doi:10.1246/cl.2011.42

Uphill Diffusion of Charged Colloidal Particles during Unidirectional Crystallization under pH Gradient

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We report that charged colloidal particles show uphill diffusion against electrostatic interparticle repulsions in the presence of pH gradient. This intriguing phenomenon is found upon unidirectional crystal growth of colloidal silica via diffusion of pyridine, by means of in situ fiber optic reflection spectrometry.

Migrations of colloidal particles under gradients of various physicochemical potentials have extensively been studied in colloid science. They include electrophoresis under electrostatic potential and thermal diffusion due to a temperature gradient.[1] It has been reported that the particles are subjected to migration forces when they are placed in a concentration gradient of adsorbing solutes.[2] This is referred to as "diffusiophoresis," which is attributed to two mechanisms. (1) Chemiphoresis is movement of particles toward regions of higher solute concentrations, in order to lower free energy. (2) When the solutes are electrolytes, their diffusion potential causes electrophoresis of the charged particles.

We have previously reported the directed crystallizations of silica colloids induced by the adsoption–diffusion of a weak base pyridine (Py)[3–5] which should result in the diffusiophoresis of the particles. The purpose of this study is to examine migrations of colloidal particles under gradients of the base concentration during unidirectional growth. By applying in situ fiber optics reflection spectroscopy, here we find that the particle concentrations became transiently nonuniform because of particle diffusion against the Py concentration gradient.

The mechanism of this crystallization of the colloidal silica can be explained as follows. The surfaces of the silica particles are covered by silanol groups (≡Si–OH). Since silanols are weak acids, their degree of dissociation and consequently, the charge number of the silica particles increases with the addition of a base. As a result, the silica colloids undergo charge-induced crystallization under appropriate conditions. Py is a weak base for which pK_a is 5.42 at 25 °C ($\mathrm{py} + \mathrm{H_2O} \rightleftharpoons \mathrm{pyH^+} + \mathrm{OH^-}$, where py and $\mathrm{pyH^+}$ denote the undissociated Py and the pyridinium ion, respectively). Upon addition to colloidal silica, some Py molecules provide charges on the silica surface ($\equiv\mathrm{Si{-}OH} + \mathrm{py} \rightleftharpoons \equiv\mathrm{Si{-}O^-} + \mathrm{pyH^+}$), while other Py molecules remain in the dispersion medium as a mobile species. When colloidal silica was set in contact with a reservoir of an aqueous solution of Py through a semipermeable membrane, the crystal region expanded because of the reaction–diffusion of Py.[3,5] In Figure 1a, a schematic of the experimental system is shown.

Colloidal silica KE-W10 was purchased from Nippon Shokubai Co., Ltd. (Osaka, Japan) and purified by a method described in a previous paper.[5] The particle diameter estimated by dynamic light scattering was 110 nm. The effective charge number Z, as determined from the measured electrical conductivity was 170. Unidirectional crystallization was carried out in the absence of extraneous salts for a particle volume fraction $\phi = \phi_0 = 0.034$. The water used was purified by using a Milli-Q Simpli-Lab system (Millipore, Billerica, MA, U.S.A.), and the conductivity of the water was 0.4–0.6 µS cm^{-1}.

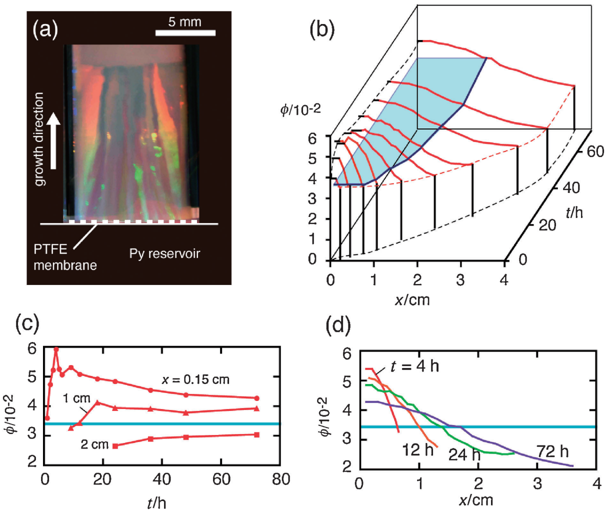

Figure 1. (a) Colloidal silica crystals obtained by unidirectional growth via diffusion of pyridine ($[\mathrm{Py}]_0 = 10$ mM) and (b) variations in the ϕ–x plot with time. The projections on the ϕ–t and ϕ–x planes are shown in (c) and (d), respectively.

The crystal growth experiments were conducted in sample cells that were in contact with a reservoir of aqueous Py solution (500 mL) through semipermeable poly(tetrafluoroethylene) (PTFE) membranes having a thickness of 0.1 mm. To achieve vertically upward crystal growth, we used a poly(methyl methacrylate) cell (inner dimensions: 1 × 1 × 4.5 cm^3), which has been described in a previous paper.[5] However, such a cell was not suitable for use in experiments on the horizontal growth of crystals, because the gravitational settling of the crystals caused macroscopic flows in the sample. As a result, the boundary between the crystal and noncrystal regions became remarkably inclined. Therefore, we used a thinner quartz cell (inner dimensions: 0.1 × 1 × 4.5 cm^3) to minimize the settling and achieve horizontal growth.

Right-angle reflection spectra were measured for circular areas on the crystals; these areas had diameters of approximately 1 mm. The spectra were obtained using a fiber-optic spectrophotometer MCPD-8600 (Photal Co., Ltd., Osaka, Japan). Typical reflection spectra of the crystals have been presented as Supporting Information 1.[9]

Figure 1a shows an overview of the crystals obtained by unidirectional vertical crystal growth in the upward direction at time t of 19 h. The concentration of Py in the reservoir (hereafter denoted by $[\mathrm{Py}]_0$) was 10 mM. The colloid crystallized for a Py concentration greater than 40 µM ($Z \approx 200$).[6] The crystal regions consisted of columnar crystal grains having millimeter-sized width, which showed iridescent color due to Bragg diffraction. A red shift in the Bragg wavelength, λ_B, occurred as the crystal height increased, as shown in Figure 1a.

The particle concentration profiles in the crystal region were determined from the λ_B values measured at intervals of 1 to 2 mm in the following manner. We confirmed that the crystals had body-centered-cubic (BCC) lattice symmetry and that their {110} planes were oriented parallel to the cell wall.[7] Then, we obtained the relationship between the lattice spacing, d_{110}, and λ_B by using the Bragg relation for right-angle first-order diffraction, i.e., $2d_{110} = \lambda/n_r$ (n_r: refractive index of the colloidal dispersion). Because of the low values of ϕ, we adopted the volume-averaged refractive index: $n_r = (1 - \phi)n_{r,w} + \phi n_{r,p}$, where $n_{r,w}$ (1.33) and $n_{r,p}$ (1.45) are the refractive indexes for water and the silica particles, respectively. In the case of the BCC geometry, the relationship between ϕ and d_{110} is given by $\sqrt{2}d_{110} = (8\pi/3\phi)^{1/3}a_p$ (a_p: the particle radius).

In Figure 1b, ϕ values for vertical crystal growth in the upward direction at various times t (shown in red) are plotted against the distance from the PTFE membrane (x) ($[\mathrm{Py}]_0 =$ 10 mM): these values were determined by spectroscopy. The plane shaded in blue corresponds to a constant value of ϕ ($\phi_0 = 0.034$). The black dashed curve on the x–t plane represents the crystal growth. Figures 1c and 1d present the projections of several data shown in Figure 1b on the ϕ–t and ϕ–x planes, respectively (the blue lines correspond to $\phi = \phi_0$). From Figures 1b–1d, it is clear that the colloidal silica particles were first concentrated in the region near the PTFE membrane. For $x = 0.15$ cm and $t = 5$ h, the value of ϕ was double that of ϕ_0 (Figure 1c). However, after a sufficiently long period of time, these nonuniform particle concentrations approached uniform values.

During the vertical crystal growth described above, we expected that the crystals would be subjected to gravitational compression because of the high density of the silica particles (approximately 2.1).[5] We then carried out crystal growth in the horizontal direction (See Supporting Information 2[9]). Although the crystal growth in the horizontal direction was more uniform than that in the vertical direction, for both types of crystal growth, the value of ϕ decreases at large x and the growth becomes increasingly uniform over time. Figure 2 shows the ϕ–x curves corresponding to the horizontal growth for $[\mathrm{Py}]_0$ of 100 mM. At this high value of $[\mathrm{Py}]_0$, the rate of crystal growth was high, thus we observed the time evolution of the ϕ–x curves. We can clearly see that initially a transient nonuniform distribution of ϕ exists. Subsequently, this concentration profile approaches uniformity (shown by the arrows in Figure 2). The inset of Figure 2 shows the dependence of the average value of ϕ at the time t; this dependence is represented as reduced value by ϕ_0, $\langle\phi/\phi_0\rangle$, in the crystal region. It is obvious that the silica particles were concentrated within a short period of time.

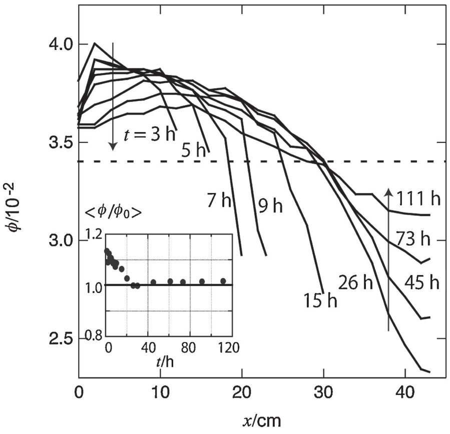

Figure 2. Time evolution of the ϕ–x plots for the horizontal crystallization ($[\mathrm{Py}]_0 = 100$ mM). The inset shows the variation of the averaged value of ϕ (reduced values by ϕ_0).

It should be noted that because of the high charge number, the magnitude of electrostatic interaction between the particles is higher at smaller values of x. Therefore, the present findings imply that the silica particles are subjected to a considerably strong uphill (that is, toward a region with higher ϕ) migration force against the electrostatic interparticle interactions. This migration force appears to be closely related to the gradient in Py concentration in the colloids since the particle concentration approached a uniform one over time. We attribute the above-mentioned behavior to diffusiophoresis. Further studies of this mechanism, including measurements of diffusion potential and 2D-image-spectroscopy of the microscopic nonuniformity, are in progress.

A part of this study was performed as a 3DPC Space Experiment Project of Japan Aerospace and Exploration Agency (JAXA). The authors express sincere gratitude to all the members of the project for their helpful discussion.

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