Photonic pigments from white particles and black ink

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Abstract. In this paper, white silica nanoparticles with a diameter of 346 nm were prepared using the Stöber method. Mixed with different concentrations of black ink, the silica nanoparticles were self-assembled into structurally coloured photonic crystal films by gravity sedimentation at different temperature. The effects of temperature, the concentration of black ink and the viewing angle on the structural colour were investigated. The result showed structural colours can be produced by mixing white silica particles and commercial black ink, and this provided a novel strategy to make non-iridescent photonic pigments.

1. Introduction

Structural colour, which can be divided into two parts as the iridescent colour and non-iridescent colour [1]. Iridescent photonic crystal (PC) has great limitations when it comes to some fields that need to be angle-independent, such as printing pigments and chemical dyes. The internal structure of non-iridescent PC is not arranged periodically, and the photonic band gap is incomplete, so the material is given a soft and bright colour rendering effect that does not change with angle [2]. Non-iridescent PC has the characteristics of colour stability, non-fading, and environmental protection. Researchers started to apply it to textile printing and dyeing [3], which is a highly polluting industry, with a view to reduce sewage discharge and a lot of energy consumption.

Currently, the preparation methods of non-iridescent PC can be classified as plate etching, colloidal particle self-assembly, template method and phase separation [4]. The preparation methods of non-iridescent PC are continuously optimized. Xiao et al. [5] used polydopamine (PDA) to synthesize melanin nanoparticles. Similar to natural melanin, the nanoparticles have a high refractive index and wide light absorption, and can be used to make coloured films. Ara et al. [6] applied photonic-crystal-based nanocoatings to wood surface for an aesthetic appeal. Iwata M et al. [7] used black polystyrene to reduce the background brightness and appropriately control the thickness of the array to increase the saturation of structural colours, and realized the preparation of amorphous photonic crystal (APC) with low angle dependence. Katagiri et al. [8] fabricated tunable iridescent coloured film with silica, PDA and carbon black as the main materials, this method increased the mechanical wear resistance of the film.

In order to improve colour saturation of the structural colour, researchers often introduce carbon black into the colloidal system. However, the application of commercial ink as a reagent to prepare non-iridescent PC has been not found yet. This paper introduces a method for preparing non-iridescent PC by self-assembly of colloidal particles. Firstly, silica nanoparticles (SNPs) solution with good dispersion was prepared by Stöber method. Then adding a certain mass fraction of ink to the silica suspension, the structural colours saturation of the PC films was improved.
2. Experimental

2.1. Materials
TEOS (> 99%) (superior pure, Shanghai Macklin Biochemical Technology Co., Ltd., ammonia water (25%) (Merck Co., Ltd.), anhydrous ethanol (≥ 99.9%) (chromatography pure, Yonghua Chemical Technology (Jiangsu) Co., Ltd.), distilled water (280 ml / bottle, Watsons), M&G cartridge black ink bag (190mg / ml), (M&G Chenguang Stationery Co., Ltd.).

2.2. Synthesis of silica particles
In this experiment, TEOS was used as a precursor, ethanol as solvent, ammonia as catalyst, distilled water as hydrolysis agent [9]. Uniform SNPs were prepared by hydrolysis and polymerization of TEOS. Firstly, 8 ml of ammonia, 3 ml of distilled water and 90 ml of ethanol were added to a 250 ml round-bottom flask, this device was placed in a water bath, and then stirred and mixed with a magnetic stirrer. When the temperature of the mixture solution reached 30℃ and remained constant, 6 ml TEOS was rapidly added to the solution. After 2 hours of reaction, uniform SNPs were finally synthesized.

2.3. Preparation of non-iridescent PC films
The prepared silica solution was doped with ink of a certain mass fraction and dispersed for half an hour using a vortex oscillator (VORTEX-BE1). The SNPs suspension mixed with ink was uniformly settled on the cover glass by gravity sedimentation, PC films were obtained at a certain temperature.

2.4. Characterization
Hitachi S-4800 scanning electron microscopy (SEM) was used to observe the morphology of SNPs and structurally coloured films. The particle size and distribution of silica were measured by Malvern Zetasizer Nano S dynamic light scattering (DLS) device. Images of the coloured samples were taken with Sony Alpha 7 III digital camera. The optical property of the film samples was analyzed by using a NH300 colorimeter.

3. Results and Discussion

3.1. Morphology of SNPs and PC films
Figure 1 shows the SEM images of PC films prepared from bare SNPs (Figure 1a) and those mixed with black ink particles (Figure 1b). It can be seen from Figure 1a that bare silica particles are uniform in size, round in shape, well dispersed and regularly arranged, the particle diameter of the bare silica was measure as 346 nm and PDI was 0.116. However, in Figure 1b, the black ink particles are dispersed in larger silica particles, the adding of black ink particles disturbed its original periodic arrangement as shown in Figure 1a, resulting in a short-range ordered but a long-range disordered crystal structure, this amorphous structure gives non-iridescent structural colour effect. The effect of the self-assembly temperature and concentration of black ink on the colour will be discussed in the following sections.

Figure 1. SEM images of PC films composed of bare 346 nm sized SNPs (a) and those mixed with black ink (b).
3.2. The effect of temperature on structural colour
Figure 2 shows the pictures of PC films prepared using bare SNPs and those mixed with black ink at different temperatures. It can be seen that when black ink was added, the contrast of the films is enhanced and the coffee ring effect occurs. When the temperature was 40°C, the PC film is the most uniform, and the coffee ring effect has the least influence on the formation of the structurally coloured film. At the temperature of 20°C, the phenomenon of coffee ring was obvious and individual particles were found. When the high temperature of 60°C was used, more coffee rings were produced due to the accelerated self-assembly process, affected the uniformity of the film.

![Figure 2](image)

Figure 2. Photographs of films prepared using bare SNPs at temperature of 20°C (a), 40°C (b), 60°C (c); Photographs of films prepared using SNPs and mixed with black ink at temperature of 20°C (d), 40°C (e), 60°C (f).

3.3. The effect of concentration of black ink on structural colour
Figure 3 shows the photographs of PC films prepared from white silica particles mixed with different concentrations of black ink. When the concentration was increased, the saturation of the structural colour also increased, and the green colour with lower brightness can be obtained, the colour of the film became dimmer and dimmer. It can be concluded that the most uniform of the PC film was obtained when the black ink concentration was 0.07%.

![Figure 3](image)

Figure 3. Photographs of PC films prepared from white silica particles mixed with concentration of 0%, 0.03%, 0.05%, 0.07%, 0.1% black ink from left to right, respectively.

**Table 1.** L*, a*, b*, C*, h° values of PC films added with concentration of 0%, 0.03%, 0.05%, 0.07%, 0.1% commercial black ink (at 40°C).

| Black ink concentration | L*  | a*  | b*  | C*  | h°   |
|-------------------------|-----|-----|-----|-----|------|
| 0.00%                   | 28.50 | -0.92 | -1.44 | 1.71 | 237.38  |
| 0.03%                   | 21.68 | 0.53  | -1.24 | 1.50 | 238.83  |
| 0.05%                   | 22.15 | -1.07 | -1.48 | 1.84 | 237.47  |
| 0.07%                   | 20.23 | -0.52 | -0.97 | 1.96 | 237.95  |
| 0.10%                   | 19.45 | -1.25 | -3.29 | 3.32 | 238.34  |
Table 1 shows $L^*$, $a^*$, $b^*$, $C^*$, $h^\circ$ values of PC films added with concentration of 0%, 0.03%, 0.05%, 0.07% and 0.1% M&G black ink. The lightness, $L^*$, is represented on the z-axis in the colour space, the $a^*$ and $b^*$ values describe the degree of the colour in term of red ($+a^*$) to green ($-a^*$) and yellow ($+b^*$) to blue ($-b^*$), which are represented on the x-axis and y-axis, respectively. $C^*$ represents the chroma value and $h^\circ$ represents the hue angle of the coloured sample.

It can be seen from table 1 that as the black ink concentration increased, the $L^*$ value will decrease, which means the lightness became lower. The $C^*$ value gradually increased because the addition of carbon black can absorb visible light, eliminating incoherent light scattering, the saturation of the colours increased. The $h^\circ$ value basically remains unchanged, indicating the hue of the coloured film did not change. According to Bragg's law [9], the peak wavelength of the colour (hue) is mainly determined by the particle size, as long as the particle size remains the same, the hue value should not change.

3.4. The effect of viewing angle on structural colour
In this work, the addition of black ink produced non-iridescent PC films with short-range ordered and long-range disordered amorphous structure. It can be seen from Figure 4, the films were observed at different viewing angles of 0°, 30°and 60°, when the viewing angle increased, the bare silica PC films changed its colour from green to blue, while the PC films containing 0.07 % black ink did not change its colour at different viewing angles, which means the structural colour has a non-iridescent effect. In addition, it can be seen that the films are uniform and vivid in colour.

![Figure 4. Photographs of films prepared using bare SNPs at viewing angles of 0° (a), 30° (b), 60° (c); Photographs of films prepared using SNPs and mixed with black ink at viewing angles of 0° (d), 30° (e), 60° (f).](image)

4. Conclusions
Structurally coloured PC films was successfully self-assembled by gravity sedimentation from white silica particles and black ink materials. The adding of black ink absorbed incoherent light scattering within the film, producing films with enhanced color contrast and non-iridescent effect. The optimum conditions to produce a uniform non-iridescent PC films are the temperature of 40 °C and black ink concentration of 0.07 %. This kind of non-iridescent film can be used for photonic pigments, coatings, fashion, displays and other colour related applications.

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