

## Pressure controlled self-assembly of high quality three-dimensional colloidal photonic crystals

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A concise pressure controlled isothermal heating vertical deposition (PCIHVD) method is developed, which provides an optimal growing condition with better stability and reproducibility for fabricating photonic crystals (PCs) without the limitation of colloidal sphere materials and sizes. High quality PCs are fabricated with PCIHVD from polystyrene spheres with diameters ranging from 200 nm to 1  $\mu\text{m}$ . The deep photonic band gap and steep photonic band edge of the samples are most favorable for realizing ultrafast optical devices, photonic chips, and communications. This method makes a meaningful advance in the quality and diversity of PCs and greatly promotes their wide applications. © 2007 American Institute of Physics. [DOI: 10.1063/1.2435613]

Photonic crystals have the properties of confining and controlling the propagation of light due to the existence of photonic band gaps in these periodic dielectric structures.<sup>1,2</sup> The unique optical properties make them have wide applications in optical communications, photonic computing, switching, sensing, lasing, and solar cells.<sup>3-7</sup> To realize these utilizations, significant efforts have been devoted to fabricate photonic crystals.<sup>8-19</sup> Among them, the colloidal sphere self-assembling provides a simple, cost-efficient approach to fabricate three-dimensional (3D) photonic crystals (PCs).<sup>12-19</sup> Vertical deposition method, developed by Jiang *et al.*<sup>12</sup> is widely used to form large scale single-crystalline PCs with controllable thickness and superior quality compared to other self-assembly methods.<sup>8-19</sup> Recently, some effectively improved approaches based on the vertical deposition method have been developed to break through its two limitations: sedimentation of large colloidal spheres and long evaporation time.<sup>20</sup> Vlasov *et al.* added a vertical temperature gradient to enhance convective flows in sphere dispersions and successfully produced colloidal crystal films with 855 nm silica spheres.<sup>21</sup> Kitaev and Ozin *et al.*<sup>22</sup> applied accelerated evaporation technique to assemble surface patterns of binary colloidal crystals. A great development was made by Wong *et al.*<sup>20</sup> in their isothermal heating evaporation-induced self-assembly (IHEISA) method. They successfully assembled high quality colloidal crystal films from 1  $\mu\text{m}$  silica spheres in a short time. However, two side effects were yielded due to the fixed high isothermal heating temperature which is slightly above the boiling point of solvent: (1) the heavy necking of polystyrene (PS) spheres during deposition,<sup>20</sup> which are widely used to fabricate tunable band gap photonic crystals and the template for inverse opal, and (2) the non-adjustable solvent evaporation rate. The current issue is that none of the self-assembly methods available is suitable for

assembling colloidal spheres of various materials and different sizes. Moreover, the quality of photonic crystals made by these methods cannot meet the practical optical applications yet, which need deep photonic band gaps (PBGs) and steep photonic band edges (PBEs).<sup>6</sup> It is well known that holding the evaporation rate at an optimal value is crucial for the regular assembling of colloidal spheres.<sup>13,14</sup> The excessively high or low speed of the solvent evaporation induced the as-grown defects and disorders in the growing crystals. In the methods mentioned above, only one parameter (e.g., temperature or pressure) can be adjusted during deposition, which makes it difficult or even impossible to obtain the optimal growing condition for PC growth. Therefore, a self-assembly method with more controllable growth parameters is necessary for keeping the optimal evaporation rate steady.

As will be discussed and formulated later, the evaporation rate depends on both temperature and pressure. According to the relation between the boiling point of solvent and pressure, a concise pressure controlled isothermal heating vertical deposition method is proposed herein, which stemmed from the IHEISA method, in which the isothermal heating temperature and the pressure in the growth chamber can be adjusted simultaneously. By maintaining the critical condition of near boiling to form an enhanced convective body flow, as shown by IHEISA,<sup>20</sup> the colloidal spheres are kept uniformly dispersing in solution. Meanwhile, the boiling point of solvent can be significantly changed by adjusting the pressure. Hence, the isothermal heating temperature and evaporation rate can be adjusted in a wide range, which is limited in IHEISA. Therefore, an optimal evaporation rate can be precisely obtained for fabricating high quality 3D PCs. In addition, the materials for making PCs can be greatly extended by reducing the temperature.

3D PCs are fabricated by means of pressure controlled isothermal heating vertical deposition (PCIHVD) method from aqueous solutions of PS spheres with diameters of 235 nm, 360 nm, 451 nm, 596 nm, and 1  $\mu\text{m}$ . (PS spheres with diameter of 235 nm are supplied by Beijing Technical

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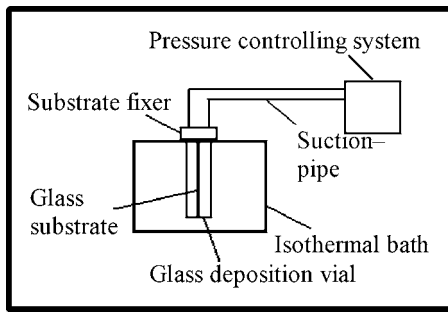


FIG. 1. Schematic of the experiment equipment for PCIHVD method to fabricate colloidal photonic crystals.

Institute of Physics and Chemistry, Chinese Academy of Science. Other PS spheres are purchased from Duke Scientific Corporation.) The aqueous dispersions of PS spheres are placed in cylindrical glass vials, respectively. Concentrations ranging from 0.05 to 3 wt % are diluted with de-ionized water. The vials containing the diluted colloidal dispersions are immersed in an isothermal deposition bath. Glass microscope slides are cleaved into two equal pieces lengthwise, cleaned with ethanol for several times, and dried in a stream of nitrogen. The glass slide is fixed in the center of the vial with the PS dispersion. Finally, the vial is sealed and connected to the pressure controlling system. The schematic of the experiment setup for the PCIHVD method is shown in Fig. 1. The pressure controlling system is just a vacuum pump connected to the deposition vial with a soft suction pipe. The pressure in the growth chamber is measured using a mercury vacuum gauge. The vacuum pump is started and the pressure is precisely adjusted in the growth chamber with a needle valve. The temperature and the pressure in the deposition vial will become steady in 3 min.

In order to obtain the optimal growth condition, the evaporation rate is altered by adjusting the pressure and is measured during experiments. It is found that the evaporation rate  $\dot{m}_1$  increases considerably with the elevation of boiling point in our method and can be well described by Stefan's law,<sup>23</sup>

$$\dot{m}_1 = (Dl/R_1T) \ln[(P - P_{1s})/(P - P_{1w})], \quad (1)$$

where  $D$  is the diffusion coefficient of water vapor in air,  $l$  is the distance from the liquid surface to the open end of the vial,  $R_1$  is the gas constant of water vapor,  $T$  is the temperature at the liquid surface, and  $P$ ,  $P_{1s}$ , and  $P_{1w}$  are the total pressure in the growth chamber and the water vapor pressure at the open end of the vial and at the liquid surface, respectively. Table I shows the calculated (Calc.) and average experimental (AE) evaporation rates at different growing conditions, as well as the corresponding optical qualities of the resulting samples by taking 235 nm PS spheres, for example.

TABLE I. Influence of different growing conditions on the quality of PS PCs made with the PCIHVD method (see explanations in Ref. 24).

Heating temperature (°C)	20.0	30.0	35.0	40.0	50.0	
Pressure (mm Hg)	16.1	29.3	39.0	51.3	85.9	
$\dot{m}_1$ (g/cm <sup>2</sup> hd)	Calc.	0.27	0.45	0.67	0.93	1.3
	EA	0.30	0.48	0.71	1.02	1.45
Typical PBG depth (%)	65–70	70–75	>80	60–65	50–60	
Typical maximal PBE slope (%/nm)	4.0–4.5	5.0–5.5	>7.0	3.0–3.5	2.0–2.5	

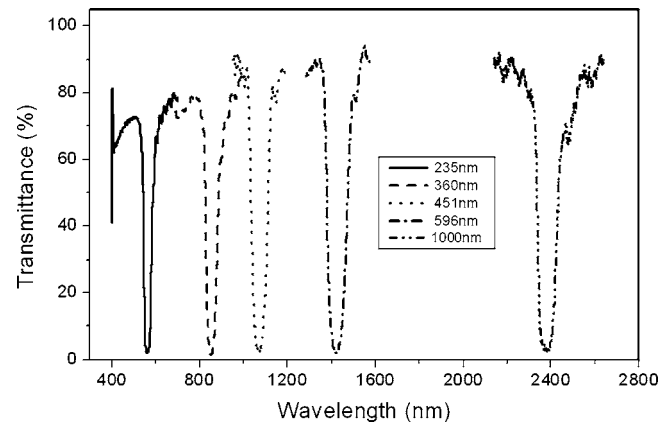


FIG. 2. Transmittance spectra of the PCs formed from 235 nm, 360 nm, 451 nm, 596 nm, and 1  $\mu$ m PS spheres by PCIHVD method under the optimal growth condition.

It indicates that at the optimal growth condition of 35.0 °C and 39.0 mm Hg, in which the evaporation rate is determined to be about 0.71 g/cm<sup>2</sup> h, 3D PS PCs with the largest PBE slope and PBG depth are fabricated. While increasing or decreasing the evaporation rate, the optical quality of the resulting samples worsens gradually.

In the transmittance spectra for all of the samples made in the optimal condition (Fig. 2), the transmittances at the center of the PBGs and in the passbands are below 2% and above 80%, respectively, and the largest slopes of shortwave PBE exceed 5 %/nm. Especially, the maximal slope of the PBE for samples made with 235 nm PS spheres has exceeded 7 %/nm, owing to their better polydispersity (below 1%) compared to other PS spheres used in our experiments (3%). The steep PBE and deep PBG of these PS PCs are especially important for producing optical devices based on PBE or PBG shift of tunable photonic band gap crystals such as the ultrafast all-optical switch,<sup>6,7</sup> which is extensively applied in optical communications and photonic chips. In addition, the well defined Fabry-Pérot fringes in the transmittance spectra demonstrate the high uniformity of the film.<sup>12</sup> From the Fabry-Pérot fringes, the thicknesses of PCs are figured out to be about 25–35 layers,<sup>25</sup> which coincides with the inspection of the SEM images. As shown apparently in the top view scanning electron microscopy (SEM) images (Fig. 3), these samples have a high degree of hexagonal ordering; almost no defects are observed over the measured scales. The colloidal crystal film thickness can range from several to nearly 50 layers, approximately linear with the increase of the concentration of PS sphere in a single deposition. Figure 4 shows the cross-section SEM images of colloidal crystals and the dependence of the thickness of colloidal crystals on the concentration of spheres in dispersion by taking 235 nm PS spheres, for example, the high-degree vertical ordering maintains well throughout the whole thickness in PCs. The nearly perfect PCs with sufficient thickness guarantee the deep PBGs and steep PBEs.<sup>26</sup>

In our method, not only are the advantages of previous methods such as the enhanced body flow and fast growth rate preserved but we can also benefit more from controlling the pressure and the temperature simultaneously in the growth chamber. Firstly, the optimal condition for making high quality PCs can be easily found through changing the evaporation rate in a wide range by adjusting the pressure. Secondly, the growing conditions are more controllable and shielded

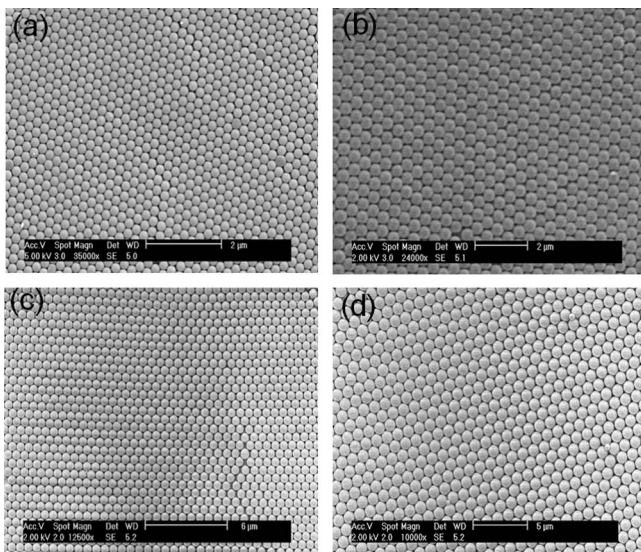


FIG. 3. Top view SEM images of the PCs formed from (a) 235 nm, (b) 451 nm, (c) 596 nm, and (d) 1  $\mu\text{m}$  PS spheres by PCIHVD method under the optimal growth condition.

from outside disturbance by the close deposition system, which provides the growing process with better stability and reproducibility. Furthermore, the heating temperature can be significantly altered by changing the pressure. Therefore, the distortion, conglutination, and damage to the material properties of colloidal spheres due to high temperature can be effectively avoided through reducing of the temperature to an appropriate range. As a result, the materials of building blocks are largely extended, especially for organic and biological active materials.

In conclusion, we develop an efficient, facile, and well reproducible PCIHVD method for fabricating 3D PCs. The superior optical quality of large PBE slope and PBG depth and the structural perfection of the resulting PS PCs have

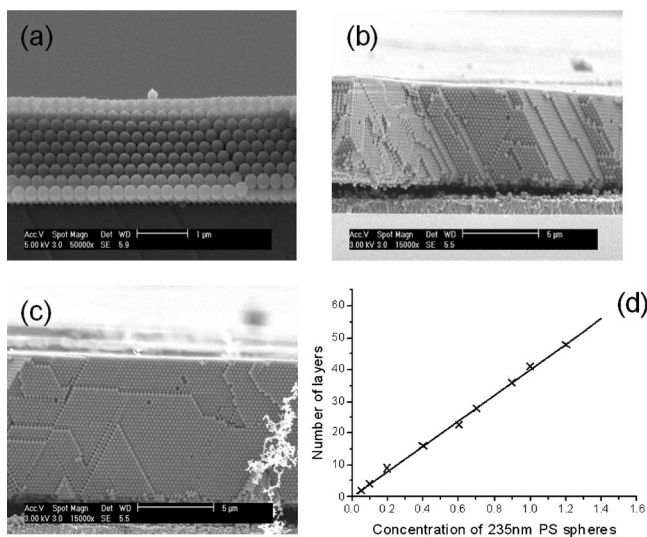


FIG. 4. Cross-section SEM images [(a)–(c)] of colloidal photonic crystals made by PCIHVD method under the optimal growing condition from 235 nm PS spheres. The nether right plot (d) shows the dependence of the thickness of colloidal crystal films (plotted as the number of layers) on the concentration of 235 nm PS spheres in dispersion.

confirmed the success of this method. More importantly, the wide applicability of this method can hardly be overemphasized because it is free of the limitations of materials and sizes of colloidal spheres. We believe that the PCIHVD method makes a meaningful advance in the quality and diversity of PCs and will greatly promote the practical applications of PCs in many areas.

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