Applied Surface Science 273 (2013) 457–464

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Effect of annealing temperature on the microstructural, optical and electrical properties of CeO_2 nanoparticles by chemical precipitation method

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ARTICLE INFO

Article history:
Received 25 December 2012
Received in revised form 2 February 2013
Accepted 18 February 2013
Available online 24 February 2013

Keywords:
Cerium oxide
Optical
Structural
Electrical properties

ABSTRACT

Highly uniform and well-dispersed cerium oxide nanoparticles are successfully synthesized by simple precipitation method using cerium nitrate and ammonia. Effect of annealing temperature on the crystallite growth of cerium oxide nanoparticles is investigated by PL, XRD, FTIR, SEM, TEM, XPS, TG–DTA and *I–V* studies. Cubic fluorite crystallites are detected by X-ray diffraction pattern with preferred orientation along (1 1 1) direction. Annealing temperature affects the crysrallinity and structural parameters like grain size, texture coefficient, and dislocation density. The activation energy of cerium oxide (CeO_2) nanoparticles during annealing is found to be 1.004 eV. PL spectra revealed that strong and broad emission band is observed at 425 nm due to the presence of blue shift in the visible region. Large agglomerated spheroid crystallites are obtained with the typical size in the range 4–12 nm. XPS spectrum confirms the existence of Ce^{4+} oxidation states in Cerium oxide nanoparticles. The activation energy is calculated as 0.984 eV.

1. Introduction

Nanomaterials contain particles with one dimension in the nanometer regime. Now days, there is a growing interest from the scientific community in the applications of these nanomaterials which is 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 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].

Several methods have been adopted for the preparation of ultrafine ceria nanoparticles including azeotropic distillation [6], Co precipitation [7], glycine–nitrate combustion [8,9], glycothermal decomposition [10], hydrothermal [11–13], pyrolysis [14], reverse micelles [15], sol–gel [16,17], sonochemical [18,19], solvothermal [20] and simple precipitation method [21–24]. Among these methods, ammonia precipitation method is widely adopted in laboratories because of its low preparation cost and simple process. It has fascinated substantial attention of researchers because of its wide band gap and considered as a promising material for automobile exhaust [25], buffer layers [26], catalyst [27,28], filters [29], gas sensors [30,31], NO removal [32], solid oxide fuel cells (SOFC) [33–35].

In the present work, the crystallographic structures, surface morphology, optical properties and *I–V* characteristics as a function of annealing temperatures prepared by chemical precipitation method using cerium nitrate as the source material are investigated and presented.

2. Experimental details

Cerium oxide (CeO_2) nanoparticles are prepared using cerium nitrate and aqueous ammonia purchased from HIMEDIA, Mumbai. In the process of synthesis, 0.1 M of cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) is dissolved in 50 ml of deionized water and strongly stirred for 30 min, then 25 ml of aqueous ammonia solution is added dropwise to the above solution for 20 min and stirred for 10 h at room temperature. Interesting changes appeared in color

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http://dx.doi.org/10.1016/j.apsusc.2013.02.062

of the solution when precipitant was added to cerium nitrate solution. Initially at low pH slurry is light brown, possibly due to Ce^{3+}, which is turned into light white–black in 2 h, then turned into brown after 3 h, then light or orange for 5 h, finally light yellow due to the formation of Ce^{4+} in the presence of oxygen. The obtained slurry is filtered and washed several times with deionized water and ethanol. The washed precipitate is dried in oven at 60 °C for 3 h. The dried powders are well grinded for 15 min using mortar pestle and annealed to 450 and 900 °C for 2 h to enhance the crystallinity of the samples. The synthesis mechanisms may be described by the following reactions.

$$Ce(NO_3)_3 \cdot 6H_2O + 2NH_4OH \xrightarrow{450-900\,^{\circ}C} CeO_2 + 2NH_4(NO_3) \uparrow + NO_2 \uparrow + 7H_2O \uparrow$$

A precipitate is obtained by adding solution to NH_4OH. The formation of cerium hydroxide after oxidation of Ce^{3+} to Ce^{4+} at high pH is obtained and then cerium hydroxide is converted into cerium oxide with the removal of hydroxyl group [22].

Several complementary methods are used to characterize the properties of the obtained samples. The vibrational measurements are carried out at room temperature using the normal KBr disc technique. IR spectra are taken with a Bruker IFS Table 88 spectrometer in the range 4000–400 cm^{-1}. The as-prepared and annealed samples are characterized for their purity and crystallinity by X-ray powder diffraction (XRD) using XPERT-PRO, Bruker AXS D8 Advance X-ray diffractometer. TG/DTA measurements are carried out with the help of SII nanotechnology, TG/DTA 6200 at nitrogen atmosphere. Samples weighing 20.0 ± 0.1 mg are heated in a ceramic sample boat up to 900 °C at 20 °C/min and in a stream (40 ml/min) of nitrogen gas. Surface morphology of the samples are analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using JEOL Model JSM-6390 LV instrument for high resolution surface imaging and Philips CM20 super twin microscope respectively. Specimens for TEM are prepared by ultrasonic dispersion of some powder sample in ethanol and putting a droplet of the suspension on a copper microscope grid covered with carbon. XPS is a straight forward and nondestructive technique for the investigation of chemical and electronic structure of materials. An important advantage of XPS is its ability to characterize the variations in the binding energies of the core level or chemical shifts of the samples. *I–V* characteristics are analyzed with the help of Keithley electrometer 6517B.

3. Results and discussion

3.1. Optical properties

Room temperature photoluminescence spectra of cerium oxide nanoparticles were annealed at 120 °C, 450 °C and 900 °C shown in Fig. 1. The spectra have been recorded at room temperature with an excitation wavelength of 325 nm. It exhibits strong blue emission with a photoluminescence peak at 425 nm and relative weak green emission bands at 466 nm [35]. The investigation showed that the emission bands ranging from 400 to 500 nm for cerium oxide samples are attributed to the hopping from different levels of the range from Ce 4f and O 2p band [36]. The strong emission of the cerium oxide samples at 466 nm is related to the abundant defects like dislocations, which are helpful for fast oxygen transportation. The defects energy levels between Ce 4f and O 2p are dependent on the temperature and density of defects in the crystal [37]. The annealed sample at 900 °C show the strong and sharp emission bands at 425 nm in the blue visible region.

Fig. 2 shows the FTIR spectum of cerium oxide nanoparticles was annealed at 120 °C. It reveals that the group of strong intense bands

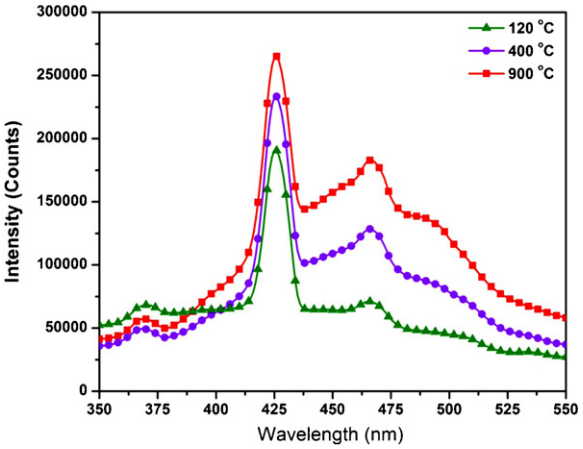

Fig. 1. PL spectra of cerium oxide nanoparticles.

are observed at 3391, 1616 and below 700 cm^{-1}, low intensity groups are observed at 2930–2840 and 1170–1000 cm^{-1} respectively. The observed bands can be assigned as follows: the intense bands at 3391 and 1616 cm^{-1} correspond to γ(O—H) mode of water molecules and γ(OH) respectively. Residual water and hydroxyl groups are usually observed in as-prepared samples and can be eliminated during heat treatment. A group of weak intensity bands centred at 2930 and 2840 cm^{-1} are assigned to γ(C—H) mode of organic moieties and $\gamma(CH_2)$ respectively. Additional bands around 1170–1000 and 960–850 cm^{-1} are most probably associated to the presence of residual organic or the formation of "carbonate-like" species on the ceria surface. A strong band at 700 cm^{-1} which is due to the envelope of the phonon band of the metal oxide (CeO_2) network is also observed [38].

DTA and TGA spectra of the cerium oxide nanoparticles were annealed at 120 °C is shown in Fig. 3. It is observed that Fig. 3, the DTA curves exhibit three major peaks at 68, 188 and 598 °C. The first exothermic peak corresponds to the desorption of physically absorbed water and organic solvent, the second exothermic peak corresponds to the combustion of residual organic species and the third endothermic peak corresponds to decomposition of some residual absorbed species and oxygen loss at higher temperature. TGA curves reveal that the major weight loss upto 4% occurs at 400 °C due to the decomposition of absorbed water and organic species, then small amount of weight loss upto 1% is observed at

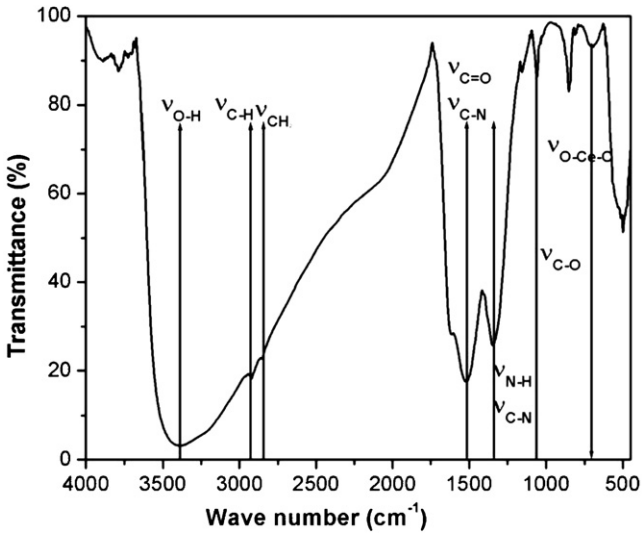

Fig. 2. FTIR spectrum of cerium oxide nanoparticle.