FOCUS REVIEW

Fusion materials for biomimetic structurally colored materials

Yukikazu Takeoka

This review addresses recent developments in structurally colored materials composed of submicrometer-sized fine particles, where the structural color is not angle-dependent. Recently, studies on colloidal crystals of submicrometer-sized fine particles for structurally colored materials applications have drawn great attention. Materials researchers have become aware that many living things exhibit bright structural colors that arise from amorphous arrays of particles, pores and fibers, and are now engaged in research related to this phenomenon. In particular, colloidal amorphous arrays composed of submicrometer-sized fine particles, which can display vivid structural color without angle dependence, have become a popular topic of study within recent years. In this paper, I review the possibility of using colloidal amorphous arrays as stimuli-responsive colored materials based on the properties of colloidal amorphous arrays that have been elucidated in recent experimental investigations.

Polymer Journal (2015) 47, 106–113; doi:10.1038/pj.2014.125; published online 17 December 2014

INTRODUCTION

Numerous objects appear colored due to wavelength-specific optical interference, despite their lack of light-absorbing pigments and dyes. Such color is generally referred to as structural color because the color essentially results from a microstructure with dimensions that are comparable with the wavelength range of visible light, such that the structure interacts with light through optical phenomena such as interference, diffraction and scattering.¹ Recently, structural colors have attracted much attention in a wide variety of disciplines. Previously, however, the word ‘iridescence’ has been used instead of ‘structural color’ to describe a surface that appears to change color as the viewing angle or the angle of light illumination changes. Thus, people who are aware of the concept of interference color have a strong impression that all structurally colored materials change hues when viewed from different angles, as indicated by the term ‘iridescence.’ In fact, many structurally colored objects change their hue depending on the viewing and light illumination angles because most of these structural colors are derived from Bragg reflection. Such angle dependence represents a barrier to the development of displays and sensors made with structurally colored materials.²

Yet, examples exist of angle-independent structurally colored entities in nature. Some of these examples have been subjected to study for a long time; however, the interpretations of the color mechanisms remain a matter of debate.^{3–5} For example, the mechanism associated with the angle-independent structural coloration of blue bird feathers has been debated for over a century.³ Until quite recently, the blue color was thought to be caused by Tyndall or Rayleigh scattering. However, Prum *et al.*³ demonstrated that the observed blue color is caused by the constructive interference of light by submicrometer-sized fine air cavities through spatially distributed

scattering. Numerous other living things, such as mammals and insects, display angle-independent structural colors produced in a similar manner.⁵ These colorations can also be caused by constructive interference owing to the presence of amorphous arrays of submicrometer-sized particles and fibers with short-range order (Figure 1).

This idea is now influencing materials scientists who study optical materials and colored materials.^{6–18} Since the discovery of the photonic crystal, the presence of a periodic dielectric structure has been widely believed to be a precondition for the presence of a photonic band gap (PBG) or pseudo-PBG (p-PBG) in the visible region of the electromagnetic spectrum, which causes structural color but with angle dependence.^{19,20} The effects of both the PBG and the p-PBG are explained by Bragg scattering of photons by the periodic dielectric structure. Colloidal crystals composed of submicron-sized particles are periodic arrays that exhibit both long-range and short-range order and thereby display angle-dependent structural color arising from a PBG or p-PBG.^{21–24} In contrast, amorphous arrays of particles and pores possess only short-range order and lack periodicity.^{25,26} However, despite such conditions, certain amorphous arrays display vivid structural colors (Figure 1).¹² This revelation must amaze many researchers.

When viewed from the perspective of materials chemistry, structurally colored materials are ideal for use in energy-saving reflective displays and sensors because structural color does not fade and because no energy is lost as a result of the color-producing mechanism. Furthermore, structurally colored materials prepared by environmentally friendly methods are not only fadeless but also safe pigments. By employing the principles discussed above, we may be able to obtain new man-made, stimuli-sensitive structurally colored

Figure 1 Schematic of various living things and a colloidal amorphous array that display angle-independent structural color. A full color version of this figure is available at *Polymer Journal* online.

materials never observed in living matter; furthermore, such materials may have novel functions.

In this paper, I discuss our recent study into the preparation and optical properties of amorphous arrays of submicrometer-sized particles that mimic structures observed in living organisms. Using and fusing stimuli-responsive materials, including polymers and inorganic and organic materials, to prepare amorphous arrays, we can obtain 'smart' structurally colored materials that are sensitive to changes in their environment, developed on the basis of the principles observed in nature using resources not found in biological systems.

COLLOIDAL AMORPHOUS ARRAYS FOR ANGLE-INDEPENDENT STRUCTURALLY COLORED MATERIALS

Colloidal amorphous arrays of submicrometer-sized hard particles

Colloidal amorphous arrays of hard colloidal particles are difficult to fabricate because submicrometer-sized hard particles have a strong tendency to crystallize.^{9,27} By mixing two different types of submicrometer-sized hard particles such as SiO_2 and polymeric colloidal particles, we can easily prepare colloidal amorphous arrays with short-range order but no long-range order or periodicity.⁷ The discrete ring in the two-dimensional Fourier transform of the scanning electron microscope image in Figure 2a (left), which is also shown in Figure 2a (right), indicates that the microstructure of an aggregate composed of SiO_2 particles is isotropic and has short-range order.³ The size variation of the hard colloidal particles causes them to be arranged in a disordered state. The short-range order in the colloidal amorphous arrays causes them to coherently scatter light, and thus the arrays exhibit structural color. Simply varying the ratio of the two different-sized particles during mixing controls the hue of the angle-independent structural color (Figure 2b) because of the change in the short-range order distance.^{2,9} However, the colors emitted from these colloidal amorphous arrays are very pale because the incoherent light scattering across the entire

visible region is very strong in colloidal amorphous arrays of high-refractive-index contrast (that is, the difference in the refractive index of the particle relative to the gap portion), such as the air-filled SiO_2 colloidal array.²⁶ Moreover, the thickness of membranal-colloidal amorphous arrays critically affects their color, with the appearance of such a membrane becoming whitish as it increases in thickness. Even colloidal amorphous arrays composed of monodisperse fine colloidal particles with the diameter of 280 or 360 nm, prepared by the spray method or another appropriate method, have whitish, faint structural colors (Figure 2c).⁹ The dielectric contrast can be controlled by filling the gap portion with dielectric fluids to suppress the incoherent light scattering and to enhance the structural color of colloidal amorphous arrays.⁷ For example, when the gaps in colloidal amorphous arrays composed of SiO_2 particles that have an experimentally determined refractive index of ~ 1.39 are impregnated with methanol, which has a refractive index of 1.3292 at 20 °C for 589.3 nm light, the structural colors emitted from the arrays become brighter (Figure 2d).

Effect of the addition of black particles

To determine the cause of the incoherent light scattering across the entire visible region from the colloidal amorphous arrays, polarization spectra of the membranal-colloidal amorphous arrays were measured.^{9,13} The spectra were obtained using the methods shown in Figure 3a. White light passes through a linear polarizer before it reaches the colloidal amorphous array. The polarization is parallel to the scattering plane that is formed by the incident beam and the detector. The incident angle between the surface normal and the planar surface of the membrane is 0°. The detector used to collect the scattered light was fixed at 10° from the surface normal. An additional linear polarizer was placed in front of the detector and was used to change the polarization direction to be parallel (p-polarization) or perpendicular (s-polarization) to the scattering plane. The gathered polarization spectra of membranes composed of 360 nm SiO_2 colloidal particles are shown in Figure 3b. A peak at ~ 680 nm appeared in the spectrum of co-polarized light (p-polarization) scattered from the membrane. The scattering intensity of the membrane irradiated by s-polarized light is approximately constant upon the wavelength, with no peak observed across the entire visible region. Conversely, in the scattering spectrum of p-polarized light, we observed that the light scattered from the membrane did not depolarize. From these results, we conclude that a single scattering process produced the peak observed in the spectrum of the colloidal amorphous array.²⁸ However, in the case of the s-polarization scattering spectrum, we observed that depolarized light passed through the membrane was scattered as a result of a high-order scattering process. We hypothesized that light scattered multiple times in the colloidal amorphous array significantly contributes to the nearly uniform scattering observed in the scattering spectrum of the s-polarized light passed through the membrane.

To reduce the contribution of multiple-scattered light rays to the overall scattering spectrum and to enhance the structural color of the colloidal amorphous array, a black component, that absorbs light uniformly across the entire visible region can be incorporated into the array. Carbon black (CB) is one of the most common and environmentally preferable black component available; it reflects very little light in the visible region of the spectrum. Therefore, we prepared membranal-colloidal amorphous arrays using suspensions of the SiO_2 colloidal particles mixed with various small amounts of CB that had an average particle size of 28 nm.⁹ Figure 4a shows the membranes obtained by changing the amount of CB added. The saturation of the

Figure 2 (a) Left: scanning electron microscope image of a colloidal amorphous array made of 90 wt% 310 nm SiO_2 particles and 10 wt% 220 nm SiO_2 particles. The scale bar is 1 μm . Right: two-dimensional Fourier power spectra from the scanning electron microscope image of the colloidal amorphous array in (a). (b) Plots showing the λ_{max} of the transmission spectra as a function of the doping concentration of 220 nm SiO_2 particles in each colloidal amorphous array. (c) Optical photographs of membranes composed of 280 nm SiO_2 particles and 360 nm SiO_2 particles. (d) Optical photographs showing the structural color of the colloidal amorphous arrays made of 310 nm SiO_2 particles doped with 220 nm SiO_2 particles at different ratios (upper: 10 wt% of 220 nm, middle: 30 wt% of 220 nm, and lower: 40 wt% of 220 nm) in methanol. The number written on each column represents the angle of illumination and the scale bar is 1 mm.

colors observed on membranes composed of 280 or 360 nm SiO_2 colloidal particles increased with increasing amount of CB added to the suspension. The peak intensities of the reflection spectra were only slightly diminished, whereas the scattered intensities, owing to the incoherent scattering across the entire visible region, were greatly reduced (Figure 4b). The color of the membrane can be controlled by the diameter of the SiO_2 colloidal particles (Figure 4c). Because of the amorphous structure of the membrane, the colors do not depend on the observation angle during illumination.

In addition, we prepared colloidal amorphous arrays that exhibited vivid, angle-independent structural color from SiO_2 colloidal particles that contained magnetite as a black particle; the performance of the resulting arrays was variable.⁸ Magnetite is a commonly used, non-toxic and environmentally friendly black particulate material. Figure 5a shows secondary particles of colloidal amorphous arrays prepared using suspensions of the 360 nm SiO_2 colloidal particles that include a small amount of magnetite. These secondary particles exhibit a bright red color. Because magnetite is magnetic, we moved and collected the colored secondary particles using an external magnetic field (Figure 5b). When we placed the larger droplets of the aqueous solution, which are approximately a few millimeters in diameter and include both SiO_2 particles and a small amount of magnetite, into oil at 60 °C during the preparation of the secondary particles, the heavier magnetite (5.2 g cm^{-3}) accumulated at the bottom of the droplet

before drying. As a result, we obtained flattened Janus secondary particles with the diameter of about 1 mm, where one side was white and the other side was green or red when we prepared them using 280 or 360 nm colloidal SiO_2 particles, respectively (Figure 5c). Because the colored portion contained the magnetite, the Janus secondary particles faced the same direction in the presence of an external magnetic field (Figure 5d). The skin color of specific species of fish can change with changes in the active concentration or dispersion of pigment granules in the interior region of the pigment cells. An analogous color change in artificial materials can be achieved using stimuli-responsive structurally colored pigments.

Consequently, we obtained vivid, angle-independent, structurally colored colloidal amorphous arrays by mixing black components into white colloidal particles. Incidentally, black melanin granules also exist in the blue bird feathers mentioned previously. However, the melanin granules are located below the nanostructure of the blue bird feathers,²⁹ whereas the CB and magnetite present in our systems are distributed throughout the colloidal amorphous array. Thus, the melanin granules in the bird feathers function to prevent light scattering from below; however, the CB and magnetite reduce the total scattering within the film. In the near future, our research group will report this biomimetic system displaying vivid, angle-independent structural color.

Figure 3 (a) Schematic of the instrument setup used to obtain the p-polarization and s-polarization spectra. (b) Polarization spectra of the structural-colored membranes. The p-polarization and s-polarization reflection spectra of the membranes composed of 360 nm SiO_2 particles. A full color version of this figure is available at *Polymer Journal* online.

STIMULI-RESPONSIVE COLLOIDAL AMORPHOUS ARRAYS DISPLAYING ANGLE-INDEPENDENT STRUCTURAL COLOR

Photo-responsive system using TiO_2 -Ag particle composites

Tunable, angle-independent structural color saturation of a colloidal amorphous array was established using a photo-induced Ag/Ag^+ redox reaction (Figure 6a).¹⁰ When UV light is incident on anatase-type titanium oxide (TiO_2), an electron in the valence band of the TiO_2 is excited into the conduction band, a free hole is created in the valence band, and an electron-hole pair is generated.³⁰ As a result, the UV-light-induced charge-separated excited electron and hole contribute to a reduction reaction and an oxidation reaction at the surface of the TiO_2 , respectively. If, for example, Ag ions are present in the vicinity of the TiO_2 particle surface in the charge-separated state, they are reduced to metallic Ag and are deposited as tiny particles onto the TiO_2 particle. Ag particles exhibit strong absorption bands in the visible-light region because of surface-plasmon resonance that depends upon the size and shape of the silver particles and the local refractive index around the silver particles. If various sizes and shapes of Ag particles are deposited onto the surface of the TiO_2 via the application of UV light, the resulting TiO_2 -Ag particle composite can absorb light across the entire visible region. This composite system can serve as an appropriate black component to enhance the structural color of a colloidal amorphous array.

However, in the case of TiO_2 -Ag particle composites, irradiation with visible light can also induce charge separation.³¹ This charge separation is induced by localized surface-plasmon resonance of the Ag particles because TiO_2 does not absorb visible light. An optical electric field vibrates the free electrons in the Ag particles. These electrons are excited only when they are irradiated with light matching their resonant wavelength. In the case of Ag particles, the excited electron is transferred to oxygen in the air; thus, the silver particles are oxidized to colorless Ag^+ ions. When the TiO_2 -Ag particle composite is irradiated with white light, the intensity of its black color decreases.

Using systems, similar to the one previously discussed, a change in the brightness of the structural color can be repeatedly controlled by applying UV and white visible lights.¹⁰ Composite colloidal

Figure 4 (a) Optical photographs showing the color change in membranes composed of 280 nm particles with various quantities of CB and 360 nm SiO_2 particles with various quantities of CB. (b) Reflection spectra of the membranes shown in **a** obtained using an integrating-sphere measurement. (c) Optical photographs of membranes composed of 230, 280 and 360 nm SiO_2 particles with 1.7 wt% CB.

Figure 5 (a) Secondary particles composed of 360 nm SiO₂ particles with the addition of magnetite. (b) The secondary particles, composed of 360 nm SiO₂ particles and magnetite, were collected by applying an external magnetic field. (c) Flattened Janus secondary particles, characterized by one white side and one red side, composed of 280 nm SiO₂ particles (left) and 360 nm SiO₂ particles (right). (d) Flattened Janus secondary particles composed of 360 nm SiO₂ particles face the same direction in the presence of an external magnetic field. A full color version of this figure is available at *Polymer Journal* online.

amorphous arrays were prepared using fine SiO₂ particles as the main component, and a small amount of TiO₂ particles display a change in structural color when irradiated with light. The composite colloidal amorphous array soaked with silver nitrate aqueous solution exhibited a bright structural color under 313 nm UV light. We observed a strong increase in the saturation of the color upon increasing the UV light intensity (Figure 6b). Moreover, the saturation of the color of composite colloidal amorphous array diminished again when irradiated with white visible light. This process for changing the saturation of the structural color was repeatable. In our system, the color saturation of the colloidal amorphous array was controlled by the deposition and dissolution of black silver particles that decrease incoherent multiple-light scattering within the array. Composites that display various bright hues also can be prepared using SiO₂ colloidal particles with different sizes. These compounds can be useful in the manufacture of sensors, displays and cosmetic products.

Fabrication of a stimuli-responsive system using hydrogel particles

We have demonstrated that condensed gel particle suspensions in amorphous states display angle-independent structural color.⁶ Practically, the preparation of amorphous arrays from hard colloidal particle suspensions is more complicated than expected and is one of the greatest challenges in the large-scale production of such arrays. Indeed, handling a soft-gel particle suspension during the preparation of an amorphous array is substantially easier.^{32,33} In this case, an amorphous array can be prepared by simply evaporating the water from a diluted gel particle suspension. Unlike hard-particle suspensions, the viscosity of the gel particle suspension gradually changes with the particle concentration. Eventually, the deformed soft-gel particles are packed tightly together with short-range order. Consequently, a soft-gel particle

amorphous array displays tunable structural colors and hues that depend on the concentration of the soft-gel particles (Figure 7). Because the gel particles can be prepared from stimuli-responsive polymers, the environment can be used to control their size. As a result, we obtained stimuli-responsive colloidal amorphous arrays displaying angle-independent structural color. A specific example of stimuli-responsive colloidal amorphous arrays is presented in the next section.

Preparation of a thermo-responsive system using core-shell particles

Numerous authors have previously reported that reversible changes in the position and the strength of a PBG or p-PBG can be achieved by altering the Bragg reflection that is observed from colloidal crystals composed of environmentally responsive particles.^{34–37} Conversely, the literature contains few reports of amorphous arrays consisting of such environmentally responsive particles exhibiting a change in the position and the magnitude of the p-PBG as the environmental conditions change.¹³ It was only recently found that amorphous arrays also exhibit p-PBGs, which explains why the environmentally responsive p-PBG of the amorphous arrays composed of environmentally responsive particles has not been reported. Recently, we prepared an amorphous array composed of thermo-responsive fine core-shell particles, where monodisperse SiO₂ colloidal particles make up the core and the shell is a high-density polymer brush of uniform thickness made from thermally responsive poly(*N*-isopropylacrylamide; Figure 8a).¹¹ We observed that the position and magnitude of the angle-independent p-PBG of the array reversibly changed depending on the environmental temperature (Figures 8b and d). Because core-shell particles tend to aggregate in water, even at temperatures below the lower critical-solution temperature of linear

Figure 6 (a) Schematic diagram for the photo-responsive change in the angle-independent structural color saturation of the colloidal amorphous array. (b) Left: the change in the reflection spectra and the optical images of the colloidal amorphous array containing an aqueous solution of silver nitrate under 313 nm UV light passed through a bandpass filter. The incident angle relative to the normal of the planar surface of the colloidal amorphous array was 0°. The measurement angle, θ , was 10° relative to the normal of the planar surface of the colloidal amorphous array. Right: optical images of the colloidal amorphous array that was irradiated with visible light ($\lambda > 420 \text{ nm}$) for 12 h under the conditions shown in the images on the left. A full color version of this figure is available at *Polymer Journal* online.

Figure 7 Optical images of gel particle suspensions with different polymer contents. These images were taken at angles different from the direction of incident light.

Figure 8 (a) TEM image of thermo-responsive polymer brush-coated SiO₂ particles with poly(*N*-isopropylacrylamide; PNIPA) of $M_n = 6.18 \times 10^4$, and with 269 nm SiO₂ core particles. Scale bar = 100 nm. (b) Schematic diagram for the change in the short-range-order distance of the amorphous array composed of thermo-responsive polymer brush-coated SiO₂ particles. (c) Transmission spectra of a thin membrane of the amorphous array composed of thermo-responsive polymer brush-coated SiO₂ particles with 207 nm SiO₂ core particles and PNIPA of $M_n = 2.55 \times 10^4$ measured at various angles at 25 °C. (d) Temperature dependence of the transmission spectra of the thin membrane composed of thermo-responsive polymer brush-coated SiO₂ particles with 207 nm SiO₂ core particles and PNIPA of $M_n = 2.55 \times 10^4$ measured at 0° between 30 and 39 °C. A full color version of this figure is available at *Polymer Journal* online.

poly(*N*-isopropylacrylamide),³⁸ the amorphous array of the core-shell particles did not decompose into particles at low temperatures; it instead exhibited a temperature-reversible change in the short-range order distance, maintaining its aggregation state (Figure 8b). As a result, the amorphous array demonstrated a reversible change in its faint angle-independent structural color that depended on the temperature of water used in the array. Figures 8c and d show the angle dependence and temperature dependence of the transmission spectra of the thin amorphous array membrane, respectively. The $\lambda_{\max}$ was positioned at 668 nm at 0° and was nearly independent of the observed angle (θ) from 0° to 45°. Additionally, a reversible change in the position and the magnitude of the p-PBG was observed when the temperature was varied. The structural color of the aggregate also changed slightly on the basis of the properties of the p-PBG and is therefore dependent on the temperature. In this amorphous array, a faint color was visible, irrespective of the membrane thickness. Relatively low refractive-index contrast owing to the presence of water between the core-shell particles is thought to suppress the multiple light scattering phenomenon.

SUMMARY

Recent advances in the preparation of many types of submicrometer-sized fine particles have introduced exciting new possibilities for developing unprecedented new materials. Stimuli-responsive colloidal amorphous arrays displaying various angle-independent structural colors are one of these interesting new materials. Similar to the humans yearning to fly like birds and eventually developing airplanes, we may be able to develop new fusion materials for optical applications; such materials may be beyond what can be synthesized in natural systems and may someday be useful for enhancing our quality of life. We look forward to the development of materials with similar exciting functions stemming from future advances in the field of materials science.

ACKNOWLEDGEMENTS

I acknowledge the support of a Grant-in-Aid for Scientific Research (No. 23245047 and No. 22107012) on Innovative Areas: 'Fusion Materials' (Area no. 2206) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT).

- 1 Kinoshita, S. & Yoshioka, S. Structural colors in nature: the role of regularity and irregularity in the structure. *Chemphyschem* **6**, 1442–1459 (2005).
- 2 Harun-Ur-Rashid, M., Seki, T. & Takeoka, Y. Structural colored gels for tunable soft photonic crystals. *Chem. Rec.* **9**, 87–105 (2009).
- 3 Prum, R. O., Torres, R. H., Williamson, S. & Dyck, J. Coherent light scattering by blue feather barbs. *Nature* **396**, 28–29 (1998).
- 4 Prum, R. O. & Torres, R. H. A Fourier tool for the analysis of coherent light scattering by bio-optical nanostructures. *Integr. Comp. Biol.* **43**, 591–602 (2003).
- 5 Prum, R. O. & Torres, R. H. Structural colouration of mammalian skin: convergent evolution of coherently scattering dermal collagen arrays. *J. Exp. Biol.* **207**, 2157–2172 (2004).
- 6 Takeoka, Y., Honda, M., Seki, T., Ishii, M. & Nakamura, H. Structural colored liquid membrane without angle dependence. *Acs Appl. Mater. Interfaces* **1**, 982–986 (2009).
- 7 Harun-Ur-Rashid, M., Imran, A. B., Seki, T., Ishii, M., Nakamura, H. & Takeoka, Y. Angle-independent structural color in colloidal amorphous arrays. *Chemphyschem* **11**, 579–583 (2010).
- 8 Takeoka, Y., Yoshioka, S., Teshima, M., Takano, A., Harun-Ur-Rashid, M. & Seki, T. Structurally coloured secondary particles composed of black and white colloidal particles. *Sci. Rep.* **3**, 2371 (2013).
- 9 Takeoka Y., Yoshioka S., Takano A., Arai S., Nueangnoraj K., Nishihara H., Teshima M., Ohtsuka Y. & Seki T. Production of colored pigments with amorphous arrays of black and white colloidal particles. *Angew Chem. Int. Ed. Engl.* **52**, 7261–7265 (2013).
- 10 Hirashima, R., Seki, T., Katagiri, K., Akuzawa, Y., Torimoto, T. & Takeoka, Y. Light-induced saturation change in the angle-independent structural coloration of colloidal amorphous arrays. *J. Mater. Chem.* **2**, 344–348 (2014).
- 11 Gotoh, Y., Suzuki, H., Kumano, N., Seki, T., Katagiri, K. & Takeoka, Y. An amorphous array of poly(*N*-isopropylacrylamide) brush-coated silica particles for thermally tunable angle-independent photonic band gap materials. *New J. Chem.* **36**, 2171–2175 (2012).
- 12 Takeoka, Y. Angle-independent structural coloured amorphous arrays. *J. Mater. Chem.* **22**, 23299–23309 (2012).
- 13 Takeoka, Y. Stimuli-responsive opals: colloidal crystals and colloidal amorphous arrays for use in functional structurally colored materials. *J. Mater. Chem.* **1**, 6059–6074 (2013).
- 14 Ge, D. T., Yang, L. L., Wu, G. X. & Yang, S. Angle-independent colours from spray coated quasi-amorphous arrays of nanoparticles: combination of constructive interference and Rayleigh scattering. *J. Mater. Chem.* **2**, 4395–4400 (2014).
- 15 Ge, D. T., Yang, L. L., Wu, G. X. & Yang, S. Spray coating of superhydrophobic and angle-independent coloured films. *Chem. Commun.* **50**, 2469–2472 (2014).
- 16 Park J. G., Kim S. H., Magkiriadou S., Choi T. M., Kim Y. S. & Manoharan V. N. Full-spectrum photonic pigments with non-iridescent structural colors through colloidal assembly. *Angew Chem. Int. Ed. Engl.* **53**, 2899–2903 (2014).
- 17 Rotstein, R., Mitragotri, S., Moskovits, M. & Morse, D. E. Progressive transition from resonant to diffuse reflection in anisotropic colloidal films. *J. Polym. Sci. Pol. Phys.* **52**, 611–617 (2014).
- 18 Shi, L., Zhang, Y., Dong, B., Zhan, T., Liu, X. & Zi, J. Amorphous photonic crystals with only short-range order. *Adv. Mater.* **25**, 5314–5320 (2013).
- 19 Miguez, H., Meseguer, F., Lopez, C., Blanco, A., Moya, J. S., Requena, J., Mifsud, A. & Fornés, V. Control of the photonic crystal properties of fcc-packed submicrometer SiO₂ spheres by sintering. *Adv. Mater.* **10**, 480–483 (1998).
- 20 Miguez, H., Meseguer, F., Lopez, C., Lopez-Tejeda, F. & Sanchez-Dehesa, J. Synthesis and photonic bandgap characterization of polymer inverse opals. *Adv. Mater.* **13**, 393–396 (2001).
- 21 Aguirre, C. I., Reguera, E. & Stein, A. Tunable colors in opals and inverse opal photonic crystals. *Adv. Funct. Mat.* **20**, 2565–2578 (2010).
- 22 Fudouzi, H. & Xia, Y. N. Colloidal crystals with tunable colors and their use as photonic papers. *Langmuir* **19**, 9653–9660 (2003).
- 23 Furumi, S., Fudouzi, H. & Sawada, T. Dynamic photoswitching of micropatterned lasing in colloidal crystals by the photochromic reaction. *J. Mater. Chem.* **22**, 21519–21528 (2012).
- 24 Arsenault, A. C., Puzzo, D. P., Manners, I. & Ozin, G. A. Photonic-crystal full-colour displays. *Nat. Photon.* **1**, 468–472 (2007).
- 25 Garcia, P. D., Sapienza, R. & Lopez, C. Photonic glasses: a step beyond white paint. *Adv. Mater.* **22**, 12–19 (2010).
- 26 Forster, J. D., Noh, H., Liew, S. F., Saranathan, V., Schreck, C., Yang, L., Park, J.-G., Prum, R. O., Mochrie, S. G., O'Hern, C. S., Cao, H. & Dufresne, E. R. Biomimetic isotropic nanostructures for structural coloration. *Adv. Mater.* **22**, 2939–2944 (2010).
- 27 Garcia, P. D., Sapienza, R., Blanco, A. & Lopez, C. Photonic glass: a novel random material for light. *Adv. Mater.* **19**, 2597–2602 (2007).
- 28 Noh, H., Liew, S. F., Saranathan, V., Prum, R. O., Mochrie, S. G., Dufresne, E. R. & Cao, H. Double scattering of light from Biophotonic Nanostructures with short-range order. *Opt. Express* **18**, 11942–11948 (2010).
- 29 Shawkey, M. D. & Hill, G. E. Significance of a basal melanin layer to production of non-iridescent structural plumage color: evidence from an amelanotic Steller's jay (*Cyanocitta stelleri*). *J. Exp. Biol.* **209**, 1245–1250 (2006).
- 30 Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37–38 (1972).
- 31 Ohko, Y., Tatzuma, T., Fujii, T., Naoi, K., Niwa, C., Kubota, Y. & Fujishima, A. Multicolour photochromism of TiO₂ films loaded with silver nanoparticles. *Nat. Mater.* **2**, 29–31 (2003).
- 32 Nakanishi, T., Naito, M., Takeoka, Y. & Matsuura, K. Versatile self-assembled hybrid systems with exotic structures and unique functions. *Curr. Opin. Colloid. & Inter. Sci.* **16**, 482–490 (2011).
- 33 Mattsson, J., Wyss, H. M., Fernandez-Nieves, A., Miyazaki, K., Hu, Z., Reichman, D. R. & Weitz, D. A. Soft colloids make strong glasses. *Nature* **462**, 83–86 (2009).
- 34 Hu, J., Zhao, X.-W., Zhao, Y.-J., Li, J., Xu, W.-Y., Wen, Z.-Y., Xu, M. & Gu, Z.-Z. Photonic crystal hydrogel beads used for multiplex biomolecular detection. *J. Mater. Chem.* **19**, 5730–5736 (2009).
- 35 Kumoda, M., Watanabe, M. & Takeoka, Y. Preparations and optical properties of ordered arrays of submicron gel particles: interconnected state and trapped state. *Langmuir* **22**, 4403–4407 (2006).
- 36 Ge J. P. & Yin Y. D. Responsive photonic crystals. *Angew Chem. Int. Ed. Engl.* **50**, 1492–1522 (2011).
- 37 Kim, S. H., Lee, S. Y., Yang, S. M. & Yi, G. R. Self-assembled colloidal structures for photonics. *Npg Asia Mater.* **3**, 25–33 (2011).
- 38 Suzuki, H., Nurul, H. M., Seki, T., Kawamoto, T., Haga, H., Kawabata, K. & Takeoka, Y. Precise synthesis and physicochemical properties of high-density polymer brushes designed with poly(*n*-isopropylacrylamide). *Macromolecules* **43**, 9945–9956 (2010).