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The photonic opal – the jewel in the crown of optical information processing

Photons have many advantages over electrons as carriers of information. They are faster and can convey huge amounts of data with low power losses. A new class of materials called photonic crystals have the potential to steer light in the same way as electrons are manipulated in semiconductor chips. Fabricating these devices is proving extremely challenging. Nevertheless, an ingenious chemical approach is being exploited by research groups such as that of **Geoffrey Ozin** at the University of Toronto, which may not only contribute to the development of the all-optical computer but also stimulate the expansion of a new field of materials science. Nina Hall discusses Professor Ozin's contribution.

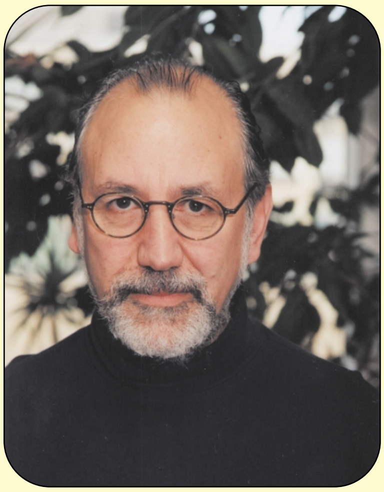
WHEN it comes to developing new technologies, a comment often made is that chemists and physicists need to talk more. Focused discussion can open up new scientific vistas glowing with potential. This is what Geoffrey Ozin found when first accosted by his physicist neighbour in the lab opposite, Sajeev John. To those in the know, Professor John is the world-leading theorist who had, along with Eli Yablonovitch, kicked off the fledgling field of photonic bandgap crystals – materials that are the optical analogues of semiconductors. Physicists are excited about them because they could revolutionise telecommunications and put optical computing on a sound footing. John had a precise theoretical blueprint for making a useful photonic crystal. Ozin, together with Francisco Meseguer in Valencia, Spain, had the chemical experience needed to fabricate it. The result was a joint paper in *Nature* in 2000 describing the large-scale synthesis of a silicon photonic crystal with a complete three-dimensional bandgap.[2] Three-dimensional photonic crystals had been made in silicon using lithography but were just a few periodic layers thick.[3]

Photonic bandgaps

The concept of an optical bandgap was first proposed in 1987 by Yablonovitch,[4] then at Bell Communications in New Jersey, and independently by John,[5] then at Princeton. The idea somehow seems obvious now, that – just as the periodic atomic structure of a semiconductor causes Bragg-like diffraction of propagating electrons resulting in a forbidden range of energies, the bandgap – photons propagating through a periodic dielectric can also scatter and interfere, resulting in a photonic bandgap. An appealing aspect is that, unlike the Schrödinger equation for interacting electrons in semiconductors, Maxwell's equations describing the behaviour of light in periodic dielectric can be solved exactly. Furthermore, there is no fundamental scaling length – the periodicity is not limited to an atomic lattice and can be on any scale.

However, nobody had actually created a photonic bandgap. What was needed was a material exhibiting a regular variation in dielectric constant, or refractive index – a photonic crystal (Fig. 1). Yablonovitch's first effort in 1991 involved simply drilling a large-scale 3D array of millimetre-sized air holes in a slab of material with a refractive index of 3.6. This blocked out light in the microwave region – not particularly practical but it created a sensation.[6]

To be useful for communications, the spacing of the photonic lattice needs to be comparable with the wavelength of infrared light, at around a micrometre or



Professor Ozin received a BSc in chemistry from King's College London and a DPhil in inorganic chemistry from the University of Oxford in 1967. He was ICI Fellow at the University of Southampton from 1967 to 1969 before joining the University of Toronto in 1969; he became full professor in 1977 and University Professor in 2001. Professor Ozin is Honorary Professorial Fellow at The Royal Institution of Great Britain and University College London, and is a Government of Canada Research Chair in Materials Chemistry.

The focus of Professor Ozin's materials chemistry research is on supramolecular chemistry (chemistry beyond the molecule), materials self-assembly over all scales (chemistry approaches to inorganic materials with complex form), biomimetic inorganic chemistry (copying the chemistry of biomineralisation), nanochemistry (chemistry at the nanometre scale), inorganic-organic hybrid materials (chemistry strategies to nanocomposites), inclusion compounds (host-guest nanomaterials chemistry) and photonic materials chemistry (chemical approaches to control the flow of light).

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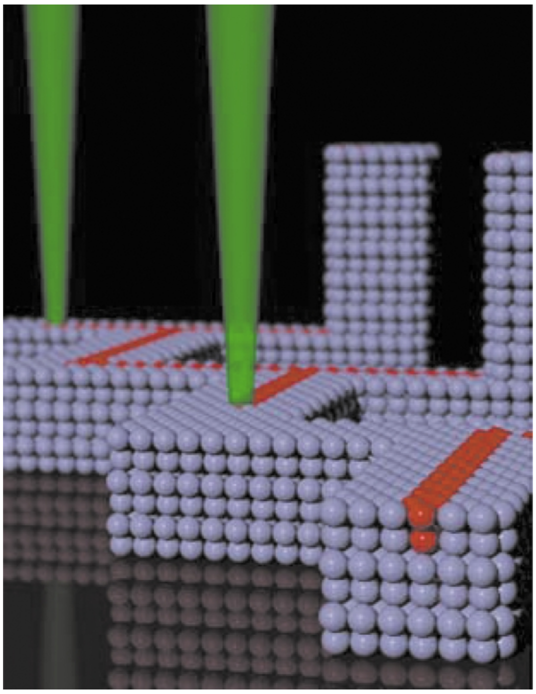

Fig. 1 Graphical representation of an all-optical chip using opal photonic structures. It is based on Joannopoulos's futuristic concept of a photonic 'micropolis'.[1] Reproduced with permission from *Adv. Mater.* (ref. 20), copyright 2003 Wiley-VCH.

so. And ideally the photonic crystal should be based on the electronics engineer's first love – silicon, or possibly gallium arsenide. The 1990s saw a surge of activity as physicists and materials scientists thought up imaginative schemes of microfabrication to make photonic materials with the right scale-lengths. There have been some successes, mostly in one and two dimensions. Ingeniously-made optical fibres with a one-dimensional photonic bandgap look promising for carrying more data,[7] but materials with a two-dimensional bandgap are not likely to be practical as they leak light from the third dimension.

One of the problems is that the required photonic lattice-scale is difficult to reach using the traditional top-down fabrication methods of the semiconductor industry. Here, however, something can be learnt from Nature who, as ever, mastered the assembly of photonic materials first – in iridescent butterfly wings, in the hairs of the sea mouse and even in the scales of the ancient coelacanth. Significantly, the shimmering colours of the opal are due to a partial photonic bandgap caused by the close-packing of silica spheres, a fraction of a micrometre across.

Microengineering opal structures

Chemists, of course, are adept at exploiting the same natural principles through which directed self-assembly achieves a precise matching of structural complexity to application. Indeed, the opal structure concept, combined with clever but established chemical manipulation, soon suggested a promising approach to making 3D photonic lattices. In 1998, two research groups, one at the University of Minnesota and one at the University of Amsterdam, had prepared opal-like porous materials with photonic crystal characteristics.[8,9] The principle was to prepare a template of self-assembled latex spheres, of an order of a micrometre or less, and allow a metal alkoxide (such as titanium ethoxide) to permeate the voids between the balls. The composite was then dried, and calcined to remove the latex spheres leaving behind a 3D framework of the oxide. The resulting periodic array of air spaces represents an inverted opal structure on the required micrometre scale – just what the physicists needed. Carbon inverse opals were also similarly prepared by Ray Baughmann and colleagues at AlliedSignal in New Jersey.[10]

At first, these structures looked like an interesting idea, but fraught with problems. It was not clear that they could be made with sufficient optical quality. They were usually filled with vacancies and stacking faults, and tended to crack. Which was why Ozin was more than a little dubious about John's demanding request to sculpt a perfect silicon photonic crystal of exactly the right polymorph with a precise lattice dimension between 0.5 and 1.5 micrometres and defined network topology. "At first I said: 'No, it can't be done'", recalls Ozin, "But I agreed to do it and soon realised the potential of the work."

Meseguer's group had already done a great deal of work on developing a method to create mechanically stable large-sphere opals.[11–13] They started with silica spheres, between 0.6 and 1 micrometre across, made by the base-catalysed hydrolytic polycondensation of tetraethoxyorthosilicate in a two-stage growth process. The balls were encouraged to settle slowly in a solvent into close-packed face-centred cube colloidal crystal. Small necks were then formed by sintering to hold the structure rigid and create a network topology. These materials were used by Ozin to introduce silicon into the voids by chemical vapour deposition (CVD) using disilane, and annealed. Calculations had showed that to obtain the best bandgap the opal template needed to be made of spheres of 860 nanometres diameter and filled to 86 per cent. The silica template was then etched away using a fluoride-based agent to give a silicon inverted opal with a full bandgap near 1.5 micrometres, the wavelength of choice for optical telecommunications (Fig. 2).

Much effort by several groups has gone into maximizing structural, optical and mechanical quality, by growing silica microspheres of uniform size and establishing the optimum physical method for preparing the colloidal crystal. Recent research has shown that the best crystals are obtained on a substrate held vertically in an ethanol dispersion of the silica microspheres.[14,15] As the ethanol

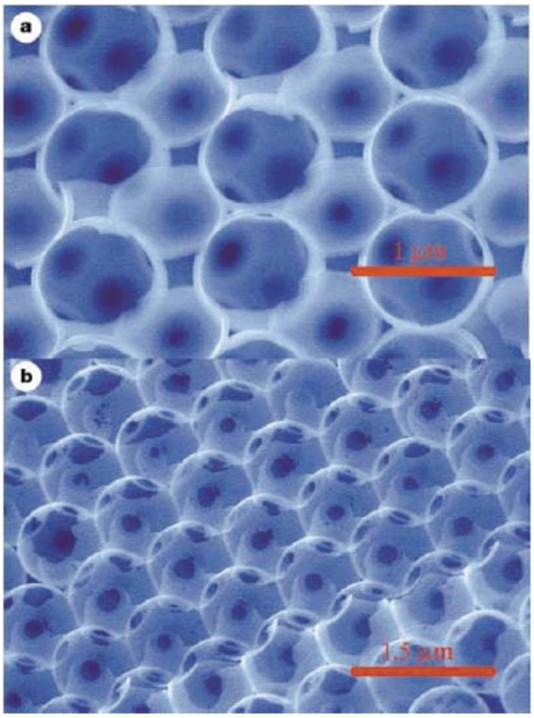

Fig. 2 SEM images of an inverse silicon opal. Reproduced with permission from *Nature* (ref. 2), copyright 2000 Nature Publishing Group (http://www.nature.com/).

evaporates, and aided by convective and shear forces (such as from a stir bar), the spheres collect at the meniscus where capillary action causes them to slide up the substrate while self-assembling into a colloidal crystal film. Cracking at the silica necks is another problem, and this has been minimised by depositing further layers of silica on the spheres *in situ* using CVD (with silicon tetrachloride vapour undergoing acid-catalysed hydrolytic polycondensation); this additional process gives further control over connectivity and pore size.[16,17]

The group has experimented with other structures and topologies, creating complex patterns comprising spheres of two different sizes – for example, hexagonally close-packed layers of large spheres with a superimposed arrangement of much smaller spheres confined in the interstices (Fig. 3).[18] Ozin has also developed a new photonic crystal topology by making an inverted silica opal (starting with a latex colloidal crystal) and coating the air cavities with silicon using CVD. Dissolving away the silica leaves behind a 3D structure made of spherical silicon shells interconnected by cylindrical channels in an air background. Ozin dubs the technique MISO (micro-moulding in inverse silica opals) (Fig. 4). The different arrangement of necks between the spheres means that the optical band properties are different but the opal structure still has a complete photonic bandgap.[19]

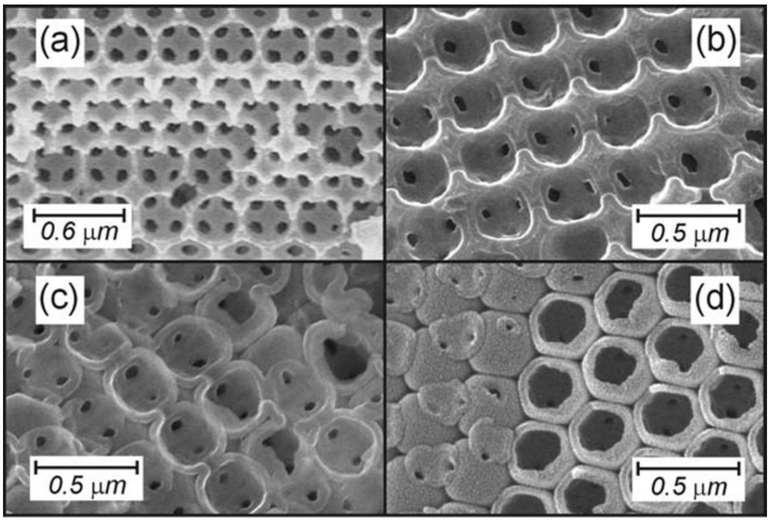

Fig. 4 SEM images of the different steps in the MISO process (*a*) an inverse silica colloidal crystal micro-mould; (*b*) an inverse silica-silicon composite colloidal crystal; (*c,d*) a silicon colloidal crystal with novel topology. Reproduced with permission from *Adv. Mater.* (ref. 19), copyright 2003 Wiley-VCH.

Making a real device

These remarkable materials with their precise optical properties represent a major breakthrough in condensed matter physics. But photonic crystals are of little use unless, like semiconductors, you can introduce defects, which modulate the band structure, allowing light to be manipulated. These include point or line vacancies at the length-scale of the photonic lattice constant, needed for waveguides or microlasers, and larger defect architectures which can couple or switch light in specific regions of the photonic lattice. As a step in this direction, Ozin's group has devised a method to build patterns of refractive index contrast (the defects) in a polycrystalline or amorphous silicon photonic crystal. By using a laser attached to a scanning optical microscope to perform laser microwriting and microannealing, a controlled crystalline phase change, and therefore refractive index change, could be induced in defined regions of the crystal over a range of length scales.[20]

The next step has been to make well-defined photonic crystal shapes on or within a typical planar device like a silicon wafer, so as to create lasers, transistors, waveguides and other microoptical devices that could be integrated in an all-optical chip. This was done by subtly combining soft lithography with colloidal crystal self-assembly. Ozin's group fashioned V-shaped, rectangular and square channels in a silicon wafer and filled them with opal photonic crystals (Fig. 5).[21] A line-patterned master of polydimethylsiloxane (PDMS) was inked with an alkanethiol in ethanol and printed onto a silicon wafer coated with gold and an adhesive layer of titanium. The exposed gold surface and the underlying silicon were sequentially etched away to form grooves. Silica microspheres dispersed in ethanol were then coaxed by capillary forces into the tunnels by directed evaporation-induced self-assembly or by placing a flat piece of PDMS over the grooves. As the ethanol evaporated, the microspheres collected into lines with the desired fcc crystal structure. Another approach that the team has worked on was to use spin-coating (the wafer is spun round while centrifugal forces spread the silica dispersion over it) to guide the spheres into sets of pre-formed channels or pits in the substrate. The pit dimensions can be designed so that they are commensurate with an integral number of spheres, resulting in well-defined ordering.[22]

A whole range of opal structures can be

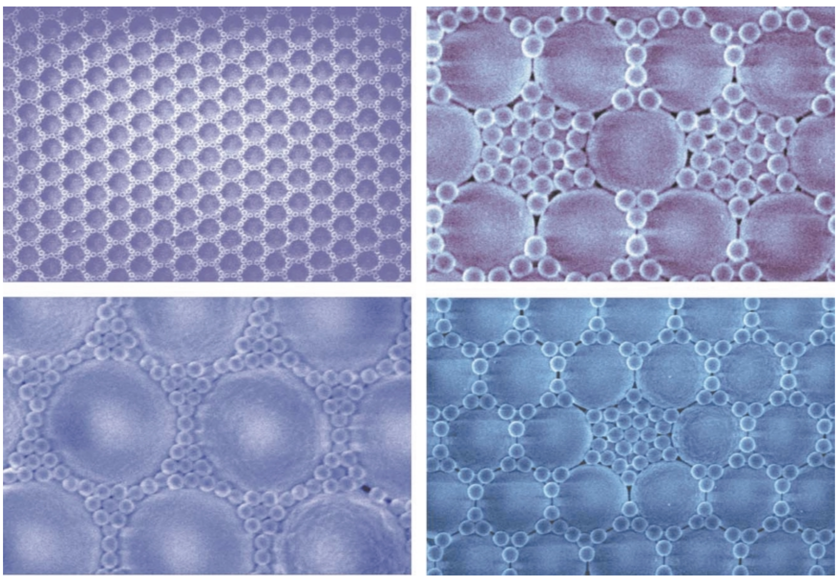

Fig. 3 Examples of binary colloidal crystal patterns and defects. Reproduced with permission from *Adv. Mater.* (ref. 18), copyright 2003 Wiley-VCH.

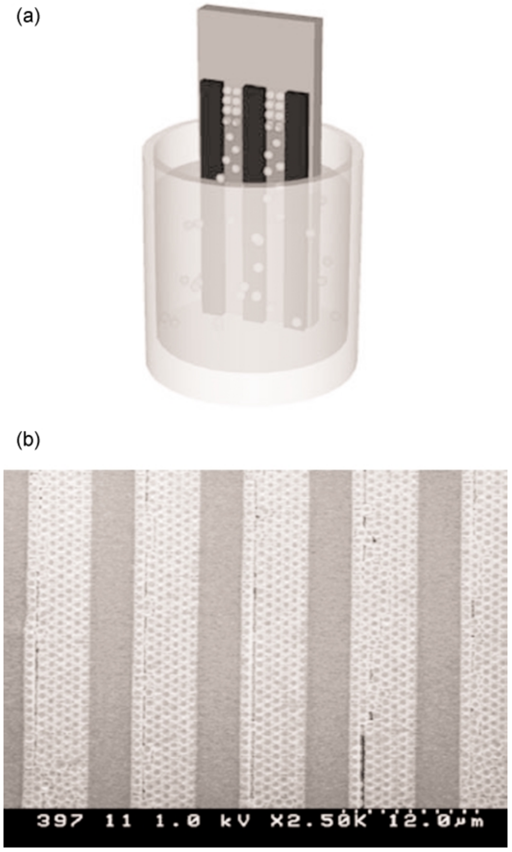

Fig. 5 (*a*) Opal crystals forming inside rectangular-shaped microchannels on a flat substrate; (*b*) an SEM of the structures that form. Reproduced with permission from *Adv. Funct. Mater.* (ref. 21), copyright 2002 Wiley-VCH.

made in this way using various surface relief patterns, including free-standing microfibres (Fig. 6)[23] and heterostructures consisting of two sizes of spheres suitable as optical filters and mirrors. There's also the potential to introduce other active molecules such as liquid crystals and luminescent guests, or to use other materials. An all-optical transistor could, for example, be based on the large refractive-index change accompanying the metal-to-nonmetal transition induced in an inverse colloidal crystal of vanadium dioxide by a femtosecond laser. A serious problem still to be overcome is how to get light in and out of a photonic crystal and with minimal light scattering losses. One approach Ozin is working on is to create connecting structures with a refractive index gradient using the laser writing technique.

Other applications of opal technology

Although the opal approach to optical circuits and computers is promising, Ozin admits that it may not be the final answer. However, he is convinced that the underlying chemical methodology, based on 50 years of colloid chemistry, has great potential in many other areas, from battery materials to visual displays. It has already been shown that the efficiency of tin dioxide gas sensors[24] and solar cells[25] based on dye-sensitised titanium dioxide can be improved by preparing the active material as an inverse opal microstructure.

However, for the chemist, perhaps the most exciting possibilities arise from the colour-tunability presented by opal photonic crystals. "Chemists can now produce colours based on refractive index contrast rather than chromophores," says Ozin. Since the diffraction colour depends on the photonic crystal lattice constant, changing the distance between the microspheres changes the colour. This can be achieved by filling the interstitial spaces of the colloidal crystal with a polymer gel that swells or shrinks in response to an external effect. The process could be used in a sensor or even to make a photonic ink (P-Ink).[26] In the latter, the distance between the unattached spheres is determined by a redox-active metallopolymer gel (partially cross-linked polyferrocenylsilane). The redox state of the iron atoms, which can be controlled electrochemically, reversibly changes the amount of solvent the polymer absorbs, on a sub-second switching time.

It's interesting to note the many directions in which the original work, based on specific physics, has taken someone with a background in inorganic and materials chemistry. Ozin hopes that other chemists will be stimulated to look at

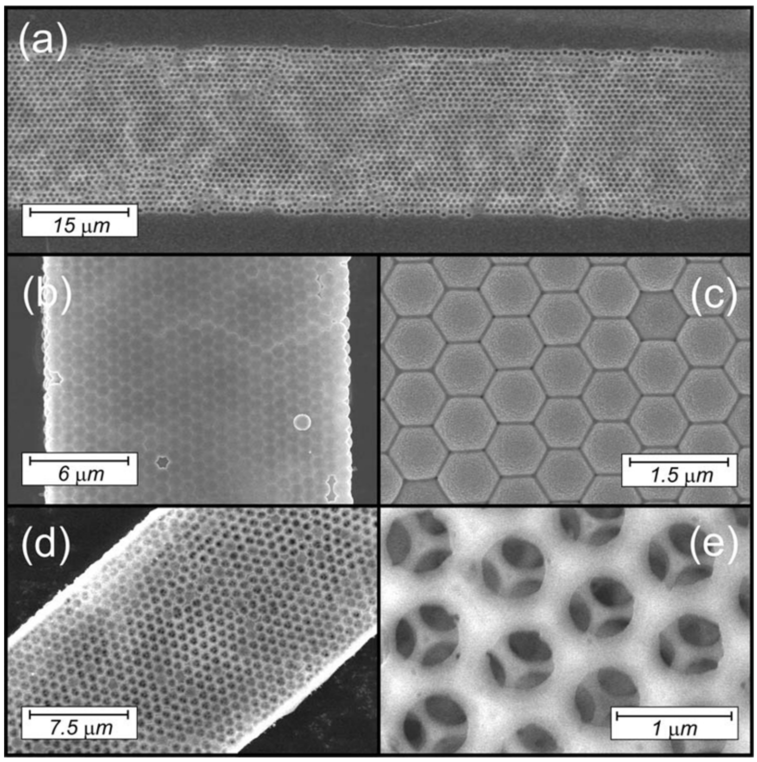

Fig. 6 SEMs of silicon–silica composite and inverted silicon colloidal crystal fibres at different magnifications. Reproduced with permission from *Adv. Mater.* (ref. 23), copyright 2002 Wiley-VCH.

this novel approach to chemical manipulation, whereby chemical form and physical function are so happily married at the nano and mesoscopic level.

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