Structural colours controlled by mixing two sized silica nanoparticles

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Abstract. Structural colour has attracted much attention because of its features of never fading, high saturation, high brightness, green environmental protection, the application of structurally coloured photonic crystal (PC) materials as pigments and coatings is becoming more and more mature. In this work, silica nanoparticles (SNPs) with two particle diameters were prepared by using Stöber method, PC films were fabricated by mixing two sized SNPs with different mixing ratios, the result showed that the structural colours of the photonic films had a blueshift when the ratio of the smaller sized SNPs increased, i.e. the structural colours changed from red to orange, yellow, yellow-green and green for the five selected increased ratios. In addition, PC films with uniform SNPs give iridescent structural colours, while those with mixed SNPs give non-iridescent structural colours. The method of producing different structural colours from two sized SNPs is simple and fast, and it can be applied to the development of a wide range of colourful photonic pigments.

1. Introduction
There are two main sources of colour in nature: pigmentary colour and structural colour. Unlike pigmentary colour, structural colour is produced by interference, diffraction and scattering of light. Many colours in nature belong to structural colour, for example, peacock, butterfly, dragonfly, and opal [1-3]. Structural colour can be divided into two groups depending on relationship between colour and viewing angle: iridescent and non-iridescent. The former type of colour is dependent on the viewing angle (angle-dependent), while the latter is independent on the viewing angle (angle-independent) [4,5].

Photonic crystal (PC) is a kind of dielectric material with periodically changing refractive index. The periodic change in refractive index produces a photonic band gap, which controls the propagation of light in PC, producing angle-dependent structural colours. Amorphous photonic crystal (APC) is a special type of PC with defects, it can produce the structural colour which is not affected by the viewing angle, i.e. the angle-independent structural colour. The widely used technique to prepare photonic pigments is through the self-assembly of colloidal particles [6]. Liu et al. made photonic crystal inks from poly (styrene-methacrylic acid) microspheres with different sizes and prepared photonic crystal structural colours on the fabric surface by ink-jet printing [7]. Li et al. used atomization deposition of silica nanoparticles (SNPs) to prepare non-iridescent APC coatings, also, the colours are changeable by using different sized silica colloidal particles [8]. By vertical deposition, Liu et al. used polystyrene microspheres with various sizes were used to fabricate different colours of photonic crystals on cotton fabrics, photonic crystals after the vertical deposition, the resultant cotton fabrics presented bright structural colours and strong hydrophobicity, achieved the coloration and hydrophobicity of cotton fabrics by one-step processing [9]. There are more and more studies on making different PC structural...
colours by using colloidal particles with different particle sizes, but few studies have been conducted on the preparation of colours by mixing two sized SNPs with different mixing ratios.

In this paper, a range of PC films with low angle-independent structural colours were fabricated by gravity sedimentation self-assembly of SNPs mixed with two different diameters. The factors that affect the structural colour of the prepared silica films, such as SNPs diameter, mixing ratio of two sizes and viewing angle were studied. The optical properties of spectrum reflectance and angle dependence were analysed.

2. Experimental

2.1. Materials
Tetraethyl orthosilicate (TEOS) (>99%) was purchased from Shanghai Macklin Biochemical Co., Ltd.; Ammonia (NH₃, 25% in H₂O) was obtained from Merck KGaA; Ethanol (EtOH) (99.9%) was supplied by Yonghua Chemical Technology (Jiangsu) Co., Ltd.; Distilled water was bought from Guangzhou Watson’s Food & Beverage Co., Ltd.. All the chemical materials were used as received without any further purification.

2.2. Synthesis of silica colloids
Uniform silica colloids were synthesized using Stöber method [10], and Gao found other reaction conditions remained unchanged, homogeneous and controllable SNPs could be obtained by simply changing the volume of EtOH [11], we adopted this solvent control method. Typically, a mixed solution containing certain EtOH, ammonia and distilled water was prepared in a 250 ml round-bottom flask under vigorous stirring, when the temperature of the solution reached the set temperature, the TEOS was added quickly, the solution was stirred for 2 h until the reaction completed, during the experiment, the only variable was the volume of EtOH. The obtained two silica colloids were respectively centrifuged and washed, and then dispersed into ethanol for different concentrations.

2.3. Self-assembly of silica colloids into PC and APC films
The prepared silica colloids was transferred to a petri dish for gravity sedimentation, placing the petri dish in the drying oven at 40 ºC to accelerated the particles self-assembly rate and resulted in solid silica PC films exhibiting structural colours. Silica colloids with two sizes were mixed in different ratios, and the APC films were produced according to the above method.

2.4. Characterisation of SNPs, PC and APC films
The SNPs diameter and dispersity were determined using a Malvern Zetasizer Nano S dynamic light scattering (DLS) device. The morphology of the PC and APC films were examined using a TESCAN-CEGA3 scanning electron microscope (SEM). Images of the structural coloured films were captured using a Sony Alpha 7 III digital camera. Reflection spectra of the film samples were measured using a X-Rite Ci-60 spectrophotometer.

3. Results and Discussion

3.1. The effect of silica size on the structural colour
Stöber method is a simple method to prepare uniform SNPs by using ammonia as catalyst and TEOS as silicon source. In this study, the temperature was controlled at 30 ºC, the volume of EtOH was inversely proportional to silica diameter, and the prepared SNPs were uniform.

To confirm the arrangement of the particles, we observed the microstructure of the films composed of SNPs using SEM. SEM images of the PC films are shown in Figure 1, silica particles had uniform size and smooth surface, the structure of PC presented an ordered hexagonal arrangement.

When light propagates, it is influenced by Bragg diffraction, which leads to create band structure, band gaps between the bands prevent light from entering the PC and thus produce colour. The SNPs
with 330 nm and 255 nm were deposited into the petri dish for gravity sedimentation, and the structural colours of PC films were obtained, as shown in Figure 2a and 2e. It can be seen from the two images that with the decrease of silica diameter, the structural colour changed from red to green, this’s blueshift, which conformed to the Bragg equation (1) [12]. In the equation, other variables remain the same, $\theta$ is inversely proportional to $\lambda$ and $\lambda$ corresponds to the structural colour.

$$m\lambda = 2d(n_s^2 - \sin^2\theta)^{1/2}$$

where $m$ is the order of the diffracted beam, $\lambda$ is the wavelength of the reflectance peak of the PC film, $d$ is the separation of the planes of atoms, $n_s$ is the refractive index of the PC, and $\theta$ is the angle between the normal and the incident light (the viewing angle).

![Figure 1. SEM images of SNPs with 330 nm (a), 255nm (b).](image)

3.2 The effect of mixing ratio on structural colour
Two silica colloids were mixed in different ratios, respectively, 330/255= 10:0, 7:3, 5:5, 3:7, 0:10, and the mixed colloids proceeded gravity sedimentation at 40 ºC to form the structural colours. The photos of its films were shown in Figure 2a-e, colours were respectively, red, orange, yellow, yellow-green, green. In the reflectance spectrum, the wave crest of the reflection spectrum became decreased after mixing, the five wave crest basically changed linearly, and the mixing of two particle sizes increased the peak width (see the inset in Figure 2f and Figure 2g). With the increase of wt% SNPs with 255 nm, the average particle size after mixing decreased (show in Figure 2h), the corresponding structural colours appeared blueshift, this means that the average particle size affects the structural colour. It can be inferred that a series of structural colours can be obtained by changing the mixing ratio of two SNPs with different sizes.

![Figure 2. Reflectance spectra and graph of structural colours.](image)
Figure 2. (a-e) Photos of films with different mixing ratios of 330 nm and 255 nm SNPs in vertical angle, respectively, 330/255=10:0, 7:3, 5:5, 3:7, 0:10. (f) Reflection spectra of films with different ratios of 330 nm and 255 nm SNPs in vertical angle. (g) Plots showing the position of the crest wavelength in the reflection spectra (c) versus wt% for 330 nm SNPs. (h) Plots showing the average particle sizes versus wt% for 255 nm SNPs.

3.3. The effect of viewing angle on the structural colour
In addition to particle size and mixing ratio, the effect of viewing angle on the structural colour was also studied. Figure 3a shows that PC structural colour was prepared using SNPs of 255 nm size, structural colour from green to white depending on the viewing angles changed from 0º to 90º. This phenomenon indicated that the PC structural colour changed with the viewing angles, and this could be explained with Bragg equation.

The mixed SNPs with two sizes reduced the surface order of PC and took shape APC, but the face-centered cubic structure still appeared in the short range, as shown in Figure 3b. Compared with the long-range ordered arrangement of PC, APC presents a long-range disordered and short-range ordered arrangement, this results in an isotropic defect structure, which reduces the angle dependence of the APC. In Figure 3c, APC with three mixing ratios, respectively, 330/255=7:3, 5:5, 3:7, the colours of APC respectively were orange, yellow, yellow-green at an viewing angle of 0º, and the structural colours remained the same when the angle was 10º, but the dispersion of mixed SNPs were too high, APC appeared white when viewing angle exceeded 10º, in addition, compared with PC structural colour, the APC structural colour is dimmer.
Figure 3. (a) The images of PC film with SNPs of 255 nm size at different viewing angles. (b) SEM images of mixed SNPs 330/255=7:3. (c) The images of APC films with three mixing ratios at two viewing angles, respectively, 330/255=7:3, 5:5, 3:7, and viewing angle was 0°, 10° and 20°.

4. Conclusions
SNPs were prepared by Stöber method, and structural colours were prepared by gravity sedimentation self-assembly. A series of APC structural colours can be obtained by changing the mixing ratio of two sized SNPs, and theses colours have low angle-dependence, while PC films with uniform SNPs can produce structural colour are dependent on viewing angle. The method is simple and effective, and can be used for the preparation of a variety of non-iridescent colours, adding it has the characteristics of non-fading and green environmental protection, it can be widely used in the field of pigments and coatings.

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