

Preparation of a Three-Dimensional Ordered Macroporous Titanium Dioxide Material with Polystyrene Colloid Crystal as a Template

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ABSTRACT: Polystyrene (PS) photonic colloid crystals were assembled from PS spheres prepared by emulsion-free polymerization through an improved vertical deposition method that could shorten the assembly time efficiently. The monodispersity of the spheres was appraised according to the standard deviation. The results showed that the PS spheres had a high monodispersity with a standard deviation of 3.7% and a dispersion coefficient of 0.02. The morphology and bandgap structure were observed with scanning electron microscopy images and transmission spectra, respectively. The mechanism of verti-

cal deposition was analyzed simply. As an application of PS colloid crystals, ordered macroporous TiO₂ photonic crystals were prepared, and the structure and properties of macroporous TiO₂ were also studied with various analytical methods, which provided some values for the fabrication of photonic crystals with a complete bandgap. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3903–3908, 2008

Key words: colloids; emulsion polymerization; polystyrene; self-assembly

INTRODUCTION

Polymer colloid spheres have been widely researched because of their various applications in the fields of chemistry, physics, medicine, biology, and so forth. In recent years, assembling submicrometer-sized monodisperse polymer colloid spheres into colloid photonic crystals with a periodically varying index of refraction at appropriate conditions has been a hot research topic. Colloid photonic crystals have a close-packed and three-dimensional periodical structure that can produce a photonic bandgap and control the behavior of photons. It is also considered an effective and promising method for the preparation of three-dimensional photonic crystals in the wave range of close-infrared light, visible light, and shorter wavelength light. The preparation of colloid crystals usually includes two parts: the synthesis of monodisperse polymer colloid spheres and the ordered assembly of the spheres. Emulsion polymerization is the traditional method for preparing polymer colloid spheres,^{1,2} but prepared spheres have a comparatively wide distribution of sizes. Moreover, the emulsifier will be largely consumed and is difficult to remove from the resultant product. Consequently, emulsifier-free polymerization has attracted great interest because the polymer colloid spheres prepared by this method have the characteristics of

good monodispersity, a narrow distribution of sphere sizes, clean sphere surfaces, and so forth.

In this article, polystyrene (PS) colloid spheres were synthesized by emulsifier-free polymerization and were assembled into colloidal photonic crystals by an improved vertical deposition method. In comparison with the previous method,^{3–6} the prepared time for the PS colloid crystal was reduced to only 2 days from beginning to end of the assembly, and there were no manipulated processes or complicated apparatus. The mechanism of vertical deposition was analyzed, and it would be beneficial to the synthesis of high-quality photonic crystals. The prepared PS colloid crystal with a submicrometer size has Bragg diffraction in the range of visible light, and multicolors can be seen from different angles, so it can be used as a photonic crystal with a corresponding photonic bandgap. On the other hand, the prepared colloid crystal has a face-centered cubic (fcc) close-packed structure with 26% porosity theoretically and can be infiltrated by various materials, so it can be used as a template to synthesize three-dimensional ordered macroporous (3DOM) materials.^{7–11} Among the multitudinous 3DOM materials, particular attention has been paid to macroporous titania (TiO₂) because of its higher refractive index (>2.5), which is very important for photonic crystal applications. With the PS colloid photonic crystal prepared in this study as a template, 3DOM TiO₂ materials were synthesized, and the optical properties were measured.

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EXPERIMENTAL

Materials

Styrene (St), potassium persulfate (KPS), sodium *p*-styrene sulfonate (SSS), sodium bicarbonate (NaHCO₃), tetrabutyl titanate [Ti(BuO)₄], and anhydrous ethanol were all analytically pure and obtained from China National Medicines Corp., Ltd. (Shanghai, China).

St was purified by distillation under reduced pressure before use.

Synthesis of the PS colloid spheres and assembly of the PS colloid crystal

PS colloid spheres were synthesized by emulsifier-free polymerization. Water (200 mL) was added to a three-mouth flask and heated to 70°C. NaHCO₃ (0.14 g) and 0.0356 g of SSS were introduced into the three-mouth flask, and the solution system was kept stable for 30 min. Then, 18.5 mL of St was introduced into the solution, which was stirred for another 30 min. At last, 0.162 g of KPS was introduced, and the whole system was refluxed under constant stirring and a nitrogen atmosphere for 28 h to form a white PS colloid sphere suspension.

After the reaction, PS colloid spheres were assembled into PS colloid crystals by an improved vertical deposition method. The PS emulsion was diluted to 0.9 wt % by a 25 wt % ethanol solution and dispersed ultrasonically for 30 min. Then, the diluted PS emulsion was put into a beaker, and simultaneously, a cleaning quartz slide loader was inserted vertically. The assembly process was finished at 55°C, and the evaporation speed of the solvent was 3.5 mm/day for 2 days through control of the ring-size (6 cm) of the beaker; a beautiful multicolored film with an area of 1.5 × 1 cm² was obtained.

Preparation of 3DOM TiO₂

The PS colloid crystal, used as a template, was heat-treated at 100°C for 5 min to increase the intensity of the PS template. The mixed solutions of Ti(BuO)₄ and ethanol with volume ratios of 1 : 2 and 2 : 1 were used as precursors, and it was possible to adjust the viscosity and hydrolysis/condensation rates of the alkoxide by dilution in ethanol. The PS templates were immersed in the mixed solutions, and the coated templates were dried at room temperature. This immersion procedure was repeated several times to ensure the complete infiltration. After infiltration, the coated templates were calcined at 300°C for 2 h and at 550°C for 6 h in air at the heating rate of 2°C/min. The samples of 3DOM TiO₂ were obtained after the decomposition of the PS template.

Analytical methods

The scanning electron microscopy (SEM) images were obtained with an FEI Quanta 200 scanning electron microscope (Holland) operating at 30 kV. Transmission spectra were recorded with a TU1901 ultraviolet–visible spectrophotometer (Beijing, China). The crystalline form of 3DOM TiO₂ was identified by a powder X-ray diffraction (XRD) pattern collected from a diffractometer (X'Pert Pro, Holland) with Cu Kα radiation (40 kV, 40 mA). The pore structure of 3DOM TiO₂ was measured by the nitrogen adsorption/desorption isotherm at 77.4 K with a Micromeritics ASAP 2010 sorption analyzer.

RESULTS AND DISCUSSION

PS colloid crystal analysis and characterization

The uniformity of PS spheres is the premier condition for assembling a three-dimensional ordered colloid crystal. When the standard deviation that characterizes the monodispersity of the spheres is less than 5%, the spheres can possibly be assembled into an ordered colloid crystal structure.^{12,13} The SEM images of PS are shown in Figure 1. One hundred PS spheres were chosen randomly, and the diameter of each sphere was measured from Figure 1. Then, the standard deviation (δ) was calculated as follows:

$$\delta = \left[\sum (d_i - d)^2 / (n - 1)^{1/2} \right] \quad (1)$$

where n is the number of spheres and d_i and d are the diameter of each sphere and the average diameter, respectively. After calculation, δ was 3.7%, and the dispersion coefficient (ε) was 0.02:

$$\varepsilon = \delta / d_{\text{average}} \quad (2)$$

where d_{average} is the average diameter. It could be concluded that the PS spheres had a uniform size, and the average diameter of the PS spheres, which had a clear boundary and an ordered array, was 270 nm.

There are three main packing forms for polymer colloid crystals: fcc close-packed structure, body-centered close-packed structure, and hexagonal close-packed structure.¹⁴ Woodcock¹⁵ simulated the behavior of the sediment of spheres with a computer and considered the fcc packing structure to be the most stable array. The synthesized PS spheres in this study displayed a hexagonal array on the whole, which indicated the most stable state of thermodynamics, although there were some point defects, line defects, and stacking defects in local places. There was some dislocation between the first layer and inner layer through the point defect in Figure 1(b),

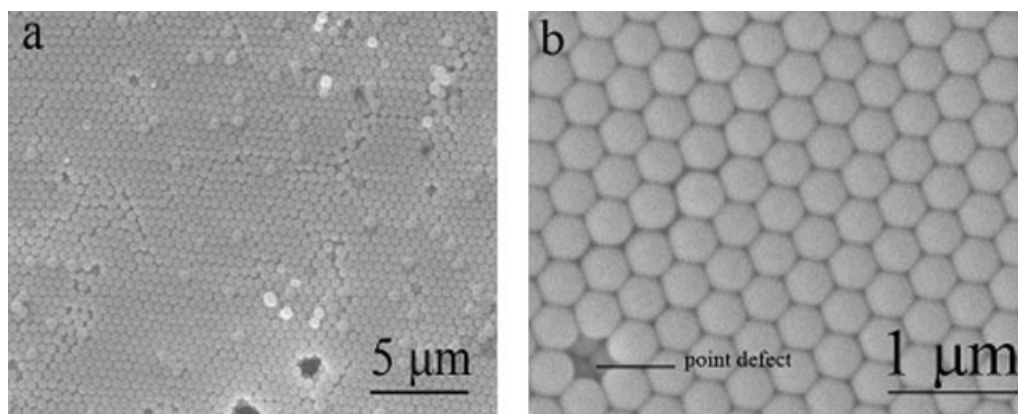


Figure 1 SEM images of PS colloid crystal with (a) low magnification and (b) high magnification.

which was considered to be a typical characteristic of the fcc packing structure.

Mechanism of vertical deposition

Ordered self-assembly by the process of vertical deposition depended on the effects between the spheres themselves and between the spheres and meniscus surface, which was caused by the evaporation of the solvent from the substrate. According to the Yang–Laplace equation, there were long-range interaction forces between the spheres. When the interaction force appeared on the solid–liquid interface, the liquid layer became gradually thinner with evaporation, and the capillary force between spheres became stronger and stronger. When the center of the liquid surface had a thickness equivalent to the diameter of the spheres, the meniscus surface was formed between the spheres, and the spheres congregated to form a crystal core by the capillary force. Then, the spheres that were located in the thicker part of the liquid layer moved to the vicinity of the crystal core, and a new boundary was formed because of the connection of the crystal core and ambient spheres. After the evaporation of the solvent was finished, the ordered PS colloid crystal was assembled on the substrate. This process could be divided two steps: (1) the formation of the crystal core, which was caused by the capillary force, and (2) the growth of the crystal, which developed with the process of evaporation. The temperature of 55°C was chosen as the evaporation temperature because of the equilibrium between the formation of the crystal core, transmission of spheres, and crystal.³ In other words, the formation of the PS colloid crystal by the vertical deposition method was caused by the interaction of the capillary force and surface tension that resulted from the meniscus surface. Jiang et al.¹⁶ used colloid spheres to prepare a multilayer film successfully by this method.

Optical property of the PS colloid photonic crystal

The transmission spectrum of the prepared PS colloid crystal was measured, and the spectral curve is shown in Figure 2. The photonic bandgap of the samples was located at 638 nm, which was the experimental value. The theoretical value could be obtained with the Bragg equation:

$$\lambda_c = 2n_c d_{hkl}$$

where λ_c is the light wavelength of normal incidence, n_c is the effective refractive index of composite of PS spheres and air and d_{hkl} is the crystal plane spacing. The d_{111} crystal surface of the fcc structure was $0.816d_{\text{average}}$, so d_{111} was 220.32 nm. n_c could be calculated as follows:

$$n_c = [n_{\text{PS}}^2 f + n_{\text{air}}^2 (1 - f)]^{1/2} \quad (3)$$

where f , which is the filling fraction of the fcc structure, is 0.74 and n_{PS} and n_{air} are 1.6 and 1.0, respectively. λ_c was 646 nm by the Bragg equation and was very close to the value in the transmission spec-

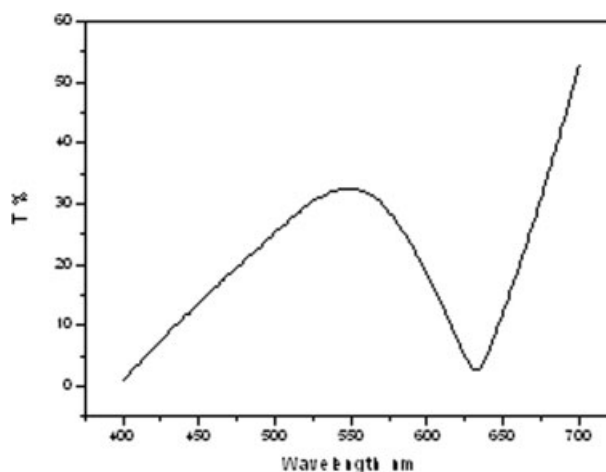


Figure 2 Transmission spectrum of the PS colloid crystal.

tra despite some differences. The differences were probably caused by the size deviation of the PS spheres and various defects, which were not avoided under the present experimental conditions and did not influence the fcc packing structure of the PS colloid crystal on the whole. The PS colloid crystal itself can be used as a kind of photonic crystal and has potential applications in light filters, light switches, chemical or biological sensors, and so forth. On the other hand, the photonic bandgap range of this kind of photonic crystal with a close-packed structure can be limited by the lower ratio of the refractive index between two composite materials. However, the colloid crystal can be used as an ideal template to prepare 3DOM materials, which can be considered as promising materials for amplifying the range of the photonic bandgap and even forming a complete photonic bandgap. Through calculation,¹⁷ the colloid crystal does not appear to have a complete photonic bandgap until the ratio of the refractive index reaches 4.0, whereas the ratio of the refractive index for its reverse structure to form a complete photonic bandgap is only 2.8. Therefore, the preparation of 3DOM materials is more important than the colloid crystal itself.

Structure and properties of 3DOM TiO₂

Titania is a promising material for preparing photonic crystals because of its higher refractive index. Consequently, 3DOM TiO₂ was obtained by the use of the prepared PS colloid crystals as templates.

Figure 3 shows SEM images of 3DOM TiO₂ with different magnifications and experimental conditions. 3DOM TiO₂ was an inverse replica of the PS colloid crystal template with a uniform pore size when the mixture of Ti(BuO)₄ and ethanol with a volume ratio of 1 : 2 was used as the precursor, as shown in Figure 3(a,b), which indicated the sufficient infilling of the template. However, when the volume ratio of Ti(BuO)₄ to ethanol was 2 : 1, the orderliness of the prepared macroporous TiO₂ was lowered obviously, and there were some ruptures in the pore wall from Figure 3(c), which indicated that the precursor solution still had a higher viscosity. The higher viscosity could cause the insufficient and uneven infiltration in the inner template and form the distortion and cleavage of the macroporous structure in the process of synchronous shrinkage of both the PS template and precursor during calcination. The precursor of Ti(BuO)₄ and ethanol with a volume ratio of 1 : 2 was considered to be the most

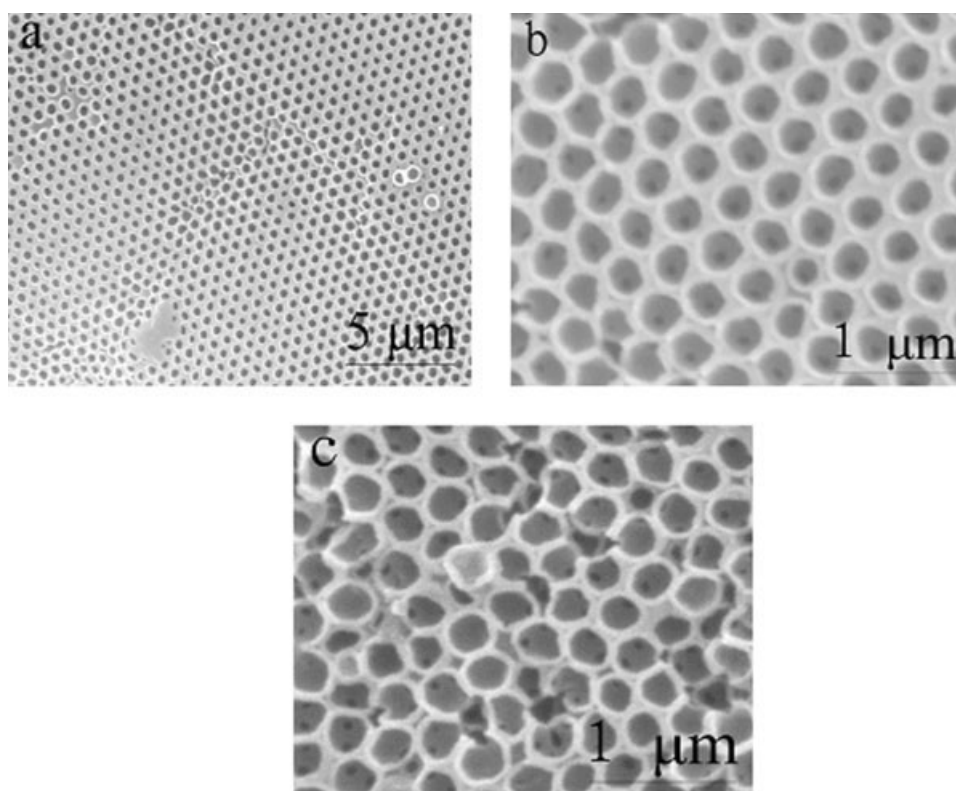


Figure 3 (a,b) SEM images of 3DOM TiO₂ from the precursor of Ti(BuO)₄ and ethanol with a volume ratio of 1 : 2 with low and high magnifications, respectively, and (c) SEM image of macroporous TiO₂ from the precursor of Ti(BuO)₄ and ethanol with a volume ratio of 2 : 1.

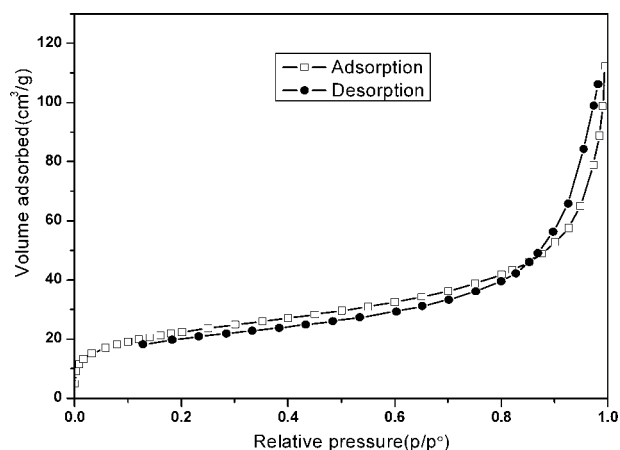


Figure 4 Adsorption/desorption isotherm of 3DOM TiO₂ from the precursor of Ti(BuO)₄ and ethanol with a volume ratio of 1 : 2.

favorable for fabricating 3DOM TiO₂. In theory, each macropore should have 12 small windows, but only 3 could be observed because of the limitation of the visual field. According to Figure 3(a,b), the average diameter of the macropores was 210 nm, and the shrinkage was approximately 22%. The pore structure of 3DOM TiO₂ was further analyzed by nitrogen adsorption and desorption measurements at 77.4 K, and the adsorption/desorption isotherm, an IV-type isotherm, is shown in Figure 4. The inflexion appeared at the low partial pressures, and the adsorbed volume increased slowly; this indicated the existence of some micropores, and single-molecular-layer saturated adsorption was finished rapidly. Simultaneously, the isotherm exhibited hysteresis loops in a large range of partial pressures, indicating that there were abundant mesopores on the macropore wall, which agreed with the SEM images.

The XRD pattern of the 3DOM TiO₂ product is shown in Figure 5. Four sharp peaks can be seen at

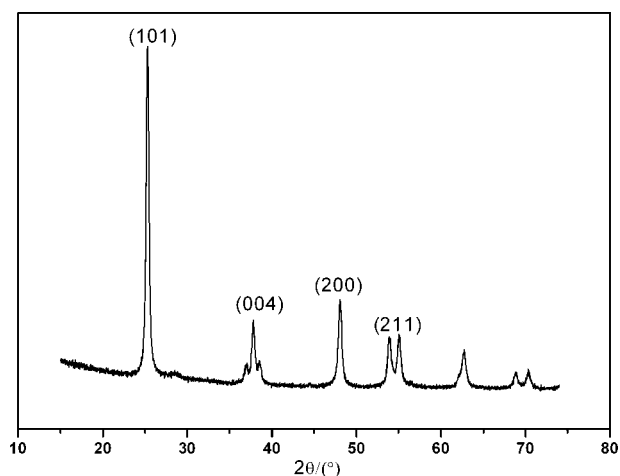


Figure 5 XRD pattern of 3DOM TiO₂.

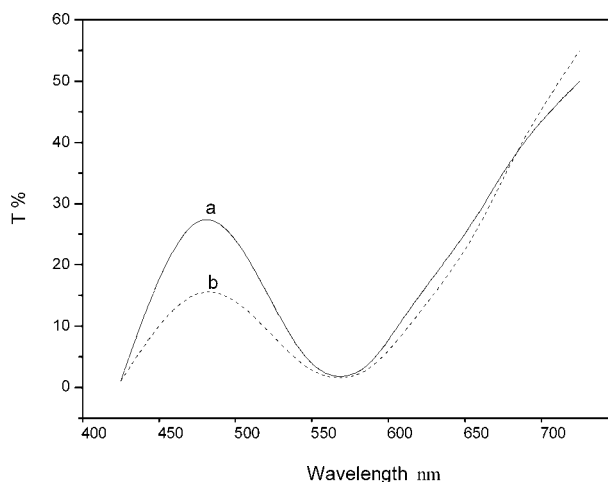


Figure 6 Transmission spectra of macroporous TiO₂ from different precursors: (a) the precursor of Ti(BuO)₄ and ethanol with a volume ratio of 1 : 2 and (b) the precursor of Ti(BuO)₄ and ethanol with a volume ratio of 2 : 1.

the positions of 25.32, 37.61, 48.10, and 53.76°, which represent the anatase crystal planes (101), (004), (200), and (211), so the wall crystallinity of 3DOM TiO₂ was the anatase phase. The crystal size was 25.8 nm, as calculated with the Debye-Scherrer formula.

The transmission spectra of the macroporous TiO₂ products prepared by two kinds of precursors were determined, as shown in Figure 6. The broadened bandgaps could be observed around 550 nm in two curves. The appearance of broadened bandgaps resulted from many factors, including the error in replicating the template, the difference in the pore size, and the volume shrinkage. However, in comparison with the bandgap structure in Figure 6(a), the property of the bandgap in Figure 6(b) is obviously weak. The reason is that the orderliness of macroporous TiO₂ from the mixture of Ti(BuO)₄ and ethanol with a volume ratio of 1 : 2 was reduced. Although there is no complete bandgap structure, the preparation of 3DOM TiO₂ has attracted interest.

CONCLUSIONS

Monodispersed PS colloid spheres with an average diameter of 270 nm were synthesized by emulsifier-free polymerization and self-assembled into an ordered colloid crystal by improved vertical deposition. The prepared PS colloid crystal was demonstrated to be an fcc structure with good orderliness. This improved method could reduce the assembly time efficiently, and the whole process consumed only 2 days from beginning to end; therefore, this was beneficial for the development of photonic crystals. At the same time, the PS colloid crystal tem-

plate was the foundation of the fabrication of 3DOM materials, and macroporous TiO₂ photonic crystals were synthesized with different viscous precursors and studied with transmission spectra. 3DOM TiO₂ could be the inverse replica of the colloid crystal template, and the pore size could be adjusted easily through the synthesis of templates with different diameters. The preparation of 3DOM TiO₂ is an important application for PS colloid crystals and is beneficial for the formation of photonic crystals with a complete bandgap.

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