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Bio-inspired intelligent structural color materials

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Bioinspired structural color materials represent a curiosity-led, technology-driven field with multi-disciplinary research studies aiming at mimicking and recapitulating natural coloration and functions. Over the past several decades, great achievements have been made, including natural structural coloration mechanisms, fabrication of artificial structural color materials, and their applications in extensive areas. In very recent years, research has been propelled forward towards making structural color materials intelligent by incorporating fascinating functions such as self-healing, autonomous regulation, shape memory, etc. These accomplishments create a great leap for structural color materials being applied in real-life scenarios and devices such as in anti-counterfeiting, displays, sensors, soft robots, wearable electronics, organ-on-a-chip platforms, etc.

1. Introduction

Structural color is a type of coloration which arises from visible light interference with certain structural features at the micro- or nano-scale.¹ It is defined in contrast to pigmentary coloration as the former originates from the physical properties of light while

the latter involves energy consumption and conversion between light and electrons.^{2–4} Structural coloration is a widespread phenomenon in natural creatures, which contributes to camouflage, reproduction, signal transmission, etc., and emerges through a long-time evolution dating back from the Cambrian explosion.⁵ Scientific studies of structural coloration began with the pioneering works done by Hook and Newton in the 17th century, while a deep understanding was not achieved until the establishment of electromagnetic theories and direct observation of the nanostructures by electron microscopy.⁶ The definite interpretation of the relationship between structure and coloration provides a principle for on-demand materials design. By tailoring the structures at the nanoscale, photonic materials could be constructed with specific optical properties and functions, which are unachievable in bulk materials.

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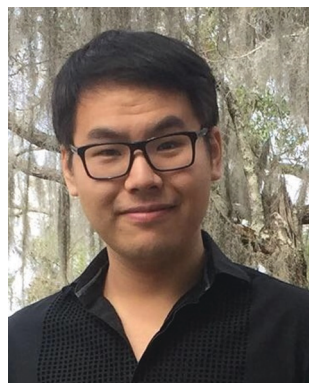
Through top-down processing techniques such as lithography and bottom-up methods including controlled self-assembly, structural color materials have been fabricated and find applications in a large number of fields.^{7–12} Due to their brilliant colors, they could be applied in decoration, printing, and displays.¹³ Besides, they serve as light wave guiding units for photonic communication and in optoelectronic devices.^{14,15} In addition, they could be made responsive and thus used as sensors in anti-counterfeiting and chemical/biomedical analysis.^{16–18}

Despite these achievements, it is still a challenge that current artificial structural color materials cannot meet the marvelous features seen in natural creatures. Indeed, natural structural coloration plays vital roles in multiple aspects far from just contributing to external appearance. In addition, it remains in the laboratory stage as the systems tend to be complex and technically demanding and thus the real-world applications are limited. Therefore, efforts have been made in developing next-generation structural color materials with smart biomimetic functions such as self-healing, autonomous regulation, on-demand adaptability, *etc.*^{19–26} Such materials not only possess the irreplaceable value of visualization, but also show durability, portability, and robustness. These signs of progress provide highly promising avenues for structural color materials being used in real-life products including soft robots, wearable electronics, organ-on-a-chip devices, *etc.* Herein, we provide a review of recent progress in intelligent structural color materials with biomimicking functions and real-life applications. In the sections that follow, we introduce natural structural coloration phenomena, including static and dynamic systems. Then we present artificial structural color materials with smart bio-inspired functions, followed by their cutting-edge applications. Finally, a summary and perspectives are proposed, discussing the remaining challenges and future trends of structural color materials.

2. Natural structural colors

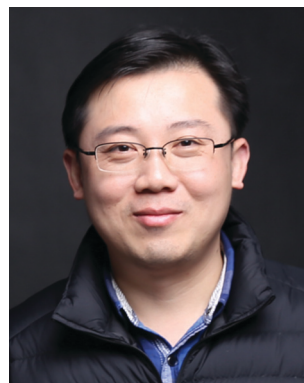
2.1 Static structural colors in natural creatures

Natural structural coloration exists in a rich variety of organisms, ranging from invertebrates, insects, plants, *etc.*^{27–31} Unlike pigments or dyes, which involve photo-electrical energy consumption and conversion and thus suffer from dissipative loss, structural color can be exempt from fading because it originates from the physical interaction of structural features with light. Different photonic nanostructures are naturally present from one-dimension (1D) to three dimensions (3D). By utilizing such sophisticated nanoscale architectures, the propagation of light could be well controlled. As a result, light within a certain range of wavelengths shows high reflectivity and is perceived by the human eye due to selective spectral sensitivities of photoreceptors in the retina. The underlying mechanisms of light–structure interactions include combinations of several fundamental optical processes including film interference, diffraction grating, photonic crystal effect, and organized light scattering. The principle of film interference is wave interference when the light is reflected off the boundaries of layers consisting of two media with different refractive indices. Many insects and birds apply multi-layered structures with alternatively piled thin films with periodic variation of the refractive index in one spatial dimension.^{32,33} The constructive or destructive interference behavior determines the preferential reflection wavelength and the appearing color. The diffraction grating effect corresponds to a unique surface structure with periodic corrugations with a certain amplitude. It has been discovered in invertebrates and many iridescent flowers.^{34,35} White light could be diffracted from successive rings or grooves into constituent wavelengths, thus creating a rainbow-like reflectance. The photonic crystal effect is attributed to an ordered arrangement of two media with refractive index contrast on the submicron scale. The periodic variation of the refractive index results in the generation of a photonic bandgap (PBG).



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Light of a certain wavelength located in this gap could not propagate and show high reflectivity, thus producing colors. According to the spatial dimensionality of the periodicity, photonic crystal structures could be categorized into 1D film-like stacks, 2D pillar-like arrays, and 3D sphere-like lattices, which have been discovered in butterfly wings, worms, plants, *etc.*^{36–38} Another source of structural coloration comes from scattering. It is based on a disordered isotropic structure that emits diffusive light and has been considered as part the reason for blue coloring seen in insects and birds' feathers.³⁹ It should be noted that the above-described mechanisms might be combined in natural structural coloration systems, corresponding to complex geometries seen in some organisms such as the butterfly wings.⁴⁰

2.2 Dynamic structural colors in natural creatures

While natural structural coloration is generally static, it can also be dynamic that allows some organisms to adapt most to the needs for living, social interaction, and reproduction, through functions including signaling, camouflage, *etc.* The fast and reversible color alternation behavior usually corresponds to a structure change including the spacing of the structural units, *i.e.* the nano-reflectors, or the average refractive index, in response to environmental stimuli such as stress, light, temperature, *etc.* One of the most prominent examples is chameleons, whose rapid color shifting capacity has long been intriguing and recently been elucidated by Milinkovitch and co-workers.⁴¹ They studied the color shifting behavior of panther chameleon *Furcifer pardalis*. As shown in Fig. 1A, under combat conditions, an adult male chameleon turns its skin background color from green to yellow and changes the mid-body stripe color from blue to whitish color. By combining electron microscopy and histological methods, they further confirmed that in an adult male individual, there are two layers of dermal iridophore cells which contain guanine nanocrystals packed into a face-centered cubic lattice (Fig. 1A(ii)). During excitation, the spacing of the nanocrystals increased, causing a shift of preferential reflectivity from short to long wavelength and the corresponding color change (Fig. 1A(iii)). A similar adaptive iridescence mechanism has also been identified in some fish species by tuning the spacing of multilayer reflecting stripes.⁴² In addition to regulation of dimensions, in some squid species, the plasma membrane could be invaginated into iridophore cells, forming an array of alternating refractive indices, and a reversible swelling and shrinking process could be triggered, which causes a rapid change in both lattice constant and dielectric contrast.⁴³ Besides, in some species, a change in structural color even triggers a more complex optical process. Whitney *et al.* investigated the light-responsive structural color vanishing phenomenon in the brown alga *Cystoseira tamariscifolia*.⁴⁴ As shown in Fig. 1B, this alga exhibits green to blue colors due to the presence of opal-like lipid photonic crystals being surrounded by cylindrical chloroplasts in the photosynthetic cells. The packing of the photonic crystals could shift from an ordered to a random mode in the dark or under bright light illumination, respectively, thereby controlling light transmission and reflectance.

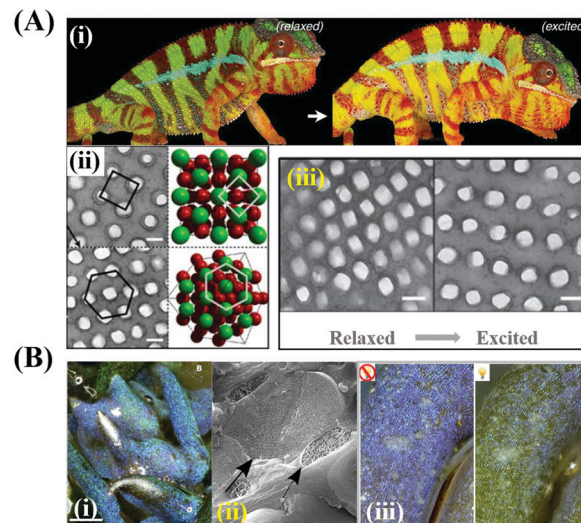


Fig. 1 Dynamic structural colors in natural creatures. (A) (i) Color change in a mature male chameleon during excitation, as depicted by the white arrow. (ii) TEM images of the guanine nanocrystals showing the FCC lattice in two orientations. (iii) TEM images showing the nanocrystal spacing difference in relaxed and excited states, respectively.⁴¹ The scale bars are 200 nm. (B) (i) Structural color of alga *C. tamariscifolia*. (ii) Cryo-SEM image showing intercellular photonic crystals (solid arrow) and the chloroplasts (dashed arrow). (iii) Structural color faded upon illumination, corresponding to a disordered packing formation.⁴⁴ The scale bar is 500 μm .

Such dynamic behavior allows for control of light flux towards the chloroplast aligned parallel to the sunlight, and thus contributes to adaptive photosynthetic behaviors in an environment with fluctuations in light intensity.

3. Bio-inspired intelligent structural color materials

3.1 Responsiveness

3.1.1 External stimuli. Inspired by the fast and reversible color-shifting phenomena in natural creatures, synthetic responsive structural color materials have attracted notable research interest as they allow for modulation of the colors for on-demand applications including sensors, displays, anti-counterfeiting, smart devices, *etc.*^{17,45} In principle, tuning of the optical signals is mainly achieved through three strategies which determine the transmission and reflection of visible light: variation of the refractive indices, tilting the glancing angle, and manipulating the photonic nanoarchitectures. Such variations are usually induced in response to external triggers, such as temperature, light, ionic or molecular concentration, electric or magnetic field, mechanical strain, *etc.*^{46–51} and correspondingly, active substances with stimuli-responsive modalities are employed as building blocks, matrix, or filtrating ingredients. One of the most common examples is by using polymers, such as hydrogels, polyelectrolytes, and elastomers, as the substrate material to accommodate periodically arranged or amorphous photonic crystal building blocks.^{52–54} Upon being triggered by environment fluctuations such as temperature, ionic/molecular

concentration, electric voltage, mechanical force, *etc.*, the polymer undergoes reversible and large deformation or volume change, thus causing a variation of the diffracting plane spacing or resulting in an order–disorder transition. In addition to volume or shape change, phase transition inorganic materials, such as semiconductors, ferroelectrics, photoisomers, and liquid crystals, have been utilized as filler materials to induce fast regulation of the refractive index or lattice structure.^{55–58} Besides, field-sensitive materials, for example magnetically responsive materials, could be employed as building blocks for controllable assembly at different lattice spacings, orientations, or degrees of ordering.^{59–61}

3.1.2 Autonomous regulation. While stimuli-responsive structural color materials have been intensively investigated, self-regulating materials with autonomous color regulation capacity have been created very recently, which shed light on next-generation photonic devices. A group led by Zhao *et al.* got inspiration from the active tuning mechanism of the guanine nanocrystal lattice in chameleon, and fabricated a chameleon skin-like hydrogel film with embedded photonic crystal structures.¹⁹ Live cardiomyocyte tissues were assembled on the film and could recover autonomic beating ability due to good compatibility of the substrate material. Thus, through rhythmic cell contraction and relaxation, the elastic film could switch synchronously between the tensioned state and the original state, as shown in Fig. 2A. The resultant volume and morphology changes of the biohybrid film gave rise to an alternation of both the diffracting plane spacing and the glancing angle, therefore contributing to a color change. By using a mask mold with a shaped pattern, the originally free-standing film could be immobilized in a fixed plane, thus ensuring even morphology changes and constant glancing angle. As shown in Fig. 2B–D, the film exhibited uniform color changing behavior during myocardial cycles, and the reflection peak shifted periodically, with its frequency corresponding to that of cardiomyocyte beating.

3.2 Self-healing

In addition to responsiveness, other important features of next-generation structural color materials are resistance to deterioration and accumulative damage, long-term duration, and environmental tolerance. Although these abilities are difficult to obtain and have been overlooked in the early research studies, recent studies have made them possible by drawing inspiration from the self-healing phenomena in nature. Self-healing properties are ubiquitous in natural materials, such as in skins and bones, and have been implemented in synthetic polymer materials by incorporating healing agents into the polymeric architectures through covalent reactions or physical crosslinking including hydrogen-bonding, ionic bonding, hydrophobic bonding, *etc.*^{62,63} Accordingly, Zhao *et al.* constructed a self-healing structural color hydrogel by combining a photonic crystal framework with a protein repairing filler agent.²¹ As shown in Fig. 3A(i), a 3D inverse opal hydrogel film scaffold was first fabricated by using a methacrylated gelatin (GelMA) hydrogel to replicate the silica colloidal crystal templates. Then, a glutaraldehyde cross-linked bovine serum

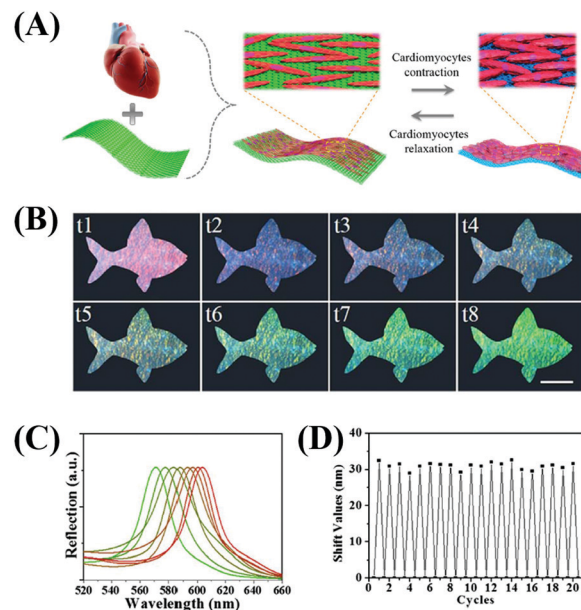


Fig. 2 Self-regulating structural color material. (A) Scheme of the fabrication process of the biohybrid autonomous color tuning film composed of synthetic inverse opal hydrogels topped with a layer of live cardiomyocyte tissues. (B) Optical microscope images of the immobilized fish-shaped biohybrid structural color film during one myocardial cycle. The scale bar is 1 mm. (C) Reflection spectra of the film in (B), viewed at a fixed angle. The curves from left to right correspond to t8 to t1, respectively. (D) Relationship between the reflection shift and the cardiomyocyte beating cycles.¹⁹

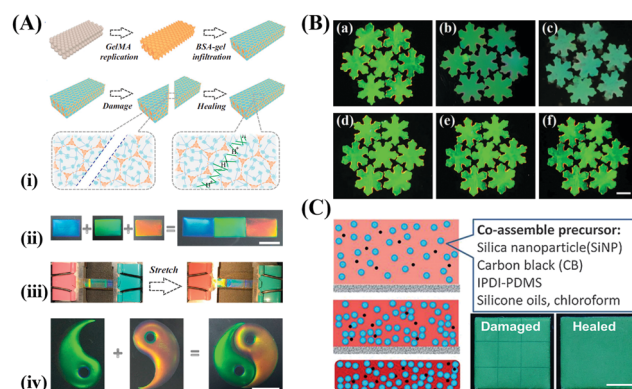


Fig. 3 Self-regulating structural color materials. (A) (i) Scheme of the generation and self-healing process of the structural color protein hydrogel. (ii) Integrated self-healing structural color hydrogel showing resistance to tensile force. The scale bar is 5 mm. (iii) A Chinese Taiji pattern generated by two pieces of a self-healing structural color hydrogel. The scale bars are 5 mm.²¹ (B) Optical images of the (a–c) AgNP-free and (d–f) AgNP-tagged self-healing structural color hydrogels during 20 day storage. The scale bar is 500 μm .⁶⁴ (C) Scheme of the synthesis of the organogel structural color membrane and the self-healing ability after crisscross cut.⁶⁶ The scale bar is 0.5 cm.

albumin (BSA) hydrogel with enzyme additives was infiltrated into the nanovoids of the film. Due to the periodic photonic crystal structure, the composite film exhibited iridescent structural color. In addition, because of the reversible imine covalent interactions between glutaraldehyde and the residues

on BSA as well as the additives, the hydrogel possessed self-healing ability. Based on this strategy, segments of such hydrogels with different colors could be integrated into an intact composite with unique patterns, retaining their original elasticity, as shown in Fig. 3A(ii–iv). In one of their subsequent studies, the self-healing structural color hydrogel was further imparted with anti-bacterial ability for long-term survivability.⁶⁴ By integrating antibacterial silver nanoparticles (AgNPs), the above-described protein hydrogels could be protected from bacterial adhesion and proliferation, thus restoring the structural color and self-healing ability for a long time, as shown in Fig. 3B. A similar strategy has also been implanted into a 1D photonic crystal film composed of cholesteric cellulose nanocrystal (CNC) assembly and a poly(vinyl alcohol)–polyacrylamide (PVA–PAM) hydrogel.⁶⁵ The dynamic bonds of boronic esters gave rise to the self-healing property, and the resultant composite hydrogel could be stitched into patterns/stacked architectures.

In addition to hydrogels, the feature of self-healing has also been realized in organogel-based structural color materials. Yao *et al.* developed such kind of organogel nanocomposite membrane that combined photonic structures and self-healable supramolecular gel substrates.⁶⁶ As illustrated in Fig. 3C, the supramolecular polymer was prepared by condensation of isophorone diisocyanate (IPDI) and amino terminated poly(dimethylsiloxane) (NH_2 -PDMS- NH_2) in a solvent together with silicone oil and was co-assembled with octadecyl-modified oleophilic silica nanoparticles and carbon black nanoparticles. After solvent evaporation, the organogel nanocomposite was formed and SiNPs assembled into an amorphous morphology, which gave rise to structural color with an angle-independent feature. The dynamic crosslinking from urea groups contributes to the self-healing performance at the molecular level through hydrogen bonding. In addition, the presence of carbon black could improve color saturation due to broad-spectrum absorption and specific coherent scattering. Compared with hydrogel materials, such organogel membranes also provided slippery and water-repellent features, which were compliant with outdoor environments.

3.3 Shape memory

Shape memory is a property by which materials could “memorize” a permanent shape after deformation into a “fixed” temporary shape, and reform without additional mechanical efforts. Inspired by the intelligent shape-shifting behaviors in natural systems, shape memory materials have aroused widespread attention as they allow for reconfigurable and complex structures and adaptive functions. Specifically, shape memory in polymers could be achieved by a process of programming, storage, and recovery, during which external triggers are usually applied such as temperature, light, solution, electric/magnetic field, *etc.*^{67,68} Recently, shape-memory structural color polymers have been put forward with regard to on-demand programming and retaining of the colors without continuous application of external input, which are highly desirable in constructing energy-efficient and reusable displays or wearable materials.^{69–72} Smoukov *et al.* created chameleon-inspired opals with a

shape-memory polymer embedded in the matrix, which could be programmed into fixed colors.⁷³ Vignolini *et al.* reported a thermo-mediated shape memory photonic crystal film by embedding CNC assembly within a polydiolcitrate elastomer which undergoes melting transition upon heating.⁷⁰ The resultant film could fix at a programmed, temporary shape after a heating–mechanic deformation–cooling process, and then recover to its permanent shape. In addition to temperature control, Jiang *et al.* conducted a series of research studies on vapor-mediated shape-memory photonic crystals that enable ‘cold’ programming as well as instantaneous shape recovery. As shown in Fig. 4A(i), an inverse opal membrane of ethoxylated trimethylolpropane triacrylate-*co*-polyethylene glycol diacrylate (ETPTA-*co*-PEGDA) copolymer was fabricated by replicating silica colloidal crystal templates, which possessed an original crystalline array of macroporous structures and showed iridescent color.²⁰ By evaporating water from the scaffold, the membrane would be deformed into a temporary, collapsed porous structure and would lose the color due to the large capillary pressure. Subsequently, by applying a small contact pressure, the permanent ordered structure could be recovered. Based on this strategy, arbitrary structural color patterns could be printed on the membrane, as shown in Fig. 4A(ii). In addition, upon being exposed to low surface tension vapors such as ethanol and acetone, shape recovery of the deformed membrane could be activated, along with a gradual color-shifting process, as shown in Fig. 4B.⁷⁴

In addition to the “memory” of the internal ordered structures at the microscale, structural color materials could be engineered and reprogrammed into complex 3D macroscale structures by using origami-designed, self-folding templates. Origami is an ancient design principle by which a flat sheet of material could be folded into 3D shapes.^{75,76} By combining a shape memory polymer Nafion with the origami technique, Chen *et al.* presented a reconfigurable molding route for 3D shaping of structural color objects.⁷⁷ Specifically, a sheet of Nafion composite was first generated with prescribed geometric patterns composed of a

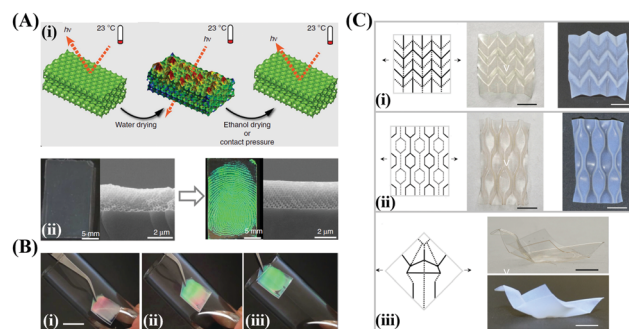


Fig. 4 Shape memory structural color materials. (A) (i) Scheme of the pressure or vapor-responsive shape memory photonic crystals. (ii) Photograph and SEM images of (left) a translucent film with a disordered structure and (right) a green-colored fingerprint with a crystalline ordered structure.²⁰ (B) Photographs showing a shape memory photonic crystal membrane being exposed to acetone vapor at different positions.⁷⁴ The scale bar is 1 mm. (C) 3D shaped photonic crystals created by spray coating on a master mold with prescribed patterns of (i) Miura-ori origami, (ii) bow-tie origami, and (iii) bird origami.⁷⁷ The scale bars are 5 mm.

dispersed unlocked phase and a matrix locked phase, which were derived from protonated and deprotonated Nafion, respectively. Due to the difference in the thermal relaxation temperature between the two phases, 3D shapes could be generated as a result of differential shrinkage upon heating, and the shape could be removed through acid–base treatment and re-programmed into other on-demand configurations. The resultant stable origami structures then served as master molds for 3D shaping of various materials, including photonic crystals, by spray-coating of monodispersed polystyrene nanospheres. The nanospheres assembled into a quasi-amorphous structure and gave rise to angle-independent blue color, as shown in Fig. 4C.

3.4 Others

Superwetttable structural color systems exist widely in natural organisms such as bird feather, fish skin, flower petals, *etc.*, which contribute to higher tolerance to various living environments.^{78,79} Inspired by this, recent years have seen a tendency of tailoring structural color materials with superwettability features. In principle, surface wettability could be adjusted by tailoring multiscale geometrical structures and chemical compositions. This could be facily implemented in structural color materials due to their intrinsic geometrical features. For example, 3D photonic crystal materials could be further obtained with hierarchical nanostructures through micromachining such as lithography and reactive ion etching.^{80,81} Also, the surface chemical properties could be tuned by infusing liquids.⁸²

Besides, novel functional ingredients or dopants could be incorporated into structural color materials to enhance the optical performances or introduce new properties. For example, Omenetto *et al.* created silk inverse opals by using natural silk fibroin to replicate colloidal crystal templates.⁸³ The resultant materials showed excellent color tunability and biocompatibility and could be easily functionalized or doped with gold nanoparticles, demonstrating enhanced absorption as well as patterned laser heating. Snaith *et al.* reported a structural colored perovskite solar cell constructed by integrating a photonic crystal scaffold within the photoactive layer.⁸⁴ Graphene⁸⁵ or poly-dopamine⁸⁶ doping into amorphous photonic structures helped in creating noniridescent structural colors with improved brightness.

4. Cutting-edge applications

4.1 Anti-counterfeiting

Anti-counterfeiting is the technique of identifying the authentication of products, which is essential for many concerns including economic security and human health. Development of anti-counterfeiting tags that are sufficiently complex, not to be readily copied, while cost-efficient for use in commodities is highly anticipated.^{8,87,88} Among many kinds of anti-counterfeiting materials, structural color materials stand out mainly due to their easy-perceivable and stable optical signals. In addition, structural color materials could be graphically designed with arbitrary patterns and engineered on different

substrates with relatively low cost, benefiting from various manufacturing technologies such as photolithography and ink-jet printing.^{18,89} These features, together with their stimuli-responsive ability, make structural color materials excellent choices in anti-counterfeiting applications. For example, an anti-counterfeiting photonic stripe was generated by the fast assembly of discrete colloidal crystal arrays in a glass capillary.⁹⁰ The nonsynchronous process of colloidal assembly and the descent of solid–liquid–air interface resulted in discrete colloidal crystal rings on the capillary wall, as shown in Fig. 5A(i). By co-assembly of particles with different sizes, a stripe could be generated with a heterogeneous pattern composed of different colors. In addition, by integrating with a graphene oxide hydrogel, the stripe could serve as anti-counterfeiting tags through a NIR-light-responsive color change, as shown in Fig. 5A(ii).

Compared with 1D stripes, 2D structural color patterns carry more abundant information. Zhao *et al.* designed a dynamic molding strategy for the generation of structural-colored photonic crystal bead (PCB) patterns.⁹¹ Specifically, a series of spherical PCBs could be prepared through droplet microfluidics or flow lithography with highly controllable shape and structure,⁹² and could then be precisely positioned by sequentially filling into an array of microholes, which were created through stepwise spacing out of a microhole-array mold from a complementary microcylindrical-array mold in the vertical direction, as shown in Fig. 5B(i). By horizontally expanding the microhole array mold, the PCBs could be arranged into 2D patterned objects, which demonstrated anti-counterfeiting capacities in various daily-life commodities, as shown in Fig. 5B(ii). Besides, more complex and accurate structure color graphs could be generated with the aid of printing or lithography techniques. For example, Gu *et al.* used colloidal nanoparticles for

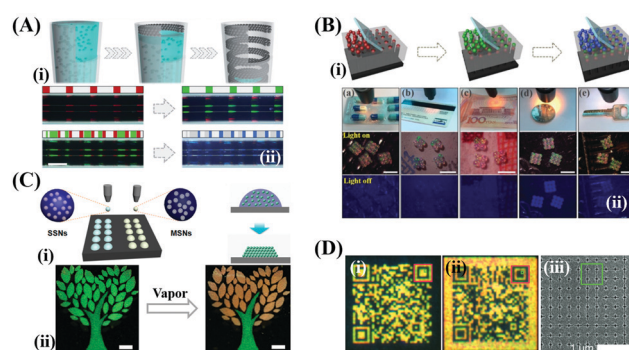


Fig. 5 Patterned structural color materials as anti-counterfeiting tags. (A) (i) Scheme of the colloidal crystals self-assembling into a striped pattern in glass capillaries. (ii) Dynamic color shifting of the stripes under NIR scanning.⁹⁰ The scale bar is 500 μm . (B) (i) Scheme of the stepwise filling of PCBs into the microhole array. (ii) Anti-counterfeiting capability of the 2D photonic barcodes on different substrates including a piece of (a–e) pharmaceutical packaging, credit card, paper currency, coin, and key, respectively. The scale bars are 1 mm.⁹¹ (C) (i) Scheme of the ink-jet printing process. (ii) Responsive color change of a printed pattern upon being saturated in EtOH vapor. The scale bars are 1 μm .⁹³ (D) (i and ii) Contrast view of a plasmonic filter based QR code when illuminated under (i) x polarized light and (ii) y polarized light, respectively. (iii) SEM image showing the right corner of the code. The scale bar is 1 μm .⁹⁴

ink-jet printing, after which the particles could assemble into well-ordered structural color patterns on both soft and rigid substrates.⁹³ As shown in Fig. 5C(i), latex droplets of solid (SSNs) and mesoporous (MSNs) silica nanoparticles were printed with a pre-designed pattern. Due to the strong vapor-responsive color shifting ability of the MSNs, implicit images could be revealed upon exposure to certain vapors (Fig. 5C(ii)). Moreover, Clark *et al.* created ultra-resolution images using polarization multiplexed plasmonic color filters.⁹⁴ Arbitrary images would be encoded into an array of pixels composed of cross-shaped nanoapertures in an aluminum film. Based on the resonant photon–electron interaction, each aperture could exhibit two arbitrary color signals. By doing this, high-density QR codes were fabricated, which possessed optically-readable outputs with polarization switching ability, as shown in Fig. 5D.

4.2 Optical display

The rapid development of mobile and electronic devices places a huge demand for advanced display technology, which is becoming increasingly important in daily life. Structural color materials are highly promising for constructing optical display devices as they allow for low-power consumption as well as full-color emission.^{95–97} Specifically, the generation of a tunable pattern with well-arranged primary color (red, green, and blue, RGB) units is anticipated, which can be achieved through micro-molding, printing, or lithography. For example, Kim *et al.* created a multi-colored inverse opal micropattern combining colloidal self-assembly with the photolithography technique.⁹⁸ Colloidal crystals were first assembled and embedded within a negative photoresist (SU-8) matrix through thermal annealing. Then, an inverse opal pattern with bright colored pixels was created after photolithography and colloid removal, as shown in Fig. 6A(i and ii). By performing double or multiple steps of the above-described process, dual-colored or multi-colored pixels could be prepared, which is highly feasible for reflective color displays (Fig. 6A(iii and iv)). In addition, photonic crystal beads (PCBs) could be used as color units for display applications through assembling on a substrate.⁸ By incorporating magnetic nanoparticles, switchable behavior could be achieved in alignment with the magnetic field.⁹⁵ Besides, due to the spherical symmetry of the PCBs, their reflective spectral peak remained constant despite rotation of the axes.⁹⁹ Based on this, a photonic paper composed of hydrogel films was prepared by replicating an array of PCBs, which displayed identical colors when observed at various angles, as shown in Fig. 6B(i).¹⁰⁰ By using the salt solution as ink, such a film enabled flexible writing and erasing due to the ionic-responsive color change behavior of the hydrogel-based inverse opal structure (Fig. 6B(ii)).

The feature of high visibility is also highly desired for advanced display applications. Recent studies take inspirations from melanin granules existing in birds' feathers, which serve as both structural color components and broadband absorbers. Biomimetic artificial melanin photonic crystals are achieved by using polydopamine as synthetic melanin^{101–103} or using core-shell nanoparticles with adjustable refractive index contrast (*e.g.* polystyrene@polydopamine,¹⁰⁴ melanin@silica,¹⁰⁵ hollow

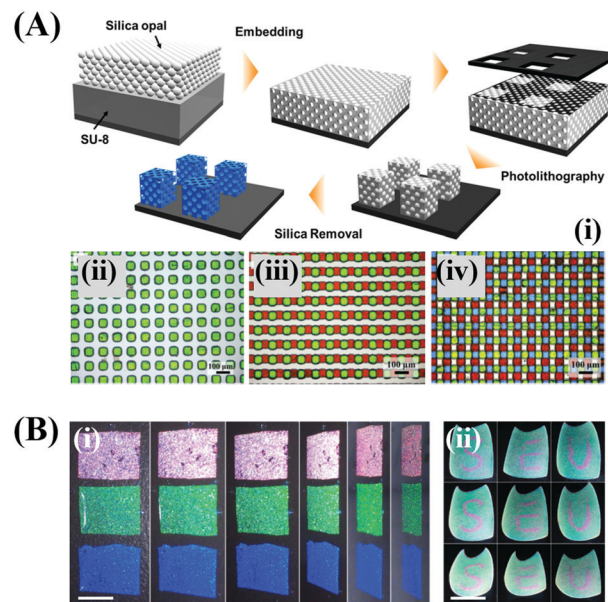


Fig. 6 Structural color display materials. (A) (i) Scheme of the fabrication of inverse opal pixel patterns. (ii–iv) A pixelated inverse opal panel showing (i) single, (ii) double, and (iii) triple colors, respectively.⁹⁸ The scale bars are 100 μm . (B) (i) A photonic paper when viewed at different angles. From left to right: 90°, 75°, 60°, 45°, 30°, 20°, respectively. (ii) A green photonic paper with red ink mark of characters “S”, “E”, and “U”.¹⁰⁰ The scale bars are 1 cm.

polydopamine,¹⁰⁶ *etc.*) as components for assembly. Iridescent color could be achieved through a crystalline assembly and non-iridescent color could be generated through an amorphous assembly.

4.3 Sensors

There is huge interest in exploring advanced sensing methodologies for probing complex systems, including in the food/pharmaceutical industry, environmental monitoring, and medical diagnostics, with high specificity, sensitivity, as well as low cost.^{107–109} Structural color sensors have become particularly attractive in recent years, using which a responsive color-shift readout is employed for identification and/or quantification of a certain parameter.^{17,110} According to the type of the stimulus, they can be categorized into physical and chemical sensors. Physical sensors typically involve responsive behaviors under mechanical strain, temperature or humidity alternation, external fields, *etc.*^{23,111,112} Elastomeric materials could be engineered into 1D stacks or 3D colloidal crystals to enable color tuning under mechanical strain.^{54,113} For example, Park *et al.* constructed a strain visualization device based on a mechanochromic block copolymer structural color (BCP SC) film sensor.¹¹⁴ As shown in Fig. 7A(i), a sensing layer composed of BCP SC and ionic gel (IG) being embedded in PDMS medium (BCP SC: IG in PDMS) was sandwiched between ionic hydrogel electrodes and protected by elastomeric VHB. The BCP SC could respond to strain by a dimensional change of its periodic lamellae structure, and allowed for full visible range monitoring of strain up to 100% (Fig. 7A(ii)). In addition, by using environment-sensitive hydrogels,

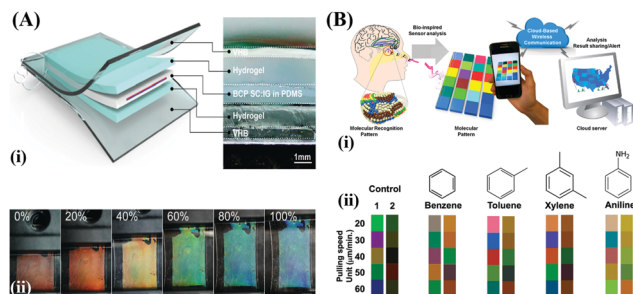


Fig. 7 Structural color sensors. (A) (i) Scheme of a strain sensor based on a block copolymer structural color film. (ii) Photographs of the sensor under different strains up to 100%. The scale bars are 1 cm.¹¹⁴ (B) (i) Scheme of the smart chemical sensor platform inspired by human's smell perception mechanism. (ii) Fingerprint pattern in the sensor arrays corresponding to benzene, toluene, xylene, and aniline, respectively.¹²³

a color shift could be triggered through volume change, thus enabling humidity sensing.¹¹⁵ Besides, by incorporating electrolyte or magnetic particles either in solution or in the polymer matrix, electric/magnetic based sensors have been explored (Table 1).^{46,57,59}

A chemical sensor, on the other hand, involves monitoring of chemicals including small molecules, charged species, as well as biomacromolecules. One of the key points is sensitivity and the ability to recognize different analytes. Song *et al.* introduced a beetle-inspired photonic crystal chip with patterned wettability features to realize ultratrace assays.¹¹⁶ They further created a rainbow-like structural color matrix chip with abundant sensing information, by which twelve saccharides can be distinguished.¹¹⁷ Li *et al.* reported a “breathing” metal-organic framework (MOF) inverse opal film. When exposed to various gases, the refraction index and/or the ordered structure of the MOF skeleton could be changed specifically, therefore enabling “self-reporting” vapor sensing performances.¹¹⁸ Lotsch *et al.* further prepared MOF-based Bragg stacks (BSS) for combinatorial vapor sensing with high analyte specificity by arranging dual MOF BSS in one platform.¹¹⁹ For the recognition of ions or biomolecules, the specificity of the sensors could be enhanced by functionalizing with certain binding agents including complementary DNA or antibody, molecular imprinting polymers, *etc.*^{52,120,121} Moreover, for distinguishing a broad range of chemicals, research studies have recently focused on

electronic noses/tongues by drawing lessons from mammalian's olfactory system, which relies on a pattern recognition process occurring in the brain.¹²² For example, Lee *et al.* fabricated a structural color array based on a phage-mediated liquid-crystalline nanofiber assembly.¹²³ After being functionalized with specific receptors, a fingerprint-like pattern could be generated upon exposure to certain volatile toxic chemicals, as shown in Fig. 7B. The results could be analyzed automatically through MATLAB image processing, and a smartphone-based wireless network system could be established, from which the images could be disseminated and interpreted against a fingerprint color pattern database.

4.4 Soft robotics

Robots are machines with desired abilities to perform tasks in real-life scenarios for human services including movement, perception, communication, *etc.* Soft robots, as one of them, refer to those constructed with intrinsically soft and deformable body materials. Compared to their rigid counterparts, soft robots behave in a way more like biological systems and allow for higher compliance for the interaction with humans.^{124,125} As one of the segments in a robot, the actuation system plays a vital role, and structural color-based actuators have recently attracted attention. Zhang *et al.* integrated photonic crystals with deformable materials to enable humidity responsive bending actuation.¹²⁶ Wei *et al.* developed a thermally triggered photonic crystal actuator by using an inverse opal/liquid crystal elastomer (LCE) bilayer film.¹²⁷ The thermally driven alternation of the nematic LCE order caused asymmetric shrinkage/expansion behavior of the bilayer, thus resulting in bending deformation and color change of the film. In addition to thermal actuation, Chen *et al.* reported a light-triggered actuator through a laminated film composed of a PDMS infiltrated colloidal crystal layer and a single-walled carbon nanotube (SWCN)-LCE layer, being separated by a PDMS glue.¹²⁸ Due to the photothermal properties of the SWNTs, the film could undergo a series of localized actuation upon infrared (IR) irradiation. Guo *et al.* further created a structural colored bionic hand performing complex and selective actuation by coupling a LCE inverse opal and graphene oxide (GO) as a thermal-mechanical unit and photothermal-conversion component, respectively.¹²⁹ The alternating pattern

Table 1 Examples of different structural color sensors

Stimulus/ analyte	Material components	Mechanism	Ref.
Mechanical	Block copolymer lamellae Elastomeric inverse opal Metastable colloidal crystal gel	Change of periodic structure Change of the lattice spacing Change of the interparticle spacing	114 47 and 54 112
Humidity	Liquid crystal-hydrogel composites Nanocrystal multilayers in hydrogel film Hydrogel inverse opal	Change of the helical pitch Change of the Bragg stacks lattice spacing Change of the lattice spacing	48 and 50 51 115
Temperature	Liquid crystal elastomer	Alternation of the nematic order	127
Light	Liquid crystal nonsymmetric dimer	Phase transition due to photoisomerization	56
Electric field	Ionic liquid-swollen block copolymer films	Electric-driven swelling/deswelling due to ions transport	112
Magnetic field	Magnetic colloidal crystals	Change of the interparticle distance	60
Small molecules	Metal-organic frameworks based inverse opal	Change of the effective refractive index	118
Ions	Colloidal crystal array in aptamer functionalized hydrogel	Hydrogel shrink due to specific binding	52 and 120
Biomolecules	Molecularly imprinted inverse opal hydrogel	Change of the lattice spacing and the refractive index	121

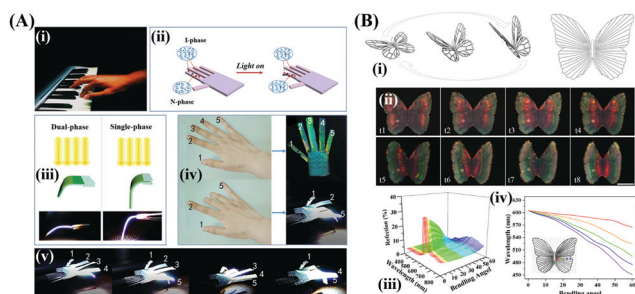


Fig. 8 Structural color soft robotics. (A) (i) A prototype of human finger playing piano. (ii and iii) Scheme of the bionic hand with alternating N-phase and I-phase and (iii) different bending performances of the films containing dual phase shown in (ii) and a single N-phase. (iv) Finger action of a real hand and the bionic hand. (v) A series of finger movement behaviors upon light irradiation.¹²⁹ (B) (i and ii) Scheme and optical microscopy images of the 3D artificial Morpho butterfly in one myocardial cycle. The scale bar is 2 mm. (iii) Dynamic reflective spectra at a fixed position of the wing's outer edge during one myocardial cycle. (iv) Relationship between the bending angle and the reflection peak values at different positions.¹⁹

of the nematic (N) and isotropic (I) phases contributed to versatile actuation modes and the resultant deformation behaviors. Thus, finger actions were achieved that recapitulated real hand performances, as shown in Fig. 8A.

Different from the above-described methods, which rely on external triggers, Zhao *et al.* introduced a self-actuated, 3D artificial Morpho butterfly.¹⁹ It was crafted using a biohybrid structural color hydrogel with radial microgroove patterns for laminar assembly of cardiomyocytes. The anisotropic cell contraction and relaxation behaviors triggered swinging of butterfly wings, as shown in Fig. 8B(i and ii). Meanwhile, the bending of the wings caused a gradual blue-shift of the reflection peak from the inside to the outer edge when observed at a fixed observation point. Also, during one myocardial cycle, for a certain fixed position, the different bending angles corresponded to specific reflection wavelengths, which served as unique structural color fingerprints, as shown in Fig. 8B(iii and iv).

4.5 Wearable electronics

Wearable electronic devices are desired to be conformally attached to the skin or organ for the real-time monitoring of health status by measuring and quantifying the signals generated from human activities. It offers a great opportunity for future development of personalized and preventive medicine.^{130–132}

In general, these systems should be stretchable, light-weight, and highly sensitive, for mimicking the human skin.¹³³ Structural color materials have been designed to meet these requirements. For example, Zhou *et al.* created an organogel photonic nanocomposite with high bending flexibility and deformation-insensitive structural colors based on the enormous mechanical contrast between the matrix material and the photonic aggregates.¹³⁴ Gu *et al.* reported a multifunctional wearable sensor based on a composite inverse opal acetylcellulose (IOAC) and oxide graphene (rGO) film to monitor human motion and sweat.¹³⁵ As shown in Fig. 9A(i), an rGO film was first generated through droplet casting and chemical

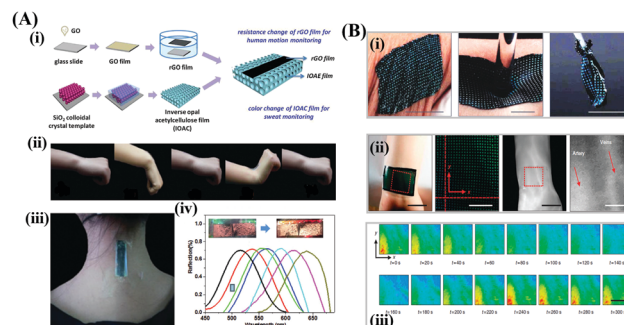


Fig. 9 Structural color wearable electronics. (A) (i) Scheme of preparation of the composite rGO-IOAC device. (ii and iii) Photographs showing the rGO-IOAC device attached on (ii) the wrist joint undergoing a series of movements and (iii) the neck. (iv) Color change and reflection spectra shift in response to different concentrations of NaCl in sweat.¹³⁵ (B) (i) Pictures showing the flexible e-TCL device under various deformation. Scale bars represent 3 cm, 1 cm, and 2 cm, respectively, from left to right. (ii) Optical images showing the e-TCL device on the wrist for reactive hyperaemia test and infrared images showing the spatial distributions of temperature. Scale bars represent 3 cm, 1 cm, 3 cm, and 1 cm, respectively, from left to right. (iii) Spatio-temporal mapping of temperature fluctuations during (starts at $t = 0$ s) and after (ends at $t = 160$ s) vascular occlusion. Scale bar represents 2 cm.¹³⁶

reduction, which was then transferred and fixed onto an IOAC film generated through a silica colloidal crystal template. The rGO layer served as a strain sensor for motion monitoring through a resistance change, and the IOAC layer was used for sweat ion concentration analysis through a color shift caused by the refractive index change (Fig. 9A(iv)). The resultant device was highly flexible to be mounted directly onto various parts in the human body such as the finger, wrist, neck, *etc.* (Fig. 9A(ii and iii)). In addition to motion recording, Rogers *et al.* developed a photonic device for thermal measurements by patterning thermochromic liquid crystals (TCL) into pixelated arrays on a stretchable elastomer substrate, as shown in Fig. 9B.¹³⁶ The thermal-responsive phase transition of the liquid crystal dots provided a colorimetric readout of the sensor, and the flexible and elastic nature of the substrate allowed for the device to be attached to the skin (Fig. 9B(i and ii)). By integration of electronics, it enabled radio localized heating by radio frequency signals. The resultant e-TCL device could be used for reactive hyperaemia assessment through spatio-temporal mapping of blood flow-related temperature fluctuations (Fig. 9B(iii)).

4.6 Organ-on-a-chip system

Organ-on-a-chip engineering aims at recapitulating organ-level cell functions *in vitro* and establishing models for human physiology or diseases.^{26,137} It is a rising field beginning with several early attempts in the 1990s^{138–140} and was formally termed by Donald Ingber in 2010.¹⁴¹ Since then, organ-on-a-chip research has been thriving, as it shows the potential for creating human surrogates instead of animal models for drug screening, clinical test, *etc.* In principle, organ-on-a-chip systems combine tissue engineering with advanced processing techniques including microfluidics, 3D printing, *etc.*, through

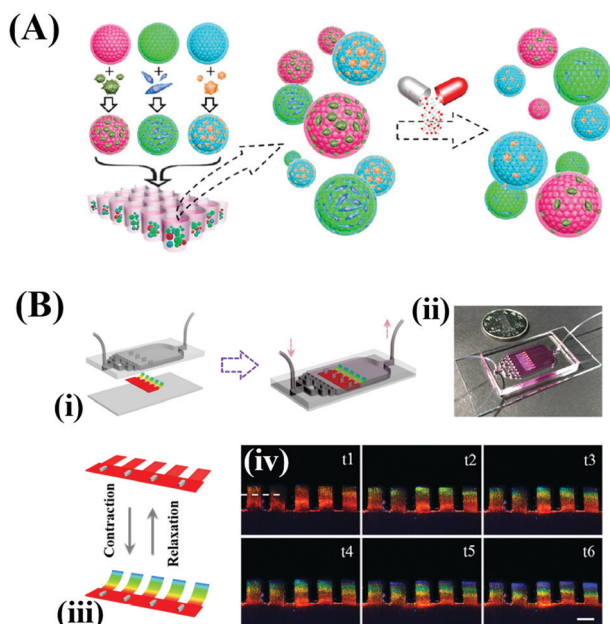


Fig. 10 Structural color organ-on-a-chip system. (A) Schematic of the photonic barcode-based suspension chip for drug screening.¹⁴⁵ (B) (i and ii) (i) scheme and (iii) photograph of the heart-on-a-chip device. (iii) The mechanism of the photonic sensor in (i). (iv) Dynamic bending and color shifting behavior of the sensor during one myocardial cycle. The scale bar represents 1 mm.¹⁹

which customized cellular microenvironments and tissue architectures could be constructed within a microfabricated device, thus enabling reproduction of organ-level organization, functions, and interactions.^{142–144} Structural color materials, as intelligent barcodes or sensors, could be incorporated into organ-on-a-chip systems to provide physiological readouts. For example, a suspension chip for drug screening was reported by using biocompatible photonic crystal particles as encoded barcodes.¹⁴⁵ As shown in Fig. 10A, three types of cell spheroids (including tumor and normal cells) were cultured on differently colored barcodes, respectively, and were then mixed and incubated in different drug solutions for cytotoxicity testing. Cellular responses could be distinguished by the barcode color. Such a coculture system provided a platform for cellular interaction and helped in establishing a hepatic-tumorous model for complex drug metabolism analysis. Besides, the photonic barcode-based suspension chips have also been employed for capture and detection of circulating tumor cells, as well as enzyme cascade reaction assays.^{146,147} In addition to suspension chips, microfluidic-based organ-on-a-chip devices were developed with responsive structural color materials being incorporated as built-in sensors. Zhao *et al.* developed a self-reporting heart-on-a-chip device by incorporating a biohybrid cardiomyocyte-inverse opal sensor into a bifurcated microfluidic chip containing cell culture medium and cardiac stimulants such as isoproterenol (Fig. 10B(i and ii)).¹⁹ The activities of cardiomyocytes under different stimulant concentrations could be detected based on the responsive bending and color shifting behaviors of the sensor, as shown in Fig. 10B(iii).

5. Conclusion and perspective

Taking inspiration from nature's masters of light, structural color materials have been widely studied in the past few decades. Great achievements have been made including understanding the fundamental mechanism of light-matter interaction, fabrication of artificial structural color materials, and exploring their applications in extensive fields. In very recent years, nature has continued to inspire researchers for endowing structural color materials with novel and remarkable functions such as self-healing, autonomous regulation, shape memory, *etc.* These break-through developments revolutionized the field of structural color materials by endowing them with not only appealing visual effects but also dynamic and adaptive properties. Structural color materials thus help create coloration-mediated human-environmental interactive systems and devices, and find applications in real-life scenarios such as anti-counterfeiting, displays, sensors, soft robots, wearable electronics, organ-on-a-chip platforms, *etc.* We herein provide a review of intelligent structural color materials with biomimicking functions and real-life applications. We focused on very recent discoveries of dynamic structural color phenomena in natural organisms, bioinspired intelligent functions integrated into synthetic structural color materials, and their applications in various frontier areas.

Although much progress has been accomplished in recent years, there remain challenges as well as huge space for development. First, the study on natural structural coloration is never enough. The intriguing color production and perception process are closely associated with multiple-level biological life activities including in physiology, behavioral ecology, and evolution. A deeper understanding of these behaviors would thus provide substantial implications of coloration-related biological functions far from just visual appearance. Besides, for the fabrication of bioinspired artificial structural color materials, some of the coloration-related nanostructures in natural organisms are very intricate, which but brings extremely high complexity for reproducing. To address such problems, novel manufacturing strategies are anticipated, such as by combining “top-down” techniques with “bottom-up” strategies, and by drawing support from additive manufacturing, or even genetic engineering. In addition, regarding their properties, synthetic structural color materials could go beyond nature. By incorporating novel materials, such as plasmonic or metal nanoparticles, combined optical effects or other features could be anticipated that are unavailable in nature. Moreover, there is still much room for improvement as for the applications. With a function-oriented design and feedback system, the next-generation devices could become even more intelligent to accommodate more complicate environmental interactions and implement customized integration tasks. Finally, before stepping out of the lab and getting into the market, the durability, portability, robustness, and scalability of structural color materials should never be neglected. By rational integration of mathematics, structural mechanics, surface chemistry, and rapidly developing engineering techniques, future structural color platforms or devices could become even more advanced.

Overall, the ability to modulate light propagation is the most significant and irreplaceable property of structural color materials, which should make them shine brilliantly in addressing future global challenges in health, energy, environmental, and other fields.

Conflicts of interest

There are no conflicts to declare.

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