Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 131 (2014) 556–563

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis and characterization of ZrO_2–CuO co-doped ceria nanoparticles via chemical precipitation method

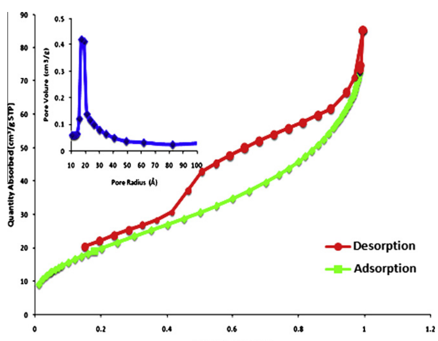
G. Viruthagiri *, E. Gopinathan, N. Shanmugam, R. Gobi

Department of Physics, Annamalai University, Annamalai Nagar, 608 002 Tamil Nadu, India

HIGHLIGHTS

- We have synthesized nanostructures of ZrO_2–Cuo doped with CeO_2 by simple chemical precipitation method.
- The PL emission has emission bands at UV and visible regions as a result of 2p → 4f transition.
- In Surface analysis crystalline size of nanosized powders were calculated using BET techniques.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 February 2014
Received in revised form 11 April 2014
Accepted 22 April 2014
Available online 30 April 2014

Keywords:
Ceria
Nanocrystals
Fluorite
Quantum confinement
UV-DRS

ABSTRACT

In the present study, the fluorite cubic phase of bare and ZrO_2–CuO co-doped ceria (CeO_2) nanoparticles have been synthesized through a simple chemical precipitation method. X-ray diffraction results revealed that average grain sizes of the samples are within 5–6 nm range. The functional groups present in the samples were identified by Fourier Transform Infrared Spectroscopy (FTIR) study. Surface area measurement was carried out for the ceria nanoparticles to characterize the surface properties of the synthesized samples. The direct optical cutoff wavelength from DRS analysis was blue-shifted evidently with respect to the bulk material and indicated quantum-size confinement effect in the nanocrystallites. PL spectra revealed the strong and sharp UV emission at 401 nm. The surface morphology and the element constitution of the pure and doped nanoparticles were studied by scanning electron microscope fitted with energy dispersive X-ray spectrometer arrangement. The thermal decomposition course was followed using thermo gravimetric and differential thermal analyses (TG-DTA).

Introduction

Nanomaterials contain particles with one dimension in the nanometer regime. Recently, there is a growing interest from the scientific community in the applications of these nanomaterials, which are sometimes referred to as "the next industrial revolution" [1]. Nanoparticles have received much attention in the field of material science because of their fascinating mechanical and physico-chemical properties which are entirely different from their bulk counterparts. Semiconductor nanoparticles are of great interest due to their electronic and optical properties [2]. Among these semiconductor nanoparticles, cerium oxide has been of great interest in versatile applications due to its chemical stability and close lattice parameter with silicon [3]. It is a noticeable functional material with an extraordinary capacity to store and release oxygen with cubic fluorite structure [4]. Among oxides, the cubic CeO_2 phase (fluorite) has long been considered as one of the most

* Corresponding author. Tel.: +91 9486223626.
E-mail address: gvgiri2002@gmail.com (G. Viruthagiri).

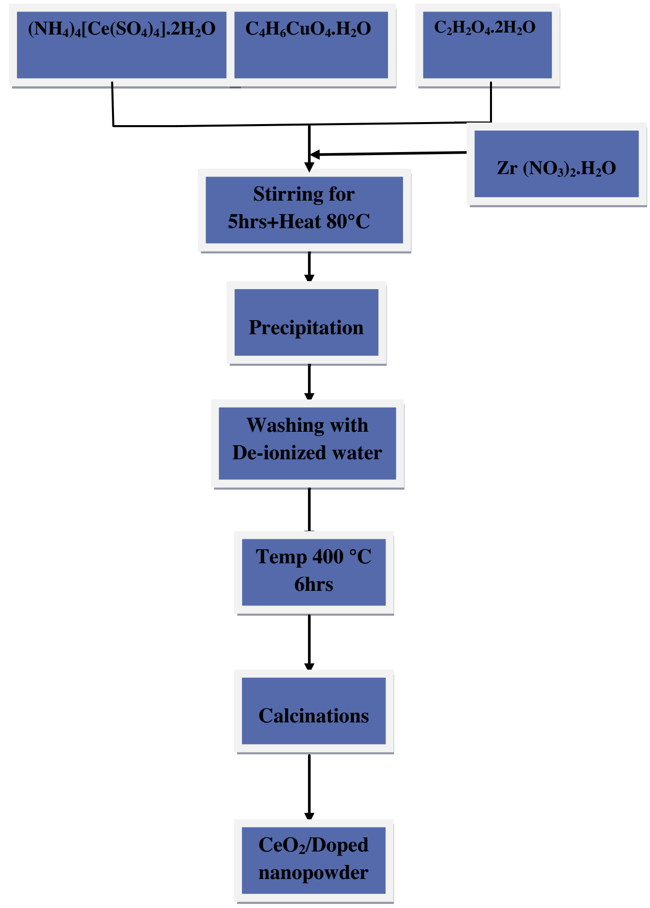
http://dx.doi.org/10.1016/j.saa.2014.04.117
1386-1425/

promising materials because of high refractive index, good transmission in visible and infrared regions, strong adhesion, and high stability against mechanical abrasion, chemical attack and high temperatures [5]. Cerium oxide (CeO_2) particles have been extensively studied owing to their potential uses in many applications, such as UV absorbents and filters [6,7], buffer layers with silicon wafer [8], gas sensors [9], photo catalysts in the fuel cell technology [10–12], catalytic wet oxidation [13], engine exhaust catalysts [14], NO removal [15], and photo catalytic oxidation of water [16]. However, the material performances in practical uses are strongly influenced by the properties of constituent CeO_2 particles. Many methods have been employed to produce doped-cerium oxide nanoparticles such as the chemical precipitation, sol–gel method, microwave-assisted hydrothermal processes [17–23], mechano-chemical processing [24], polyvinyl pyrrolidone (PVP) solution route [25], electrochemical synthesis [26], combustion method [27], direct sono-chemical route [28] and gas–liquid co-precipitation [29]. In this study, we have used the chemical-precipitation method to synthesize bare and co-doped CeO_2 powders. The main advantage of the chemical precipitation technique has the capability of producing ultrafine powders with high purity and homogeneous phase composition at lower temperatures. Recently, simultaneous doping of two kinds of atoms (co-doping) into semiconductor materials has attracted considerable interest, as it could result in a higher photocatalytic activity and special characteristics compared with single element doping into semiconductor oxides, such as Ag^+ and La^{3+}, metallic silver and V, Ga/Al/Co co-dopants [30–32].

In the present work, we have synthesized ZrO_2–CuO co-doped ceria nanoparticles and the effects of doping on the structural and optical properties of CeO_2 were analyzed.

Materials and method

In the chemical precipitation method the, stoichiometric ratios of the materials Ammonium Ceric Sulfate ($(NH_4)_4$ $[Ce(SO_4)_4]\cdot 2H_2O$), Oxalic acid ($C_2H_2O_4\cdot 2H_2O$), Copper acetate ($C_4H_6CuO_4\cdot H_2O$), Zirconium nitrate ($Zr(NO_3)_2\cdot H_2O$) were used as precursors. All chemicals were used as received in analytical reagent (AR) grade with 99% purity. 0.2 M of ($(NH_4)_4$ $[Ce(SO_4)_4]\cdot 2H_2O$) was dissolved in 25 ml of deionized water and then stirred the solution vigorously. Next the solution 0.2 M of ($C_4H_6CuO_4\cdot H_2O$) and ($Zr(NO_3)_2\cdot H_2O$) was dissolved in 10 ml of deionized water was added drop wise to the solution. Finally 0.3 M of ($C_2H_2O_4\cdot 2H_2O$) was dissolved in 25 ml of deionized water was added drop wise to solution under vigorous stirring. The solution was heated at 60 °C and continuously stirred for 5 h using magnetic stirrer. By gradually mixing these of solutions a pale blue precipitate were formed. After the obtained precipitate was washed repeatedly with deinosied water and then filtered. The precipitate was dried in hot air oven at 100 °C for 1 h, and then the product was annealed at 400 °C in muffle furnace for 6 h to get phase pure and doped ceria nanopowders. The possible chemical reactions are given below:



Scheme 1. Schematic representation for preparation of ceria Nps.

Results and discussion

Powder X-ray diffraction study (XRD)

The XRD pattern of bare and ZrO_2–CuO–CeO_2 is given in Fig. 1(a and b). All the marked diffraction peaks of CeO_2 can coincidently be indexed by the standard CeO_2 (JCPDS card No: 81-0792). The crystallographic phase of bare CeO_2 belongs to the face-centered cubic (FCC) fluorite type and the space group Fm-3m. The relatively high intensity of the plane (1 1 1) is indicative of anisotropic growth and implies a preferred orientation of the crystallites. Fig. 1b shows the XRD pattern of ZrO_2–CuO–CeO_2 nanoparticles. It is different from that of bare CeO_2 pattern. In the ZrO_2–CuO–CeO_2 system, there is a shift in the diffraction peaks which correspond to ZrO_2–CuO. These shift at high angle side due to the dopant ions take interstitial positions of host matrix (or) placed on a metal surface. This confirms the loading of ZrO_2–CuO on CeO_2. Broadening of diffractograms indicate that the reduction of the size of the particle when compared to bare CeO_2.

$$Ce\,(NH_4)_4\bullet(SO_4)_4\bullet H_2O + \begin{matrix}COOH\\ |\\ COOH\end{matrix}\bullet H_2O \longrightarrow CeO_2 + H_2O + CO_2 + H_2SO_4$$

$$C_4H_6CuO_4\bullet H_2O + Zr(NO_3)\bullet H_2O + Ce(NH_4)_4\bullet(SO_4)_4\bullet H_2O + \begin{matrix}COOH\\ |\\ COOH\end{matrix}\bullet H_2O \longrightarrow ZrO_2 - CuO - CeO_2 + CH_3COOH + NH_4(NO_3) + CO_2 + H_2O$$

The preparation of bare and co-doped CeO_2 nanoparticles by the chemical precipitation method is illustrated in Scheme 1.

The crystallite size of the ceria nanoparticles was determined using Scherrer's equation,