Fabrication of Effect Pigments with Full Visible Photonic Crystal Colors via Shear-Induced Assembly of Multinary Colloidal Nanoparticles

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This text includes a supplementary table showing size characteristics of obtained PS@P(EA-co-AA) nanoparticles and supplementary Figure S1-15.

Experimental Section

Materials

Styrene (St) and ethyl acrylate (EA) from Sinopharm Chemical Reagent Co., Ltd. was purified twice using alkaline alumina column to remove polymerization inhibitor before use. Sodium persulfate (SPS), sodium dodecylsulfate (SDS), acrylic acid (AA), potassium hydroxide (KOH), ethylene glycol dimethacrylate (EGDMA), 2-hydroxy-2-methylpropiophenone were purchased from Aladdin for using without further purification. Dowfax 2A1and CO436 surfactants were purchased from Dow Chemicals. Butanediol diacrylate (BDDA) was purchased from Tokyo Chemical Industry, Shanghai used for cross-linker. Deionized water was purified using a Millipore Milli-Q Synergy. Polydimethylsiloxane (PDMS) and the cross-linker (Sylgard 184 elastomer kit) were provided by Dow Corning. Polyurethane resin and varnish were purchased from BSAF Advanced Chemicals Co., Ltd.

Characterization Methods

Dynamic light scattering instrument (DLS, Malvern Zetasizer Nano ZS90) was used to record the hydrodynamic particle size and distribution of PS@P(EA-co-AA) nanoparticles under a helium-neon laser light source. Transmission electron microscopy (TEM, Tecnai G2 20 TWIN, FEI) was used to characterized PS seeds, PS cores and PS@P(EA-co-AA) nanoparticles sizes at an operating voltage of 120 kV. Field emission scanning electron microscopy (FESEM) micrographs were collected with a Zeiss Ultra 55 operated at a 3 kV and a working distance of 5.0-8.0 mm. The well-prepared samples were coated with Au at 10 mA for 120 s using a spray coater before measurement. Portable fiber spectrometer (Ideaoptics PG2000-Pro) was used to carry out the reflective and transmission spectra, and the standard aluminum mirror (100% reflection) was used as a reference. Photographs were taken illuminated with a LED light source against a dark background using a smartphone. Ultrasmall angle X-ray scattering (USAXS) characteristic was carried out in the Shanghai Synchrotron Radiation Facility (SSRF), China and analyzed by FIT 2D (v12.077).

Tables:

Table S1 TEM and DLS data of PS@P(EA-co-AA) core/shell nanoparticles.

Sample Name		TEM (nm)	Z-Ave. (nm)	Zeta potential (mV)	PDI
Red	Seed	/	72	-17	0.149
	Core	207	225	-32	0.080
	Core/shell	/	246	-35	0.033
Yellow	Seed	/	58	-22	0.135
	Core	183	202	-33	0.085
	Core/shell	/	225	-36	0.072
Yellow-green	Seed	/	56	-18	0.108
	Core	176	193	-35	0.056
	Core/shell	/	216	-37	0.067
Green	Seed	/	52	-22	0.072
	Core	161	178	-35	0.083
	Core/shell	/	207	-32	0.032
Blue	Seed	/	50	-19	0.072
	Core	148	172	-32	0.095
	Core/shell	/	192	-28	0.052
Violet	Seed	/	49	-19	0.119
	Core	128	165	-28	0.151
	Core/shell	/	182	-31	0.045
Ultraviolet	Seed	/	42	-21	0.129
	Core	100	139	-25	0.263
	Core/shell	/	158	-29	0.096

Figures:

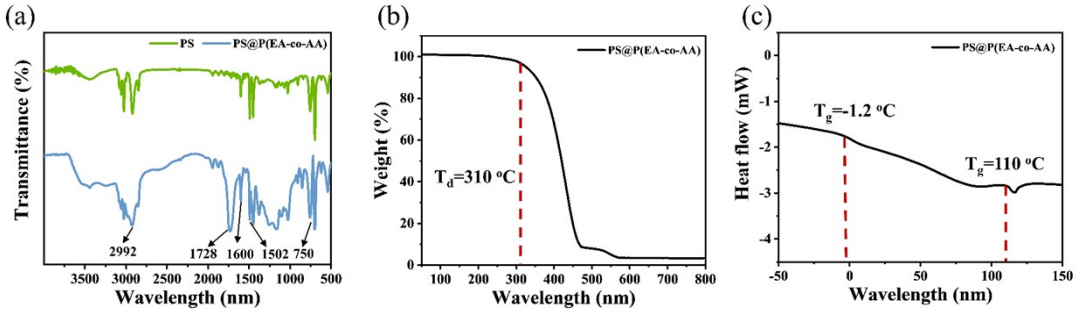

Figure S1 (a) FT-IR, (b) TGA and (c) DSC curves of PS@P(EA-co-AA) nanoparticles.

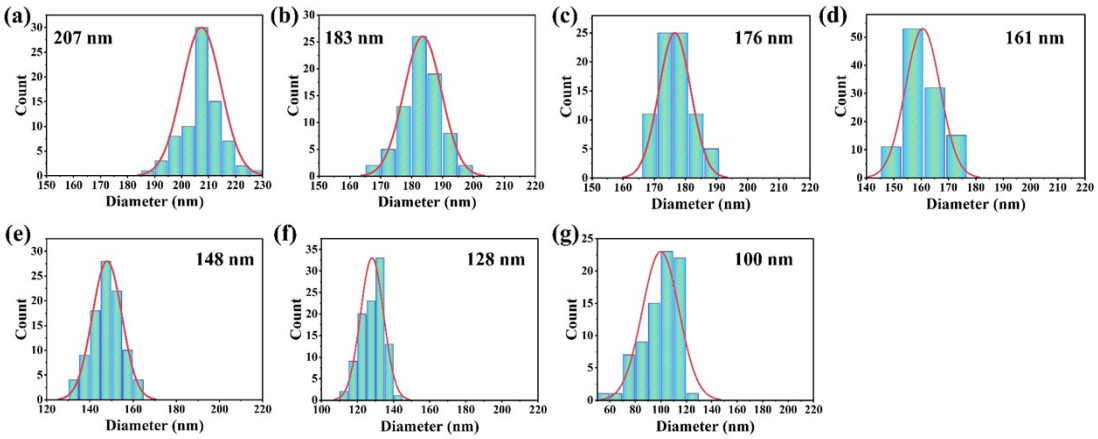

Figure S2 The diameter distribution histograms of PS core with (a) 207 nm, (b) 183 nm, (c) 176 nm, (d) 161 nm, (e) 148 nm, (f) 128 nm, and (g) 100 nm, respectively.

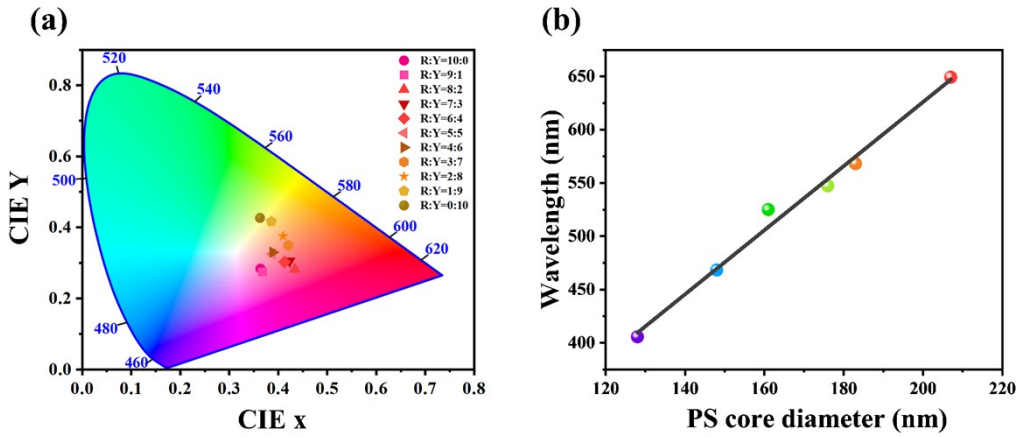

Figure S3 (a) The CIE chromaticity diagram of films for various blending ratios. (b) The peak wavelengths of the photonic films as a function of PS core diameters.

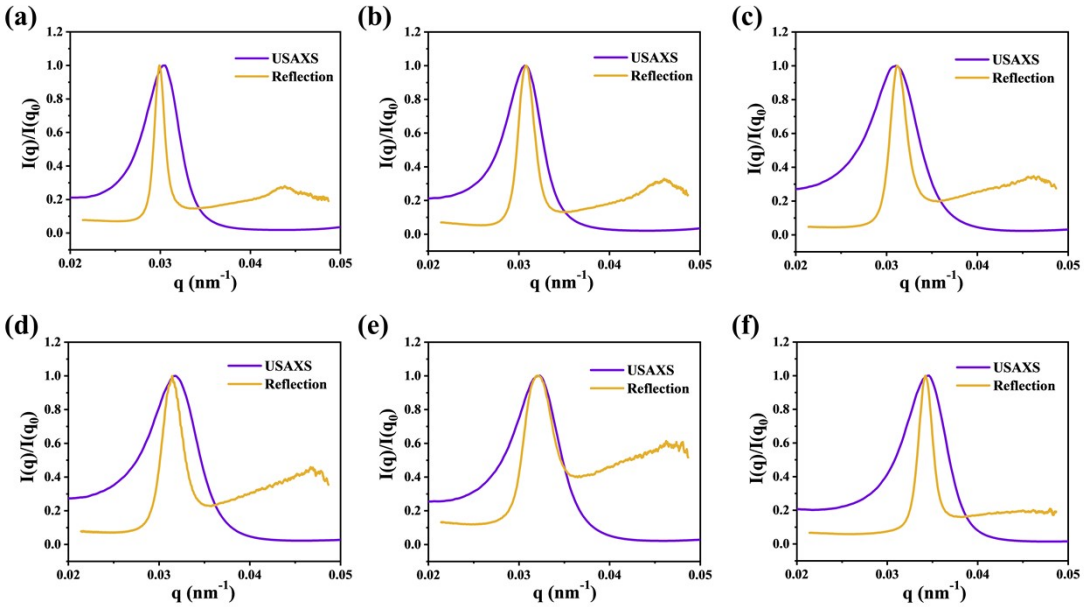

Figure S4 The azimuthal average of the experimental USAXS pattern and obtained reflection data of binary photonic films containing varied contents of 207-nm nanoparticles with (a) 100 wt%, (b) 80wt%, (c) 70 wt%, (d) 60 wt%, (e) 50wt% and (f) 0 wt%, as a function of the wavevector *q*.

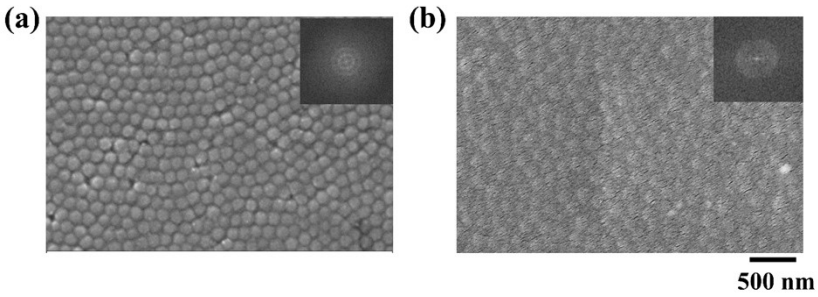

Figure S5 SEM images of films containing (a) 20 wt% of 207 nm and 80 wt% of 176 nm and (b) 40 wt% of 207 nm and 60 wt% of 161 nm.

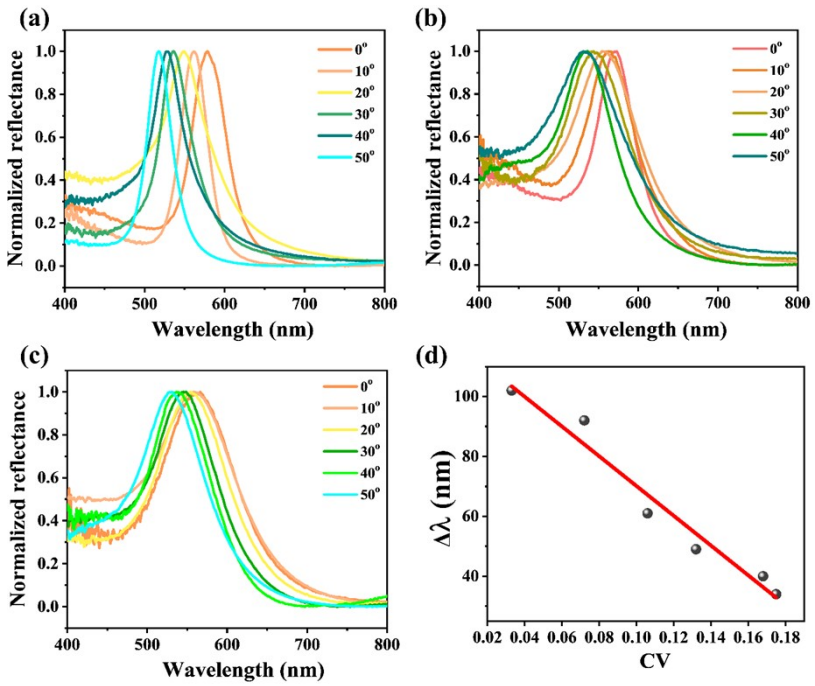

Figure S6 Reflection spectra of the photonic films with different coefficient of variation (CV) values of (a) 0.106, (b) 0.168 and (c) 0.175 at various detection angles from 0° to 50°. (d) The blue-shift values (Δλ) as a function of CV values.

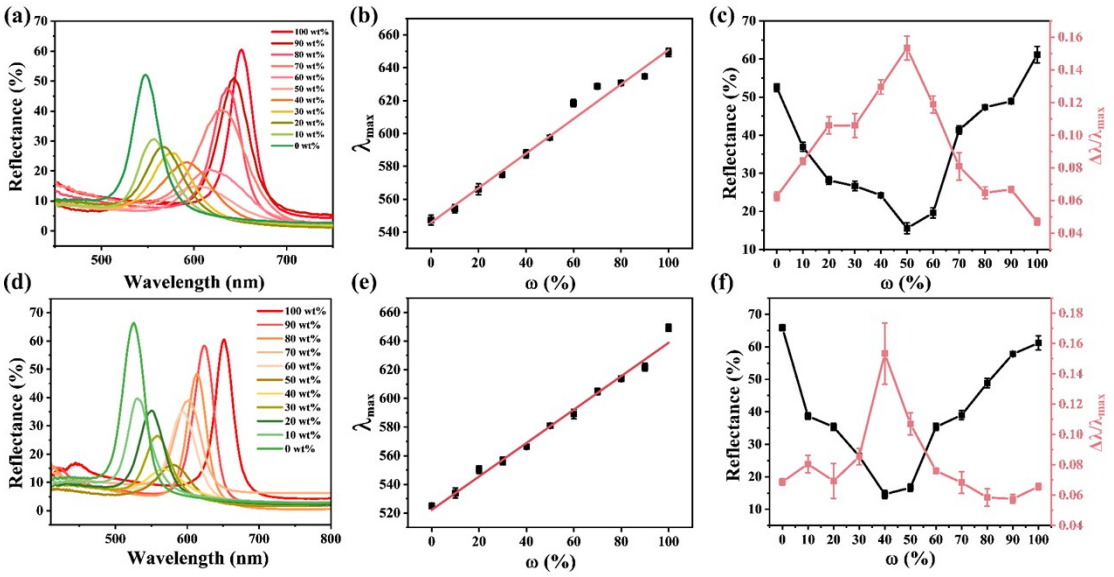

Figure S7 Reflectance spectra of the photonic films for various blending ratios of (a) 207 nm and 176 nm, (d) 207 nm and 161 nm. Reflectance peak position, λ_{max}, as a function of 207-nm weight percentage (ω) in the binary of (b) 207 nm and 176 nm, (e) 207 nm and 161 nm. Reflectivity and normalized full width at half-maximum, as a function of 207-nm weight percentage (ω) in the binary of (c) 207 nm and 176 nm, (f) 207 nm and 161 nm.

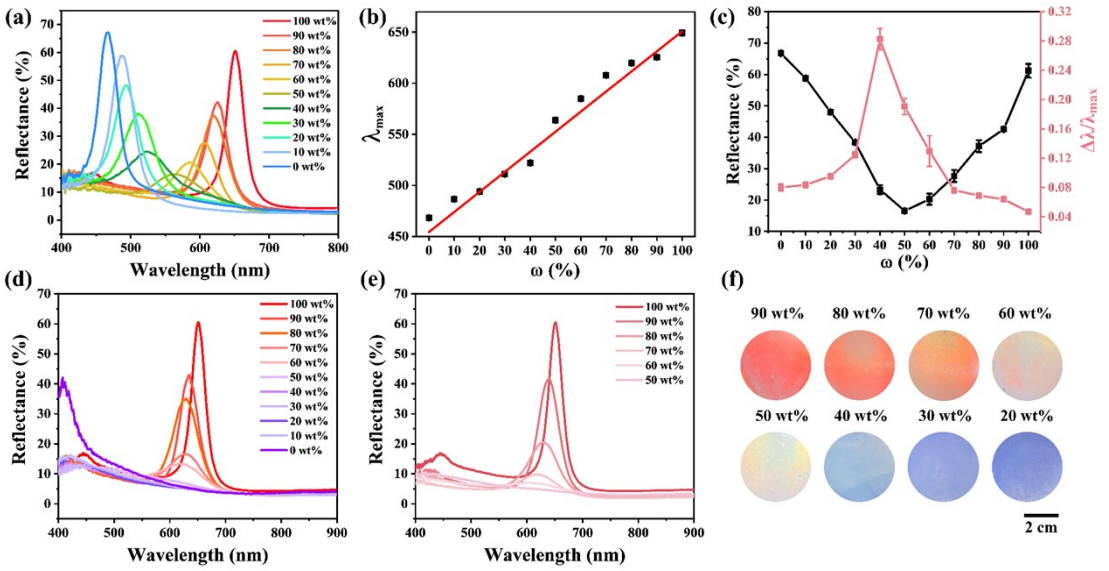

Figure S8 Reflectance spectra of the films for various blending ratios of (a) 207 nm and 148 nm, (d) 207 nm and 128 nm, (e) 207 nm and 100 nm. (b) Reflectance peak position and (c) reflectivity and normalized full width at half-maximum as a function of 207-nm weight percentage (ω) in the binary of 207 nm and 148 nm. (f) Photographs of prepared films from various mass fractions of 207-nm when blending particles with diameters of 207 nm and 100 nm.

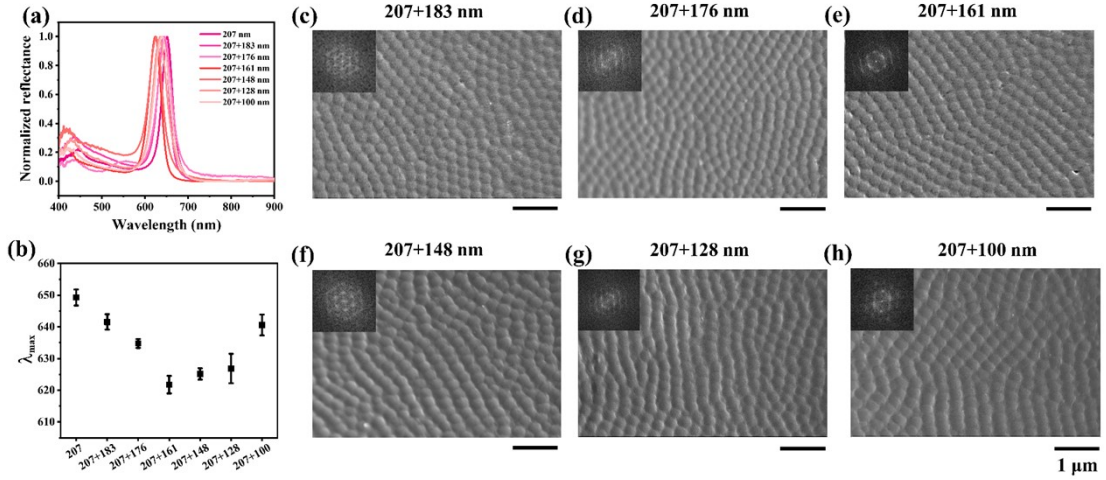

Figure S9 (a) Reflectance spectra and (b) peak position of photonic films when weight percentage of 207-nm particles is 90 wt%. SEM images of binary colloidal arrays with (c) 207 and 183 nm, (d) 207 and 176 nm, (e) 207 and 161 nm, (f) 207 and 148 nm, (g) 207 and 128 nm and (h) 207 and 100 nm when ω=90 wt%.

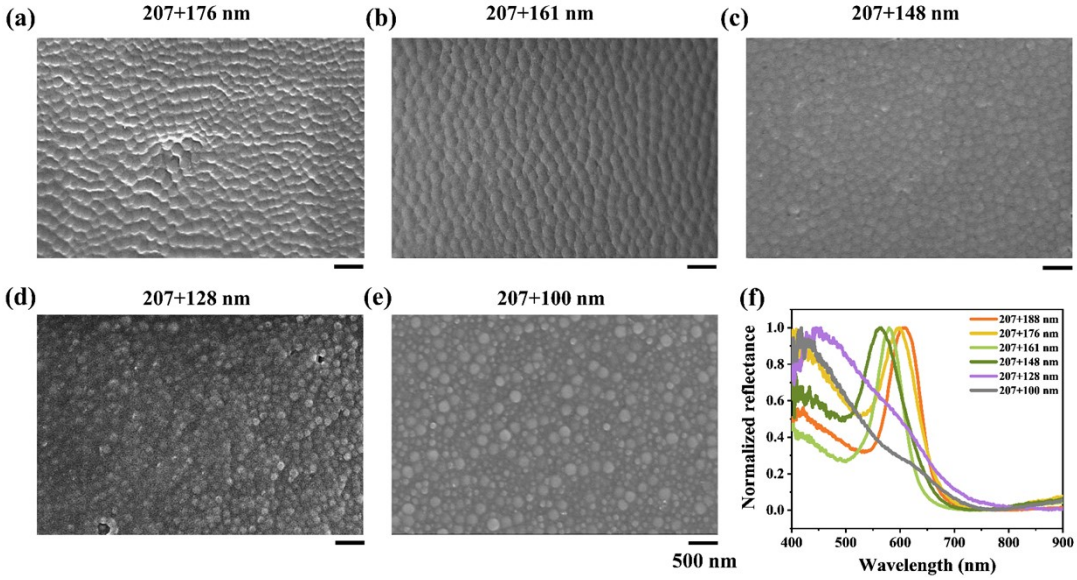

Figure S10 SEM images of binary colloidal arrays with (a) 207 and 176 nm, (b) 207 and 161 nm, (c) 207 and 148 nm, (d) 207 and 128 nm and (e) 207 and 100 nm when ω=50 wt%. (f) Reflectance spectra of the films when weight percentage of 207-nm particles is 50 wt%.

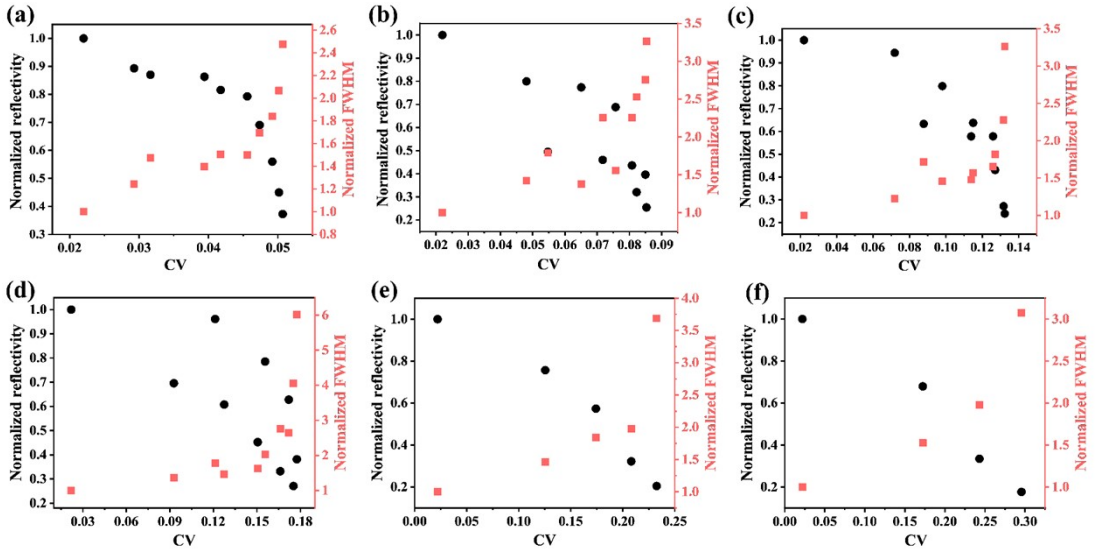

Figure S11 Normalized reflectance and full width at half-maximum as a function of coefficient of variation (CV) value at various blending sets of (a) 207 and 183 nm, (b) 207 and 176 nm, (c) 207 and 161 nm, (d) 207 and 148 nm, (e) 207 and 128 nm and (f) 207 and 100 nm

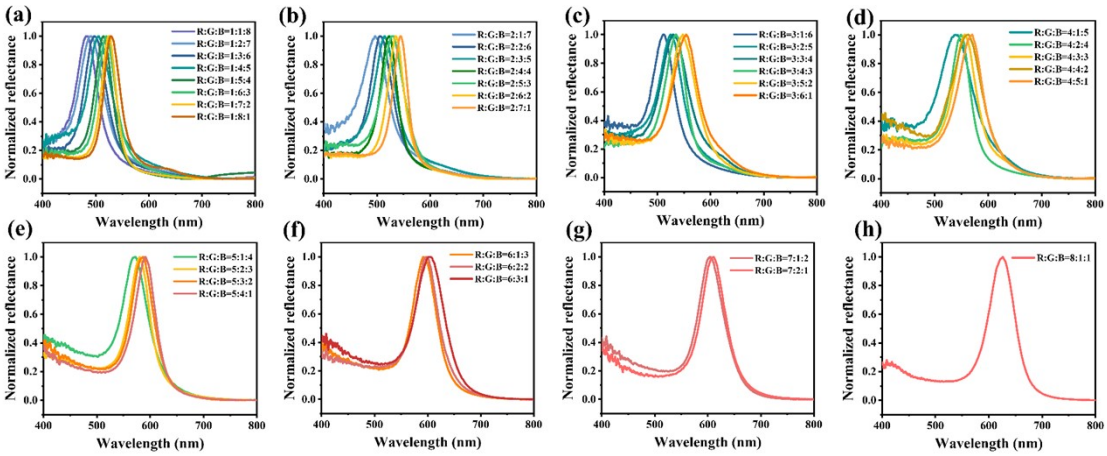

Figure S12 Reflectance spectra of the films for various ternary blending ratios of nanoparticles with diameters of 207 nm, 161 nm and 148 nm.

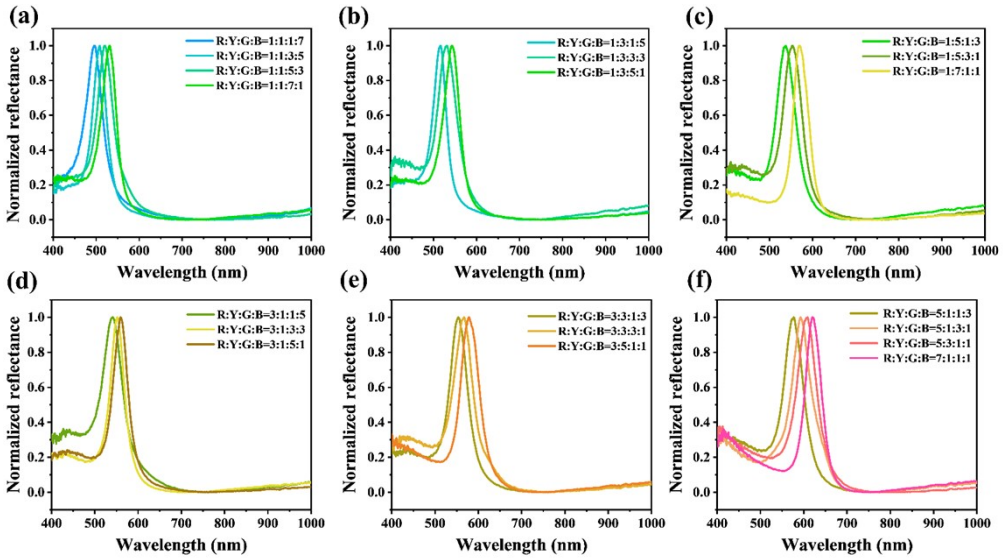

Figure S13 Reflectance spectra of the films for various quaternary blending ratios of nanoparticles with diameters of 207 nm, 183 nm, 161 nm and 148 nm.

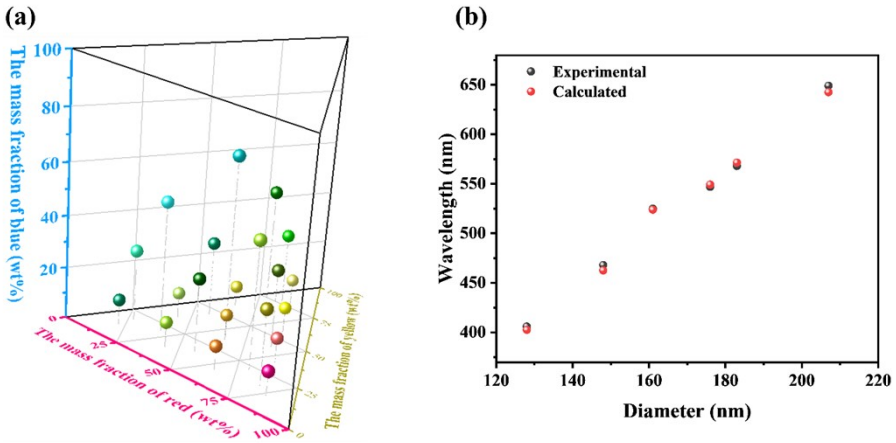

Figure S14 (a) Partial quaternary diagram of films with different components of 207-

nm, 183-nm, 161-nm and 148-nm. (b) The experimental and calculated peak wavelengths of different nanoparticles following the similar value.

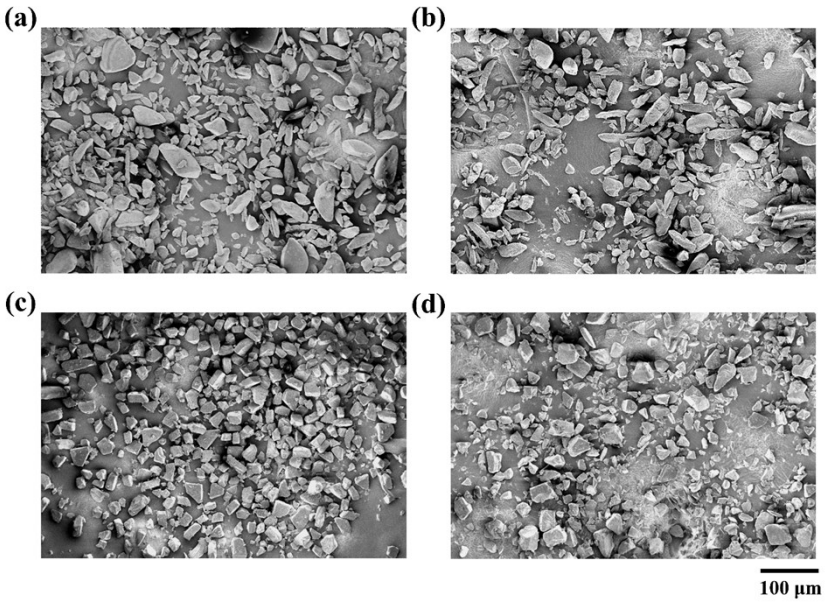

Figure S15 SEM images of the size distribution of the resultant photonic pigments of (a) blue, (b) green, (c) yellow and (d) red.

Figure S16 Photonic coatings containing different blending pigments of the same mixing ratios with (a) Y + G + B (1:1:1), (b) R + Y + G (1:1:1) and (c) R + G + B (1:1:1) when weight percentage of pigments is 4 wt%.