Novel processing for improving monodispersity of ceramic spheres and colloidal crystallinity

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Abstract

We recently proposed that an aging of starting solutions for ceramic nanoparticles synthesis can be a factor to control the nucleation of the nanoparticles. Silica spheres are the most suitable material to learn the aging effect due to their easy to handle and their definite shape that can be measured accurately. The size and the uniformity (or, monodispersity) of silica spheres are essentially enhanced with aging time of several days. In this work, a series of colloidal crystal (opal) films were prepared from variously monodispersed silica spheres. The starting solutions (an ethanolic solution of tetraethylorthosilicate and that of ammonia water) were aged for a week or so, and then reacted. Besides the aging method, spheres with slightly different size were mixed into commercial spheres at different ratio to change the monodispersity. For efficient crystallization on substrate we used three methods, namely, natural drying, silicone oil-covered drying and dip-coating. Among these, silicone oil-covered drying and dip-coating processes showed similar high crystallinity, which we defined from the transmission spectrum of the film. Relationship between the monodispersity of spheres and the opal crystallinity was found to be in a single exponential curve for a variety of silica suspensions.

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1. Introduction

So much has been reported upon 3D (or, 2D and 1D) -array processing for colloidal crystal or photonic crystal with which most of the researchers use commercial monodispersed spheres made of silica or polystyrene\textsuperscript{[1--6]}. Monodispersity within several percent of the median sphere size is considered to be necessary for a well-crystallized opal structure. However, there have been few reports on quantitative discussion on the deviation of sphere size and the colloidal crystallinity.

It is said that the industrial fabrication of silica spheres involves a two-step process, i.e., synthesis and classification (or sieving) to achieve high monodispersity. It must be more favorable to synthesize the spheres with high monodispersity in one-step processing. In the previous work of ours \textsuperscript{[7--9]}, we proposed a simple but novel approach to enhance monodispersity with one step; i.e., several days’ aging of starting solutions before reaction has been found to enhance monodispersity of the spheres. We assume that this amazing result is attributable to microscopic homogenization in the starting solution followed by suppression of nucleation \textsuperscript{[7,10]}.

In this work, we made a 3D arrangement for an opal structure from the silica spheres that were prepared by ourselves from the aged solutions. Commercial spheres were occasionally used to change the monodispersity. Semi-quantitative relationship between colloidal crystallinity and monodispersity will be presented.

2. Experimental

For the silica spheres synthesis, two starting solutions were prepared. One is an ethanolic solution involving tetraethylorthosilicate (TEOS), the other is an ethanolic solution involving ammonia water. All chemical reagents were used without further purification. Needless to say,
both TEOS and ammonia water is very soluble with ethanol and it was quite easy to obtain the two solutions which are clear and homogeneous. In order to enhance microhomogeneity of them and to tailor the monodispersity of product, they were sealed in a brown glass container and aged at room temperature in a shade for 0–7 days. Molar concentration after the two solutions were mixed was fixed at TEOS: NH$_3$:H$_2$O = 0.2: 0.6: 3.2 (mol/L) in ethanol solvent as a whole. Reaction was carried out at 50°C for 80 min with a magnetic stirring. After the reaction, the products were centrifuged, substituted by ethanol, and then dispersed in distilled water by using an ultrasonic cleaner. Solid content in the aqueous suspension was about 1.5 mass%.

The sphere size was determined by measuring ~300 particles from a scanning electron micrograph of each sample. Monodispersity D10/D90 was defined from the size distribution curve at accumulative of 10% and 90% as shown in Fig. 1.

Substrate slide glass (25 × 25 mm) was carefully washed by detergent and water, and then cleaned up by firing at 600°C in air. This process to remove organics on the substrate is necessary for the spheres to move smoothly. In this study, three methods to prepare colloidal crystal film were compared. One is to drop the suspension on the glass and to leave it at room temperature (natural drying). The second one, developed by Fudouzi [3], is to cover the dropped suspension with silicone oil (density 0.965 g/cm$^3$) and to dry in a 55°C oven (oil-covered drying). The third one is, what is called, dip-coating method (pull-up angle = 90°, pull-up speed = 20 μm/min).

Crystallized film was evaluated by a UV–vis spectrophotometer (Hitachi, U-3300). A hand-made jig to tilt the incident angle from 0° to 40° was used to confirm the refractive index and the d-value (plane distance) of the film [3].

![Fig. 1. A typical size distribution curve of the synthesized spheres. The size ratio D10/D90 was used as an index to present the monodispersity of spheres.](image)

3. Results and discussion

3.1. Aging effect on sphere size and monodispersity

Fig. 2 shows the monotonous increment of the sphere size and the monodispersity as a function of aging time. Comparing the size of spheres prepared from fresh solutions ($D_{\text{fresh}} = 350$ nm) and that from the 7-days-aged solution ($D_{7d} = 380$ nm), the increment is only 11.4%. But we should remember that this is a one-dimensional parameter. Since the reaction time of 80 min is quite enough to complete the reaction, we can simply convert this value into the number ratio of nucleus; that is, let the nucleus number generated in the reaction with fresh solutions be $N_{\text{fresh}}$ and let that with the 7-days-aged solutions be $N_{7d}$, the ratio ($N_{7d}/N_{\text{fresh}}$) is equal to $(D_{7d}/D_{\text{fresh}})^3$. From this simple calculation we find that $N_{7d} = 0.78 \times N_{\text{fresh}}$. This means that the nucleation in the aged condition was above 20% less than that in the fresh. As we discussed in the previous work [7], the results in Fig. 2 are not due to mere contamination such as moisture in ethanol, but we assume that microheterogeneity (or, variously sized clusters) in the fresh starting solutions could induce heterogeneous nucleation to reduce the number of nucleus and to uniformalize the nucleation.

3.2. Evaluation of colloidal crystallinity

Fig. 3 shows a typical transmission spectrum from a well-crystallized opal film measured with the incident light normal to the substrate. As shown in Fig. 3, we notice that a specific wavelength has not been transmitted due to Bragg reflection in the opal film. Herein, the depth ($h$) and the width ($d$) of the dip will be used to evaluate the colloidal crystallinity semi-quantitatively.

In order to prepare opal films with different crystallinity, the following experiment was run. Commercial silica spheres, whose median size and monodispersity ($D10/D90$) were 302 nm and 0.927, respectively, were mixed with synthesized spheres of 294 nm. The mixed of the
synthesized spheres was 5, 10, and 20 mass%. A mixed suspension was dispersed and mixed by an ultrasonic cleaner for 10 min, and then crystallized by the oil-covered drying method.

Unsurprisingly, the monodispersity of the mixed spheres simply decreased with increasing amount of the mixed sphere. As a consequence, we obtained four different samples with the monodispersity varying from 0.875 to 0.927. Fig. 4 shows the values of $h$ and $\delta$ in the transmission spectra as a function of monodispersity. The depth tends to increase, while the width tends to decrease with the increasing monodispersity. To take both into account in practice, a new parameter, $h/\delta$, is now assumed to present the colloidal crystallinity of the opal film. For example, the highest crystallinity in Fig. 4 is more than 10 ($\mu$m$^{-1}$) for pure commercial spheres. Since the unit in the blanket in the former sentence is not significant, the relative value such as 10 will be used in the following text. The refractive index and the plane distance of this film estimated by the
method previously shown [3] were 1.36 and 241 nm, respectively. The latter value is close to the theoretical value (246 nm) of the plane distance assuming the closest packing among the sphere of 302 nm. This means that the opal crystallization process here was done adequately.

3.3. Effect of crystallization methods

In comparison, the $h/d$ values for the natural drying, the oil-covered drying, and the dip coating were found to be 2, 14, and 13, respectively. Microstructure of those opal films are shown in Fig. 5. Low crystallinity value in the natural drying method is obvious in Fig. 5(a). The oil-cover method and the dip-coating provided similarly high crystallinity and ordered microstructure in the opal film. Fig. 6 shows zoom-out micrographs for the oil-covered coating and the dip coating. Owing to the shrinkage during drying, the formation of cracks (or, domain boundaries) is inevitable. To make the crack boundaries in the micrograph clear, supplementary lines are drawn in Fig. 6. Due to the pulling process in the dip-coating method, unidirectional domains of 10–30 μm width were formed. On the other hand, what we call polycrystalline-like domains of 50–200 μm in size were formed in the oil-covered drying process. Judging from the $h/d$ values of the two films so far, the domain size is does not much influence colloidal crystallinity assumed in this work. An exact analysis should be made by controlling the exact thickness of the film, and has not been successfully accomplished in the present work.

3.4. Relationship between monodispersity and colloidal crystallinity

Fig. 7 shows a plot for the monodispersity defined in Fig. 1 versus the colloidal crystallinity defined by the $h/d$ values in Fig. 3. Hollow plots are data obtained by blending the spheres, and the solid ones are data for the aging-controlled runs. Although the deviation is not so small, a general tendency can be expressed as a single curve.

It may be natural but should be noted that the curve increased exponentially. This means that only a small increment in the monodispersity above ~0.92 could have a prominent effect upon the crystallinity and the optical properties of the film. Awfully simple method to enhance the monodispersity by aging starting solutions would be a new aspect in nanoparticles synthesis from a liquid phase.

4. Summary

(1) A method to tailor the monodispersity in one-step process (i.e., aging of starting solutions) and a primitive method to vary the monodispersity by simple mixing spheres of slightly different sizes were compared in terms of opal crystallization.

(2) A simple method to determine the crystallinity from a transmission spectrum is suggested.

References

[1] H. Fudouzi, Y. Xia, Adv. Mater. 15 (2003) 892.
[2] F. Tang, H. Fudouzi, T. Uchikoshi, Y. Sakka, J. Euro. Ceram. Soc. 24 (2004) 341.
[3] H. Fudouzi, J. Colloid Interface Sci. 275 (2004) 277.
[4] Y. Masuda, T. Itoh, K. Koumoto, Langmuir 21 (2005) 4478.
[5] Y. Masuda, T. Itoh, K. Koumoto, Adv. Mater. 17 (2005) 841.
[6] Y. Masuda, M. Itoh, T. Yonezawa, K. Koumoto, Langmuir 18 (2002) 4155.
[7] N. Enomoto, A. Kumagai, J. Hojo, J. Ceram. Soc. Jpn. 113 (2005) 340.
[8] N. Enomoto, A. Kumagai, J. Hojo, J. Ceram. Process. Res. 5 (2004) 391.
[9] N. Enomoto, A. Kumagai, J. Hojo, J. Ceram. Process. Res. 6 (2005) 286.
[10] N. Enomoto, J. Shiihara, T. Hongo, Z. Nakagawa, J. Ceram. Soc. Jpn. 107 (1999) 278.