Features of the deposition of photonic crystal films of polystyrene and silica

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Abstract. The paper presents the results of research in the field of deposition technology for self-organizing colloidal films. Such structures can be used in the manufacture of controlled photonic crystal devices. Therefore, it is important to determine methods and modes of obtaining high-quality ordered periodic opal structures. We compare the methods of vertical deposition and electrophoresis and discuss the features of their application in the deposition of films formed from colloidal particles of polystyrene and silica. We have found that vertical film deposition when the substrate is pulled out of the colloidal suspension is the most technologically convenient and suitable for both materials. The electrophoresis method is more difficult to implement, but it allows you to control the deposition process in dynamics. In this article, we present the identified rational modes of obtaining photonic crystal films by both methods.

1. Introduction
Self-organization of colloidal particles is the most technologically advanced way to obtain photonic crystals. The optical properties of smart photonic crystal (PhC) structures based on colloidal films can be switched by the action of gases and liquids, electric and magnetic fields, mechanical stress and temperature changes [1-4]. In this respect, colloidal films, composite and inverse structures obtained by introducing functional materials into the pores between the colloidal particles and then removing these particles, respectively, are of interest [5-7].

Colloidal photonic crystal films are obtained by deposition a suspension containing monodisperse spherical particles by gravitational sedimentation, centrifugation, vertical deposition, electrophoresis and Langmuir-Blodgett methods [8]. Self-assembly of polymer or silica (SiO$_2$) colloidal particles with diameter in the range from 200 to 1000 nm plays the main role in the formation of PhC structure [9, 10]. The ordering of the structure is determined by the ability of the particles to coagulate (adhere to each other), which is determined by surface external charge of the microspheres. Various strategies have been developed to direct the self-assembly of colloidal particles, but fabrication of PhC large area films without cracks and defects remains an unsolved task [11]. In this work methods of vertical deposition and electrophoresis were used, since these methods are characterized by the presence of controlled modes. The quality of the obtained films is determined by a large number of factors; therefore, special attention must be paid to the reproducibility of the deposition technological processes. We solve this problem by using special automated equipment [12, 13]. Thus we could regulate the parameters of the deposition processes.
2. Methods and materials description

We used commercial polystyrene monodisperse carboxylated latex (PS) and silica made by us. The method for producing a silica suspension was a modified Stöber method. The essence of the method is hydrolysis of tetraethoxysilane Si(OEt)₄ (TEOS) in an aqueous-alcoholic suspension by ammonia catalyst as it shown in the Figure 1.

![Figure 1. Schematic representation of the Stöber method. At the final stage of the process, nanoclusters grow and turn into colloidal particles with a size of hundreds of nanometers.](image)

The vertical deposition method has gained great interest because of its simplicity and ability to vary the conditions. Usually in this process the substrate is placed vertically in a particles suspension and is gradually exposed by evaporation or other slow solvent removal. We implemented the vertical deposition method by vertically lifting the substrate from a colloidal suspension. The method of electrophoresis is the deposition of colloidal particles on one of the electrodes immersed in the suspension. Figure 2 shows the general schemes of both methods. Films were deposited on ceramic, quartz, polycor and silica substrates. To implement electrophoretic deposition a thin film of a conductive material, copper or silver, was preliminarily applied to the substrates in thermal evaporation in a vacuum.

![Figure 2. The general scheme of the vertical deposition method (a) and electrophoresis (b).](image)

In our experimental studies we used suspensions with different particle diameters in the range from 100 nm to 600 nm and their concentration from 1 % to 5 %. When depositing films by the vertical stretching method, we changed the substrate speed from 0.1 mm/min to 10.0 mm/min. When using electrophoresis, the voltage supplied to the electrodes was changed from 0.8 V to 6.0 V, deposition time was varying from 5 min to 10 min; pH was equal to 7.

Each method has its own advantages and disadvantages in terms of technology. The vertical stretching method does not require any preliminary preparation of the substrate except for its cleaning. Electrophoresis is possible if there is a conductive substrate or an underlayer on it. On the other hand, the film deposition in this process can be controlled by varying the duration of the process, while in vertical deposition the film thickness is determined by a combination of a large number of factors and is difficult to determine it theoretically.
3. Results

It was revealed that the method of vertical lifting is more inherent in single-crystallinity of the deposited films than electrophoresis. PS particles, when deposited by the method of vertical stretching, form single-crystal regions tens of microns in size. The best quality structures have been obtained for particles diameters varying from 220 nm to 330 nm, lifting velocity of 0.3 mm/min and suspension concentration of 5%. The reflection spectrum and the surface structure for 300 nm particles film are shown in figure 3.

![AFM image of PS film](image1)

![Reflection spectrum of the polystyrene film](image2)

Figure 3. Vertical lifting method: (a) AFM image of PS film, hereinafter dimensions in micrometers are plotted along the image axes, (b) the reflection spectrum of the polystyrene film.

The electrophoresis method is more complicated to implement, but it is interesting for the possibility of obtaining an ordered monolayer of colloidal particles and depositing films on curved surfaces. Figure 4a shows an AFM image of a PS film obtained by electrophoresis with a voltage of 1.6 V.

The properties of a suspension of silica particles are highly dependent on the storage time. We recommend using a “freshly” prepared suspension that has been stored for no longer than 3...5 days. Silica particles have a tendency to coagulate, which is especially evident when using electrophoresis. For this material the most successful samples were obtained by the vertical lifting method, AFM-image of such a film is shown in Figure 4b.

![AFM image of PS film deposited by electrophoresis](image3)

![AFM image of silica film deposited by vertical lifting](image4)

Figure 4. Colloidal films: (a) AFM image of PS film deposited by electrophoresis, (b) AFM image of silica film deposited by vertical lifting.
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Presented films show opalescence: reflected colors that come from the Bragg diffractions in the periodic distribution of microspheres. The reflection spectrums of the samples demonstrate the presence of a photonic band gap. Reflection in its region depends on the area of single-crystal areas. The most successful samples had a reflection of 20 ... 30 %.

4. Conclusion
We managed to obtain samples of colloidal films with a photonic crystal structure of opal matrices. The methods and process parameters used for this are presented in the work. The overall dimensions of local single-crystal regions in these films are tens of micrometers. Experiments have shown that it is necessary to work out not only the modes of film deposition, but also the synthesis and storage of colloidal suspensions.

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