Electronic Supplementary Information (ESI)

Size-controlled synthesis of monodisperse zinc gallium oxide particles via coprecipitation under a hydrothermal condition using trisodium citrate

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HR-TEM image of the ZGO particle

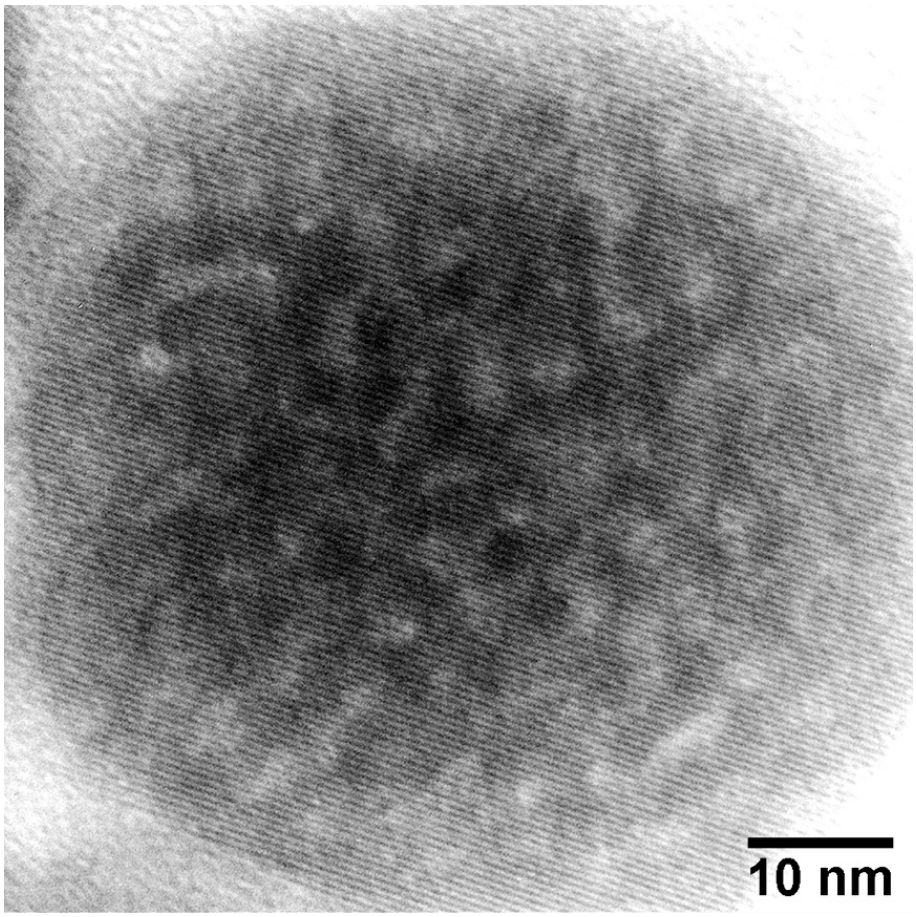

Fig. S1 HR-TEM image of the ZGO particle hydrothermally prepared in the presence of trisodium citrate at 150 °C for 24 h. The reaction condition of C_{Ga}/C_{Zn} = 2.0 ($C_{Zn} + C_{Ga}$ = 30 mmol/L) and C_{cit} = 30 mmol/L ($f_{Ga/Zn}$ = 1.70).

TEM-EDX spectra for the ZGO particles

Fig. S2 indicates TEM-EDX spectra, obtained with EDAX Genesis XM2T equipped to the Hitachi H-7650 TEM, for the ZGO particles hydrothermally synthesized at C_{Ga}/C_{Zn} = 2.0. The peak intensities estimate the Ga/Zn atomic ratio as $f_{Ga/Zn}$ = 1.89 and 1.52 for C_{cit} = 0 mmol/L and 40 mmol/L, respectively. The values agree with those estimated from the AAS measurement of the supernatant solutions ($f_{Ga/Zn}$ = 1.90 and 1.55 for C_{cit} = 0 mmol/L and 40 mmol/L, respectively).

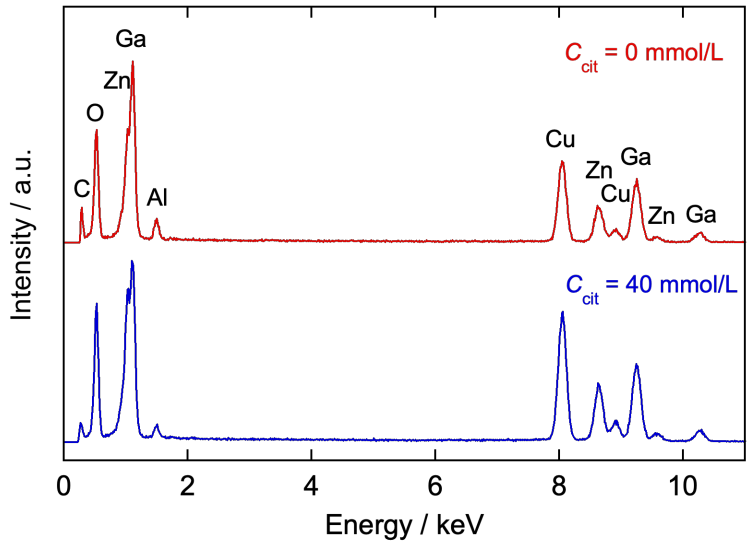

Fig. S2 TEM-EDX spectra of the ZGO particles synthesized at C_{Ga}/C_{Zn} = 2 in the absence and presence of Na_3-Cit (150 °C for 24 h). The Cu and Al signals are derived from the sheet mesh and the specimen folder, respectively.

The white precipitate formed at 40 °C in the absence of Na_3-Cit

The white precipitate for characterization was prepared in the same manner as the ZGO synthesis without applying hydrothermal treatment in the absence of Na_3-Cit ($C_{Zn} + C_{Ga}$ = 30 mmol/L, C_{Ga}/C_{Zn} = 2, C_{NaOH} = 0.084 mmol/L, C_{cit} = 0 mmol/L). After mixing the reactant solutions and keeping them at 40 °C under magnetic stirring for 60 min, the precipitate formed was repeatedly washed with distilled water using a centrifuge.

The XRD pattern of the white precipitate is indicated in Fig. S3, suggesting the precipitate is the layered double hydroxide (LDH), rather than the spinel ZGO phase. If assuming the rhombohedral lattice ($R\bar{3}m$) as literature, the peaks at 2θ = 11.8° and 23.7° of the 003 and 006 reflections, respectively, enable us to estimate the lattice parameter c as c = 22.5 Å, which agrees with the value in literature (c = 22.99 Å)[1]. The lattice parameter a is also close to the value in

the literature (a = 3.112 Å)[1] from the diffraction angle for the 012 reflection (2θ = 34°). However, it includes some uncertainty due to its broad and somewhat asymmetrical peak profile. In addition, the 015 and 018 reflections, which are expected to appear at about 39° and 46°, respectively, are not clearly observed. The misalignment of the stacked hydroxide layer could cause it.

It should be noted that the XRD pattern, however, does not ensure the white precipitate consists of a single phase of the LDH, as amorphous solids indicate no clear peaks of reflection, even if they are present. Rather, it would be reasonable to consider that the present white precipitate also contains amorphous hydroxides, since the fraction of Ga^{3+} seems to be too rich to regard it as a single LDH phase, as mentioned in the main text.

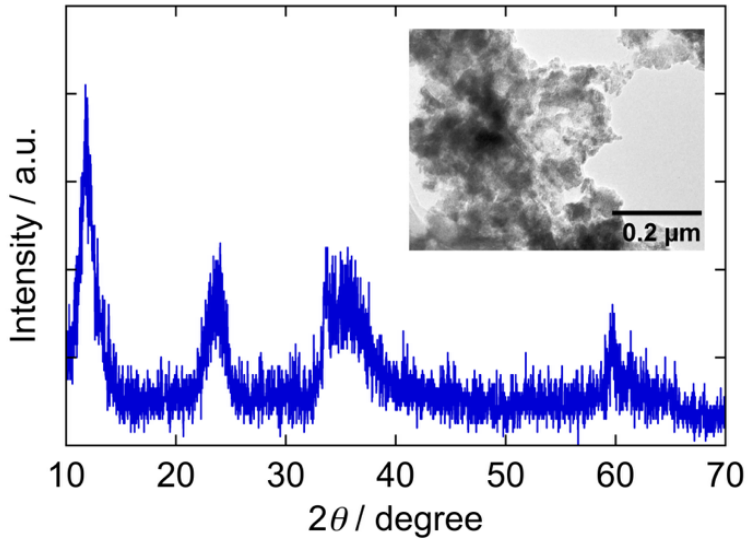

Fig. S3 XRD pattern of the white precipitate formed at 40 °C in the absence of Na_3-Cit. The inset is its TEM image.

Estimation of the solubilities for $Zn(OH)_2$ and $Ga(OH)_3$ from the equilibrium constants

The solubility of $Zn(OH)_2$ precipitate in NaOH aqueous solution is governed by the equilibrium constants of the solubility product, K_{sp}, and the stability constants for hydroxide complexes, β_n. The equilibrium constants enable us to formulate the molar concentrations of the free Zn^{2+} ion and of its hydroxide complexes:

$$[Zn^{2+}] = K_{sp}^{Zn}/[OH^-]^2$$
$$[[ZnOH]^+] = \beta_1^{Zn}[Zn^{2+}][OH^-]$$
$$[[Zn(OH)_2]] = \beta_2^{Zn}[Zn^{2+}][OH^-]^2$$

$$[[\mathrm{Zn(OH)_3}]^-] = \beta_3^{\mathrm{Zn}}$$
$$[[\mathrm{Zn(OH)_4}]^{2-}] = \beta_4^{\mathrm{Zn}}[\mathrm{Zn^{2+}}][\mathrm{OH^-}]^4$$

The molar solubility of $Zn(OH)_2$ precipitate, s^{Zn}, is the sum of the concentrations, thus

$$s^{\mathrm{Zn}} = [\mathrm{Zn^{2+}}] + [[\mathrm{Zn(OH)_2}]] + [[\mathrm{Zn(OH)_3}]^-] + [[\mathrm{Zn(OH)_4}]^{2-}]$$
$$= K_{\mathrm{sp}}^{\mathrm{Zn}}\left(\frac{\beta_1^{\mathrm{Zn}}}{[\mathrm{OH^-}]} + \beta_2^{\mathrm{Zn}} + \beta_3^{\mathrm{Zn}}[\mathrm{OH^-}] + \beta_4^{\mathrm{Zn}}[\mathrm{OH^-}]^2\right)$$

Similarly, the solubility of $Ga(OH)_3$ precipitate, s^{Ga}, is also given by

$$s^{\mathrm{Ga}} = K_{\mathrm{sp}}^{\mathrm{Ga}}\left(\frac{\beta_1^{\mathrm{Ga}}}{[\mathrm{OH^-}]^2} + \beta_2^{\mathrm{Ga}}[\mathrm{OH^-}] + \beta_3^{\mathrm{Ga}} + \beta_4^{\mathrm{Ga}}[\mathrm{OH^-}]\right)$$

As long as the hydroxide precipitate remains, $[Zn^{2+}]$ and $[Ga^{3+}]$ are functions of $[OH^-]$ (thus of pH), as shown in Fig. S4, where the assumed values of equilibrium constants[2] are $pK_{sp} = 17.0$, $\log\beta_1 = 5.1$, $\log\beta_2 = 11.1$, $\log\beta_3 = 13.6$, and $\log\beta_4 = 14.9$ for Zn^{2+} and $pK_{sp} = 35.2$, $\log\beta_1 = 11.3$, $\log\beta_2 = 21.8$, $\log\beta_3 = 31.3$, and $\log\beta_4 = 38.8$ for Ga^{3+}. Also $pK_w = 14.00$ was used to convert pH to $[OH^-]$.

To establish the homogeneous solution phase, the concentrations of $Zn(NO_3)_2$ and $Ga(NO_3)_3$ in the reacting solution must be lower than the respective solubility levels. The estimated solubility curves indicate that, at pH ~9, all Ga^{3+} ions are in the solution phase by sufficient formation of the anionic complex, but not for Zn^{2+} ions. Introducing citrate ions assists in increasing the solubility by forming citrate complexes with the metal ions, in addition to the hydroxide ones, to maintain the homogenous state before applying the hydrothermal treatment.

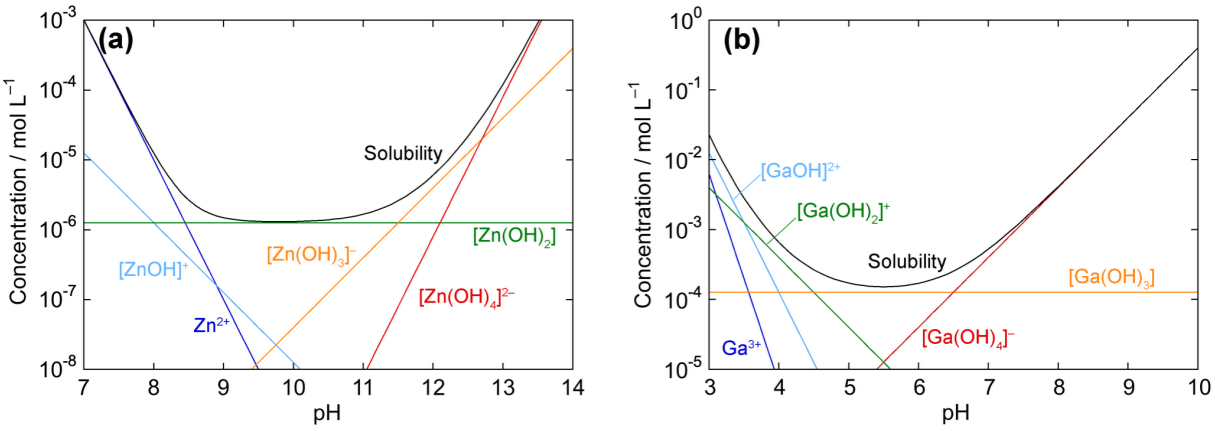

Fig. S4 pH dependence of the solubility for (a) $Zn(OH)_2$ and (b) $Ga(OH)_3$ precipitate as the sum of the free metal ion and its hydroxide complexes estimated from the equilibrium constants at 25 °C.

Size distributions of the ZGO particles synthesized under different Na_3-Cit concentrations (C_{Ga}/C_{Zn} = 2.57).

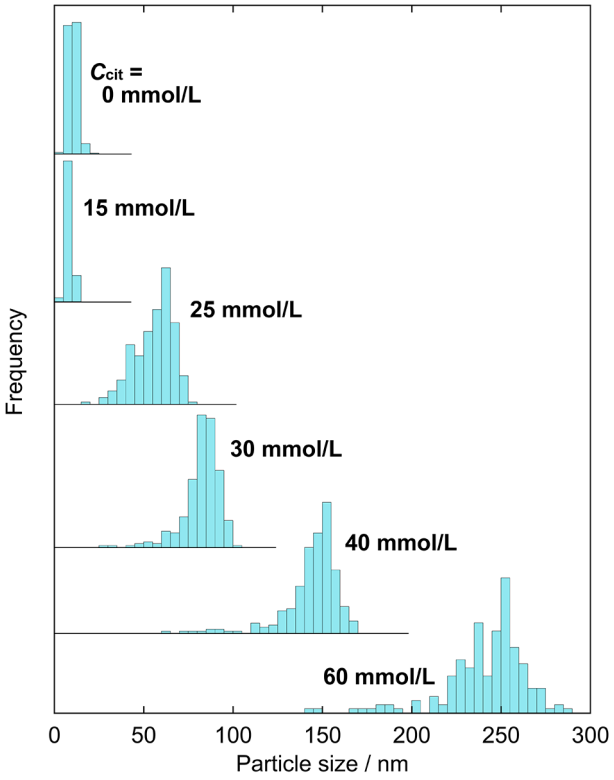

Fig. S5 Histograms of particle size for the ZGO particles shown in Fig. 3, indicating the effect of Na_3-Cit concentration on the size distribution. The width of each class is 5 nm.

Table S1 Estimated values of the average size (D), the standard deviation of size (σ), and the coefficient of variation (COV) from the size distribution data in Fig. S5 for the ZGO particles shown in Fig. 3.

C_{cit} / mmol L^{-1}	D / nm	σ / nm	COV / %
0	10	2.6	25
15	8	1.7	21
25	56	11	19
30	83	10	13
40	144	16	11
60	242	23	9

Effect of $f_{Ga/Zn}$ on the XRD pattern of the ZGO particles

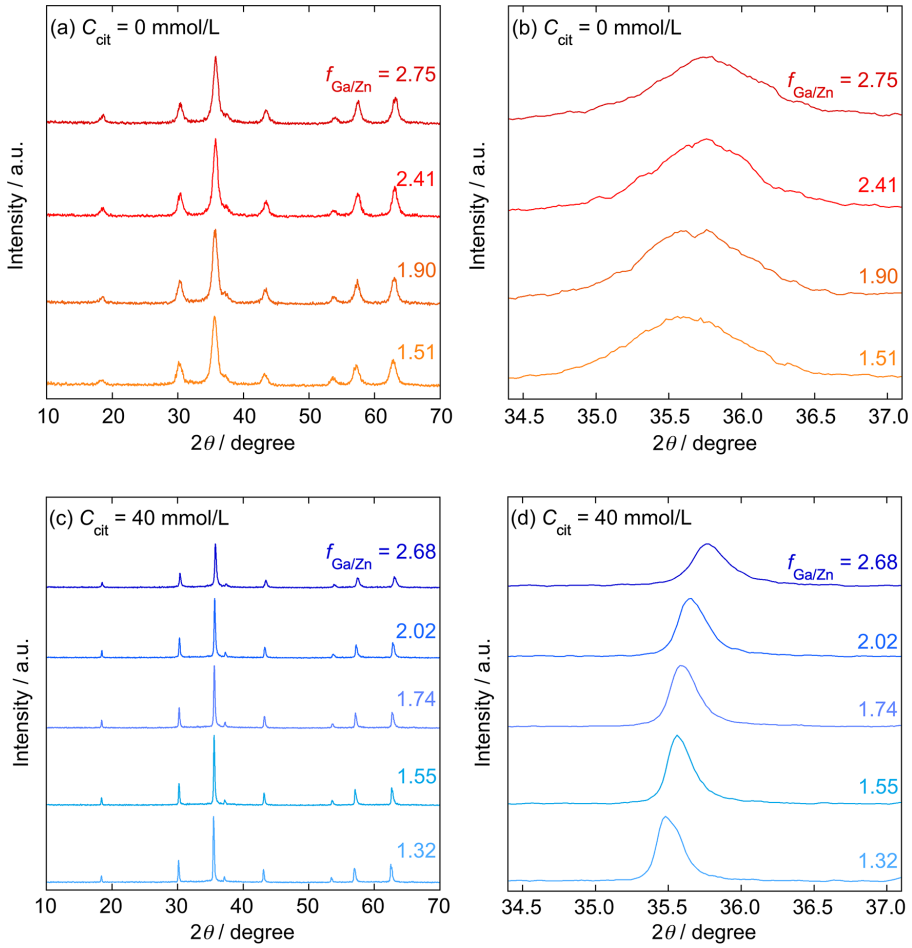

Fig. S6 XRD patterns for the ZGO particles hydrothermally synthesized at (a)(b) C_{cit} = 0 mmol/L and (c)(d) C_{cit} = 40 mmol/L, where (a)(c) show the whole scanned range and (b)(d) expand around the strongest peak (the 311 reflection). The lattice parameter, a, in Fig. 6 in the main text is estimated from the relationship $1/a^2 = (h^2 + k^2 + l^2)/d^2$ for the cubic lattice where $h = 3$, $k = 1$, and $l = 1$. (Cu Kα radiation, λ = 1.5418 Å)

Determination of the band gap energy for the ZGO particles with different $f_{Ga/Zn}$ values.

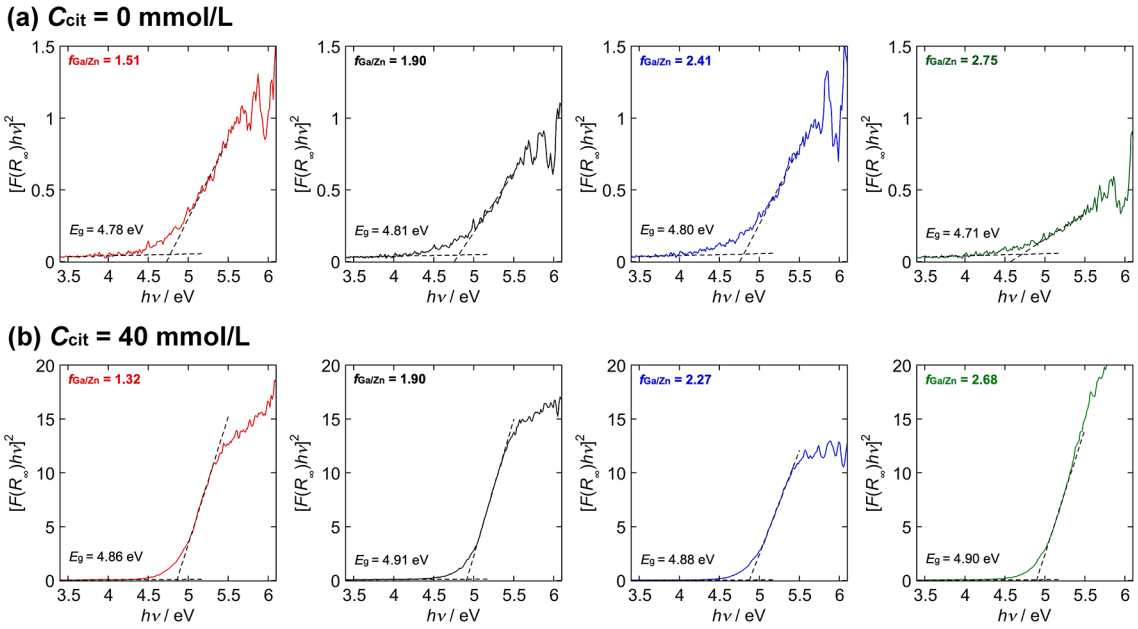

Fig. S7 Tauc's plots for ZGO particles of different $f_{Ga/Zn}$ obtained at (a) C_{cit} = 0 mmol/L and (b) C_{cit} = 40 mmol/L.

Reference

1. K. Fuda, N. Kudo, S. Kawai and T. Matsunaga, *Chem. Lett.*, 1993, 777.
2. Y. F. Orlov and E. I. Belkina, *Russ. J. Inorg. Chem.*, 2011, **56**, 975.