A colloidal crystal double-heterostructure fabricated with the angle controlled inclined deposition method*

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(Received 14 July 2011; revised manuscript received 2 March 2012)

A self-assembly method, named the angle controlled inclined deposition method, is developed for fabricating well-ordered silica and polystyrene colloidal crystals. A high-quality colloidal crystal with a flat and uniform surface over a large area can be produced rapidly using a minute quantity of suspension and without any additional equipment. By controlling the inclined angle, we can fabricate colloidal crystals with diverse numbers of layers. A colloidal crystal double-heterostructure (composed of three different colloidal photonic crystals) can be rapidly fabricated with this method. Both experimental and simulation results show that the photonic band gap of the double-heterostructure is not a simple superposition of that of the compositional colloidal crystals along the stacking direction.

Keywords: colloidal photonic crystal, self-assembly method, band gap, heterostructure

PACS: 81.10.Dn, 42.70.Qs, 73.20.At **DOI:** 10.1088/1674-1056/21/7/078103

1. Introduction

Photonic crystals (PCs) characterized by dielectric periodicities have attracted a great deal of attention due to their novel potential applications in many fields.[1−6] Recently, colloid PC heterostructures have been reported.[7−10] The vertical deposition (VD) method[9−12] appears to be an effective and economic way to fabricate three-dimensional (3D) PCs. However, it is hard to self-assemble silica particles over a large area using this method because the silica colloid spheres will deposit at the bottom during fabrication. In addition, it is expensive, because a large amount of polystyrene (PS) colloid suspension or special equipment (e.g., a peristaltic pump[10]) are needed.

In this paper, we develop a procedure, the angle controlled inclined deposition method, which can be used to produce well-ordered silica and PS colloid crystals. Compared with the previously reported procedure, both silica and PS colloid crystals can be fabricated rapidly (less than 2 h) over a large area (2 cm×2 cm) with only a minute quantity of colloidal suspension. We can control the thickness at the layer level without any additional equipment. Furthermore, we fabricate a double PC heterostructure by stacking three different colloidal PCs. The experimental measurement results are compared with the numerical simulations based on the finite-difference time-domain technique (FDTD). A tunneling peak is observed in the transmission spectrum of the double-heterostructure.

2. Experiment

Colloidal crystals A, B, and C were fabricated from PS colloidal spheres with average diameters of 227 nm, 250 nm, and 312 nm, respectively. Colloidal crystal D was fabricated using silica colloid spheres with an average diameter of 256 nm.

The solution containing the colloidal spheres and a small amount of surfactant was sonicated for 20 min. A few drops of colloidal suspension were dropped on a tilted glass substrate (the tilted angle was less than 15°), and the temperature of the experiment was sta-

*Project supported by the Guangdong Province Natural Science Foundation, China (Grant No. 8151063101000030), the National Natural Science Foundation of China (Grant No. 10504008), and the Key Project of Chinese Ministry of Education (Grant No. 209091).

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bilized at 50 °C. The thickness of the colloidal crystal film could be controlled by the tilted angle of the substrate and the concentration of the suspension. A large flat colloidal crystal film could be obtained in a few hours. Then the samples were put into a calciner at a temperature of 80 ° for 1 h and subsequently annealed to firm the films. With the same method, we could obtain double-heterostructure D/A/B.

A scanning electron microscope (SEM, JSM-6330F) was used to examine the microstructures of the samples, and an ultraviolet–visible spectrometer (HITACHI U-3310) was used to measure the optical transmission spectra.

3. Results and discussion

3.1. Inclined deposition method for fabricating colloid crystals

Figure 1 shows the process of inclined deposition self-assembly.

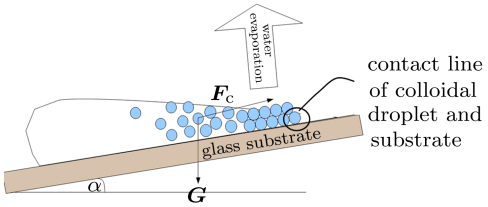


Fig. 1. (colour online) The process of inclined deposition self-assembly.

We incline the substrate to form a substrate-suspension angle, which is equal to the inclined angle. The water influx transports the colloidal particles toward the edge, where they are assembled into an ordered structure because of lateral capillary force. In general, the silica particles sink to the bottom, and it is hard to fabricate a large well ordered pattern. However, in this method, the substrate-suspension angle is so small that the contact line declines faster than the sinking rate of the silica particle. In addition, the lateral capillary force and the gravity are not in the inverse directions, so the lateral capillary force is large enough to array the particles. For PS, the particles suspend in water, and the lateral capillary force and gravity not only array the particles but also make them compress mutually, resulting in a deformation, as shown in Fig. 2.

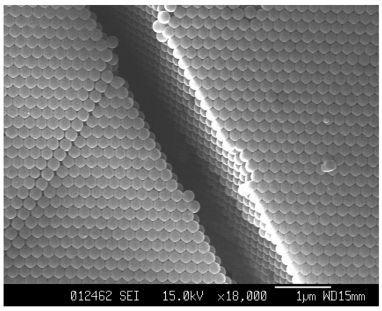


Fig. 2. SEM image of the colloid crystal.

Figure 3 shows the normal-incidence transmission spectra (along the [111] direction) of the individual colloidal photonic crystals. Samples A, B, C, and D each have an obvious photonic band gap (PBG). The center wavelengths of these band gaps are 515 nm, 551 nm, 670 nm, and 554 nm, respectively. The positions of the transmission peaks are not very consistent with the results calculated using Bragg's law for the (1 1 1) family of planes

$$\lambda_c = 2\sqrt{2/3}D\sqrt{fn_{\text{sphere}}^2 + (1-f)n_{\text{air}}^2}, \qquad (1)$$

where λ_c is the wavelength of the peak, D is the diameter of the PS/SiO2 sphere, f is the dielectric filling ratio (for an ideal face center cubic structure, $f = 0.74$), and n_{sphere} and n_{air} are the refractive indexes of the colloidal sphere and air (in the theoretical calculation, we use $n_{SiO_2} = 1.45$, $n_{PS} = 1.59$, and $n_{\text{air}} = 1$), respectively. The center positions of the PBGs calculated using Bragg' s law are 535 nm, 589 nm, 674 nm, and 560 nm, respectively. The reason for this phenomenon is that the shapes of the colloidal spheres are changed on account of the mutual compression during the process of self-assembly, and then the distances among the spheres become smaller, and the dielectric filling ratio increases. The competition between the changes in distance and the filling radio determines the shift of the location of the PBG. The larger the size of the sphere, the greater the deformation and the greater the shift of the PBG location will be. But for sample D, the position of the PBG agrees well with Bragg's law. This is because the silica particles are too hard to be compressed. It can also be seen from the transmission spectra that there are Fabry–Perot (FP) fringes on both sides of the PBG, which means that the surfaces of the sample are smooth, flat, and uniform.[7]

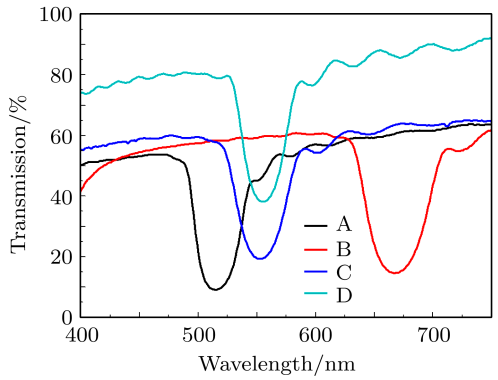


Fig. 3. (colour online) The normal-incidence transmission spectra of individual PS colloidal photonic crystals A (diameter 227 nm), B (diameter 250 nm), and C (diameter 312 nm), and silica colloidal photonic crystal D (diameter 256 nm).

Figure 4 shows the normal transmission spectra of colloidal photonic crystal C produced with inclined angles of 5°, 10°, and 15°, respectively. The depth of the photonic gap increases as the inclined angle increases. On the other hand, the depth of the photonic gap increases as the number of colloid crystal layers increases. This means that the number of particle layers increases with the increase in the inclined angle.

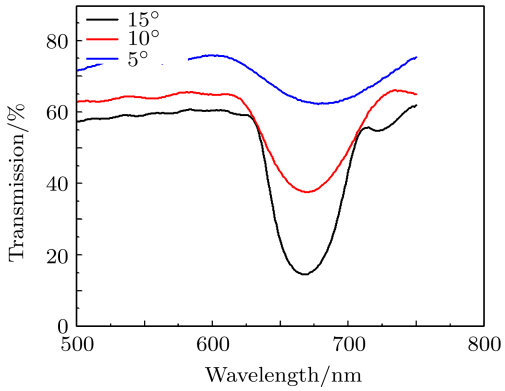


Fig. 4. (colour online) The normal-incidence transmission spectra of colloidal photonic crystal C produced with different inclined angles.

In the study of the self-assembly of colloidal spheres into two-dimensional (2D) arrays on a solid substrate using the LB technique, Dimitrov and Nagayama[13] derived a mathematic model to describe the formation of 2D arrays

$$k = \frac{\beta L}{0.605} \frac{j_{\mathrm{e}}\phi}{dV_{\mathrm{w}}(1-\phi)}, \tag{2}$$

where k is the number of layers, β is a constant depending on particle–particle and particle–substrate interactions, L is the meniscus height depending on the capillary constant,[14] d is the particle diameter, ϕ is the particle volume fraction of the colloidal suspension, j_{e} is the solvent evaporation rate, and V_{w} is the withdrawal velocity of the contact line. In our experiment, the contact line withdraws as the solvent evaporates from the surface of the colloidal solution. Supposing that the surface of the colloidal solution is $s_1 + s_2$, the declined angle is α, and the decreasing rate of the solution is V_{s}, as shown in Fig. 5, then we can obtain

$$V_{\mathrm{s}} = j_{\mathrm{e}}(s_1 + s_2) \approx j_{\mathrm{e}} s_1 (1+\alpha), \tag{3}$$

and

$$V_{\mathrm{s}} = s_1 V_{\mathrm{w}} \sin\alpha. \tag{4}$$

So from Eqs. (2)–(4), we have

$$k = \frac{\beta L}{0.605} \frac{\phi \sin\alpha}{d(1-\phi)(1+\alpha)}. \tag{5}$$

Equation (5) shows that the number of k layers depends on the particle diameter d, the particle volume fraction of the colloidal suspension ϕ, and the declined angle α. When $\alpha \leq 64°$, the number of k layers increases with the increase in the inclined angle α. Hence, the depth of the forbidden gap increases as the inclined angle increases, as shown in Fig. 4.

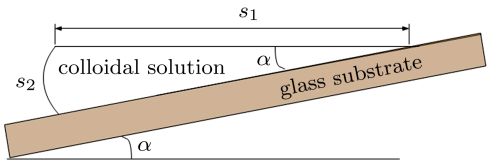


Fig. 5. (colour online) Illustration for the derivation of withdrawal velocity V_{w}.

3.2. Double-heterostructure

Figures 6(a) and 6(b) show cross-sectional SEM images of heterostructure D/A and double-heterostructure D/A/B, respectively. As shown in Fig. 6, each colloidal crystal layer exhibits a highly ordered structure with its (111) planes parallel to each other. Figure 7 shows the transmission spectra along the (111) direction for each step of the preparation of the double-heterostructure and individual crystal B. The final photonic crystal D\A\B (double-heterostructure) exhibits a wider stop band, and a tunneling peak appears within the band at 549 nm. Obviously, the tunneling peak within the optical stop band is not generated by simple overlapping of the spectra of their components. This phenomenon agrees with the previous reports.[15–17] On the one hand,

the superposition of the photonic band of the compositional colloidal crystal will obviously enlarge the stop band of the heterostructure. On the other hand, colloidal crystal A sandwiched between D and B can be treated as an asymmetric photonic quantum well, since the band gaps of colloidal crystals D and B are almost overlapping.

In order to confirm our experimental data, we performed 3D numerical simulations for double-heterostructure D/A/B and individual crystals A, B, D. We compared the simulated transmission spectra with the measured ones. MIT's free program Meep, based on the FDTD method, was used in the numerical simulations. A perfectly matched boundary condition was employed in the simulations. The numbers of sphere layers along the (111) direction for crystals D, A, and B were chosen to be 10, 14, and 10, respectively. The simulated result is presented in Fig. 8, and the simulated spectrum basically agrees with our experimental result. The tunneling peak at 554 nm is much more evident. The difference between the simulated result and the measured one is due to the fact that the number of sphere layers in the calculated model is more or less different from that in the actual model. Figure 9 shows the simulated transmission spectra for double-heterostructure D/A/B and individual crystals A, B, D. As shown in Fig. 8, the tunneling peak would not emerge if the photonic band structure of heterostructure D/A/B is a simple superposition of those of individual crystals A, B, D.

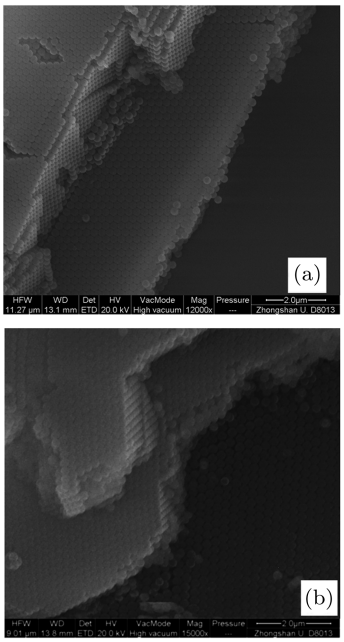


Fig. 6. (colour online) SEM images of (a) heterostructure D/A and (b) double-heterostructures D/A/B.

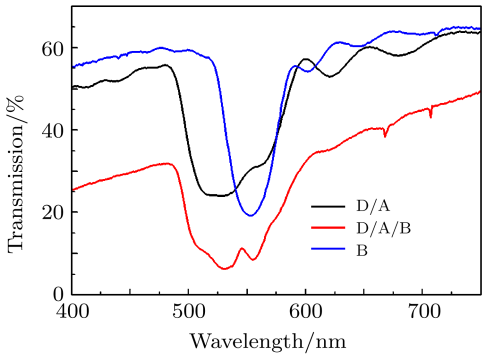


Fig. 7. (colour online) The normal-incidence transmission spectra for each step of the preparation of double-heterostructure D/A/B and individual crystal B.

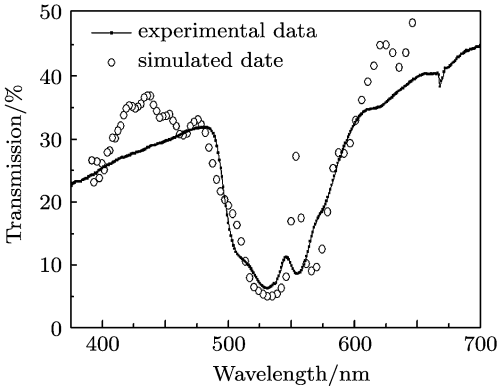


Fig. 8. (colour online) Comparison between the experimental and simulated transmission spectra for double-heterostructure D/A/B.

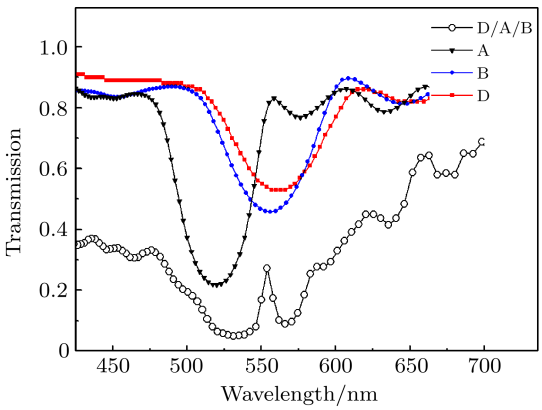


Fig. 9. (colour online) Simulated transmission spectra for double-heterostructure D/A/B and individual crystals A, B, D.

We can explain the appearance of a tunneling peak with the resonant cavity theory as follow. The light with a specific wavelength between the overlapping PBGs of crystals D and B will be reflected back by crystal D or B on its surfaces. So crystal A, which is sandwiched between crystals B and D, can be treated as a resonant cavity for the specific wavelength. When

the wavelength and the thickness of the cavity (the thickness of crystal A) satisfy certain conditions, a resonance can occur, and a resonant state will be generated. Consequently, the tunneling peak can be regarded as a resonant tunneling state, which appears within the overlapping PBGs of top crystal D and bottom crystal B at 549 nm.

4. Summary

In summary, we use a simple method to fabricate colloidal crystals. Such a method is valid for both silica particles and PS particles. The position of the PBG of the PS colloidal crystal shifts to a shorter wavelength because of the manual compression of the PS particles. With this method, the thickness of the colloidal crystal can be controlled by the inclined angle. We also use this method to fabricate a double-heterostructure composed of three different colloidal PCs. A resonant tunneling state within the overlapping PBGs of the top and bottom PCs is observed in the transmission spectrum of the double-heterostructure.

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