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Growth and UV Absorption of 5 mol% Zn-doped CeO_2 Nanoparticle Synthesized with A Simple Precipitation Process

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Abstract. Nanoparticles of the 5 mol% Zn-doped CeO_2 have been synthesized with a simple precipitation process from aqueous/alcoholic solution of cerium nitrate and zinc nitrate mixture at room temperature. Dried precipitates were calcined at 300-700^oC for 2 hours. The structure and growth of 5 mol% Zn-doped CeO_2 was investigated using X-ray diffraction measurement. All peaks in the X-ray diffraction patterns were identified and indexed as single crystalline phase of cubic fluorite CeO_2. The rise in calcination temperature increases the crystallite size from 5.51 to 15.56 nm and improves their crystallinity. The low activation energy for crystallite growth of the 5 mol% Zn-doped CeO_2 is found to be 10.85 kJ/mol. The UV-Vis spectrophotometer measurement showed that the UV absorption property of the 5 mol% Zn-doped CeO_2 is enhanced with increasing calcination temperature. The 5 mol% Zn-doped CeO_2 nanoparticle calcined at a temperature of 600^oC is found to be more effective as UV-blocker.

Introduction

Nanometer size rare earth oxides have prompted wide research from their synthesis, structure and properties to their applications. Among the rare earth oxides, CeO_2 has been extensively studied and considered as a promising material because of its high refractive index, good transmission in visible light region, excellent UV absorption and high stability. Those properties are dominated by defect chemistry. Hence, doping with a second element can have a significant effect on many applications such as UV absorbent [1]. Currently, TiO_2 and ZnO are used as commercial UV absorbents for effective UV protection. Protection against UV radiation requires broad-spectrum UV-blocker material with an appropriate level of UV-A protection. CeO_2 nanoparticle powders have considerable potential to be used as broad spectrum UV absorbent/filter/blocker [2, 3]. Nano-sized CeO_2 has excellent UV absorption compared to TiO_2 and ZnO. For those applications, the crystallite size and morphology of CeO_2 nanoparticle significantly influence its absorption property. Several efforts have been made to improve UV-shielding with low photo catalytic activity of nano-sized CeO_2. The effect of crystallinity on the optical properties of nano-sized CeO_2 powder has been studied by Ko et al. [2]. CeO_2 nanoparticles were incorporated into polystyrene matrix to prevent inter-particle aggregation. It shows excellent UV-shielding with potential application for polymers such as varnish, fiber coating and plastic [4]. ZnO: CeO_2 has higher UV absorption and transparency in visible light region and lower photo catalytic activity than TiO_2. Pure CeO_2 and ZnO were prepared by non-alkoxide sol-gel method [5]. The combination of panthenol and nano-ceria more effectively protects biological object from reactive oxygen species (ROS) and UV irradiation [3].

This article is mainly aimed at studying the crystallite growth and UV absorbance of 5 mol% Zn-doped CeO_2 nanoparticles synthesized by precipitation process. X-ray diffraction is carried out to analyze crystallinity, phase and crystallite size of nanoparticle that is calcined at different temperatures. The UV absorbance was measured to evaluate the ability of 5 mol% Zn-doped CeO_2 nanoparticles to absorb broad-spectrum UV. In addition, the crystallite growth of the 5 mol% Zn-doped CeO_2 nanoparticles was also studied and correlated to that of UV absorption properties.

Experiment

Nanoparticles of the 5 mol% Zn-doped CeO_2 were precipitated from cerium nitrate solution with additional zinc nitrate. A solution of 0.08 M cerium nitrate was prepared in demineralized water/isopropanol mixed solvent with a volume ratio of 1:6. NH_4OH was then added drop wise under stirring into the solution until a pH value of 10 was reached. Precipitates were repeatedly washed by ethanol. The precursor powders were then dried at 60^o for 2 hours in an oven. Finally, the dried powders were calcined at various temperatures in the range of 300-700^{o}C for 2 hours.

The crystallinity and phase of the 5 mol% Zn-doped CeO_2 nanoparticles were characterized by X-ray powder diffractometric (XRD) with $Cu_{K\alpha}$ radiation (λ = 1.54060 A) at 10-90^o. In addition, UV-Vis absorption of the 5 mol% Zn-doped CeO_2 nanoparticles was examined using UV-Vis spectrophotometer.

Results and discussion

Crystallite growth. Fig. 1 shows the x-ray diffraction pattern of 5 mol% Zn-doped CeO_2 calcined at various temperatures for 2 hours. The spectra clearly shows diffraction peaks corresponding to face-centered cubic (fcc) CeO_2 which is in good agreement with the Joint Committee on Powder Diffraction Standard (JCPDS- No. 34-394). Four preferred diffraction peaks of (111), (200), (220) and (311) planes are observed for all calcination temperatures. Weak and broad peaks of samples which are calcined at temperatures of 300-500^{o}C imply low crystallinity and fine grains distributed in 5 mol% Zn-doped CeO_2. The additional diffraction peaks of (222), (400), (331), (420) and (422) planes appear when calcination temperature is increased to 600^{o}C. Furthermore, when calcination temperature is increased from 600^{o}C to 700^{o}C, the diffraction peaks became sharper and stronger. It suggests that crystallinity of 5 mol% Zn-doped CeO_2 is improved and the crystallite size is increased with increasing calcination temperature. In addition, no other peaks related to impurities or other phases are detected in the spectra which confirm that precipitated powders are single phase crystalline of CeO_2.

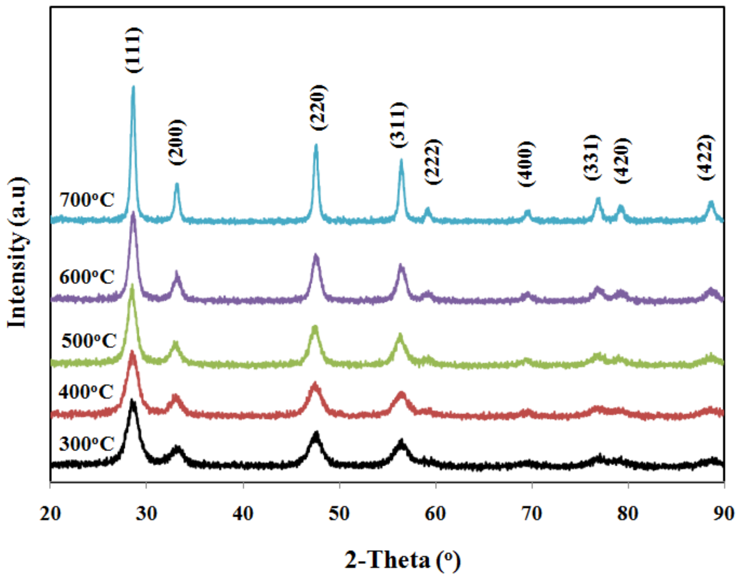

Figure. 1. X-ray diffraction pattern of 5 mol% Zn-doped CeO_2 nanoparticle calcined at different temperatures for 2 hours

The crystallite size (*D*) of 5 mol% Zn-doped CeO_2 calcined at different temperatures is calculated from the X-ray line broadening by using full width at half maximum (FWHM) value of (111) peak to Scherrer equation as described by Eq.1.

$$D = \frac{0.89\lambda}{\mathrm{FWHM}\cos\theta} \quad (1)$$

where λ is the wavelength of incident of X-ray and θ is the diffraction angle of (111) plane. The lattice constant (a) of 5 mol% Zn-doped CeO_2 calcined at different temperatures is also calculated by using Eq. 2 for diffraction peak of (111) plane.

$$a = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin\theta} \tag{2}$$

where h, k and l are Miller indices of the Brag diffraction. Here, $h = k = l = 1$. Fig. 2 depicts the graph of crystallite size and lattice constant of 5 mol% Zn-doped CeO_2 calcined at different temperatures. As can be seen in the X-ray diffraction pattern, the FWHM value of (111) plane is decreased with increasing calcination temperature. As a consequence, the crystallite size is increased from 5.51 to 15.56 nm. The crystallite growth is slow at calcination temperature of 300–500°C. However, when Zn-doped CeO_2 is calcined from 500 to 700°C, the crystallite size rapidly increases. It was also observed that lattice constant is reduced linearly with increasing calcination temperature. The decreasing lattice constant can be correlated to the increasing crystalite size [6].

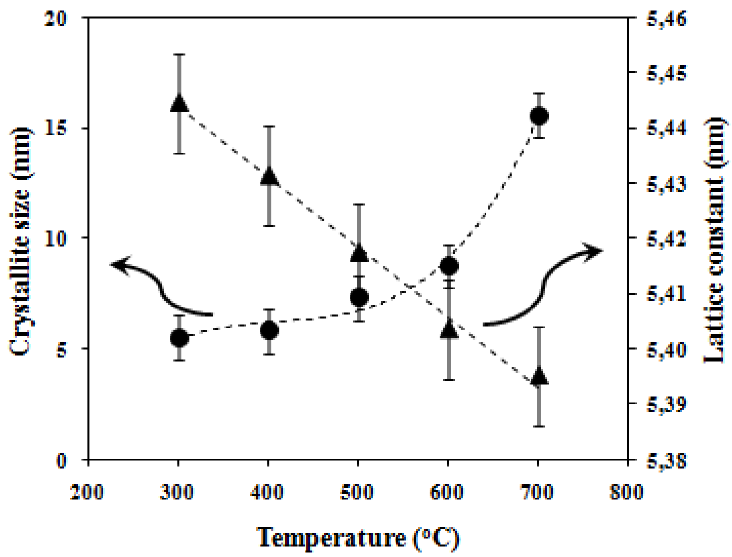

Figure. 2. Crystallite size and lattice constant of the 5 mol% Zn-doped CeO_2 nanoparticle calcined at different temperatures for 2 hours.

Activation energy for crystalllite growth of the 5 mol% Zn-doped CeO_2 was estimated by applying Arrhenius equation as given in Eq. 3.

$$D = k\exp\left(\frac{-E}{RT}\right) \tag{3}$$

where D is crystallite size of the 5 mol% Zn-doped CeO_2, R denotes universal gas constant, E is activation energy, T is calcination temperature and k is a constant which may depend on the initial value of crystallite size. The plot of ln (D) versus $1/T$ is shown in Fig. 3. The activation energy is calculated from the slope of linear regression to be 10.82 kJ/mol which is much lower than the result of precipitated CeO_2 nanocrystal (24.85 kJ/mol) calcined at temperatures in the range 300-700°C[7]. However, that value is close to 11.54 kJ/mol for crystallite growth of CeO_2 during a synthesis by ammonia precipitation at temperatures of 30-80°C. Other experimental results reported activation energies of 17.48 kJ/mol and 16.0 kJ/mol for CeO_2 nanopowder precipitated at pH 8 and pH 9, respectively [8]. These mean that high pH precipitation results in low activation energy for crystallite growth. In this study, the activation energy for 5 mol% Zn-doped CeO_2 is lower than that of CeO_2 which was previously reported by other researchers. This may be because the precipitation was carried out at pH 10. Hence, the formation of cerium hydroxide after oxidation Ce^{3+} to Ce^{4+} is easier at high pH that the crystallite growth is straightforward [9].

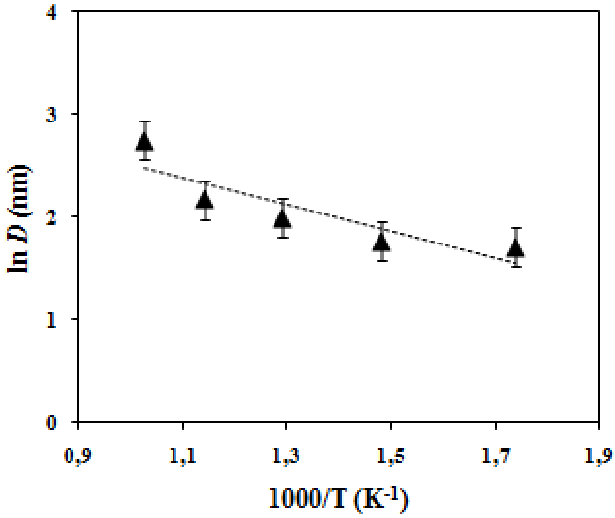

Figure. 3. Arrhenius plot of crystallite size with resiprocal calcination temperature of the 5 mol% Zn-doped CeO_2 nanoparticle

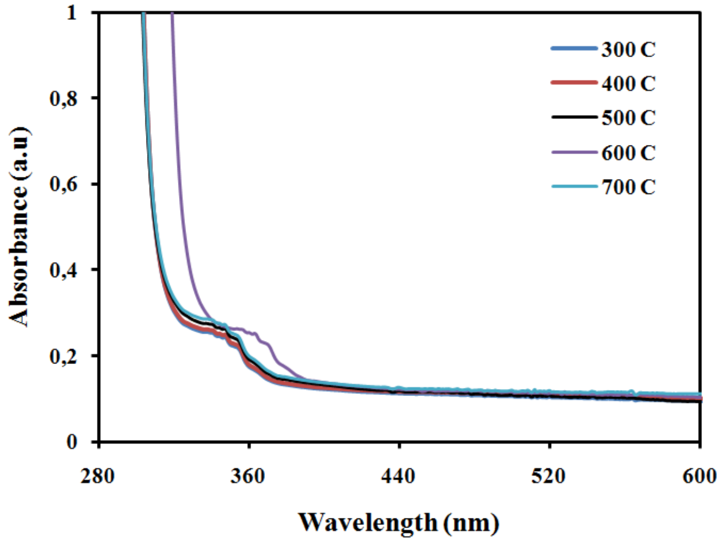

Figure. 4. The UV-Vis absorbance spectra of the 5 mol% Zn-doped CeO_2 nanoparticle calcined at different temperatures for 2 hours.

UV-Vis absorbance. The UV-Vis absorbance spectra of the 5 mol% Zn-doped CeO_2 nanoparticle calcined at different temperatures for 2 hours are shown in Fig. 4. All samples show similar behaviors of absorption property i.e. high absorbance in the UV (B-A) region and low absorbance in the visible region. It indicates that 5 mol% Zn-doped CeO_2 nanoparticles is good for UV absorption and is transparent in visible light region. The UV absorbance increases slightly with increasing calcination temperatures from 300°C to 500°C, and then it increases rapidly at a calcination temperature of 600°C. However, the UV absorbance for calcination temperature of 700°C is the same with the sample which is calcined at 300-500°C. The strongest UV absorption is found for 5 mol% Zn-doped CeO_2 nanoparticle calcined at a temperature of 600°C. Moreover, it was observed that the absorption peak in the UV-A region shifts to the higher wavelength (the peak at 358 nm for the sample calcined at 600°C and ~ 340 nm for the other samples). In other words, increasing calcination temperature leads to the red-shift phenomenon. This phenomenon has been reported for 20 mol% Zr-doped CeO_2 nanoparticle prepared by hydrothermal process [1]. Ko et al. [2] have also found a small amount of the red-shift in pure CeO_2 nanoparticles after calcination at

1073K for 15 to 120 minutes. They say it was due to prolonged calcination duration that induces increased crystallinity, leading to intense absorption. Similar explanation also applies to 5 mol% Zn-doped CeO_2 nanoparticle in this study. Increasing calcination temperature causes improved crystallinity and large crystallite size and they in turn lead to strong absorption.

Summary

The growth and UV absorbance of the 5 mol% Zn-doped CeO_2 nanoparticles were investigated by analyzing x-ray diffraction patterns and UV absorbance spectra. The results indicate that nanoparticle contains single phase CeO_2 cubic. The crystallite size is slightly increased for calcination temperatures of 300 to 500°C and rapidly increased for calcination temperatures of 500°C to 700°C. The activation energy for crystallite growth is found to be 10.82 kJ/mol. The UV absorbance spectra reveals the red-shift phenomenon from 340 nm for nanoparticle calcined at 300°C to 358 nm for nanoparticle calcined at 600°C. The absorption property of the nanoparticle in the UV-B and UV-A regions is enhanced with increasing calcination temperature up to 600°C. These results suggest that 5 mol% Zn-doped CeO_2 nanoparticles are suitable for broad-spectrum UV-absorption.

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