

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

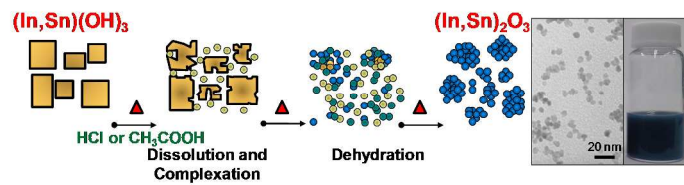
Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

SYNOPSIS TOC.

Large quantities of water based ITO nanoparticles with size of 5 nm were prepared in 2-octanol-HCl/CH₃COOH system at atmospheric pressure.



Large-scale Synthesis of ITO Nanoparticles in Alcohol System Assisted by Acids

Jhon L. Cuya Huaman,^a Koji Tanoue,^b Hiroshi Miyamura,^a Takatoshi Matsumoto^c and Balachandran Jeyadevan^{*,a}

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Co-precipitation of indium and tin salts in aqueous media followed by the heat treatment of the products provides a versatile route to obtain tin-doped indium oxide (ITO) nanopowders in large quantities. However, the high temperature treatment that is need for getting well-crystallized powders provokes particle growth through sintering and leads to poor dispersibility. In this study, ITO NPs were obtained by the dehydration of In,Sn hydroxide precursor and subsequent crystallization of the same in acidified 2-octanol solution under atmospheric conditions and at low reaction temperature, 180 °C. This process yields grams of well-dispersed ITO nanoparticles with an average size of ~5 nm and a tin content of ~10 %. In addition, pellets made of ITO nanoparticles and annealed at 200 °C in vacuum exhibited a conductivity of 1.3 Ω-cm.

Introduction

Doping of In₂O₃ by ions such as Sn⁴⁺ generates electrons on its conduction band and possess n-type semiconductor properties with a wide optical band gap of 3.3 eV as well as low electrical resistivity of 10⁻⁴ Ω-cm.¹⁻⁷ In addition, the excellent transparency and wear resistance properties of tin-doped indium oxide (ITO) is an essential material to fabricate devices such as, smart or touching panels, liquid crystal and organic light emission displays, sensors and photocells, etc.⁶⁻⁸

The techniques for preparing conducting ITO films are based mainly on high temperature processes such as sputtering, spray pyrolysis and evaporation^{4,5,9,10}. However, in recent years, there is a trend to prepare conducting and semiconducting films by depositing nanoparticles on flat substrates.¹¹⁻¹³ This is due to the fact that the melting temperature of nanoparticles are lower than their bulk counterpart, which is one of the profound advantage of using nanoparticles. Consequently, films using NPs could be fabricated on low melting point substrates.⁶ In addition to cheaper processing techniques, nanoparticles could be handled efficiently and the loss of raw materials, especially the scarcely and costly indium metal, could be minimized.^{11,12,14} However, in order to obtain highly dense and chemically homogeneous films, the nanoparticles should be stably suspended in a liquid solvent to be uniformly injected or sprayed on desired substrates. To materialize the above applications, it is necessary to prepare ITO particles with average sizes around 20 nm and below, and narrow sized distribution;¹² a physical characteristic commonly observed in conducting metal-based nanoinks, which are highly stable over extended time period.

To prepare ITO nanoparticles, techniques such as sol-gel, microemulsion, and thermal decomposition have been proposed and utilized.¹⁵⁻²¹ However, co-precipitation of metallic salts is the most common and highly preferred chemical synthesis technique.²²⁻²⁵ Though this technique could facilitate high

mass production, the resulting products are constituted of amorphous In and Sn hydroxides requiring high temperature post-heat treatment to achieve chemically homogenous and highly crystalline ITO particles. Although, this technique has been modified with the aim to tune the optical and electrical properties through controlling size and composition of ITO particles; the sintering and particle growth during post-heat treatment seriously affects the particle size and size distribution and as a consequence the dispersability in solvents is lost. On the other hand, the thermal decomposition technique, where the size and shape could be controlled by changing the reaction temperature or salt precursors or using additives such as hydroxyl ions, is also being actively pursued. However, this technique too requires a post-heat treatment to convert the In, Sn hydroxides or oxyhydroxide products into oxides.²⁶⁻²⁸

In contrast to the above techniques, ITO nanoparticles have been successfully obtained through solvothermal routes when water is replaced by alcohols such as ethanol, butanol, benzyl alcohol, ethylene glycol, diethylene glycol, polyethylene glycol or other alcohols.^{11,29-33} Though the crystallization of ITO is achieved at elevated temperatures and prolonged reaction time or using microwave heating system, under these nonaqueous conditions, the massive production is considered difficult.³⁴ In addition to the above synthesis routes, recently, crystallized ITO in small quantities was produced at atmospheric pressure and at relatively low reaction temperature using 1-heptanol and metal ions with the assistance of hydroxyl ions.³⁴ It should be noted that the formation of crystallized ITO was not realized in the absence of hydroxyl ions or using other alcohols such as ethylene glycol or trimethylene glycol. However, the above process demonstrated the capability of alcohol in hydrating the metallic salts and subsequently dehydrate the hydroxide products, which is considered the key to obtain ITO nanopowders directly.

Based on the results of the above study, we believed that the selection of the appropriate alcohol could lead to the direct synthesis of ITO without the necessity of any further heat

treatments. Consequently, we succeeded in the synthesis of multigram quantity of ITO nanoparticles (~15 g per batch) with particle size less than 5 nm. Here, metal hydroxides precursors are converted to oxide in an acidified solution of 2-octanol at ~180 °C. The results showed that long-chain alkyl alcohol is an excellent media for the condensation of In, Sn hydroxide powders from the precursor prepared by the co-precipitation of their metal salts. In addition, the presence of hydrochloric or acetic acid assisted the dehydration through the following two steps: (1) dissolution of the precursor and (2) formation of intermediate complexes. The crystal structure of the final product was similar to In_2O_3 with a tin content of ~10 %. On the other hand, ITO pellets prepared using these nanoparticles and annealed in air at 200 °C showed an electrical resistivity of 1.3 $\Omega\cdot\text{cm}$. It should be noted that the main advantages of the proposed technique are (a) large-scale high temperature processing step-free synthesis of ITO nanoparticle and (b) preparation of water-based ITO ink dispersing nanometer sized particles.

Experimental Section

Synthesis of ITO precursor

ITO precursor were synthesized by treating the In, Sn hydroxide precursors in long chain alcohol. First, the hydroxides were prepared by mixing, indium chloride tetrahydrate (or indium nitrate tetrahydrate) and tin chloride dihydrate in a ratio of 10:1 at 40 °C in aqueous solution, under vigorous stirring and rapid addition of specific amounts of ammonia solution (25%). Then after 30 min, the precipitate was collected by centrifuging and washed with distilled water.

Synthesis of ITO nanoparticles

0.10 mol/L of (In, Sn) hydroxide and 80 mL of 2-octanol were introduced into a two necked glass reactor (Chemist Plaza). It was then heated to 180 °C (boiling point of 2-octanol) and maintained at this temperature for 5 hours. During heating, specific concentrations of acid (0.005, 0.01 and 0.02 mol/L) is dissolved in 20 mL of 2-octanol and introduced into the reaction vessel. Once the reaction was completed, the solution was cooled down to room temperature. The settled particles were recovered by centrifugation and then washed with ethanol several times. Finally, the particles were dried overnight under vacuum. For comparison, the synthesis of ITO powders was attempted in different alcohols (1-heptanol and 1-octanol) and polyol (ethylene glycol) at near the boiling points of solvents for 5 hours.

Characterization

Crystallographic phases present in the powder were identified by analyzing the X-ray powder diffraction (XRD) patterns of the samples obtained using the Rigaku Multiflex Diffractometer with $\text{Cu K}\alpha$ -radiation. The size and morphology of the particles were analyzed by using transmission electron microscope (FE-TEM Hitachi HF-2000). The optical properties of the liquid and solid products were analyzed using ultraviolet-visible spectrophotometer (UV-Vis, Hitachi U2000)

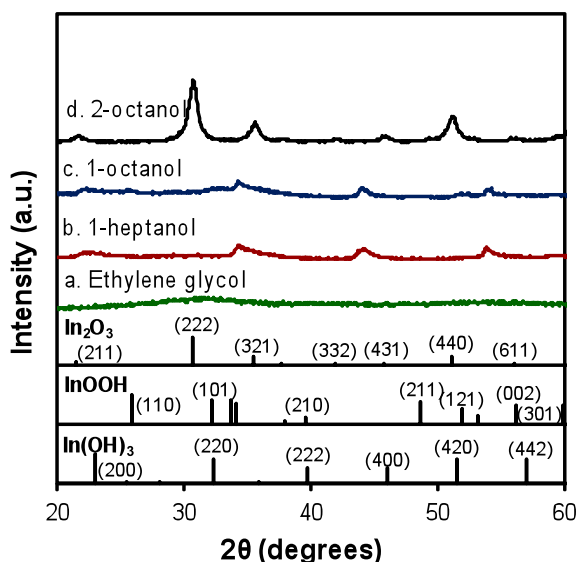


Fig. 1 XRD patterns of the products obtained after treating indium tin hydroxides in (a) ethylene glycol, (b) 1-heptanol, (c) 1-octanol and (d) 2-octanol at temperatures near their boiling points for 2 h.

in the range of 200 to 900 nm and Fourier transform infrared spectrometer (FTIR, Thermolite Scientific Nicolet-IS5) in the range of 500 to 4000 cm^{-1} . The conductivity measurements of ITO pellets were carried out using 4-point method on a Loresta-GP (Mitsubishui Chemical Analytech Co., Ltd). ITO pellets with a diameter of 10 mm were prepared by pressing the powder under a pressure of 1.0 ton cm^{-2} and subsequently annealing the same at 200 °C in vacuum. Furthermore, the composition of the powder determined by analysing the ITO dissolved solution using mainly inductive coupled plasma (ICP, Perkin Elmer Optima 3300XL).

The ratio between $\text{SnO}_2/(\text{SnO}_2+\text{In}_2\text{O}_3)$ were calculated as follows: The ITO powders were dissolved in acid and the solution was analyzed by ICP to obtain the concentration of Sn. Then, the amount of SnO_2 was calculated considering the stoichiometric oxygen value. Then, the ITO powders were dissolved in acid and the solution was re-precipitated by introducing ammonia. The precipitate was filtered and heat-treated for measuring the total weight of ($\text{In}_2\text{O}_3 + \text{SnO}_2$), assuming that the In and Sn form In_2O_3 and SnO_2 , respectively. The chloride ion concentration was calculated by analyzing the supernatant solution obtained after dissolving ITO powder in water, by ion chromatography.

Results and Discussion

The direct synthesis of ITO nanoparticles from their metallic salts have been a challenge for the researchers in the field of chemical synthesis. The use of alcoholic solvents in closed vessel (solvothermal method) have proved to be successful in to producing ITO from their metallic salts. The crystallinity of the product has been found to depend on the type of alcohol, reaction temperature and duration.²⁹⁻³³ However, the syntheses of ITO using alcohols as solvents under atmospheric pressure

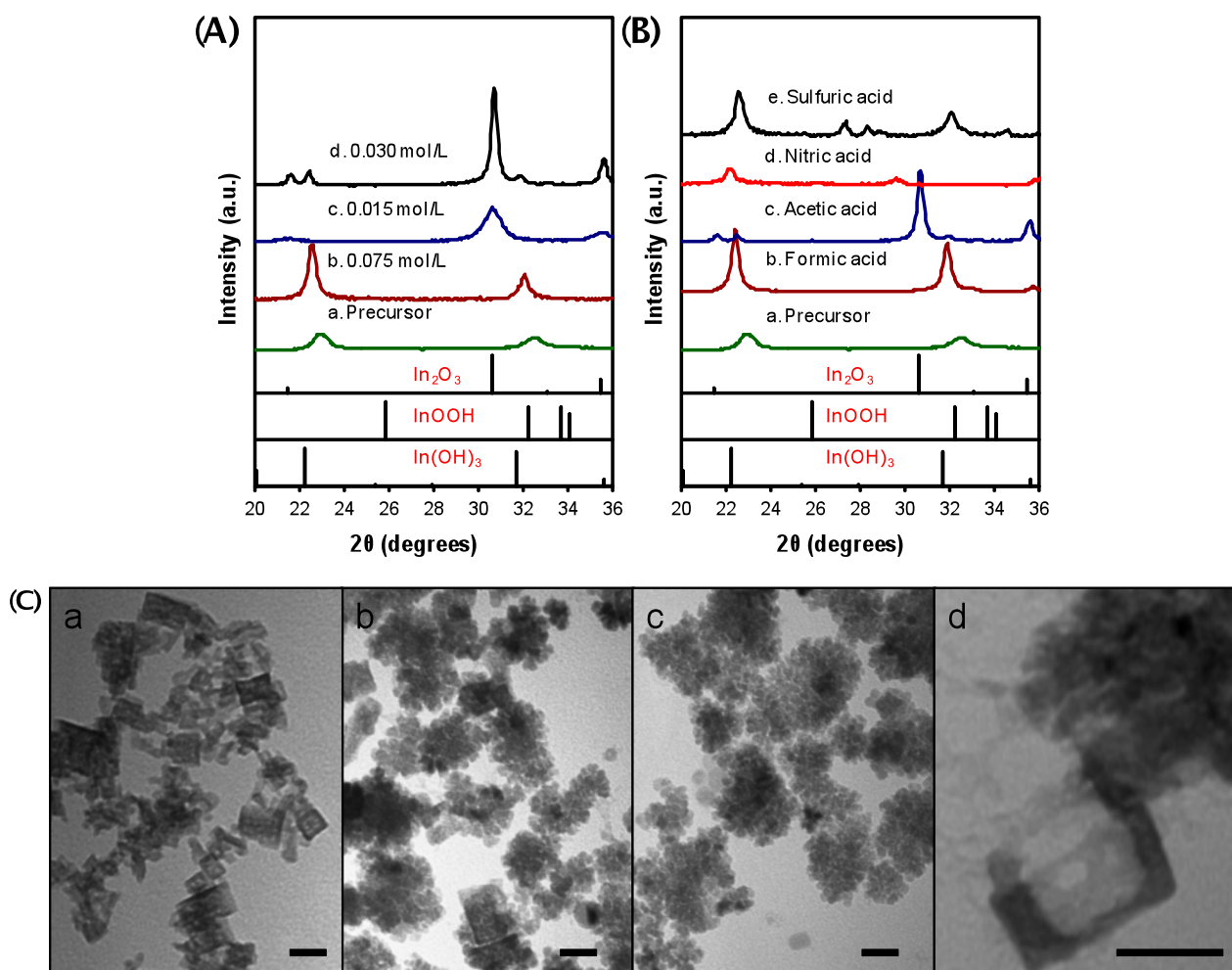


Fig. 2 (A) XRD pattern of the (a) as-prepared precursor and products obtained after heating hydroxide precursor at 180 °C for 2 h in 2-octanol with different hydrochloric acid concentrations: (b) 0.005, (c) 0.01, and (d) 0.02 mol/L of HCl. (B) XRD pattern of the (a) as-prepared precursor and products obtained after treating the precursor with different acids: (b) formic acid (c) acetic acid, (d) nitric acid and (e) sulfuric acid. (C) TEM images of products obtained after treating the precursor with different hydrochloric acid concentrations: (a) 0.005, (b) 0.01, and (c) and (d) 0.02 mol/L. Scale bar: 20 nm.

have been rarely reported.^{11,34} This is due to the fact that the redox potential difference between In and Sn favors the formation of In and Sn oxides separately. Thus it is necessary to introduce hydroxyl ions into alcohol to get chemically homogeneous ITO through dehydration.³⁴ However, in case of using 1-heptanol as solvent, the process failed, when the amount of metallic salts were increased in order to obtain large quantities of well-crystallized oxides. It seems that the alcohols used in these experiments were not suitable to dehydrate the hydroxides completely. Hence, in this study, we demonstrate the synthesis of ITO nanoparticles in large quantities from their hydroxide precursors using 2-octanol as solvent, and the results are compared with other alcohols such as 1-heptanol, 1-octanol and ethylene glycol.

Effect of Alcohol

Fig. 1 shows the XRD patterns of products obtained when (In, Sn) hydroxides were reacted with alcohols such as (a) ethylene glycol, (b) 1-heptanol, (c) 1-octanol or (d) 2-octanol at temperatures near their boiling points. Here, the hydroxide precursor was prepared by using indium and tin (II) chlorides

as metal sources. When ethylene glycol was used as the solvent, the XRD peaks of the precipitate were broadened and centered near angles, 30.9 degrees, corresponding to the main plane (222) of cubic In_2O_3 (JCPDS No. 06-0416). The lattice parameter of this sample was determined to be 9.699 Å, which is lower than the reported value, 10.118 Å. It could be ascribed to the reduction of lattice spacing caused by Sn doping where ionic radius of Sn^{4+} is smaller than In^{3+} . However, it may also be due to the poor crystallinity. On the other hand, in cases of 1-heptanol and 1-octanol, the products exhibited unknown phases that could be ascribed only partially to dehydrated $\text{In}(\text{OH})_3$ compounds (JCPDS No. 16-0161) or other In and Sn, containing compounds. On the other hand, in the case of 2-octanol, the peaks corresponding to planes (211), (222), (321), (332), (431) and (440) of cubic crystal structure of In_2O_3 were observed at angles of 21.6, 30.1, 35.6, 42.0, 45.9, and 51.2 degrees that are in good agreement with the values reported in the JCPDS No. 06-0416. The lattice parameter was calculated to be 10.094 Å, slightly smaller and confirms the presence of Sn into the In_2O_3 structure. The reason for adequacy of 2-octanol over other alcohols/polyols in obtaining crystallized

ITO powders is not clear. Although, the size and crystallinity of the products have been reported to depend on the viscosity of the solvent,³¹ it could be also related to the solubilities of water and hydroxide in alcohols and polyols. In solvothermal techniques, the use of short-chain alkyl alcohols such 1-butanol instead of ethylene glycol resulted in the formation of oxide mixtures, and oxyhydroxide.³²⁻³³ This could be due to the presence of dissolved water in 1-butanol because the synthesis of pure ITO has been proved possible in ethanol. In fact, the effect of water in ethylene glycol has been also examined and the formation intermediate products such hydroxide and oxyhydroxide has been found to be promoted depending on the amount of water in the system. It seems that water content in the alcoholic solution inhibits the formation of ITO and favors the conversion of the already formed oxides into hydroxides ($\text{In}(\text{OH})_3 \leftrightarrow \text{In}_2\text{O}_3$). In case of 2-octanol, at higher reaction temperatures, water or hydroxyl ions is not retained in the system. As a consequence, complete dehydration is facilitated leading to the formation of oxides.

Effect of acid concentration

Due to the use of metal chloride salts for the synthesis of the In, Sn hydroxides where a 14000 Cl ppm was determined by ion chromatography, hydroxide precursor was washed several times to remove the chloride ions. However, the synthesis of ITO was not realized when the content of chloride ions was very low. Thus, it was assumed that chloride ions assisted the synthesis of ITO nanoparticles in a similar way as it is used to function in the formation of oxides through hydrolysis in acidified aqueous solution.^{35,36} Thus, in order to determine the role of chloride ions in the formation of oxides, In, Sn hydroxide was prepared using indium nitrate and tin (II) chloride as metal sources and was treated in 2-octanol with different hydrochloric acid concentrations. For clarity, the XRD patterns in the region from 20 to 36 degrees, where the main peaks of oxide, hydroxide and oxyhydroxide appear are shown in Fig. 2A. The XRD patterns revealed the formation of ITO only when the HCl concentrations were 0.01 and 0.02 mol/L, but not at 0.005 or 0 mol/L. At low HCl concentrations, the initial cubic $\text{In}(\text{OH})_3$ structure (JCPDS No. 16-0161) was retained.

In addition, the TEM images of these samples were analyzed and shown in Fig. 2C. At low acid concentrations, the sample was constituted of cubic-shaped particles, similar to the precursor and its average particle size was determined to be approximately around 18 nm. However, at higher acid concentrations, agglomerates constituting smaller sized particles (about 5 nm) were observed. But in some areas the cubic-shaped precursor particles could also be observed. This accounts for the presence of peaks corresponding to the precursor in the XRD patterns. On the other hand, the figure 2C(d) taken at shorter reaction time shows a partially dissolved cubic particle. This suggests that prior to the formation of oxides, the precursor particles undergo dissolution and reprecipitation. Subsequently, the resultant compound is dehydrated to form new smaller sized ITO particles.

We also experimentally verified whether this phenomena could occur with other acids such as formic, acetic, nitric, and

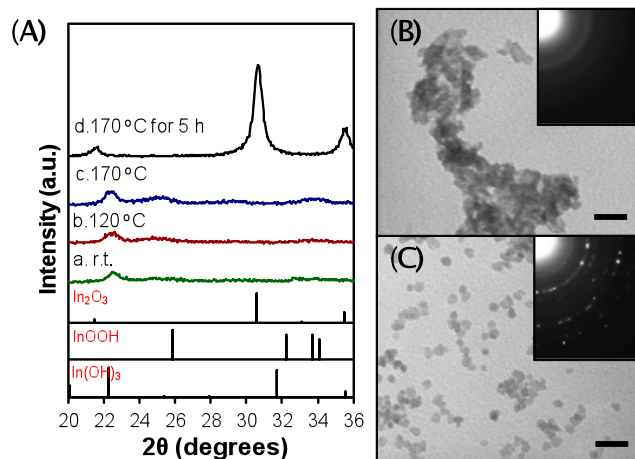


Fig. 3 (A) XRD patterns of (a) precursor and products obtained by heating the same in 2-octanol at (b) 120, (c) 170 and (d) 170 °C for 5 h. TEM images with their respective SAED patterns of products obtained after heating at 170 °C for (B) 0 and (C) 5 h. Scale bar: 20 nm.

sulfuric under similar experimental conditions. Here, the molar acid concentration was fixed at 0.01 mol/L. The XRD patterns of the products indicated that ITO powders can only be obtained when acetic acid was used. These results suggested that hydrochloric acid and acetic acid have the capability in forming stable compounds in contrast to other acids considered in this study. With these results, we partially concluded that the dissolution of the metal hydroxide particles and the formation of metal complex occur prior to the precipitation of ITO. However, it is necessary to elucidate the mechanism of ITO formation in order to optimize reaction conditions such as temperature and duration. Thus, the reaction was monitored at different temperatures and reaction durations and the samples were characterized by different techniques such as XRD, TEM, FT-IR and UV-vis spectrometry.

Elucidation of Reaction Mechanism

Different mechanisms have been proposed to explain the formation of ITO nanoparticles in solvothermal methods.^{29,31,33} Recently, Joseyphus et al.,³⁴ reported that the process is composed of two steps: (1) the hydroxylation of metallic salts and (2) the hydroxide condensation, under continuous purging of N_2 gas. However the process studied here is quite different, since In, Sn hydroxides are used as precursors. Thus, in order to understand the formation of well crystallized ITO, the process was monitored at different reaction temperatures and durations. Fig. 3(A) shows the XRD patterns of powders obtained at different reaction temperatures when the precursor was heated for 5 hours. The XRD pattern for the hydroxide precursor (Fig. 3(A)(a)) exhibited a poorly crystallized structure with peak position similar to the one corresponding to the (200) plane of $\text{In}(\text{OH})_3$. However, the peaks corresponding to hydroxide or oxyhydroxide, which appear at angles below 32 degrees, were not recorded. We believe that this is due to either poor crystallinity or the formation of complex phases such as $\text{In}(\text{OH})_{3-x}\text{Cl}_x$ or similar compounds as observed by other researchers during the hydrolysis of metal salts in presence of

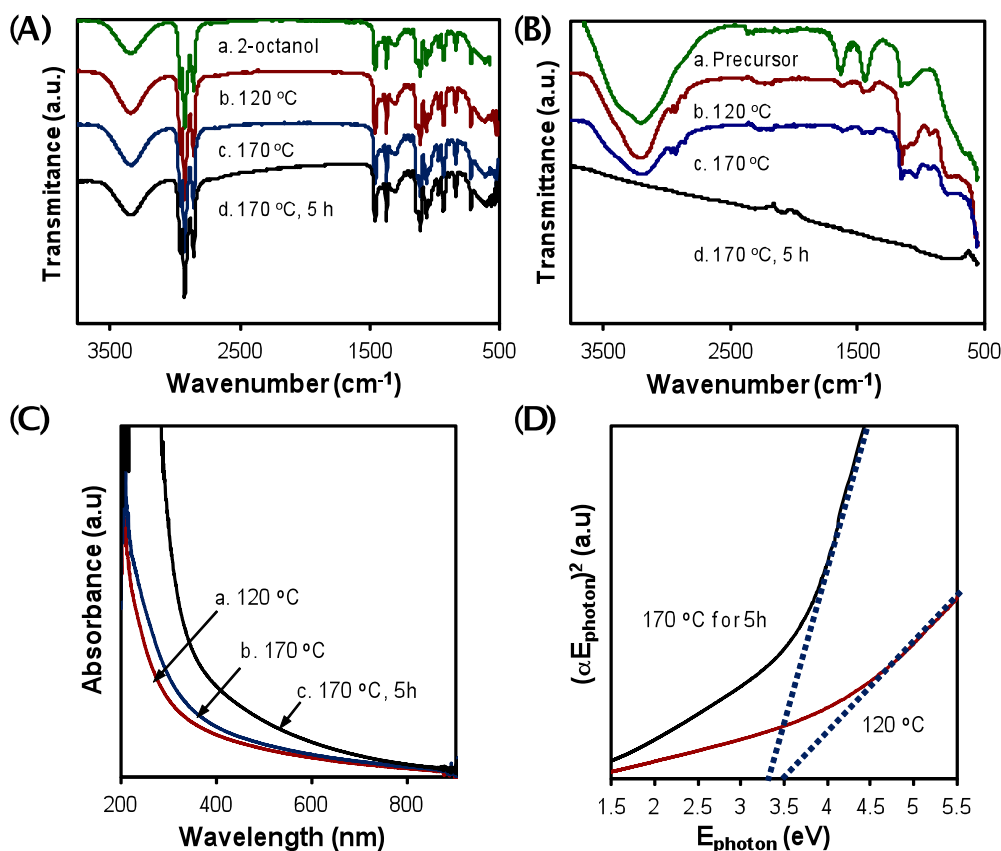


Fig. 4 FTIR spectra of (A) liquid samples and (B) dried powder taken at different reaction temperatures: (a) room temperature, (b) 120 °C, (c) 170 °C and (d) 170 °C for 5 hours. (C) UV-vis spectra of the samples treated at different temperatures. (D) $(\alpha E_{\text{photon}})^2$ against E_{photon} plots of products obtained at 120 °C and 170 °C.

chloride ions.³⁷ Whereas $((\text{H}_2\text{O})_3\text{In})\text{Cl}_3$ were observed in the synthesis of InOOH by a diglycol-mediated solvothermal process.³⁸ On the other hand, complexation is also reported in benzylalcohol solution containing In acetylacetonate and Sn butoxide, prior to the formation of ITO.³¹ However it should be noted that the transformation of the metal complex to ITO occurs only at 170 °C, but within reasonably short period of time. Thus, ITO is formed within an hour and further heating only enhances the crystalline phase instead of the particle growth. On the other hand, a lattice parameter of 10.084 Å was calculated using (222) diffraction peak. Whereas a grain size of 5.3 nm was evaluated by using the Debye-Scherrer equation.

Figure 3B and C are the microphotographs of the products obtained at (a) 0 and 5 h at after the solution reached 170 °C. As observed in Fig. 3B, the sample is constituted of irregularly-shaped particles with sizes around 17 nm. On the other hand, the particles in Fig. 3C was also irregularly-shaped, but has well defined borders and their average size was around 5 nm which is similar to those obtained in the XRD analysis. These results indicate clearly that the hydroxide particles underwent dissolution in the alcoholic solution and reprecipitated. The insets in the microphotographs (Figs. 3B and C) correspond to small area diffraction (SAED) patterns, which indicate that the crystallization of the samples increases as the reaction progresses and the rings correspond to the planes of cubic phase of In_2O_3 : (211), (222), (400), (411), (332), (431) and

(440).

FT-IR spectroscopic measurements of the liquid and solid powders obtained at different reaction temperatures were also analyzed (Fig. 4A and B) to better the understand the reaction scheme. The spectra of the liquid products were compared with that of pure 2-octanol and showed in (Fig. 4A) (curve (a)). The spectra corresponding to liquid samples obtained at different temperatures exhibited peaks characteristic of 2-octanol, which are ascribed to the O-H stretching vibration band at 3336 cm^{-1} , the symmetric and asymmetric CH_2 stretching vibration peaks between 2959 and 2856 cm^{-1} and those corresponding to CH_3 bending vibration at 1458 and 1375 cm^{-1} . Careful analysis of these results, suggested that the solvent does not undergo any changes and also presence of other compounds such as 2-octanone, which is formed through the oxidation was not observed. It should be noted that the formation of 2-octanone has been recorded during the synthesis of Ni nanoparticles.³⁹ The above results suggest the following possibilities; either there is no oxidation reaction taking place in this system or the oxidized products are too volatile to be collected and analyzed.

Furthermore, the FTIR spectra of the as-prepared hydroxide powders and their products were also analyzed (Fig. 4B). In case of hydroxide precursors, in addition to OH deformation bands corresponding to the hydroxide^{40,41} at 1153 and 1095 cm^{-1}

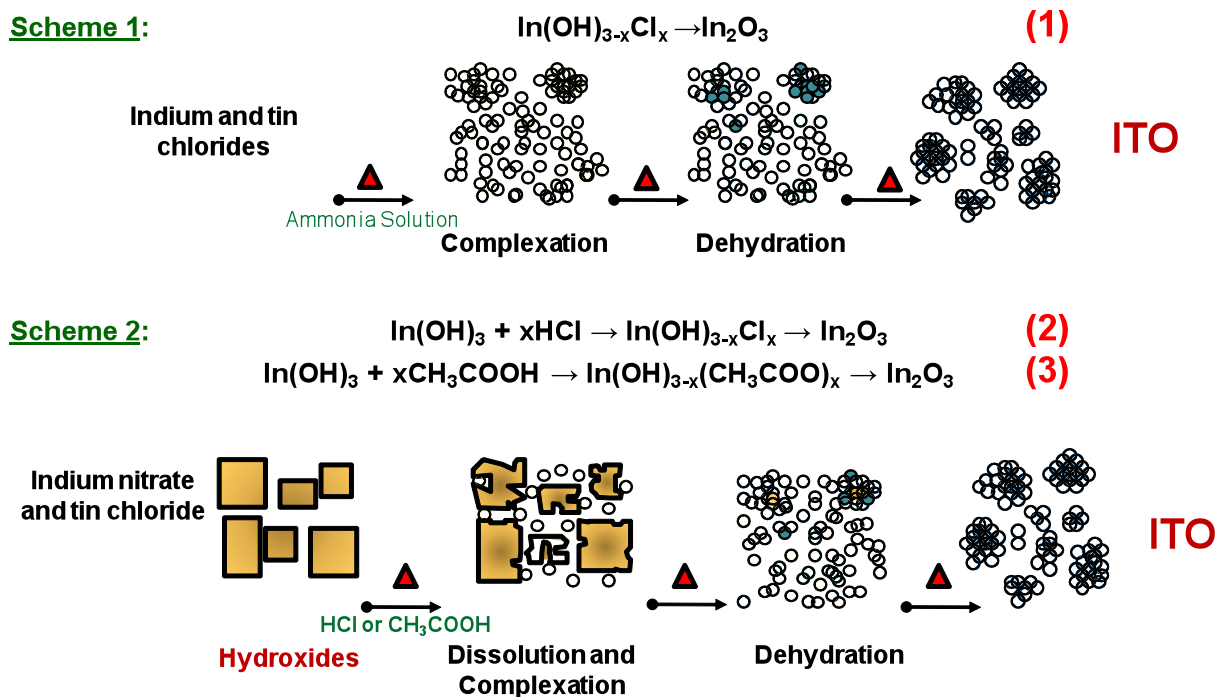


Fig. 5 Reaction schemes proposed for the synthesis ITO nanoparticles using hydroxide cake prepared using (1) In and Sn chlorides and 2-octanol and (2) In nitrate and Sn chloride in acidified 2-octanol.

¹, a broad band characteristic of OH stretching vibrations due to structural hydroxyl ions and adsorbed water were observed in the range between 3000 and 3600 cm^{-1} . The presence of peaks corresponding to In-OH bending band at 1434 and water at 1623 cm^{-1} , confirmed the presence of hydroxide precursor and adsorbed water.^{40,41} When the solution/suspension was subjected to heat, the product underwent some changes and this is reflected in the spectra. The intensities of the peaks corresponding to hydroxide decreased, especially the removal of free or adsorbed water could be inferred. At 170 °C, the peaks corresponding to adsorbed water and In-OH disappeared indicating a total dehydration of the hydroxide and conversion to ITO. The above observation was in accordance with the XRD pattern obtained at this temperature and reaction duration (Fig. 3A, 5 h)

In addition, the optical properties of the powders were examined (Fig. 4C). Here also the changes observed at temperatures below 170 °C were negligible. However, the absorption spectra of the sample obtained after a prolonged reaction duration, shifted to higher wavelength due to the transformation of the hydroxide to ITO. The band gap was calculated from the plot of $(\alpha E_{\text{photon}})^2$ as a function of E_{photon} for the samples obtained at 120 and 170 °C and shown in Fig. 4(D). From the extrapolated values of linear section (the point of intersection of the straight lines with the x axis), the band gap (B_g) of the samples were estimated to be 3.3 and 3.5 eV for ITO and its precursor at 120 °C, respectively. The band gap value obtained for the samples collected at 170 °C is comparable to ITO nanoparticles reported in the literature.^{1,2}

While the band gap of the samples obtained at 120 °C is very low and considered as that of In(OH)_3 (~5.0 eV)⁴², but close to that of InOOH (3.7 eV).⁴³ Probably, the difference could be ascribed to the doping of Sn or the formation of complexes with Cl⁻ ions. Further investigation is necessary to verify the same.

Based on the results of structural and spectroscopic analyses, the possible mechanism for the formation of ITO nanoparticles in 2-octanol-acid system can be proposed as follows: (1) when In and Sn chloride were used as precursors for preparation of hydroxide cake, $(\text{In,Sn})(\text{OH})_{3-x}\text{Cl}_x$ is formed and this subsequently gets dehydrated to form ITO; (2) when In nitrate and Sn chloride were used as precursor, the $(\text{In,Sn})(\text{OH})_3$ cake thus formed undergoes dissolution, followed by complexation to form $(\text{In,Sn})(\text{OH})_{3-x}\text{Cl}_x$ or $(\text{In,Sn})(\text{OH})_{3-x}(\text{CH}_3\text{COO})_x$ and subsequently undergoes transformation to precipitate ITO. Schematic representation is shown in Fig. 5.

Electrical properties of ITO pellets

Advantage of this method is that we could obtain 15 g of stably-dispersed ITO nanoparticles in a single batch under optimum conditions. The photograph of the powder obtained and the ITO suspension in water are shown in Fig. 6. The ITO dispersion in water was stable for days and precipitation of solids was not observed. Thus we believe that it would remain for prolonged period of time. However, detailed study is necessary.

The electrical measurements of the pellets made of ITO powders and annealed in vacuum at 200 °C showed a conductivity of 1.3 $\Omega\text{-cm}$ (Table 1). Its value is relatively high

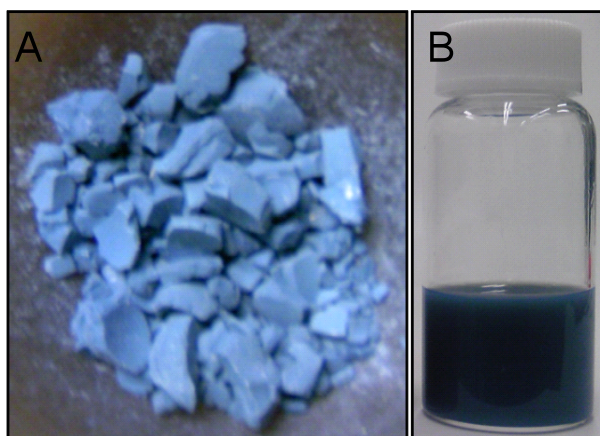


Fig. 6 Photographs of (A) ITO powders (~15 g) produced by 2-octanol and (B) their stable dispersion in water.

compared to the bulk value ($1 \times 10^{-4} \Omega\text{-cm}$)² as well as the product obtained by Hammarberg et al.¹¹ using diethyleneglycol as solvent, $1 \times 10^{-2} \Omega\text{-cm}$. The low electrical conductivities could be ascribed at the presence of chloride ions or surface adsorption of the by-products generated during the formation of ITO in alcohol system. Likewise, enhancement in conductivity is also attempted through annealing at higher temperatures or heating for longer periods of time as reported by other researchers working in chemical synthesis of ITO;^{11,30,31,33} however, it should be noted this will make the use of these materials in low substrate difficult and alternative solutions are necessary. Work melting point is in progress to develop techniques such as plasma etching to remove the impurities during the washing step.

Table 1 Tin content and electrical resistance of the ITO samples prepared (a) without acid (prepared using chloride metal sources) and with (b) hydrochloric and (c) acetic acids.

Samples	SnO ₂ (SnO ₂ + In ₂ O ₃) (%)	Pellet Density (g .cm ⁻³)	Electrical Resistance (Ω.cm)
a. W/o Acid	8.3	3.3	1.4
b. Hydrochloric Acid	11.2	3.4	15.0
c. Acetic Acid	11.5	3.6	1.3

Conclusions

It was demonstrated that the synthesis of ITO nanoparticles can be realized by heat treating In, Sn hydroxides using long chain alcohol. The solubility of water is considered to be the decisive factor in the selection of the solvent. Among the alcohols and polyols investigated, 2-octanol result to be suitable solvent to produce high quantities of ITO nanoparticles in a batch at relatively low reaction temperature and under atmospheric pressure. In addition, the presence of chloride or acetate ions has been found to play a key role in the dissolution of the

hydroxide, which facilitates the subsequent metal complexation. The reaction mechanism has been elucidated and the formation of ITO has been found to undergo through the (a) dissolution of the In-Sn hydroxide, (b) metal-complexation, (c) transformation and (d) precipitation of ITO. The ITO particles annealed at 200 °C exhibits a conductivity of 1.3 Ω-cm, which could be further enhanced by removing the impurities adsorbed on the surface of ITO particles.

Acknowledgments

This study was supported by Grant-in Aid for Basic Research #(B) 22310064 and #(B) 22655066 from the Ministry of Education, Science, Culture and Sport of Japan.

Notes

^a Department of Material Science, School of Engineering, The University of Shiga Prefecture, Hikone, Japan. Fax: 81 749 28 8486; Tel: 81 749 28 8352; E-mail: jevadevan.b@mat.usp.ac.jp, cuya.j@office.usp.ac.jp

^b DOWA Holdings Co. Ltd., Tokyo, Japan. Fax: 81 495 25 6936; Tel: 81 495 25 6934; E-mail: tanoue@dowa.co.jp

^c Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan. Fax: +81 22 217 5108; Tel: +81 22 217 5108; E-mail: matsu@tagen.tohoku.ac.jp

References

- H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jagdish, *Semiconducting Transparent Thin Films*, IOP Publishing, Bristol, 1995.
- I. Hamberg, C. G. Granqvist, *J. Appl. Phys.* 1986, **60**, R123-159.
- P. P. Edwards, A. Porch, M.O. Jones, D. V. Morgan, R. M. Perks, *Dalton Trans.*, 2004, 2995-3002.
- J. W. Bae, H. J. Kim, J.S. Kim, N. E. Lee, G. Y. Yeom, *Vacuum*, 2000, **56**, 77-81.
- A. Kono, Z. Feng, N. Nouchi, F. Shoji, *Vacuum*, 2009, **83**, 548-551.
- T. Minami, *Thin Solid Films*, 2008, **516**, 5822-5828.
- C. G. Granqvist, A. Hultaker, *Thin Solid Films*, 2002, **411**, 1-5.
- Y. Yang, Q. Huang, A. W. Metz, J. Ni, S. Jin, T. J. Marks, M. E. Madsen, A. DiVenere, S.-T. Ho, *Adv. Mater.* 2004, **16**, 321-324.
- M. J. Chuang, H. F. Huang, C. H. Wen, A. K. Chu, *Thin Solid Films*, 2010, **518**, 2290-2294.
- J. Ma, D. Zhang, J. Zhao, C. Tan, T. Yang, H. Ma, *App. Surf. Sci.* 1999, **151**, 239-243.
- E. Hammarberg, A. Prodi-Schwab, C. Feldmann, *Thin Solid Films*, 2008, **516**, 7437-7442.
- J. Puetz, N. Al-Dahoudi, M. A. Aegerter, *Adv. Eng. Mater.*, 2004, **6**, 733-737.
- J.-W. Kim, J. Choi, S.-J. Hong, *J. Korean. Phys. Soc.*, 2010, **57**, 1794-1798.
- S. G. Chen, Y. F. Huang, Y. Cheng, Q. Xia, H. W. Liao, C. G. Long, *Mater. Lett.*, 2008, **62**, 1634-1637.
- Z.-H. Li, Y.-P. Ke, D.-Y. Ren, *Tans. Nonferrous Met. Soc. China*, 2008, **18**, 366-371.
- M. J. Alam, D.C. Cameron, *Thin Solid Films*, 2002, **420-421**, 76-82.
- A. Solieman, *J. Sol-Gel Sci. Technol.*, 2011, **60**, 48-57.
- R. A. Gilstrap, C. J. Capozzi, C. G. Carson, R. A. Gerhardt, C. J. Summers, *Adv. Mater.*, 2008, **20**, 4163-4166.
- D.-W. Kim, S.G. Oh, J.-D. Lee, *Langmuir*, 1999, **15**, 1599-1603.
- D. Gallager, F. Scanlan, R. Houriet, H. J. Mathieu, T. A. Ring, *J. Mater.*, 1993, **8**, 3135-3144.
- P. S. Devi, M. Chatterjee, D. Ganguli, *Mater. Lett.*, 2002, **55**, 205-210.
- H. Wang, X. Xu, J. Zhang, C. Li, *J. Mater. Sci. Technol.*, 2010, **26**, 1037-1040.
- D. Zhanlai, A. Cunran, L. Qiang, H. Zhezhe, W. Jianqiang, Q. Haibo, Q. Fangjuan, *J. Nanomater.*, 2010, 543601.

24. X.-B. Zhu, T. Jiang, G.-Z. Qiu, B.-Y. Huang, *Trans. Nonferrous Met. Soc. China*, 2009, **19**, S752-756.
25. R. Seoudi, A. B. El-Bially, A. A. Shakaba, S. Abd El-Mongy, N. A. M. Shahan, S. M. K. Meki, *J Appl. Sci. Res.*, 2012, **8**, 3530-3538.
26. C. P. Udawatte, K. Yanagisawa, *J. Solid State Chem.*, 2000, **154**, 444-450.
27. K. Yanagisawa, C. P. Udawatte, *J. Mater. Res.*, 2000, **15**, 1404-1408.
28. C. P. Udawatte, K. Yanagisawa, *J. Am. Ceram. Soc.*, 2001, **84**, 251-253.
29. J.-S. Lee, S.-C. Choi, *J. European Ceram. Soc.* 2005, **25**, 3307-3314.
30. J. Ba, D. Fattakhova Rohlfiing, A. Feldhoff, T. Brezesinski, I. Djerdj, M. Wark, M. Niederberger, *Chem. Mater.*, 2006, **18**, 2848-2854.
31. J. Ba, A. Feldhoff, D. Fattakhova Rohlfiing, M. Mark, M. Antonietti, M. Niederberger, *Small*, 2007, **3**, 310-317.
32. Y. Endo, T. Sasaki, K. Kanie, A. Muramatsu, *Chem. Lett.*, 2008, **37**, 1278-1279.
33. T. Sasaki, Y. Endo, M. Nakaya, K. Kanie, A. Nagatomi, K. Tanoue, R. Nakamura, A. Muramatsu, *J. Mater. Chem.*, 2010, **20**, 8153-8157.
34. R. Justin Joseyphus, B. Jeyadevan, *J. Phys. Chem. Solids*, 2011, **72**, 1212-1217.
35. L.-T. Cheng, M.-Y. Tsai, W. J. Tseng, H.-I. Hsiang, F.-S. Yen, *Ceramic Int.*, 2008, **34**, 337-343.
36. W. Dong, S. Xu, D. Chen, X. Jiang, C. Zhu, *Chem. Lett.*, 2000, 496-497.
37. D. Ferri, *Acta Chem. Scand.*, 1972, **26**, 747-759.
38. S. G. Chen, Y. F. Huang, Y. Cheng, Q. Xia, H. W. Liao, C. G. Long, *Mater. Lett.*, 2008, **62**, 1634-1637.
39. J. L. Cuya Huaman, N. Hironaka, S. Tanaka, K. Shinoda, H. Miyamiura, B. Jeyadevan, *CrysEngComm*, 2013, **15**, 729-737.
40. J. Yang, H. Cheng, W. N. Martens, R. L. Frost, *Appl. Spectroscopy* 2011, **65**, 113-118.
41. S. Kim, S. B. Kim, H. C. Choi, *Bull. Korean Chem. Soc.* 2012, **33**, 194-198.
42. F. V. Motta, R. C. Lima, A. P. A. Marques, M. S. Li, E. R. Leite, J. A. Varela, E. Longo, *J. Alloy Compounds*, 2010, **497**, L25-28.
43. Z. Li, Z. Xie, Y. Zhang, L. Wu, X. Wang, X. Fu, *J. Phys. Chem. C*, 2007, **49**, 18348-18352.