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Optimal process of preparation of inverse opal zirconia

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Polystyrene colloidal template was prepared by evaporation deposition method with as-prepared polystyrene microspheres with the size of 340±10nm as raw material and inverse opal zirconia was fabricated by colloidal crystal-templating method. The optimal process of preparation of polystyrene colloidal template and inverse opal zirconia were deeply studied via orthogonal experiment design and range date processing. The factors, which affect the morphology of polystyrene template and inverse opal zirconia, and the corresponding values were considered, respectively and the primary and secondary order of factors were also determined. The results showed that the optimal process of preparation of polystyrene colloidal template was that self-assembly temperature was 55 °C, emulsion height was 1.5 cm, emulsion consistence kept 4.0% and container diameter was Φ6.0 cm. It also found that the as-prepared polystyrene template showed bright green color and the better polystyrene template structure was, the brighter green color can be obtained. The optimal process of preparation of inverse opal zirconia was that impregnation time was once, mass ratio of polystyrene template and precursor kept 1 : 15, precursor ratio of zirconium acetate and methanol kept 1 : 1 and calcination temperature was 450 °C.

Key words: Polystyrene, Inverse opal, Zirconia, Structure color, Optimal process.

Introduction

Photonic crystals are highly ordered structures with a periodically modulated refractive index, with periods typically on the length scale of optical wavelengths (380-750 nm) [1-3]. This periodic arrangement may exist in one, two, or three dimensions and affect the propagation of electromagnetic waves in the material resulted in a photonic band gap, because of the Bragg diffraction on lattice planes [4-5]. All common colloidal crystal-templating methods to fabricate inverse opal photonic crystals result in structures based on a HCP-arrangement of spherical particles [6-9]. It is known that an inverse opal has superior photonic properties than a"direct" artificial opal made of the same material [10-12]. We are interested in inverse opal structures because of their novel ability in optical properties that are useful in structure color application.

Polystyrene (PS)-based colloidal photonic crystals based on self-assembly method have an incomplete photonic band gap and typically appear iridescent in the visible range [13-15]. PS was widely applied in making inverse opal structure as template, but the optimal process to fabricate PS template with good HCP-arrangement and inverse opal structure was less reported.

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In this article, PS crystal templates were fabricated by evaporation deposition method. Orthogonal tests were designed to obtain the optimal process to fabricate PS template and inverse opal zirconia. Various factors and the corresponding values which affect the morphology and color performance of PS template as well as inverse opal zirconia were considered, respectively.

Experimental Procedure

Fabrication of polystyrene colloidal template

The monodisperse PS microspheres were prepared by soap-free emulsion polymerization method with styrene monomer as raw material. The factors of consistence, height of PS emulsion, self-assembly temperature and area and the corresponding values, which listed in Table 1, on the morphology and color performance of PS colloidal template were investigated by orthogonal test. The orthogonal table of L_9 (3^4) was selected to design experiment and data processing was

Table 1. Various factors and the corresponding values for fabrication of PS template.

Number of values	Factors			
	A (consistence)	B (height)	C (temperature)	D (diameter)
1	3.5%	2.0 cm	60 °C	Φ4.0 cm
2	4.5%	1.0 cm	65 °C	Φ6.0 cm
3	4.0%	1.5 cm	55 °C	Φ9.0 cm

shown in Table 2

One-hundred-mark system was taken to evaluate the combined performance of PS templates and 1 on 100 scales was the worst, 100 on 100 scales was the best. Each sample was given an average score shown in table 2 and range analysis was taken to find out the remarkable influencing factors of each judging target.

Fabrication of inverse opal zirconia

Zirconium acetate was mixed with methanol in a

Table 3. Various factors and the corresponding values for preparation of inverse opal zirconia.

Number of values	Factors			
	A (Precursor ratio)	B (Dipping times)	C (Mass ratio)	D (Calcinations temperature)
1	1 : 1	1	1 : 15	600 ºC
2	1 : 0.8	2	1 : 10	450 ºC
3	1 : 1.2	3	1 : 20	700 ºC

Table 2. Experiment design and range analysis of preparation of PS template.

Number of samples	A (Consistence)	B (Height)	C (Temperature)	D (Diameter)	Performance score
1#	3.5%	2.0 cm	60 ºC	Φ4.0 cm	62
2#	3.5%	1.0 cm	65 ºC	Φ6.0 cm	24
3#	3.5%	1.5 cm	55 ºC	Φ9.0 cm	96
4#	4.5%	2.0 cm	65 ºC	Φ9.0 cm	22
5#	4.5%	1.0 cm	55 ºC	Φ4.0 cm	84
6#	4.5%	1.5 cm	60 ºC	Φ6.0 cm	74
7#	4.0%	2.0 cm	55 ºC	Φ6.0 cm	90
8#	4.0%	1.0 cm	60 ºC	Φ9.0 cm	70
9#	4.0%	1.5 cm	65 ºC	Φ4.0 cm	50
k_1	60.6	58	68.7	65.3	
k_2	60	65.3	38	68.7	/
k_3	70	73.3	90	62.7	
Range (R)	10	15.3	52	6	/
Primary and secondary order of factors			C > B > A > D		
Optimal process			$A_3B_3C_3D_2$		

Table 4. Experimental design and range analysis of preparation of inverse opal zirconia.

Number of sample	A (Precursor ratio)	B (Dipping times)	C (Mass ratio)	D (Calcinations temperature)	Performance score
1#	1 : 1	1	1 : 15	600 ºC	96
2#	1 : 1	2	1 : 10	450 ºC	72
3#	1 : 1	3	1 : 20	700 ºC	20
4#	1 : 0.8	1	1 : 10	700 ºC	80
5#	1 : 0.8	2	1 : 20	600 ºC	56
6#	1 : 0.8	3	1 : 15	450 ºC	46
7#	1 : 1.2	1	1 : 20	450 ºC	70
8#	1 : 1.2	2	1 : 15	700 ºC	52
9#	1 : 1.2	3	1 : 10	600 ºC	26
k_1	62.7	82	64.7	59.3	
k_2	60.7	60	59.3	62.6	/
k_3	49.3	30.7	48.7	50.6	
range (R)	13.4	51.3	16	12	
Primary and secondary order of factors			B > C > A > D		
Optimal process			$A_1B_1C_1D_2$		

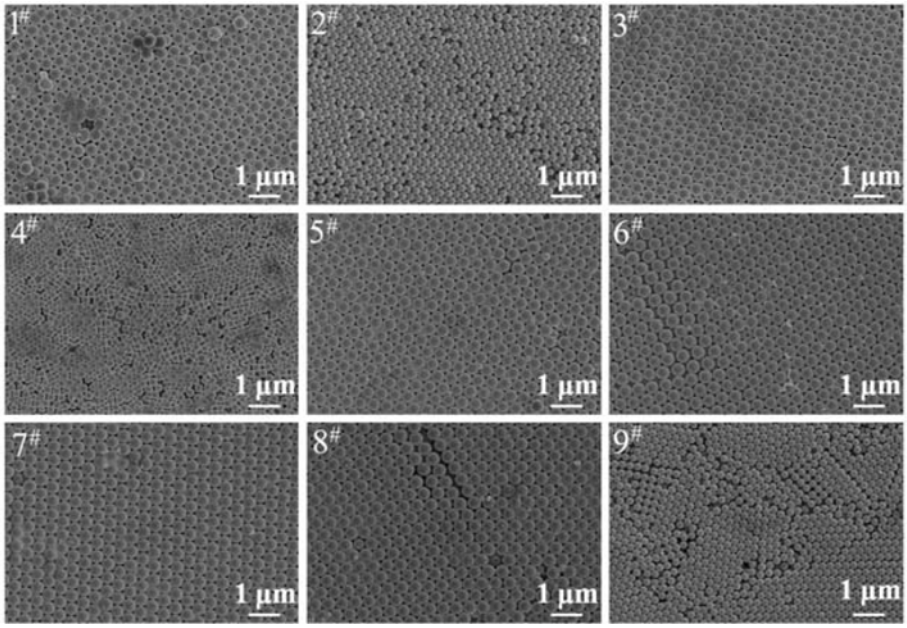

Fig. 1. SEM images of as-prepared PS colloidal crystal template by orthogonal test.

certain proportion as precursor of zirconia. Inverse opal zirconia was prepared by dipping-filtration-calcination PS template as crude material. The influence of precursor ratio of zirconium acetate and methanol, dipping times, mass ratio of PS template and precursor and calcination temperature and the corresponding values, which listed in Table 3, on the morphology and the phase and purity of as-prepared inverse opal zirconia was investigated. Select the orthogonal table of L_9 (3^4) to optimize the process of preparation of inverse opal zirconia.

The morphology of as-prepared inverse opal zirconia was analyzed by score given by three expert people, respectively, based on the regularity of three-dimensional ordered structure, and defects they had. We also took one-hundred-mark system to evaluate the morphology of inverse opal zirconia and 1 on 100 scale was the worst, 100 on 100 scale was the best. Each sample was given an average score shown in table 4 and range analysis was taken to find out the remarkable influencing factors of each judging target. Experimental design and data processing were showed in Table 4.

The morphology of as-prepared PS templates and inverse opal zirconia were observed by scanning electron microscopy (S4800, Japan). Color performance of PS template was showed by a digital camera (Canon, Japan). Moreover, X-ray diffraction (D/max2200PC, Japan) was used to characterize the phase and purity of as-prepared inverse opal zirconia.

Results and Discussion

The morphology of polystyrene colloidal template

It can be seen from Fig. 1 ($4^{\#}$) that PS microspheres did not self-assemble completely and there were vacancies between them. Fig. 1($2^{\#}$) showed that PS microspheres were like a multi-domain structure in some certain region where they were arranged in close-packed hexagonal structure. Compared with that was in Fig. 1($2^{\#}$), PS microspheres were more orderly arranged and there were more close-packed hexagonal structure, while there was still unstable tetragonal arrangement structure in Fig. 1($9^{\#}$). The remaining six groups of PS templates showed long-range order. It can also be seen that there were still a few of PS microspheres which were not arranged, agglomerated and dispersed in Fig. 1($1^{\#}$), meanwhile, there were a few of vacancies and dislocations caused by individual PS spheres in Fig. 1($8^{\#}$). Some vacancies and FCC structure which were looser than HCP structure and were unstable in law of thermodynamic, were existed in Fig. 1($6^{\#}$). Few of hexagonal stacking which were not close-packed arranged was observed in Fig. 1 ($5^{\#}$). It was found that PS microspheres were well-arranged in hexagonal structure and there were almost no vacancy and dislocation in Fig. 1($7^{\#}$) and Fig. 1($3^{\#}$), while the distribution of PS microspheres in Fig. 1($3^{\#}$) were more uniform than that was in Fig. 1($7^{\#}$), which meant that it was the optimal process to fabricate PS template.

Color performance of polystyrene colloidal template

We analyzed the color performance of PS colloidal template by orthogonal test shown in Fig. 2. As it was observed in Fig. 2($4^{\#}$), PS template showed white color under visible light. A little bit bright green color in the edge area of PS colloidal template was found in Fig. 2($2^{\#}$), and the other part was still white color. Compared with that was in Fig. 2($2^{\#}$) and Fig. 2($1^{\#}$), more areas and brighter of green structural color was

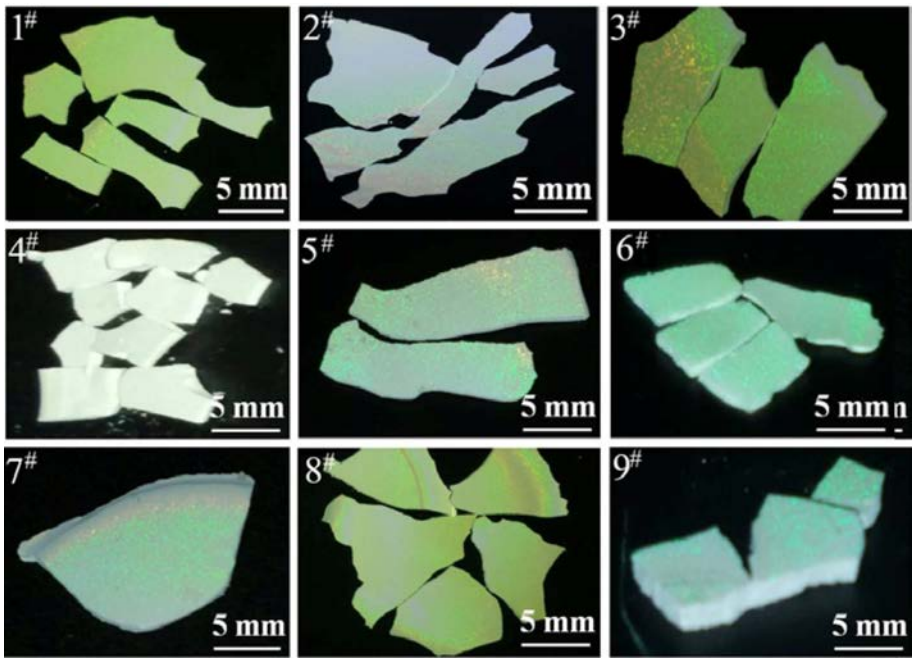

Fig. 2. Color performance of PS colloidal crystal template by orthogonal test.

observed in Fig. 2(9#), while, there were still a little white color area. The surface of the entire PS template was faint green color both in Fig. 2(6#) and Fig. 2(5#). It was also found that brighter, higher saturation and more uniform of green color on the whole surface of PS template was found in Fig. 2(3#), compared with that was in Fig. 2(7#).

The combined color performance and the morphology of PS template were analyzed comprehensibly. The combined performance scores of these PS templates were given by three expert people, respectively, based on the regularity of PS micros spheres, arrangement of PS template and the color performance.

From table 2, the orthogonal experiment results and range analysis indicated that the most significant influence on the combined performance of PS templates was C, and the primary and secondary order of factors was C, B, A and D. As for factor A, since $k_3 > k_2 > k_1$, A_3(emulsion consistence was 4.0%) was the optimal values. Similarly, $A_3B_3C_3D_2$ was the optimal process to fabricate PS temperate, which meant that emulsion consistence was 4.0%, emulsion height was 1.5 cm, self-assembly temperature kept 55 ºC and container diameter was Φ6.0 cm.

Optimal process of polystyrene template

Compared optimal process $A_3B_3C_3D_2$ obtained by range analysis of preparation of PS template with the number 3# sample obtained in orthogonal test shown in Fig. 3. PS microspheres were more orderly and tightly arranged, and there were less defects in Fig. 3(c) than that was in Fig. 3(d). We can see obviously that it was more uniform, higher brightness and saturation in Fig. 3(a) than that was in Fig. 3(b), indicating that

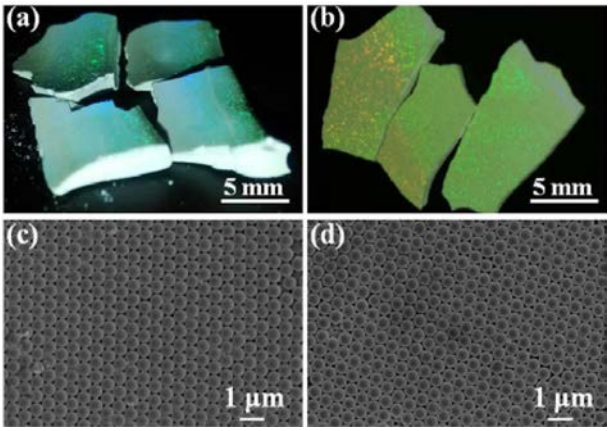

Fig. 3. Optical photograph and SEM images of PS template (a, c) by $A_3B_3C_3D_2$ obtained by range analysis; (b, d) 3# sample in orthogonal test.

$A_3B_3C_3D_2$ was the optimal process of preparation of PS template.

The morphology of inverse opal zirconia

We analyzed the morphology of as-prepared inverse opal zirconia shown in Fig. 4. It can be seen that there was curved face with a little holes and almost no inverse opal structure at all in Fig. 4(3#). It was arrangement with HCP structure, while it seems irregular due to too many times impregnation. Meanwhile, there were some residual inorganic substance as shown in Fig. 4(3#) and Fig. 4(6#). Some arrangement defects were observed in Fig. 4(8#) and Fig. 4(5#).As shown in Fig. 4(7#), Fig. 4(2#), Fig. 4(4#) and Fig .4(1#), these was obvious and compact HCP arrangement, while there were some residual inorganic matter existed in the aperture gap.

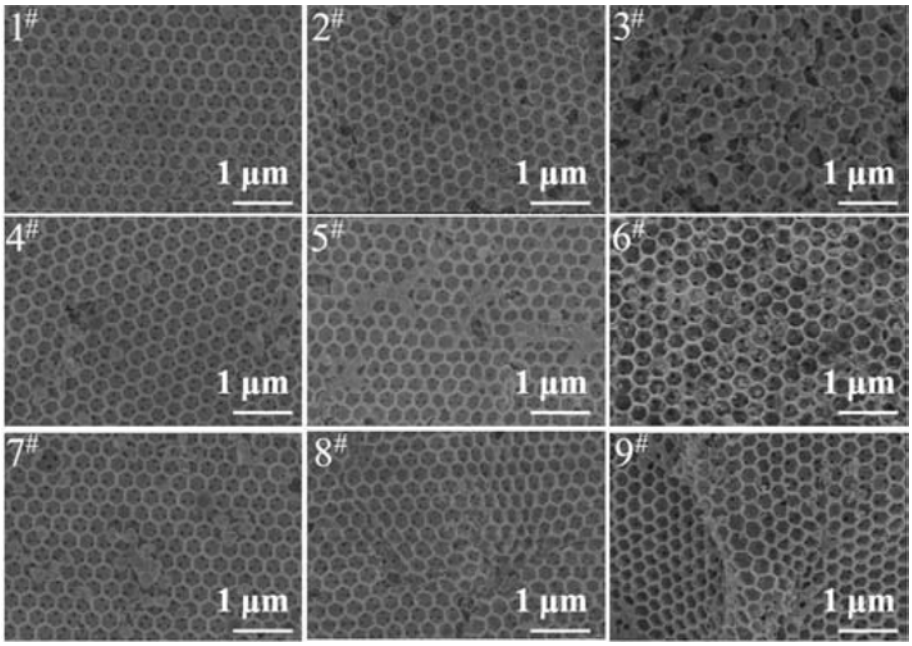

Fig. 4. SEM images of as-prepared inverse opal structure zirconia by orthogonal test.

Some deformation occurred in Fig. 4(2#) due to too many times of impregnations. Good HCP arrangement structure and clear channel between the two aperture gaps were observed both in Fig. 4(4#) and Fig. 4(1#), however, there were more structure defects and residual inorganic matters in Fig. 4(4#) than that was in Fig. 4(1#), which meant that it was the optimal process to fabricate inverse opal zirconia.

It was obvious from table 4 that the most significant influence on the morphology of as-prepared inverse opal zirconia was B, and the primary and secondary order of factors was B, C, A and D. As for factor A, since $k_1 > k_2 > k_3$, A_1 was chosen the best values. Similarly, the optimal experimental process to fabricate inverse opal zirconia was $A_1B_1C_1D_2$, suggesting that precursor ratio was 1 : 1, impregnation time kept once, mass ratio of PS template and precursor was 1:15 and calcination temperature was 450 ºC.

Optimal process of inverse opal zirconia

Fig. 5 was XRD patterns of the sample prepared by optimal process $A_1B_1C_1D_2$ obtained by range analysis and 1# sample obtained in orthogonal test. It can be seen that all the diffraction peaks of the as-prepared inverse opal zirconia powder agreed well with the standard JCPDS card no.50-1089 when it was sintered at 450 ºC, while, there was some other phases which agreed with standard JCPDS card no.37-1484 when it was sintered at 600 ºC, suggesting that with increasing the sintered temperature, tetragonal phase changed to monoclinic phase zirconia.

A comparison test was conducted between $A_1B_1C_1D_2$ and 1# sample and SEM images of the as-prepared inverse opal zirconia was showen in Fig. 6. It can be

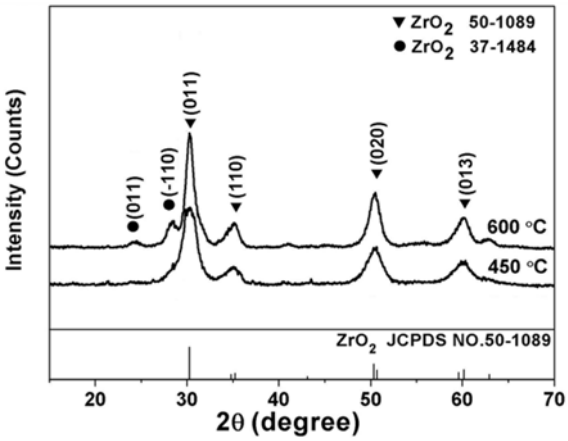

Fig. 5. XRD images of as-prepared zirconia (a) by $A_1B_1C_1D_2$ obtained by range analysis; (b) 1# sample in orthogonal test.

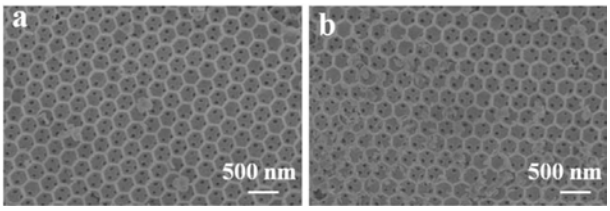

Fig. 6. SEM images of as-prepared zirconia (a) by $A_1B_1C_1D_2$ obtained by range analysis; (b) 1# sample in orthogonal test.

found in Fig. 6(a) that there was uniform size of opening of holes, tight and ordered HCP arrangement and there were almost no defects and cracks, compared with that was in Fig. 6(b), suggesting that a perfect inverse opal structure was obtained. While, there were still some residual inorganic substance found in Fig. 6(b), which can be conformed further that $A_1B_1C_1D_2$

was the optimal process to fabricate inverse opal zirconia.

Conclusions

In summary, the optimal process for preparation of PS template and inverse opal zirconia were studied via orthogonal experiment design and range date processing by choosing four factors and the corresponding values. Firstly, the remarkable influencing factor and the primary and secondary order of factors, which affected the morphology of PS template and inverse opal zirconia were obtained, respectively. The optimal process to fabricate PS template was that self-assembly temperature was 55 ºC, emulsion height kept 1.5 cm, emulsion consistence kept 4.0% and container diameter was Φ6.0 cm. The optimal process to fabricate inverse opal zirconia was that impregnation time kept once, mass ratio keep was 1 : 15, precursor ratio kept 1 : 1 and calcinations temperature was 450 ºC. It was also found that PS templates showed bright green structural color and the brightness and saturation were severely influenced by the quality of the arrangement. Meanwhile, the color changed with the changing of incidence angle.

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