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Fabrication and Optical Properties of Photonic Crystals of LiCl Modified SiO_2 Colloidal Spheres

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Abstract. LiCl was used to improve the surface charge of SiO_2 colloidal spheres prepared by stöber method. And vertical deposition method was used to synthesize the photonic crystal with modified SiO_2 colloidal spheres. The micromorphology, electrical properties and optical properties were characterized by scanning electron microscope (SEM), zeta potential instrument and UV/VIS/NIR spectrophotometer. The surface charge of SiO_2 colloidal spheres can be improved by LiCl solution, and the Zeta potential increases with the increment of LiCl concentration and NH_3 concentration. The position of the transmission dip of the photonic crystals is close to the experimental value.

1. Introduction

Photonic crystal is a metamaterial with ordered structure, and it restricts certain wavelengths of light to pass through which give rise to photonic band gaps [1-3]. Therefore, photonic crystal has brilliant structural color. Such ordered nano-, submicro- or micro-structure has technological applications, including those in photonic materials [4, 5], sensers [6] and filters [7]. Self-assembling is a simple and useful method to prepare the photonic crystal with face-centered cubic structure. Many research groups have developed self-assembling processes for fabricating photonic crystal [8, 9]. The microstructure and surface charge of colloidal spheres are important for synthesizing the photonic crystal via self-assembing method, such as vertical deposition method, electrophoresis-assisted self-assembly method, air-water interfacial floating method, horizontal deposition, Langmuir-Blodgett and so on.

In the present work, stöber method was applied to prepare SiO_2 colloidal spheres, and LiCl was applied to improve the surface charge of spheres. Then, SiO_2 colloidal crystal was fabricated via vertical deposition method. The reaction conditions including LiCl and NH_3 concentration were investigated. The microstructure and photonic band gap property of photonic crystals obtained by different modified SiO_2 colloidal spheres were analyzed. This study has general implications in the surface modification and self-assembling of photonic crystal.

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2. Experimental Procedure

2.1Synthesis

SiO_2 colloidal spheres were synthesized via Stöber method [10] using ammonium hydroxide as a catalyst. In a typical synthesis operation, 50 mg LiCl was added in 50mL distilled water, and then LiCl solution and ammonium hydroxide was added in 25mL ethanol. The solution was dropped into one solution containing TEOS and 25mL ethanol under vigorous magnetic stirring. The reaction was allowed to continue for 22 h at 25℃. Then the mixture was washed with ethanol and distilled water followed by drying at 60℃. The detailed synthesis conditions of our reaction system are presented in Table 1. The photonic crystals were prepared via vertical deposition method following the process of S.F. Sun et al [11]. We used colloidal suspensions of SiO_2 spheres dispersed in ethanol with a concentration of 1wt%. All processes were performed at 40℃ in a vacuum oven.

TABLE1 THE LICL MODIFIED SILICA COLLOIDAL PARTICLES PREPARED BY STÖBER METHOD

Samples	TEOS [mL]	ammonium hydroxide [mL]	LiCl solution [mL]	Particle size [nm]
C1	2.5	2.5	2	185
C2	2.5	3.5	1	130
C3	2.5	3.5	2	220
C4	2.5	3.5	3	230
C5	2.5	6	1	211
C6	2.5	7	1	202

2.2Characterization

FE-SEM (S-4800, Japan) was utilized to examine the morphology of the SiO_2 particles and photonic crystals. The values of zeta potential of LiCl modified SiO_2 particles were determined by Zetasizer Nano ZS. Optical transmission spectrum was obtained using a Perkin-Elmer Lamda 950 UV/VIS/NIR Spectrophotometer.

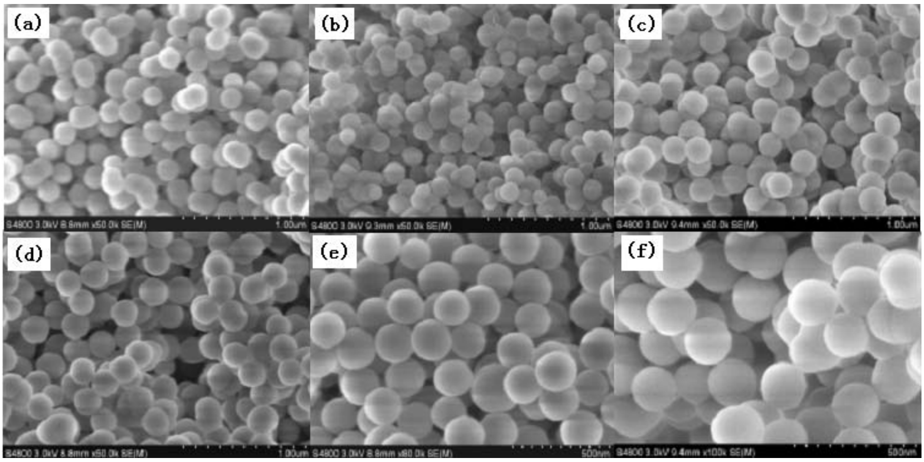

Fig. 1 The SEM images of SiO_2 colloidal spheres: (a) C1, (b) C2, (c) C3, (d) C4, (e) C5, (f) C6

3. Results and Discussion

Fig. 1 shows the SEM images of LiCl modified SiO_2 colloidal spheres. All the obtained SiO_2 particles are spheres. As shown in table 1 and Fig.1, when LiCl solution is 1 mL or 2mL, increasing NH_3 concentration can increase the particle size. And the particle size of colloidal spheres also increases significantly with the increment of LiCl concentration (Fig.1 (b)-(d)). Aggregates are formed at low LiCl concentration and high NH_3 concentration.

Table 2 shows the Zeta potential of LiCl modified SiO_2 spheres. It is obvious that when V_{NH3} is 3.5 mL, increasing LiCl concentration benefits the improvement of the Zeta potential of SiO_2 spheres. And the Zeta potential increases significantly with the increment of NH_3 concentration. According to the electric double layer theory，the Zeta potential is influenced by charge density and electric double layer. When increasing LiCl concentration, the electric double layers of modified SiO_2 colloidal spheres become thicker, so the Zeta potential becomes higher. This is benefit for self-assembling of colloidal spheres.

TABLE 2 RESULTS OF ZETA POTENTIAL OF LICL MODIFIED SIO_2 SPHERES

Samples	C2	C3	C4	C5	C6
Zeta potential /mV	-1.592	-7.541	-7.917	-13.75	-18.33

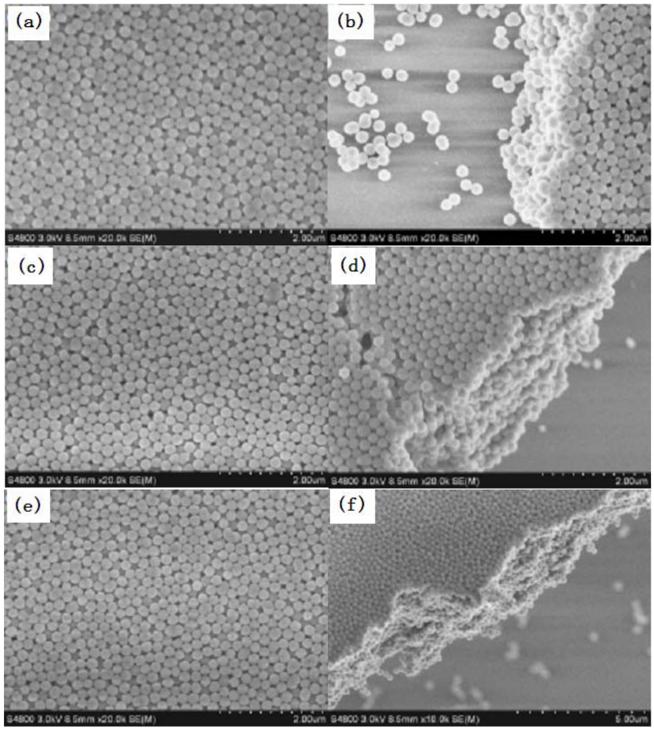

Fig. 2 The SEM images of photonic crystals prepared by colloidal spheres:

(a) , (b) C4; (c), (d) C5; (e), (f) C6

Fig. 2 shows the SEM images of photonic crystals obtained by LiCl modified SiO_2 spheres, which exhibits fcc structure with the [111] direction normal to the sample surface. As shown in table 2, the Zeta potentials of samples C4, C5 and C6 are -7.917, -13.75 and -18.33 respectively. As the results (Fig. 3), the photonic crystal obtained by spheres C6 is more ordered than that synthesized by spheres C4 or C5. And the number of layers increases with the increment of the Zeta potential. Higher Zeta potential results in higher interaction force between SiO_2 spheres, which is benefit for ordered structure.

As shown in Fig. 3, the optical images of SiO_2 photonic crystals present different colors. And the photonic crystal prepared by spheres C6 is obviously brighter and more uniform than the other two photonic crystals. This also proves that the photonic crystal prepared by spheres C6 has more ordered structure.

Photonic band gap is the most important characteristic of the SiO_2 photonic crystals. Typical transmission spectrum from samples acquired at normal incidence to the (111) plane is shown in Fig. 4. The photonic crystals assembled by LiCl modified SiO_2 colloidal spheres C4, C5 and C6 exhibit absorption peaks at 518 nm, 465 nm and 437 nm respectively.

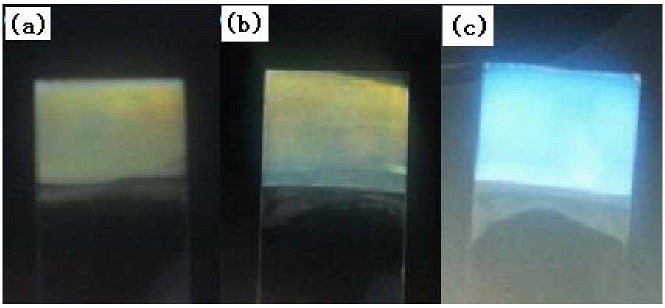

Fig.3 Optical images of SiO_2 photonic crystals obtained by (a) C4, (b) C5, (c) C6

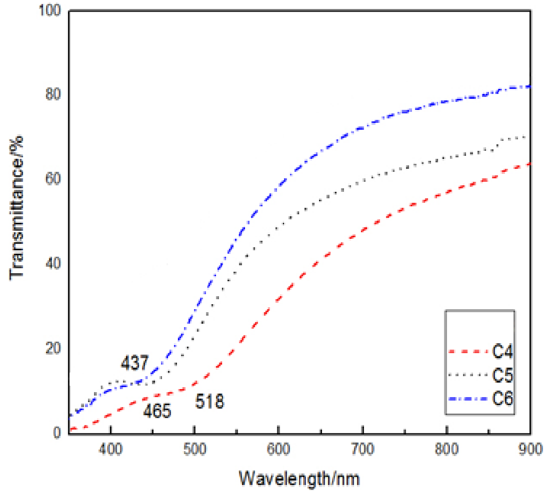

Fig.4 Transmission spectrum of the photonic crystals

For FCC structure, position of the transmission dip (λ) can be estimated using the Bragg law:

$$\lambda = 2d_{(111)}\left(\varepsilon_e - \cos^2\theta\right)^{1/2} \tag{1}$$

where $d_{(111)}$ is the distance between (111) crystalline planes, $d_{(111)}$ = 0.816D (D is the particle size of the SiO_2 spheres). θ is the angle between the incident light and the surface of the sample, θ=90°. ε_e is the effective refractive index of the SiO_2/air composite, and can be approximated by the following expression:

$$\varepsilon_e = \varepsilon_{silica} f + \varepsilon_{air}(1-f) \tag{2}$$

where f is the dielectric filling ratio (f=74% in FCC structure), ε_{silica} and ε_{air} are the refractive indices of the SiO_2 spheres and the air respectively (ε_{silica}=2.1, ε_{air}=1). Therefore, the transmission peaks of the photonic crystals assembled by SiO_2 colloidal spheres C4, C5 and C6 can be easily calculated to be 504 nm, 462 nm and 442 nm respectively, which are close to the experimental value.

4. Conclusions

In this paper, the SiO_2 colloidal spheres with particle size of about 130 nm ～ 230 nm could be synthesized by stöber method with LiCl as surface charge control agent. Increasing NH_3 concentration or LiCl concentration can increase the particle size of SiO_2 colloidal spheres. And the Zeta potential of SiO_2 spheres can be improved by increasing NH_3 concentration or LiCl concentration. The obtained photonic crystal exhibits fcc structure with the [111] direction normal to the sample surface. The photonic crystal prepared by SiO_2 spheres C6 which has higher Zeta potential is more ordered, uniform and obviously brighter than the other photonic crystals. The photonic crystals exhibit absorption peaks at 518 nm, 465 nm and 437 nm respectively, which are close to the calculated values.

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