Polyhedron 28 (2009) 3005–3009

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Pure cubic $ZrO_2$ nanoparticles by thermolysis of a new precursor

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ARTICLE INFO

*Article history:*
Received 28 April 2009
Accepted 7 June 2009
Available online 23 June 2009

*Keywords:*
Nanomaterials
Zirconium oxide
Thermolysis
Inorganic materials
Characterization methods

ABSTRACT

Zirconia ($ZrO_2$) nanoparticles have been synthesized through the thermolysis of bis-aqua, tris-2-hydroxyacetophenato zirconium (IV) nitrate, $[Zr(HAP)_3(H_2O)_2](NO_3)$, as a precursor in oleylamine ($C_{18}H_{37}N$) and triphenylphosphine ($C_{18}H_{15}P$). The combination of $C_{18}H_{37}N$ and $C_{18}H_{15}P$ was added to act as surfactants to control the particle size. $C_{18}H_{37}N$ and $C_{18}H_{15}P$ play an important role in preventing aggregation of $ZrO_2$ nanoparticles. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL) and Fourier transform infrared (FT-IR) spectroscopy to depict the phase and morphology. The synthesized $ZrO_2$ nanoparticles have a cubic structure. The FT-IR spectrum showed the purity of obtained cubic phase $ZrO_2$ nanocrystals.



## 1. Introduction

Zirconia ($ZrO_2$), because of its surface characteristics of possessing both acid–basic and redox functions, has been widely used as a catalyst in numerous chemical reactions. $ZrO_2$ has three different crystal phases, monoclinic, tetragonal and cubic, that strongly influence the catalyst's activities and selectivities [1,2].

Generally, the tetragonal phase of zirconia is preferentially formed relative to the monoclinic phase during the crystallization of amorphous hydrous zirconia. So, upon increasing the calcination temperature, firstly most amorphous zirconia precursors convert to the tetragonal phase and then transform to the monoclinic phase at higher temperatures (~600 °C). The transformation is completed at temperatures more than about 800 °C [3–5].

$ZrO_2$ has been synthesized via different routes, for example by the microwave plasma method [6], chemical vapor synthesis [7], sol–gel method [8–10], precipitation [11], hydrothermal synthesis [12], *etc.* [13–15]. Several year ago we initiated a research work aimed at the synthesis of metallic [16,17] and metal oxide nanoparticles [18–20] by thermal decomposition of inorganic complexes as precursors. With this thermolysis method, the utilization of simple, facile, cheap, air-stable and less-toxic molecular precursors is expected to greatly facilitate the large-scale production of oxide nanocrystals for the above applications. A major interest at the moment is in the development of organometallic or inorganic compounds for preparation of nanocrystals. Using novel compounds can be useful and can open a new way for preparing nanomaterials whilst controlling the nanocrystal size, shape and distribution size.

A variety of zirconium complexes have been prepared successfully and modified [21–24]. These precursors can be good candidates for the synthesis of $ZrO_2$ nanomaterials. Herein, we report on the facile synthesis of $ZrO_2$ nanocrystals via thermolysis of the new precursor bis-aqua, tris-2-hydroxyacetophenato zirconium (IV) nitrate; $[Zr(HAP)_3(H_2O)_2](NO_3)$; in oleylamine and triphenylphosphine (TPP). To the best of our knowledge, this is the first report on the synthesis of $ZrO_2$ nanocrystallites with this precursor. In this process, oleylamine was used as both the medium and the stabilizing reagent.

## 2. Experimental

### 2.1. Materials

Zirconyl nitrate pentahydrate ($ZrO(NO_3)_2.5H_2O$), 2-hydroxyacetophenone (HAP), oleylamine, triphenylphosphine (TPP), toluene, hexane, and ethanol were purchased from Aldrich and used as received. The precursor complex $[Zr(HAP)_3(H_2O)_2](NO_3)$ was prepared according to the procedure described previously [25]: 0.01 mmol $ZrO(NO_3)_2{\cdot}5H_2O$, 0.06 mmol of 2-hydroxyacetophenone and 10 ml of 2-methoxy ethanol were added to a 250 ml Erlenmeyer flask to give a turbid solution. To this suspension 10 ml of acetonitrile was added and the solution was refluxed for 12 h to yield white crystals. The crystalline product was purified by washing with dry diethylether to yield 80% of the product (m.p. 99 °C). Anal. Calc. for $ZrO_{11}C_{24}H_{25}$ N: C, 48.47; H, 4.24; N, 2.36; Zr, 15.34. Found: C, 48.29; H, 4.80; N, 2.41; Zr, 15.32%.

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doi:10.1016/j.poly.2009.06.032

### 2.2. Characterization

XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Elemental analyses were obtained from Carlo ERBA Model EA 1108 analyzer. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscope. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) of the as-prepared products was measured on an ESCA-3000 electron spectrometer with non-monochromatized Mg Kα X-ray radiation as the excitation source. Room temperature photoluminescence (PL) was studied on an F-4500 fluorescence spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the complexes were taken on a Shimadzu UV–Vis scanning spectrometer (Model 2101 PC).

### 2.3. Synthesis of $ZrO_2$ nanoparticles

The current synthetic procedure is a modified version of the method developed by the Hyeon group for the synthesis of various nanoparticles of metals and oxides, which employs the thermal decomposition of metal–surfactant complexes in hot surfactant solution [26]. A stock solution of $[Zr(HAP)_3]$–surfactant complex, prepared by reacting 0.6 g of bis-aqua, tris-2-hydroxyacetophenato zirconium (IV) nitrate, $[Zr(HAP)_3(H_2O)_2](NO_3)$, with 5 ml of oleylamine at 150 °C, was slowly injected into 5 g of triphenylphosphine (TPP) under vigorous stirring at 250 °C. The mixture was heated at 250 °C and the resulting solution was stirred at this temperature for 90 min. The initial white color of the solution slowly turned yellow, indicating that nanoparticles were generated. The reaction mixture was then cooled to room temperature and the white nanoparticles were retrieved by adding 30 ml of ethanol, followed by centrifugation. The final products were washed with ethanol at least three times to remove impurities, if any, and dried at 100 °C. The retrieved powder form of the nanoparticles could be easily redispersed in non-polar organic solvents such as hexane or toluene (Scheme 1).

## 3. Results and discussion

### 3.1. Thermogravimetric analysis of the $[Zr(HAP)_3(H_2O)_2](NO_3)$ precursor

The TGA curve for the decomposition of $[Zr(HAP)_3(H_2O)_2](NO_3)$ was recorded in air atmosphere and is shown in Fig. 1. As shown in Fig. 1, a total of two weight losses were observed. A weight loss of 9% occurred between 100 and 180 °C, and this weight loss is indicative of the loss of one coordinated $H_2O$ molecule. The TG curve of the complex shows a gradual loss of weight of about 70% around 460 °C to give a residual mass consisting of about 30%, close to that expected for a complete conversion to $ZrO_2$. The weight loss from 250 to 460 °C is linked with burning of 2-hydroxyacetophenato (exothermic) to acetone, $CO_2$ and $H_2O$ [27]. There was no organic residue left after 450 °C, as confirmed by the FT-IR spectrum of the residual mass.

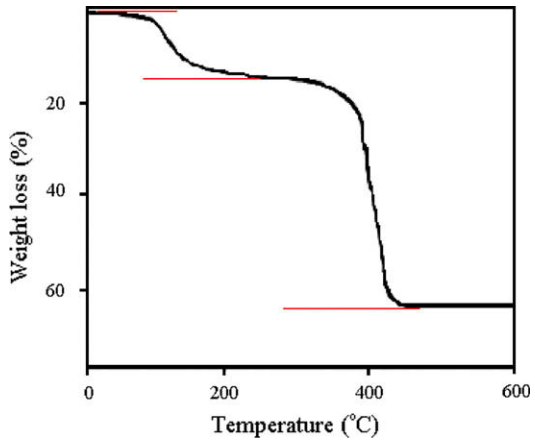



**Fig. 1.** TG curve of the $[Zr(HAP)_3(H_2O)_2](NO_3)$ precursor in air.

### 3.2. XRD analysis of the products

The XRD diffraction pattern of the $ZrO_2$ was recorded for the identification of the product (Fig. 2). From the XRD data, the crystallite size ($D_c$) of the as-prepared $ZrO_2$ particles was calculated to be 40 nm using the Debey–Scherrer equation [28],

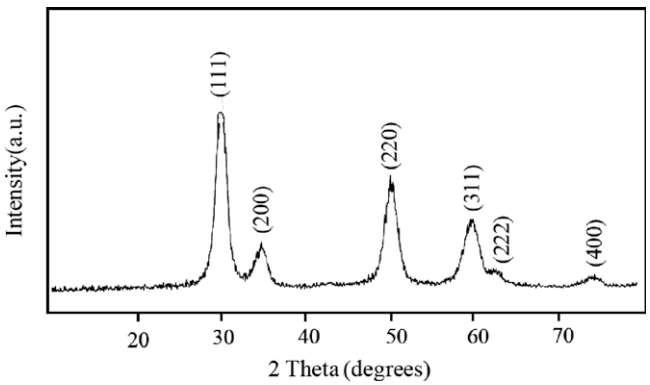
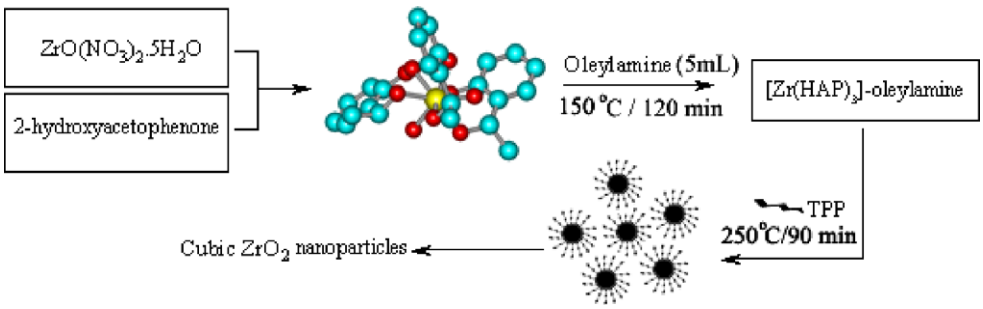



**Fig. 2.** XRD patterns of $ZrO_2$ nanoparticles.




**Scheme 1.** Synthetic procedure for $ZrO_2$ nanoparticles.