UV-Light absorption and photocatalytic properties of Zn-doped CeO2 nanopowders prepared by ultrasound irradiation

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UV-Light Absorption and Photocatalytic Properties of Zn-doped CeO_2 Nanopowders Prepared by Ultrasound Irradiation

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Abstract. Ceria (CeO_2) nanopowders doped with various Zinc (Zn) compositions were synthesized from solution by irradiating ultrasound waves. Ultrasound waves were irradiated to aqueous/isopropanol solution of cerium nitrate and zinc nitrate mixtures. Aqueous solution of ammonium hydroxide was droped into that solution until pH becomes 10. Dried precipitates were calcined at 100^{o}C to form CeO_2 nanopowders. X-ray Diffraction (XRD) analysis shows the CeO_2 nanopowder possess fluorite cubic structure. Ultrasound irradiation resulted in nano-metric powder of CeO_2 with spherical in shape. The addition of Zn into CeO_2 reduces the particle size and shows strong absorbance in the ultra–violet (UV) region. Moreover, the addition of 20 mol% Zn is inhibiting photocatalytic activity of CeO_2 under sunlight irradiation. These results suggest that Zn-doped CeO_2 is more promising for UV radiation protection with no presence photocatalytic activity.

Introduction

Ceria (CeO_2) nanoparticles are extensively studied through the last few decades due to effective for many applications such as absorbent, UV filter and blocker [1-2]. This material become one of the most attractive nanomaterials for research objectives, one of which is because of its interesting properties for UV radiation protection. For these application, CeO_2 with low photocatalytic ability is needed. CeO_2 nanoparticles are oxide material with fluorite cubic structure. The properties of that CeO_2 can be changed by doping Zn. The inserting Zn into CeO_2 lattice can reduce that particle size. As consequnce, it reduce catalyst and photocatalyst activity, the evolution of molecular oxygen and preventing degradation of organic materials [3]. In recent years, many effort have been made to synthesize CeO_2 nanoparticles through different approaches. These methods include sol-gel, precipitation, and sonochemical method [4-6] etc. Sonochemical method has many advantages including easy of operation, being fast, low cost, high efficiency, convenient, time saving, and enviromental friendly [6]. Chemical reaction of the starting materials occured in the presence of an applied high-frequency ultrasonic waves. These method has been employed for several purpose, in various organic and inorganic reactions and fabrication of nanostructured materials [7]. The chemical effect of ultrasonic irradiation arise from acoustic cavitation, in other words, the formation, growth and impolsive collapse of bubbles in a liquid medium, which result in an instantaenously high temperature and pressure pulse [8,9]. These special conditions of high temperature, pressure and local intense micromixing attained during acoustic cavitation lead to many unique properties in the irradiated solution [10].

Zn-doped CeO_2 nanopowders were synthesized from solution assisted by ultrasound irradiation. Generally, the irradiation performes in solution with water solvent. In this paper, we use mixed solvent system (aqua/isopropanol) to obtain cerium and zinc precursor solution. It is expected to produce the fine particle and strong UV absorbance. Phototacalytic of Zn-doped CeO_2 nanopowders were examined to methylene blue (MB) degradation under sunlight irradiation. The Zn-doped CeO_2 nanopowders show excellent UV absorption and lower photocatalytic activity than TiO_2. This result indicates that Zn-doped CeO_2 nanopowders are promising as an alternative UV radiation protection materials.

Experimental Procedure

CeO_2 and Zn-doped CeO_2 nanopowders were synthesized from solution of Cerium (III) nitrate (0.07 M) and Zinc nitrate in a mixture of aqua DM and isopropanol solvent with volume ratio of 1:6. Ammonium hydroxide (3M) was droped into that solution until pH 10. Ultrasound wave was irradiated to the solution with frequency of 40 kHz for 60 minutes. The result of irradiated solution was then washed and calcined at 100°C for 3 hours.

X-ray Diffraction (XRD) measurement was used to analysize structure of nanopowders. Optical properties of nanopowders were measured using ultraviolet-visible (UV-vis) spectroscopy. Photodegradation of 32 ppm MB solution under sunlight irradiation for 120 minutes was carried out to evaluate photocatalytic activity of nanopowders. Particle morphology of the synthesized nanopowders were observed by scanning electron microscopy (SEM).

Result and Discussion

Structural Analysis. The diffraction patterns of undoped CeO_2 and Zn-doped CeO_2 nanopowders are shown in Fig.1. Various of diffraction peaks were observed in all the powders indicating the polycrystalline structure. All the diffraction peaks of the samples correspond to a pure fluorite cubic structure of CeO_2 (JPDS 43-1002). The (111), (200), (220), (311) dominant diffraction peaks could be seen in all of the samples. The sharp of those peaks is indicating that CeO_2 well crystallized. Moreover, the intensity of all the diffraction peaks is increased with increasing Zn content. The peaks become more broader with increasing Zn content than undoped CeO_2. The broadening of peak is expected due to decreasing in the particle size. It indicates that Zn-doped CeO_2 nanopowders are consist of nanometric size particle. The other peaks of (222), (400), (311), (420), and (422) with small intensity were also observed in the pure CeO_2 diffraction pattern and that peaks is not appearing in the Zn-doped CeO_2. The diffraction patterns of both pure CeO_2 and Zn-doped CeO_2 do not show the peaks corespond to others phase, so that Zn is successful substituted into CeO_2.

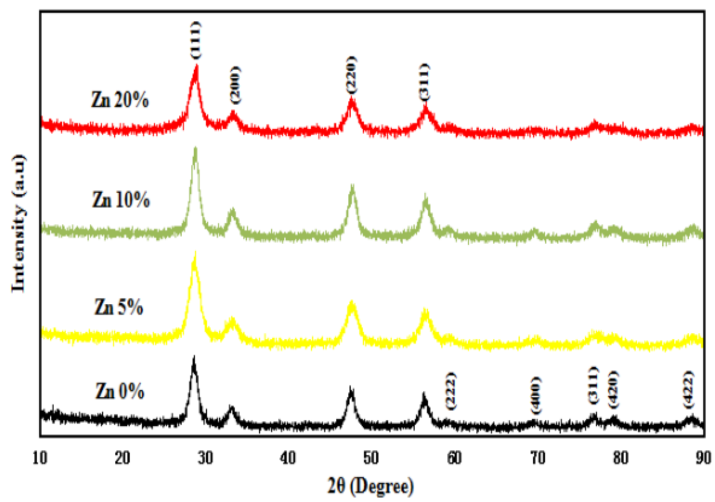

Fig. 1. X-ray diffraction patterns of Zn-doped CeO_2 with Zn content of 0%, 5%, 10%, 20%

The lattice constant of CeO_2 nanopowders can be determined by using Equation (Eq.) 1.

$$a = \frac{\lambda}{2\sin\theta}\sqrt{h^2 + k^2 + l^2} \quad (1)$$

where a is the lattice constant, λ = 1,54056 Å, h, k, l is miller index and θ is the diffraction angle. The values of lattice constant were calculated by Eq. 1 ranging from 5.4006 Å to 5.4211 Å. These values still indicates Zn-doped CeO_2 nanoparticles have fluorite cubic structure. The value of lattice constant decreases as the diffraction angle shifts to the right. The relationship between Zn content with lattice constant of CeO_2 nanopowders was shown in Fig. 2. It can be seen that lattice constant decreases with increasing Zn content in CeO_2. This decreasing shows that the volume of the CeO_2 cell has decreased due to the Zn^{2+} effective ionic radius (0.74 Å) which is smaller than Ce^{4+} ionic radius (0.97 Å) [11].

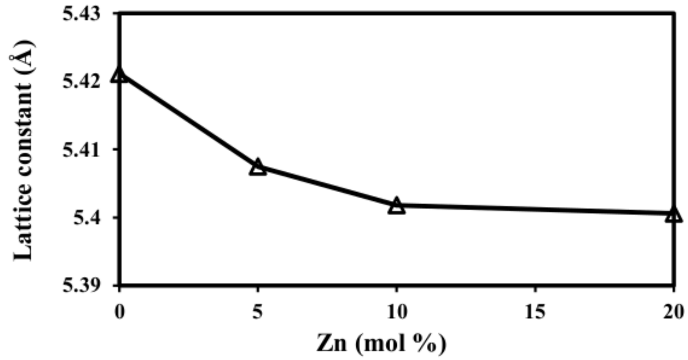

Fig. 2. Lattice constant of Zn-doped CeO_2 nanopowders vs Zn content.

Particle Morphology. Fig. 3 shows SEM image of undoped and Zn-doped CeO_2 nanopowders. The surface morphology of all that nanopowders appears to be rough and look spherical in shape. In this study, the estimation of average grain size are 37 nm for undoped CeO_2 and 28 nm for the 20 mol% Zn-doped CeO_2. The addition of Zn content 5% and 10 % was not estimated because the grain boundaries couldnot be clear seen. The average of grain sizes is reduced due to Zn doping.

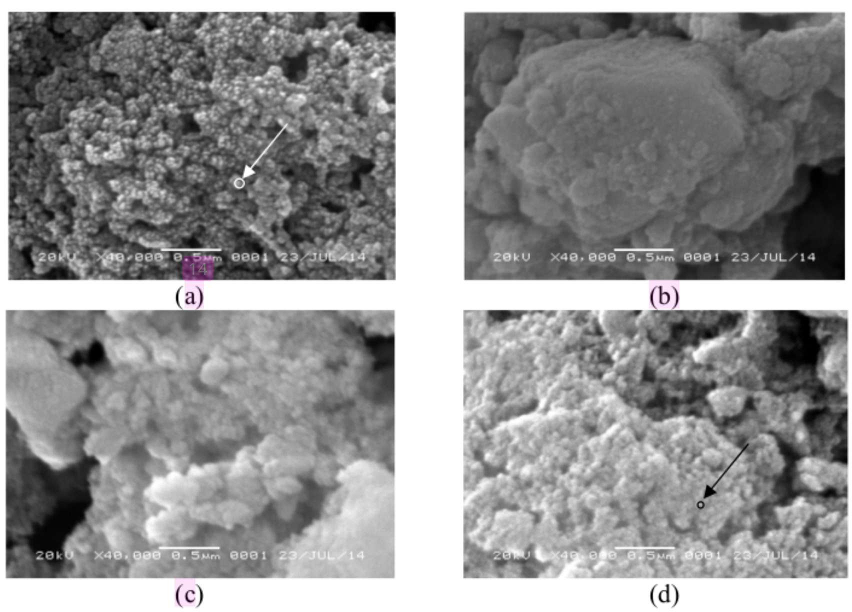

Fig. 3. SEM images of (a) undoped CeO_2 and Zn-doped CeO_2 nanopowders with Zn content (b) 5%, (c) 10%, (d) 20%

Optical Properties. The UV absorption spectra of undoped and Zn-doped CeO_2 nanopowders is shown in Fig. 4. CeO_2 nanopowders have strong absorption properties in the ultraviolet region. The undoped and Zn-doped CeO_2 increase slightly in the UV absorption. The change in optical properties of CeO_2 due to presence Zn dopant in the lattice CeO_2 are related to the particle size and the aggregation condition of particle [4]. The smoother particle surface is better light scattered than the rougher particle surface. It can be correlated by the results of SEM image. The surface morphology of undoped and the 20 mol% Zn-doped CeO_2 are more smoother than the 5 and 10 mol% Zn-doped CeO_2. It causes that the UV absorption of undoped CeO_2 is more little stronger than the others. It is caused by 5 and 10 mol% Zn-doped CeO_2 nanopowders have a little agglomeration as can be seen in SEM image.

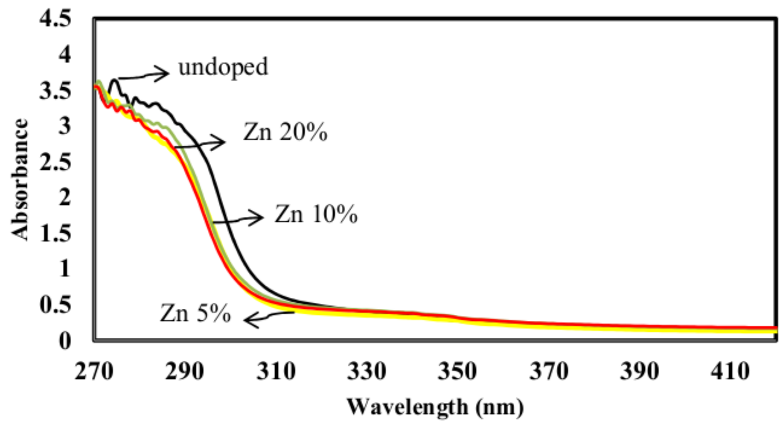

Fig. 4. UV absorbance spectra of CeO_2 nanopowders with Zn content of 0% (undoped), 5%, 10% and 20%.

The effect of Zn dopant to photocatalytic activity of CeO_2 was evaluated by the photodegradation of MB under sunlight irradiation for 120 minutes. The photocatalytic activity of Zn-doped CeO_2 nanopowder is also compared to the photocatalityc activity of TiO_2 comercial. The degradation of MB solution was calculated by Eq. 2

$$\text{Degradation (\%)} = \frac{Ao-A1}{Ao} \times 100\% \quad (2)$$

where A_0 and A_1 are absorbance of MB solution before irradiation (t = 0 minutes) and after irradiation for t = 120 minutes, respectively.

Degradation of MB solution under sunlight irradiation is shown in Fig. 5. By comparison to MB solution without photocatalyst material, the degradation of MB solution in the presence undoped and Zn-doped CeO_2 is almost equal. In the other hand, MB solution with TiO_2 posses high degdradation. These result shows that the photocatalytic of undoped and Zn-doped CeO_2 is lower than TiO_2. The lowest degradation is achieved for MB with 20 mol% Zn content in CeO_2. It can be correlated to vacancies resulted from Zn^{2+} incorporation into Ce^{4+} lattice. That explaination can be showed from the decreasing of lattice constant. That vacancies act as trap for the charge [4]. The charge can not achieve to the particle surface to induce free radicals formation. This charge is responsible for MB degradation. The decreasing of charge on particle surface causes the inhibits MB degradation.

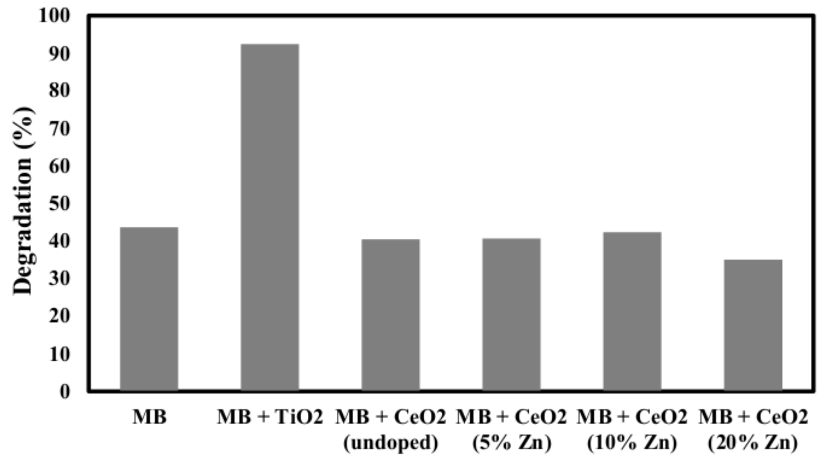

Fig. 5. The MB degradation under sunlight irradiation for 120 minutes.

Summary

Undoped and doped with various Zn compositions (5%, 10%, 20%) of CeO_2 nanopowders were synthesized from solution by ultrasound irradiation. The effect of Zn doping on the structural, morphological and optical properties of that CeO_2 were investigated. The diffraction peaks in XRD pattern show that both undoped and Zn-doped CeO_2 were well crystalline and posses fluorite cubic structure. It is found that CeO_2 nanopowders consist of spherical particle. The addition of Zn into CeO_2 results in decrease in particle size. The undoped and Zn-doped CeO_2 nanopowders have strong absorption properties in the ultraviolet region. This results show that Zn-doped CeO_2 is excellent UV absorber and almost no presence photocatalytic activity.

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