Pigments

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Production of Colored Pigments with Amorphous Arrays of Black and White Colloidal Particles**

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There are many technical and industrial applications for colored pigments with nonfading properties. The development of a low-cost, high-volume production method for nonfading pigments with low toxicity and minimal environmental impact may promote their widespread use. To accomplish this goal, pigments need to be prepared using abundant and environmentally friendly compounds. Here, we report on the variously colored aggregates formed by spraying fine, submicrometer-sized spherical silica particles. The microstructure of the aggregate is isotropic with a short-range order on a length scale comparable to optical wavelengths, and exhibits an angle-independent structural color as a result of wavelength-specific constructive interference.[1–5] Interestingly, the color saturation of these aggregates can be controlled by the incorporation of a small amount of conventional black particles, such as carbon black (CB). We demonstrate that a Japanese-style painting can be successfully drawn with this method.

Silicon dioxide, which is a major component of silica particles, is chemically stable and used in scientific glassware suitable for chemical experiments. It is also a primary component of soil and found in abundant supply in nature. Furthermore, in vivo toxicity of silica particles that are greater than 300 nm in diameter has not been detected.[6] Therefore, submicrometer-sized silica particles are one of the best candidates for fabricating environmentally friendly materials.

Fine submicrometer-sized spherical silica particles usually appear white to the human eye when they are in powdered form. However, assemblies of these particles can appear colored because of wavelength-specific optical interference,[1,4,5,7] despite the absence of light-absorbing pigments and dyes. Such color is generally referred to as structural color, because it is essentially caused by the microstructure through optical phenomena, such as interference, diffraction, and scattering.[8,9] Crystalline arrays of fine submicrometer-sized spherical silica particles (colloidal crystals) are well known examples of assembled particles that have structural colors as a result of a very high reflectance at a certain wavelength of light. However, the structural colors produced by colloidal crystals show distinct variations, which depend on viewing and light illumination angles.[7,10] Such iridescence makes the use of colloidal crystals as pigments[11] difficult, because typical pigments generally require a constant color at different viewing angles.

The iridescences of the colloidal crystals originate from Bragg reflection, which is the reflection mechanism that occurs as a result of the long-range order in the particle arrangement. Thus, if the arrangement is changed from the crystalline structure to the amorphous state, which has only a short-range order, iridescence is expected to be suppressed. In fact, amorphous aggregates of colloidal particles have been reported to exhibit angle-independent structural colors.[1,4,5,12] However, amorphous colloidal arrays are difficult to fabricate because submicrometer-sized particles have a strong tendency to crystallize.[13] Previously, amorphous colloidal arrays have been prepared by mixing two different kinds of submicrometer-sized silica particles.[1,4,5,13] These mixtures exhibit structural colors, but the colors are very pale.[1,4,5] Therefore, such amorphous colloidal arrays are unsuitable for use as brightly colored pigments. A simple synthetic method for the preparation of assemblies of submicrometer-sized particles with angle-independent brilliant structural colors for use as pigments has not yet been reported.

Herein, we report a simple and reproducible synthetic procedure for the preparation of pigments that exhibit angle-independent, bright structural colors from amorphous colloidal arrays by spraying fine submicrometer-sized spherical silica particles of uniform size. We added a small amount of black particles to the colloidal amorphous array to enhance the saturation of the structural color by reducing incoherent-light scattering across the entire visible spectrum. Variously

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colored pigments were prepared by varying the diameter of the silica particles.

First, we prepared a suspension of fine submicrometer-sized spherical silica particles. Methanol was used as the dispersion medium. The choice of solvent was important, as rapid evaporation was necessary to obtain an amorphous state of the colloidal particles, as described below. The suspension was air-sprayed onto a glass plate positioned approximately 30 cm from the outlet of the spraying nozzle. Because the solvent evaporated rapidly, the silica particles were dried in air and were evenly coated in a powdery state on the glass plate to form a membrane, the thickness of which could easily be controlled up to 1 mm. When the nozzle and the glass plate were too close to each other or when an involatile solvent was used, spraying of the suspension resulted in the formation of a thin liquid layer on the glass surface.[14,15] In these cases, the colloidal particles crystallized on the glass plate during the evaporation of the solvent and appeared iridescent. Thus, the characteristics of the membrane fabricated by the spray method depended on the temperature, pressure, and humidity of the surrounding air, all of which affected the volatilization of the solvent that was used.

The color of the membrane depended on the size of the silica particles that were used. Membranes with whitish-green and whitish-pink colors were prepared using particles of 280 nm and 360 nm size, respectively (Figure 1 a). These membranes were approximately 0.2 mm thick. For very thin membranes, the thickness was found to affect the appearance of the color: a distinct color was observed for membranes thinner than approximately 0.05 mm, whereas the color appeared whiter for a thicker membrane. The prepared membranes (with an average diameter, D_{ave}, of 280 nm and 360 nm) exhibited distinct peaks at approximately 460 nm and 610 nm, respectively, in the reflection spectra, which were measured using an integrating sphere (Figure 1 b). Figure 1 c shows the transmission spectra of a membrane composed of 360 nm-sized silica particles. The spectra were measured at various incident angles relative to the surface of the membrane, and a dip occurred at 610 nm, corresponding to the same peak position observed in the reflection spectrum (Figure 1 c, right). The position of the dip did not depend on the angle from 0° to 40°. The reflectance peak was considered to originate from wavelength-specific constructive interference,[16,17] and its angle independency implied that the silica particles formed an amorphous array with only short-range order.

To confirm the arrangement of the particles, we visualized the microstructure of the membrane composed of 360 nm silica particles using a scanning-electron microscope (SEM) and a transmission-electron microscope (TEM). SEM images of the membrane are shown in Figure 1 d and e. The silica particles formed raspberry-like secondary particles of various sizes, and the colloidal particles on the surface of the secondary particles did not appear to have crystallized when viewed under higher magnification (Figure 1 e). In addition, TEM micrographs (Figure S1) also confirmed that the colloidal particles inside the secondary particles did not crystallize either. Two-dimensional Fourier analyses of the SEM and TEM images resulted in ring patterns (see the inset

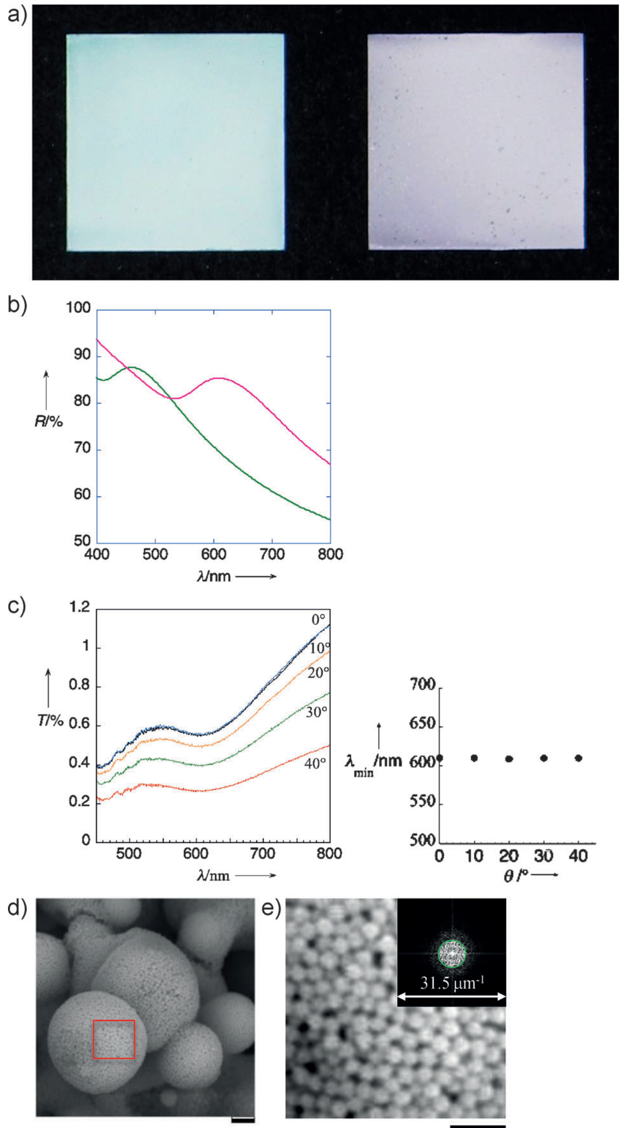

Figure 1. Optical properties and microstructure of structural-colored membranes composed of silica particles. a) Optical photographs of membranes composed of silica particles with D_{ave} = 280 nm (left) and 360 nm (right). b) Reflection spectra of the membranes shown in (a) with D_{ave} = 280 nm (green) and 360 nm (pink), measured using an integrating sphere. c) Transmission spectra of a membrane composed of silica particles with D_{ave} = 360 nm, measured at various incident angles relative to the surface of the membrane. Right: Plots of the position of the dip wavelength (λ_{min}) versus the incident angle (θ). d) SEM image of a membrane composed of 360 nm-sized silica particles. Scale bar = 2 μm. e) Magnified view of the red-framed region of the SEM image shown in (d). Scale bar = 1 μm. Inset: Two-dimensional Fourier power spectra obtained from the SEM image in (e).

in Figure 1 e, and Figure S1b in the Supporting Information), thus indicating that the silica particles formed an isotropic amorphous array without any long-range order.[18] We suggest that this amorphous state was realized by rapid evaporation of the solvent during preparation,[19] because slow solvent evaporation results in a highly ordered crystalline structure.[20] Thus, the aggregation in the spray method resembles the glass transition in the sense that the glassy state is realized by rapid cooling during which liquid molecules are not given sufficient time to crystallize.

The membrane exhibited, albeit faintly, structural color caused by coherent-light scattering because of the short-range order of the amorphous colloidal array. However, the reflectance spectra in Figure 1b demonstrate that incoherent-light scattering was also strong; there is the background-like component across the entire visible region that gradually increases as the wavelength decreases. This component largely affects the perceived color. The three types of cone cells in the retina of the human eye can respond to light of certain wavelengths in the visible region, which peaks at approximately 430 nm, 540 nm, and 570 nm.[21] Each cone cell can detect blue, green, and red light. The differences in the signals received from the three cone cells allow the brain to perceive all possible colors through the opponent process of color vision. Objects that scatter light across the entire visible region appear white because all three cone cells respond to the light. Therefore, for the angle-independent reflectance peak to appear as a saturated color, incoherent-light scattering should be reduced.

To accomplish this goal, the incorporation of black substances that can uniformly absorb light across the entire visible region into the membrane was identified as an effective approach.[22–24] CB is one of the most common and environmentally friendly black substances and reflects very little light in the visible region of the spectrum. Therefore, we fabricated membranes using a suspension of silica particles with varying small amounts of CB of an average size of 28 nm. Figure 2a shows the membranes obtained by varying the amount of CB added. The color saturation of the membranes was found to greatly increase with CB incorporation. A quantitative reflectance spectrum was obtained (Figure 2b and c). The overall magnitude of the reflectance greatly decreased with CB incorporation, while the intensity of the peak component seemed to remain constant. We fit the reflectance spectrum using two empirical functions for the peak and the background-like component. The results showed that the ratio of the amplitudes of the peak to the background increased by a factor of three when 1.7 wt% CB was added to the suspension (see Figure S3 in the Supporting Information). Consequently, we were able to observe the angle-independent reflectance peak with the naked eye in the form of saturated structural colors.

The polarization-dependent reflectance spectra of the membranes were measured to investigate the light-reflection processes occurring inside the amorphous array in more detail. The spectra were obtained using the methods shown in Figure S6. White light was passed through a linear polarizer before being illuminated onto the membrane. The incident angle relative to the normal of the planar

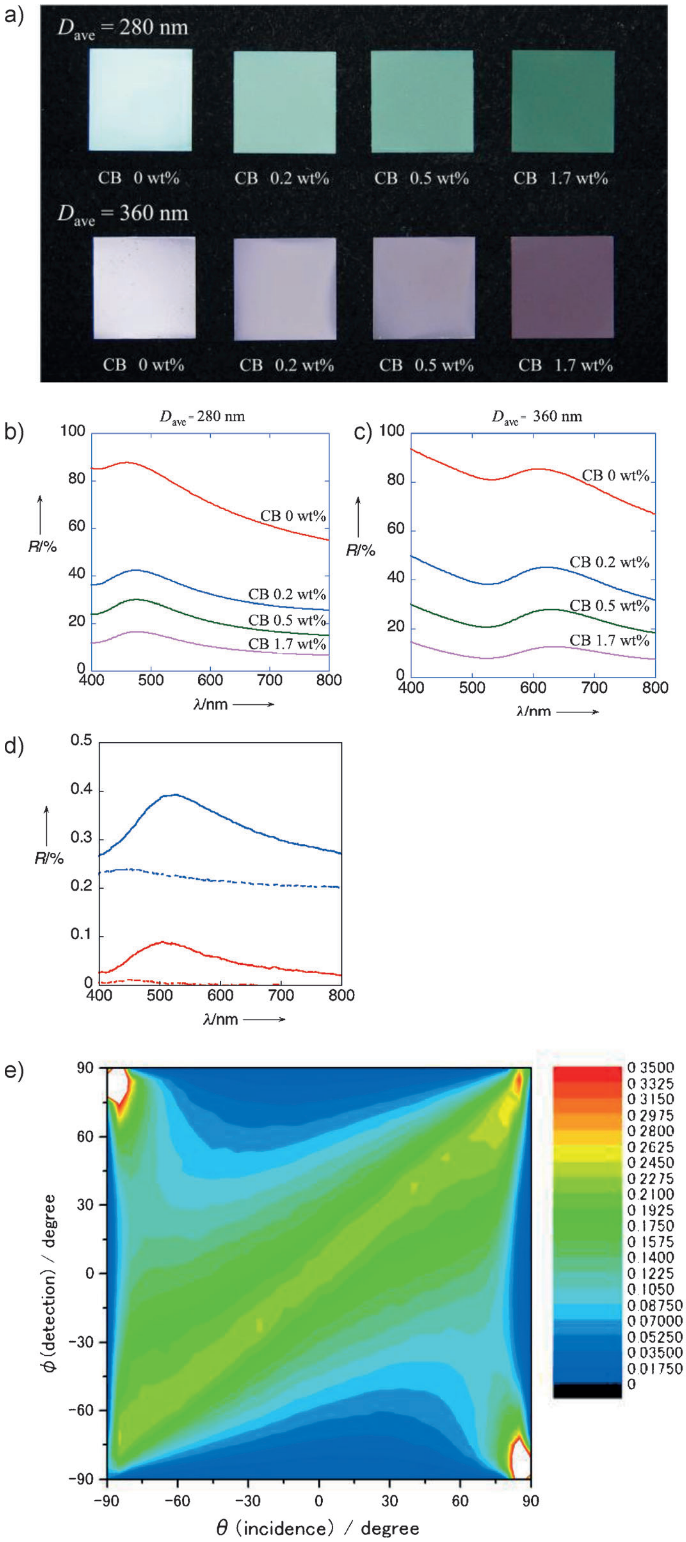

Figure 2. Optical properties and microstructures of structural-colored membranes composed of silica particles and CB. a) Optical photographs showing the color change in particle membranes with varying quantities of CB. b,c) Reflection spectra of the membranes shown in (a), measured using an integrating sphere. d) Co-polarization and cross-polarization reflection spectra of membranes composed of 280 nm-sized silica particles with/without CB (see Figure S7 for the results with 360 nm-sized silica particles); solid blue line: p-polarization without CB, dotted blue line: s-polarization without CB, solid red line: p-polarization with CB (1.7 wt% CB), dotted red line: s-polarization with CB (1.7 wt% CB). e) Contour map of the reflectance versus the θ-ϕ coordinate at the peak wavelength in the reflection spectra for a membrane composed of 280 nm-sized silica particles with 1.7 wt% CB.

surface of the membrane was 0°. The polarization of the incident light was parallel to the scattering plane containing the incident beam and the detector. The detector was placed at a fixed angle of 10° to the surface normal. Another linear polarizer was placed in front of the detector, and the direction of the polarization was changed to be parallel (p-polarization) or perpendicular (s-polarization) to the scattering plane. Figure 2d shows the polarization spectra obtained for membranes composed of 280 nm silica particles with and without CB addition. In the spectrum of the co-polarized light scattered from the membranes, a spectral peak was observed at approximately 510 nm, regardless of whether CB was added, while the s-polarized spectra showed a nearly flat spectral shape across the entire range of investigated wavelengths. The wavelength and width of the peak in Figure 2d appear to be slightly different from those in Figure 1b and Figure 2b. These differences are a result of the different optical geometries of the measurements: the polarized spectrum was obtained for a fixed reflection angle, whereas the spectra in Figure 1b and Figure 2b were obtained using an integrating sphere that collected omnidirectionally reflected light.[3] The fact that the reflectance peak was only observed in the co-polarization spectra implies that the peak was produced by optical interference of single scatterings from individual particles,[25] because single scattering processes do not depolarize light. On the other hand, the depolarized (cross-polarization) spectrum included high-order scattering. Thus, multiple and incoherent-light scattering by the colloidal amorphous array contributed significantly to the background-like component observed in the cross-polarization spectrum, which was greatly reduced by the incorporation of CB.

It is known that an angle-independent pseudo-photonic band gap (p-PBG) can be caused by the evanescent coupling of Mie scattering by individual particles in an amorphous state.[16,17] However, a large difference in refractive index is necessary for the creation of the *p*-PBG; it has been reported that suppression in the density of optical states is not clearly observed when the difference in refractive index in the amorphous photonic structure is less than 2.45.[16] In our case, the refractive index difference was approximately 1.4. Thus, the reflectance peak is thought to be produced by single scattering process with wavelength-specific constructive interference rather than by the presence of *p*-PBG that requires multiple scattering during its formation.

We also measured the bidirectional reflectance distribution function (BRDF) to investigate the optical properties of the membrane as a colorant using an optical system similar to that described previously.[26] The incidence angle, θ, and the reflection angle, ϕ, were defined with respect to the surface normal of the membrane (Figure S8). Figure 2e shows a contour map of the reflected intensity versus the θ-ϕ coordinate at the peak wavelength in the reflection spectra for membranes composed of 280 nm silica particles with CB (1.7 wt%). The strongest light reflectance for the membrane occurred at positions where $\theta = \phi$. This result indicates that the irradiated light was less scattered in the specular direction, while being more backscattered at the peak wavelength in the reflection spectra. Backscattering is a desirable characteristic for colorants because the coloration in the specular direction can become unsaturated as a result of wavelength-independent reflection at the air surface for large illumination angles. It is interesting to note that the wings of *Morpho* butterflies are an example of a naturally occurring structural-colored material with strong backscattering.[27]

The color of the membrane can be controlled by the diameter of the silica particles used in the spray method. For example, blue, green, and red membranes were prepared using different-sized particles, as shown in Figure 3a, where the diameters were 230 nm, 280 nm, and 360 nm, respectively, with 1.7 wt% added CB. Because of the amorphous structure of the membrane, the colors do not depend on the observation angle during illumination (Figure 3a). Thus, one promising way to obtain membranes of various bright colors is the use of silica particles with different diameters by the spray method.

If, however, we need faint or dusky colors, there is a simple way: we previously reported that the peak position in the reflection spectra for membranal amorphous colloidal arrays composed of two different sizes of silica particles can

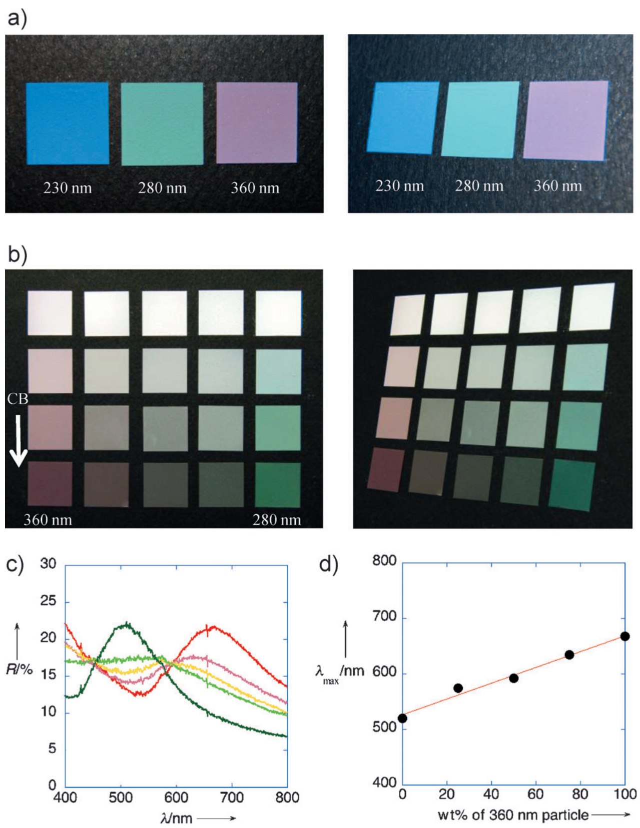

Figure 3. Variously colored membranes composed of silica particles and CB. a) Optical photographs of membranes composed of silica particles with a size of 230 nm, 280 nm, and 360 nm, and 1.7 wt% CB. b) Optical photographs showing the color change of membranes achieved by varying the ratio of the relative quantities of silica particles of two different sizes (cross direction) and by varying the amount of CB (longitudinal direction). c) Reflection spectra of membranes with different ratios of 280 nm and 360 nm silica particles (100% 360 nm (red), 100% 280 nm (dark green), 360/280 = 2:1 (rose), 1:1 (yellow), and 1:2 (bright green)) and 1.7 wt% CB. d) Plots showing the position of the peak wavelength in the reflection spectra (c) versus wt% for 360 nm silica particles in each colloidal amorphous array.

be shifted depending on the mixing ratio of the two particles.[1] All colors from the membranes are quite faint. Based on this result, dusky colored membranes were prepared by simply adding CB to the mixed amorphous colloidal arrays.[4] The fabricated membranes showed intermediate colors depending on the mixing ratio, and the color saturation could be controlled by varying the CB quantity (Figure 3 b). In the reflectance spectrum, changes in the mixing ratio induced a continuous shift in the wavelength of the peak, while decreasing the magnitude of the reflectance and increasing the peak width (Figure 3 c and d). As a result, the colors of the mixed amorphous colloidal arrays are faint or dusky.

Structural color is generally associated with dazzling and iridescent colors. However, in this study, we found that muted and noniridescent structural colors can be produced by an amorphous array of fine white silica particles with a small quantity of black particles. Faint or dusky colors can also be created using the mixed amorphous colloidal arrays and CB. Thus, both intensely colored pictures and Japanese-style paintings with faint and dull colors can be produced with our technology (Figure 4).

In conclusion, variously colored pigments without angular dependence were prepared by a spray method, which is a remarkably simple method using submicrometer-sized silica particles and carbon substances. Various vividly colored pigments can be produced from fine silica particles with sizes between 200 nm and 400 nm. The use of a polyelectrolyte that adheres to the particles can stabilize the structure of the colloidal amorphous arrays to create highly stressable, nonfading pigments. This newly prepared, angle-independent structural-colored colloidal amorphous array composed of submicrometer-sized silica particles and carbon substances presents an environmentally friendly and nonfading pigment; thus, these colored materials may have potential applications in various fields where highly toxic heavy-metal-containing pigments are currently in use.

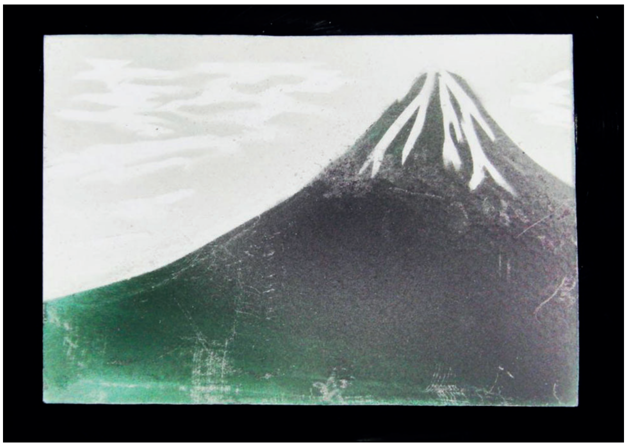

Figure 4. A color picture of Mount Fuji drawn by spraying suspensions of silica particles and CB.

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