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CONTENTS

Producing coloured materials with amorphous arrays of black and white colloidal particles

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There are many technical and industrial applications for coloured pigments with anti-fading properties. The development of a low-cost, high-volume production method for anti-fading pigments with low toxicity and minimal environmental impact may promote their widespread use. To accomplish this goal, we need to prepare pigments using abundant and environmentally friendly chemical compounds. Here, we report on the aggregates of various colours formed by spraying fine, submicron spherical silica particles. The aggregate microstructure is isotropic with short-range order on a length scale comparable to optical wavelengths and exhibits an angle-independent structural colour due to wavelength-specific constructive interference. Interestingly, the colour 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 and that an interesting effect is obtained that can be applied to steganography.

This paper reports on a simple and reproducible synthetic procedure for preparing novel structural-coloured pigments that exhibit angle-independent, bright structural colours from amorphous colloidal arrays [1–13] by spraying one size of fine submicron spherical silica particles. We added a small amount of black particles to the colloidal amorphous array to enhance the structural-colour saturation by reducing incoherent light scattering across the entire visible spectrum. Various coloured pigments were prepared by varying the diameter of the silica particles. Furthermore, we demonstrated an interesting application: Initially inconspicuous patterns drawn by successive spraying of different-sized silica particles can be later colourised by carbon vapour deposition.

First, we prepared a suspension of fine submicron 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 exit 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 a non-volatile solvent was used, spraying the suspension resulted in a thin liquid layer forming on the glass surface. In these cases, the colloidal particles crystallised on the glass plate during the solvent evaporation and appeared iridescent. Thus, the characteristics of the membrane fabricated by the spray method depended on the temperature, pressure, and humidity, all of which affected the volatilisation of the solvent used.

The colour of the membrane depended on the size of the silica particle used. Membranes with whitish green and whitish pink colours were prepared using 280-nm particles and 360-nm particles, respectively (Fig. 1a). These membranes were approximately 0.2 mm thick. For very thin membranes, the thickness was found to affect the appearance of the colour: a distinct colour tended to be observed for membranes thinner than approximately 0.05 mm, whereas the colour appeared whiter for a thicker membrane. It was found that both the prepared membranes exhibited distinct peaks at approximately 460 nm and 610 nm in the reflection spectra, which were obtained using an integrating sphere measurement (Fig. 1b). Fig. 1c presents the transmission spectrum of a membrane composed of 360-nm silica particles, which was measured at various incident angles relative to the membrane surface. A dip in the transmission spectra occurred at 610 nm, corresponding to the same peak position observed in the reflection spectrum. 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, and its angle independency implied that the silica particles formed an amorphous array with only short-range order.

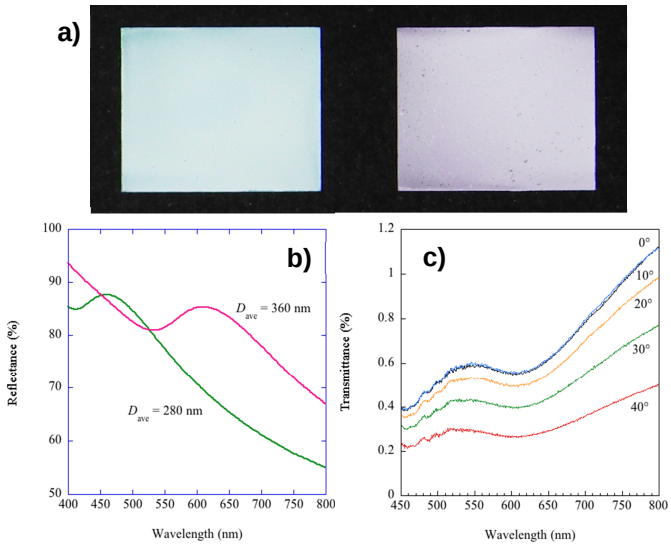

Figure 1. a) Optical photographs of whitish structural-colour membranes composed of 280-nm silica particles and 360-nm silica particles, b) Reflection spectra of the membranes shown in Fig. 1a, which were obtained using an integrating sphere measurement, c) Transmission spectra of the membranes shown in Fig. 1a, which were measured at various incident angles relative to the surface of the membrane.

The membrane exhibited, albeit faintly, structural colour caused by coherent light scattering due to the short-range order of the amorphous colloidal array. However, the reflectance spectra in Fig. 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 colour. 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. 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 colours through the opponent process of colour 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 colour, 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. CB is one of the

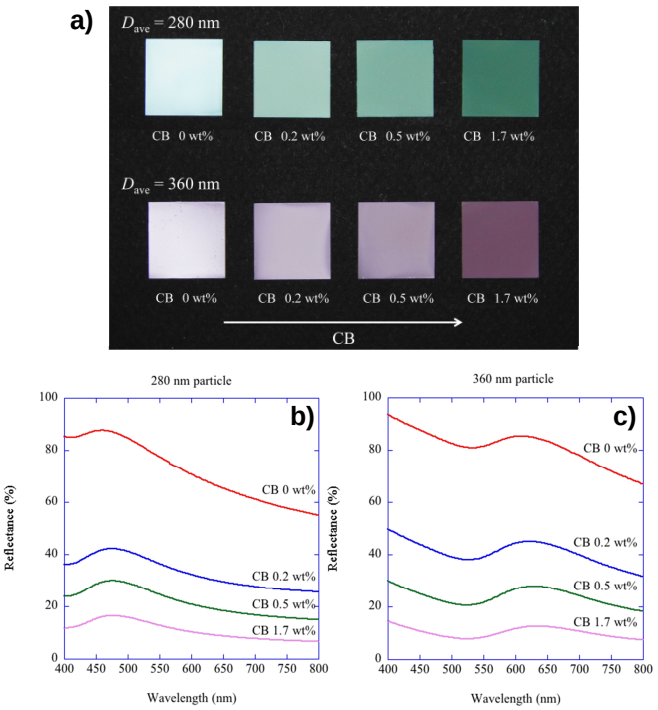

Figure 2. a) Optical photographs showing the colour change in membranes composed of 280-nm particles with varying quantities of CB and 360-nm silica particles with varying quantities of CB, b), c) Reflection spectra of the membranes shown in Fig. 2a, were obtained using an integrating sphere measurement.

most common and environmentally preferable 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. Fig. 2a shows the membranes obtained by varying the amount of CB added. The colour saturation of the membranes was found to greatly increase with CB incorporation. A reflectance spectrum was quantitatively obtained, as shown in Figs. 2b and 2c. 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. Consequently, we were able to observe the angle-independent reflectance peak with the naked eye in the form of saturated structural colours.

MATERIALS AND METHODS

The structural-coloured membrane was formed by spraying a suspension of silica particles (6.0 g) and methanol (9.0 g) using an airbrush system with a 0.2-mm bore, at pressures ranging from 0.1 to 0.3 MPa. Brighter structural-coloured membranes were obtained by adding a small quantity of CB to the suspension. The absolute reflectance was measured by a spectrophotometer (Nippon Bunko Company, V-670) equipped with a 6-cm-diameter integrating sphere. The membrane was illuminated with a spot size of a few millimetres at an incidence illumination angle of 8°. The reflectance was determined by dividing the observed spectrum by that of the reflection standard (Labsphere, Spectralon). The transmittance, relative reflectance, and polarisation spectra were measured by an Ocean Optics USB2000 fibre optic spectrometer and a UV-vis spectrometer (Nippon Bunko Company, V-670), equipped with an absolute reflectance measurement unit (ARMN-735). A digital camera was used to photograph the structural colours of the samples.

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