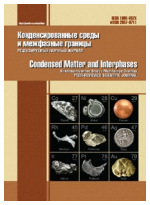

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Specifics of the formation of regular opal structures from spherical silica particles in various colloidal solutions

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Abstract

Photonic crystal opal matrices are bulk spatial periodic structures based on amorphous spherical silica particles whose size is compatible with the wavelengths of the visible light spectrum. These structures are very promising and can be used as matrices for new functional materials.

The article studies the formation of a regular opal structure on dielectric substrates by means of the evaporation of droplets and layers of colloidal solutions based on water and ethanol with various concentrations of spherical SiO_2 particles with a diameter of about 250 nm synthesised using the Stöber method.

Keywords: Opal structures, Evaporation-induced self-assembly method, Tetraethoxysilane, Sedimentation, Lyophilic medium, Iridescence

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1. Introduction

An opal matrix is a face-centred cubic lattice (FCC) formed by densely packed spheres of amorphous silicon dioxide (SiO_2) with similar diameters and the size of 0.1–1.0 μm. The space between the SiO_2 spheres is occupied by a void sublattice, which can be filled with other materials. Such structures serve as a basis for photonic crystals with the electromagnetic band gap blocking the waves with wavelengths compatible with the parameters of the periodic structure. By filling the voids between the structural elements of an opal matrix with various substances, we can create periodic nanocomposites of optically active materials to be used in optoelectronics, semiconductor engineering, opal-semiconductor based photonic media, magnetic recording systems, etc. [1–11].

In order to obtain regular opal structures, first we need to synthesise spherical particles of silica, whose size should not vary by more than a few percent. In this regard, the Stöber method is considered to be the most appropriate [12]. This method is based on the hydrolysis of tetraethoxysilane (TEOS) in an aqueous-alcoholic medium in the presence of ammonium hydroxide serving as a catalyst. This method was first described by *G. Kolbe* in 1956 [13] and then elaborated by *W. Stober* et al. The method allows for the synthesis of SiO_2 particles of almost ideal spherical shape in a wide range of diameters: from tens of nanometres to several micrometres. The size and sphericity of the particles depend on the purity and concentrations of the reagents, the temperature, and the composition of the colloidal solution, which is most commonly based on ethyl alcohol. The next important and equally difficult task is to obtain ordered 2D and 3D microstructures with linear dimensions of up to several millimetres. The most popular method for the creation of such structures is the method of natural sedimentation in alcoholic colloidal solutions. In this case the particles deposit on a flat horizontal substrate at a rate determined according to Stokes' law [1]. It takes several weeks to obtain opal layers of several millimetres.

The evaporation-induced self-assembly method proved to be quite effective for alcoholic media [8, 9]. This method involves the deposition of spherical silica particles on an inclined or vertical substrate during the evaporation of the alcoholic suspension. Although opal films obtained during the formation of a regular structure in alcoholic media are more perfect than bulk samples, the number of cracks and dislocations in the obtained samples is still very large. In fact, there are hardly any 1 mm^2 regions with no dislocations. The film obtained using this method demonstrated a mesh of horizontal and vertical bands [10], which the authors explained by the fluctuations in the temperature and the concentration of particles in the solutions being evaporated under conditions which are difficult to control.

D. V. Kalinin et al. developed a promising technique for obtaining regular structures from spherical submicron silica particles [1, 5]. The technique involves packing the particles in a droplet or a 0.1–0.5 mm thin layer in a lyophilic medium based on dimethyl sulfoxide. To increase the mobility of the silica spheres, a plasticiser (namely isopropanol) is added to the quite viscous suspension. During its formation in the suspension, the structure demonstrates plasticity, which significantly enhances the regularity of packing and reduces the chance of microcracks resulting from the shrinkage of the film during drying. This method can be used to obtain 3D opal structures with the width of tens of layers of SiO_2 particles over an area of 1–2 cm^2.

The existing literature does not provide enough comparative data on the formation of regular opal structures by submicron silica particles from various suspensions depending on the concentrations of the solutions. Therefore, the purpose of our study was to compare the suspensions most commonly used by other researchers as the media for obtaining regular opal structures based on ethyl alcohol and water. In our study, we investigated the possibility of using a 50% aqueous solution of ethanol as a solvent, because there is very little information about it in the literature. To maintain the accuracy of our experiments, we used silica particles synthesised by means of the Stöber method in the laboratory.

2. Experimental

The starting materials for the synthesis of spherical silica particles were: 95% ethanol by Alfa-him, 25% ammonia (P.A.), tetraethoxysilane by

various Russian and international manufacturers (P.A. and E.P.), and distilled water.

For the distillation of TEOS, a special unit was assembled consisting of a three-neck flask and a refrigerator made of heat-resistant glass. To enhance the accuracy of the fractionation of the reagents, the flask was placed on a specially designed electrical furnace regulated by means of a RIF-101 based precision temperature controller. To control the temperature, we used a platinum-rhodium thermocouple placed at the inlet of the refrigerator. Each TEOS composition was divided into 4–5 fractions in the range of 165–173 °C. Each fraction was used separately in the experiments. The best results were obtained when the most volatile fraction of TEOS was used.

To prevent the formation of moisture during the distillation process, we passed argon through the system and used a tube with calcined calcium chloride. The silica particles were synthesised in a 50–200 ml glassware by mixing the components at 20 °C. The solution was stirred on a MM-5 magnetic stirrer or a Meos Praha T2 vibrating plate for 1–2 hours, after which the particles were formed within an interval of 8–24 hours without any mechanical influences. The synthesised spherical silica particles were separated from the alcoholic solution in a centrifuge (Elecon R10-01 or TsUM-1) with the rotation speed of 1500–2000 rpm, which was reconfigured for 50 ml test tubes. The obtained precipitates containing the minimum amount of moisture were put into containers with: a) ethyl alcohol (C_2H_5OH), b) 1:1 aqueous-alcoholic solution, and c) distilled water - in order to obtain suspensions with the concentration of silica particles from 15 to 0.5 wt%.

The layers and droplets of the suspensions with various concentrations of silica particles were put on a 24×24×0.17 mm glass plate (microscope slides) using a glass rod, a pipette, or a brush. The relative change in the weight of the substrate before and after the application of the suspension was registered by means of VLA-200 analytical scales with an accuracy of 0.2 mg. We also registered the time of evaporation of the colloidal solution and the area of drop spreading. This helped us to calculate the thickness of the solution layer and the film of the silica spheres after drying out the suspension. Either visually or via an MBS-2 microscope, we observed the presence of an interference pattern from the film (iridescence), when the SiO_2 spheres were regularly packed at a reflection angle of about ~5°. We also determined the crack density of the film on a BIOLAM transmission microscope at 50× and 200× magnifications. The surface structure of the films was studied using a Carl Zeiss EVO LS 10 electron microscope.

3. Results and discussion

In our study, we determined, as did the authors of [7, 11], that the reproducibility of the experiments on the synthesis of monodisperse silica particles heavily depends on the quality of TEOS. The use of TEOS of different manufacturers under identical conditions resulted in silica particles of different shape and size, which could hardly be used to obtain ordered regular structures. The diameters of the silica particles differed by 2–4 times (Fig. 1).

Only the use of TEOS purified from high-temperature fractions resulted in reproducible monodisperse silica particles. In our further analysis, we used 250±10 nm particles. Table 1 presents the characteristics of the films of spherical silica particles formed from an alcoholic suspension depending on the concentration of SiO_2. We determined that the height of the droplets decreases with smaller concentrations of the suspension. The average thickness of the silica films also decreases significantly: it is about 5 μm for the 10% suspension, and about 1 μm for the

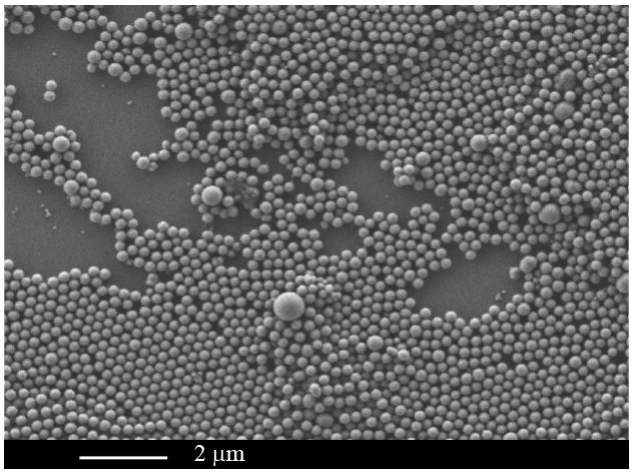

Fig. 1. SiO_2 spheres of various diameters obtained when using the commercial reagent of TEOS (evaporation-induced self-assembly in a 10% alcoholic suspension)

2.5% suspension. Since for all the compositions with the concentration of the suspension of over 1% we clearly observed iridescence (both visually and via a microscope with the reflection angle of about ~ 5°), we can conclude that submicron SiO_2 particles are regularly packed in dried droplets of alcoholic suspension. The defects include radial beam-like cracks in the direction from the periphery to the centre. The results of our study are consistent with the results obtained in [11]. The latter study modelled the process of particles packing using various methods and demonstrated the identity of the formation of the SiO_2 film from alcoholic suspensions by means of the evaporation-induced self-assembly method and the droplet evaporation method.

Our study demonstrated the difference between the formation of regular opal structures in a layer or in a droplet of an alcoholic suspension depending on the concentration of silica particles. The structure of the iridescent layer with the silica particles the concentration in the suspension of over 10 % is not uniform, as shown in [6]. The periphery of the film is significantly thinner, which indicates the maximum iridescence, which then decreases towards the centre (Fig. 2).

Droplets of the alcoholic suspension with the concentration of SiO_2 particles below 10 wt% demonstrated larger drop spreading with the thickness being significantly more uniform. The thickening of the outer ring in the droplet's periphery is almost imperceptible,

Table 1. Characteristics of the films of spherical silica particles formed from the alcoholic suspension depending on the concentration of SiO_2

Solvent C_2H_5OH	Silica concentration, wt%									
	15	10		5		3		1		0.5
Droplet weight, mg	6.7	11	5.5	8.8	4.4	8	4	1	2.6	5
Droplet area, cm^2	0.8	2.5	0.8	4.0	2.2	3.8	2.3	1.2	2.1	3
Suspension density, g/cm^3	0.9	0.85	0.85	0.82	0.82	0.8	0.8	0.79	0.79	0.79
Droplet height, μm	93	50	80	26	24	26	22	10	16	12
Height of the SiO_2 nanosphere layer, μm		5.6		1.3		1.2				
Film iridescence	+	+	+	+	+	+	+	слаб.	слаб.	? -

Table 2. Characteristics of the films of spherical silica particles formed from the aqueous suspension depending on the concentration of SiO_2

Solvent H_2O	Silica concentration, wt%					
	15	10	5	2.5	1	0.5
Droplet weight, mg	15.8	16.3	15.8	12.8	15.8	15.0
Droplet area, cm^2	0.5	0.7	0.7	0.8	1.1	0.6
Suspension density, g/cm^3	1.06	1.04	1.02	1.01	1.0	1.0
Droplet height, μm	300	224	220	170	145	135
Film iridescence	+	+	+	слаб.	-	-

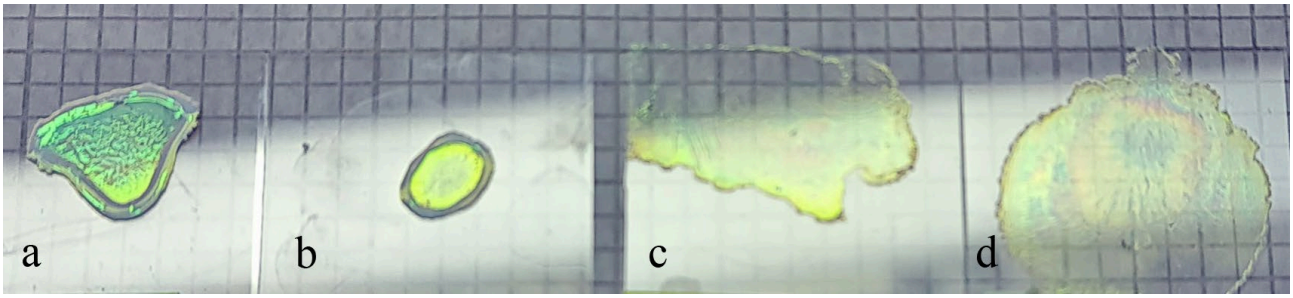

Fig. 2. Films of spherical SiO_2 particles obtained by the evaporation of the droplets of the alcoholic suspension of SiO_2 with various concentrations of submicron silica spheres (see Table 1): a – SiO_2 concentration: 15 %; b – SiO_2 concentration: 10 %; c – SiO_2 concentration: 5 %; d – SiO_2 concentration: 3 %

Таблица 3. Характеристики пленок из сферических частиц кремнезема, сформированных из водно-спиртовой суспензии, в зависимости от концентрации SiO_2

Solvent $C_2H_5OH(50\%)+H_2O(50\%)$	Silica concentration, wt%								
	15	10		5		3	2.5	1	0.5
Droplet weight, mg	15.8	16.3	14.1	15.8	16.3	13.8	14.8	15.6	15
Droplet area, cm^2	0.55	0.7	0.7	0.7	0.9	0.8	0.85	1.0	0.9
Suspension density, g/cm^3	0.96	0.94	0.94	0.92	0.92	0.91	0.9	0.9	0.9
Droplet height, μm	300	250	210	240	195	190	190	170	185
Height of the SiO_2 nanosphere layer, μm			1.2		1.1		0.2		
Film iridescence	+	+	+	+	+	+	+	слаб	?

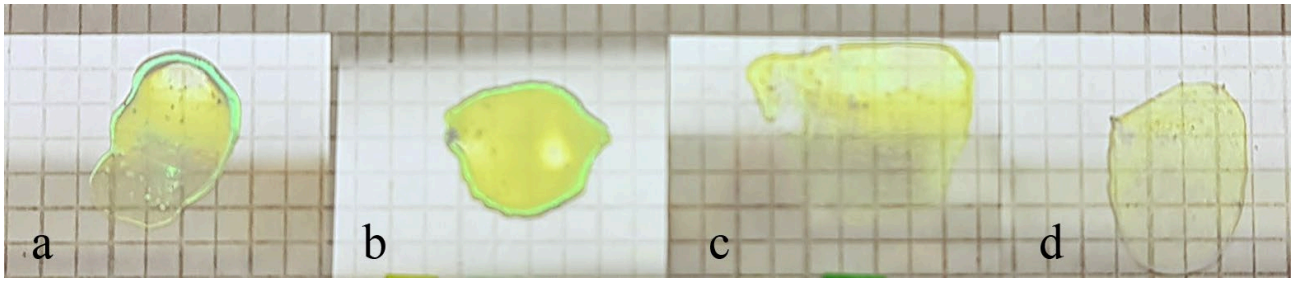

Fig. 3. Films of spherical SiO_2 particles obtained by the evaporation of the droplets of the 50 %C_2H_5OH – 50 % H_2O suspension with various concentrations of submicron silica spheres: a – SiO_2 concentration: 10 %; b – SiO_2 concentration: 5 %; c – SiO_2 concentration: 2.5 %; d – SiO_2 concentration: 1 %

and the homogeneity of the films increases over the spreading area. Table 2 presents the characteristics of the films of spherical silica particles formed from an aqueous suspension depending on the concentration of SiO_2.

The study demonstrated that it takes 4-6 hours for a droplet to evaporate, and the homogeneity of the films is higher than that of the films obtained from alcoholic compositions with larger concentrations (> 10 wt%). The iridescence, which is less bright than the iridescence in alcoholic suspensions, is only observed in thick suspensions with concentrations of SiO_2 of over 5 %.

Using aqueous-alcoholic suspensions (with a 50% concentration of C_2H_5OH), we obtained films similar to those formed during the evaporation of the alcoholic suspension (Fig. 3).

Table 3 presents the characteristics of the films of spherical silica particles formed from an aqueous-alcoholic suspension depending on the concentration of SiO_2. The average evaporation time was 25–30 minutes, which is several times more than the time required for the evaporation of alcoholic suspensions, but is an order of magnitude less than the time required for the evaporation of an aqueous suspension. The thickness of the iridescent films with a minimum concentration of SiO_2 is lower than the thickness

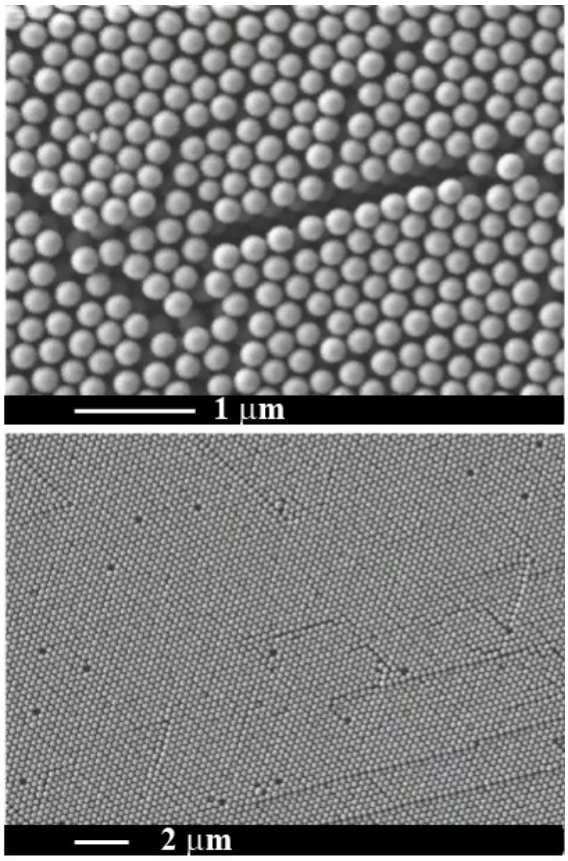

Fig. 4. Regular structure of the layer of 250±10 nm silica spheres obtained during the evaporation of a 10% aqueous-alcoholic (50%) suspension on a horizontal substrate

of films obtained from alcoholic suspensions, and the spread of the droplets of the suspension with concentrations of 2.5 and 1 % is more uniform (Fig. 3).

Fig. 4 shows the image of a film consisting of silica spheres obtained during the evaporation of an aqueous-alcoholic suspension layer on a horizontal glass substrate.

4. Conclusions

The films consisting of submicron silica spheres obtained by means of evaporation of colloidal aqueous, alcoholic, and aqueous-alcoholic (50%) solutions of various concentrations are characterised by concentric and radial banding. [10] suggests that this (as well as a series of horizontal and vertical bands appearing when using the evaporation-induced self-assembly method) is caused by a single reason: then change in the concentration of silica particles in the suspension. Comparing the surface of the films obtained under identical conditions by means of the evaporation-induced self-assembly method on an inclined substrate and the droplet evaporation of the suspension on a horizontal substrate, we can see that in the latter case there are much fewer bands or other defects. We suppose that using aqueous-alcoholic suspensions of spherical silica particles in order to obtain opal layers on a horizontal substrate is a promising method that can be used to enhance the regularity and the quality of films.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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