Synthesize of Cerium-doped ZnO nanoparticles as antioxidant agent

by Iis Nurhasanah

Synthesize of Cerium-doped ZnO nanoparticles as antioxidant agent

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Abstract. Zinc oxide nanoparticles are potential metal oxide for antioxidant agent. This paper investigates antioxidant activity of cerium-doped zinc oxide (Ce-doped ZnO) nanoparticles. Ce-doped ZnO nanoparticles was prepared by precipitation method with calcination temperature of 200°C. The product of precipitate was characterized by X-ray diffraction measurement, and UV-Vis spectrophotometer. The antioxidant activity of Ce-doped ZnO nanoparticles was investigated using 1,1-diphenyl-2-pcrylhydrazyl (DPPH) method. The X-ray diffraction pattern showed the growth of Ce-doped ZnO crystalline structure of hexagonal wurtzite with crystallite size of 42 nm. UV-Vis absorbance spectrum analysis revealed the band gap energy of Ce-doped ZnO nanoparticles was smaller than band gap energy of bulk ZnO. Ce-doped ZnO nanoparticles could scavenge DPPH free radicals and exhibited moderate antioxidant activity.

1. Introduction

Nanometric materials such as nanoparticles have been widely developed and applied in various fields because of their superior physical and chemical properties. The large surface to volume ratio of nanoparticles compared to their bulk lead to high reactivity nanoparticles. Therefore, nanoparticles possessed high possibility to interact with the surrounding environment [1]. Zinc oxide (ZnO) nanoparticles is one of the most nanoparticles that has been developed for biomedical applications due to its excellent biocompatibility, non-toxic and safe for human use [2]. Several studies of ZnO nanoparticles in the biomedical application including anti-inflammatory [3], antibacterial [4], antifungal [5], antimicrobial and antioxidant [6], anticancer [7] were found in the literatures.

Application of ZnO nanoparticles as antioxidants demonstrated the dependence of its antioxidant activity on the surface area [1]. ZnO nanoparticles with larger surface area showed better antioxidant activity [8]. A large surface area is owned by small size nanoparticles, hence the antioxidant activity can be increased by reducing the nanoparticles size. Doping with rare earth elements was found as an effective attempt to reduce the size of ZnO nanoparticles. Sheydaei et al. reported that Cerium (Ce) doping into ZnO resulted in reduction size and morphological changed of ZnO nanoparticles [9]. However, the small size nanoparticles tend to agglomerate and generated large secondary particles. In another report, nanoparticles with high crystallinity showed less agglomeration [10].

Numerous methods have been employed to synthesize Ce-doped ZnO nanoparticles including the sol-gel process [11], precipitation [12] and hydrothermal [13]. Commonly, formation of Ce-doped ZnO nanoparticles with great crystallinity required heat treatment at high temperature. In the precipitation method, crystallization take place at the calcination stage. Calcination at a relatively low temperature

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succeeded in formation of Ce-doped ZnO nanocrystals which were synthesized by precipitation method combined with ultrasonic irradiation [12].

This study aims to synthesis Ce-doped ZnO nanoparticles for antioxidant agent using a precipitation method followed by ultrasonic irradiation. The characteristics of the Ce-doped ZnO nanoparticles were analysed using X-ray diffractometer and UV-Vis spectrophotometer. The antioxidant property of Ce-doped ZnO nanoparticles was examined using *1,1-diphenyl-2-picrylhydrazil* (DPPH) method.

2. Experimentals

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 6H_2O$) and cerium nitrate hexahydrate $Ce(NO_3)_3 6H_2O$, 1,1-diphenyl-2-picrylhydrazil (DPPH) of Sigma Aldrich, ammonium hydroxide 25%, methanol and ethanol of Merck, demineralized water, distilled water.

2.2. Synthesis

Precipitation method was utilized to produce Ce-doped ZnO nanoparticles as described previously [12]. The precursor solution was made by dissolving $Zn(NO_3)_2 6H_2O$ and $Ce(NO_3)_3 6H_2O$ with molar ratio (Ce/Ce+Zn)=3% in 200 ml demineralized water. The homogeneous precursor solution was prepared at room temperature by stirring using a magnetic stirrer. Furthermore, 3 M of ammonium hydroxide was added into a precursor solution up to a pH of 10 and followed by ultrasonic irradiation. The product of precipitate was washed using ethanol and distilled water, then calcined at 200°C for 3 h.

2.3. Characterization

The X-ray diffractometer (Rigaku miniplex 600) was used to analyse crystal structure of Ce-doped ZnO nanoparticles. UV-Vis spectrophotometer (Genesys 150) was used to record absorption spectrum of Ce-doped ZnO nanoparticles in the range 300-800 nm. The antioxidant activity was evaluated by DPPH free radical method.

3. Results and Discussion

3.1. Structure of Ce-doped ZnO nanoparticles

The formation of Ce-doped ZnO nanoparticles was analysed based on X-ray diffraction (XRD) measurement. Fig. 1 displays XRD pattern of Ce-doped ZnO nanoparticles. The several peaks are seen at 2θ = 31.91°; 34.60°; 36.41°; 47.69°; 56.75°; 63.01°; 66.54°; 68.08°and 69.21°. Those peaks were indexed as the (100), (002), (101), (102), (110), (103), (200), and (112) planes (JCPDS Card No. 36-1451), respectively [1, 14, 15]. It exhibited the growth of Ce-doped ZnO crystalline structure of hexagonal wurtzite. The sharp and high intensity of diffraction peaks indicated that Ce-doped ZnO nanoparticles possessed high crystallinity.

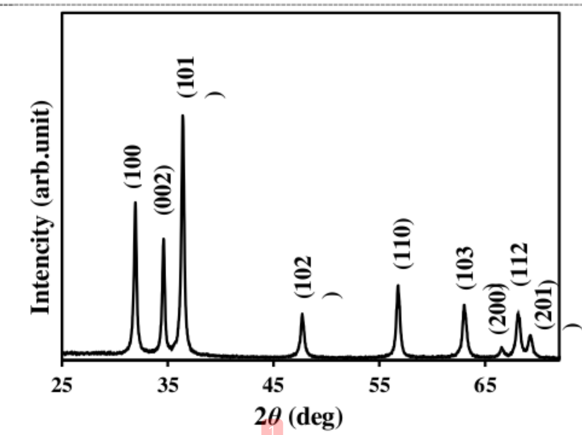

Figure. 1. XRD pattern of Ce-doped ZnO nanoparticles

The formation of Ce-doped ZnO nanoparticles was further analysed based on lattice parameter of hexagonal structure determination using the equation (1) [17].

$$\frac{1}{d_{hkl}{}^2} = \frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} \quad (1)$$

Where, h, k and l are Miller indices, d_{hkl} is spacing between planes with given Miller indices, a and c are the lattice parameters and λ is wavelength of X-ray radiation (1.54059 Å). The lattice parameters a and c were calculated for diffraction peak of (100) and (002) planes using equation (2) and (3) [15-16]. The obtained lattice parameter a and c of Ce-doped ZnO nanoparticles were 3.235 Å and 5.180 Å [15].

$$\alpha = \frac{\lambda}{\sqrt{3}\, Sin\, \theta_{(100)}} \quad (2)$$

$$C = \frac{\lambda}{Sin\, \theta_{(002)}} \quad (3)$$

The Williamson-Hall (W-H) equation (4) [15] was applied to determine the crystallite size and strain of Ce-doped ZnO nanoparticles.

$$\beta Cos\theta = \frac{k\lambda}{D} + 4\varepsilon\, sin\theta \quad (4)$$

Where β is full width at half of maximum (FWHM), k expresses the shape factor (0.9), D and ε are crystallite size and the lattice strain. Plotting the W-H equation yield a straight line as can be seen in Fig. 2. The crystal size of 42 nm was obtained from the intercept of W-H plot. It indicated that Ce-doped ZnO composed by nanometric particles. Meanwhile the lattice strain was found to be 8 x 10^{-4} from the gradient of W-H plot. The presence of lattice strain is a consequence of the incorporation of larger Ce ion into smaller Zn ion lattice [15].

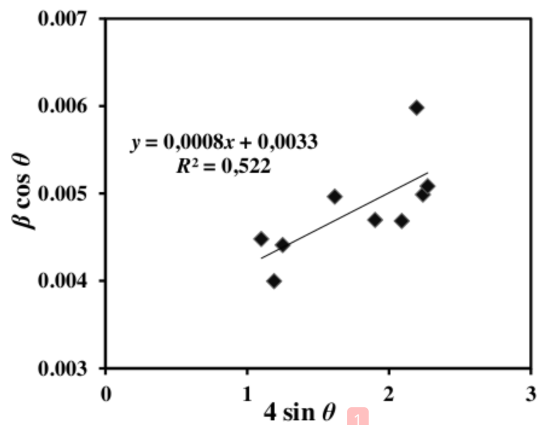

Figure. 2. Williamson–Hall plots of Ce-doped ZnO nanoparticles

3.2. Optical properties of Ce-doped ZnO nanoparticles

UV-Vis absorbance spectrum as depicted at Fig. 3(a) was used to analyze optical properties of Ce-doped ZnO nanoparticles. The strong absorption property observed in the wavelength region of 300 to 500 nm. It is also seen a sharp absorption peak at 377 nm which was identified as absorption characteristic of ZnO. Those absorption peak is attributed to the band to band electronic transition corresponding to band gap energy of ZnO [17].

Fig. 3(b) shows determination of the band gap energy for Ce-doped ZnO nanoparticles using Tauc's plot method. The Ce-doped ZnO nanoparticles possessed band gap energy of 2.7 eV which is smaller than the band gap energy of bulk ZnO [18]. The energy band gap reduction is the result of Ce doping into lattice of ZnO as previously reported [14].

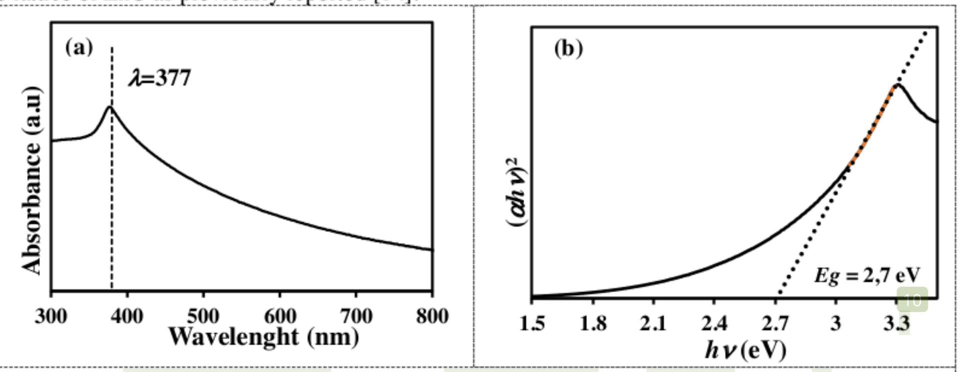

Figure. 3. (a) Uv-Vis absorption spectrum and (b) the band gap energy of Ce-doped ZnO nanoparticles

3.3. Antioxidant activity of Ce-doped ZnO nanoparticles

Antioxidant activity is a quantity that measures the ability of a substance to scavenge free radicals. The radical scavenging ability of Ce-doped ZnO nanoparticles was tested by DPPH free radicals. The Ce-doped ZnO nanoparticles demonstrate radical scavenging activity with inhibitory concentration (IC_{50}) of 163.08 µg/mL. These IC_{50} value revealed moderate antioxidant activity of Ce-doped ZnO nanoparticles. The antioxidant property of Ce-doped ZnO nanoparticles was attributed to the release of proton (H^+) and electron (e^-) to nanoparticles surface and interact with DPPH radical [19].

This result shows that combination of precipitation method with ultrasonic irradiation favoured to produce Ce-doped ZnO nanoparticles crystalline at low temperature. Nanometric crystallite size of about 42 nm and band gap energy of 2.7 eV facilitated the high release of proton (H^+) and electron (e^-) to surface of Ce-doped ZnO nanoparticles. Those characteristic contributed to the antioxidant activity of Ce-doped ZnO nanoparticles.

4. Conclusion

The precipitation method combined with ultrasonic irradiation was successfully used to produce high crystalline of Ce-doped ZnO nanoparticles at low temperature. The Ce-doped ZnO nanoparticles composed of crystallites with a size of 42 nm. The Ce-doped ZnO nanoparticles possessed antioxidant activity with IC_{50} of 163.08 µg/mL.

Acknowledgment

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