# Vapor Pressure-Responsive Nanostructured Photonic Patterns with Reversibly Tunable Colors for Anticounterfeiting and Information Encryption Applications

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**ABSTRACT:** The information encryption and decryption, using optical principles and techniques, are of significant importance to extensive anticounterfeiting applications, ranging from anticounterfeiting tags, information security and authentication, image watermarking to decorative applications. Owing to the antiphotobleaching capability and exceptional ease of precept, structural optical materials, such as holographic gratings, have been employed worldwide for optical encryption, and have achieved long-term commercial success. However, most commercial anticounterfeiting materials and methodologies can be readily imitated or copied in recent years. Herein, this study reports an innovative strategy to realize optical encryption and decryption. A roll-to-roll compatible self-assembly methodology is developed to fabricate macroporous poly(ethoxylated trimethylolpropane triacrylate) (poly(ETPTA)) photonic crystals. 2-Hydroxyethyl methacrylate monomer/ethanol mixtures are then utilized as inks for designing and



building chromogenic patterns onto the poly(ETPTA) photonic scaffold, followed by polymerization of the monomers. Upon exposure to water or common chemical vapors, the swelling of poly(2-hydroxyethyl methacrylate) (poly(HEMA)) coating layer brings about a drastic color change of the nanostructured photonic patterns. The dependences of the corresponding reflection peak shift on vapor partial pressure, poly(HEMA) layer thickness, the pore size of the photonic scaffold, response time, and reusability are also investigated in this research.

KEYWORDS: anticounterfeiting, self-assembly, vapor pressure-responsive, swelling, photonic crystals

# INTRODUCTION

Counterfeits are fabricated deliberately to replicate the originals with trusted trademarks, and to profit illegally from the commercial reputation of legal entities. In the past few decades, the production and distribution of counterfeited products have become fast-growing global issues, which significantly harm legitimate businesses and the economy as a whole.<sup>1,2</sup> Apart from the economic impact, most pirated goods are produced using low-grade materials, and are with scant regard to relevant health and environmental regulations. To address the issues, miscellaneous anticounterfeiting methodologies, including but not limited to single-layered and multilayered approaches, have been well-established.<sup>3</sup> Among these strategies, single-layered anticounterfeiting labels, such as watermarks, bar codes, QR codes, and holograms, have been extensively exploited.<sup>4-6</sup> The encrypted information can be either identified straightforwardly by the naked eye or detected using mobile applications on smartphones and tablets. However, many existing single-layered labels are readily copied, as a result of the rapid progress and commercialization of high-resolution equipment. To enhance information security, more unique and complicated anticounterfeiting labels are engineered using multilayered approaches, e.g., radio frequency identification, surface-enhanced Raman scattering, quantum dots inkjet printing, security printing, and electrochemical technologies.<sup>7–11</sup> Nevertheless, powerful information processing systems and sophisticated analytical instruments are required to meet the needs of information encryption and decryption.

Recently, diverse luminescent materials and fluorescent materials have gathered interest in designing and building optics-based anticounterfeiting patterns.<sup>12–17</sup> The patterns exhibit distinctive optical signal outputs on exposure to external stimuli, including heat, ultraviolet radiation, mechanical forces, electric/magnetic fields, and chemicals, and therefore can serve as security labels. Even though the labels permit easy probing

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Over 800 million years of evolution, living organisms have developed diversified nanoscale and/or microscale features for survival. For instance, certain insects, such as shining leaf chafer beetles and blue Morpho butterflies, are covered with periodically arranged nano/microstructures.<sup>20</sup> The structure arrays possess forbidden photonic bandgaps, and hence prevent the propagations of electromagnetic radiation with particular wavelength ranges falling within the energy bandgaps.<sup>21,22</sup> As a result, these insects display iridescent structural colors, derived from the diffraction of incident light, in order to attract mates and to ward off predators. Inspired by these creatures, numerous photonic bandgap materials, also known as photonic crystals, have been created and utilized to manipulate the propagation of light, especially for miniature systems.<sup>23,24</sup> Previous studies have demonstrated that the photonic crystals can be exploited as anticounterfeiting materials.<sup>25,26</sup> The resulting structural colors cannot be simply imitated using pigments or dyes, and even remain unaffected by photobleaching. Unfortunately, their applications are limited by unchangeable photonic bandgaps and dull colorings.

Benefiting from the progress of material synthesis techniques, reconfigurable photonic crystals with tunable lattice spacings and effective refractive indices have been invented.<sup>27-33</sup> Their structures can be temporarily deformed in response to a variety of chemical and physical stimuli, allowing their energy bandgaps and corresponding structural colors to be altered. Accordingly, the endowed patterns can be revealed or concealed on demand. Such dynamic color changes undoubtedly render much easier visual readouts, and hence are more favorable to optical encryption and decryption.<sup>34,35</sup> Despite that, the optical contrasts of most encrypted patterns with surrounding backgrounds are perceptible, which poses a challenge to ensure invisibility. Moreover, many existing reconfigurable photonic crystals are restricted by incomplete reversibility after prolonged use, slow responses to external stimuli, and high costs of painstaking lithography-based nanofabrication technologies for producing photonic crystals and creating patterns. To eliminate the issue, a number of colloidal self-assembly methodologies, including gravitational sedimentation, electric/magnetic-fieldassisted assembly, physical confinement, capillary-force-induced assembly, etc., have been developed to render an inexpensive and relatively simple strategy to fabricate photonic crystals.<sup>36–39</sup> However, current self-assembly technologies still suffer from laboratory-scale and time-consuming productions.

Herein, we present an innovative optics-based anticounterfeiting strategy that integrates a scalable colloidal self-assembly methodology and vapor pressure-responsive polymeric materials. A roll-to-roll compatible technique is developed to assemble macroporous photonic crystals, which serve as a structural scaffold to be patterned using vapor pressure-responsive polymers. The iridescent color of the nanostructured photonic pattern can be drastically changed on demand by manipulating the swelling degree of vapor pressure-responsive polymer coating on exposure to common household chemical vapors. Thanks to the presence of photonic scaffolds, the pattern

## EXPERIMENTAL SECTION

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Reagents and Materials. The chemicals applied for the Stöber synthesis of colloidal silica particles, including tetraethyl orthosilicate  $(\geq 99.5\%)$ , ammonium hydroxide  $(\geq 23.8\%$  ammonia in water), absolute ethanol (200 proof), and deionized water ( $\geq$ 18.4 M $\Omega$ ), are obtained from Thermo Fisher Scientific, and a Milli-Q HX 7000 water purification system (Merck KGaA), respectively. UV-curable ethoxylated trimethylolpropane triacrylate (ETPTA) monomers (SR 454, ≥99.5%), 2-hydroxyethyl methacrylate (HEMA) monomers  $(\geq 97.0\%)$ , methacrylic acid (MMA) monomers  $(\geq 97.0\%)$ , and 2hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) (≥97.5%), are provided by Arkema Sartomer, PolyScience, Merck KGaA, and Ciba-Geigy AG, respectively. Aqueous hydrofluoric acid (HF) (48.0–51.0% in water) is acquired from Merck KGaA. All the reagents are of analytical grade, and utilized without further purification. Corning glass substrates (0.9-1.1 mm in thickness), supplied by Merck KGaA, are rinsed with deionized water before use. Copper shielding foil (~0.04 mm) is collected from 3 M Company.

Self-Assembly of Macroporous Photonic Crystals Using a Doctor-Blade-Coating Technology. Monodispersed silica colloids, with mean diameters of 350, 285, and 180 nm (<5% standard deviations), are synthesized in the Stöber sol-gel process.<sup>40</sup> The assynthesized spherical silica colloids can be cleansed with absolute ethanol through 5 dispersion/centrifugation cycles, and then be redispersed in a mixture of UV-curable ETPTA monomers and HMPP using a Thermolyne Maxi Mix II Vortexer (Marshall Scientific). In the colloidal suspension, the volume fractions of silica colloids, ETPTA monomers, and HMPP are controlled to be 74, 25, and 1 vol %, respectively. Afterward, the suspension is coated on a poly(ETPTA) wetting layer-coated glass plate at a constant coating rate of 5 cm/min by an Elcometer 4340 motorized/automatic film applicator (Elcometer), while a unidirectional shear force is generated to align the colloids. The monomers are subsequently cured by UV radiation for 5 s in an XLite 500Q chamber (OPAS). The self-assembled silica colloidal crystals, embedded in the poly(ETPTA) matrix, are finally wet-etched by immersing the composite in a hydrofluoric acid solution (1.5 vol % in water) for half an hour to create macroporous poly(ETPTA) photonic crystals.

Patterning of Vapor Pressure-Responsive Chromogenic Macroporous Photonic Crystals. The as-prepared macroporous photonic film is further dipped into a HEMA monomer/MMA monomer/HMPP/absolute ethanol mixture. In this mixture, the volumetric ratio of HEMA monomers, MMA monomers, and HMPP are adjusted to be 98:1:1. The excess mixture retained on the film surface can then be removed through spinning the macroporous film at 500 rpm for 3 min using a WS-650-23B spin-coater (Laurell Technologies), during which the ethanol trapped within the pores is completely evaporated. After that, a patterned copper shielding foil is placed on the film, and serves as a photomask under UV irradiation for 5 s. The HEMA/MMA monomers in defined regions can be photopolymerized on exposure to UV radiation, whereas the monomer mixture in unexposed regions remains unchanged during the patterning process, and is subsequently rinsed off with absolute ethanol. As a consequence, a poly(HEMA)-patterned macroporous poly(ETPTA) photonic film is developed. The corresponding vapor pressureresponsive chromogenic performance is further evaluated in a modified VWR 1400E vacuum oven (Marshall Scientific), which is evacuated and then backfilled with a water vapor or an ethanol vapor with a specific vapor partial pressure at 25 °C. Nitrogen is subsequently introduced to make the total vapor pressure maintain at 1 atm.

**Characterization.** Photographic and scanning electron microscopy (SEM) images of the samples are captured by a HX99 camera (Sony) and a JSM 6320FZ field-emission scanning electron microscope (JEOL), respectively. The samples are sputtered with platinum prior to



Figure 1. Schematic illustration of the experimental procedures for engineering vapor pressure-responsive tulip cartoon-patterned macroporous photonic crystals.



**Figure 2.** (a) Photographic image of a 285 nm silica colloidal crystal/poly(ETPTA) composite self-assembled by the doctor-blade-coating technology. (b) Cross-sectional SEM image of the specimen in (a). The inset shows a magnified top-view SEM image. (c) Photographic image of the macroporous poly(ETPTA) photonic crystals, templated from 285 nm silica colloidal crystals. (d) Cross-sectional SEM image of the specimen in (c). The inset shows a magnified top-view SEM image of the specimen in (c). The inset shows a magnified top-view SEM image.

the SEM imaging to avoid any electron charging using a Cressington 108 auto sputter coater (Ted Pella). Reflection spectra in the wavelength range from 350 to 800 nm of the specimens are carried out by an HR4000 high-resolution fiber-coupled spectrometer (Ocean Optics) with a DT-MINI-2-GS light source. At least 10 reflection spectra over different spots on each sample are recorded to determine the average reflection peak position. Fourier transform infrared (FTIR) spectra of the samples are characterized by a Spectrum 100 Optica FTIR spectrometer (PerkinElmer).

# RESULTS AND DISCUSSION

The fabrication procedures for developing vapor pressureresponsive anticounterfeiting materials are illustrated in Figure 1. A colloidal suspension, consisting of silica colloids (74 vol %), UV-curable ETPTA monomers (25 vol %), and HMPP as a photoinitiator (1 vol %), is doctor-blade-coated on a poly-(ETPTA) wetting layer-covered glass plate using a motorized film applicator, while a unidirectional shear force is generated to align the silica colloids into a hexagonally close-packed arrangement. It is worthy to note that the application of poly(ETPTA) wetting layer greatly improves the wettability of the glass substrate, and therefore facilitates the spreading of colloidal suspension over the substrate uniformly. In addition, the doctor-blade-coating speed, the blade gap, and the rheological behaviors of colloidal suspension can be adjusted to determine the thickness of colloidal crystals.<sup>41</sup> After photopolymerization of the ETPTA monomers under UV irradiation, the silica colloidal crystals, utilized as structural templates, are wet-etched to create macroporous poly(ETPTA) photonic crystals. The three-dimensionally interconnected pore network can be considered as a structural scaffold for designing and building vapor pressure-responsive chromogenic patterns. In the patterning process, the macroporous poly(ETPTA) film is dipped into a UV-curable HEMA monomer/ethanol mixture,



**Figure 3.** Photographic images and SEM images of tulip cartoon-patterned (a, b) macroporous 10% poly(HEMA)/poly(ETPTA) photonic crystals, (c, d) macroporous 15% poly(HEMA)/poly(ETPTA) photonic crystals, (e, f) macroporous 20% poly(HEMA)/poly(ETPTA) photonic crystals, and (g, h) macroporous 25% poly(HEMA)/poly(ETPTA) photonic crystals, templated from 285 nm silica colloidal crystals. (b, d, f, g) Cross-sectional SEM images of the patterned poly(HEMA)/poly(ETPTA) regions in (a, c, e, h), respectively. The inserts show magnified top-view SEM images.

of which limited amounts of HMPP and MMA monomers are included as a photoinitiator and a polymeric toughener, respectively. After ethanol evaporation, a patterned copper shielding foil is placed on the HEMA monomer-covered poly(ETPTA) scaffold, and serves as a photomask. The HEMA monomers in defined regions can be photopolymerized on exposure to UV radiation, whereas the unpolymerized ones are subsequently eliminated by rinsing with absolute ethanol. As a consequence, poly(HEMA)-patterned macroporous poly-(ETPTA) photonic crystals are engineered.

As shown in Figure 2a, the doctor-blade-coated 285 nm silica colloidal crystal/poly(ETPTA) composite presents a reddish color under natural light illumination. The uniform color is attributed to the Bragg diffraction of incident light from the hexagonally close-packed silica colloids (Figure 2b). Even though a few defects are observed, the long-range highly ordered

silica colloidal crystals, embedded within a poly(ETPTA) matrix, are clearly evidenced. Interestingly, the film drastically turns green after removing the silica colloids through a wetetching treatment (Figure 2c,d). This striking structural color even suggests that the three-dimensional crystalline lattice is well-remained. To better understand the crystalline structures, normal-incidence reflection spectra of the specimens are carried out using a fiber-coupled spectrometer. It is recognized that the measured reflection peak position of the composite is located at 665 nm, which is consistent with the one, represented as a black arrow (666 nm), theoretically calculated according to the Bragg's eq (Figure S1).<sup>42</sup> In this equation, the reflection peak position ( $\lambda_{peak}$ ) is expressed as a function of the effective refractive index ( $n_{eff}$ ) of the medium and the interlayer lattice spacing (d).



**Figure 4.** Dependences of (a, b) the reflection peak position shifts and (*c*, d) the calculated condensed liquid layer thicknesses of macroporous poly(ETPTA) photonic crystals and macroporous poly(HEMA)/poly(ETPTA) photonic crystals, templated from 285 nm silica colloidal crystals, on ethanol vapor partial pressures and water vapor partial pressures. (e, f) Dependence of the  $\ln(\frac{P}{P_{sat}})$  on the 1/r, where *P*,  $P_{sat}$ , and *r* indicate the vapor partial pressure, the saturated vapor pressure, and the radius of curvature of the swollen poly(HEMA) coating layer, respectively.

$$\begin{split} \lambda_{\text{peak}} &= 2 \times n_{\text{eff}} \times d \times \sin 90^{\circ} \\ &= 2 \times \left( f_{\text{silica}} \times n_{\text{silica}}^2 + f_{\text{poly}(\text{ETPTA})} \times n_{\text{poly}(\text{ETPTA})}^2 \right)^{1/2} \\ &\times \left( \sqrt{\frac{2}{3}} \times D \right) \times \sin 90^{\circ} \end{split}$$
(1)

where the  $f_{\rm silica}$  (0.74),  $n_{\rm silica}$  (1.42),  $f_{\rm poly(ETPTA)}$  (0.26),  $n_{\rm poly(ETPTA)}$  (1.46), and *D* (285 nm) denote the volume fraction of silica, refractive index of silica, volume fraction of poly-(ETPTA), refractive index of poly(ETPTA), and silica colloid size of the composite, respectively. Similarly, the theoretical reflection peak position of the corresponding macroporous poly(ETPTA) photonic crystals can be estimated as below.

$$\lambda_{\text{peak}} = 2 \times (f_{\text{air}} \times n_{\text{air}}^2 + f_{\text{poly(ETPTA)}} \times n_{\text{poly(ETPTA)}}^2)^{1/2} \\ \times \left(\sqrt{\frac{2}{3}} \times D\right) \times \sin 90^{\circ}$$
(2)

where the volume fraction and refractive index of air are symbolized by  $f_{\rm air}$  (0.74) and  $n_{\rm air}$  (1.00). It is apparent that the estimated reflection peak position, represented as a red arrow (530 nm) in Figure S1, agrees well with the measured one (531 nm). The results once again confirm the hexagonally close-packed arrangements of the doctor-blade-coated photonic crystals. It is worth mentioning that the macroporous photonic crystals exhibit a much higher reflection intensity, resulting from

the larger refractive index difference between the  $n_{\rm poly(ETPTA)}$  and  $n_{\rm air}$ 

Tulip cartoon patterns are subsequently printed onto the macroporous poly(ETPTA) photonic films by using HEMA monomer/ethanol mixtures as printing inks. In the patterning process, mixtures with varying HEMA monomer volume fractions ( $\varphi_{\text{HEMA}}$ ) from 10 to 25 vol % are introduced to determine the optimal poly(HEMA) coating thickness on the poly(ETPTTA) scaffolds. As a 10 vol % HEMA monomer/ ethanol mixture is applied as the printing ink, the tulip cartoonpatterned macroporous poly(ETPTA) photonic crystals, referred as the macroporous 10% poly(HEMA)/poly(ETPTA) photonic crystals, display a homogeneous green color (Figure 3a). Compared with the wall thickness of unpatterned macroporous poly(ETPTA) voids (Figure 2d), a slight increase in that is found on the poly(HEMA)-coated voids (Figure 3b). Crucially, its tulip cartoon pattern cannot be distinguished by the naked eye. On the other hand, the application of HEMA monomer/ethanol mixture with a higher  $\varphi_{\rm HEMA}$  leads to the formation of thicker poly(HEMA) coating layer and less air in the pores after the ethanol trapped within the pores is completely evaporated and an even more obvious color change (Figures 3c-h and S2). The color change can be expounded by the following equations derived from the Bragg's law, where  $n_{\rm poly(HEMA)}$  equals to 1.45.

$$\begin{split} \lambda_{\text{peak}} &= 2 \times \left( f_{\text{poly(ETPTA})} \times n_{\text{poly(ETPTA})}^2 + f_{\text{poly(HEMA})} \right. \\ &\times n_{\text{poly(HEMA)}}^2 + f_{\text{air}} \times n_{\text{air}}^2 \right)^{1/2} \\ &\times \left( \sqrt{\frac{2}{3}} \times D \right) \times \sin 90^{\circ} \\ &= 2 \times \left( 0.26 \times 1.46^2 + \left( 0.74 \times \varphi_{\text{HEMA}} \right) \times 1.45^2 \right. \\ &\left. + \left( 0.74 \times \left( 1 - \varphi_{\text{HEMA}} \right) \right) \times 1^2 \right)^{1/2} \\ &\times \left( \sqrt{\frac{2}{3}} \times 285 \right) \times 1 \end{split}$$
(3)

As the  $\varphi_{\text{HEMA}}$  increases from 0 to 25 vol %, the reflection peak position gradually shifts from 530 to 570 nm, and eventually falls on the spectrum between yellow and green light wavelength regions. On that account, a yellowish-green tulip cartoon pattern appears on the macroporous 25% poly(HEMA)/poly(ETPTA) photonic crystals. Obviously, this photonic film is unsuitable for optical encryption and decryption. Moreover, it is found that the red-shifts remarkably agree with the experimental values supplemented by normal-incidence reflection spectra of the macroporous poly(HEMA)/poly(ETPTA) photonic crystals (Figure S3). The findings disclose that the poly(HEMA) coating layers are with uniform thicknesses.

Fourier-transform infrared (FTIR) spectroscopy is further employed to characterize the functional groups of the tulip cartoon-patterned macroporous poly(HEMA)/poly(ETPTA) photonic crystals (Figure S4). For the unpatterned region, absorption peaks of the carboxylate group (C-O, 1185 cm<sup>-1</sup>), bipyridine group (C=C, 1620 cm<sup>-1</sup>), and carbonyl group (C=O, 1726 cm<sup>-1</sup>) are noticed. Besides these peaks, it is evidenced that an absorption band is located between 2873 and 2960 cm<sup>-1</sup>, which is assigned to the C-H stretching vibrations of methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) groups.<sup>43</sup> Compared with that, an additional adsorption band, centered at 3450 cm<sup>-1</sup>, appears for the macroporous poly(HEMA)/poly(ETPTA) region. This broadband is associated with the O-H stretching vibrations of poly(HEMA).<sup>44</sup> Owing to the presence of hydroxyl groups, the appearance of the tulip cartoon pattern can be transformed in response to a spectrum of chemical vapors used in daily life, such as vaporized alcohols and water vapors.

To evaluate the sensitivity of the vapor-responsive chromogenic materials, normal-incidence reflection spectra of these macroporous photonic crystals exposed to either ethanol or water vapor are conducted. The condensation of vapor into the macropores even for vapor pressures below its saturated vapor pressure  $(P_{sat})$  leads to a reduced refractive index contrast between the polymeric matrix and the enclosed materials, and generates an increased effective refractive index of the medium as well. Accordingly, the reflection peak positions of the macroporous specimens red-shift as the vapor partial pressures vary from 0 to 1.0  $P_{sat}$ , while the corresponding reflection intensities decrease monotonically with the increases of vapor partial pressures (Figure S5). It is of vital importance that the condensed vapor molecules are able to diffuse into the crosslinked poly(HEMA) within a short time, which facilitates the condensation of more vapor molecules and the swelling of the poly(HEMA) network. As a result, the application of a thicker poly(HEMA) coating layer brings about a larger effective refractive index and a more obvious red-shift on exposure to ethanol or water vapor (Figure 4a,b). It is noteworthy that the red-shifts of the poly(HEMA)-coated macroporous photonic crystals exposed to ethanol vapors are even larger than those exposed to water vapors. The red-shift differences can be expounded using the Flory-Huggins solution theory.<sup>45</sup> Benefiting from a more favorable Gibbs energy change for mixing poly(HEMA) with ethanol than that with water, the poly(HEMA) coating layer exhibits a higher swelling degree in response to ethanol vapors.<sup>46</sup> To acquire a more profound understanding, the Ostwald-Freundlich equation (  $\ln \frac{P}{P_{ret}} = -\frac{2\gamma V_m}{RT} \times \frac{1}{r}$  is applied to evaluate the resulting swelling.<sup>47</sup> In this equation, P,  $\gamma$ ,  $V_{\rm m}$ , R, T, and r denote the vapor partial pressure, the liquid/vapor surface tension, the ideal gas constant, the absolute temperature, and the radius of curvature of the swollen poly(HEMA) coating layer, respectively. By presuming that the coating layer swells uniformly, the r can be computed using the following equations expressed by the Bragg's law.

$$\begin{split} \lambda_{\text{peak}} &= 2 \times \left( f_{\text{poly(ETPTA})} \times n_{\text{poly(ETPTA})}^2 + f_{\text{poly(HEMA})} \right. \\ &\times n_{\text{poly(HEMA)}}^2 + f_{\text{liquid}} \times n_{\text{liquid}}^2 + f_{\text{air}} \times n_{\text{air}}^2 \right)^{1/2} \\ &\times \left( \sqrt{\frac{2}{3}} \times D \right) \times \sin 90^{\circ} \\ &= 2 \times \left( 0.26 \times 1.46^2 + \left( 0.74 \times \varphi_{\text{HEMA}} \right) \times 1.45^2 \right. \\ &+ f_{\text{liquid}} \times n_{\text{liquid}}^2 + \left( 0.74 \times \left( 1 - \varphi_{\text{HEMA}} - f_{\text{liquid}} \right) \right) \\ &\times 1^2 \right)^{1/2} \times \left( \sqrt{\frac{2}{3}} \times 285 \right) \times 1 \end{split}$$

(4)

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**Figure 5.** (a) Illustration of the concept of vapor pressure-responsive chromogenic photonic crystals. Photographic images of the tulip cartoonpatterned macroporous 20% poly(HEMA)/poly(ETPTA) photonic crystals, templated from 285 nm silica colloidal crystals, exposed to ethanol vapors with varied vapor partial pressures of (b) 0  $P_{\text{Sat. EtOH}}$  (c) 0.2  $P_{\text{Sat. EtOH}}$  (d) 0.5  $P_{\text{Sat. EtOH}}$  and (e) 0.7  $P_{\text{Sat. EtOH}}$ .

$$\begin{aligned} \text{liquid thickness} &= \frac{285}{2} \\ &- \left[ \frac{285}{2} \times \left( 1 - \left( 1 - \varphi_{\text{HEMA}} \right)^{1/3} \right) \right] \\ &- \left[ \frac{285}{2} \times \left( 1 - \varphi_{\text{HEMA}} - \frac{f_{\text{liquid}}}{0.74} \right)^{1/3} \right] \\ & (5) \end{aligned}$$

$$\begin{aligned} &\frac{1}{r} = \frac{1}{\frac{285}{2} \times \left\{ 1 - \left[ \left( 1 - \left( 1 - \varphi_{\text{HEMA}} \right)^{1/3} \right) \right] - \left[ \left( 1 - \varphi_{\text{HEMA}} \right)^{1/3} - \left( 1 - \varphi_{\text{HEMA}} - \frac{f_{\text{liquid}}}{0.74} \right)^{1/3} \right] \right\} \end{aligned}$$

$$(6)$$

As summarized in Figure 4c,d, the estimated condensed ethanol layer thicknesses are greater than the condensed water layer thicknesses under varied vapor partial pressures. The thicker condensed ethanol layer assuredly results in the formation of larger 1/r (Figure 4e,f). Since the  $\frac{2\gamma V_m}{RT}$  remains constant at a fixed temperature, the ln  $\frac{P}{P_{sat}}$  shall be linearly proportional to the 1/r. Evidently, this theoretical prediction matches well with the experimental data points of the macroporous poly(ETPTA) photonic crystals. By contrast, discrepancies are observed and get larger under higher ethanol

vapor partial pressures for the poly(HEMA)-coated macroporous photonic crystals. The results once more confirm the high swelling degree of poly(HEMA) on exposure to ethanol vapors. As a consequence, the macroporous 20% poly(HEMA)/ poly(ETPTA) photonic crystals can be considered as optimal anticounterfeiting materials on exposure to ethanol vapors.

The ethanol vapor-responsive chromogenic performance of the tulip cartoon-patterned macroporous 20% poly(HEMA)/ poly(ETPTA) photonic crystals is further characterized in this study. Compared with the unpatterned macroporous poly-(ETPTA) region, the poly(HEMA)-patterned macroporous



**Figure 6.** (a) Photographic image of a 350 nm silica colloidal crystal/poly(ETPTA) composite self-assembled by the doctor blade coating technology. (b) Cross-sectional SEM image of the specimen in (a). The inset shows a magnified top-view SEM image. (c) Photographic image of the macroporous poly(ETPTA) photonic crystals, templated from 350 nm silica colloidal crystals. (d) Cross-sectional SEM image of the specimen in (c). The inset shows a magnified top-view SEM image. (e) Photographic image of the tulip cartoon-patterned macroporous 20% poly(HEMA)/poly(ETPTA) photonic crystals, templated from 350 nm silica colloidal crystals. (f) Cross-sectional SEM image of the specimen in (e). The inset shows a magnified top-view SEM image. Photographic images of the specimen exposed to ethanol vapor with a vapor partial pressure of (g) 0.7  $P_{\text{Sat. EtOH}}$  followed by exposure to (h) pure nitrogen.

poly(ETPTA) region allows more condensed ethanol molecules to be trapped within the macropores, and hence leads to a visible color change (Figure 5a). Apparently, an iridescent yellow tulip cartoon pattern appears as the macroporous photonic crystals exposed to ethanol vapor with a vapor partial pressure of 0.2  $P_{\text{Sat. EtOH}}$ , whereas the appearance of the unpatterned region remains nearly unchanged (Figure 5b,c). Importantly, the difference of condensed ethanol layer thickness becomes even larger upon exposure to ethanol vapors with higher vapor partial pressures. The corresponding structural color of the tulip cartoon therefore turns from yellow (0.2  $P_{\text{Sat. EtOH}}$ ), orange (0.5  $P_{\text{Sat. EtOH}}$ ) to red (0.7  $P_{\text{Sat. EtOH}}$ ) under varied ethanol vapor partial pressures (Figure 5d,e). To express the pattern color change in a more standardized way, the Commission Internationale de L'Eclairage (CIE) chromaticity values of the patterned macroporous 20% poly(HEMA)/poly(ETPTA) photonic crystals, exposed to ethanol vapors with varied vapor partial pressures of 0, 0.2, 0.5, and 0.7  $P_{\text{Sat. EtOH}}$ , are depicted in Figure S6. Obviously, the resulting CIE chromaticity diagram indicates that the patterns exhibit a virtually distinguishable color change. To further find out the response time, optical responses of the macroporous 20% poly(HEMA)/poly-(ETPTA) photonic crystals are evaluated under a fixed ethanol vapor pressure (0.2  $P_{\text{Sat. EtOH}}$ ). As shown in Figure S7, the reflection peak position dramatically shifts in a few seconds and then stays in the same position. Moreover, the pattern disappears gradually in few minutes once the macroporous specimen is transferred to a dry nitrogen atmosphere (Figure S8). The findings disclose that the structural colors of the patterns can be easily converted at short notice, which renders a facile strategy to realize optical encryption and decryption. To verify the feasibility for designing and building arbitrary photonic crystal patterns, the NCHU logo and the Mona Lisa image are drawn on the macroporous poly(ETPTA) photonic films using the HEMA monomer/ethanol mixture ( $\varphi_{\text{HEMA}}$  = 20%) as a painting ink. Remarkably, the complicated patterns are revealed and concealed instantaneously through manipulating the vapor partial pressures (Figure S9(a-d)). It is worthy to mention that multicolored patterns can be created as well by applying HEMA monomer/ethanol mixtures with varied  $\varphi_{\mathrm{HEMA}}$ as painting inks (Figure S9(e,f)). The application of HEMA mixture with a higher  $\varphi_{\rm HEMA}$  undoubtedly brings about a more significant color change.

The interlayer spacing of photonic crystals can be considered as another variable in determining the structural color. To investigate the interlayer spacing effect, macroporous poly-(ETPTA) scaffolds are templated from doctor-blade-coated 350 nm silica colloidal crystals and 180 nm silica colloidal crystals, respectively, followed by using a 20 vol % HEMA monomer/ ethanol mixture as the printing ink (Figures S10 and S11). It is found that the reflection peak position of the self-assembled 350 nm silica colloidal crystal/poly(ETPTA) composite locates at 816 nm, which falls in the near-infrared region of the electromagnetic spectrum (Figure S12). On that account, the composite film appears clear under natural light illumination (Figure 6a,b). As expected, the reflection peak position blueshifts after wet-etching the silica templates; thus, the visual appearance of the resulting macroporous poly(ETPTA) photonic film turns red (Figure 6c,d). It is worth noting that either of the reflection peak positions of the macroporous poly(ETPTA) photonic crystals and the corresponding poly-(HEMA)-coated macroporous photonic crystals are located in the red light wavelength region. Thereupon, the poly(HEMA)patterned macroporous poly(ETPTA) photonic crystals present a homogeneous red color (Figure 6e,f). Crucially, the diffractive colors of the NCHU logo and tulip cartoon pattern are transferred from shining iridescence to near transparency upon exposure to ethanol vapors with a vapor partial pressure of 0.7  $P_{\text{Sat. EtOH}}$ , and once again, turn red in a dry environment (Figure 6g,h). Furthermore, it is evidenced that the pattern on the macroporous 20% poly(HEMA)/poly(ETPTA) photonic film, templated from 180 nm silica colloidal crystals, can be switched swiftly between bluish and transparent colors (Figures S13 and S14). The results even suggest that the pattern color can be determined through adjusting the pore size of the macroporous photonic crystals.

To achieve a deeper comprehension, normal-incidence reflection spectra of these macroporous photonic crystals, templated from 350 to 180 nm silica colloidal crystals, are conducted under varied ethanol vapor partial pressures (Figure S15). As demonstrated previously, the poly(HEMA) coating ones are more sensitive to ethanol, and hence display larger redshifts of reflection peak positions on exposure to ethanol vapors (Figure S16). In addition, the introduction of larger pore size leads to the formation of a thicker poly(HEMA) coating layer, which facilitates the ethanol vapor condensation. The increased condensed ethanol layer thickness further results in an even greater red-shift appearing on the macroporous 20% poly-(HEMA)/poly(ETPTA) photonic crystals, templated from 350

nm silica colloidal crystals. As a consequence, a large discrepancy between the experimental data points and the theoretical prediction according to the Ostwald–Freundlich equation is recognized under high ethanol vapor partial pressures (Figure S17). It is significant to indicate that the condensed ethanol can be fully evaporated, which allows the iridescent patterns to be concealed simultaneously. The indiscernible patterns are revealed once again on exposure to ethanol vapors. Critically, the application of macroporous poly(ETPTA) as a scaffold effectively prevents any considerable inhomogeneous deformation of poly(HEMA) hydrogel in the optical information concealing and revealing processes. On account of that, the visual appearances of the printed patterns can be converted reversibly (Figure S18). As evidenced in Figure 7, the reflection



**Figure 7.** Reversible reflection peak position shifts of macroporous 20% poly(HEMA)/poly(ETPTA) photonic crystals, templated from 350 nm silica colloidal crystals, 285 nm silica colloidal crystals, and 180 nm silica colloidal crystals, respectively. The specimens are exposed to ethanol vapor with a vapor partial pressure of 0.7  $P_{\text{Sat. EtOH}}$ , followed by exposure to pure nitrogen. The operating conditions are switched for 100 cycles.

peak positions of the 20% poly(HEMA)/poly(ETPTA) photonic crystals can even be switched for 100 cycles regardless of the pore size. This finding further verifies their high durability.

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To conclude, we have developed an optical encryption and decryption mechanism by using HEMA monomer/ethanol mixtures as printing inks for designing and building vapor pressure-responsive chromogenic patterns on doctor-bladecoated macroporous poly(ETPTA) photonic crystals. On exposure to ethanol vapors, the diffusion of condensed ethanol molecules into the cross-linked poly(HEMA) coating layer significantly changes its swelling degree. As a result, the nanostructured photonic patterns display controllable visible readouts with a fast response rate by manipulating the ethanol vapor partial pressures. Importantly, the optical responses can be further improved by adjusting the poly(HEMA) layer thickness and the interlayer spacing of the poly(HEMA)-patterned macroporous poly(ETPTA) photonic crystals. Owing to the presence of poly(ETPTA) scaffold, the pattern revealing/ concealing operations can be switched reversibly. Such reusable vapor pressure-responsive nanostructured materials will ultimately contribute to innovative photonic crystal devices,

chromogenic chemical sensors, high-density optical data storage media, biometric materials, information encryption, and anticounterfeiting applications.

# ASSOCIATED CONTENT

## **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.4c04930.

Video S1 (MP4)

Video S2 (MP4)

Schematic illustration of the experimental procedures for engineering patterned vapor pressure-responsive macroporous photonic crystals; photographic images, SEM images, and normal-incidence reflection spectra of the asfabricated silica colloidal crystal/poly(ETPTA) composites, macroporous poly(ETPTA) photonic crystals, and macroporous poly(HEMA)/poly(ETPTA) photonic crystals; pore size distributions and Fourier-transform infrared spectra of the macroporous poly(ETPTA) photonic crystals and macroporous poly(HEMA)/poly-(ETPTA) photonic crystals; the changes in normalincidence reflection spectra and color coordinates for the macroporous poly(HEMA)/poly(ETPTA) photonic crystals under varied ethanol vapor partial pressures and water vapor partial pressures; the changes of reflection peak position shifts, calculated condensed liquid layer thicknesses, and appearances of the macroporous poly-(ETPTA) photonic crystals and macroporous poly-(HEMA)/poly(ETPTA) photonic crystals with time (PDF)

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## Notes

The authors declare no competing financial interest.

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