

## Two thermolysis routes to ThO<sub>2</sub> nanoparticles from thorium nitrate

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**Abstract.** Two thermolysis routes (that is, solvothermal treatment in toluene at 180 °C for 24 h and direct heating in air at 200 °C for 5 h) were proposed to prepare ThO<sub>2</sub> nanoparticles, by using thorium nitrate (Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O) as the precursor. The as-prepared products were characterized by X-ray diffraction and transmission electron microscopy. The characterization results suggested that both of the proposed thermolysis routes can be used to prepare ultrafine ThO<sub>2</sub> nanoparticles from thorium nitrate.

### Introduction

Nanoparticles can exhibit quite different properties from their bulk counterparts, and in some fields (such as adsorption and catalysis, etc.), they usually showed better performance [1–3]. Nevertheless, the size of nanoparticles play an important role in their properties and applications. Therefore, in order to meet the requirements for specific purposes, the size-controlled synthesis of nanoparticles is highly desirable.

ThO<sub>2</sub> can be used in ceramics, catalysts, sensors, electrodes, solid electrolytes, optical materials, and nuclear industry, etc. [4–10]. However, due to the radioactivity of thorium, the synthesis and properties of ThO<sub>2</sub> have been seldom studied so far [4–10].

Solvothermal technique is a versatile method for synthesizing nanomaterials at temperatures generally below 200 °C. It not only enables to produce crystalline products at low temperatures, but also can easily control the size and morphology of the resultant products [11–16]. On the other hand, when a suitable precursor is selected, direct thermolysis in air may be a simpler and cheaper way of preparing nanomaterials. Herein, we report the two thermolysis routes for the synthesis of ThO<sub>2</sub> nanoparticles, by using thorium nitrate (Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O) as the precursor. The obtained products are characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

### Experimental

All the chemical reagents used are of analytical grade. In the solvothermal preparation, 1.5 g of Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O powder was weighted into a 50 ml Teflon-lined stainless steel autoclave, and subsequently 40 ml of toluene was added in. The autoclave was sealed and maintained at 180 °C for 24 h in an electric oven, then cooled to room temperature naturally. The resulting precipitate was filtered, washed with ethanol and distilled water for several times, and dried in air at 80 °C.

On the other hand, for the direct thermolysis route, 1.5 g of Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O powder was heated in air at 200 °C for 5 h, then cooled to room temperature naturally. The residue powder was collected directly as the final product.

The resultant products were characterized by XRD (German Bruker AXS D8 ADVANCE X-ray diffractometer) and TEM (Holland Philips Tecnai-12 microscope).

### Results and discussion

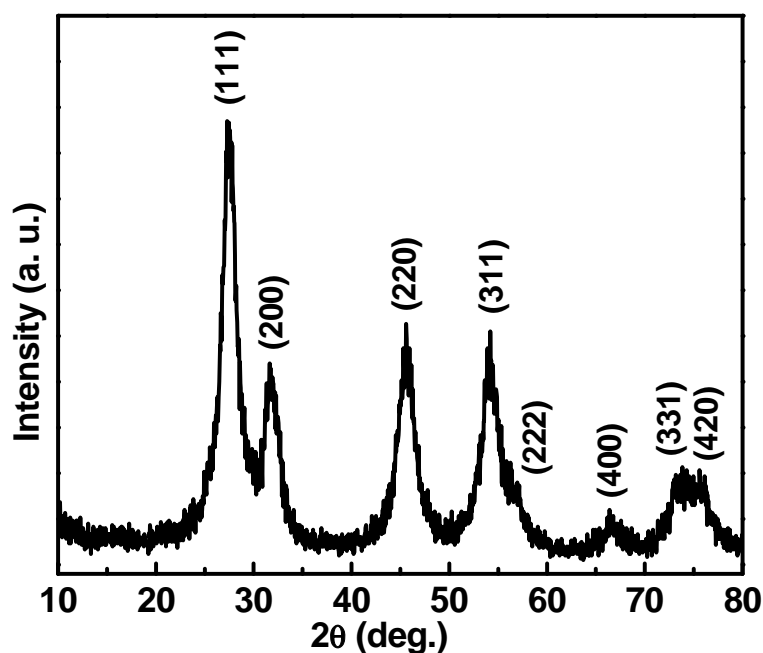


Fig. 1. XRD pattern of the product obtained via solvothermal treatment of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in toluene at 180 °C for 24 h.

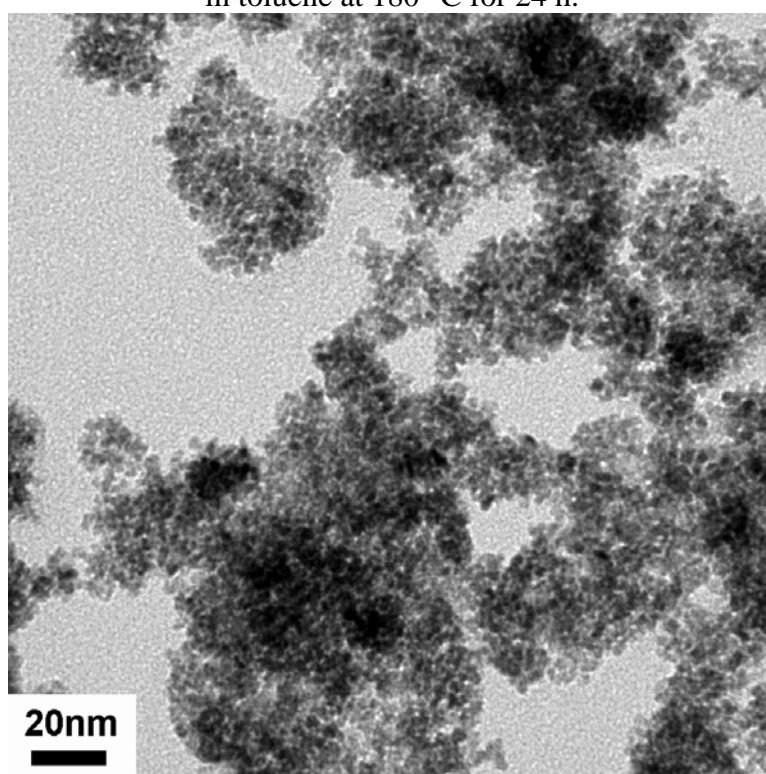


Fig. 2. TEM image of the  $\text{ThO}_2$  nanoparticles obtained via solvothermal treatment of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in toluene at 180 °C for 24 h.

Fig.1 shows the XRD pattern of the product obtained via solvothermal treatment of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in toluene at 180 °C for 24 h. All its XRD peaks can be indexed to cubic phase  $\text{ThO}_2$  (JCPDS card no. 03-065-0289), indicating the formation of phase-pure  $\text{ThO}_2$  under the current solvothermal condition. The widening behavior of the XRD peaks of this sample suggests that its crystal size is very small. Using the well-known Scherrer formula based on the half-width of (111) peak in its XRD pattern (Fig. 1), the crystal size of this sample was estimated to be 2 nm.

Fig. 2 shows the TEM image of the  $\text{ThO}_2$  nanoparticles obtained via solvothermal treatment of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in toluene at 180 °C for 24 h. It can be seen that this sample consists of ultrafine nanoparticles of 2–4 nm, which is consistent with the calculated result using Scherrer formula. Because of the extremely small dimension and high surface energy of the

solvothermally-synthesized  $\text{ThO}_2$  nanoparticles, it is easy for them to aggregate as seen in Fig. 2.

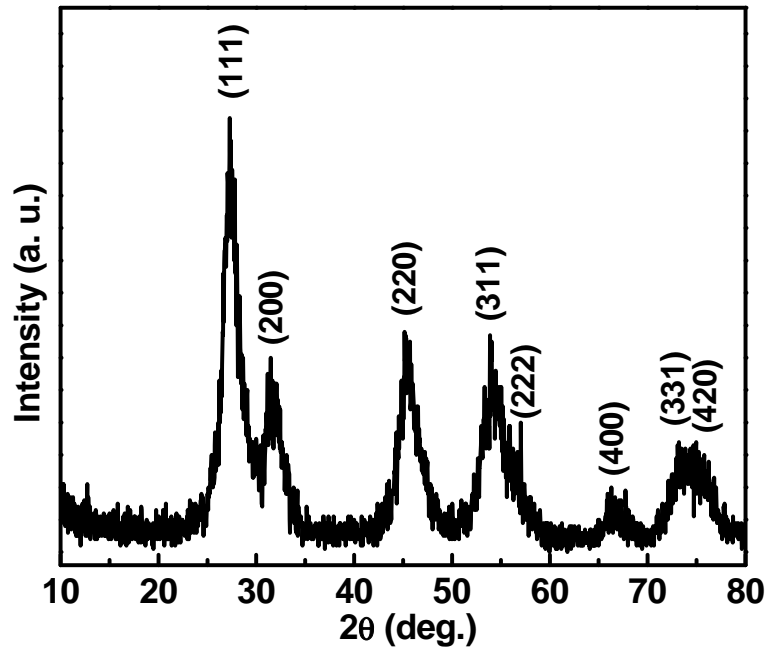


Fig. 3. XRD pattern of the product obtained via heating  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in air at 200 °C for 5 h.

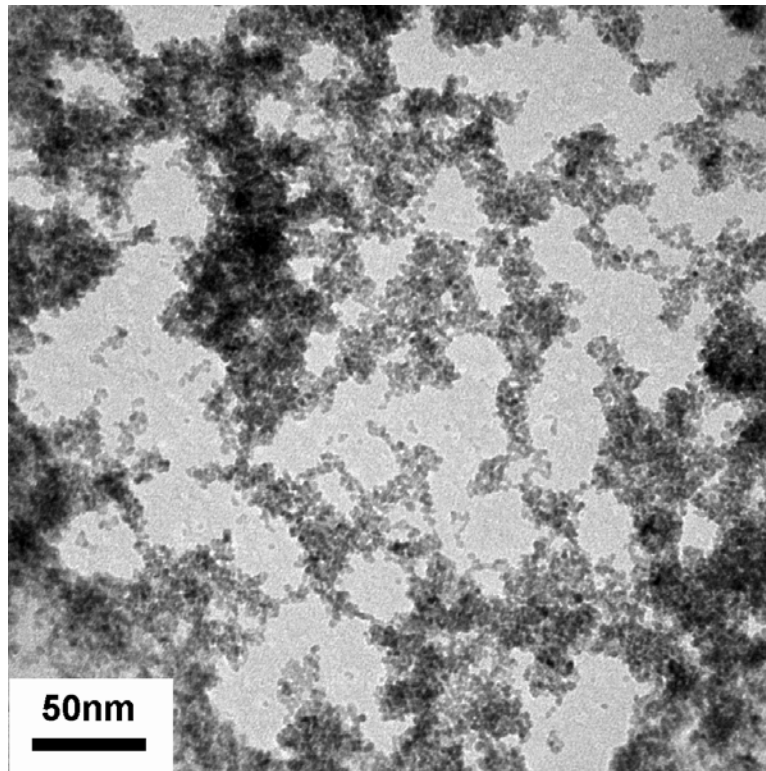


Fig. 4. TEM image of the  $\text{ThO}_2$  nanoparticles obtained via heating  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in air at 200 °C for 5 h.

Fig. 3 shows the XRD pattern of the product obtained via heating  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  powder in air at 200 °C for 5 h. As can be seen, this product displays only the characteristic XRD peaks of cubic phase  $\text{ThO}_2$ . Using the Scherrer formula based on the half-width of (111) peak in its XRD pattern (Fig. 3), the crystal size of this product was estimated to be 2 nm. Besides, the TEM image in Fig. 4 shows that this product comprises ultrafine nanoparticles of 2–4 nm.

From the above results, we can conclude that both of the two thermolysis routes (that is, solvothermal treatment in toluene at 180 °C for 24 h and direct heating in air at 200 °C for 5 h) can prepare ultrafine  $\text{ThO}_2$  nanoparticles from thorium nitrate. Moreover, the products prepared by these two routes seem to have no much difference in size. However, the in air direct thermolysis route is

more preferable for industrial production, because the solvothermal route needs the use of toxic toluene as the solvent and autoclave as the reactor, which cause higher cost and environmental risk.

## Conclusions

ThO<sub>2</sub> nanoparticles of several nanometers can be prepared via: (1) solvothermal treatment of Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O powder in toluene at 180 °C for 24 h; and (2) direct heating Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O powder in air at 200 °C for 5 h. It is believed that the in air direct thermolysis way is more economical and efficient for large scale production of multifunctional ThO<sub>2</sub> nanoparticles.

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