrast between PS ($n_{PS} \approx 1.6$) and P2VP ($n_{P2VP} \approx 1.6$) domains as more SiO_2 ($n_{SiO_2} \approx 1.22-1.46$)[20] is incorporated into the P2VP domains.[14] Samples with long aging time ($\tau_a > 1$ h) showed another peak in the short wavelength region other than the primary peak. This peak can be attributed to the second-order peak, since it satisfies the relationship $\lambda_{first\ peak} = 2\lambda_{second\ peak}$.[21] The existence of the higher order peak indicates that the lamellar structures have good long-range order after the SiO_2 infiltration process.

Scanning electron microscopy (SEM) of the *f*-photonic gels confirmed that the swollen lamellar structures were successfully fixed by SiO_2 (Figure 2). Samples for cross-sectional imaging were

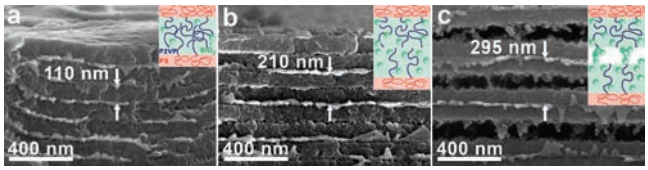

Figure 2. SEM images of *f*-photonic gels prepared at (a) τ_a =15, (b) 45, and (c) 120 min. Samples for SEM imaging were prepared by fracturing *f*-photonic gels immediately after freezing in liquid nitrogen. SEM images were taken after osmium coating. Inset cartoons show the P2VP/SiO_2 layers as thicker green layers and the glassy PS blocks as thin red layers. With increasing amounts of silica in the P2VP layers, the silica particles bridge across from the P2VP layers, forming a third layer comprised of silica and solvent (air after drying).

prepared by fracturing *f*-photonic gels immediately after freezing in liquid nitrogen. In this case, layers defining the PS and P2VP/SiO_2 domains are revealed due to their different mechanical properties.

The thin, bright layers in the images are the PS domains, and the thicker, somewhat darker layers correspond to the P2VP/SiO_2 domains. As shown in Figure 2, the thickness of the P2VP/SiO_2 layers increases with aging time, while that of the glassy PS layers remains constant. At τ_a = 15 min, the periodicity, the distance between the two thin PS layers marked with arrows, was 110 nm, which is slightly larger than that of the original photonic gels (d = 100 nm).[14] The periodicity increased to 210 nm and to 295 nm when the aging time increased to τ_a = 45 min and 2 h, respectively. These images directly prove that SiO_2 was infiltrated into the P2VP domains, further confirmed by energy dispersive X-ray spectroscopy analysis (Figure S5, Supporting Information). Interestingly, at higher loadings of silica ($\tau_a > 45$ min), the originally interdigitated P2VP chains were split into two parts and subsequently induced void regions with silica bridges connecting P2VP layers. Currently we are investigating its mechanism.

In conclusion, we have demonstrated a facile method of fabricating robust photonic crystals from modest-molecular-weight block copolymers which takes advantage of a swelling and freezing process. Controlled infiltration of SiO_2 within the swollen P2VP domains allows fixating and tailoring the stop bands across the full visible portion of the spectrum (400−800 nm). We are currently investigating other *f*-photonic gels infiltrated with metal oxides, such as TiO_2, ZnO, Al_2O_3, and ZrO_2. We propose that this method could provide a simple avenue to fabricating hybrid organic/inorganic photonic crystals using block copolymers as a template.

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Supporting Information Available: Experimental details for preparation and fixation of photonic gels, UV−vis spectra for swollen photonic gels, SEM images for other *f*-photonic gels, and the results of EDS analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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