An invisible photonic crystal (PC) pattern encrypted at the dry state and decrypted by solvent is a new anticounterfeiting material system, but its diversity and complexity in response are still required to be increased to enhance the anticounterfeiting effect. Herein, a triple-state invisible pattern encrypted in hollow-silica/polyurethane (h-SiO2/PU) film with two decryption mechanisms is developed based on the asymmetric solvent response of h-SiO2/PU with different SiO2 shell thicknesses. The pattern is printed via etching SiO2 shell in the designed region, which creates an etched “pattern” containing thin-shell h-SiO2 particles and an unetched “background” containing thick-shell particles. Different from the traditional invisible PC patterns, the current system possesses triple states, including a “dry” invisible state composed of two close inverse opal structures, a “wet” invisible state composed of inverse opals filled with water, and an ethanol-soaking visible state due to the prevention of solvent diffusion by the thicker shell. The invisible patterns are reversibly and randomly switched among these three states, which suggest that they are decrypted from the dry invisible state through selective solvent infiltration or from the wet invisible state through selective extraction. Such increased diversity and complexity make this invisible PC pattern ideal material for anticounterfeiting applications.

1. Introduction

Invisible photonic crystal (PC) patterns with dynamic displaying characteristics have attracted great interest due to their applications in anticounterfeiting. Generally, the invisible PC pattern is unseen under a normal state due to its close optical signal. However, it could be revealed by many external stimuli, such as the diffusion of solvent and vapor, change of pH, temperature, the tuning of magnetic and electric field, and mechanical strain, where the refractive index contrast or the lattice spacing changed asymmetrically to these stimuli. An ideal invisible PC pattern was expected to meet the following requirements simultaneously. 1) The difference of structural colors between the pattern and background should be as small as possible for a better hiding effect. 2) The color contrast should be large enough to show the invisible pattern once the external stimuli are applied. 3) The PC prints should be durable in practical usage, and the PC pattern could be reversibly shown and hidden for many cycles.

A primary strategy to prepare an invisible PC pattern was creating two PC structures on a premade photonic paper, which responded asymmetrically to the external stimuli and thereby showed different structural colors. This strategy was broadly adopted by researchers since the early report of a “soaking-revealed” invisible PC pattern in 2012. For example, Ge et al. fabricated a “deformation-revealed” invisible pattern via regionally crosslinking the mechanochromic PC gel composed of silica particle, poly(ethylene glycol) methacrylate, and ethylene glycol. In the stretching or squeezing mode, the crystal lattice of the uncrosslinked region responded to the deformation whereas that of the crosslinked region was unchanged, which formed a significant color contrast to show the invisible pattern immediately. Song et al. encrypted a “vapor-revealed” invisible pattern on the hydrophobic hollow-silica PC film through oxygen plasma etching in the designed regions. In a dynamic flow of water stream but not in a static environment with high humidity, the invisible pattern could be revealed due to the color contrast between the hydrophilic pattern and the hydrophobic background caused by the selective infiltration of water into the colloidal PC. Recently, Ge et al. also developed a “solvent-revealed” invisible pattern on the collapsed-inverse opaline macroporous polyurethane (IOM-PU) film via wet and dry heating treatment to the pattern and the background, respectively. The pattern was highly invisible in a dry state as both collapsed IOM structures are transparent. It could be revealed in the soaking of ethanol/water because the wet-heated film showed structure color due to the recovery of the ordered IOM structure,
whereas the dry-heated film remained transparent as the collapsed structure was permanently fixed by heating.\textsuperscript{131}

Another strategy for the fabrication of an invisible PC pattern was stacking a responsive PC with good masking capability on top of a premade PC pattern, which could be revealed once the top PC film turned transparent under external stimuli.\textsuperscript{112} For example, Zhang et al. reported a “solvent-revealed” invisible pattern based on the bilayer-inverse opaline PEG-acrylate PC film.\textsuperscript{126} The pattern at the bottom layer was invisible due to the masking of the top PC layer. However, it could be revealed in the soaking state as the top layer became transparent due to the swelling-induced shifting of reflection into the infrared zone. Similarly, a “rotation-revealed” invisible pattern was developed based on the bilayer-inverse opaline poly(vinylidene fluoride) PC film. When the sample was tilted, the pattern could be revealed as the top layer became transparent due to the significant decrease in reflection intensity.\textsuperscript{126}

The invisible PC pattern was naturally good anticounterfeiting material as it was invisible at normal state and decryptable by specific stimuli. Although various invisible PC patterns based on different working mechanisms have been developed in the past few years, diversity and complexity were still desired as they were the key requirements for anticounterfeiting applications. Traditional invisible PC patterns were usually fabricated based on two states and two conversion processes. Once multiple states and more responding processes were introduced to the same material system, it would be more difficult to mimic all the dynamic effects so that the anticounterfeiting capabilities could be further improved.

In this work, a triple-state invisible pattern encrypted in the hollow-silica/polyurethane (h-SiO$_2$/PU) PC film was developed for anticounterfeiting applications. (Figure 1) The h-SiO$_2$/PU film, as the PC paper to record the pattern, was first prepared by embedding the preassembled h-SiO$_2$ colloidal crystals in the polyurethane matrix. The invisible pattern was then printed on it through controlled etching of the SiO$_2$ shell in the regions without the protection of the adhesive mask, which created two similar h-SiO$_2$/PU photonic structures with the part of thinner SiO$_2$ shell as “pattern” and the thicker shell as the “background.” The pattern was invisible at the dry state, as the slight change of shell thickness through etching only induced a small difference in the reflection signal and structural color. The pattern could be revealed in the ethanol-soaking state because the thicker SiO$_2$ shell could block the entrance of the solvent into the hollow particle whereas the thinner shell could not, which lead to an asymmetric optical response and apparent color contrast. A unique characteristic of the current system was that the pattern was also invisible in the water-soaking state, as water molecules diffused into the hollow particles through both the thick and the thin shells. This new feature not only provided the third “wet” invisible state but also brought six conversion processes among these three states, which produced a more complicated system compared with the traditional solvent-revealed invisible pattern with two states and two conversions. The structural color changing with six conversions was fully reversible, which suggested that the state of the PC pattern could be “randomly” switched among the three states. Therefore, the pattern could be revealed from the “dry” invisible state through solvent infiltration or from the “wet” invisible state through solvent extraction. All these new features rendered the triple-state invisible PC pattern more diverse optical responses to the solvents, which became its advantages as new materials for anticounterfeiting applications.

2. Results and Discussion

A hollow SiO$_2$ (h-SiO$_2$) particle is an interesting nanostructure, where the diffusion or transportation of solvent molecules through the SiO$_2$ shell are tightly relevant to the shell thickness and species of the solvent. This phenomenon originated from the fact that the pore structures of the SiO$_2$ shell changed with its thickness. Using the same polystyrene particles as sacrificial templates, one could prepare h-SiO$_2$ particles with a thickness of 14, 26, and 42 nm, respectively (Figure 2a-c). Nitrogen

![Figure 1](https://www.advancedsciencenews.com)

**Figure 1.** Schematic illustration of a) the preparation of h-SiO$_2$/PU PC film with an invisible pattern, b) which could be revealed by ethanol soaking and hidden in the dry state and water-soaking state.
adsorption–desorption tests revealed that there were a relatively larger amount of mesopores (0.68 cm$^3$ g$^{-1}$) and micropores (0.027 cm$^3$ g$^{-1}$) in the 14 nm SiO$_2$ shell (Figure S1, Supporting Information). However, as the shell thickness increased to 42 nm, the total volume of mesopores (0.065 cm$^3$ g$^{-1}$) and micropores (0.005 cm$^3$ g$^{-1}$) dramatically decreased ten and five times. Therefore, the thin SiO$_2$ shell favored the transportation of the solvent across the shell, whereas the dense shell usually would not.

When these h-SiO$_2$ particles were assembled into colloidal PCs, they formed solvent responsive photonic structures with changeable structural colors. There were two types of solvent responses, which corresponded to the filling of interparticle voids by solvent and the further filling of the interior cavities. For the first case, the PC’s reflection usually red shifted with increased intensity because both the effective refractive index ($n_{eff}$) and the contrast of refractive index ($\Delta n$) increased along with the replacement of air by solvent in the interparticle voids. For the second case, the h-SiO$_2$ PC became colorless and transparent when its reflection intensity decreased dramatically because further filling of the interior cavities would decrease $\Delta n$ to nearly zero and close the photonic bandgap.

For PCs assembled from identical h-SiO$_2$ particles only with different shell thicknesses, their response to the same solvent could be different (Figure 2d–i, Figure S2, Supporting Information). For example, when ethanol was dripped onto the purple h-SiO$_2$ PC with a shell thickness of 14 nm, the PC film became transparent immediately, and the reflection band disappeared in the dynamic reflection spectra (DRS). It suggested that the solvent filled both the interparticle voids and the interior cavities in the PC. However, when ethanol was dripped onto the blue and green h-SiO$_2$ PCs with a shell thickness of 26 and 42 nm, the PC films turned to green and red with reflection bands being raised about 60 nm in the DRS pattern. In these cases, the solvent only filled the interparticle voids, and the silica shell prevented its further diffusion. The responses of h-SiO$_2$ PC to water had a similar trend, except that the effective blocking of solvent diffusion required a thicker shell.

The asymmetric solvent response of h-SiO$_2$ PCs with different shell thicknesses provided a new strategy to create invisible but solvent decryptable photonic patterns. In this work, an h-SiO$_2$/polyurethane PC film instead of h-SiO$_2$ PC was used as photonic paper to print the pattern due to its better durability in the repeated usages. The h-SiO$_2$/PU film was prepared by the infiltration of DMF solution of PU to the interparticle voids of the h-SiO$_2$ PC film, followed by evaporation of DMF at 90 °C. The PC structure was retained with the reflection peak red shifted.
strengthened, and broadened due to the increase of $n_{\text{eff}}$ and $\Delta n$ after the replacement of air with PU in the interparticle voids (Figure S3, Supporting Information). Polyurethane (PU) was compatible with many solvents, which ensured the free diffusion of the solvent in the polymer matrix and no interference with the solvent response.

The printing of the invisible PC pattern, which could be understood as the selective tuning of SiO$_2$ shell thickness in specific regions of the h-SiO$_2$/PU film, was realized by controlled etching of the SiO$_2$ shell with HF acid. The scanning electron microscope (SEM) images of the h-SiO$_2$/PU film and transmission electron microscope (TEM) images of h-SiO$_2$ particles revealed the change of structures during etching. Through the comparison of SEM images, one could find that the ordered arrangements of particles were retained after etching, and the etched SiO$_2$ shell became more porous and partially broken at some places (Figure 3a-d). To achieve a more precise description of the structural changes, the original film and the etched film were both dissolved by DMF to release the h-SiO$_2$ particles. Their TEM images showed that the shell thickness decreased from 23 to 9 nm by etching, and a small number of h-SiO$_2$ fragments could also be observed. All these results proved that it was feasible and controllable to produce a contrast of SiO$_2$ shell thickness by the etching process.

The unetched h-SiO$_2$/PU film with a thick SiO$_2$ shell and the etched film with a thin shell presented the same optical signals in the dry state and in the soaking of water but different optical signals in the soaking of ethanol (Figure 3e–j, Figure S4, Supporting Information). Here, h-SiO$_2$ particles with an average diameter of 253 nm and shell thickness of 23 nm were assembled and embedded in the PU matrix to form the original h-SiO$_2$/PU PCs, which showed typical reflection at 530 nm and green colors by observation. In the dry state, both the unetched and the etched h-SiO$_2$/PU showed the same reflection and color because the etching process didn’t change the inverse opal structure, and the distributions of two major dielectric materials (PU and air) were almost unchanged after etching. In the soaking of ethanol, the unetched film changed to yellow with reflection wavelength red shifted to 567 nm, as the crystal lattice increased due to the swelling of PU by ethanol. However, the etched film changed to red with reflection wavelength red shifted to 600 nm, because ethanol further diffused into the interior cavity.

Figure 3. SEM images of the a) unetched and c) etched h-SiO$_2$/PU films. TEM images of the corresponding b) unetched and d) etched h-SiO$_2$ particles with thicknesses of 23 and 9 nm. The colloid arrangement and the reflection spectra of these two h-SiO$_2$/PU films in e, h) dry state, f, i) ethanol-soaking state, and g, j) water-soaking state.
to increase $n_{\text{eff}}$ of the whole PC film. The same color in the dry state but different colors in the soaking state were similar to previous reports of invisible PC patterns revealed by soaking. A unique response for the current system was that both the unetched and etched h-SiO$_2$/PU showed the same red color with reflections at around 595 nm in the soaking of water, as water could diffuse into the hollow particle even through a thicker shell. It provided another “invisible” state for such PC prints. The 23 nm SiO$_2$ shell presented specific selectivity in diffusion for different solvents, which rendered the current PC prints more diversities in solvent response and more difficulties to mimic its dynamic effect.

A PC-based “flower” pattern, printed by the selective etching of h-SiO$_2$/PU film, exhibited “randomly” showing and hiding among three states, including a dry invisible state, a wet invisible state in water, and a visible state in ethanol (Figure 4a, Video S1, S2, Supporting Information). The showing and hiding of patterns or the structural colors could be reversibly switched between any two of these three states in any sequence, which suggested that “six” dynamic processes instead of two for the traditional invisible PC pattern should be investigated to confirm the showing and hiding. Therefore, the time evolution of the reflection wavelength of the pattern (etched) and the background (unetched) was studied when the sample was switched among three states in a clockwise and counterclockwise directions.

In a clockwise direction (Figure 4b-d, Process 1–3), when the dry film was soaked in ethanol, the invisible flower pattern was immediately revealed because the $\lambda$ of pattern and background red shifted to 600 and 563 nm, respectively, which formed an apparent color contrast. The diffusion of ethanol was blocked by the thick SiO$_2$ shell in the background region. When the ethanol-soaked film was directly soaked in water, the flower pattern was hidden, and the whole PC film turned red because $\lambda$ of pattern blue shifted and $\lambda$ of background red shifted to the same value at around 592 nm. The same distribution of dielectric substances and the same PC structure would be achieved after ethanol is exchanged and water is infiltrated into the whole h-SiO$_2$/PU film, including the cavity of hollow particles, no matter whether their shell thickness is 23 or 9 nm. Finally, when the sample was completely dried, it changed back to the green film with the pattern still being hidden, as both the pattern and background recovered the h-SiO$_2$/PU inverse opal structure.

In a counterclockwise direction (Figure 4e–g, Process 4–6), when the green dry film was soaked in water, it changed to a

![Figure 4.](image-url)
red film with the pattern hidden due to the same explanation for Process 2. When the water-soaked film was directly soaked in ethanol, the flower pattern was revealed because the $\lambda$ of the pattern red shifted to 600 nm and the $\lambda$ of the background blue shifted to 560 nm, respectively. The red shift of $\lambda$ for the etched h-SiO$_2$/PU with a thin shell (pattern) was attributed to the relatively larger swelling of the PU film by ethanol than water. At the same time, the blue shift of $\lambda$ for the unetched h-SiO$_2$/PU with thick shell was caused by the extraction of water out of the hollow particles by ethanol due to the aforementioned selectivity of solvent diffusion for the 23 nm SiO$_2$ shell. Finally, after the sample completely dried, it also changed back to the pattern-invisible green film. Besides the three states, the PC pattern had angular-dependent colors (Figure S5, Supporting Information), which was also a useful characteristic for anticounterfeiting applications. When revealed by ethanol, the color of the background changed from yellow, green, to blue, whereas that of the pattern changed from red to green accordingly. The angular-dependent color changes had no influence upon the revealed PC pattern, as there was always a contrast of reflection wavelength between the pattern and the background at different angles.

For the current invisible PC prints with triple states and multiple responses, ethanol was the critical solvent to “show” the invisible pattern, no matter through the selective entrance to the h-SiO$_2$ particles or selective extraction of water from the h-SiO$_2$ particles with thin/thick shells. Therefore, soaking experiments were designed to explore why ethanol was capable of showing and what solvents could be the substitutes? Here, different solvent including water, methanol (MeOH), ethanol (EtOH), ethylene glycol (EG), butanol (BuOH), hexanol (HeOH), and propylene carbonate (PCb) were dripped to the dry h-SiO$_2$ (23 nm shell) PC film, whose reflection spectra were recorded to investigate the solvent diffusions (Figure 5). H-SiO$_2$/PU film was not used here to exclude the interference from PU matrix. According to the reflection spectra changes in 2 min, all the tested solvents could be categorized into two groups. One group included EtOH, EG, BuOH, HeOH, and PCb, which only filled the interparticle voids and induced reflection red shifts of 50–60 nm and increased intensities ($R$). Another group included water and methanol, which filled the voids and further diffused into the hollow particles so that $\lambda$ red shifted even more, but $R$ decreased. The successful diffusion of water and methanol into h-SiO$_2$ might be attributed to their good affinity with silica. In addition, both water and methanol have a small molecular size, which is beneficial to diffusion through the silica shell with only a small amount of micropores (1.3 nm, 0.015 cm$^3$ g$^{-1}$). As shown

![Figure 5. a) Schematic illustration of the selective diffusion of solvents into the hollow particle. Changes of b) reflection wavelength and c) intensities after the solvents were dripped onto the h-SiO$_2$ PC. d) $\Delta \lambda$ and e) $\Delta R$ of h-SiO$_2$ PC at 100 s, and comparison of the measured $\Delta \lambda$ with the theoretical $\Delta \lambda$.](image-url)
in Table S1. Supporting Information, a comparison of the measured $\Delta \lambda$ with the calculated $\Delta \lambda$ of the void-filled and the fully filled h-SiO$_2$ PC also supported the above deduction where most solvents were blocked by the SiO$_2$ shell, and only water and methanol could diffuse across the shell. The converse change of reflection intensities for the two groups of solvents further confirmed the statement because the filling of interparticle voids would increase $\Delta n$ and $R$, whereas the filling of both voids and cavities of h-SiO$_2$ particles would decrease $\Delta n$ and $R$, considering that solvent had a closer refractive index to that of silica than air. All these results suggested that EG, BuOH, HeOH, and PCb were also capable of showing the invisible pattern in Process 1, as they showed similar diffusion behavior with ethanol.

In another showing process based on the selective extraction of water, the working mechanism of ethanol and its possible substitutes were also investigated by spectra measurements. Here, solvents with different dielectric constants, including PCb (64.9), EG (37), EtOH (24.5), PrOH (21.8), BuOH (17.8), DeOH (n-decanol, 8.1), and CYH (cyclohexane, 2.0), were dripped onto a water-soaked h-SiO$_2$ (23 nm shell) PC film, whose reflection spectra were recorded to monitor the transfer of water. (Figure 6) According to the reflection spectra changes in 2 min, it was found that the addition of polar solvents caused a blue shift of reflection wavelength for about 20–30 nm and a dramatic increase in reflection intensity, about 70–90%, compared with the water-soaked h-SiO$_2$ PC film. The earlier changes in reflection proved the extraction of water from the hollow particle by these polar solvents, as the replacement of water by air in the hollow particle would decrease the effective refractive index ($n_{\text{eff}}$) and increase the contrast of refractive index ($\Delta n$). On the contrary, the addition of a less polar solvent led to very small changes of reflection wavelength and intensity, which indicated that water was not extracted by them. All these results suggested that most polar solvents with good affinity to water were capable of showing the invisible pattern in Process 5. Combined with the discussion of Figure 5, it could be concluded that some polar solvents, such as EG and BuOH, were qualified substitutes for ethanol, as they could also reveal the patterns from the dry or wet invisible state (Figure S6, Supporting Information).

The etched and unetched h-SiO$_2$/PU film had reproducible optical responses and color changes upon drying and soaking so that the invisible patterns could be reversibly shown and hidden for many times. In a test for reversible conversions, the sample was periodically placed in the dry state, water-soaking state, and ethanol-soaking state for ten cycles, when the reflection signals were recorded accordingly. (Figure 7) After being used ten times, the showing and hiding of the invisible PC pattern still functioned well, and no apparent difference could be found by

![Figure 6](image-url)

Figure 6. a) Schematic illustration of the selective extraction of water from the hollow particle by proper solvents. Changes of b) reflection wavelength and c) intensities after the solvents were dripped onto the water-soaked h-SiO$_2$ PC. d) $\Delta \lambda$ and e) $\Delta R$ of h-SiO$_2$ PC at 100 s.
When the h-SiO$_2$ colloidal PCs with different shell thicknesses were soaked in the dry state, water-soaking state, and ethanol-soaking state, the pattern and the background region as the sample was periodically placed in the dry state, water-soaking state, and ethanol-soaking state for ten cycles.

![Image](Figure 7. a) Digital photos of the patterned h-SiO$_2$/PU film in the first and tenth cycle of soaking and drying. b) Change of the reflection wavelength of the pattern and the background region as the sample was periodically placed in the dry state, water-soaking state, and ethanol-soaking state for ten cycles.)

In summary, a triple-state invisible pattern encrypted in h-SiO$_2$/PU film was fabricated for anticounterfeiting applications.

3. Conclusion

In summary, a triple-state invisible pattern encrypted in h-SiO$_2$/PU PC film was fabricated for anticounterfeiting applications. When the h-SiO$_2$ colloidal PCs with different shell thicknesses were soaked by the same solvent, they showed different optical responses and color changes as the diffusion of solvent molecules through the SiO$_2$ shell was affected by the shell thickness. Based on the asymmetric solvent response of h-SiO$_2$ PCs with different shell thicknesses, we have prepared solvent decryptable invisible patterns on h-SiO$_2$/PU film via etching the SiO$_2$ shells in designed regions with the assistance of an adhesive mask. The controlled etching actually created an etched “pattern” containing h-SiO$_2$ particles with thin shells and an unetched “background” containing particles with thicker shells. Different from the previous solvent-revealed invisible PC patterns, the current PC pattern possessed triple states, including a dry invisible state, a water-soaking invisible state, and an ethanol-soaking visible state, which could be explained by the solvent diffusion, extraction, and thereby distribution of dielectric substances in different cases. The invisible patterns could be reversibly shown and hidden along with the “random” switching among three states. Regionally selective solvent diffusion or extraction was the intrinsic physical change behind the pattern decryption from the invisible dry or water-soaking states. Further investigations suggested that some polar solvents could be replacements for ethanol to realize the same showing and hiding effect. Triple states and six conversion processes increased the diversity and complexity of the invisible PC pattern in solvent response, which made it ideal materials for anticounterfeiting applications.

4. Experimental Section

**Materials**: Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (NH$_3$·H$_2$O, 28%), ethanol (EtOH, 99.7%), methanol (MeOH, 99.5%), N,N′-dimethyleformamide (DMF, 99.5%), cyclohexane (CYH, 99.7%), and hydrofluoric acid (HF, 40%) were purchased from Sinopharm Chemical Reagent Co. Ltd. N-decanol (DeOH, 98%), propylene carbonate (PCb, 99%), propanol (PrOH, 99.7%), and butanol (BuOH, 99.7%) were purchased from Aladdin Co. Ltd. Ethylene glycol (EG, 99%) was purchased from J & K Co. Ltd. N-hexanol (HeOH, 99%) was purchased from TCI Co. Ltd. Glycol (Gly, 99%) was purchased from Rich Joint Chemical Reagent Co. Ltd. Polyether-based thermoplastic polyurethane (TPU, Elastollan 1195 A) was obtained from BASF Co. Ltd. All chemicals were used as received without further treatment.

**Preparation of Hollow Silica (h-SiO$_2$) Particles**: Polystyrene–silica core–shell (PS@SiO$_2$) particles with narrow size distributions were synthesized by a reaction in the mixture of ethanol and water at room temperature, which used PS particles as templates, TEOS as silica source, and NH$_3$·H$_2$O as a catalyst. In a typical synthesis of PS@SiO$_2$ particles with an average diameter of 265 nm, PS particles (0.3 g, 215 nm) were first dispersed in a mixture of ethanol (200 mL) and water (10 mL) by sonication. Then, NH$_3$·H$_2$O (3.5 mL) was added to the solution under magnetic stirring for 30 min, after which TEOS (1.5 mL) was quickly injected to initiate hydrolysis and coating. After a 12 h reaction, the PS@SiO$_2$ particles were collected by centrifugation and washed with water and ethanol three times. Finally, h-SiO$_2$ particles were obtained after removing the PS template by calcination at 500 °C in air for 6 h. The particle’s diameter decreased to 253 nm due to the shrinkage at high temperature, and the shell thickness was measured to be 23 nm. Hollow SiO$_2$ particles with thicknesses of 14, 26, and 42 nm were produced by similar procedures using the same PS template, except that the amount of TEOS was changed to 0.9, 1.7, and 3 mL, and the hydrolytic reaction was conducted at 12, 12, and 24 h, respectively.

**Preparation of h-SiO$_2$/PU Film**: Hollow SiO$_2$ PC films were converted from the liquid-colloidal PCs coated on the glass substrate. First, a homogeneous suspension containing h-SiO$_2$ particles (0.06 g), EG (100 μL), and ethanol (1.0 mL) were prepared by sonication. After being heated at 90 °C for 2 h, ethanol was evaporated, leaving behind a supersaturated h-SiO$_2$/EG colloidal solution. Then, the colloidal solution (35 μL) was spread onto a pretreated hydrophilic glass slide via blade coating, where the thickness of the liquid film was controlled at 40 μm by intervals. After being placed at room temperature for several minutes, h-SiO$_2$ particles spontaneously precipitated to form h-SiO$_2$/EG liquid-colloidal PCs, which converted to the solid h-SiO$_2$ PC film after EG evaporated at 90 °C.

**Preparation of h-SiO$_2$/PU Film**: First, thermoplastic polyurethane (PU, 2.0 g) was dissolved in DMF (20 mL) at 90 °C to form a homogeneous solution. The solution (5 mL) was then poured onto the h-SiO$_2$ PC film (7 × 2 cm), which was placed for 15 min to allow the full infiltration of the naked eye compared with its first use. Even in the spectros- copy measurement, the reflection wavelength of the pattern and the background in three states showed little fluctuation, which proved that the optical response was highly repeatable. Furthermore, the as-prepared h-SiO$_2$/PU PC film with invisible patterns was self-supported due to the good mechanical property of polyurethane, which also ensured its durability in repeated usage.
the DMF solution of PU into the voids of h-SiO$_2$ PC by capillary force. Finally, h-SiO$_2$/PU film was obtained after evaporating DMF at 90 °C for 4 h.

Printing Invisible Patterns on h-SiO$_2$/PU Film: In a typical printing process, an adhesive mask with a hollowed pattern was first placed on the h-SiO$_2$/PU/PC film. HF solution (2.8%) was then spread onto the h-SiO$_2$/PU film to accomplish etching in about 10 s. HF solution was immediately removed by washing with water and ethanol three times. Finally, invisible patterns on h-SiO$_2$/PU film were prepared after removing the masks.

Characterizations: The spatially resolved reflection spectra (SRRS) were recorded by an Ocean Optics Maya 2000 Pro spectrometer coupled to a six-around-one reflection probe. The optical microscopy (OM) images were obtained by an Olympus BXFM reflection-type microscope that operated in dark-field mode. The particle sizes and morphology were determined by an FEI Tecnai G2 F30 TEM. The top-view and cross-sectional microstructure of the PCs were analyzed by Hitachi S4800 SEM. Nitrogen adsorption–desorption isotherms and Brunauer–Emmett–Teller (BET) surface areas were measured by a Belsorp-Max analyzer at 77 K.

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

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

Keywords
anticounterfeiting, hollow silica/polyurethane, invisible patterns, photonic crystals, triple states

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