ISSN 1067-8212, Russian Journal of Non-Ferrous Metals, 2018, Vol. 59, No. 1, pp. 111–116. © Allerton Press, Inc., 2018.

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

Fabrication of Cerium Oxide Nanoparticles by Solution Combustion Synthesis and Their Cytotoxicity Evaluation[1]

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Received April 17, 2017

Abstract—The diverse abilities such as the antioxidant effect of cerium oxide nanoparticles (CeO_2-NPs) have encouraged researchers to pursue CeO_2-NPs as a therapeutic agent to treat a number of diseases, including cancer and diabetes. The synthesis method of CeO_2-NPs affected on its abilities. In this study, nanosize ceria powders were synthesized by combustion of aqueous containing corresponding cerium nitrate, ammonium nitrate, and glycine redox mixtures. Solution combustion synthesis is a fast and cost-efficient process with high purity product. The crystallite structures were characterized by various methods, including X-ray diffraction technique, high-resolution scanning electron microscopy, transmission electron microscopy, and UV–vis spectroscopy technique. The combustion was flaming and yields voluminous oxides with nano size (20–30 nm). In addition, no diffraction patterns that are characteristic of impurities were observed, indicating the purity of the CeO_2-NPs. In vitro cytotoxicity studies on L929 cells, a non-toxic effect in all concentration (up to 1000 μg/mL) was indicated and it can be believed that this nanoparticle will have viable applications in different medical fields.

Keywords: CeO_2, nanoparticle, solution combustion synthesis, cytotoxicity

DOI: 10.3103/S1067821218010170

1. INTRODUCTION

Ceria (cerium oxide, CeO_2) is a cubic fluorite-type oxide in which each cerium site is surrounded by eight oxygen sites in fcc arrangement and each oxygen site has a tetrahedron cerium site. Recently [1], vacancy-engineered ceria nanoparticles have emerged as a fascinating material due to its wide applications and unique properties such as UV absorbing ability [1], high thermal stability [2], high hardness, specific chemical reactivity [1], ability to store and transport oxygen as large oxygen storage capacity [3], high refractive index, and the quick and expedient mutation of the oxidation state of cerium between Ce(III) and Ce(IV) [3, 4], polishing materials [5] and medicine [5]. A further advance in nanoceria or cerium oxide nanoparticles (CNPs) are gaining interest in plants to increase photosynthesis via suppression of reactive oxygen species (ROS) [6]; also as an antioxidant, there are a number of reports and Biomedicine concerning the protective effects of nanoceria in certain neurological disorders [7], to provide cells protection from radiation [8], to be cytotoxic to cancer cells [9] and show promise for addressing the various radical associated problems driving and resulting from diabetes [9].

Several synthesis routes have been developed to produce nanocrystalline CeO_2-based powders, including hydrothermal synthesis [10, 11], sol–gel method [5, 12], microwave-assisted sol–gel [13], mechanochemical synthesis [14], polyvinyl pyrrolidone (PVP) solution route [15] electrochemical synthesis [16] and combustion synthesis [17, 18]. However, most of these techniques usually include many sophisticated processes and consume much longer time. Moreover, they have not received much commercial attention due to lacking reproducibility, reliability, and cost-effectiveness [19]. Solution combustion synthesis has an edge over other methods as it is considered simple, instantaneous, single-step, and energy saving [20, 21]. Combustion synthesis (CS) is characterized by the fact that once the initial exothermic reaction mixture is ignited by means of an external thermal source, a rapid (typically from 0.1 to 10 cm/s) high-temperature (1000–3000°C) reaction wave propagates through the heterogeneous mixture in a self-sustained manner leading to the formation of the solid material without involving any additional energy. A combination of CS and reactive solution approaches

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lead to solution combustion (SC) synthesis methods [21]. Typically, SC involves a self-sustained reaction in solutions of metal nitrates and different fuels, which can be classified based on their chemical structure, i.e. the type of reactive groups (e.g. amino, hydroxyl, and carboxyl) bonded to the hydrocarbon chain. The reaction between fuel and oxygen containing species, formed during the decomposition of the nitrate species, provides high-temperature rapid interaction. In a typical scheme, an initial liquid solution of desired reagents, after preheating to a moderate temperature (150–200°C), self-ignites along the whole volume (VCS mode) leading to the formation of fine solid products with tailored composition [22].

Mokkelbost et al. [18] studied the synthesis of high-quality CeO_2-NPs-based powders by the glycine/nitrate combustion method. In this study, CeO_2-NPs was produced after calcination of as-SC prepared powder at 550°C for about 12 h and the average size was about 22 nm. In another study, Ravishankar et al. [20] reported the synthesis of CeO_2 nanoparticles using ceric ammonium nitrate as an oxidizer and ethylenediaminetetraacetic acid (EDTA) as a fuel. These nanoparticles exhibit good photocatalytic degradation and antibacterial activity. The average size of the nanoparticles is found to be 42 nm.

As mentioned above, nanoscale CeO_2 is increasingly used for industrial and commercial applications. Because of its increasing potential for consumer and occupational exposures, a comprehensive toxicological characterization of this nanomaterial is needed [23]. While most in vitro cellular assays show minimal toxicity for CeO_2-NPs but Demokritou et al. [23] reported that CeO_2-NPs can induce the cytotoxic effect. A recent study by Pulido-Reyes et al. [6] demonstrated that neither shape, concentration, surface charge (ζ-potential), synthesis method nor the nominal size of CeO_2-NPs had any influence in the observed toxic effects. Karakoti et al. [24] have reviewed the effect of the preparation method on CeO_2 toxicity and have indicated that a synthesis at low temperature often leads to less toxic ceria particles. They also found that the effects of chemicals can be altered by high temperatures. This was also observed by Peng et al. [25] who compared the cytotoxicity of CeO_2-NPs synthesized by either hydrothermal or precipitation methods. The hydrothermally prepared CeO_2-NPs produced cytotoxicity effect.

In most studies, CeO_2-NPs were synthesized with cerium nitrate as an oxidizer and inorganic component as a fuel. In this study, we report the synthesis of CeO_2-NPs using cerium(III) nitrate hexahydrate, glycine, and ammonium nitrate. In a previous study [18], the influence of glycine/nitrate ratio on crystallite size, surface area, and carbonate species remaining from the combustion reaction has been studied. In this study, we added ammonium nitrate to glycine/nitrate solution for the first time to evaluate carbonate species remaining after solution combustion. Ammonium nitrate was used as a fuel because it is cheap and rich in nitrogen, hydrogen, and oxygen without carbon which is released as their corresponding oxides during combustion and no carbonate species formed. The release of produced gases leads to the formation of highly porous CeO_2-NPs with a greater surface area. The structural features of the CeO_2-NPs were determined by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and UV–vis absorption spectroscopy. Also, in this study, an attempt was made to evaluate cytotoxic effect of synthesized CeO_2-NPs by MTT assay.

2. EXPERIMENTAL PROCEDURE

All the raw materials used were of analytical grade and were utilized without any purification. Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and glycine were purchased from Merck (Germany) and ammonium nitrate was purchased from Fluka (Germany). All glasswares utilized in the experiments were cleaned with ethanol, washed thoroughly with distilled water, and dried before use. Double distilled water was used in all experiments.

CeO_2-NPs were synthesized by the combustion of aqueous solutions containing stoichiometric amounts of cerium(III) nitrate, glycine and ammonium nitrate. Stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valences of the oxidizer and the fuel keeping the O/F ratio unity [26]. The aqueous solution containing the redox mixture in a glassware when introduced in a hot plate with magnetic stirrer price heated to 150°C, boils, foams and undergoes combustion with a flame to produce the ceria. The products of combustion are similarly fluffy and voluminous.

If combustion reaction was done completely, the theoretical reaction for the formation of ceria with ammonium nitrate and glycine can be written as a reaction (1):

$$\begin{aligned} Ce(NO_3)_3{-}6H_2O_{(eq)} + 2C_2H_5O_2N_{(eq)} \\ + NH_4NO_{3(eq)} \rightarrow CeO_{2(s)} \\ + 4CO_{2(g)} + 13H_2O + \frac{7}{2}N_{2(g)}. \end{aligned} \quad (1)$$

Specified fuel, such as glycine also form complexes with metal ions to modify the mixing rate of the reactants [27].

The phase evaluation after solution combustion synthesis was investigated by X-ray diffraction analysis using a Philips X'PERT multipurpose X-ray diffractometer (Philips Analytical BV, Almelo, The Netherlands) with CuK_α radiation (0.15405 nm). The crystallite size was estimated from X-ray line broadening measurements, the calculation was done by (110) dif-

fraction line of CeO_2 crystal according to the Scherrer formula [28]:

$$D = 0.9\lambda/\beta\cos\theta, \quad (2)$$

where D is the crystallite size, λ is the wavelength of the X-ray diffraction, β is the FWHM, and θ is the angle of diffraction.

The morphology and particle size of synthesized CeO_2-NPs were characterized by high-resolution scanning electron microscopy (MIRA3 TESCAN) and transmission electron microscopy (Philips EM208S). The absorption of the CeO_2-NPs in the UV region was performed by UV–vis (Evolution 300® Thermo Fisher Scientific).

To evaluate toxicity of synthesized CeO_2-NPs, L929 cells (Pasteur Institute, Tehran, Iran) were maintained in a 90% humidified atmosphere containing 5% carbon dioxide at 37°C. Cells were cultured in high-glucose Dulbecco's modified Eagle's medium (DMEM) (4.5 g/L) with 10% (v/v) fetal bovine serum, 100 units/mL penicillin and 100 mg/mL streptomycin. The cell viability was obtained by a modified 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium (MTT) assay [29]. For MTT assay, five thousand cells were seeded in each well of a 96-microwell plate and treated with various concentrations of CeO_2-NPs (0–1000 mg/mL) for 24 h. MTT solution in phosphate-buffered saline (PBS, 5 mg/mL) was added to a final concentration of 0.05%. After 3 h, the formazan precipitate was dissolved in DMSO. The absorbance at 570 and 620 nm (background) was measured using a StatFAX303 plate reader [11]. All experiments were performed in triplicate; the percentage of viable cells was calculated as the mean ± SD and as a percentage of non-treated control groups, which was assumed to be 100% and morphological deformations of the cells were also examined.

3. RESULTS AND DISCUSSION

A combustion synthesis reaction is influenced by the type of fuel and the fuel-to-oxidizer ratio. Depending upon the fuel used and the type of metal ion involved, the nature of combustion differs from flaming (gas phase) to non-flaming (smoldering and heterogeneous) type. Flaming reactions could be attributed to the generation of gaseous products like nitrogen oxides (NO_x) by metal nitrates and HNCO, NH_3, CO, etc., generated by fuels like urea [21]. In this study, glycine and ammonium nitrate were used as fuels for the first time and the nature of combustion was the flaming type.

Figure 1 showed XRD pattern of product synthesized using the solution combustion process from the redox mixture of cerium(III) nitrate, glycine and ammonium nitrate were performed to identify crystalline phases and estimate the crystalline size. As presented in Fig. 1, the characteristic peaks of powders

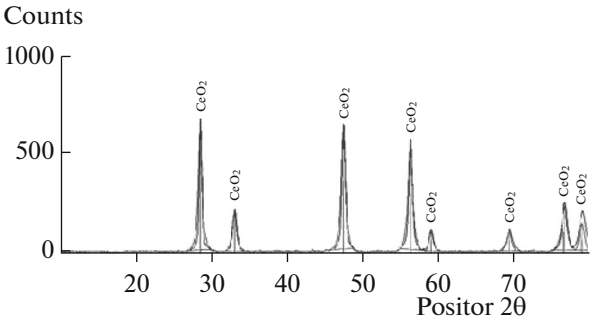

Fig. 1. The XRD pattern of synthesized CeO_2-NPs.

agree well with those of ceria (CeO_2, JCPDS 00-034-0394), confirmed that the main crystal phase of the combustion synthesized powders is ceria. The CeO_2-NPs is a kind of typical calcium fluoride (CaF_2) crystalline structure with space group Fm3m [5]. The represented peaks of cubic fluorite structure of CeO_2 correspond to the (111), (200), (220), (311), (222), (400), (331) and (420) at 2Θ = 29.2°, 33.1°, 47.5°, 57.6°, 59.0°, 64.5°, 76.7°, 79.2° and 88.4°, respectively that indicated using the standard data [30, 31]. Also, the synthesized CeO_2-NPs represent very well-defined crystalline lattice fringes and the XRD peaks are acuminate, indicating that the crystallinity of CeO_2-NPs is obtained during solution combustion synthesis without additional processes such as calcination, etc. In addition, no diffraction patterns of any other phases detected such as cerium hydroxides, carbonate species, and other byproducts phases as an impurity, indicating the high purity of the product. In a previous study [18], CeO_2-NPs with carbonate species as an impurity was synthesized. To remove this impurity and production of high purity CeO_2-NPs, synthesized CeO_2-NPs were thermally treated at 550°C. Whereas, high purity CeO_2-NPs were synthesized in this study by addition of ammonium nitrate as fuel.

The mean size of ordered ceria crystallite obtained by Debye–Scherrer equation as presented in the Eq. (2). It was obtained that the average diameter of the CeO_2-NPs crystal was about 18 nm.

Optical response of the ceria nanoparticles was evaluated via UV–vis absorption spectroscopy, and the result was presented in Fig. 2. The absorbance spectra were recorded for the nanoparticles dispersed in water. The good absorption of the ceria nanoparticles located at 318 nm. Also, at the UV region due to the charge-transfer transitions from O 2*p* to Ce 4*f*, which overruns the well-known f–f spin–orbit splitting of the Ce 4*f* state [1–5]. The good absorption of the ceria that prepares by SCS in the UV region corroborated the applicability of this CeO_2-NPs in such biomedical application such as sunscreen protective or disinfection in ointments [5].

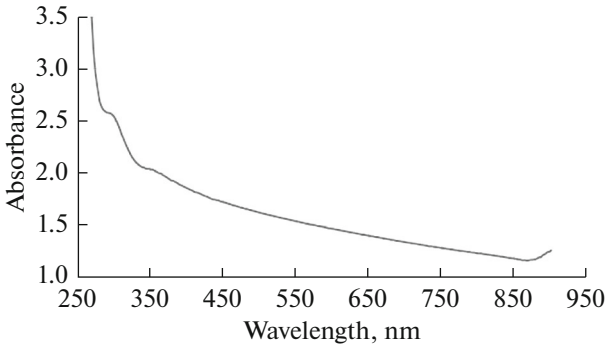

Fig. 2. UV–vis absorption spectroscopy of CeO_2-NPs.

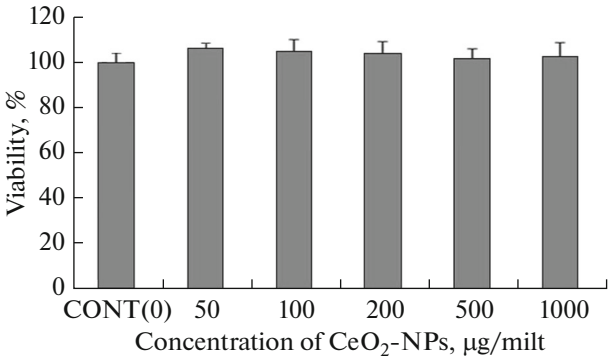

Fig. 4. The cytotoxicity effect of CeO_2-NPs.

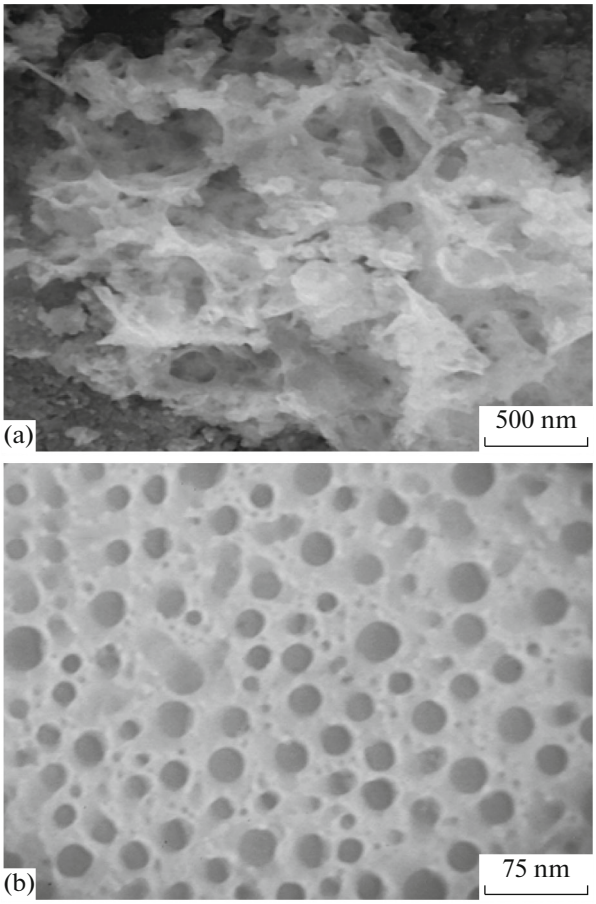

Fig. 3. Microscopy images of CeO_2-NPs synthesized via solution combustion method. (a) FESEM image and (b) TEM bright field image.

Figure 3a show the FESEM images of CeO_2-NPs synthesized by solution combustion method. This type of porous network with a lot of voids is typical of combustion-synthesized powders due to escaping gases. The TEM bright field image (Fig. 3b) shows that the particles are almost spherical in shape, and the average nanoparticle size is found to be 20 nm. The particle size of synthesized CeO_2-NPs in this study is less than previous studies which used one fuel such as Ravishankar et al. (42 nm) [20] and Mokkelbost et al. (22 nm) [18]. This result confirmed that more escaping gases reduced the particle size.

The cytotoxicity effect of CeO_2-NPs was evaluated on L929 cell line. This cell line was treated for 24 h with different concentrations of CeO_2-NPs (0–1000 μg/mL). As seen in Fig. 4, in all concentrations, no significant cytotoxic effect was observed in the L929 cell line. This result confirmed that CeO_2-NPs synthesized via SCS have the potential to medicinal applications. Significant differences were established at $p < 0.05$. Recent findings suggest that further complicating toxicity interpretations are the effects of the synthesis methodology; various manufacturing processes may incorporate additives and solvent chemicals that are not completely removed from the final product [32]. Bushra Alam et al. [33] reported that synthesized CeO_2-NPs by sol–gel method with three different raw materials as the source of cerium, ($Ce(NO_3)_3$, $CeCl_3$, and $Ce(CH_3COO)_3$) were toxic. In contrast, investigations by other researchers concluded that there was no apparent toxicity due to CeO_2 nanoparticles [17, 20]. Differences in reported toxicity can be ascribed to many factors. These can include the origin of the raw materials and methods used for their synthesis as well as the procedures employed to evaluate toxicity and can make it difficult to form conclusions.

Based on the results of this study, the solution combustion synthesis appears to be well suited for the synthesis of CeO_2-NPs the salient features including preparation of CeO_2-NPs at very low temperatures, homogenous and crystalline powders, less agglomeration and large quantities of CeO_2-NPs can be synthesized relatively cheaply. Also, this method is really fast and causes to synthesize high purity CeO_2-NPs with no cytotoxicity effect by using cheap raw materials. Moreover, CeO_2-NPs synthesized in this study had no toxicity.

4. CONCLUSIONS

In this study, the following conclusions can be made from the present research:

• Solution combustion synthesis method has been successfully established for the synthesis of CeO_2-NPs. This method is found to be rapid, convenient and efficient.

• One interesting point of this study is that the average particle size of synthesized powder calculated with the help of XRD pattern and TEM images is less than 30 nm.

• No impurity phases such as cerium hydroxides and other byproducts phases were observed and high pure CeO_2-NPs were synthesized.

• The MTT assay results confirmed that CeO_2-NPs have no significant cytotoxic effect in the L929 cell line and have the potential to medicinal applications.

ACKNOWLEDGMENTS

This study was supported by Arak University.

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