Supporting Information

Multicolored photonic barcodes from dynamic micromolding

*Yuxiao Liu, Luoran Shang, Huan Wang, Han Zhang, Minhan Zou and Yuanjin Zhao**

Experimental Section

Materials. SiO_2 nanoparticles with different sizes were purchased from NanJing DongJian Biological Technology Co., Ltd. The Sylgard 184 (PDMS) was purchased from Dow Corning Corporation. Ethoxylated trimethylolpropane triacrylate (ETPTA), sodium alginate, and calcium chloride were purchased from Sigma Aldrich Co. The egg white pregel solution were self-prepared in the laboratory. The Rabbit IgG, Goat IgG, Human IgG, and the FITC-tagged anti-human IgG were all purchased from Beijing Biosynthesis Biotechnology Co., Ltd. Deionized water with a resistivity of 18.2 MΩ·cm-1 was obtained from a Millipore Milli-Q system. All other chemical reagents were of the best grade available and used as received and the deionized water was used in all experiments. The purity of the used chemical reagents are all analytically pure.

Fabrication of the micromolding molds. The negative microhole-array molds were obtained from microfabrication technique. The Sylgard 184 was used to generate the positive microcylindrical-array mold. The base (part A) and the curing agent (part B) were mixed in 10:1 mass ratio. Then the mixture was put in a culture dish and the negative mold was pushed down to the dish bottom to make the microhole arrays filled with the mixture. After one-hour standing for removing air bubbles, the dish was put in an oven for 4 hours at 80℃ to solidify the PDMS pregel. Finally, the solidified PDMS was peeled off from the negative mold and the positive mold with microcylindrical array was obtained.

Fabrication of PhC microparticles. The PhC microparticles were fabricated by the single-emulsion microfluidics. The 50cSt silicon oil and the aqueous suspension of the SiO_2 nanoparticles were pumped into a capillary microfluidic device. The concentration of the used silica nanoparticles was 0.2g/mL. The injection speeds of the continuous and dispersed phase were 5mL/h and 0.3mL/h, respectively. Due to the effects of the fluid shear force, the SiO_2 aqueous suspension was sheared into droplets by the continuous phase in the capillary channel. The resultant SiO_2 droplets were collected in a plastic container filled with 500cSt silicon oil. Then the silica nanoparticles in the droplets self-assembled into hexagonal packed structure during the evaporation process at 75℃ in an oven, which lasted overnight. Later, the silicon oil was gently and thoroughly washed out from the PhC microparticles. Finally, the PhC microparticles were calcined at 800℃ for 3 hours in order to improve the mechanical strength. The optical and SEM images of the PhC microparticles have been demonstrated in **Fig. S6**.

Fabrication of the photonic barcodes. The mask plates were generated through nicking on the aluminized paper. Firstly, the positive PDMS substrate was immobilized in a fixed position and the complementarily negative mold (with double-hole array) was just fitted on the substrate. Later, we put the mask plate on the negative mold to shade half of the hole unit and lifted the mold up out of the substrate with a certain distance. Then the first kind of PhC particles were settled in the hole arrays by a wiper blade. Later, we removed the mask plate and put the second

kind of particles into the array. Next, the negative mold continued to lift up to a distance for the assembling of second particle layer. All the PhC particles were first immersed in the ETPTA pregel solution (containing 1 w/v % SiO_2 nanoparticles and 1 v/v % HMPP), and when the assembling process was finished, the particle array was fixed by polymerizing the pregel under UV radiation. Finally, the fixed 2×2 barcodes were pushed out by pressing the negative mold down to the bottom of the PDMS substrate. The barcodes with 3×3 structures were fabricated with similar process.

Anti-counterfeiting applications. The photonic barcodes were immobilized on the surfaces of the pharmaceutical packaging, credit card, paper currency, coin, and key. The specific structural colors of the barcodes could be observed by a microscope under halogen cold light source (XD-302, Shanghai optical instrument factory).

Multiplexed bioassay applications. We choose four different kinds of barcodes with 2×2 particle arrays (green & red, all blue, blue & red, all red). First, these barcodes were under plasma treatment for 3 minutes. Then they were immersed in the 0.1 mmol/L NaOH for 10 minutes, so as to activate the silanol group on the surface. Later, the barcodes were transferred into 5 v/v% APTMS aqueous solution and stirred slightly for 4 hours to graft amino groups on the surfaces. Then the barcodes were washed by the PBS buffer (PH=7.4) and immersed in the PBS solution of 2.5 v/v% glutaraldehyde for 4 hours. Finally, the resultant barcodes were thoroughly washed by the PBS buffer. The treated barcodes were put into the 0.5mg/mL PBS solution of IgG and incubated for 12 hours at 4℃. Specifically, the green & red barcodes, all blue barcodes, blue & red barcodes and all red barcodes were incubated with R-human IgG, G-rabbit IgG, B-goat IgG, and pure PBS solution, respectively. After incubation, the barcodes were treated by the PBS solution of 1% BSA for 2 hours at room temperature. Finally, these barcodes were transferred into the 20mg/mL PBS solution of FITC-anti-human IgG for 3 hours at 31℃. The FITC-anti-human IgG could only match with the R-human IgG, and thus the fluorescence was able to be observed merely on the green&red barcodes.

Fabrication of edible photonic barcodes. The original PhC microparticles were immersed in the egg white pregel solution for 5 hours, in order to make the solution thoroughly fill the nanovoids in the PhCs. Then, the pregel was polymerized by the constant temperature water bath at 80℃ and the solid hydrogel was exposed under the UV radiation in order to kill the potential germs. Later, the egg white hydrogel hybrid microparticles were stripped out from the egg white hydrogel in the deionized water. Finally, the egg white inverse opal particles were generated after removing the silica template by immersed in hydrofluoric acid (4%, v/v) overnight. The generation process of the inverse opal barcodes was similar to the above-mentioned barcodes preparing method, while just changing the ETPTA to sodium alginate for polymerizing the inverse opal particles. The inverse opal particles were immersed in the 2% sodium alginate solution and when the assembling process was finished, the 2% calcium chloride solution was spread in the holes on the negative mold. Due to the chelation between calcium ion and alginate, the calcium alginate hydrogel was formed and encapsulated the photonic particles.

Supporting Figures:

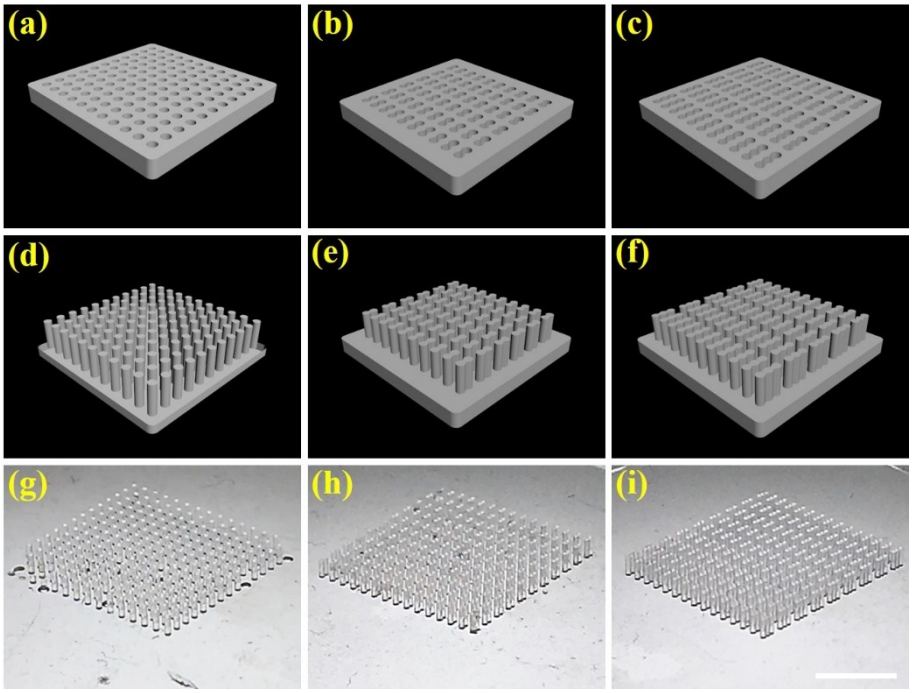

Figure S1. (a-c) The stereo illustrations of the negative molds with different hole arrays; (d-f) the stereo illustration of the positive molds with different cylindrical arrays; (g-i) the images of the real PDMS positive molds. The scale bar is 0.5cm.

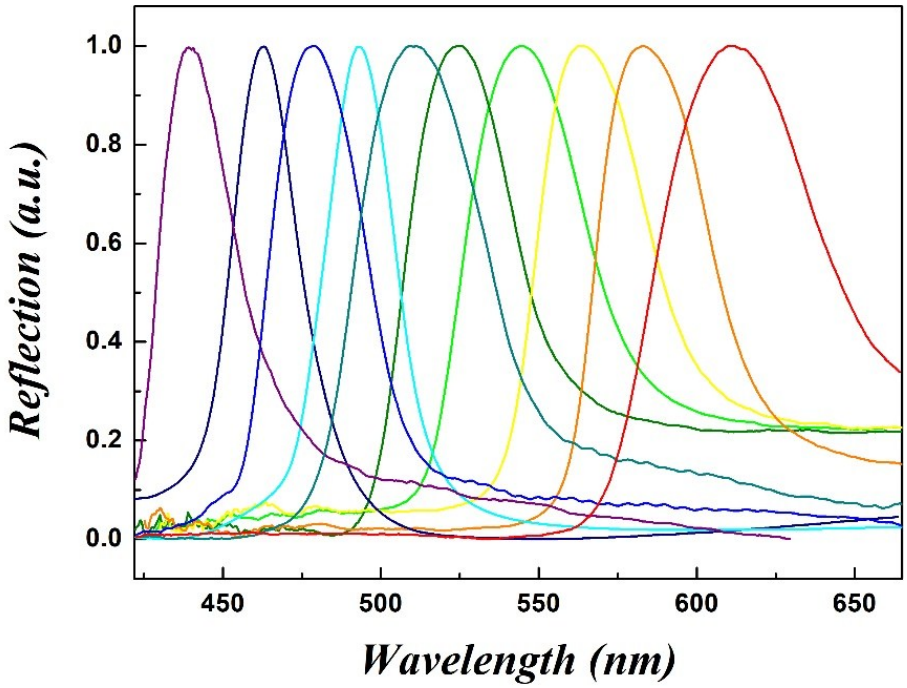

Figure S2. The reflection spectra of different kinds of PhCs.

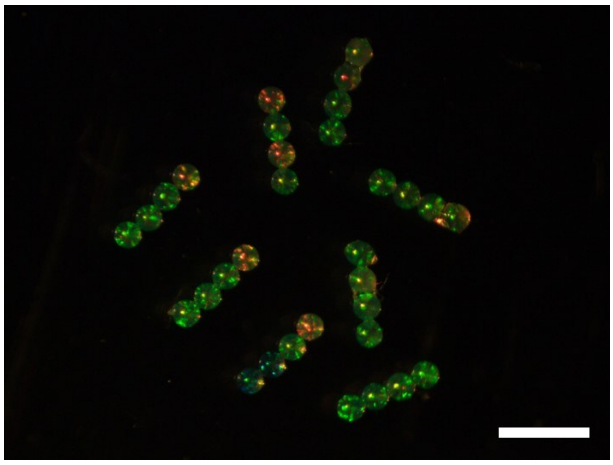

Figure S3. The photonic sequences with different color arrangements. The scale bar is 1mm.

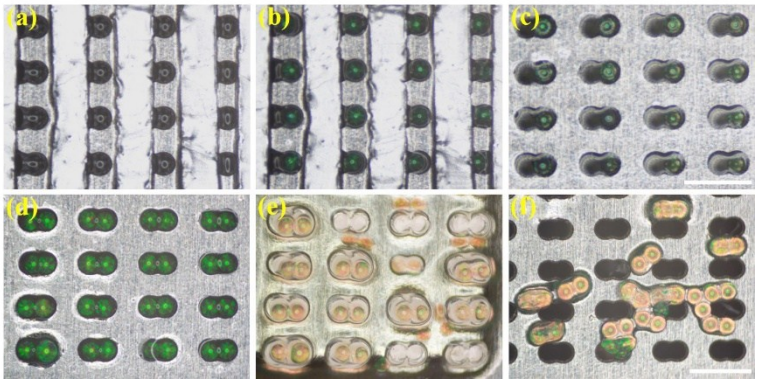

Figure S4. (a-f) The real images of the generation process of the photonic barcodes in the double-hole negative mold. The scale bars are 1mm.

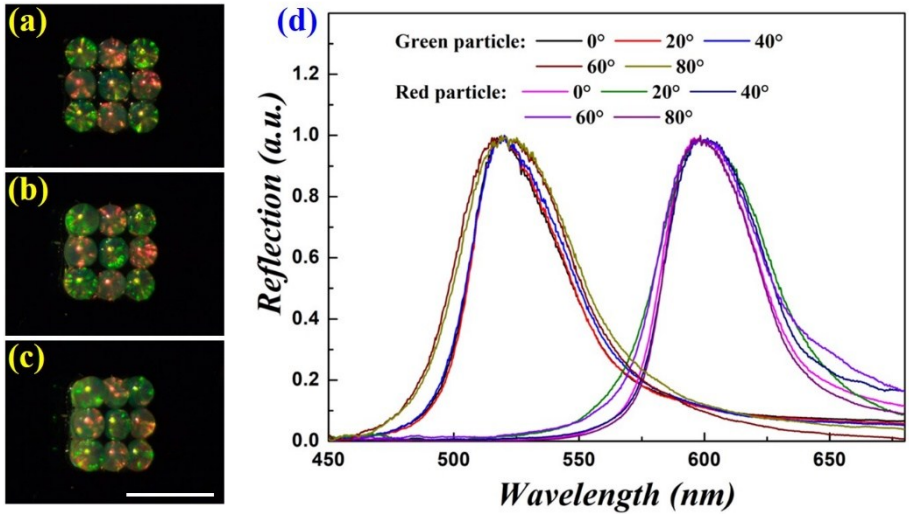

Figure S5. (a-c) The optical image characterizations about the angle-independent property of the photonic barcodes. The observing angles (angle between the horizontal plane and the 3×3 barcode) are 0°, 20° and 40° in

(a-c) respectively. The scale bar is 1mm; (d) the spectra of the reflection peaks about the green and red particles in the barcode with changing observing angles.

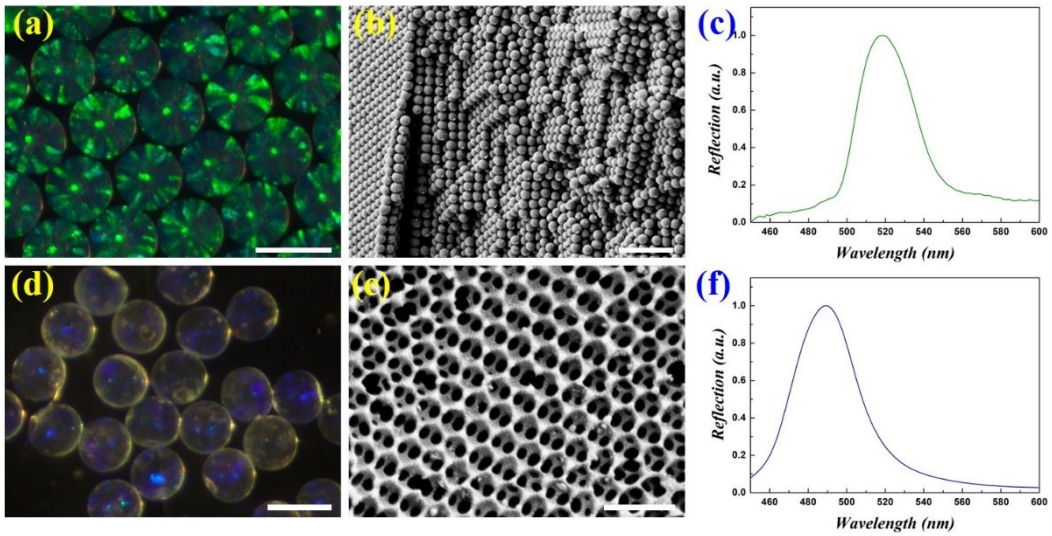

Figure S6. (a-b) The optical (a), microstructures (b) and spectral (c) images of the PhC microparticles; (d-f) the optical (d), microstructures (e) and spectral (f) images of the egg white inverse opal particles. The scale bars are 300 μm in (a, d), 1 μm in (b) and 500 nm in (e).