**Strobilanthes crispus** (B.) leaf extract-assisted green synthesis of ZnO-La$_2$O$_3$ composite and preliminary study of its photocatalytic activity

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**Abstract.** In this study, ZnO-La$_2$O$_3$ composite as photocatalyst was synthesized via facile sol-gel route using biomaterial as a weak base source and a capping agent. ZnO-La$_2$O$_3$ composite was successfully formed through the reaction of Zn(NO$_3$)$_2$ (aq), La(NO$_3$)$_3$ (aq) and *Strobilanthes crispus* (B.) aqueous leaf extract. ZnO and La$_2$O$_3$ vibration modes of ZnO-La$_2$O$_3$ composite was analysed by Fourier Transform Infra Red (FTIR) at 400 – 700 cm$^{-1}$ wavenumber. Optical band gap of ZnO-La$_2$O$_3$ composite determined by using Tauc plot method was about 5.21 eV. X-Ray Diffraction (XRD) pattern of ZnO-La$_2$O$_3$ composite confirmed a combination of the diffraction patterns of ZnO particle and La$_2$O$_3$ particle. Photocatalytic activity of ZnO-La$_2$O$_3$ composite and ZnO particle were observed with methylene blue using UV light irradiation. The percentage of methylene blue degradation using ZnO-La$_2$O$_3$ composite and ZnO particle were 81.75 % and 74.87 %, respectively. This result shows that La$_2$O$_3$ was improving the activity and stability of the ZnO photocatalyst.

**Keywords:** green synthesis, methylene blue, photocatalyst, *Strobilanthes crispus* (B.), ZnO-La$_2$O$_3$ composite

1. **Introduction**

Zinc oxide (ZnO) has high potential in many applications, such as nanolasers, sensors, transistors, nanogenerators and solar cells [1]. ZnO is an n-type semiconductor with a band gap of 3.20 to 3.37 eV, has been used as material for photocatalytic process [2,3]. ZnO was found as an active catalyst in photodegradation process [4]. Common procedure mostly applied for the photocatalytic activity improvement in ZnO is to encounter the doping with another semiconductors [5,6]. La$_2$O$_3$ is known to offer an efficient result for the improvement of the catalyst’s activity and stability [7]. The previous reports associated with ZnO-La$_2$O$_3$ catalysts have been applied in monocrotophos degradation and phenol photodegradation [8,9].

On the other hand, there are several methods reported for the synthesis of composites, such as co-precipitation, sol-gel, and hydrothermal [10–12]. Sol-gel method has been widely used for the synthesis of metal oxide, because sol-gel is an efficient method for controlling the morphology and reactivity of solids [13]. Sol-gel method usually used in toxic hydrolysis agent like NaOH and organic solvents, and they are harmful to the environment. Green synthesis of composites is one of the promising and environmentally friendly method. In the previous report, green synthesis method was conducted using plant extract, fungi, microbes, and extracts of fruit and vegetables [14]. Green synthesis of nanoparticle and nanocomposite using plants such as *Phyllanthus emblica*, *Calotropis procera*, *Theobroma cacao*, *Oldenlandia corymbosa*, *L. Physalis angulata*, and *Terminalia catappa* have been reported [14–19]. However, there was no report on ZnO-La$_2$O$_3$ composite synthesis using green synthesis method.

*Strobilanthes crispus* (B.) is one of medical plants in Indonesia [20]. This plant has secondary metabolite compounds that can be used to synthesize metal oxides composite. *Strobilanthes crispus*
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(B.) leaf extract (SCBE) had been previously reported to contain the alkaloid, flavonoid, and saponin compounds which act as a weak base source and stabilizing agent in metal oxide composites formation [21].

In this research, ZnO-LaO composite was synthesized through a simple green route using SCBE as a weak base source and capping agent. ZnO-LaO composite was characterized by using UV-Vis Diffuse Reflectance Spectroscopy (DRS), Fourier Transform Infrared (FT-IR), and X-Ray Diffraction (XRD). Furthermore, ZnO-LaO composite was evaluated for photocatalytic degradation of methylene blue (MB)

2. Materials and methods

2.1. Materials

Strobilanthes crispus B. (SCB) was obtained from Cimanggis, Depok, West Java, Indonesia and has been determined at Indonesian Institute of Sciences (LIPI), Bogor, West Java, Indonesia. Methylene blue (MB) was obtained from Merck. Methanol and n-hexane were obtained from PT. Brataco. Analytical-grade of lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) and zinc nitrate pentahydrate (Zn(NO₃)₂·4H₂O) were obtained from Merck, Germany.

2.2. Preparation of leaf extract

250 mL of methanol was added to the dried leaves powder of SCB and macerated for 7 days at room temperature. Methanol extract of SCB leaves was partitioned using hexane. The filtrate was then concentrated using vacuum rotatory evaporator. Distilled water was added to the concentrated methanol to obtain a stock solution of SCBE for composite synthesis.

2.3. ZnO-LaO composites synthesis

Synthesis of ZnO-LaO composite using SCBE refers to the method from the previous research [9]. Zn(NO₃)₂ and La(NO₃)₃ precursors were mixed and stirred continuously at 80 °C for 1 h. After that, SCBE was added to the mixture drop wise, then stirred simultaneously at 80 °C for 4 h. The colloidal was heated at 100 °C for 1 h and annealed at 700 °C for 3 h. ZnO-LaO crystal was obtained as white powder. ZnO particles were synthesized using the same method, but without La(NO₃)₃ precursor.

2.4. Characterization

Band gap measurements were determined by UV-Vis diffuse reflectance spectra (Shimadzu 2450). The functional group of compound was analyzed by FTIR (Shimadzu, Prestige 21). The diffraction pattern information was determined by XRD (Shimadzu 610) at 2θ of 20–60° with Cu Kα (λ = 0.1546 nm) radiation. The UV-Vis absorption spectrum was recorded using UV-Vis spectrophotometer (Shimadzu 2600).

2.5. Photocatalytic activity

ZnO-LaO composite was added to methylene blue of 3.0 × 10⁻⁴ M. The mixture was stirred under UV light irradiation. The reaction was observed through the absorbance change using a UV-Vis spectrophotometer for 120 min. For comparison, the photocatalytic activity of ZnO nanoparticles was evaluated using the same method.

3. Results and discussion

3.1. FT-IR analysis

Identification of functional groups of SCBE, ZnO, La₂O₃, and ZnO-LaO composite were recorded by FTIR spectroscopy at 400-4000 cm⁻¹ range. Figure 1a shows broad vibrations band at 3361.1 cm⁻¹ which corresponds to −OH stretching of flavonoid and saponin compounds [22, 23] and vibrations band at 1080.2 cm⁻¹ which corresponds to C-N stretching of alkaloid compounds [24].

Figure 1b shows a typical Zn-O stretching vibration mode of ZnO particles at 453.0 cm⁻¹ and La-O stretching vibration mode of La₂O₃ particles at 640.8 cm⁻¹. These results conform to the previous literatures [16,25]. Meanwhile, ZnO-LaO composite shows two vibration modes of ZnO particles and La₂O₃ particles at 453.0 and 640.8 cm⁻¹, respectively, indicating ZnO-LaO composite was successfully synthesized.
3.2. UV-Vis DRS analysis
The determination of band gap energy value of ZnO-La$_2$O$_3$ composite was obtained through the characterization of UV-Vis DRS. The UV-Vis DRS result presents the reflectance data which then converted into Kubelka Munk equation by plotting the curve F(R) against Eg (eV) as shown in figure 2. According to the calculation, ZnO-La$_2$O$_3$ composite has a band gap energy (Eg) of 5.21 eV.

3.3. XRD analysis
The diffraction patterns and average crystalline size of ZnO-La$_2$O$_3$ composites are shown in figure 2 (b). The diffraction patterns of ZnO crystallites (blue line) and La$_2$O$_3$ crystallites (red line) are matched with the COD 96-230-0113 and COD 96-200-2287, respectively. The XRD results of ZnO-La$_2$O$_3$ composites (green line) shows ten diffraction patterns at 2θ of 26.06°; 27.25°; 27.94°; 29.90°; 31.71°; 34.36°; 36.20°; 39.40°; 47.48° and 56.54°, which demonstrated the combination of diffraction pattern of ZnO crystallites and La$_2$O$_3$ crystallites. The crystallite size of ZnO-La$_2$O$_3$ was calculated using the Debye-Scherer’s formula. According to the calculation, ZnO-La$_2$O$_3$ composite has the crystallite size of 45.59 nm.
3.4. Photocatalytic activity

The photocatalytic activity of ZnO-La₂O₃ composite was investigated by the degradation of MB under UV light irradiation. Figure 3 shows the degradation spectra of MB in 120 minutes. Investigation of MB degradation was indicated by the decreasing absorbance of UV-Vis spectra at λmax of 665 nm and the decreasing colour intensity of MB. Figure 3 shows that ZnO-La₂O₃ composite and ZnO particle without photocatalyst are able to degrade MB under UV light irradiation, yielding MB degradation of 81.75% 74.87%, and 9.17% respectively. This result shows that La₂O₃ was improving the activity and stability of the ZnO photocatalyst.

When a semiconductor is irradiated by light, it will produce e- (electron) on the conduction band (CB) and h+ (hole) on the valence band (VB), which is caused by the excitation of electron from VB to its CB. The hole will then react with water (H₂O), which will cause the formation of hydroxyl radicals (OH•) and H⁺ ion. Meanwhile, the electron on the CB will react with the water-dissolved O₂, which eventually will form superoxide radical, O₂•. This radical ion will react with H⁺ ion to form hydroxyl radicals. The hydroxyl radicals will react with one and another to form hydrogen peroxide (H₂O₂) and also react with MB to degrade it and form various intermediate products such as phenol and benzene sulfonic acid compounds, before producing H₂O and CO₂ gas [26]. Figure 3a shows the appearance of a new absorption peak at the wavelength of 277 nm. This result indicates the presence of carboxylic acid groups and aromatic chromophore groups [27]. The formed hydrogen peroxide will react with the light and cause a photolysis reaction, so the hydrogen peroxide will split into hydroxyl radicals or the hydrogen peroxide, which will react with electron on CB of the composites forming hydroxyl ions and radicals.

4. Conclusions

The ZnO-La₂O₃ composite prepared using Strobilanthes crispus B. leaf extract has been studied. FT-IR result showed that ZnO-La₂O₃ composite was successfully formed at 453.0 and 640.8 cm⁻¹ which corresponds to the specific vibration mode of Zn-O and La-O, respectively. The optical band gap of ZnO-La₂O₃ composite was 5.21 eV. XRD result of ZnO-La₂O₃ composite showed a combination diffraction peak of ZnO and La₂O₃ particle with crystalline size of 45.59 nm. The ZnO-La₂O₃ composite and ZnO particle showed the photocatalytic activity in the methylene blue degradation at 81.75 % and 74.87 %, respectively.

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