value — 41.0% at pH 8.5 instead of 88%, the value given in ref. 1. As the pH decreases, the quantum yield drops to about 5% (at pH 5.8). This is a very important finding for researchers studying bioluminescence. It is worth noting that despite the large difference between the new and previously reported values, the revised quantum yield is still higher than that of other bioluminescent systems.

To quantitatively describe the bioluminescence spectra, the authors analysed the spectra using gaussian-curve fitting and found that the whole spectra can be decomposed into three components peaking at around 2.2 eV (560 nm), 2.0 eV (620 nm) and 1.85 eV (670 nm). The first two peaks coincide with the well-known values of green-yellow and red bioluminescence maxima, whereas the weak peak at 670 nm was observed for the first time. Unfortunately, the origin of this 670-nm peak is not yet known.

By analysing the spectra in detail (in particular, the absolute integrated areas of the three components) the authors concluded that the red emitter (2.0 eV) and deep-red emitter (1.85 eV) are sensitive to pH and only the green-yellow component (which peaks at 2.2 eV) is strictly pH-sensitive. This interpretation conflicts with previous explanations of the pH-dependence of firefly bioluminescence spectra and suggests that they should be re-examined.

In my opinion, however, these results are not contradictory but in fact fully compatible with the results from other groups. The reason is that all the emitting components at each pH value have to be in equilibrium. This means that it is necessary to consider the relative areas of each component at each fixed pH rather than the absolute values.

At each pH, the total number of photons is equal to 100%, and the relative contribution of each emitter (the percentage of the total number of photons emitted) is different. Figure 1 shows the relative contribution of different components towards the total number of photons as a function of the pH value. This figure shows that up to pH values of 6.5 the red-emission components (which peak at 2.0 eV and 1.85 eV) prevail, whereas at higher pH values the yellow-green component dominates. As the pH increases, the relative content of the red components drops, whereas the relative contribution of the green emitter (2.2 eV) rises.

Figure 1 (taken from the supplementary information accompanying ref. 3) demonstrates that the two components at 2.2 eV and 2.0 eV co-exist even at neutral and basic pH levels. For example, at pH 8.0 the input of the green emitter (2.2 eV) accounts for about 70%, and the combined input of the other two is about 30%. Similar data have been obtained for the Luciola mingrelica firefly luciferase. The wild-type enzyme in this firefly (for which λ_{max} is 566 nm) also showed the presence of a red emitter (about 20%) in the bioluminescence spectra at basic pH levels. Thus, from my point of view, the results of Ando et al. support the results from the other groups.

In any case, the quantitative studies by Ando et al. are of great value to the bioluminescence community and will inspire further studies of wild and mutant luciferases, thus helping to advance studies of the origins of bioluminescence colour.

References

PHOTONIC CRYSTALS

Acclaimed defects

Defect engineering is crucial for realizing all-optical integrated circuits from self-assembled photonic crystals. A two-photon polymerization strategy paves the way towards incorporation of arbitrary defects in silicon inverse opal photonic crystals.

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Photonic crystals are periodic dielectric structures that prevent the propagation of electromagnetic waves within a select band of frequencies (the photonic bandgap). Colloidal particles can spontaneously form such crystalline structures, a process that has occurred in nature for millions of years and results in the growth of gemstone opals. This provides a useful method for creating three-dimensional (3D) photonic crystals for manipulating light at the technologically important telecommunication wavelengths; a method that is much easier than the expensive and painstaking nanolithography alternative. Well-defined defects need to be incorporated into photonic crystals to realize functional optical devices. Although nanolithography enables quite simple construction of arbitrary defects, controlled incorporation of engineered defects in colloidal photonic crystals has proven to be a greater challenge. On page 52 of this issue, Stephanie Rinne...
A second consideration is the refractive index of the crystal. When the index is sufficiently high, a complete photonic bandgap exists that could prevent light at frequencies within the bandgap from propagating through the crystal from any direction of incidence\(^4,5\). Once a photonic crystal with a complete 3D photonic bandgap is available, engineered defects need to be introduced to achieve various optical functionalities. A point defect (Fig. 1a) in an otherwise perfect 3D crystal functions as a microcavity to localize light and enables low-threshold lasing. A line defect (Fig. 1b) acts as an optical channel for light to travel from place to place on a miniaturized optical circuit. A planar defect (Fig. 1c) plays the role of a planar waveguide. It is quite straightforward to create structural defects using top-down nanolithography techniques (electron-beam lithography, for example) by a precise, but time-consuming, step-by-step patterning process\(^1\). By contrast, bottom-up colloidal self-assembly can easily construct a multilayer crystal in a single step\(^5\), but incorporating arbitrary defects is a major technical challenge preventing the realization of practical optical devices and has been the focus of intense research\(^6\). A common strategy is to combine the bottom-up and top-down approaches: defects can be patterned using standard microfabrication on a self-assembled colloidal multilayer, which is then covered with a second 3D crystal. This multi-step coating process is much easier than nanolithography and has been used to create point, line and planar defects in colloidal photonic crystals. But it suffers from a major drawback: the presence of the intentional defect could affect the crystalline quality of the second colloidal multilayer, especially in regions close to the defect. It is well known that the photonic bandgap is sensitive to such inadvertent imperfections (they can be thought of as intrinsic defects) and that they can destroy the bandgap if the defect density is high enough. Therefore, the dimension of the intentional (or extrinsic) defect needs to be commensurate with the crystalline lattice of the bottom crystal to ensure a single-crystalline-like second coating. This is not an easy task using standard lithographic patterning.

Rinne et al.\(^3\) tackle the problem of defect doping from the opposite direction. As shown in Fig. 2, they create defects directly inside a single self-assembled colloidal crystal by a two-photon polymerization process. The planar colloidal silica crystal (Fig. 2a) is formed by a vertical deposition method\(^7\) and then infiltrated with a photosensitive monomeric material. This material can be polymerized in a highly controlled manner by scanning a tightly focused laser beam inside the crystalline lattice. As polymerization only occurs over a small volume at the focal point of the laser beam, arbitrary 3D defects with submicrometre dimensions are easily achieved after dissolving any unexposed monomer (Fig. 2b). To provide the high-refractive-index contrast necessary for opening complete photonic bandgaps, the interstitial regions between silica colloids are infiltrated with high-refractive-index amorphous silicon using a relatively low-temperature (325 °C) chemical-vapour-deposition process (Fig. 2c). The silica-sphere template and micropatterned polymer defects are removed by wet etching and calcination, respectively, leaving behind a silicon inverse opal with incorporated air-core defects.
a wet etch and calcination, respectively, to create the so-called inverse opals\textsuperscript{2,7} with arbitrary air-core defects (Fig. 2d).

This technique ensures that the crystal lattice around the defects is retained during the TPP and the subsequent removal of the template. Most importantly, in situ confocal monitoring is possible during direct defect ‘writing’ by adding a fluorescent dye to the monomer solution, which enables submicrometre-scale registration accuracy of the defects with the surrounding crystal lattice. The team use their technique to create various high-quality structural defects with sub-100-nm edge resolution. These include vertical and multi-bend waveguides, Y-shaped splitters, and planar cavities, all of which are incorporated into 3D silicon inverse opals with a complete photonic bandgap. Rinne et al.\textsuperscript{3} also show light localization in planar cavities and waveguiding of telecommunication-wavelength light along a line defect with two 90° bends.

The significance of this work is that both passive and active optical components, which are crucial for all-optical integrated circuits, could be easily and cheaply created using this mainly self-assembly-based approach. Optically active materials, such as quantum dots, nonlinear materials or even liquid crystals, could be incorporated into 3D photonic crystals to provide on-demand light manipulation. To achieve practical photonic-crystal devices for next-generation optical telecommunication and high-speed optical computing, the geometry of the embedded defects needs to be well-defined by both experiment and theoretical modelling, and the optical performance of the components (for example, insertion and propagation losses and the polarization and dispersion of the coupled light) need to be quantitatively characterized. Fortunately, both optical modelling and characterization techniques for microphotonic crystals are already available and relatively mature. Although many challenges remain before the ultimate realization of all-optical integrated circuits, Rinne and colleagues’ work represents a major advance towards this goal.

**References**


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**METAMATERIALS**

**Lost in space**

When you think of metamaterials, wormholes might not be the first things that spring to mind. But scientists working in the USA and the UK are suggesting that these materials could actually be used to make devices that act as invisible tunnels for electromagnetic waves (Phys. Rev. Lett. 99, 183901; 2007).

The concept of a wormhole is familiar in cosmology. Now Allan Greenleaf and colleagues describe how to build a device that affects the propagation of electromagnetic waves in such a way that the topology of space seems to change. They consider a wormhole manifold made from two components ‘glued’ together: a space containing two holes located some distance apart, and a curved handle-shaped tunnel or wormhole that connects those two holes.

With special combinations of the electric permittivity and magnetic permeability in this system, the researchers describe how electromagnetic waves can be made to behave as if they travel through the curved handle from one hole to the other. In practice, metamaterials could be used to specify the electromagnetic parameters as needed. Of course, there is no tearing apart and gluing together of space; rather the researchers are meeting certain mathematical electromagnetic field conditions (using metamaterials as their basis) to make waves behave as if they pop from one hole to the other through the tunnel without being seen by an external radiation probe or observer.

The paper outlines a number of applications that could result from wormhole devices. A wormhole device, for example, could function as an invisible optical tunnel or cable. Such a cable could be used to measure electromagnetic fields without disturbing them, as the tunnel does not radiate energy to the outside world except from its ends.

Alternatively, electromagnetic wormholes could be used in light-based computers, where active components could be placed inside the tunnels with only visible exits for the input and output of signals. The research might also have implications for magnetic resonance imaging (MRI). Scientists could use a wormhole to build a tunnel or ‘scope’ that does not disturb the uniform magnetic field needed for imaging. Instead, the scope would make it possible to have metals, magnetic materials or other components in the area being imaged without disturbing the MRI process, perhaps even as part of a medical procedure.

Finally, these wormholes could give rise to virtual magnetic monopoles. By enabling a magnetic field to enter one end of the wormhole and disappear inside, the other end of the tunnel would behave as a magnetic monopole. Intriguing work.

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