

Preparation of two-dimensional direct opals by controlled assembly of silica spheres*

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This paper has been devoted to the preparation of hard colloidal crystals by a self-assembly process. The aim of the study has been to find the precise conditions governing this process, in order to make it controllable. To accomplish our goal, we have studied the influence of factors such as: the type of solvent, system temperature, particle volume fraction and size of the silica spheres. These are synthesized following a Stöber procedure where the size is precisely controlled by a seeded-growth technique. In some of the experiments, the silica spheres are deposited in the presence of different surfactants (SDS, CTAB), thus varying the magnitude of the ζ -potential. The material of the substrate (glass or silicon) also plays a crucial part in the deposition process and during the sintering procedure. The structural regularity is characterized by scanning electron microscopy and optical absorption spectra.

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1. Introduction

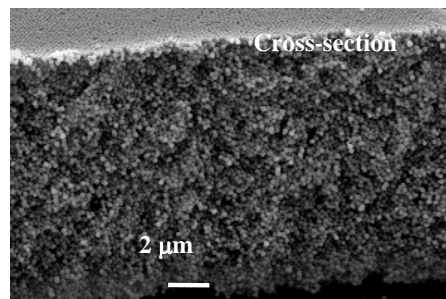
Recently, the preparation of hard colloidal crystals in the dry state, commonly termed as direct opals, has received tremendous attention, because direct opals are the ideal templates to synthesize porous materials. The latter have promising applications in photonics, optoelectronics, data storage, as sensors etc.

Common techniques for the fabrication of direct opals are lithographic methods [1], a self-assembly process [2, 3] or the recently introduced holographic lithography [4]. Lithographic methods are very versatile in terms of the symmetry of the ordered structure and controlled disorder, but they use expensive technology and are time consuming. In contrast, the self-assembly process does not require any expensive instrumentation since it is based on the natural tendency of monodisperse colloidal particles to self assemble into face-centred cubic (fcc) arrays, by capillary forces. Up to now, many techniques which exploit self-assembly have been developed, such as gravitational sedimentation, vertical deposition and the Langmuir-Blgett method. Among them, the vertical deposition method has proved the most effective, as the thickness and surface morphology can be controlled. In our research, vertical deposition is used to study the influence of the following factors: the type of solvent, temperature, particle volume fraction and size of the silica

spheres. The role of surfactants and the substrate material in governing the process is also taken into account.

2. Experimental

Silica microspheres were synthesized following the Stöber procedure [5], where the size is precisely controlled by seeded-growth technique proposed by Bogush et al. [6]. The latter technique was used to prepare both larger particles and a high volume fraction of silica.



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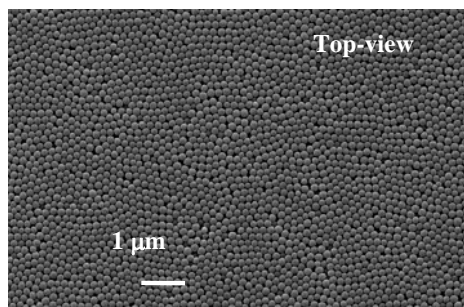


Fig. 1. Scheme of the overall synthetic procedure (TEOS – tetraethoxysilane).

Fig. 1 summarizes the overall synthetic procedure developed to obtain monodisperse silica particles. The optimal reaction conditions were studied in our previous work [7]. The spheres were washed six times with ethanol and water by repeated centrifugation/dispersion cycles. Then they were dispersed in a suitable solvent for self-assembly. A very important step, preceding the deposition of the silica spheres, was their microfiltration through filters with a pore size ranging from two to four times the particle diameter. Thus, the particle aggregates were removed.

The substrates employed were clean hydrophilic glass microscope slides or pieces of silicon wafer. The glass slides were washed with detergent and subsequently placed either in a chromic mixture overnight or in an organic solvent (acetone) for half an hour. The silicon wafers were washed with detergent and then immersed in an HCl/H₂O₂ solution (1:1 vol.) for half an hour. Afterwards, they were rinsed with plenty of bi-distilled water and dried. In a typical experiment, the substrate was placed in a 25 mL beaker containing from 8 to 10 mL of a silica suspension dispersed in the desired solvent (usually water or ethanol – 96 %), as shown in Fig. 2.

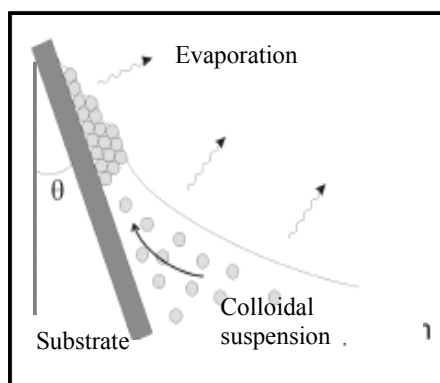


Fig. 2. Scheme of the vertical deposition method. A substrate (dark grey) is inclined at an angle θ .

The beaker was placed inside an oven, where the temperature was kept constant with a precision of 1°C. The fabrication of the silica opals lasted long enough to allow for growth over a distance of 1cm along the vertical direction. In order to study the factors involved in the

assembly process, we varied the particle volume fraction (0.4 - 1 % vol.), the system temperature (35 – 50 °C), and the type of material (glass slides or silicon wafers). The influence of different surfactants (Cetyl Trimethyl Ammonium Bromide, CTAB, and Sodium Dodecyl Sulfate, SDS) on the layer formation and growth was studied as well. We paid attention to the effect of the silica sphere size (with sizes in the range 300-450 nm) and surface charge density on the quality and optical properties of the ordered arrays. The structural morphology of the direct opals was observed with a Scanning Electron Microscopy (SEM) JEOL JSM 5510 and the optical transmittance spectra were measured with a Jenway (model 6400) spectrophotometer, in the range 320 to 1100 nm.

3. Results and discussion

We prepared direct opals of silica particles with diameters of about 300 and 400 nm. For spheres with diameters above 400 nm, sedimentation decreased the sphere concentration during the growth process, and yielded poor quality samples. The parameters that influence the layer formation and growth were varied to determine their effect on the regularity of the fabricated arrays. The latter was characterized by SEM and absorbance spectra.

Typical top-view and cross-section SEM images of opals, obtained by the present self-assembly method, are shown in Fig. 3.

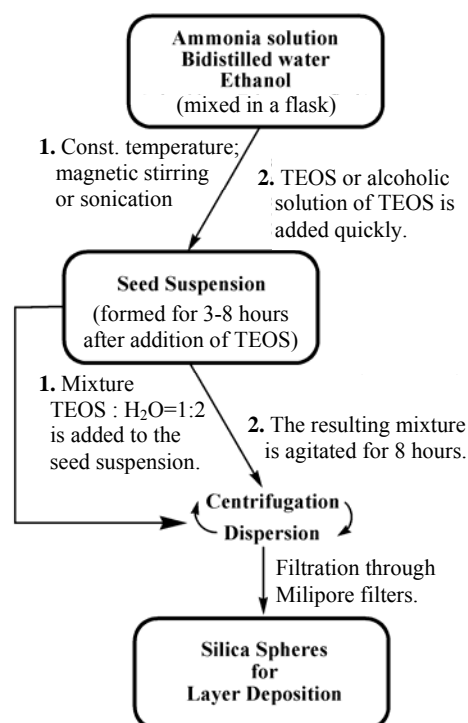


Fig. 3. Typical SEM images of the fabricated opals.

The opals possess a fcc symmetry, showing ordered stacking and characteristic hexagonal facets (111).

Fig. 4 and Fig. 5 show the optical density and transmittance spectra along normal incidence to the (111) planes parallel to the surface. A photonic band-gap effect in the absorbance spectra is observed, which results from Bragg diffraction due to the location periodicity of spheres in the opals. The height of the optical density maximum (or the depth of the transmittance minimum) was used to evaluate the number of defects. The height was lowered in the presence of defects. On the other hand, a smaller full width at half maximum (FWHM) was related to a thicker layer.

3.1. Effect of solvent type, temperature and particle volume fraction on the layer formation

The effects of the studied factors are represented by the optical density spectra of the silica opals, as given in Fig. 4.

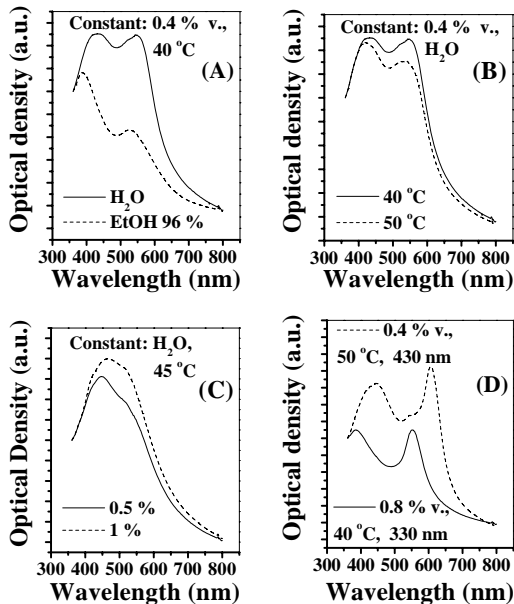


Fig. 4. Optical density spectra of direct silica opals obtained varying: (A) the solvent type; (B) temperature; (C) particle volume fraction and (D) multiple variables. The silica sphere diameter was 330 nm except where stated.

As observed from Fig. 4A, the height of the absorbance maximum when an aqueous suspension was used for vertical deposition is greater than that for the case of the opal grown from alcoholic suspension. This is the reason why the use of volatile solvents with low surface tension, such as ethanol, leads to the fabrication of 2D-arrays with smaller monocystal domains. This is due to

the higher evaporation rate of ethanol than water, and thus the rapid production of a thinner layer with uncontrollable defects. Another reason for the better regularity of the direct opal grown from water dispersion is due to the surface tension effect, which offers a greater stacking force during the drying process.

The higher temperature leads to thicker layer, but with more defects than the lower one. The layer thickness is evaluated from the FWHM of absorbance spectra in Fig. 4B. These effects are due to the more intense Brownian motion of the particles, the decrease in the water surface tension with temperature increase, and to the higher evaporation rate.

Similarly to the temperature effect commented upon above, the layer thickness and number of defects increase simultaneously with increasing particle volume fraction. However, this effect is negligible, as can be estimated from Fig. 4C. As a consequence of this, the multiple effects presented by the optical spectra in Fig. 4D can be understood. The higher temperature leads to a convective flow of larger particles, and thus prevents their sedimentation. A layer with better quality is produced compared to the case of smaller particles.

3.2. Influence of the size and annealing temperature of the silica spheres

Following Bragg's law (Eq. (1)), when the particle size increases, the optical density maxima are red-shifted (Fig. 5):

$$\lambda = 2d_{111}n_{\text{eff}} = 2\sqrt{\frac{2}{3}}D\sqrt{fn_{\text{SiO}_2}^2 + (1-f)n_{\text{air}}^2} \quad (1)$$

where λ is the wavelength, d_{111} is the distance between the crystal planes in the (111) direction, n_{eff} is the volume averaged refractive index of composite, D is the silica sphere diameter, f is the filling fraction ($f = 0.74$ for fcc), $n_{\text{SiO}_2} = 1.45$ is the silica refractive index and n_{air} is the air refractive index.

The thermal treating of silica spheres leads to pore contraction, and thus to a slight reduction in the particle diameter. However, at the same time, the spherical morphology of the silica remains unchanged. This is the reason why the particle annealing temperature effect is similar to the size effect, but less pronounced in that the size is negligibly changed. The opals obtained from calcinated silica particles at different temperatures possess similar regularity as observed from the photonic band depth (Fig. 5B).

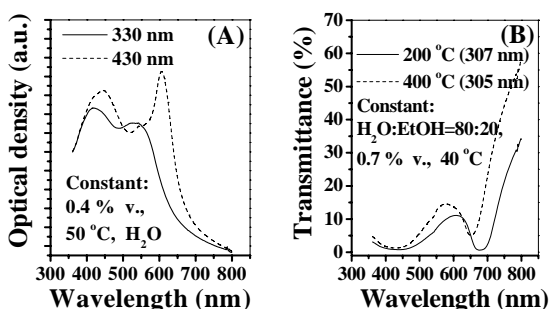


Fig. 5. Optical density (A) and transmittance spectra (B) demonstrating the sphere size and annealing temperature effect, respectively.

An excellent agreement between the calculated Bragg wavelength of the transmittance minimum ($\lambda_{Bragg}=675$ nm) and the experimentally determined one ($\lambda_{exp}=677$ nm) is observed for the spectrum in Fig. 5B, for silica spheres calcinated at 200 °C.

3.3. Opals produced on glass slides or silicon wafers and in presence of surfactants

The mechanical stability of opals depends significantly on the hydrophilicity of the substrate material. Regardless of the washing procedure, the opals grown on silicon wafers appeared to present no deposit in certain regions.

In order to vary the ζ -potential, we used cationic (CTAB) or anionic (SDS) surfactants. When SDS was used, narrow well-ordered domains were formed, which surrounded large and less ordered areas with organic impurities. Coagulation was not observed (Fig. 6).

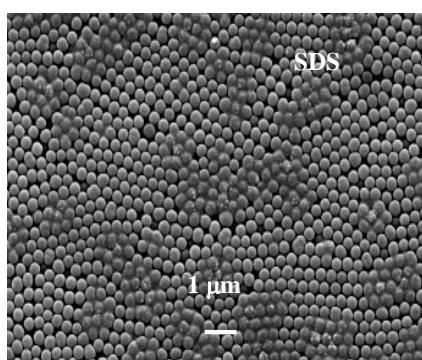


Fig. 6. SEM image of a direct opal grown in the presence of SDS.

In the presence of CTAB, the silica particles are adsorbed on the glass surface before their incorporation in

the array. This causes defects in the 2D-crystal. Another drawback is the adsorption of surfactant molecules on the negatively charged silica particles, which suppresses the electrostatic repulsion and leads to particle coagulation.

4. Conclusions

Monodisperse silica spheres (200 - 450 nm) with a high volume fraction were synthesized by a controlled seeded growth Stöber procedure.

Vertical deposition was applied for the fabrication of 2D-direct opals on both glass and silicon substrates. The silica arrays showed greater adhesion to the hydrophilic glass slides, in comparison to that for the silicon wafers.

The temperature and presence of a more volatile solvent had the greatest effect on the layer thickness and degree of ordering, compared to the other studied parameters. Direct opals with larger monocrystal domains were prepared at low temperatures from water suspensions.

The use of both anionic and cationic surfactants was found inappropriate for a high quality of the deposited layer.

Acknowledgements

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