Dual-Modal Invisible Photonic Crystal Prints from Photo/Water Responsive Photonic Crystals

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Invisible photonic crystal prints (IPCPs) are appealing for anti-counterfeiting and information protection due to their capability in hiding and showing the encrypted information under specific conditions. Herein, the dual-modal IPCPs based on responsive photonic crystals (PCs) with tunable photoluminescent (PL) and structural colors are reported. The responsive PCs are prepared by the self-assembly of dyes doped silica particles into non/swellable polymers. The independent design and control over the optical response of the PL of the particles and structural colors of PCs enable the successful encryption of dual-modal patterns. Under normal conditions, the as-fabricated IPCP shows a fake pattern with uniform structural colors and thus hides the encrypted pattern due to the similar particles size, lattice constant, and refractive index of each region. In striking contrast, PL and structural colors-based new patterns can be instantly and reversibly revealed when the IPCP is exposed to UV illumination or soaked in water. This work provides a new concept in designing and fabricating dual-modal IPCPs, and facilitates their applications in the fields of color display, antifake package, and multilevel anti-counterfeiting.

1. Introduction

Photonic crystals (PCs) exhibit potential applications in the field of color display,[1–7] pigment,[8–11] printing/pattern,[12–18] sensing,[19–35] chemical separation,[19,36–39] anti-counterfeiting,[38–53] and photocatalysis,[54–57] benefiting from the unique periodic structures.

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DOI: 10.1002/adpr.20200197

The color of the PC comes from the diffraction, interference, and scattering of light by its ordered structures, which can be altered by the lattice constant, refractive index, and orientations of the crystal.[25,58–63] Therefore, PC-based patterns with visible color contrast between the background and pattern can overcome the photobleaching and environmental pollution compared to that of conventional patterns from organic dyes and inorganic pigments. In contrast to the conventional visible patterns, invisible photonic crystal prints (IPCPs) first proposed and demonstrated by Ge’s group[60] have attracted growing interests due to their ability in hiding and revealing the encrypted information at normal conditions and external stimulus, respectively.

Recently, various approaches based on cross-linking,[41,46,66–70] wetting,[46,66,72] bilayer PC films,[42,73] and functional particles[28,45,74,75] are developed to prepare IPCPs. The information or patterns of the IPCPs can be hidden at the normal condition but revealed in the presence of solvents,[41,42,46,66,69–72] vapors,[28] mechanical force,[67,68] UV light,[45] and viewing angles.[73,75] The working mechanism of these methods is to create asymmetric optical response between the pattern and background under specific stimulus, while maintaining the similar colors of the pattern and background. For example, cross-linking strategy is widely used to fabricate IPCPs by regionally restricting the swellable or deformable properties of PCs using the cross-linker, leading to the dissimilar optical response between the pattern and background. Despite their success in fabrication, only a single pattern can be encrypted into the IPCP, which will limit its practical applications.

Here, we demonstrate that dual-modal IPCPs can be fabricated by the combination of photo- and water-responsive PCs, which were prepared by the self-assembly of dyes doped silica particles into the functional polymers. The fabrication is considerably straightforward and efficient, and IPCPs with any desired patterns can be obtained in a simple way. The key to the construction of IPCP is to regulate the optical response of PCs by UV illumination and water, respectively. The photoluminescent (PL) and water responsiveness of IPCPs is determined by the species of dye in silica particles and the swelling behavior of the polymer, respectively. In the beginning, the as-fabricated IPCP exhibits a fake pattern with similar structural colors. A new pattern with different PL colors can be immediately shown as the UV light is illuminated on the IPCP. Interestingly, another
new pattern with different structural colors can be revealed once the IPCP is immersed in water due to the swelling effect of PCs. The hiding and revealing of the pattern into the IPCP between the pristine and UV irradiation/swelling state is instant and reversible. Although the combination of fluorescence and structural color has been reported previously,[77–79] these works focused on the enhancement of fluorescence by PC or detection, which are quite different from this work. The IPCP prepared by this work provides a new concept in the design and fabrication of multiresponsive IPCPs and will promote their application in multistage anti-counterfeiting, information storage, and delivery.

2. Results and Discussion

Figure 1 shows the schematic illustration of the fabrication processes of the IPCP, which includes 1) the synthesis of dye-doped silica particles; 2) the self-assembly of the PL silica particles into PCs that can respond to UV irradiation and water, respectively; and 3) arrangement of these PCs with designed patterns in a desired way.

The PL silica particles with diverse fluorescent colors are prepared simply by the introduction of silane dyes into the reaction system of Stöber silica particles. Here, we use the (3-aminopropyl)triethoxysilane (APS) to form a covalent bond with the fluorescein isothiocyanate isomer I (FTIC) or rhodamine B isothiocyanate (RITC) through the click reaction between the amidogen from APS and isothiocyanate groups from dyes. The covalent bond can prevent leakage of dye from the particle, thereby contributing to the steady fluorescent intensity of the particles. For easy comparison, the FITC- and RITC-doped silica particle are named as F-SiO₂ and R-SiO₂, respectively. The transmission electron microscope (TEM) and scanning TEM (STEM) images (Figure 2a) of the F-SiO₂ demonstrate the high uniformity of the particles. Furthermore, the element mapping images of the particles prove that Si, O, N, and S are uniformly dispersed across the particles, implying the dyes are homogeneously doped into the particles. When the FITC was replaced by RITC or the fabrication is in the absence of dye, R-SiO₂ and SiO₂ particles with uniform size was also obtained (Figure 2b), respectively. These particles with or without dyes show similar particle size, polydispersity index (<0.03), and ζ-potential (Figure 2c), suggesting that the encapsulation of dyes into silica particles has negligible effect on the size and the surface property of the silica particles. Similar to the Stöber silica particles, the size of the dye doped silica particles can be easily adjusted through controlling the reaction parameter, such as the amount of ammonium hydroxide (Figure S1, Supporting Information).

Dissimilar to the whitish color of Stöber silica, the F-SiO₂ and R-SiO₂ particles show yellow and pink appearance, respectively, due to their diverse absorption characteristics at visible range (Figure S2, Supporting Information). The weak absorption spectra of R-SiO₂ and F-SiO₂ can be attributed to the low concentration of the organic dyes into the particles and scattering of light by the colloidal particles. Since the low concentrations of dyes are embedded into the particles, the light was significantly scattered by the colloidal particles during the absorption test, thereby contributing to the weak absorption. In the view of following encryption, taking F-SiO₂ as an example, it is better to select UV light than the visible light (Ex,max: 495 nm) as the excitation wavelength because the visible light may disturb the showing of information. Therefore, we select UV light (365 nm) as excitation wavelength as the light source for the fluorescent. Under the excitation of UV light (365 nm, Figure 2d,e), the F-SiO₂ and R-SiO₂ colloidal solutions exhibit brilliant green and orange colors with
corresponding PL peak located at 522 and 584 nm, respectively. The RITC molecules are chemically doped into the network of silica particles with strong covalent bonding, which means that the RITC molecules will not escape from the particles and thus possesses a stable fluorescent intensity. The transparent supernatant solution (Figure S3, Supporting Information) separated from the R-SiO2 colloidal solution by centrifugation after being stored for 6 months firmly demonstrates the stability of the R-SiO2 particles. The mass fractions of RITC and FITC in the particles are 0.054% and 0.195%, respectively, implying the dye molecules are probably isolated from each other and thus avoid the aggregation efficiently. For example, the fluorescence of the R-SiO2 particles is much brighter than that of RITC powder (Figure S4, Supporting Information), strongly supporting the aforementioned assumption. In contrast, the pure Stöber silica particles show negligible PL property. The aforementioned results demonstrate that dyes doped silica particles with uniform size, different appearances, and PL properties can be fabricated in an efficient and simple way.

PCs can be prepared when the dye-doped silica particles are self-assembled into the ordered structures. Here, the F-SiO2, R-SiO2, and SiO2 particles are used to be assembled into the poly(ethylene glycol) methacrylate (PEGMA) to fabricate PCs, respectively, which are named as PC–F–MA, PC–R–MA, and PC–MA, accordingly, where F/R and MA represent the F/R–SiO2 and PEGMA, respectively. The volume fraction of the particles and PEGMA is designed to be 40% and 60%, respectively. The as-prepared PCs show similar reflection wavelengths around at 525 nm and thus vivid green colors (Figure 3a,b). The microscope image of the PC–R–MA (Figure 3c) shows that the reflection signal is originated from the numerous microcrystals with bright green color. These microcrystals with similar size can be regarded as colloids assemblies through the stacking of particles at microscale. When the volume fraction of particle exceeds to a critical value (20% for most case), the particles will spontaneously be precipitated out from the solution and self-assembled into ordered structures through balancing the electrostatic repulsion and attraction interactions between the particles. The assembly of the particles will be stopped once the volume fraction of the particles is below to 20%. This means not all the particles are participated into the ordered structures, and small part of them are randomly dispersed into the system.

The ordered structures of PC–R–MA can be confirmed by its SEM images and angle-dependent reflection spectra. Under SEM (Figure 3d), the particles of the most top layer are packed into long-range ordered structure. Different from the close packed structures of traditional PCs, the particles are nonclosely packed with PEGMA filled between the interparticle gaps. The cross-sectional SEM images (Figure 3e,f) indicate both the (100) and (111) planes with large areas can be observed, indicating the particles are assembled into face center cubic structure. The angle-resolved reflection spectra of PC–R–MA show that its reflection wavelength blueshifts from 524 to 428 nm (Figure 3g,h) as the incident detector angle simultaneously varied from 0 to 60°, further suggesting its highly ordered structure. Except for PEGMA, the dyes doped silica particles also can be assembled into other acrylates with distinct structures, such as trimethylolpropane ethoxylate triacrylate (ETPTA) and poly(ethylene glycol) diacrylate (PEGDA). For example, PC–R–DA and PC–F–DA showing similar structural colors and reflection wavelengths to that of...
Based on the aforementioned results, we can achieve two basic conclusions: 1) the monodispersed functional silica particles with diverse PL colors can be prepared in a straightforward and efficient way, which provides a PL channel for construction of IPCPs and 2) PCs with similar structural colors can be prepared using particles with different PL colors and acrylates with different structures. The independent control of the PL color and structures of the acrylate allows us a new chance in fabricating IPCPs with dual-modal patterns in response to the UV light and another stimulus, respectively.

The as-prepared PCs with similar structural colors show diverse and abundant optical response when exposed to UV illumination and water (Figure 4a). Six PCs, including PC–R–MA, PC–F–MA, PC–MA, PC–R–DA, PC–F–DA, and PC–R–DA with different optical response to the external stimulus, can be obtained by the combination of functional particles and acrylates.

**Figure 3.** a) Reflection spectra and b) digital photos of PC–F–MA, PC–R–MA, and PC–MA. c) Microscope image, d–f) SEM images, g) angle-resolved spectra of PC–R–MA. h) Reflection wavelength as function of viewing angles varied from 0 to 60° of PC–R–MA.

PC–R–MA and PC–F–MA can be prepared when the PEGMA was replaced by PEGDA.
Through careful observation, one can find that: 1) for the PC, its PL colors only depend on the fluorescent property of the particles; 2) for the PEGMA-based PCs, their structural color changes from green to red when they are immersed in water; and 3) for the PEGDA-based PCs, their structural colors keep constant no matter in dried or wetted state.

The PC–R–MA is investigated to show and reveal the distinctive optical response of PCs to the UV light and water. Under ambient white light, the PC–R–MA exhibits green structural color with a reflection peak position at 525 nm (Figure 4b). In striking contrast, the PC–R–MA shows bright orange color when it is illuminated by UV light. The PL wavelength of the PC is located at around 584 nm (Figure 4c), similar to that of R-SiO₂ particles, indicating the ordered structures of the PC has a little effect on its PL property. The structural and PL color can be reversibly and instantly switched under the alternative illumination of white and UV light, respectively (Figure 4d).

The PC–R–MA can further respond to the water due to the swelling effect of PEGMA. The reflection wavelength of this PC redshifts from 525 to 624 nm (Figure 4e) and corresponding color turns form green to red in seconds when it was immersed in water. In contrast, no obvious change in reflection signal can be observed when the PC–R–MA is replaced by PC–R–DA (Figure 4f). The different shift of the reflection peak position between the PC–R–MA and PC–R–DA can be ascribed to the dissimilar swelling behavior of PEGMA and PEGDA. The PEGMA has abundant hydrophilic groups (-OH), which contributing to the good swelling, leading to the expansion of lattice constant and thus the redshift of reflection wavelength of the PC into water. This can be well explained by the modified Bragg–Snell law: \( m \lambda = 2d \left( n^2 - \sin^2(90 - \theta) \right)^{1/2} \), where \( m \) and \( \lambda \) are the diffraction order and reflection wavelength, respectively. The \( d \) and \( n \) are the lattice constant and refractive index of PCs, respectively. \( \theta \) is angle between the incident/reflective light and sample. Under SEM, the lattice constants of PC–R–MA at pristine and swelling state are determined to be 146.0 and 168.3 nm (Figure 4g,h), respectively. The increase in lattice constant of PC will lead to the redshift of the reflection wavelength and thus

![Figure 4](https://example.com/figure4.png)
a red structural color. Conversely, the PEGDA cannot be swelled due to the lack of hydrophilic groups, thereby almost no change can be observed in the aspect of the appearance and reflection signal of PC–R–DA. It is worth noting that the large color contrast of PC–R–MA between the pristine and swelling state is benefiting from the large volume fraction of PEGMA (60%) in the PC. Both the dynamic microscope images (Figure 4i) and reflection spectra (Figure 4j) of PC–R–MA swelled in water suggest the swelling process can be accomplished instantly within 30 s. After drying, the appearance and reflection of the PC–R–MA would return back to the pristine state due to the shrinkage of the lattice constant of the PC. Similar to that of UV–visible light cycles, the switch of the reflection signal of the PC–R–MA between the dried and swelling state is fully reversible (Figure 4k). In addition, we test the R–PC–R–Ma film after repeated use for 20 times in encryption environment of water. The similar fluorescence intensity before and after repeated usage (Figure S5, Supporting Information) suggests the good stability of the fluorescent PCs.

Through careful observation, one may find that the swelling structural color and fluorescent color are not consistent under the same conditions. For instance, PC–R–MA and PC–R–DA should exhibit same fluorescent color under UV (but yellow and pink in the article); SiO2, R-SiO2, and F-SiO2 in PC–PEGMA system should exhibit same swelling structural color (but yellow, brown, and red in the article). Moreover, the original color of the pattern is green, whereas the fluorescent color of F-SiO2 particle is also green. Therefore, fluorescent emission overlaps with the photonic bandgap, probably preventing the outward emission of fluorescence. The reasons may be very complicated probably due to the complex interactions between the PC and organic dyes. The colors of the PC composites encapsulation of organic dyes are not pure reflective, transmissive, or fluorescent color, but probably the mixture of them. Especially, the effect of photonic bandgap on the absorption and emission of organic dyes is still unclear and need numerous efforts and investigations in the future. Fortunately, for all the PCs, they have similar green colors, which is extremely important for the encryption process.

IPCP can be fabricated by the combinations of PCs with similar structural color but dissimilar PL and water-responsive structural colors. Here, IPCP with two encrypted patterns was achieved through the region selective assembly process (Figure 5a), which allows us to modify the optical response of the PCs of each region in a straightforward and efficient way. The W, KY, E, US, and L of the IPCP is composed by PC–R–DA, PC–MA, PC–R–MA, PC–F–DA, and PC–DA, respectively. At normal conditions, the

![Image](https://www.advancedsciencenews.com/)

**Figure 5.** a) Schematic illustration of fabrication of IPCP. b–e) Digital photos IPCPs at b,e) pristine state, c,f) under UV illumination, and d,g) soaked in water. The PC of e) from left to right: PC–R–DA, PC–F–MA, PC–DA, PC–R–MA, and PC–F–DA.
as-prepared IPCPs (Figure 5b) shows the pattern of “WKEYULS” with similar structural colors, and the encrypted information cannot be recognized at this state. In the presence of UV irradiation, the “WE” and “US” with brilliant yellow and green PL colors, respectively, can be instantly revealed (Figure 5c). In contrast, new patterns of “KEY” with bright red color (Figure 5d) are shown in seconds when the IPCP is immersed into the water. The encrypted information can be hid again into the background after removing the UV light or drying, and the switch between the pristine and UV illumination/drying state is fully reversible. In addition, other IPCPs (Figure 5e) also can be fabricated with similar procedures but different designed patterns (Figure 5f,g), which exhibit reversibly dual-modal color contrasts under UV light and water.

3. Conclusion

In summary, IPCPs with dual-modal invisible patterns were generated by the integration of the UV light and water-responsive PCs, which was prepared by the assembly of the dyes doped silica particles into the PEGMA/PEGDA with tunable swelling ability. The independent control over the optical response of the PCs by UV illumination from the PL particles and swelling in water caused by the polymer is the key to the successful fabrication. At normal conditions, the IPCP shows a fake pattern with similar structural color of each region. A new PL pattern was obtained when the IPCP is exposed to the UV light. In addition, another new pattern was achieved once the IPCP is soaked into water due to the swelling effect of PCs. The hiding and showing of the encrypted patterns between the pristine and PL/swelling state is instant and reversible. This work demonstrates a new insight and way in the construction of multifunctional IPCPs and will facilitate their applications in display, information protection, and high-level anti-counterfeiting.

4. Experimental Section

Materials: Fluorescein isothiocyanate isomer I (FITC) and RITC were purchased from Sigma-Aldrich. Tetraethyl orthosilicate (98%), ethanol (EtOH, 99%), and aqueous ammonia (28%) were purchased from J&K. PEGMA (Mn: 360), PEGDA (Mn: 250), and 2-hydroxy-2-methylpropionic acid (photoinitiator, 97%) were obtained from Sigma-Aldrich. All the chemicals were used as received without further purifications.

Synthesis of SiO2, F-SiO2, and R-SiO2 Particles: FITC (0.1 mmol) and RITC (0.02 mmol) were dissolved into ethanol solution (20 mL) containing APS (0.2 mL), respectively. The mixed solutions were stirred for 12 h to form APS–FITC and APS–RITC precursors before usage. Afterward, TEOS (64 mL) and the APS–FITC (20 mL) [or APS–RITC solution (20 mL)] precursor solutions were added into the mixture containing ethanol (800 mL), H2O (56 mL), and NH4OH (32 mL). After stirring for 5 h, the products were purified by centrifugation-washing process with excess ethanol. The F-SiO2 and R-SiO2 particles showed yellow and pink colors, respectively. The Stöber silica particles were synthesized by similar procedures with TEOS as the silane resource.

Fabrication of IPCPs: For the fabrication of PC–F–MA, F-SiO2 particles (0.04 mL) were dispersed into the mixture of ethanol (1 mL) and PEGMA (0.06 mL) containing 5% photoinitiator. Then, the mixed solution was heated at 373 K for 1 h and a nearly transparent precursor solution was obtained. This precursor solution was sandwiched between two glass slides with an interval of 0.09 mm, followed by UV light illumination (365 nm, 4.8 mW cm−2) for 3 min. One side of the PC–F–MA film was fixed on the glass by the commercially available NOA61 with the help of UV light. The PC–F–DA film can be obtained with similar procedures when the PEGMA was replaced by PEGDA. Other PCs, such as PC–R–MA, PC–R–DA, PC–MA, and PC–DA, can be fabricated with similar protocols when the R-SiO2 and SiO2 particles were used to replace F-SiO2 particles. The pattern of the PCs can be controlled through the well-developed region selective polymerization strategy with the help of mask. Therefore, the IPCPs were prepared by integration of different PCs onto the substrate.

Characterization: The morphologies of F-SiO2, R-SiO2, SiO2, and the assembly structures of PCs were investigated by the HITACHI SEM-SU8010. The optical microscopic images and microscopic reflectance spectra were obtained on an Olympus BXFM reflection-type microscope operated in darkfield mode. The reflectance and backscattering spectra at different angles were measured by a NOVA spectrometer (Hamamatsu, S7031). The UV–vis absorption spectra were conducted on SHIMADZU UV-3600Plus spectrophotometer. The PL spectrum was recorded on HORIBA Instruments Incorporated Fluorolog-3 instrument. The zeta-potential and particle sizes of dye-doped silica particles were determined by Zetazizer Nano ZS90 (Malvern Instruments Ltd.) at a fixed angle of 90°. Dynamic scattering of light (DLS) of the samples were prepared freshly before the measurement by diluting the products with water.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

C.J.X. and D.P.Y. contributed equally to this work. This work was financially supported by the NSFZJ for Distinguished Young Scholars (LR16B010002), the National Natural Science Foundation of China (21673160, 51372173, 5120105002, 51920105004, and 11574058), and the General Program of the Natural Science Foundation of Guangdong Province (2019A1515011563). D.P.Y., L.L., and S.M.H. supervised this work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

anti-counterfeiting, dual-modal, invisible photonic crystal prints, UV illumination and water responsive

Received: December 21, 2020
Revised: March 6, 2021
Published online:

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