Green-synthesis of CuO-doped SnO₂ nanoparticles using pelawan (*Tristaniopsis merguensis*) leaf extract

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Abstract. CuO-doped SnO₂ nanoparticles were successfully synthesized using biosynthetic methods with the pelawan leaf extract. This method is a modification of the sol-gel process by utilizing antioxidant compounds from the leaf extract as a trap matrix for tin oxides. This research was conducted based on variations in CuO doping. The characteristics of tin oxide observed in this study were a phase, crystallite size, and crystallinity, which determined based on x-ray diffraction method. It is expected that the method proposed in this study can be developed to synthesize SnO₂ nanoparticles that are environmentally friendly.

1. Introduction
The Bangka Belitung Islands is the three largest tin producers in the world thus the economic activity in the province is dominated by the mining sector. In 2014, tin production on Bangka Island has reached 19,719.32 tons/year. Although tin mining has a negative impact on the environment, tin mining in Bangka Belitung is still rife [1,2].

With a dense population, especially in urban areas, the air in Indonesia has been heavily polluted by carbon monoxide emissions from motor vehicles and industrial machinery. Carbon monoxide (CO) is a toxic gas that is invisible, odorless and tasteless. The impact of CO varies depending on the level of CO that is inhaled, CO can inhibit blood in transporting oxygen (O₂) and the heart works harder [3]. In high levels of CO inhaled can cause fainting and even death. Because it cannot be detected by the human senses, a gas sensor is needed to detect the presence of CO. One type of material that can be used to detect gas is tin oxide nanoparticles (SnO₂). Tin oxide can provide a good response to the presence of CO gas [4,5].

There are various methods to synthesize nanoparticle such as coprecipitation, sol-gel, hydrothermal, and green-synthesis. Green-synthesis is an interesting method to produce nanoparticles because it provides an opportunity to create nanoparticles that are environmentally friendly and low-cost [6].

Previous research has developed green-synthesis method various kinds of plant extract [7-9]. One of abundant tree in Bangka Belitung Island is Pelawan. Pelawan is fast-growing species and it contain flavonoids, terpenoids, tannins, and saponins which have the potential to reduce particle size [10].

To optimize the performance of SnO₂ nanoparticles in detect gas some experiments add copper oxide as doping, considering that CuO is a p-type semiconductor [11]. Therefore, in this article, a study of green-synthesis of SnO₂ nanoparticles with CuO-doped and pelawan extracts as mediator was...
carried out. The characteristics observed in this study include the effectiveness of the addition of CuO to the crystal.

2. Methods

To make an extract, we use two grams of pelawan leaves. The leaves were then mashed and 20 ml of ethanol was added and stirred using a magnetic stirrer for 30 minutes. Dark green leaf extract was filtered using Whatman paper No. 1 and used for the further process. A total of 3 grams of SnCl₂·2H₂O were dissolved in 100 ml of distilled water. 0.5 M NaOH was added to reaches pH=7 and the solution transforms to gel.

Furthermore, the gel formed is filtered using Whatman paper No. 1 and washed using distilled water. The gel obtained is dried at 70°C. The powder crushed for 30 minutes and added CuO (doping) with variations 15% wt and 10% wt. The precursor calcined at 500°C for 3 hours. Characteristics of samples are determined based on x-ray diffraction (XRD) analysis.

3. Results and Discussion

After the calcination process was carried out, can be obtained SnO₂ powder as shown in Figure 1. The color of SnO₂ without doped after calcined is dark gray. For SnO₂ with 15%-CuO the color produced was similar with SnO₂ powder without doping. It indicates the powders still contains leaves extract or precursor incompletely calcined. Different things for SnO₂ with10%-CuO, it appears that the color is whiter.

Figure 1. SnO₂ powder (a) without doping, (b) Cu-doped: 10% and (c) CuO-doped: 15%

Figure 2 shows the pattern of XRD analysis of SnO₂ nanoparticles based on variations in CuO doping. XRD results were analyzed using the X’Pert HighScore Plus software with reference pattern for SnO₂ (PDF 2 – Ref. Code: 01-070-4176) and CuO (PDF 2 – Ref. Code: 00-045-0937). According to results can be stated that all three pH variation of synthesis of SnO₂ nanoparticles has produced SnO₂ and CuO phases with tetragonal crystal system and space group P42/mnm. The lattice parameter of SnO₂ (Å) is \( a = b = 4.7390; \ c = 31.83 \) with \( a = \beta = \gamma = 90 \degree \). The peaks of the four samples are related to CuO peaks and SnO₂ peaks.

Furthermore, the relationship of variations in doping with the size of crystallite (\( \tau \)) is calculated according to the Debye-Scherrer equation,

\[
\tau = \frac{K\lambda}{B\cos \theta}
\]

where \( K \) is the nanoparticle form factor (in this study we assume \( K = 0.9 \)), \( \lambda \) is the x-ray wavelength, \( B \) is FWHM, and \( \theta \) is the Bragg angle. The result of the average crystallite size is given in Figure 3. For non-doped SnO₂ the crystallite size is 11.36 nm. As information in this study, we used CuO that has a size of 28.86 nm. For SnO₂ with 10%-CuO, the crystallite size is 26.18 nm. While the addition of 15%-CuO the crystallite size is 28.86 nm. In Figure 3, it can be seen that there is a linear increase in the crystallite size.
Based on Figure 4, it can be seen that the crystallinity of non-doped SnO$_2$ is 32.89%; while the 10%-CuO the crystallinity is 32.82%; and for 15%-CuO the crystallinity is 32.81%. According to these results, it can be seen that the more percentage of CuO-doped, the lower level of crystallinity.
Figure 4. Relationship between the of crystallinity with the percentage of CuO-doped

3. Conclusions
Based on XRD analysis, CuO-doped decreases the level of crystallinity and increases the size of the crystallites. In addition, doping treatment also resulted in the appearance of SnO$_2$ and CuO phases without a new phase of the impurity.

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