

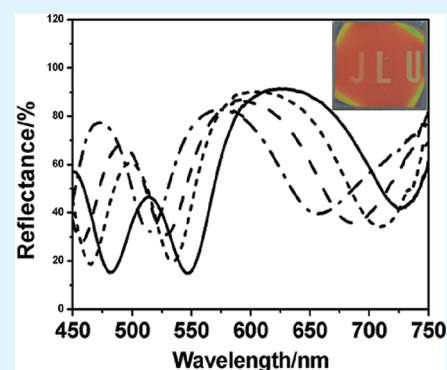
Patterning Organic/Inorganic Hybrid Bragg Stacks by Integrating One-Dimensional Photonic Crystals and Macrocavities through Photolithography: Toward Tunable Colorful Patterns as Highly Selective Sensors

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Supporting Information

ABSTRACT: Herein, we report a simple method to fabricate patterned organic/inorganic hybrid 1DPCs by top-down assisted photolithography. Versatile colorful pattern with different size and shape can be produced by selectively exposing the 1DPCs under UV light with predesigned photomask directly. The period change, especially the thickness variation of the top polymer layer, is the main reason for the colorful pattern generation. Because of the swelling property of the polymer layers, the pattern color can be modulated by introducing or taking off organic solvents, leading the as-prepared patterned 1DPCs to be effective sensors with high selectivity.



KEYWORDS: one-dimensional photonic crystals, UV irradiation, pattern, macrocavity, sensors

INTRODUCTION

Among numerous research studies on fabrication of photonic band gap materials,¹ patterning photonic crystals can be regarded as a key step in the developing road from colloidal crystals² as the original material to the final integrated optical circuits,³ which can be achieved by self-assembly,⁴ lithographic approaches,⁵ inkjet printing,⁶ and so on. Among them, self-assembling colloidal crystals in microchannels and different kinds of substrates is a comprehensively used method.^{7–23} Whitesides and his colleagues, for the first time, have produced high-quality artificial opals in microchannels by evaporating the liquid medium from colloidal suspension, and fabricated inverse opal structures by using the colloidal as templates.⁷ Yang et al. has described a high-speed crystallization process to build colloidal photonic crystals inside microchannels by using centrifugal microfluidics platforms.^{9b} As alternatives, vertical dip-coating of colloidal particles on patterned substrates, capillary force-induced deposition and microfluidic fabrication have been demonstrated for patterned colloidal microstructures, which has been reported by Ozin team.^{3a,9d} Except colloidal crystals self-assembly, various lithography provides another platform for fabricating patterned photonic crystals, including holographic lithography, electron beam lithography, soft lithography, and so on.^{5,9,10} Rogers group has constructed micromixers or optical filters inside microfluidic channels by near field phase shift lithography using a thick negative

photoresist.¹⁰ Yang and co-workers have also developed a new strategy to fabricate hierarchically patterned photonic crystals by integrating holographic lithography with soft-lithography.^{9a} Our group has built up many kinds of patterned photonic crystal and related nanostructured materials through employing lift-up soft-lithography.²

Patterning photonic crystals draws extensive attention because of their broadly promising applications in photonic paper,²⁴ displays,²⁵ microfluidic devices,⁹ sensors,²⁶ and optical analysis.²⁷ Kwon and Yin groups employ magnetically tunable photonic crystals to demonstrate rapid production of high-resolution patterns and achieve precise structural color printing.²⁸ Yang group employ electro-responsive tunable colloidal crystals to fabricate a reflective mode display device capable of repeatedly changing the color of a pattern of characters with fast response and clear boundaries over large area.²⁵ A special kind of patterned photonic crystal known as photonic nose reported by Ozin and co-workers, is manufactured through selectively etching the nanoparticle one-dimensional photonic crystals (1DPCs) with a patterned mask and can be used as a platform for molecule and bacteria identification.²⁶

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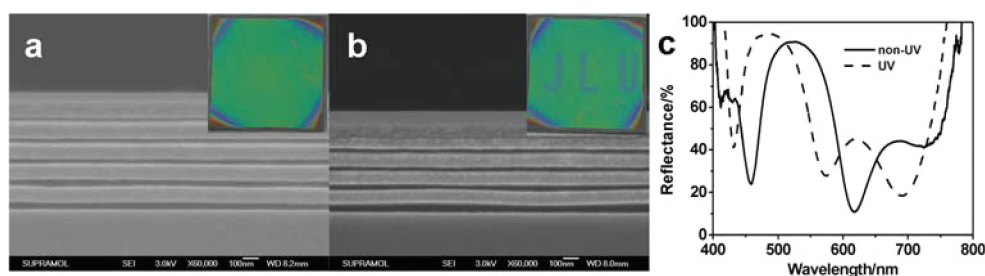


Figure 1. Cross-linking SEM images, photographs, and their corresponding reflective spectra of a photonic crystal irradiated with JLU patterned mask for 10 min. The size of the photograph is about 20 mm × 20 mm.

At present, most of the reported patterned photonic crystals are based on three-dimensional opal and inverse opal structures from colloidal crystals self-assembly, while little work has been reported about 1DPCs patterning. 1DPCs, also known as Bragg stacks or Bragg mirrors, consist of ordered multiple layers of two alternating materials with varying dielectric constants along the direction normal to the substrate upon which the layers are deposited.^{29–48} Interference of light reflected at the interfaces of the dielectric layers leads to strong reflection in a well-defined wavelength range resulting in pronounced structural coloration.²⁹ Simple configurations are realized by sequential coating of thin solid films of alternating refractive index. The spectral response can be finely tuned by varying the refractive index,^{30,31} thickness,^{37–40} and number of the alternating layers,^{30,31} and by introducing defects.^{47,48} Our group has successfully fabricated several kinds of organic/inorganic hybrid 1DPCs by alternating responsive polymer and nanoparticles, whose optical properties can be tuned by reversibly introducing or taking off external stimuli.^{49–51} Thanks to the simple ordered layer structure, 1DPCs are easily processed to achieve their patterning with the help of state-of-the-art lithographic techniques, which promises them many potential applications such as highly selective sensor, security label, and photonic paper.^{26,52}

By introducing defects into the 1DPC structure, an obvious optical macrocavity can be produced, which modifies the optical properties and colors of 1DPCs.^{47,48} In this paper, we report a simple method to fabricate patterned organic/inorganic hybrid 1DPCs through top-down assisted photolithography, during which an optical macrocavity is produced promising the Bragg Stacks color patterned and structure disordered. Diverse colorful patterns with versatile size and shape are produced through careful choice of photomask. The pattern resolution can achieve micrometer level. Because of the solvent sensitivity of the polymer layer, the color of the pattern can be modulated, which suggests that the patterned Bragg Stacks can be used as a signal for colorful detecting solvents.

EXPERIMENTAL SECTION

Materials. Methyl methacrylate (MMA, 99.5%), 2-hydroxyethyl methacrylate (HEMA, 99.5%) and ethylene glycol dimethacrylate (EGDMA, 99.5%) were distilled under vacuum and stored at -4°C before using. Azobisisobutyronitrile (AIBN) was recrystallized twice in 95% alcohol before using. Ethanol, acetonitrile, acetone, butanone, and dimethyl formamide (DMF) were used as received. The silicon wafers (100) were cut into 20 mm × 20 mm pieces, soaked in the mixture of 98% H_2SO_4 /30% H_2O_2 (volumetric ratio 7:3) for 20 min under boiling (*caution: strong oxide*), and then rinsed with deionized water several times, at last dried with N_2 stream.

Preparation of the 1DPCs and Their Patterning. Preparation of titania sol: The titania sol was prepared according to reference.⁵³

Briefly, 4 mL of tetrabutyl titanate was dissolved into 2 mL of isopropanol (IPA) in a conical flask for 5 min; 0.21 g of water and 17 μL of concentrated HCl were mixed with 4 mL IPA for 5 min, and then the mixing solution was dipped into the above conical flask for about 10 min, and stirred 12 h at room temperature.

Preparation of the copolymer: The copolymer was prepared by solution radical polymerization. In detail, 1 mL of HEMA, 1 mL of MMA, 0.3 mL of EGDMA, and 10 mg of AIBN were dissolved into 25 mL of butanone, and the solution was then bubbled with N_2 for 30 min and put into 60°C oil for 6 h of reacting. To get different thickness films, we diluted the titania sol by different volume of IPA and the polymer solution was diluted by different volume of butanone.

Preparation of the 1DPCs and their patterning: The 1DPCs were fabricated by spin-coating the titania sol and the polymer precursor alternatively at 3000 rpm for 60 s on silicon wafer. Each layer was baked at 135°C for 10 min. The first layer was polymer layer and the last layer was titania layer in all our experiments. The number of total layers of the film materials was 10. The pattern was produced by exposing the 1DPCs below the UV light with a mask. The power of the UV light is 1000 W and the distance between the UV source and the film surface is 19 cm.

Characterization. SEM micrographs were taken with a JEOL FESEM 6700F electron microscope with primary electron energy of 3 kV. The samples were sputtered with a thin layer of Pt prior to imaging. A Shimadzu 3600 UV–vis–NIR spectrophotometer with standard mirror optics was used to measure the reflectance in the 200–1600 nm range at the incidence angle of 5 degree. An Optics spectrofluorometer (USB4000) was employed to detect reflection spectrum in the 400–800 nm at normal incidence. The *ex situ* determinations of layer thicknesses and optical constants of layers were carried out using an ellipsometer (Woollam XLS-100) at an angle of 70° and within a spectral range of 315–720 nm. The thicknesses of the films were also determined using a Dektak150 surface profiler (Veeco).

RESULTS AND DISCUSSION

Patterning Organic/Inorganic Hybrid 1DPCs by Photolithography. Organic/inorganic hybrid 1DPCs were fabricated through alternating thin films of poly methyl methacrylate-co-hydroxyethyl methacrylate-co-ethylene glycol dimethacrylate (PMMA-co-PHEMA-co-PEGDMA) and titania nanoparticle sol by spin-coating. Both of the titania sol and the polymer precursor layer were baked at 135°C for 10 min, which avoided the as-coated layers were destroyed by the following layers. Due to the higher refractive index of titania layer (1.831) compared with polymer layer (1.497) and ordered layer structure (Figure 1a), obvious photonic stop band and vivid color can be easily obtained in several layers.^{30,49} (Figure 1a,c) Its position is determined by the thickness of the polymer and/or the titania layer which can be tuned by changing the spin-coating rate and the precursor concentration. The film color is very uniform over a large area with minimal adventitious striations, cracks, and comets. (Figure 1a,b)

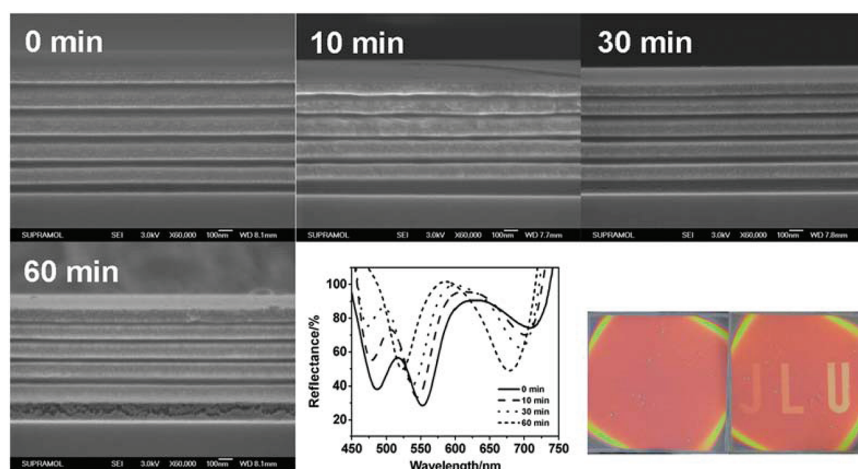


Figure 2. Cross-linking SEM images, photographs, and their corresponding reflective spectra of a photonic crystal irradiated with JLU patterned mask for different lighting time (J, 10 min; L, 30 min; U, 90 min). The size of the photograph is about 20 mm × 20 mm.

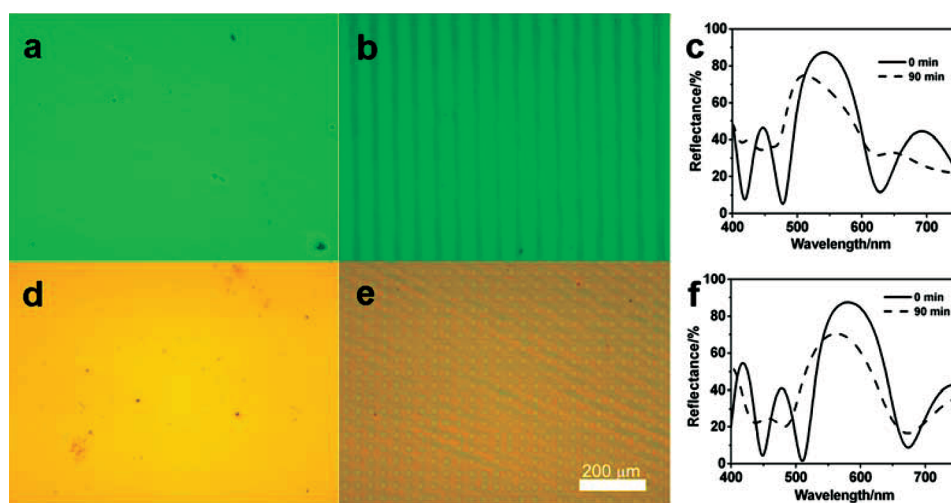


Figure 3. Microscopy images of two 1DPCs (a, d) before and (b, e) after UV irradiation and (c, f) their corresponding reflective spectra.

As the 1DPC is irradiated directly by UV light with a predesigned photomask, corresponding pattern is produced with color distinct from the substrate (Figure 1b). The color of pattern boundary is extremely clear. A shift of the photonic stop band is also observed simultaneously (Figure 1c). SEM images a and b in Figure 1 show that the top-layer polymer is etched before and after UV irradiation, indicating the ordered structure is destroyed, which leads to the shift of photonic stop band and the change of color.^{30,47,48} All of the “JLU” regions are lighted for 10 min during this patterning process, which results in the generation of the same color pattern. By contrast, different colored pattern can be achieved when the exposed regions are irradiated for different time. As demonstrated in Figure 2, the thickness of the top layer decreases with the increased irradiation time, leading the structure more and more disordered, which results in the blue shift of the photonic stop band gradually and the generation of different colored pattern.

The resolution of the pattern prepared by this method can achieve micrometer scale, which can be confirmed in Figure 3. The ordered macroscale strip and circle patterns are produced by using the corresponding size photomask, which illustrates that various colorful patterns with versatile size and shape can

be prepared through careful choice of photomask. (Figure 3a, b, d, and e) The corresponding optical property change is shown in panels c and f in Figure 3, displaying that the photonic stop band shifts to blue and the symmetry of the photonic stop band decreases. In addition, the intensity of the Bragg peak also reduces for the reason that the thickness of the top layer polymer in the lighted region becomes thinner. The change in reflective spectra of the patterned 1DPCs before and after irradiation may be owing to the collaborative contribution of the unexposed part and exposed part. Micrometer scale patterned 1DPCs can combine with microfluidic technology to prepare optofluidics that may possess potential applications in bioassay.

Patterning Mechanism. To clarify the patterning mechanism clearly, thickness changes of a single polymer layer and titania layer with UV irradiation are investigated first. From Figure S1 in the Supporting Information, we can see that a single polymer layer with different thicknesses can be degraded completely after enough irradiation time, whereas thickness change of a single titania layer decreases first and then keeps constant with increased etching time. The polymers we used are methyl acrylate and their derivatives which can be degraded with the final product as carbon dioxide and methane or carbon

monoxide and methanol under UV irradiation.^{54,55} The titania layer is a thin organic/inorganic hybrid film. Its thickness change is caused by the removal of organic groups under the UV light because the organic components in the hybrid materials suffer from photochemical decomposition.^{56,57}

The color of the 1DPC variation originates from the structure and optical property change during the patterning process, which comes from the degradation of the polymer and titania layer under UV light. Figure 4 displays the cross-section

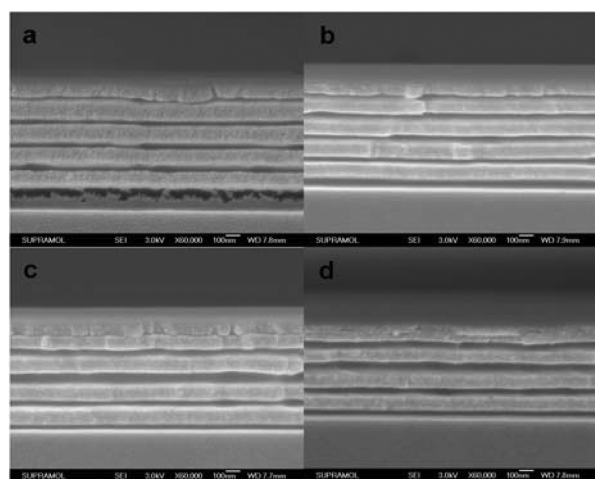


Figure 4. Cross-section SEM images of the photonic crystal at different irradiation time. (a) 0, (b) 40, (c) 80, and (d) 120 min.

SEM image of the 1DPC at different lighting time, from which we can see the change of the period. The original thicknesses of the titania layer and the polymer layer are 121 and 42 nm on average, respectively. The thickness of the top layer polymer decreases gradually with increased etching time, for which the ordered photonic structure is destroyed. The top-layer polymer is etched completely after 120 min. (Figure 4d) Thickness changes of the titania layers during the etching process are summarized in Table S1 in the Supporting Information, from which we can see that titania layer thickness change to 58, 70, 86, 104, and 110 nm from the top layer to the bottom layer, respectively. Furthermore, the titania nanoparticle profile becomes more and more clear with increased irradiation time. Thickness change of the titania layer may be caused by the degradation of the left organic compositions under UV irradiation. The decrease in the titania layer thickness causes separation of the adjacent polymer and titania layer, which results in the increase of the distances between the two-layer

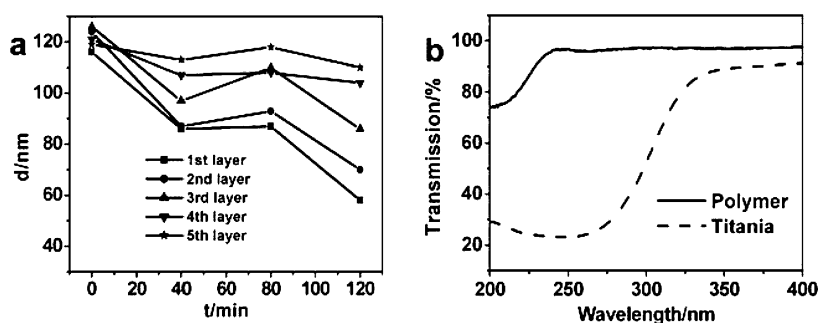


Figure 5. (a) Relation curve between the thickness of the titania layer and irradiation time. (b) Transmission spectra of a single polymer and titania layer.

titania. Through calculation conclusion can be got that the total thicknesses of the 1DPC are 855 and 644 nm, respectively, before and after etching. So the total thickness change is 211 nm. The thickness change of the total titania layer is 177 nm during the etching, therefore the total thickness change of the polymer layer during the etching is 34 nm, which is close to the thickness of the top polymer layer. Hence, during the etching only the top-layer polymer is etched while other polymer layers keep their thicknesses almost constant.

Figure 5a presents the relation curve between the thickness of the titania layer and irradiation time, indicating that the thickness of each titania layer has been changed. The top layer is etched fastest and the etching speed decreases gradually from the top layer to the bottom layer. This is because that the titania layer has strong UV absorption (Figure 5b, the dash line), the intensity of the UV light transmitted from top to bottom reduces gradually. Since the UV light is largely absorbed by the titania layer, other polymer layers can not be degraded. The top polymer layer is almost etched completely during the last 40 min etching, brings about the total reflective intensity reduced and more UV light transmitted. The solid line in Figure 5b shows the transmission spectra of a single polymer layer, which displays that the polymer layer has little absorption in the UV region. Because the etching process is controlled by UV irradiation, the polymer layer has little influence on its degrading.

Optical property change of the patterned photonic crystal is demonstrated in Figure 6, showing the reflective spectra and

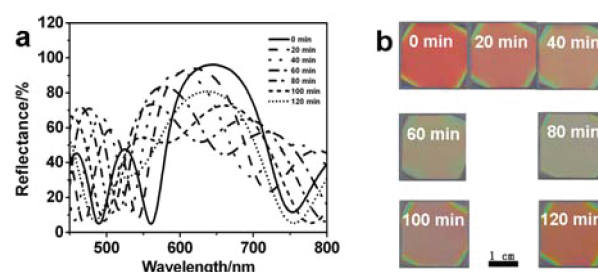


Figure 6. (a) Reflective spectra and (b) its corresponding photograph of a photonic crystal exposed for different time. The size of the photograph is about 20 mm × 20 mm.

the corresponding color change of the 1DPC at different lighting time. The solid line of Figure 6a shows the reflective spectra of a 1DPC consisting of 121 nm titania and 42 nm polymer with photonic stop band at 650 nm. With increasing the exposure time, the thickness of the titania layer and the top

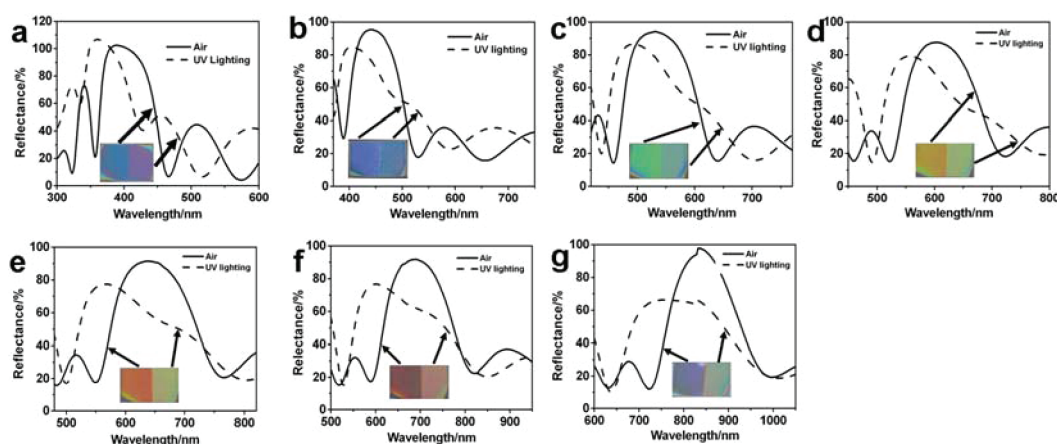


Figure 7. Reflective spectra of the patterned photonic crystal and its corresponding photograph in different solvents. (a) Air, (b) water, (c) ethanol, (d) acetonitrile, (e) butanone, (f) acetone, and (g) dimethyl formamide. The size of the photograph is about 10 mm × 20 mm.

polymer layer decreases, which leads to the decrease of the period. Therefore the photonic stop band shifts to the shorter wavelength. As the lighting time increases to 40 min, the ordering of the 1DPC structure is destroyed largely, thus the photonic stop band is not obvious. By contrast, a photonic pass band appears at 670 nm. The thickness of the top polymer layer continues to decrease with the continually increased irradiation time, resulting in the pass band also proceeds to shift. As the lighting time increases to 120 min, the top polymer layer is etched completely. During this process, the first two titania layers combine together with its thickness close to that of other titanias; therefore, the photonic stop band recovers to its original position. As the number of the total layers decreases, the intensity of the reflectivity reduces. Color changing during the UV lithography is shown in Figure 6b. The original and final color of the film is red. After 120 min lighting, we can achieve a color cycle. When there is a photonic pass band arising, the color changes to gray, because the light within the range of original stop band region is transmitted.

From the above discussions about the structure and optical property change, the thickness changes of the top layer polymer and all the titania layers during photolithography process result in the variation of the photonic period, which causes the color change and the photonic stop band shift. Because of the color difference from the exposed regions and substrates can be easily captured by naked eyes, colorful patterns can be created by carefully choosing the photomask.

Evolution of Optical Properties of the Patterned 1DPCs in Organic Solvents. Because of the sensitivity of the polymer layer to solvents,⁵⁸ incorporating organic solvents into the polymer network changes the refractive index and increases the thickness of the polymer layer, which leads to the changing of 1DPCs' optical properties.⁵¹ Color from the patterned 1DPCs can be reversibly tuned by introducing or taking off different organic solvents. The pattern color change in organic solvents can be captured by naked eyes directly, verifying it as a colorful signal for visual detection of organic solvent. Figure S2 in Supporting Information shows the cross-section SEM image of a patterned 1DPC with half a part irradiated by UV light for 30 min. The original 1DPC possesses 70 nm titania and 20 nm polymer (see Figure S1a in the Supporting Information). The top polymer layer is etched completely after 30 min (see Figure S1b in the Supporting Information), which results obvious change in the reflective spectra and corresponding photograph.

(Figure 7a) When dipping the patterned 1DPC into water, ethanol, acetonitrile, butanone, acetone, and dimethyl formamide respectively, the patterned 1DPC changes to different color accompanying the photonic stop band red shifts to different positions. (Figure 7b–g) The patterned 1DPC possesses special colored pattern and stop band in each other solvent. Color difference in organic solvents depends on different swelling degrees of the polymer layer in solvents. Swelling behavior of solvents to polymers is determined by the solvent solubility parameter,⁵⁹ which describes different interactions between the polymer and solvent molecules, resulting that the shift of the photonic stop band increases with the solvent solubility parameter increasing.⁵¹ The color of the unexposed region in water and dimethyl formamide is very similar, which is caused by the second diffraction peak position in dimethyl formamide is very close to the first diffraction peak position in water. Furthermore, most of this two photonic stop bands are overlapping (see Figure S3 in the Supporting Information). However, we can also easily differentiate these two solvents by naked eyes because the exposed part colors of the patterned 1DPC in them are different. Compared with the existing photonic sensors, this phenomenon confirms that our photonic sensitive system possess much higher selectivity. More elaborate features such as four or more colors integrating together can be realized with further modification of the patterned 1DPCs, which may be used as a highly selective sensor for substances with similar properties.

CONCLUSIONS

In conclusion, diverse kinds of patterned organic/inorganic hybrid photonic crystals with different size and shape are produced by top-down assisted photolithography. The color of the pattern can be reversibly modulated by introducing/taking off organic solvents, combining with simple fabricating method, low cost, and large area production, which promises the patterned Bragg stacks to be used as efficient sensors with high selectivity.

ASSOCIATED CONTENT

Supporting Information

Cross-section SEM images, thickness changes of single polymer and titania layers and reflective spectra of a patterned 1DPC (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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