La$_2$O$_3$ nanoparticles formation using *Nothopanax scutellarium* leaf extract in two-phase system and photocatalytic activity under UV light irradiation

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Abstract. La$_2$O$_3$ nanoparticles (NPs) have been formed using *Nothopanax scutellarium* leaf extract (NSE) and lanthanum precursor in two-phases system (n-hexane/water) with high-speed stirring method. Alkaloids as a secondary metabolite compound in NSE were used as a hydrolyzing agent and the other substances, namely saponin and tannin as a capping agent. All characterizations in this study were undertaken by Fourier transform infrared (FT-IR), UV-Vis DRS, X-Ray diffraction (XRD), scanning electron microscopy energy-dispersive X-Ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM) and UV-Vis spectrophotometer. UV-Vis DRS characterization showed that La$_2$O$_3$ NPs has a bandgap value of 5.59 eV. The particle size of La$_2$O$_3$ NPs was around 84.3 nm confirmed by TEM. UV-Vis spectrophotometer was utilized to analyze the photocatalytic activity of La$_2$O$_3$ NPs for the degradation of malachite green (MG) as a modelling of dye. The degradation percentage of MG using La$_2$O$_3$ NPs was 87.32 % for 120 min under UV light irradiation.

Keywords: La$_2$O$_3$ nanoparticle, *Nothopanax scutellarium* leaf extract; two-phases system; photocatalytic activity; malachite green

1. Introduction

Recently, research related to the green synthesis of nanoparticles had been well developed. It uses materials such as microorganisms, enzymes, plants, and plant extracts [1]. A biological research reported that plant extract can serve as a reducing and stabilizing agent in metal nanoparticle synthesis [2].

Two-phases system is commonly used for complex formation of metal and ligand to dissolve them in polar and non-polar solvents, respectively. This method has advantages, such as simple and cheaper synthesis process and low energy requirement [3].

Metal nanoparticles green synthesis, namely gold nanoparticles and copper (II) oxide nanoparticles using *Tinospora crispa* plant extracts have been recorded. Besides, metal oxide nanoparticles such as titanium oxide using *Averrhoa bilimbi* then metal oxide transition such as silver oxide and nickel oxide also had been successfully synthesized using *Vernonia amygdalina* and *Ageratum conyzoides*, respectively. Also, Cerium and lanthanum metal oxide nanoparticles had been successfully synthesized using *Datura metel L* and *Physalis angulata* leaf extract, respectively, in one phase system [4-10].
Rare earth elements, as materials with high thermal conductance, melting point, and conductivity, as well as unique physical and chemical properties, have been extensively applied in electronics, biomedical, and agronomic fields [11]. Lanthanide oxide nanoparticles (La₂O₃ NPs) are rare earth metal oxide and semiconductor materials with a bandgap range of 4.3–5.8 eV. La₂O₃ NPs are potentially useful materials for various optical and electronic applications, such as capacitors, optical filters and waveguides [12].

*Nothopanax scutellarium* is an ornamental plants or hedges grown wild in field and river banks. In the previous study, it is a local medicinal plant for a hair growth contained about 11% of alkaloids and other secondary metabolites such as flavonoid, saponin, and tannin [13]. Alkaloids served as a hydrolysis agent (weak base source of OH⁻). Meanwhile, the other secondary metabolite such as saponins and tannins act as a capping agent for La₂O₃ NPs growth [14].

In this study, the synthesis of La₂O₃ NPs were carried out using *Nothopanax scutellarium* leaf extract (NSE) in a two-phase system (n-hexane / water), which is not reported in the previous study yet. Also, La₂O₃ NPs were tested for the photocatalytic activity for degradation of malachite green under UV light irradiation.

2. Materials and method

Lanthanum nitrate hexahydrate (La(NO₃)₃.6H₂O), malachite green, and NSE were applied as the primary raw materials. (La(NO₃)₃.6H₂O) and malachite green were purchased from Merck, and *Nothopanax scutellarium* plant obtained from the conservation unit of biopharmaca (UKBB) center study for tropical, LPPM IPB, Bogor, Indonesia.

2.1. Preparation of NSE
The leaves were cleaned and dried at room temperature. Fifty g of leaves powder was macerated in 250 mL of n-hexane for a week by stirring every day. Next, the filtrate was separated and partitioned by aquadest. Then, the formed n-hexane and water phases were identified by the phytochemical test.

2.2. Synthesis of La₂O₃ NPs
La₂O₃ NPs were synthesized by a sol-gel method with slight modification [9]. 2 mmol of La(NO₃)₃ precursor was mixed into n-hexane phase of NSE by high-speed stirring method at 23,000 rpm. Then, the water phase changed its color from clear to turbid, and the turbid layer was separated. The result was dried at 120 °C and calcined at 700 °C for 2 h to form white powders of La₂O₃ NPs.

2.3. Photocatalytic activity of La₂O₃ NPs
Three mg of La₂O₃ NPs was dispersed in 25 mL of malachite green 6 x 10⁻⁶ M and stirred for 120 min under UV light irradiation. The degradation result was monitored by UV-Vis spectrophotometer every 10 min irradiation.

2.4. Characterization of La₂O₃ NPs
Fourier transform infrared (FT-IR) spectroscopy (IR Prestige-21 Shimadzu) was used to identify the functional groups of La₂O₃ NPs in the range of 400–4000 cm⁻¹. UV-Vis diffuse reflectance (UV-Vis DRS, Shimadzu 2600) was utilized to determine the band gap value of La₂O₃ NPs. The degradation of malachite green were observed by UV-Vis spectrophotometer (Shimadzu 2600). The crystallinity of La₂O₃ NPs was determined by X-Ray diffraction (XRD, Shimadzu). The particle size distribution of La₂O₃ NPs was defined by particle size analyzer (PSA, Zetasizer nano ZS 90). The morphology and element composition of La₂O₃ NPs were determined by scanning electron microscopy-energy dispersive X-Ray spectroscopy (SEM-EDX, JED-2300). The particle size of La₂O₃ NPs was investigated by transmission electron microscopy (TEM, JEOL JEM 14000).
3. Results and discussion

3.1. Characterization of La$_2$O$_3$ NPs

La$_2$O$_3$ NPs and NSE functional groups are presented in FT-IR spectra in figure 1. The spectrum of NSE shows that the vibration of O-H stretch, C-H sp$^3$ stretch, -NH stretch, C-C stretch, N-O stretch, and N-H Wagg-stretch appeared at the wavenumbers of 3450, 2960, 1646, 1462, 1387 and 810 cm$^{-1}$, respectively. The N-H Wagg-stretch indicates the presence of alkaloids. Meanwhile, the functional groups of -OH and C-H sp$^3$ indicate the presence of saponins. Also, the C-C stretch is derived from steroids compound [15-17]. Besides, the spectrum of La$_2$O$_3$ NPs shows that there was a La-O stretch at 645 cm$^{-1}$ [18].

The band gap value was determined by using a % reflectance, which is converted into Kubelka-Munk function. A linear regression equation for $F(R)^2 = 0$ is found and made by plotting $F(R)^2$ to $E_g$ [19]. Based on the linear regression equation, the bandgap value of La$_2$O$_3$ NPs was 5.59 eV, as shown in figure 2. XRD pattern of La$_2$O$_3$ NPs shows that there were some peaks at the $2\theta$ of 15.72° (1 0 1); 27.36° (2 2 2); 28.12° (3 0 0); 39.62° (4 0 0) and 48.69° (6 2 2), as shown in figure 3.

Figure 1. FTIR spectra of NSE (green line) and La$_2$O$_3$ NPs (blue line).

Figure 2. Curve of F(R) to $E_g$ of La$_2$O$_3$ NPs.

Figure 3. XRD pattern of La$_2$O$_3$ NPs.
These values are corresponded to JCPDS data of La$_2$O$_3$ no. 04–0856 [20]. According to the data, La$_2$O$_3$ had the hexagonal crystal structure. Besides, the crystalline size of La$_2$O$_3$ was calculated by Debye-Scherrer equation using the full-width at half maximum $\beta$ of the diffraction peaks [21],

$$ D = \frac{0.9 \lambda}{\beta \cos \theta}, $$

where $\lambda$ is the X-Ray wavelength and $\theta$ is the Bragg angle diffraction. According to the calculation, La$_2$O$_3$ had a crystalline size of 29.67 nm. Moreover, La$_2$O$_3$ NPs were characterized by PSA to determine the average particle size distribution. The average distribution particle size of La$_2$O$_3$ NPs was 55.76 nm, as shown in figure 4. The morphology was investigated by SEM characterization with 500 nm scale bar, as shown in figure 5a. For further characterization, TEM was utilized to determine the particle size of La$_2$O$_3$. It can be seen that the particle size of La$_2$O$_3$ NPs was about 84.3 nm, as presented in figure 5b.

3.2. Photodegradation activity of malachite green

Figure 6a shows a UV-Vis absorption spectra of malachite green degradation using La$_2$O$_3$ NPs. The degradation was observed with UV-Vis spectrophotometer by monitoring the decrease of absorbance at the maximum wavelength of 617 nm. Also, figure 6b shows the plotting of % degradation versus time. The degradation percentage was calculated by equation 1.

$$ \% D = \frac{[C]_0 - [C]_t}{[C]_0} \times 100 \% $$  \hspace{1cm} (1)

where $[C]_0$ is the initial concentration of MG and $[C]_t$ is MG concentration of each time interval by UV light irradiation [22]. According to the calculation, the degradation percentage of MG photodegradation using La$_2$O$_3$ NPs was 87.32 % for 120 min under UV light irradiation.

![Figure 4](image4.png)

Figure 4. Particle size distribution of La$_2$O$_3$ NPs.

![Figure 5](image5.png)

Figure 5. (a) SEM image of La$_2$O$_3$ NPs with 30,000x magnification, and (b) TEM image of La$_2$O$_3$ NPs.
4. Conclusion
La₂O₃ NPs have been synthesized using NSE in the two-phase system (n-hexane/water). The NSE phytochemical test presents the secondary metabolite compounds such as alkaloids, saponin, and steroids, which are used as a weak base source and capping agent for La₂O₃ NPs formation. The XRD analysis confirms that La₂O₃ had the hexagonal crystal structure. Finally, La₂O₃ NPs have a nanometer scale and photodegradation activity on malachite green of 87.32 % under UV light irradiation.

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