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Preparation and characterization of pyrochlore oxide $Y_2Ti_2O_7$ nanocrystals via gel-combustion route

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Abstract

Pure-phase pyrochlore oxide $Y_2Ti_2O_7$ nanocrystals with good dispersity were successfully synthesized via a glycine-nitrate gel-combustion approach. The preparation process and products were monitored and characterized by Fourier transform-infrared spectra, thermogravimetry-differential scanning calorimetry, X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy. The detailed results suggested that the phase and nature of as-obtained products are highly dependent of the pH value of the precursor solution and the amount of glycine. Under the appropriate conditions that the pH value of the precursor is 2.0, the fuel-to-oxidant ratio is 2.0, and the calcination temperature is 800 °C, the as-prepared products are almost sphere-like or ellipsoid, exhibits perfect crystalline phase, good dispersity and a narrow particle distribution with an average size diameter of 20–30 nm. This soft-chemistry route can be also extended to prepare $Y_2Ti_2O_7$-based functional nanomaterials and other pyrochlore-oxide nanocrystals.

Keywords: Gel-combustion synthesis; Yttrium titanate; Nanocrystals; Characterization

1. Introduction

Owing to its unique structural and physio-chemical characteristics, $Y_2Ti_2O_7$ (YTiO), one of the typical titanate pyrochlore oxides, recently has received considerable attention as potential applications, as host materials for efficient luminescence [1,2], photocatalysts for splitting water to generate H_2 [3], alternative candidates to immobilize nuclear solid waste [4], ceramic pigments [5] and oxygen-ion conductor [6]. More often than not, rare earth titanates have been prepared by conventional solid state reaction, *i.e.* by heat treatment of a stoichiometric mixture of rare earth oxides and titania at elevated temperature for long reaction time (1500 °C for several hours or 1300 °C for 40 h) [7]. Additionally, repeated cycles of grinding and firing of starting constituents are required to complete the solid-based reaction. In spite of this, it is difficult to obtain chemical and microstructural homogenous products. Although a new solid-based approach for the rapid low-temperature synthesis (*i.e.* 700 °C for 2 h) of nanocrystalline $Y_2Ti_2O_7$ was developed [8], nanoparticle powders of Y_2O_3 and TiO_2 were used as the starting materials. Compared with bulk materials, nanoscale ones exhibit outstanding physico-chemical properties, it, therefore, is of great significance to develop novel alternative procedures to synthesize pyrochlore oxide nanocrystals under mild conditions. Recently, several solution chemistry routes like co-precipitation [9], sol–gel process [10,11] and hydrothermal/solvothermal methods [2,12], have been exploited to prepare nanoscale pyrochlore oxides at relatively low temperatures.

Another versatile solution-based technique, *i.e.* the gel-combustion synthesis, is a time- and energy-saving, and cost-effective strategy [13,14]. This process involves an intimate mixing of suitable fuel (*i.e.* glycine, urea or citric acid) and metal nitrates in an aqueous solution, and a self-sustained and exothermic redox reaction between fuel and oxidizers (*i.e.* nitrates). The nature and amount of the fuel chosen, and the pH of the precursor solution are important factors in inhibiting selective precipitation and/or phase separation during the evaporation of solvents, which may in turn depend on the powder characteristics [13]. Glycine (NH_2CH_2COOH), one of the simplest and cheapest amino acid, has an

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amino group at one end and a carboxylic acid group at the other end. Such types of zwitterionic character can effectively complex various metal ions, which aids in preventing them from precipitating selectively and thus keeps the compositional homogeneity among the constituents [15]. Furthermore, glycine can also serve as a fuel in the combustion reaction, being oxidized by nitrates. Namely, metal nitrates coupled with glycine as complexing agent are highly promising in synthesis of a variety of amorphous and nanocrystalline oxides [16–18]. To the best of our knowledge, however, the synthesis of titanate pyrochlore oxide nanocrystals via gel-combustion has not been reported so far.

Taking these into considerations, the aim of this present work is to exploit the glycine-nitrate gel-combustion (GNC) to prepare pyrochlore-type YTiO nanocrystals at low calcination temperature. The effect of pH values of the precursor solution and the fuel-to-oxidant ratio on the powder characteristics such as crystallite sizes, morphologies and agglomeration are described.

2. Experimental procedure

2.1. Preparation of YTiO powders

All the chemical reagents in the present experiment were of the analytical purity. Yttrium oxide (Y_2O_3) and tetra-*n*-butyl titanate (Ti(O-*n*-Bu)$_4$) were used as the starting materials, and glycine was chosen as the fuel. The molar ratio of Ti/Y was controlled at 1:1. Firstly, a given amount of Y_2O_3 was dissolved with concentrated HNO_3 to convert into $Y(NO_3)_3$ solution completely. Titanyl nitrate ($TiO(NO_3)_2$) was prepared *in situ* by the hydrolysis of Ti(O-*n*-Bu)$_4$ followed by the treatment of HNO_3 as follows:

$$Ti(O-n-Bu)_4 + 3H_2O \rightarrow TiO(OH)_2 + 4n-BuOH \quad (1)$$

$$TiO(OH)_2 + 2HNO_3 \rightarrow TiO(NO_3)_2 + 2H_2O \quad (2)$$

The two solutions above was then mixed, and a given amount of glycine was added. The pH values of mixture solution (*i.e.* precursor solution) was adjusted by adding either dilute ammonia or dilute nitric acid as required. After evaporation and dehydration on a hot plate (80 °C), the precursor solution was transformed into viscous gel, which was placed in a preheated furnace maintained at 210 °C. The gel underwent swelling, decomposition and auto-ignition, and the foamy and voluminous ashes obtained could be readily crushed into the precursor powders. The combustion was complete in less than a few seconds. The combustion reaction can be balanced by the reducing and oxidizing valences of glycine and metal nitrates based on the concept of propellant chemistry [19]. In the case of this combustion system, the fuel-to-oxidant ratio, $\psi = 50/18 = 2.78$, is called the stoichiometric amount. When ψ is less than 2.78, the combustion is fuel-lean, and when ψ is greater than 2.78, it is a fuel-rich reaction. The redox reaction during auto-combustion can be written as follows.

$$Y(NO_3)_{3(aq)} + TiO(NO_3)_{2(aq)} + \psi NH_2CH_2COOH_{(aq)} + (9\psi/5 - 25/4)O_{2(g)} \rightarrow 1/2Y_2Ti_2O_{7(c)} + (\psi/2 + 5/2)N_{2(g)} + 2\psi CO_{2(g)} + 5\psi/2H_2O_{(g)} \quad (3)$$

Where the subscripts aq, c and g denote the aqueous, solid, and gaseous phase, respectively. In order to eliminate carbonaceous residues and improve the crystallinity, the crushed powders were calcined at 600–1000 °C for 1.0 h in air and the final white products were prepared. By varying the pH of the precursor solution and ψ value, a series of YTiO powders was obtained. The schematic diagram of synthesis of YTiO powders by GNC is shown in Fig. 1.

2.2. Characterization and instrumentation

The binding reaction of glycine and metal ions prior to decomposition was examined by Fourier transform infrared spectra (FT-IR, Avatar 380, Thermo Nicolet Corporation, USA) with the scan range of 4000–400 cm^{-1}. The decomposition behavior and the nature of combustion reaction were investigated by thermogravimetry-differential scanning calorimetry (TG-DSC, Netzsch STA 449C, Germany) operated with the heating rate of 5 °C/min in static air (the mass of the samples mounted into the TGA-DSC sample pan is in the

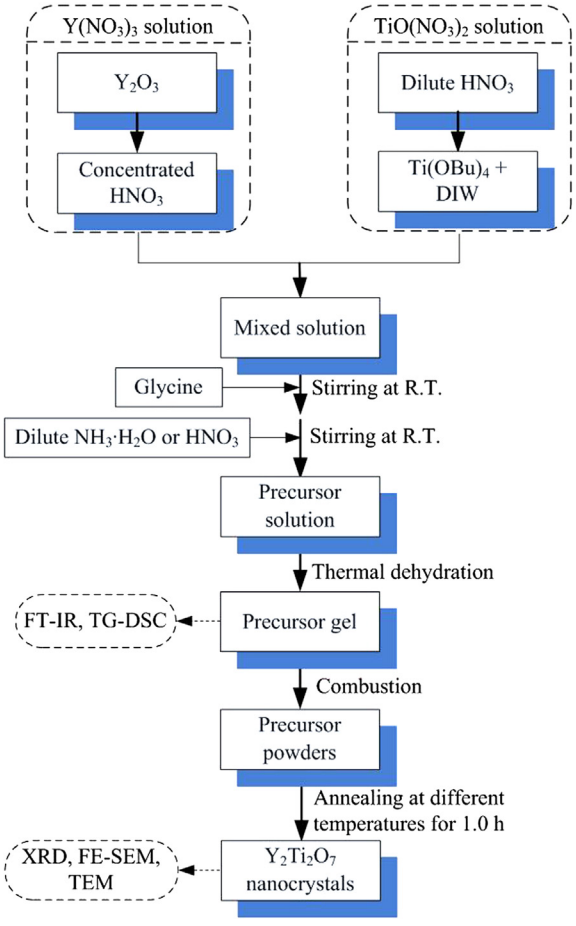

Fig. 1. Schematic diagram of the synthesis of $Y_2Ti_2O_7$ nanocrystals by GNC.

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