Supporting Information

Dual Photonic-Bandgap Optical Films towards Generation of Photonic Crystal-Derived 2-Dimensional Chemical Codes

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1. Experimental Section

1.1 Chemicals and Materials.

Potassium persulfate (KPS), polyvinylpyrrolidone (PVP), acrylamide (Am), N-Isopropylacrylamide (NIPAm), N, N’-Methylenebisacrylamide (MBA), diethoxyacetophenone (DEAP), tetraethylorthosilicate (TEOS, 98%), methanol, ethanol, hexane, tetrahydrofuran (THF), chloroform, carbon disulfide (CS$_2$), concentrated HCl (37% in water), methacrylic acid (MAA) and butyl acrylate (BA) were of analytical grade and used as received. Styrene (St) was purified by distillation under reduced vacuum to remove inhibitor. Purified water with resistance greater than 18 MΩ·cm$^{-1}$ was used in all experiments.

1.2 Characterizations.

The microstructures of as-synthesized microspheres were examined by using transmission electron microscopy (TEM) (JEOL JEM-2100). The sample was placed on a copper grid, which was left to dry before being transferred into the TEM sample chamber. Scanning electron microscope (SEM) observations were measured by using a HITACHI S-4800 scanning electron microscope. The samples for TG analysis were
prepared by drying under vacuum for water removal, and the analysis was carried out at a heating rate of 10 °C/min from 30 to 600 °C in nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer. The samples were ground with KBr crystals, and the mixture was then pressed into a disk for IR measurement. UV-Vis transmission and reflection spectra of the RPC-derived 2D codes were measured by the optic spectrometer (Ocean Optics, USB4000). The reflex peak spectra were measured at normal incidence to the (1 1 1) planes of the 2D optical code films. Photographs were taken with an optical microscope (ZEISS, Axio Scope A1).

1.3 Formula Derivation.

The corresponding shift amounts of the sensing reflex peak for 2D RPC codes in the presence of different solvent liquids can be calculated by Bragg’s law [Eq. (1)]:\[3\]

\[ m \cdot \lambda = 2d \cdot n_{avg} \cdot \sin \theta \]

where \( \lambda \) denotes the sensing reflex peak position, \( m \) is the order of Bragg diffraction, \( d \) is the spacing between close-packed planes of voids, \( \theta \) is the Bragg angle and \( n_{avg} \) is the average RI of the inverse RPC layer. As the reflex peak spectra were measured at normal incidence to the (1 1 1) planes, a Bragg angle \( \theta \) of 90° was fixed here and the term \( \sin \theta = 1 \), while \( n_{avg} \) could be calculated by [Eq. (2)]:\[4\]

\[ n_{avg} = \Phi n_{silica} + (1 - \Phi)n_{solvent} \]

where \( \Phi \), \( n_{silica} \), and \( n_{solvent} \) are the solid fraction and the RI values of the silica wall and filling solvents, respectively. Substituting Eq. 2 to Eq. 1, a linear expression of
the wavelength shift ($\Delta\lambda$) versus the solvent RI can be obtained [Eq. (3)]:

$$\Delta\lambda = \lambda - \lambda_0$$

$$= (2d / m)(1-\Phi)n_{\text{solv}} + (2d / m)\Phi n_{\text{silica}} - \lambda_0$$

where $\lambda_0$ corresponds to the control peak of the 2D RPC code. Accordingly, a linear relationship should be observed between $\Delta\lambda$ and $n_{\text{solv}}$ with $(2d/m) (1-\Phi)$ as the slope.

1.4 Synthesis of polystyrene (PS) microspheres.

Monodispersed PS microspheres with different diameters were prepared according to our previous work.\cite{1, 2} The synthesis processes were carried out in a four-necked round-bottomed flask equipped with a water-cooled reflux condenser, a mechanical stirrer, a nitrogen inlet and a stirrer. Briefly, 0.20 g PVP, 135 mL purified water, and 5.0–15.0 g styrene were first added into the four-necked round-bottomed flask. After the mixture was heated to 98 °C, 0.04 g of KPS in 15 mL H$_2$O was added to initiate the polymerization reaction. The reaction was terminated after about 2 h, and the resulting colloid dispersion was filtered through 200-mesh nylon net to remove minor traces of large agglomerates.

1.5 Preparation of bi-layer opal RPC templates.

The bi-layer opal RPC templates were fabricated via a vertical deposition method on a quartz glass that was treated with a Piranha solution to ensure clean surface.\cite{5-7} To be
specific, a special unit with a beaker that can be divided into two small independent spaces by the quartz glass was first made to conduct the deposition process. Then, two kinds of PS colloid dispersions with different sizes at a concentration of 0.2% were injected into the two isolated spaces of the beaker separately. To initiate the deposition process, the beaker was placed into a sealed chamber with the constant temperature (80°C) and humidity (60%). After the evaporation of water, bi-layer opal RPC templates were finally obtained.

1.6 Preparation of SiO$_2$-based bilayer-structure 2D optical codes$^{[8]}$

The bilayer-structure 2D optical codes were constructed via a template method. First, the SiO$_2$ sol was prepared by adding 10.5 mL TEOS into a mixture of 30 mL ethanol and 0.06 mL HCl at room temperature with an aging time of 4 h. Then, the as-obtained opal RPC templates were vertically immersed into the SiO$_2$ sol for about 3 min, and slowly lifted up at a speed of 2 mm/min. The impregnation processes were repeated for three times to fully fill the opal interstices. After the RPC template was remove by calcination at 500°C for 4 h, the SiO$_2$-based bilayer-structure 2D optical codes with double brilliant structural colors were finally obtained.

1.7 Synthesis of acrylic resin-grafted hard-core/soft-shell microspheres.

The synthesis of acrylic resin-grafted PS microspheres in this work was achieved by seeded emulsion copolymerization from micrometer-sized PS seed microspheres and acrylic monomers. Briefly, 130 mL of deionized water was first poured into a four-
necked flask equipped with a condenser, a nitrogen inlet, a thermometer and a stirrer. Then, 0.24 g of PVP, 0.03 g of KPS and 4.0 to 6.5 g of purified styrene were added into the flask under stirring in nitrogen atmosphere. Then, the reaction was initiated by increasing the temperature to 98 °C. After the reaction was kept at 98 °C for 2 h, 0.5 g of styrene, 0.05 g of MAA, 0.95 g of BA and 0.01 g of KPS in 30 mL of deionized water were added dropwise, and the reaction was terminated after about 4 h to give the final acrylic resin-grafted PS microspheres, and the products were purified by dialysis to remove impurities before utilization.

1.8 Preparation of 2D optical barcodes on flexible substrates via hand coating.

The preparation of 2D optical barcodes on flexible substrates was achieved via hand print with the 30 μm-depth roll bar. First, the printing “ink” was prepared by enriching the concentration of acrylic resin-grafted lattice to ca. 30 wt%. Then, the ink was quickly cast onto the PET film or the A4 coated fine paper, and scratched through the substrate. After the evaporation of water, the first optical layer was attained. Accordingly, 2D optical barcodes on flexible substrates were prepared via repeating the hand-coating process. All experiments were carried out at a temperature of 15 °C and a humidity of 50 %.

1.9 Preparation of the bistriate-structure 2D optical codes.

To prepare the polymerized bistriate-structure 2D optical codes, polyacrylamide (PAm)-co-polyacrylic acid (PAA) copolymers and poly (N-Isopropylacrylamide)
(PNIPAm) hydrogels were gradually introduced to a colloidal crystal array. To be specific, a PS colloid dispersion with diameter of 190 nm was first purified by dialysis against water to remove excess ions and surfactants before utilization. Then, 30 μg AA, 0.08 g Am, 0.001 g MBA, 0.001 g DEAP and 1 mL of purified PS dispersion (40 wt%) were poured into the interstice of the two glass substrates. After the exposure of UV light for 15 min, the PAm-co-PAA encapsulated colloidal RPC was prepared. Next, immerse the PAm-co-PAA encapsulated colloidal RPC into a solution containing 0.5 g NIPAm, 0.005 g MBA, 0.005 g DEAP and 5 g H2O for 24 h, and the polymerized bistriate-structure 2D optical code was finally obtained after photo-polymerization under a mask with fringe patterns.

2. Supporting Figures

2.1 The fabrication process for bilayer-structure 2D optical code film and its SEM images
Figure S1. a) Schematic illustration for preparing bilayer-structure 2D optical code films. b, e) SEM images for the code film with 111 crystal planes and colloid sizes of 
(b) 266 and (e) 390 nm, respectively. The top view (c, f) and side view (d, g) of the corresponding code film structures of (b) and (e). Inset images correspond to their optical images. Scale Bar = 1 μm.

The bilayer-structure 2D optical codes were constructed via a template method. Firstly, a container centrically isolated by the quartz glass was set up to construct the bi-layer opal RPC templates via a vertical deposition method. Then, the interstices of the RPC templates were impregnated with the SiO$_2$ sol via a dip-coating method. Followed by the calcination at 500 °C for 4 h, the bilayer-structure 2D optical code with inverse opal structures were finally obtained (Figure S1a). Figure S1b and S1e show the typical SEM images of the bi-layer RPC templates. Both sides of the quartz glass are uniformly covered by hexagonally arranged PS particles with the diameter of ~266 nm and ~390 nm, respectively, presenting brilliant red and pale structural colors (Figure S1b and S1e insets). Figure S1c and S1f reveals that the as-obtained bilayer-structure 2D optical codes were with homogeneous pore sizes and consistent wall thickness, exhibit blue and yellow structural colors, respectively (Inset images in Figure S1c and S1f). In order to further probe into the microstructures of these pores, the cross-sections of the bilayer-structure 2D optical code were dissected. As shown in Figure S1d and S1g, several smaller windows link micropores to be an integrative structure, forming sufficient spaces to adsorb analytes for detection.
2.2 UV-Vis transmission and reflection spectra of the $A_{410}^+A_{410}^-$-typed bilayer-structure 2D optical code

![UV-Vis transmission and reflection spectra](image)

**Figure S2** UV-Vis transmission and reflection spectra of the $A_{410}^+A_{410}^-$-typed bilayer-structure 2D optical code film with its bottom side stripped.

From the UV-Vis transmission spectrum, we can see that more than 90 percent of the light, that does not located in the photonic band gap ($\sim 410$ nm), can pass through the top layer of the $A_{410}^+A_{410}^-$-typed 2D code film. Thus, as for the bi-layer RPC-derived 2D code, the reflex peak originating from the bottom layer could be detected, providing the feasibility to integrate two photonic bandgap signals into a single material unit.

2.3 SEM characterization of the as-obtained PS microspheres
**Figure S3** SEM characterization of the as-obtained PS colloids. (a) The PS microspheres with a diameter of 190 nm were used for the construction of the bistriate-structure 2D code. (b, d) The PS microspheres with diameter of 266 and 390 nm were used for the preparation of bilayer-structure 2D code. (b, c, e) The microspheres with diameter of 266, 315 and 420 nm were used for the development of encoded libraries with different spectra codes. Scale bar = 500 nm.

**2.4 Research on correlation between the spectrum intensity and the refractive index (RI) of the solvents filled into the 2D optical code**

**Table S1** The detailed optical spectra of the $A_{410}^+A_{410}^-$-typed code after infused with different solvents

<table>
<thead>
<tr>
<th>M</th>
<th>$\lambda_0$(nm)</th>
<th>$\lambda_f$(nm)</th>
<th>$\Delta\lambda$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>415</td>
<td>530</td>
<td>115</td>
</tr>
<tr>
<td>Ethanol</td>
<td>415</td>
<td>538</td>
<td>123</td>
</tr>
<tr>
<td>Hexane</td>
<td>415</td>
<td>548</td>
<td>133</td>
</tr>
<tr>
<td>THF</td>
<td>415</td>
<td>558</td>
<td>143</td>
</tr>
<tr>
<td>Chloroform</td>
<td>415</td>
<td>569</td>
<td>154</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>415</td>
<td>613</td>
<td>198</td>
</tr>
</tbody>
</table>
Figure S4 The relationship between the maximum intensity of the reflection spectrum and the refractive index (RI) of various filling solvents.

The solvent fluids used to conduct the experiment were, in order of increasing RI: methanol (n=1.329), ethanol (n=1.360), hexane (n=1.375), THF (n=1.407), chloroform (n=1.473), and CS$_2$ (n=1.630). The results show that the reflection intensity of the 2D code reduced first and then increased along with the increase of RI. The weakest intensity point occurred when it was filled with the chloroform (n=1.473), where the RI of the solvent was quite approximate to that of the silica wall (~1.46).

2.5 Reflection spectra of the A$_{410}^+\!A_{410}$-typed 2D optical code upon immersing with the glucose solution with various concentrations
Figure S5 The corresponding reflex spectra of the A\textsubscript{410}+A\textsubscript{410}-typed 2D optical code film upon immersing with the glucose solution with various concentrations.

Table S2 Summary of experimental data for the real-time detecting of the glucose

<table>
<thead>
<tr>
<th>Num</th>
<th>c (wt%)</th>
<th>(\lambda_0) (nm)</th>
<th>(\lambda_1) (nm)</th>
<th>(\Delta\lambda) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>415</td>
<td>520</td>
<td>105</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>415</td>
<td>523</td>
<td>108</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>415</td>
<td>528</td>
<td>113</td>
</tr>
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<td>3</td>
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</tr>
<tr>
<td>5</td>
<td>45</td>
<td>415</td>
<td>545</td>
<td>130</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>415</td>
<td>547</td>
<td>132</td>
</tr>
</tbody>
</table>

The experiment was conducted with the A\textsubscript{410}+A\textsubscript{410}-typed 2D optical code film. \(\lambda_0\) and \(\lambda_1\) correspond to the control peak and sensing peak, respectively.

2.6 FT-IR spectrum and SEM characterization of the bistriate-structure 2D optical code
In order to prepare the bistriate RPC, were first copolymerized to encapsulate the colloidal RPCs. Subsequently, N-isopropylacrylamide (NIPAm) was selectively introduced under a striping-patterned mask to obtain final bistriate RPC via the Radiation induced polymerization. As for the as-obtained bistriate RPC-based 2D code, a strong adsorption peak at 1705 cm\(^{-1}\) and a broad band peak in the range 3700–3100 cm\(^{-1}\) were noted, indicating the successful introduction of the salt- tracked carboxyl units. The SEM image in Figure S6b shows that the colloids in the PAm-co-PAA hydrogel-encapsulated RPC were still arranged orderly, implying the maintenance of its periodical PC structure.

2.7 TEM characterization of the PS seed microspheres and acrylic resin-grafted hard-core/soft-shell latices
Figure S7 TEM images of (a, b) pure PS seed microspheres and (c, d) acrylic resin-grafted PS colloids. Scale bar 200 nm.

Figure S7a and S7c show that both of the pure PS seed microspheres and acrylic resin-grafted PS colloids were highly monodispersed with diameter of 220 nm and 235 nm. Figure S7b and S7d correspond to their amplified TEM images. It can be seen that compared to the pure PS seed microspheres, the diameter of acrylic resin-grafted PS colloids increases and meanwhile their surface become obviously rough after grafting, indicating the successful incorporation of resin components.

2.8 FT-IR characterization of the PS seed microspheres and acrylic resin-grafted hard-core/soft-shell lattices
Figure S8 FT-IR characterization of the pure PS seed microspheres (a) and acrylic resin-grafted PS colloids (b).

Compared to the pure PS seed microspheres, the FT-IR spectrum of the acrylic resin-grafted PS colloids displays a strong adsorption peak at 1,732 cm$^{-1}$, which is attributed to the typical characteristic peak of C=O originated from the acrylic resin shell.

2.9 TGA characterization of the PS seed microspheres and acrylic resin-grafted hard-core/soft-shell latices

Figure S9 The TGA curves of the pure PS seed microspheres and acrylic resin-grafted PS colloids.
The TGA curves of pure PS seed microspheres (the black line) and acrylic resin-grafted PS colloids (the red line) were shown in Figure S9. It reveals that, a decreased thermal stability is noted after resin grafting, indicating the successful introduction of soft acrylic resin.

2.10 SEM characterization of the 2D optical code film on the PET flexible substrate constructed from the hard-core/soft-shell latices

![SEM characterization of the 2D optical code film on PET substrate constructed from the hard-core/soft-shell PS latices. Scale bar 1 μm.](image)

**Figure S10** SEM characterization of the 2D optical code film on PET substrate constructed from the hard-core/soft-shell PS latices. Scale bar 1 μm.

2.11 UV-Vis transmission and reflection spectra for the top layer of the RPC on PET substrates
Figure S11 UV-Vis transmission and reflection spectra of the monolayer RPC on PET substrate.

3. Supporting Video Instructions

3.1 Video S1: the preparation of the 2D RPC code on A4 paper via hand coating

3.2 Video S2: stability testing of the 2D RPC code under the rinse of water

3.3 Video S3: bending test of the 2D RPC code on PET substrates

4. References