Temperature-tuned photonic bandgap in polymer synthetic opals

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Much interest has been emerging in photonic bandgap (PBG) structures or photonic crystals (PCs) because of their capability to control the propagation of electromagnetic waves [1–3]. Some important applications have been proposed in several scientific and engineering fields, such as zero-threshold lasers, highly efficient light-emitting diodes and integrated optical waveguides. Photonic crystals are the structures where the refractive index is a periodic function in space, which create a band of frequencies where the propagating modes are forbidden in all directions (absolute band gaps) or limited range of directions (incomplete band gaps). Based on this concept, many structures have been fabricated successfully to meet the periodic function requirement including "Yablonivite" mode [4], " woodpile" or "log-pile" [5] structure and opal, inverse opal structure [6, 7].

Photonic crystals could be applied in the range of microwave to optical frequency. Engineering of the structures could be easily applied in microwave domain by drilling [8], micro-machining [9] and semiconductor processing techniques [9]. But in optical application, it is a challenge to fabrication process because the feature size of periodicity reduces to hundreds of nanometers. To meet this challenge, self-assembled systems of colloid sphere are used. This self-assembly process has been used in synthesizing opal and inverse opal structures successfully. There are two steps in this process: (1) obtaining a monodisperse microsphere suspension and (2) gravitational sedimentation of the particles, usually combined with drying of the suspension. Silica and polystyrene microspheres are the major types of particles used for colloidal crystal assembly, because they are both highly monodispersive and relatively cheap. Some groups demonstrated that it was possible to fine-tune the bandgap properties of synthetic opal photonic crystals of silica or polymer colloids by sintering or annealing the samples at elevated temperature [6, 10, 11].

Thereafter, we fabricated photonic crystals of polystyrene spheres by gravitational sedimentation of the particles combined with drying of the suspension, and treated the templates in air at different temperatures. The aim of this study is to investigate the influence of annealing temperatures on templates' microstructures and photonic bandgaps in air. Our study showed that by increasing annealing temperature, the polystyrene spheres' surface shape transforms to dodecahedron, and the peaks of reflection spectra are blue-shifted.

Our fabrication of photonic crystal structures was similar to that reported previously [12], the monodisperse colloidal suspension (5% solid content) of polystyrene microspheres with a homogenous size of 270 nm was prepared in water. A few drops of this suspension were spread on a quartz glass substrate and left to dry slowly in humidity chamber at a temperature of 40 °C and relative humidity of 80%. The microspheres were self-assembled into a face-centered cubic (FCC) with the (111) plane, parallel to the substrate, to form templates after five days. The templates were placed in drying cabinet and treated at different temperature intervals of 10 °C between 60 and 110 °C for 24 h separately.

JSM-6301F scanning electron microscope (SEM) was used to determine the microstructures of the opal samples. Optical properties of the samples are evaluated by measuring their reflection spectra at an incidence angle of 5 °, using an UV-visible spectrometer (unicam UV540, thermo, USA).

The micrograph of the opals treated at different temperatures are shown in Fig. 1. After drying the sample at 60 °C for 24 h, the microspheres retain their original shape and well-ordered opal structure (Fig. 1a). On increasing the annealing temperature, the surface shape of the polystyrene microsphere transforms to hexagon, and the particles are in the intermediate state of sphere and polyhedron when the template is treated at 80 °C for 24 h (Fig. 1b). Fig. 1c shows that the surface shape of the particles treated at 100 °C for 24 h is hexagon, and there is small residual air void among the particles. After being treated at 110 °C for 24 h, polystyrene particles melt to form a disordered film (Fig. 1d) and the sample is transparent without reflecting light.

Fig. 2 shows the optical reflection spectra of the templates treated at different temperatures with 5 °-incidence angle. The peak of reflection spectra focus between 635 and 637 nm when the templates are treated at the temperatures from 60 to 80 °C, and shift to 622 nm when the templates are treated at 90 °C. The result shows that the reflection peaks are blue-shifted with increasing annealing temperatures. In the range of 80–100 °C, the shift rate is accelerated. No reflection peak is found when the templates are treated at 110 °C. This corresponds with that observed in SEM analysis: the polystyrene microspheres' deformation process is

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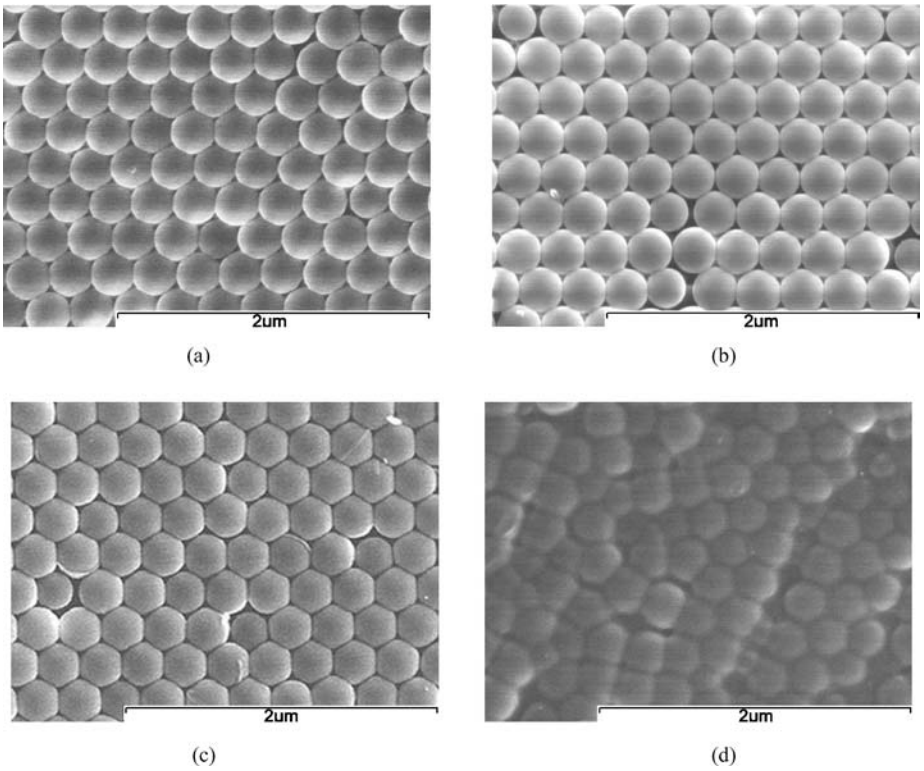

Figure 1 SEM micrographs of the polymer synthetic opal treated at different temperatures: (a) 60 °C, (b) 80 °C, (c) 100 °C and (d) 110 °C.

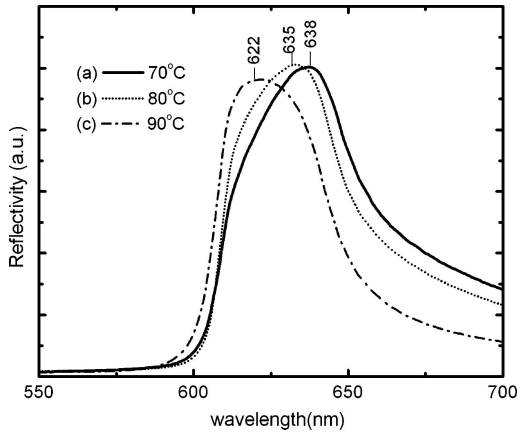

Figure 2 UV-spectra of the polymer synthetic opal treated at different temperatures.

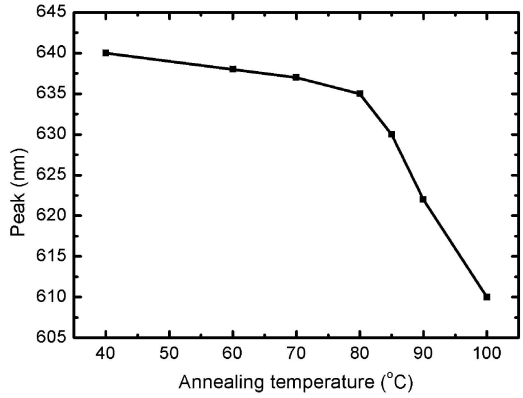

Figure 3 Plot of the reflection maximum wavelength versus the treating temperatures.

notable between 80 and 100 °C, and the film is disordered when treated at 110 °C.

For theoretical simulation, an approximate expression for the reflection peak position is given by the Snell's law, shown as Equation 1 [13]:

$$\lambda = 2d\left(n_{\text{eff}}^2 - \sin^2\theta\right)^{1/2} \tag{1}$$

where n_{eff} is the effective refractive index, λ the free-space wavelength of light, d the inter-planar spacing, and θ the incidence angle measured from the normal to the planes. The inter-planar spacing, d can be expressed in terms of the unit cell parameter a, and the Miller indices by, $d = a/(h^2 + k^2 + l^2)^{1/2}$. In FCC lattice the diameter of the spheres, D is related to the lattic parameter by $a = \sqrt{2}D$.

n_{eff} is determined by Equation 2, where n_{sphere} is the relative refractive index of polystyrene spheres, n_{air} is that of the air, and f is the filling ratio [6].

$$n_{\text{eff}}^2 = \varepsilon = n_{\text{sphere}}^2 f_{\text{sphere}} + n_{\text{air}}^2(1 - f_{\text{sphere}}) \tag{2}$$

In the well-ordered opal composed by ideal microspheres, the value of n_{eff} obtained as 1.46 corresponds to a polystyrene volume fraction of 26% assuming that the refractive index of polystyrene is 1.59. Assuming that the reflection peaks are associated with the (111) planes of FCC lattice, we obtain the bandgap wavelength position of 640 nm, which is in reasonable agreement with the reflection peak of 637 nm and is shown in spectra analysis.

The inter-planar spacing, d decreases and the effective refractive index n_{eff} increases with the increasing annealing temperature, accompanied with the polystyrene spheres in opal structure, which transform to dodecahedrons. The shift tendency of the reflection

peak was determined by the dominant factor, either d or n_{eff}. Calculations show that the bandgap position is red-shifted with increasing annealing temperature if $n_{\text{eff}} > 2$, but when n_{eff} is lower, the bandgap position will have a contrary tendency.

If polystyrene spheres' deformation reaches the maximum, it means that the cells' contact mode changes from point-contact to surface-contact and air void reduces to the extent that the air volume could be ignored, but the cells remain separate and the lattice retains the FCC structure. The lattice parameter can be obtained by Equation 3 as the volume of polystyrene cells remains unchanged:

$$a'^3 = \frac{16}{3}\pi\left(\frac{D}{2}\right)^3 \tag{3}$$

So the inter-planar spacing, $d' = \frac{a'}{\sqrt{3}} = \frac{\sqrt[3]{2\pi}D}{\sqrt[3]{3}\sqrt{3}} = 199$ nm, $n_{\text{eff}} = n_{\text{sphere}} = 1.59$. The bandgap position is $\lambda = 634$ nm. Calculation shows that the peak is blue-shifted corresponding to that observed in the experiment. But the measured value (622 nm) is smaller than the ideal calculation. This may be due to the inhomogeneity of the microsphere size and the anisotropy in shrinking process.

In summary, the optical properties of polystyrene opal photonic crystals were influenced drastically by the annealing temperature. On increasing the annealing temperature, the polystyrene spheres' shape transforms to dodecahedron, and the reflection peak is blue-shifted.

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