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SHORT COMMUNICATION

Colloidal photonic crystals with a graded lattice-constant distribution

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Abstract In this work, a gradient polystyrene colloidal photonic crystal was fabricated by annealing in a graded temperature field. The lattice constant of the gradient crystal gradually varied along the temperature-gradient direction. The positional bandgap wavelength as well as the attenuation of the bandgap wavelength could be tuned dependent on the position of the gradient colloidal crystal along the gradient direction because of the lattice-constant variation.

Keywords Colloidal crystal · Photonic crystal · Gradient

Introduction

Two- or three-dimensional colloidal structures assembled from monodisperse microspheres or nanospheres possess periodically dielectric structures and exhibit visible photonic crystal properties [1–5]. These colloidal arrays are promising in application to novel advanced materials and devices including photonic bandgap crystals [3–5], optical switches and filters [6, 7], chemical and biochemical sensors [8, 9], optoelectronic devices [10], and templates for ordered microporous materials [11–13], etc. A primary requirement for the success of these applications is the ability to direct particle assembly to form ordered arrays over large domains on the flat or patterned substrates. Various strategies of colloidal assembly have been developed to obtain these colloidal structures, including gravity sedimentation [14, 15], using capillary force [16, 17], the fluidic cell method [18], dewetting [3, 19], electrostatic interaction [20], electric field [21], microcontact printing [22], vertical deposition [23], and other novel methods [24, 25].

Recently, gradient colloidal crystals have also attracted much attention because of the potential application such as photonic crystals, sensing materials, coatings, biomaterials, and microfluidic devices for sensing and catalysis [26–29]. For example, Park et al. [27] have prepared a photonic crystal structure with a graded refractive-index distribution in which an infiltrated polymer in a colloidal crystal causes a gradual increase in the refractive index. Positional refractive-index variation in the gradient crystal was achieved using interfacial gel polymerization and a high-index dopant, leading to the positional bandgap tunability. von Freymann et al. [28] have also fabricated gradient colloidal photonic crystals with a lattice constant gradient by plasma etching. These gradient colloidal structures can serve as a new type of bandgap-tunable photonic crystal based on positional variations without the need to apply any external fields. Especially, the gradient photonic crystals with a lattice-parameter gradient can realize the reduction in the group velocity of light [28, 30]. It has previously been demonstrated that the lattice parameters and the stop band positions of colloidal crystals can be easily tuned by annealing them [5, 31, 32]. In this work, for the first time, we fabricated a gradient polystyrene (PS) colloidal photonic crystal by annealing in a graded temperature field. The lattice parameters of the gradient crystal gradually varied along the temperature-gradient direction. The positional bandgap wavelength could be tuned dependent on the position of the gradient colloidal crystal.

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Experimental

Monodisperse PS microspheres with a diameter of 242 nm were made by a surfactant-free emulsion polymerization process using potassium peroxysulphate as the initiator [33]. PS colloidal crystals were prepared by the vertical deposition technique [23]. A precleaned glass slide was vertically dipped into the suspension of the PS microspheres in ethanol. After ethanol was evaporated at 35 °C for 4 days, PS microspheres self-organized to form PS colloidal crystals on the glass substrates. By annealing in a graded temperature field by heating one end at about 130 °C for 36 h and keeping the other end at room temperature, the PS colloidal crystals with a graded lattice-constant distribution was obtained, as shown in Fig. 1.

Scanning electron microscopy (SEM) micrographs were taken using a Philips XL-30-ESEM-FEG instrument operating at 20 kV. The samples for SEM were coated with a 20–30 Å layer of Au to make them conductive. Optical absorption spectra of the gradient colloidal photonic sample were measured to probe the existence of stop bands on a HITACHI U-4100 spectrophotometer at room temperature.

Results and discussion

When microspheres are assembled into 3D crystalline arrays, the resulting highly ordered, periodic colloidal structures can strongly diffract light, and each of them exhibits a stop band in its spectrum. It has previously been demonstrated that it is possible to accurately control the optical properties of colloidal photonic crystals through thermal treatment [5, 31, 32, 34]. By annealing PS colloidal crystals at temperatures in the range of room temperature to 100 °C, the position of its stop band was continuously blue shifted in a controllable fashion. That is to say, the position of its stop band can be determined in the tunable range via changing the annealing temperatures. Therefore, it is possible to integrate these optical properties at different annealing temperatures into a gradient PS colloidal photonic crystal.

As shown in Fig. 1, the PS gradient colloidal crystal was fabricated through placing the PS colloidal crystal composed of 242-nm PS microspheres in the graded temperature field by heating one end at about 130 °C for 36 h and keeping the other end at room temperature. The diffractive optical properties of the gradient colloidal crystal film have been characterized using the absorption spectra in normal incidence. To examine the detailed optical properties of the gradient PS colloidal crystal, the tunability of the stop-band wavelength with respect to the position of the gradient crystal was measured as shown in Fig. 2. All absorption measurements were carried out with a normal incidence at each point with 1 mm spacing of the gradient crystal. Depending on the positions from the unheated end to the other end at 130 °C on the gradient PS colloidal crystal, the peak wavelength of its stop band was continuously blue shifted from 594 to 568 nm, and the attenuation of this stop band was gradually reduced. As shown in Fig. 2b, the optical changes on the gradient crystal can be divided into three regions according to the shifting rate of the peak wavelength along the gradient direction. In I region, the diffracted peak wavelength varies from 594 to 584 nm; in II region, the peak wavelength varies from 584 to 582 nm; and finally in III region, the peak wavelength varies from 582 to 568 nm.

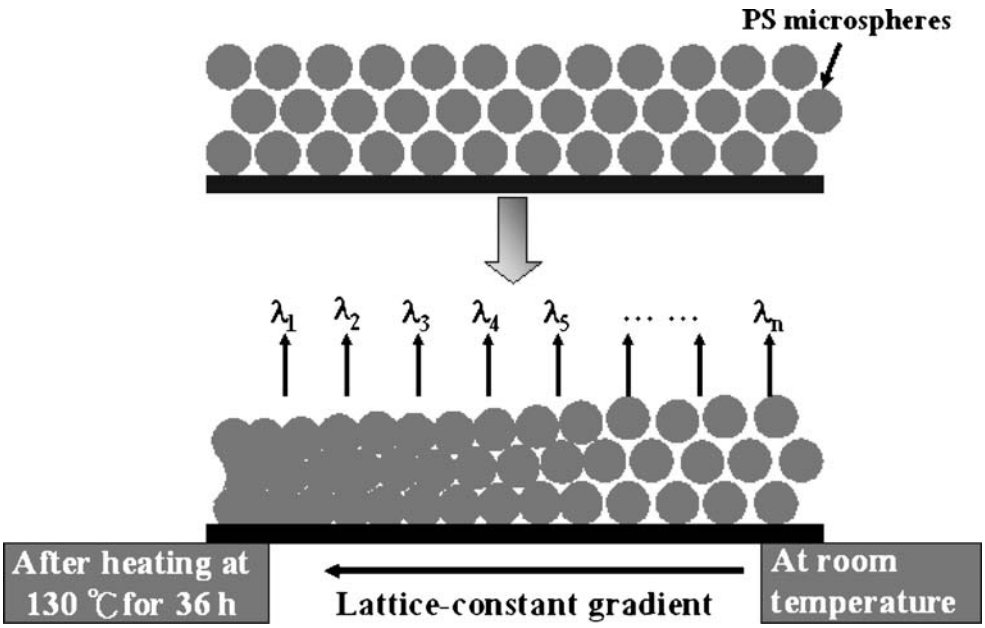

Fig. 1 A schematic illustration of the process of preparing the polystyrene colloidal photonic crystals with a graded lattice-constant distribution in a graded temperature field

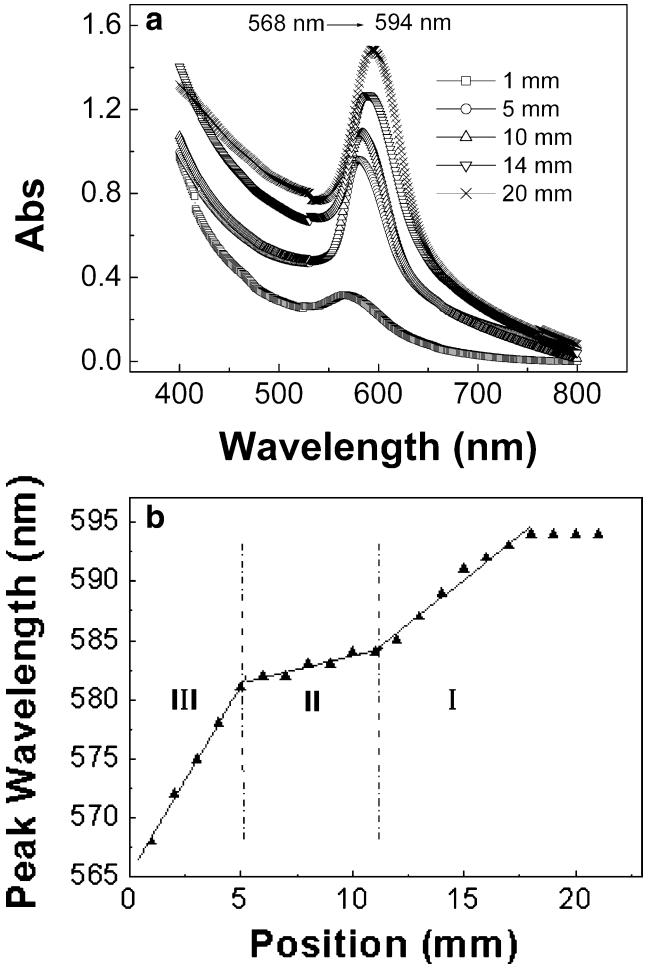

Fig. 2 **a** Positional absorption spectra of the PS gradient colloidal crystal annealed in a graded temperature field from room temperature to 130 °C. **b** Positional stop-band peak vs the position of the PS gradient colloidal crystal

It is believed that the positional optical properties reported above are accompanied by some morphological changes. In the process of preparing the gradient PS colloidal crystal in the graded temperature field, the colloidal crystal went through the three different stages of annealing, which corresponded to the three regions shown in Fig. 2b. Figure 3 exhibits SEM micrographs of different parts of the gradient PS colloidal crystal along the gradient direction. Figure 3a displays the I region of the gradient crystal, in which there is an interparticle separation of about 6 nm from the electrostatic repulsion on the surface of the PS microspheres [31, 32, 34]. In I region, a gradual increase in the temperature causes a gradual shrinkage between the separate gap between the neighboring PS microspheres and a reduction in the center-to-center distance between the PS beads (Fig. 3a), which can result in a blue shift of stop bands of the colloidal crystals. The shrinkage of the center-to-center distance does not stop until the microspheres have reached a state in which they are all in physical contact. The SEM micrograph in Fig. 3b shows the II region, in which the center-to-center distance between the neighboring PS microspheres continuously decreased. But the decrease rate of the center-to-center distance in II region is lower than that in I region. II region will last until the temperature is raised above the T_g of PS (~93 °C). In III region, the center-to-center distance is further reduced as a result of the viscoelastic deformation of PS beads (Fig. 3c) [31, 35]. In this region, the temperature was higher than T_g, the polymer chains in the PS microspheres could move at a low velocity, which resulted in the PS microspheres to begin to collapse at their locations, and necks formed between the neighboring microspheres. After heating the film for 36 h, the relatively close-packed multilayer microstructure disappeared gradually. Finally, the air voids between the neighboring microspheres vanished and a relatively flat surface formed, as shown in Fig. 3d. In Fig. 3c and d, the top surface of the PS spheres was deformed by the intrinsic forces of surface tension and became very rough [35]. Therefore, the center-to-center distance of the gradient colloidal crystal gradually decreases from about 248 to 221 nm along the gradient direction from the lower annealing temperatures to the higher ones. At the same time, the filling ratio of PS microspheres gradually increased from ~74 to near 100% along the temperature-gradient direction [31].

When the incident light is normal with respect to the surface (111) of the PS opals, the peak wavelength of the stop band can be described by the Bragg's law:

$$\lambda = 2\overline{n}d \tag{1}$$

where d is the lattice constant, i.e., the spacing between crystalline planes in the (111) direction. In the case of the PS opal, this spacing is related to the center-to-center distance D between the neighboring microspheres by $d = \sqrt{2/3}D$ for the f.c.c structure. And $\overline{n}$ is the average refractive index, can be approximated by the equation:

$$\overline{n} = \sqrt{f_{\text{spheres}} {n_{\text{spheres}}}^2 + f_{\text{voids}} {n_{\text{air}}}^2} \tag{2}$$

where f_{spheres} and f_{voids} are the filling ratio for the PS microspheres and the air voids, respectively. Here, the refractive index of the PS microspheres is approximately $n_{\text{spheres}}=1.59$ and that of the air voids is $n_{\text{air}}=1.0$. With the increase in the filling ratio of the PS microspheres in the colloidal crystal, the average refractive index $\overline{n}$ of the photonic systems will increase. As a result, the peak wavelength of the stop band will shift to longer wavelength according to the Bragg's law. However, the peak wavelength of the stop band will shift to the shorter wavelength as the center-to-center distance between the neighboring microspheres reduces. On the gradient colloidal crystal along the temperature-gradient direction from room temperature to 130 °C, the center-to-

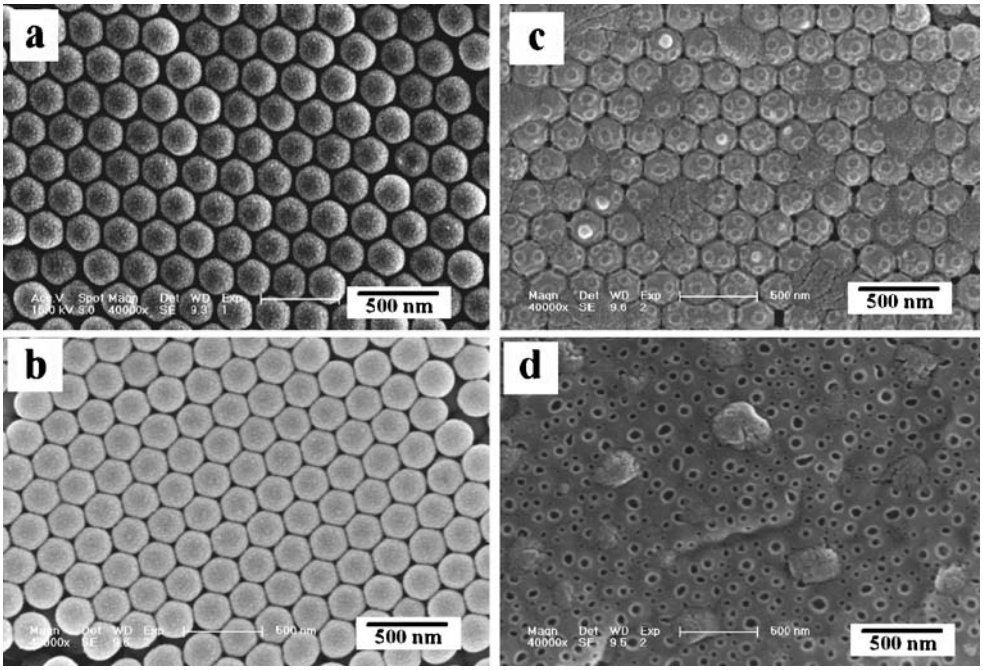

Fig. 3 SEM micrographs of the polystyrene gradient colloidal crystals in the graded temperature field from room temperature to 130 °C. Along the gradient direction, there are three regions of morphological changes corresponding to the three regions of optical variations in Fig. 2b, respectively. **a** I region: there is a separate gap between the neighboring PS colloidal microspheres; **b** II region: the neighboring microspheres are all in physical contact; **c** III region: polystyrene microspheres have been deformed by the visco-elasticity; **d** a rough transparent film formed at the end of 130 °C because of the fusion of polystyrene microspheres

center distance between the neighboring microspheres will gradually decrease, which results in the peak wavelength of the stop band gradually shifting to the shorter wavelength. At the same time, along the gradient direction, the filling ratio of the PS microspheres will gradually increase, which results in the peak wavelength of the stop band gradually shifting to the longer wavelength. Because of the contribution of the two opposite actions, the peak wavelength of the stop band is calculated to gradually shift from 589 to 567 nm by the Bragg's law, which is similar to the experimental data. In I region, f_{spheres} is 0.74 and the center–center distance between two neighboring microspheres reduces from 247 to 242 nm. So, the peak wavelength is calculated to shift from 589 to 577 nm by Eq. 1. In II region, the peak wavelength is calculated to be 577 nm adjacent to the experiment data of 582–584 nm. In III region, PS spheres' deformation gradually 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. As the volume of PS cells remains unchanged in this region, the interplanar spacing can be obtained by the equation as follows: $d = \frac{\sqrt[3]{2}}{\sqrt[3]{3}\sqrt{3}} D$ [34]. So, d can be calculated to be 178 nm and $\overline{n}$ approximates n_{spheres}=1.59. The peak position of stop band is calculated to be 567 nm. At the same time, the increase in the filling ratio of PS spheres is responsible for the observed decrease in the attenuation of the mid-gap as the annealing temperature increases. Therefore, the optical properties of the three regions in Fig. 2b reflect the morphologies of the three regions of the gradient colloidal crystal in Fig. 3. The experiment and theory clearly show that the stop band could be successfully tuned depending on the position of the gradient crystal because of the variation of the lattice constant.

Conclusions

In summary, we fabricated the PS colloidal photonic crystal by annealing in a graded temperature field. The lattice constant and the filling ratio of the gradient crystal gradually varied along the temperature-gradient direction. The positional bandgap wavelength could be tuned dependent on the position of the gradient colloidal crystal along the gradient direction because of the lattice-constant variation. This increase in the filling ratio of PS spheres is responsible for the observed gradual decrease in the attenuation of the mid-gap along the gradient, increasing direction of the annealing temperature. The gradient colloidal crystal integrates the optical properties of PS colloidal crystals at different annealing temperatures and may be used for tunable optical filters that can modulate the wavelengths.

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