Amino Acid Assisted Hydrothermal Synthesis of $\text{In}(\text{OH})_3$ Nanoparticles Controlled in Size and Shape

Takafumi Sasaki, Masafumi Nakaya, Kiyoshi Kanie* and Atsushi Muramatsu*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Size and shape controlled indium hydroxide ($\text{In}(\text{OH})_3$) nanoparticles are readily obtained by amino acid assisted hydrothermal synthesis from an aqueous system. The shape control is achieved by the utilization of adsorption of amino acid on the growing surfaces of the nanoparticles, and rod- and cubic-shaped $\text{In}(\text{OH})_3$ nanoparticles are selectively formed in the presence of glycine and L-aspartic acid, respectively. Furthermore, by utilization of two-step aging technique in L-aspartic acid system, originally developed by the gel-sol method, the cubic-shaped $\text{In}(\text{OH})_3$ nanoparticles with narrow size distribution are successfully obtained. [doi:10.2320/matertrans.M2009236]

(Received July 6, 2009; Accepted September 11, 2009; Published November 11, 2009)

Keywords: amino acid, hydrothermal synthesis, indium hydroxide, nanoparticle, size and shape control

1. Introduction

Recent remarkable progress in synthetic chemistry of inorganic nanoparticles enabled us to obtain various types of the inorganic nanoparticles with controlling their shapes and sizes.^{1–3)} In particular, solution based synthetic systems have large advantages for the precise shape and size control of the inorganic nanoparticles.^{4–8)} The gel-sol method, we have recently developed, is a particle deposition system from solution for the preparation of monodispersed nanoparticles in large quantities.^{9–21)} In this system, once formed gels consist of an intermediate of the desired nanoparticles prevent coagulation of growing nanoparticles. Furthermore, by the formation of the gels, concentration of direct precursors of the solid particles in the solution is kept low state among the particle growth. These two points play critical roles to obtain monodispersed nanoparticles. For example, by using the gel-sol method, monodispersed hematite, $\alpha\text{-Fe}_2\text{O}_3$, nano- and fine-particles are produced from ferric hydroxide gel through a two-step phase transformation from $\text{Fe}(\text{OH})_3$ gel to a solid intermediate, $\beta\text{-FeOOH}$, of a medium solubility and from $\beta\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$.^{9–16)} Among the dissolution-recrystallization processes, shape control, leading to obtain various shapes of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, is easily achieved. The shape control is usually performed by adsorption of shape controllers on the specific crystal planes during the particle growth period. The shape controllers such as anions, organic molecules, and surfactants inhibit the particle growth towards perpendicular to the adsorbed crystal planes. This particle preparation technique is applicable to the preparation of shape-controlled anatase-type TiO_2 nanoparticles.^{17–20)} In this case, amines, carboxylic acids, and amino acids are effective for the introduction of anisotropic shapes.

In the present study, we have succeeded in precise size and morphology control of $\text{In}(\text{OH})_3$ nanoparticles in the presence of amino acids in a hydrothermal reaction system based on the gel-sol technique. The $\text{In}(\text{OH})_3$ nanoparticles can be applied as a precursor of indium tin oxide (ITO)

nanoparticles.^{22–24)} ITO is one of the most representative transparent conductive oxide materials, and it has been extensively investigated owing to many ITO applications.²⁵⁾ However, only a few examples have been reported so far for the direct synthesis of ITO nanoparticles with controlling the shapes.^{8,26)} In this regards, preparation of size and shape controlled $\text{In}(\text{OH})_3$ nanoparticles would lead to the efficient procedure for the preparation of size and shape controlled ITO nanoparticles with highly conductivity.

2. Experimental Procedure

All reagents of the highest commercial quality were purchased from Wako Pure Chemical Industries, Ltd. and were used as received, unless otherwise noted. Water was doubly distilled, deionized, and filtered prior to use. X-ray diffraction (XRD) measurements were carried out on a Rigaku Ultima-IV system using $\text{CuK}\alpha$ radiation (40 kV, 40 mA) equipped with a D/teX Ultra detector. TEM observations were performed by using a Hitachi H7650 system with an acceleration voltage 100 kV.

The experimental procedure for the preparation of $\text{In}(\text{OH})_3$ nanoparticles was as follows. An indium chloride (InCl_3) aqueous solution (1.0 mol L^{-1}) was filtered through a $0.2 \mu\text{m}$ PTFE filter prior to use to remove insoluble particulates. A sodium hydroxide (NaOH) aqueous solution (3.0 mol L^{-1}) was added dropwise to 3.5 mL of the InCl_3 solution under agitation at 0°C to adjust pH from 8 to 10 in a screw-capped Pyrex bottle so that the white-colored suspensions were formed. After the total volume of the suspensions was adjusted to 7.0 mL with H_2O , the suspensions were mixed under the agitation with 7.0 mL of aqueous amino acid solution (0.10 mol L^{-1}) such as glycine (**Gly**), L-aspartic acid (**Asp**), L-serine, and L-lysine. By the addition of NaOH solution (3.0 mol L^{-1}), pH of the amino acid solutions was pre-adjusted to 8–10. Here, the total concentrations of In^{3+} and amino acid were 0.25 and 0.050 mol L^{-1} , respectively. The resulting suspensions were aged at 100°C for 24 h. Solid precipitates from the aged suspensions were collected by centrifugation at 18,000 rpm for 10 min, and the sediments were washed three times with water followed by centrifuging. The resulting precipitates were dried at 60°C , and the

*Corresponding authors: kanie@tagen.tohoku.ac.jp, mura@tagen.tohoku.ac.jp

powders were characterized by XRD measurements. Particle morphology was checked by TEM observations. Almost all the reactants were consumed as the final product, $\text{In}(\text{OH})_3$, as ascertained by weighing the solid separated after the synthesis for all the runs in the present study.

3. Results and Discussion

3.1 Effect of pH on the synthesis of $\text{In}(\text{OH})_3$ nanoparticles in the presence of amino acids

Indium hydroxides suspensions obtained by the mixing of InCl_3 solution with NaOH one were aged at 100°C for 24 h in the presence of 0.050 mol L^{-1} **Gly** or **Asp** and its absence. Figure 1 shows TEM images of the particles obtained at different initial pH. The products in the absence contained mixture of rectangular- and cubic-shaped particles regardless the initial pH (Fig. 1(a)–(c)), whose structure was identified as $\text{In}(\text{OH})_3$ (JCPDS No. 076-1464) in a single-phase by XRD analysis. The mean particle size was drastically decreased from several μm to ca 100 nm with increasing the initial pH from 8 to 10. In contrast, as shown in Fig. 1(d), particles of irregular shape and rough surfaces with less than 50 nm in the diameter were formed for 0.050 mol L^{-1} **Asp** at initial pH 8. Cubic-shaped particles with the relatively broad size distribution in 40–70 nm were predominantly formed at pH 9 (Fig. 1(e)), in contrast to the formation of the rectangular-shaped particles in the absence of amino acids (Fig. 1(b)). The size of the cubic-shaped particles was decreased to 20–30 nm by increasing in **Asp** concentration to 0.25 mol L^{-1} . The particles shape became rod-like with the further increase in initial pH to 10 (Fig. 1(f)). XRD measurements showed that the solid particles mainly consisted of $\text{In}(\text{OH})_3$ crystal structure with few undefined solid phase when the initial pH was adjusted to 8 and 10 in the presence of 0.050 mol L^{-1} **Asp**. In contrast, only the $\text{In}(\text{OH})_3$ phase was observed at pH 9 for **Asp** systems.

Fig. 1 TEM images of the particles synthesized in the absence of amino acid (a), (b), (c), and in the presence of **Asp** (d), (e), (f) and **Gly** (g), (h), (i) under different initial pH condition: (a), (d), (g): pH 8; (b), (e), (h): pH 9; (c), (f), (i): pH 10.

On the other hand, for **Gly** systems (Fig. 1(g)–(i)), all of the particles were assigned as $\text{In}(\text{OH})_3$ as a single-phase by the XRD measurements, only rod-shaped particles with the major axis about 50 nm were formed at initial pH 9 and 10 (Fig. 1(h), (i)). Such rod-shaped particles were also formed by using L-serine or L-lysine. The average particle size increased from 50 nm to about $1.0 \mu\text{m}$ with decreasing in pH from 9 to 8, as shown in Fig. 1(g). Generally speaking in the synthesis of metal oxide nanoparticles from aqueous solutions, the higher initial pH results in the more number of nuclei due to higher OH^- concentration: namely, the as-prepared particle size is the smaller. In fact, the mean particle size was decreased with increasing the initial pH, except for **Asp** systems. In contrast, in the case of **Asp** systems, the particle shape was significantly affected by the initial pH. The aspect ratio of cubic-shaped particles formed in **Asp** system at the initial pH 9 is smaller than that of rectangular-shaped particles. This shape control may be due to the suppression to the growth by the specific adsorption of **Asp** on the surface. In fact, Ninhydrin tests of the supernatant solutions after 24 h aging at 100°C in the **Asp** systems with the initial pH 9 and 10 indicated 25% and 10% uptake of original **Asp** feed on the particle surface. This difference seems due to the strong dependence of the adsorption behavior of **Asp** on pH, because of the relationship between the dissociation state of **Asp** and surface charge of the particles.^{27–29} The cubic particles, obtained in the present study, were bounded by {100} planes, determined by high resolution TEM observation. The specific adsorption of **Asp** onto {100} surface of the $\text{In}(\text{OH})_3$ particles may be stronger than the other ones. In this regard, the shape control to cube on $\text{In}(\text{OH})_3$ nanoparticles must be achieved by the specific adsorption of **Asp**. The detailed formation mechanism is now under the investigation, in particular, on particle morphology change on precise shape control of the $\text{In}(\text{OH})_3$ nanoparticles. It can be summarized that we have succeeded in the size- and shape-control of $\text{In}(\text{OH})_3$ nanoparticles to form both cubic- and rod-shapes by changing amino acids and the optimization of the initial pH.

3.2 Effect of aging period on the particle formation

Figure 2 exhibits TEM images of the products formed after different aging times at 100°C in amino acids free systems at the initial pH 9. The products formed just after mixing of InCl_3 solution with NaOH seemed amorphous $\text{In}(\text{OH})_3$, and no crystalline $\text{In}(\text{OH})_3$ particles were observed (Fig. 2(a)). After 30 min, $\text{In}(\text{OH})_3$ nanoparticles of rectangular, cubic, and irregular shapes were formed as shown in Fig. 2(b). The particles clearly grew with aging time and finally the mean particle size reached 100 nm after 24 h (Fig. 2(c)). The XRD patterns of the products before aging at 100°C indicated amorphous phase because of no crystalline peak. The crystalline $\text{In}(\text{OH})_3$ was confirmed as a single phase after 30 min. The crystallinity was improved by the extension of aging time. Thus, XRD results were consistent with the TEM observations.

TEM photos in Fig. 3 show time evolution of the products with aging time at 100°C in the presence of **Asp** at the initial pH 9. Figure 3(a) indicates that the initially formed precipitates before aging at 100°C were amorphous like gel. After

Fig. 2 TEM images of the precipitates in samples aged for 0 h (a), 0.5 h (b), and 24 h (c) at 100°C in the absence of amino acids. The scale bar in (a) is common for all images.

Fig. 3 TEM images of the solid particles formed by aging for 0 h (a), 0.5 h (b), 3 h (c), 6 h (d), 8 h (e), and 72 h (f) at 100°C in the presence of 0.050 mol L⁻¹ Asp. The scale bar in (a) is common for all images.

30 min, the particles with both of irregular and thin plate shapes were observed (Fig. 3(b)). No cubic-shaped $\text{In}(\text{OH})_3$ particle was found in the products aged until 3 h (Fig. 3(c)). The cubic-shaped $\text{In}(\text{OH})_3$ particles were clearly recognized in the products formed after aging for 6 h (Fig. 3(d)). The cubic nanoparticles grew with the aging time, while the other particles, such as thin plate-like and irregular ones, were decreased (Fig. 3(e)). The thin plate-like particles were completely disappeared after 24 h, and no irregular-shaped particles were observed after 72 h (Fig. 3(f)). The XRD patterns of the products at different aging time are shown in Fig. 4. No crystalline phase was found at 0 h (Fig. 4(a)). Peaks of $2\theta = 22.2, 35.5$, and 45.4° in the XRD patterns of the products obtained after more than 30 min can be assigned as $\text{In}(\text{OH})_3$, but undefined peaks ($2\theta = 27.3, 28.8, 32.4, 39.8$, and 54.2°) were also found until 8 h aging: They are not matched with JCPDS data. By the aging, the undefined peaks were decreased, and peaks derived from $\text{In}(\text{OH})_3$ were increased. Finally, the undefined peaks were totally disappeared at 24 h aging, and the $\text{In}(\text{OH})_3$ was formed in a single phase. This behavior was consistent with the morphological changes shown in Fig. 3. Thus, it can be identified that the

Fig. 4 XRD patterns of the precipitates in samples aged for 0 h (a), 0.5 h (b), 3 h (c), 6 h (d), 8 h (e), and 24 h (f) at 100°C in the presence of 0.050 mol L⁻¹ Asp.

undefined peaks were derived from the formation of thin plate-like solid, which is, we believe, an intermediate to final product, $\text{In}(\text{OH})_3$. Such an intermediate was only observed in the presence of Asp. Regarding this behavior, the cubic-shaped $\text{In}(\text{OH})_3$ nanoparticles were formed through dissolution of the undefined solid intermediates with thin-plate morphology. In the case of Gly system, $\text{In}(\text{OH})_3$ particles were nucleated and grew through direct deposition without any formation of an intermediate, similar to amino-acid free systems.

3.3 Intermediate-assisted size distribution control of cubic-shaped $\text{In}(\text{OH})_3$ nanoparticles

As mentioned above, during the generation of $\text{In}(\text{OH})_3$ nanoparticles in the presence of Asp, the formation of undefined solids as an intermediate was ascertained. Beneficial use of a solid intermediate as a reservoir of precursor complexes to desired product in the gel-sol method, is one of the most powerful tools for the preparation of mono-dispersed fine particles.¹³ Based on the idea of the gel-sol method, we focused on the utilization of the undefined solid intermediate for the further size-control to obtain monodispersed $\text{In}(\text{OH})_3$ nanoparticles. Initially, we have investigated the effect of aging temperatures in Asp system to predominantly obtain the solid intermediate. The TEM images and the XRD patterns of the products obtained at 50 and 70°C for 24 h are shown in Fig. 5(a)–(b) and 6(a)–(b), respectively. The products formed at both temperatures mainly consisted of the thin plate precipitates, which were confirmed as the

Fig. 5 TEM images of the solid particles obtained at different aging temperature in the presence of **Asp**. (a) 50°C, 24 h; (b) 70°C, 24 h; (c) 50°C, 24 h then 100°C, 48 h; (d) 100°C, 48 h. The scale bar in (a) is common for all images.

Fig. 6 XRD patterns of the precipitates formed at different aging temperature in the presence of **Asp**. (a) 50°C, 24 h; (b) 70°C, 24 h; (c) 50°C, 24 h then 100°C, 48 h.

same intermediate as shown in Fig. 3(b). However, peak at 22.2° derived from the formation of $\text{In}(\text{OH})_3$ was also observed by the aging at 70°C (Fig. 6(b)). Thus, we set the first aging temperature to 50°C for 24 h as an optimized condition to predominantly obtain the solid intermediate. To accelerate $\text{In}(\text{OH})_3$ nucleation in a short period through dissolution of once formed solid intermediate, the aging temperature was rapidly increased to 100°C , and aged for 48 h at the temperature. The TEM image and the XRD pattern of the resulting solid particles, obtained by the two-step aging, are shown in Fig. 5(c) and 6(c), respectively. The solid particles can be identified as crystalline $\text{In}(\text{OH})_3$ as a single-phase. As shown in TEM images (Fig. 5(a) and 5(c)), the

solid intermediate obtained by aging at 50°C for 24 h was transformed into cubic-shaped $\text{In}(\text{OH})_3$ nanoparticles through the dissolution and precipitation. The average size of the nanoparticles is calculated as 47 nm with a standard deviation of 7 nm (15%) by counting 100 particles taken by TEM observation. In contrast, average size of the particles synthesized by one-step aging at 100°C for 48 h is 53 nm with a standard deviation of 15 nm (27%), as shown in Fig. 5(d). Such improvement of the size distribution utilizing dissolution control of an intermediate has been reported in the preceding studies of the gel-sol method.¹⁰⁾ Also in the case of the present report, the nucleation and growth of $\text{In}(\text{OH})_3$ nanoparticles might be clearly separated with use of once-formed solid intermediate as reservoir of precursor to them, which can decrease the super-saturation in the system to avoid the spontaneous nucleation during the particle growth. Thus, the amino acid-assisted two-step hydrothermal synthesis seems favourable for the preparation of monodispersed $\text{In}(\text{OH})_3$ nanoparticles.

4. Conclusion

In summary, shape-controlled highly crystalline $\text{In}(\text{OH})_3$ nanoparticles were successfully prepared by amino acid-assisted hydrothermal synthesis. The rod-shaped $\text{In}(\text{OH})_3$ nanoparticles with the major axis about 50 nm were mainly formed by using **Gly** as a shape controller, while both of rod and cubic-shaped particles were formed in the absence of amino acid. On the other hand, only cubic-shaped $\text{In}(\text{OH})_3$ nanoparticles were formed by using **Asp** and adjusting the initial pH. The size distribution of the cubic-shaped nanoparticles was improved by two-step aging based on the gel-sol technique. The particle deposition system utilizing dissolution-recrystallization process of solid intermediate based on the gel-sol technique would be a quite effective and promising procedure for the preparation of highly monodispersed nanoparticles in large quantities.

Acknowledgements

This work was financially supported by METI & NEDO Rare Metal Substitute Materials Development Project.

REFERENCES

- 1) T. Kasuga, M. Hiramatsu, A. Hosono, T. Sekino and K. Niihara: *Langmuir* **14** (1998) 3160–3163.
- 2) M. Niederberger: *Acc. Chem. Res.* **40** (2007) 793–800.
- 3) T. Teranishi, M. Saruyama and M. Kanehara: *Chem. Lett.* **38** (2009) 194–199.
- 4) L. Gou and C. J. Murphy: *Nano Lett.* **3** (2003) 231–234.
- 5) S. Yang and L. Gao: *J. Am. Chem. Soc.* **128** (2006) 9330–9331.
- 6) J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama and T. Adschiri: *Adv. Mater.* **19** (2007) 203–206.
- 7) O. Durupthy, J. Bill and F. Aldinger: *Cryst. Growth Des.* **7** (2007) 2696–2704.
- 8) R. A. Gilstrap Jr., C. J. Capozzi, C. G. Carson, R. A. Gerhardt and C. J. Summers: *Adv. Mater.* **20** (2008) 4163–4166.
- 9) T. Sugimoto and K. Sakata: *J. Colloid Interface Sci.* **152** (1992) 587–590.
- 10) T. Sugimoto, K. Sakata and A. Muramatsu: *J. Colloid Interface Sci.* **159** (1993) 372–382.

- 11) T. Sugimoto, M. M. Khan and A. Muramatsu: *Colloid Surf. A* **70** (1993) 167–169.
- 12) T. Sugimoto, S. Waki, H. Itoh and A. Muramatsu: *Colloid Surf. A* **109** (1996) 155–165.
- 13) K. Kanie, A. Muramatsu, S. Suzuki and Y. Waseda: *Mater. Trans.* **45** (2004) 968–971.
- 14) S.-K. Kwon, K. Kimijima, K. Kanie, A. Muramatsu, S. Suzuki and E. Matsubara: *Mater. Trans.* **46** (2005) 155–158.
- 15) T. Sugimoto: *Monodispersed Particles*, (Elsevier, Amsterdam, 2001).
- 16) Y. Waseda and A. Muramatsu, eds.: *Morphology Control of Materials and Nanoparticles*, (Springer, Berlin, 2003).
- 17) T. Sugimoto, K. Okada and H. Itoh: *J. Dispersion Sci. Technol.* **19** (1998) 143–161.
- 18) T. Sugimoto, X. Zhou and A. Muramatsu: *J. Colloid Interface Sci.* **259** (2003) 43–52.
- 19) T. Sugimoto, X. Zhou and A. Muramatsu: *J. Colloid Interface Sci.* **259** (2003) 53–61.
- 20) K. Kanie and T. Sugimoto: *Chem. Commun.* **14** (2004) 1584–1585.
- 21) K. Kanie, H. Sakai, J. Tani, H. Takahashi and A. Muramatsu: *Mater. Trans.* **48** (2007) 2174–2178.
- 22) H. Zhu, Y. Wang, N. Wang, Y. Li and J. Yang: *Mater. Lett.* **58** (2004) 2631–2634.
- 23) H. Zhu, K. Yao, Y. Wo, N. Wang and L. Wang: *Semicond. Sci. Technol.* **19** (2004) 1020–1023.
- 24) Q. Tang, W. Zhou, W. Zhang, S. Ou, K. Jiang, W. Yu and Y. Qian: *Cryst. Growth Des.* **5** (2005) 147–150.
- 25) R. B. H. Tahar, T. Ban, Y. Ohya and Y. Takahashi: *J. Appl. Phys.* **83** (1998) 2631–2645.
- 26) Y. Endo, T. Sasaki, K. Kanie and A. Muramatsu: *Chem. Lett.* **137** (2008) 1278–1279.
- 27) H. Tanaka, K. Miyajima, M. Nakagaki and S. Shimabayashi: *Chem. Pharm. Bull.* **37** (1989) 2897–2901.
- 28) C. E. Giacomelli, M. J. Avena and C. P. D. Pauli: *Langmuir* **11** (1995) 3483–3490.
- 29) J. Ikhsan, B. B. Johnson, J. D. Wells and M. J. Angove: *J. Colloid Interface Sci.* **273** (2004) 1–5.