

Fabrication of BaTiO₃ Inverse Opal Photonic Crystal

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Abstract: The colloidal crystal template or opal with a closed-packed face centered cubic (fcc) lattice, was prepared from monodisperse polystyrene (PS) spheres by gravity sedimentation. The template was used for the generation of photonic crystal. The template provided void space for infiltration of liquid precursor composed of titanium butyloxide, barium acetate, ethanol, and acetic acid. The opal composite was hydrolyzed, dried, sintered by heating for completely removing PS spheres to form BaTiO₃ photonic crystals with inverse opal structure. The PS spheres were replaced by air spheres, which interconnected each other through the windows on the BaTiO₃ wall. So both the BaTiO₃ wall and air void constitute continuous phases.

Keywords: Photonic crystal, barium titanate, opal, inverse opal.

Photonic crystals (PCs) are a type of materials, in which the dielectric constant is patterned with a periodicity. These materials can create a range of 'forbidden' frequencies called a photonic bandgap, analogous to the electronic bandgap in a semiconductor¹. The bandgap provides the opportunities to shape and mould the flow of light for photonic technology and photonic computer in the future.

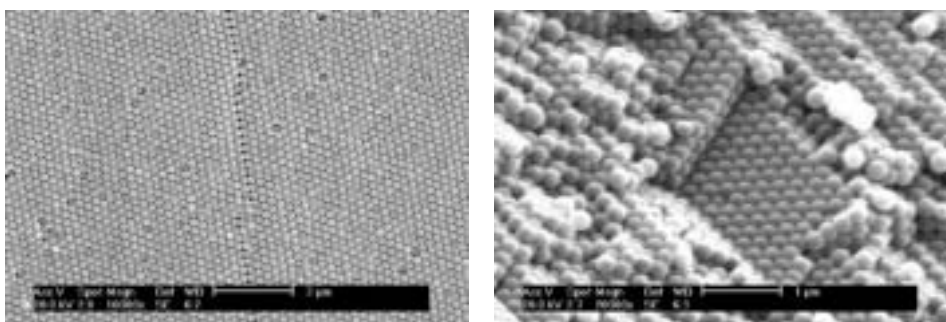
Visible and near infra-red photonic crystals impose challenges to traditional lithographic techniques, which normally can not produce the three-dimension lattice. An alternative route, self-assembly of spheres, solves the problems and can form opal-like photonic crystals²⁻⁴. However theory analysis shows that inverse opal would show much better photonic bandgap properties than the opals⁵. BaTiO₃ is a kind of ferroelectric materials with high dielectric constant, and its relative dielectric constant is changeable as external electric field or temperature, which gives an opportunity to make optical tunable (or bandgap tunable) photonic crystal. Tunable photonic crystals are useful in the optical elements such as optical switch or optical filter, so much attention was paid to it recently⁶. In this paper, BaTiO₃ inverse opal photonic crystal was fabricated by template-infiltration method.

Monodisperse (better than 5%) polystyrene (PS) spheres with an average diameter of 250 nm were prepared by emulsion polymerization. The dispersity of the spheres is very important because it controls the characters of the inverse opal. To grow PS opal (or template), 20% colloidal suspension of PS spheres was sedimentated and dried for

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about 4 months on a glass slice, during which the temperature and humidity were controlled to prevent the template from broken. The template showed a close-packed face centered cubic (fcc) lattice with a long-range order as shown in **Figure 1**, though some point and linear defects were observed. The defects are always observed in photonic crystals^{3,4,7}, but they were so small that large crystal domain was not disrupted by the defects. The defects in **Figure.1** were reduced by controlling the humidity of the sample chamber during the formation of PS opal, in comparison with the opal produced by ordinary gravity sedimentation as reported^{3,4}.

Figure 1 SEM photo of the PS opal



Once the template was formed, the voids among the PS spheres in the template were filled with BaTiO₃, a material with high dielectric constant, by sol-gel methods, using a solution precursor of titanium butyloxide, barium acetate and acetic acid with ethanol as solvent.

Figure 2 SEM photo of BaTiO₃ inverse opal

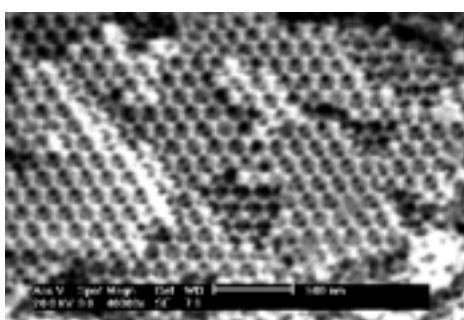
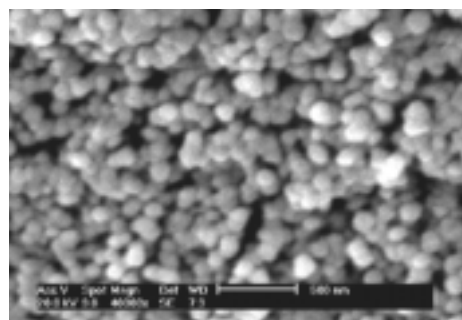


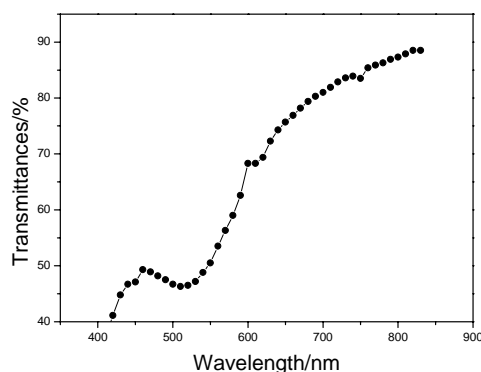
Figure 3 SEM photo of over-heated opal composite



The template was put and soaked in the precursor for about 1 h, and filled with the precursor in the interstices motivated by capillary forces. After infiltration, the template was taken out and put in the air to allow the precursor reacting with the vapor in the air for about 1 day. The process was repeated seven times to obtain high filled template. The infiltrated template (or opal composite) was heated in an oven. The temperature was increased from room temperature to 450°C at a rate of about 20°C/h, then it was kept this temperature for about 3 h to remove PS spheres completely. Further, the

temperature was kept rising until it arrived at 600°C. Finally, the BaTiO₃ inverse opal was obtained by cooling down (**Figure.2**). When temperature exceed 700°C, the inverse opal structure was destroyed as shown in **Figure 3** owing to the recrystallization of BaTiO₃. The long-range order of the template has been imprinted in the BaTiO₃ inverse opal. PS spheres were removed and replaced by void spheres during the calcination, but 25~30% shrinkage in diameter occurred. BaTiO₃ forms the wall of the air spheres. We can find windows on the BaTiO₃ walls, through which the neighbor air spheres were connected. Theoretical calculations reveal that these windows can enlarge the photonic bandgap⁸. **Figure 4** is the transmittance of the opal photonic crystal. There is an attenuation peak at 570 nm, which is corresponding to Bragg diffraction. This shows that the bandgap is in the visible region. The bandgap of BaTiO₃ inverse opal and its electrically tunable property are under study.

Figure 4 Transmittance spectrum of opal photonic crystal



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