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SHORT COMMUNICATION

Video-tape observation of the crystal growth and morphology of colloidal single crystals

Tsuneo Okubo

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Abstract Crystal growth and morphology of colloidal crystals of silica spheres (81.2 nm in diameter) are observed directly on a video-tape camera. Crystal growth from the round-shaped, small single crystals to the angular-shaped ones is clear. It is observable that the single crystals are packed densely and separated from each other with the grain boundaries. The morphology of colloidal crystals is quite similar to that of typical crystals such as metals, proteins, and ice.

Keywords Video-tape observation · Colloidal crystallization · Morphology · Colloidal silica spheres

Introduction

Colloidal suspensions display structures in particle distributions, such as gas-, liquid-l, and crystal-like structures, especially in deionized suspensions [1–15]. Suspensions showing crystal-like structures are named as *colloidal crystals* and are ideal for model studies of metals and protein crystals, as the colloidal structures are analyzed much conveniently with optical techniques and even with the naked eyes. A study of the colloidal crystals is helpful in understanding the fundamental properties of states of substances and electrostatic intersphere interactions. The important factors causing the colloidal crystallization are an electrostatic intersphere repulsion and the extended electrical double layers around the spheres in the deionized state. Many researchers have studied colloidal crystals both experimentally and theoretically [1–15].

Direct observations of colloidal crystal growth processes have been studied by several researchers hitherto [2, 10, 11, 13, 16–29]. However, little work has been reported on the morphology (shape, size, and mutual arrangement) of the colloidal single crystals, because the size of the crystals was not large enough and the mutual arrangement of the single crystals was not clear using the usual techniques of video-tape observation and microscopy. In this work, the author changed the incident-light angle very slightly in the video-tape observation and succeeded to distinguish the nearest-neighbored single crystals. The other reason for the scarcity of the work is the fact that it has been difficult to obtain thoroughly deionized suspensions, which contain the charges from the particles, their counterions, and H^+ and OH^- from the dissociation of water. The deionized suspension is believed to contain no contaminant ions from air, glass, etc. To obtain the thoroughly deionized suspension, highly effective mixed beds of cation- and anion-exchange resins such as Bio-Rad resins have to coexist in a suspension for a long time, *more than* 10 *years*. From our experiences, the deionization process of suspension with resins is unexpectedly slow. This may be due to the fact that the deionization reaction takes place between solid (colloidal particles)–solid (resins) phases via a liquid medium. It is interesting to note that large colloidal crystals are formed at the very low sphere concentrations for the thoroughly deionized suspensions [30–41]. We observed very large single crystals, 2 to 8 mm in size, by the complete deionization of a colloidal suspension with the ion-exchange resins coexisted for more than 10 years [33, 36, 40].

T. Okubo (✉)
Institute for Colloidal Organization,
Hatoyama 3-1-112,
Uji, Kyoto 611-0012, Japan
e-mail: okubotsu@ybb.ne.jp

T. Okubo
Cooperative Research Center, Yamagata University,
Johnan 4-3-16,
Yonezawa 992-8510, Japan
e-mail: okubo@yz.yamagata-u.ac.jp

In this work, rather small colloidal silica spheres, 81.2 nm in diameter, were deionized thoroughly with Bio-Rad ion-exchange resins [AG501-X8(D), 20–50 mesh] for more than 10 years, and a video-tape observation was made for studying colloidal crystal growth processes and their morphology.

Experimental

Materials

CS61 silica spheres were kindly donated by Catalysts & Chemicals Industries (Tokyo). The diameter, standard deviation from the mean diameter, and polydispersity index of the spheres were 81.2 nm, 11.5 nm, and 0.14, respectively. These size parameters were determined on an electron microscope (transmission electron microscope, Hitachi, H8100) in our laboratory. The charge density of the spheres was determined by conductometric titration with a Horiba conductivity meter, model DS-14 (Kyoto). The strongly acidic and weakly acidic charge densities were 0.60 and 4.90 $\mu C/cm^2$, respectively. The spheres were carefully purified several times using an ultrafiltration cell (model 202, membrane: Diaflo-XM300, Amicon). Then, the stock sample suspension was treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8 (D), 20–50 mesh] for more than 10 years before use. The water used for the sample preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA, USA).

Close-up video-tape observation

A close-up video-tape observation was made with a video camera recorder (CCD-V800, Sony). The sample suspensions were prepared by dilution of the stock suspension in the absence of ion-exchange resins coexisted in a round bottle-type densitometer, 100 ml in volume (code 1857, TOP Co. Tokyo). The suspension was coexisted with a spin bar, which was set in the bottom of the cell on the magnetic rotating device. Sphere concentration was rather high,

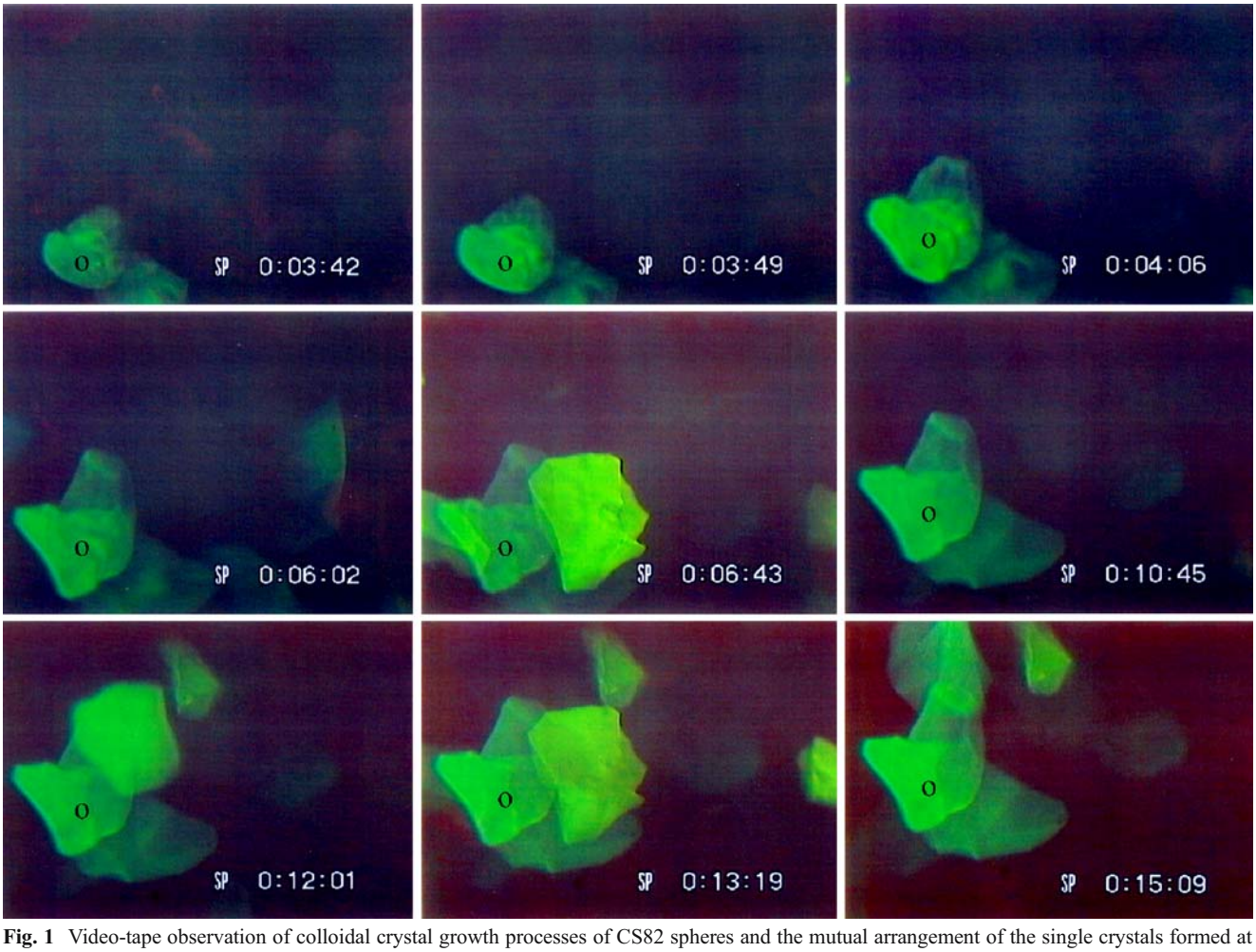

Fig. 1 Video-tape observation of colloidal crystal growth processes of CS82 spheres and the mutual arrangement of the single crystals formed at 23 °C. ϕ=0.0215; the frame size of the each picture is 1.3×1.8 mm

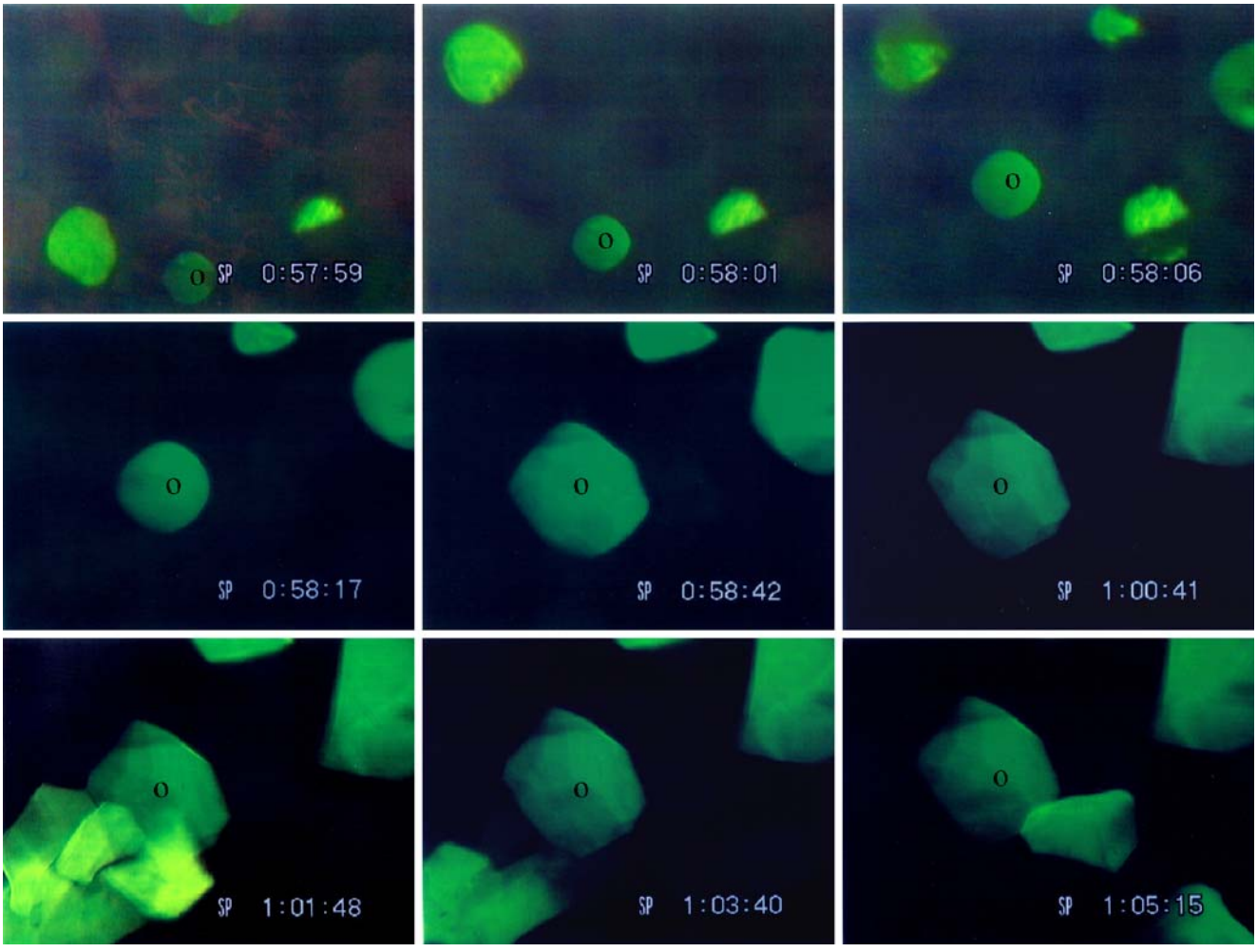

Fig. 2 Video-tape observation of colloidal crystal growth processes of CS82 spheres and the mutual arrangement of the single crystals formed at 23 °C. ϕ=0.0215; the frame size of the each picture is 1.3×1.8 mm

0.0215 in volume fraction. In this sphere concentration, small-sized single crystals, 0.05 to 0.4 mm, were formed stably for several years even without coexistence of the ion-exchange resins. When the agitation of the suspension ceased, crystal grew. The mutual arrangement of the single crystals was observed from the very slight change of the incident angle of light. Colored pictures were reproduced from the video films with a color printer (NV-MP1, Panasonic) and scanned on a Color Scanner & Printer (Pixus MP800, Canon). The light source for the video-tape observation was a pocket-type flashlight (BF-775, Xenon 4, National).

Results and discussion

Figure 1 shows the crystal growth process (from 0:03:42, which means 3 min 42 s, to 0:06:02 in the frame clock) and mutual arrangement of single crystals (from 0:06:02 to 0:15:09). A certain single crystal, which always appeared in all the frames, was marked with an open circle for the convenience of the readers to see the mutual arrangement of the single crystals as easy as possible. The primary crystal growth processes completed at 0:06:02 in the frame clock. In the beginning stage of crystal growth, which is not shown in Fig. 1, blinking of the small single crystals (or "crystallites") was marked; very small single crystals from the homogeneous nucleation mechanism appeared at one moment. However, they disappeared in the next moment, and new crystals appeared in other places [34]. The blinking phenomenon is undoubtedly due to the rotational and translational Brownian movement of crystallites, which are surrounded in a liquid-like structure of suspension. During the blinking of the crystallites, growth of the crystals was also observed clearly with the naked eyes, though taking pictures of the assigned crystals was extremely difficult. In the crystal growth processes, the single crystals from the *homogeneous* nucleation in the bulk phase far from the cell wall and also those from the *heterogeneous* nucleation mechanism along the cell wall

came to touch to each other. The single crystals were packed densely and separated from each other by the grain boundaries. It should be noted here that this state corresponds to the *primary* crystallization step, where the meta-stable single crystals are formed.

The first frame in Fig. 1 shows the single crystals in contact with each other and then the primary crystallization process was in progress. In this case, most of the local position of each single crystal did not change. At 0:06:02, crystal growth seems to be complete. Then, the author changed the incident angle of the flashlight very slightly and carefully one after another. The frames from 0:06:43 to 0:15:09 show the single crystals thus observed. The single crystals repeated to appear and disappear depending on the very small change in the incident light angle. It is now clear that only the single crystals matching with the Bragg condition are observable with the naked eyes, and the mutual arrangement of the each single crystals is clearly observed from several frames of the pictures taken from 0:06:43 to 0:15:09. It is understood from the pictures that the single crystals are packed densely and separated from each other with the thin grain boundaries. It should be noted here that the kinetic analysis of colloidal crystallization from the video-tape observation shown in Figs. 1, 2, 3, and 4 was impossible, because the pictures of the specified single crystals in the beginning stage of crystallization were not taken by the blinking phenomena described above. Kinetic analyses have been made successfully from the spectroscopic measurements such as reflection spectroscopy [42–45] and time-resolved small-angle X-ray analysis [46].

Figure 2 shows the other example of the video-tape pictures. From 0:57:59 to 1:00:41, the incident angle of a flashlight was fixed. The location of several single crystals in the frames moved upward slightly, as the suspension flow did not stop completely by stopping the rotation of the spin bar. However, the several single crystals kept to be observable, though only a few crystals still appeared and/or disappeared especially in the beginning several frames. These observations again mean that all the single crystals are packed densely already at 0:57:59. Several important features are observed in Fig. 2: (a) single crystals changed their shapes from a round to an angular shape in the course of crystallization and (b) crystal growth takes place in the densely packed condition. The change in the single crystals

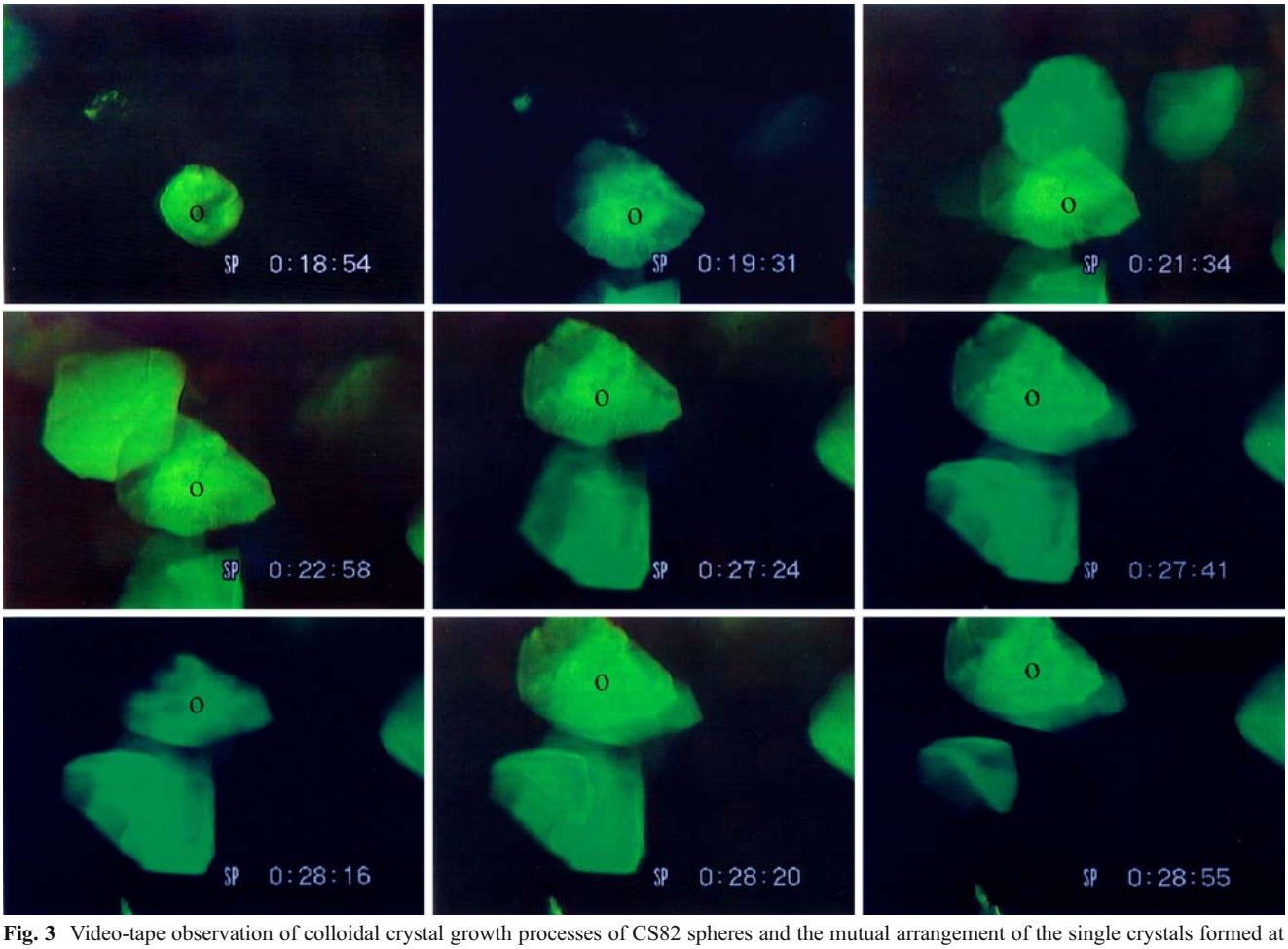

Fig. 3 Video-tape observation of colloidal crystal growth processes of CS82 spheres and the mutual arrangement of the single crystals formed at 23 °C. ϕ=0.0215; the frame size of the each picture is 1.3×1.8 mm

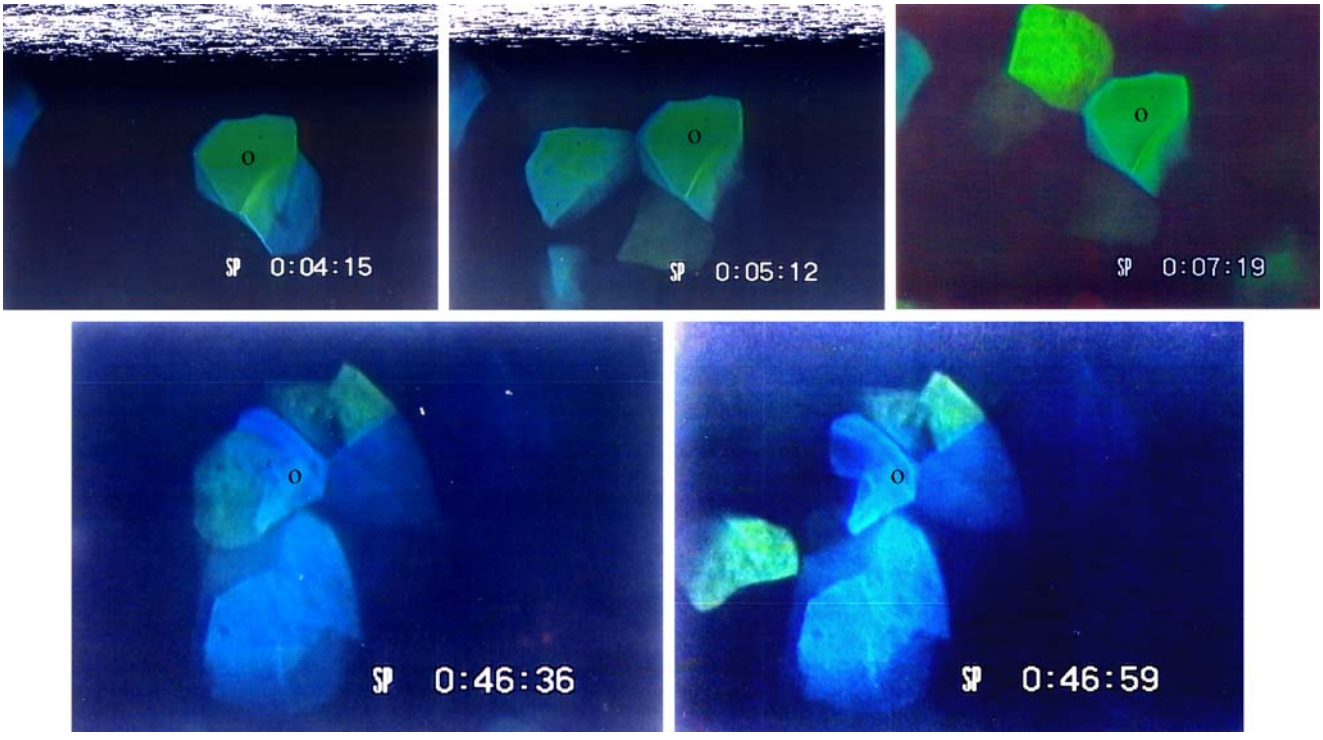

Fig. 4 Video-tape observation of the mutual arrangement of the single crystals formed at 23 °C. ϕ=0.0215; the frame size of the each pictures is 1.3×1.8 mm. The *upper three* and *lower two* pictures are for the different colloidal single crystals

from round to angular shape supports that the germinal single crystals are round. When the neighbored crystals contact with each other, crystal growth proceeds further toward the dead space, where the sphere distribution is still liquid-like. It should be mentioned here that the Ostwald ripening processes, i.e., the larger crystals come much larger and the smaller ones come smaller and even disappear in the final stage of crystallization, start after the contact of the growing crystals intermediated with the grain boundaries. Thus, the total number of single crystals should decrease in the course of crystallization. Concerning the first result, it should be noted further that the association-type and lozenge-shaped single crystals were formed for CS61 spheres [36], where sphere concentration was low, 0.0044 in volume fraction. On the other hand, the shape of the single crystals in Figs. 1 and 2 was block-like and an angular one. In the present work, the sphere concentration is rather high, ϕ=0.0215, and the ion-exchange resins are not coexisted. These different experimental conditions will be the reason for the difference in the morphology of the single crystals. Three frames from 1:01:48 to 1:05:15 were observed by changing the incident light angle, and they demonstrate clearly the mutual arrangement of single crystals. It should be noted further here that the size distribution of the single crystals was significant in the pictures. This supports the idea that the Ostwald ripening processes do not proceed completely, though the reason is not clear yet.

Figure 3 also shows the crystal growth and the mutual arrangement of the single crystals formed. In this case, the incident light angle was not changed but fixed during observation times from 0:18:54 to 0:28:55. Round-shaped single crystals grew up to the angular-shaped ones as is demonstrated by the crystals marked by an open circle, for example. It should be mentioned here that most kinetic measurements of colloidal crystallization have observed an induction period, after which the crystal growth starts, especially in diluted suspensions. This observation supported the explanation of the kinetics of colloidal crystallization by the classical diffusive crystallization theory, including nucleation and crystal growth processes [42–45]. It is further interesting to note that the crystal marked by a small cycle in the frame at 0:28:16 is very small compared with the other crystals marked by the small cycles in the other frames. This supports that the marked single crystal is not single but composed of two crystals overlapped in front and rear. Thus, the picture further supports again that the single crystals are packed densely.

Figure 4 shows two examples demonstrating the mutual arrangement of single crystals. The upper and lower pictures show that one of the single crystals marked by an open circle is surrounded by other many neighbored single crystals. It should be mentioned here that this work demonstrates that single crystals are packed densely and denies the *island–sea* and/or *void* model for the completed colloidal crystals [12, 15]. It should be noted here, however,

that the "island–sea" model is undoubtedly correct in the processes of crystallization, as the colloidal single crystals born and that grow in the sea of liquid-like distribution of colloidal spheres.

Lastly, we should note that the colors of the single crystals observed in this work (see Figs. 1, 2, 3, and 4) were blue or green and quite monotonous, which is in contrast to the colorful single crystals reported often hitherto. This is clearly due to the fact that the most neighbored intersphere distance and the Bragg reflection peak wavelength at 90° in the incident light angle in this work are calculated to be 264 and 487 nm, respectively, just in the range of ultraviolet light, when the calculation was made assuming the face-centered cubic lattices. Thus, the colors observed in Figs. 1, 2, 3, and 4 must be weakly bluish, and the colors from the secondary and/or tertiary Bragg diffractions are also very weak.

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