Structural Analysis of Nanoceria Powder Precipitated in Different pH

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ABSTRACT

Nanoceria has been proposed as inorganic material for sunscreen product because of its excellent UV absorpsition ability. Fine particle nanoceria and non-aglomeration determines comport and covering capability on human skin. Particle size and aglomeration could be controlled by parameters and medium synthesis. In the present work, nanoceria powders were synthesized using precipitation method in different pH of 7 and 10. Precipitation was caried out in water/isopropanol mixed solvent. Cerium nitrate and amonium hydroxide was used as source of cerium and precipitation agent, respectively. Crystal structure of nanoceria was examined using x-ray diffraction (XRD). Scanning electron microscope (SEM) was used to observe morphology of nanoceria. Diffraction pattern analysis shows that the precipitates were single phase of nanoceria with cubic fluorite structure and lattice contants of 0.5429 nm and 0.5419 nm. Crystallite size and lattice strain were obtained from Williamson-Hall method. Precipitation in pH of 7 resulted in smaller crystallite size which correlated to the larger lattice strain and lattice constant. SEM image shows spherical morphology with less agglomeration occuring for nanoceria precipitated in pH 10.

Keyword : nanoceria, precipitation method, XRD, SEM, agglomeration

ABSTRAK

Kemampuan absorpsivitas UV yang baik serbuk nanoceria menjadikannya sebagai material inorganik tabir surya. Serbuk nanoceria yang halus dan tidak bersifat aglomerasi menentukan kenyamanan penggunaannya. Ukuran nanoceria dan sifat aglomerasi dapat dikontrol oleh parameter dan medium sintesis. Serbuk nanoceria pada penelitian ini disintesis menggunakan metode presipitasi pada pH 7 dan 10 dalam campuran pelarut aquades/isopropanol. Cerium nitrate dan amonium hidroksida berturut-turut digunakan sebagai sumber cerium dan presipitan. Stuktur kristal nanoceria diuji menggunakan difraksi sinar-x. *Scanning electron microscope* (SEM) digunakan untuk mengamati morfologi nanoceria. Analisis pola difraksi menunjukkan bahwa hasil presipitasi merupakan fase tunggal nanoceria berstruktur kubik fluorite dengan konstanta kisi 0,5419 nm dan 0,5429 nm. Kondisi presipitasi pada pH 7 menghasilkan ukuran kristalit yang lebih kecil. Ukuran kristalit yang kecil berkorelasi dengan regangan kisi dan konstanta kisi yang lebih besar. Citra SEM menggambarkan morfologi nanoceria berbentuk sferis dan aglomerasi lemah tampak pada nanoceria hasil presipitasi pada pH 10.

Kata kunci : nanoceria, metode presipitasi, XRD, SEM, aglomerasi

INTRODUCTION

Ceria has been used in many applications, such as: fuel cell [1], gas sensor and pollutant reduction [2-3], and anticorrosive coating [4]. Recently, extensive investigation has been performed on potential ceria as nanobiomaterials [5]. Because of excellent uv absorption ability, low photocatalytic, non-toxic and low refractive index is relatively transparent to visible light, ceria is proposed as inorganic sunscreen material [6]. Three of the most important keys for sunscreen material are effective broad spectrum uv absorption, comport and safety when applied on human skin. For those reasons, fine particle and non-agglomeration ceria is required.

Several methods have been used to synthesize nanoceria with controlled of properties. Precipitation method is the most attracted attention due to its advantages, such as: simple process, easy to scale-up, uniform particle size and low cost. In addition, diameter and distribution of particle size and morphology can be easilly controlled by pH of synthesis. However, it is not easy to produce fine nanoceria using preipitation because of high degree agglomeration. Homogeneous precipitation with surfactant and precipitation in aqueous/alcohol mixed solvent are two approach which proposed to solve disadvantages of these method [7-9]. Usually, conventional precipitation method used water as a solvent. The addition of low dielectric solvent to the aqueous solution would result in reducing particle size and size distribution of resulting particles. Chen et al. employed six alcohols as the dielectric regulators of water/alcohol mixed solvents [9]. In other report, Sudjana used acetone as low dielectric medium and mixed with aqueous medium to prepare nanoceria by surfactant mediated precipitation method [10]. In the present work, nanoceria is synthesized using precipitation process in water/isopropanol mixed solvent with volume percentage of isopropanol was kept at 60% as previous reported [11]. Precipitation condition was adjusted in different pH. Structure and morphology of precipitates were studied.

EXPERIMENT

A solution of 0,08 M cerium nitrate hexahydrate (strem, 99,9%) was prepared in water/isopropanol (merck, 99,9 %) mixed solvent system. Nanoceria powder were obtained through precipitation process by dropwise 3 M amonium hydroxide (merck) into cerium solution and stirred simultaneously under controlled pH of 7 and 10. The precipitates were washed with water and isopropanol. Finally, precipitates were dried at 60^oC and then calcined at 300^oC for 2 hours resulting in light yellowish powder. The structural characterization was performed by X-ray diffraction (Phillips PW 1710) using CuKα radiation. The morphology of powder was examined using a scanning electron microscope (JEOL, JSM 6360).

RESULTS AND DISCUSSION

The powder XRD patterns of nanoceria precipitated in different pH of 7 and 10 are shown in Figure 1. All the samples showed difraction peaks of (111), (200), (220), (311), (222), (400), (331), (420) and (422) correspond to fluorite structure of ceria (JCPDS card no.43-0394). No secondary phase peak is found in the XRD pattern, which suggests that all samples are pure ceria. The diffraction peaks become narrower and sharper with increasing of precipitation pH, indicating the improvement of crystallinity.

Lattice constant for FCC structure was calculated by following equation:

$$= \frac{\lambda\sqrt{h \quad + \quad +}}{2\sin} \qquad (1)$$

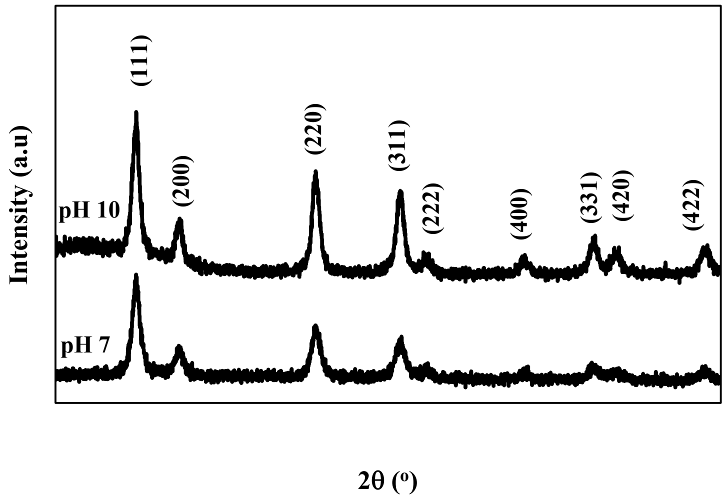

Figure 1. X-ray diffraction patterns of nanoceria precipitated in (a) pH 7, (b) pH 10

where, a is lattice constant of cubic crystal lattice, h, k and l Miller indices of the peak diffraction, λ denotes X-ray wavelenght and θ the diffraction angle. From the XRD pattern, the full width at half maximum (FWHM) of all peak diffractions for nanoceria were also determined. The crystallite size and lattice strain were calculated according to Williamson-Hall equation as follow:

$$\frac{\cos}{\lambda} = - + 2\ \frac{2\sin}{\lambda}$$

or

$$\Delta\ = \frac{0.89}{} + 2 \qquad (2)$$

In equation (2) Scherrer constant k is 0,89 for spherical particle, β denotes FWHM of peak diffraction and ε the lattice strain[12]. Plots of Williamson-Hall equation are shown in Figure 2.

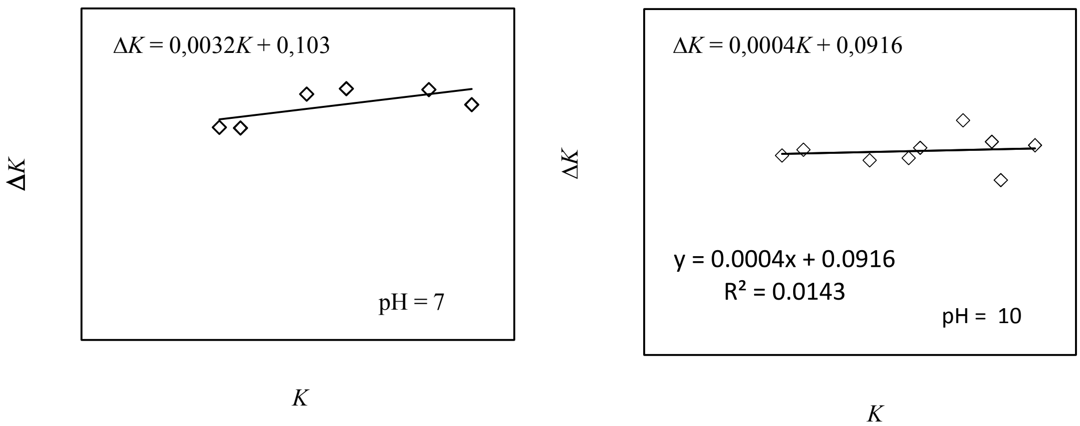

Figure 2. Williamson-Hall plots of nanoceria precipitated in (a) pH 7 and (b) pH 10

Table 1 summarizes crystallite size, lattice strain and lattice constant of nanoceria precipitated in pH 7 and pH 10 according to equation (1) and (2). Based on JCPDS card no. 43-0394, lattice constant of cubic phase ceria is 0.5411 nm. From the Table 1, it can be seen that lattice contants are 0.5429 nm and 0.5419 nm for nanoceria precipitated in pH 7 and pH 10 respectively. The lattice constants are higher than that record on JCPDS card, indicate occuring lattice expansion. Its well known, generally nanoparticle of oxide exhibits lattice expansion with reduction in particle size. Therefore, the larger lattice constant of nanoceria precipitated in pH 7 is expected due to smaller crystallite size. As can be seen in Tabel 1, the crystallite sizes are 8.73 nm and 9.72 nm, respectively for pH 7 and pH 10. The precipitation condition in pH 7 resulting in smaller crytallite size which agreed to broader peak diffraction. The dependence of lattice constant to the crystallite size was also observed by Goharshadi et al. for nanoceria prepared by microwave method. An increase in lattice constant was correlated to a decrease in crystallite size [13].

Table 1. Crystallite size, lattice strain and lattice constant of nanoceria precipitated in pH 7 and pH 10

pH	*D* (nm)	ε (x 10^{-3})	*a* (nm)
7	8,73	1.50	0.5429
10	9.72	0.20	05419

Figure 3 exhibits the spherical morphology of particle with diameter of about 10 nm - 30 nm which larger than that calculated crystallite size from XRD analysis. It is indicated that particle consists of one - three crystallite agregates. Its also observed that particle size of nanoceria precipitated in pH 10 smaller than nanoceria precipitated in pH 7 suggesting that precipitation condition in pH 10 resulted in nanoceria with less agglomeration. These phenomenon can be explained as follow. Agglomeration is driven by surface energy. Smaller crystallite size is corelated to higher surface area and consequently the increase of that surface energy. Therefore, smaller crystallite size trends for hard agglomeration.

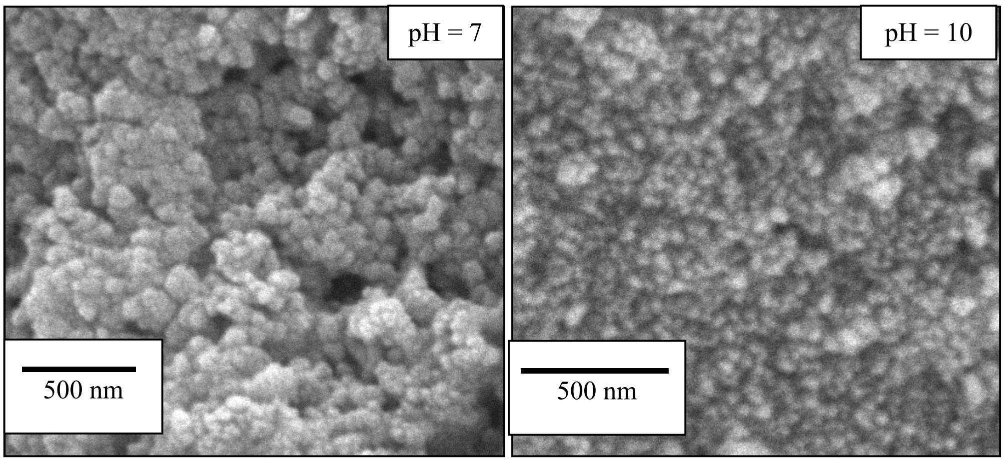

Figure 3. SEM images of nanoceria precipitated in (a) pH 7, (b) pH 10

CONCLUSION

Nanoceria powders can be prepared through precipitation process in pH of 7 and 10. The structure and morphology of nanoceria have been investigated by XRD and SEM. The prepared nanoceria had highly crystalline structure of cubic fluorite. pH of precipitation influences on crystalynity, crystallite size and agglomeration degree of nanoceria. Precipitation in pH 10 leads to bigger crystallite size and lattice constant closer to the reference. It also results in nanoceria with higher crystalinity and less agglomeration.

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