require the nondrug components of the device to occupy minimal volume. Suitable candidate drugs should be potent, should be formulatable as highconcentration preparations, and should be stable for extended periods at body temperature.

Materials

The materials of construction of an implantable device need to meet a wide range of requirements. Originally, the substrate was silicon, but the category is no longer limited to silicon-based devices. Polymers have superior properties to silicon for BioMEMS applications with regard to cost and versatility of physical properties. To provide more design flexibility, biocompatible polymers like polymethylmethacrylate (PMMA) and polydimethylsiloxane (PDMS) are being investigated as alternative materials to silicon.

The exterior of the device must be biocompatible. The primary materials and associated leachables must be nontoxic over long device use periods. The materials must be stable in contact with physiological fluids and tissues. In particular, the metal and/or polymer in contact with the body must have minimal leachables and be hypoallergenic.

Future Work

MEMS and miniaturization technologies have been used for producing novel stimuli-responsive drug delivery microchips that require minimal invasiveness of the medical procedures. Future development of ideal implantable drug delivery microchips requires several subsystems to provide all necessary functions: electrical components for selectively addressing individual reservoirs, biosensors for information acquisition, wireless communication hardware for remote control and a power source. These drug delivery microchips will be tailored for personalized medicine and other unmet medical need.

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Stimulus-Responsive Polymeric Hydrogels

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Strain Gradient Plasticity Theory

Plasticity Theory at Small Scales

Structural Color in Animals

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Synonyms

Animal coloration; Biological photonic structures; Biological structural color; Bio-optics; Bio-photonics

Definition

Intense and bright colors result from the interaction of light with periodic micro- and nanostructures that cause color by interference, coherent scattering, or diffraction. These colors are termed structural colors, and structures that cause color by modulation of light are called photonic structures. Photonic structures are usually composed of regular lattices with periodicities on the order of the wavelength of light. Various organisms in nature are known to use intriguingly diverse photonic structures.

Introduction

Structural Colors and Photonic Structures

Structural colors in the animal kingdom have attracted increasing research interest in recent years. Biological organisms offer an enormous variety of periodic micro- and nanostructures that by specific interaction with light provide distinct coloration. This sometimes dynamic reflectivity is tailor-made for the organism's purpose within its natural illumination environment. Intriguing photonic structures have been identified on the wing cases and armors of beetles, the scales of butterflies, the feathers of birds, in the shells of marine animals, or even within the skin of mammals. Nature offers a huge choice of blueprints for novel artificial optical materials and photonic structures. The strongest color contrasts are achieved by a combination of different physical effects, including multilayer interference, diffraction, coherent scattering, and spatially confined absorption [1-3]. A common design concept in natural photonic systems is the complex interplay of structural regularity on the length scale of the wavelength of visible light combined with structural disorder on a larger scale [4]. In many cases, the complex interaction of these hierarchical structures with incident light lead to an outstanding, dynamic coloration, bright reflectivity that is perceivable in a wide angular range, brilliant whiteness, or enhanced transmission [5, 6]. While photonic structures can be made entirely from transparent materials, the incorporation of absorbing pigments deposited under or incorporated into a photonic structure is frequently used in nature to prevent spurious reflections. This improves the contrast leading to an enhancement of the color perceived from the photonic system [7]. Biological micro- and nanostructures that cause structural color are very diverse and often show periodicities on several length scales. This makes the optical characterization of a biological photonic system and the determination of the optical properties of its constituent materials (e.g., refractive index) very challenging. A set of useful techniques for the determination of the complex refractive indices of materials in biological photonic structures has recently been reported and successful attempts have been made to determine the complex refractive index of the organic cuticle material in the scales of butterflies and the armor of beetles [8].

Occurrence and Purpose of Structural Colors in Nature

Structural colors can be found in the feathers and skin of various birds [9-11], in the shells, spines, and scales of marine animals [12, 13], and in the skin of some mammalian species [14]. They are probably most abundant in species of the insect orders Lepidoptera and Choleoptera that comprise butterflies, moths, and beetles [15–19]. The different purposes of structural colors are as diverse as the organisms that use them [20]. Intense colors with stark contrast to their environment can serve in interspecies interaction including agonistic displays to confuse or scare away potential predators, while structural colors are also applied to induce a cryptic coloration for camouflage. For other animals, they are playing an import role for intraspecies communication such as competition between males of the same species for territory and/or females. Structural colors often provide sexual dichroism between males and females and are believed to have a function in sexual selection. They might also play a role in temperature regulation. While the physics and functioning of photonic structures found in many different organisms are mostly understood, it is frequently very challenging to clearly identify the specific benefit for the animal, which often remains mysterious.

The Physical Effects Underlying Structural Colors

Bright, pure, and intense colors arise from strong reflectivity in narrow spectral bands caused by highly ordered structures including multilayers, surface diffraction gratings, and photonic crystals. While many biological photonic structures are based on multilayer assemblies and two- or three-dimensional photonic crystals [1], diffraction gratings are rare in nature, possibly because they do not display a specific color but give rise to a range of colors depending on light incidence and observation direction [4]. The contrast of structural colors in their environment is often increased by the placement of absorbing elements spatially under or around the photonic structure. Intense blacks are achieved in nature by structurally assisted pigmentation as in the case of the butterfly *Papilio* ulysses [7]. In some avian species the pigments are incorporated directly into the photonic structure [9]. Brilliant white is achieved by multiple, incoherent scattering caused by highly disordered structures of random size, aperiodically arranged on the length scale of the wavelength of visible light [6]. Intense, spatially homogenous, angle-independent colors arise from coherent scattering caused by structures of welldefined size comparable to the wavelength of light, such as air pores of a narrow size distribution dispersed randomly in the volume of a material. This, for example, gives rise to the strong blue of the feathers of several different bird species [11]. High transparency is achieved by graded refractive index surfaces, involving arrays of conical protrusions found in moth eyes [5].

In the following, the structural designs, which give rise to strong coloration, ultrahigh blackness, or brilliant whites are discussed with emphasis on the interplay of different structural, hierarchically assembled elements. Specific natural organisms that apply these particular structural combinations are presented in an exemplary manner, without recounting all the animals known to apply the same or very similar concepts. First, static systems that induce structural colors based on "simple" multilayer elements are discussed before progressing to more and more sophisticated two- and three-dimensional structural arrangements. Attention is paid to combinations of different photonic elements and to the interplay of order and disorder in hierarchical structures on the nano- and microscale, a powerful concept occurring in natural structural colors.

Static Structural Colors in Animals

Multilayer Structures of Varying Complexity in Natural Photonic Systems

Thin film interference and multilayer interference are among the most common phenomena inducing structural color in animals. Light reflected from periodic stacks of multiple planar, optically distinct, transparent layers (often called Bragg mirrors) is colored, provided the thickness of the individual layers is comparable to the wavelength of light in the visible spectrum. The color, its intensity, and purity depend on the refractive index contrast of the multilayer materials, the individual layer thicknesses, and the number of layers in the stack [2]. Furthermore, the perceived color strongly varies with the angle of light incidence and the observation direction. The peak wavelength λ_{max} of light reflected from a multilayer in air composed of two materials with refractive index n_1 , n_2 and film thicknesses d_1 , d_2 upon incidence at an angle θ is given by the relation

$$m \cdot \lambda = 2 \cdot (n_1 d_1 \cos \theta_1 + n_2 d_2 \cos \theta_2), \qquad (1)$$

where *m* is a positive integer and the angles θ_1 , θ_2 of the light path in the materials are given by Snell's law $n_{\text{air}} \sin \theta = n_1 \sin \theta_1 = n_2 \sin \theta_2$. In this case the rays reflected from the family of $n_1 - n_2$ -interfaces interfere constructively with each other, if the light has the wavelength λ_{max} . The same holds for light rays reflected from the $n_2 - n_1$ -interfaces in the stack. If a second relation given by

$$\left(m + \frac{1}{2}\right) \cdot \lambda = 2n_1 d_1 \cos \theta_1 = 2n_2 d_2 \cos \theta_2 \qquad (2)$$

is also satisfied, the multilayer stack is referred to as an ideal multilayer. This relation signifies the fact that in an ideal multilayer the light rays reflected from the $n_1 - n_2$ -interfaces interfere constructively with the rays reflected from the $n_2 - n_1$ -interfaces, which is not the case for a "nonideal" multilayer. The reflectance of a nonideal multilayer is therefore lower compared to an ideal multilayer made of the same materials, with an equal overall layer number and equal periodicity $d_1 + d_2$. Most multilayer arrangements found in nature are nonideal in the sense of this classification. In some cases this may even be beneficial for the organism since nonideal multilayers have a narrower bandwidth compared to ideal multilayers, which increases the purity of the reflected color.

The wood-boring Japanese jewel beetle Chrysochroa fulgidissima found in the forests of Japan during summer displays a vivid ventral and dorsal coloration (Fig. 1a). This color originates from interference of light in a multilayer stack of about 20 alternating layers (Fig. 1d) with refractive indices of 1.5 and 1.7 incorporated in the epicuticle of the beetle's wing cases [4]. The perceived coloration strongly depends on the orientation of the beetle with respect to the incident light and the observation direction, as expected for a multilayer structure (Fig. 1a). Nevertheless, the beetle's surface does not act like a colored mirror, as expected from a perfectly flat multilayer



Structural Color in Animals, Fig. 1 Natural photonic systems based on multilayer arrangements. (a) The wing cases and the ventral side of the Japanese Jewel beetle Chrysochroa fulgidissima display bright and iridescent colors that show a strong angular color variation (b, c). The surface of the wing cases shows irregular corrugations on the 100 μ m scale (**b**, scale bar $\sim 100 \ \mu\text{m}$) and more regular indentations on the 10 μm scale (c, scale bar 10 μ m). (d) Cross-sectional transmission electron micrographs reveal the stack of alternating high and low refractive index layers that causes multilayer interference, resulting in the beetle's iridescent color, scale bar 400 nm (Pictures (a-d) reproduced with permission of S. Kinoshita and IOP Publishing © 2008 Kinoshita et al. [1]). (e) The Madagascan moth, Chrysiridia rhipheus, displays a range of bright shimmering colors on its wings. (f) Different wing regions are covered by patterns of colorful scales reflecting green, yellow, red, or violet light. The scales are highly curved so that the observer only perceives light reflected from part of the scales, which creates the impression of texture caused by the juxtaposition of bright and dark regions, scale bar 200 µm. (g) The scales are spanned by parallel micro-ribbed ridges, scale bar 2 μ m. (h) Cuticle layers of well-defined thickness that are spaced by small struts extend between and under the ridges, forming a regular multilayer arrangement with air as the low refractive index material,

scale bar 500 nm. (i) The butterfly Papilio blumei displays lucid green stripes on its upper and lower wing pairs. (j) At higher magnification, the green scales show regions of distinct blue or yellow color, scale bar 100 μ m. (k) The yellow color from the centers of concavely shaped surface corrugations disappears when the scales are imaged between crossed polarizers while the blue from the edges of the concave shapes persists due to polarization rotation upon reflection, scale bar 5 µm. (I) Concave surface corrugations on the scales, scale bar 2 µm. (m) A crosssection through one of the concavities reveals cuticle layers of well-defined thickness and regular spacing forming a multilayer reflector, scale bar 1 μ m (Figure (m) reproduced with permission of P. Vukusic and Springer Science+Business Media © 2009 Vukusic [19]). (n) The South American butterfly Morpho rhetenor. (0) Bright blue scales cover the wing membrane like tiles on a roof top, scale bar 100 μ m. (**p**) Top and cross-sectional view of the ridges running along each scale, scale bars 500 and 100 nm. (q) A cross-section through a scale exposes the intricate design of the ridges, scale bar 1 µm. The horizontal extensions on each ridge act as a multilayer reflector tuned for the blue spectral range with air as the low refractive index medium (Figures (o and q) reproduced with permission of P. Vukusic and Springer Science+Business Media (C 2009 Vukusic [19])

arrangement. Minute hexagonally arranged holes and indentations are distributed in the multilayer on the 10 μ m length scale (Fig. 1c) and the areas bordered by the micro-holes vary in their inclination. On the 100 μ m length scale, the surface shows a strongly irregular corrugation (Fig. 1b). This structural irregularity leads to the scattering of light reflected from the multilayer, giving the beetle its characteristic color in a larger angular range around the specular reflection

direction thus increasing its visibility.

The scales of the Madagascan moth Chrysiridia rhipheus (also called sunset moth because of the two bright yellow-orange-violet spots on the lower wing pair) display intense, beautiful colors ranging from green to red, similar to the jewel beetle's hues (Fig. 1e, f). The different, similarly bright colors result from a multilayer incorporated into the body of the moth's wing scales (Fig. 1h). The multilayer is made from layers of one single material (cuticle) spaced by perpendicular struts, effectively creating a controlled air spacing between the cuticle layers. Including air as the second component in the multilayer stack leads to the maximization of the refractive index contrast, providing intense reflection with a much smaller number of layers compared to the Japanese jewel beetle, where the refractive index contrast is much lower. The air spacing varies in the differently colored regions of the moth's wing with the smallest spacing found in the green areas and the largest spacing seen in the red wing spots. The multilayered scales show a strong curvature along their long axis. This curvature superimposed onto the photonic multilayer structure leads to a high visibility of the colors from various directions and also introduces multiple reflection effects between adjacent scales, leading to an increased purity of the reflected color and to interesting polarization effects [21]. Overall, caused by the interplay of the highly reflective air-cuticle multilayer and the pronounced scale curvature, the moth wing displays bright colors with a velvety, textile-like shimmer.

Air-cuticle multilayers of even more complex shapes can be found on the wing scales of butterflies of the genus *Papilio*. The South-East Asian Emerald Swallowtail *Papilio palinurus* and the Green Swallowtail *Papilio blumei* (Fig. 1i) display bright green spots on their wings resulting from a concavely shaped multilayer architecture on the individual scales (Fig. 11, m). The vivid green originates from a superposition of blue and yellow reflected from the edges and the centers of the multilayer concavities, respectively (Fig. 1j, k) [22]. Different colors result from distinct regions of the concavely shaped multilayer due to the spatially varying angle of light incidence on the edges and in the center of the concavities. Light reflected from the edges can undergo multiple reflections within a single concavity, inducing a change in polarization. The butterfly Papilio ulysses displays concavely shaped multilayer structures on its scales that have less curvature and smaller cuticle and air gap thicknesses, resulting in a lucid blue color. While in the case of Papilio palinurus and Papilio blumei the higher local concavity wall curvature results in the juxtaposition of yellow and blue reflected from different regions forming green (a color that might have a purpose in camouflage), the shallower concavities of Papilio ulysses do not produce the same effect but rather diffuse the reflected light into a wide angular range for higher visibility [19].

The possibly most sophisticated and intensely studied multilayer structure giving rise to bright animal coloration is found on the wing scales of butterflies belonging to the genus Morpho. These butterflies that are native to South and Central America are known for their intense, widely visible coloration. Among them, Morpho rhetenor is the most striking example of vivid bright blue structural color (Fig. 1n, o). The intriguing hue of its wings results from the interference of light caused by ridge structures (Fig. 1p) on the wing scales that have a Christmas-tree like cross-section (Fig. 1p, q). The horizontal periodic protrusions of the ridges cause "quasi"-multilayer interference [4, 5]. The term "quasi" is used in this context, because light not only interferes when reflected from protrusions of the same ridge but also when reflected from protrusions on different adjacent ridges. As for the moth *Chrysiridia rhipheus* and the butterflies of the genus *Papilio*, the incorporation of air layers into the multilayer structure leads to a large refractive index contrast and consequently to a bright reflection in a wide spectral band. The ridges are spaced by $\leq 1 \,\mu m$ on average, which in the past lead to the assumption that they also act as a diffraction grating. However, local variation between the ridges in height and distance and in the orientation of entire scales confines the diffraction to individual ridges and inhibits the manifestation of a pronounced diffraction grating effect in reflection [4]. Nevertheless, this randomization seems to have a beneficial side effect: despite its origin from multilayer reflection, the



Structural Color in Animals, Fig. 2 Natural photonic systems based on diffraction. (a) The torso of the spider *Cosmophasis thalassina* shows two broad metallic golden-greenish stripes in air. (b) The color changes to purple-silvery when immersed in water. (c) The structure on the spider torso that causes these colors consists of a combination of surface striations superimposed on a chirped multilayer reflector (not shown here), scale bar 5 μ m. (d) A schematic of the interaction of light with the spider's photonic structure. Blue light is very efficiently scattered by the striations while light of higher

blue color of the *Morpho rhetenor* is very illumination and observation angle insensitive and perceivable from all points in space above the wing plane, only changing to violet at very high angles of light incidence or observation.

Diffractive Elements

Diffraction from surface gratings is believed to be rare in nature. This might be due to the fact that diffraction gratings with periodicities of 400 nm-2 μ m need longrange order on the 60 μ m scale (the spatial coherence of sun light) in order to be efficient, a criterium that is hard to meet in the natural context where irregularity is usually predominant at this length scale. During the past decade some animals, mostly invertebrates, have been shown to employ diffraction gratings, however [12]. As opposed to multilayer reflectors, which reflect light in a relatively narrow spectral band, diffraction gratings split incident light into its spectral components and redirect each color into a different direction. Consequently, diffraction gratings are less suitable for providing spectrally well-defined colors in a

wavelength interferes with the multilayer stack. Red is specularly reflected in the top section of the chirped mirror where the layers are thicker while green is reflected by the thinner layers further down the stack. (e) The hairs of the first antenna of the seed shrimp *Azygocypridina lowryi* show strong iridescence caused by grating diffraction. (f) The diffraction grating on a single *setule* (hair) of the antenna, scale bar 1 μ m (Images (d modified) reproduced with permission of A. R. Parker, IOP Publishing © 2003 Parker and Hegedus [23] and The Royal Society © 2005 Parker [13])

wide angular range (which is better achieved with a multilayer reflector combined with some irregularity on the micron-scale). While diffraction gratings made from transparent materials efficiently create vivid colors in transmission, they have to be made from (or backed by) reflective materials to produce strong colors in reflection, which seems to be less efficient for the organism.

Periodic grating-like surface structures on an underlying chirped broadband multilayer reflector have been found on the torso of spiders [23]. In a chirped multilayer the thicknesses of the individual layers decrease or increase gradually from the top to the bottom of the stack. Constructive interference occurs for the reflection of light of a particular color/wavelength range at a specific depth in the stack (Fig. 2d) where the layer thicknesses fulfill the condition discussed above (Eq. 1) thereby leading to a broadband reflection usually resulting in a silver or golden color. In the case of the spider *Cosmophasis thalassina* (Fig. 2a, b), the striations (Fig. 2c) mainly serve the purpose to disperse blue light before it interacts with the underlying reflector (Fig. 2d), thereby biasing the color of the spider's body toward a golden appearance, instead of the more silvery shine which it would have without the striations. Fourier analysis shows that there is no pronounced long-range order in these striations and consequently the striations do not create strong grating diffraction. The striations are likely to disperse light reflected from the multilayer reflector into a wider angular range. This represents a good example of the interplay of different structures with varying length scales to achieve a specific optical response.

The use of periodic diffraction gratings as surface structures seems particularly beneficial on narrow cylindrical geometries where the implementation of multilayers might be impractical or impossible. The thin hairs (*setae*) of some Crustacean species including the antenna of the male seed shrimp, *Azygocypridina lowryi* (Fig. 2e), display vibrant colors resulting from periodic surface structures [12, 13]. In the antenna of *Azygocypridina lowryi* the grating is formed by regular undulations of the hair thickness with a periodicity of 600–700 nm (Fig. 2f).

A curious structure causing diffraction with a reverse angular color sequence was recently found on the wings of the male butterfly *Pierella luna* [24]. The ends of the scales in the central portions of this butterfly's forewings are curled upward, enabling regularly arranged, on average 440 nm spaced cross-ribs to act as an upward-directed diffraction grating in transmission, resulting in this intriguing phenomenon of "inverse" diffraction. As opposed to a conventional diffraction grating, these structures make the central forewing regions appear red for small angles of observation (measured from the surface normal), changing to yellow, green, and finally blue as the observation angle is increased.

Two-Dimensional Photonic Crystals

Two-dimensional photonic crystals that cause structural colors have been found in marine animals [13, 25, 26], birds [9, 10], and mammals [14]. This part of the review focuses on two-dimensional photonic systems found in nature that induce the striking color in some animals. The *setae* of the polychaete worm *Pherusa* sp. (Fig. 3a, b) show a vivid play of colors originating from the periodic two-dimensional hexagonal arrangement of cylindrical channels (Fig. 3c, d) with a well-defined lattice constant within a single *seta* [26]. This system is strikingly similar to artificial photonic crystal fibers. A very similar arrangement was found earlier in the spines of the sea mouse *Aphrodita* sp. [25] (Fig. 3e–h).

The feathers of kingfishers, peacocks, ducks, pigeons, and trogons among various other birds display strong blue and green colors that reportedly have attracted the interest of scientists for more than 300 years [1, 4, 18]. The bright blues and greens result from well-ordered melanin granules in a dense keratin matrix [9] or a spongy keratin network with regular air pores [11] of varying dimensions and structural complexity within the birds' feather barbules. These structures have been classified and investigated in great detail in the last three decades [9]. The order of the layers of the solid or hollow melanin granules or the pores in the keratin matrix varies from species to species. Consequently, the physical effect causing the bright color was repeatedly identified as incoherent scattering for the less ordered randomly distributed structural elements with well-defined sizes or as coherent scattering (for instance, multilayer interference) in structures of quasi-ordered arrangements with higher spatial order. In many bird species not only the feather barbules but also the skin on different body parts show strong color. These colors are based on coherent scattering caused by two-dimensional photonic crystal structures, consisting of regular arrays of collagen fibers in the dermis of the birds (Fig. 3i-l). The dimensions of the collagen fibers are very well defined with a narrow distribution in fiber diameter for each species, while the extent of spatial order varies from species to species (compare Fig. 3j, 1).

Three-Dimensional Photonic Crystals

The first discovered biological three-dimensional photonic crystal is a solid, hexagonally close-packed array of transparent spheres of 250 nm diameter in a matrix of hydrated chitinous material found inside the scales of the Australian weevil *Pachyrhynchus argus* [28] (Fig. 4a–c). Similar to the ordered arrangement of silica spheres in precious opal, this structure gives the beetle a metallic coloration visible in any direction. Recently, a similar structure was also observed in the Asian longhorn beetle *Pseudomyagrus waterhousei* (Fig. 4d–f).

Inverse opal photonic structures have been identified in various butterfly and beetle species. The beetle *Pachyrrhynchus congestus pavonius* [30] displays vivid patches of orange color on its body (Fig. 4g, h)



Structural Color in Animals, Fig. 3 Structural colors based on two-dimensional photonic crystals. (a) The *setae* of the polychaete worm *Pherusa* sp. show a remarkable structural color (*white arrow*). (b) Micrograph of a *seta* of the worm. (c) A crosssectional transmission electron micrograph of a *seta*, scale bar 5 μ m. (d) High-magnification image of the regular structure in the *seta*, scale bar 2 μ m (Image (a) reproduced with permission of A. R. Parker, 1995. Images (b–d) reproduced with permission of P. Vukusic and The American Physical Society © 2009 Trzeciak and Vukusic [26]). (e) The colorful spines (*white arrow*) of the sea mouse *Aphrodita* sp. (Image courtesy of D. Harasti). (f) Optical micrograph of one of the colorful spines. (g, h) Side view and cross-section of the tubular structures in the spine, scale bars 2 µm and 1 µm (Images (**f**–**h**) reproduced with permission of A. R. Parker and The Royal Society © 2004 Parker [27]). (**i**) The bright green wattle (*white arrow*) of the Madagascan bird *Philepitta castanea* (velvet asity). (**j**) A transmission electron micrograph of a cross-section of the nanostructured arrays of dermal collagen fibers responsible for the wattle's green color, scale bar 500 nm. (**k**) The blue eye spot (*white arrow*) of the Madagascan bird *Terpsiphone mutata* (Madagascar paradise flycatcher). (**l**) A cross-section of the collagen fiber array that causes the blue color around the bird's eye, scale bar 500 nm (Images (**i**–**l**) adopted from Prum and Torres [10] with permission of R. O. Prum and T. Schulenberg (**k**))



Structural Color in Animals, Fig. 4 Structural colors based on three-dimensional photonic crystals. (a) Dorsal view of the Australian weevil Pachyrhynchus argus showing the green metallic spots (white arrow) on its back side. (b) Scanning electron micrograph of the beetles scales, scale bar 50 μ m. (c) Cross-section of a scale revealing the opaline structure responsible for the beetle's metallic coloration, scale bar 1 µm (Images (a-c) reproduced with permission of A.R. Parker and The Royal Society © 2004 Parker [27]). (d) The South-East Asian bright blue longhorn beetle Pseudomyagrus waterhousei. (e) Micrograph of the iridescent drop-shaped scales on the beetle's body, scale bar 50 µm. (f) Scanning electron micrograph of a crosssection through a single scale revealing the origin of the iridescent blue color, regularly sized, closely packed spherules forming a direct opal, scale bar 1 µm (Images (d-f) reproduced with permission of J. P. Vigneron and The American Physical Society © 2011 Simonis and Vigneron [29]). (g) The beetle Pachyrrhynchus congestus pavonius. (h) Micrograph of the highly conspicuous annular spots on the beetle's thorax. The

that originate from the interference of light within the beetle scales, which consist of a multilayered cortex surrounding an inverse opal photonic crystal (Fig. 4i). This is an example of the superposition of different structural geometries, in this case a multilayer mirror and a three-dimensional photonic crystal. The light reflected from a regular multilayer mirror results in an iridescent color while the interference of light with a polycrystalline three-dimensional photonic crystal usually leads to a uniform color over wide angular ranges. However, the precise influence of each

scales of different colors are clearly visible. (i) Scanning electron micrograph of the cross-section of a scale, revealing the photonic structure consisting of a combination of a multilayer reflector on top of a three-dimensional face-centered cubic photonic crystal, scale bar 1 µm (Images (g-i) reproduced with permission of J. P. Vigneron and The American Physical Society © 2007 Welch et al. [30]). (i) The South American butterfly Parides sesostris, commonly called Emerald-patched Cattleheart due to the bright green patches on its upper wing pairs (white arrow). (k) Scales in the green areas of the butterfly's wings, scale bar 100 µm. (I) SEM image of a crosssection of the three-dimensional photonic structure found within a single scale, scale bar 1 µm. (m) Transmission electron micrograph of the cross-section of a scale showing the superficial ridging and the domains of the underlying of photonic crystal, scale bar 2 µm (Images (j, l, m) reproduced with permission of P. Vukusic and Springer Science+Business Media B.V © 2009 Vukusic [19]. Image (k) courtesy of M. Doolittle)

structural component on the overall appearance of this particular beetle, *Pachyrrhynchus congestus pavonius*, remains to be investigated in detail. The wings of the butterfly *Parides sesostris* display patches of bright green angle-independent color (Fig. 4j, k), resulting from the interaction of light with a polycrystalline, three-dimensional photonic crystal structure that is buried under the superficial ridging in the body of the butterfly's wing scales (Fig. 41, m). The individual crystallites were shown to have cubic symmetry and recent research suggests that they consist in fact of



Structural Color in Animals, Fig. 5 Deep blackness and brilliant whiteness. (a) The butterfly *Papilio ulysses* shows regions of deep black (*white arrow*) surrounding the bright blue spots on its wings. (b) The scales in the black regions carry cuticle microstructures that trap light. The inset shows a cross-section of a scale revealing the dense network of pigment-loaded cuticle, scale bars 2 μ m. (c) The brilliant white

a bi-continuous regular gyroid network [31]. The different orientations of the photonic crystal domains and the light scattering induced by the superposed ridge structure ensure that the reflected color is independent of observation angle.

Structurally Assisted Blackness and Brilliant Whiteness

The natural photonic structures presented so far serve the organisms to display a distinct coloration. The contrast of a color is often enhanced in nature by placing it against a black background and color purity is ensured by absorption of undesired spectral light components in regions beneath or around the color creating photonic elements. Consequently, optimized absorption plays an important role for natural structural colors. The scales of various butterflies that display structural colors are supported on a surface containing melanin pigments. The pigments absorb the light that passes through photonic structures of the scales, suppressing spurious reflection and consequently preventing the desaturation of the reflected color.

Very strong blackness can be achieved by an optimized interplay of pigment absorption and structure. A particularly good example is the butterfly *Papilio ulysses* [7]. The bright blue patches on the butterfly's wings are surrounded by very dark scales that show strong light absorption induced by melanin-containing microstructures (Fig. 5a). These pigment-filled structures act as light traps that are tailored to prevent light from escaping once it enters the scales (Fig. 5b). This maximizes the interaction with the pigment, resulting beetle *Cyphochilus* spp. compared to other beetles. (**d**) The intense white results from incoherent diffuse scattering from an interconnected network of filaments within the body of each beetle scale, scale bar 1 μ m (Inset in (**b**), images (**c**) and (**d**) reproduced with permission of P. Vukusic, The Royal Society © 2004 Vukusic et al. [7] and The Optical Society of America © 2009 Hallam et al. [32])

in the extremely low reflectivity of the butterfly's black scales.

Materials with a high structural irregularity, a random distribution, orientation, and size of individual transparent or highly reflective scattering elements on the scale of the wavelength of light are known to equally scatter light of any color into a broad angular range, thereby creating an intense white appearance. An extra-ordinary example of brilliant structural whiteness has been discovered in the case of the *Cyphochilus* spp. beetle [6]. The insect's intense white (Fig. 5c) is based on the incoherent scattering of light from a random network of about 250 nm thick interconnected filaments that are randomly distributed within the ultrathin beetle scales (Fig. 5d). Despite the fact that the scales are only about 5 µm thick, an optimized void fraction, high aperiodicity, and the large refractive index contrast of about 0.56 ensure that light of all colors is very efficiently scattered in all directions.

Dynamically Variable Structural Colors in Animals

The most interesting structural color systems in nature are the ones that show aspects of intentional color tuning, like the photonic structure employed by the beetle *Charidotella egregia* (Fig. 6a). In situations of distress, for instance, caused by predator attacks [33], the beetle can change its appearance from a bright golden shine to a striking red color (Fig. 6c) within 2 min. The structure inducing this phenomenon is



Structural Color in Animals, Fig. 6 Dynamically tunable structural color. (a) The golden beetle *Charidotella egregia*. (b) Transmission electron micrograph of the chirped multilayer reflector in the outer layer of the beetle's armor, showing the density variation of irregularly distributed porous and solid areas within the stack, scale bar 1 μ m. (c) When threatened the beetle can change its golden color to a striking red within less than 2 min (Images (**a**–c) reproduced with permission of J.P. Vigneron and The American Physical Society (**c**) 2007 Vigneron et al. [33]). (d) The squid *Logilo peadeii*. (e) Microscope images of the squid's skin show the brown and reddish pigmented chromatophores and the underlying iridescent iridophores shimmering in colors from green

to orange. (f) A sketch of the arrangement of chromatophores (c), iridophores (i), and leucophores (l) in the skin of cephalopods (Images (\mathbf{d} -f) reproduced with permission of L. Mäthger, Springer Science+Business Media (\odot 2007 Mäthger and Hanlon [34] and The Royal Society (\odot 2009 Mäthger et al. [35]). (g) Optical microscope images, and (**h**, i) transmission electron micrographs of active iridophores of the squid *Lolliguncula brevis* reveal the variation in reflection and the ultrastructural changes in the iridophore platelets when switching between non-reflective (*left*) and reflective (*right*) states, scale bars 1 µm (**h**), 250 nm (**i**) (Images (**g**-**i**) reproduced with permission of R. T. Hanlon and Springer Science+Business Media (\odot 1990 Cooper et al. [36]) a multilayer buried in the exocuticle of the beetle's transparent armor (Fig. 6b). The multilayer is chirped which results in reflection of light in a broad wavelength range, leading to the golden appearance of the beetle. Internally, the multilayer structure shows a random distribution of porous regions and channels within the layer planes and perpendicular to the layers. In the default state, these irregularly distributed voids are filled with liquid leading to a homogenous refractive index within each layer thereby suppressing scattering and allowing interference of light in the chirped multilayer, which results in the golden metallic color. Beneath the multilayer resides a layer of bright red pigment. When under a potential threat the beetle resorts to an aposematic protection mechanism. It can withdraw the liquid from the porous regions in the multilayer which strongly increases the scattering thereby rendering the layer stack translucent and revealing the bright red color of the underlying pigments, which serves as a warning signal.

The impressive camouflage and signaling capacities of cephalopods (squid, cuttlefish, and octopus) result from an intricate interplay of mainly three different functional elements within the skin of the animals [35]. Chromatophores are small pigment-filled organs that can be stretched and compressed by radially attached muscle strands. The squid Logilo pealeii (Fig. 6d) can vary the size of its chromatophores from 1.5 mm in the expanded state to about 0.1 mm when retracted [34]. A distinct layer of iridophores buried in the skin beneath the chromatophores provide spectrally selective reflection (Fig. 6e, f). The iridophores are colorless cells, which contain stacks of thin platelets (iridosomes) that reflect light by multilayer interference. Among the iridophores, cuttlefish and octopus employ additional structural elements, so-called leucophores (Fig. 6f). These cells are made up of disordered spherical assemblies with particles ranging from 250 to 1,250 nm in diameter (leucosomes). They induce diffuse broadband scattering and are responsible for the white patterns on cuttlefish and octopus. While the leucophores are passive elements, cephalopods have a high physiological control over chromatophores and iridophores [35]. The chromatophores can be expanded or retracted within a fraction of a second. In the expanded state they display the pigment color (red, yellow/orange, or brown/black depending on the species) and hide the underlying iridophores and leucophores from interfering with the incident light. When the chromatophores are retracted iridophores and leucophores are revealed and determine the reflected color. Squids are able to change the iridescence of the iridophores with shifts of over 100 nm in the reflected wavelengths observed for some species. This reflectance change progresses much slower than the actuation of the chromatophores and can take several seconds to minutes. The change in iridophore reflection can result from two different processes. The platelets in the iridophores, which are made of a protein called reflectin, can change their refractive index by a change in state of the protein conformation [36] (Fig. 6g-i). Furthermore, the thickness of the plates can change to tune the reflection. In addition to the described passive optical elements, some cephalopod species make use of structurally very complex light-emitting photophores that can be highly directional in their emission. The emission of photophores is often enhanced by the incorporation of multilayer back-reflectors. More complex photophores contain filters and light guides that help to channel and direct the emitted light. In summary, cephalopods use an extensive repertoire of actively tunable optical elements that rely on a range of physical effects in order to manipulate incident light, including absorption, light interference, bioluminescence, and scattering, which makes them the uncontested masters of color, light manipulation, and camouflage in nature.

Conclusions

In the course of evolution, various organisms in nature have developed a huge variety of photonic systems that by interference, diffraction, coherent, and incoherent scattering cause distinct color. While the bearers of such photonic structures come from very different animal orders, common design principles can be identified across the distinct taxonomic groups. Regular periodic multilayer arrangements and two- or threedimensional photonic crystals build the base for strong color, while disordered arrays of particles and filaments cause bright whiteness. Pigment-loaded structures with corrugations on different length scales act as efficient light traps that render surfaces deep black. Strong blackness and brilliant whiteness are frequently employed in nature to provide contrast for intriguing patterns of color on wings and bodies of insects, scales and shells of marine animals, and feathers of birds. The coordinated interplay of regularity and irregularity on different length scales plays an important role in the function of many natural photonic systems [4, 9]. Well-defined, structural regularity and periodicity on the submicron scale ensures the reflection of strong bright colors, while irregularity on the scale of several microns inducing random scattering often mediates color stability and conspicuousness in a wide angular range.

By looking at organisms in nature new insight and knowledge can be gained for the design of materials that show specific and efficient interaction with light. This fact is widely acknowledged in the scientific community [15, 27]. Researchers show increased interest in the development of bio-inspired photonic systems. The current techniques and tools used in the industry, research, and everyday life for light harvesting, optical signaling, data transfer, and processing might soon benefit from a better understanding of the composition and functioning of biological photonic structures.

Cross-References

- Biomimetics of Optical Nanostructures
- ► Moth-Eye Antireflective Structures
- Nanostructures for Coloration (Organisms other than Animals)
- ► Nanostructures for Photonics

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Structural Color in Nature

Biomimetics of Optical Nanostructures

Structural Colors

► Nanostructures for Coloration (Organisms other than Animals)

Structure and Stability of Protein Materials

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Synonyms

Nanostructure; Thermostability

Definition

Protein-based materials are polymeric biomaterials comprising amino acid subunits that are connected together by peptide bonds. These materials are usually biomimetic, self-assemble into higher-order nanometerscale architectures, and can interact with biological entities. Determination of their structure and stability is an important component of assessing their utility and function.

Protein-Based Nanomaterials

The control of architecture at the nanoscale is a challenge in which nature has been highly successful. Since genetic manipulation enables the definition of every monomer in a polymeric protein structure, giving far greater control than conventional chemical synthesis, one approach in materials synthesis is the use of protein engineering to create biologically inspired materials [1]. By combining natural scaffolds, structural elements, and biologically reactive sites, materials with novel architectures and properties can be obtained. These materials are fabricated in microorganisms as recombinant proteins comprising amino acid units. Furthermore, proteins often self-assemble into complex, higher-order nanostructures, which include fibrous and spherical architectures [2, 3]. Protein-based materials have been evaluated for a wide variety of applications, such as tissue engineering scaffolds, templates for nanomaterials synthesis, and drug delivery carriers. The evaluation of structure and stability in these protein-based nanomaterials is primarily established using techniques developed for general proteins.

Structure

The structures of proteins span several length scales, and different methods are used depending on the type of structure being evaluated [4]. The *primary structure* of proteins describes the sequence of individual amino acids, or monomer residues, covalently coupled by peptide bonds to form a polypeptide chain. There are 20 known natural amino acids, each differing in their side chain identity, thereby imparting different physicochemical characteristics at each location along the polymer. One can also incorporate "unnatural" amino acids, which expands the functionalization of the protein-based material with useful chemical components that are not native [5, 6]. When the protein materials have been created in a recombinant system (such as in microorganisms), the DNA encodes for the protein sequence. Primary