31

Biomimetics: Photonic Nanostructures

31.1 Introduction

Three centuries of research, beginning with Hooke and Newton, have revealed a diversity of optical devices at the nanoscale (or at least the submicron scale) in nature. These include structures that cause random scattering, 2D diffraction gratings, 1D multilayer reflectors, and 3D liquid crystals (Figure 31.1a through d). In 2001, the first photonic crystal was identified as such in animals, and since then the scientific effort in this subject has accelerated. Now we know of a variety of 2D- and 3D-photonic crystals in nature (e.g., Figure 31.1e and f), including some designs not encountered previously in physics.

Biomimetics is the extraction of good design from nature. Some optical biomimetic successes have resulted from the use of conventional (and constantly advancing) engineering methods to make direct analogues of the reflectors and antireflectors found in nature. However, recent collaborations between biologists, physicists, engineers, chemists, and material scientists have ventured beyond merely mimicking in the laboratory what happens in nature, leading to a thriving new area of research involving biomimetics via cell culture. Here, the nano-engineering efficiency of living cells is harnessed, and nanostructures such as diatom “shells” can be made for commercial applications via culturing the cells themselves.

31.2 Engineering of Antireflectors

Some insects benefit from antireflective surfaces, either on their eyes to see under low-light conditions, or on their wings to reduce surface reflections in transparent (camouflaged) areas. Antireflective surfaces, therefore, occur on the corneas of moth and butterfly eyes and on the transparent wings of hawkmoths. These consist of nodules, with rounded tips, arranged in a hexagonal array with a periodicity of around 240 nm (Figure 31.2b). Effectively they introduce a gradual refractive index profile at an interface between chitin (a polysaccharide, often embedded in a proteinaceous matrix; r.i. 1.54) and air, and hence reduce reflectivity by a factor of 10.

This “moth-eye structure” was first reproduced at its correct scale by crossing three gratings at 120° using lithographic methods. It has been employed on the surfaces of solar panels, providing a 10% increase in energy capture through reducing the reflected portion of sunlight. Again, this device is embossed onto plastic sheets using holographic techniques.

31.3 Engineering of Iridescent Devices

Many birds, insects (particularly butterflies and beetles), fishes, and lesser-known marine animals display iridescent (changing color with angle) and/or “metallic” colored effects resulting from
photonic nanostructures. These appear comparatively brighter than the effects of pigments and often function in animals to attract the attention of a potential mate or to startle a predator. An obvious application for such visually attractive and optically sophisticated devices is within the anticounterfeiting industry. For secrecy reasons, work in this area cannot be described, although devices are sought at different levels of sophistication, from effects that are discernable by the eye to fine-scale optical characteristics (polarization and angular properties, for example) that can be read only by specialized detectors. However, new research aims to exploit these devices in the cosmetics, paint, printing/ink, and clothing industries. They are even being tested in art to provide a sophisticated color-change effect.

Original work on exploiting nature’s reflectors involved copying the design but not the size, where reflectors were scaled up to target longer wavelengths. For example, rapid prototyping was employed to manufacture a microwave analogue of a *Morpho* butterfly scale that is suitable for reflection in the 10–30 GHz region. Here the layer thicknesses would be in the order of 1 mm rather than 100 nm as in the butterfly, but the device could be employed as an antenna with broad radiation characteristics, or as an antireflection coating for radar. However, today techniques are available to manufacture nature’s reflectors at their true size. Nanostructures causing iridescence include photonic crystal fibers, opal and inverse opal, and unusually sculpted 3D architectures. Photonic crystals are ordered, often complex, sub-wavelength (nano) lattices that can control the propagation of light at the single-wave scale in the manner that atomic crystals control electrons. Examples include opal (a hexagonal or square array of 250 nm spheres) and inverse opal (a hexagonal array of similar-sized holes in a solid matrix). Hummingbird feather barbs contain variation ultrathin layers with variations in porosity that cause their iridescent effects, due to the alternating nanoporous/full dense ultrastructure. Such layers have been mimicked using aqueous-based layering techniques. The greatest diversity of 3D architectures can be found in butterfly scales, which can include micro-ribs with nano-ridges, concave multilayered pits, blazed gratings, and randomly punctate nano-layers.

![FIGURE 31.1](image_url)
The analogues of the famous blue Morpho butterfly (Figure 31.4a) scales have been manufactured. These have been replicated in titania for specialized coatings, where a mimetic sample can be compared with the model beetle and an accurate variation in spectra with angle is observed (Figure 31.3). The titania mimic can be nanoengineered for a wide range of resonant wavelengths; the lowest so far is a pitch of 60 nm for a circular Bragg resonance at 220 nm in a Sc$_2$O$_3$ film (Ian Hodgkinson, pers. com.).

Biomimetic work on the photonic crystal fibers of the Aphrodita sea mouse is underway. The sea mouse contains spines (tubes) with walls packed with smaller tubes of 500 nm, with varying internal diameters (50–400 nm). These provide a bandgap in the red region, and are to be manufactured via an extrusion technique. Larger glass tubes packed together in the proportion of the spine’s nanotubes will be heated and pulled through a drawing tower until they reach the correct dimensions. The sea mouse fibre mimics will be tested for standard PCF applications (e.g., in telecommunications) but also for anticounterfeiting structures readable by a detector.

Biomimetics: Photonic Nanostructures

31.4 Cell Culture

Sometimes nature’s optical nanostructures have such an elaborate architecture at such a small (nano) scale that we simply cannot copy them using current engineering techniques. Additionally, sometimes they can be made as individual reflectors (as for the Morpho structure), but the effort is so great that commercial-scale manufacture would never be cost-effective.

An alternative approach to making nature’s reflectors is to exploit an aspect other than design—that the animals or plants can make them efficiently. Therefore we can let nature manufacture the devices for us via cell-culture techniques. Animal cells are in the order of 10 μm in size and plant cells up to about 100 μm, and hence suitable for nanostructure production. The success of cell culture depends on the species and on type of cell from that species. Insect cells, for instance, can be cultured at room temperature, whereas an incubator is required for mammalian cells. Cell culture is not a straightforward method, however, since a culture medium must be established to which the cells adhere, before they can be induced to develop to the stage where they make their photonic devices.

The current work in this area centres on butterfly scales. The cells that make the scales are identified in chrysalises, dissected, and plated out. Then the individual cells are separated, kept alive in culture, and prompted to manufacture scales through the addition of growth hormones. Currently we have cultured blue Morpho butterfly scales in the lab that have identical optical and structural characteristics to natural scales. The cultured scales...
FIGURE 31.3  (a) A Manuka (scarab) beetle with (b) titania mimetic films of slightly different pitches. (c) Scanning electron micrograph of the chiral reflector in the beetle’s cuticle. (d) Scanning electron micrograph of the titania mimetic film. (Reproduced from DeSilva, L. et al., *Electromagnetics*, 25, 391, 2005. With permission.)

FIGURE 31.4  (a) A *Morpho* butterfly with (b) a scanning electron micrograph of the structure causing the blue reflector in its scales. (c) A scanning electron micrograph of the FIB-CVD-fabricated mimic. A Ga⁺ ion beam (beam diameter 7 nm at 0.4 pA; 30 kV), held perpendicular to the surface, was used to etch a precursor of phenanthrene (C_{14}H_{10}). Both give a wavelength peak at around 440 nm and at the same angle (30°). (From Watanabe, K. et al., *Jpn. J. Appl. Phys.*, 44, L48, 2005. With permission.) (d) Scanning electron micrograph of the base of a scale of the butterfly *Ideopsis similes*. (e) Scanning electron micrograph of a ZnO replica of the same part of the scale in (d). (Reproduced from Zhang, W. et al., *Bioinspir. Biomim.*, 1, 89, 2006. With permission.)
could be embedded in a polymer or mixed into a paint, where they may float to the surface and self-align. Further work, however, is required to increase the level of scale production and to harvest the scales from laboratory equipment in appropriate ways. A far simpler task emerges where the iridescent organism is single-celled.

31.5 Diatoms and Coccolithophores

Diatoms are unicellular photosynthetic microorganisms. The cell wall is called the frustule and is made of the polysaccharide pectin impregnated with silica. The frustule contains pores (Figure 31.5a through c) and slits that give the protoplasm access to the external environment. There are more than 100,000 different of species of diatoms, generally 20–200 μm in diameter or length, but some can be up to 2 mm long. Diatoms have been proposed to build photonic devices directly in 3D. The biological function of the optical property (Figure 31.5d) is at present unknown, but may affect light collection by the diatom. This type of photonic device can be made in silicon using a deep photochemical-etching technique (initially developed by Lehmann) (e.g., Figure 31.5e). However, there is a new potential here since diatoms carry the added advantage of exponential growth in numbers—each individual can give rise to 100 million descendents in a month.

Unlike most manufacturing processes, diatoms achieve a high degree of complexity and hierarchical structure under mild physiological conditions. Importantly, the size of the pores does not scale with the size of the cell, thus maintaining the pattern.

Fuhrmann et al. showed that the presence of these pores in the silica cell wall of the diatom Coscinodiscus granii means that the frustule can be regarded as a photonic crystal slab waveguide. Furthermore, they present models to show that light may be coupled into the waveguide and give photonic resonances in the visible spectral range.

The silica surface of the diatom is amenable to simple chemical functionalization (e.g., Figure 31.6a through c). An interesting example of this uses a DNA-modified diatom template for the control of nanoparticle assembly. Gold particles were coated with DNA complementary to that bound to the surface of the diatom. Subsequently, the gold particles were bound to the diatom surface via the sequence-specific DNA interaction. Using this method up to seven layers were added showing how a hierarchical structure could be built onto the template.

Porous silicon is known to luminesce in the visible region of the spectrum when irradiated with ultraviolet light. This photoluminescence (PL) emission from the silica skeleton of diatoms was exploited by DeStafano in the production of an optical gas sensor. It was shown that the PL of Thalassiosira rotula is strongly dependent on the surrounding environment. Both the optical intensity and peaks are affected by gases and organic vapors. Depending on the electronegativity and polarizing ability, some substances quench the luminescence, while others effectively enhance it. In the presence of the gaseous substances NO₂, acetone, and ethanol, the photoluminescence was quenched. This was because these substances attract electrons from the silica skeleton of the diatoms and hence quench the PL.

![Figure 31.5](image-url)
Nucleophiles, such as xylene and pyridine, which donate electrons, had the opposite effect, and increased PL intensity almost ten times. Both quenching and enhancements were reversible as soon as the atmosphere was replaced by air.

The silica inherent to diatoms does not provide the optimum chemistry/refractive index for many applications. Sandhage et al.22 have devised an inorganic molecular conversion reaction that preserves the size, shape, and morphology of the diatom while changing its composition. They perfected a gas/silica displacement reaction to convert biologically derived silica structures such as frustules into new compositions. Magnesium was shown to convert SiO₂ diatoms by a vapor phase reaction at 900°C to MgO of identical shape and structure, with a liquid Mg₂Si byproduct. Similarly, when diatoms were exposed to titanium fluoride gas, the titanium displaced the silicon, yielding a diatom structure made up entirely of titanium dioxide; a material used in some commercial solar cells.

An alternative route to silica replacement hijacks that native route for silica deposition in vivo. Rorrer et al.23 sought to incorporate elements such as germanium into the frustule—a semiconductor material that has interesting properties that could be of value in optoelectronics, photonics, thin film displays, solar cells, and a wide range of electronic devices. Using a two-stage cultivation process, the photosynthetic marine diatom Nitzschia

![FIGURE 31.6](https://example.com/figure31.6)

**FIGURE 31.6** Modification of natural photonic devices. (a)–(c) Diatom surface modification. The surface of the diatom was silanized, then treated with a heterobifunctional cross-linker, followed by attachment of an antibody via a primary amine group. (a) (i) Diatom exterior surface (ii) APS (iii) ANB-NOS (iv) primary antibody (v) secondary antibody with HRP conjugate. Diatoms treated with primary and secondary antibody with (b) no surface modification (c) after surface modification. (d and e) Scanning electron micrographs showing the pore pattern of the diatom *C. wailesii* (d) and after growth in the presence of nickel sulphate (e). Note the enlargement of pores, and hence change in optical properties, in (e). (f) “Photonic crystal” of the weevil Metapocyrtus sp., section through a scale, transmission electron micrograph; scale bar: 1 μm (see Parker33). (g) A comparatively enlarged diagrammatic example of cell membrane architecture: tubular christae in mitochondria from the chloride cell of sardine larvae. Evidence suggests that preexisting internal cell structures play a role in the manufacture of natural nanostructures; if these can be altered then so will the nanostructure made by the cell. (From Threadgold, L.T., *The Ultrastructure of the Animal Cell*, Pregamon Press, Oxford, U.K., 1967.)
frustulum was shown to assimilate soluble germanium and fabricate Si-Ge-oxide nanostructured composite materials.

Porous glasses impregnated with organic dye molecules are promising solid media for tunable lasers and nonlinear optical devices, luminescent solar concentrators, gas sensors, and active waveguides. Biogenic porous silica has an open sponge-like structure and its surface is naturally OH-terminated. Hildebrand and Palenik24 have shown that rhodamine B and 6G are able to stain diatom silica in vivo, and determined that the dye treatment could survive the harsh acid treatment needed to remove the surface organic layer from the silica frustule.

Now attention is beginning to turn additionally to coccolithophores—single-celled marine algae, also abundant in marine environments. Here, the cell secretes calcitic photonic crystal frustules, which, like diatoms, can take a diversity of forms, including complex 3D architectures at the nano- and microscales.

### 31.6 Iridoviruses

Viruses are infectious particles made up of the viral genome packaged inside a protein capsid. The iridovirus family comprises a diverse array of large (120–300 nm in diameter) viruses with icoshedral symmetry. The viruses replicate in the cytoplasm of insect cells. Within the infected cell the virus produces a paracrystalline array that causes Bragg refraction of light. This property has largely been considered esthetic to date, but the research group of Vernon Ward (New Zealand), in collaboration with the Biomaterials laboratory at Wright–Patterson Air Force base, is using iridoviruses to create biophotonic crystals. These can be utilized for the control of light, with this laboratory undertaking large-scale virus production and purification as well as targeting the manipulation of the surface of iridoviruses for altered crystal properties. These can provide a structural platform for a broad range of optical technologies, ranging from sensors to waveguides.

Virus nanoparticles, specifically *Chilo* and *Wiseana* Invertebrate Iridovirus, have been used as building blocks for iridescent nanoparticle assemblies. Here, virus particles were assembled in vitro, yielding films and monoliths with optical iridescence arising from multiple Bragg scattering from closely packed crystalline structures of the iridovirus. Bulk viral assemblies were prepared by centrifugation followed by the addition of glutaraldehyde, a cross-linking agent. Long-range assemblies were prepared by employing a cell design that forced virus assembly within a confined geometry followed by cross-linking. In addition, virus particles were used as core substrates in the fabrication of metallic dielectric nanostructures. These comprise a dielectric core surrounded by a metallic shell. More specifically, a gold shell was assembled around the viral core by attaching small gold nanoparticles to the virus surface using inherent chemical functionality of the protein capsid.25 These gold nanoparticles then acted as nucleation sites for electroless deposition of gold ions from solution. Such nano-shells could be manufactured in large quantities, and provide cores with a narrower size distribution and smaller diameters (below 80 nm) than currently used for silica. These investigations demonstrated that direct harvesting of biological structures, rather than biochemical modification of protein sequences, is a viable route to create unique, optically active materials.

### 31.7 The Mechanisms of Natural Engineering and Future Research

Where cell culture is concerned it is enough to know that cells do make optical nanostructures, which can be farmed appropriately. However, in the future an alternative may be to emulate the natural engineering processes ourselves, by reacting to the same concentrations of chemicals under the same environmental conditions, and possibly substituting analogous nano- or macro-machinery.

To date, the process best studied is the silica cell wall formation in diatoms. The valves are formed by the controlled precipitation of silica within a specialized membrane vesicle called the silica deposition vesicle (SDV). Once inside the SDV, silicic acid is converted into silica particles, each measuring approximately 50 nm in diameter. These then aggregate to form larger blocks of material. Silica deposition is molded into a pattern by the presence of organelles such as mitochondria spaced at regular intervals along the cytoplasmic side of the SDV.26 These organelles are thought to physically restrict the targeting of silica from the cytoplasm, to ensure laying down of a correctly patterned structure. This process is very fast, presumably due to optimal reaction conditions for the synthesis of amorphous solid silica. Tight structural control results in the final species-specific, intricate exoskeleton morphology.

The mechanism whereby diatoms use intracellular components to dictate the final pattern of the frustule may provide a route for directed evolution. Alterations in the cytoplasmic morphology of *Skeletonema costatum* have been observed in cells grown in sublethal concentrations of Mercury and Zinc,27 resulting in swollen organelles, dilated membranes, and vacuolated cytoplasm. Frustule abnormalities have also been reported in *Nitzschia liebethrutti* grown in the presence of mercury and tin.28 Both metals resulted in a reduction in the length to width ratios of the diatoms, fusion of pores, and a reduction in the number of pores per frustule. These abnormalities were thought to arise from enzyme disruption either at the silica deposition site or at the nuclear level. We grew *Coscinodiscus wailesii* in sublethal concentrations of nickel and observed an increase in the size of the pores (Figure 31.6d and e), and a change in the phospholuminescent properties of the frustule. Here, the diatom can be "made to measure" for distinct applications such as stimuli-specific sensors.

Further, trans-Golgi-derived vesicles are known to manufacture the coccolithophore 3D "photonic crystals."29 So the organelles within the cell appear to have exact control of (photonic) crystal growth (CaCO\textsubscript{2} in the coccolithophores) and packing (SiO\textsubscript{2} in the diatoms).30,31 Indeed, Ghiradella suggested that the employment of preexisting, intracellular structures lay behind the development of some butterfly scales, and Overton32
reported the action of microtubules and microfibrils during butterfly-scale morphogenesis. Further evidence has been found to suggest that these mechanisms, involving the use of molds and nano-machinery (e.g., Figure 31.6f and g), reoccur with unrelated species, indicating that the basic “eukaryote” (containing a nucleus) cell can make complex photonic nanostructures with minimal genetic mutation.\(^{33}\) The ultimate goal in the field of optical biomimetics, therefore, could be to replicate such machinery and provide conditions under which, if the correct ingredients are supplied, the optical nanostructures will self-assemble with precision.

For further information on the evolution of optical devices in nature, including those found in fossils, or when they first appeared on earth, see references.\(^{34,35}\)

### Acknowledgments

This work was funded by The Royal Society (University Research Fellowship), The Australian Research Council, European Union Framework 6 grant, and an RCUK Basic Technology grant.

### References


