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SHORT COMMUNICATION

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Preparation of colloidal crystals with polyhedral building blocks through post-polymerization

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Abstract An alternative approach was adopted to prepare colloidal crystal with polyhedral building blocks. First, monodisperse polystyrene particles that contained about 30% wt of monomer were obtained by emulsifier-free emulsion polymerization at 38 °C. These monomer-containing particles were used to prepare colloidal crystal on the surface of dispersion, before the spherical particles in the colloidal crystals underwent deformation between two quartz plates at 75 °C for 40 min by interfacial tensions, and finally the deformed particles were "frozen" through post-polymerization.

Keywords Colloidal crystal · Non-spherical · Surface tension

Introduction

Colloidal crystals are promising structures for applications in optical devices and photonic bandgap (PBG) crystals [1, 2], and most colloidal crystals are made up of spherical building blocks. Under appropriate conditions, PBG crystals may exhibit a forbidden bandgap, which can be applied to control and guide the propagation of light. Computational studies have suggested conditions for the PBG crystals to exhibit full bandgap in the optical regime [3, 4, 5, 6], and also suggested that the use of non-spherical objects as the building blocks in constructing the face-centered cubic lattice may lead to full bandgap under specific conditions. In addition, the formation of non-spherical building blocks can be used to fine-tune the band gap of a PGB crystal [7].

Two strategies could be used for preparing 3D colloidal crystals with non-spherical building blocks. One possible way is to fabricate the non-spherical particles first, and then assemble the building blocks into ordered structures [8]. The other one involves the reversed procedure, for example, López et al. [9] have demonstrated the possibility of obtaining the colloidal crystals with slightly deformed silica particles by sintering the sample at elevated temperature, so that the stop band position can be fine tuned. Xia and co-workers [7] used a similar procedure to prepare the colloidal crystals with polyhedral polystyrene building blocks; the stop band position of their colloidal crystals could also be fine tuned just by annealing the samples at a temperature (~100 °C) slightly above the glass transition temperature (T_g) of polystyrene.

In this work, by using monomer-containing polystyrene particles, we developed an alternative approach for fabricating the colloidal crystals with polyhedral building blocks, in which the capillary pressure was thought to be the main driving force for the deformation of these polymer particles.

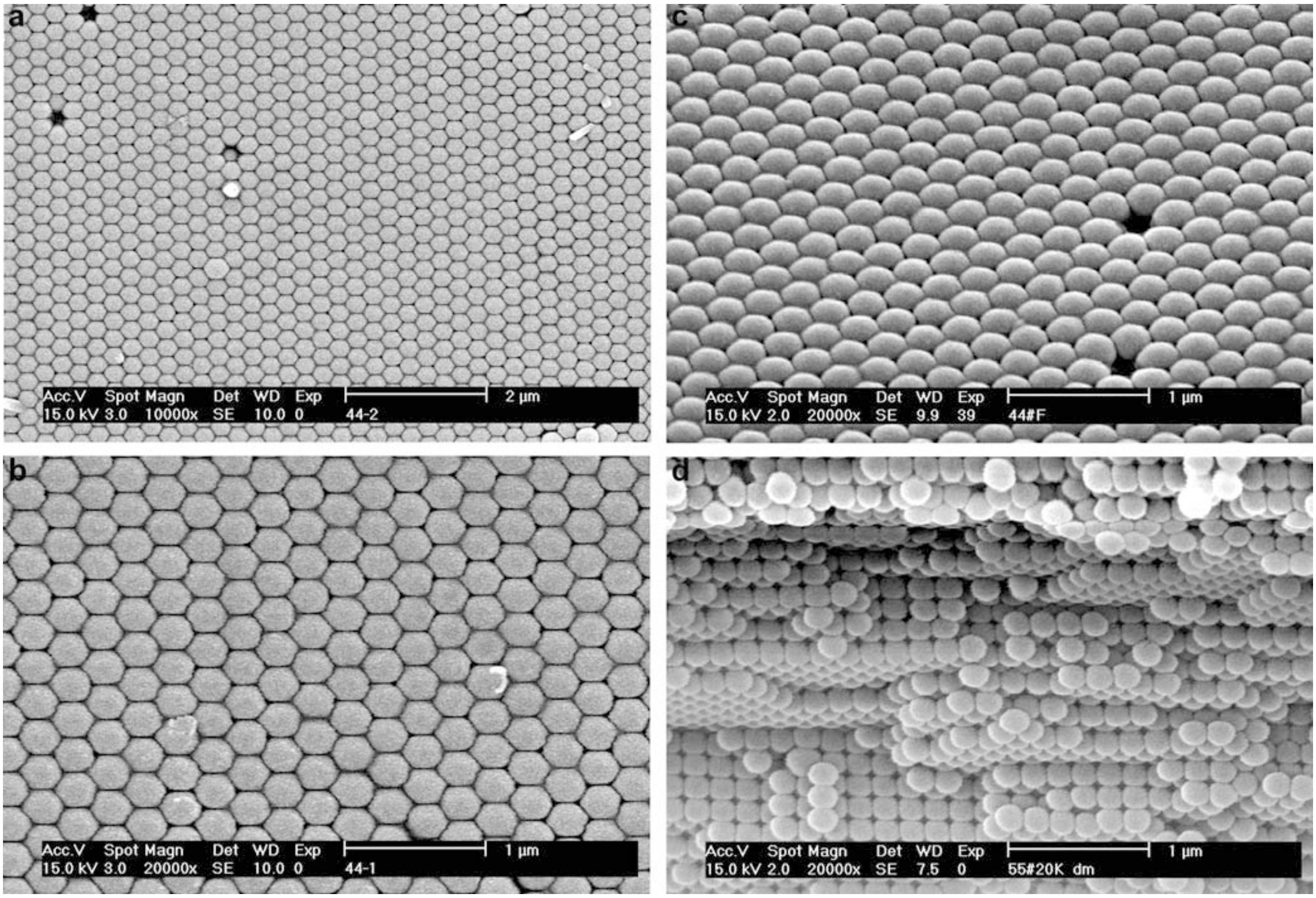
Materials and methods

Materials. Styrene (Aldrich) was distilled under reduced pressure of nitrogen at 40 °C. Sodium styrene sulfonate (NaSS), potassium persulfate ($K_2S_2O_8$) and sodium bisulfite ($NaHSO_3$) were all obtained from Aldrich and were used as received. Acetone, *p*-dihydroxybenzene, divinyl benzene and sodium bicarbonate were commercial analytical reagents and used as received. The water was double distilled and deionized with a Millipore water purification device and was used throughout.

Preparation of spherical colloids. The crosslinked spherical polystyrene particles were prepared through emulsifier-free emulsion copolymerization of styrene, NaSS and divinyl benzene at 38 °C with water/acetone as the reaction medium and $K_2S_2O_8/NaHSO_3$ as the redox initiators. We followed the procedure of Kim et al. [10] for the emulsifier-free polymerization, except that the water/acetone mixture was used as the reaction medium to reduce the polydispersity of the particle diameter [11]. After 2 h of polymerization, a portion of latex was taken out for preparing colloidal crystals, and then the temperature of the remaining latex was increased to 80 °C to make the final conversion nearly 100%. Two samples were prepared and used in this study, with diameters of 190 nm and 250 nm respectively.

Assembling colloidal crystal. The detailed procedure for assembling colloidal crystals has been described elsewhere [12]. Immediately after the emulsifier-free polymerization, 50 ml fresh latex was moved into a glass container and 0.05 ml *p*-dihydroxybenzene was dropped into the glass container to deactivate the initiators. The dispersion was then moved into a thermostat oven at about 65 °C. About 15 min later, a thin film with bright iridescence formed on the surface of the dispersion and a quartz plate was used to take a part of the film (about 0.1 mm in thickness) from the surface.

Fig. 1a–d Scanning electron microscope images of colloidal crystals with non-spherical building blocks. **a** General morphology of first layer. **b** Magnification of **a. c** Image from a tilting angle of 30°. **d** Morphology of cross-section of colloidal crystal



Preparation of non-spherical colloidal crystals. The colloidal crystal stuck to quartz plate was placed in a Buchner filter connected with vacuum line and then washed with 30 ml ethanol three times to remove the residual *p*-dihydroxybenzene, and dried in air. The mass difference between original colloidal crystal and washed colloidal crystal was within 5% wt of the original one. The aqueous solution of $K_2S_2O_8$ (0.5% wt) was then dropped onto the colloidal crystal sample, and the sample was covered with another quartz plate through two 0.2 mm spacers. The sample thus prepared was moved into a thermostat oven with a temperature of about 75 °C. Upon being heated for about 40 min, the quartz set was dismounted and the structure of the colloidal crystal sample was observed on a Philips XL30 scanning electronic microscope (SEM) after the sample was dried in air.

Results and discussion

Figure 1 presents the SEM images of colloidal crystals with non-spherical building blocks. Remarkable differences can be found between spherical [12] and non-spherical building blocks. Figure 1a shows the long-range order of a colloidal crystal with non-spherical particles. In an enlarged image, as shown in Fig. 1b, it can be clearly seen that the building blocks of the crystal exhibit hexagonal shape in (111) plane, and there are distinct boundaries between the building blocks, while looked from an angle of 30° as presented in Fig. 1c, the surface of upper part of each particle is not flat. Figure 1d is the SEM image for the cross section of a colloidal crystal on the (100) plane, which shows that those particles having contact with other particles underwent deformation, and that some particles, being in contact with four other particles in the plane exhibit a tetragonal shape, while those having no contact with other particles remain spherical. Figure 1 indicates that the colloidal crystals we prepared were composed of non-spherical building blocks.

Previous studies by other groups have shown that upon being heated to a temperature higher than its T_g, the polystyrene beads can be deformed into space-filling shapes by intrinsic forces of surface tension [7]. In this work, we employed an alternative method to realize the deformation of colloidal spheres. The schematic diagram for preparing this kind of colloidal crystals is demonstrated in Fig. 2 (following the sequence a-b-c-d). The particle deformation process of this method is somewhat like the film-forming process of latex. It is generally accepted that above the minimum film formation temperature (MFFT) of the latex, the film-forming process occurs in three stages [13]: (1) evaporation of the water until the particles reach close-packing, which is similar to the situation demonstrated in Fig. 2b, except that there was no upper cover for film formation, (2) formation of particle contacts and deformation of the latex particles into polyhedral shape, similar to that in Fig. 2c, and (3) interdiffusion of macromolecular chains between particles as the deformation goes further, and then the disappearance of the interface between particles (see Fig. 2e). As for the driving forces for the particles' deformation, Bradford and coworkers [14] thought the deformation was caused by Frenkel viscosity flow of contracting polymer spheres under polymer/air and polymer/water interfacial tensions. Brown [15] first pointed out that water also contributed to the deformation process through capillary compression of the polymer assemblage by the water/air surface tension. In the early 1980s, Lamprecht [16] recognized that film formation was actually a viscoelastic process. Then Dobler et al. [17] concluded that although the polymer/water interfacial tension alone could drive the latex to coalesce, the major driving force was that from the capillary pressure from the water/air interface.

In this study, we also made use of these interfacial tensions to drive the monodisperse polystyrene particles to undergo a viscoelastic deformation. However, to obtain the colloidal crystal with deformed particles, the building blocks should be "frozen" before they become the continuous film shown in Fig. 2e. To do that, we prepared monodisperse polystyrene particles containing a relatively large amount of "residual" styrene monomer via emulsifier-free emulsion polymerization at low temperature (38 °C), at which the monodisperse particles can be obtained, and the conversion rate of the polymerization for the particles was kept at a low level (about 70%). At this level the reaction was almost

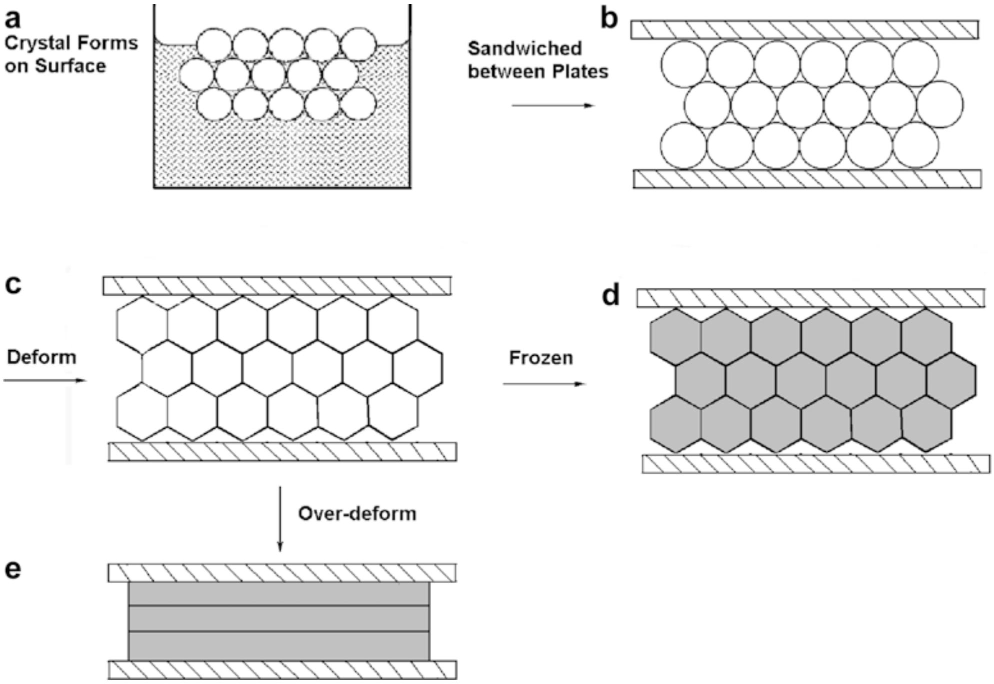


Fig. 2 Schematic process for formation of colloidal crystal with non-spherical particles. *a* Ordered spherical particles formed on surface of dispersion, *b* colloidal crystal was sandwiched between two quartz plates, *c* deformation occurred due to evaporation of water at higher temperature, *d* particle shape was frozen by post-polymerization, *e* particles form continuous film if not frozen

stopped since the reaction temperature was close to the T_g of the polymer/monomer mixture [11].

Then we adopted a simple method recently developed by our group [12] to assemble these particles as a crystal, in which a thin film of close packed crystal was formed on the surface of the dispersion driven by the static repulsive forces between the adjacent particles and the lateral capillary forces, as shown in Fig. 2a. At this stage, the monomer could not be re-initiated in the presence of inhibitor.

As the close packed colloidal crystal was formed, it was washed to remove inhibitor, sandwiched between two quartz plates, and then filled with initiator solution. The purpose of using two quartz plates is to retain water inside the interstitial spaces and prevent the water evaporating too fast during heating. When heated to 75 °C, a temperature that is higher than both the T_g of the polystyrene/styrene mixture and the MFFT of polystyrene/styrene latex, the water in the interstitial spaces between the particles evaporated and the particles could undergo deformation and gradually turn into polyhedrons, like other latexes do during their film formation process (stage 2), as shown in Fig. 2c. We suppose the predominant driving force for the deformation of our samples was from the capillary pressure, i.e. from the negative radius of curvature of water occurring during water evaporation in the interstitial space between particles [18]. Figure 1d shows that no deformation occurred on those particles that did not contact with other particles, because no negative radius of curvature of water could be formed for these particles and thus there was no capillary pressure to cause the particle deformation.

At the same time, the monomer inside the deforming particles was re-initiated by $K_2S_2O_8$ solution around the particles at this temperature, and the polymerization proceeded gradually, the conversion finally reaching over 95%. As a result, the deformed particles could be frozen since at this time the T_g for the particles is close to or even higher than the environment temperature and the deformation could not go further. Therefore, the shape of the building blocks ended up with the polyhedrons shown in Fig. 2d rather than the continuous film in Fig. 2e.

The shape of the deformed particles was complex. In the first layer of colloidal crystal (111 plane), during the deformation each particle contacted and occupied the free spaces as if they "squeezed" the other six adjacent particles in this layer during deformation, and each particle therefore had a tendency to exhibit a hexagonal shape, while for the particles within (100) plane in the one cross section of the colloidal crystal, as shown in Fig. 1d, they exhibited a tetragonal shape in the plane for similar reasons. In Fig. 1a, the irregular shape of particles around the defect was probably caused by the asymmetrical "squeezing" forces. The shape of most particles below the first layer would be the complex polyhedrons since one particle would be "squeezed" by 18 adjacent particles in the three-dimensional space.

Figure 3 gives the transmission spectra of the colloidal crystals with spherical and non-spherical building blocks respectively. The positions of the diffraction peaks for these two samples were 518 nm and 480 nm respectively. Blue-shift occurred as the particles underwent deformation. This result indicates that the layer separation (spacing between two planes) was decreased as a result of particle deformation. The positions of the diffraction peaks ($\lambda_{\max}$) in the spectra can be approximately identified by using Bragg equation for first order diffraction [19]:

$$\lambda_{\max} = 2d\left(n_a^2 - \sin^2\phi\right)^{1/2} \tag{1}$$

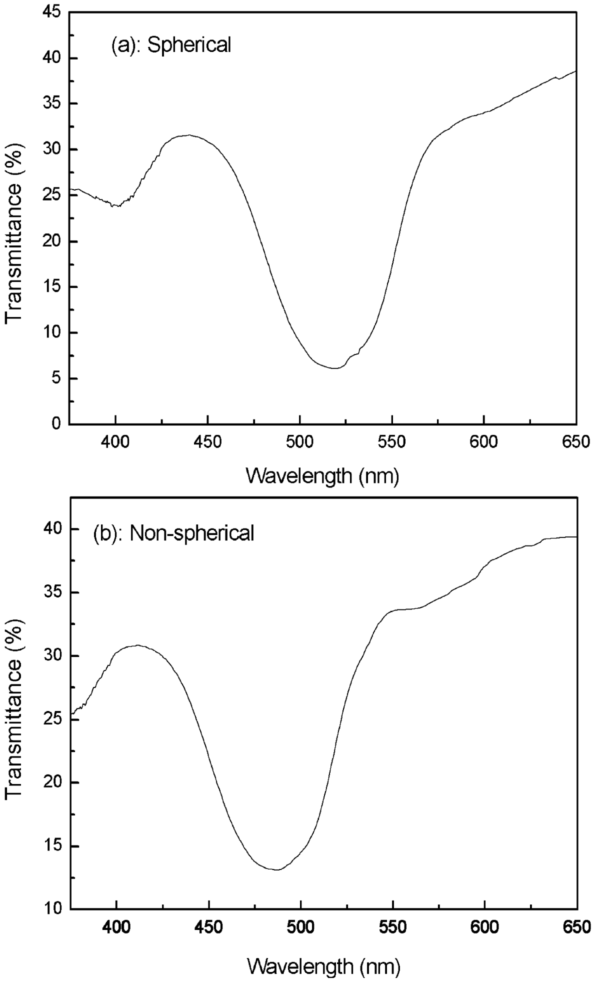


Fig. 3a, b The transmission spectrum of **a** colloidal crystal with spherical building blocks assembled from 190 nm monodisperse polystyrene particles and **b** colloidal crystal with non-spherical building blocks from 190 nm monomer-containing polystyrene particles where n_a is the refractive index of the crystalline assembly; ϕ is the angel between incident light beam and the normal to the surface of the crystal; d is the spacing between two adjacent crystalline planes (layer separation). In this study, where $\sin\phi$ is 0, n_a is 1.489, and (111) plane is parallel to the substrate, then d is the spacing between (111) planes, and Eq. 1 becomes:

$$\lambda_{max} = 2d_{111}n_a \tag{2}$$

In this study, if we assume the packing density of polystyrene particle is 74%, for spherical colloidal crystal, $d_{111} = (2/3)^{1/2}\ a$, where a is the diameter of colloidal particles (~190 nm). For non-spherical colloidal crystals, we could not obtain the layer separation between (111) planes from SEM pictures, and the shape for the deformed particles is very complicated, so we assume the center-to-center distance of adjacent particles in plane (100) (~178 nm, see Fig. 1d) as the value ***a*** to calculate d_{111}. Both the observed and calculated λ_{max} are given in Table 1; the difference between the observed and the calculated values we suppose is due to the assumptions for the calculation, especially the one that the particles are closely packed. In the UV-visible transmission spectra, the full widths at half-minimum of the peaks are relatively high (~60 nm) for the samples, reflecting that in some spaces the colloidal crystals are not regularly packed. Despite the difference between observed and calculated values, we can still attribute these diffraction peaks to the first-order Bragg diffraction of the colloidal crystals.

Table 1 Calculated and observed transmittance valley wavelength (λ_{max}) for spherical and non-spherical colloidal crystals

Colloidal crystal	d_{111} (nm)	λ_{max} (observed) (nm)	λ_{max} (calculated) (nm)
Spherical	156	518	465
Non-spherical	146	480	434

In conclusion, we prepared the colloidal crystal with polyhedral building blocks through an alternative approach, in which monomer-containing monodisperse particles were used as the building block to assemble colloidal crystal on the surface of the dispersion, and then the spherical particles underwent deformation at moderate temperature by interfacial tensions, and the deformed particles were "frozen" through post-polymerization. The colloidal crystal thus prepared can be used as a template to fabricate photonic crystals.

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