

Effects of medium composition on optical properties and microstructures of non-close-packed colloidal crystalline arrays

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Abstract The effects of medium composition on the optical properties and microstructures of non-close-packed silica colloidal crystalline arrays have been demonstrated. Water–alcohol mixtures were used as dispersion media for these arrays. Optical properties and microstructures were examined using angle-resolved reflection spectra measurements. The Bragg diffraction peaks of the colloidal crystalline arrays shifted with changing of concentration or hydrocarbon number of alcohol. With an increase in concentration or hydrocarbon number of alcohol, the effective refractive index of the dispersion increased and the interplanar spacing of the colloidal crystalline array decreased. The increase in effective refractive index was caused by an increase in the refractive index of the mixed medium with the change in solvent. The decrease in interplanar spacing of the array was caused by decreased electrostatic repulsions between the silica spheres with decreasing dielectric constant. The current work suggests new possibilities for the control of optical properties and microstructures of colloidal crystalline arrays.

Keywords Colloidal crystalline array · Bragg diffraction · Medium composition · Refractive index · Interplanar spacing

Introduction

Colloidal crystalline arrays are three dimensionally periodic lattices of self-assembled monodisperse colloidal spheres. These periodic structures have been actively explored as functional components in fabricating new types of diffractive devices such as optical filters and chemical sensors [1–4], mechanical sensors [5–9], and photonic bandgap structures [10–15]. Recent studies on the unique optical properties of these materials, often referred to as photonic bandgap crystals [16–18], have now evolved into a new, exciting field of research.

Two methods of manipulating monodisperse colloidal spheres for the generation of colloidal crystals have emerged. One approach involves assembly of the spheres into close-packed crystalline arrays through sedimentation or solvent evaporation [19–26], and the second utilizes the long-range electrostatic interactions of charged colloidal spheres dispersed in a liquid medium to make non-close-packed crystalline arrays [27–33].

The latter array will self-assemble from a dispersion of monodisperse colloidal spheres containing ionizable surface functional groups. If these spheres are dispersed in a polar medium such as water, the surface groups ionize to form spherical macroions, which are surrounded by a diffuse counterion cloud (electrical double layer). If the solution medium is pure and contains few other ionic species, the electrostatic interaction between spherical macroions can be significant over macroscopic distances greater than 1 μm [34–37]. The methodology based on electrostatic interactions seems to be the most powerful and successful for generating multilayer assemblies and producing large single-crystalline domains of mesoscale particles [38, 39]. This method, however, requires very strict experimental conditions such as the density of charges on the surface of

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the particles, the concentration of particles, and the concentration of free electrolyte molecules in the dispersion medium. The effects of charge density of the particles and the concentration of free electrolyte molecules on these interactions have been previously investigated [40–42], and the microstructures of colloidal crystalline arrays can be explained by electrostatic interactions.

In this work, effects of medium composition on optical properties and microstructures of non-close-packed silica colloidal crystalline arrays have been examined. Water–alcohol mixtures were used as the dispersion medium of the arrays. Optical properties and the microstructures of the non-close-packed colloidal crystalline arrays were estimated by angle-resolved reflection spectroscopy. Changes in optical properties and microstructures with medium composition were investigated for opening up new possibilities for the control of the structures and properties of such arrays.

Experimental

Colloidal crystalline arrays in various suspension media

Monodisperse colloidal silica spheres KEW10 (diameter 90 nm) were purchased from Nihon Shokubai, Japan. The non-close-packed silica colloidal crystalline arrays were dispersed in water–alcohol mixtures. The volume fraction of the silica spheres was 4 vol%, and the alcohol content of the dispersions was 0–40 wt%. The alcohols used were methanol, ethanol, 1-propanol, and 1-butanol. The spheres were shaken in the dispersion with an excess of mixed-bed ion-exchange resin [AG501-X8(D), Bio-Rad Laboratories, Hercules, CA, USA] to reduce ionic impurities and to form the non-close-packed colloidal crystalline arrays.

Measurements

Optical properties of the non-close-packed colloidal crystalline array were evaluated by measuring their reflection spectra at normal incidence using a multichannel spectrometer (Soma Optics, Fastevert S-2650). The arrays in water–alcohol mixtures were injected into a quartz cell, and structural analysis was performed by angle-resolved reflection spectroscopy [43–46]. Angle-resolved reflection spectra were measured by changing the angle of incidence θ between the beam and the normal of the sample surface from 9° to 46° and by collecting the light scattered in the Bragg configuration. The Bragg equation is given by Eq. 1:

$$m\lambda_{\text{peak}} = 2d_{111}(n_{\text{eff}}^2 - \sin^2 \theta)^{1/2} \quad (1)$$

where m is the order of diffraction; λ_{peak} is the wavelength of the diffraction peak; d_{111} is the interplanar spacing

between (111) planes; θ is the angle between the incident light and the normal to the diffraction planes (at normal incidence, $\theta=0^\circ$); and n_{eff} is the mean effective refractive index of the dispersion. λ_{peak} was plotted against θ . d_{111} and n_{eff} were determined by fitting the Bragg condition to the plotted data.

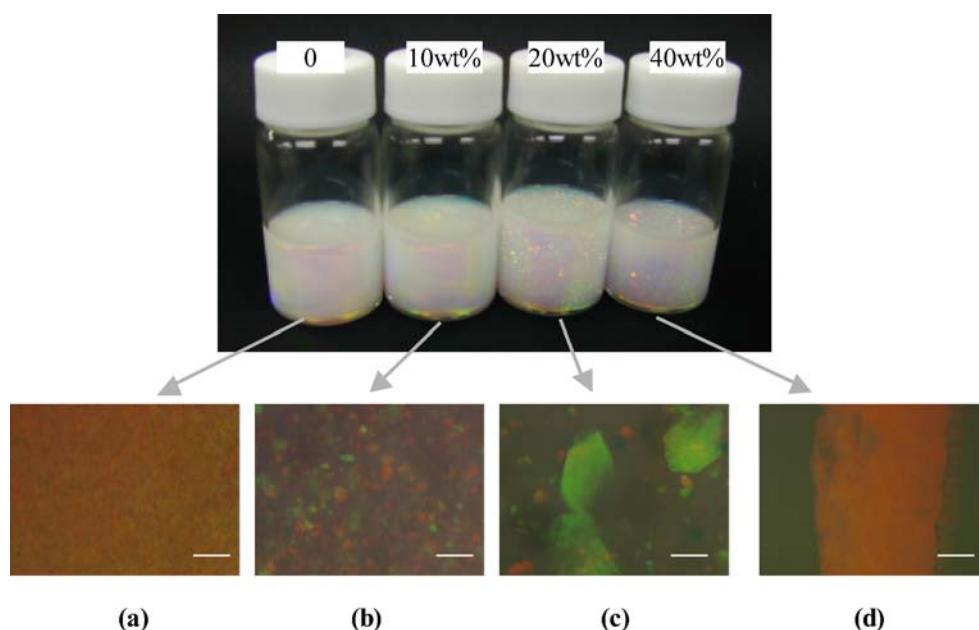
Results and discussion

Figure 1 shows the appearance of the non-close-packed silica colloidal crystalline arrays in mixed media with varying 1-propanol content. Crystalline arrays formed in all dispersions, as indicated by visible range Bragg diffractions caused by the ordered arrays, whose size increased with increasing 1-propanol content. This must have been caused by an increase in dispersion viscosity, as 1-propanol is more viscous (η :2.26 Pas) than water (η :1.00 Pas). In a previous paper, nucleation and crystallization rates of non-close-packed colloidal crystalline arrays decrease as the fraction of ethylene glycol increases in the mixture with water by viscosity of solvent [47], because the viscous solvent caused friction, which strongly dampens the lattice vibrations of the arrays [48]. When the dispersion viscosity was low, many crystalline array nuclei formed simultaneously throughout the dispersion. As the viscosity of the dispersion increased, the nuclei of the colloidal crystal are going to be difficult to make because of restraint of particle moving and the number of nuclei decreases consequently. In other words, colloidal crystalline arrays formed more slowly and more uniformly, and grew into larger one.

Figure 2 shows the reflection spectra of the non-close-packed silica colloidal crystalline arrays in mixed media containing various proportions of 1-propanol. Peak positions and peak heights in the reflection spectra shifted with increasing 1-propanol content.

In these measurements, the incident light and detector were both oriented perpendicular to the (111) plane of this lattice. The interplanar spacing between (111) planes of the crystalline array, d_{111} , and the mean effective refractive index, n_{eff} , of this dispersion were derived from the angle dependence of the reflection spectra (Fig. 3a). The spectrum evolved gradually with increasing angle θ . Clear attenuation bands corresponding to the (111) Bragg reflection peaks could be observed [band (1) 650–550 nm], along with weaker peaks [band (2) 370–380 nm]. As the angle increased, band (1) shifted to shorter wavelengths according to the Bragg law, whereas band (2) shifted a little to longer wavelengths. To clarify the factor responsible for this shift, angle-resolved reflection spectra measurements were performed. The equilibrium crystalline array structure for these dispersions with the present

Fig. 1 The appearance of non-close-packed colloidal crystalline arrays made of silica particles in water/1-propanol dispersions with varying 1-propanol content: **a** 0 wt%, **b** 10 wt%, **c** 20 wt%, **d** 40 wt%. The scale bar in the inset corresponds to 100 μm



volume fraction and the particle diameter is known to be face-center-cubic (fcc) [49, 50]. When the incident light was rotated toward the (111) surface of the crystal within the zx and zy planes, the position of the diffraction peak shifted to shorter wavelengths. As both spectra indicated a shift to shorter wavelengths, it could be concluded that these colloidal crystalline arrays were fcc structures. The latter band could be explained as a (220) reflection [43]. The interplanar spacing d_{111} and n_{eff} were determined by fitting the (111) Bragg reflection peaks to the Bragg diffraction Eq. 1.

Figure 3b shows the relationship between incident angle and peak of band (1) reflection spectra of the non-close-packed colloidal crystalline arrays. The very close fit also indicates that these structures diffracted based on the Bragg law. From the fitting of Eq. 1, n_{eff} and d_{111} of the colloidal crystalline array were found to be 1.343 and 239.2 nm, respectively. In the same way, n_{eff} and d_{111} of the arrays in media with various contents of 1-propanol were derived

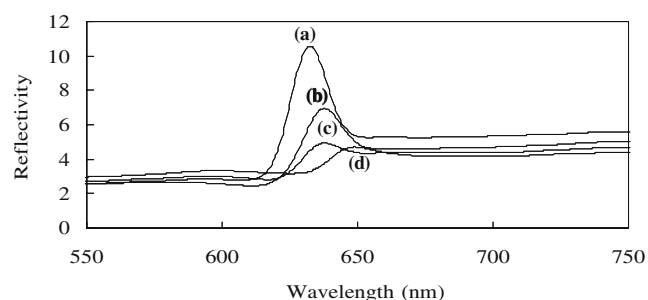


Fig. 2 The reflection spectra of non-close-packed colloidal crystalline arrays made of silica particles in water/1-propanol dispersions with varying 1-propanol content: **a** 0 wt%, **b** 10 wt%, **c** 20 wt%, **d** 40 wt%

from angle-resolved diffraction spectra (Fig. 4). The refractive index of the arrays increased with increasing 1-propanol content, whereas interplanar spacing decreased. As the refractive index of 1-propanol (1.39) is larger than that of water (1.33), we supposed that the refractive index of the dispersion increased as the content of 1-propanol increased. The Bragg diffraction equation

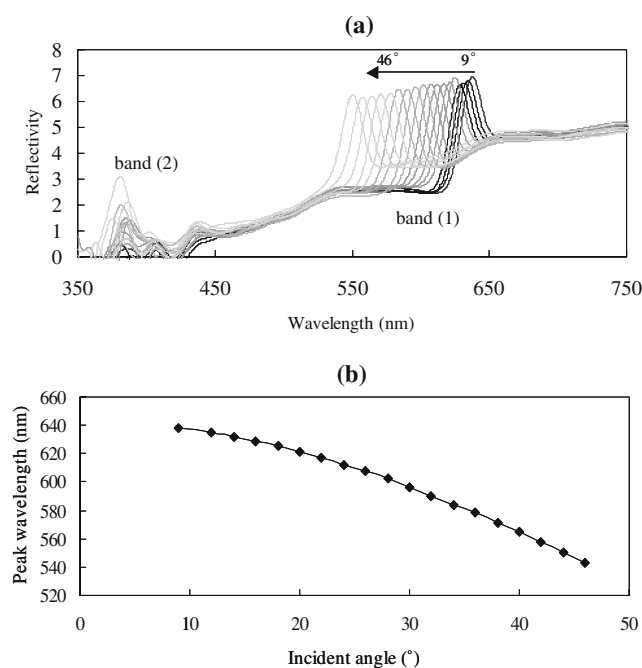


Fig. 3 Angle-resolved reflection spectra of non-close-packed colloidal crystalline arrays made of silica particles in a water/1-propanol dispersion with 10 wt% 1-propanol. **a** Reflection spectra, **b** the relationship between incident angle and peak of reflection spectra

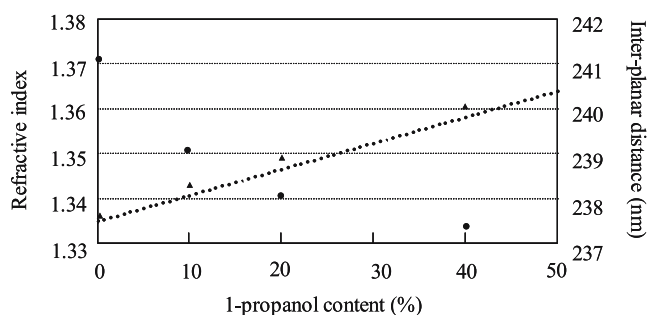


Fig. 4 Effective refractive index n_{eff} , calculated refractive index n_{calc} , and interplanar spacing d_{111} of non-close-packed colloidal crystalline arrays made of silica particles in water/1-propanol dispersion. Filled circle: d_{111} ; filled triangle: n_{eff} ; dotted line: n_{calc}

can be applied to these systems together with the effective medium approximation,

$$n_{\text{eff}} = n_{\text{particle}}\phi + n_{\text{solvent}}(1 - \phi), \quad (2)$$

where ϕ is the filling fraction of the volume occupied by the particles, and n_{particle} and n_{solvent} are the refractive indices of particle and solvent, respectively.

$$n_{\text{solvent}} = n_{\text{water}}\phi_{\text{water}} + n_{1\text{-propanol}}\phi_{1\text{-propanol}} \quad (3)$$

where n_{water} and $n_{1\text{-propanol}}$ is the refractive index of water and 1-propanol, ϕ_{water} and $\phi_{1\text{-propanol}}$ is the filling fraction of the volume occupied by the water and 1-propanol, respectively, and Eq. 2 is substituted in Eq. 3 to obtain Eq. 4:

$$n_{\text{eff}} = n_{\text{particle}}\phi_{\text{particle}} + n_{\text{water}}\phi_{\text{water}} + n_{1\text{-propanol}}\phi_{1\text{-propanol}}(1 - \phi_{\text{particle}}). \quad (4)$$

The dashed line in Fig. 4 shows n_{eff} calculated from Eq. 4, substituting $\phi_{\text{particle}}=0.04$, $n_{\text{particle}}=1.45$, $n_{\text{water}}=1.33$ and $n_{1\text{-propanol}}=1.39$. Experimental values of n_{eff} were almost identical to calculated values, suggesting that the increase in n_{eff} was caused by the increase in refractive index of the mixed medium. On the other hand, the decrease in interplanar spacing d_{111} must have been caused by the decrease in electrostatic interactions with decreasing dielectric constant of the mixed medium. The colloidal crystalline arrays were formed mainly by electrostatic repulsion between the electrical double layers of the spheres. Thickness of electrical double layers is characterized by the Debye-Hückel screening parameter κ^{-1} calculated from Eq. 5

$$\kappa^{-1} = (\epsilon kT / 2e^2 n_0 Z^2)^{1/2}, \quad (5)$$

where ϵ is dielectric constant, k is Boltzmann constant, T is absolute temperature, e is elementary electric charge, n_0 is number of ions, and Z is the ionic valence. With a decrease in dielectric constant ϵ , κ^{-1} also decreases. ϵ decreased

Table 1 Effective refractive index n_{eff} , calculated refractive index n_{calc} and interplanar spacing d_{111} of non-close-packed colloidal crystalline arrays made of silica particles in water/alcohol dispersions with various alcohols; (a) no alcohol (water only), (b) methanol, (c) ethanol, (d) 1-propanol, (e) 1-butanol

Co-solvent	n_{eff}	n_{calc}	d_{111}
No (water)	1.336	1.335	241.2
Methanol	1.334	1.335	240.5
Ethanol	1.338	1.34	239.2
1-propanol	1.343	1.342	238.2
1-butanol	1.352	1.343	236.4

with increasing 1-propanol content, as ϵ of 1-propanol is smaller than that of water (Table 1). In water/1-propanol mixtures, thickness of electrical double layers κ^{-1} decreased and electrostatic repulsions decreased with increasing 1-propanol content. On the other hand, decrease of the peak height is caused from decrease of the volume fraction of colloidal crystalline array in the dispersion with increasing concentration of 1-propanol because of decreasing interparticle electrostatic interaction.

Figure 5 shows the reflection spectra of the non-close-packed silica colloidal crystalline arrays in mixed media with various alcohols. Peak positions and peak heights in the reflection spectra shifted with changes in the alcohol used. n_{eff} and d_{111} of non-close-packed silica colloidal crystalline arrays containing various alcohols were derived from angle-resolved diffraction spectra (Table 1). n_{eff} of the dispersion increased with increasing hydrocarbon number of the alcohol, whereas d_{111} of the crystalline array decreased. As the refractive index of alcohol increased with increasing hydrocarbon number of the alcohol (Table 1), we supposed that the refractive index of the dispersion increased as well. In fact, experimental values of n_{eff} corresponded well to calculated values.

This suggested that the increase in n_{eff} was caused by an increase in the refractive index of mixed medium. And the decrease in interplanar spacing d_{111} of the crystalline array must have been caused by a decrease in electrostatic interactions, because κ^{-1} and electrostatic interactions

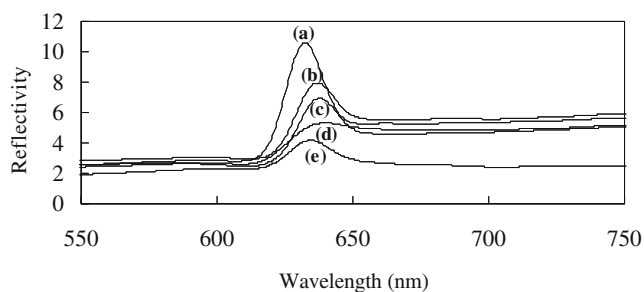


Fig. 5 Reflection spectra of non-close-packed colloidal crystalline arrays made of silica particles in water/alcohol dispersions with various alcohols: a no alcohol (water only), b methanol, c ethanol, d 1-propanol, e 1-butanol with alcohol content 10 wt%

decreased with increasing hydrocarbon number of alcohol because of the decreasing dielectric constant of the mixed medium. On the other hand, decrease of the peak height is caused from decrease of the volume fraction of colloidal crystalline array in the dispersion with increasing hydrocarbon number of alcohol because of decreasing interparticle electrostatic interaction.

Conclusions

Effects of medium composition on optical properties and microstructures of non-close-packed silica colloidal crystalline arrays have been demonstrated. Various water–alcohol mixtures were used as the medium of dispersion for these arrays, whose optical properties and microstructures were examined using angle-resolved reflection spectra measurements. Bragg diffraction peaks of the arrays shifted with changing concentration or hydrocarbon number of alcohol. With increasing concentration or hydrocarbon number of alcohol, the effective refractive index of the mixed medium increased and the interplanar spacing of the colloidal crystalline array decreased. The increase in effective refractive index was caused by the increase in the refractive index of the mixed medium with the change. The decrease in interplanar spacing was caused by an decrease in electrostatic repulsions between the silica spheres with decreasing dielectric constant. The current work suggests new possibilities for the control of optical properties and microstructures of colloidal crystalline arrays.

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