Sm$_2$O$_3$ nanoparticles preparation using caesalpinia pulcherrima leaf extract, characterization and photocatalytic activity

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Abstract. In this research, Sm$_2$O$_3$ nanoparticles (NPs) have been prepared via Caesalpinia pulcherrima leaf extract (CPE), whichh contains secondary metabolites contained as a weak base source and a capping agent. The nanoparticles were confirmed by UV-Vis DRS, FT-IR spectroscopy, XRD, PSA and TEM. FT-IR spectrum showed that CPE contains the secondary metabolites which play an essential role in the preparation of Sm$_2$O$_3$ NPs. UV-Vis DRS result showed that the bandgap value of Sm$_2$O$_3$ NPs was approximately 4.76 eV which works in the UV region. Based on the XRD analysis, Sm$_2$O$_3$ NPs have a structure of cubic. PSA characterization showed that the average particle size distribution of Sm$_2$O$_3$ was around 84.47 nm. TEM image confirmed that Sm$_2$O$_3$ was in nanoscale with the particle size of 73.27 nm. Finally, Sm$_2$O$_3$ NPs have been tested for the photodegradation of malachite green (MG) under UV light illumination. The degradation percentage of MG using Sm$_2$O$_3$ NPs photocatalyst was 80.14 % for 2 h.

Keywords: Sm$_2$O$_3$ nanoparticles, Caesalpinia pulcherrima (L.) Sw, characterization, photocatalytic activity

1. Introduction

Nanoparticles have an average size of < 100 nm with some beneficial characteristics such as large surface area and equally distributed composition of cell units. Also, nanoparticles are mostly applied in the fields of health, agriculture, and electronics due to their unique physical, chemical, thermal and electrical properties, which makes the nanomaterial more preferable than the bulk material [1]. Semiconductor-nanoscale materials are important and promising to be developed because of their good optical, photocatalytic, and magnetic properties, especially metal-semiconductors [2]. Also, metal oxides and their semiconductor-based composites are excellent materials for catalytic and antimicrobial activity [3].

Rare-earth metal nanoparticles have unique magnetic, luminescent and electrochemical properties [4]. Samarium oxide (Sm$_2$O$_3$) is a wide bandgap rare-earth metal oxide [5]. Recently, metal oxide nanoparticles have been synthesized using fungi, bacteria, or plant extracts as the desired biogenic agent [6] since the presence of toxic chemicals could be adsorbed on the material surface and has an adverse effect on health [7]. Plant extracts are widely utilized to synthesis metal oxide nanoparticles and surfactants such as Tinospora crispa, Datura metel L, Pandanus amaryllifolius, Ageratum
conyzoides L., Orthosiphonaristatus (Blume) Miq, Morinda citrifolia L. [8-12]. Caesalpinia pullcherima has a rich phytochemical content. Some isolated compound from the extract of this plant are alkaloid, saponin, flavonoid [13]. In this work, we reported the synthesis of Sm$_2$O$_3$ NPs using *Caesalpinia pullcherima*, the characterization and their photocatalytic activity for MG degradation under UV light illumination.

2. Materials and method

The CPE solution was prepared by an extraction method, as reported in our previous work [9]. Fifty g of dried *Caesalpinia pullcherima* powders were macerated into methanol for 7 days. The mixture was then stirred for 20 min every day. The result was partitioned using n-hexane to obtain the n-hexane and methanol fractions. The methanol fraction was evaporated, then dissolved into distilled water to obtain the CPE solution. All fractions were further tested by phytochemical screening.

Sm$_2$O$_3$ NPs were synthesized by adding 0.02 M Sm(NO$_3$)$_3$ into 10 mL of CPE 1.85 % (w/v). The mixture was stirred for 4 h at 80 °C. The formed colloid was heated at 120 °C to form a gel, then calcined at 600 °C to form a white powder [14]. The obtained Sm$_2$O$_3$ NPs was confirmed by UV-Vis spectrophotometer, UV-Vis DRS, FT-IR, XRD, PSA and TEM. Photocatalytic activity tests were carried out by adding Sm$_2$O$_3$ NPs into 25 mL of malachite green $6 \times 10^{-6}$ M and stirred up to 120 min under visible light radiation. The degradation result was observed by a UV-Vis spectrophotometer every 10 min [15].

3. Results and discussion

FTIR characterization was performed to identify the functional groups of Sm$_2$O$_3$ NPs and a water fraction of CPE. The water fraction of CPE has vibrational spectrum at wavenumbers of 3341, 2941, 1700, 1353, 1231 and 843 cm$^{-1}$, which were attributed to O-H stretching, C-H stretching, N-H amine bending, N-O stretching, C-N stretching, N-H wagging-stretching, respectively, as shown in figure 1. Amine bending, N-H functional groups, C-N stretching indicate the presence of alkaloid compound [16]. Meanwhile, O-H stretching, C-H sp$^3$ stretching, and C=C stretching show the presence of saponins [17]. The secondary metabolite compounds in the CPE water fraction have an important role, alkaloids act as a source of weak bases, while saponins act as a capping agent in the nanoparticle synthesis. Also, the absorption at 534 cm$^{-1}$ shows the bending vibration of Sm-O bond. This result has conformity with the previous research, which indicates that the bending vibration of Sm-O bond is in the wavenumber range of 593–475 cm$^{-1}$[14].

XRD characterization of Sm$_2$O$_3$ NPs was performed to determine their diffraction patterns, as shown in figure 2. The diffraction patterns of Sm$_2$O$_3$ NPs were presented at 2θ of 25.96$^\circ$; 28.49$^\circ$; 30.83$^\circ$;

![Figure 1. FTIR spectra of Sm$_2$O$_3$ NPs (black line) and CPE (green line).](image1)

![Figure 2. XRD pattern of Sm$_2$O$_3$ NPs.](image2)
38.93°; 40.74°; 42.48° and 48.90° (COD Entry Number 96-101-0341) with the miller index of 310, 222, 321, 323, 422, 501 and 503, respectively. According to this result, it can be concluded that Sm$_2$O$_3$ was well-matched with a cubic crystal structure.

PSA characterization was conducted to determine the average particle size distribution of Sm$_2$O$_3$ NPs. The characterization result is shown in figure 3. The average particle size of Sm$_2$O$_3$ NPs was 84.47 nm. These results proved that Sm$_2$O$_3$ NPs were synthesized using CPE.

The bandgap energy is determined by the UV-Vis DRS characterization. The determination was conducted by converting a % reflectance into a bandgap value using Kubelka-Munk function. The F(R)$^2$ and Eg were plotted by finding and making a linear regression equation with F(R)$^2$ against Eg (eV) [18], as shown in figure 4. From the linear regression equation, the bandgap energy of Sm$_2$O$_3$ NPs was 4.76 eV. This result showed that Sm$_2$O$_3$ NPs have good absorption in the UV region.

TEM characterization was used to analyze the morphology and particle size of Sm$_2$O$_3$ NPs. TEM images were presented in a magnification of 20,000 times, as shown in figure 5. According to the analysis result, Sm$_2$O$_3$ NPs had an average of particle size approximately 73.27 nm. This result demonstrates that Sm$_2$O$_3$ NPs has the particle size in nano-scale.

The photocatalytic activity of Sm$_2$O$_3$ NPs was tested in the degradation of malachite green under UV light illumination for 120 min. The results of UV-Vis absorption spectra for the photodegradation of malachite green using Sm$_2$O$_3$ NPs are shown in figure 6.

The wavelength shift occurs at $\lambda_{\text{max}}$ of 318 to 250 nm, as shown in figure 6. A peak shift around 250–254 nm indicates the presence of carboxylic acid and aromatic chromophore groups [19].

![Figure 3. Particle size distribution of Sm$_2$O$_3$ NPs.](image3)

![Figure 4. UV-Vis DRS of Sm$_2$O$_3$ NPs.](image4)

![Figure 5. TEM mage of Sm$_2$O$_3$ NPs.](image5)
Figure 6. UV-Vis absorption spectra of malachite green degradation.

Figure 7. Mechanism of photocatalytic activity.

The absorbance value obtained every 10 min irradiation was used to obtain the concentration of malachite green. Then, the degradation percentage was calculated using equation 1 [20].

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Depgradation\% = \left( \frac{[C]_0 - [C]_t}{[C]_0} \right) \times 100\%
\]

([C]₀ is the initial concentration of malachite green and [C]ₜ is the concentration of malachite green at each time interval under UV light illumination. According to the calculation, the degradation percentage of malachite green using Sm₂O₃ NPs was 80.14 % for 120 min under UV light illumination. Furthermore, the photocatalytic activity of Sm₂O₃ NPs is presented in figure 7 [21].

When Sm₂O₃ NPs were irradiated by UV light, it will produce e⁻ (electrons) in the conduction band (CB) and h⁺ (hole) in the valence band (VB) due to an electron excitation from the valence band to the conduction band, as presented in figure 7. The hole in the valence band reacts to H₂O to form the hydroxyl radicals (OH⁻) and H⁺ ions, while the electrons in the conduction band react to O₂ dissolved in water to form superoxide radicals (O₂⁻). Both hydroxyl and superoxide radicals can degrade the molecule of malachite green.
4. Conclusion

The green synthesis of Sm$_2$O$_3$ NPs was carried out using a water fraction of *Caesalpinia pulcherrima* leaves extract (CPE). Flavanoid and saponin in extract act as capping agent and alkaloid as a weak base source to synthesize the metal oxide nanoparticles. According to TEM characterization, Sm$_2$O$_3$ has the particle size in nanoscale. Also, the photocatalytic activity of Sm$_2$O$_3$ NPs works at $E_g$ of 4.76 eV, which operates in the UV area. In the next work, we expect that Sm$_2$O$_3$ NPs could be utilized as materials, which could be active in the visible area.

Acknowledgments

The authors would like to thank Universitas Indonesia for funding this research through PIT-9 Grant Universitas Indonesia with contract number: NKB-0037/UN2.R3.1/HKP.05.00/2019.

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