

Supplementary Information

Permanent Irreversible Structural Color Based on Core-Shell Chemically Bonded SiO₂@P(St-BA) Particles

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Experimental Section

Materials

Tetraethylorthosilicate (TEOS), ammonia (NH₃·H₂O, 28%), vinyl triethoxysilane (VTES), and anhydrous ethanol were purchased from Shanghai Macklin Biochemical Co., Ltd. Styrene (St), Butyl acrylate (BA), sodium dodecyl sulfate (SDS) and potassium peroxydisulfate (KPS) was purchased from Aladdin Co. Ltd. All chemicals were used as received without further treatment.

Fabrication of Vinyl-Grafted SiO₂ Nano Particles

The vinyl-grafted SiO₂ particles were synthesized by a modified Stöber method. In brief, mixture A consisted of 2 mL NH₃·H₂O, 48 mL deionized water, and 50 mL anhydrous ethanol and was stirred vigorously (1500 rpm) for 30 mins. Mixture B was composed of 82 mL of ethanol and 16 mL of TEOS was poured quickly into the system, then the speed was down low to 600 rpm and the process was run for 4 h and 2 mL of VTES was added into the system, and then keep stirring for 2 h. Finally, the particles were washed with ethanol three times and then prepared into about 8 wt% ethanol suspensions.

Fabrication of the PS and P(St-BA) Particles

The pure PS particles and P(St-BA) were synthesized by a classical emulsion polymerization method. In brief, St (5g), SDS (30 mg), water (100g), initiator (KPS 0.3g) were added into a 250 ml flask and stirred at 300 rpm. after a homogeneous solution was obtained at ambient temperature, the mixture was placed in a oil bath thermostated. When the temperature was increased to 75°C, 0.3 g KPS was added into the system and then keep reaction for 5 h. Finally, the PS particles with diameter about 195 nm were fabricated. The diameter of particles can controlled by tuning the mass of St monomer. The different mass of BA (0-1g) monomer was introduced into the above system to prepare the P(St-BA) particles.

Fabrication of the Core-Shell SiO₂@PS and SiO₂@P(St-BA) Particles

The core-shell $\text{SiO}_2@\text{PS}$ and $\text{SiO}_2@\text{P}(\text{St-BA})$ particles are synthesized by using an emulsion polymerization²⁵⁻²⁷. In brief, 10 mL of the 8wt% vinyl-grafted SiO_2 suspensions, 150 mL deionized water, 30 mg of SDS, and 5 mL St were charged into a round-bottom flask, after a homogeneous solution was obtained at ambient temperature, the mixture was placed in a water bath thermostated. When the temperature was increased to 75°C, 1.5 g KPS was added into the system and then keep reaction for 5 h. In this process, the SiO_2 particles were vinyl-modified by VTES. The contained C=C double bond will copolymer with St and BA monomers upon initiation, and then grow to the core-shell $\text{SiO}_2@\text{PS}$ and $\text{SiO}_2@\text{P}(\text{St-BA})$ particle. The obtained $\text{SiO}_2@\text{PS}$ and $\text{SiO}_2@\text{P}(\text{St-BA})$ particles were thoroughly washed with ethanol three times by centrifugation. The diameter of the polymer shell can be tuned by controlling the amount of the monomer. The glass transition temperature (T_g) can be tuned by controlling the BA content and calculated by the classical Fox equation (detail formula see Table S1).

Preparation of Structural Colors and Patterned Structural Colors

The structural color films were prepared by the dip-coating method. In brief, the 70 mL, 8 wt% particles ethanol suspensions were ultrasonicated for 1 h before use and then transferred into a 100 mL beaker, and then the beaker was placed in a Coater from HeatMent (SYDC-100H DPI, SAN-YAN Instrument Co. Ltd., Shanghai). And then the cleaned glass substrate was placed vertically into the $\text{SiO}_2@\text{PS}$ nanosphere suspensions. The pulling rate was set as $2 \mu\text{ms}^{-1}$ at 25 °C, and the entire procedure was carried out two times. The patterned structural colors were prepared by a hot-pressing printing method, firstly, the metal stamp was heated to different temperatures (120 and 80 °C), and then it was put on the samples and cooled to room temperature naturally.

Characterization

The morphology of SiO_2 , $\text{SiO}_2@\text{PS}$, and $\text{SiO}_2@\text{P}(\text{St-BA})$ particles and the self-assembly microstructure of structural colors were sputtered with platinum and then characterized by scanning electron microscopy (FE-SEM, ZEISS ULTRA 55). The core-shell structure of $\text{SiO}_2@\text{P}(\text{St-BA})$ particles was characterized by transmission electron microscopy (TEM). The reflectance and transmission spectra were recorded using a Hitachi U-4100 spectrophotometer. The schematic of the measurement setup and the measurement steps have been given in detail in the Supporting Information. The digital photographs of the structural colors of PCs were taken by a cell phone under different incident angles. The specific method and steps of taking photos have been detailed in the Supporting Information. The morphology of

the prepared samples was obtained by using a Nova NanoSEM 450 field emission scanning electron microscope.

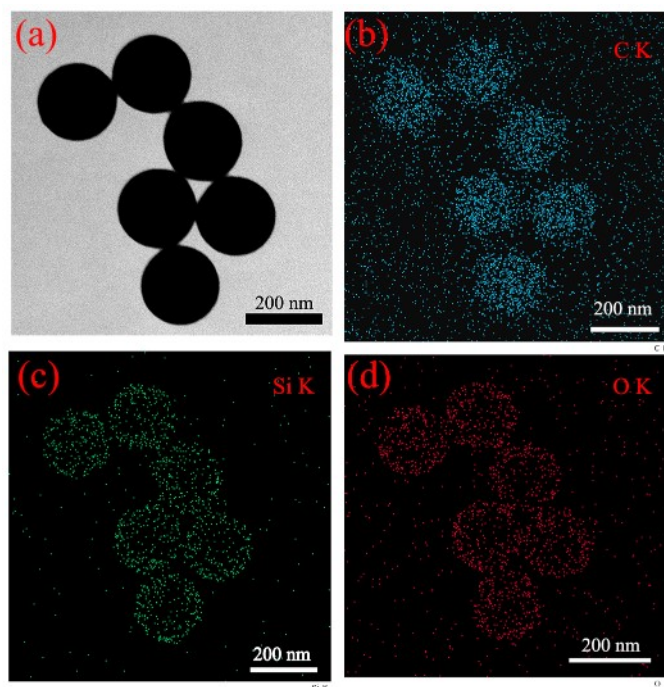


Figure S1. (a) STEM image of vinyl-grafted SiO₂ nano particles. (b-d) element distribution of C, Si and O, respectively.

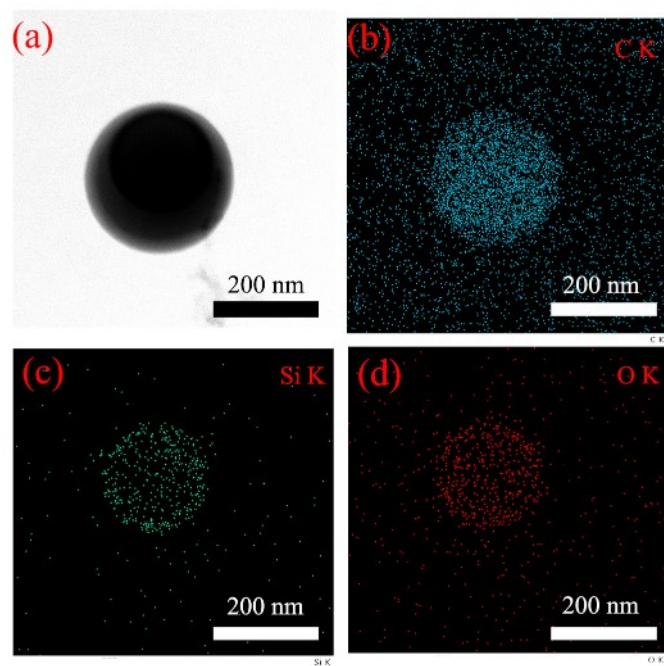


Figure S2. (a) STEM image of SiO₂@P(St-BA) particles nano particles. (b-d) element distribution of C, Si and O, respectively.

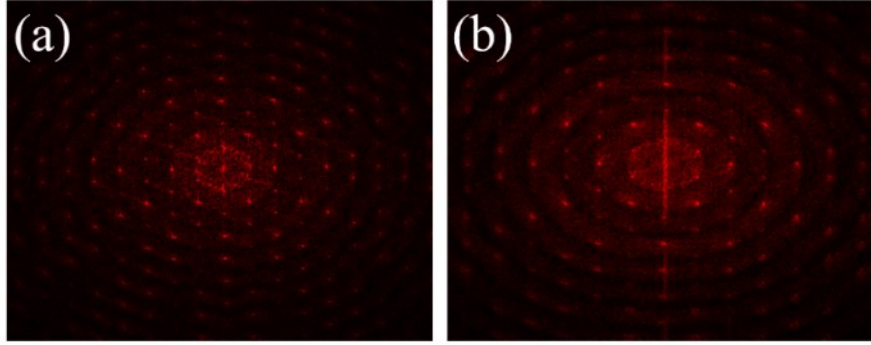


Figure S3. 2D FFT images of the photonic crystal with green (a) and red (b) colors, showing the high quality of structural colors.

Fabrication of the core-shell SiO₂@PS and SiO₂@P(St-BA) nanoparticles: firstly the 10 mL of the 8wt% vinyl-grafted SiO₂ were used as seeds to prepare the SiO₂@PS and SiO₂@P(St-BA) core-shell particles. The T_g can be controlled by tuning the BA content in the system and then calculated according to the following formula:

Table S1. The detailed formula of polymer shell with different T_g.

Samples	St/g	BA/g	Theory T _g / °C	Measured T _g
SiO ₂ @PS	5	0	100	100.2
SiO ₂ @P(St-BA)-1	4.6	0.4	80.1	80.5
SiO ₂ @P(St-BA)-2	4.2	0.8	62.3	64.5
SiO ₂ @P(St-BA)-3	4	1	54.0	55.7

As we can see from Table S1, the value of measured T_g is a litter higher than the theory, which may be caused by the incomplete reaction of the BA monomer.

According to Bragg's law, the effective refractive index can be calculated according to the:

$$\lambda \propto dn_{eff} \quad (1)$$

$$n_{eff} = \sqrt{f_{Air} n_{Air}^2 + f_{Shell} n_{Shell}^2 + f_{Core} n_{Core}^2} \quad (2)$$

Where d is the center-to-center distance between two neighboring crystalline planes. n_{eff} is the effective refractive index of SiO₂@PS core-shell particles (n_{shell} equals $n_{PS} = 1.59$; n_{core} equals $n_{silica} = 1.46$), which can calculate by equation (2). In the classical 3D photonic crystal structure, the microsphere filling

factor is $f_{shell} + f_{core} = 0.74$, $f_{void} = f_{air} = 0.26$, respectively.

The f_{core} can be calculated by the following equation:

$$f_{core} = \frac{V_{core}}{V_{particle}} * 0.74 = \left(\frac{\frac{1}{6}\pi D_c^3}{\frac{1}{6}\pi D_p^3} \right) * 0.74 \quad (3)$$

where D_c and D_p are the diameter of the core and the $\text{SiO}_2@PS$ particles ($D_c = 193$ and $D_p = 263$).

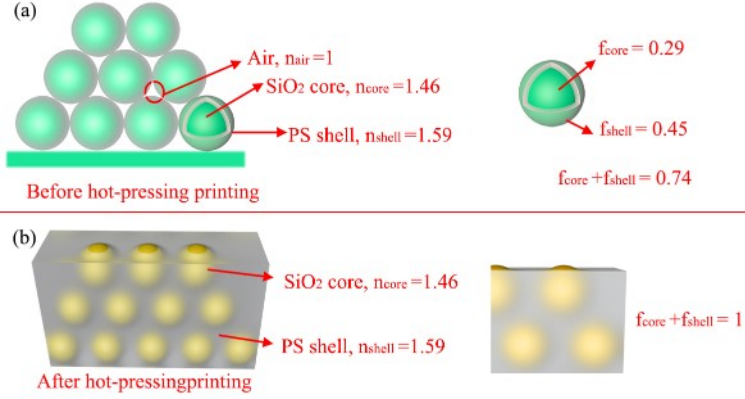


Figure S4. The schematic of calculation of the effective refractive index. (a)

Therefore, the f_{core} equals 0.29 and the f_{shell} calculated by $(0.74 - f_{core})$ equals 0.45. Therefore, the n_{eff} in classic 3D structural colors equals 1.33.

$$n_{eff} = \sqrt{0.26 * 1^2 + 0.45 * 1.59^2 + 0.29 * 1.46^2} = 1.33$$

However, when the sample was treated by hot-pressing printing, the f_{void} will decrease gradually or even to zero. The particles seem like a hexagonal non-close-packed arrangement and the air in gaps was squeezed out. In this case, we normalize the volume fraction as the following equation: $f_{core} = 0.39$; and the f_{shell} calculated by $(1 - f_{core})$ equals 0.61. Therefore, the n_{eff} equals 1.55 after hot-pressing printing.

$$n_{eff} = \sqrt{0.68 * 1.59^2 + 0.32 * 1.46^2} = 1.55$$

Therefore, the bandgap of structural colors was redshift after the hot-pressing printing treatment.