콜로이드 결정을 이용한 다공성 고분자 주형의 제조

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Preparation macroporous polymer template from colloidal crystals

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Introduction

Many novel properties can be engineered in periodic dielectric materials by controlling the symmetry and length of scale of a sample's microstructure.[1] This idea is technologically important because they can be potentially used, for instance to greatly improve the performance of semiconductor lasers and many other kinds of quantum electronic device. Also that has motivated researchers and fabricate photonic band gap materials in order to investigate possible applications in optics and optoelectronics, catalysis[2][8].

Recently, colloidal crystals have renewed attention as an avenue to acheving controlled periodicity. colloidal crystals are regular crystalline arrays of highly monodisperse spheres dielectric materials such as silica and polymers. In this case, crystalline quality is among the most important parameters in determining the performance of colloidal crystals in optical applications.

Recent work of Nagayama et al. has exploited capillary forces to drive to assembly larger polystyrene colloids on flat surfaces. This method, which is conceptually similar to the Langmuir-Blodgett methods for film deposition, creates ordered monolayer films on nearly any vertical surface. Under the appropiate solvent and colloid conditions Nagayama et al. showed patches to bi and trilayer arrays could also be formed[3].

In this study, a self assembly technique which relies on capillary force to organize colloids is used to fabricate colloidal crystal multilayers. and extending this method, We will create macro-porous polymer film.

Experimental and Results

There are several aspects involved in producing these colloidal crystals. First, monodisperse homogeneous silica spheres are inquired. The size of the particles must be controllable. A procedure insuring self-assembly into the appropriate structure must be obtained. and the structure must be characterized structurally and optically to guarantee that suitable properties are present[4].

Monodisperse, sub micrometer silica spheres prepared by hydrolysis and condensation of tetra alkoxy silanes according to a method developed by Stober et al. have been used as a model system in many different fields such as ceramics, catalysis.

The Stober methode for producing monodispersed particles of a specific Size

was used. Tetra ethyl ortho silicate (TEOS) was added to controlled solutions of ammonium hydroxide and ethanol is used to make all volumes equal in accordance to the equation.

$$Si(OC_2H_5)_4+4H_2O \longrightarrow Si(OH)_4+ 4C_2H_5OH \quad [1]$$

$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O \quad [2]$$

The reaction covered by Eq 1 are ester exchange, hydrolysis and its reversal, esterification, It is generally accepted that the base catalyzed reactions.[1] proceed through a bimolecular nucleophilic attack on the silicon atom. The nucleophile attacking the silicon atom in the hydrolysis reaction is OH−: an increase in the concentration of this catalyst results in an increase in reaction rate. Therefore, the hydrolysis rate increase if the concentration of NH_3 and or H_2O increase[5].

The stober method can very simply and reliably provide a means for producing monodispersed silica colloidal. when particles are synthesized from this method, they assemble into spheres, Mean and standard deviation of diameters can be controlled by careful stochiometry. This is important because of the issue of monodispersity which is defined as the condition for which standard deviation of sphere diameter falls within 5%. Care must be taken to ensure monodispersity, as widely dispersed particle will not segmentally self assemble into any regular lattice. We made the monodisperse silica particle of 250nm and 285nm size shown to figure 1(a),(b).

And before deposition the silica alcholsols are washed by repeated centrifugation and ultralsonic dispersion cycle in order to remove impurities , such as amonia, unreacted tetraethoxysilan. 3 or 4 cycles are usually performed. The samples are diluted or concentrated using a centrifuge −redisperse cycle to the required volume fraction. Thicker films are fabricated by successive stacking as shown to figure 1(c).

After monodispersed colloidal solutions have been obtained in desired size ranges, the colloids will be self−assembled in confinement cell or on slide glass surface.

The spheres will self assemble in to an FCC(face−centered cubic) lattice, as a result of energetic preference due to entropy consideration. Experimentally, hard sphere−like colloidal dispersions are known to crystallized with a random stacking of closed packed planes[7]. But theoretically, it is not clear what the thermodynamic equilibrium phase is; also computer simulations have not been determine whether FCC or HCP (hexagonal close packed) or random stacking is favoured[6].

However we found in this work that crystals that form through sedimentation have a random stacking with closed packed planes perpendicular to gravity. Ordered periodic dielectric structures(opals) are found in nature and can be produced artificially from stacking monodisperse silica. it is necessary to find a sphere which must be located simultaneously in three different crystal planes. An analysis of spatial structure shows that each lattice point of the fcc connects with two different kinds of (111) planes, such as (010), (001), etc.

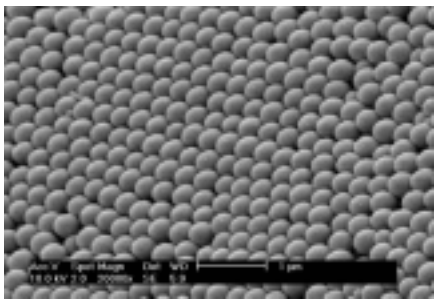
In addition, in SEM image of Figure 1(a) and (c) we have taken from cleaved surfaces this relationship is always satisfied. We believe that this is the most direct evidence to confirm the fcc structure of artificial opals. However, the size of a single crystal of opal is still quite small. The reduction of defects and dislocations therefore become a challenge. Spheres of either larger or smaller diameter can destroy the regular alignment of the opal. Moreover, in solution the aggregation and adhesion of the same spheres can be seen from time to time,

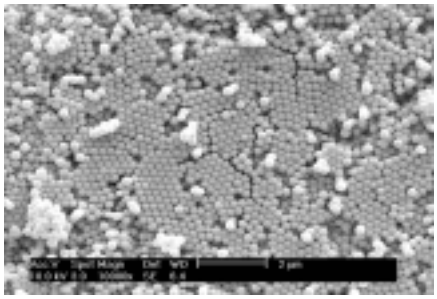
The sample used in this study are closed-packed crystals of monodisperse silica spheres containing few crystalline defects. the silica sphere are synthesized using standard methods. with controllable diameter from 200-400nm. The silica /air composites can be used as templates for the growth of polymer films. the interstitial regions of silica film are filled with low viscosity monomer, which is then photopolymerized. When the silica is etched away , the remaining structure is a macroporus polymer, consisting of a close packed array of air spheres. Because of the direct templating of a original silica film the macroporous polymers maintain the high crystalline equality of the precursor silica film. Figure 1(d) shows secondary electron microscopes of these sample.

Summary

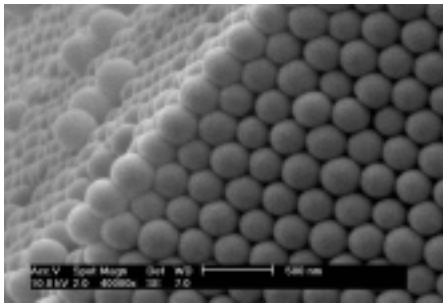
In conclusion, we have prepared SiO_2 oplas of higher quality, achieved by procedure of stricter selection of SiO_2 spheres. We confirmed that good monodispersity of the spheres is one of th major factors for obtaining opals with fine optical properties and large size. The silica-air composites can be used as templates for the growth of polymer films. The interstitial regions of silica film are filled with low viscosity monomer. When it is inverted by HF solution, macroporous polymer films suitable for optical application can be made using silica colloidal crystal.

(a) (b)





(c) (d)



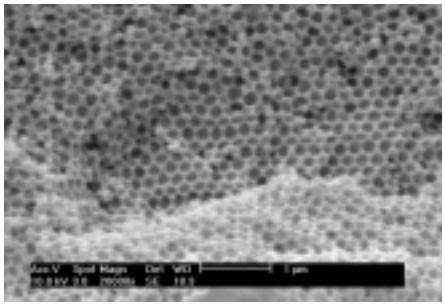


Figure1. Typical scanning electron microscope(SEM)image of
(a)Top view showing sphere 250nm diameter.
(b)Top view showing sphere 282nm diameter.
(c)Cross-sectional image stacking from solutions with volume fraction(10wt%) of (b) sample.
(d)Macroporous poly(methyl acrylate) membranes.

Reference

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