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Supporting Information

Controlling the shape of wedge-like α-GaOOH particles formed by a hydrolysis process using sodium acetate as a growth modifier

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Change of pH by the formation reaction of α-GaOOH particles

Figure S1(a) shows change of pH with time during the formation process of α-GaOOH particles shown in Fig. 7. In Fig. S1(b), pH values at 168 h (pH_{fin}) are plotted to those at 5 min (pH_{ini}) for all the tested conditions in the presence of AcONa. When $pH_{ini} \geq 4.13$ ($C_{Ac} \geq 0.175$ mol L^{-1}), pH is almost unchanged during the 168 h reaction due to the buffering effect of acetic acid (pK_a 4.75 at 25 °C). At $pH_{ini} \leq 3.56$ ($C_{Ac} \leq 0.15$ mol L^{-1}), on the other hand, pH is somewhat decreased by the consumption of OH^- ions, since buffering effect is no longer expectable in the pH region.

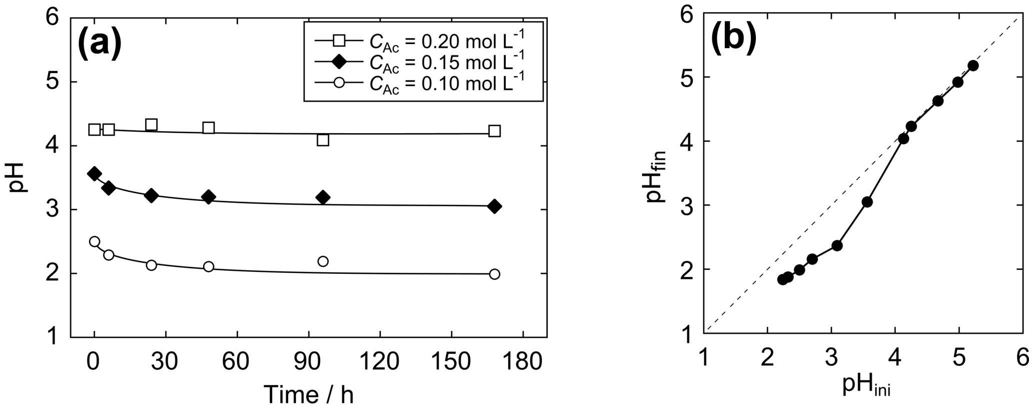

Fig. S1 Change of pH by the formation reaction of α-GaOOH particles. (a) Time evolution of pH at $C_{Ac} = 0.1$, 0.15, and 0.2 mol L^{-1}. (b) Relationship between pH values at 5 min (pH_{ini}) and at 168 h (pH_{fin}).

Comparison of morphology between the α-GaOOH particles synthesized in the presence and absence of AcONa under comparable pH conditions

To elucidate the contribution of AcONa to formation of the wedge-like morphology, NaOH instead of AcONa was employed to adjust the pH condition to a comparable condition with the AcONa system. Figure S2 indicates SEM images of α-GaOOH particles prepared with AcONa (C_{Ac} = 0.140 mol L^{-1}) and NaOH (C_{NaOH} = 0.135 mol L^{-1}). The pH changes are quite similar as pH 3.09, 2.60, and 2.37 at 5 min, 24 h and 168 h, respectively, for the former, whereas pH 3.05, 2.64, and 2.36, respectively, for the latter.

In spite of the virtually same pH conditions, the morphology of particles is different: wedge-like particles in the AcONa system (L_{b} = 0.34 μm, L_{c} = 0.42 μm, $L_{\mathrm{c}}/L_{\mathrm{b}}$ = 1.2) and needle-like particles in the NaOH system (L_{b} = 0.19 μm, L_{c} = 2.14 μm, $L_{\mathrm{c}}/L_{\mathrm{b}}$ = 11.3). On the other hand, as shown in Fig. S3, identical SAED patterns are obtained from both particles. The Laue pattern for the latter indicates that the needle-like morphology is a result of preferential growth along *c*-axis. Thus it is strongly suggested that the formation of the wedge-like morphology is attributed to the presence of AcONa, rather than pH itself, by suppressing the growth along the *c*-axis, probably by the adsorption on the {212} face.

Here, the smaller L_{b} in the NaOH system is probably due to the *flow out effect* of the reactants from the vicinity of the {110} faces to the *ab*-faces.[S1] The very fast consumption rate of reactants could cause a concentration gradient at just around the particle to promote the flow of the reactants, resulting in the lack of reactants for the growth of the {110} faces.

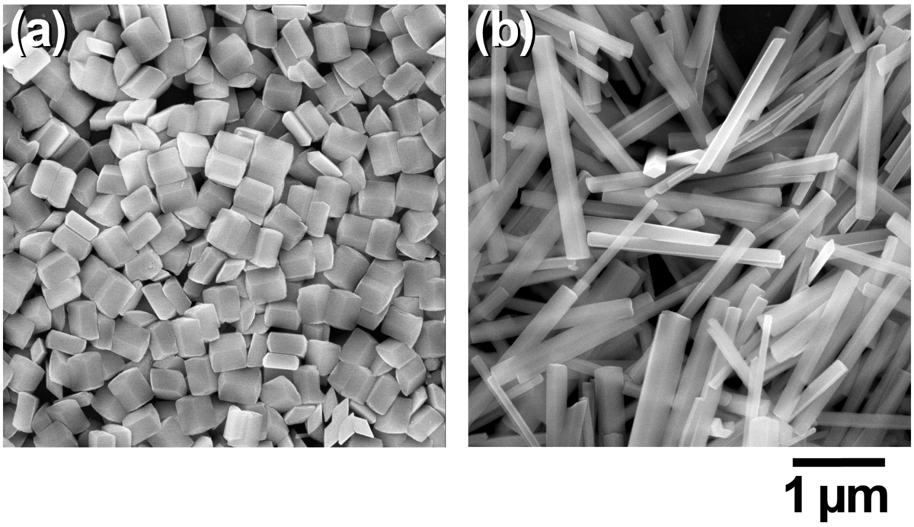

Fig. S2 FE-SEM images of α-GaOOH particles synthesized at 70 °C for 168 h with (a) AcONa at $C_{\mathrm{Ac}} = 0.140$ mol L^{-1} and (b) NaOH at $C_{\mathrm{NaOH}} = 0.135$ mol L^{-1}. The pH values at 5 min, 24 h, and 168 h for (a) are 3.09, 2.60, and 2.37, respectively, whereas those for (b) are 3.05, 2.64, and 2.36, respectively.

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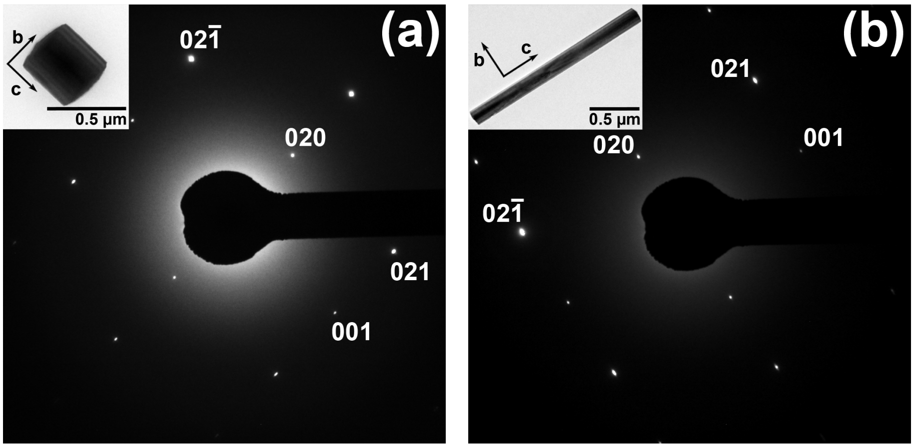

Fig. S3 SAED patterns for single α-GaOOH particles prepared with (a) AcONa at $C_{\mathrm{Ac}} = 0.140$ mol L^{-1} and (b) NaOH at $C_{\mathrm{NaOH}} = 0.135$ mol L^{-1}.

Time evolution of L_c/L_b ratio during the growth of α-GaOOH particles

Figure S4 shows evolution of L_c/L_b ratio with time during the growth process, where L_c/L_b ratio is calculated from the L_b and L_c values in Fig. 8. At each C_{Ac} condition, L_c/L_b ratio tends to decrease with time.

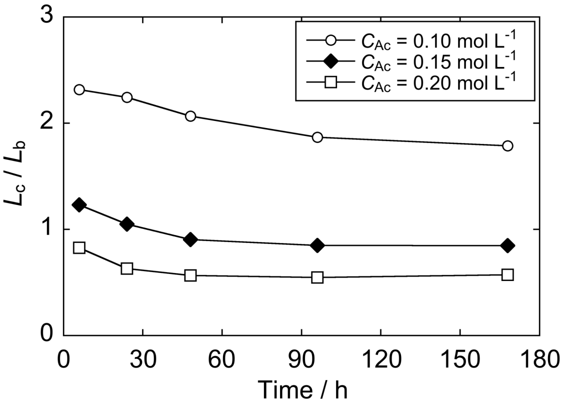

Fig. S4 Evolution of L_c/L_b ratio of wedge-like α-GaOOH particles with time during the growth process at C_{Ac} = 0.1, 0.15, and 0.2 mol L^{-1}.

Change of XRD pattern of the precipitate during the formation process

Figure S5 shows XRD patterns of precipitate at 6, 24, 48, 96, and 168 h (C_{Ac} = 0.2 mol L^{-1}). Reflecting the volume increase of α-GaOOH phase, intensity of the peaks increases with time of the reaction. Moreover, all the peaks are identified to those for α-GaOOH, implying other kinds of crystalline phase are not present. In other words, the gel-like precipitate existing at early stage of this C_{Ac} condition (see Fig. 7) is in amorphous structure.

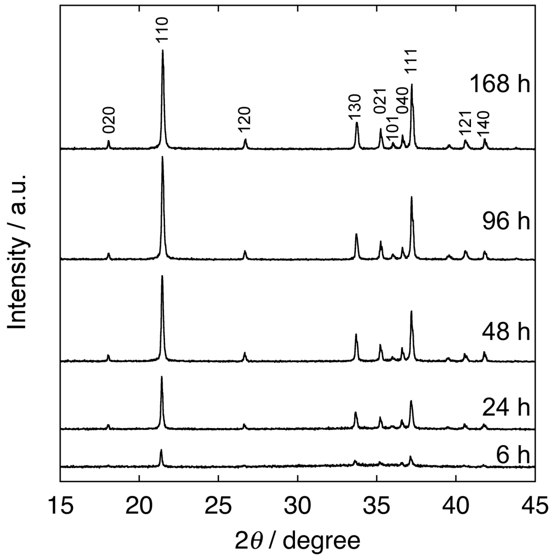

Fig. S5 XRD patterns of the precipitates at different reaction time (C_{Ac} = 0.2 mol L^{-1}, CuKα radiation, λ = 1.5418 Å).

Time change of total concentration of soluble Ga^{3+} species remaining in the aqueous phase

Figure S6 shows time changes of the total concentration of the soluble Ga^{3+} species in the forms of free Ga^{3+} ion and Ga(OH)$_n^{(3-n)+}$ complexes remaining in the aqueous phase, [Ga^{3+}]$_{\mathrm{tot}}$, at $C_{\mathrm{Ac}} \leq 0.15$ mol L^{-1}. The value of [Ga^{3+}]$_{\mathrm{tot}}$ was estimated colorimetrically as described below. The chemical reaction rate seems to be somewhat faster at higher C_{Ac} (i.e. higher pH), probably due to increase of [OH^{-}], although the difference is not so significant. Note that, at $C_{\mathrm{Ac}} \geq 0.175$ mol L^{-1}, Ga^{3+} was not detectable by the colorimetry, since almost all Ga^{3+} was preserved in the form of hydroxide gel in the C_{Ac} region.

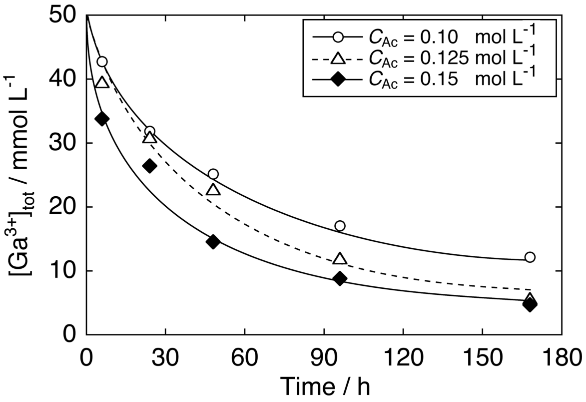

Fig. S6 Time change of total concentrations of Ga^{3+} species, $[Ga^{3+}]_{tot}$, remaining in the aqueous during the hydrolysis reaction at C_{Ac} = 0.1, 0.125, and 0.15 mol L^{-1}. $[Ga^{3+}]_{tot}$ = 50 mmol L^{-1} at 0 h from the reaction condition.

Procedure of the colorimetric estimation of Ga^{3+} in the aqueous phase

The values of $[Ga^{3+}]_{tot}$ in Fig. S6 were determined by a colorimetric analysis using xylenol orange (XO; Dojindo, Kumamoto, Japan).

The supernatant solution for analysis was obtained by centrifuging the reacting solution to separate from the precipitate. A certain volume of the supernatant solution and 1 mL of XO solution (1 mmol L^{-1} dissolved in 0.1 mol L^{-1} HNO_3) was introduced into a volumetric flask that contained 2 mL of HNO_3 (1 mol L^{-1}). After adjusting the volume to 20 mL with distilled water, the mixed solution was placed in a water bath at 50 °C for about 1 h. Then the absorbance at 552 nm was measured while keeping the temperature as possible.

Arrangement of Ga atoms on the {212} plane of α-GaOOH

Figure S7 illustrates the atomic arrangement in a unit cell of α-GaOOH, where the yellow line indicates the {212} plane of α-GaOOH. It should be noted that the atoms are in contact with each other actually and thus the space in the cell is filled with them. This figure hence shows that all the four Ga atoms are effectively located in the {212} plane, although there are small positional shits for two of the four atoms.

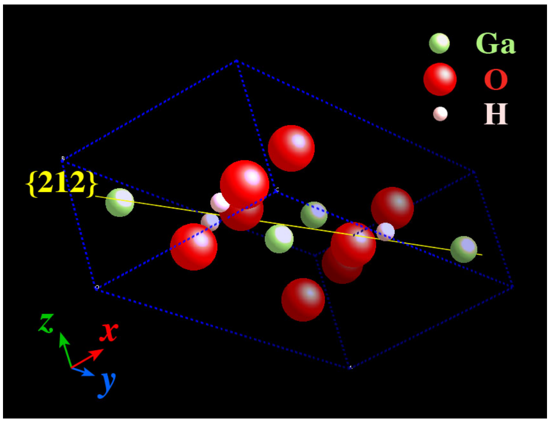

Fig. S7 Atomic arrangement in a unit cell of α-GaOOH, where the yellow line indicates the {212} plane.

Reference

S1. T.-G. Kim and B. Park, *Inorg. Chem.*, 2005, **44**, 9895.