

***Garcinia Mangostana* Peel Extract as Sustainable Fuel Source on Ceria Synthesis under Hydrothermal Condition**

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ABSTRACT

Cerium (IV) oxide or ceria (CeO_2) was fabricated by heating an aqueous extract of *Garcinia mangostana* and cerium (III) nitrate in hydrothermal autoclave reactor at 200 °C for 3 hours, followed by calcination at 600 °C for 5 hours. The powder X-ray diffraction (XRD) pattern of the precipitate from cerium(III) nitrate under hydrothermal reaction conditions shows no clear XRD peaks, indicating its amorphous nature. In contrast, the products from the calcinated samples exhibit XRD peaks, which correspond to cubic fluorite structure with an average crystal size of 7.55 nm. The elemental mapping using the energy-dispersive X-ray (EDX) analysis reveals the main elements present were cerium and oxygen, with minor impurities in low amounts. The presence of *Garcinia mangostana* extract is predicted to be the key component and fuel source to obtain CeO_2 particles with narrow crystal size.

Key word: ceria, CeO_2 , fuel source, *Garcinia mangostana*, hydrothermal.

INTRODUCTION

The hydrothermal method is one of the most popular techniques for the synthesis of cerium(IV) oxides (CeO_2) or ceria due to its simplicity and low cost. A number of developments and modifications of this methodology have been reported. One of the such approaches is the hydrothermal synthesis of ceria from cerium(IV) and cerium(III) salts. It has been shown that the CeO_2 product obtained from Ce(IV) salts was isolated as fine powder whereas the same material obtained from Ce(III) salts was coarse [1]. A big challenge in the production of ceria is avoiding the aggregation of particles. As a result, a number of methods such as addition of surfactant [2] capping agent, modifying the reaction temperature and calcination have been reported [3].

At present, much attention is given to the development of methods for the production of advanced materials based on bio-resources. The main reasons for this are the necessity to decrease the use of costly synthetic agents, reduction of the preparation time and improvement of the quality of the target materials. Green synthesis methods for the production of ceria are preferred as they offer advantages of cost-effectiveness and simplicity. Other benefits of using ecological approaches include high yields and reduced production time [4]. Much of the current literature focuses on the development of green synthetic methods for the production of rare earth oxides, particularly ceria. Some examples

of such approaches include synthesis of ceria nanoparticles using *Aloe barbandosis* Miller gel [5], *Paseolus vulgaris* [6], *Gloriosa superb* [4], and *Azadirachta indica* [2] extracts. In addition, agarose polymers have been shown to mediate the synthesis of CeO₂ via a sol–gel method [7]. Starch has also been described as a capping agent to give ultrafine and uniform CeO₂ nanoparticles [8]. Furthermore, dextran has been used for coating and stabilizing of CeO₂ nanoparticles [9]. A different established approach involves the use of the *Olea europaea* plant extract as a bio-capping agent. Ceria produced using this methodology showed good photocatalytic properties and excellent biocompatibility for phyto-cultures [10-11]. Moreover, ceria synthesized using *Salvia macrosiphon* seed extract displayed good photocatalytic properties on the rhodamine B degradation. The hydroxyl and superoxide anion radicals resulting from the ceria reaction react with organic dye molecules and cause decomposition of the substance [12]. It is noteworthy that the development of synthetic methods for the production of CeO₂ remains a challenge for researches. In this study, we utilized the *Garcinia mangostana* peel extract as a fuel for the synthesis of ceria.

EXPERIMENT

Chemicals and instrumentation

Cerium(III) nitrate was purchased from Merck and used without further purification. *Garcinia mangostana* (mangosteen) peel was obtained from a traditional market in Bengkulu, Indonesia. Demineralized water was used to make the mangosteen peel extract and to wash the precipitated materials obtained at the end of hydrothermal reaction. The product was analyzed using X-ray diffraction (XRD) (XPRT POWDER PANalytical PW30/60; $2\theta = 10^\circ - 80^\circ$), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM 6510 LA), and Fourier-transform infrared spectroscopy (FTIR) (Bruker, scan range of $4000\text{ cm}^{-1} - 500\text{ cm}^{-1}$).

Experimental Procedure and Product Characterization

Typically, mangosteen peel extract was obtained by boiling the peels powder (2 g) in demineralized water (50 mL) for 20 minutes. The CeO₂ particles were prepared using the following procedure: cerium(III) nitrate (5 g) was dissolved in a mangosteen peel extract solution (25 mL). The mixture was transferred to a hydrothermal autoclave reactor equipped with a magnetic bar. The autoclave was heated to 200 °C for 3 hours using oil batch. The resulting precipitate was separated by decantation and washed with demineralized water twice. The resulting black powder was calcinated at 600 °C for 5 hours to produce a pale-yellow solid as the final product.

RESULT AND DISCUSSION

It was observed that when the mixture of cerium(III) nitrate in an aqueous extract of *Garcinia mangostana* peels was heated in a hydrothermal autoclave reactor at 200 °C for 3 hours, black precipitate was formed. The precipitate was speculated to be a mixture composed of carbonized materials from the extract and intermediate compounds from the production of CeO₂. It is noteworthy that the hydrothermal reaction was proceeded without addition of any base. The powder XRD analysis was performed on the solid material collected from the hydrothermal reactor as well as on the corresponding materials after calcination (Figure 1).

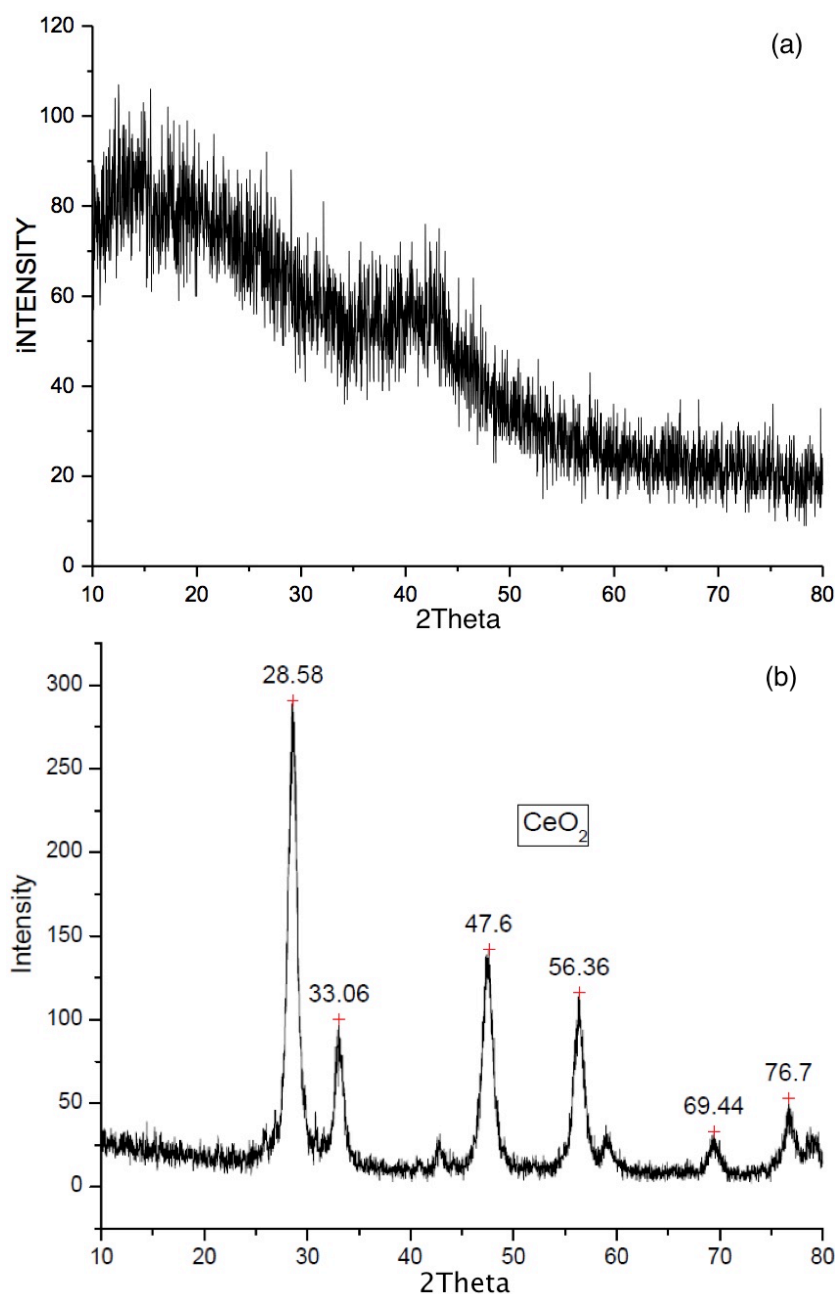


Figure 1. (a) XRD diffractogram of solid materials collected from hydrothermal autoclave reactor, and (b) solid material after calcination at 600 °C for 5 hours

As shown in Figure 1a, no peaks were observed for the solid sample collected from the hydrothermal autoclave reactor before calcination. This result indicated amorphous nature of the analyzed material. In contrast, when the calcinated samples were analyzed using XRD, clear peaks at 28.58°, 33.06°, 47.6°, 56.36°, 69.44°, and 76.70° were observed (Figure 1b). Based on the data in literatures, the peaks present correspond to planes of 111, 200, 220, 311, 400 and 331, respectively [5, 13-14].

The pattern of the peaks allowed for the estimation of the crystal size to be made. This was based on the Full Width at Half Maximum (FWHM) and the results of this analysis are presented in Table 1. As shown in Table 1, the average crystal size was 7.55 ± 1.16 nm. The methodology described herein utilizes the *Garcinia mangostana* peel extract in a

hydrothermal autoclave reactor at 200 °C for 3 hours, followed by calcination at 600 °C for 5 hours. These conditions have proved to be crucial in minimizing the ceria crystal size through inhibition of nucleation of the crystal [13].

Table 1. Ceria (CeO_2) crystal size estimation using XRD data

No.	$2\theta/^\circ$	FWHM / $^\circ$	Crystal Size/nm
1	28.58	1.01	8.40
2	33.06	0.98	8.84
3	47.60	1.30	6.98
4	56.36	1.26	7.48
5	69.44	1.26	8.02
6	76.70	1.89	5.60

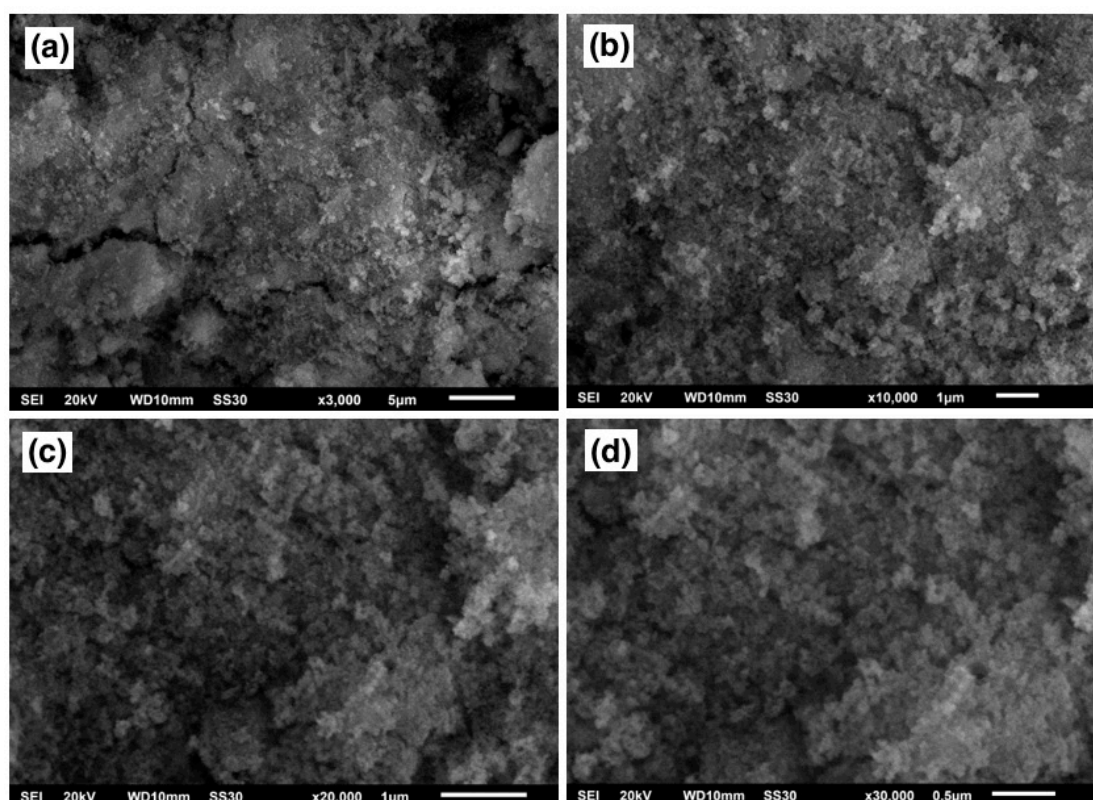


Figure 2. SEM images of CeO_2 particles (a) 3000x (b) 1000x (c) 2000x (d) 30000x

The morphology of the CeO_2 particles obtained in this work is depicted by the SEM images shown in Figure 2. As indicated by the SEM images presented in Figures 2a to 2d, the morphology of the obtained CeO_2 particles is spherical with slight random agglomeration [15]. It is possible that the agglomeration occurred during the high temperature calcination removes the carbonized materials. The chemical composition of the obtained material was analyzed using EDX, as shown in Figure 3. The results confirm the presence of cerium and oxygen as major elements. Some impurities including phosphorus, sulfur, potassium, and copper are usually present in small amounts. Although not exact, it is presumed that the impurities appeared from the autoclave cleaning system or other possibilities.

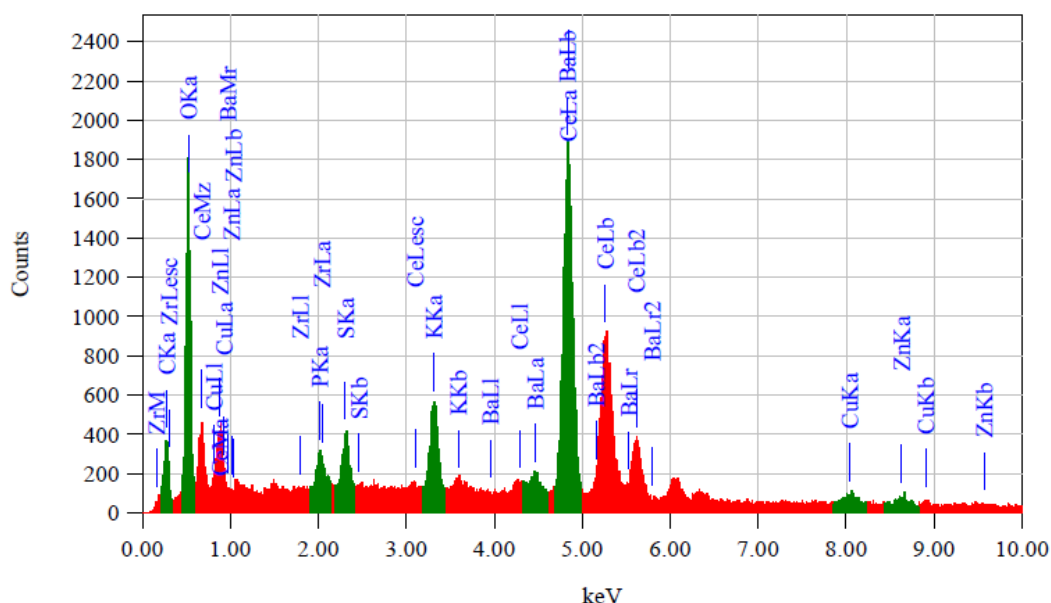


Figure 3. EDX pattern of CeO₂ synthesized using *Garcinia mangostana* peel extract as fuel

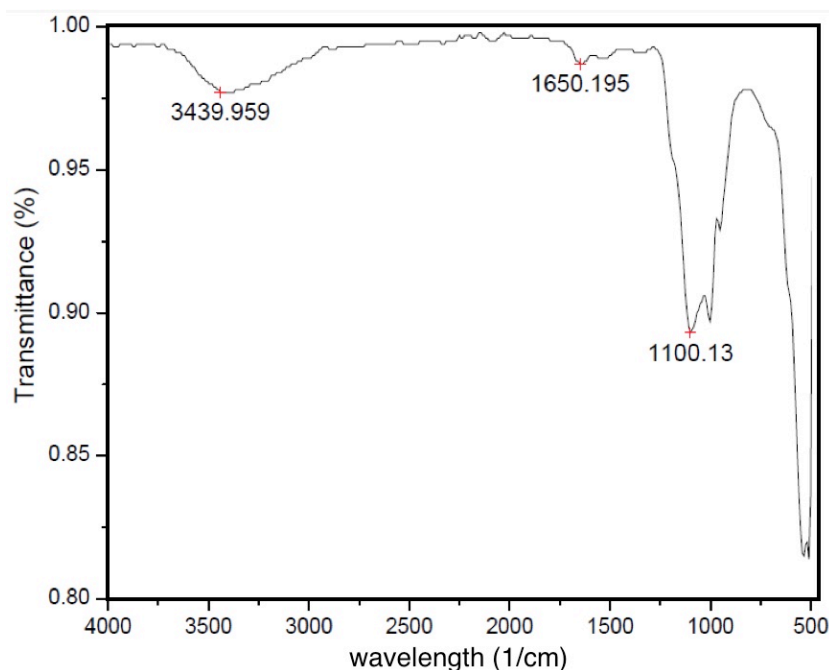


Figure 4. FTIR spectra of ceria sample synthesized using *Garcinia mangostana* peel extract as fuel

The appearance of two peaks at 3439 cm⁻¹ (stretching vibration) and 1650 cm⁻¹ (bending vibration) is indicative of water chemisorption on the surface of the ceria particles. Presences of a peak at 1100 cm⁻¹ as well as neighboring peaks correspond to the Ce-O stretching vibration. This was further supported by the presence of a sharp peak at 500 cm⁻¹ (bond stretching of Ce-O) [14, 16, 17].

CONCLUSION

Solid particles of CeO₂ were synthesized from cerium(III) nitrate using a simple and eco-friendly method exploiting *Garcinia mangostana* peel extract as sustainable fuel. The synthesis began with a hydrothermal reaction without addition of any base, followed by calcination at 600 °C. Based on the powder XRD analysis, the resulting solid product was confirmed as cerium (IV) oxide. The average crystal size of 7.55 nm was determined based on the FWHM data.

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CONFLICT OF INTEREST

Author declare no competing interests.

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