

Using Cuttlefish Ink as an Additive to Produce Non-iridescent Structural Colors of High Color Visibility

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In recent years, amorphous photonic structures (APSSs) that possess only short-range order have received considerable attention due to their unique structural features, resulting in many interesting optical properties such as unusual light scattering, transport, and localization.^[1–9] Moreover, APSSs can produce vivid non-iridescent structural colors when the structural feature sizes are comparable to the visible wavelengths, resulting from an isotropic photonic pseudogap.^[8,9] In contrast, conventional photonic crystals (PCs) with both short- and long-range order produce iridescent structural colors due to the photonic bandgap effect.^[10–15] Those non-iridescent structural colors produced by APSSs may have important potential applications in color-related fields such as paints, cosmetics, textile, and displays.

Interestingly, striking non-iridescent structural colors can be found in living organisms.^[16–21] For example, the feather barbs of the scarlet macaw show a non-iridescent blue color because of the amorphous diamond photonic structures.^[19] Random close-packed and spinodal-decomposition structures are also found in the scales of some longhorn beetles, showing bright non-iridescent colors.^[20,21] These natural APSSs could provide us with great sources of inspiration to design and fabricate novel color-related optical materials and devices.^[22–26]

To mimic non-iridescent structural colors in nature, self-assembling methods have been mostly used to obtain large-area 3D APSSs.^[22–26] Normally, self-assembling monodisperse spheres tend to form highly ordered face-centered cubic structures due to the sphere–sphere electrostatic repulsive force.^[7,27,28] In order to obtain APSSs, it is necessary to modify the conventional self-assembling methods. By strictly controlling the concentration of charged spherical particles in liquid gel, artificial APSSs with non-iridescent colors were first realized in liquid phase.^[29] Strategies such as adding ions into the gel,^[30–33] using static electric field^[34] or coating soft polymer on the colloidal spheres^[35–37] in order to further control the

interactions among spheres have been proposed. For dried colloidal APSSs, self-assembling two different-sized spheres was proposed.^[22,38] In the presence of salt in the suspension of single-sized spheres, dried APSSs could be obtained.^[39,40] By choosing highly volatile solvents to speed up evaporation, APSSs could even be fabricated by a spray method.^[41–43] All these modifications can suppress the long-distance electrostatic interactions among spheres and break down the long-range order of these colloidal structures. However, these dried artificial APSSs usually have a low color visibility. To enhance the color visibility, one can add carbon black or iron oxide black particles,^[22,39–41] or directly self-assemble synthesized black spheres of polydopamine.^[44]

Here, based on a drop-coating method a new strategy by using cuttlefish ink as an additive is proposed to produce mass APSSs with a high color visibility. The APSSs obtained by self-assembling the mixture of monodisperse polystyrene (PS) spheres and cuttlefish ink particles show vivid non-iridescent structural colors and can offer a delicate color palette with tunable hues that can cover the visible spectrum. The color hues of the APSSs are strongly related to the diameter of the PS spheres, while their spectral purity can be controlled by the proportion of the PS spheres to the cuttlefish ink particles. The whole technical procedure is rather simple: an aqueous mixture of PS spheres and appropriate amount of cuttlefish ink is dropped onto a substrate such as paper, glass, and plastic, and then dried under ambient temperature and humidity.

Cuttlefish species usually use ink to evade predators. Scanning-electron-microscopy (SEM) observations show that the cuttlefish ink is composed of non-spherical melanin particles with an average size about 110 nm, as shown in **Figure 1a**. The non-spherical geometry and size dispersity of the ink particles (**Figure S1**, Supporting Information) are amiable to realize APSSs by mixing PS spheres without any elaborate refining process. Another intriguing optical property of cuttlefish ink is the broadband high absorption (**Figure 1b**), which is important to attain APSSs with a high color visibility. Obviously, the average absorption of the cuttlefish ink powder is about 99% in the visible range, in accordance with its black appearance (inset of **Figure 1b**). Furthermore, the ink particles can be well dispersed in water (inset of **Figure S1c**, Supporting Information) due to the hydrophilicity of ink particles, making the self-assembly of PS spheres and ink particles in aqueous solutions possible. **Figure 1c** shows a typical SEM image of a self-assembled APSS consisting of 200 nm PS spheres and cuttlefish ink particles, showing a very good structure quality with a homogeneous distribution of both particles. The introduction of ink particles can break down the long-range ordered arrangement of the PS spheres, eventually leading to APSS structures, due to the size

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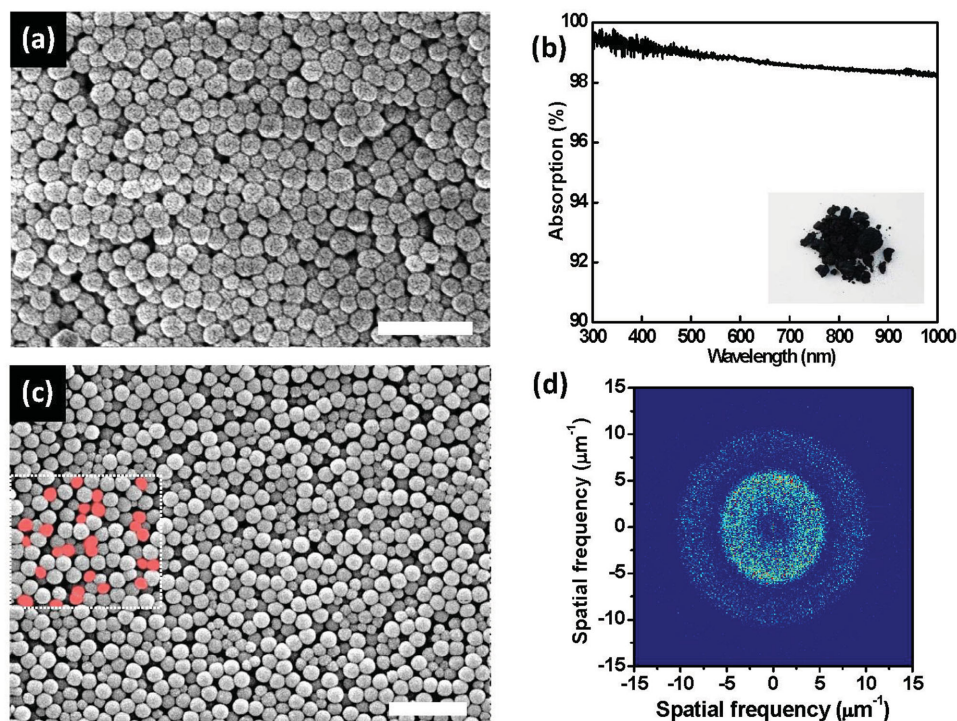


Figure 1. a) SEM image of dried cuttlefish ink powder consisting of non-spherical melanin particles. b) The absorption of 0.1 g dried cuttlefish ink powder. Inset is the optical image of the ink. c) SEM image of an APS composed of 200 nm PS spheres mixed with cuttlefish ink particles. In the dashed box, ink particles are marked by red. d) 2D Fourier transform of the SEM image in (c). Scale bars: a) 500 nm and c) 1 μm .

difference between the PS spheres and the ink particles,^[22,38] as well as the non-spherical shape of the ink particles. Figure 1d shows the 2D Fourier transform of the SEM image of an APS. A ring-like feature of the Fourier components reveals that the structure has the well-defined short-range order. SEM images taken from both the interior and the surface of samples show that the whole structure is quite homogeneous (Figure S2, Supporting Information).

Figure 2a shows the images of different APS structures on a white paper, displaying blue, green, and red colors, taken under the conditions of diffuse light illumination. Because the average size of the ink particles is approximately equal or less than a half of the diameter of the PS spheres, the ink particles would be located interstitially in the packing voids of the PS spheres. The proportion of ink particles is about 30%, 33%, and 38% for the blue (200 nm PS spheres), green (240 nm PS spheres), and red (280 nm PS spheres) APS structures, respectively. Obviously, the color visibility of the APS structures is quite high by considering that these images were taken in the white background. As indicated in previous studies,^[8,9,16] the non-iridescent structural colors of APSs originate from the coherent scattering due to the short-range order. Thus, the colors of APSs can be tuned by the characteristic length of the short-range order. In other words, different colors can be obtained by using PS spheres with different diameters. One interesting feature of structural colors is the color change with the change in the dielectric environment. In fact, the brown color of an APS consisting of 260 nm PS spheres becomes red after dropping a drop of water (Figure S3, Supporting Information). The response of this color change is rather fast due to the hydrophilicity of cuttlefish ink particles.

Films of PCs composed of only PS spheres of the same diameters as the corresponding APSs were also fabricated by the same process for comparison (Figure S4, Supporting Information). These opaline samples show matte whitish colors under the condition of diffuse light illumination, due to not only the abundant defects inside the PC structures but also the iridescent feature of the PC structures. Reflection spectra of these APS and PC samples were measured by an integrating sphere as shown in Figure 2b. For PC samples, although reflection peaks due to the partial photonic band gap exist, the overall reflection is rather high in the whole visible range, leading to whitish colors. In contrast, the overall reflection of the APS samples is rather low on both sides of the reflection peaks, leading to a high color visibility. The high color visibility of the APS samples can be understood as follows. Coherent scattering due to the short-range order in the APSs leads to a photonic pseudogap,^[8,9,19–21] within which a reflection peak is expected. In general, the introduction of ink particles would absorb scattered light in a wide wavelength range, leading to an overall low reflection of the APSs. Due to the lack of photonic density of states, the absorption for wavelength within this pseudogap should be much lower than for wavelength outside. Thus, the colors of the APSs have a good visibility in a white background.

Both the angle-resolved specular reflection and scattering spectra of the fabricated APSs were measured. The reflection-peak shifts for both the specular reflection and scattering in the blue-colored sample are rather small, as shown in **Figure 3a,b**. This indicates that the colors of the fabricated APSs are nearly angle-independent, i.e., non-iridescent. In contrast, the PC samples with only PS spheres show a strong angle dependence

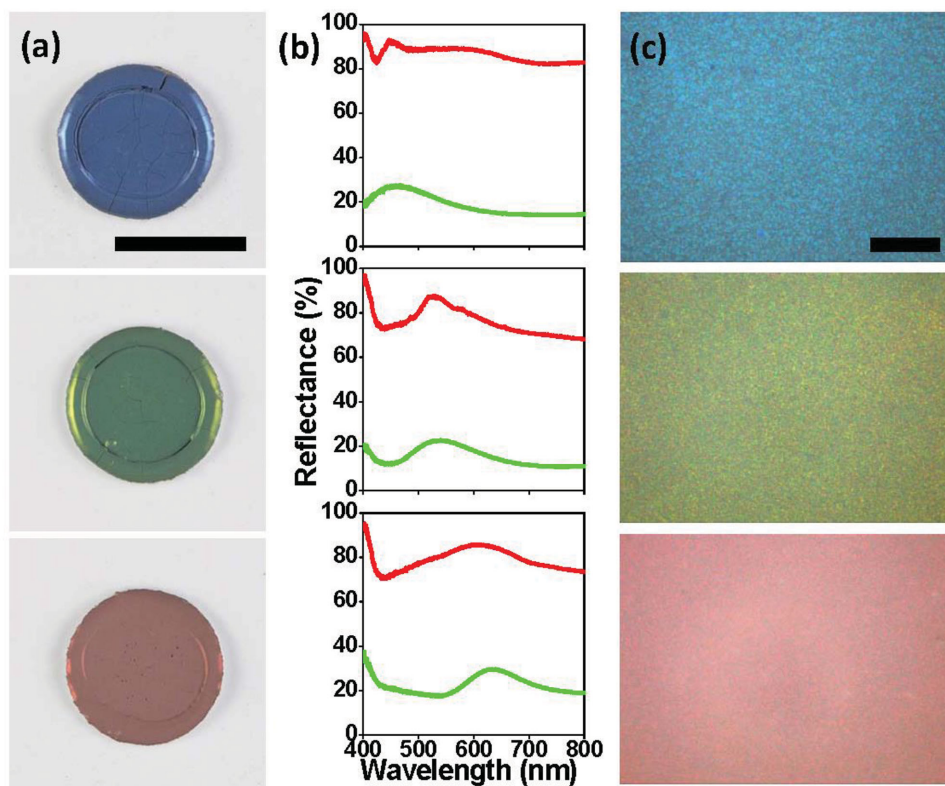


Figure 2. a) Self-assembled films of APSs on a white paper with different diameters of the PS spheres (from top to bottom: 200, 240, and 280 nm). b) Corresponding measured reflection spectra. Green lines stand for APSs with introduced ink particles and red lines represent those for PCs with only PS spheres of the same diameters as the corresponding APSs. c) Corresponding microscopic optical images of the samples in (a) with 500 \times magnification. Scale bars: a) 5 mm and c) 50 μ m.

(Figure S5, Supporting Information). The green and red APS samples show the similar results (Figures S6 and S7, Supporting Information). Moreover, by observing the red-colored APS sample under a microscope with a large numerical aperture objective, the uniform reddish color could still be seen due to the non-iridescent character of APSs. However, for the PC samples a whitish color is observed (Figure 2c and Figure S7, Supporting Information). This distinct property of APSs is important for some applications, e.g., the microscopic color display. As a demonstration of the angle independence, these artificial structural colors produced by the drop-coating method were used to manifest the logo of our university, shown in Figure 3c,d. Six colors, namely, blue, cyan, green, brown, red, and purple were used, which are realized by using 200, 220, 240, 260, 280, and 300 nm PS spheres mixed with cuttlefish ink particles, respectively. It is obvious that no color differences can be observed under normal and oblique observations.

With PS spheres of different sizes and different proportions of cuttlefish ink particles, APSs with different non-iridescent colors can be obtained, offering a fine color palette as shown in Figure 4a. The design strategy is as follows. The color hues are tuned by the diameter of PS spheres while the spectral purity is tuned by the relative proportion of ink particles. A series of colors ranging from blue to purple red have been realized by using PS spheres of diameter varying from 200 to 300 nm. It is found that the reflection peak positions scale almost linearly

with the diameter of PS spheres (Figure S8, Supporting Information). When the relative proportion of ink particles is high, the produced colors are slightly darkish, but still non-iridescent. However, when the relative content of cuttlefish ink particles decreases, the produced colors tend to be bright and gradually become iridescent because of the ordering tendency of the PS sphere packing. To see the color variations with the diameter and the proportion of ink particles, the measured reflection spectra of these APSs were converted into the Commission Internationale de l'Eclairage (CIE) chromaticity values,^[20] shown in Figure 4b. To the best of our knowledge, our offered color palette might be the best palette of non-iridescent structural colors so far.

Interestingly, these artificial non-iridescent structural colors can be used as physical pigments. In fact, even ground into powder with a grain size comparable to commercial pigments, the color appearance of these artificial APSs is still unaltered (Figure 5a). As for the mechanical properties, they can be improved by adding commercial water glues. The glues influence little on the color rendering as confirmed by both the visual inspection and the reflection measurement. Meanwhile, the samples can be stretched or bent after the firmness strengthened (Figure 5b).

It is noteworthy to point out that the color saturation of our artificial APSs is not very high, especially for the red colors due to the strong Mie scattering of individual spheres in the visible

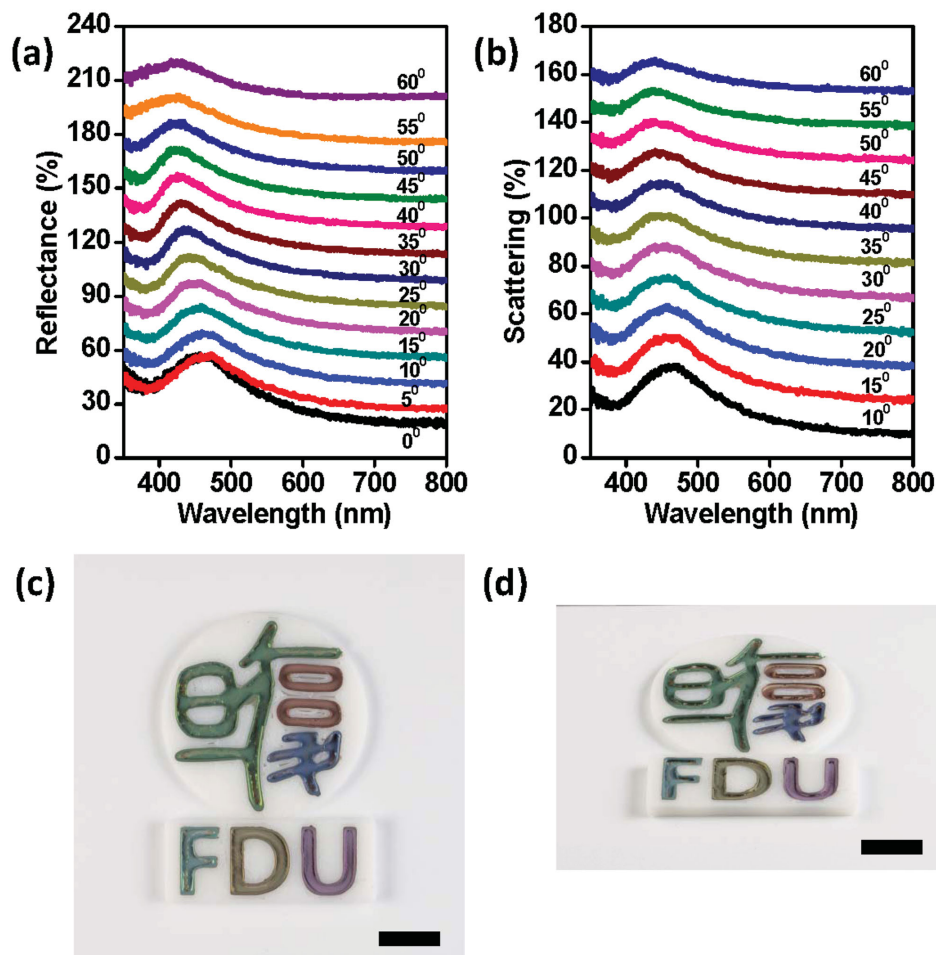


Figure 3. a) Measured angle-resolved specular reflection and b) scattering spectra of the blue-colored APS sample in Figure 2a. Each spectrum is equal-offset shifted (15%) for comparison. In scattering spectrum measurements, incident light is normal to the sample surface and the labeled scattering angles are with respect to the surface normal. c,d) Our university logo colored by six non-iridescent structural colors under normal and oblique observations, respectively. Scale bars: c,d) 1 cm.

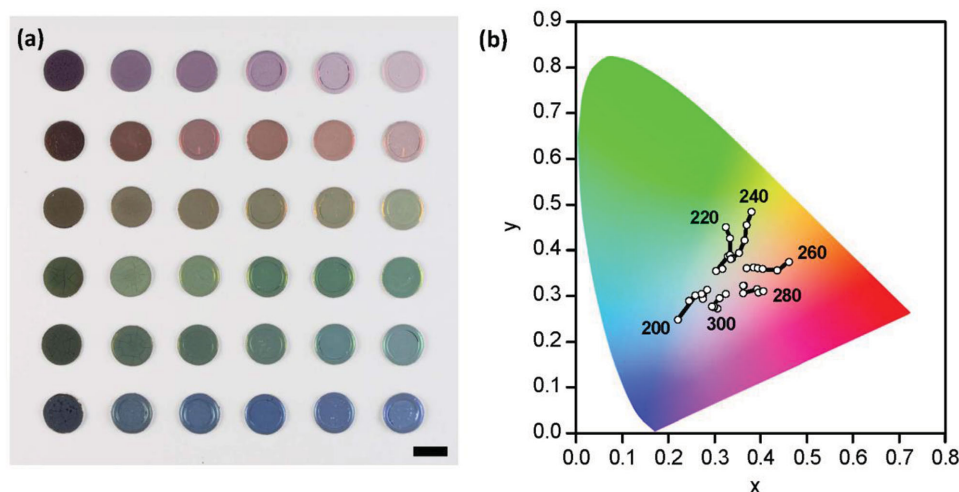


Figure 4. a) Color palette offered by the fabricated APSs. In general, the diameter of PS spheres in the APSs increases from bottom to top panels while the proportion of ink particles decreases from left to right. b) CIE chromaticity x and y values for the colors in the color palette. Each line stands for the APSs with the same diameter of the PS spheres (labeled in units of nm) but with a different proportion of ink particles (increasing from the point close to the white center $x=y=0.33$). Scale bar: a) 5 mm.

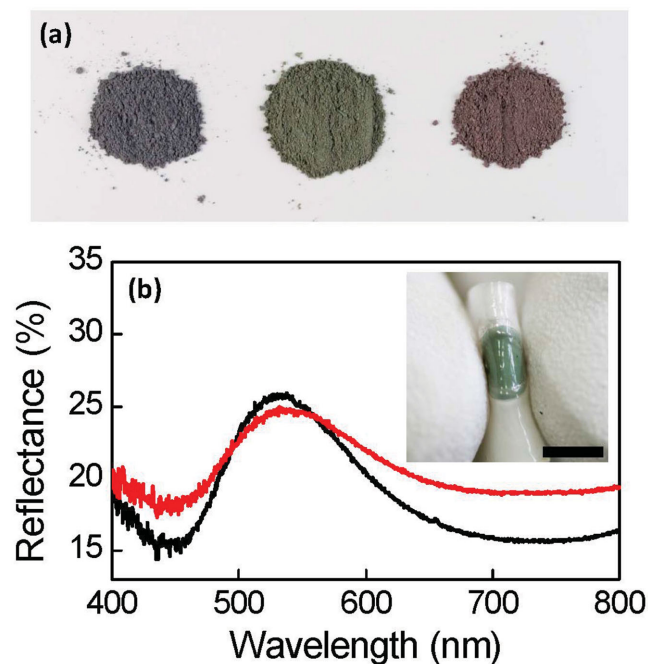


Figure 5. a) Powders of three colored samples. b) Measured reflection spectra of the powder of a green-colored sample with (red line) and without a water glue added. The glued sample film can be stretched as shown in the inset. Scale bar: b) 5 mm.

short wavelength range (Figure 2b and Figure S7, Supporting Information).^[45] This is similar to the scales of the longhorn beetle *Anoplophora graafi* where the red colors are more likely purple.^[20] To enhance the color saturation, several ways can be tried. We can further improve the structural quality to obtain APSs with better short-range order. As a result, the color saturation can be improved due to the enhanced scattering from the short-range order.^[22] By using spheres of higher refractive index or by inverting APSs, one can shift the reflection peak stemming from the Mie scattering of individual particles outside the visible range to suppress the Mie scattering.^[45] Finally, we could spin-coat a thin polymer layer doped with absorptive dye on top of APSs, similar to the strategy adopted in the green feathers of rosy-faced lovebird (*Agapornis roseicollis*) where this green color is a mixed color resulting from blue structural color and yellow color in cortex layer containing yellow pigments.^[46]

In conclusion, a simple and large-area fabrication method for producing non-iridescent structural colors is proposed and demonstrated by using cuttlefish ink particles as an additive to break down the long-range ordering of self-assembled colloidal structures. APSs with a high color visibility are obtained by coassembling PS spheres and cuttlefish ink particles of appropriate proportions. The obtained structural colors are non-iridescent due to the good short-range ordering of the APSs. The color hue and its visibility can be tuned by adjusting the diameter of the PS spheres and the proportion of ink particles. The obtained colors can be coated on any substrates without the limitation of black backgrounds. The color samples can even be ground into powder to obtain physical pigments. These artificial colors may have potential applications in paints, cosmetics, textile, and displays.

Experimental Section

Materials and Methods: Monodisperse PS spheres suspensions ($CV \leq 5\%$, 10% solids by weight) were purchased from Thermo Fisher Scientific Corp. (diameter: 200, 220, 240, 260, and 300 nm) and Bangs Laboratories, Inc. (280 nm). The cuttlefish ink was taken from the bodies of died cuttlefish purchased from the market. The purchased PS aqueous suspensions were directly used to be self-assembled into PC samples through natural-evaporation. The APSs were fabricated in the following procedure. First, 1 g of dried ink powder was dispersed into 5 g of deionized water and ultrasonicated for 30 min. Second, a syringe was used to take 0.2, 0.4, 0.7, 1.0, 2.0, and 3.0 g of PS suspension of each the six diameters, respectively, and then a fixed amount of 0.1 g of ink suspension was dropped into the prepared PS suspensions and the mixed suspensions ultrasonicated for 5 min. Finally, a small amount of the mixed suspensions was dropped onto white round photopapers and left overnight for drying.

Optical and Structural Characterization: The optical photographs and microscopy images of the fabricated APSs were taken by a digital camera (Canon EOS 6D) and an optical microscope (Leica DM6000 M) connected with a CCD camera, respectively. The white balance was corrected by a mension standard 18% gray board. The microstructures of the APSs were characterized by scanning electron microscopy (SEM) (Philips XL30 FEG).

Spectra Measurement: The angle-resolved reflection and scattering spectra of different color samples were measured by home-built angle-resolved optical spectroscopy at Fudan University,^[8] a Xenon lamp was used as light source covering a wavelength range from 250 to 800 nm. A standard white board (Spectralon Reflectance Standards) for APS samples and an aluminum mirror for PC samples were used as reference.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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