Multi-functional flexible 3D photonic crystals

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The International Society

for Optical Engineering

Three-dimensional photonic crystals have properties that may make them useful for sensing physical strain. This paper discusses a novel way to make such crystals, using polystyrene spheres. The process enables various types of nanoparticle to be incorporated in the lattice, making it possible to dramatically alter the optical properties of the resultant crystal. Stretching the crystalline films also modifies their photonic characteristics, suggesting they could be used in strain sensing.

Photonic crystals have attracted a lot of interest since it was first proposed that they could capture light.^{1,2} This property is a result of the way the dielectric constant of a crystal is periodically modulated by its structure, preventing light propagating through it in certain directions. This effect could lead to remarkable applications in optical communications and sensing, and is also important in fundamental quantum optics.

Although the theory of photonic band gap (PBG) materials has developed rapidly in recent years, it is still difficult to make them, especially in 3D. We present a straightforward way to make such 3D photonic crystals. Our nanostructures are artificial opals consisting of hard polystyrene (PS)—polymethylmethacrylate (PMMA) spheres—surrounded by a soft polyethylacrylate (PEA) material. The PMMA interlayer is needed to ensure the PEA grafts to the PS core in the precursor sphere.³ The photonic-crystal film is made by compression-molding the precursor-polymer core-shell spheres, allowing them to self-assemble. Subsequent steps can include cross-linking to make the film elastic. Such shear-enhanced assembly of the multishelled polymer sphere precursor, at elevated temperature and pressure, produces a 3D periodic array as shown in Figure 1(a) and (b).

Figure 1(c) shows a transmission electron microscope (TEM) image of the ordered lattice plane. The film thickness is varied from 100 to 300μ m and the PS sphere diameter from 150 to 300nm. A beautiful feature of a PBG effect is shown in Figure 1(d), where the color of the resonantly-reflected light changes with the angle of incidence.

The flexibility of these nanostructures can be exploited in sensing applications.⁴ The structural changes with strain are illustrated in Figure 2(a). Stretching the sheet laterally brings the (111) lattice planes (parallel to the sample surface) closer to each



Figure 1. (*a*) *Precursor polymer composition.* (*b*) *Diagram of the fabrication.* (*c*) *TEM image of an ordered sample plane.* (*d*) *Images of the sample surface.*



Figure 2. (*a*) *Diagram of the strain influence on the lattice planes.* (*b*) *Measured reflection (left) and transmission (right) shifts with increasing strain.*

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other. This is readily seen in Figure 2(b), which shows the measured shift of the Bragg-scattering resonance to shorter wavelengths in both the normal-incidence reflectivity (left) and transmission (right) of the film. The steep slope of the transmission roll-off across the band gap retains its shape throughout (strains 0 to 13%). Strain sensing with these materials is realised by monitoring how the light throughput changes as a function of strain.

The steep slope in transmission has been engineered into the film using nanoparticle doping. Typically, polymer-based photonic crystals exhibit only partial PBGs. This is true for our structures, where the reflective-index contrast is 1.59 (PS) to 1.49 (PEA). However, the most attractive features of our nanostructures are the scalability of the PS sphere size (controlled by the precursor-emulsion polymerization process), and the relative ease of incorporating nanoparticles to create multi-functional crystals. The PS sphere size directly affects the lattice parameter in the resulting face-centered-cubic lattice. This means we can tune the optical activity of the structure over the whole range of visible wavelengths.

Electromagnetic variational theory shows that, as the wavelength is scanned across the band gap from short to long, the electric-field distribution shifts from the low-refractive-index PEA material to the high-refractive-index PS spheres. In the manufacturing process, additional absorbing nanoparticles are incorporated in the soft PEA material surrounding the PS cores. This means the optical field interacts much more with the nanoparticles at short wavelengths, creating the steep transmission edge. The inclusion of nanoparticles could lead to both very interesting new physics and a plethora of applications.

We have discussed a versatile way to make 3D polymer photonic crystals that, by controlling the precursor sphere size and nanoparticle inclusions, gives extensive control of their optical properties. We have already investigated using these crystals as strain sensors. Future experiments will explore the effect of crosslinking on the photonic properties as well as the incorporation of gold and semiconductor nanoparticles in the structures to observe plasmonic effects in such metamaterials.

This work was supported by the EPSRC-GB Portfolio Partnership EP/C51178 6/1, The Foundation of Technology Finland, and Merck KGaA. We are grateful for support and collaboration from H. Winkler and T. Ruhl.

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