Gold nanoparticles supported on Al₂O₃ using Tabebuia aurea leaf extract and catalytic properties for methylene blue reduction

A Maulidya, Y Yulizar, T Utari and D O B Apriandana

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

Corresponding author’s e-mail: yokiy@ui.ac.id

Abstract. In this research, we reported a cost-effective and an environmentally friendly technique for synthesis of gold nanoparticles supported on alumina (Al₂O₃/AuNPs) using Tabebuia aurea leaf extract (TAE) as non-toxic reducing agent, efficient stabilizer, and weak base source without adding any surfactants. Al₂O₃/AuNPs was characterized using various techniques including UV-Visible Spectrophotometer, Fourier-transform Infrared (FT-IR) spectroscopy, X-Ray diffraction (XRD), and Particle Size Analyzer (PSA). AuNPs was successfully synthesized using HAuCl₄ as precursor. The characterization of UV-Vis Spectrophotometer shows that AuNPs colloidal was formed at 0.15 % TAE. FTIR characterization of Al₂O₃ shows Al-OH band at 1505 cm⁻¹ and Al-O band at 680 cm⁻¹. Phase of Al₂O₃ was amorphous confirmed by XRD. The particle size distribution average of Al₂O₃/AuNPs was about 43 nm. The reduction percentage of methylene blue using Al₂O₃/AuNPs catalyst was 70.41 % for 120 min.

Keywords: Al₂O₃/AuNPs, Tabebuia aurea, catalytic activity, methylene blue reduction

1. Introduction
Aluminum oxide (Al₂O₃) is a well support catalyst material due to its inert properties, good thermal stability, capable to bind with metals as catalyst, has high surface area and evenly dispersed pores on the surface [1-4]. On the other hand, gold nanoparticle (AuNPs) has important roles in several catalytic processes such as in reduction of nitro-aromatic compounds and azo dyes, low temperature CO oxidation, and organic synthesis [5-8]. However, the use of metal nanoparticles like AuNPs can cause some problems such as homogeneity, reusability, and catalyst separation from the system [9]. Thus, some previous researchers have conducted many studies of metal nanoparticle immobilization on the support material [10-11]. This result is in line with the property of Al₂O₃ as a support catalyst. AuNPs may enhance the catalytic activity of Al₂O₃ due to its active site. The immobilization of AuNPs on Al₂O₃ surface can convert AuNPs phase from colloidal into solid phase [12].

Tabebuia aurea is one of the medicinal plants in tropical countries like Indonesia [13]. This plant has secondary metabolite compounds that can be used to synthesize the nanoparticle. Tabebuia aurea leaf extract have been previously reported to contain alkaloid, flavonoid, polyphenols and saponins compounds which act as a weak base source and stabilizing agent in nanoparticles formation [14]. Green synthesis method has been widely used for both metal and metal oxide synthesis. In previous study, we prepared both metal and metal oxide by green synthesis approach using plant [15-19].

To the best of our knowledge, we reported about cost-effective and environmentally friendly synthesis and immobilization of AuNPs on Al₂O₃ surface (Al₂O₃/AuNPs) using TAE. The catalytic activity of Al₂O₃/AuNPs was observed in methylene blue reduction.

2. Materials and methods
2.1. Materials
Tabebuia aurea (TA) was obtained from Jagakarsa, South Jakarta, Indonesia and has been determined at Lembaga Ilmu Pengetahuan Indonesia (LIPI), Bogor, West Java, Indonesia. Methanol and n-hexane were analytical grade from PT. Brataco, Indonesia. HAuCl₃·H₂O was purchased from Sigma-Aldrich. Al(NO₃)₃·9H₂O and methylene blue were obtained from Merck, Germany.

2.2. Preparation of leaf extract
Dried powder of Tabebuia aurea (TA) leave was added into methanol of 300 mL and macerated for 7 days at room temperature. The result was then partitioned by n-hexane. The methanol fraction was evaporated then added by distilled water to obtain TA extract (TAE) for nanoparticles fabrication.

2.3. AuNPs synthesis
0.05, 0.10, and 0.15% of TAE (w/v) were added dropwise into 1.0 x 10⁻⁴ M HAuCl₃ until forming a violet colloidal. The colloidal was further characterized using a UV-Vis spectrophotometer.

2.4. AlO synthesis
0.15% of TAE was added dropwise into 0.03 M Al(NO₃)₃ solution in volume ratio (1:3) and stirred continuously at 80 °C for 5 h to form a white colloid. The colloid was heated at 100 °C for 1 h and annealed at 500 °C for 4 h to obtain white powder of AlO.

2.5. AlO/AuNPs synthesis
AlO powder was dispersed into 30 mL of 1.0 x 10⁻⁴ M HAuCl₃ with sonication for 20 min. TAE 0.15% (w/v) was added dropwise into the previous mixture and stirred continuously for 100 min at room temperature. The dispersed system was annealed at 500 °C for 4 h to obtain the violet powder of AlO/AuNPs.

2.6. Characterization
TAE optimum concentration for synthesis of AuNPs and catalytic activity analysis were observed by UV-Vis Spectrophotometer (Shimadzu 2600). The functional group of AlO/AuNPs was examined by Fourier Transform Infrared (FT-IR) (Shimadzu, Prestige 21). The crystal phase of AlO was characterized by X-Ray Diffraction (XRD) Shimadzu 610 at 20 range of 20°–60° with Cu Kα (λ = 0.1546 nm) radiation. The particle size distribution of AlO/AuNPs was characterized by Particle Size Analyzer (PSA) Malvern Zetasizer 1600.

2.7. Catalytic activity analysis
5 mg of Au/AlO. NPs was added into the mixture of 5 mL of 2.0 x 10⁻⁴ M methylene blue and 0.1 M NaBH₄. The catalytic activity was observed by measuring the absorbance change using UV-Vis spectrophotometer for 120 min.

3. Results and discussion

3.1. Optimization of AuNPs
Synthesis of AuNPs was varied in TAE concentrations of (0.05, 0.10 and 0.15) %. It aims to observe the effect of TAE concentration in AuNPs formation. The formation of AuNPs is signed by the presence of absorption peak at the maximum wavelength of 500–550 nm due to the SPR peak formation [20,21]. A color change of colloidal occurs from yellow to violet in the AuNPs formation. AuNPs formation can be described by UV-Vis absorption spectra as shown in figure 1.

0.15 % TAE was the optimum concentration in AuNPs formation. Since this concentration resulted the absorption peak at the smallest maximum wavelength of 540 nm called by blue shift region. It has the conformity with the previous research that the maximum wavelength shift at blue region will produce the small size of nanoparticle [22]. Furthermore, 0.15 % TAE was used as optimum concentration for AlO/AuNPs fabrication. The particle size of AuNPs was further observed by PSA characterization.
3.2. FT-IR spectroscopy and XRD analysis

Functional groups of TAE, AlO, and AlO/AuNPs were identified by FT-IR as shown in figure 2a. TAE has broad vibrations band at 3318.7 cm⁻¹ corresponds to –OH stretching of polyphenols, flavonoids and saponins that act as capping and reducing agents in AuNPs formation [19,22,23]. The vibrations band at 1384.0 cm⁻¹ assigns to C-N stretching from alkaloids compound that plays a role as weak base source for the synthesis of metal oxide nanoparticle [15]. Figure 2 shows that both AlO and AlO/AuNPs reported the typical Al-O stretching vibration at wavenumber of 715.6 and 713 cm⁻¹, respectively. Based on figure 2b, XRD pattern of AlO shows no sharp peak, indicating the amorphous phase. The amorphous form of AlO has an excellent performance on catalysis due to its better adsorption ability [24].

3.3. Particle size analyzer

PSA characterization was performed to determine the average of particle size distribution of AlO/AuNPs as presented in figure 3. Figure 3 shows that AlO and AlO/AuNPs were distributed at particle size average of 37.76 and 43.29 nm, respectively. These results demonstrate that both of AlO and AlO/AuNPs are nanoparticles.
Figure 3. PSA result of (a) Al₂O₃ and (b) Al₂O₃/AuNPs.

Figure 4. (a) Decreasing of UV-Vis absorption spectra and (b) reduction percentage of MB with NaBH₄ for 120 min using Al₂O₃/AuNPs catalyst.

3.4. Catalytic activity
Figure 4 shows the reduction percentage of MB calculated from the reduction of MB with NaBH₄ through the observation of the fading blue color and the decrease of its absorbance. MB was reduced to be a leuco methylene blue (LMB) presented by a new absorption as shown in figure 4a. The formation of LMB occurs at the wavenumber of 300 nm [25]. The reduction percentage of MB using Al₂O₃ and Al₂O₃/AuNPs are 60.26 % and 70.41 %, respectively, as shown in figure 4b. The presence of AuNPs can accelerate the reduction of MB solution. AuNPs plays important role in electron transfer from BH₄⁻ as a donor to MB as an electron acceptor. BH₄⁻ are nucleophilic, while MB are electrophilic [26].

4. Conclusions
Al₂O₃/AuNPs has been successfully synthesized using TAE. FTIR characterizations show that there are alkaloid and flavonoid in TAE, which can act as reducing and capping agents as well as weak base source in synthesis of Al₂O₃/AuNPs. AuNPs may enhance the catalytic activity of Al₂O₃ significantly. According to all discussions, we demonstrate that Al₂O₃/AuNPs has a good catalytic activity in the reduction of MB using NaBH₄ with reduction percentage of 70.41 %.

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