Fabrication of Gd\textsubscript{2}O\textsubscript{3} nanoparticles in hexane-water system using *Myristica fragrans* Houtt leaves extract and their photodegradation activity of malachite green

A Eprasatya, Y Yulizar, R T Yunarti and D O B Apriandani

Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: yokiy@sci.ui.ac.id

**Abstract.** This study aims to fabricate the Gd\textsubscript{2}O\textsubscript{3} nanoparticles (NPs) using *Myristica fragrans* Houtt leaves extract (MFE) in hexane-water phases system by high-speed stirring method. We performed a phytochemical test to qualitatively confirm that MFE contained the secondary metabolite of alkaloid, steroid and saponin as a weak base source (OH\textsuperscript{-}), a stabilizing agent, and a capping agent in the Gd\textsubscript{2}O\textsubscript{3} NPs fabrication, respectively. According to SEM image, the morphology of Gd\textsubscript{2}O\textsubscript{3} NPs was spherical shape in agglomeration. UV-Vis DRS result shows that Gd\textsubscript{2}O\textsubscript{3} NPs has a large bandgap which was found to be 5.1 eV. XRD characterization shows that the diffraction pattern of the formed nanoparticle was well-matched with the data source of Gd\textsubscript{2}O\textsubscript{3}. The particle size of Gd\textsubscript{2}O\textsubscript{3} NPs was approximately 40 nm confirmed by PSA. Photocatalytic activity of Gd\textsubscript{2}O\textsubscript{3} NPs was tested for dye degradation. In this study, malachite green was utilized as a modelling of dye. The photodegradation percentage of malachite green using Gd\textsubscript{2}O\textsubscript{3} NPs catalyst was 75.15\% for 120 min under UV light irradiation.

**Keywords:** Gd\textsubscript{2}O\textsubscript{3} NPs, *Myristica fragrans* Houtt, hexane-water phases, photocatalytic activity malachite green

1. Introduction

Nanoparticle has been developed due to its versatility in many aspects. The synthesis of nanoparticle has been reported with various methods such as co-precipitation, sol-gel method, microemulsion, hydrothermal/solvothermal, or also electrochemical [1]. But mostly, these methods are expensive and not environmentally friendly because it uses a lot of chemical compounds which harms the human body and environment [2]. On the other hand, green synthesis is a nanomaterial synthesis method, designed as a cost-effective alternative in the fields of chemistry and physics [3]. Green synthesis of metal nanoparticles is an environmentally friendly procedure, free from strong, hazardous, and high cost chemicals [4].

The use of plants in the nanoparticle synthesis is related to the content of both secondary metabolites and antioxidant activity. These antioxidants make plants as an alternative material to environmentally friendly reduce the use of hazardous chemicals [4]. Another advantage of using plants for nanoparticle synthesis are readily available, non-toxic, and have a wide variability in metabolites to prevent the agglomeration of nanoparticles and the formation of surfactants, respectively [3, 5, 6].
The hexane-water phase system is a common method to form a complex of metal and ligand since metal ion can dissolve in polar substance, and ligand can dissolve in nonpolar. The advantage of using a hexane-water phase to synthesize nanoparticles are relatively low costs and energy [7].

Gadolinium oxide (Gd$_2$O$_3$) is one of the members of lanthanide oxide group which has a high density (7.6 g/cm$^3$), a crystallographic stability up to 2325 °C, a high mechanical strength, and a large optical band gap (5.4 eV) [8]. Also, Gd$_2$O$_3$ is well-known as an n-type semiconductor for photocatalysis. Due to their highly chemical stability, UV absorptivity and efficient photon-to electron conversion, Gd$_2$O$_3$ is widely used for the degradation of organic pollutants and water splitting [9-11].

Nanoparticles formation by hexane-water phases system has not been widely reported yet. Therefore, in this research, Gd$_2$O$_3$ NPs was synthesized using Myristica fragrans Houtt leaves extract (MFE) in hexane-water phase system by high-speed stirring method. Also, their photocatalytic activities were tested for the degradation of malachite green.

2. Materials and method

2.1. Materials

Materials used in this research were Myristica fragrans Houtt leaves from Pusat Studi Biofarmaka Tropika IPB, Bogor, West Java. The chemicals of gadolinium nitrate hexahydrate (Gd(NO$_3$)$_3$.6H$_2$O), malachite green, n-hexane, HCl, Wagner reagent, H$_2$SO$_4$, chloroform, lead acetate were all from Merck, and distilled water.

2.2. Method

2.2.1. Myristica fragrans (MF) leaves extraction. MF leaves were washed, cut, dried, then blended to obtain powders [12]. MF leaf powder was macerated into hexane and stirred every day for a week. The mixture was sieved to produce the crude extract, which was further partitioned by distilled water to obtain the hexane fraction as MFE for nanoparticle synthesis [13, 14].

2.2.2. Phytochemical test. MF leaf extract was tested phytochemically to determine the content of active substances qualitatively. Phytochemical tests were carried out on several classes of compounds, such as alkaloids, steroids, terpenoids, saponins, tannins, polyphenols and flavonoids [15].

2.2.3. Gd$_2$O$_3$ nanoparticles synthesis. Gd(NO$_3$)$_3$ solution was mixed with MFE 0.46 % (w/v) with the high-speed stirring method at 23000 rpm for an hour to form Gd(OH)$_3$ colloids. The result was filtered, rinsed, and dried at 120 °C for 5 h, and calcinated at 600 °C for 5 h. [7].

2.2.4. Gd$_2$O$_3$ nanoparticles characterization. Gd$_2$O$_3$ NPs were characterized by FT-IR spectroscopy (IR Prestige-21 Shimadzu), UV-Vis spectrophotometer Shimadzu 2600, UV-Vis DRS Shimadzu 2450, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX JED-2300), transmission electron microscopy (TEM JEOL JEM 1400), X-ray diffraction (XRD Shimadzu 2700), and particle size analyzer (PSA Zetasiser Nano ZS 90).

3. Results and discussion

3.1. Phytochemical test of Myristica fragrans leaves extract

Phytochemical tests were conducted to qualitatively determine the secondary metabolites in MFE, such as alkaloids, flavonoids, saponins, tannins, polyphenols, steroids, and terpenoids. According to the result, MFE positively contained alkaloids, saponins, and steroids. Positive result of alkaloid compounds in MFE indicated by the appearance of red sediment, saponin was shown from stable bubbles on the solution surface, while the steroid compounds were noticed by the bluish-green color solution.
3.2. Characterization of Gd$_2$O$_3$ NPs using FT-IR Spectroscopy

FTIR characterization was conducted to identify the functional groups of the Gd$_2$O$_3$ NPs and MFE. FTIR data of MFE have the vibrational spectra at wavenumbers of 3456; 2962; 1645; 1466; 1380 and 720 cm$^{-1}$, which indicate the presence of O-H stretching, C-H sp$^3$ stretching, N-H amine bending, C-C stretching, N-O stretching and N-H wagging stretching, respectively, as shown in figure 1. The N-H amine bending indicates the presence of alkaloid. Also, the O-H stretching, C-H sp$^3$ stretching and C=C stretching show the presence of saponins. These secondary metabolite compounds have an important role in the synthesis of nanoparticles. Alkaloids act as a source of weak bases, and saponins act as a capping agent [16]. FTIR spectrum of Gd$_2$O$_3$ NPs shows the absorption at wavenumber 556 cm$^{-1}$, which indicates the bending vibration of Gd-O. This result is in accordance to the previous research that the Gd-O bond has a vibration at the wavenumber range of 563–547 cm$^{-1}$ [8].

3.3. Characterization of Gd$_2$O$_3$ NPs using XRD

XRD characterization was conducted to investigate the diffraction pattern and crystallinity of the synthesized Gd$_2$O$_3$ NPs. X-ray diffractograms present the diffraction of 2$\theta$ as shown in figure 2. The 2$\theta$ value of synthesized Gd$_2$O$_3$ was compared to the data from COD Number 96-101-1289, which were well-matched at 28.71; 33.08; 35.20; 42.48; 47.51; 56.50 and 76.88 deg. This result indicates that Gd$_2$O$_3$ nanoparticles have been synthesized using MFE hexane fraction.

3.4. Characterization of Gd$_2$O$_3$ NPs using PSA

PSA identification was carried out to study the particle size distribution of Gd$_2$O$_3$ NPs. PSA result of Gd$_2$O$_3$ NPs is shown in figure 3. The average size distribution of Gd$_2$O$_3$ NPs was 40 nm.

![Figure 1. FTIR spectra of MFE and Gd$_2$O$_3$ NPs.](image1)

![Figure 2. XRD pattern of Gd$_2$O$_3$ NPs.](image2)

![Figure 3. Particle size distribution of Gd$_2$O$_3$ NPs.](image3)
3.5. Characterization of Gd$_2$O$_3$ NPs using SEM-EDX
SEM characterization aims to determine the surface morphology of the Gd$_2$O$_3$ NPs, which were appeared as an agglomeration rice-like materials, as shown in figure 4. Meanwhile, EDX analysis aims to determine the atomic composition on the surface of Gd$_2$O$_3$ NPs. According to the EDX spectrum, Gd$_2$O$_3$ NPs contained Gadolinium atom (Gd) of 46.87 %, and oxygen atom (O) of 32.55 %, as shown in figure 5.

3.6. Characterization of Gd$_2$O$_3$ NPs using UV-Vis DRS
UV-Vis DRS identification was carried out to determine the bandgap value of Gd$_2$O$_3$, which is defined by converting a % reflectance using Kubelka-Munk function. According to the calculation, the obtained bandgap energy of Gd$_2$O$_3$ was 5.1 eV (figure 6), which included in UV light range. This result indicates that Gd$_2$O$_3$ has a good absorption in the UV region which has absorption range between 270-325 nm.

3.7. Characterization of Gd$_2$O$_3$ NPs using TEM
TEM identification was conducted to define the particle size of Gd$_2$O$_3$ NPs. The results were presented at magnification of 43,000x and 97,000x, as shown in figure 7. Based on TEM characterization, Gd$_2$O$_3$ NPs were observed with particle size around 150 nm. That size shows that Gd$_2$O$_3$ NPs form aggregate of nanoparticles.

![Figure 4](image1.png)
![Figure 4](image2.png)

Figure 4. SEM images of Gd$_2$O$_3$ NPs with magnification of (a) 30,000x and (b) 10,000x.

![Figure 5](image3.png)

Figure 5. EDX spectrum of Gd$_2$O$_3$ NPs.

![Figure 6](image4.png)

Figure 6. UV-Vis DRS analysis of Gd$_2$O$_3$ NPs.
3.8. Photocatalytic activity analysis of Gd$_2$O$_3$ NPs
The photocatalytic activity of Gd$_2$O$_3$ NPs was carried out for the degradation of malachite green under the UV light area for 120 min with the observation every 15 min. The results of UV-Vis absorption spectra of malachite green degradation are shown in figure 8. The wavelength shifts were observed at $\lambda_{max}$ range of 318 to 250 nm. The absorption peak at 250–254 nm indicates the presence of aromatic chromophore and carboxylic acid groups [17]. According to the calculation, the photodegradation percentage of malachite green using Gd$_2$O$_3$ NPs for 120 min was 75.15%.

4. Conclusion
The synthesis of Gd$_2$O$_3$ NPs using a hexane fraction of Myristica fragrans extract (MFE) has been successfully synthesized. The phytochemical test results show that a hexane fraction of MFE contained alkaloids, steroids, and saponins. PSA characterization shows that the average particle size distribution of Gd$_2$O$_3$ was around 40 nm. The results of UV-Vis DRS characterization show that Gd$_2$O$_3$ has a...
bandgap energy of 5.1 eV. The photocatalytic activity of Gd₂O₃ NPs was observed for the degradation of malachite green with the percentage of 75.15 % for 120 min under UV light irradiation.

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.

References
[1] Jamkhande P G, Ghule N W, Bamer A H, Kalaskar M G 2019 J. Drug Delivery Sci. Tech. 53 101174
[2] Yedurkar S, Maurya C and Mahanwar P 2016 Open J. Synthesis Theory Applications 5 1-14
[3] Parveen K, Banse V and Ledwani L. 2016 AIP Conf. Proc. 1724 020048
[4] Iravani S 2011 Green Chem. 13 2638-50
[5] Abbas M, Sari N, Utari T, Yulizar Y and Apriandanu D O B 2018 AIP Conf. Proc. 2023 020100
[6] Tania T C D, Deastri Y N, Utari T, Yulizar Y and Apriandanu D O B 2018 AIP Conf. Proc. 2023 020103
[7] Yulizar Y, Monjushiro H, and Watarai H 2004 J. Colloid Interface Sci. 275 560-9
[8] Tamrakar R K, Bisen D P, and Brahme N 2014 Res. Chem. Intermediates 40 1771-9
[9] Mamba G, Mbianda X Yand Mishra A K 2016 Mater Res. Bull. 75 59-70
[10] Ayawanna J, Teoh W T, Niratisairak S and Sato K 2015 Mater. Sci. Semicond. Process. 40 136-9
[11] Ledwaba M, Masilela N, Nyokong T and Antunes E 2015 J. Mol. Catal. A-Chem. 403 64-76
[12] Yulizar Y, Kusriini E, Apriandanu D O B and Nurdini N 2020 Surf. Interfaces 19 100437
[13] Yulizar Y, Sudirmian, Apriandanu D O B and Wibowo A P 2019 Compos. Commun. 16 50-6
[14] Apriandanu D O B and Yulizar Y 2019 Nano-Struct. Nano-Objects 20 100401
[15] Edrah S M, Elzaedi Y M, Kahel F and Alkhumsi S I 2016 ICCPGE 1, 25-30
[16] Yulizar Y, Latifah I, Bakri R and Apriandanu D O B 2018 AIP Conf. Proc. 2023 020097
[17] Chen C C, Lu C S, Chung Y C and Jan J L 2007 J. Hazard. Mater. 141 520-8