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Green synthesis of Co_3O_4 nanoparticles using *Euphorbia heterophylla* L. leaves extract: characterization and photocatalytic activity

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Abstract. In this research, Co_3O_4 NPs were prepared by green synthesis method using *Euphorbia heterophylla* L. leaves extract (ELE). ELE contains secondary metabolite compounds like alkaloid, as weak base source, and saponin, as capping agent, in the synthesis of Co_3O_4 nanoparticles. The Fourier- Transform Infrared (FTIR) spectrum of ELE depicted some peaks at 3245, 1610 and 1071 cm^{-1} which represented hydroxyl group, carbonyl group (C=O) and C-N group, respectively. Co_3O_4 NPs were characterized by FTIR Spectrometry, UV- Vis Spectroscopy, Particle Size Analyser (PSA), X- Ray Diffraction (XRD) and UV- Vis DRS. The FT-IR results showed the presence of Co (II)- O bond and Co (III)- O bond at the wavenumber of 574 and 699 cm^{-1}, respectively. UV-Vis characterization spectroscopy indicated the typical peak of Co_3O_4 NPs found at the range wavelength of 200- 350 nm and 380- 600. The particle size of Co_3O_4 NPs was 69.75 nm confirmed by Particle Size Analyser. XRD characterization showed that Co_3O_4 NPs had diffraction peaks at 31.1953°; 38.5401°; 44.8076°; 50.2027°; 59.2743° and 65.1419°. The band gap energy of Co_3O_4 NPs was 1.53 eV confirmed by UV-Vis DRS. TEM image showed that morphology of Co_3O_4 NPs was spherical shaped with the particle size of ~17 nm. Co_3O_4 NPs had a photocatalytic activity in the degradation of methylene blue about 63.105% for 3 hours.
Keywords: Co_3O_4 nanoparticles, *Euphorbia heterophylla* L., green synthesis, photocatalytic, methylene blue

1. Introduction

Co_3O_4 is a type of metal oxide nanomaterials. Nanomaterials, the type of functional materials, had many applications and have been developed broadly [1-3]. Co_3O_4 is a p-type semiconductor with spinel crystal structure [4, 5]. Applications of Co_3O_4 have used in catalysis field, sensor, battery, electrochromic films, heterogeneous catalytic materials, magnetic materials, electrochemical and solar selective absorbers [6-13]. The direct optical band gaps of Co_3O_4 nanoparticles were about 1.48 and 2.19 eV [14] and it can be used as photocatalyst to degrade organic pollutant using visible light [15].

Synthesis of Co_3O_4 nanoparticles have been reported using some methods such as sol-gel method, synthesis based on surfactant, decomposition using temperature, large molecule-bond assisted synthesis, chemical spray pyrolysis processing, template method, reflux method by microwave, solvothermal and hydrothermal technique [16-22]. These methods need more energy and high cost [1]. In addition, Co_3O_4 nanoparticles could be synthesized by green synthesis. This method is environmentally friendly, low cost and effective. It used raw materials like microscopic organism especially a bacterium or fungus, polymeric substance occurring in living organism-alginate and bioactive molecule contained in plants

[23-26]. Co_3O_4 nanoparticles have been synthesized by green synthesis method using plants such as *Calotropis gigantea*, *Moringa oleifera*, *Aspalathus linearis*, *Terminalia chebula*, *Sageretia thea*, *Calotropis procera*, *Manihot esculenta Crantz* [1, 27-32]. *Another oxide metals were successfully synthesized by Graptophyllum pictum* (Fe_3O_4) [33], *Oldenlandia corymbosa L.* (CuO) [34], *Imperata cylindrica L.* (ZnO) [35], *Terminalia Catappa* (Nd_2O_3) [36], *Physalis angulata* (La_2O_3 and NiO) [37, 38], *Parkia speciosa Hassk* (CdO) [39].

Indonesia is known as a country rich in biodiversity. One of natural plant from Indonesia is *Euphorbia heteropyhlla L.* Its leaves contained the secondary metabolites such as alkaloid, flavonoid, saponin, tannin and other compounds [40]. The presence of alkaloid could be used as a weak base source for Co_3O_4 nanoparticles synthesis and no report before about Co_3O_4 nanoparticles synthesis using *Euphorbia heteropyhlla L.*

2. Materials and Method

2.1. Material
Cobalt nitrate hexahydrate, $Co(NO_3)_2.6H_2O$, was purchased from Merck (Germany). *Euphorbia heterophylla* L. leaves were collected from Conservation Unit and Cultivation Biopharmaca IPB Bogor, Indonesia. All reagents and solvents for synthesis were analytical grade.

2.2. Preparation of Euphorbia heterophylla L. leaves extract (ELE)
Euphorbia heterophylla L. leaves were washed completely and dried at indoor temperature. The dried leaves were ground to get leaves powder, then that powder was macerated using methanol. The mixture was stirred in each day for a week and then separated using hexane (1:1) (m/v) to get methanol and hexane fractions. Methanol fraction was evaporated and dissolved into aquabidest to obtain the aquoeus fraction of *Euphorbia heterophylla* L. leaves extract (ELE) [41]. The metabolite secondary of ELE was identified by phytochemical analysis.

2.3. Synthesis of Co_3O_4 nanoparticles using Euphorbia heterophylla L. leaves extract (ELE)
Euphorbia heterophylla L. leaves extract (ELE) was added dropwise into $Co(NO_3)_2$ and stirred at 80ºC during 2 hours and calcinated at 550°C for 4 hours.

2.4. Characterization of Co_3O_4 nanoparticles (NPs)
Co_3O_4 NPs and *Euphorbia heterophylla* L. leaves extracted were characterized using Prestige-21 Shimadzu FT-IR Spectrometry to identify functional group. Shimadzu 2600 UV-Vis Spectroscopy was used to identify the absorption spectra of nanoparticles. The particle size distribution was determined by Malvern Zetasizer Particle Size Analyser. The crystallinity was performed by XRD Empyrean diffractometer. The band gap energy was identified by Shimadzu 2450 UV-Vis DRS. The morphology and particle size of Co_3O_4 NPs was determined by TEM (JEOL JEM 1400).

2.5. Photocatalytic activity of Co_3O_4 nanoparticles (NPs)
Co_3O_4 NPs of 3 mg was reacted into 25 mL methylene blue $2x10^{-5}$ M under visible light irradiation for 3 hours. The photocatalytic activity of Co_3O_4 NPs was observed using UV-Vis characterization spectroscopy.

3. Results and Discussion
According to the phytochemical analysis, ELE contained secondary metabolite such as alkaloid, saponin, flavonoid, tannin and polyphenol. FTIR spectrum of ELE showed the peaks at the wavenumber of 3245, 1610 and 1071 cm^{-1}, which is related to the hydroxyl, carbonyl and functional group of C-N respectively. These functional groups were from alkaloid of ELE. FTIR spectrum of Co_3O_4 NPs indicated Co (II)-O bond, Co (III)-O bond at the wavenumber of 574 and 699 cm^{-1}, respectively. The presence of C-N functional group was assigned at the wavenumber of 1045 cm^{-1} as shown in Fig. 1a.

This result was demonstrated that Co_3O_4 NPs still contain the remain of alkaloids from ELE. Alkaloid contained in ELE has a role as hydrolysing substance in Co_3O_4 nanoparticles formation which has been shown by the presence of C–N bond [42].

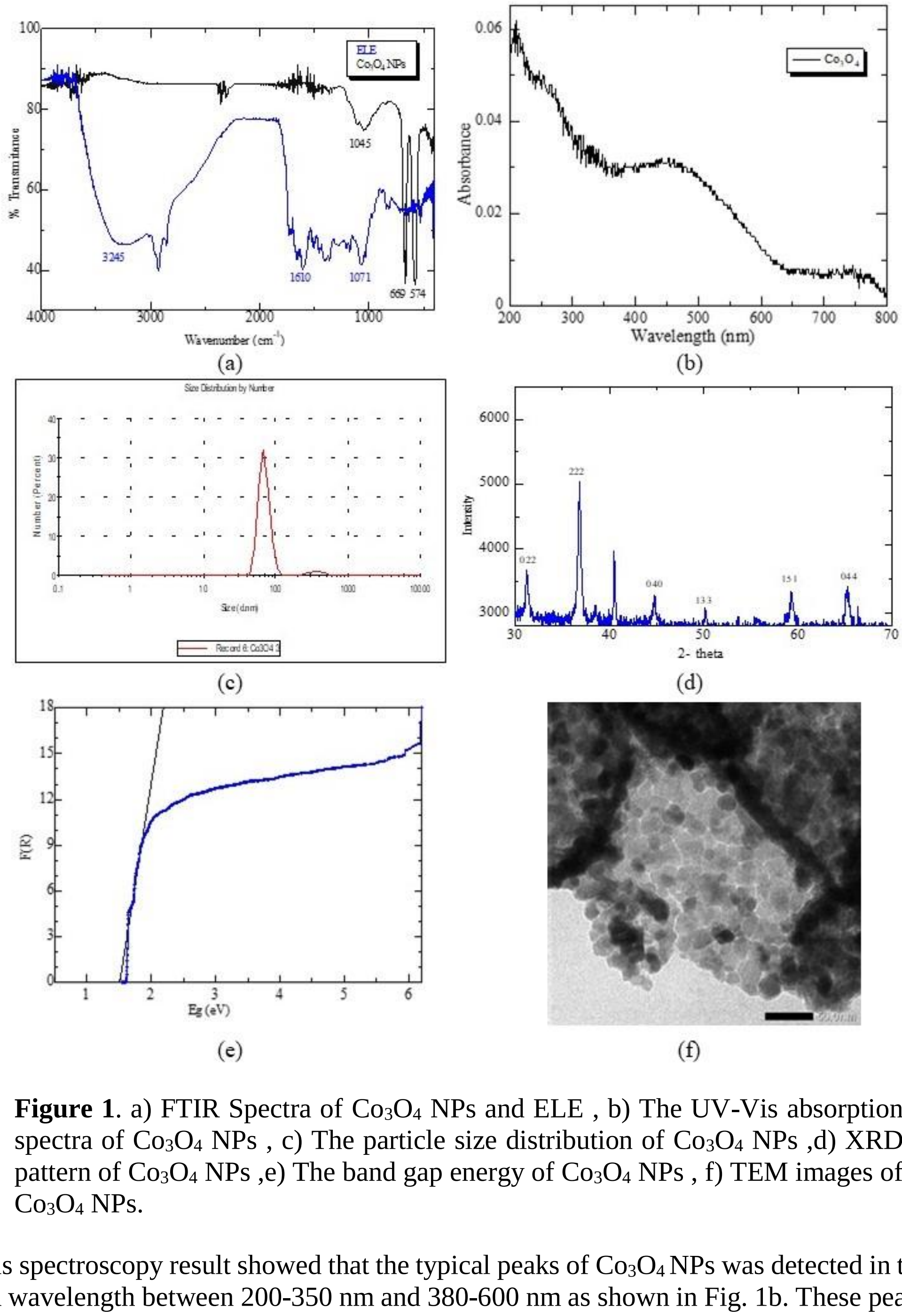
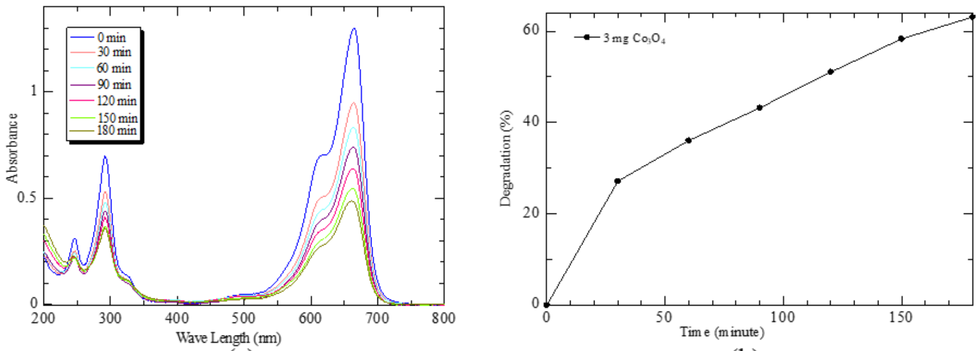


Figure 1. a) FTIR Spectra of Co_3O_4 NPs and ELE , b) The UV-Vis absorption spectra of Co_3O_4 NPs , c) The particle size distribution of Co_3O_4 NPs ,d) XRD pattern of Co_3O_4 NPs ,e) The band gap energy of Co_3O_4 NPs , f) TEM images of Co_3O_4 NPs.

UV-Vis spectroscopy result showed that the typical peaks of Co_3O_4 NPs was detected in the range of maximum wavelength between 200-350 nm and 380-600 nm as shown in Fig. 1b. These peak indicated the transfer processes of Co (II) and Co (III) with oxygen, respectively [43]. The particle size distribution of Co_3O_4 NPs was 69.75 nm. The XRD pattern showed that Co_3O_4 NPs had the diffraction peaks at 2θ of 31.1953°; 38.5401°; 44.8076°; 50.2027°; 59.2743° and 65.1419° corresponded to the miller indices of 022; 222; 040; 133; 151 and 044, respectively. These diffraction peaks have been matched with the reported values (COD data of Co_3O_4 96-153-8532) with cubic crystal system and Fd-3m space group.

This XRD result was good agreement in literature [43]. The particle size of Co_3O_4 NPs using Debye-Scherer equation was ~39.99 nm. The band gap energy of Co_3O_4 NPs was 1.53 eV corresponded to the literature [14] as shown in Fig. 1e. TEM image showed that morphology of Co_3O_4 NPs was spherical shape with diameter ~17 nm as shown in Fig. 1f. This result has conformity with the literature [44].



(a) (b)

Figure 2. a) The UV-Vis absorption of the methylene blue degradation, b) The percentage degradation of methylene blue.

Co_3O_4 NPs was modelled as photocatalyst in the methylene blue degradation under irradiation of visible light for 3 hours. Fig. 2a showed the absorbance decreasing of methylene blue in the wavelength of 665 nm as the absorption characteristic of methylene blue. Fig. 2b showed the relation between the percentage of degradation versus the time. According to the Fig. 2b, the photocatalytic activity of Co_3O_4 NPs was performed for the degradation of methylene blue was about 63.105% under visible light irradiation for 3 hours.

4. Conclusions

Co_3O_4 NPs was successfully synthesized by *Euphorbia heterophylla* L. leaves extract (ELE) which contained alkaloid as a weak base source for Co_3o_4 NPs synthesis. FT-IR spectrometry showed the presence of Co (II)-O and Co (III)-O bond at the wavenumber of 574 and 699 cm^{-1}, respectively. UV-Vis Spectroscopy indicated the typical peak of Co_3O_4 NPs was found at the maximum wavelength range of 200-350 and 380-600 nm. The particle size distribution of Co_3O_4 NPs was 69.75 nm. XRD result of Co_3O_4 NPs had the 2θ diffraction peaks at of 31.1953°; 38.5401°; 44.8076°; 50.2027°; 59.2743° and 65.1419°. The Co_3O_4 NPs band gap energy was 1.53 eV. TEM image showed that morphology of Co_3O_4 NPs were spherical shaped with the size of particle about ~17 nm. The photocatalytic activity of Co_3O_4 NPs was carried out for the methylene blue degradation in 63.105% under irradiation of visible light for 3 hours.

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