

Electronic Supplementary Information

Materials

All materials employed in the paper were commercially available. Tetraethyl orthosilicate (TEOS), Dopamine hydrochloride (DA·HCl), Tris(hydroxymethyl)aminomethane (Tris), and Polyethyleneimine (PEI, $M_w=600$) were purchased from Aladdin (Shanghai, China). Ammonium hydroxide (25-28 %) and absolute ethyl alcohol were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Glass substrates were purchased from Shangzhuo Technology Company (Henan, China). All solvents used in the synthesis were used without further purification.

Preparation of PDA@SiO₂ NPs:

SiO₂ NPs were synthesized by the well-known Stöber method. SiO₂ NPs of different sizes were used to prepare dispersions with the mass fraction of 20 wt.%. A certain amount of the SiO₂ NPs dispersion was added into 200 mL Tris buffer (pH~8.5) for ultrasonic until the dispersion was uniform. A certain amount of DA·HCl was added for stirring at 30 °C for 18 h. Then the system was centrifuged at 6000 rpm for 10 min. After discarding the supernatant, the PDA@SiO₂ NPs were resuspended in deionized water and centrifuged again. Repeated 3-5 times to obtain PDA@SiO₂ NPs dispersion at the mass fraction of 20 wt.%. The microstructures of the nanoparticles were obtained by the scanning electron microscope (S-4700, Hitachi). Two-dimensional Fourier Transform for SEM image was conducted by the image analyzing software ImageJ. The specific surface area of nanoparticles was measured by the automatic surface area and porosity analyzer (ASAP 2020, Micromeritics). The infrared spectrums of nanoparticles were measured by Fourier Transform Infrared spectroscopy (Nicolet 6700, Thermo Scientific).

Preparation of the metastable photonic pigments

A certain amount of the obtained PDA@SiO₂ NPs dispersion was loaded into the airbrush system at a fixed working pressure of 0.1 MPa and a working distance of 10 cm. The dispersion was uniformly sprayed on the clean glass substrate to obtain the single-component metastable photonic pigments. For the preparation of binary photonic pigments, two kinds of PDA@SiO₂ NPs dispersion with known corresponding reflection wavelength were mixed in a certain volume ratio for ultrasonic until the dispersion was uniform. The same airbrush system was used to obtain the binary metastable photonic pigments. The optical photographs of the photonic pigments were captured by the camera of an iPhone XR. The corresponding reflection spectrums were measured by the reflectance mode of the UV-visible spectrophotometer (Lambda 750, PerkinElmer). The simulation of photonic structures and calculation of their optical properties were conducted by Lumerical FDTD Solutions.

Calculation of brightness of the metastable photonic pigments

The light source was set as D50 and field of view was set as 2 °, and the reflection spectrums of photonic pigments were substituted into formula (1-1, 1-2) to obtain the corresponding tristimulus values X, Y, Z.

$$X = K \int_{380}^{780} S(\lambda) \bar{x}(\lambda) R(\lambda) d\lambda$$

$$Y = K \int_{380}^{780} S(\lambda) \bar{y}(\lambda) R(\lambda) d\lambda \dots\dots\dots(1-1)$$

$$Z = K \int_{380}^{780} S(\lambda) \bar{z}(\lambda) R(\lambda) d\lambda$$

$$K = \frac{100}{\int_{380}^{780} S(\lambda) \bar{y}(\lambda) R(\lambda) d\lambda} \dots\dots\dots(1-2)$$

where $S(\lambda)$ is relative spectral energy distribution of light sources, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ are CIE 1931 color matching functions, $R(\lambda)$ is the reflection spectrum of objects.

Then, CIE 1976 $L^*a^*b^*$ color space was used to calculate the brightness of photonic pigments. The brightness (L^*) was obtained by substituting the previous tristimulus values into formula (1-3, 1-4).

$$\begin{cases} L^* = 116f(Y/Y_0) - 16 \\ a^* = 500[f(X/X_0) - f(Y/Y_0)] \\ b^* = 200[f(X/X_0) - f(Z/Z_0)] \dots\dots\dots(1-3) \end{cases}$$

$$f(I) = \begin{cases} (I)^{\frac{1}{3}} & I > (6/29)^3 \\ (841/108)I + 4/29 & I \leq (6/29)^3 \dots\dots\dots(1-4) \end{cases}$$

where X, Y, Z are tristimulus values of objects, X_0 , Y_0 , Z_0 are tristimulus values of CIE standard light source.

Stabilization of the metastable photonic pigments

A certain amount of PEI was dissolved in Tris buffer (pH~8.5), and the prepared photonic pigment was immersed in the solution and reacted for 30 min. After the reaction, the stabilization of photonic pigment was completed after natural drying. The water contact angles of photonic pigments were measured by the automatic optical contact angle meter (JGW-360A, Dataphysics). The infrared spectrums of photonic pigments were measured by Fourier Transform Infrared spectroscopy (Nicolet 6700, Thermo Scientific).

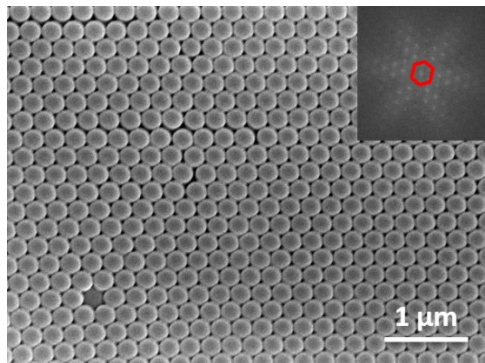


Figure S1. SEM image of the photonic crystals prepared by SiO₂ NPs. Inset: the corresponding 2D FT pattern of the SEM image.

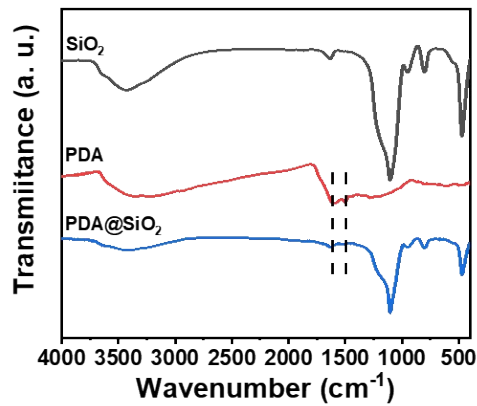


Figure S2. FT-IR spectrums of SiO₂ NPs, PDA, and PDA@SiO₂ NPs.

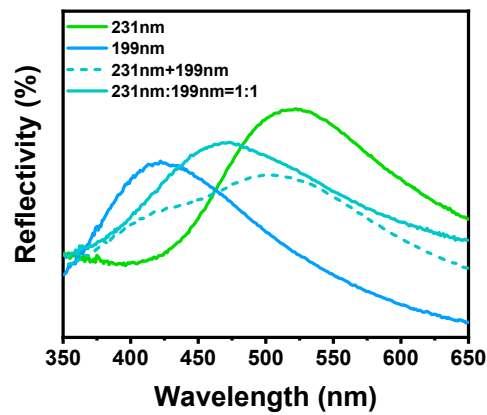


Figure S3. Reflection spectrums of binary photonic pigments prepared by 231 nm and 199 nm PDA@SiO₂ NPs (Dotted line: the simulate reflection spectrum)

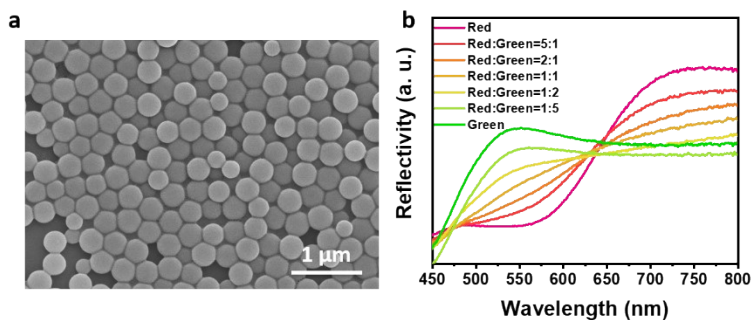


Figure S4. (a) SEM image of binary photonic pigments prepared by PDA@SiO₂ NPs with low roughness; (b) Reflection spectrums of binary photonic pigments prepared by PDA@SiO₂ NPs with low roughness in different volume fractions.

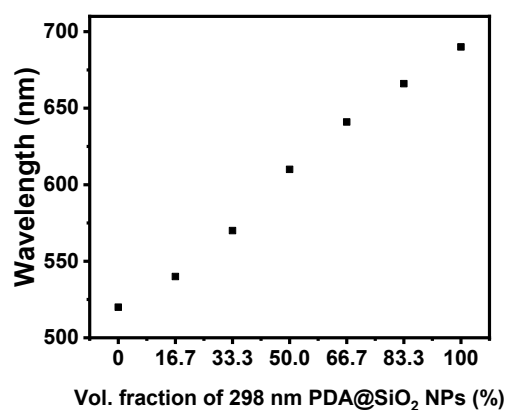


Figure S5. Wavelength values at the dominant reflection peaks of photonic pigments as a function of volume fraction of 298 nm PDA@SiO₂ NPs.

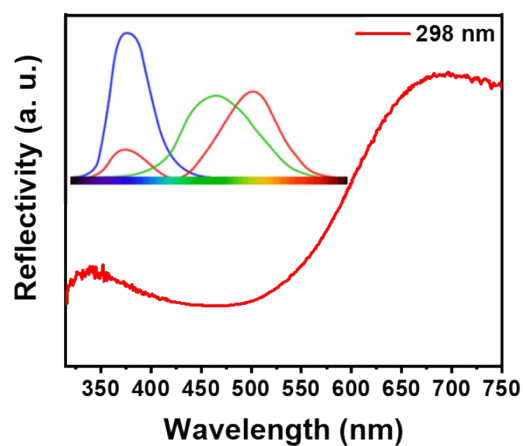


Figure S6. Reflection spectrum of single-component photonic pigment prepared by 298 nm PDA@SiO₂ NPs. Inset: CIE 1931 color matching function.

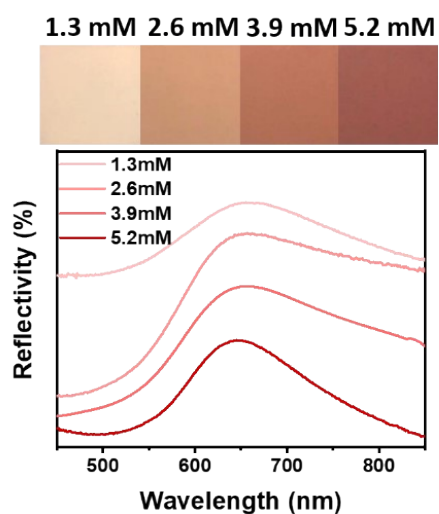


Figure S7. Optical images and reflection spectrums of photonic pigments prepared by PDA@SiO₂ NPs with different DA contents.