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Effect of Gd dopant concentration on the defect engineering in ceria nanostructures

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ABSTRACT

In this study, the fabrication and characterization of pure and gadolinium (Gd) doped ceria nanostructures ($Ce_{1-x}Gd_xO_{2-\delta}$ where $x = 0.05$, 0.1 and 0.2) are investigated. The origin of defect formation has been systematically investigated by XRD and UV-Visible Raman. All the fabricated ceria are found to be "Nanosponge" morphology which is observed by using FESEM technique. The charge transfer of O^{2-} ions and Ce^{3+}/Ce^{4+} in the ceria host due to these defect structures are studied by UV–DRS. Impedance analysis is showed an enhanced ionic conductivity for 5% Gd doped ceria compared to other concentration of Gd, revealing that the dopant concentration is a critical parameter in engineering a large number of vacancy defects in ceria nanostructures.

1. Introduction

Scaling down the conventional materials from microscale to nanoscale has drawn much attention in material research as they show interesting phenomenon at the nanoscale. In particular, the metal oxides nanomaterials have received enormous attention owing to their multifunctional properties. Among the metal oxides, interests in ceria (cerium oxide, CeO_2)-based nanomaterials have been growing very rapidly as it is one of the most reactive rare-earth metal oxides in the lanthanide series of the periodic table. Ceria based materials at the nanoscale show enhanced activity which finds applications in solid oxide fuel cell, catalysis and oxygen storages [1–4]. These applications emerge due to the formation of oxygen vacancy defects in the material. Engineering of such defect architectures is highly desirable at the nanoscale to enhance such phenomena [4]. In the past decade, rare earths (RE) such as La, Pr, Sm, Gd, Tb, Er, Dy and Nd modified ceria have been extensively utilized in the field of catalysis and solid oxide fuel cells (SOFCs) [5–10]. Many of these applications are promoted due to the presence of oxygen vacancy defects which are created due to the insertion of RE ions into the CeO_2 lattice [11,12]. Efforts have also been made to investigate the effect of these dopants on the amount, mobility and distribution state of oxygen vacancy defects in CeO_2 based nanomaterials [13,14].

Besides, the preparation route also determines structural and surface defect properties of cerium oxide and thus there is a growing interest in obtaining unique morphologies and controlling such morphologies to enhance the properties at nanoscale. For the past few years, cerium oxide nanostructures have been produced by room temperature solution precipitation [15], sonochemical synthesis [16], hydrothermal crystallization [17], micro-emulsion [18], mechano-chemical processing [19], thermal decomposition [20], spray pyrolysis [21], sol–gel method [22], thermal hydrolysis [23], solvothermal synthesis [24], simple solid–liquid interface reaction route [25] by etching $Ce(OH)_3$ nanotubes/nanorods with H_2O_2 [26] and using carbon nanotubes as templates by a liquid phase deposition methods [27–29]. These techniques are rely mainly on salt–solvent mediated high temperature or high pressure or surface capping agent or templates. For these reasons, an alternate simple approach for low-cost, room-temperature, large-scale, controlled growth of ceria nanostructures at atmospheric pressure is essential. Also, well-defined ceria nanostructures with different morphologies have been successfully fabricated by above mentioned methods. Recently, Sun et al. prepared monodispersed flowerlike CeO_2 microspheres from ethanol steam by a novel hydrothermal method [30]. However, engineering oxygen vacancy defects in the ceria is very essential as it plays a significant role in the reactivity of the cerium oxide surface for their catalytic applications [30,31]. This oxygen vacancy defect is mainly concerned with the migration of oxygen ions in the ceria host which creates the ionic conduction. It has been shown that the ionic conductivity of doped ceria can be significantly influenced by the dopant type [32–34]. Also it is reported that

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there exists an *optimum radius* of the dopant for the enhanced ionic conduction [35–37]. For an example, in a comparative study of Gd and Y-doped ceria, the larger conductivity of ceria is observed when the Gd concentration is lower than 25% and smaller conductivity observed for Gd concentration is greater than 25% compared to the Y doped ceria at the same concentration level. Zhang et al. [38] explained that this trend has occurred due to the ionic conduction in heavily doped ceria is dominated by the formation of nanosized domains, instead of being dominated by the dopant-oxygen vacancy association.

Therefore, to address these such interesting issues, this present study reports a conceptual approach to enhance the ionic conductivity of ceria by engineering vacancy defects by doping with rare earth element gadolinium with different concentrations. Consequently, this study reveals that, along with the so-called *optimum radius*, there exists an *optimum concentration* of the dopant for the better ionic conduction. It is also found that, even the range of concentrations of a single dopant (e.g. gadolinium) introduced in ceria, can influence the ionic conductivity. Therefore, the samples of pure and Gd doped ceria ($Ce_{1-x}Gd_xO_{2-\delta}$) with different concentrations of Gd (5%, 10% and 20%) are prepared by the precipitation method. Subsequently, the thermal decomposition temperature is estimated by thermo-gravimetric analysis (TGA) (NETSCH STA 409C). The structural and morphological analyses are done by powder X-ray diffraction (XRD) (Pananalytical Instruments) and FESEM techniques (Hitachi S6600) respectively. The surface defect information and optical properties are obtained by UV-Visible Raman spectroscopic (HORIBA scientific) and UV-Diffuse reflectance spectroscopic analysis (Perkin Elmer UV-Vis 650). Finally, the ionic conductivity is measured using the impedance spectroscopic technique (PSM 1735).

2. Experimental

Fig. 1 depicts the preparation flow chart of pure and Gd doped ceria. To prepare the samples, cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) is dissolved in isopropyl alcohol (IPA) and triethanolamine ($(C_2H_5OH)_3N$) is used to precipitate the solution. To introduce gadolinium (Gd) ions into CeO_2 host, gadolinium nitrate (Gd $(NO_3)_3{\cdot}6H_2O$) is taken in required concentrations ($Ce_{1-x}Gd_xO_{2-\delta}$ where $x = 0.05, 0.1$ and 0.2) and added in the reaction mixture. In the typical procedure, 0.1 M of cerium (III) nitrate hexahydrate is dissolved in 50 ml of IPA and then the solution is dripped in 0.3 M of triethanolamine under vigorous stirring at room temperature until a homogeneous solution is obtained. The stirring is continued for 3 h for the complete precipitation and the solution is filtrated out. Subsequently, the precipitate is washed with solvent IPA and allowed to dry at room temperature. The dried precipitate is annealed at 600 °C for 3 h. The final powders obtained are pale yellow in color. The same procedure is repeated to prepare Gd doped CeO_2 nanostructures. The gadolinium nitrate of required quantity is taken in the cerium nitrate-IPA solution and precipitated by triethanolamine (All chemicals used for synthesis are from Alfa Aesar with 99.9% purity).

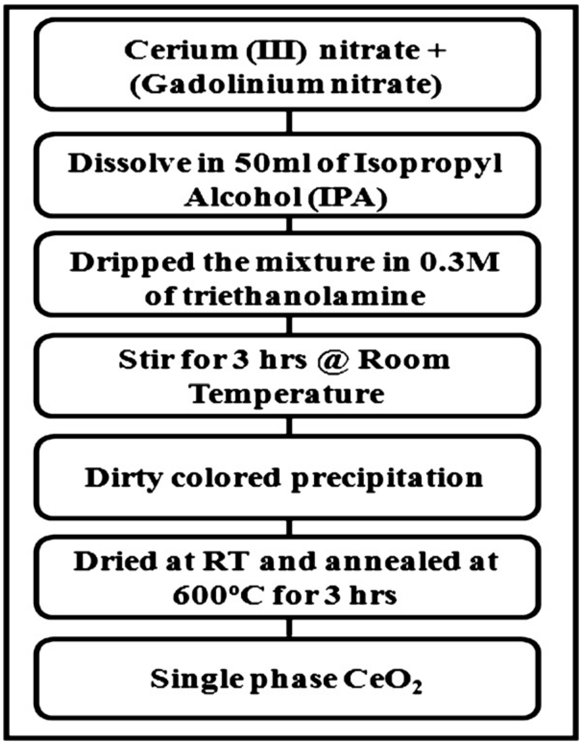

Fig. 1. Synthesis flowchart of pure and Gd doped ceria nanoparticles.

3. Results and discussion

3.1. Thermal decomposition study

The freshly as prepared product is subjected to thermo-gravimetric analysis (TGA) to find out the decomposition temperature (Fig. 2). It is observed that there are three stages of weight loss in the temperature range from 100 to 200 °C, at 270 °C and 300 to 600 °C. The TG curve shows a minor weight-loss step in the temperature range 100 °C and 200 °C which is due to the loss of water and nitrate ions. The drastic weight loss at 270 °C is due to the loss of carbon and triethanolamine contents. The weight loss observed between 300 °C and 600 °C is due to the loss of residual carbon. Almost no weight loss is observed above 600 °C which suggests the formation of impurity free CeO_2 phase. Hence, the annealing temperature is fixed as 600 °C and all the Gd doped ceria are annealed at this same temperature for 3 h. The XRD results are revealed that the estimated annealing temperature and time are optimum to yield pure and doped ceria with good crystallinity and impurity free.

3.2. Morphological analysis

Fig. 3(a–d) depicts the FESEM images of the undoped and doped ceria nanostructures. In all nanostructures, the "*Nanosponge*" with porous morphology is observed. However, the porous morphology of ceria tend to decrease with the increase of Gd concentrations. Messing et al. [39] have reported that powders derived from metal

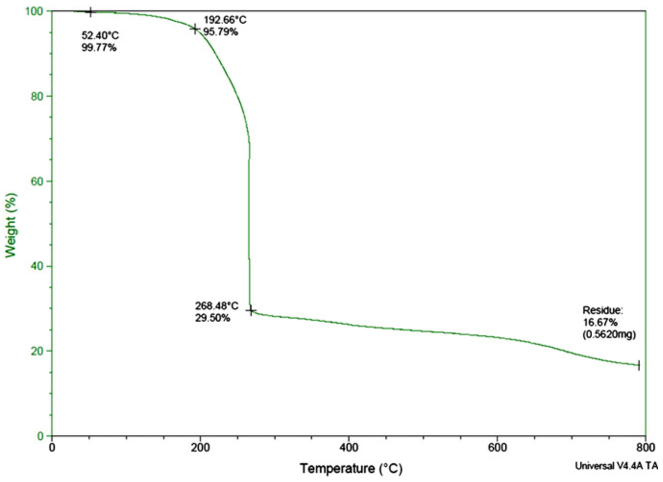

Fig. 2. TGA analysis of the as prepared ceria samples.