

## Electronic Supplementary Information

### Direct solution synthesis of corundum-type $\text{In}_2\text{O}_3$ : effects of precursors on products

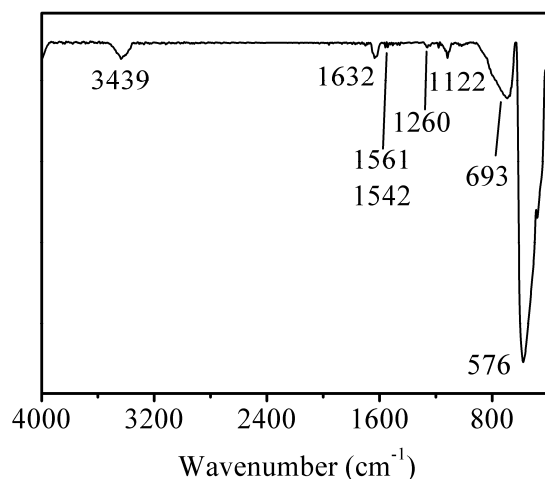
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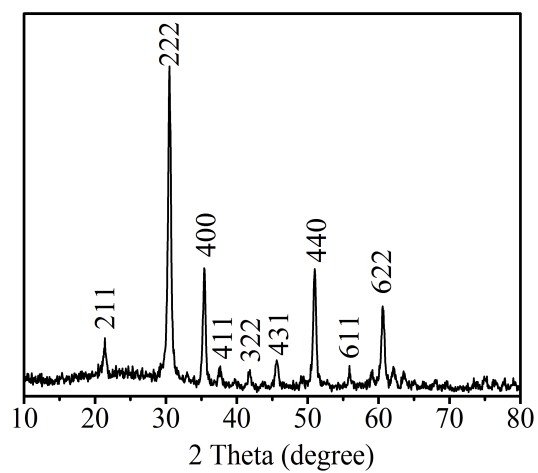
#### Preparation of $\text{In}_2\text{O}_3$ precursors.

Citric acid,  $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and acetylacetonone (Hacac) were used as reagents. All chemicals were analytical grade and were used as received without further purification. 3.73 g (10 mmol)  $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  and 2.10 g (10 mmol) citric acid were dissolved into 20.0 mL deionized water. After adjusting pH value of the solution to 9.6 through adding 1:1 aqueous ammonia, 3.0 g (30 mmol) acetylacetonone was added. Of course the white indium acetylacetonate precipitate was formed. The precipitate was collected by filtration, washed with deionized water for several times, and then dried at  $90^\circ\text{C}$  in air for 2.0 h to obtain the C- $\text{In}_2\text{O}_3$  precursor. To obtain the H- $\text{In}_2\text{O}_3$  precursor, the precipitate washed with water was dipped in the mixture of methanol and water (volume ratio 4:1) to prolong the drying time and let the methanol contact with the  $\text{In}(\text{acac})_3$  completely. Then the mixture was dried at  $90^\circ\text{C}$  in air for 2.0 h.

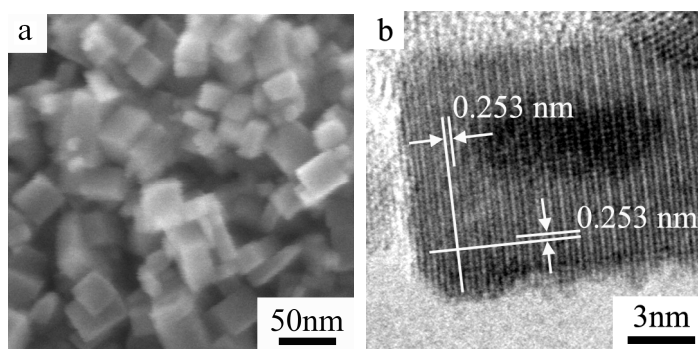
Fig. S1. IR spectrum of the as-prepared H- $\text{In}_2\text{O}_3$ .



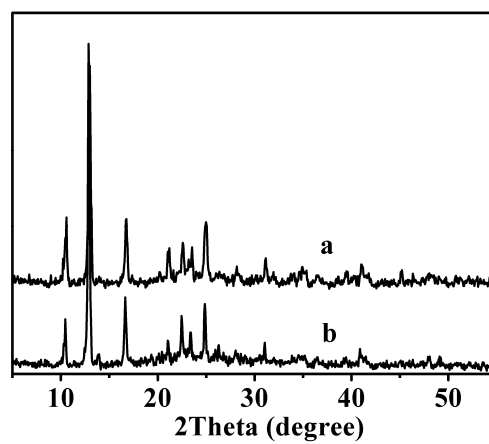
**Fig. S2.** XRD pattern of the as-prepared C-In<sub>2</sub>O<sub>3</sub>.



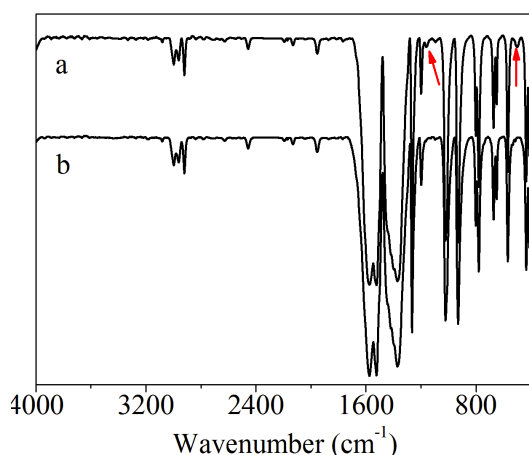
**Fig. S3.** FE-SEM (a) and HR-TEM (b) images of the as-prepared C-In<sub>2</sub>O<sub>3</sub>.



**Fig. S4.** XRD patterns of H-In<sub>2</sub>O<sub>3</sub> precursor (a) and C-In<sub>2</sub>O<sub>3</sub> precursor (b).



**Fig. S5.** FT-IR spectra of the H-In<sub>2</sub>O<sub>3</sub> precursor (a) and C-In<sub>2</sub>O<sub>3</sub> precursor (b).



The IR spectrum of C-In<sub>2</sub>O<sub>3</sub> precursor shows the bands around 2998, 2962 and 2920 cm<sup>-1</sup>, which can be ascribed to the C-H vibrations of acetylacetonate species. The strong absorptions at 1568 and 1529 cm<sup>-1</sup> should be attributed to the C=O vibrations from the acetylacetonate species. All absorption assignments of C-In<sub>2</sub>O<sub>3</sub> precursor are listed below.<sup>[S1]</sup>

Absorption /cm <sup>-1</sup>	Assignment	Features functional groups	Absorption /cm <sup>-1</sup>	Assignment	Features Functional Groups
2998	$\nu_{as}$ C-H	CH <sub>3</sub>	1022	$\rho r$ CH <sub>3</sub>	CH <sub>3</sub>
2962	$\nu_{as}$ C-H	CH			
2920	$\nu_s$ C-H				
2132	$\nu$ C=C	C=C=O	930	$\nu$ C-CH <sub>3</sub>	C-CH <sub>3</sub>
1575	$\nu$ C=O	C=O	803	$\nu$ C-CH <sub>3</sub>	C-CH <sub>3</sub>
1524	$\nu$ C=C	C=C	780	$\pi$ C-H	C-H
1445	$\delta_{as}$ C-H	CH <sub>3</sub>	673	$\nu$ C-CH <sub>3</sub>	C-CH <sub>3</sub>
1390	$\delta_s$ C-H			+ Ring deformation	+ $\pi$ ring
1372	$\delta$ C-H	CH <sub>3</sub>	649	$\nu$ C-CH <sub>3</sub>	CH <sub>3</sub>
1266	$\nu$ C-CH <sub>3</sub>	C-CH <sub>3</sub>	434	$\nu$ In-O	In-O
	+ $\nu$ C=C	C=C			
1198	$\nu$ C-H	C-H	404	Ring deformation	$\pi$ ring
	+ $\nu$ C-CH <sub>3</sub>	C-CH <sub>3</sub>			

For the C-In<sub>2</sub>O<sub>3</sub> precursor, all the IR absorptions are consistent with those of In(acac)<sub>3</sub>. However, two new absorptions around 1156 and 506 cm<sup>-1</sup> appeared on the IR spectrum of H-In<sub>2</sub>O<sub>3</sub> precursor besides those of the C-In<sub>2</sub>O<sub>3</sub> precursor. The two bands are attributed to the C-O and In<sup>3+</sup>-O vibrations of -OCH<sub>3</sub> coordinated with In(III), indicating the existence of the -OCH<sub>3</sub> groups in the H-In<sub>2</sub>O<sub>3</sub> precursor.

**Fig. S6.**  $^1\text{H}$  NMR (DMSO as solvent) spectra of H- $\text{In}_2\text{O}_3$  precursor (a) and C- $\text{In}_2\text{O}_3$  precursor (b).<sup>[S2]</sup>

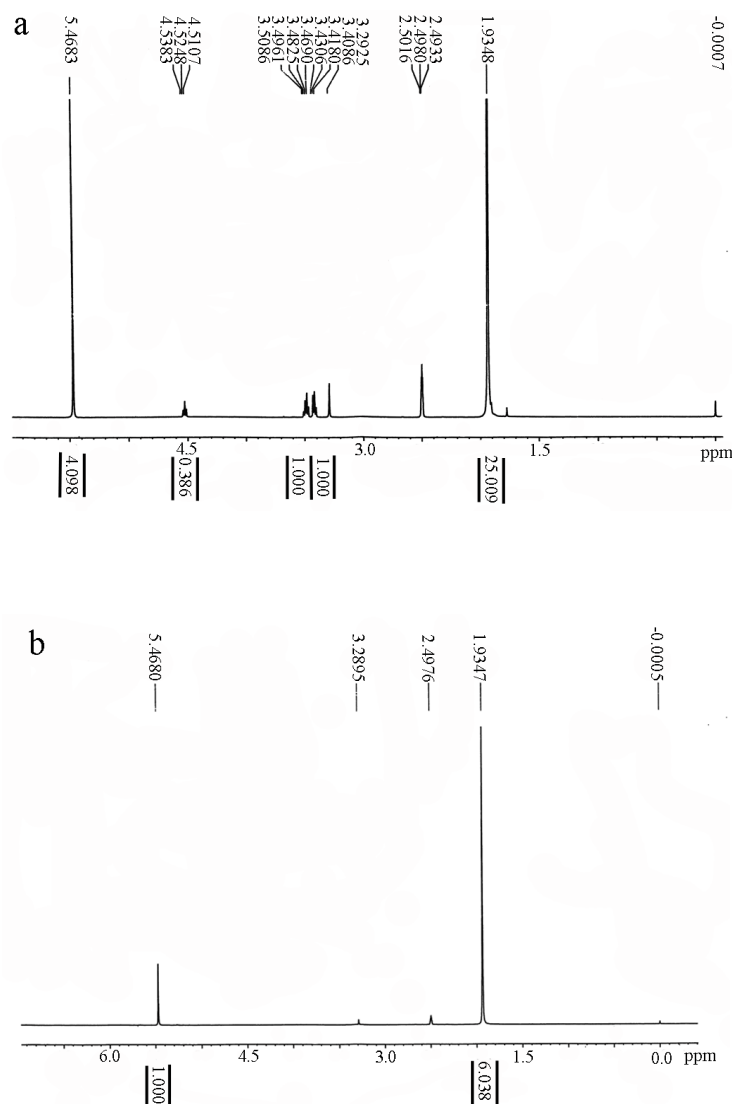
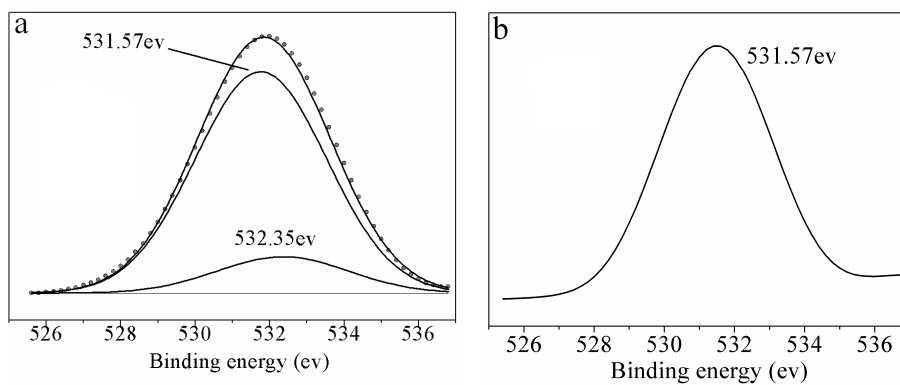
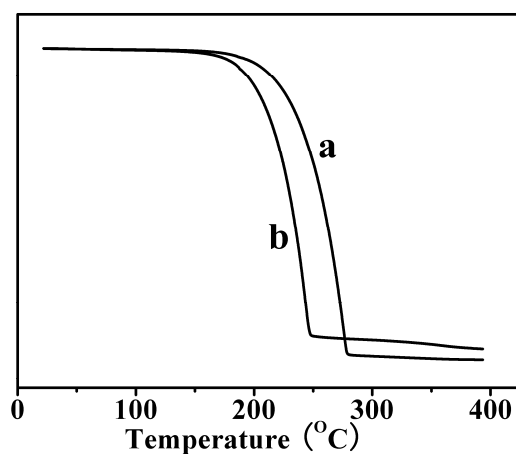


Figure S6b shows the  $^1\text{H}$  NMR chemical shifts at 1.93 and 5.47 ppm and the molar ratio is 6/1, which can be ascribed to H atom in  $\text{CH}_3$  and CH and reveals the C- $\text{In}_2\text{O}_3$  precursor is pure indium acetylacetonate. Comparing with that of the C- $\text{In}_2\text{O}_3$  precursor,  $^1\text{H}$  NMR spectrum of the H- $\text{In}_2\text{O}_3$  precursor shows a signal at 3.42 ppm ascribed to the H atoms in  $-\text{OCH}_3$  besides the  $^1\text{H}$  NMR chemical shifts at 5.47 and 1.97 ppm. (Figure S6a) The molar ratio of H-atoms in  $-\text{CH}-$  to those located in terminal  $\text{CH}_3$  is 4/25, which is less than the theoretical value of  $\text{In}(\text{acac})_3$ . It is because a small quantity of  $-\text{acac}$  species in the  $\text{In}(\text{acac})_3$  complex are replaced by  $-\text{OCH}_3$  during drying at 90  $^\circ\text{C}$  in the presence of the mixture of methanol and  $\text{H}_2\text{O}$ . Chemical shifts at 3.47 and 4.52 ppm are ascribed to H atom of  $-\text{CH}_3$  and  $-\text{OH}$  in methanol molecules. Signals at 2.501 ppm and 3.292 ppm in both precursors should be ascribed to  $\text{H}_2\text{O}$  or HOD in solvent DMSO.

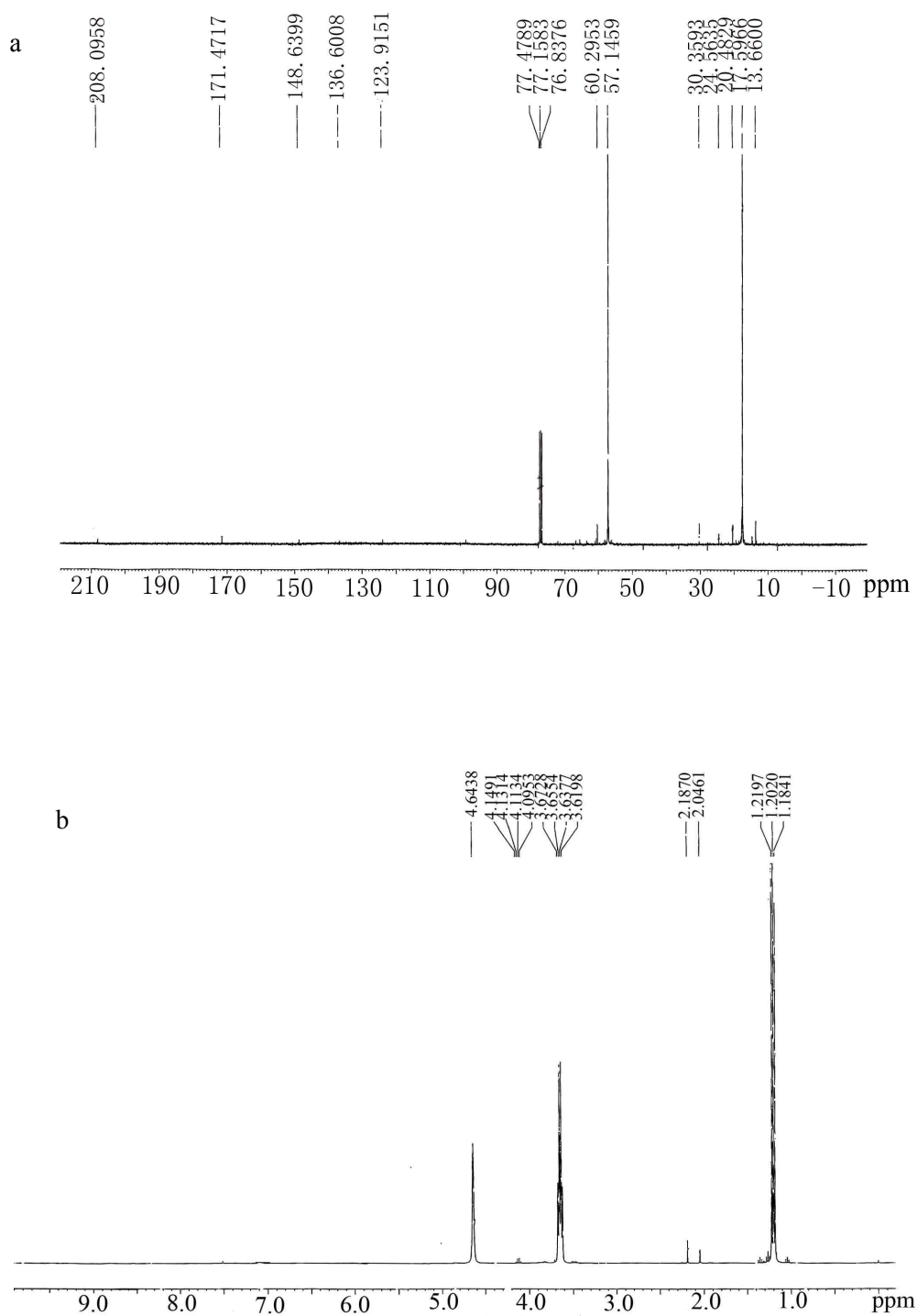
**Fig. S7.** XPS patterns of O1s in the H-In<sub>2</sub>O<sub>3</sub> precursor (a) and C-In<sub>2</sub>O<sub>3</sub> precursor (b).



**Fig. S8.** TG curves of the H-In<sub>2</sub>O<sub>3</sub> precursor (a) and C-In<sub>2</sub>O<sub>3</sub> precursor (b).



**Fig. S9.**  $^{13}\text{C}$  (a, c) and  $^1\text{H}$  NMR (b, d) spectra of the reaction solutions with different precursors. H- $\text{In}_2\text{O}_3$  precursor (a, b) and C- $\text{In}_2\text{O}_3$  precursor (c, d) ( $\text{CDCl}_3$  as solvent)



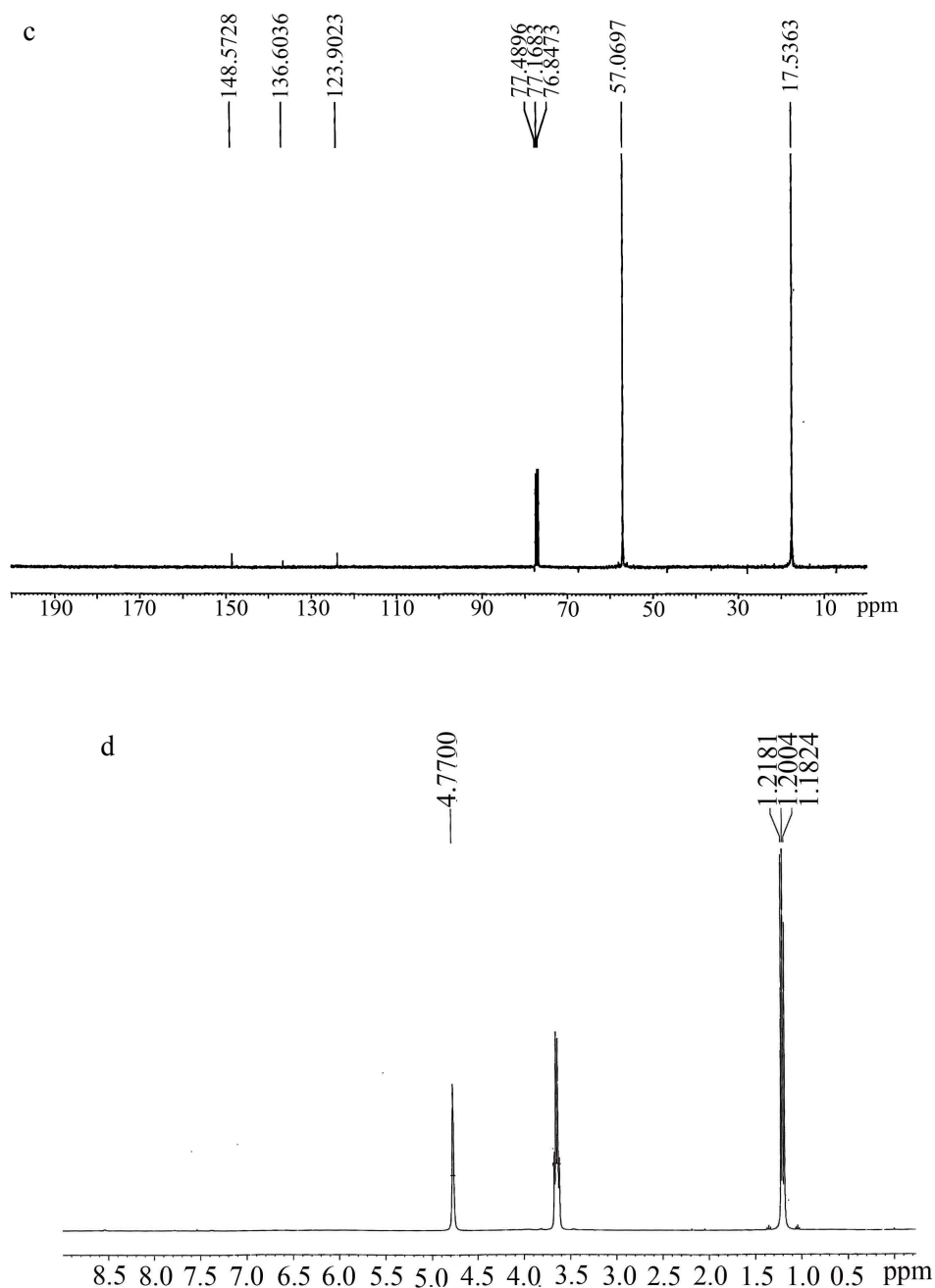


Figure S9 shows the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the final reaction solutions with different precursors. It can be seen that after solvothermal treatment the  $^{13}\text{C}$  NMR spectrum of the C- $\text{In}_2\text{O}_3$  reaction solution (Figure S9c) indicates the existence of the aryl compound (148.6, 136.6, 123.9 ppm) other than the signals of the  $^{13}\text{C}$  in ethanol (57.1, 17.5 ppm), which is the thermal decomposition product of  $\text{In}(\text{acac})_3$ .  $^1\text{H}$  NMR spectrum (Figure S9d) only shows the  $^1\text{H}$  NMR signals of ethanol (3.6, 1.2 ppm). As to the  $^{13}\text{C}$  NMR spectrum of the H- $\text{In}_2\text{O}_3$  reaction solution (Figure S9a), several new signals appeared except the signals of ethanol and aryl compound, which can be assigned to acetone (30.3, 208.1 ppm) and ethyl acetate (60.3, 170.5 ppm), and the signals of aryl compound obviously decreased.  $^1\text{H}$  NMR spectrum (Figure S9b) also

indicates the existence of acetone (2.2 ppm) and ethyl acetate (2.0, 4.1 ppm). Based on the  $^{13}\text{C}$  and  $^1\text{H}$  NMR analyses of the reaction solutions, it can be concluded that only thermal decomposition of  $\text{In}(\text{acac})_3$  carried out during the formation of the  $\text{C-In}_2\text{O}_3$ , which resulted in the formation of the aryl compound. While hydrolysis of indium acetylacetonate firstly formed the Hacac which can react with ethanol to form acetone and ethyl acetate. Then it can be concluded the formation of the  $\text{C-In}_2\text{O}_3$  went through the thermal decomposition of  $\text{In}(\text{acac})_3$ , while hydrolysis of indium acetylacetonate occurred during the formation of the  $\text{H-In}_2\text{O}_3$ .

## References

- S1 (a) K. Nakamoto, C. Udovich and J. Takemoto, *J. Am. Chem. Soc.*, 1970, **92**, 3973; (b) J. P. Fackler, M. L. Mittleman, H. Weigold and G. M. Barrow, *J. Phys. Chem.*, 1968, **72**, 4631; (c) X. Xing, S. Chen and S. Me, *The Workable Index of IR Spectra (in Chinese)*, Tianjin Science & Technology Press, Tianjin, 1992.
- S2 (a) H. E. Gottlieb, V. Kotlyar, A. Nudelman *J. Org. Chem.*, 1997, **62**, 7512; (b) N. Wang, *NMR Spectroscopy--Application in Organic Chemistry (in Chinese)*, Chemistry Industry Press, Beijing, 2006; (c) Q. Deng, L. Liu and H. Deng, *Spectrum Analysis Tutorial (in Chinese)*, Science Press, Beijing, 2007.