Solvent Effects in Colloidal Crystal Deposition

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The effects of solvent in the deposition of opal films from colloidal suspensions of polystyrene spheres have been studied with respect to the newly developed capillary deposition method and the well-known vertical deposition method. Both the surface morphology and the fine structure of the opal films are influenced by the solvent significantly. An optimized solvent mixture for fabrication of high-quality opal films has been found, and possible influence mechanisms of solvent are discussed.

1. Introduction

The strong interest in photonic crystals stems from their potential to confine and control the propagation of light in ways that were previously impossible.[1–4] Self-assembly of colloidal spheres is one of the most promising approaches to three-dimensional opaline photonic crystals.[5,6] Very often it exploits capillary forces for sphere self-assembly.[7–9] The vertical deposition method (VD method) is a very successful and versatile example of the use of capillarity for the preparation of opal films.[10] Several modifications, such as temperature gradient[11] or isothermal heating,[12] have also been applied to the vertical deposition process in order to extend the application of this promising method and improve the quality of the opal films. In most of the preparations by the VD method ethanol or water has been utilized as solvent.

Recently, an improved method for the growth of opal films was found.[13] This capillary deposition method is also based on self-assembly; yet, efficient control during the fabrication of opal films is possible. Opal films with controlled crack alignments and lateral opal heterostructures consisting of different-sized polystyrene (PS) spheres have been successfully produced using this method.[13,14]

Even though intense efforts have been done to control the deposition process and improve the quality of the opal films, the film quality is far from the requirement for practical applications;[15] therefore, the control of morphology and quality improvement are still challenges in the preparation of colloidal crystals. When opals are deposited onto solid substrates by a self-assembly process, contraction phenomena during drying lead to crack formation.[16,17] The reason for the contraction is a little separation between the spheres in the wet opal which disappears in the dry opal. Although the mechanisms of drying were well understood for gels,[18] the basic mechanisms in the case of suspensions are still being researched.[19] Some basic questions, for example, the influence of viscosity and surface tension on the morphology (crack distribution and film thickness) and fine structure (ordering of the spheres) of the opal films, are still unclear or even controversial.[20] The properties of the solvent, such as its surface tension, viscosity, and volatility, can be easily tuned when a mixed solvent is used. Varying the ratio of the components in such a mixed solvent[21] changes these properties and enables the study of the solvent effect in the process of opal deposition. The choice of solvent could be a versatile possibility of tuning the assembly process.

In this article we investigate the solvent effects based on the newly developed capillary deposition method using different ethanol/water mixtures. Several solvent-related phenomena in the opal film fabrication are described in the Results section and analyzed in the Discussion section. The results obtained from the vertical deposition method are presented for comparison.

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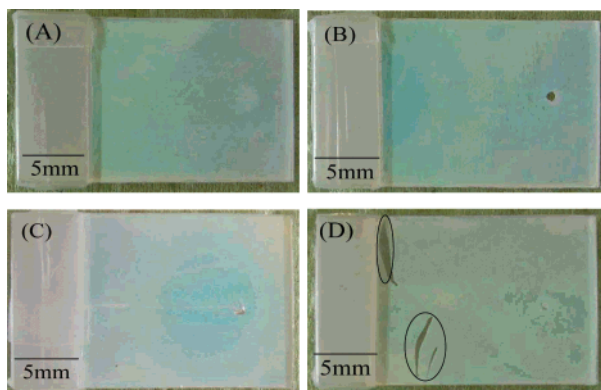(21) *Handbook of Chemistry and Physics*, 43rd ed.; CRC Press: Boca Raton, FL, 1961; pp 111 and 133.

Figure 1. Overviews of the opal films made from 260 nm PS suspensions of different solvents: (A) H$_2$O, (B) 1/4 ethanol/water, (C): 1/1 ethanol/water, (D) pure ethanol (positions of the voids are marked).

2. Experimental Section

Materials. Suspension of 10 wt % 0.26 μm PS spheres (deviations smaller than 3%; Duke Scientific) was used as received. Ordinary glass slides and glass slides with a 1 mm hole were cleaned in 5% Labosol (Neolab) aqueous solution for 0.5 h and then rinsed with deionized water completely. After rinsing the slides were dried under an air flow. Corresponding capillary tubes with a 1 mm external diameter and 20 mm length have been used.

Capillary Cells. A planar capillary cell with three open sides was mounted using two glass slides of the same size separated by a strip of thin spacer (e.g., Hostaphan RN, Pütz GmbH Folien KG, Germany). One of the glass slides was provided with a hole 1 mm in diameter. A detailed scheme of the setup is shown in refs 13 and 14.

Opal Film Deposition. The original 10 wt % 0.26 μm polystyrene suspensions were diluted with pure water, pure ethanol, or ethanol/water mixtures of different ratios to obtain diluted PS suspensions of 0.5 vol % in each case. The diluted suspensions were used for the opal film deposition by both the capillary deposition method and the VD method. In the first case, capillary cells were filled with the suspension, allowing the opal self-assembly. In the case of vertical deposition, single slides were vertically immersed into the suspension and exposed to evaporation.

3. Results

3.1. Capillary Deposition Method. *3.1.1. Overview Images.* Figure 1A−D shows the global views of the 75 μm thick opal films obtained from the different solvents by the capillary deposition method. From the images we can see that they are quite similar, except that the film made from ethanol suspension shows a few voids. The voids are likely formed due to the low surface tension and viscosity of ethanol (see section 4.1.2). It should be noted that film thickness and thickness homogeneity are crucial for the comparability of the different films. Variations in them influence other properties of the film, making the comparison more complicated and even unreliable. Control of the film thickness by simply changing the spacer regardless of solvent and suspension concentration is one of the advantages of the capillary deposition method.[13] This advantage ensures a homogeneous and well-defined thickness of opal films made from different suspensions.

3.1.2. Crack Distributions. As shown in Figure 2 the capillary deposition method provides opal films with regular crack alignments. The spacing between cracks can be used for studying the influence of solvent. Parts A, B, C, D, E, and F show the crack distributions in films prepared from suspensions in water, 1/4 (v/v) ethanol/water, 1/2 ethanol/water, 1/1 ethanol/water, 4/1 ethanol/water, and ethanol, respectively. An average spacing between cracks of 120, 165, 185, 200, 175, and 130 μm, respectively, has been observed using an optical microscope. The relationship between the average spacing and the volume fraction of ethanol in the mixed solvent has been plotted in Figure 3. Maximum average spacing is reached for a 1/1 mixing ratio.

3.1.3. SEM Overviews. To get more details on the crack distributions in the opal films, SEM investigations have been carried out. Figure 4 shows the low-magnification SEM images of the corresponding opal films described in Figure 2. The average spacing between cracks observed from these SEM images is consistent with the values obtained from the optical microscope. The images also reveal that the solvent influences not only the average distance between cracks, but
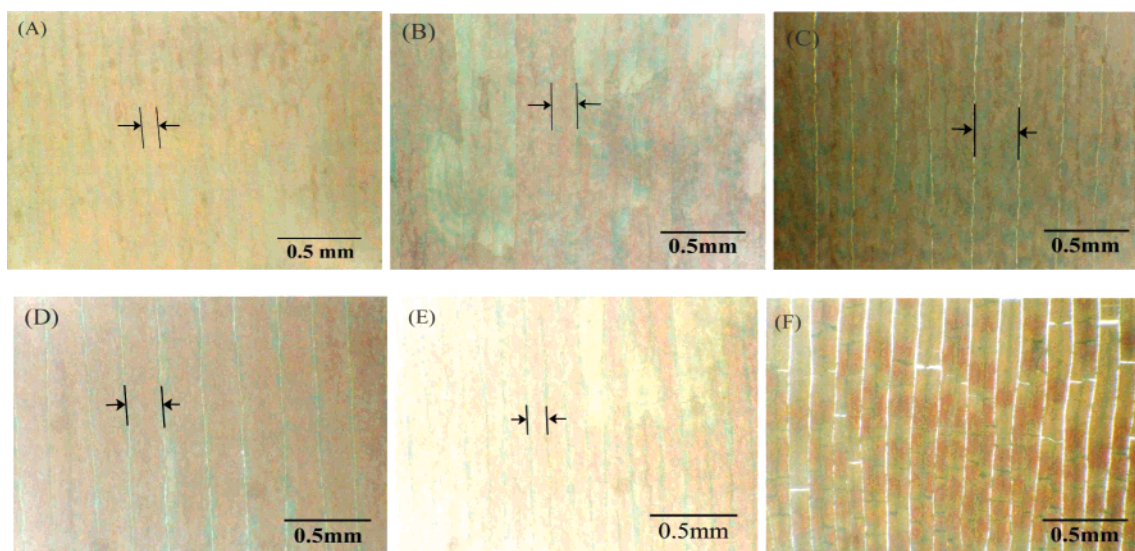

Figure 2. Crack patterns in the opal films derived from 260 nm PS suspensions using different solvents: (A) water, (B) 1/4 (v/v) ethanol/water, (C) 1/2 ethanol/water, (D) 1/1 ethanol/water, (E) 4/1 ethanol/water, (F) ethanol.
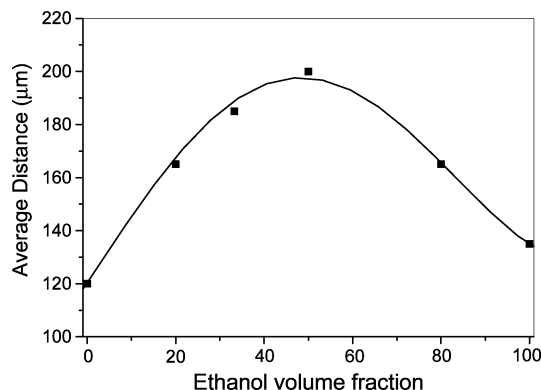
Figure 3. Average spacing between the cracks as a function of the ethanol volume fraction in the mixed solvent.

also the crack distribution. For a pure aqueous suspension, the cracks are aligned parallel to each other and perpendicularly to the open sides of the capillary cells. Few short cracks normal to the main cracks are also observed. For the films prepared from PS suspension of 1/4, 1/2, and 1/1 ethanol/water mixture solvent, the cracks are most regular. When pure ethanol is used as solvent, most irregular cracks have been observed in the film (Figure 4F).

SEM requires direct access to the surface of interest which is why one substrate slide must be detached. Such a detachment peels off parts of the top layer, resulting in structures visible in Figure 4C−E. This has been verified by the high-magnification SEM observations of both substrate slides.

3.1.4. Fine Structures. Does the solvent influence only the surface morphology of the films or can it also modify the fine structure of the opal films? To answer this question high-magnification SEM images were made to see the detailed structures (Figure 5A−F). Obviously, the fine structure of the opal films is influenced by the solvent. The defect densities of the opal films have been determined by counting the visible defects per unit area and related to the ethanol fraction in the solvent as shown in Figure 6. The least defects are observed for 1/4 ethanol/water. Films derived from pure

water show a defect density similar with those obtained from the 1/2 ethanol/water suspension. Pure ethanol is not a suitable solvent for the preparation of thick opal films as the film is mostly disordered (Figure 5F).

3.1.5. Optical Properties. Optical properties can also be used to assess the quality of the opal films. Here we use two parameters to compare the qualities of the spectra: the Bragg peak intensity and the background. In principle, for opal films with the same thickness, an intense Bragg peak and a low background reflect the perfection of the opal structure. Figure 7 shows the UV−Vis−NIR spectra of the samples derived from different suspensions. The intensities of the Bragg peaks increase in the series pure ethanol, 4/1 ethanol/water, 1/1 ethanol/water, pure water, 1/2 ethanol/ water, and 1/4 ethanol/water. The opal film prepared with 1/4 ethanol/water as solvent shows the highest intensity and the lowest background, which means the quality of this film is the best one among them. The film made from 4/1 ethanol/ water suspension shows a reduced peak intensity and the highest background. The opal film with the worst quality made from the ethanol suspension shows almost no peak. Its relatively low background can be explained as being due to the large cracks inside the film. The UV−Vis−NIR spectra results are consistent with the direct SEM observations.

3.2. Vertical Deposition Method. *3.2.1. Overviews.* Both the capillary deposition method and the widely used VD method exploit capillary forces during the deposition process, but the practical aspects are in contrast. Therefore, we investigated the vertical deposition method with different solvents in order to understand the solvent effects in the different processes of opal film deposition.

Figure 8A−D shows overviews of the films prepared by the VD method from different solvents. The black lines in the pictures indicate roughly the immersion levels of the slides upon insertion into the suspensions. The immersion depths of the four slides are the same; however, the resulting film morphologies are quite different. The films derived from
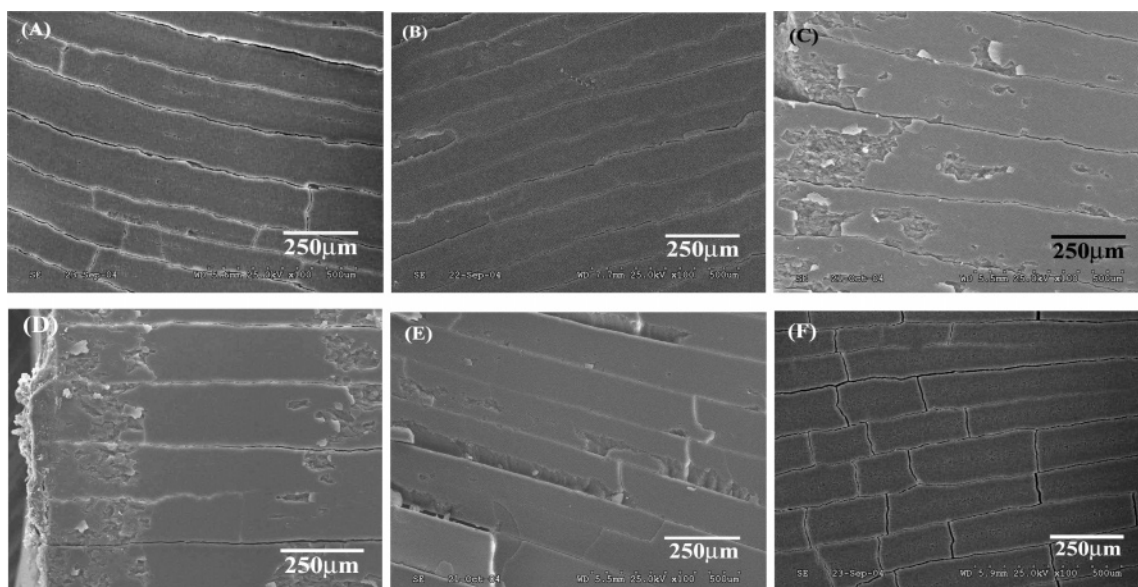

Figure 4. SEM overviews of the opal films derived from suspensions of different solvent: (A) water, (B) 1/4 (v/v) ethanol/water, (C) 1/2 ethanol/water, (D) 1/1 ethanol/water, (E) 4/1 ethanol/water, (F) ethanol.
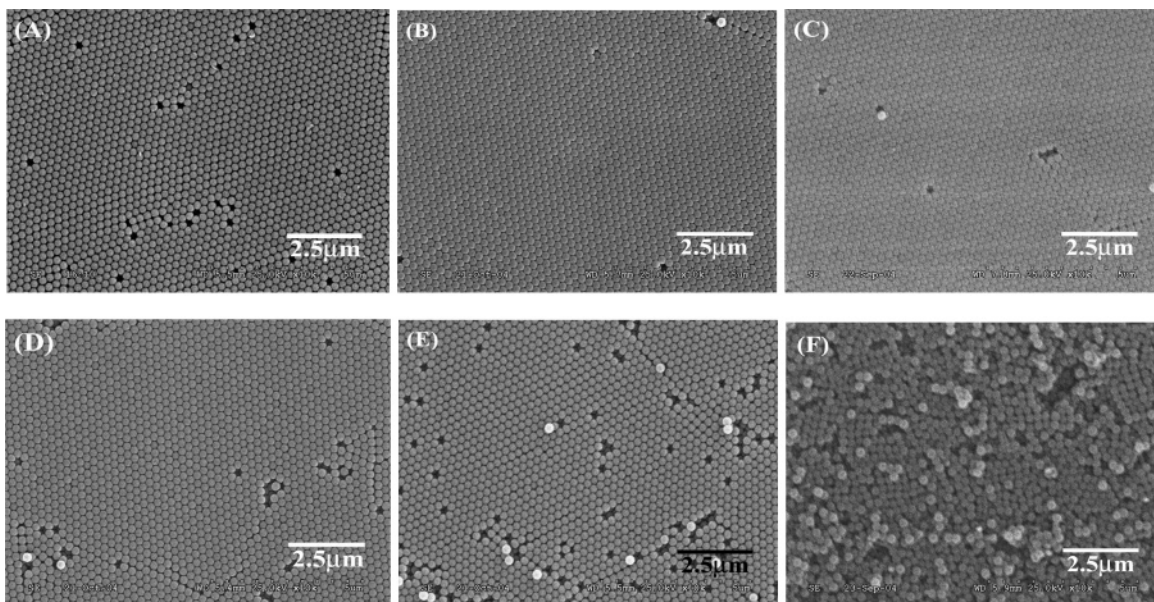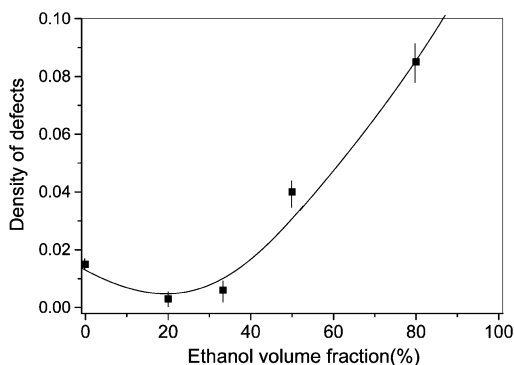
Figure 5. High-magnification images of the opal films derived from 260 nm PS suspensions of different solvents: (A) water, (B) 1/4 (v/v) ethanol/water, (C) 1/2 ethanol/water, (D) 1/1 ethanol/water, (E) 4/1 ethanol/water, (F) ethanol.

Figure 6. Relation between defect density and ethanol volume fraction. The error bars result from an assumed $\sqrt{N}$ mistake for N counted defects.
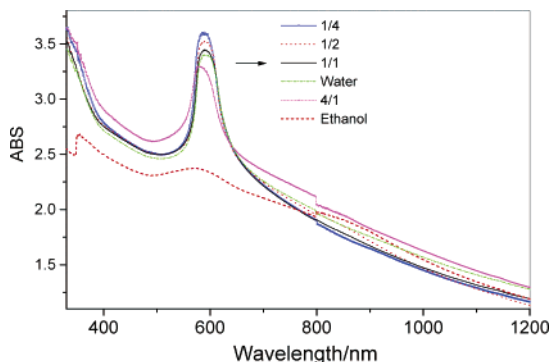

Figure 7. UV−Vis−NIR spectra of the opal films made from 260 nm PS dispersed in solvents with different mixing ratios (indicated).

Figure 8. Overviews of the opal films made by the VD method from 260 nm PS in different solvents: (A) water, (B) 1/4 ethanol/water, (C) 1/2 ethanol/water, (D) pure ethanol. The black lines show the initial level of immersion of the slides, and the arrow in A indicates the film growth direction. At the right side of the black line in B and C a filmless area is observed.

the aqueous and ethanol suspensions are more homogeneous than those obtained from suspensions of the ethanol/water mixtures. The films obtained from ethanol/water mixtures show a basically filmless area with some film residues just below the immersion level. This naked area is larger for the film prepared from 1/2 ethanol/water suspension than for the others.

Even though the same initial concentration of PS has been used for the film depositions, the thicknesses of the four samp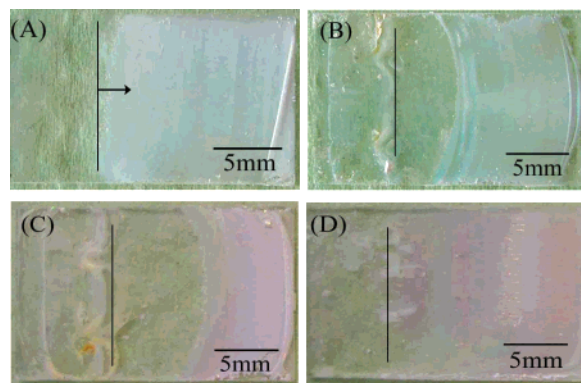les are obviously quite different. Simultaneously, the yield of opal deposition (amount of PS deposited on the slide per used PS in the suspension) varies. For water as solvent the yield is about 80%; however, the yields decrease with the increasing amount of ethanol in the solvent. The opal film derived from the ethanol suspension shows a very low yield, and most of the PS spheres are deposited on the bottom of the container.

3.2.2. Optical Microscopy Images. Figure 9A−D shows the optical microscopy images of the four opal films described in Figure 8. In all samples grid-shaped cracks cover the films. Their appearance is much different from the parallel cracks in the opal films derived from the capillary deposition method. The cracks separate areas of perfect order with different size for the four films. However, this size is related not only to the solvent parameters but also to the obtained thickness. It has been observed that thicker opal film regions have larger perfect areas. The opal film derived from ethanol suspension shows very tiny perfect areas. Very likely this can be related predominantly to the low opal film thickness.
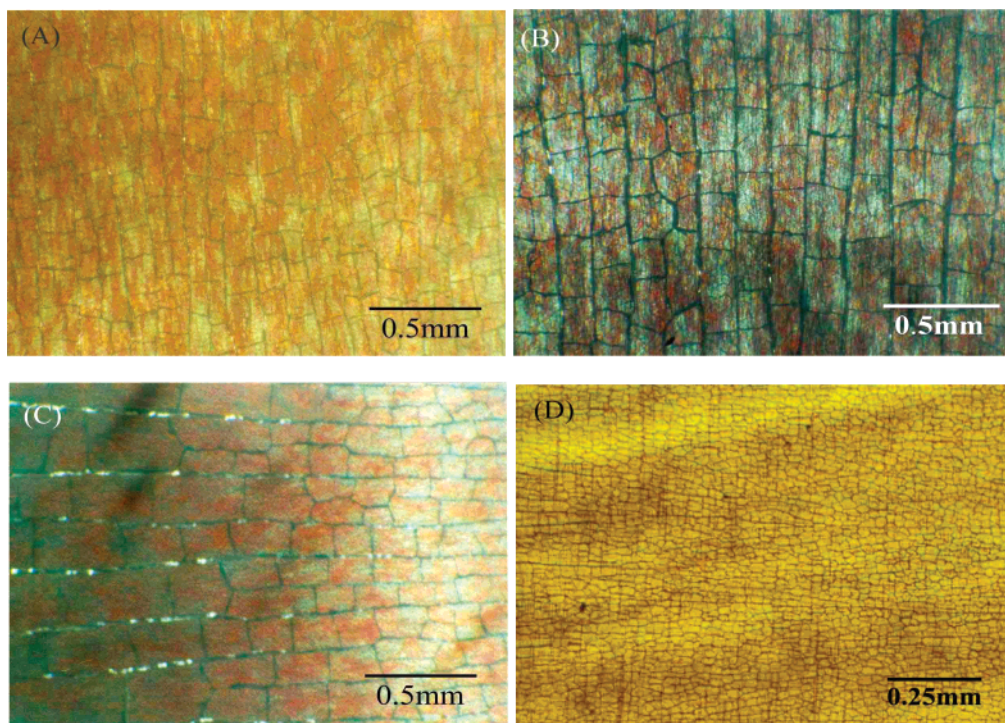
Figure 9. Optical microscopy images of the opal films made by the VD method from 260 nm PS colloids in different solvents: (A) water, (B) 1:4 (v/v) ethanol/water, (C) 1:2 ethanol/water, (D) pure ethanol.
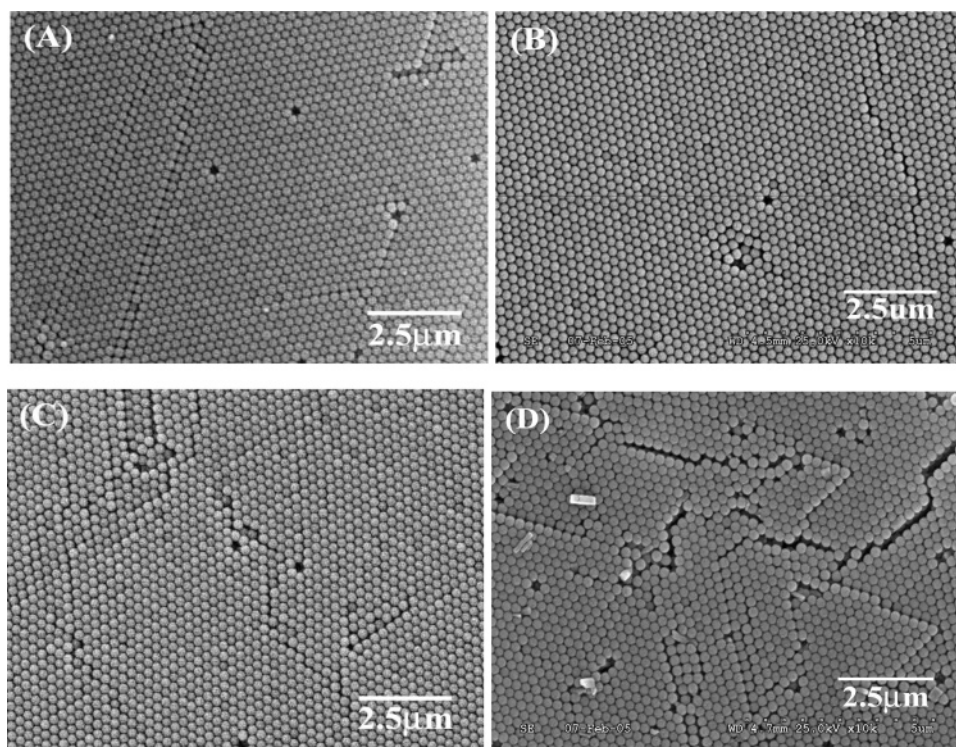

Figure 10. SEM images of the opal films made by the VD method from 260 nm PS colloids of different solvents: (A) water, (B) 1:4 (v/v) ethanol/water, (C) 1:2 ethanol/water, (D) pure ethanol.

At this point it becomes clear that the control of the vertical deposition method by variations of the solvent is not very convenient due to the resulting thickness inhomogeneity, the yield variations, and the uncontrolled cracks.

3.2.3. SEM Images. SEM investigations have been carried out to reveal the fine structure of the films from different suspensions by the VD method. Figure 10 shows the typical images of them. The film obtained from the 1/4 ethanol/

water mixture suspension shows the best quality (Figure 10B) visible in the lowest number of point and line defects. Lower and higher ethanol concentrations lead to an increase of the defect numbers. The difference between them has also been reflected in their optical properties (see section 3.2.4). The highest number of lattice defects results in films produced from pure ethanol suspensions. SEM investigations show that the influence of solvent on the quality of opal films prepared
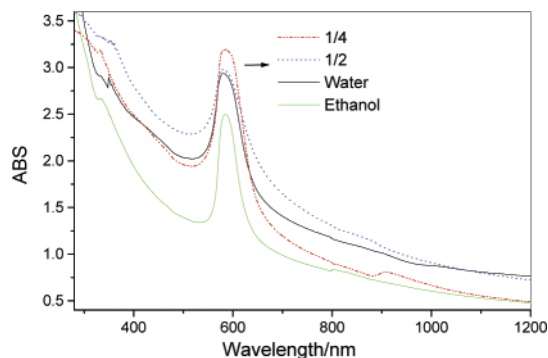
Figure 11. UV−Vis−NIR spectra of the opal films made by the VD method from 260 nm PS in different solvents.

by the VD method is very similar to that observed for the capillary deposition method.

3.2.4. UV−Vis−NIR Spectra. Figure 11 shows the transmission spectra of the opal films made from different suspensions. The comparison of opal quality based on their optical properties is difficult for the VD-prepared opal films because they have nonconstant thickness. The film thickness influences the Bragg peak intensity and the scattering background of the spectra decisively but in a different manner. The Bragg peak results from the ordered structure and is partially destructed by any opal defect. The peak height rises with thickness during the transition from a few layers to a 3D PhC. However, for thick opal layers (thicker than 10 layers or 3 μm) it is expected to be constant because it represents only a reflection loss for the incident beam at the opal surface. Here its height (above the background) is therefore a measure for the opal quality independent of the thickness. The background originates from the scattering at the defects on the path of light through the opal film. Therefore, it depends on defect concentration and more strongly on the thickness. It is much less suited for comparing the opal quality when the thickness is undefined.

For the investigated samples the Bragg peak heights are 1.1, 1.5, 0.9, and 1.25 for films prepared by 0/1, 1/4, 1/2, and 1/0 ethanol/water mixtures, respectively. This is the same trend as we found from the SEM pictures except for the film made from pure ethanol. Very likely the consideration of further optical effects such as sieve effects with the cracks in the opal film and the limited detection limit of the spectrometer could explain this difference. Nevertheless, the opal films made from the 1/4 mixture showed the best properties for both methods, SEM and optical spectroscopy.

4. Discussion

The results show the significance of solvent for opal film fabrication from colloidal suspensions and provide a possibility for controlling the resulting morphology and quality of the opal films. Although detailed theoretical explanations to all of the observations are difficult because of the intrinsic complexity of the processes accompanying deposition of spheres and crack formation, we will try to understand the observations based on the available parameters of the solvents.

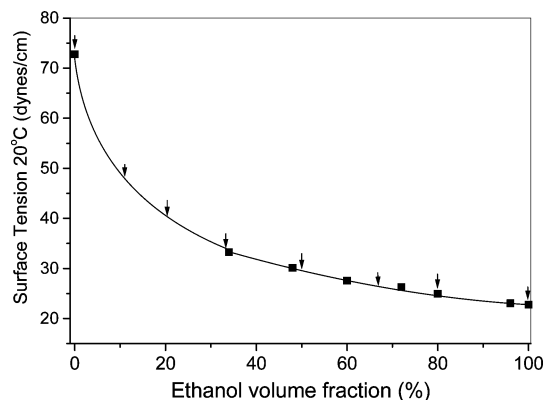**4.1. Capillary Deposition Method.** *4.1.1. Surface Morphology of the Opal Films.* As we can see from sections

Figure 12. Surface tension vs volume fraction of ethanol in an ethanol/water mixture. The squares are the literature data used to plot the curve;[21] the arrows indicate the compositions of the solvents used in our experiments.
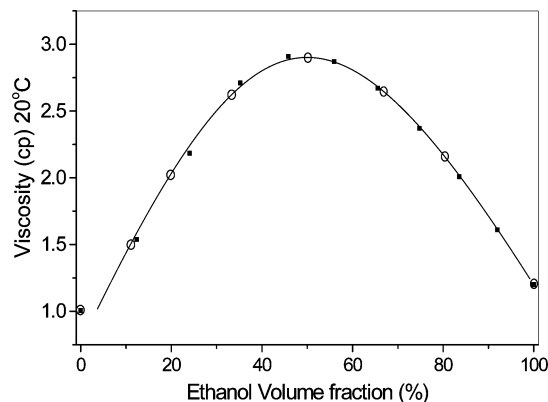

Figure 13. Viscosity vs volume fraction of ethanol in the ethanol/water mixture. The squares are the literature data used to plot the curve;[21] the circles show the compositions of the solvents used in our experiments.

3.1.2 and 3.1.3, the change of solvent results in different crack patterns in the opal films. The average spacing between cracks reaches its maximum for an ethanol fraction of about 50%. In a former paper it was observed that the cracks are formed during film drying.[13] The process of crack formation is fast; therefore, we assign it to solvent loss from the interstitial spaces between the particles rather than from a potential swelling of individual particles. Since the kind of solvent influences the drying decisively, changing the solvent must affect the cracks.

The changed solvent composition influences at least the following three properties of the solvent: surface tension (γ), viscosity (η), and volatility. As we can see in Figure 12, the surface tension decreases with the increasing volume fraction of ethanol in the mixtures in a hyperbolic-like manner. There is however no direct coincidence between the surface tension and the average spacing between cracks. Figure 13 shows the relationship between viscosity and ethanol volume fraction in the mixture. The viscosity reaches its maximum for an ethanol fraction of about 50%. This curve is similar to the spacing trend observed in Figure 3.

To understand the roles of surface tension and viscosity in the process of crack formation, we use the theoretical model of crack formation developed by C. Allain and L. Limat (AL).[22] They investigated a 2D scalar model and concluded that the competition between stress relaxation due

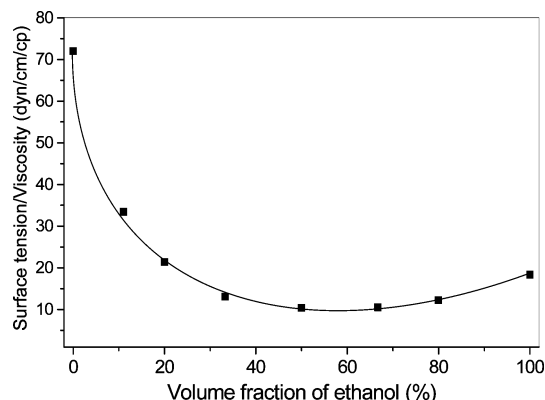(22) Allain, C.; Limat, L. *Phys. Rev. Lett.* **1995**, *74*, 2981.

Figure 14. Surface tension/viscosity ratio vs volume fraction of ethanol.

Figure 15. The average film growth velocity vs volume fraction of ethanol in the solvent. The bars are the estimated errors in the velocity measurements.

to crack opening and stress increase due to loss of solvent defines the spacing between cracks. In the environment of one crack a stress field is generated which originates the next crack. The parameters of this stress field are determined by the flux of solvent K. Therefore, a direct relation between the spacing between cracks and K was found.

K is inversely proportional to an effective diffusion coefficient D related to the transport of solvent through the opal film. D is proportional to the capillary characteristic velocity ($\cong \gamma/\eta$).[23] Therefore, K is predicted to be inversely proportional to the surface tension-to-viscosity ratio (γ/η).

Figure 14 shows the relationship between γ/η and the respective ethanol volume fraction. From the plot we can see that the γ/η value reaches a minimum at a volume fraction of about 55% ethanol. It corresponds well with the volume fraction of ethanol at which the spacing maximum appears (see Figure 3). The model provides a surprisingly good explanation to our experimental observations, although it has not considered some important aspects of the real system. For example, it is assumed that the double layer responsible for the repulsion between the particles is not very influenced by the solvent. The properties of this layer determine the solvent content of the wet opal film (determining $C\infty$ in AL). The ionic concentration is likely the same, but the dielectric constant is solvent dependent. However, this change is monotonic and can, therefore, only produce a small shift in the curve for the AL prediction of the crack frequency.

4.1.2. Fine Structure of the Opal Films. The influence of solvent on the film fine structure in the capillary deposition method can happen at two separate steps: the wet film deposition and drying.

(1) Wet Film Deposition. During the wet opal formation the arrangement of the spheres requires time for perfecting the order. Such an effect is partially visible in our experiments.

Figure 15 shows the growth velocity of the opals for different solvents. Although a precise determination of the growth velocity is difficult, a clear trend is visible. The initial decrease of growth velocity with ethanol fraction turns to an increase after reaching a local minimum at about 0.1. In this region high-quality opal films were obtained, which is
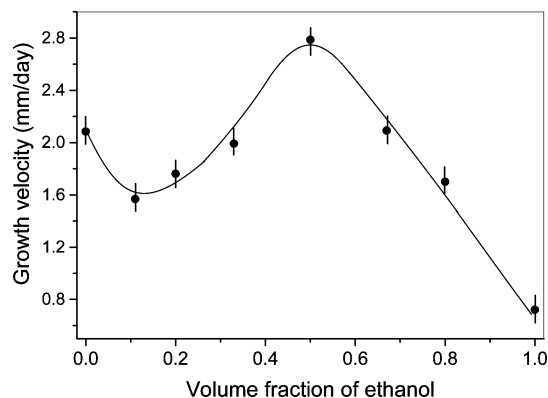
in accordance with the deposition velocity minimum. At the volume fraction of about 0.5 the growth velocity reaches its maximum and then decreases again with increasing ethanol volume fraction. In this region the film quality does not improve, indicating a more complex influence of the solvent parameters than via the deposition speed. We assign this to the drastic decrease of surface tension and viscosity, which result in weaker driving forces for the self-assembly process. However, a detailed theoretical explanation of the roles of these two solvent properties in the wet opal film deposition is complex and beyond the scope of this paper.

(2) Drying of the Film. An advantage of the capillary deposition method is that deposition and drying processes can be controlled separately.[13] First, a wet opal film is formed inside the capillary cell and then, if no solvent is supplied, the drying process follows. As described in section 4.1.1, the drying process determines the crack distribution inside the opal film. Besides the cracks, drying may also modify the quality of the local sphere arrangement.

During the drying capillary forces between spheres compress the arrangement of the spheres locally.[7,8] The change of surface tension of the solvent will modify the capillary forces between the spheres. However, this influence very likely has no defined direction with respect to defect concentration because the capillary forces will cure some vacancies or line defects formed during wet opal deposition, but on the other hand, new defects can be introduced. The reason for this ambivalent action is the relative rigidity of the wet opal arrangement. It will likely not allow large-scale movements and structural optimizations. Therefore, we believe that the solvent effect during drying is much weaker than during the deposition process.

4.2. Vertical Deposition Method. *4.2.1. Surface Morphology.* As it has been shown in parts A–D of Figure 8, the four samples prepared from PS suspension of different solvents have different surface morphologies. The difference can be assigned to an instability of the meniscus related to the Marangoni effect.[24-28]

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The influences of solvents on the crack distribution in the case of the films prepared by the VD method are not as regular as those observed for the capillary deposition method (compare Figure 8 and Figure 2) since the deposition and drying processes take place simultaneously in the former case while they happened separately in the latter case. All four samples in Figure 9 show grid-shape cracks with different areas between the cracks. In thicker films larger areas between the cracks have been observed even in the same film with inhomogeneous thickness; therefore, it is difficult to separate the solvent effects from the influences of thickness.

4.2.2. Fine Structure. The influence of solvent on the fine structure of opal films prepared by the VD method shows quite similar results with that observed in the capillary deposition method (see sections 3.2.3 and 3.2.4). Addition of a little ethanol can increase the quality of the opal film but only to some point. Further addition results in decreasing quality. The deposition mechanisms of the capillary deposition method and the VD method are different; however, the optimal solvent for high-quality opal films is quite similar. An obvious difference between the VD method and the capillary deposition method is that the opal film derived from ethanol suspension by the VD method is ordered, while the film prepared by the capillary deposition method from the same suspension is completely disordered. Since both the hydrodynamic drag force and the capillary force play a role in the assembly of PS spheres by the VD method,[20] changing the solvent composition modifies the self-assembly of the spheres by changing the surface tension, viscosity, and volatility of the solvent, resulting in the optimal opal deposition condition for high-quality opal films.

5. Conclusion

The solvent plays a very important role in the deposition of opal films from colloidal suspensions. For the newly developed capillary deposition method the spacing between the cracks and the quality of the final opal films can be modified by changing the volume fraction of ethanol in the ethanol/water mixture. Changing the volume fraction of ethanol modifies the surface tension and viscosity of the mixed solvent. These changes in turn modify the competition between the stress relaxation due to crack opening and the stress increase due to solvent loss, which takes place during the drying process and determines the spacing between cracks inside the final opal films.

For the VD method sphere assembly and drying take place simultaneously. Therefore, the solvent effect in the preparation via the VD method is different from that by the capillary deposition method. The solvents do not influence the crack distribution inside the films qualitatively, but they influence the surface appearances of the final films and their fine structures.

The solvent effects in the self-assembly of PS spheres provide opportunities to control the morphology and improve the quality of the opal films in a flexible way. It can also provide information for understanding the working principles of the different methods of opal film deposition.

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