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Colloidal Crystallization of Polystyrene Induced by a New Drop-Slide Method

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Summary

Colloidal crystals of mono-dispersed polystyrene spheres in aqueous solvent were formed by a new drop-slide method. The optical properties of the colloidal crystal array (CCA) were characterized by reflection spectroscopy. The very strong intensity of reflectance was obtained by the new method. The maximum of the diffraction peak is highly symmetric and has a relatively narrow line width of about 52.0 nm when the CCA is in the wet state. An in-situ real time investigation on the formation of the CCA was performed. The reflection maximum was found to be 566.4nm, which blue shifted to 486.5 nm over the first drying phase and finally to a minimum of 432.3nm upon reaching the final stable state. The shifts of peak position were determined to be 4.1 nm / min at the first drying phase. The analysis of the diffraction maximum with calculation shows that the colloidal particles can crystallize into a face-centered-cubic (fcc) structure. The scanning electron micrograph image of the polystyrene spheres after is completely dried shows a face centered cubic formation.

Introduction

Colloidal crystals or opals are defined as a large, area-ordered, nano-structured material with periodicity in the sub-micrometer range. The self assembly of the colloids has many potential applications in photonics, optics and sensor development industries (1-4). These planar crystals exhibit a periodic spatial variation of refractive index with lattice constants on the order of the wavelength of light, thus exhibiting a well defined photonic band gap (PBG) (5-6). Prior investigation of CCAs have shown that in order for the submicron particles to function as photonic crystals, the synthetic opal crystals should be arranged into special architectures in order to be integrated into micro devices. Only then will CCAs behave as photonic circuits, switches, mirrors, filters, waveguides or sensors (7-10). Structures exhibiting full photonic band gaps in the microwave, millimeter, and sub-millimeter regimes have already been fabricated, but scaling these structures down to the optical level has remained a challenge. The photonic crystal considered here is a three dimensional dielectric structure with a periodic modulation of its dielectric constant with spatial periods of the order of the wavelength of light (11).

Owing to this periodicity, light incident along a particular direction will be Bragg diffracted by the crystal planes for a certain range of frequencies, forming stop bands. When the stop bands are wide enough and overlap for both polarization states along all crystal directions, the material possesses a complete photonic band gap. To build such a structure there are several important parameters that need to be controlled: lattice type, filling fraction, and dielectric contrast between the low and high dielectric regions. The 3D arrays can be prepared by a number of different methods like natural sedimentation, electrostatic repulsion, template assisted assembly, physical confinement, and capillary forces induced convective self assembly (12-14).

Typical fabrication of a photonic crystal suitable for Bragg diffraction of visible light is achieved by growing colloidal crystals formed from an aqueous suspension of sub-micrometer polystyrene micro spheres. The photonic crystals grown for this work were 210nm in diameter and were mono-dispersed in water to obtain the desired concentration. A unique and easy method for the self assembly of colloidal PS spheres into opaline crystalline lattice arrays was introduced in this study. The reflectance study was done continuously over a period of 70 minutes and the blueshift of the reflectance peak was monitored with respect to time in minutes. The CCA’s formed exhibited high stability at room temperature and the increasing stability was reflected in the change in Bragg reflection with time.

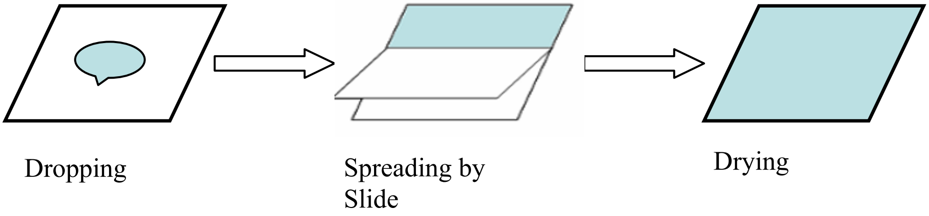
Experimental Procedures

Materials

For the preparation of the CCA, we obtained OptiBind® polystyrene micro particles (PS-MPs – Seradyn Inc, IN, USA) which are uniformly sized (0.210 μM) stable colloids and are considered to be mono dispersed spheres. The specific gravity of polystyrene is 1.05 g/mL. Polystyrene colloidal spheres were centrifuged seven times. The final product is an iridescent opal colored colloidal micro gel. The gel mainly reflects light in the green to red region. The particles are supplied at nominal 10% solids after dilution with distilled water from the original polymerization mixture. The stability of the colloids (ie maintaining spheres as separate particles) requires a minimum amount of surface negative charge. The slide and cover glasses (Fisher) used for creating a uniform thin layer of the colloids were first treated with freshly prepared piranha solution (H_2SO_4 / H_2O_2, ratio of 3:1). The glass substrates were rinsed copiously with distilled water and subsequently dried under the flow of N_2. Such chemical modification of the substrate surfaces is known as an effective way to facilitate the preparation of laterally patterned colloidal crystals (15).

New Drop-Slide method to form a CCA

A new and easy drop and slide technique was used to form the CCA as shown below. Micro droplets of the aqueous colloidal spheres (50% v/v) were first placed on a glass slide and a cover glass slip then slightly interfaced with the colloids. Immediately when the particles come in contact with the cover glass they spread along the long edge of the cover glass manually. The cover glass is then very slowly slipped right along the length of the glass slide causing the colloidal particles to thinly and uniformly spread on the substrate. Although this method provides a relatively easy route to ascertain uniformly spread crystal lattice, it has no provisions for the control of thickness based on sliding speed and hence has room for improvement. This method is analogous to that used by Ko et.al (16), however here we used a pipette to deposit the particles horizontally on the substrate and then spread them with a cover slip. The self assembly of the CCA from the wet to the dry state was monitored by taking reflection spectra at normal incidence using an Ocean Optics USB 2000 fiber optic spectrometer. Usually, the high optical quality of the film can be judged by the naked eye due to the opalescence. The reflection spectra were obtained in the region from 350nm – 1000nm. The reflection spectra were obtained over selected time intervals (2 and 4 minutes) from the placement of the colloidal particles on the substrate until the dry state was ascertained- indicated both visibly and by a strong Bragg reflection in the visible region. In order to determine morphology of the films, scanning electron microscopy (SEM, JSM-5900) was used.



Results and Discussion

Crystalline quality of the polystyrene CCA particles obtained by a new drop slide method is shown in Figure 1. The SEM image shows the perfect close-packed order extending over areas. The SEM image elucidates the highly ordered structures with the hexagonal packing on the film surface of the face centered cubic (fcc) structure on Figure 1(a). As shown Figure 1(b), the SEM image with the low magnification shows the crack distributions on the film. The reflection spectra were obtained in the region from 350nm – 1000nm for the polystyrene film as soon as the colloids started to form into a highly ordered crystalline structure (17). The formation of the crystal depends on several factors such as the substrate, temperature, humidity and concentration, diameter and the charged nature of the colloid. The formation was observed to be more rapid in high volume fraction (ie 50% v/v in aqueous solvent) and also for colloids which have a high net negative surface charge inherently present in them (18). For the normal kind of polystyrene spheres placed on the substrate as a micro droplet the colloids start to self assemble into the crystalline state in about 6 ~ 8 min of settling time. A reflection spectrum observed in the spectral region from 350nm – 1000nm for the CCA, after 8 minutes of settling time from the time the material is placed on the substrate is shown in Figure 2. As seen in the figure a very strong intensity was obtained by the new method. The spectrum exhibits the symmetric as well as the relatively narrow line width of the reflection maximum. The reflection maximum was found to be at 554nm and the relative stop bandwidth ($\Delta\lambda/\lambda_0$ = 52.4 nm) which is about 9 % of the center wavelength of the peak (λ_0). This value agrees with the theoretical calculation result for an FCC crystal structure by Tarhan and Watson (19).

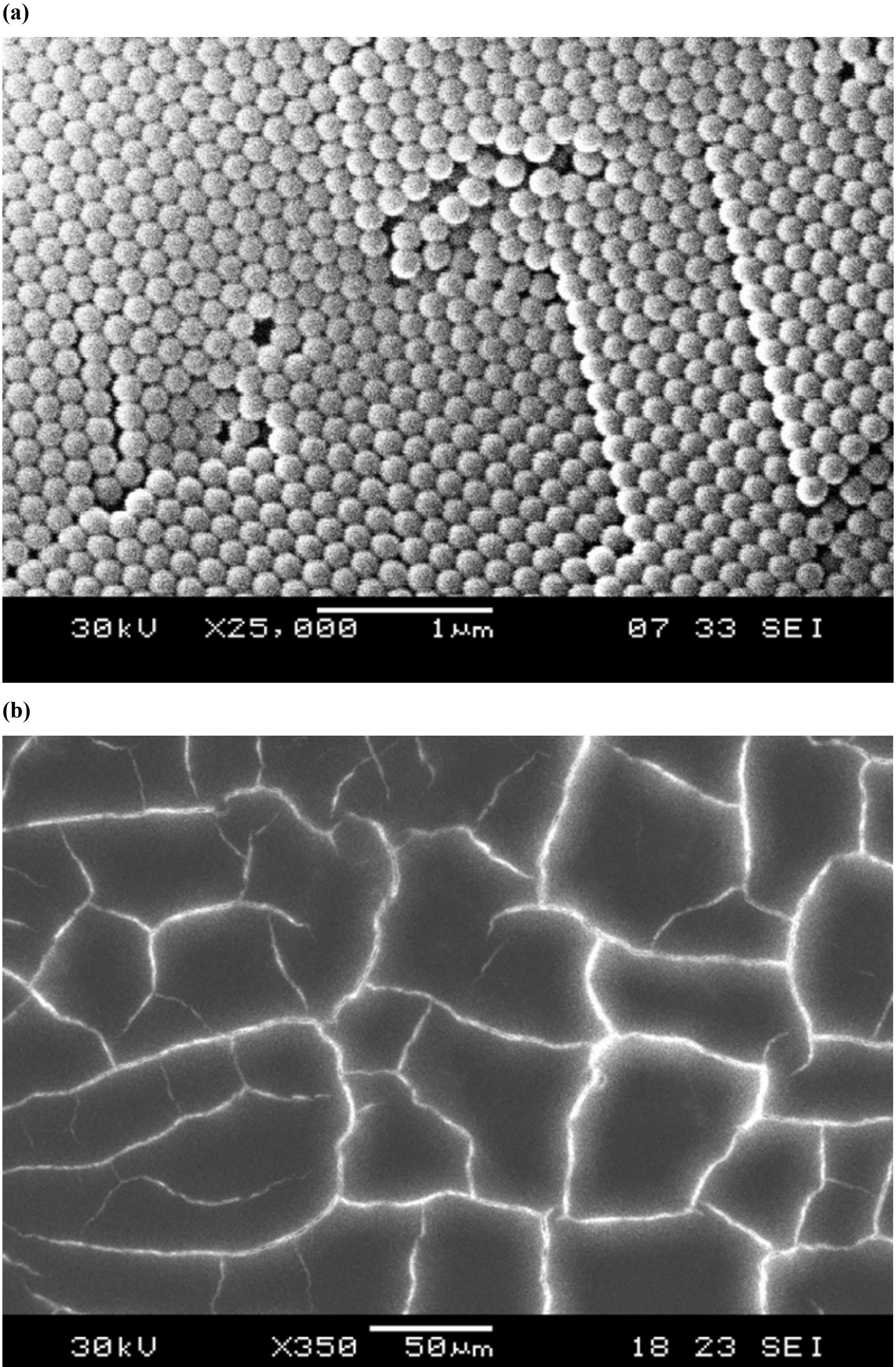


Figure 1. A Scanning Electron Micrograph of the polystyrene showing self assembly into CCA

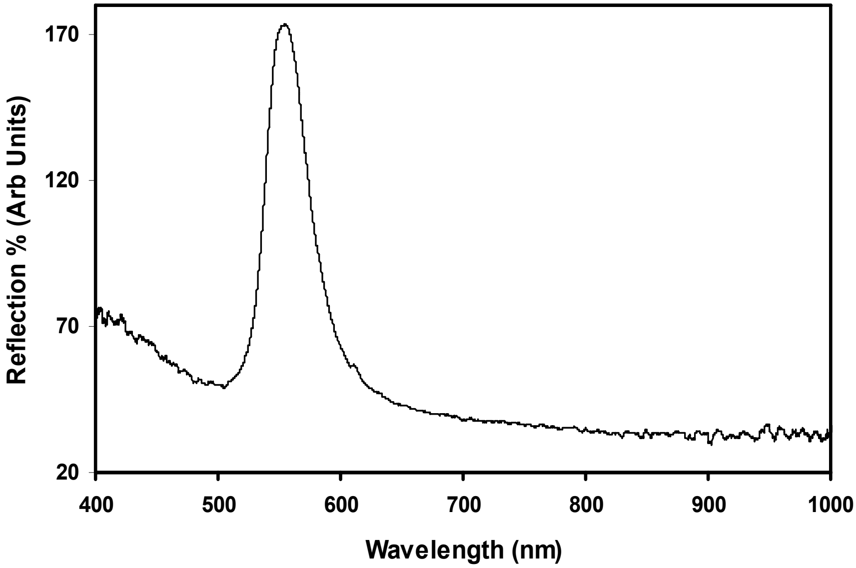


Figure 2. Bragg reflection spectrum from Polystrene CCA's formed on a glass substrate

In situ reflectance spectroscopy was performed to characterize the self assembly process during drying as have been illustrated by Koh's group (20). These experiments were conducted by positioning the reflectance probe normal to the substrate on which colloid material was assembled. Figure 3(a) shows the spectra that were obtained after 6 minutes settling time and up to 20 minutes drying time. An initial diffraction peak is observed at 566.4 nm which blue-shifted to 486.5 nm after 20 minutes. The intensity of peak was sharply decreased over time. A near linear shift in the peak position was observed as the film approached as shown on Figure 3(b). The slope for shifts of peak position was determined to be 4.1 nm / min. The linear response of the reflectance maximum during the early drying phase implies that the particles are in a metastable state which interparticle distance of CCA is very close to the diameter of particles. The nearest-neighbor intersphere distance l was determined from wavelength maxima (λp) using equation $l = 0.460\,\lambda$p (21). A change in intersphere distance from 260.5 nm to 223.8 nm was calculated at the first drying phase. Figure 4(a) shows the spectra obtained from the metastable state at 25 minute to the completely dry which is stable and compact state of CCA at 70 minute. At 25 min, the peak was observed at 486.5 nm which blue-shifted to 432.3nm upon reaching the stable state (second drying phase). The peak shifts are exponentially dependent on time for the second drying phase as shown on Figure 4(b). In this final stage, the intersphere distance was further decreased to 198.9 nm which is smaller then the diameter of particle of polystyrene in solution. The two different behaviors observed during the drying process can be expressed with two different equation types as shown in figures 3b and 4b. This behavior can only be explained due to a complex physical phenomenon that occurs during the drying process. The reflection maximum initially has a close to linear behavior suggesting that the mono disperse colloidal particles will self assemble in solution into highly ordered, non-close-packed three dimensional array. With the gradual loss of water an almost linear shift to a higher energy state is preserved during the drying process. As soon as most of the solvent has evaporated and air begins to fill the interspaces a non-linear pattern develops. This pattern is further enhanced by the dehydration of the particles themselves and their consequent reduction in size.

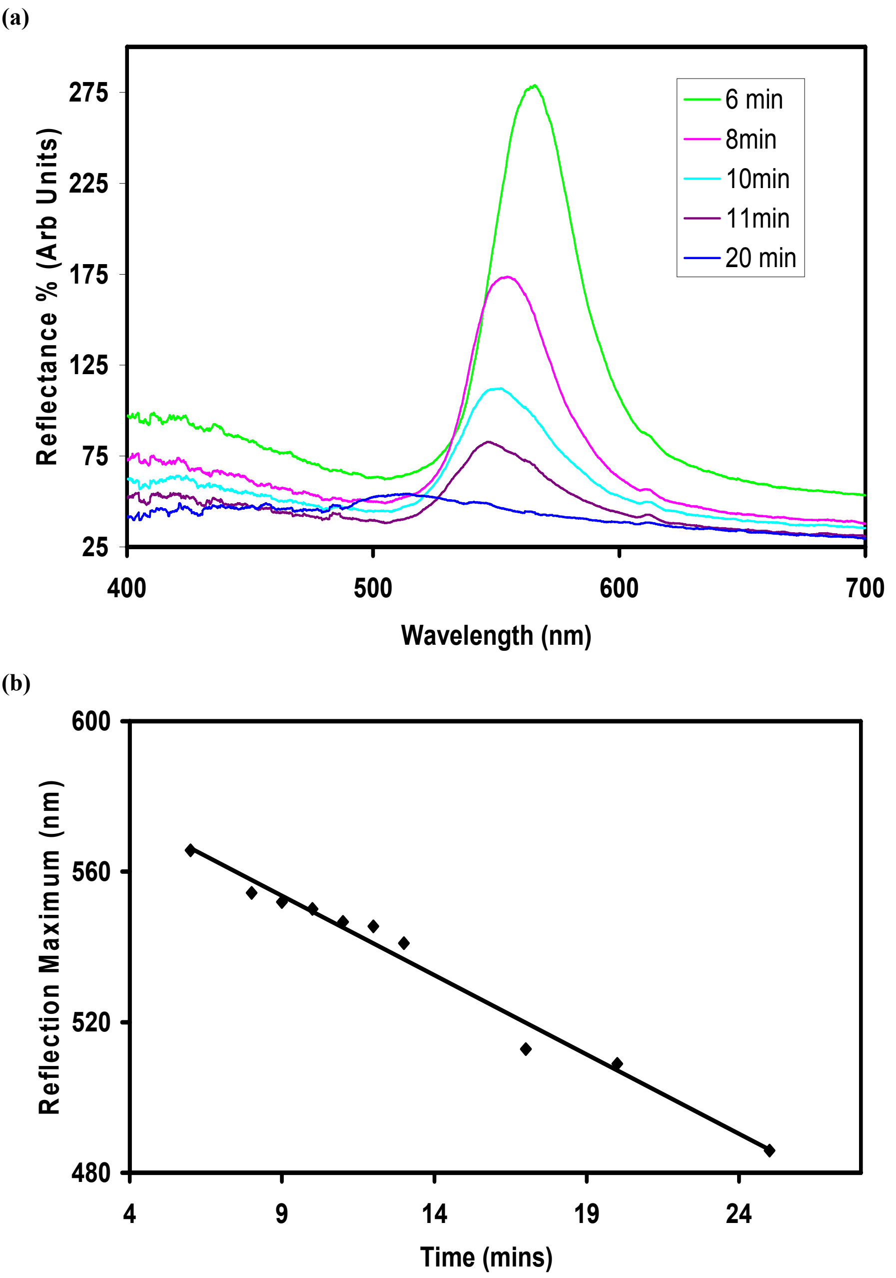
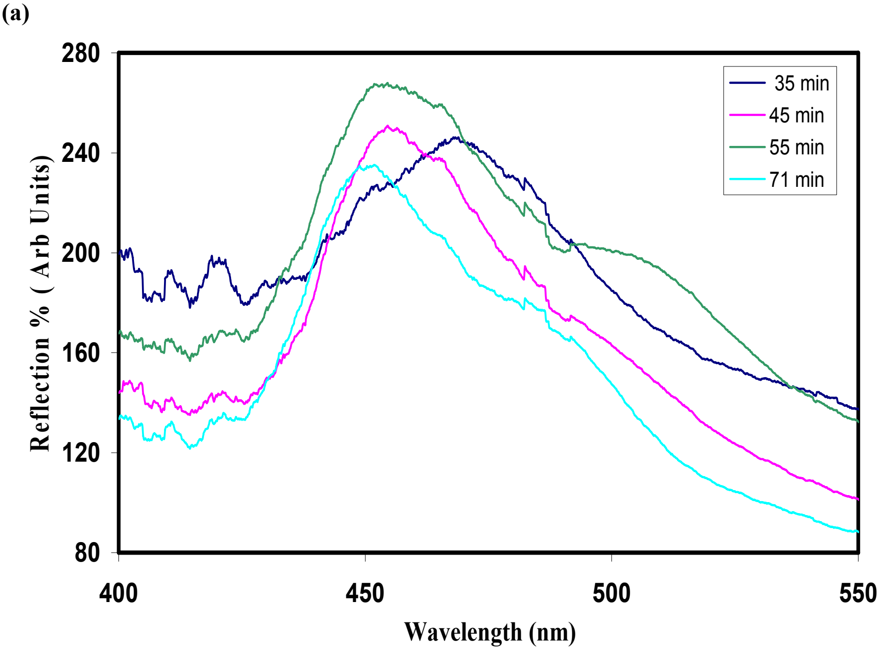


Figure 3. (a) The time resolved shifts of the primary Bragg reflection of CCA during the first stage of drying process and (b) The behavior of the reflection maximum of the first stage of drying process



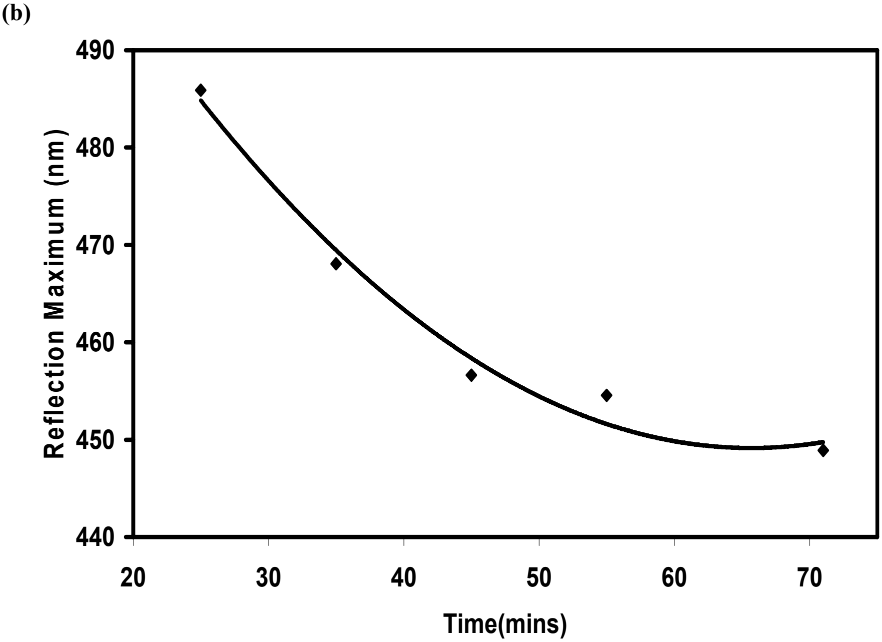


Figure 4. (a) The time resolved shifts of the primary Bragg reflection of CCA during the second stage of drying process and (b) The behavior of the reflection maximum of the second stage of drying process

The diffraction characteristics of these systems are most accurately predicted through the application of dynamic Bragg diffraction theory. The Bragg wavelength was predicted using a scalar wave approximation for periodic dielectric structures, which shows that it depends on the volume fraction of the material, its refractive index, and also the refractive index of air/solvent, which also governs the distance, d_{111}, between the planes of the face-centered cubic lattice.

At normal incidence on the film, the reflectance peak position is given by (22)

$$\lambda_{max} = 2\, d_{111} n_{eff} \qquad [1]$$

n_{eff} is the effective refractive index of the CCA formed. In a face centered cubic lattice,
$d_{111} = (2/3)^{1/2}$ D, where D is the particle diameter (210nm),

$$n_{eff} = [74\% \, (n_{ps})^2 + 26\% \, (n_{sol})^2]^{1/2} \qquad [2]$$

$n_{ps} = 1.59$ given by manufacturer and $n_{sol} = 1.33$ for water.

Bragg relation gives a reflection maximum value of $\lambda = 523.3$ nm for the wet CCA against an experimentally observed value of $\lambda_{wet} = 554.4$ nm as shown in Figure 1. When the CCA starts to dry owing to the evaporation of the solvent, the experimental peak position monotonically blue shifts to $\lambda_{dry} = 424.0$ nm at which time, the inter spacing between colloids becomes filled with air and therefore the refractive index $n_{sol} = 1$, hence the calculated value of the reflection maximum at this time becomes 500.5 nm. The free volume for hard spheres in a hexagonal close packed (HCP) or face centered cubic (FCC) crystal lattice (maximum packing volume fraction of 74%) is greater than that of disordered spheres (maximum packing volume = 64%), Y. Xia et al (23). The variation in the peak maximum between experimental and the calculated values is probably due to fact that the peak positions in the spectra depend on the angle between normal vector of the substrate and the detecting light which is found to shift to shorter wavelength with increasing detection angles as are given by a modified Bragg formula (18). The relationship between reflection spectra and the detecting angle were obtained continuously and hence as the film starts to dry the angle of incidence of the light can vary. The reflection spectra have been obtained non stop and hence no adjustments could be made to collimate the light into the fiber probe and hence the time resolved peak appears weaker in reflection intensity. The relation for calculation of reflection maximum given by this study (17) is

$$\lambda_{max} = (8/3)^{1/2} D \, [\, (n_{ps})^2 \; V_{ps} + (n_{void})^2 \, V_{void} - \sin^2\theta \,]^{1/2} \qquad [3]$$

where V_{ps} is the volume fraction of the polystyrene and n_{void} and V_{void} are the refractive index and volume fraction of the void spaces. The variation in peak position against the illuminating angle has also been recently explained by Burkert, K.et al (24) by yet another similar relation to the above equation 3.

Conclusions

We demonstrated a drop slide method for the fabrication of high quality colloidal crystal arrays. The Bragg reflection maximum is obtained in real time as the CCA is being formed and until it became stable state. The effect of the evaporation of the solvent on the reflection maximum was observed and a detail analysis states that the CCA transforms a stable FCC structure. The two different equations were obtained for the drying processes. The formation of the CCA is instantaneous and is highly favorable for higher volume fraction of the material. The prepared colloidal arrays form the basis for further developments towards a potential chemical sensor from determining surface charge effects. As a bio-sensor ie protein array sensor where the changes in the mean refractive index of the CCA upon binding ligands from solution to proteins immobilized in the interstitial sites could be used to realize detection of the protein ligand interactions (25).

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