Biomimetics of photonic nanostructures

Biomimetics is the extraction of good design from nature. One approach to optical biomimetics focuses on the use of conventional engineering methods to make direct analogues of the reflectors and anti-reflectors found in nature. However, recent collaborations between biologists, physicists, engineers, chemists and materials scientists have ventured beyond experiments that merely mimic what happens in nature, leading to a thriving new area of research involving biomimetics through cell culture. In this new approach, the nanoengineering efficiency of living cells is harnessed and natural organisms such as diatoms and viruses are used to make nanostructures that could have commercial applications.

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Three centuries of research, beginning with Hooke and Newton, have revealed a diversity of optical devices at the submicrometre scale in nature[1]. These include one-dimensional multilayer reflectors, two-dimensional diffraction gratings and three-dimensional liquid crystals. In 2001 the first photonic crystal in an animal was identified[2] and since then the scientific effort in this subject has accelerated. Now we know of a variety of two-dimensional and three-dimensional photonic crystals in nature, including some designs not encountered previously in physics.

However, some of the optical nanostructures found in nature have such an elaborate architecture at the nanoscale that we simply cannot copy them using current engineering techniques or, if they can be copied, the effort involved is so great that commercial-scale manufacture would never be cost-effective. An alternative approach is to exploit the fact that plants and animals can make these designs very efficiently (for example, ref. 3). Therefore we can let nature manufacture the devices for us through cell-culture techniques.

Animal cells are about 10 μm in size and plant cells can have sizes of up to about 100 μm, so they are both of a suitable scale for nanostructure production. Although the overall size of the structures produced by a single cell is about the size of the cell itself, these structures can involve sub-structures on a smaller scale (typically of the order of 100 nm). The success of cell culture depends on the species and on the type of cell. Insect cells, for instance, can be cultured at room temperature, whereas an incubator is required for mammalian cells. It is also necessary, where solid media are involved, to establish a culture medium that the cells can adhere to in order for them to develop to the stage where they can make photonic devices.

This article will first describe progress in the conventional engineering approach to optical biomimetics, and then discuss the more recent cell-culture approach at greater length.

ENGINEERING ANTI-REFLECTORS AND IRIDESCENT DEVICES

Some insects benefit from anti-reflective surfaces, either on their eyes to see in low-light conditions, or on their wings to reduce surface reflections from transparent structures for the purpose of camouflage. Anti-reflective surfaces are found, for instance, on the corneas of moth and butterfly eyes[4] and on the transparent wings of hawkmoths[5]. These surfaces consist of cylindrical nodules with rounded tips arranged in a hexagonal array with a periodicity of around 240 nm (Fig. 1a). Effectively they introduce a gradual refractive index profile at an interface between chitin (a polysaccharide with a refractive index, n, of 1.54 that is often embedded in a proteinaceous matrix) and air ($n = 1.0$), and reduce reflectivity by a factor of about ten.

This 'moth-eye structure' was first reproduced at its correct scale by crossing three gratings at 120° using lithographic techniques, and has been used as an anti-reflective surface on glass windows in Scandinavia[6]. Here, plastic sheets bearing the anti-reflector were attached to each interior surface of triple glazed windows using refractive-index-matching glue to provide a significant difference in reflectivity. Today the moth-eye structure can be made extremely accurately using electron-beam etching[7] (Fig. 1c), and is used commercially on solid plastic and other lenses.

A different type of anti-reflective device, in the form of a sinusoidal grating of 250 nm periodicity, was discovered on the cornea of a 45 million-year-old fly preserved in amber[8] (Fig. 1b). This type of grating is particularly useful where light is incident at a range of angles (within a single plane, perpendicular to the grooves of the grating), as demonstrated by a model made in a photoresist using lithographic methods[8]. Consequently it has been used on the surfaces of solar panels, providing a 10% increase in energy capture by reducing the reflected portion of sunlight[9]. Again, this device is embossed onto plastic sheets using holographic techniques.

Many birds, insects (particularly butterflies and beetles), fishes and lesser-known marine animals exploit photonic nanostructures on their surfaces to make their colour change with viewing angle (iridescence) and/or appear 'metallic'. These visual effects appear more pronounced than those produced by pigments and are used to attract the attention of potential mates or to startle predators.

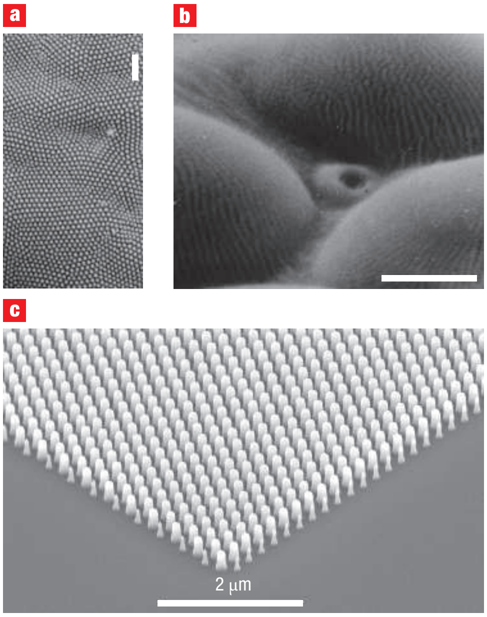

Figure 1 Natural and fabricated anti-reflective surfaces. **a**, Scanning electron micrograph of an anti-reflective surface from the eye of a moth. Domains corresponding to individual cells are evident in this image Scale bar = 1 μm. **b**, Anti-reflector with ridges on three facets on the eye of a 45 million-year-old fly (dolichopodid). Scale bar = 3 μm. Courtesy of P. Mierzejewski. **c**, This biomimetic replica of a moth eye[7] was fabricated with ion-beam etching. Although the replica is accurate, it can only be fabricated over areas of a few micrometres across, whereas a natural device has the potential to be larger as the size is limited by the number of appropriate cells present. Scale bar = 2 μm. Copyright (2006) IEEE.

An obvious application for such visually attractive and optically sophisticated devices is within the anti-counterfeiting industry[10]. Although much of the work in this area is not published, researchers are developing devices with different levels of sophistication, from effects that are discernable by the eye to fine-scale optical characteristics (such as polarization and angular properties) that can be read only by specialized detectors.

However, new research — such as the replication of an iridescent beetle cuticle by Vigneron *et al.*[11] — aims to exploit these devices in the cosmetics (including packaging), paint, printing and clothing industries. Interestingly, the range of refractive indices available in artificial structures is much larger than those found in natural reflectors: n can be as high as 4 for a semiconductor, compared with a maximum of around 1.8 for natural materials. This could make these structures considerably more useful for applications, even if the natural structure geometry is maintained.

Original work exploiting the reflectors found in nature involved copying the design but not the size, with reflectors being scaled-up to work at longer wavelengths. For example, the *Morpho* butterflies — a group of large, usually blue, butterflies from Central and South America — typically possess optical structures with a 'Christmas tree' profile. A microwave analogue of this structure, which could be used as an antenna or as an anti-reflection coating for radar, has been manufactured using rapid prototyping. The layers in these devices are about 1 mm thick, compared with 100 nm in the butterflies. However, techniques are now available to manufacture natural reflectors at their true size.

Nanostructures causing iridescence include photonic crystals and unusually sculpted three-dimensional architectures. Photonic crystals are materials with an ordered subwavelength structure that can control the propagation of light, only allowing certain wavelengths (or ranges of wavelengths) to pass through the crystal, just as atomic crystals only allow electrons with energies in certain ranges to propagate[12]. Examples include opal (a hexagonal or square array of 250 nm spheres) and inverse opal (a hexagonal array of similar sized and shaped holes in a solid matrix). Hummingbird feather barbs provide an example of unusually sculpted three-dimensional architectures, with the iridescence often caused by variations in porosity. Such devices have been mimicked using aqueous-based layering techniques[13].

The greatest diversity of three-dimensional architectures can be found in butterfly scales, which can include micro-ribs with nanoridges, concave multilayered pits, blazed gratings and randomly punctuated nanolayers[14–16]. The cuticles of many beetles contain chiral films that produce iridescent effects with circular or elliptical polarization properties[17]. These have been replicated in titania for specialized coatings (Fig. 2). 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_2O_3 film (I. Hodgkinson, personal communication).

Biomimetic work on the photonic crystal fibres of the *Aphrodita* sea mouse is underway. The sea mouse contains spines (tubes), the walls of which are packed with smaller tubes that are 500 nm in diameter and have varying internal diameters (50–400 nm). These provide a bandgap in the red region, and will be manufactured by an extrusion technique. Larger glass tubes, arranged proportionally, will be heated and pulled through a drawing tower until they reach the correct dimensions.

Analogues of blue *Morpho* butterfly (Fig. 3a) scales have also been manufactured. *Morpho* wings typically contain two layers of scales — a quarter-wave stack to generate colour and another layer above it to scatter the light. Early copies of the *Morpho* wing did not have this scattering layer: rather, the quarter-wave stack was deposited onto a roughened substrate, and the resulting roughness in the stack scattered the light[18]. Nevertheless, these devices closely matched the butterfly wings, with the colour changing only slightly as the angle was varied over 180°. This effect, which is actually quite difficult to achieve, is useful for various types of optical filter.

Recently, focused ion beam chemical vapour deposition (FIB-CVD) has been used to make more accurate reproductions of the *Morpho* Christmas tree structures[19] (Fig. 3c), but this method is not suitable for low-cost mass production, so the nanostructures produced are currently limited to high-cost items, such as filters for flat-panel displays. Recently the scales of butterfly wings have been used as templates for replicating these structures in ZnO (ref. 20). This technique involves sacrificing a scale to make each replica, but the enhanced optical properties of the replacement materials could make that profitable.

CELL CULTURE TECHNIQUES AND EARLY SUCCESSES WITH DIATOMS

An alternative approach to optical biomimetics involves harnessing the actual processes inside cells that make natural optical devices, rather than trying to use conventional fabrication techniques. Below we discuss the use of diatoms and viruses to make optical nanostructures, and in the section "Lessons from cell engineering" we discuss an alternative manufacturing approach based on the emulation of natural engineering processes.

Current work on cell-culture techniques centres on butterfly scales. The cells that make the butterfly scales are identified in chrysalises, dissected and plated out. The individual cells are then separated, kept alive in culture and prompted to manufacture scales through the addition of growth hormones. We have cultured blue *Morpho* butterfly scales in the lab that have optical and structural

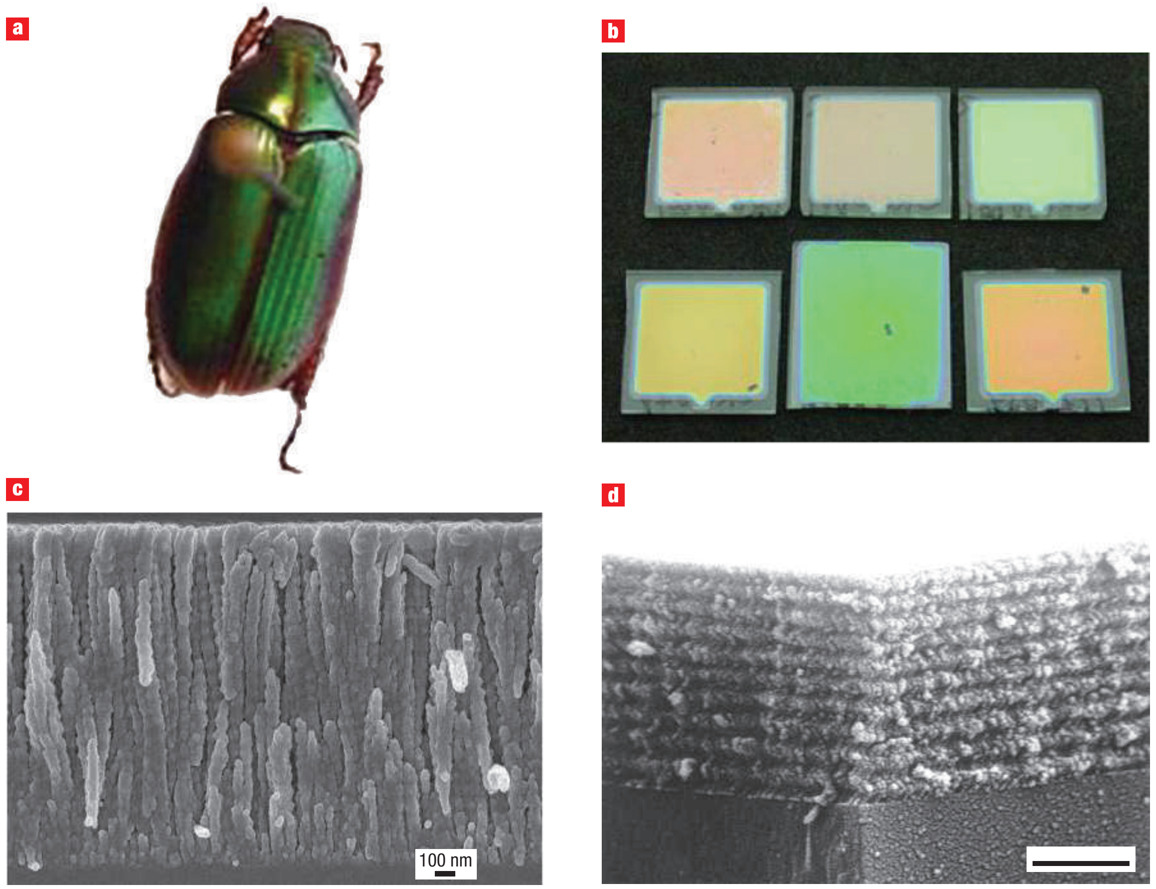

Figure 2 Replicating the iridescent cuticle of a beetle. **a**, The Manuka (scarab) beetle exploits chiral films in a manner similar to a liquid crystal to make its cuticle iridescent. **b**, Biomimetic replicas (each around 2 cm^2) made of titania have different colours depending on the pitch of the film. The colour of the replica varies with angle in the same way as the cuticle of the beetle. The circular polarization properties of the replica and the beetle are also the same. **c**, A scanning electron micrograph of the chiral reflector in the cuticle of the beetle and **d**, the replica. Scale bar = 400 nm. Reproduced with permission from ref 17. Copyright (2005) Taylor and Francis.

characteristics that are identical to those found in natural scales. The cultured scales could be embedded in a polymer or mixed into a paint, where they may float to the surface and self-align. There are also applications in optical sensors for vapours[21]. However, if cultured scales are to be used in real-world applications, further work is needed to increase the level of production and to find better ways of harvesting the scales from laboratory equipment.

It is, however, much easier to work with single-celled organisms, such as diatoms. A diatom is a photosynthetic micro-organism and its cell wall (called the frustule) is made of pectin, a polysaccharide, impregnated with silica. The frustule contains pores (Fig. 4a) and slits that give the protoplasm in the cell access to the external environment. There are more than 100,000 different species of diatoms, which are generally 20–200 μm in diameter or length, but can be up to 2 mm long. Diatoms have been proposed to build photonic devices directly in three-dimensions[22]. The biological function of the optical effect (Fig. 4b) is at present unknown but it may affect light collection by the diatom. This type of photonic device can be made in silicon using a deep photochemical etching technique that was initially developed by Lehmann and co-workers[23] (see also Fig. 4c). However, it is possible to exploit the fact that the number of diatoms grows exponentially with time — 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.*[22] 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 (Fig. 4d,e). An interesting example of this uses a DNA-modified diatom template for the control of nanoparticle assembly[24]. 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[25]. This photoluminescence (PL) emission from the silica skeleton of diatoms was exploited by DeStafano[26] in the production of an optical sensor. It was shown that the PL of *Thalassiosira rotula* is strongly dependent on the surrounding environment.

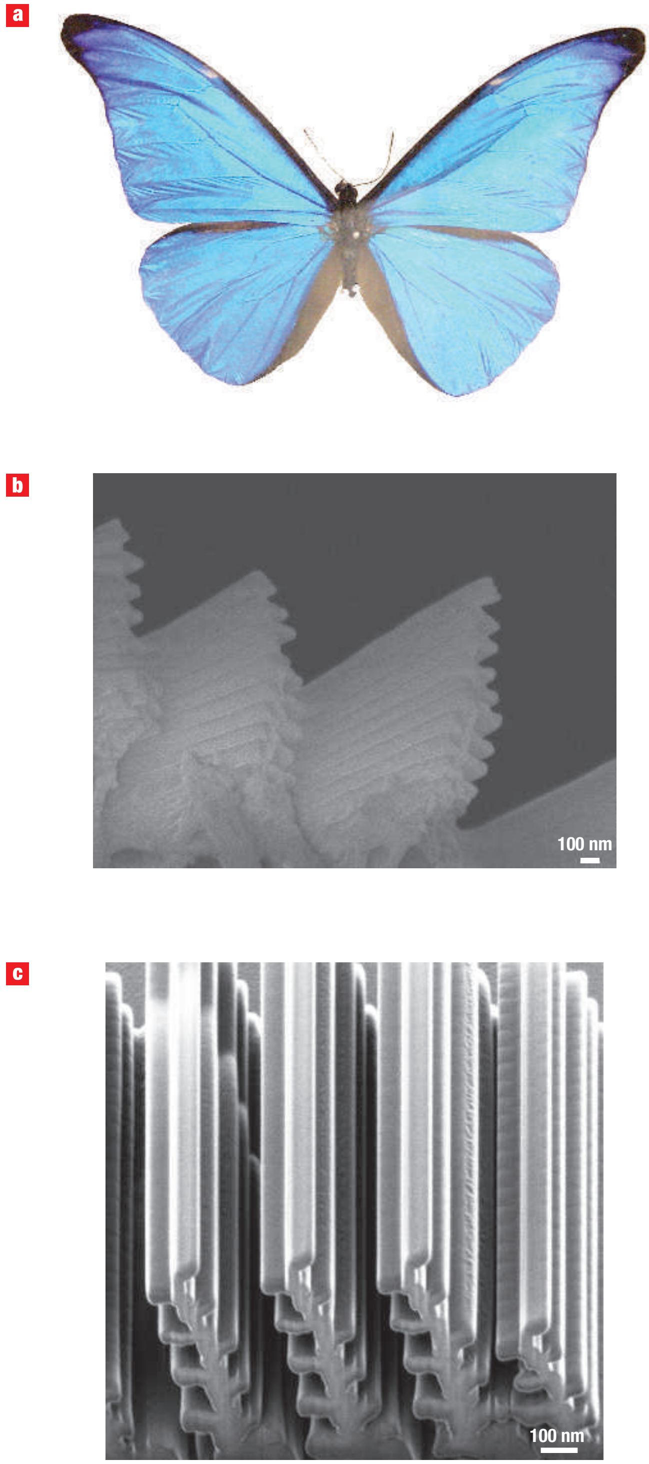

Figure 3 The iridescent wings of a *Morpho* butterfly. **a**, The complex nanoarchitecture found in the wings of this *Morpho* gives them a distinctive iridescent blue colour and presents significant challenges to researchers trying to make replicas. **b**, Scanning electron micrographs of the structures in the scales of the wing that reflect blue light. **c**, A mimic fabricated with the FIB-CVD method. Both structures give a wavelength peak at around 440 nm at an angle of about 30°. However, the replica can only be made to cover areas in the order of micrometres, whereas the butterfly wings are several centimetres across. Reproduced with permission from ref. 19. Copyright (2004) Japanese Society of Applied Physics.

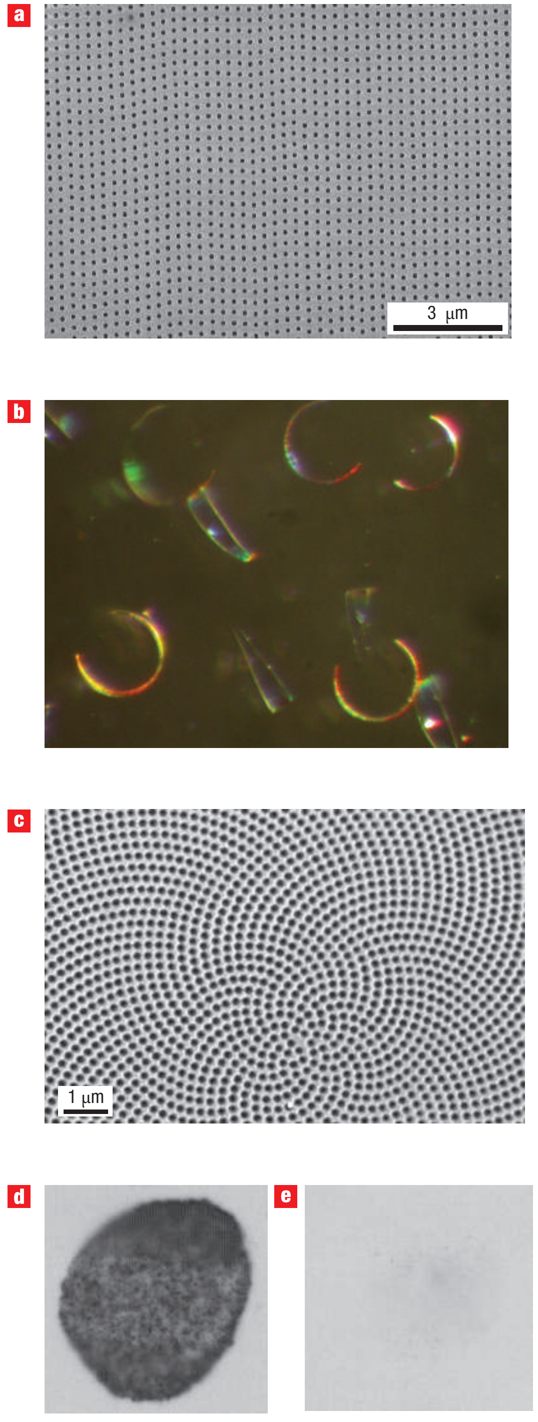

Figure 4 The periodic structures found in the walls of some diatoms could have useful optical properties for applications. **a**, A scanning electron micrograph of the girdle band (which form the side wall of the frustule) of *Coscinodiscus granii*. **b**, The iridescent effect of several isolated girdle bands. **c**, A scanning electron micrograph of a replica of a diatom frustule made by deep photochemical etching. This method has been patented for photonic crystal applications. Reproduced with permission from ref. 46. Copyright (2006) Royal Society. **d**,**e** The surface of the diatom can also be chemically modified for specific applications. For example, silanization of the surface followed by treatment with a heterobifunctional crosslinker allows an antibody to be attached. These modified diatoms can be used to reveal the presence of a secondary antibody (**d**), whereas non-modified diatoms cannot (**e**).

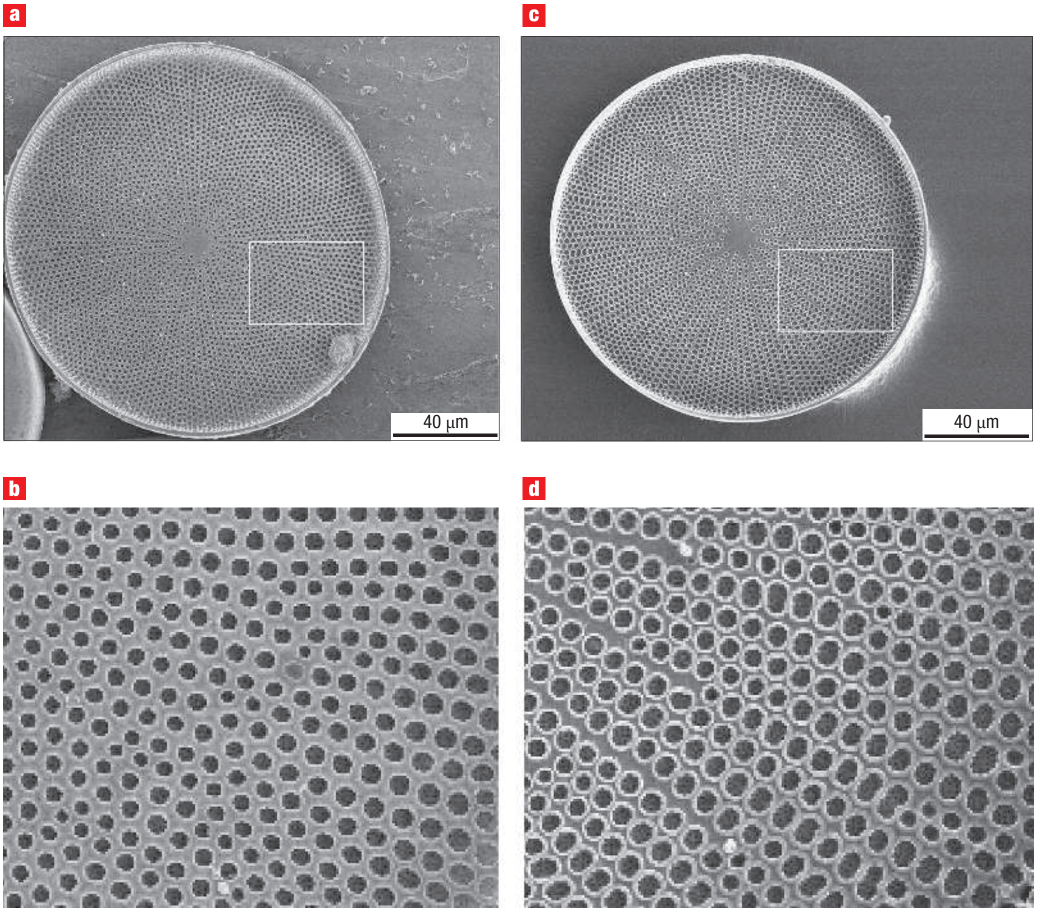

Figure 5 Made-to-measure structures in cell walls. **a**,**b**, Scanning electron micrographs showing the pore pattern in the silica-based cell wall of the diatom *Coscinodiscus wailesii* grown under ordinary conditions. **c**,**d**, If the growth takes place in the presence of nickel sulphate, the pores become much larger. The influence of the environmental conditions on the physical properties of the walls could be exploited in applications. For instance, an optical sensor could detect the change in the pore size from their effect on light, thus providing information about the environmental conditions.

Both the optical intensity and peaks are affected by gases and organic vapours. In the presence of NO_2, acetone and ethanol, the photoluminescence was quenched because these substances attract electrons from the silica skeleton of the diatoms and hence quench the PL. On the other hand, substances that donate electrons, such as xylene and pyridine, 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.*[27] have devised an inorganic molecular conversion reaction that preserves the size, shape and morphology of the diatom whilst changing its composition. They perfected a displacement reaction to convert biologically derived silica structures such as frustules into new compositions. Magnesium was shown to convert SiO_2 diatoms by a vapour phase reaction at 900 °C to MgO of identical shape and structure, with a liquid Mg_2Si by-product. 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. Recently, this group extended its work on silica diatoms to work at lower temperatures (650 °C; ref 28).

An alternative approach is to 'hijack' the process that deposits the silica into the frustule so that another material is deposited instead. Rorrer *et al.*[29] have used this *in vivo* approach to incorporate germanium directly into the frustule. Using a two-stage cultivation process the photosynthetic marine diatom *Nitzschia frustulum* was shown to assimilate soluble germanium and fabricate Si–Ge oxide nanostructured composite materials. As germanium is a semiconductor, these structures could have applications in electronics, optoelectronics, photonics, thin-film displays and solar cells.

Porous glasses impregnated with organic dye molecules are promising solid media for tuneable 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 Palenik[30] have shown that Rhodamine B and 6G are able to stain diatom silica *in vivo*, and have 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 to coccolithophores — single-celled marine algae that are also abundant in marine environments. These cells secrete calcitic photonic crystal frustules that, like diatoms, can take a diversity of forms[31].

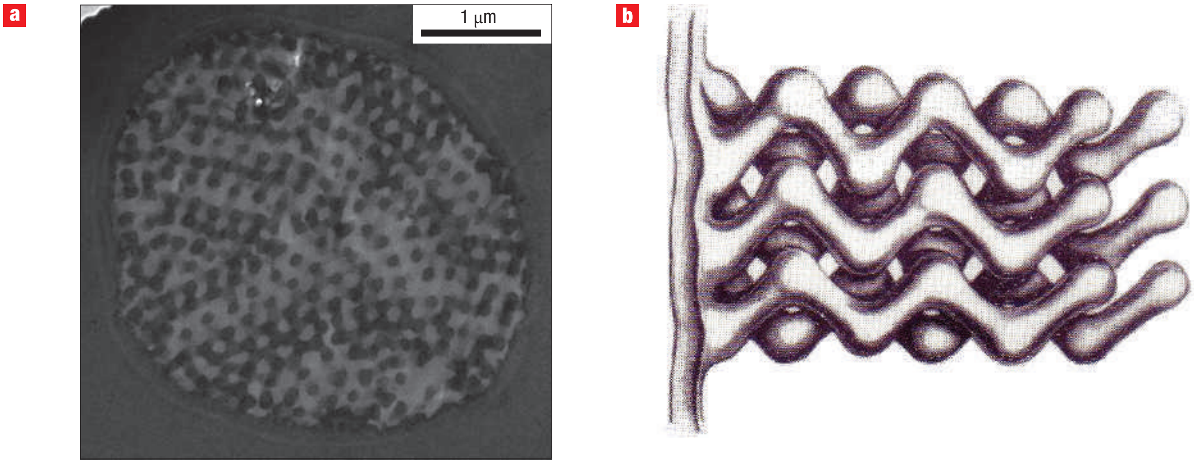

Figure 6 The basic elements of cell engineering. **a**, A transmission electron micrograph of the inverse-opal-type photonic crystal of the weevil *Metapocyrtus* sp. **b**, Illustration of tubular christae in mitochondria from the chloride cell of sardine larvae as an example of animal intracellular membrane form. Evidence suggests that pre-existing internal cell structures play a role in the manufacture of natural nanostructures. If these internal structures can be altered, the cell will produce different nanostructures. Reproduced with permission from ref. 47.

BUILDING OPTICAL DEVICES WITH 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 icosahedral symmetry. The viruses replicate in the cytoplasm (the watery matrix) of insect cells. Within the infected cell the virus particles form a paracrystalline array that causes Bragg refraction of light. This property has largely been considered aesthetic to date but now iridoviruses are being used to create biophotonic crystals. These can be used for the control of light, with researchers at the Wright–Patterson Air Force Base in the US undertaking large-scale virus production and purification, as well as exploring ways to change the properties of the crystals by manipulating the surfaces of the iridoviruses. This work could have applications in a broad range of optical technologies, ranging from sensors to waveguides[32].

Virus nanoparticles, specifically *Chilo* and *Wiseana* Invertebrate Iridovirus, have been used as building blocks for iridescent nanoparticle assemblies. Virus particles were assembled *in vitro*, yielding films and monoliths with optical iridescence arising from multiple Bragg scattering from close-packed crystalline structures of the iridovirus. Bulk viral assemblies were prepared by centrifugation followed by the addition of glutaraldehyde, a crosslinking agent, and long-range assemblies were prepared using a cell design that forced virus assembly within a confined geometry followed by crosslinking.

In addition, virus particles were used as core substrates in the fabrication of nanostructures that 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[33]. These gold nanoparticles then acted as nucleation sites for electroless deposition of gold ions from solution. Such nanoshells 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.

LESSONS FROM CELL ENGINEERING

Where cell culture is concerned it is enough to know that cells do make optical nanostructures, which can be farmed appropriately. In the future, however, it may be possible to emulate the natural engineering processes ourselves by reacting the same concentrations of chemicals under the same environmental conditions, perhaps with the help of purpose built nanomachinery.

For the Manuka beetle we already have some insights into the influence of micro-environmental conditions on the growth of the 'liquid crystal' reflectors in its cuticle. The elongated chitin molecules that make up the reflector gradually self-assemble into a liquid crystal arrangement, during drying (as the molecules become closer to each other)[34]. Here, the precise shape of the chitin molecules becomes important. Chitin has also been shown to form submicrometre spheres, such as those that make up the opal structure in a weevil's scales[35], simply by varying the pH[36].

To date, however, the process that is best understood is the formation of the frustule in diatoms. The frustule is 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, and these particles then aggregate to form larger blocks. The silica is deposited in a pattern that appears to be defined by the presence of organelles, such as mitochondria, that are spaced at regular intervals along the cytoplasmic side of the SDV[37]. These organelles are thought to physically prevent the silica reaching specific parts of the silica cell wall, thus leaving a space. This process is very fast, presumably because conditions are optimal for the synthesis of amorphous silica. The involvement of the cell organelles as obstacles during the silica deposition process results in a final species-specific cell wall with intricate architecture.

The mechanism whereby diatoms use intracellular components to dictate the final pattern of the frustule may provide a route for directed evolution. Growth of *Skeletonema costatum* in sublethal concentrations of mercury and zinc[38] results in cells with swollen organelles, dilated membranes, and membrane-bound cavities. Frustule abnormalities have also been reported in *Nitzschia liebethrutti* grown in the presence of mercury and tin[39]. Both metals resulted in a reduction in the length-to-width ratios of the diatoms, fused 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 (Fig. 5a,b) and a change in the phospholuminescent properties of the frustule, which could have applications in sensing.

Other structures in cells called 'trans-Golgi-derived vesicles' are known to manufacture three-dimensional photonic crystals in coccolithophores[40]. The organelles in cells therefore appear to precisely control (photonic) crystal growth (of calcium carbonate in coccolithophores) and packing (of silica in the diatoms)[41,42]. Indeed, Ghiradella[14] suggests that structures within the cell play a role in the development of some butterfly scales, as does Overton[43], reporting that microtubules and microfibrils also play an important role. Studies of the diversity of photonic crystals produced by different cells also suggest such internal cell structures are used as moulds and nanomachinery (Fig. 6).

Indeed, the same few designs are found again and again within highly unrelated species, suggesting that the basic eukaryote cell contains an array of pre-existing structures that can be called upon to play a role in the manufacture of complex photonic nanostructures in any taxon[44]. If the same moulds, scaffolds, templates or machinery are used each time, it is not surprising that the photonic devices show similarities. Equally, if similar physical processes are involved, such as molecular self-assembly, then similar nanoarchitectures could be expected to reoccur[44].

The ultimate goal in the field of optical biomimetics, therefore, could be to replicate such nanomachinery and/or to provide conditions under which, if the correct ingredients are supplied in suitable quantities, the optical nanostructures will self-assemble with precision. DNA machines are already made by self-assembly[45], so this goal is not unrealistic.

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