

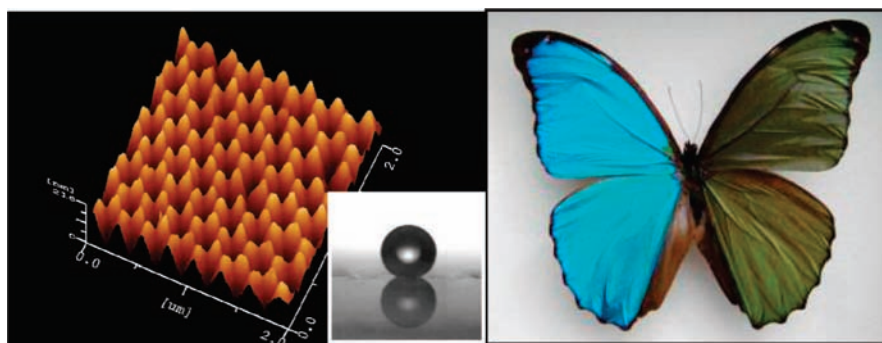
Structural Color Films with Lotus Effects, Superhydrophilicity, and Tunable Stop-Bands

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CON SPECTUS



The structural blue color of a *Morpho* butterfly originates from the diffraction of light and interference effects due to the presence of the microstructures on the wing of the butterfly. Structural color on the surface of a damselfish reversibly changes between green and blue. Inspired by these creatures, we have been trying to prepare high-quality and functional structural color films. We describe our efforts in this Account.

A useful technique to prepare such structural color films in colloidal solution is a “lifting” method, which allows us to quickly fabricate brilliant colloidal crystal films. The thicknesses of the films can be controlled by precisely adjusting the particle concentration and the lifting speed. Moreover, in order to prepare a complicated structure, we have used template methods. Indeed, we have successfully prepared the inverse structure of the wing of a *Morpho* butterfly with this technique. Initially, however, our structural color films had a whitish appearance due to the scattering of light by defects in the colloidal crystal film. Later, we were able to prepare a non-whitish structural color film by doping an appropriate dye in the colloidal particles to absorb the scattering light.

In addition to the structural blue color, the wing of the *Morpho* butterfly has superhydrophobic properties. According to Wenzel’s equation, the hydrophobic and hydrophilic properties are enhanced when the roughness of the hydrophobic and hydrophilic surface is increased, respectively. Based on this mechanism, we have successfully prepared structural color films with superhydrophobic properties, as well as with superhydrophilic properties.

Another important property that can be seen in nature is tunable structural color, such as the color change that can be seen on the surface of a damselfish. In order to mimic such color change, we have developed several tunable structural color films. In particular, we have successfully prepared phototunable photonic crystals using photoresponsive azobenzene derivatives.

In order to apply these structural color films, we developed a technique for patterning them by taking advantage of the wettability of the substrate surface. These materials can be used in the future for self-cleaning pigments and tunable photonic crystals.

Introduction

There has been great interest in the study of colloidal crystal films with lattice parameters comparable

to the wavelength of visible light because of their possible application to photonic crystals and coating materials.^{1–4} In particular, the preparation of



FIGURE 1. Photograph of *Morpho menelaus* butterfly. Inset, the right wing of the butterfly is wetted with ethanol.^{50,51} The change in the refractive index induces the color change from blue to green.

functional colloidal crystal films that display brilliant structural colors, such as demonstrated here by the wing of a *Morpho* butterfly, has recently attracted great attention.^{5–7} Figure 1 shows a *Morpho* butterfly, which displays a blue color on its wings. The wings of the butterfly contain ordered microstructures. The structural blue color originates from the diffraction of light and interference effects due to the presence of the microstructures. Threads, pigments, and sensing materials have recently been developed that take advantage of these brilliant colors. Along these lines, we have been studying preparation techniques for various structural color films and have succeeded both in developing a number of preparation methods and in preparing films that display brilliant and “nonwhitish” structural colors, one example being a replica of the wing of a *Morpho* butterfly.

Elsewhere, superhydrophobic and superhydrophilic surfaces have also recently attracted great attention.^{8–13} One reason for this interest is that materials with such superhydrophobic and superhydrophilic surfaces can exhibit self-cleaning properties. A typical example with such a superhydrophobic surface can be found on the surfaces of lotus leaves. Furthermore, the wing of the *Morpho* butterfly is also superhydrophobic. When water is dropped on a superhydrophobic surface, it forms spherical drops and is able to roll off the surface. Any dust on the surface can then be removed along with the water drop, by which means the surface can be kept clean. It has been reported that the microstructure of the surface plays an important role in making the surface superhydrophobic or superhydrophilic. Hence, if an ideal microstructure could be fabricated on the surface of a colloidal crystal film, then self-cleaning films that display brilliant structural colors could be prepared. Indeed, we have succeeded in preparing such

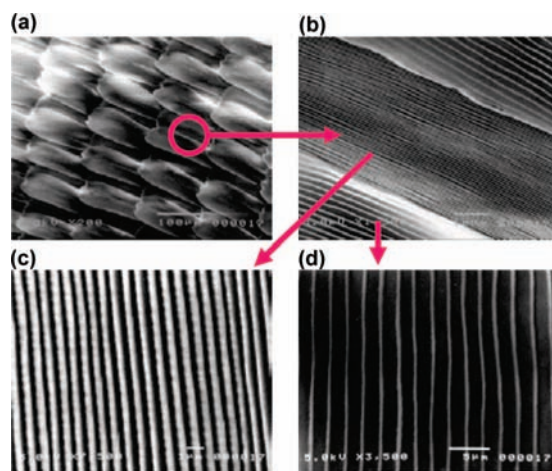


FIGURE 2. SEM images of the wing of *Morpho menelaus*: (a) low magnification image; (b) high magnification image; (c) image of the ground scales; (d) image of the cover scales.

superhydrophobic and superhydrophilic structural color films by mimicking the wings of a *Morpho* butterfly.

Additionally, it is important to be able to control the stop-band (or structural color) of colloidal crystals for practical applications such as switches and display devices.^{14–18} Tunable stop-bands can be seen on the surfaces of damselfish.^{19,20} These structural color-change mechanisms play an important role in both protective and warning colorations. In order to mimic this dynamic character of the stop-band, we have prepared tunable structural color films by making use of the large changes that occur in the refractive indices of liquid crystals.

We have organized this Account as follows. First, we describe the preparation of colloidal crystal films and the preparation of a structured film using the wings of a butterfly as a template. Second, the preparation of colloidal crystals that display either superhydrophobic character (resembling the *Morpho* butterfly) or superhydrophilic character is described. Next, a technique for patterning the colloidal crystal films is explained. Finally, a method by which tunable structural color devices that resemble the surfaces of damselfish can be fabricated is described.

Preparation of High-Quality Structural Color Films

Structural color originates from the diffraction of light due to periodic microstructures. Figure 2 shows the well-ordered scales of the *Morpho menelaus* butterfly.⁷ It is well-known that there are two types of scales on the wings of a butterfly. These are known as “cover scales” and “ground scales”.^{7,21} The structural color of the butterfly originates from the ground scales. The ridges on the ground scales are aligned in parallel with each other. Furthermore, every ridge is further structured by

the presence of cuticles. The periodic structure of the cuticles contributes to the interference effects. In this case, the results of both the diffraction effects and the interference effects mean that blue light with a peak wavelength of ca. 495 nm is selectively reflected.⁷

The mechanism that causes the coloration of the wing is consistent with that of the coloration of colloidal crystals. Hence, films that display structural color in the same way as the wings of a butterfly could be prepared by using colloidal crystals.⁵ The peak position caused by the optical stop-band in colloidal crystals can be calculated approximately by using the equation for Bragg diffraction under normal incidence:

$$\lambda = (8/3)^{1/2} d (n_{\text{sphere}}^2 V_{\text{sphere}} + n_{\text{void}}^2 V_{\text{void}})^{1/2}$$

where λ is the peak position, d is the diameter of the colloidal particles, and n_{sphere} and n_{void} are the refractive indices of the spheres and of the media occupying the voids within the opal films, respectively.

Several methods for the preparation of the colloidal crystals have been reported so far.^{22–27} The most versatile method is the “vertical deposition” method.²⁶ This method is both very simple and convenient. However, it takes much time to prepare the films on the substrates in this way. Hence, we used a much-quicker “lifting” method to fabricate high-quality colloidal crystal films.⁵ As shown in Figure 3a, the substrate is lifted under constant speed instead of relying on the evaporation of the solvent. The speed is generally 0.1–10 $\mu\text{m/s}$, which is still slow but is generally much faster than the vertical deposition method. Hence, the concentration of particles essentially remains unchanged during the film formation, so the thickness of the films is relatively uniform. Furthermore, the thicknesses of the films can be changed from just a single layer to several tens of layers by precisely controlling the particle concentration and the lifting speed.⁵

Figure 3b,c shows that the particles are well-arranged three-dimensionally and that the films display brilliant structural color. This result clearly shows that the lifting method is a useful technique for fabricating high-quality colloidal crystal films that display distinct structural colors.

Brilliant and “Nonwhitish” Structural Color Films Inspired by the *Morpho* Butterfly

Although the structural color films described above are of high-quality, they are somewhat “whitish” in appearance. This is because any colloidal crystal films prepared from suspension contain a range of defects, including boundaries between the spheres and the surrounding air, from which light can be scattered. These shortcomings impose a limit on their poten-

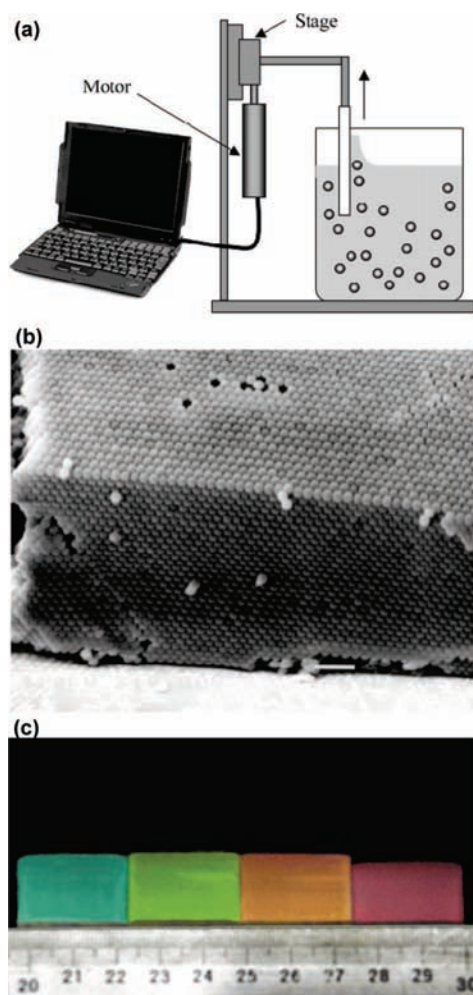


FIGURE 3. (a) Outline of the film fabrication technique. The dipping apparatus is an automation stage. The speed of movement of the stage is precisely controlled by a computer. (b) Cross-sectional images of colloidal crystals composed of spheres with a diameter of 246 nm. The film was fabricated at a speed of 0.1 $\mu\text{m/s}$ using a 3% (v/v_0) suspension. The thickness is 31 layers. (c) Photograph of colloidal crystal films composed of polystyrene spheres of different sizes. The diameters of the spheres are 211, 233, 246, and 263 nm from left to right, respectively.

tial applications. However, when we look at the color of the wing of the *Morpho menelaus* butterfly, it is not whitish in appearance.^{21,28,29} It has been reported that the differences between the wings of a butterfly and colloidal crystal films originate from the presence of melanine pigment in the butterfly’s wing. The melanine pigment absorbs light over the whole visible region, and because it absorbs the diffuse light, which is the origin of the whitish color, the structural color of a “natural” wing looks more brilliant than is generally the case with colloidal crystal films.²¹ This suggests that similar brilliant and nonwhitish colloidal crystal films can be prepared by doping the films with an appropriate dye.



FIGURE 4. Photograph of colloidal crystal films composed of nigrosine-doped (bottom) and undoped spheres (top) with diameters of 220, 198, and 248 nm from left to right. These films were fabricated by drying the suspension at 60 °C.

Inspired by the *Morpho* butterfly, we have tried to prepare colloidal crystal films that do not have the whitish cast.²⁹ The dye that we used was nigrosine. The dye was doped into poly-(methyl methacrylate-co-divinylbenzene-co-methacrylic acid) nanoparticles, and colloidal crystal films were then fabricated using these dye-doped nanoparticles. For comparison, colloidal crystal films prepared using both undoped and doped particles are shown in Figure 4.²⁹ The colloidal crystal films consisting of undoped spheres exhibit a “pearly” appearance due to the influence of defects such as cracks, point defects, and disclination lines. On the other hand, the nigrosine-doped colloidal crystal films do not have the same whitish cast. This clearly shows that doping with an appropriate dye that absorbs light over the whole visible region is effective in suppressing light scattering, and hence the films do not have a whitish cast and the colors appear to be more brilliant.

Inverse *Morpho* Butterfly

We have succeeded in preparing colloidal crystal films that possess brilliant structural colors. However, their overall structures are very simple compared with the structure of the wings of a butterfly. Because the microstructures that occur in nature are quite complicated in many cases, it is not easy to fabricate the same microstructures by synthetic means. One possible method of fabricating such a complicated structure is to replicate it by using the original structure as a template. Indeed, we have succeeded in preparing the inverse structure of the wing of a *Morpho* butterfly by using just such a replication technique.⁷

The preparation method is as follows. First, the wing of a butterfly was dipped into a 10% w/v TiO₂ nanoparticles/water suspension. The wing was then withdrawn from the suspension at a rate of 3.6 μm/s. The TiO₂ nanoparticles are infiltrated into the voids of the wing during this process. After drying in air, the wing was rinsed with deionized water and sintered at 450 °C. In this way, an inverse pattern of a *Morpho* butterfly wing could be obtained, which was blue in color.

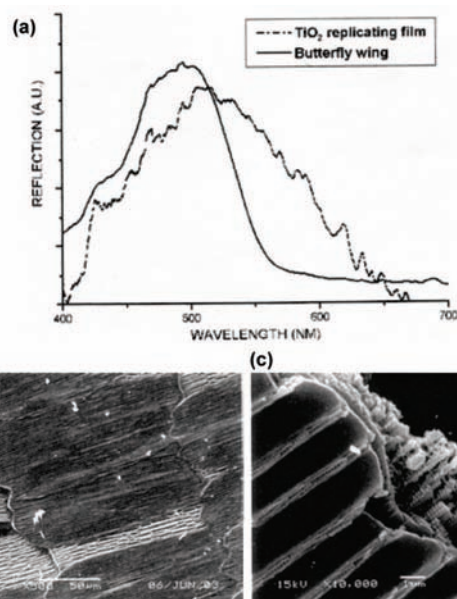


FIGURE 5. (a) Reflection spectra of a butterfly wing (solid line) and its replication by TiO₂ (dashed line). The reflection intensity from the replicated wing is much weaker than that from the original *Morpho* scale. In order to compare the two, the reflection spectrum from the replicated wing is expanded in this figure. (b) SEM image of the replicated butterfly wing, top image. (c) SEM image of the replicated butterfly wing, cross-section image.

The reflection spectra of the butterfly wing and that of the inverse *Morpho* butterfly wing are shown in Figure 5a. A reflection peak was observed at 510 nm.

Figure 5b,c shows that the wing can be replicated accurately, although it would be difficult to fabricate by using other approaches.

Structural Color and Superhydrophobicity (Lotus Effect)

In addition to the structural blue color, the wing of the *Morpho* butterfly has another important property, that is, waterproof character. As described above, there are two types of scales on the wing. The ground scales are responsible for the structural color, while the cover scales act as a waterproof layer, which prevents the wings from being wetted.

These superhydrophobic surfaces have self-cleaning properties. Water forms spherical droplets on a hydrophobic surface, which minimizes the area of the solid–liquid interface. Because dust tends to attach itself to the surfaces of the droplets, they are able to carry dust away from the surfaces of the scales, resulting in the “cleaning-up” of the surfaces of the scales.

These waterproof and superhydrophobic properties can be seen not only on the wings of butterflies but also on the surface of a lotus leaf. Hydrophobic character that originates from

the microstructure of a surface is thus known as the "lotus effect".^{13,30} Furthermore, the legs of the creatures known as water striders are also known to be superhydrophobic.³¹

In order to fabricate thin films that display both structural color and lotus effects, we fabricated inverse opal films by the lifting method using nanoparticles. The reason why we used inverse opal to obtain hydrophobic surfaces is that its surface roughness can enhance the hydrophobic properties of the surface.

Wenzel proposed an equation concerning the contact angle of a rough surface.³² Wenzel's equation is expressed as follows:

$$\cos \theta' = r \cos \theta$$

where θ is the contact angle on a flat solid surface, θ' is the contact angle on a rough surface, and r is the roughness factor, which is larger than 1. Hence, this equation means that the hydrophobic properties are enhanced when the roughness of the hydrophobic surface is increased. Furthermore, it also shows that the hydrophilic properties are enhanced when the roughness of the hydrophilic surface is increased.

By taking advantage of this mechanism, we have succeeded in fabricating structural color films with superhydrophobic properties.¹¹ Figure 6 shows the hydrophobic properties of the inverse opal films that we fabricated.¹¹ As shown in Figure 6, the contact angle of the inverse opal is 155° , while it is only 100° for flat glass. This clearly shows that rough surfaces contributed greatly to the enhancement of the hydrophobic properties of the material. Moreover, the AFM images show that small particles had accumulated in the voids between the spheres, forming a bumped structure. The specific bumped structure obtained when using the nanoparticles greatly enhanced the superhydrophobic properties of the surface. Hence, our preparation method using nanoparticles is suitable for the fabrication of superhydrophobic structural color films.

Note that an important characteristic of our fabrication method is that the inverse opal films were prepared from a suspension containing spheres of two different sizes.¹¹ The general belief has been that when the size of the particles is not uniform, high-quality films cannot be obtained because of the presence of defects. However, we found that when the diameter ratio of the small particles is less than 0.15, well-ordered colloidal crystal films could be formed (Figure 7). By using this technique, well-arranged inverse opal films constituted of nanoparticles could be prepared.

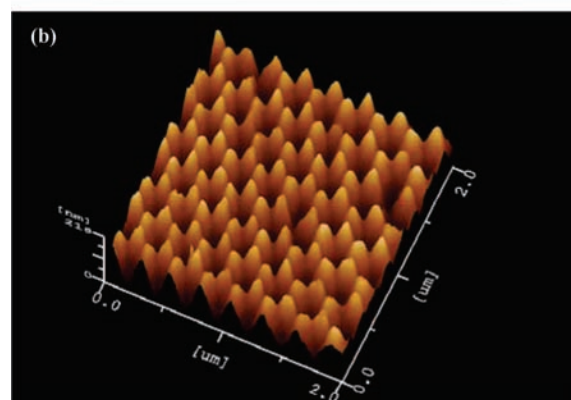
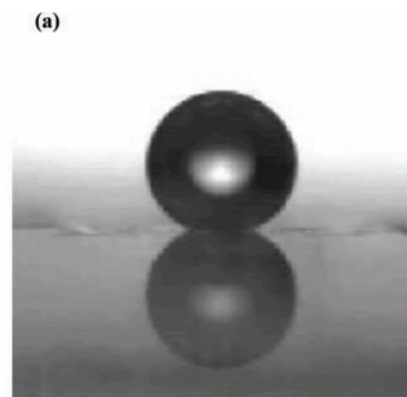


FIGURE 6. (a) Water drops on an inverse-opal coated glass substrate modified with fluoroalkylsilane, which displays the enhanced hydrophobic character of the inverse opal film. (b) AFM image of the surface topography of an inverse opal film.

Structural Color and Superhydrophilicity

Superhydrophilicity is another important property of surfaces. When water flows on a superhydrophilic surface, it can insinuate itself into the spaces between the substrate and any dust that is present, and hence the dust can be removed from the surface. Therefore, superhydrophilic films that display structural color can be used as self-cleaning pigments.

As described above, according to Wenzel's equation, the hydrophilic properties are enhanced when the roughness of the hydrophilic surface is increased. Hence, in order to prepare a superhydrophilic surface with structural color, we prepared inverse opal films composed of titanium dioxides (TiO_2).³³ This is because TiO_2 can exhibit photocatalytic and photoinduced superhydrophilic properties.^{34,35}

The fabrication was performed as follows. First, polystyrene opal films were coated onto glass substrates by a vertical-lifting method, followed by a "hydrophilic treatment" of the surface of the polystyrene using a 7% solution of polyethylenimine in ethanol. After that, 15 nm diameter titania nanoparticles were infiltrated into the voids of the polystyrene opal, which was then heated to 500°C to remove the polymer spheres in order to form TiO_2 inverse opal films.

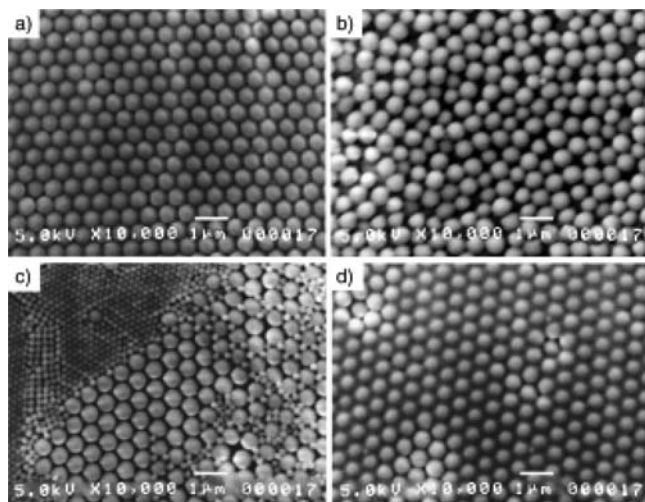


FIGURE 7. SEM images (a) of a film composed of polystyrene spheres with a diameter of 680 nm and (b–d) of a film composed of polystyrene spheres of two sizes. The diameter of the larger spheres is 680 nm in each case. The diameters of the smaller spheres are 580 (b), 230 (c), and 48 nm (d). The SEM image in panel d shows that the 680 nm spheres are arranged as well as those in panel a. Careful observation of the structure of the film in panel d shows that the small particles have infiltrated the voids between the 680 nm particles.

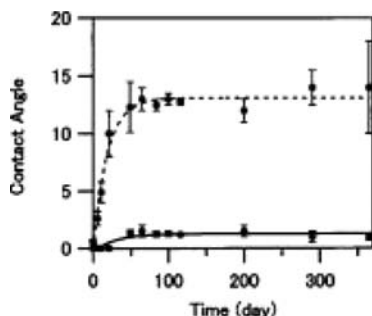


FIGURE 8. Change of the contact angle with the time. The solid line is the nanoporous TiO₂ film, and the dashed line is the ordinal TiO₂ film without pores. For the ordinal film, the superhydrophilicity declines over three months, while it is maintained for over one year for the nanoporous film.

When titanium dioxide films are irradiated with UV light, their surfaces become superhydrophilic.³⁵ The contact angle after irradiation is 0°. When such a film is kept in the dark after irradiation, the contact angle changes from 0° to 14° over a period of 3 months (Figure 8). After that, the angle is maintained and does not change further. However, the contact angles of inverse opal films can be suppressed compared with those of “conventional” TiO₂ films. That is, even if the film is kept under dark for ca. 3 months, the increase in the contact angle is only 1° or 2° (Figure 8). The superhydrophilic properties can be maintained for more than 1 year, which is an advantage over TiO₂ films in general.

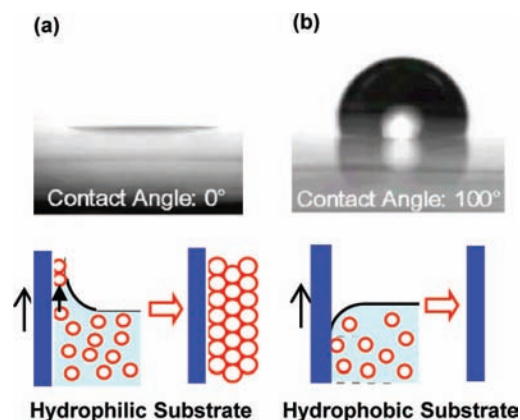


FIGURE 9. (a) When the substrate surface is hydrophilic, colloidal crystal films are formed on the substrate; (b) when the substrate surface is hydrophobic, colloidal crystal films are not formed on the substrate.

When water is dropped onto TiO₂ inverse opal, the water penetrates into the inverse opal due to capillary forces. As long as the water can infiltrate into the pores, no water can exist in the form of water droplets. Hence, even when the hydrophilicity of the TiO₂ surface declines, the contact angle can be kept below 1° or 2°.

Structural Color with Specific Pattern

For practical applications of the structural color films, it is essential to be able to deposit the thin films onto substrates in specific patterns. Along these lines, we studied patterning techniques for colloidal crystals and found that patterned structures can be obtained by controlling the wettability of the substrate surfaces.³⁶

When a substrate with a hydrophilic surface is dipped into a suspension containing colloidal particles, the liquid surface is concave above the hydrophilic surface. That is, the solution forms a meniscus with an angle smaller than 90°. Such a meniscus contributes to the generation of capillary forces, which causes the spheres to assemble on the hydrophilic surface (Figure 9). On the other hand, when the substrate surface is hydrophobic and hence the slope of the meniscus is greater than 90°, the capillary forces that are responsible for the assembly of the colloidal particles disappear. Hence, colloidal crystal films are not formed on areas with hydrophobic surfaces (Figure 9). Through this mechanism, patterned structures can be prepared.

The key to our method of preparing hydrophilic and hydrophobic patterns on substrate surfaces is our use of the photocatalytic and photoinduced superhydrophilic properties of TiO₂.^{34,35} The preparation method is as follows. Glass substrates were first coated with a thin film of TiO₂. The surface of the TiO₂ film was then modified with fluoroalkylsilane

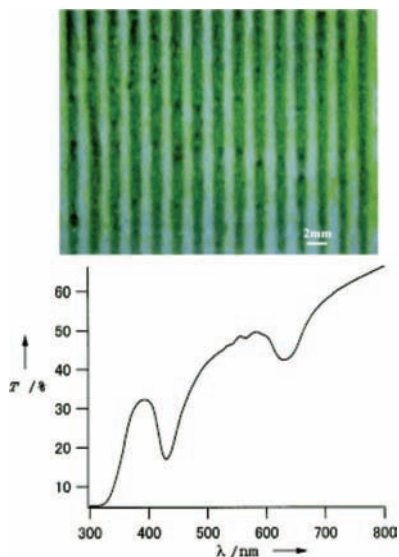


FIGURE 10. Top, a pattern of alternate lines composed of two different types of silica spheres. The green lines are films composed of spheres of 275 nm diameter, between which are films composed of spheres with a diameter of 195 nm. The difference in colors comes from the change in the wavelength of the diffraction peaks. The patterned film could be obtained repeatedly. Bottom, transmission spectrum of the line pattern. The two peaks can be assigned to lines composed of spheres with diameters of 195 and 275 nm, respectively.

$\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ whereupon the surface became hydrophobic with a contact angle larger than 100° . When the substrate was irradiated with ultraviolet light through a photomask, the irradiated area became superhydrophilic due to the photocatalytic and photoinduced superhydrophilic properties of the TiO_2 . The contact angle of the irradiated area was 0° . Hence, surfaces with large contrasts in wettability could be obtained using the unique properties of the TiO_2 .

When glass with a large contrast in wettability is used as a substrate, we expect to obtain patterned colloidal crystal films. Indeed, when such a substrate was inserted into a suspension containing silica spheres (or polystyrene spheres), colloidal crystal films were formed only on the hydrophilic surfaces.

Furthermore, when the patterned colloidal crystal films were treated with fluoroalkylsilane and then irradiated with UV light, patterned films on which the TiO_2 surfaces were hydrophilic and the silica (or polystyrene) surfaces were hydrophobic could be obtained. After that, when the substrates were immersed in a suspension containing silica spheres (or polystyrene spheres) with different diameters, the colloidal crystal films were deposited only on the TiO_2 surfaces, allowing the formation of patterned colloidal crystal films constituted of two kinds of particles with different diameters (Figure 10). It is

anticipated that this simple technique could enable the application of colloidal crystals to a new generation of decorative materials.

Tunable Structural Color

Structural color is not always static. Changes in color can be seen on the surface of various animals. For example, the color of a damselfish changes between green and blue. Structural color-change mechanisms play an important role in the protective and warning coloration of some animals.^{19,20} These structural color changes originate from changes in the microstructures on the surfaces of the animals' bodies.

In order to mimic these color changes, several tunable structural color systems have been developed.^{14,37–49} A possible method for controlling color is to change the refractive indices of the microstructures. Figure 1 (inset) shows color changes on the wings of a butterfly.^{50,51} This color change was induced by dropping ethanol on one of the wings. That is, the refractive index is changed from that of air to that of ethanol. As a result, the observed color changes from blue to green.^{50,51} When the ethanol evaporates, the color of the wing is restored to the original blue.

In order to induce changes in the refractive index, we fabricated inverse opal films and then infiltrated liquid crystals (LCs) into the voids in the structures.^{41,42} The LC used here is 4-pentyl-4'-cyanobiphenyl (5CB). The composite film was opaque at room temperature. However, a bright structural color appeared when the sample was heated to 34°C , which corresponds to the phase transition temperature of 5CB.

In the nematic phase, the liquid crystal molecules are aligned parallel to the surfaces of the spherical voids of the inverse opal and form a bipolar structure. The axes of the bipolar structures are different in each of the voids. Hence, the film was opaque overall because the light was scattered due to the nonuniform anisotropic refractive indices in the voids. On the other hand, the anisotropy disappeared when the LC was converted to the isotropic phase. Therefore, the film consisted of periodic refractive indices for LC and inverse opal, and a stop-band due to the selective diffraction of light was observed in the spectrum. Hence, inverse opal films infiltrated with LC are thermally tunable structural color materials.

In order to apply these tunable structural color systems, the switching speed should be high. Hence, we have studied various phototunable structural color films and have succeeded in preparing some of them using azobenzene derivatives.

The phototunable structural color film that we proposed consists of an inverse opal structure infiltrated by a mixture of 5CB and 4-butyl-4'-methoxyazobenzene (AzoLC). When it was

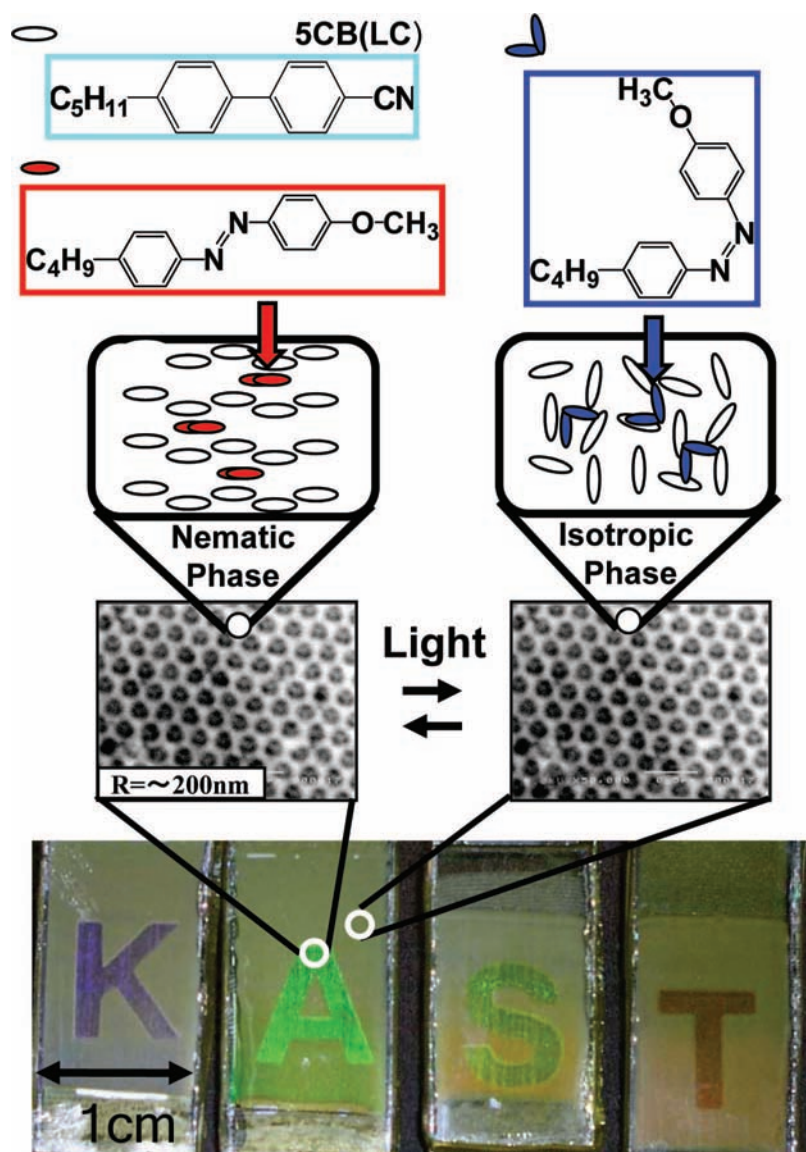


FIGURE 11. Photograph of patterns stored in liquid crystal infiltrated inverse opal films with diameters of 200, 220, 240, and 260 nm from left to right.

irradiated by light, *trans*–*cis* photoisomerization of the AzoLC was induced in the voids. Because the *cis*-form of azobenzene has a “bent” shape, the nematic phase is disorganized by the *cis*-azobenzene, resulting in a phase transition from the nematic phase to the isotropic phase.^{52,53} Hence, as in the case of the thermally induced color change, this change in color can be induced by light. When the composite film was irradiated by UV light (light intensity = ca. 1.5 mW/cm²) through a photomask, a stop-band appears at the irradiated position (Figure 11).

Furthermore, in order to enhance the stability of the color change, Moritsugu et al. used polymer liquid crystal.^{44,54} When these were irradiated by linearly polarized light, the azo-molecules aligned perpendicular with respect to the polarization direc-

tion of the light. The azo-molecules that align parallel to the polarization direction can absorb light. Hence, this material undergoes *trans*–*cis* photoisomerization. On the other hand, when the molecules align perpendicular to the linearly polarized light, the molecules cannot absorb light, so the material does not undergo photoisomerization. Hence, when the molecules are irradiated by linearly polarized light, those perpendicular to the light polarization are enriched during the *trans*–*cis* and *cis*–*trans* photoisomerization, and finally the overall conformation becomes perpendicular to the polarized light. As a result, changes in refractive index due to conformation changes are induced in the liquid crystals.

An important point is that the conformation of the azo-molecule is the *trans*-form, both before and after irradiation. A

weak point of the azo-derivatives is that the cis-form is relatively unstable and hence the cis-form reverts to the trans-form with time, even in the dark. Hence, devices prepared using azo-molecules are generally not stable. However, in the present case, because the azo-molecules take the trans-form, the change is quite stable. Furthermore, reversible changes can be induced by alternately irradiating with linearly polarized light and circularly polarized light. When the circularly polarized light is used, the orientation of the azo-molecules is randomized. Hence, the refractive index of the liquid crystal changes, resulting in changes in the structural color.

Tunable structural color films can also be prepared using only a photochromic dye instead of liquid crystals.^{38,40} When a spiro derivative, which forms J-aggregates, was introduced into the voids in the inverse opal and photoirradiation was carried out, a shift in the stop-band was clearly observed. This change was as large as 37 nm.

Concluding Remarks

We have reported the preparation of colloidal crystal films that display brilliant structural color. High-quality opal films could be obtained by using a lifting method. Furthermore, we could successfully prepare "nonwhitish" colloidal crystal films by doping the colloidal particles with dyes that absorb light over the whole visible region. Moreover, we have shown that complicated structures such as the wings of a butterfly can be replicated by introducing template techniques.

Colloidal crystals that exhibited lotus effects were fabricated by "particle mixing" methods. The superhydrophobic properties of the inverse opal films were derived from the rough surfaces of the inverse opal structures. Moreover, a "bumped" structure on the surface greatly enhanced the hydrophobic properties. On the other hand, colloidal crystals with superhydrophilic properties could be obtained by preparing inverse opal films using TiO₂. An important characteristic of this technique is that the superhydrophilic properties could be maintained for more than one year, which is more stable than TiO₂ films with flat surfaces. Furthermore, we showed that patterned colloidal crystals can be prepared by controlling the wettability of the substrate.

Tunable structural color devices could be obtained by using liquid crystals. The color changes were derived from changes in the refractive indices due to changes in the orientation of the molecules in the liquid crystal or to interconversions between the liquid crystal and the isotropic phase.

The materials described above can be used as phototunable photonic crystals in which the propagation of light can be controlled by light. However, in order to actually apply this technique for switching devices, the switching speed should be

increased to faster than the microsecond range. Furthermore, the quality of films prepared via self-assembling methods using colloidal particles is not as good as those prepared by lithography methods using an electron beam. Hence, a new technique to prepare higher quality films with much lower defect levels needs to be developed.

Furthermore, structural color films with superhydrophobic and superhydrophilic surfaces can find applications as pigments with self-cleaning properties. Generally available pigments composed of organic dyes discolor with time because of the decomposition of the dyes. On the other hand, the inorganic particles that are the components of the structural color films do not easily decompose. Moreover, because of their self-cleaning properties, the time required to clean these materials can be reduced. However, because the particles interact with each other by physical adsorption, it is not clear whether the films can be used over a period of many years. Hence, for practical applications, the particles should be bound tightly by modifying their surfaces, which is an important challenge for the future.

Furthermore, it was recently reported that *Morpho* butterfly wing scales have a highly selective vapor response.⁶ This suggests that the replicated films might be used as sensing devices. In particular, we can change the component materials for the replicated butterfly wings, allowing for the optimization of their optical properties as sensing devices. This means that sensors could become an important application of replicated wings.

Note Added after ASAP. This paper was released to the web on October 7, 2008 with missing references. The revised version was posted on November 4, 2008.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

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