

Synthesis of corundum-type In_2O_3 nanocrystals via hydro/solvothermal route and their photocatalytic properties

Guodong Liu*, Weidong Wu, Chengcheng Li, Xinjin Shi, KeKe Gao, Min Li, Yuan Tian

Department of Chemistry and Chemical Engineering, Jining University, Jining 273155, China

*Corresponding author e-mail: liugd615@163.com

Abstract. The understanding of the polymorphism of In_2O_3 has evoked recent interest in terms of fundamental scientific and technological aspects. A simple yet effective hydro/solvothermal route was introduced for the preparation of In_2O_3 nanocrystals with different phases using $\text{In}(\text{acac})_3$ as indium source. Through adjusting the systemic amount of water, the hydrolysis reaction of In^{3+} can be efficiently controlled. Moreover, the phases and morphologies of products can also be regulated. Meanwhile, the photocatalytic property of the prepared corundum-type In_2O_3 was also measured, which showed superior photocatalytic performance on the decomposition of phenol compared to that of cubic phase In_2O_3 nanocubes.

1. Introduction

Until now, nanoscale metal oxides have received great attention in a myriad of research fields such as chemical sensors, photonic devices, drug delivery carriers, field emission displays, photocatalyst, and lithium-ion batteries, owing to their unique morphologies and physicochemical properties which are different from their bulk counterparts.^[1-3] As one of the most important part of new research area of functional materials, metastable materials, physical and chemical properties being different from their stable phase, are becoming ever more essential to resolve new problems.^[4, 5]

As a key n-type III-VI semiconductor, Indium oxide (In_2O_3), has attracted considerable attention because of the peculiar electronic and optical properties and increasingly extensive applications in solar cells, sensors, electrocatalyst and nanoscale transistors etc.^[6, 7] Normally, In_2O_3 prefers to crystallize in the form of cubic structure (C- In_2O_3), whereas metastable corundum-type In_2O_3 (H- In_2O_3) was obtained by the phase transition method under high temperature and high pressure (HTHP) conditions.^[3] The understanding of the polymorphism of In_2O_3 has evoked recent interest both due to fundamental scientific and technological aspects.^[8]

Here, we aimed at exploring a novel low-temperature hydrothermal & solvothermal methods to synthesize metastable phases of functional materials, and studying the formation mechanism of the metastable phases under the hydrothermal & solvothermal conditions. Among so many solution synthesis routes reported, the calcination of corresponding hydrolysis precursors (such as $\text{In}(\text{OH})_3$ and InOOH) is necessary, which can be concluded that the amount of H_2O and hydrolyzation of In^{3+} play a crucial role in the process. So far, the influences of reactional precursors, temperature, and time, surfactants on morphologies, sizes, as well as phases of products have been deeply researched. In our



previous work, the influence of H₂O in solution system was reported.^[9] As a polar solvent, H₂O plays several roles in hydro/solvothermal process, which can be summarized: (i) As solvent: Reaction substances dissolved and temperature and pressure transferred medium. (ii) As reaction substance: take part in the hydrolysis reaction to form oxide or hydroxide. (iii) Influence the number of hydroxyl on the surface of obtained nanocrystals, and further affect the ir aggregation. Hence, How to use the adjustment of systemic H₂O to control solution-phase synthesis nanomaterials has an important research value. Now we use indium acetylacetonates (In(acac)₃) to synthesis InOOH, the precursor of H-In₂O₃. In previous reports, In(acac)₃ was frequently used as a precursor to prepare In₂O₃ through a solvothermal process, and C-In₂O₃ rather than H-In₂O₃ was obtained.^[10, 11] Herein, a simple hydro/solvothermal route to the In₂O₃ nanocrystals with different phase by using In(acac)₃ as indium source was introduced. Through adjusting the systemic amount of water, the In³⁺ hydrolysis reaction can be controlled. Of course, the phases and morphologies of products also can be controlled. Furthermore, the photocatalytic property of the prepared H-In₂O₃ was also studied, which shows superior photocatalytic performance on the decomposition of phenol compared to the prepared C-In₂O₃ nanocuboids.

2. Experiments

2.1 Synthesis

In a typical synthesis, 0.206 g (0.5 mmol) of In(acac)₃ was added to 20.00 mL of ethanol. The reaction mixture was transferred into a 30 mL inner volume stainless autoclave with Teflon liner, and different amount of water was injected into the reaction system before solvothermal reaction. The reaction was maintained at 200 °C for 24 h in a furnace. The resulting products were centrifuged, and washed with ethanol for several times, and subsequently being dried in air at 60 °C. The as-prepared InOOH nanocrystals were calcined in a boat crucible at a temperature of 500 °C and maintained for 2 h in air with rate temperature of 5 °C min⁻¹.

2.2 Characterization.

X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (Rigaku D/Max 2200PC) with a graphite monochromator and CuK α radiation ($\lambda=0.15148$ nm) in the range of 10-80° at room temperature while the voltage and electric current were held at 40 kV and 20 mA. The morphology and microstructure of the products were determined by transmission electron microscopy (TEM, JEM-100CXII) with an accelerating voltage of 80 kV and high-resolution TEM (HR-TEM, GEOL-2010) with an accelerating voltage of 200 kV.

3. Results and Discussion

Table1. Phases and Morphologies of Products obtained from different system

Volume of Mixed Solvent	H ₂ O (x mL)	Product	Morphology
20+x mL	0-50 μ L	C-In ₂ O ₃	Nanocubes
	0.05-0.10 mL	C-In ₂ O ₃	Nanoparticles
	0.50-1.50 mL	InOOH	Nanoparticles
	1.50-5.00 mL	InOOH & In(OH) ₃	Nanoparticles
	>5.00 mL	In(OH) ₃	Nanoparticles

Through adjusting the systemic amount of water, different kinds of products were obtained. (See Table 1) The XRD pattern of the sample obtained in ethanol solvothermal route, which is denoted as sample a, can be indexed to the cubic In₂O₃ (JCPDS, No. 65-3170), no other peaks can be observed, revealing its phase-pure cubic structures. The size of sample is 23 nm calculated from the Scherrer equation. Further calculation revealed that the cell parameters of the sample is 1.0142 nm, which is in

well agreement with the reported data of $a=1.0140$ nm (JCPDS, No. 65-3170). The data was collected using KCl as standard graph and the scan speed was one degree per minute. TEM images (Figure 2a) of the samples obtained from ethanol solvothermal route show that the nanocuboids are with smooth and regular quadrangle surface. FE-SEM images (Figure 3a) of sample a indicate that the In_2O_3 nanocrystals show as regular nanocubes with the size ca. 25 nm and thickness ca. 8-9 nm.

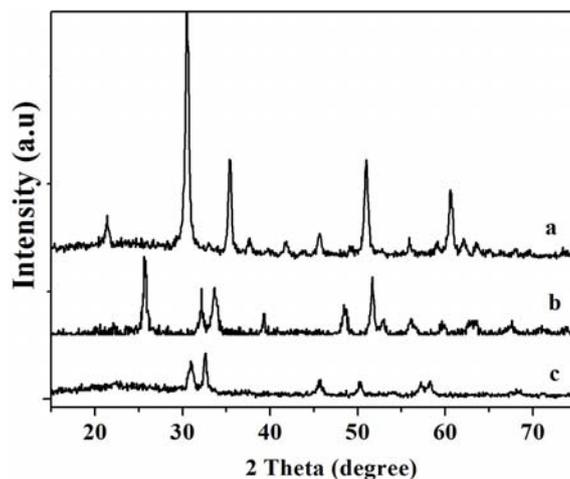


Figure 1 XRD patterns of $\text{C-In}_2\text{O}_3$ (a) InOOH (b) and its calcined product $\text{H-In}_2\text{O}_3$ (c)

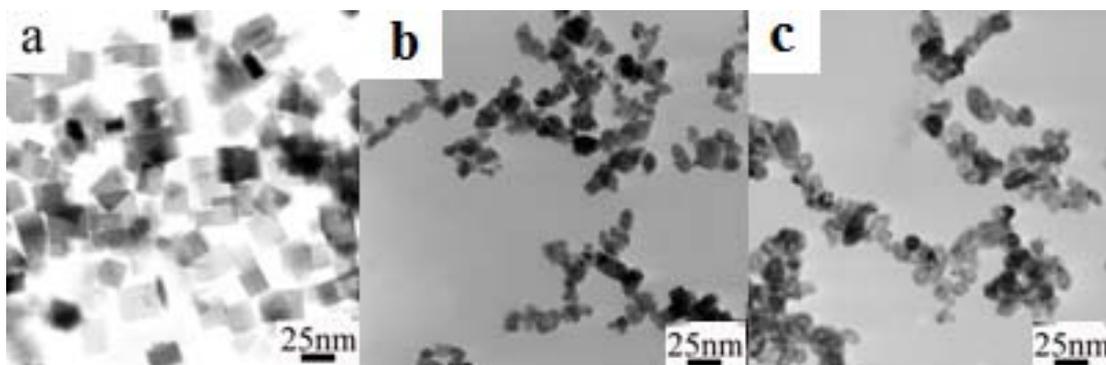


Figure 2 TEM image of $\text{C-In}_2\text{O}_3$ (a), InOOH (b) and its calcined product $\text{H-In}_2\text{O}_3$ (c)

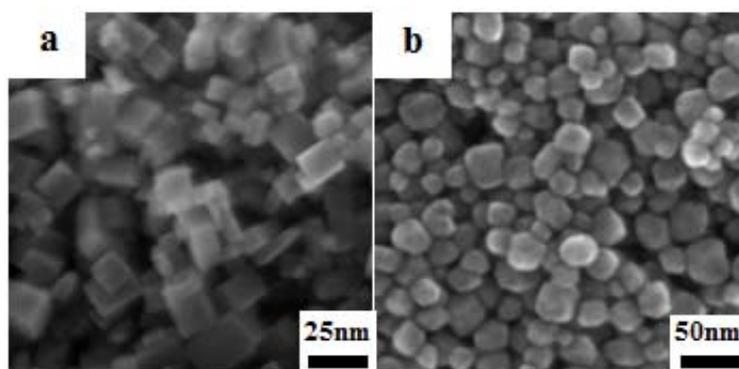


Figure 3 FE-SEM image of $\text{C-In}_2\text{O}_3$ (a) and $\text{H-In}_2\text{O}_3$ (b)

As known, the metal indium ion easily hydrolyzes to form metal hydroxide or oxide. In ethanol solvothermal reaction system, When 50 μL of H_2O water added, hydrolysis reaction between In^{3+} and H_2O were occurred to form indium hydroxide. From the XRD patterns of products obtained from different time during solvothermal procedure, we can know the generated $\text{In}(\text{OH})_3$ from hydrolysis of indium salt further dehydrated to form C- In_2O_3 nanocrystals which can be proposed as a “dissolution-recrystallization” mechanism, and the driving force is the lower solubility of the In_2O_3 compared to the $\text{In}(\text{OH})_3$ in the system. (See Figure 4) The reaction equations are as follows:

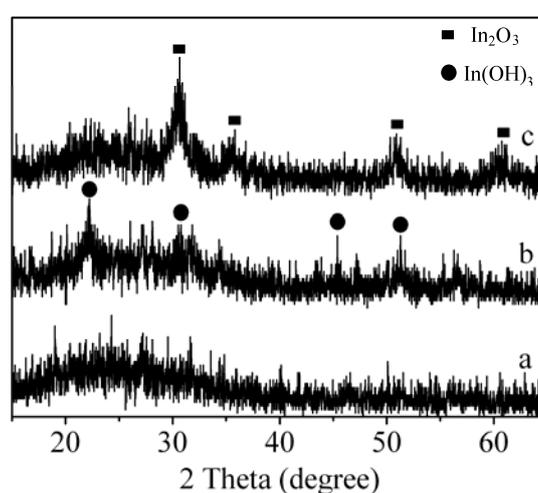
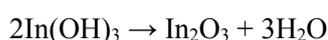
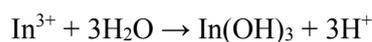
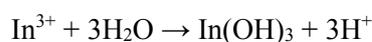
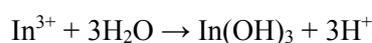


Figure 4 XRD patterns of Products obtained from different time during solvothermal procedure (When 50 μL mL H_2O water added). (a)0.5 h, (b)1.0 h, (c) 3.0 h.

When 0.50-1.50 mL water was added, InOOH nanoparticles with size about 20 nm (See Figure 1b and Figure 2b) were obtained. Because the amount of water is not enough in this system, the dehydration reaction of $\text{In}(\text{OH})_3$ is occurred. InOOH can be regarded as the result of part-hydrolysis of indium ion. The reaction equations are as follows:^[12]



After calcining the as-prepared InOOH nanocrystals in a boat crucible at a temperature of 500 $^\circ\text{C}$ and maintained for 2 h in air, phase-pure metastable In_2O_3 nanocrystals were obtained. The XRD pattern of the product (Figure 1c) was in good agreement with that of H- In_2O_3 (JCPDS, No.73-1809). All reflections show high intensity, which reveals its high crystallinity, of which size is about 20-30 nm. (See Figure 1c, Figure 2c and Figure 2b) When more water was added, the system adequately hydrolyzed and $\text{In}(\text{OH})_3$ nanoparticles were obtained. The reaction equations are as follows:



Through adjusting the systemic amount of water, the In^{3+} hydrolysis reaction can be controlled. Of course, the phases and morphologies of products also can be controlled. Herein, a simple hydro/solvothermal route to the In_2O_3 nanocrystals with different phase by using $\text{In}(\text{acac})_3$ as indium

source was introduced instead of $\text{In}(\text{NO}_3)_3$, which is not similar to our previous report.^[9] $\text{In}(\text{acac})_3$ was frequently used as a precursor to prepare In_2O_3 . As a stable indium complex, $\text{In}(\text{acac})_3$ can release indium ion slowly under hydro/solvothermal environment in our system, where hydrolysis reaction speed can be controlled.

The IR spectra of $\text{C-In}_2\text{O}_3$ and $\text{H-In}_2\text{O}_3$ were shown above (Figure 5). The IR spectrum of $\text{C-In}_2\text{O}_3$ indicated that the bands around 3400 and 1630 cm^{-1} can be ascribed to the $-\text{OH}$ vibrations of absorbed water and ethanol. The bands around 2925 , 2858 and 1416 cm^{-1} can be ascribed to the C-H vibrations of methyl and methylene. The bands around 1050 cm^{-1} can be ascribed to the C-O vibrations. The bands around 500 cm^{-1} can be ascribed to the In-O vibrations of In_2O_3 .^[13, 14] All data shown above indicated that some acetylacetonate molecular and ethanol on the surface of $\text{C-In}_2\text{O}_3$ through coordination bond. On the contrary, the IR spectrum of $\text{H-In}_2\text{O}_3$ is simple which indicated that their surface is very clean after calcining process.

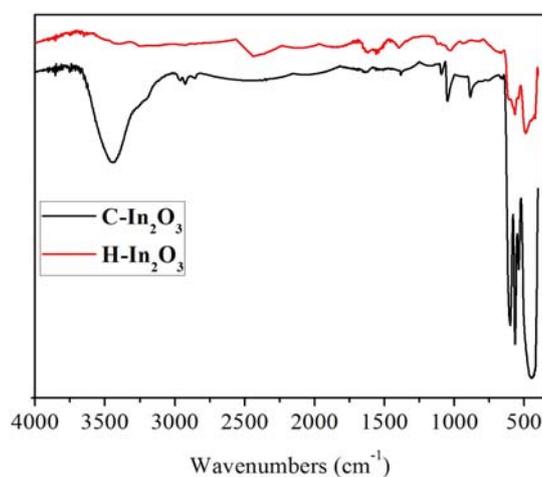


Figure 5 IR spectra of $\text{C-In}_2\text{O}_3$ and $\text{H-In}_2\text{O}_3$

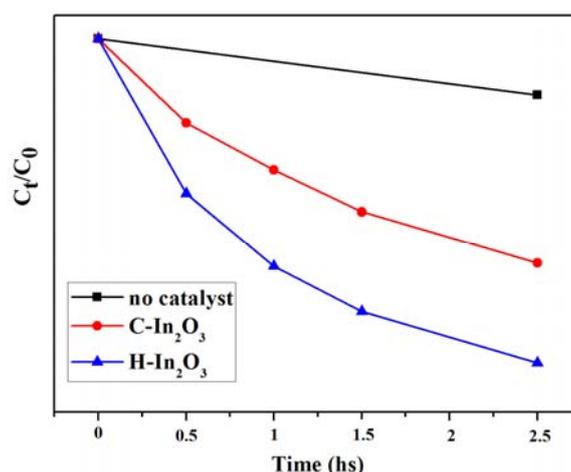


Figure 6 Photo-degradation graphs of phenol solution (1.0 mmol/L , 75.00 mL) under UV light ($300\text{--}400\text{ nm}$, 125 W).

Moreover, the photocatalytic performances of $\text{C-In}_2\text{O}_3$ and $\text{H-In}_2\text{O}_3$ nanocrystals were compared by the degradation of phenol under UV irradiation. As shown in Figure 6, the phenol hardly decomposes after irradiation with UV light for 2.5 h without catalyst. $\text{C-In}_2\text{O}_3$ exhibits a relatively poor catalytic performance with only 52% phenol decomposing, while higher catalytic activity is

obtained with H-In₂O₃ as catalyst and ca.70% of the phenol decomposes under the same conditions. The higher photocatalytic activity of H-In₂O₃ compared to that of the as-prepared C-In₂O₃ might relate to their UV absorptions. Further experiments show that as a photocatalyst, H-In₂O₃ is stable and can be repeatedly used many times. N₂ adsorption experiment gives the BET surface areas of 32 and 26 m² g⁻¹ for C-In₂O₃ and H-In₂O₃, and no adsorption of the phenol on the In₂O₃ nanoparticle's surface was detected. Then, it is proposed that the high catalytic performance of the H-In₂O₃ may relate to its high atom density of the (001) plane.^[15]

4. Conclusion

In summary, the H-In₂O₃ nanoparticles with high crystallinity have been synthesized by a simple hydro/solvothermal method. The micro-difference of the amount of water added would result in the different reaction mechanisms and form different polymorphs. Moreover, the H-In₂O₃ exhibited high photocatalytic activity for the degradation of phenol.

Acknowledgements

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