Natural photonics for industrial inspiration

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There are two considerations for optical biomimetics: the diversity of submicrometre architectures found in the natural world, and the industrial manufacture of these. A review exists on the latter subject, where current engineering methods are considered along with those of the natural cells. Here, on the other hand, I will provide a modern review of the different categories of reflectors and antireflectors found in animals, including their optical characterization. The purpose of this is to inspire designers within the $2 billion annual optics industry.

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1. Introduction

The evolution of optical reflectors in animals began soon after the first eye evolved. Trilobites are the first animals known to host image-forming eyes, of ca 521 Ma (figure 1); eyes that contain efficient optics in their own right (Parker 1998, 2003). In the absence of vision, any incidental iridescence appearing before the Cambrian period would have been neutrally selective. But with the evolution of the eye, the size, shape, colour and behaviour of animals were revealed for the first time. Consequently, adaptive optical devices in nature were born.

Soon after the first eyes, at least by 508 Ma (Parker 1998; new date for the Burgess Shale fossils), animals began to evolve sophisticated optical reflectors—nanostructures that interact with (reflect, refract and diffract) light rays, such as surface corrugations or internal stacks of thin layers. Today we find an array of optical reflectors in animals that have resulted from millions of years of evolutionary ‘fine-tuning’. For example, the corrugations on the surface of cypridinid ostracod (crustacean) setae that diffract a spectrum used as a courtship display have improved in optical efficiency throughout the evolution of the group (Parker 1995). Maybe, then, nature’s optical designs can be useful for commerce. Indeed, the first butterfly scale reflectors have been reproduced recently using industrial methods (Wong et al. 2003; Parker & Townley 2007).
The relatively bright, directional effect of most optical reflectors in nature (including their ultraviolet component) is termed structural colour, which separates it from the comparatively duller, diffuse effect of chemical pigments. However, matt colours, similar to those of pigments, are also known to result from some structures (e.g. Kertész et al. 2006). Traditionally, biologists have found helpful the classification of structural colours into the categories of (random) scattering, diffraction gratings, multilayer reflectors and liquid crystals. The last paper thoroughly reviewing these structures in nature, beginning with the first identified (Newton’s study of peacock feathers in 1704) and detailing their diversity and biological functions, was published in 2000 (Parker 2000). All of these structures fall into a category of optical devices that I will term ‘simple’ optics because the single-scattering approximation (or ‘first Born approximation’) applies to them. That is, once a light ray is scattered/reflected for the first time within the structure, it is not scattered again. This is an estimation—indeed, wavelength is a factor (this approximation is even more appropriate for X-rays, which are difficult to scatter, but less appropriate for electrons)—but provides justification to employ non-rigorous physics to explain reflections. This is particularly useful for biologists. However, in 2001 the first reflector requiring ‘complex’ optics was identified in animals (Parker et al. 2001), which attracted groups of physicists and engineers to the subject. In complex optical reflectors, each individual light ray is scattered more than once (sometimes many times, depending on the complexity of the nanostructure)—it is reflected from optical boundary to optical boundary.

2. Simple optical reflectors

(a) Scattering structures

Forms of random scattering can result in either a white, diffuse appearance, or a blue coloured, diffuse effect (red when the system is viewed in transmission).
White scattering structures

Simple, equal scattering of all spectral wavelengths results in the observation of a diffuse white effect. This commonly arises from the effects of some non-periodic arrangements of colloidally dispersed matter where the different materials involved have different refractive indices (e.g. figure 2), or from solid colourless materials in relatively concentrated, thick layers (Fox 1976). In some colloidal systems, where the particles are larger than the wavelength of light and are spaced at distances greater than their size, they can be thought of as mirrors oriented in all directions. The reflection is polarized unless the incident light is at normal incidence on the system and, in the colloidal system, spherical or randomly arranged particles are involved.

Many white bird feathers are so coloured due to non-periodic arrangements of reflecting elements, causing the random scattering of all wavelengths into all directions and thus a diffuse white reflection.

From some scales of extant butterfly wings, light is scattered uniformly and completely in all directions, due to the chaotic disposition of the surfaces. Matt or pearly whites may be observed depending on the complexity or the arrangement of the structures, which affects the relative degree of scattering (Mason 1927).

The colloidal system involves either a gas-in-solid, gas-in-liquid, liquid-in-liquid (emulsions) or solid-in-liquid (Fox 1976). For example, the gas-in-liquid system is partly responsible for the white body and/or tentacles of certain anemones today (Fox 1976). Light is reflected and refracted at the surfaces of the particles of matter or spaces (with dimensions greater than 1 \( \mu m \); Mason 1927). An unordered (as opposed to periodic) group of closely spaced setae, such as those in patches on the extant fly Amenia sp., may form a white reflection via random scattering or reflection.

Reflection and refraction that occur at the interfaces of strata with different refractive indices may result in the display of white light. The degree of whiteness depends on the difference in refractive indices (Fox 1976). This mechanism is evident in the shells of many lamellibranch molluscs (Verne 1930). Between the outer, often pigmented layer and the mantle is a thick middle layer of crystalline calcium carbonate. In most species, these laminations are sufficiently thick (greater than 1 \( \mu m \)) to render the inner lining white.

Figure 2. Diagrammatic representation of a scattering system. Horizontal lines represent incident light, other lines are scattered light.
(ii) Blue scattering structures

Tyndall or Mie scattering occurs in a colloidal system where the particle size approximates the wavelength of light. Here, diffraction is important. Light is diffracted from the scattering elements but the reflection is inversely proportional to the fourth power of the wavelength. This means that shorter wavelength blues are diffracted more than the longer wavelength reds, and the reflection appears blue (the transmitted portion appears red). Rayleigh scattering may also occur in molecules in a two-photon process by which a photon is absorbed and raises the molecule to an exited electronic state from which it re-radiates a photon when it returns to the ground state. Diffraction is not involved here.

Tyndall scattered light is polarized under obliquely incident light. The relative sizes of particles determine the shade of blue. If the particles responsible for the scattering coalesce to form particles with a diameter greater than approximately 1 μm, then white light is observed (see §2a(i) above). A gradation from blue to white scattering (‘small’ to ‘large’ particles) occurs on the wings of the extant dragonfly Libellula pulchella (Mason 1927).

Scattered blues can also be found in other extant dragonflies. In the aeschnids and agrionids, the epidermal cells contain ‘minute’ colourless granules and a dark base. The males of libellulids and agrionids produce a waxy secretion that scatters light similarly over their dark cuticle. The green of the female Aeschna cyanea is the combined result of Tyndall scattering and a yellow pigment, both within the epidermal cells (degradation of the yellow pigment turns the dead dragonfly blue; Fox & Vevers 1960).

Scattered blues are also observed from the skin of the extant cephalopod (Mollusca) Octopus bimaculatus (Fox 1976), where a broad blue ring surrounds ocelli. Blue light is scattered from this region as a result of fine granules of purine material within cells positioned above melanophore cells (Fox 1976). The colour and conspicuousness of the ring are controlled by the regulation of the melanophores, by varying the distribution of melanin and consequently the density of the absorbing screen. The squid Onychia caribaea can produce rapidly changing blue colours, similarly (Herring 1994). Importantly, there is no constructive interference between the reflected rays from both white and blue scattering systems where their particles are dispersed at distances larger than their diameter—they are known as ‘incoherent’ reflectors.

Not all assumptions of blue scattering are correct, however. As far back as 1934, C. V. Raman doubted that scattering was the cause of all blue bird feathers (Raman 1934). Then, in 1971 Jan Dyck suggested that the reflecting elements within blue bird feathers (such as small air spaces within a spongy matrix) may actually provide a coherent reflection, whereby they act as ‘layers’ within a multilayer reflector (Dyck 1971). Rick Prum and his colleagues substantiated this idea to great effect using a two-dimensional Fourier analysis to demonstrate that the blues of some extant bird feathers, previously thought to result from scattering structures, were in fact the result of coherent reflectors (Prum et al. 1998, 1999; see §2d,e).

(b) Diffraction gratings

When light interacts with a periodic surface consisting for example of a series of parallel grooves, it may be deviated from the direction of simple transmission or reflection. For this to happen, the light that is scattered or diffracted from

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successive grooves should be out of phase by integral values of $2\pi$. This occurs when for a given direction of propagation the optical path difference via successive grooves is $m\lambda$, where $m$ is an integer known as the diffraction order. This may be expressed by the grating equation

$$2w(\sin \theta_i - \sin \theta_m) = m\lambda,$$

where $\theta_i$ and $\theta_m$ are the angles of incidence and diffraction, respectively, and $w$ is the period (figure 3).

A diffraction grating gives rise to coloration because constructive interference for different wavelengths is fulfilled under different angles according to the above equation. For a ‘non-blazed’ grating, although the effect changes with angle of incidence it is less critical than it is with multilayer reflectors (see below) and the visual appearance is different. For a parallel beam of white light incident upon a multilayer, a family of wavelengths will be reflected as determined by the so-called ‘Bragg condition’, although often only one of these wavelengths falls within the visible range. The same beam incident upon a non-blazed grating will be dispersed into spectra. The complete spectrum reflected nearest to the perpendicular (grating normal) is the first order. The first-order spectrum is reflected over a smaller angle than the second-order spectrum, and the colours are more saturated and appear brighter within the former. Diffraction gratings have polarizing properties, but this is strongly dependent on the grating profile.

The earliest known examples of diffraction gratings, or indeed any form of structural colour, are from the Cambrian period and belong to the famous Burgess Shale animals of the Canadian Rockies, 508 Ma (Parker 1998). These linear, two-dimensional diffraction gratings have not survived in their entirety, rather as mosaics (e.g. figure 4), but always run in the same direction relative to a spine, even where it curves (suggesting that the gratings are not artefacts of geological processes). Therefore, to observe the original colours, the surface must be reconstructed in photoresist. Most colours in sunlight would have existed in the original environments of the Burgess animals, and their colours probably functioned as warnings to predators with eyes—to emphasize the strong, protective spines on which they are accommodated.

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Today diffraction gratings are particularly common in butterflies (Ingram & Parker 2008; Ingram et al. 2008) and on the setae or setules (hairs) of crustaceans. The ostracod (seed shrimp) *Euphilomedes carcharodonta*, for example, houses a diffraction grating on the rostrum, a continuous flattened area of the carapace that is corrugated to form periodic ridges. Cylindroleberidid ostracods possess a comb on their maxilla bearing numerous fine setules on each

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Cypridinid ostracods (Myodocopida) contain diffraction gratings on their halophores (setules) of their first antennae (Parker 1995). This character is sexually dimorphic and employed by males as a courtship display (figure 5). Also, many polychaetes possess gratings on their setae. For example, the opheliid Lobocheisis longiseta bears gratings with periodicities of the order of 500 nm.

(c) ‘Liquid crystals’

Chiral forms of liquid crystals are found in nature. The helicoidal arrangement of the microfibrils comprising the outer 5–20 μm of the cuticle (the ‘exocuticle’) of certain scarab beetles, such as Plusiotis resplendens, gives rise to metallic colours (Neville & Caveney 1969). Here, the fibrils are arranged in layers, with the fibril axis in each layer arranged at a small angle to the one above, so that after a number of layers the fibrillar axis comes to lie parallel to the first layer. Thus, going vertically down through the cuticle, one corresponding peak and trough of a diffraction grating will be encountered with every 360° rotation of the fibrils—the ‘pitch’ of the system. Polarized light encounters an optically reinforcing plane every half turn of the helix. The system provides a peak reflectance at $\lambda=2nd$, where $d$ is the separation of analogous planes, or half the pitch of the helix (figure 6). In fact, it approximates a diffraction grating except for the polarization properties; the helical arrangement of fibrils reflects light that is circularly or elliptically polarized (Nassau 1983).

(d) Narrowband (coloured) multilayer reflectors (including single thin films)

Light may be strongly reflected by constructive interference between reflections from the different interfaces of a stack of thin films (of actual thickness $d$) of alternately high and low refractive index ($n$). For this to occur,
the reflections from successive interfaces must emerge with the same phase and this is achieved when the Bragg condition is fulfilled (figures 7 and 8). The optical path difference between the light reflected from successive interfaces is an integral number of wavelengths and is expressed in the equation

\[ 2nd \cos \Theta = (m + 1/2)\lambda, \]

from which it can be seen that the effect varies with angle of incidence (\( \Theta \), measured to the surface normal), wavelength (\( \lambda \)) and the optical thickness of the layers (\( nd \)). There is a phase change of half a wavelength in waves reflected from every low-to-high refractive index interface only (figure 7). The optimal narrowband reflection condition is therefore achieved where the optical thickness (\( nd \)) of every layer in the stack is a quarter of a wavelength. In a multilayer consisting of a large number of layers with a small variation in index, the process is more selective than one with a smaller number of layers with a large difference of index. The former therefore gives rise to more saturated colours corresponding to a narrow spectral bandwidth and these colours therefore vary more with a change of angle of incidence. Both conditions can be found in animals—different coloured effects are appropriate for different functions under different conditions. For an oblique angle of incidence, the wavelength of light that interferes constructively will be shorter than that for light at normal incidence. Therefore, as the angle of the incident light changes, the observed colour also changes. Iridescence caused by such interference disappears after (complete) gold coating because transmission of light through the outer surface is prevented.

If the dimensions of the multilayer system deviate from the quarter-wave condition (i.e. \( nd \) is not equal for all layers), then the reflector is known as ‘non-ideal’ (Land 1972) in a theoretical sense (but may be ideal in a behavioural sense). Non-ideal reflectors provide a reduced proportional reflectance and narrower bandwidth for a given number of layers. However, a narrow bandwidth, and a less conspicuous reflection, is sometimes selected for in animals.
Multilayer reflectors polarize light incident at Brewster’s angles. This is approximately $54^\circ$ for a quarter-wave stack of guanine and cytoplasm. At very oblique angles, all wavelengths are strongly reflected from a multilayer.

Single-layer reflectors are found commonly in nature today, where light is reflected, and interferes, from the upper and lower boundaries (figure 7). A difference in the thickness of the layer provides a change in the colour observed from unidirectional polychromatic light. The wings of some houseflies act as a single thin film and reflect different wavelengths as a result of this phenomenon (Fox & Vevers 1960). A single quarter-wavelength film of guanine in cytoplasm, for example, reflects approximately 8 per cent of the incident light (Land 1978).

Figure 7. Light rays affected by a single thin layer, such as a fly’s wing, in air. The layer is shown in cross section; the light ray path and wave profiles are illustrated as solid lines (incoming light) and dashed lines (reflected light).

Figure 8. A narrowband (‘ideal’) multilayer reflector composed of thin (approx. 100 nm thick) layers of alternating refractive index, where the light rays reflected from each interface in the system superimpose either constructively or destructively (some degree of refraction occurs). Reflected rays are in phase when all the layers are approximately a quarter of their wavelength in optical thickness.
However, in a multilayer reflector with 10 or more high index layers, reflection efficiencies can reach 100 per cent (Land 1972; figure 9b). Thus, animals possessing such reflectors may appear highly metallic.

Multilayer reflectors are the most common form of structural colour in animals today. They are usually extracellular, produced by periodic secretion and deposition, but sometimes occur within cells. Guanine (n=1.83) is a common component in invertebrate reflectors because it is one of the very few biological materials with a high refractive index and is readily available to most invertebrates as a nitrogenous metabolite (Herring 1994). However, arthropods, including insects, crustaceans and spiders, have largely ignored guanine in favour of pteridines (Herring 1994). Also surprising is that the reflector material of closely related species, e.g. the molluscs Pecten (scallop) and Cardium (cockle), may differ (Herring 1994).

Multilayers produce optical effects in living and fossil beetle cuticle from highly metallic colours (‘ideal’ system) to rather dull greens (non-ideal system in combination with scattering; Parker et al. 1998a; Parker & McKenzie 2003; Vigneron et al. 2005, 2007). They are also responsible for the colours reflected from the wings of many butterflies (Ingram & Parker 2008), where layers of chitin (n=approx. 1.56) are supported by ribs protruding vertically from the scales. Air (n=1.0) fills in the spaces and provides the alternate layers of the system. A layer of melanin (a black or brown pigment) often underlies the reflector and intensifies the metallic coloured effect by absorbing the transmitted portion of incident light. For example, in beetles the elytra of Anoplognathus parvulus appear metallic gold, green or yellow in reflected light and diffuse brown in transmitted light (Parker et al. 1998a). Individual butterfly scales have been examined in detail to reveal a number of variations in quarter-wave stacks, sometimes in combination with other optical structures, to provide a range of coloured effects (e.g. Ghiradella 1989; Vukusic et al. 2000; Kinoshita et al. 2002). Butterfly scales are three-dimensional submicrometre structures in their basic form, and this has provided a foundation for evolution to produce the most diverse array of optical devices in any taxon, forming a subject in their own right.

Figure 9. Transmission electron micrograph of the iridescent cuticle of the swimming crab Ovalipes molleri. Layers are approximately 100 nm thick.
The crustaceans *Limnadia* (Conchostraca), *Tanais tenuicornis* (Tanaidacea), *Ovalipes molleri* (Decapoda) and the males of *Sapphirina* (Copepoda) all bear multilayer reflectors in their cuticles, in different forms. In contrast to the usual continuous thin layers, male sapphirinids have 10–14 layers of interconnecting hexagonal platelets within the epidermal cells of the dorsal integument (Chae & Nishida 1994). The reflector of *O. molleri* comprises layers that are corrugated and also slightly out of phase (figure 9). The corrugations function to broaden the reflectance band, at the expense of reducing the intensity of reflection (Parker et al. 1998).

(e) Broadband multilayer reflectors (silver and gold ‘mirrors’)

‘Broadband’ multilayer reflectors (figure 10), as opposed to the narrowband types described above, reflect a broad range of wavelengths, such as all of those in white light, thus forming a mirror effect. Simply, they contain layers of different optical thicknesses that each reflects a different wavelength in a given direction. The different wavelengths combine to form an optical effect with a broad range of colours. When all the wavelengths in white light are reflected, the appearance is silver, and when all but blue and violet are reflected, the appearance is gold, for instance. The metallic effect (e.g. silver rather than white) is due to the directional nature of the reflectance; since all rays are reflected into the same direction, the relative intensity is high (the reflection appears bright).

Broadband reflectors, or mirrors, are employed in animals such as the chrysalis of the butterfly *Euploea core*, the tortoise beetle and many silvery fishes to provide camouflage. The surrounding environment is reflected from the mirrored surface so that the animals cannot be seen (Denton 1970; Land 1972;
Parker 1999b; Vigneron et al. 2007). However, this means of camouflage can only be achieved in an environment with diffuse light to prevent a strong, direct reflection from the Sun. *Euploea core* indeed lives in forests with diffuse light conditions. Many fishes take advantage of such conditions, to achieve the same effect, in the sea (Denton 1990). Similarly, iridophores camouflage the parts of squids and cuttlefishes that cannot, by their nature, be made transparent, such as eyes and ink sacks (Land 1972).

### 3. Antireflectors: zero-order gratings

When the periodicity of a grating reduces much below the wavelength of light, it becomes a zero-order grating and its effect on light waves changes (see Hutley 1982). This difference in optical effect occurs because when the periodicity of the grating is below the wavelength of light, the freely propagating diffracted orders are suppressed and only the zero order is reflected when the illumination is normal to the plane of the grating. To describe accurately the optical properties of a zero-order grating, rigorous electromagnetic theory is required. In an optical system that accepts only the zero order, what is seen is white light minus that diffracted into the ±1 order. This may result in no reflection at all (i.e. total transmission), where the structures become ‘antireflective’.

In 1976, in Poland, a 45-million-year-old fly’s eye preserved in Baltic amber was photographed in an electron microscope to demonstrate the detail of preservation (figure 11). An unusual feature of the cornea was a series of fine parallel ridges. A model of the corneal surface was made in photoresist by lithographic methods and its reflectivity was compared with the same photoresist material with a smooth surface. The fly eye model was found to have excellent antireflective properties over a wide angular range, at least 60° on either side of the surface normal (Parker et al. 1998c). This would have aided the fly’s vision by permitting more light to pass through the surface of the eye and therefore reach the retina. However, it was found that this new antireflector design provides a 10 per cent increase in energy capture when applied to the surfaces of solar panels (Parker 1999a). Hence, this fly eye antireflector is now manufactured, moulded on large plastic sheets with refractive index matching glue.

Zero-order diffraction gratings that cause total transmission (i.e. there is no reflection) are also found on the corneal surface of *Zalea minor* (Diptera) today. The periodicity of the corneal gratings of this fly, which have the same profile as that of the Eocene fly above, is 242 nm (Parker et al. 1998c).

Another form of antireflection grating is found on the transparent wings of the hawkmoth *Cephalonodes hylas* (Yoshida et al. 1996) and on the corneal surface of each ommatidium of the compound eyes of moths (Miller et al. 1966) and butterflies (e.g. figure 12). Here, optical impedance matching is achieved by means of a hexagonal array of tapered cylindrical protuberances, each of approximately 250 nm diameter (Miller et al. 1966), thus forming a ‘tri-grating’ with grooves transecting at 120° (figure 12). The protuberances provide a graded transition of refractive index between the air and the cornea/wing. Hence, the refractive index at any depth is the average of that of air and the corneal/wing material.
4. Complex optical reflectors: photonic crystals

In the 1980s the photonic crystal concept was introduced within physics. Photonic crystals are ordered, often complex, subwavelength (nano) lattices that can control the propagation of light at the single wave scale in the manner that atomic crystals control electrons (see Yablonovitch 1999). This is because light of a certain wavelength is completely reflected, regardless of the direction of the incident light.
Photonic crystals are complex optical reflectors, where a single wave is scattered more than once, even leading to rays of certain wavelengths becoming trapped when surrounded by ‘forbidden zones’ (regions where rays of some wavelengths are inadmissible) within the structure. Here, the light of a certain wavelength encounters a region from where it is back reflected in every direction it can travel. To identify a photonic crystal, rigorous electromagnetic scattering theory must be applied (such as the ‘multipole’ method; see Parker et al. 2001), since all the probabilities for ray paths should be considered rather than simply the average ray path as considered in simple optical reflectors. For such complex optical structures, the single-scattering approximation is no longer appropriate due to the multiple scattering of a single light ray. Nonetheless, all reflectors found in nature (when described by wave optics rather than light ray scattering) remain solvable by Maxwell’s equations, and so do not require quantum optical methods. New collaborations between biologists and optical physicists are realizing that some of nature’s reflectors may involve at least partial band gaps, where a forbidden zone for a ray’s path exists in some but not all directions.

An introduced ‘nanotunnel’ (known as a ‘defect’) in the photonic crystal can open up a pathway, along which light of the wavelength affected must travel. This is what ‘controlling’ the path of light means; an achievement previously reserved for the considerably larger fibre optics (see Joannopoulos et al. 2008). Defects are yet to be found in natural photonic crystals, however.

Forbidden zones are the product of periodic arrays of elements, or variations in refractive index, in two or three dimensions within a submicrometre structure (a multilayer reflector has a periodicity in only one dimension). Consider again a quarter-wave stack, where alternating thin layers (a quarter of the wavelength of light in thickness) of different refractive indices are stacked (this happens to be the type of multilayer reflector shown in figure 8, where alternate layers are equal in thickness; see Land 1972). A photonic crystal is the generalization of this principle for submicrometre structures with periodic arrays in two or three dimensions. If the periodicity is constant in two or three dimensions, at approximately twice the wavelength of light, light rays may be forbidden to propagate in many or all directions (the latter case is known as a complete or full photonic band gap; the former case is partial)—in some or all directions it will encounter a forbidden zone. Therefore, a complete photonic band-gap structure will reflect light of a certain wavelength of any polarization incident at any angle. Note that in physics ‘reciprocal space representations’ (or ‘band diagrams’) are made to represent the photonic band-gap effect. Such diagrams are given for some of the photonic crystals in this paper, and so I will provide a brief explanation for a two-dimensional lattice below (three-dimensional lattices complicate matters considerably).

(a) Band diagrams

Each component of a photonic crystal, such as a single nanotube, is considered in cross section and marked with a point at its centre. A ‘Bragg plane’ is drawn as a line that is perpendicular to, and transects at its centre, the line connecting this point to one of its nearest neighbours. If four points are equidistant to the original point, then four Bragg planes are drawn, forming a square (figure 13a). The first ‘Brillouin zone’ for the original point is the area within the square.
A right-angled triangle is constructed by drawing a line from the centre point of the square to one corner and then to the halfway of one side—this is known as the ‘irreducible zone’ (figure 13b). Now the energy dispersion relation for a photon within the structure can be calculated and revealed diagrammatically, as shown in figure 13c. The momentum (or wavevector) of the photon moving along the perimeter of the triangle is exposed for different wavelengths of light (or energy). Horizontal gaps in this diagram represent wavelength regions where propagating photons are not allowed and will find it impossible to traverse the structure—\emph{this is a photonic band gap}. If the gap is continuous across

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the diagram (i.e. along the entire perimeter of the irreducible zone), then the photonic band gap is known as ‘full’; if the gap covers only part of the diagram it is known as ‘partial’.

(b) The sea mouse Aphrodita and a bee

In 2001, the first ‘photonic crystal fibre’ (a two-dimensional photonic crystal) in nature was identified as such in *Aphrodita* sp. (a sea mouse)—a marine polychaete worm (Parker et al. 2001). The sea mouse is covered in iridescent hairs (neurochaetae) and spines (notochaetae) that approximate photonic crystal fibres (figure 14a), causing the coloured effect to change dramatically with orientation of the hairs/spines with respect to the light source (figure 14b,c). Exactly 88 submicrometre tubes make up the wall of a spine (itself a tube), which have consistent external diameters of 510 nm and a precise packing constant (figure 14d,e). A multipole method was applied to this lattice and used to explain this reflectance pattern and reveal a photonic band gap (figure 14f,g; Parker et al. 2001). Essentially, the stack of submicrometre tubes forms a multilayer reflector in any direction within the transverse plane of the spine, although light reflected by this reflector will meet further optical boundaries in the form of the curved surfaces of surrounding submicrometre tubes. Hence, individual light rays will be reflected multiple times. This does not apply, however, to light incident in the longitudinal plane (along the length) of the spine.

Preliminary investigations have revealed ‘photonic crystal fibres’ within the setae of a diversity of polychaetes. A further example has been discovered in a blue-banded bee, *Amegilla* sp. (Fung 2005). The scales on the dorsal surface of these insects vary from green to yellowish green as the light source is rotated around them by 90°, achieving a peak reflectivity of 63 per cent (i.e. 63% of the incident light is reflected when the orientation of the scale is most compliant; Fung 2005). Within each scale exists a hexagonal array of submicrometre tubes, each 200–80 nm in external diameter, which, when packed together, form an effective stack of nanoholes approximately 10 layers deep and with a slight tilt with respect to the scale surface (figure 14e; Fung 2005). This cross-sectional architecture (figure 14e) is considered for its effect on light rays just as the architecture shown in figure 13c; only here rays reflected for the first time encounter optical boundaries in the horizontal as well as vertical direction. Hence, they are likely to be reflected again. Such multiple reflection events complicate mathematical modelling significantly. A similar two-dimensional stack of fibres was identified as the cause of iridescence in the ctenophore *Beroe cucumis*, although here the fibres were parallelogram packed (Welch et al. 2005). Reflectance was modelled using a ‘transfer matrix’ approach, based on a two-dimensional ‘Bravais’ lattice (Welch et al. 2005).

(c) Peacock feathers

Another two-dimensional ‘photonic crystal’ (figure 15a–d) has been revealed as the cause of peacock iridescence (Zi et al. 2003). The surface of the barbules of the feather consists of a thin keratin layer. Beneath the surface keratin layer there is a photonic crystal-like structure composed of an array of short rods, running parallel to the barbule surface, connected by keratin. The remaining hollows in the structure are air holes, although these represent spaces between...
Figure 14. ‘Photonic crystals’ of (a–d) the sea mouse *Aphrodita* sp. (Polychaeta) and (e) the bee *Amegilla* sp. (Insecta). (a) Scanning electron micrograph of an abraded cross section through the wall of a spine (notoseta), constructed of submicrometre tubes; internal diameters of the individual submicrometre tubes increase systematically with depth in the stack. (b,c) Light micrographs of the length of the spine showing the different colours obtained when the direction of the light source changes by 90° (light is incident along the length of the spine in (b) and from the side in (c)). (d) Transmission electron micrograph of a section through a hair (neuroseta); internal diameters of the submicrometre tubes are constant. (e) Transmission electron micrograph of a section through a dorsal scale (micrograph by K. K. Fung, reproduced with permission). (f) Modelled reflectance ($R$) of both polarizations (‘$E$’, solid curve; ‘$H$’, dashed curve) at normal incidence for an *Aphrodita* sp. spine. A multipole method was used to calculate the scattering matrix of each layer, and a transfer matrix method was used to calculate the properties of the stack. (g) Band diagram for the *Aphrodita* sp. spine in ‘$E$’ polarization. A multipole method was used to calculate the photonic band diagram for an idealized model corresponding to an array whose geometric parameters correspond to the average from the micrograph in (a) (Parker et al. 2001; McPhedran et al. 2003). Scale bars: (a) 8 μm, (d) 5 μm and (e) 1 μm.
juxtaposed rods, rather than holes within nanotubes as in the previous examples. Cylindrical, hexagonally packed holes, however, have been identified in the feather barbules of the black-billed magpie (Vigneron et al. 2006). Similar to those unidentified micrographs of butterfly ‘photonic crystals’, bird reflectors previously thought to be multilayer reflectors may reveal photonic band gaps (e.g. figure 15e), and feathers may become a common subject of quantum optics in the future. Indeed, electron micrographs of bird reflectors have been published widely, and most reveal either semi-ordered spongy lattices (e.g. Prum et al. 1998) or ordered stacks of rods (e.g. Land 1972) that probably also accommodate partial band gaps.

Figure 15. The barbule structures of a peacock feather. (a–d) Scanning electron micrographs. (a) Transverse cross section of a green barbule; the outer cortex layer contains a periodic structure, the central part is the medullar layer. (b,c) Transverse cross section of the cortex under higher magnification is shown for the green (b) and brown (c) barbules. The rods embedded in the surface keratin layer can be seen clearly. (d) Longitudinal cross section of the green barbule with the surface keratin layer removed. (e) Calculated photonic band structure of an infinite two-dimensional photonic crystal based on the rods (although the nanorods in the peacock feather are of finite length), for E (solid lines) and H (dashed lines) polarizations. Frequency is in units of \( c/a \), where \( c \) is the speed of light in vacuum and \( a \) is the lattice constant. The inset of (e) shows the irreducible Brillouin zone; \( \Gamma \), \( X \) and \( M \) are the centre, edge centre and corner of the first Brillouin zone, respectively. Note that the \( \Gamma-X \) direction is along the direction normal to the cortex surface. From Zi et al. (2003), with permission from the authors. Scale bars: (a) 2 \( \mu m \), (b,c) 500 nm and (d) 1 \( \mu m \).
(d) Weevils containing ‘opal’

Opal is an example of a three-dimensional photonic crystal that both occurs naturally and was identified as a photonic crystal soon after the concept was formed. The ultrastructure of opal was originally revealed in 1964 as a square or more usually hexagonally close packed array of spheres approximately 250 nm in diameter (Sanders 1964). Many Australian fossils have become opalized, particularly those from the Late Cretaceous period, \( \text{ca} \) 110 Ma (e.g. figure 16a). Although this opal had no biological origin, recently opal has been discovered in a live animal—a beetle. That this opal is made by a living organism has important implications—the optical engineer is presented with a manufacturing process that may be copied.

To demonstrate the optical effect of opal, it is worthwhile making the contrast with the effect of a multilayer reflector in other species of beetle. In tropical forests, many beetles employ structural colours for display purposes (Schultz 1986). Where multilayer reflectors are involved, only part of the beetle is visible (as a ‘spot’ of light) from any direction in direct sunlight because such structures cause mirror-like reflections from its curved surfaces. However, a beetle (weevil) does exist with metallic coloration visible from all body regions from every direction, due to a photonic crystal with a structure analogous to that of opal (Parker et al. 2003). The weevil *Metapocyrtus* sp. (formerly identified as *Pachyrhynchus* sp.) possesses scales, approximately 0.1 mm in diameter, occurring in patches on the top and sides of its ‘hemispherical’ body. Individually, the scales are flat, lying parallel with the body, and consist of two parts—an outer shell and an inner structure. The inner structure of the scales is a solid array of transparent spheres, each 250 nm in diameter (Parker et al. 2003; figure 16b). These spheres are arranged in flat layers and have a precise, hexagonal close-packing order. They cause reflection of a narrow range of wavelengths over a wide range of angles of incidence (figure 16c). *Metapocyrtus* sp., however, is currently the only animal known with the opal-type photonic crystal.

(e) Butterflies and weevils containing inverse opal

Three-dimensional photonic crystals in the form of inverse opal (figure 17a), with the same periodicities as the opal lattice, have been observed in electron micrographs of butterfly scales for some time (e.g. Ghiradella 1989) but have only recently received photonic band-gap identification (McPhedran et al. 2003; Ingram & Parker 2008). This has followed considerable effort to manufacture the inverse opal lattice (see Shore et al. 1997).

The weevil *Eupholus nickerli* (figure 17b; unrelated to *Metapocyrtus* sp.) is again covered in thin flat scales, which also provide the same structural colour to *Metapocyrtus* sp. (i.e. the visual effect is equal for all directions of incident light), except here the lattice within the scales is the inverse—the nanospheres are in this case spaces, and the spaces are here chitin (figure 17c). Several recent investigations have revealed further cases of this ‘inverse opal’ in weevils and butterflies (e.g. Kertész et al. 2006).

5. Evolutionary research

Optical reflectors can make suitable phenotypes for the study of evolution, since, unlike many other morphologies, they can be quantified. This has led to the
conclusion that some invertebrate taxa may have evolved with light as the major stimulus. In this situation, the evolution of structural colours may correlate with the evolution of species.

Many species of cypridinid ostracods (seed shrimps) possess diffraction gratings on the halophores (the setules) of their first antennae, which cause iridescence (figure 5a). The least derived living cypridinid appears to be *Azygocypridina* (approx. 350 Myr old; Parker 1995). The subsequent evolution of Cypridinidae reveals a consistent improvement in the physics of the diffraction gratings. One group of cypridinids continued this trend to the point where the most derived species have very dense ‘iridescent fans’ (collection of iridescent hairs) with theoretically near-perfect reflectors in males. The females of these derived species, such as *Skogsbergia* sp., possess very sparse iridescent fans, appearing similar to those of less derived male and female species of Cypridinidae. The males’ iridescence is known to be functional. In at least one species of *Skogsbergia*, when a male ostracod approaches a female its iridescent fan is displayed, which is otherwise held within the carapace that encloses the body (figure 5b). The female then becomes sexually receptive to the light displayed and mating follows (Parker 1995). Divergence in sexual light displays may have generated sufficient sexual isolation among populations to lead to
speciation (see Verrell 1991). In fact, the whole of the Cypridinidae appear to have evolved with light as the major stimulus (Parker 1995).

Also, in butterflies, optical structures are known to be involved in speciation through influencing population structures (Bálint et al. 2005) and in sexual selection (Bálint et al. 2006).

A new aim in the study of animal optical structures is to decipher and emulate the animal’s manufacturing process. Animals contain the ultimate factories—they engineer via nanomachinery and molecular self-assembly, and the results are perfect, as demonstrated by the micrographs in this paper. Maybe, in the not-too-distant future, living cells can be cultured and photonic crystals ‘grown’ and harvested. This in turn would provide an opportunity for novel evolutionary study.

Self-assembly and the engineering processes within cells are not easy to decipher. Considering the lessons learnt from the construction of the tobacco mosaic virus, there may be intermediate stages involved in the manufacture of nature’s photonic crystals—stages that are not evident from the finished article. However, research on the self-assembly of the Aphrodita sp. and Metapocyrtus sp. photonic crystals is underway, beginning with live-cell imaging (e.g. figure 18). Then there are plans to probe the genome of the sea mouse and find the genes that code for its photonic crystals. When compared with the genotypes and phenotypes of its sister species, this will help to explain the evolution of morphologies. This would contrast well with current evolutionary developmental biological studies where patterns on butterflies’ wings are considered (e.g. Xi et al. 2001). Patterns result from the concerted actions of groups of cells, and the study of their development through the life history of the animal is very much distinct from the consideration of individual scale manufacture by individual cells (individual scales provide colour; combined scales provide pattern shapes).

The first study of the manufacture of a specific phenotype by a single cell has been made already, where a model for the development of butterfly scales containing a three-dimensional optical reflector (now known to be inverse opal) was proposed (Ghiradella 1989). Here, the smooth endoplasmic reticulum (ER)
was considered to form a lattice with the architecture of the inverse opal itself. This would draw in the cell membrane to form a ‘negative’ of the lattice, into which chitin would be secreted to form the ‘positive’ structure (Ghiradella 1989). If this idea can be confirmed using live-cell imaging techniques, and coupled with the genetic data to code for the structure, we may learn much about the complete process of evolution, where the much overlooked engineering capabilities of the cell are influential. This may, for instance, explain how a butterfly and a weevil—two unrelated insects—can evolve identical photonic crystals (as shown in figure 17a,c). At first sight, these appear as highly complex structures that require the control of many genes and consequently significant evolutionary steps. However, if the cells themselves carry out much of the work then such structural parallelism, and consequently evolutionary convergence, is not so surprising. This is because the ability to manufacture this photonic crystal could be inherent within insect cells in general, where only (minimal) mutation in the genes to control the developmental process is required. The limited range of photonic crystals found in animals, in comparison with the potential range in physics (where lattices may also contain sharp edges and corners, etc.), further substantiates this idea. So, as a consequence of their production by single cells, photonic crystals make ideal phenotypes for evolutionary study in the future.

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**References**


