Preparation and Modification of Inverse Opal Zirconia Pigment

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Abstract:
Inverse opal zirconia pigment prepared by traditional process has the disadvantages of low color saturation and variegated color which restrict its further application. In this work, the inverse opal zirconia pigment was prepared by colloidal crystal template fabricated using polystyrene microspheres with particle size of 340 ± 10 nm as raw material and further modified by sintering at 600 °C for 2 h with heating rate of 2 °C/min in an atmosphere tube of 0.8 L min⁻¹ nitrogen flow. The morphology, phase crystallinity and color performance of the inverse opal zirconia pigment before and after modification were characterized in detail and the modified mechanism was investigated. The results showed that morphology of the inverse opal zirconia pigment before modification was basically a highly ordered porous structure, the phase was relatively pure, and the overall appearance was variegated color. Some parts of the samples exhibited low color saturation and different areas showed various colors, indicating that the samples had certain angle dependence. After modification, the samples showed bigger-area single blue-green color, suggesting that the color saturation was significantly improved and the angle dependence was reduced evidently. The mechanism for modification was that the zirconia precursor and polystyrene templates were carbonized when sintered in nitrogen atmosphere. The generated in-situ carbon remained in the samples and absorbed the tray background light, which significantly suppressed the multiple scattering of structural defects.

Keywords: Zirconia; Pigment; Color saturation; Modified; In situ carbon.

1. Introduction

The inverse opal material has photonic band which incident light irradiate in is not reflection. There is structural color when the inverse opal material’s stop band is at 380-750 nm [1]. The structural color is also called physical color which is produced by purely physical process [2]. Structural colors have attracted wide attention from scholars at home and abroad because of their high brightness, iridescent effect and never fade [3-5]. However, certain unavoidable defects in the inverse opal material decrease the reflectivity of the photonic stop band and scatter the light outside the band, resulting in an opalescent appearance. Moreover, in the process of color rendering, people not only see the light wave of stop band position, but also background light [6, 7]. So, the inverse opal materials greatly restrict their further application in pigment due to the problem of weak color and low color saturation [8-10].

In previous studies, many strategies have been brought up to improve the color property of the opal materials. For example, Wang [11] obtained large-scale polymer crystal...
films with intense and tunable structural colors by doping carbon black into the system of colloidal silica. Aguirre [12] prepared opal material by mixing poly methyl methacrylate colloidal photonic crystals with carbon nanoparticles and finally obtained the pigment with a well-defined color and low angle dependence. Compared with opal materials, inverse opal materials show high mechanical stability and provide a selection of the materials, so it is more suitable for the development of structural color.

Polystyrene (PS) are widely used in the preparation of inverse opal materials due to the low preparation cost, mild processing condition method and has the advantage that raw materials can be easily obtained [13, 14]. Zirconia as an important strategic material with a large dielectric constant, good chemical and photo-chemical stability and high optical transparency holds considerable potential for realizing a wide photonic band gap and is an important material for constructing inverse opal materials [15, 16].

Building on advances that demonstrated the benefit of including carbon within the opal structure, in this study, we employed the samples sintered in nitrogen atmosphere with flow rate of 0.8 L min\(^{-1}\) to produce in situ carbon which could modify the inverse opal zirconia pigment and improve the color saturation, making it have a broader application prospect.

2. Materials and Experimental Procedures
2.1 Preparation and modification of the inverse opal zirconia pigment

Firstly, the PS colloidal crystal template was obtained by evaporation self-assembled method using the PS microspheres with particle size of 340 ± 10nm as raw material. Zirconia precursor solution was obtained by adding zirconia acetate to methanol in a 100 mL beaker and mixing at a molar ratio of 1:1. Then the precursor solution was stirred at room temperature with a magnetic stirrer for about 10 h. About 1g the PS colloidal crystal template was broken into pieces and placed on the filter paper in the Buchner funnel which was installed on the suction filtration flask. About 15g of the zirconia precursor was dripped onto the crystal template from one corner and permeated into the whole template to ensure that all the colloidal crystal templates pieces were wetted. Then, it was soaked, extracted for about 5 min, placed at room temperature for 24 h, and divided into two groups. One group of the samples named 1\# were sintered at 600 °C in air with a heating rate of 2 °C/min and held for 2 h to remove the PS templates.

Another group of the samples named 2\# were sintered at 600 °C in an atmosphere tube furnace with nitrogen flow rate of 0.8 L min\(^{-1}\) and heating rate of 2 °C/min to remove the PS templates and converted the filtrated zirconia precursor into the inverse opal zirconia. All the samples were kept warm for 2 h and cooled to room temperature.

2.2 Characterization

The morphology of the PS template and the inverse opal zirconia pigment were measured by scanning electron microscopy (SEM). SEM images were taken from an angle normal to the samples surface using a field emission scanning electron microscope (S-4800, Tokyo Japan). The particle size of the PS microspheres was evaluated by measuring the SEM photos of the PS microspheres with Smileview software and it was taken by the average of multiple pore measurements [16].

Moreover, the crystalline phases of the samples were examined with X-ray powder diffraction (D/max2200PC, Japan) using CuK\(_\alpha\) radiation (\(\lambda = 1.54056 \text{ Å}\)) in the range of 2\( \theta = 10\)-80° and a scanning rate of 5° min\(^{-1}\). Reflectance spectra of the samples in the visible range
were characterized by spectrometer (1050, Lambda). In addition, the color performance of the samples was characterized by a SLR camera (5D Mark III, Japan).

3. Results and Discussion

3.1 Morphology and phase analysis of the inverse opal zirconia

Fig. 1a shows SEM image of the PS microspheres. According to the measurement results of Smileview software, the particle size of the PS microspheres was about $340 \pm 10$ nm, which had obvious uniformity. It can be observed from Fig. 1a that the surface of the PS microspheres was smooth and the particle size was uniform, which was conducive to being used as PS template material in subsequent experiments. From the side view of the PS colloidal crystal template (Fig. 1b), it can be seen that the PS microspheres were highly ordered.

![Fig. 1. SEM images of (a) PS microspheres; (b) PS colloidal crystal template.](image)

SEM images of the sample 1# sintered in air (unmodified) showed uniform, interconnected and ordered porous structure, which was similar to the PS template (Fig. 2a). In the interior of the ordered macropores, much smaller pores with uniform size and orderly arrangement were also found, showing a "smiling face" shape as a whole. In addition, due to the volume shrinkage of the PS template and zirconia precursor during sintering, the average particle size of the sample 1# measured by Smileview software was about 294 nm, which was 9 % smaller than that of the original PS microspheres. Fig. 2b shows the effect of sintering at a flow rate of 0.8 L min$^{-1}$ in nitrogen atmosphere on the morphology of the sample 2# (modified). It was observed that the sample 2# still showed ordered porous structure. Compared with the sample 1# sintered in air, the periodic morphology of the sample 2# sintered in nitrogen atmosphere decreased slightly, and some deformation and deformation were observed. The average pore diameter of the sample 2# measured by Smileview software was about 288 nm (Fig. 2b), which was smaller than of the sample 1#.

The diffraction peaks of the unmodified sample 1# were consistent with the tetragonal structure of zirconia (JCPDS no. 50-1089) as shown in Fig. 2c. The high and sharp peak of the main phase indicated that the pure tetragonal zirconia phase was obtained. When the modified sample 2# was sintered in nitrogen, the diffraction intensity of the main peak decreased slightly, forming a new phase. The hexagonal phase Zr3O1-x (JCPDS no. 37-1484) appeared on (012) crystal face and the diffraction intensity of each crystal surface decreased. Since both zirconium acetate and polystyrene were easy to carbonize in nitrogen atmosphere, the carbon formed was trapped in the zirconia wall, which reduced the crystallinity of the modified zirconia.
Fig. 2. SEM images of the samples (a) sintered in air (1#); (b) sintered in nitrogen (2#); (c) XRD diffraction pattern of the samples 1# and 2#.

Fig. 3 represents the amount of elemental content of the sample 1# and 2# and EDS analysis are given in Table I. The contents of Zr, O and C in the sample 1# were 81.38 %, 16.27 % and 2.35 % respectively, while those in the sample 2# were 72.02 %, 14.01 % and 13.97 % respectively, which indicated that after sintered in nitrogen atmosphere, the atomic percentage of Zr and O decreased, while the content of C increased nearly 5 times as much as that sintered in air. It also showed that carbon was successfully prepared by nitrogen modified process.

Fig. 3. EDS spectrum of the samples (a) 1#; (b) 2#.
Tab. I Element content of the samples 1\(^\#\) and 2\(^\#\).

| Samples | Zr (wt\%) | O (wt\%) | C (wt\%) |
|---------|-----------|----------|----------|
| 1\(^\#\) | 81.38\%   | 16.27\%  | 2.35\%   |
| 2\(^\#\) | 72.02\%   | 14.01\%  | 13.97\%  |

3.2 Color performance of the inverse opal zirconia

Fig. 4 displays color performance and visible reflection spectra of the sample 1\(^\#\) and 2\(^\#\). The sample 1\(^\#\) showed weak green, blue, red and other mixed colors, and some areas were almost colorless (Fig. 4a), indicating that the overall color saturation of the sample 1\(^\#\) was low and angular dependent. After sintered in nitrogen, the sample 2\(^\#\) showed a large area of bright single blue-green (Fig. 4b), indicating that the color saturation and angle dependence of the sample 2\(^\#\) were significantly improved. The comparison of the reflection spectra of the sample 1\(^\#\) and 2\(^\#\) is shown in Fig 4c. When the sample 2\(^\#\) was sintered in nitrogen atmosphere, the position of band gap peak in reflection spectrum was different from that in air. According to Fig. 4c, after sintered in air, the band gap peak of the sample 1\(^\#\) was at 528 nm, while after sintered in nitrogen, the band gap peak of the sample 2\(^\#\) was at 468 nm, indicating a 60 nm blue shift.

![Image of color performance and spectra](image_url)

Fig. 4. Color performance of the samples (a) 1\(^\#\); (b) 2\(^\#\); (c) visible reflection spectrum of the samples 1\(^\#\) and 2\(^\#\).

3.3 Modification mechanism of the inverse opal zirconia

Before modification, when a bunch of natural light irradiates on the surface of the sample, the wavelength which in the stop band is not allowed to enter the sample to be reflected, and the light of the residual wavelength could enter the interior of the sample and the reflected light and the background reflected light of the final forbidden band part are
received by the human eye [17, 18]. Among them, the background light of stray light could reduce color performance of the sample, and the carbon produced could adjust the weakening degree of the background light, so as to adjust the proportion of the visible light component of human eye.

After modification in nitrogen atmosphere, carbon components were produced on the surface and inside of the sample 2⁹. When the incident light irradiated on the sample 2⁹, the carbon on the sample surface would absorb a small amount of light in the forbidden band, while the carbon in the sample would absorb a large amount of stray light. The influence of carbon leaded to the decrease of band gap intensity and background reflectance, which indicated that the carbon in the sample 2⁹ significantly inhibited the strong multiple scattering of structural defects, thus highlighting the reflection color of Bragg. Finally, the color saturation and angle dependence of the inverse opal zirconia pigment were improved significantly by sintering at a flow rate of 0.8 L min⁻¹ in nitrogen atmosphere.

4. Conclusion

A single blue-green inverse opal zirconia pigment was successfully prepared by sintering at 600 °C for 2 h in an atmosphere tube with nitrogen flow rate of 0.8 L min⁻¹ and heating rate of 2 °C/min. When sintered in nitrogen atmosphere, zirconia precursor and the PS template were carbonized to form in-situ carbon, which could significantly inhibit the strong multiple scattering of structural defects, significantly improve the color saturation and reduce the angle dependence of the inverse opal zirconia pigment.

It was also found the modified inverse opal zirconia pigment showed a large area of blue-green color, which indicated that sintering in an atmosphere tube with nitrogen flow rate of 0.8 L min⁻¹ was an effective way to solve the low color saturation, variegated color and to obtain single color of the inverse opal zirconia pigment. It is believed that the successful preparation of enhanced color saturation zirconia pigment makes it possible to apply structural pigment in anti-counterfeiting, display, sensing and the like.

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5. References

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позадинско светло, што значајно смањује расејање светлости у структурним дефектима.

Кључне речи: цирконијум, пигмент, сатурација боја, модификација, угљеник.

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