



Bulk synthesis of nanocrystalline urania powders by citrate gel-combustion method



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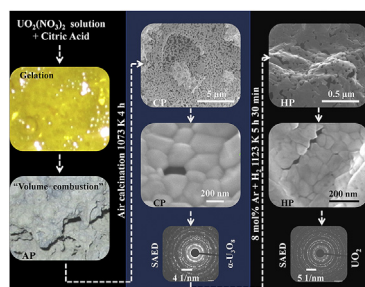
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HIGHLIGHTS

- Bulk quantities of nanocrystalline urania were prepared for the first time using citrate gel combustion method.
- Volume combustion was observed in mixtures with fuel to nitrate ratio (R) 0.25.
- The value of R was found to significantly influence the characteristics of the final product.
- Typical exfoliated microstructure and nanopores were observed.
- Established correlation between particle size distribution and bulk density, X-ray crystallite size and lattice strain.
- Relationship between fuel to nitrate (R) mole ratio and physical characteristics of powders were also established.

GRAPHICAL ABSTRACT



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ABSTRACT

Bulk quantities (60 g) of nanocrystalline (nc) free flowing urania powders with crystallite size ranging from 38 to 252 nm have been synthesized for the first time by the citrate gel combustion method. A systematic study of the influence of the fuel (citric acid) to oxidant (nitrate) ratio (R) on the characteristics of the urania powders has been carried out for the first time. Mixture with an “R” value of 0.25 exhibited a vigorous auto-ignition reaction. This reaction was investigated with Differential Scanning Calorimetry (DSC) and in-situ thermogravimetry coupled with differential thermal analysis and mass spectrometry (TG-DTA-MS). The bulk density, specific surface area, X-ray crystallite size, residual carbon and size distribution of particles of this powder were unique. Microscopic and microstructural investigation of selected samples revealed the presence of nanocrystals with irregular exfoliated morphology; their Electron Energy Loss Spectra testified the covalency of the U–O bond.

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1. Introduction

Synthesis of nanocrystalline (nc) oxide powders with “unique” microstructural and morphological characteristics for different technological applications has been the subject of active research in the past two decades [1–10]. Nanocrystalline UO_2 has attracted the attention of nuclear technologists owing to its unique properties that stem from its nanocrystallinity [11–21] and relevance to high burn-up structures (HBS) [22–27] observed in irradiated fuels. However, investigations on the synthesis of nc-actinide oxides are rather limited [11–18,28]. T. Pavelkova et al. [13] reported the synthesis of nanocrystalline UO_2 by photo induced irradiation method. V. Tyrpekl et al. [27] reported the synthesis of nc- UO_2 through oxalate precipitation. Even though these authors have not specified the scale at which the preparation was carried out, this method could be used in principle for the bulk preparation of nc- UO_2 . However, so far no direct investigations have been reported in which nc- UO_2 has been synthesized in bulk quantities (60 g).

Recent investigations by Spino et al. [25] have revealed that the high burn up structure (HBS) formed during the irradiation of UO_2 in thermal reactors, is in fact a nanoscopic phase. This phase is likely to exhibit a higher resilience to radiation damage, higher plasticity and greater fission gas retentivity. These properties are most suitable for achieving a higher burn-up. In order to prove its pertinence to advanced nuclear fuel fabrication, simulation experiments were carried out by Spino et al. [25] on partially stabilized nanocrystalline zirconia doped with 4 mol % yttria (nc- Y_2O_3). These authors observed that actual tests on nc- UO_2 have not been reported so far. In this context the preparation of nc- UO_2 gains prominence and is thus relevant to advanced nuclear fuels research. There are many methods, by which nanocrystalline UO_2 could be synthesised. These include non-aqueous colloidal synthesis [11], hydrothermal method [16], sulphate mediated synthesis [17] and laser ablation [19]. These methods are expensive, yield agglomerated powders with larger grains (μm) and contain substantial impurities. These attributes are not desirable for fabricating pellets with tailored properties. Further, only a few milligrams of the product have been obtained so far in laboratory scale investigations cited in Refs. [11,16,17]. In addition, these methods invariably generate large quantities of liquid waste. Hence, there is a need to identify a simple inexpensive method for preparing nc- UO_2 .

Citric acid being a good chelating agent [29,30], has been used in the synthesis of nanomaterials by thermal decomposition of its metal ion complexes through combustion synthesis. This technique has been extensively studied and has been used for the preparation of simple binary and ternary oxides. It is an elegant method and has been used in the preparation of complex nc-oxides viz., hydroxyapatite [31], barium ferrites [32] and LiFePO_4 [33]. Jianguo Huang et al. [32] have reported that by tuning the composition of the combustion mixture, the particle size and magnetic coercivity of the product (barium ferrites) could be tailored. Similarly, Kuei-Feng Hsu et al. [33] have reported that properties of the citrate gel-combustion derived powders are strongly dependant on calcination temperatures.

Citric acid has also been used in the preparation of nano nuclear ceramics. Chandramouli et al. [34] have reported the combustion synthesis of ThO_2 powders through citrate gel combustion. These authors also studied the effect of different modes of heating (viz. hot plate and microwave) on the product. Combustion synthesis of solid solutions of uranium with other binary oxides viz. ThO_2 [35], CeO_2 [36] and Ln_2O_3 [37–39] (Ln = Lanthanide) have also been reported.

In spite of these extensive investigations, no study has so far been reported in which nc- UO_2 powders were prepared through

citrate gel-combustion. Hence, in this study we undertook to investigate the suitability of this method for the preparation of bulk quantities of nc- UO_2 . In addition an attempt was made to identify the optimum value of R by studying the influence of the latter on the properties of the product.

2. Experimental

2.1. Starting materials

Uranium oxide of nuclear grade purity was procured from Nuclear Fuel Complex, Hyderabad, India. Ferrioin (AR 0.025 M) and citric acid (AR) (>99.5% pure) were obtained from Loba chime Pvt. Ltd, Mumbai, India. Ammonium iron (II) sulfate hexahydrate (GR 99.0%) was procured from Merck Ltd, Mumbai, India.

2.2. Powder synthesis

Uranyl nitrate was prepared afresh from the urania stock by using the following procedure. First, the urania powder was converted quantitatively into U_3O_8 by heating the former for 4 h at 773 K in air. This powder was cooled and stored in a dessicator. An appropriate amount of U_3O_8 required for preparing 60 g of UO_2 was dissolved in 12 M HNO_3 and heated on a hot plate to dryness to obtain uranyl nitrate crystals. These crystals were dissolved in distilled water and the concentration of NO_3^- in this solution was estimated by titrimetry. For this estimation, a known quantity of uranyl nitrate solution was taken along with 25 mL of 0.2 N ferrous ammonium sulphate (FAS), acidified with 10 mL (12.2 M) HCl and 25 mL H_2SO_4 (18.4 M) and titrated against $\text{K}_2\text{Cr}_2\text{O}_7$ (0.1 N) by using ferrioin indicator under ice cold condition [40]. The exact quantity of the fuel required to carry out the combustion reaction with a particular value of citric acid (fuel) to nitrate (oxidant) mole ratio (R) was calculated by using the estimated value of the concentration of nitrate.

In a typical experiment, desired quantities of oxidant and fuel were dissolved in a minimum quantity of distilled water and warmed on a hot plate. Mixtures with R values 0, 0.055, 0.10, 0.25, 0.50, 0.75, 0.90 and 1.00 were prepared. In a typical combustion synthesis experiment, the desired mixture was allowed to gelate on a hot plate. Subsequently this gel got dehydrated, and an auto ignition reaction ensued leaving behind a carbonaceous powder. The powders obtained at the end of the combustion syntheses were termed as the “as prepared” powders. These were calcined in air at 1073 K for 4 h by using a furnace equipped with SiC heating elements. All the calcined powders were reduced in flowing hydrogen at 1123 K for 5 h 30 min at a pressure of 49–98 kPa (flow rate = 6.67 mL s^{-1}), in a custom made furnace equipped with inconel sample holders.

These powders were designated with different labels by using the following nomenclature. The suffices “A”, “C” and “H” were used to identify the “as prepared”, “calcined” and “hydrogen reduced” powders respectively. All these indices bore a prefix U_C to denote urania powders prepared by using citrate gel-combustion. Each mixture used for carrying out the gel-combustion synthesis were identified with the help of two unique digits “XX” which referred to the value of R expressed in percentage. Powders prepared without the use of fuel were devoid of the label “C”. Thus, typically the powders that were prepared from a mixture with an R value of 0.25 would be designated as U_C25A , U_C25C and U_C25H to indicate that these are the “as prepared”, “calcined” and “hydrogen reduced” products respectively.

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