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Control of crystallization of ionic silica particles in aqueous dispersions by sodium hydroxide

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Crystallization behavior of colloidal silica particles in aqueous dispersion (particle diameter = 0.12×10^{-6} m) is examined at a silica volume fraction of 3×10^{-2} and various sodium hydroxide and salt concentrations. We report that the crystallization could be controlled by adding 10^{-5} to $10^{-4}M$ sodium hydroxide, which increased the surface charge density, σ, of the silica particle. Conditions for crystallization were determined as a function of σ and salt concentration. The grain size was large near the phase boundary between crystal and liquidlike regions. The structure of the crystals was studied using an ultra-small-angle x-ray scattering method. Several orders of Bragg reflection having a sixfold symmetry was observed for large grains. For small grains, the scattering profile was powderlike. In both cases, the crystals had body-centered-cubic lattice structures. The observed closest interparticle distances were smaller than average interparticle distance, suggesting the non-space-filling nature of the crystal. [S1063-651X(96)51105-0]

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I. INTRODUCTION

Ionic colloidal particles form crystals in dispersions, due to a strong electrostatic interparticle interaction [1]. Aqueous dispersions of colloidal silica have been frequently studied [2–4]. Since the driving force of the crystallization is electrostatic, it is expected that the crystals are formed when the salt concentration, C_s, is low, and the surface charge density, σ, is high. Experimental studies on the crystallization have usually been performed at deionized conditions, with coexisting ion-exchange resin beads in the dispersions. However, as we have reported earlier [5], the σ value of the colloidal silica is quite small (less than 10^{-7} C cm^{-2}) at deionized conditions, and crystallization is unfavored. Therefore, previous studies have been performed under quite limited experimental conditions. For example, Konishi *et al.* [3,4] reported that it took several months to obtain silica crystals by deionizing dispersions with coexisting ion-exchange resin beads. It is thus hoped to study colloidal silica particle with high σ values.

It has been reported that the σ value of colloidal silica can be controlled by addition of hydroxides of alkali metal in the dispersion [6]: The surface of silica particle is covered by weakly acidic silanol groups. By adding the hydroxide, the degree of dissociation of the silanol groups, and thus σ value, increases. Although most of previous experiments on the surface charge of colloidal silica have been performed at relatively high salt conditions, we have recently found out that the σ value of silica could be controlled by sodium hydroxide without changing C_s value in bulk, when [NaOH] was smaller than $2.5\times10^{-4}M$ and the volume fraction of silica, ϕ, was larger than 2.6×10^{-3} [5]. On the basis of this finding, in the present work we studied the crystallization behavior of colloidal silica at various [NaOH]'s and C_s's. Here we report that the crystallization of colloidal silica particles could be controlled by 10^{-5} to $10^{-4}M$ sodium hydroxide in the dispersion. We find that when σ values were sufficiently high, the silica crystals could be easily formed in a few minutes even in the presence of salt.

Previous studies have shown that the lattice constants of colloidal crystals were of the order of 0.1–1 μm [1], which could not be precisely determined by light and neutron scattering methods. Recently an ultra-small-angle x-ray scattering (USAXS) method, by which an electron density fluctuation of several μm is detectable, has been developed and it has made it possible to perform detailed studies on the crystal structure [3.4]. In the present paper, we report the preliminary USAXS study at several surface charge densities and salt concentrations.

II. EXPERIMENTAL SECTION

The colloidal silica, Seahoster KE-P10W, was kindly donated by Nippon Shokubai Co., Ltd. (Osaka, Japan) in the form of an aqueous dispersion stabilized by ammonium hydroxide. The dispersion was purified by dialysis and ion-exchange methods, as described earlier [5]. The diameter of the particles was $(0.12\pm0.01)\times10^{-6}$ m, which was estimated by fitting the USAXS profile under high salt conditions to the form factors for isolated spheres. Water was purified by using Milli-XQ system (Millipore Co., Ltd., Bedford, MA) and by bubbling with argon gas, and had an electrical conductivity of $(0.2–0.3)\times10^{-6}$ S cm^{-1}. To avoid ionic impurities from the glass wall, polystyrene and polyethylene apparatuses, which were carefully cleaned and rinsed with the purified water, were used in sample preparation. They were washed with the purified water just before use, conductivities of which were measured to examine whether the cleanings were satisfactory. A stock solution of sodium hydroxide was prepared just before use, whose concentration was determined by performing electrical conductivity titrations. The

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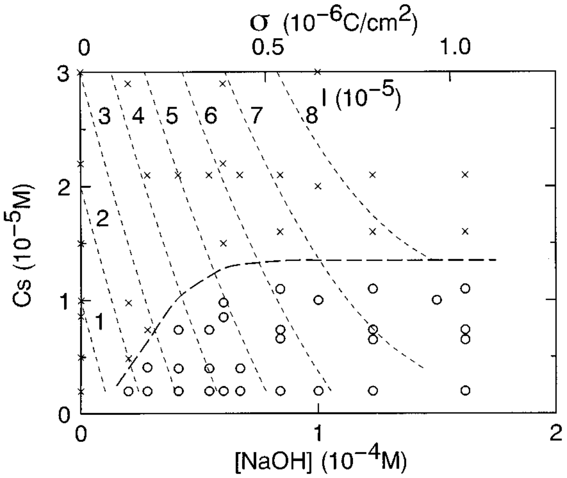

FIG. 1. Conditions for crystallization of KE-P10W colloidal silica particles in aqueous dispersions ($\phi=3\times10^{-2}$) at room temperature. Surface charge density, σ, was calculated from the concentration of coexisting NaOH. ○: crystal formation; ×: no crystal formation. Dashed lines show conditions where effective ionic strengths, I, are constant.

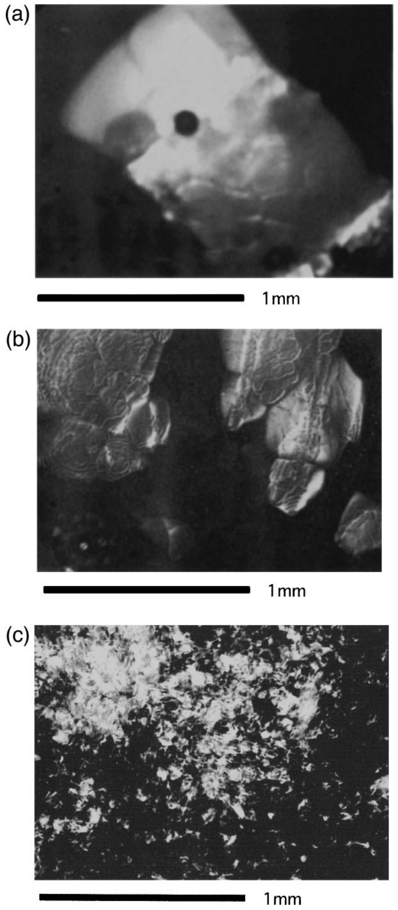

FIG. 2. Polarizing reflection optical micrographs of the colloidal crystals at (a) $[\mathrm{NaOH}]=2\times10^{-5}M$, (b) $6\times10^{-5}M$, and (c) $9\times10^{-5}M$. $C_s=2\times10^{-6}M$ in all cases.

volume fraction of silica was 3.0×10^{-2}.

Observations of the dispersions were performed at room temperature under argon atmosphere. Polarizing reflection micrographs were taken by using a metallurgical microscope (Optiphot, Nikon Co., Ltd., Tokyo) and specially designed polyacrylate cells. A Bonse-Hart USAXS apparatus with a newly designed channel-cut germanium single crystal was constructed, whose details were fully described elsewhere [7,8]. The beam height and width were approximately 1 and 8 mm, respectively. Sample dispersions were introduced into a quartz capillary cell having an inner diameter of 2 mm and a thickness of 0.2 mm. After argon gas was introduced, the capillary was doubly sealed by using plastic films and chemical paste, and used for the measurements within 1 day. The capillary was held horizontally during the measurement. Temperature was controlled at 25±0.5 °C.

III. RESULTS AND DISCUSSION

A. Conditions for crystallization

Crystallization of the silica particles in aqueous dispersions was examined at various sodium hydroxide and salt concentrations. Figure 1 is the phase diagram, which was constructed by observing iridescence due to the crystal formation. Hereafter we denote these two regions as crystal and liquidlike regions, respectively. The value of C_s was estimated from the sum of concentrations of coexisting sodium chloride and protons in the water used ($2\times10^{-6}M$). Our previous results [5] showed that concentrations of free Na and OH ions in the bulk were negligibly small at $[\mathrm{NaOH}]\leqslant2.5\times10^{-4}M$ and at $\phi\geqslant2.6\times10^{-3}$. Under the present condition, we can safely assume that the (analytical) charge density of the silica particle is proportional to [NaOH] [9]. The value of σ calculated from [NaOH] is also shown in Fig. 1. It was also confirmed that dissolution of silica particle to be monosilicate was negligible at present condition. An effective ionic strength of the dispersion, I, was estimated by an equation

$$I=C_s+f[\mathrm{NaOH}]$$

where f is a fraction of free counterions. The values of f at various [NaOH]'s were estimated from the f-σ plot (Fig. 10 in Ref. [10]) determined experimentally by using H-type latices whose diameters were close to that of the present silica [10]. Conditions where I values were constant (isoionic lines) are also shown in Fig. 1.

Without sodium hydroxide, the crystal was not formed even at $C_s=2\times10^{-6}M$. On the other hand, at 10^{-5} to $10^{-4}M$ sodium hydroxide, crystals were formed in a few minutes. The crystallization was observed even in the presence of extraneous salt. However, it was inhibited at C_s's larger than $1.5\times10^{-5}M$. Thus we could control the crystallization of silica particles by varying the surface charge density of the particle and salt concentration of the dispersion. The present system is useful for the study of the charge density dependence of various properties in ionic colloidal dispersion. Palberg *et al.* [11] have reported another system using polymer latex particles, whose charge densities were varied by addition of ionic surfactants.

The crystal consisted of grains whose size increased when the boundary between crystal and liquidlike regions was approached. This trend on the grain size is consistent with that expected from currently accepted theory on nucleation and growth for atomic and molecular systems [12]. Figure 2

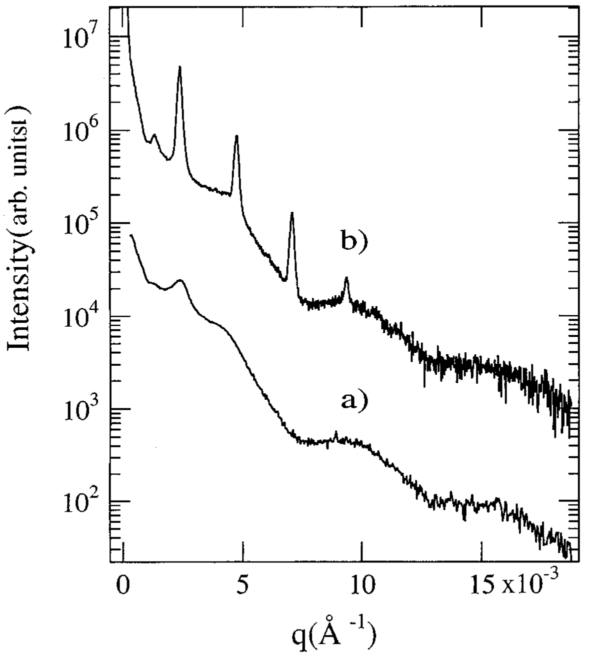

FIG. 3. Ultra-small-angle x-ray scattering (USAXS) profile for aqueous dispersions of the silica at (a) [NaOH]=0*M* and (b) $1.5\times10^{-4}M$. $C_s=10^{-5}M$.

shows polarizing reflection micrographs at $C_s=2\times10^{-6}M$ at three [NaOH]'s. At $[\mathrm{NaOH}]=2\times10^{-5}M$, which was very close to the boundary, large grains (1–2 mm) were formed. It was observed that large grains grew from the cell wall under this condition. At $[\mathrm{NaOH}]=9\times10^{-5}M$, the grain size was smaller than 0.1 mm.

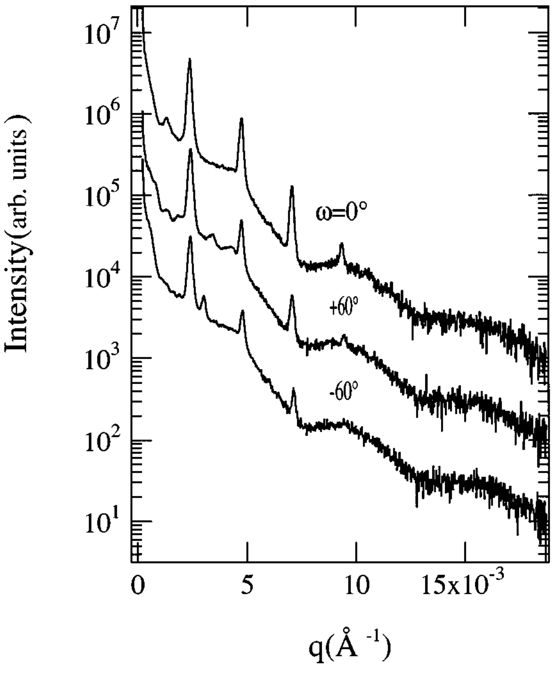

FIG. 4. USAXS profile for an aqueous dispersion of the silica at three rotation angles, *ω*, around the capillary axis. $[\mathrm{NaOH}]=1.5\times10^{-4}M$, $C_s=10^{-5}M$.

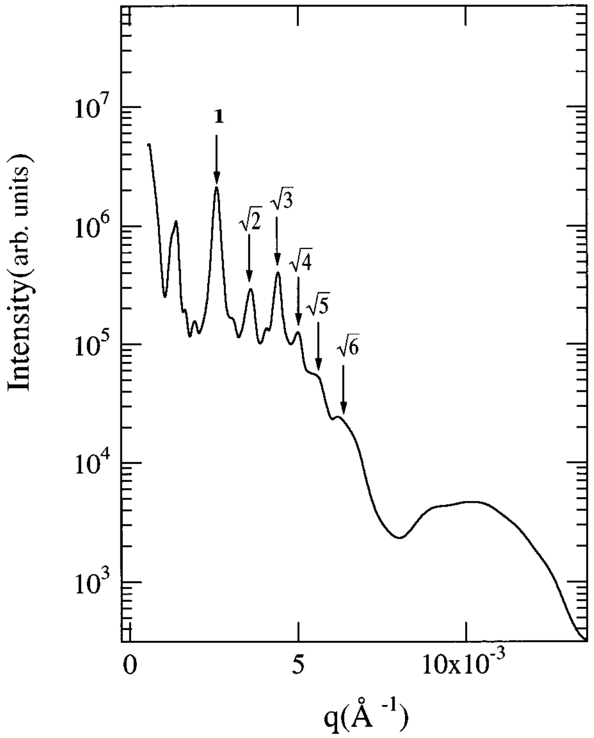

FIG. 5. USAXS profile for the silica dispersion at $[\mathrm{NaOH}]=10^{-4}M$ and at $C_s=2\times10^{-6}M$.

B. USAXS measurement

The USAXS measurements were performed at several C_s's and [NaOH]'s. Figure 3 shows the scattering intensity versus scattering vector (q) plot at $C_s=10^{-5}M$ and at two [NaOH]'s, which corresponded to the liquidlike and the crystal regions.

In the liquidlike region ($[\mathrm{NaOH}]=0M$), a broad peak due to interparticle interference, resulting from an electrostatic interaction, was observed in addition to the form factor of an isolated particle. The closest interparticle distance, $2d_{\mathrm{expt}}$, estimated from the 2θ value using Bragg equation, was 0.286×10^{-6} m. On the other hand, sharp peaks were observed in the crystal region ($[\mathrm{NaOH}]=1.5\times10^{-4}M$; grain size=1–2 mm) at $q=2.4n\times10^{-3}$ Å^{-1}, n being an integer from 1 to 4. These were ascribed to the first to the fourth orders of Bragg diffractions. The measurements were further performed by rotating the sample with respect to the capillary axis. Similar scattering profiles were observed at each multiple angle of 60°, which indicated that the crystal structure had a sixfold symmetry. The profiles at rotation angle, $\omega=0,\pm60°$ are shown in Fig. 4. Several small peaks other than the Bragg peaks did not show the sixfold symmetry. They appear to be due to smeared scatterings from other small grains which coexisted in the sample [3,4,13].

The presence of a sixfold symmetric structure in the colloidal silica crystals has been reported by Konishi *et al.* [3]. They performed detailed USAXS studies at $\phi=3.76\times10^{-2}$ on large grains which were formed after the sample (the same batch of silica as the present one) had been kept standing under the deionized condition for several months. They found out that the diffraction of the sixfold symmetry was attributable to the (110) plane of a body-centered-cubic (bcc) structure, which was maintained parallel to the capillary wall with the $[1\overline{11}]$ direction being vertically upward. The scattering profile presently obtained can be ascribed to the same structure. The distance between the (110) planes, d_{110}, and the lattice constant, a, were 0.266×10^{-6} m and 0.376×10^{-6} m, respectively. The $2d_{\mathrm{expt}}$ value was calculated to be 0.326×10^{-6} m.

The measurements were further performed under conditions where small grains were formed. In Fig. 5, a desmeared scattering profile at $C_s=2\times10^{-6}M$ and at $[\mathrm{NaOH}]=10^{-4}M$ (grain size<0.1 mm) is shown. Except for a small peak at $q=1.5\times10^{-3}$ Å^{-1}, which was due to the smearing effect [3,4,13], the scattering profiles did not markedly change with rotation of the sample with respect to the capillary axis. The ratios of the q values of each peak are also shown in Fig. 5. It is clear that the profile can be attributed to the powderlike pattern of a bcc lattice [14]. The values of d_{110}, a, and $2d_{\mathrm{expt}}$ estimated by assuming a bcc lattice, were 0.248×10^{-6} m, 0.351×10^{-6} m, and 0.304×10^{-6} m, respectively.

As seen above, the USAXS profiles obtained under various conditions were consistent with the finding on liquid like-crystal transition mentioned in the previous section. It should be noted that the closest interparticle distances, $2d_{\mathrm{expt}}$, in the crystals were smaller than the average interparticle distance, $2d_0$ (0.331×10^{-6} m, in the present case), which was estimated by assuming homogeneous distribution of the particles with a bcc symmetry. This confirms the non-space-filling nature of the crystal [3,4].

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[14] The present observation suggests that randomly oriented grains, which give a powderlike scattering pattern, coexist with highly oriented ones, which cause a smearing effect. The former might result from homogeneous nucleation, while the latter seems to be due to inhomogeneous nucleation from the capillary wall.