LETTER www.rsc.org/njc | New Journal of Chemistry

Controlled preparation of In_2O_3, InOOH and $In(OH)_3$ *via* a one-pot aqueous solvothermal route†

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Received (in Montpellier, France) 3rd June 2008, Accepted 31st July 2008
First published as an Advance Article on the web 12th August 2008
DOI: 10.1039/b809313j

Pure cubic In_2O_3, orthorhombic InOOH and cubic $In(OH)_3$ nanocrystals were separately synthesized *via* a one-pot aqueous solvothermal route at low temperature by simply regulating the amount of water in the ternary system H_2O–DMF–$In(NO_3)_3\cdot 4.5H_2O$.

Indium hydroxide ($In(OH)_3$), oxyhydroxide (InOOH) and oxide (In_2O_3), which have optical band gap energies (E_g) of 5.15, 3.50 and 3.67 eV, respectively,[1–3] are important n-type semiconductor materials, and have been widely applied in many fields. Nanostructural $In(OH)_3$ and InOOH have shown superior photocatalytic behavior to TiO_2 for the degradation of aromatic hydrocarbons under UV irradiation.[4–6] In_2O_3 has applications in many areas, including catalysis,[7] photocatalysis,[8] sensors[9,10] and solar cells.[11] The structure-, morphology- and size-controlled preparation of these indium-based materials are very important to their various applications. Numerous methods, such as CVD,[12] sonohydrolysis,[1] or hydrothermal routes,[2,13] *etc.*, have been developed for their preparation. $In(OH)_3$ can be easily and directly synthesized by hydrolysis and hydrothermal routes, InOOH is usually derived from the decomposition of $In(OH)_3$ at high temperature, and In_2O_3 is only obtainable through the calcination of $In(OH)_3$ or InOOH.[14,15] Whether In_2O_3 and InOOH nanocrystals of a desired structure and morphology can be directly synthesized from a simple system at low temperature is still under research, although there have been some reports of their direct synthesis.[16,17] A study of the detailed mechanism of formation is still in progress. Herein, we report a one-pot controllable synthesis of In_2O_3, InOOH and $In(OH)_3$ nanocrystals by an aqueous solvothermal route. The reaction temperature is as low as 150 °C, and a simple reaction system containing only indium nitrate and a binary solution of water and *N*,*N*-dimethylformamide (DMF) are confirmed as being feasible for achieving In_2O_3, InOOH and $In(OH)_3$ nanocrystals. By tuning the amount of water, the composition of the products can be manipulated from In_2O_3 to InOOH, and then to $In(OH)_3$, along with a spontaneous variation in their size and morphology.

The crystal phases of the products were characterized by XRD. As shown in Fig. 1, the XRD patterns of the as-synthesized samples vary greatly, depending on the amount of water in the reaction solution. When no water was added, the products could be easily indexed as the pure cubic structure of In_2O_3 (JCPDS no. 76-0152) (Fig. 1(a)). When the volume fraction of water was increased from 2.9 to 8.8%, the resulting solids could be clearly indexed to pure orthorhombic InOOH (JCPDS no. 71-2283) (Fig. 1(b) and (c)). Interestingly, when the volume fraction of water was increased to 20.6%, the products were a mixture of two crystal phases: orthorhombic InOOH and cubic $In(OH)_3$, with characteristic diffraction peaks at $2\theta = 22.3$ and 31.7° (JCPDS no. 76-1463) (Fig. 1(d)). When the dosage of water was set to higher than 32.4%, the resulting solids were pure cubic $In(OH)_3$ (Fig. 1(e)), and its diffraction peaks were enhanced by further increasing the water content. When water was used as the sole reaction medium (*i.e.* no DMF), a highly pure phase of $In(OH)_3$ was formed (Fig. S1 in the ESI†). The water-dependent formation of the different indium compounds was also testified by Raman characterization of the resulting samples (Fig. S2 in the ESI†).

The additive water in the reaction system not only influenced the phase of the products, but also had an effect on their morphology. A further investigation on the morphology of the obtained products by TEM is given in Fig. 2. No

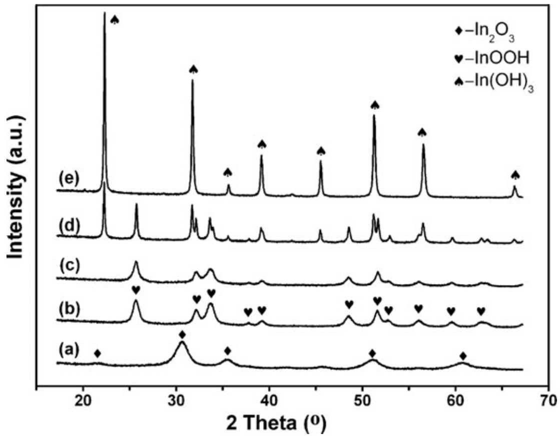

Fig. 1 XRD patterns of the products synthesized as a function of the volume fraction of water in the H_2O–DMF solution: (a) 0, (b) 2.9, (c) 8.8, (d) 20.6 and (e) 32.4%. The total volume of the solution was 17 mL.

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† Electronic supplementary information (ESI) available: XRD pattern of $In(OH)_3$, Raman spectra, HRTEM and SAED of the as-synthesized products. See DOI: 10.1039/b809313j

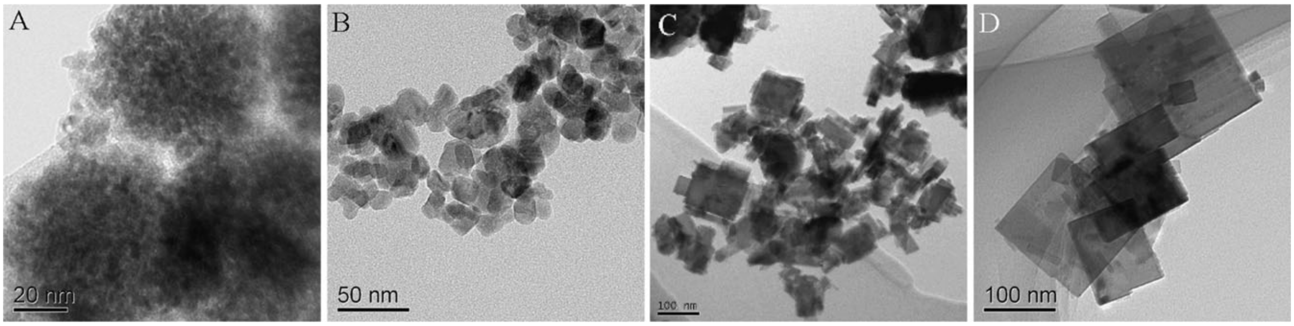

Fig. 2 TEM images of the products synthesized as a function of the volume fraction of water in the H_2O–DMF solution: (a) 0, (b) 8.8, (c) 17.6 and (d) 32.4%.

addition of water to the reaction solution led to the formation of flower-like agglomerates with a coarse surface and a diameter of 60–75 nm (Fig. 2A). Clearly, the individual flower-like agglomerates are composed of smaller nanoparticles, with sizes ranging from 4–8 nm (Fig. S3-A1 in the ESI†). The HRTEM image (Fig. S3-A2 in the ESI†) of part of one nanoparticle of these flower-like agglomerates shows several lattice planes of perfect crystallinity. The lattice plane spacing of (400) is 0.253 nm. The electron diffraction pattern (SAED) of the flower-like agglomerates is consistent with cubic In_2O_3, with strong ring patterns due to (222), (400), (440) and (622) planes, respectively (Fig. S3-A3 in the ESI†). If the volume fraction of water was 8.8%, closely monodispersed and irregular small nanoparticles with an average diameter of 20 nm were obtained (Fig. 2B). The HRTEM image of a part of one particle indicates the expected lattice fringes, with an interplanar spacing of 0.34 nm that corresponds to the (110) plane of InOOH (Fig. S3-B1 in the ESI†). The SAED patterns of a number of particles coincide well with orthorhombic InOOH (Fig. S3-B2 in the ESI†). As the dosage of water was increased to 17.6%, many square nanoflakes, with an average length of about 150 nm, were obtained (Fig. 2C). Furthermore, it was also clearly seen that some small irregular particles were attached to the edges of the nanoflakes. The nanoflake morphology became more perfect if 32.4% dosage water was added (Fig. 2D). The typical SAED pattern indicates the crystalline nature of the bcc $In(OH)_3$ (Fig. S3-C in the ESI†).

Enlightened by the above XRD and TEM results, cubic In_2O_3, orthorhombic InOOH and cubic $In(OH)_3$ nanocrystals could be selectively synthesized from a solvothermal system containing $In(NO_3)_3$, DMF and water by adjusting the dosage of water and DMF. As shown in Fig. 3, In_2O_3 was obtained when only DMF was used as the medium, $In(OH)_3$ was formed in the case of a high water dosage or with pure water, while InOOH, and a mixture of InOOH and $In(OH)_3$, were produced with a low water dosage.

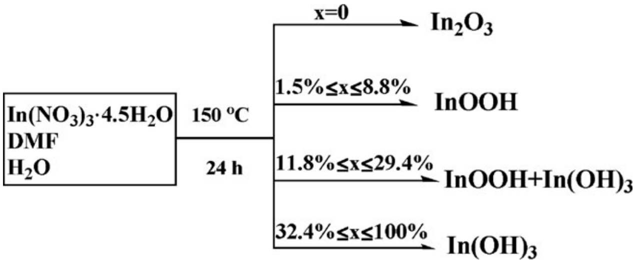

Fig. 3 Scheme of the synthetic paths for the synthesis of the various products under different conditions (x denotes the volume fraction of water in the H_2O–DMF solution).

In order to understand the effect of water and DMF on the final products, several additional experiments were performed.

The first one used anhydrous $In(NO_3)_3$ (analytical grade, further dehydrated under evacuation at 100 °C) as the starting material, while keeping the other reaction conditions constant. As shown in Fig. 4, pure In_2O_3, InOOH and $In(OH)_3$ were obtained by no adding water, adding a low amount of water (from 1.5 to 11.8%) and adding more than 29.4% water, respectively. In combination with the foregoing results, the final product seems to be dependent on the total content of water rather than the indium source. The second experiment was carried out by using anhydrous $In(NO_3)_3$ and purified DMF (distillation over 4A molecular sieves) as the indium source and medium, respectively. The obtained product was confirmed to be In_2O_3 by XRD characterization. In this condition, since no other agents were added to the starting solution, it seems that the DMF solvent was working as a reagent for the synthesis of In_2O_3. However, DMF often contains a trace amount of water, even after treatment by re-distillation,[18] and as the solvent in the synthesis of In_2O_3, it is in great excess with respect to $In(NO_3)_3$. Therefore, it is difficult to identify whether the formation of In_2O_3 is a result of a direct reaction between $In(NO_3)_3$ and DMF or a

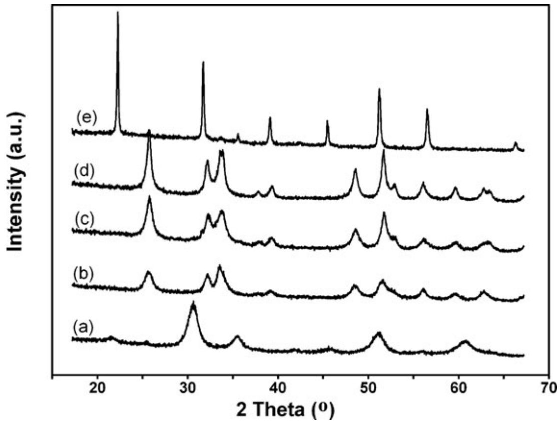

Fig. 4 XRD patterns of the products synthesized using anhydrous $In(NO_3)_3$ as the starting material as a function of the volume fraction of water: (a) 0, (b) 1.5, (c) 8.8, (d) 11.8 and (e) 29.4%.

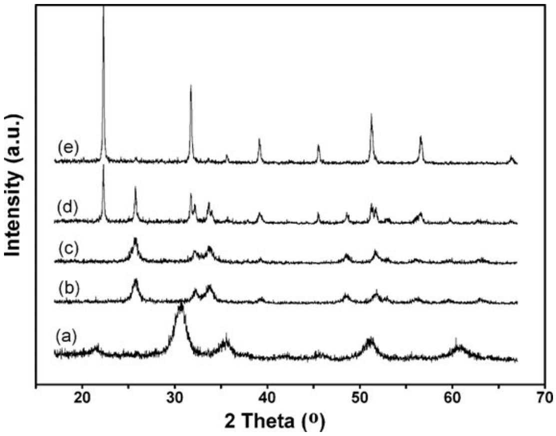

Fig. 5 XRD patterns of the products synthesized as a function of the volume fraction of water in the H_2O–en solution: (a) 0, (b) 2.9, (c) 8.8, (d) 20.6 and (e) 32.4%. The total volume of the solution is 17 mL.

hydrolysation process of $In(NO_3)_3$ by impurity water in the DMF. A clear understanding of the mechanism requires a quantitative analysis of the reaction products; work which is now in progress. Stoichiometrically, the hydrolysation of 1 mol of indium ion to $In(OH)_3$, InOOH and In_2O_3 requires 3, 2 and 1.5 mol of water, respectively, in agreement with the phase variation of the products with decreasing water content. However, it has been deduced that the formation of In_2O_3 may also be due to the participation of water. The third control experiment was performed with another solvent, ethylenediamine (en), instead of DMF. Pure phases of In_2O_3, InOOH and $In(OH)_3$ were also obtained in the en–H_2O–$In(NO_3)_3\cdot 4.5H_2O$ ternary system (Fig. 5). This result could be indirect evidence that proves that the presence of water, rather than DMF, is pivotal for the formation of In_2O_3.

It is well known that DMF is a polar aprotic solvent, with applications as a solvent in the synthesis of transition-metal oxide (Cu_2O, α-Fe_2O_3) nanocrystals having been reported.[19,20] Based on our experimental results and the literature, a possible mechanism for the formation of In_2O_3 is suggested by equations (1) and (2) in Scheme 1. Firstly, under solvothermal conditions, $NH(CH_3)_2$ forms from the hydrolysis of DMF (water molecules from $In(NO_3)_3\cdot 4.5H_2O$ or DMF water impurity). Next, the intermediate product, $NH(CH_3)_2$, reacts with indium ions and water to form In_2O_3 nanoparticles. The resulting solution after the reaction was indeed found to have a stronger odour of amines and contain a small amount of formic acid (determined by GC and NMR). A water–DMF mixture is also an appropriate medium for the smooth hydrolysis of different metal ions.[21] In mixed solution with a high water–DMF ratio, the direct hydrolysation of In^{3+} ions to $In(OH)_3$ could be dominant (Scheme 1, eqn (3)) under solvothermal conditions.[13] However, in the case of lower water contents, the $In(OH)_3$ could be dehydrolysed to InOOH as soon as it formed (Scheme 1, eqn (4)).[14,17] Unlike strongly basic solvents (such as ammonia and ethylenediamine), which rapidly react with In^{3+} in an uncontrollable manner, or neutral solvents (such as water), which result in the incomplete hydrolysis of In^{3+}, DMF provides specific basic conditions for the hydrolysis of In^{3+} in a controllable manner.

$$HCON(CH_3)_2 + H_2O \longrightarrow HCOOH + NH(CH_3)_2 \quad (1)$$

$$2In^{3+} + 3H_2O + 6NH(CH_3)_2 \longrightarrow In_2O_3 + 6NH_2(CH_3)_2^{+} \quad (2)$$

$$In^{3+} + 3H_2O \xrightarrow{DMF} In(OH)_3 + 3H^{+} \quad (3)$$

$$In(OH)_3 \longrightarrow InOOH + H_2O \quad (4)$$

Scheme 1 The possible formation mechanisms of In_2O_3, InOOH and $In(OH)_3$.

In summary, we have presented a convenient, one-pot route to In_2O_3, InOOH and $In(OH)_3$ nanocrystals under aqueous solvothermal conditions. The major advantages of this route are that (i) indium hydroxides, oxyhydroxides and oxides can be selectively synthesized by a simple route, (ii) a reaction system containing common materials and inexpensive solvents can be used and (iii) there is no need to use alkalis.

Financial support for this work from the National Natural Science Foundation of China (grant nos. 20673020, 20573020 and 20537010) and the National Basic Research Program of China (973 Program, no. 2007CB613306) is gratefully acknowledged.

Experimental

In a typical synthesis, 0.6 mmol of $In(NO_3)_3\cdot 4.5H_2O$ and the desired amount of distilled water (0–17 mL) were added to a 25 mL autoclave. DMF was then added to bring the total volume up to 17 mL. After the solution had been heated at 150 °C for 24 h, the precipitate was separated by centrifugation, washed with de-ionized water and ethanol, and finally dried at 60 °C for 10 h. X-Ray diffraction (XRD) analyses of samples were performed on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation. Raman spectra were recorded at ambient temperature on a Perkin-Elmer Spectrum 2000 R NIR FT-Raman spectrometer with a Nd/YAG laser and a InGaAs detector. Transmission electron microscopy (TEM) images were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV.

References

1 S. Avivi, Y. Mastai and A. Gedanken, *Chem. Mater.*, 2002, **12**, 1229.
2 H. L. Zhu, K. H. Yao, H. Zhang and D. R. Yang, *J. Phys. Chem. B*, 2005, **109**, 20676.
3 S. J. Wen, G. Campet, J. Portier, G. Couturier and J. B. Goodenough, *Mater. Sci. Eng., B*, 1992, **14**, 115.
4 Z. H. Li, Z. P. Xie, Y. F. Zhang, L. Wu, X. X. Wang and X. Z. Fu, *J. Phys. Chem. C*, 2007, **111**, 18348.
5 T. J. Yan, J. L. Long, Y. S. Chen, X. X. Wang, D. Z. Li and X. Z. Fu, *C. R. Chim.*, 2008, **11**, 101.
6 T. J. Yan, X. X. Wang, J. L. Long, P. Liu, X. L. Fu, G. Y. Zhang and X. Z. Fu, *J. Colloid Interface Sci.*, 2008, DOI: 10.1016/j.jcis.2008.05.065.
7 D. F. Wang, Z. G. Zou and J. H. Ye, *Chem. Mater.*, 2005, **17**, 3255.
8 K. R. Reyes-Gil, E. A. Reyes-Garcia and D. Raftery, *J. Phys. Chem. C*, 2007, **111**, 14579.
9 N. Pinna, G. Neri, M. Antonietti and M. Niederberger, *Angew. Chem., Int. Ed.*, 2004, **43**, 4345.
10 G. Neri, A. Bonavita, G. Micali, G. Rizzo, S. Galvagno, M. Niederberger and N. Pinna, *Chem. Commun.*, 2005, 6032.
11 R. Katoh, A. Furube, T. Yoshihara, K. Hara, G. Fujihashi, S. Takano, S. Murata, H. Arakawa and M. Tachiya, *J. Phys. Chem. B*, 2004, **108**, 4818.

12 C. H. Liang, G. W. Meng, Y. Lei, F. Phillipp and L. D. Zhang, *Adv. Mater.*, 2001, **13**, 1330.

13 Q. Tang, W. J. Zhou, W. Zhang, S. M. Ou, K. Jiang, W. C. Yu and Y. T. Qian, *Cryst. Growth Des.*, 2005, **5**, 147.

14 D. B. Yu, S. H. Yu, S. Y. Zhang, J. Zuo, D. B. Wang and Y. T. Qian, *Adv. Funct. Mater.*, 2003, **13**, 497.

15 R. Roy and M. W. Shafer, *J. Phys. Chem.*, 1954, **58**, 372.

16 Z. B. Zhuang, Q. Peng, J. F. Liu, X. Wang and Y. D. Li, *Inorg. Chem.*, 2007, **46**, 5179.

17 C. L. Chen, D. R. Chen, X. L. Jiao and C. Q. Wang, *Chem. Commun.*, 2006, 4632.

18 D. R. Burfield and R. H. Smithers, *J. Org. Chem.*, 1978, **43**, 3966.

19 Y. Chang, J. J. Teo and H. C. Zeng, *Langmuir*, 2005, **21**, 1074.

20 Y. H. Zheng, Y. Cheng, Y. S. Wang, F. Bao, L. H. Zhou, X. F. Wei, Y. Y. Zhang and Q. Zheng, *J. Phys. Chem. B*, 2006, **110**, 3093.

21 G. Rodríguez, P. Santiago-Jacinto, L. Rendon-Vázquez, J. Németh, I. Dékany and D. Díaz, *J. Phys. Chem. B*, 2003, **107**, 12597.