Phase system of hexane-water for SnO$_2$ nanoparticles preparation using Cassia alata leaf extract and its photocatalytic activity

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Abstract. SnO$_2$ nanoparticles (NPs) were prepared using a hexane phase of Cassia alata leaf extract (CLE) and a water phase of SnCl$_2$ precursor by high-speed stirring (HSS) method. In this study, HSS was utilized to analyze the nanoparticle formation via phase system of hexane-water. Next, the synthesized SnO$_2$ NPs were characterized by Fourier transform infrared (FT-IR) spectroscopy, particle size analyzer (PSA), transmission electron microscopy (TEM), scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX), UV-Vis diffuse reflectance spectroscopy (DRS) and X-ray diffraction (XRD). Phytochemical screening confirms that CLE contains secondary metabolites such as alkaloids as a source of base, saponins and tannin as a capping agent in SnO$_2$ NPs formation. TEM characterization shows that the particle size of SnO$_2$ NPs was approximately 25–50 nm. The photocatalytic activity of SnO$_2$ NPs was tested for methylene blue (MB) degradation under UV light irradiation. As a result, the degradation percentage of MB was 70.29 % for 160 min.

Keywords: SnO$_2$ NPs, Cassia alata leaf extract, high-speed stirring, photocatalytic activity, methylene blue.

1. Introduction

SnO$_2$ nanoparticles (NPs) are stable semiconductor materials that have been used in various fields of application such as gas sensors [1], catalysts [2], lithium batteries [3]. SnO$_2$ NPs are n-type tetragonal crystal structure with good photocatalyst materials which have bandgap value around 3.6 eV [4].

Synthesis of nanoparticles has been widely carried out by the method of hydrothermal [5], electrospinning [1] and sol-gel [2]. The sol-gel method is one technique used for nanoparticle synthesis, which has several advantages such as homogeneity, high purity, low processing temperature and the possibility of making new ceramic compositions [6]. Synthesis methods using toxic chemicals are harmful to the environment. Therefore, one of the environmentally friendly methods is green synthesis. Green synthesis is a design to reduce or eliminate the use and formation of hazardous substances that are beneficial to the environment and economy [7]. This method also has advantages such as lower cost, lower energy, temperature, and pressure requirement compared to the physical and chemical methods.

Two-phase system was used to synthesize nanoparticles for controlling the particle size [8]. Two-phase system consisting of water and organic solvents occur a reaction at the interfacial area, and
has been reported for metal oxide nanoparticles [9]. In this system, the reaction utilized a mild condition, nucleation and growth occurred together [10]. The two-phase system utilized the high-speed stirring (HSS) method that can detect the interfacial complexation of two solutions [11].

Plant parts such as leaves, roots, seeds, and stems have been used for the synthesis of metal nanoparticles and surfactants [12]. Green synthesis uses the sol-gel method by replacing chemicals into environmentally friendly materials. Green synthesis of nanoparticles using leaf extracts such as *Piper betle* L. [13], *Psidium guajava* [14], *Datura metel* L [15] and *Tinospora crispa* [16] have been reported. The leaf extracts such as *Morinda citrifolia* [17] and *Orthosiphon aristatus* (Blume) [18] plants have been used for the synthesis of surfactants.

Indonesian plants can be used as raw material in SnO$_2$ NPs synthesis. One of them is *Cassia alata*, a shrub plant known as another *tabankun*, *acon-acon*, and *ketepeng cina*. This plant is widely spread in tropical countries, stretching from tropical America to India, Malaysia and Indonesia [19]. *Cassia alata* leaves have secondary metabolite contents of alkaloids 4.06 %, saponins 4.28 % and tannins 1.54 % [20]. In the present study, SnO$_2$ NPs were synthesized with *Cassia alata* leaves. Secondary metabolites in *Cassia alata* leaves such as alkaloids, saponins, and tannins can act as a source of bases (OH$^-$) and capping agent. The SnO$_2$ NPs were tested for photocatalytic activity of methylene blue degradation under UV light.

### 2. Materials and method

#### 2.1. Materials

The main raw material was SnCl$_2$.2H$_2$O purchased from Merck. The biomaterial of *Cassia alata* plants were obtained from the conservation unit of the tropical biopharma center, LPPM IPB.

#### 2.2. Preparation of *Cassia alata* leaves extract

Two kg of *Cassia alata* leaves were washed with distilled water. They were dried for a week at room temperature by placing them indoor. The dried leaves of *Cassia alata* were milled to obtain a fine powder. Fifty grams of *Cassia alata* leaf powder was macerated in 250 mL of n-hexane for 7–10 days. Then, the filtrated crude extract in hexane was partitioned using water. The hexane fraction was used for nanoparticle synthesis. The phytochemical test was used to determine the secondary metabolite compounds in leaf extract of *Cassia alata* (CLE).

#### 2.3. Synthesis of SnO$_2$ nanoparticles

SnO$_2$ NPs were synthesized by sol-gel technique using SnCl$_2$ precursor 0.0025 M and CLE 2.15 % (w/v). High-speed stirring method with rotation rate 23000 rpm was treated for mixing of sol Sn(OH)$_2$ formation. The mixture was heated at 160 °C for 1.5 h to obtain the reaction equilibrium of Sn(OH)$_2$ and Sn(OH)$_4$ gels formation. The gels were dried, and calcined for 2 h at 500 °C to form SnO$_2$ NPs powder.

#### 2.4. Characterization of SnO$_2$ NPs

The crystallinity of SnO$_2$ NPs was identified using X-ray diffraction (XRD) Panalytical X’Pert PRO. The morphology and composition of elements from SnO$_2$ NPs were carried out by scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) JEOL JSM 6510 LA instrument. The bandgap value of SnO$_2$ NPs was determined by UV-Vis diffuse reflectance spectroscopy (Shimadzu 2450). Transmission electron microscopy (JOEL JEM-1400) image and particle size analyzer (PSA Zetasizer Nano ZS 90) were used to know the particle size and its distribution of SnO$_2$ NPs. Fourier transform infrared (FT-IR) spectroscopy (IR Prestige-21 Shimadzu) was applied to analyze the functional groups of SnO$_2$ NPs in the range of 400–4000 cm$^{-1}$. 
2.5. Photocatalytic activity

The photocatalytic activity measurement method was used with a slight modification from the previous research [21]. Seven mg of SnO2 NPs were dispersed in 25 mL of MB 4.0x10^-6 M and stirred for 160 min under UV light radiation. The degradation result of MB was determined by UV-Vis spectrophotometer every 20 min irradiation.

3. Results and discussion

The secondary metabolites of flavonoids, tannins, phenolics, steroids, saponins, terpenoids, alkaloids were tested by a preliminary phytochemical screening. The n-hexane fraction of Cassia alata leaves extract showed a positive result of saponins, alkaloids and steroids. Meanwhile, the aqueous fraction showed negative result of all secondary metabolites.

FTIR characterization was performed to identify the functional groups of SnO2 NPs and CLE. Figure 1 are attributed to the vibrations of (2916 cm^-1 ν CH sp^3 stretching), (1738 cm^-1 ν -NH amine group), (1451 cm^-1 ν C-C stretching), (1377 cm^-1 ν NO stretching), (1248 cm^-1 ν C-N stretching) and (837 cm^-1 ν wagging/bending of the -NH group), respectively. The presence of -NH stretching, C-N stretching, and C-H stretching indicate the presence of alkaloids. Besides, the spectrum of SnO2 shows that the presence of Sn-O-Sn stretch at 626 cm^-1 has the conformity with the prior work [22].

Figure 2a shows the XRD pattern, phase and average crystalline size of SnO2 NPs. SnO2 NPs had peaks with miller indices on 2θ of 26.7° (110), 34.0° (101), 38.0° (200), 51.9° (211), 54.7° (220), 57.9° (002), 61.9° (310), 64.8° (112), 66.0° (301), 71.3° (202) and 78.7° (321) which have the conformity with the previous research [22]. The SnO2 NPs had a crystalline phase with the average crystalline size of 19.01 nm calculated by Debye-Scherrer formula.

Figure 2b shows the bandgap energy of SnO2. The bandgap value was obtained by extrapolating the slope of the curve based on the modified Kubelka-Munk function (F(r)hv)^2 versus hv. The estimated bandgap energy of SnO2 was 3.21 eV which was lower than the previous report of 3.6 eV [4]. It can be concluded, SnO2 NPs with the bandgap value of 3.21eV can active to observe in UV light radiation.

Figure 3a shows that the morphology of SnO2 NPs was investigated by SEM with 500 nm scale bar in aggregate form. Figure 3b shows the elemental compositions of SnO2 NPs with % atomic of Sn, O and C were 11.08, 32.40 and 43.06 %, respectively. The C element was presented due to the remains of leave extract on the preparation process [12].
Figure 2. (a) XRD pattern of SnO$_2$ NPs, and (b) Band gap value of SnO$_2$ NPs.

Figure 3. (a) SEM image of SnO$_2$ NPs (b) EDS spectra of SnO$_2$.

TEM characterization was used to assign the shape, morphology, and particle size of SnO$_2$ NPs. Figure 4a shows the particle size of SnO$_2$ NPs was within the range of 25–50 nm. The SnO$_2$ NPs were characterized using PSA to confirm the size distribution and the particle size. According to the result, the average of particle size distribution of SnO$_2$ NPs was 98.50 nm as shown in figure 4b. The bigger size of PSA result compared the TEM image size due to the SnO$_2$ NPs was not dispersed perfectly in water.

The photocatalytic activity of SnO$_2$ NPs was tested for methylene blue (MB) degradation under UV light irradiation. Figure 5a shows UV-Visible spectra for MB photodegradation using SnO$_2$ NPs. MB displayed a strong absorption band at 664 nm [23]. The MB degradation percentage was 70.29 % for 160 min under UV light as presented in figure 5b.
Figure 4. (a) TEM image of SnO\textsubscript{2} NPs (b) Particle size distribution of SnO\textsubscript{2} NPs.

Figure 5. (a) UV-Vis absorption spectra of MB degradation (b) degradation percentage of MB.

4. Conclusion
SnO\textsubscript{2} NPs were obtained using the hexane fraction of Cassia alata leaves extract by the green synthesis method of two-phase system (hexane-water). The CLE in hexane through phytochemical test presented the secondary metabolite compounds such as alkaloids, saponins, and steroids. Based on FTIR characterization, the alkaloid and saponin compounds acted as a weak base source and capping agents in the SnO\textsubscript{2} NP synthesis. The particle size distribution of SnO\textsubscript{2} was confirmed at 98.50 nm in the aggregate form by PSA. TEM images show that the particle size of SnO\textsubscript{2} NPs was in the range of 25–50 nm. The degradation percentage of MB using SnO\textsubscript{2} NPs was 70.29 % for 160 min under UV light irradiation.

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