Urea-based hydrothermal synthesis of ITO nanopowders

X Li and G M Kale

Institute for Materials Research, The University of Leeds, Leeds, LS2 9JT, UK

Abstract. Nanosized tin-doped indium oxide (ITO) powders were prepared by hydrothermally treating either the coprecipitated hydroxides of tin and indium gels with the addition of a small amount of urea or the solution of indium and tin aqueous salts in presence of urea at 240°C for about two days followed by calcination at 600°C for one hour. The effect of urea in the two different processing routes on the crystal structure and morphology of the ITO nanopowders has been investigated. Weakly-aggregated nanosized ITO powders with the uniform spherical morphology were obtained by the calcination of the hydrothermally treated coprecipitated indium and tin gels with 10 wt.% urea. However, by directly using urea as an alkaline solution during the hydrothermal treatment, the obtained ITO powders exhibit a composite morphology consisting of spheres and rods. Both of the processing routes yield a two-phase mixture consisting of rhombohedral and cubic forms of ITO.

1. Introduction

Utilizing urea in hydrothermal conditions to provide the hydroxyl anion (OH\(^-\)) in the aqueous solution to prepare the monodispersed metal oxide nanoparticles has been the subject of several recent investigations [1-7]. In hydrothermal conditions, the OH ions are released into the aqueous medium by the decomposition of urea according to the chemical reaction:

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\text{NH}_2\text{(CO)NH}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4\cdot\text{OH} + \text{CO}_2
\]

Therefore, the cation containing gel when treated hydrothermally in presence of urea can cause in-situ crystallization, leading to the production of loosely-aggregated nanocrystalline metal oxide with controlled morphologies. This method has been successfully used to prepare monodispersed metal oxide nanoparticles of stabilized zirconia [1-3], cerium (IV) oxide [4], \(\text{ZrGeO}_4\) [5], \(\text{Ce}_{1-x}\text{Zr}_x\text{O}_2\) [6], and rod-like \(\beta\)-FeO(OH) [7].

Among the various methods that can be employed for the synthesis of nanosized tin-doped indium oxide (ITO) commonly used in optical devices and chemical gas sensors, the hydrothermal method has shown a promising way for the preparation of well dispersed nanosized ITO powders. Udawatte and co-workers [8-10] reported that the substitutional vacancy type solid solution of the spherical nanosized ITO particles could be obtained from the hydrothermally-treated coprecipitated gels using aqueous ammonia as the mineralizer and subsequently calcining the treated precipitates at temperatures lower than 700°C. Similar results have been obtained by Yu et al [11] although the hydrolysis of indium and tin was separately conducted using ethylenediamine as the mineralizer. It is interesting to note that the crystal structure of ITO synthesized by Yu et al [11] has been claimed to be the most stable corundum phase, although the obtained XRD pattern is almost same as that observed by Udawatte and co-workers [8-10]. Moreover, the ITO nanowires and nanorods with corundum structure were also obtained by Yu et al [12] using ether under hydrothermal conditions. Nevertheless, Xu et al [13] recently demonstrated that using strong alkali such as sodium hydroxide as the mineralizer, the hydrothermally treated ITO nanoparticles yielded the stable bixbyite (cubic) phase. Hence, it is clear...
that under hydrothermal conditions there is a significant influence of mineralizer on the crystal structure and morphology of the ITO nanoparticles.

Therefore, in this article we present the hydrothermal synthesis of ITO in presence of urea. Two different synthesis routes have been designed in order to investigate the influence of urea on the crystal structure and morphology of ITO nanopowders. With these two different synthesis routes, a spherical or rod-like morphology of ITO nanopowders has been obtained. To the best of our knowledge, there is no report available in the literature describing the influence of urea on the structure and formation of ITO nanopowders prepared by hydrothermal process.

2. Experiments
Two routes have been designed to synthesise nanocrystalline ITO powders by using urea as the mineralizer under hydrothermal conditions. In route 1, the precipitates of indium and tin hydroxide (Sn:In=8:92) were obtained from the aqueous solutions of indium and tin salts at pH~9.0 by gradually adding ammonia solution and washed with distilled water for several times to eliminate the anionic species such as NO$_3^-$ and Cl$^-$. The precipitate was mixed with distilled water containing 10wt. % urea and the solution was made up to the total volume of ~120ml. The mixture was vigorously stirred for ~2 hours at room temperature and then the suspension was transferred into a Teflon liner (~170ml), sealed and securely placed in an outer pressure vessel made of stainless steel. The suspension was hydrothermally treated at 240°C for ~48 hours. After hydrothermal treatment, the obtained powders were centrifuged, washed and then calcined at 600°C for 1 hour to obtain the fine powders of ITO. The obtained powder sample was labelled as 8ITOU1. More details of the synthesis procedure are reported elsewhere by Kale and co-workers [14]. On the other hand, route 2 was designed for direct hydrothermal treatment of the mixture of the metal salt solution with urea. The mixed metal salt aqueous solutions (Sn:In=8:92) were prepared and urea was added to this solution. The molar ratio of In$^{3+}$ to urea in the solution was maintained at 1:3 and the solution was stirred vigorously for ~30 minutes. The initial pH of the solution was 0.5 which was carefully adjusted to ~1.5 by adding ammonia. The mixture was subsequently hydrothermally treated for 48 hours at 240°C as described earlier. The obtained suspension was centrifuged, washed and then calcined at 600°C for one hour to obtain the ITO nanopowders. The obtained powder sample was denoted as 8ITOU2. The phase constitution of as-synthesized ITO powders was analyzed by X-ray diffraction (XRD: Philips APD 1700) using CuK$\alpha$ radiation. Philips TEM (CM200) was employed to characterize the microstructure of the obtained ITO powders. The concentration of tin in the solid solution was analyzed by the atomic absorption spectroscopy (Varian instrument).

3. Results and discussion
XRD pattern of the ITO powders (8ITOU1) synthesized through route 1 is shown in figure 1(a). It can be seen in figure 1(a) that the as-synthesized ITO crystallized into two-coexisting phases that could be indexed as cubic and rhombohedral In$_2$O$_3$ according to JCPDS no. 6-416 and no. 22-336, respectively. By deconvoluting the overlapped peaks as shown in the figure 1(a), the volume fraction of the cubic phase and the rhombohedral phase of ITO was estimated to be approximately 39 vol.% and 61 vol.% respectively by using the integrated area ratio of the peaks corresponding to (222) and (110). This result is similar to that observed by Kim et al [15] who obtained the ITO powders by calcination of the freshly co-precipitated gels. When freshly co-precipitated gels were aged for 48h prior to calcination by Kim et al [15], the resulting powders were cubic. However, in the present study, we obtained a mixture of cubic and rhombohedral forms of ITO even after aging the hydrothermally treated gels for ~30 days. This suggests that the rhombohedral to cubic phase transformation during the aging process have been possibly suppressed by the hydrothermal treatment in presence of urea. The elemental concentration of the Sn in the ITO nanopowder has been analyzed to be 5 wt.% by the Atomic Absorption Spectroscopy, which is equivalent to 6.3 wt.% tin dioxide by converting elemental Sn to SnO$_2$.

The TEM micrograph of as-synthesized ITO nanoparticles shown in figure 1(b) suggests that the ITO particles are uniformly spherical in shape with a crystallite size ranging between ~30-60nm and are also weakly aggregated. It was ensured that the hydrolysis of the indium and tin metal ions was
complete during the co-precipitation process by adding ammonia until the pH was about 9.0. Consequently, during the subsequent hydrothermal treatment, the decomposition of urea according to the reaction (1) is likely to provide the supersaturated alkaline environment for the dissolution-precipitation process [1, 4]. This is in line with the increase in pH of the solution from ~5.0 at the beginning to ~9.0 at the end. Therefore, the combination of co-precipitation and subsequent hydrothermal treatment in presence of urea could possibly separate the particle nucleation and growth processes which could result into the production of monodispersed ITO nanoparticles [16].

Figure 1. (a) XRD pattern and (b) TEM image of as-synthesized ITO (8ITOU1) by route 1.

Further investigation on the influence of urea on the morphology of ITO has been conducted by directly using urea as the alkaline source during the hydrothermal process (i.e. route 2). The XRD pattern of the synthesized ITO powders (8ITOU2) by route 2 is shown in figure 2(a). It could be observed clearly from figure 2(a) that the pattern is almost same as that of 8ITOU1 prepared through route 1 exhibiting the coexistence of cubic and rhombohedral ITO. The volume fraction of the cubic phase and rhombohedral phase was estimated to be 15 vol.% and 85 vol.%, respectively. The volume fraction of the metastable rhombohedral phase in the composite was found to increase relative to that of the sample synthesized by the route 1. However, the morphology of 8ITOU2 indicated significant difference compared to that of 8ITOU1. It could be seen from figure 2(b) that there are two different morphologies: rod-like and spherical particles coexisting in sample 8ITOU2. The diameter of the spherical particle is ~25 nm. The rod-like particles are ~200nm in length and ~50nm in width. In figure 2(b), it appears that the spherical ITO particles are probably nucleating on the rod-like particles. Clearly, the results suggest that the urea as a mineralizer play a key role in determining the morphological changes. Especially, during the second process route, i.e. route 2, urea could in situ decompose according to reaction (1) rapidly as the temperature increases. The OH produced as a result of reaction (1) could be consumed rapidly to precipitate the indium and tin ions in the solution which would lead to the decrease in the basicity of the solution. Consequently, on one hand, the
nucleation and nuclei growth would occur almost at the same time and a typical phenomenon of Oswald ripening [17] could take place which results into the non-uniformly distributed particle size of the obtained powders. On the other hand, due to various anions such as Cl\(^-\), NO\(_3\)^- and CO\(_3\)^2- still existing in the system most of which, however, would have been removed during the route 1 process, the mixed morphologies could possibly result from these coexisting anions [17]. Therefore, we believe that the above two factors acting in tandem could possibly be the cause of obtaining different morphologies and particle size distribution in the route 2 process.

4. Conclusions
In conclusion, the nanosized ITO powders with different morphologies but similar phase composition have been synthesized by employing urea-based hydrothermal method. The results indicated that under hydrothermal conditions, urea could be used to control the morphology as well as the crystallographic form of the synthesized ITO powders. The monodispersed ITO particles with spherical shape could be obtained by hydrothermally treating the mixture of the coprecipitated gels with urea as an additive and subsequently, calcining at 600°C for one hour. However, directly using urea as the mineralizer, the two coexisting morphologies such as rod-like and spherical shapes could be obtained. These results could be used to explore the phase- and morphology-dependent properties of ITO.

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References
[1] Zhang Y, Xu G, Yan Z, Yang Y, Liao C and Yan C 2002 J. Mater. Chem. 12 970-7
[2] Xu G, Zhang Y, Liao C and Yan C 2002 J. Am. Ceram. Soc. 85 995-7
[3] Vasylkiv O and Sakka Y 2001 J. Am. Ceram. Soc. 84 2489-94
[4] Hirano M and Kato E 1999 J. Am. Ceram. Soc. 82 786-8
[5] Hirano M and Sakaida N 2003 Chem. Mater. 15 2561-6
[6] Si R, Zhang Y W, Li S J, Lin B X and Yan C H 2004 J. Phys. Chem. B 108 12481-8
[7] Kajiyama A and Nakamura T 2000 Colloids and Surf. A 163 301–7
[8] Yanagisawa K, Udawatte C P and Nasu S 2000 J. Mater. Res. 15 1404-8
[9] Udawatte C P, Yanagisawa K and Nasu S 2000 J. Solid State Chem. 154 444-50
[10] Udawatte C P and Yanagisawa K 2001 J. Amer. Ceram. Soc, 84 251-3
[11] Yu D, Wang D, Lu J and Qian Y 2000 Inorg. Chem. Commun. 5 475-7
[12] Yu D, Wang D, Yu W and Qian Y 2003 Mater. Lett. 58 84–7
[13] Xu H, Zhu G, Zhou H, and Yu A 2005 J. Am. Ceram. Soc., 88 986-8
[14] Li X, Xiong W, and Kale G M 2005 Electrochem. and Solid-State Lett. 8 H27-H30
[15] Kim B C, Kim S M, Lee J H, and Kim J J 2002 J. Am. Ceram. Soc. 85 2083-8
[16] Muramatsu A 2003 Liquid-phase process Morphology Control of Materials and Nanoparticle (Advanced Materials Processing and Characterization) ed Y Waseda and A Muramatsu (London: Springer) chapter2 pp 25-60
[17] Ring T A 1996 Fundamentals of Ceramic Powder Processing and Synthesis (London: Academic Press) chapter6 pp 208-20