Tunable structural colour

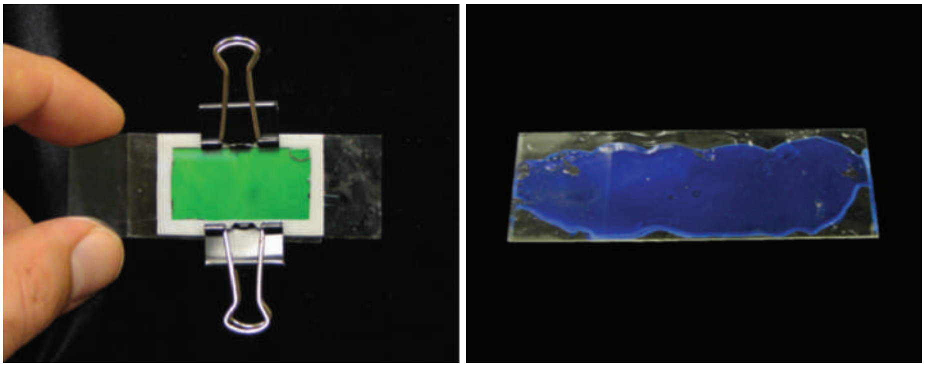
Strain gauges that change colour when stressed, bright backlight-free displays and highly sensitive biological sensors are all potential applications of tunable photonic crystal materials, reports **Duncan Graham-Rowe.**

People have long taken inspiration from nature for its ability to produce a dazzling range of colours. However, in recent years scientists have been paying close attention to a particular collection of creatures, plants and even minerals that can produce colour without the use of dyes and pigments. Instead, they use intricate structures that have features on the scale of the wavelength of light that use diffraction and photonic bandgap effects to create reflections of the desired colour. By exploiting these mechanisms it has now become possible to produce tunable coloured surfaces for a wide variety of optical applications, including backlight-free displays.

Unlike traditional plasma or liquid-crystal displays (LCDs), this new technology is intrinsically reflective, therefore, much like paper, it can be viewed in a broad range of ambient lighting conditions, even in bright sunlight. Other so-called electronic paper displays, such as the 'E-Ink display' in the Kindle electronic reader, already boast this property, but so far have struggled to produce colour without the use of filters that limit their brightness. Furthermore, the use of structural properties to produce colour in substrates can be tuned not only using electric fields (as in LCDs), but also by applying magnetic fields, chemicals, mechanical stress and temperature variations.

This opens up the potential for applications well beyond traditional displays. Researchers are now using them to develop chemical and biological sensors, as well as sensors that can detect heat and stress. The technology also paves the way for new printing applications, such as for making counterfeit-proof bank notes and for re-writable signs, posters and paper.

Such versatility comes from the simple nature in which these displays are able to produce their colour: the use of photonic crystals made from nanoscale periodic structures. From squid and *Morpho* butterflies, to opals and damselfish, such structures work by producing bandgap effects.



Inspired by the colour-changing capabilities of certain squid, researchers from MIT and Hanyang University have fabricated films from block copolymers that dramatically change their colour when subjected to different environmental conditions, such as humidity or salt.

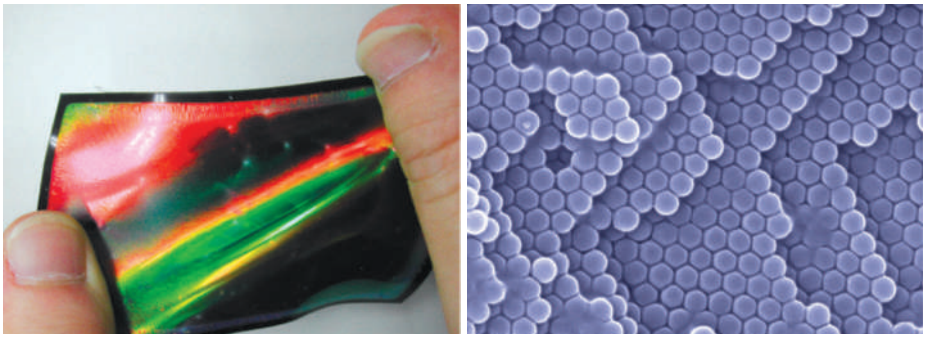
When layers of tiny nanoscale particles are organized to form regular chains, their periodicity will cause Bragg interference. When visible light is incident on the structures, the spacing determines that only certain wavelengths will be reflected, producing colour. By altering the periodicity of these photonic crystals, either through electrical, chemical, thermal or mechanical means, an induced swelling or contraction of the substrate will result in a shift in the wavelengths of light reflected — and thus a change in colour — at its surface.

To recreate such structures, Osamu Sato at the Institute for Materials Chemistry and Engineering at Kyushu University in Japan, and Zhong-Ze Gu at the State Key Laboratory of Bioelectronics at Southeast University in China, took inspiration from the periodic arrangement of cuticles on the ridged scales of *Morpho* butterfly wings. "Fabricating such complex and intricate structures is not easy," says Sato, so initially they turned to the butterfly for help. "We used butterfly wings as a substrate to replicate the structure," he says.

By using the wings as a cast they were able to create colloidal crystal films out of titanium dioxide solutions. But although these films were indeed able to recreate the vivid blue–green colour with a peak at 510 nm, similar to that of the *Morpho* butterfly, the colour was nevertheless fixed. To achieve tunable colour they turned to the opal, creating inverse casts of the structures that give these stones their characteristic iridescent appearance. However, this time they infiltrated the resulting periodic voids in their structured films with liquid crystals to create thermally switchable coloured surfaces. "Temperature changes cause the liquid crystals to go into an isotropic phase, causing a change in the refractive index, so the colour changes," says Sato. Although the colour is still fixed by the size of the voids, this approach allowed them to be switched on and off.

Besides thermal switching, Sato and Gu also found that they could switch the liquid crystals with light when they added a small amount of azobenzene, a photosensitive compound. This compound will switch between two different isomeric shapes — one straight, the other bent — when exposed to UV light. When switched to the bent state the uniform alignment of the liquid crystals in their nematic state is disrupted, causing them to take on a more disorganized isotropic phase, thus resulting in the colour change.

Using the same type of inverse-opal approach, Gu has also managed to create macromolecules with photonic crystal structures that can be used as a sensor. "We can use the porous materials as a sensor for detecting biomolecules," he says.



Hiroshi Fudouzi's soft photonic crystal films are made of an elastomer that contains an array of tiny polystyrene spheres. When stretched or stressed, the change in the spacing of the spheres alters the colour of the film. The approach could be useful for making strain gauges with a visual indicator of overloading. Images reproduced from: Fudouzi, H. & Sawada, T. *Expect. Mater. Future* **8,** 8–11 (2009).

Using silica beads laced with proteins, he created polymerized inverse casts that have nanovoids with molecular imprints of the protein templates. Because these polymerized imprints exactly match the shape of the proteins, any proteins that subsequently enter these voids have a tendency to bind to them, causing a swelling of the polymer and a shift in its refractive index. So by creating polymer beads made up of voids with different concentrations of proteins, Gu has shown that it is possible to detect very slight changes in the concentrations of proteins — as little as one nanogram per millilitre — simply by observing a change in their colour.

One of the issues with this type of inverse imprinting approach to creating photonic crystal structures is quality control, says Sato. The phototunable surfaces he has created, for example, also have potential applications in optical computing, where perhaps they could act as optical switches. But although they can already switch states quickly (in tens of microseconds), they will need to be orders of magnitude faster and, perhaps more importantly, their colour will need to be more consistent. "Our colloidal films have many defects," he says. They must therefore also improve their techniques for creating voids and making the void size more consistent to reflect the much narrower bands of wavelengths that would be required for optical switching.

However, there is another way of achieving tunable structural colour — self-assembly. Edwin Thomas, Joseph Walish and colleagues in the Department of Materials Science and Engineering at the Massachusetts Institute of Technology (MIT), and Hanyang University in Seoul, have also taken their inspiration from nature in the form of that master of camouflage — the squid. These cephalopods use chemical neurotransmitters to rapidly control the spacing or thickness of layered platelet cells to alter their colour on a short timescale. To emulate this behaviour, Thomas and colleagues used self-assembling block copolymers, chosen so that they will stack themselves into alternating layers of hydrophilic and hydrophobic monomers, thus forming the periodic lamellar structures required for photonic crystals.

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In their initial research, the group looked at how these block copolymers could be chemically tuned by exploiting the hydrophilic or hydrophobic properties of the layers to cause them to swell. By simply altering the concentrations of salt in a solvent, they achieved a tunability of 575% in the colour response, from the UV (350 nm) to the near-infrared (1,600 nm). Through careful choice of the block copolymers, this type of chemical sensor can be translated to detect a range of different substances, says Thomas. "We have made films that change colour when wet," he says, which could be used to detect ambient humidity, for example to show if food packaging has been damaged. Alternatively, it could be used to detect hazardous materials such as gasoline. Apart from its versatility, the beauty of this approach is the ease with which such high-quality photonic crystals are formed, he says. "They spontaneously self-align."

Now, to achieve their ultimate goal of creating new digital displays, the group have shown that such structures can also be electrically switched. By immersing their photonic crystals in a polyelectrolyte polymer gel they can achieve swelling through electro–chemical oxidation or reduction reactions, allowing the crystals to be tuned to produce red, green and blue. Actually creating displays is still a long way off, says Thomas, as the subsecond switching rates from one colour to another are too slow for video rates. However, it does make them suitable for other display applications such as in full-colour electronic readers, for the next generation of Kindle-type devices.

In chasing this market Thomas and colleagues already have some competition. By far the most advanced structural colour research, in commercial terms, is that carried out by Opalux. A spin-off from research at the University of Toronto by Geoffrey Ozin, Ian Manners and André Arsenault, the company has developed a simple but effective approach to creating photonic crystal displays out of silica beads embedded in sponge-like electroactive polymers. By sandwiching them between transparent electrode films it is possible to alter the spacing of these beads through voltage changes and induce a change in colour.

Like the MIT approach, the Opalux's switching technology — called Photonic Ink or P-Ink — is still too slow to achieve video rates. Even so, one major advantage of creating displays out of tunable photonic crystals such as these is that you potentially get a threefold increase in colour brightness. This is because unlike traditional displays, which require separate pixels for red, green and blue, each photonic crystal pixel can in theory be tuned to any colour. However, for now Arsenault is cautious about the digital display market. "The development of displays is a long-term endeavour," he says. "We are in negotiations with some display companies at the moment to produce some next-generation demos."

Meanwhile, in the short-term, Opalux is looking at other, more niche display applications for P-Ink, such as electrically driven colour indicators on batteries to show how much charge they have left. They are also looking at a thermally activated version of the technology that uses very precisely defined temperatures to switch colours to monitor the thermal history of samples, such as frozen food, drugs or vaccines, says Arsenault.

In Japan, Hiroshi Fudouzi at the National Institute for Materials Science in Tsukuba, is using changes in the colour of photonic crystal films to detect changes in mechanical stress. Consisting of a polydimethylsiloxane elastomer embedded within lattices of polystyrene particles, his soft opal films alter their colour depending on how much they are stretched; the periodicity of particles reducing as the thickness decreases. Because the films are flexible they should be easy to mount on surfaces for highly sensitive strain gauges, says Fudouzi.

Opalux is also looking at mechanical tuning, but with an entirely different market in mind. Its so-called Elastink is designed to change colour when pressed — a simple concept but one the company hopes has a huge market potential in helping to combat counterfeiting. "Right now many bank notes have holographic strips, but these only have a passive visual effect and are these days much easier to counterfeit than holograms or traditional watermarks," says Arsenault. But with Elastink, coloured watermarks that only appear when pressed could be embedded in notes. By using cutting-edge proprietary technology like this, producing counterfeit notes would become a lot more difficult.

The first commercial Elastink products should hit the market within the next 18 months, however with central banks being so conservative the first examples are most likely to be for anti-counterfeiting of products such as DVDs and drugs, or for secure document printing, rather than bank notes, says Arsenault.

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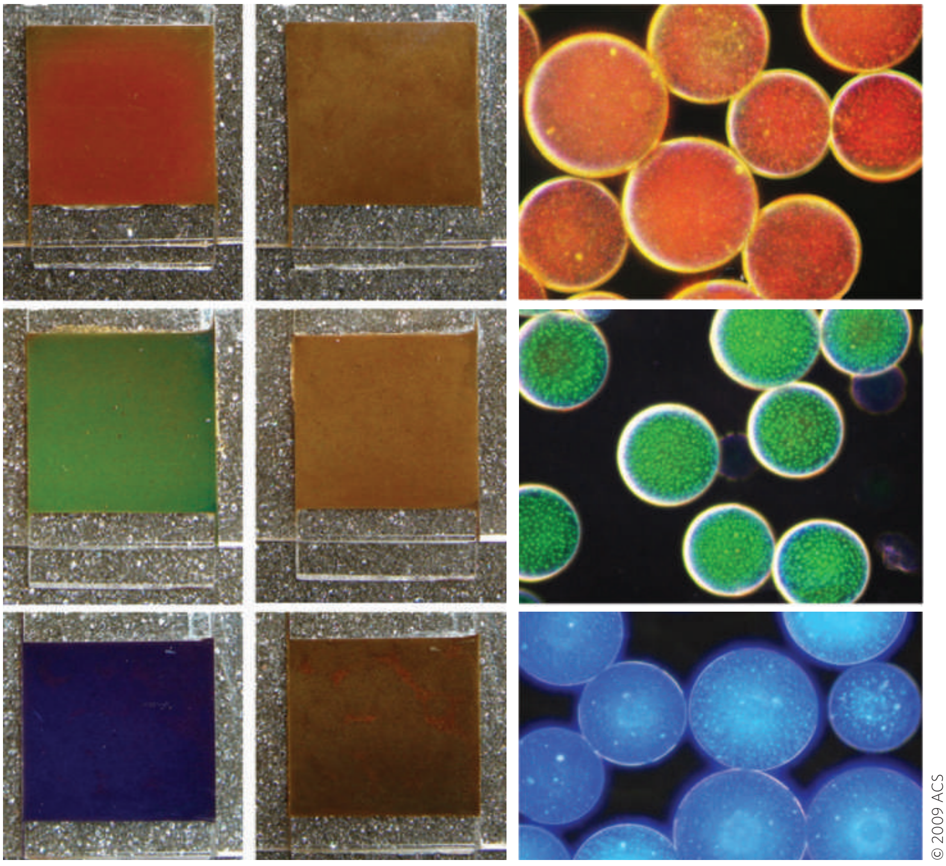
Perhaps the most unusual approach to creating tunable structural colour, which also has huge scope in printing, is the development of magnetically tunable photonic crystals. To make this possible, Sunghoon Kwon and colleagues at the Seoul National University in Korea, and Yadong Yin at the University of California Riverside, created microspheres that are tens of micrometres in size and made out of a photocurable resin embedded with periodic chains of 150-nm iron oxide particles.

The periodicity of these chains — and thus their colour — is tuned by applying a magnetic field during the UV curing-process. Once the curing process is complete the microspheres appear naturally brown, but if a second magnetic field is applied all the chains within the microspheres will align themselves with the field to produce the desired colour. However, even though the periodicity of these magnetic chains is fixed, it is still possible to tune them, says Yin. "The colour is angle-dependent, relative to the incident angle." Thus, by using the magnetic field to precisely control the orientation of the microspheres it is possible to change their colour.



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By applying a magnetic field to change the angle of orientation of chains of iron oxide particles within resin microspheres, scientists from Seoul National University and University of California Riverside have effectively made a magnetic colour-ink.

One of the positive features of this approach is the ease with which the photonic crystals are formed. "When you apply a magnetic field it induces a magnetic dipole, causing the particles to form these periodic chains," says Kwon. It also has the advantage of allowing full-field imaging to 'print' an image. "It's like taking a picture," he says. "You can print a full A4-size in full-colour in just a second."

Dubbed magnetic ink or M-Ink, this type of approach to structural colour could be used to make anything from very large re-writable signs to vehicle coatings that can change colour, says Kwon. "We are going in a few different directions. Displays are always our biggest target. But with outdoor displays we are almost there."

"Given the inherent charges within the microspheres there is even a potential to tune them using electric fields," says Yin.

But there is still work to be done. Although the colour can be tuned, there is a waveband limit on just how far you can go. By altering its orientation, a red microsphere can be made to appear green, and a green one to appear blue. "But if you start with green you can get blue, but not red," says Yin.

Whether the tuning is magnetic, thermal, mechanical or electrical, one thing seems clear: we have only just begun to scratch the surface of structural colour. And given its success in nature, it seems probable that now we have achieved it, it is likely to be an area of growing research that leads to a wide variety of applications. After all, says Thomas, these structures have already been around for millions of years in nature and have found a diverse range of uses. ❐

Duncan Graham-Rowe is a freelance science and technology journalist based in Brighton, UK.
e-mail: duncangr@gmail.com