

one of the starting points for the study of a large class of systems, ranging from molecules to crystalline solids, because it permits a clear separation of energy scales, allowing for the study of electrons and phonons individually. In addition, in ordinary metals, where non-relativistic electrons and phonons propagate, the Born–Oppenheimer approximation is supplemented by an extra factor, namely, that the electron response to an electric field is so fast that the response to the phonon motion is adiabatic, that is, can be computed as if at any time the positions of the nuclei were frozen.

Pisana and co-authors have used Raman spectroscopy to study the electron–phonon interaction, and in particular the phonon response to the application of an electric field perpendicular to the graphene crystal. They show that, unlike in ordinary metals and semiconductors where electrons are described by non-relativistic quantum mechanics, the phonon energy changes in an unusual way with the applied field, in agreement with earlier theoretical predictions<sup>8,9</sup> and experiments

by other groups<sup>10</sup>. Most importantly, the behaviour observed in these experiments shows that graphene violates the adiabatic Born–Oppenheimer approximation.

To understand the origin of this anomalous observation we have to recall the similarity between phonons in graphene and photons in QED. In graphene, phonon propagation is linked to the creation of electron–hole couples. But a hole is simply the electron antiparticle (Fig. 1b), which makes the analogy with QED almost perfect. Because the phonon propagation is so strongly connected to complex processes involving electrons, the adiabatic Born–Oppenheimer approximation — which is based on separating the motions of electrons and phonons, and consider these as frozen — cannot be valid.

The experimental observation of the strong electron–phonon coupling in graphene is not just another demonstration of the analogy with QED, and suggests that other interesting phenomena may be observed. For example, the strong electron–phonon interaction in

metals is related to the emergence of superconductivity, which indicates that even in graphene this phenomenon could occur. Despite the fact that no evidence has so far been reported of graphene superconducting, it is possible that it is on the verge of a superconducting instability, and with a slight modification, either structural or chemical, a two-dimensional graphene superconductor might be obtained. Only time and new experiments will tell whether superconductivity is really possible in this intriguing material.

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## PHOTONIC CRYSTALS

# A view of the future

Despite intense research efforts, no three-dimensional materials with a photonic bandgap for visible wavelengths have yet been fabricated. A new self-assembly strategy lays out the route towards the realization of this dream.

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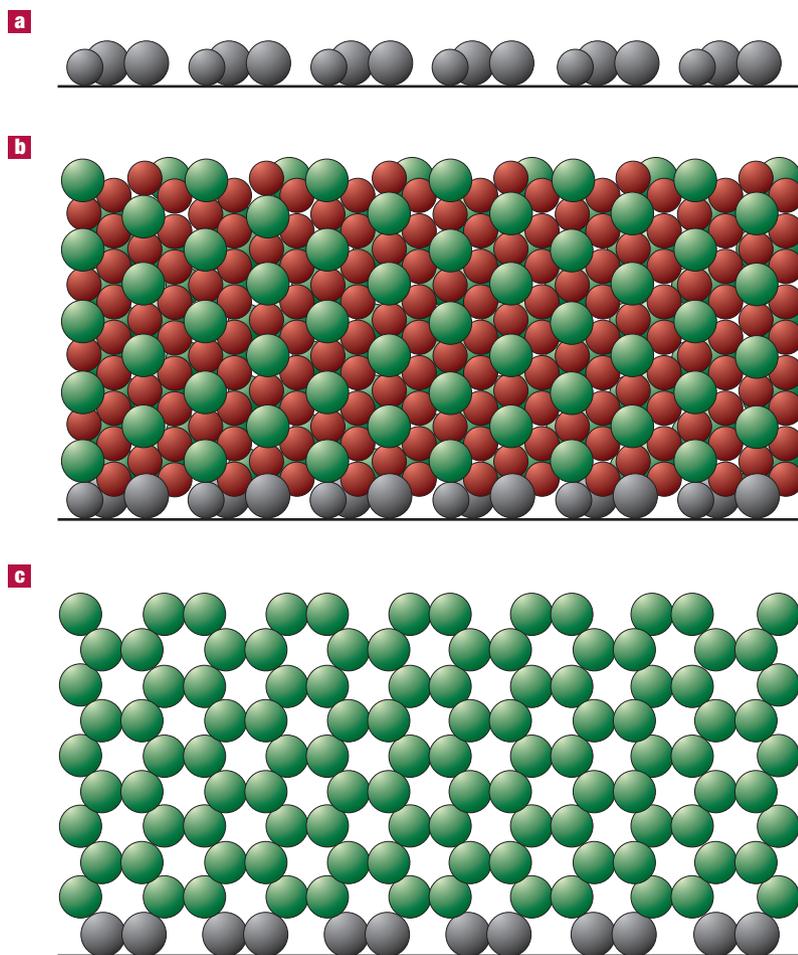
It is nearly twenty years since the possibility of materials with a photonic bandgap — where light of certain wavelengths is forbidden to propagate in any direction — was first discussed<sup>1,2</sup>. This idea has spawned the field of photonic crystals, which allows us to manipulate light in new and amazing ways. However, the original goal, a three-dimensional material with a complete photonic bandgap for visible light, has eluded us. Such a prolonged challenge often promotes creative solutions, and on page 202 of this issue<sup>3</sup>, Hynninen *et al.* propose a new route towards this aim. Their plan uses recent advances in the self-assembly of colloidal

particles into beautifully complex crystal structures. If realized, their approach may finally allow us to see a photonic bandgap with our own eyes.

In 1987, it was well known that materials that were periodically structured on a scale comparable to the wavelength of light could prohibit photons from travelling in specific directions. Inside such a structure, reflections from the periodic interfaces can cause constructive and destructive interference. A common use of this effect is for anti-reflection coatings. However, the question was whether an artificial material could forbid light from travelling in all directions simultaneously. If this occurred, a range of wavelengths, or bandgap, could be created where travelling electromagnetic waves would not be allowed to exist inside the material. Because fundamental optical properties such as fluorescence rely on

such waves, interesting implications follow from their absence.

But what is needed to obtain a photonic bandgap for visible wavelengths? Essentially, destructive interference must occur for all propagation directions. This requires a crystal from ‘atoms’ with a size similar to the optical wavelength, which for the visible is several hundred nanometres. In addition, the waves must reflect strongly from these ‘atoms’, a property determined by their index of refraction. If the refractive index could be arbitrarily high, a photonic bandgap could exist in any three-dimensional crystal. Unfortunately, we are constrained by the materials that nature provides. Because high-refractive-index materials are more readily available at longer wavelengths, several approaches have created photonic bandgaps for the near infrared<sup>4–8</sup>. For visible wavelengths, the highest available



**Figure 1** Proposed route to visible photonic bandgaps. **a**, The surface is patterned to nucleate the desired colloidal crystal. **b**, Large (green) and small (red) colloidal spheres are mixed and crystallize from the surface as the colloidal analogue of the  $\text{MgCu}_2$  structure. **c**, If the small spheres are made from a polymer such that they can be dissolved or burned away, the remaining large spheres sit on a diamond lattice. If they are made from a material such as  $\text{TiO}_2$ , they will have sufficient refractive index to yield a photonic bandgap in the visible range. Alternatively, if the large spheres in **b** are removed instead, a pyrochlore lattice of small spheres would result (not shown). This structure can also lead to a visible photonic bandgap. This approach therefore provides tremendous flexibility.

indices of refraction are more modest. Consequently, to have a chance at a visible photonic bandgap, we must not only make the 'atoms' from the most appropriate materials, but also arrange them in the optimal way. If we arrange photonic 'atoms' made from a material such as titania ( $\text{TiO}_2$ ) with a diamond or a pyrochlore crystal lattice, a visible photonic bandgap is possible.

The challenge has been to create such structures. Among the many approaches, self-assembly has been appealing because it can easily provide a crystal with the appropriate length scale. Submicrometre spheres can be synthesized with great uniformity by colloidal chemistry. These can then spontaneously form colloidal

crystals (a topic in its own right for understanding the fundamentals of crystallization). However, the spheres in the resulting structures tend to pack as densely as possible. For the spheres to crystallize on a diamond or pyrochlore lattice, both of which are quite open, another trick is needed.

Previously, it had been proposed to stack two different types of spheres<sup>9</sup>. If these 'atoms' are sized appropriately they can then form photonic-crystal analogues of metal alloys. The advantage is that the spheres can be densely packed during the assembly process, but one set of the spheres can be removed afterwards. Through this approach, more open, but still stable, crystal structures can

be obtained. Indeed, diamond colloidal crystals have been demonstrated<sup>10</sup>, however, as a micromanipulator was used to stack spheres one at a time in an electron microscope, the obtainable crystals were small.

Hynninen *et al.* propose instead a more elegant route using self-assembly. As shown in Fig. 1, they aim to use two differently sized spheres and assemble a colloidal crystal with the same structure as  $\text{MgCu}_2$ . If the 'Cu' spheres are removed after the assembly, a diamond lattice of 'Mg' spheres is obtained; if the 'Mg' spheres are removed, a pyrochlore lattice of 'Cu' spheres results. In either case, the remaining spheres are self-supporting. Thus, this one crystal can provide two interesting structures for photonic bandgaps.

Amazingly, Hynninen *et al.* also outline how to self-assemble such a complex colloidal crystal. If colloidal spheres of the proper size are mixed at the appropriate concentration, the  $\text{MgCu}_2$  structure can be obtained. However, because thermodynamics also allows two other colloidal analogues,  $\text{MgNi}_2$  and  $\text{MgZn}_2$ , to form, they propose to use a patterned surface to nucleate only  $\text{MgCu}_2$ . Indeed, their simulations show that is possible. A visible photonic bandgap material could result if one set of spheres were made, for example, from  $\text{TiO}_2$  and the other set could be dissolved or burned away.

The significance of this work is that all these steps are, in principle, now feasible. The tremendous progress in the crystallization of complex colloidal structures, surface-patterning techniques, and the synthesis of colloidal spheres with the necessary refractive index, can all be used. One remaining question is whether such spheres can be sufficiently uniform to form crystals without significant disorder, which otherwise can destroy the photonic bandgap. If this can be overcome, we may finally realize the vision of photonic-bandgap materials and be able to investigate directly the exciting fundamental physics that would ensue.

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