Green Synthesis ZnO Nanoparticles Using Rinds Extract of Sapindus rarak DC

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Abstract: The green synthesis of ZnO nanoparticles was carried out using a natural capping agent, Sapindus rarak DC rinds extract at low-temperature calcination and environmentally friendly solvent. The mixture of Zn(CH$_3$COO)$_2$, NaOH, and rinds extract was sonicated for 4 h at room temperature. The calcination was carried out at low temperature, 95°C for 8 h, and resulted in pale brown powder. XRD and SEM were used to confirm the structure and to analyze the morphology of ZnO nanoparticles respectively. XRD pattern of ZnO nanoparticles was corresponding to JDCPS card no 36-1451 with hexagonal structure. The average crystal size of ZnO nanoparticles was calculated using the scherrer equation and the average size was about 35.8 nm. From this study, the extract of the rind of Sapindus rarak DC was found to be a natural capping agent to synthesis ZnO nanoparticles because Sapindus rarak DC contain a pythochemical compound to limit the interaction between crystal seeds.

Keywords: Nanoparticles, Sapindus rarak DC, sonochemical

Introduction

In recent years, nanoparticles have become an interesting area of study for the scientist. ZnO nanoparticles are one of the inorganic materials well known as semiconductor materials with a wide bandgap which is about 3.61 eV and absorb Uv light with the wavelength ≤385 nm[1,2]. Due to the great properties of ZnO nanoparticles such as wide bandgap, high refractive index, and electrical conductivity, antifungal and antibacterial, and some optic properties have made ZnO nanoparticles used in wide areas such as gas sensors, varistor, optoelectronic device, and catalyst [3-5].

Due to the wide suitable application of ZnO nanoparticles, the scientist has studied and developed some methods to synthesize ZnO nanoparticles such as sonochemical, hydrothermal, solvothermal, and sol-gel [3, 6-8]. The sonochemical method is an excellent method for producing ZnO nanoparticles. Through sonochemical methods, ZnO crystal seeds have grown before heating. So heating can be done at low temperatures to remove solvents and organic residues. Based on the research that has been done, ZnO nanoparticles synthesized by sonochemical methods have a crystal size which is about 30-38 nm[6,9].

The other variety of capping agents were also used to alter the surface energy and control the crystal growth of ZnO to obtained the nanoparticles. Synthetic and natural capping agents have been studied in recent years. The synthetic capping agent such as polyvinyl alcohol (PVA) has been confirmed as a good capping agent in the synthesis of ZnO nanoparticles. The reaction between ZnO nanoparticles nuclei with PVA has made the different configuration to the ZnO system and the calculated crystal size is about 23-43 nm[10]. Active compounds in Moringa oleifera, such as phenolic acid, flavonoid, and vitamin have functional active groups that can act as capping agents as well as chelating agents in the synthesis of ZnO nanoparticles. The interaction of the three active compounds in Moringa oleifera obtained ZnO nanoparticles with crystal size between 12.37 – 30.51 nm [11].

Sapindus rarak DC contained phytochemical compounds such as flavonoid, saponin, alkaloid, phenol, dan tanin[12]. The functional groups of phytochemical compounds from Sapindus rarak DC were estimated to be a capping agent in the synthesis of nanoparticles. The aim of this study was to synthesize ZnO nanoparticles with a natural surfactant as a capping agent from the
extract of the rind of *Sapindus rarak DC*. The sonochemical method was chosen due to the previous research, this method can synthesize ZnO in nanoscale with environmentally friendly, fast reaction, low-temperature calcination, and nontoxic.

**Method**

**Preparation of rinds extract**

*Sapindus Rarak DC* fruits were purchased from Bogor, Indonesia. *Sapindus rarak DC* fruit used in this study were ripe fruit, first of all, *Sapindus rarak DC* fruits were washed and dried under the sun to remove water from washing. 5 grams of the dried fruits were ground and mixed with 95 mL demineralized water to obtain 5% w/v extract. The mixture was stirred at 70°C for 1 h, and the brown extract was obtained.

**Synthesis of ZnO nanoparticles using Sapindus rarak DC extract**

50 mL extract of *Sapindus rarak DC* was added to 50 mL Zn(CH$_3$COO)$_2$ 0.1 M in erlenmeyer glass. The mixture was stirred manually by a stirring rod. 50 mL NaOH 0.1 M was poured slowly into the mixture. The mixture was then sonicated using an ultrasonic bath for 4 h with the frequency of 35 kHz. After sonication, the gel was formed and then were filtered and washed by demineralized water to remove organic residues from the extract. The precipitate was dried at 95°C for 8 h to form ZnO nanoparticles. ZnO nanoparticles were characterized using XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope).

**Results And Discussion**

The reaction of Zn(CH$_3$COO)$_2$ and NaOH formed the precipitate of Zn(OH)$_2$ [6]. The ultrasonic radiation has been transformed the Zn(OH)$_2$ to be ZnO [9]. The pale brown color of ZnO nanoparticles was formed from the color of rinds extract.

The crystal structure of ZnO nanoparticles was characterized by X-Ray Diffraction (XRD). Figure 1 shows the XRD pattern of ZnO nanoparticles. Measurement was carried out with a range of 2θ from 20°-80°. The XRD pattern is in good agreement with JCPDS-card no 36-1451 with the strongest peaks at 2θ values of 31.81°; 34.41°; 36.32°; 47.61°; 56.68°; 62.90°; 67.95°; 69.07°; 77.04° with crystal structure hexagonal wurtzite. The characteristic peaks were corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (112), (201), and (202) [13]. There are other characteristic peaks were observed at 2θ values of 33.34°; and 59.35° which is corresponded with Zn(OH)$_2$ (JCPDS Card 38-0356).

![XRD pattern of ZnO nanoparticles.](image)

**Fig. 1.** XRD pattern of ZnO nanoparticles.

The average grain size of ZnO nanoparticles was calculated using the Debye Scherer equation:

$$ D = \frac{K\lambda}{\beta \cos \theta} $$

D is particle size, $\beta$ is full-width half maximum (FWHM), $\lambda$ is the wavelength of X-ray (1.546056 Å), K is a constant number of 0.9, and $\theta$ is Bragg’s diffraction angle [10].

**Table 1.** Grain size of ZnO nanoparticles at different peaks and the average grain size was about 35.78 nm.

| No | 2θ  | hkl | FWHM (β) | D (nm) |
|----|-----|-----|----------|--------|
| 1  | 31.81 | 100 | 0.20    | 54.38  |
| 2  | 34.41 | 002 | 0.32    | 25.99  |
| 3  | 36.32 | 101 | 0.12    | 69.68  |
| 4  | 47.61 | 102 | 0.16    | 54.27  |
| 5  | 56.68 | 110 | 0.24    | 37.61  |
| 6  | 62.90 | 103 | 0.40    | 23.28  |
| 7  | 67.95 | 112 | 0.48    | 19.96  |
| 8  | 69.07 | 201 | 0.40    | 24.13  |
| 9  | 77.04 | 202 | 0.80    | 12.69  |

*Sapindus rarak DC* contains phytochemical compounds such as saponins and flavonoids. Flavonoids and saponins have functional group OH as the active group. The active group of these phytochemical compounds will react like a ligand.
reaction to form a kind of polymer complex compound. The interaction between crystal seeds and the active group of rinds extract will limit the interaction between crystal seeds and then there are no crystal aggregates are formed obtaining the particles being in nano-scale [6,10,14]. The functional groups act as capping agents which can limit the rapid contacts between seeds crystal and stabilize the seeds crystal to form agglomeration [15].

Figure 2 shows the SEM image of ZnO nanoparticles. According to the XRD analysis, the size of the crystal was found to be nano-scale due to the presence of a capping agent. However, the organic residues from the extract of the rind were found to formed agglomeration in the surface of ZnO nanoparticles and were detected by SEM analysis. Since the calcinations were carried out at low temperatures, the organic residues still present in ZnO nanoparticles [16]. The sonochemical method is good enough to synthesis ZnO nanoparticles, the higher temperature calcination was required to remove the organic residues from Sapindus rarak DC extract so that the SEM image will only show the crystal without the organic residues from Sapindus rarak DC extract.

Conclusions

The purpose of this study was to investigate the effectivity of Sapindus rarak DC to be a natural capping agent in the synthesis of ZnO nanoparticles. The XRD pattern corresponded to JCPDS card no 36-1451 and there are impurities peaks to be found. The impurities peaks corresponded to Zn(OH)2. The average grain size of nanoparticles was found about 35.78 nm and indicating the extract of Sapindus rarak DC was effective as a capping agent in the synthesis of ZnO nanoparticles, however, the higher temperature calcination was needed to remove the organic residues from the extract and to decompose the impurities of Zn(OH)2 to ZnO.

Conflicts of interest

There are no conflicts to declare.

References

[1] S. Saha and A. K. Bhunia, “Synthesis and Characterization of ZnO Nanoparticles” Journal of Physical Sciences, vol. 19, pp. 109-114, December 2014.

[2] H. F. Lin, S.C. Liao, and S. W. Hung, ”The dc thermal plasma synthesis of ZnO nanoparticles for visible-light photocatalyst” Journal of Photochemistry and Photobiology A: Chemistry, vol. 174, pp. 82–87, August 2005.

[3] O. R. Vasile, I. Serdaru, E. Andronescu, R. Trusca, V. A. Surdu, O. Oprea, A. Ilie, and B. S. Vasile, ”Influence of the size and the morphology of ZnO nanoparticles on cell viability” Comptes Rendus Chimie, vol. 18, pp. 1335-1343, 2015.

[4] N. Talebian, S. M. Amininezhad, and M. Doudi, ”Controllable synthesis of ZnO nanoparticles and their morphology dependent antibacterial and optical properties” Journal of Photochemistry and Photobiology B: Biology, vo. 120, pp. 66-73, March 2013.

[5] L. He, Y. Liu, A. Mustapha, and M. Lin, “Antifungal activity of zinc oxide nanoparticles against Botrytis cinerea and Penicillium expansum” Microbiological Research, vol. 166, pp. 207-215, March 2011.

[6] A. Askarinejad, M. A. Alavi, and A. Morsali, ”Sonochemically assisted synthesis of ZnO nanoparticles: A Novel Direct Method” Iran Journal of Chemistry and Chemical Engineering, vol. 30, pp. 75–80, September 2011.

[7] E. Maryanti, D. Damayanti, I. Gustian, S. Prima S., ”Synthesis of ZnO nanoparticles by hydrothermal method in aqueous rinds extract of Sapindus rarak DC” Materials Letters, vol. 118, pp. 96-98, December 2013.

[8] T. Ghoshal, S. Biswas, M. Paul, and S. K. De, ”Synthesis of ZnO nanoparticles by solvothermal method and their ammonia sensing properties” Journal of Nanoscience and Nanotechnology, vol. 9, pp. 5973-5980, 2009.

[9] A. K. Zak, W. H. A. Majid, H. Z. Wang, R. Yousefi, A. M. Golsheikh, and Z. F. Ren, ”Sonochemical synthesis of hierarchical ZnO nanoparticles” Ultrasonic Chemistry, vo. 20, pp. 395-400, January 2013.

[10] T. K. Kundu, N. Karak, P. Barik, and S. Saha, ”Optical properties of ZnO nanoparticles prepared by chemical method using poly(vinilalcohol) (PVA) as capping agent, International Journal of Soft Computing and Engineering, vol. 1, pp. 19-24, July 2011.

[11] N. Matinise, X. G. Fuji, K. Karvijarasu, N. Mayedwa, and M. Maaza, ZnO nanoparticles via Moringa Oleifera green synthesis:
Physical properties and mechanism of formation, Applied Surface Science, vol. 406, pp. 339-347, January 2017.

[12] Y. Silviani, “Short communication: inhibitory effect of Sapindus rarak ethyl acetate extract on Staphylococcus aureus” Biotekanganiologi, vol. 14, pp. 16-18, May 2017.

[13] J. Santhoshkumar, S. V. Kumar, and S. Rajeshkumar, “Synthesis of Zinc oxide nanoparticles using plant leaf extract against urinary tract infection pathogen” Resource-Efficient Technologies, vol. 3, pp. 459-465, May 2017.

[14] A. Nafiunisa, N. Aryanti, and D. H Wardhani, “Kinetic Study of Saponin Extraction from Sapindus rarak DC by Ultrasound-Assisted Extraction Methods” Bulletin of Chemical Reaction Engineering and Catalysis, vol. 14, pp. 468-477, May 2019.

[15] A. Rahdar, “Study of Different Capping agent effect on the structural and optical properties of Mn Doped ZnS nanostructures” World Application Programming, vol. 3, pp. 56-60, 2013.

[16] M. Phrybyzewska and M. Zaborki, “The effect of Zinc Oxide nanoparticles morphology on activity in crosslinking of carboxilated nitrile Elastomer” Express Polymer Letters, vol 3, pp. 542-552, 2009.