Towards a photonic band gap for visible light

More efficient miniature lasers and other light sources, solar cells and new quantum optics are but a few examples of the exciting possibilities of so-called ‘photonic band gap’ materials. Researchers from Utrecht University report an important breakthrough towards the fabrication of materials that have a photonic band gap for visible light.

Photonic crystals are three-dimensional (3-D) structures in which the refractive index varies periodically on a length scale that is comparable to the wavelength of light. The periodicity results in an interaction between photons and the crystal that resembles the interaction of electrons with a semiconductor. Photons having an energy (or wavelength) that corresponds to a photonic band gap cannot propagate inside a photonic crystal, just like electrons that have an energy corresponding to a band gap cannot propagate inside a semiconductor. Though the concept is simple, and major breakthroughs have been realized in the fabrication of increasingly smaller structures, no material with a band gap in the visible has been fabricated yet. Researchers from the Soft Condensed Matter Group of Alfons van Blaaderen and Marjolein Dijkstra at Utrecht University have found a route that may lead to the fabrication of such materials by self-assembly of submicron particles, also known as colloids. Their results are described in *Nature Materials*, a recently introduced scientific journal having an impact factor that rocketed to the top of the list.

Despite the appealing possibilities for both fundamental and applied research, photonic crystals with a band gap in the visible have not been realized yet, which is rather puzzling. The solution to this mystery is linked to three basic properties of a photonic crystal that determine whether it has a band gap or not: 1) the refractive index contrast, 2) the crystal symmetry and 3) the lattice spacing. The first prerequisite demands that the difference in refractive index between the composite materials has to be relatively large.[1] Moreover, to be able to effectively use the optical properties of photonic crystals, absorption of light should be negligible. Unfortunately, this requirement strongly reduces the number of materials that can be used for the fabrication of photonic crystals. Silicon, for example, has a very high refractive index, but it strongly absorbs visible light. In the near-infrared (NIR) part of the electromagnetic spectrum, however, silicon is an excellent candidate, because it hardly absorbs in this wavelength range. The second prerequisite for opening up a photonic band gap is strongly related to the first one. The refractive index contrast that is required to open up a photonic band gap depends greatly on the crystal lattice symmetry and on the amount of disorder present in the actual crystal. Despite major progress in conventional microfabrication methods, including lithography, they are still incapable of fabricating 3-D structures of sufficient quality with lattice spacings on the order of 200 nm (0.0002 mm), which is necessary to meet the third requirement.

Up till now, the combination of the first and second requirements, i.e. high refractive index contrast and crystal symmetry, has rendered self-assembly as an unsuitable method for the fabrication of photonic crystals with a band gap in the visible. However, colloids with a diameter above 1 micrometer (0.0001 mm) *have* played an important role in the fabrication of photonic crystals with a band gap in the near-infrared. It so happens that colloids can self-assemble quite easily into close-packed stackings of spheres, forming so-called face-centered cubic (FCC) crystals. For an FCC structure to have a photonic band gap, it is not the spheres

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[1] The refractive index of a homogeneous slab of material is a measure of the speed of light in that material, which is always smaller than the speed of light in vacuum.

themselves that should consist of a high-index material, it is the space in between the spheres that should have a high refractive index. For example, inverse crystals of air spheres in a high-dielectric background can be fabricated by infiltrating an FCC colloidal crystal of, for example, glass spheres with a high-refractive-index material, after which the glass spheres themselves are removed by a wet chemical etch. It is not a problem to reduce the diameter of the spheres below 200 nm, thus moving the frequency range of the band gap into the visible. However, the problem is that silicon absorbs visible light. In fact, there are no materials that have a high enough refractive index for an FCC crystal of air spheres to have a band gap in the visible, which at the same time do not absorb visible light. Here is where the importance of crystal symmetry comes into play. It has been known for more than ten years that photonic band gaps can be opened up at much smaller refractive index contrasts in crystals with a diamond structure. In such crystals, even materials like titanium dioxide and zinc sulfide, which hardly absorb visible light, would open up a photonic band gap in the visible. Recent theoretical calculations showed that there is another structure, called pyrochlore after a specific mineral with the same crystal structure, in which a band gap in the visible opens up at refractive index contrasts just as low as in diamond structures.

Using computer simulations and some educated guesses, the researchers from Utrecht University managed to find conditions under which so-called binary colloidal crystals can be fabricated by self-assembly of two species of colloidal particles. The two species of colloids, from now on referred to as ‘the large colloids’ and ‘the small colloids’, only need to have a rather specific size ratio. Within the binary crystal, the large spheres form a diamond structure, while the small spheres form a pyrochlore structure (see Figure 1). Thus, both ‘optimal’ crystal structures can be realized simultaneously within one and the same structure. As the photonic band gap only opens up in diamond and in pyrochlore structures, and not in the binary crystal itself, an additional fabrication step is required. Either the large spheres must be removed, yielding pyrochlore, or the small spheres must be removed, yielding diamond. This procedure can be realized if the particles of the two different species consist of different materials. For example, if one of the species is made of organic material, such as polystyrene, while the other species consists of titanium dioxide, the organic particles can be removed from the binary crystal by heating. This method has already been used in Utrecht for other colloidal crystals. Moreover, particles with a high refractive index, including titanium dioxide or zinc sulfide particles, have previously been synthesized in Utrecht.

However, this is not the end of the story. It is not uncommon that research obeys Murphy’s Law and this research was no exception. Computer simulations by FOM[2] researcher Antti-Pekka Hynninen, currently at Princeton University, showed that the conditions under which the binary crystal would grow, would also lead to the formation of two other kinds of binary colloidal crystals. This is because the three binary structures have nearly the same degree of thermodynamic stability. Calculations by FOM researcher Job H.J. Thijssen and NanoNed[3] researcher Esther C. M. Vermolen showed that the two latter binary structures are not nearly as optimal, from a photonic point of view, as the former binary structure, from which diamond and pyrochlore can be formed. Therefore, a final trick is required to favor the growth of the optimal binary structure over the formation of the other two. The solution to this problem is as simple as it is elegant. Computer simulations proved that simply introducing a wall could do the trick, as long as the wall has been patterned with spheres such that it mimics

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[2] FOM is the Dutch Foundation for Fundamental Research on Matter (www.fom.nl).

[3] NanoNed is a national nanotechnology R&D initiative that combines the Dutch strengths in nanoscience and technology in a national network with scientifically, economically and socially relevant research and infrastructure projects (www.nanoned.nl/default.htm).

one of the crystal planes of the optimal binary structure (Figure 2). This technique, which has been developed in Utrecht and is known as *colloidal epitaxy*, has been successfully applied in several experiments. The first few steps towards experimental realization have been taken, though optimalization of growth conditions will still require loads of research. However, the prospect of low-cost fabrication of 3-D structures with a band gap in the visible provides more than enough motivation to realize the now proposed *in silico* route in a laboratory.

Figure 1. The optimal binary crystal, consisting of two species of particles having a size ratio of approximately 0.8. The two sub-structures are presented as well, one of them consisting of only large particles (*diamond*, red spheres), the other one consisting of only small particles (*pyrochlore*, yellow spheres).

Figure 2. The panel on the left-hand side shows a schematic representation of the pattern of large (red) and small (yellow) spheres that has to be applied to the wall of the container in order to obtain the optimal binary crystal (Figure 1) with a preferred orientation. The wall pattern suppresses the growth of the two other binary crystals, which are unfavorable from a photonic point of view. The panel on the right-hand side is a snapshot from a computer simulation in which the proper binary crystal (Figure 1) is growing onto the pattern that is shown in the panel on the left-hand side.