



Fuel-oxidizer ratio tuned luminescence properties of combustion synthesized Europium doped cerium oxide nanoparticles and its effect on antioxidant properties



G. Vinothkumar, R. Amalraj, K. Suresh Babu*

Centre for Nanoscience & Technology, Madanjeet School of Green Energy Technologies, Pondicherry University (A Central University), Puducherry 605014, India

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ABSTRACT

Influential role of fuel to oxidizer ratio (F/O) as the controlling parameter in combustion synthesis of europium doped cerium oxide was studied in terms of defect chemistry, optical property and antioxidant capacity. Europium (5 mol%) doped cerium oxide nanoparticles synthesized by solution combustion in fuel deficient (F/O=0.6, 1.1) and stoichiometric (F/O=1.6) conditions resulted in size ranging from 6 to 25 nm while excess fuel (F/O=2.1) lead to the lower size of 17 nm. Raman spectroscopic analysis showed the formation of intrinsic and europium ion induced extrinsic oxygen vacancies and the defect concentration was found to be decreasing with F/O ratio. Photoluminescence emission was dominated by magnetic dipole transition in F/O=0.6, 1.1 and electrical dipole in F/O=1.6, 2.1 which resulted in a persistent luminescence. Fenton reaction generated hydroxyl radical scavenging activity was influenced by the surface oxygen vacancy concentration and crystallites size. In addition to size and defect, morphology of the nanoparticle plays a significant role in determining the antioxidant efficacy.

1. Introduction

Recent advances in nanotechnology offer formulation of novel nanoparticles in which different functionalities like imaging, sensing, drug delivery and therapy *etc.*, are multiplexed together on a single platform. Cerium oxide (ceria, CeO₂) is one of the rare earth oxide, currently being investigated in biomedical applications such as in biosensing [1], antibacterial activity [2], protection of healthy cells in radiotherapy [3], ocular [4] as well as neuro protection [5] and as an antioxidant due to its superior catalytic performance and biocompatibility. The reactivity of ceria, primarily arise from its ability to switch reversibly between +3 and +4 states mediated by oxygen vacancies in the lattice [6]. When two Ce³⁺ ions replace two Ce⁴⁺ ions, the resultant net positive charge is compensated by the generation of one oxygen vacancy (O²⁻) in the ceria lattice. Bulk, stoichiometric ceria exists predominantly as Ce⁴⁺ and the ratio between the relative concentration of Ce³⁺ and Ce⁴⁺ varies with various parameters such as size, addition of divalent or trivalent dopants, exposing high energy crystal planes by morphology tuning [7,8]. However, in the nano regime, Ce³⁺ concentration increases as a function of decreasing size which makes ceria as an important therapeutic agent unlike the micron sized bulk counterpart [6,9].

Many diseases such as Alzheimer and cancer are reported to be occurring through free radical mediation. Free radicals have unpaired valence electron which makes it highly reactive. Oxygen based free radicals known as reactive oxygen species (ROS) like hydroxyl radicals (•OH) are by-products of normal metabolic processes. The ROS are extremely reactive with biomolecules which leads to oxidative stress, lipid peroxidation and permanent DNA damage [10]. The ability of ceria nanoparticle to scavenge harmful reactive oxygen and nitrogen species such as hydroxyl (•OH), superoxide anion (•O₂⁻), nitric oxide (•NO), hydrogen peroxide (H₂O₂), peroxy-nitrite (ONOO⁻) anion *etc.*, were shown to mimic the natural antioxidant enzymes like superoxide dismutase and catalase [11]. Recently, ceria and trivalent lanthanum doped ceria nanoparticles showed the influence of concentration of Ce³⁺ active sites in enhancing the hydroxyl radical scavenging activity [7,8]. Thus, enhancing the oxygen vacancy in ceria is crucial for tuning Ce³⁺/Ce⁴⁺ ratio for efficient radical scavenging activity.

In spite of the therapeutic potential of cerium oxide, poor luminescent property in the visible region limits the scope for imaging. Several reports are available on improving the visible light emitting character of cerium oxide in the presence of luminescent

* Corresponding author.

E-mail address: sureshbabu.nst@pondiuni.edu.in (K.S. Babu).

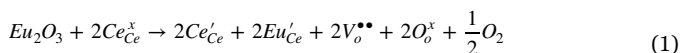
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rare-earth ions such as europium *etc.*, to combine therapeutic and imaging platforms together [12,13]. The advantage of doping rare earth europium ions include biocompatibility, reduced auto fluorescence and low signal to noise ratio [14]. The formation of oxygen vacancies ($V_o^{\bullet\bullet}$) upon doping trivalent europium ions can be represented using Kröger-Vink notation as,



where the Ce_{Ce}^x is neutral Ce in the lattice, $V_o^{\bullet\bullet}$ is the positively charged oxygen vacancy respectively. Substitutional doping of Ce^{4+} with Eu^{3+} results in charge imbalance which is neutralized by the creation of oxygen vacancy (O^{2-}) and Ce^{3+} [13].

Though increase in oxygen vacancy concentration in ceria can be beneficial as an antioxidant, the associated defects can adversely affect luminescent properties. The oxygen vacancies present at room temperature in the nanoparticle acts as luminescent quenching centers [15]. Many reports are available on improving the luminescent properties of doped ceria nanoparticles [12,13]. Our earlier report indicated an enhancement in emission by the minimization of lattice defects upon high temperature treatment albeit with an increase in crystallite size and loss of Ce^{3+} concentration [16]. Recently, it has been reported on the multifunctional ceria doped with europium and iron nanostructures exhibiting excellent luminescent properties on annealing at high temperature [17]. Though higher annealing temperature resulted in an enhancement of luminescent properties, a corresponding reduction in oxygen vacancy and Ce^{3+} concentration makes the ceria nanoparticles less active towards therapeutic application. Hence, the role of oxygen vacancies/surface defects in improving radical scavenging activity as well as quenching the emission property on a multi-functional model based system need to be critically understood for practical application.

Generation of vacancy defects in the lattice can be severely affected by the method of preparation like precipitation, hydrothermal, sol-gel, nature of precursor *etc.*, [2,18,19]. Solution combustion method is a rapid, self-propagating, one pot high temperature synthesis method, offering highly crystalline and homogeneous oxides structures with the flexibility for tailoring the size which in turn affects the associated surface area and defects. In solution combustion method, the reaction between fuel such as urea or glycine with oxidizer (metal nitrates) triggers an exothermic reaction to reach a temperature of 1000 °C in a short span of time. Any deviation from stoichiometry creates either fuel rich or lean environment which influence the resultant temperature and duration of the combustion reaction. Shi *et al.*, investigated the phosphor properties of 60 nm ceria particles with respect to europium concentration (0–16 mol%) using the mixture of nitrate: urea (1:5) and reported a multi fold increase in emission through combustion synthesis than that of conventional solid state reaction which were carried out at 1000 °C for 2 h [20]. However, the relation between fuel-to-oxidizer (F/O) ratio on tuning the size, defects, emission and potential of the material for the radical scavenging efficiency still remains to be explored.

In the present work, a solution combustion method was used to synthesize 5 mol% europium doped ceria nanoparticle with variation in F/O ratio in order to tune the size and oxygen vacancy concentration. We investigated the possibility of achieving enhanced Ce^{3+} concentration by inducing oxygen defects in the lattice through solution combustion method by varying the F/O ratio as the controlling parameter for efficient $\cdot OH$ radical scavenging activity. In addition, the role of contradicting behaviour of oxygen defects in improving antioxidant capacity, while quenching luminescent property and excited state lifetime analysis of Eu^{3+} doped cerium oxide nanoparticles were explored.

2. Experimental details

2.1. Material preparation

Analytical grade metal nitrates $Ce(NO_3)_3 \cdot 6H_2O$ (Himedia, 99.0%), $Eu(NO_3)_3 \cdot 5H_2O$ (Alfa Aesar, 99.5%) and glycine ($CH_2NH_2CO_2H$, Fisher Scientific, 98.5%) were used as oxidizer and fuel, respectively, for the combustion synthesis. The molar ratio between fuel and oxidizer known as fuel-to-oxidizer ratio (F/O) was calculated using the equation given below [21].

$$\phi = \frac{\sum(\text{Coefficient of oxidizing elements in specific formula}) \times (\text{valency})}{(-1) \sum(\text{Coefficient of reducing elements in specific formula}) \times (\text{valency})} = F/O \quad (2)$$

The F/O ratio was varied from fuel lean (0.6 and 1.1), stoichiometric (1.6) and fuel excess (2.1) condition in order to evaluate the effect of fuel content on the structural, morphological and surface properties while maintaining the europium concentration at 5 mol%. In a typical synthesis, calculated oxidizer (2.5217g of cerium nitrate and 0.1309g of europium nitrate and fuel (0.2755g of glycine) for F/O of 0.6, were dissolved in 100 ml of doubly distilled water and sonicated for 5 min. Further, the solution was heated at 80 °C in an oven until the solution becomes a transparent gel. The gel was then transferred to a hot plate maintained at 400 °C to initiate the combustion reaction. Exothermic reaction between fuel and oxidizer lead to the formation of pale yellowish powder. The resultant powder was washed thrice with double distilled water and centrifuged at 10,000 rpm and subsequently dried at 80 °C. Similar procedure was adopted to prepare samples with varying F/O ratio of 1.1, 1.6 and 2.1.

2.2. Characterization

Crystal structure of the nanoparticle was analysed by X-ray diffraction (XRD) using Rigaku Ultima IV X-ray diffractometer with monochromatic $Cu-K_\alpha$ radiation ($\lambda=0.154056$ nm) at a scanning rate of 2°/min. The mean crystallite size was calculated by Scherrer formula

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (3)$$

where β represents full width at half maximum, θ is the Bragg's angle. Surface morphological details of the sample was observed with the help of scanning electron microscopy (SEM, Hitachi S-3400N) operated at 30 keV. High resolution transmission electron microscopic (HRTEM) images were obtained by using FEI-Tecna G² 20 S-TWIN operated at 200 keV attached with Bruker XFlash 6T130 detector. Room temperature Raman spectra of the samples were recorded using confocal Raman spectrometer (Renishaw, RM 2000) with an excitation wavelength of 514.5 nm from an Ar⁺ ion laser source. Optical absorption spectra were recorded using Perkin Elmer UV Lambda S650 spectrophotometer. A Hitachi-7000 Spectrofluorimeter equipped with a 150 W Xe lamp was used to study the photoluminescence properties at room temperature. Luminescence lifetime measurements were carried out with Horiba Jobin Yvon Fluorolog-FL3 equipped with a 450 W Xenon lamp having pulsed nano LED source and a spectral resolution of approximately 2 nm.

2.3. Hydroxyl radical scavenging activity

Methyl violet (MV) dye (SR Laboratories), tris-HCl buffer (SR Laboratories, 99.0%), iron sulfate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (35% H_2O_2 , HIMEDIA) were used to elucidate the hydroxyl radical scavenging activity. A Fenton type reaction was used to generate hydroxyl radicals which can directly degrade the methyl violet dye in the absence of nanoparticles. The change in degradation of methyl

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