TOPICAL REVIEW

Material design and structural color inspired by biomimetic approach

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Abstract

Generation of structural color is one of the essential functions realized by living organisms, and its industrial reproduction can result in numerous applications. From this viewpoint, the mechanisms, materials, analytical methods and fabrication technologies of the structural color are reviewed in this paper. In particular, the basic principles of natural photonic materials, the ideas developed from these principles, the directions of applications and practical industrial realizations are presented by summarizing the recent research results.

Keywords: structural color, material design, biophotonics, biomimetics

1. Introduction

Colors are produced from various principles such as optical absorption (e.g. pigment), emission (e.g. light emitting diode (LED)), interference (e.g. bubble soap or rainbow coloration on a compact disc) or scattering (e.g. blue sky or red sunset). The ‘structural color’ is a type of coloration originating from microstructure variation at a length scale comparable to the optical wavelength. It is found in nature, for example in pearl, jewel beetle, peacock tail and fishes [1, 2]. This coloration is generally accompanied with a brilliant metallic luster, and has long attracted scientific interest [1–8]. Recently, a variety of mechanisms have been found in the nature. Some of them are related to photonic crystals [10–15], which are a new trend in photonics.

The structural color has a variety of potential applications, because of its long-term resistance to discoloration due to chemical change; furthermore, it cannot be reproduced by pigments, and pigment-free coloration is preferable from ecological viewpoint [16]. This application-wise approach can be combined well with the biomimetic one that attracts interest because of the green technology, as summarized in this journal issue.

Many coloration technologies are based on opal-like structures, which are tunable and have recently been studied for applications [17, 18], or plasmon [19], which is unrelated to the structural color. Some synthesis methods of static structural colors have already been realized and might find industrial applications. In this article, I review the biomimetic material design and fabrication techniques of structural colors by presenting the ideas and examples aiming toward practical applications; its main parts are dedicated to structures inspired by the Morpho butterflies, beetles, pearls and moth eye.

2. Color materials

2.1. Color materials inspired by Morpho butterflies

2.1.1. Principles of the Morpho-color. The brilliant blue color of some Morpho butterflies has long been an important research subject [1, 2, 5–8]. The color is produced by the wing scales, which are composed of nearly transparent cuticle proteins. The principle of this phenomenon has been referred to as grating or multilayer, which also explains the high reflectivity of the blue coloration. This blue luster is not
affected by chemical change and lasts for more than 100 years (the structural color can be found even in fossils [19]).

However, the Morpho-blue reflection spectrum cannot be explained by grating or multilayer—the color appears blue in too wide angular range (more than ±40° from the normal). The uniformity of the color in such a wide angular range contradicts the characteristics of the interference effect. The lacking multicoloration has recently been explained by the ‘discrete multilayer’ model [21]. This model contains both ordered (regular) and random (irregular) structures, which are not randomly mixed but form a specific architecture.

Figure 1 shows the wing structure a typical Morpho butterfly (Morpho didius). A cross-sectional scanning electron microscopy (SEM) image (figure 1(b)) reveals a fine and complex three-dimensional structure, with the ridges seen in a top view (figure 1(c)). This structure is characterized by one-dimensionally arrayed shelves, each composed of a multilayer. From these features, a structural model can be constructed, as shown in figure 2 in cross-sectional and top views. This model can be summarized as follows [16, 22]:

1. The blue coloration is produced by interference in a single shelf, which is composed of alternating layers of high and low refractive index materials.
2. The blue color is diffracted into a wide angular range because the width of each shelf (~300 nm) is less than the wavelength of visible light.
3. The arrangement of individual domains has randomness in height (feature 3 in figure 2(a)) and in-plane structure (figure 2(b)); this randomness suppressed the multicolor (rainbow) interference and produces the speckle-like luster. The randomness in height is within one wavelength.
4. The close proximity of neighboring domains results in high reflectivity—if the gap is much wider than the wavelength, the incident light reaches the bottom of the multilayer and is absorbed or transmitted through the substrate. For high reflectivity the gap must be narrower than one wavelength (~450 nm).
5. As shown in figure 1(c), the pattern extends along the Y-direction, but forms a random array of discrete linear sections. This quasi-one-dimensional anisotropy plays an important role in generating the high reflectivity in a limited angular range from the Y-direction. Otherwise, if the pattern is isotropic, the reflection is scattered two-dimensionally, decreasing critically at any viewing angle. The randomness also suppresses the multicolor interference, as mentioned above. As shown in figure 2(b), this quasi-1D pattern can be approximated as rectangular units of different heights distributed randomly with an interval of ~2 µm in the Y-direction.

The above model has been experimentally verified by fabricating and testing specific nanostructures, in which several parameters (figures 2(a) and (b)) were controlled at the 100 nm scale. The basic reflection properties were reproduced, i.e. high reflectivity with a wide angular distribution, anisotropy, and speckle-like brilliance [16, 22]. The functions of each part in the collective shelf structure are discussed in [23–26]. For example, the role of different kinds of disorder in the Morpho-structure was investigated using finite-difference time-domain (FDTD) method that enables analysis even for non-analytical objects. The results showed an essential role of the incoherence in the incident light. Also, the lateral and vertical randomness in the structure and the number of random components were found to have their own roles in realizing the specific Morpho-color, resulting in the anomalously low angular dependence of the color, without sharp fringes, despite an interference effect [27].

2.1.2. Fabrication of the nanosized color-producing part. The principles discussed above originate from the disorder in the arrangement of the ‘shelf’ structures, and the optical properties of a single shelf have been studied using a synthetic structure. Matsui et al fabricated a Morpho-butterfly scale using focused ion beam chemical vapor deposition (FIB-CVD) and observed brilliant blue reflection from this quasi-structure in an optical microscope (figure 3). They measured the reflection spectra from real Morpho butterfly scales and from the quasi-structure with a photonic multichannel spectral analyzer system, and found that they are similar [28].

2.1.3. Replica method. Another approach to reproduce the specific coloration of the butterfly is to fabricate directly a replica of the butterfly’s scale using atomic layer deposition (ALD) technique [29], differently from the mimetic approach.
2.1.4. Recent progress for industrial applications.

The discussed above synthesis techniques may have potential limitations for industrial applications—FIB is costly and time consuming, whereas ALD has a limited control and is hardly suited for mass production because it uses the mold (protein) made from the real butterfly scale.

For realistic applications, the design of the color material and the fabrication process should be simplified. Thus, while studying the principles on the discrete multilayer discussed in section 2.1.1), we identified the details and principles of the *Morpho*-blue butterfly wing structure. We emulated it by a dielectric multilayered nanostructure on the stepped quartz, which was fabricated by electron beam lithography and dry etching, a simple and conventional technique in the semiconductor industry [22].

Specifically, a multilayer composed of alternating layers of high and low refractive index materials (figure 5(b)) was deposited on a nanopatterned surface shown in figure 5(a). The parameters of the nanopattern, i.e. the gap, width, randomness and the quasi one-dimensionality, were set using the model system of figure 2. The most important step is then to engrave the substrate surface (figure 5(a)) by controlling the gap and width (set by parameter W in figure 5(b)) that simultaneously includes randomness and quasi one-dimensional anisotropy.

We composed a surface pattern containing randomly distributed rectangular units of $300 \times (2000 \pm \sigma) \text{nm}$ (figure 5(a)) where $\sigma = 500 \text{nm}$ is the standard deviation of the Gaussian distribution, i.e., the parameter W in figure 5(b) was set at 300 nm. The depth of the pattern ($D$ in figure 5(b)) was set at 110 nm to prevent the normal reflection of 440 nm light (blue color) from the multilayer. This depth condition helps the blue light scatter over a wide range of angles. To produce the desired surface pattern, conventional electron beam lithography and dry etching were applied to quartz substrates (figure 5(a)). The distance between the rectangular units was determined by a random number generated by a computer program.

The process was finalized by step-by-step electron-beam-assisted deposition of seven bilayers of TiO$_2$ (high refractive index layer, $\sim 40 \text{nm}$ thickness) and SiO$_2$ (low refractive index layer, $\sim 75 \text{nm}$ thickness, figure 5(b)). This simple process allowed reproducing the *Morpho*-blue wing structure. Oxides are the best materials for the multilayer deposition because of their wide range of refractive indices and because their thickness can be accurately controlled. In all experiments, the material was designed to have the reflection maximum at 450 nm.

The produced structure showed the basic optical reflecting properties described in section 2.1.1) [16, 22]. Importantly, the reproduced *Morpho*-color was found to suit a wide range of applications, as it offers a single color with a high reflectivity and wide angular range without using a pigment. It is important from the industrial viewpoint that a significant film size was combined with control of the nanoscale structure. Furthermore, a corresponding mass-production method was developed using nanoimprinting (figure 6) [31, 32].

Realistic applications require optimization of the cost, time, size, shape and optical properties (angular dispersion, colors) of the produced nanostructures [33, 34]. For this purpose, we have recently developed a new process...
Figure 4. Optical microscopy images of alumina-coated wing scales of Morpho butterfly, revealing variation of color with the thickness of deposited alumina. The uncoated scale is blue. (Reproduced with permission from [29] ©2006 American Chemical Society.)

Figure 5. (a) SEM image of a quasi-1D pattern fabricated by conventional electron beam lithography on a quartz substrate before multilayer deposition. (b) Schematic of the multilayer fabricated by depositing TiO$_2$ and SiO$_2$ layers on the structure (a) to mimic the mechanisms presented in figure 2.

Figure 6. Photographs of (a) Morpho butterfly wing, (b) replicated Morpho-blue plate, (c) synthetic Morpho-blue plate developed by nanoimprinting for mass-production.

where femtosecond laser processing is combined with electroforming. The process features fast (1000 times faster than in previous methods), large-area fabrication of the nanopattern having both random and anisotropic structures specific to the Morpho-color. It is based on self-organization and is suited for practical applications [35]. This fabrication process was combined with FDTD simulations [27] used for generating the random structure. Such simulations allow not only analyzing random optical structures but also designing their optical properties. The described above process illustrates the recent tendency in biophotonics to target not only pure science but also technology, as outlined in this review.

2.2. Glittering materials

Materials having structural metallic color are used in cosmetics, decorations in cars and watches, and some other items. Nevertheless, the biomimetic structural colors are still limited to some applications presented below.

2.2.1. Artificial opals. Opal is a representative structural color material. It is well known as a jewel found in the nature, sometimes originating from a fossilized tree or animal’s bone. In nature-mimetic research, opal has long been one of the objects to produce the specific ‘opalcent’ luster (play of color) for industrial applications. Natural opal is composed of silica spheres (100–300 nm in diameter) forming a hexagonal or cubic close-packed lattice. Iridescent colors are produced via interference and diffraction of light passing through or reflected from the ordered arrangement of spheres in opal.

One of the most common synthetic opals is Kyoto Opal (figure 7). It is produced by Kyocera using original techniques developed after the pioneering work by Pierre Gilson [36]. The Kyoto Opal has a slightly different composition than its natural counterpart. It lacks water, which is usually found in natural opal, and may contain some plastic or silica
compounds used to cement the silica spheres instead of water [37]. Cultivated with a quartz-grain structure that is identical to naturally occurring opal, the Kyoto Opal has a unique aesthetic quality that cannot be duplicated with molded resin-based products. Kyocera realized a variety of rich and subtle hues and tints using special staining techniques based on infiltration of organic compounds between the close-packed silica spheres. By surmounting the inherently brittle characteristics of naturally occurring opals, which tend to split and crack, it is possible to cut the Kyoto Opal into diverse shapes.

Flexible opal-containing composites were realized by applying a traditional Japanese technique of manipulating hard objects for kimono designs to 0.2-mm-thin sheets of Kyoto Opal. They are used in buttons for clothes and may find other applications. Synthetic opal is also used in the new G-Shock watches by Casio.

2.2.2. Cosmetics. Another important application of glittering materials is in nacreous pigments, for which another color mechanism is being developed based on the pearl-like interference. These color materials can be applied for cosmetics, decorations and paints.

Nacreous pigments are major ingredients in make-up cosmetics, owing to their pearly shine and conspicuous tone of coloration. Most nacreous pigments, which are currently used in cosmetics, contain mica coated with titanium dioxide (TiO$_2$-mica), which might be unstable to light or heating above $>50$ °C, unsafe, and limited in the spectrum of colors. TiO$_2$-mica is a combination of thin mica flakes with a low refractive index (1.5–1.6) and TiO$_2$ with a high refractive index (2.5–2.7), and its interference colors are adjusted by varying the thickness of the TiO$_2$ layer. When pigments such as iron oxide, chromium oxide or carmine are added to TiO$_2$-mica, the product is called a ‘colored nacreous pigment’.

To improve the conventional colored nacreous pigment, Kimura [38] coated mica first with a black reduced titanium oxide (TiO$_{2-x}$) or titanium oxyxnitride (TiON) and then with TiO$_2$ (figure 8). The products had an improved color tone and stability. Their colors were tuned by adjusting the thickness of the TiO$_2$ layer, i.e. via light interference rather than addition of pigments. Absence of pigments makes this new material safer to use [38].

Researchers from Kao company replaced the central mica core with void [39]. Aided by computer simulations, this design can be used to increase the reflectance, especially in the short-wavelength range [40].

2.2.3. Textiles. One of the most well-known examples of direct biomimetic applications is adding luster to fibers. The color of the resulting textile material is derived from the multilayer interference of the *Morpho* butterfly, and this is the first application of the *Morpho* butterfly’s coloration.

Tabata fabricated a non-circular structurally colored fiber by conjugated melt spinning (figure 9). The fiber had a sectional structure containing a stack of alternating layers of two polymers with different refractive indices. The unique optical characteristics of these dye-free, structurally colored fibers based on biomimetics and their application are discussed in the literature [41]. The molding of such microstructural fibers was accomplished using a setup where the molten polymers passed through a specially designed metal mold installed in a spinning head and were wound by a winder. In the metal mold, an array of counter pores alternatively provided the polymers (polyester and polyamide) that enabled fabricating the multilayer of polymers. After cladding of the multilayer by polyester, the fiber was flattened by the specific mold. The fabricated structure had a multilayer core covered by polyester, resulting in structural blue, green or red colors owing to light interference [41].
In another example [42] Sawanoi et al manufactured new polyester composites using two methods: combining a polyester resin and pearl luster pigments into fibers, and adding a colorful design to a polyester-knitted fabric with an inkjet printer. As a result, the authors established a technique of pelletizing polyester resin, which contains pearl luster pigments, and spinning it. The resulting polyester fiber contained pearl luster pigments and provided a broad angular distribution of color at moderate intensity. Also, irregularly colored polyester fibers were obtained using an inkjet printer.

2.2.4. Paint. Pigment-free paints are well known. However, most of them are based on the surface plasmon in metal nanoparticles (Au or Ag) rather than on the structural color [43, 44]. On the other hand, the mentioned above TiO$_2$-coated mica [38] or coated fiber [41] materials can be used in pigment-free paint by mixing the color materials in the liquid solvent, and their applications are not limited to cosmetics or textiles. These paints are advantageous for their safety, stability (owing to lack of colored pigments) and anisotropic and glossy color. It should be noted that the resulting color and brilliance will be affected not only by the bulk properties of the additive but also by reflections from the edges of its particles or chips. Structural-color materials have been developed for paint applications using different optical principles and are found in the market, but the use of bioinspired principles remains limited despite their various advantages. One example of bioinspired paint is the urushi (lacquer tree) coating, which is still in the development stage. The peculiar brilliant color of this coating with specific hue has been demonstrated in test samples of round trays (figure 10) [45].

2.3. Reflective color display

Biomimetic color materials serve as a color-producing device in electronic visual displays, especially in reflective color displays. Currently, most reflective color displays use E Ink (electrophoretic ink), which relies not on optical interference but on manipulation of tiny capsules with electric field. These capsules are filled with positively charged white particles and negatively charged black particles and are suspended in a clear liquid [46–48]. Qualcomm uses a new type of optical-interference-type display that consists of tiny cavities between two layers of mirrors. A tiny electromechanical switch under the bottom mirror controls the spacing between the mirrors, thereby amplifying a particular color of light, while canceling out others [49].

While not a fully biomimetic principle, a principle common with the biological color is already realized in a commercial reflective display by Fujitsu Ltd [50]. The cholesteric liquid-crystal display (LCD) of Fujitsu FLEPia operates on a principle similar to that of some beetles (figure 11). Its elements are bistable, meaning they can remain in either a reflective or non-reflective state without a need for electric power. These LCDs do not require a backlight. They consume less power and should be easier to build. However, they have limited refresh speed and are costly.

2.4. Light-emitting sources

The last direction in the applications of biomimetic structural color is light-emitting sources, i.e. LED and laser.

Hwang et al have first constructed a structure mimicking the cuticle of a beetle (Plusiottis resplendens), and by doping
Figure 11. Principle of the color production in the Fujitsu FLEPia display. (Reproduced with permission from [50] ©2011 Fujitsu Ltd.)

Figure 12. Photographs of a Plusiotis batesi beetle, which has a single helix structure and shows a conventional selective reflection, and a Plusiotis resplendens beetle, which has an anisotropic layer sandwiched between two L-helical CLC layers with the same pitch and shows total reflection. Left and right images were taken through left and right circular polarizers, respectively. An optical diode design was inspired by these beetles. (Reproduced with permission from [51] ©2005 Nature Publishing Group.)

the anisotropic defect layer with a laser dye achieved efficient lasing (figure 12). Next, they extended the studies to a new anisotropic optical-heterojunction structure consisting of an anisotropic layer sandwiched between two cholesteric liquid crystal (CLC) layers with different periodicity of helix (photonic bandgap heterostructure). With this structure, they realized both lasing and optical diode effect, that is, directional light emission [51].

The same authors also constructed a low-threshold dye-doped CLC laser with a tunable emission wavelength by developing a new dye and combining it with the above-mentioned CLC. The low threshold and the lasing spectra observed at the high-energy edge of the photonic bandgap can be attributed to the orientation of the transition dipole moment of the dye molecules. These results can be used as guidelines for designing new dyes [52].

3. Applications of moth-eye structures

This field is the most advanced among the biomimetic photonic applications.

Figure 13. Arrays of corneal nipples in the nymphalid butterfly Polygonia c-aureum (a) and the lycaenid butterfly Pseudozizeeria maha (b), showing differences in nipple height and shape. Scale bar corresponds to 500 nm. (Reproduced with permission from [53] ©2006 The Royal Society.)

3.1. Original functions of the moth-eye structure

The basic principles of moth-eye structures are discussed in recent papers from biological viewpoint. The main function of corneal nipples is presumably to reduce the eye glare of moths that are inactive during the day, thereby making them less visible to predators. Thus, this feature is subject to evolutional modifications. For example, moths might be ancestral to the diurnal butterflies, suggesting that the reduced size of the nipples in most butterfly species is a sign of a vanishing trait. This effect is extreme in papilionids, which have virtually no nipples, in line with their highly developed status (figure 13) [53].

Another type of antireflector consists of parallel ridges with a rectangular profile and is employed on solar absorbers [54], where angle-independent antireflection properties are required. Parker et al reported such a structure on the corneal surfaces of fossilized flies. This ‘fly eye grating’ acts differently from the moth-eye structure; it is an efficient antireflector of white light at angles up to 60°, and has a reduced reflection even for angles beyond 60° [55].

From the physiology viewpoint, the basic function of the moth eye is discussed in studies of the pupillary response in the superposition eye of noctuid moths while presenting incremental (light on) and decremental (light off) light stimuli. Spectral response curves for pupillary and electroretinogram responses are rather similar, suggesting that the aperture size in noctuid moth eyes is controlled by retinula cell activity [56].
3.2. Applications

Dimpled surfaces have long been studied as an attractive alternative to multilayer antireflection coatings. The surfaces imitating the moth eye and comprising arrays of subwavelength-scale pillars are applicable to solar cells, photodetectors and stealth technologies [57]. Their low reflectance extends over a wider spectral range and is more thermally stable compared to conventional multilayer dielectric coatings [58].

3.2.1. Pioneering phase. The principles of low reflection by the moth eye had been first mentioned in the early work on the light–dark adaptation in certain moth species, which showed that the presence and migration of pigment are not crucial for the light–dark adaptation of the eyes of nocturnal moths [59]. They were then explained by the inhomogeneity of the refractive index in the crystalline cone of the moth eye (figure 14) [60] and experimentally verified by measurements on a manufactured model structure [61].

Considerable technological development is still required before these principles can become a practical alternative to multilayer coatings—one needs to define the range of shapes, materials, fabrication processes and perform theoretical modeling of the properties, considering the film adherence, surface roughness and the refractive index mismatch between air and the film.

In the early application studies of the moth-eye structure, an antireflective coating was deposited on Ge which combines a polycrystalline diamond film with a surface relief of the moth eye structure. This structure exhibited several properties desirable for optical applications, such as high hardness, transparency from UV to far infrared wavelengths, chemical inertness and high laser damage threshold (figure 15) [62].

In addition to developing new antireflective structures, the existing ones can be optimized by comparing theoretical and experimental results. For example, broadband a modulated optical waveguide. An incident light wave satisfying the resonant condition is reflected by the GMRG filter, and nonresonant light waves pass through the filter. Such GMRG filter reduces reflection of nonresonant light waves in a wide spectral range [63].

3.2.2. Theoretical developments and derived structural design. In parallel with the experimental studies, theoretical basis was developed for analyzing and predicting the optical properties of the moth eye (figure 16). To test the theoretical predictions for the array structures, the reflection properties of periodically structured silicon surfaces with a varying depth, prepared by interference lithography, were examined in the wide wavelength range (200–3000 nm). The results show universal trends in the dependence of reflectivity on the optical-path to wavelength ratio and agree well with the effective medium theory (figure 16(a)) [64].

To examine the variation of the light extraction efficiency with the aspect ratio, Kasugai et al calculated the light extraction efficiency of LEDs with a moth-eye structure by the rigorous coupled wave analysis (RCWA) [65]. The results were compared for two common simulation methods, RCWA and thin-film multilayer model, and were found identical for the templated nipple arrays. Such simple bottom-up arrays are compatible with standard microfabrication procedures and can reduce the manufacturing cost of crystalline silicon solar cells [66].

A new antireflective periodic principle different from the moth-eye structure was proposed from theoretical considerations. The structure is based on a resonance domain with a period greater than the wavelength of incident light. Using rigorous coupled-wave analysis, a reflectivity of less than 0.2% was predicted for a period larger than the wavelength, when the aspect ratio is unity. The resulting optical properties were explained by a newly derived equation based on the vector theory [67].

In addition to developing new antireflective structures, the existing ones can be optimized by comparing theoretical and experimental results. For example, broadband
antireflection schemes for silicon surfaces are important for solar cells, photodetectors and stealth technologies and can result in a very low reflectance. Boden et al showed that rigorous coupled wave analysis can be used to accurately model the intricate reflectance behavior of these surfaces and explore the effects of surface feature parameters such as height, period and shape. This approach allows tailoring the surface geometry for specific light spectrum and applications [57].

Microstructures based on the moth eye have attracted attention not only for their low reflection in a wide range of wavelengths and incident angles but also for high laser-induced damage threshold. An accurate theoretical model taking into account photoionization, avalanche ionization and decay of electrons has been developed to predict the damage threshold under femtosecond laser irradiation [68].

Further improvements of the moth-eye structure are being proposed on theoretical grounds. The moth-eye structure was modeled as an array of microlenses with a near-parabolic shape, and such a coherent array of micrometer-sized close-packed microlenses was fabricated on spherical or aspherical surfaces using a compact holographic projector system (figure 16(b)) [69]. A different approach was proposed by Huang et al. They manufactured a simple aperiodic array of silicon nanotips with a sub-wavelength structure on a 6-inch wafer and demonstrated that it can suppress reflection of electromagnetic waves from the ultraviolet to the terahertz region (figure 16(c)). These antireflection properties result from changes in the refractive index caused by variations in the height of the silicon nanotips [70].

3.2.3. Advancements in the manufacturing methods. Beside the progress in device performance, theory and structural design of antireflective structures, fabrication methods have been significantly improved over the last decade (figure 17). First fabrication methods used photopolymeric resins, which were modified using an interference pattern created by a holographic projector system [69] or processed with interference lithography [64]. Then a highly ordered periodic modulation was created on the surface by reactive-ion etching. Alternatively, columns terminated by pyramid-shaped tips were deposited on silicon and steel substrates by reactive radio-frequency magnetron sputtering [71].

New techniques have emerged during the last several years, such as ‘colloidal lithography’ combined with the following etching process. Nakanishi et al used a self-assembled monolayer of nanoparticles as an etch mask. They developed a method of fabricating a homogeneous monolayer of embedded particles over a large area with a high throughput. By transferring the pattern of the particle monolayer onto the substrate, nanostructures were deposited all over the substrate. A moth-eye antireflection surface consisting of a nanocone array was fabricated on fused silica using this technique (figure 17(a)) [72].

A number of derivative methodologies have been developed afterwards using different materials [73], as summarized in review [74]. In that review, bio-inspired surface structures are presented aiming for creation of antireflective, self-cleaning and drag-reducing surfaces, as well as new types of adhesive systems. They are not limited to the moth eye, but also include leaves, shark skin and the feet of reptiles. There is also an overview of mass-production techniques of such surfaces, including master structures and surface replication methods.

Other techniques are being developed independently, for example, using fluoropolymer nipple arrays created with a soft-lithography-like process. Such arrays share the functionalities of antireflective moth eyes and super-hydrophobic cicada wings [75]. Within colloidal lithography, non-close-packed colloidal monolayers are used as etching masks to pattern subwavelength-structured nipple arrays on GaSb, aiming to develop efficient thermophotovoltaic cells [58]. A non-close-packed colloidal template was applied to crystalline GaAs wafers to create efficient solar cells or IR detectors [76]. Alumina gel films were produced with the sol–gel technique and coated on poly(methyl methacrylate); then pseudo-boehmite crystals with a size of several tens of nanometers were precipitated on the surface of the alumina gel films through immersion in hot water [77]. Roller nanoimprint lithography (NIL) [78] was used to improve conversion efficiencies of silicon solar cells (figure 17(b)), whereas UV-NIL was combined with embossed poly(vinyl chloride) template to deposit a polymer-based moth-eye structure on glass (figure 17(c)) [79]. UV-NIL is one of the most frequently applied techniques of fabricating the moth-eye structure [80], it may be combined with the thermal NIL [81] or even with the Blu-ray Disc technologies [82].
3.2.4. Range of applications. The progress of the fabrication methods is accompanied by the development of new applications (figure 18). Typical examples are (i) a liquid crystal display (figure 18(a)); (ii) a group-III nitride-based blue LED on 6H–SiC substrate, where the moth-eye structure on the LED increases the light extraction efficiency and thus the output power (figure 18(b)) [83, 84]; (iv) a GaN top cladding layer to improve the light extraction efficiency of GaN-based green LEDs [85]; and (v) two-dimensional, periodic, highly ordered array of subwavelength-sized organic LEDs (figure 18(c)) [85].

An uncommon yet original application is based on an inverse polarization phenomenon in moth eye structures that arises from TM-polarized light having a higher reflectance than TE-polarized light (here TM stands for transverse magnetic and TE for transverse electric) at angles of incidence near the Brewster angle [87]. Apart from optical effects, the surface hydrophobicity is enhanced by increasing the height of Si nanowires on optoelectronic devices [88] that can be used in a micro fluidic system containing hydrophobic and hydrophilic channels for fuel cell applications [89].

One of the biggest applications of the moth-eye structure is the optimization of the efficiency of solar cells. Optical losses in an organic solar cell with a moth-eye antireflection coating were estimated in [90]. An antireflection moth-eye structure was made of acrylic resin and deposited on a poly(ethylene terephthalate) substrate to enhance the efficiency of crystalline silicon (c-Si) solar cells [91]. A protective layer for solar cells was patterned with a nanosized moth-eye structure to increase the total conversion efficiency (figure 18(d)) [92]. A nanopattern was formed on both sides of a glass plate, which was used as the protective layer of a solar cell. This modification increased the total conversion efficiency by 2.5% [93]. A moth-eye pattern also reduced reflectance and enhanced total conversion efficiency of a GaInP/Ga(In)As/Ge solar cell [94]. Finally, a moth-eye pattern, formed on the front surface of an amorphous silicon based thin-film solar cell using NIL, not only increased the total conversion efficiency by ~3%, but also added a hydrophobic, and thus self-cleaning functionality [95].

3.2.5. Efforts for practical applications. Realistic applications require high efficiency of fabrication and homogeneity over large moth-eye surface areas. To observe the structure defects on the entire surface of a 6–8 inch wafer, an optical filtration setup has been proposed [96]. Besides, fabrication procedures were improved to cover a 12-inch silicon wafer with moth-eye structures at low cost (figure 19) [98].

4. Summary and outlook

Significant progress has been achieved recently in biomimesis and its applications. The structural color has been explored for structures, properties, manufacturing techniques and theory, although many parts need a further development aiming at industrial applications. The structural color offers several promising advantages such as the ability to produce tunable color without pigment, with a tone which cannot be achieved using pigments—brilliant luster with high reflectivity, speckle-like reflection, etc. The absence of pigments make structural color environment friendly and resistant to fading due to chemical reactions.

The color of *Morpho* butterflies was reproduced in the laboratory to study its optical principles, but it also has
many potential applications. The reflected light has both wide angular range and high reflectivity, and this rare combination is invaluable for display applications. To reiterate, nanostructures can produce tunable monochromatic color without pigments, in a wide angular range; with a high reflectivity, specific hue (without fringes) and long lifetime. They can be based on robust inorganic materials which can offer strength, resistance to heat and fire, and a wide range of refractive indices.

The applications of the structural color include cosmetics, decorations, dressing and furnishings, textures, paints, security (e.g. holograms), posters and displays. However, they are hindered by the development of fabrication processes and theoretical design.

Technology demands high-throughput, inexpensive processes. As shown in this review, conventional processes such as nanoimprinting, advanced lithography, wet processes, etc., which have long been developed in the semiconductor, electronic and/or optical industries, were applied to generation of structural color. However, dynamic control of the structural color remains problematic, and this hinders many display applications which require rapid refresh rates (more than 50 Hz). Although no direct solutions for the dynamic control have been provided yet, many new technologies are being developed, such as ‘magnetically tunable structural color printing (figure 20)’ [98] and ‘localized strain history’ [99]. While the future of display applications will depend on the improvement in the dynamic properties, the static structural color for use in posters, paints, decorations and cosmetics currently appears as the most promising application area.

Theoretical modeling of structural color is required for the analysis and optimization of photonic structures, and it has been profited from the recent progress in theoretical and numerical simulation methods, such as FDTD analysis.

Studying nature can provide solutions to the problems in realizing the structural color, and its new types have been found recently [12] owing to the rising popularity of biomimetics research. New biomimetic approaches are being developed such as ‘colour-barcode’d magnetic microparticles for multiplexed bioassays’ [100], ‘mimicking the colourful
wing scale structure of the *Papilio blumei* butterfly [101], etc. Although most of these approaches are still at the exploratory stage, they might bring new ideas to the existing applications. For example, solar cells can be modified not only with the moth-eye structure, but also with the *Morpho*-color, as the solar cell will absorb a wider range of angles and wavelengths of incident light if a *Morpho*-colored film is placed at its bottom. These considerations extend beyond optronic devices; for example, the *Morpho*-structure has been applied to gas sensors [102] and water-repelling [103] or temperature-regulating materials [104]. Such multifunctions will provide us with novel ideas, in addition to those presented in this review (figure 21).

Figure 20. Schematic of the production of multiple structural colors with a single material, which can be controlled by an external field. Under an external magnetic field, nanoparticles are assembled to form a chain-like photonic nanostucture. This structure acts as a color unit, and the color can be tuned by varying the interparticle distance through modulation of the external magnetic field intensity. (Reproduced with permission from [98] ©2009 Nature Publishing Group.)

Figure 21. Advantages of biomimetic structural coloration and potential applications.

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