

One-Directional Crystal Growth in Charged Colloidal Silica Dispersions Driven by Diffusion of Base

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Charged colloidal particles are stabilized against aggregation in their aqueous dispersions, due to electrostatic interparticle interactions. Under a weak interaction, their spatial distribution is disordered, analogous to a *liquid* state in an atomic system. When the interaction becomes sufficiently strong, the dispersions show a phase transition to the ordered *crystal* state, where the particles are regularly arranged.¹ The crystallization of the charged colloids has been extensively studied as a model of phase transition in general.^{1–3} Furthermore, in recent years the colloidal crystals have attracted much attention as photonic materials,⁴ since their lattice spacing can be visible light wavelengths.

Controlled crystallizations,⁵ e.g., shear-annealing,^{5,6} and directed growth by colloidal epitaxy,⁷ have thus far been explored to obtain well-oriented large single crystals. In ordinary atomic or molecular crystalline materials, single crystals, which have great practical importance, are generally fabricated by one-directional growth using a temperature gradient (e.g., Bridgeman or zone-melting methods). The directed crystal growth under a temperature gradient was also found for noncharged colloids.⁸ However, in general temperature is a weak variable for the charged colloids. Here we describe a novel one-directional crystal growth for colloidal silica dispersions, under a pH gradient formed by diffusion of a weak base, pyridine (Py). The crystals consisted of volume-filling, pillar-shaped grains whose height and width were in the order of centimeter and subcentimeter. The growth was explainable in terms of coupling between the reaction-diffusion process and charge-induced crystallization in this weak base/weakly acidic particle system.

The electrostatic interaction is generally governed by three major parameters: the effective surface charge density of the particle σ_e , salt concentration C_s , and particle concentration C_p . The colloidal crystals are formed under moderately high σ_e , low C_s , and high C_p conditions.^{1,2} We previously reported the charge-induced crystallization of colloidal silica with varying pH.² The silica surface is covered by weakly acidic silanol groups ($\equiv\text{Si}-\text{OH} \rightleftharpoons \equiv\text{Si}-\text{O}^- + \text{H}^+$), whose dissociation is enhanced when partly neutralized with a suitable base, e.g., NaOH.⁹ Thus, σ_e increases with pH, resulting in crystallization above a critical pH value, pH^* . When σ_e was varied within an acidic region, where the concentration of excess base in medium is negligibly small, σ_e was tunable almost independently of C_s .² Here we examine the crystal growth in the silica dispersions with the diffusion of base.

Colloidal silica (diameter = 110 nm) was purified as described elsewhere.² The crystal growth was examined for $C_s = 2 \mu\text{M}$ and $C_p = 3.22 \text{ vol } \%$, at 25 °C. In the absence of Py, the particles were slightly charged owing to the self-dissociation of silanols ($\sigma_e =$

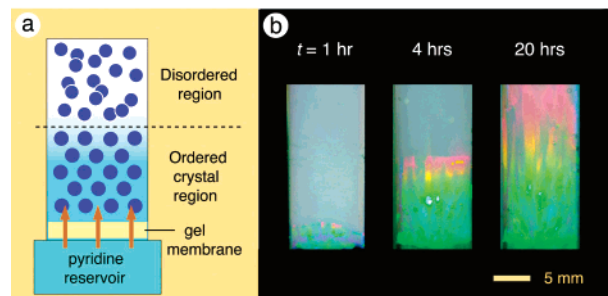


Figure 1. (a) Experimental system and (b) images of the one-directional growth process.

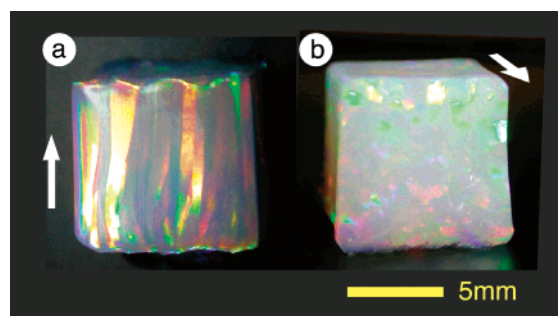


Figure 2. (a) Side view and (b) cross-sectional view of a gelled crystal. Arrows show the growth direction.

$0.07 \mu\text{C}/\text{cm}^2$), and the dispersion ($\text{pH} = 4.3$) was in a disordered state. The crystallization point was $[\text{NaOH}] = 20 \mu\text{M}$, which corresponded to $\text{pH}^* = 4.5$. All the growth experiments were performed in acidic conditions.

The experimental system is illustrated in Figure 1a. The silica dispersion was introduced into a poly(methyl methacrylate) cell (1 cm \times 1 cm \times 4.5 cm), having a poly(acrylamide)-based gel membrane (thickness = 4 mm) on its bottom, and was kept in contact with a 500 mL reservoir of an aqueous solution of Py. Figure 1b shows the one-directional, pillar-like crystal growth obtained at $[\text{Py}] = 100 \text{ mM}$, after the membrane was set in contact with the Py reservoir at time $t = 0$. The crystal region showed an iridescent color due to the Bragg diffraction of visible light, while the disordered region was opaque. The diffraction wavelength showed a red-shift with the crystal height. Further studies on this nonuniformity of the lattice spacing are currently in progress.

To examine their internal structure, we immobilized the crystals by using a gelation technique.^{10,11} The crystal was grown in the presence of UV-curable reagents, and then the medium was gelled by a photoinduced polymerization.¹¹ Parts a and b of Figure 2 show a side view (crystal height $x = 1 \text{ cm}$) and a cross-sectional view

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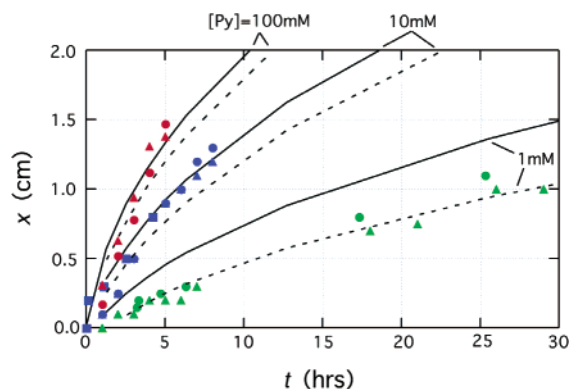


Figure 3. Observed (symbols) and theoretical (solid curves, $C_s = 2 \mu\text{M}$; broken curves, $5 \mu\text{M}$) crystal growth for three pyridine concentrations.

(at $x = 1 \text{ cm}$) of the gelled crystal ($[\text{Py}] = 1 \text{ mM}$, $t = 20 \text{ h}$). The growth direction is shown by arrows in a and b of Figure 2. The plane perpendicular to the growth direction had a mosaic-like, polygrain structure, implying that the crystals consisted of volume-filling, pillar-shaped grains.

Py is a weak base having a $\text{p}K_a$ ($\text{Py} + \text{H}_2\text{O} \rightleftharpoons \text{PyH}^+ + \text{OH}^-$) of 5.42. In the silica dispersion, Py molecules are electrostatically adsorbed onto the particle surface.⁹ Namely, a part of Py neutralizes the silanols ($\equiv\text{Si}-\text{OH} + \text{Py} \rightarrow \equiv\text{Si}-\text{O}^- + \text{PyH}^+$) to give pyridinium ions PyH^+ as counterions of the charged-up particle. The other part is present in the medium in an undissociated form, under acidic conditions where the growth experiments are performed. Potentiometric titration for homogeneous systems showed that the adsorption isotherm was Langmuir type, $S = k\Gamma C/(1 + kC)$, where S and C are molar concentrations of the adsorbed (ionized) and free (undissociated) Pys, respectively. The adsorption constant, k , and the equilibrium adsorption amount, Γ , were $8.8 \times 10^3 \text{ M}^{-1}$ and $1.15 \times 10^{-4} \text{ M}$, respectively. The one-dimensional reaction-diffusion equation for $S = S(x,t)$ and $C = C(x,t)$ is given by

$$\partial C/\partial t = [D/(1 + \partial S/\partial C)] (\partial^2 C/\partial x^2) \quad (1)$$

where D is the diffusion constant of Py. We numerically solved the diffusion equation to obtain $S(x,t)$. As described before, the crystallization point was $[\text{NaOH}] = 20 \mu\text{M}$ in a homogeneous system. This can be regarded as S value at the crystallization point, S^* , since C is nearly zero for a *strong* base. We obtained the theoretical growth curves by assuming that the crystallization takes place immediately when the local value of $S(x,t)$ reaches S^* . For more details on the theoretical growth curves, see Supporting Information. Figure 3 compares the observed (symbols) and theoretical (solid curves) growths for three $[\text{Py}]$'s. Data points in a single growth experiment are represented by the same symbol (circle, triangle, or square). Observed and calculated curves showed close agreement. The slightly larger theoretical value for x at $[\text{Py}] = 1 \text{ mM}$ might be due to a trace amount of ionic contamination, which has a more marked effect at a smaller $[\text{Py}]$. The theoretical curve for $C_s = 5 \mu\text{M}$ ($S^* = 40 \mu\text{M}$) is also shown by broken lines. We note that the averaged width of the pillar-like grains w was larger for slower growth (smaller $[\text{Py}]$), and increased with the crystal height. At $[\text{Py}] = 100$ and 1 mM , w was in the orders of 0.1 and 1 mm at $x = 1 \text{ cm}$.

As is clear from the above formalism, the presence of freely diffusing species (undissociated Py), which can extend the highly charged region forward, is essential for the present one-directional growth. In fact, with a *strong* base NaOH, for which C is nearly zero, the growth was hardly observed, if any. On the other hand, one-directional growth was found also for NaHCO_3 , a salt of a weak acid and a strong base. The $\text{p}K_a$ of the silanols in the absence of a base⁹ is about 6.4. Since this is comparable to the $\text{p}K_{a1}$ of carbonic acid (6.35), the silica particle is charged up by NaHCO_3 at a low pH ($\text{Na}^+ + \text{HCO}_3^- + \equiv\text{Si}-\text{OH} \rightarrow \text{H}_2\text{CO}_3 + \equiv\text{Si}-\text{O}^- + \text{Na}^+$). In this case, a salt NaHCO_3 in medium acts as the freely diffusing species. At a variance with the case for Py, here the local values of C_s should increase together with σ_e during the diffusion. Then S^* , which varies with C_s , depends on x and t . Analysis of the diffusion of NaHCO_3 is underway.

Diffusion of a salt of a *strong* acid and a strong base, such as NaCl, of course increases C_s solely without affecting σ_e , by which the electrostatic interaction is rather weakened. On the contrary, gradual *reduction* of C_s would produce a similar one-directional growth. By settling ion-exchange resin beads in the bottom of the charged colloids having a moderately high initial C_s value, we confirmed this phenomenon.¹² The present findings should be useful in fabricating large, single colloidal crystals which are applicable as photonic materials.

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Supporting Information Available: Numerical method for obtaining the crystal growth curve. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Note added in proof: Recently this was also confirmed independently by T. Shinohara et al. (*Langmuir*, in press.)

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