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Self-assembly of silica colloidal crystal thin films with tuneable structural colours over a wide visible spectrum

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ABSTRACT

Colloidal crystal (CC) thin films that produce structural colours over a wide visible spectrum have been self-assembled from silica nanoparticles (SNPs) using a natural sedimentation method. A series of colloidal suspensions containing uniform SNPs (207–350 nm) were prepared using the Stöber method. The prepared silica suspensions were directly subjected to natural sedimentation at an elevated temperature. The SNPs were deposited under the force of gravity and self-assembled into an ordered array. The solid CC thin films produced structural colours over a wide visible spectrum from red to violet. Visual inspection and colorimetric measurements indicated that the structural colour of the CC thin film is tuneable by varying the SNPs diameters and the viewing angles. The closely packed face-centred cubic (fcc) structure of the CC thin film was confirmed using SEM imaging and was in agreement with the intense colour observed from the film surface.

1. Introduction

As a periodic three-dimensional nanostructure system, the photonic crystal (PC) has the ability to control photon propagation [1]. This property can be used for many potential applications such as: optical switching, colour displays, biological sensors, energy storage, and solar cells [2,3]. Such a system is also known as the colloidal crystal (CC) or photonic colloidal crystal (CPC) if its periodic nanomaterial is assembled from colloidal spheres such as silica or polystyrene (PS) [4].

Natural precious opals, which consist of highly ordered silica nanoparticles (SNPs), are probably the oldest and best-known examples of CCs [5]. One of the most important and interesting properties of natural opals is the tuneable structural colour effect. This provides a novel way of producing colours without colourants [6] and has practical applications such as structurally coloured films [7–9], effect pigments [10], photonic papers and inks [11], opal fibres and fabrics [12–14].

Artificial opal CC materials have been extensively studied and fabricated using self-assembly methods: such as sedimentation [15], vertical deposition [16], physical confinement [17], spin coating [18], and most recently the dip-drawing method [19]. Current research has focused on PS-based colloids [20–23] due to the facile control of the polymer colloids size through soap-free emulsion polymerisation. This technique allows specific colours in the visible range to be produced by the self-assembly of a target polymer sphere. However, little published work shows silica CC films with structural colours that cover a wide range of the visible spectrum [16,24]. Natural opals have SNPs generally in the size range of 150–400 nm and produce a range of structural colours [25]. Due to difficulties in controlling the Stöber process, which consists of the hydrolysis and condensation of silicon alkoxide, fabricating uniform populations of SNPs in this size range has been challenging. Moreover, if the prepared colloids are not uniform in size, then additional purification processes using selection [26] or redispersion procedures [27] are required in order to improve the uniformity of the colloids.

In this paper, structurally coloured silica CC films were obtained by the gravity sedimentation self-assembly of SNPs through the drying of the prepared colloidal suspension. As the prepared SNPs in the suspensions were uniform, the suspension was used without any purification and/or modification. In addition, by only controlling the amount of solvent ethanol in the Stöber process, the diameter of the SNPs could be varied in the range of 200–350 nm. This allowed a wide range of structural colours to be produced by the CC films. The morphology of SNPs and the CC films is investigated using a SEM technique. The tuneable behaviour of structurally coloured CC films is discussed.

2. Experimental

2.1. Materials

The chemical reagents used throughout the experiments included the following. Tetraethyl orthosilicate (TEOS) (99.0%) was purchased from Sigma-Aldrich Co., LLC; ammonia (NH_3, 25% in H_2O) and ethanol (EtOH, 99.9%) were

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obtained from Fisher Scientific Co., Ltd., UK; distilled water (H2O, distilled by USF-ELGA water purifier) was dispensed from the laboratory. All the materials were used as received without any further purification.

2.2. Synthesis of silica nanoparticles

Uniform SNPs of diameter ranging from 207 nm to 350 nm were synthesized based on the Stöber method [28]. Firstly, a mother solution containing ammonia (8 ml), ethanol (47 - 73 ml), and distilled water (6 ml) was prepared in a 250 ml round-bottomed flask under vigorous stirring. When the temperature of the mixture reached 60 °C, the TEOS (6 ml) was then added into the solution. The solution was stirred under an inert atmosphere for 2 hours until the reaction completed.

2.3. Preparation of CC films by self-assembly of SNPs

Silica CC thin films were self-assembled from SNPs through natural gravity sedimentation. Specifically, the prepared silica suspension, without any purification and/or modification, was allowed to settle on a petri dish through sedimentation by gravity. The drying of suspensions at 60 °C accelerated the particles self-assembly rate and resulted in solid silica CC thin films exhibiting structural colours in approximately 10 minutes.

2.4. Characterisation of SNPs and CC films

The morphology of the prepared SNPs and CC films were recorded using a Hitachi S-3000N scanning electron microscope (SEM). The SNPs diameter and polydispersity were measured using a Malvern Zetasizer Nano S dynamic light scattering (DLS) device. Images of the structural colours were captured using a digital camera (iPhone 5s). The chromaticity coordinates of the film samples were obtained using a Konica-Minolta CS-200 Chromameter.

3. Results and discussion

3.1. SEM analysis of SNPs and CC thin film

Typical SEM images of silica nanoparticles (SNPs) with a mean diameter of 350 nm are given in Figure 1. (a) shows the isolated SNPs that were prepared using the modified Stöber method. It can be seen that the SNPs are spherical in shape and uniform in size (polydispersity index (PDI) = 0.1). Using the natural gravity sedimentation method, the SNPs were self-assembled into a CC thin film with a close-packed face-centred cubic (fcc) structure, which can be seen in Figure 1(b) and 1(c).

Figure 1(b) shows the top view of the CC film, where the hexagonal close-packed arrangement of SNPs represents the (1 1 1) plane of the fcc structure [16] and [29]. The square arrangement of SNPs on the side view represents the (1 0 0) plane of the fcc structure, which can be seen in Figure 1(c). Due to the uniform and ordered arrangement of SNPs, a particular structural colour can be observed from the surface of the CC thin film.

3.2. Structural colours tuned by particle diameter

Figure 2 shows the top view SEM images and relevant images of different coloured CC thin films. The uniform SNPs in Figure 2(a)-(e) having mean diameters of 350 nm, 282 nm, 270 nm, 249 nm, and 207 nm resulted in the CC films as shown in Figure 2(f)-(j) with variable structural colours of red, yellow-green, green, cyan, and violet at normal incidence, respectively.

It is known that silica powder is white in colour, and its suspension solution is opalescent due to scattering. However, the silica CC films show a range of vivid structural colours, which is due to the Bragg diffraction of the ordered fcc structure. The structural colour of CC films can be expressed by applying a modified Bragg's equation [30]:

$$\lambda = 2d_{(111)}d(n_{eff}^2 - \sin^2 \theta)^{1/2}, \quad (1)$$

where λ is the wavelength of the reflectance peak of the coloured CC film, d is the interplanar spacing between (1 1 1) planes, n_{eff} is the effective refractive index (RI) of the CC material, and θ is the angle between the normal and the incident light (the viewing angle).

For an opal with an fcc structure, the relationship between the (111) plane and sphere radius r or diameter d is given as:

$$d_{(111)} = 1.633r = 0.8165d, \quad (2)$$

In addition, the effective RI of the opal can be expressed using the following equation [30]:

$$n_{eff} = n_s V_s + n_a(1 - V_s), \quad (3)$$

where n_s and n_a refers to the RI of the silica sphere and the air, which is approximately 1.45 and 1, respectively; V_s is the volume fraction of the silica sphere. Taking 0.7405 as the volume fraction of the silica sphere in an fcc structure [30], the effective RI can be calculated as 1.333.

Therefore, the modified Bragg's equation is then rewritten as:

$$\lambda = 1.633d(1.333^2 - \sin^2 \vartheta)^{1/2} \quad (4)$$

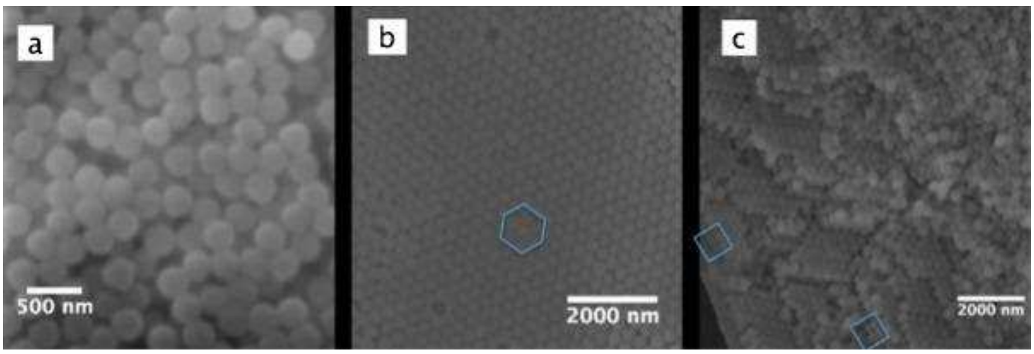

Fig. 1. SEM images of SNPs (a) and related CC films in top view (b) and side view (c).

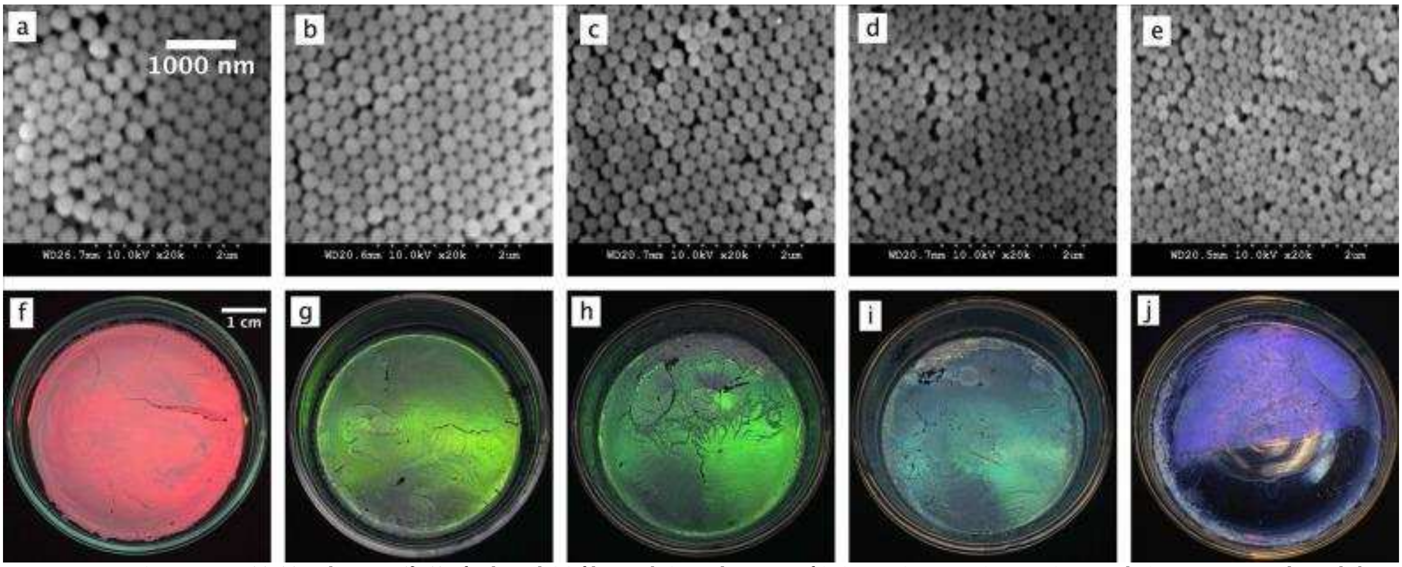

Fig. 2. Top view SEM images (a)-(e) and images (f)-(j) of coloured CC films with SNPs diameters of 350 nm, 282 nm, 270 nm, 249 nm, and 207 nm, respectively; scale bars are displayed in the first image of each set.

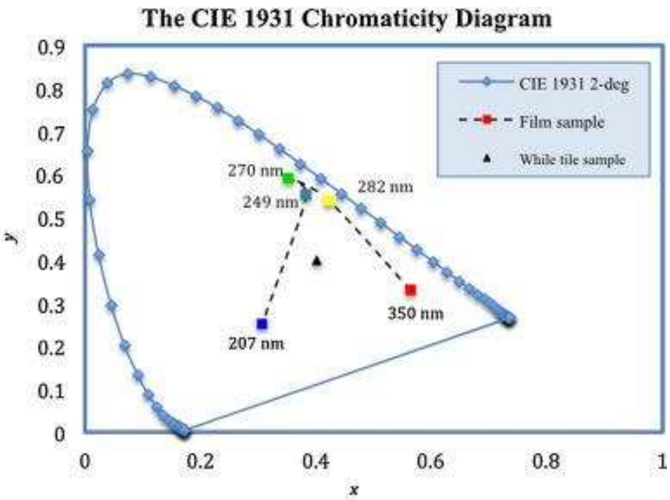

Fig. 3. CIE 1931 chromaticity coordinates of CC films with different SNP diameters measured at normal incidence.

At normal incidence, the longest wavelength λ_{max} will occur when:

$$\lambda_{max} = 1.633 d n_{eff} \approx 2.177 d \quad (5)$$

According to equation (5), it is clear that the wavelength of peak reflectance of the CC film λ has a positive correlation with the particle diameter d. Specifically, for the five coloured films (Figure 2) that have SNP diameters of 350 nm, 282 nm, 270nm, 249 nm, and 207 nm, their peak wavelengths were calculated as 762 nm, 614 nm, 588 nm, 542 nm, and 451 nm, respectively. The results are in agreement with the observed colour appearance of the CC films. The structural colours produced by the CC films in Figure 2 are tuned from red to violet with a systematically decreasing SNP diameter.

The chromaticity coordinates of the coloured CC films were plotted in a CIE 1931 chromaticity diagram as shown in Figure 3. The x and y CIE chromaticity coordinates of the film samples are connected with dashed lines and are located very close to the spectrum locus. This indicates that the film samples have produced intense structural colours and this is in agreement with the visual inspection.

3.3 Structural colours tuned by viewing angle

In addition to the particle size factor, the effect of viewing angle on the structural colours of the CC film was also investigated. In Figure 4, the CC film taken from Figure 2(f) shows different structural colours of red, yellow-green, green, and white at viewing angles of 0°, 30°, 45°, and 90°, respectively. At the 0° viewing angle, the normal incident, the increased to 30°, different structural colours were clearly observed as shown in Figure 4(b), where the CC film shows silica CC film exhibits an intense and uniform structural colour of red, as seen in Figure 4(a). When the viewing angle is polychromatic structural colours including red, orange, and green. With a further increase of the viewing angle to 45°, the structural colour of the CC film appeared uniform green, as seen in Figure 4(c).

The phenomenon of colour change with viewing angle is known as the play-of-colour [5], and it can be explained using the modified Bragg's equation. Specifically, based on the sphere diameter of 350 nm, the peak wavelength λ at different viewing angles (θ) can be calculated using equation (4), where the peak wavelength λ is calculated as 762 nm, 706 nm, 646 nm, and 504 nm, at viewing angles of 0°, 30°, 45°, and 90°, respectively. It can be seen that as the viewing angle increases, the wavelength of the reflectance peak λ will decrease, contributing to a blue shift of the structural colour. This explains the phenomenon observed in Figure 4(a)-(c), where the structural colour of the CC film gradually changed from red to green with the increase of viewing angle.

However, at a certain viewing angle (approaching 90°), total internal reflection will prevent the light source escaping from the material's surface [30], resulting in the extinction of the structural colour. This is confirmed in Figure 4(d) where at a viewing angle of 90°, the CC film exhibits a white surface colour similar to that seen in normal silica powder.

The effect of colour change with viewing angle can be represented by plotting the chromaticity coordinates of the red sample measured at several angles in the CIE 1931 chromaticity diagram, which is given in Figure 5. The colour of the marker corresponds to the observed colour of the CC film (Figure 4) and the circular marker represent the white tile sample for comparison. It can observed from the marker location that the colour shifts from the red to green region when

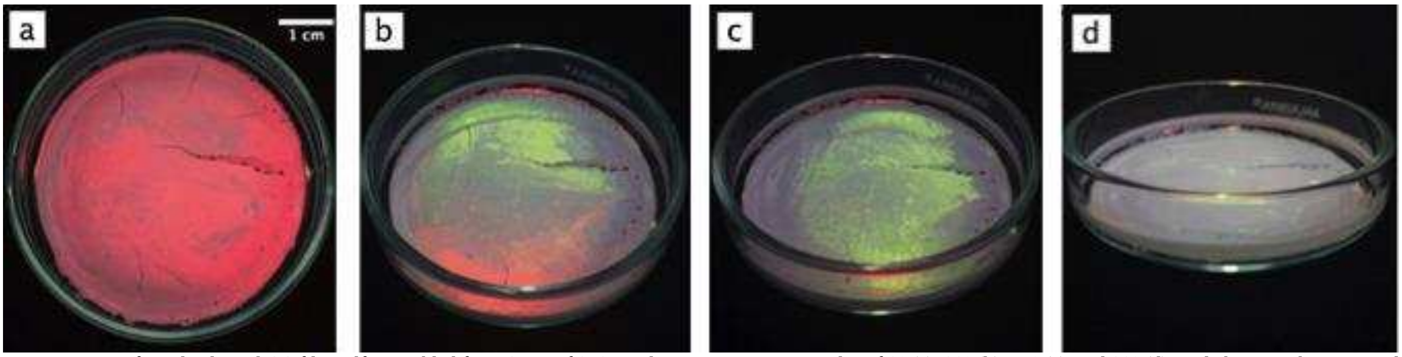

Fig. 4. Images of a red coloured CC film self-assembled from SNPs of 350 nm diameter at viewing angles of 0° (a), 30° (b), 45° (c), and 90° (d); scale bars are the same and displayed in (a).

the viewing angle is changed from 0° to 45° and this is in agreement with the visual observation, Figure 4(a)-(c).

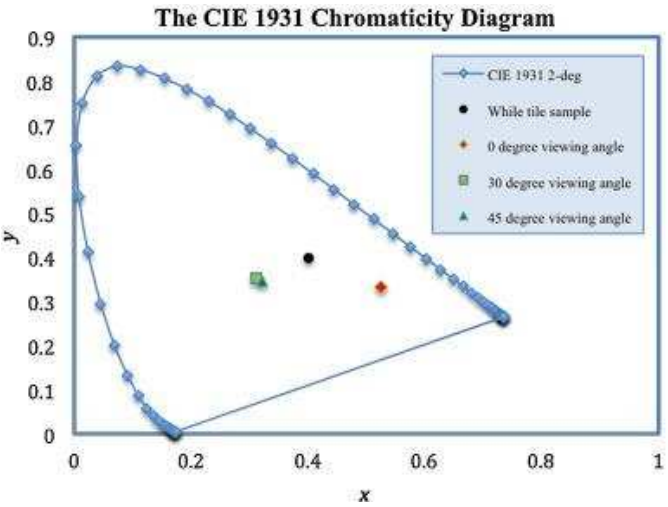

Fig. 5. CIE 1931 chromaticity coordinates of the film (Figure 4(a)) at three different viewing angles of 0°, 30°, and 45°.

4. Conclusions

CC thin films exhibiting structural colours covering a wide range of the visible spectrum have been fabricated from SNPs using a simplified sedimentation self-assembly method. The close-packed fcc structure and intense structural colour validate the method. The structural colour of CC films can be tuned by varying the particle diameter between 207 nm to 350 nm as well as by changing the viewing angle. The tuneable structural colour property of CC film is promising for fabricating photonic materials in colour- or light-related applications.

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