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# Effect of Additional Cu on Structural and Optical Properties of $TiO_2$ Synthesized with Sol-Gel Method

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**Abstract.** In this study, $TiO_2$ doped with Cu has been successfully synthesized using the sol-gel method by varying the addition of Cu and the calcination temperature. Sample preparation was started by mixing 0.75 mL of 37% HCl in 49.25 mL of 96% ethanol and stirred with a magnetic stirrer for 10 minutes. Then 10 mL of TTIP (Titanium Tetraisopropoxide) was added dropwise using a dropper and the solution was stirred again with a magnetic stirrer for 60 minutes. Then added Cu with variations of 1%, 2%, 3%, 4%, and 5% and stirred again for 60 minutes using a magnetic stirrer. The sol solution was then put into the furnace at a temperature of 100°C for 3 days. The crystalline sol solution was then mashed with a mortar to a submicron size, then washed with 50 mL of Aquades and stirred using a magnetic stirrer for 10 minutes. The washed samples were then dried in a furnace at a temperature of 100°C for 1 day. Followed by calcination for 3 hours with temperature variations of 450°C, 500°C, 550°C and 600°C to release the gases in the nanoparticles. Cu-doped $TiO_2$ nanoparticles were characterized using test equipment such as XRD, SEM-EDX, and UV-Vis. From the results of XRD analysis obtained 3 phases namely Brookite, Rutile and Anastase, and the crystal size is unstable and the shape of the sample particles is tetragonal. The results of the SEM-EDX analysis showed that the content of the sample was in accordance with the experiments that had been carried out. The results of UV-Vis analysis show that the wavelength is inversely proportional to the band gap energy.

**Keywords:** Calcination Temperature, Cu Doping, Nanoparticles $TiO_2$, Sol-Gel Method

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## 1 Introduction

Currently, technological developments require photocatalysts for all electronic components. Photocatalyst is generally defined as a light-based chemical conversion reaction due to the presence of a catalyst. In the photocatalytic process, there are electron-hole parts (e- and h+). Photocatalytic uses visible light to activate the catalyst and react near or on the surface of the catalyst with chemical compounds. The bandgap energy of the semiconductor material used must be smaller than that of visible light. This situation allows the material to generate electrons

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and holes to decompose organic or inorganic compounds. Photocatalytic materials result in electrons in the conduction band (e-) and holes in the valence band (h+). The two charge carriers give rise to reactive active types according to which hydroxyl radicals (*OH) and superoxide radicals ($*O^{2-}$) undergo redox reactions [1]. The photocatalytic process is a good solution for waste purification and photo-degradation of organic compounds as methylene blue dye in large quantities and at a more affordable price. Photocatalytic techniques are photochemical reactions that carry out chemical conversion reactions in combination with an integrated catalyst. Chemical conversion takes place on the surface of the semiconductor catalytic material and light emitted from photons with special energies is also involved. Light can decompose compounds in photocatalytic processes. The initial procedure in this process is when the catalyst surface is induced with the right light energy, electron-holes are formed. In general, semiconductor catalytic materials have been used from previous studies, specifically $TiO_2$ powder which is in the form of anatase crystals, with high photocatalytic activity, chemically stable and non-toxic [2].

Titanium dioxide ($TiO_2$) or titania is a nanoparticle material that is widely used as an alternative material in many ways. Over the past decade, titanium dioxide has been used primarily as an alternative anti-bacterial material for sterilization purposes. This is because the water and air environment that is polluted by various aspects of other pollutants often contains viral microorganisms and various types of organic compounds, and anti-bacterial materials are needed to overcome them [3]. $TiO_2$ material was chosen because $TiO_2$ has anti-bacterial properties in terms of photocatalytic activity. $TiO_2$ coating can prevent the spread of gram-positive bacteria, gram-negative bacteria, viruses, and fungi. When $TiO_2$ is irradiated with light, a band gap phenomenon occurs where electron hole pairs are formed, and a redox reaction occurs on the $TiO_2$ surface [4]. $TiO_2$ has three crystalline phases: anatase, rutile and brookite. The formation of these three crystals can be regulated by adjusting the calcination temperature and dopant ion. $TiO_2$ anatase has a relatively high photocatalytic activity and this has the potential for photocatalytic processes [5]. The band gap energy (Eg) of $TiO_2$ is 3.2 eV for anatase crystals and 3 eV for rutile. Anatase structures with higher Eg values are widely used in photocatalytic applications because they show a better redox reaction than rutile. The current problem is that commercially available $TiO_2$ has a high Eg value and therefore low photocatalytic activity. Therefore, to increase the photocatalytic activity and improve performance, it is necessary to decrease the band gap energy value of $TiO_2$ [6].

In this study, $TiO_2$ was synthesized using the sol-gel method. The sol-gel method has advantages such as ease of use, not wasteful, and effective for the synthesis of $TiO_2$ nanoparticles. In addition, the sol-gel process provides excellent access for the synthesis of various forms of $TiO_2$ nanoparticles such as wires, bulk, tubes, mesoporous, and particles [7]. In this study, the addition of Cu and varying the calcination temperature was carried out to see the development of the structural and optical properties of $TiO_2$. Analysis of the structural development of the addition of Cu to $TiO_2$ was carried out by observing the morphology with XRD test equipment and optical properties with UV-Vis. Based on the above review, an experiment was conducted on the synthesis of $TiO_2$ doped Cu with variations in the addition of Cu, namely 1%, 2%, 3%, 4%, and 5% and variations in calcination temperature, namely 450°C, 500°C, 550°C and 600°C. In this study, Cu metal dopant can act as an electron trapper of a semiconductor because its reduction potential is more positive, namely 0.34 V. The greater the reduction potential, the higher its ability as an electron trapper [8]. The result of Cu-$TiO_2$ synthesis reduces the bandgap energy of $TiO_2$ from 3.2 eV to 2.52 eV which allows Cu-$TiO_2$ to be active in visible light thereby increasing its photocatalytic activity [9]. Calculation of the maximum band gap energy (Eg) can be calculated using the following equation:

$$Eg = \frac{hc}{\lambda} \quad (1)$$

Where $Eg$ = band gap energy; $h$ = Planck's constant = $6.626\times10^{-34}$ J.s; $c$ = speed of light = $2.998\times10^{8}$ m/s, 1 eV = $1.6\times10^{-19}$ J.

## 2 Methods

The materials used in this study were Ethanol, HCl, $Ti\{OCH\ (CH_3)_2\}_4$ and $Cu(NO_3)_2$. The manufacturing process begins by measuring all the raw materials using a measuring cup. With Ethanol = 49.25 mL, HCl = 0.75 mL, $Ti\{OCH\ (CH_3)_2\}_4$ = 10 mL, and $Cu(NO_3)_2$ with variations of 0%, 1%, 2%, 3%, 4% and 5% according to the results of stoichiometric calculations. Then the ethanol and HCl were mixed into a glass beaker and stirred with a magnetic stirrer at room temperature for 10 minutes. The homogeneous solution was then added with $Ti\{OCH\ (CH_3)_2\}_4$ using a dropper dropwise and stirred again for 60 minutes. After that, $Cu(NO_3)_2$ was added with variations of 0%, 1%, 2%, 3%, 4% and 5% and stirred again using a magnetic stirrer at room temperature.

After the sol solution is formed, it is continued with the gel-making process. The sol solution was put into the furnace at a temperature of 100°C for 3 days. After the gel-making process is complete, it is followed by a washing process with distilled water for 10 minutes using a magnetic stirrer at room temperature for 10 minutes and followed by a drying process using a furnace for 24 hours to form a precipitate. Then the resulting precipitate was ground until smooth and continued in the calcination process using a furnace with temperature variations of 450°C, 500°C, 550°C and 600°C for 3 hours.

Then the sample was transferred to a sample tube to continue with the characterization process using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) tools. Then the optical properties were tested using a UV-Visual tool.

# 3 Result and Discussion

## 3.1 XRD Test Results

Identification of the highest peak list which is the characteristic peaks of a sample is carried out by testing X-Ray Diffraction (XRD) with Rigaku Brand with Cu Kα radiation. The XRD data analysis process was carried out using highscore software to determine the phase and the highest peak formed in the standard $TiO_2$ and Cu-doped $TiO_2$ samples. Data from samples obtained using x-ray diffraction are then matched with standard data in the database.

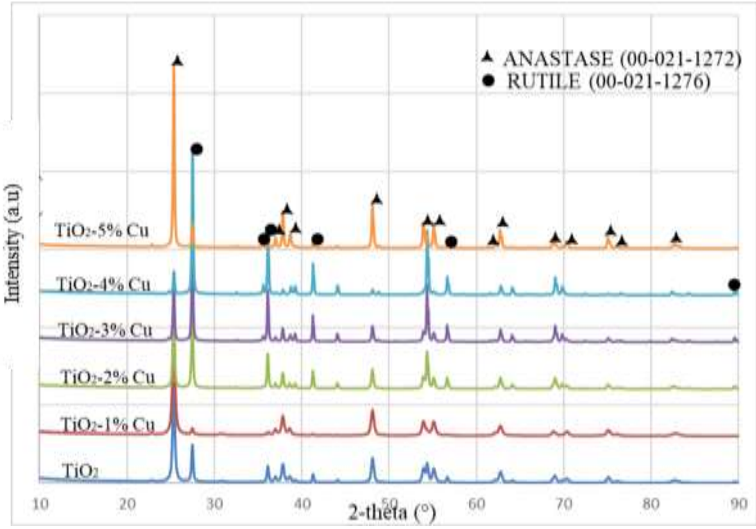



**Figure 1.** Graph of XRD Results of Cu-doped $TiO_2$ samples with various Cu content

Figure 1 shows that the sample has 2 phases formed, namely, $TiO_2$, $TiO_2$-1, $TiO_2$-2, $TiO_2$-3 $TiO_2$-4 namely rutile with a Miller index (110) and in $TiO_2$-5 the phase formed is anatase with a Miller index (101).

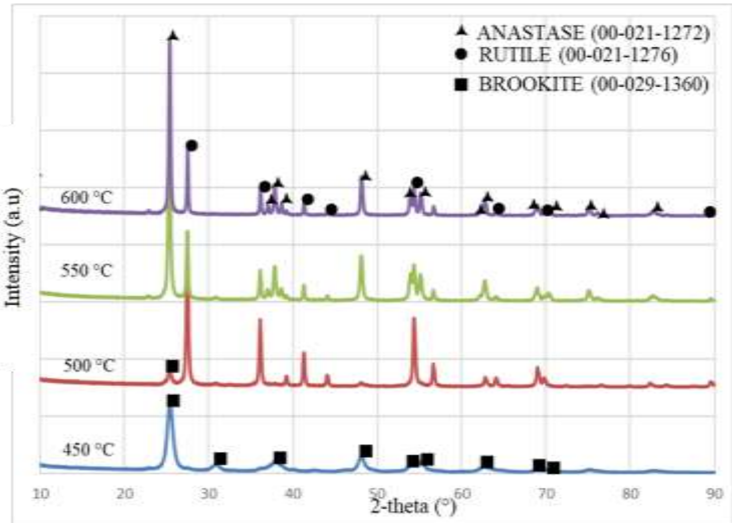


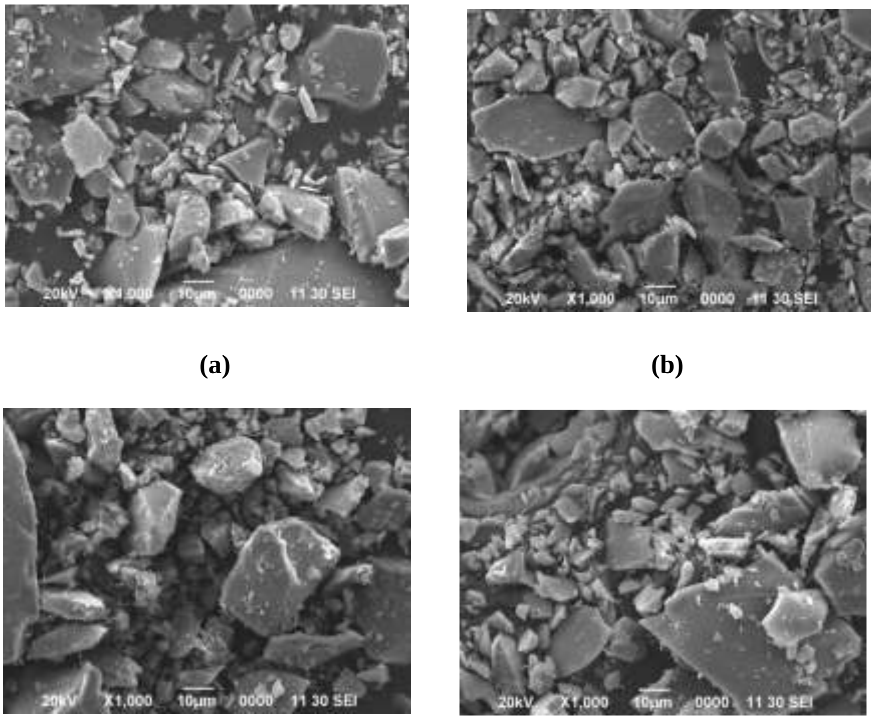

**Figure 2.** Graph of XRD Results of $TiO_2$-standard samples of calcination temperature variations

Figure 2 shows that the sample has 3 phases formed, namely, at a temperature of 450°C namely brookite with a Miller index (111) and at a temperature of 600°C the formed phase is a mixture of anatase and rutile which is more dominant in anatase with a Miller index (101).

Based on Figure 1 and Figure 2, the phase formed at each peak is the dominant $TiO_2$ phase. From the results of the analysis of the two samples, it can be seen that the phases formed are the same and different only in brookite but still more dominant in anatase.

### 3.2 SEM Characterization

Scanning Electron Microscopy (SEM) analysis was tested to determine the morphology of the particles that make up the $TiO_2$ material. The samples observed were standard $TiO_2$, $TiO_2$-1, $TiO_2$-3, and $TiO_2$-5 samples with a temperature of 550oC for 3 hours and standard $TiO_2$ samples or without doping with variations in calcination temperature, namely 450°C and 550°C. Observations on the sample were carried out with a magnification of 1000 times the magnification.




(a) (b)

(c) (d)

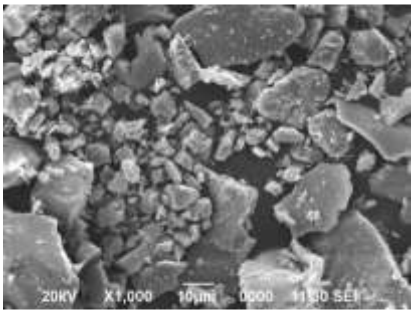
**Figure 3.** Sample Morphology (a) $TiO_2$ Standard (b) $TiO_2$-1 (c) $TiO_2$-3 (d)$TiO_2$-5

Based on Figure 3 it can be seen that all samples consist of particles small and large sizes of $TiO_2$ without doping and with Cu doping with variations of 1%, 3%, and 5% in the form of irregular and tetragonal particles, measuring 10 µm.

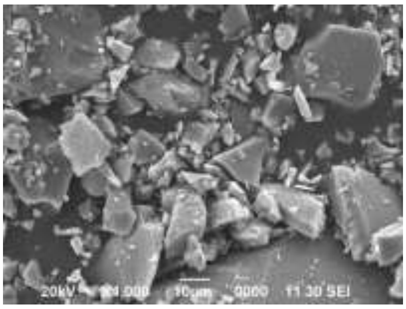
**Table 1.** Sample Content of Cu doping variation

| Sample | %Ti | %O | %Cu |
|---|---|---|---|
| $TiO_2$ | 59.80 | 40.20 | 0.00 |
| $TiO_2$-1 | 63.30 | 34.97 | 1.90 |
| $TiO_2$-3 | 60.74 | 36.17 | 3.09 |
| $TiO_2$-5 | 55.76 | 39.17 | 5.07 |

Table 1 shows the SEM-EDX test, the content contained in the sample is in accordance with the experiments that have been carried out. As in $TiO_2$-1, it can be seen that the %Cu content is 1.9%, which is almost close to the amount of Cu that was added during the research. This condition is the same as the standard $TiO_2$, $TiO_2$-3 and $TiO_2$-5 samples, 0%, 3.09%, and 5.07%.



(a)



(b)

**Figure 4.** Sample morphology (a) $TiO_2$ standard 450°C (b) $TiO_2$ standard 550°C

Based on Figure 4 it can be seen that all samples consist of small and large particles of $TiO_2$ without the addition of Cu with variations in calcination temperature of 450°C and 550°C in the form of irregular, tetragonal particles, measuring 10 µm.

**Table 2.** Content of standard $TiO_2$ Samples Calcination Temperature Variation

| Sample | %Ti | %O |
|---|---|---|
| 450 | 63.65 | 36.35 |
| 550 | 59.80 | 40.20 |

In Table 2, it can be seen that the SEM-EDX test can be seen what the percentage of Ti and O is respectively. The percentage of each sample content does not have such a different distance, as it can be seen that at a temperature of 450°C the Ti content is 63.65% and at a temperature of 550°C that is 59.8%.

### 3.3 Ultraviolet-Visible Spectroscopy (UV-Vis) Testing

UV-Vis test to find out measuring the band gap energy of titanium dioxide, which is shown in Figure 5 and Figure 6.

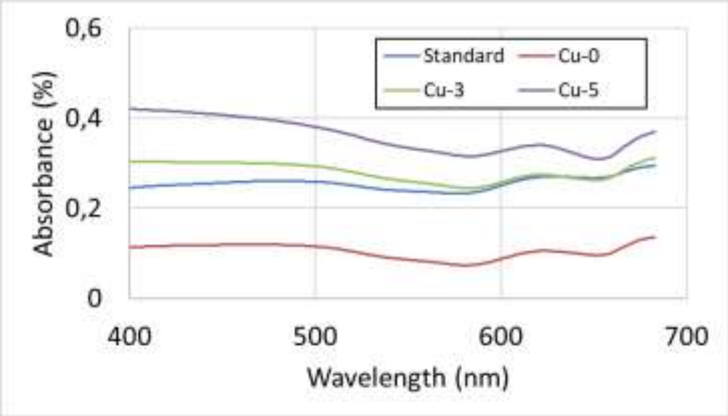



**Figure 5.** Spectra of Cu-doped $TiO_2$ SRUV with variations in Cu content

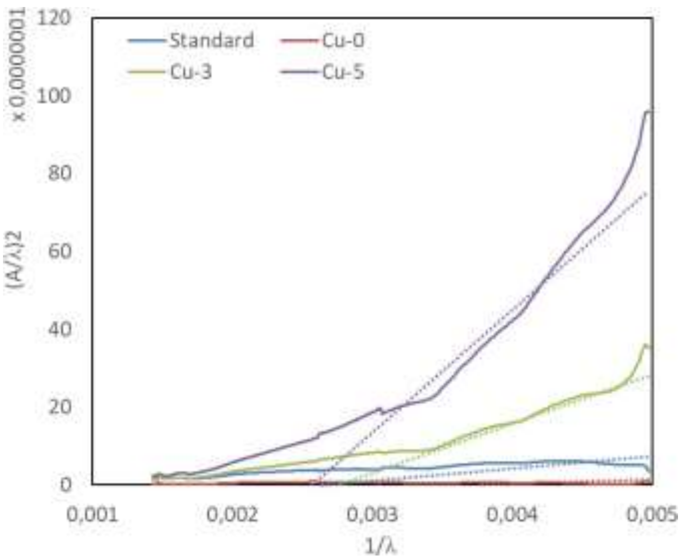



**Figure 6.** AFS of Cu-doped $TiO_2$ nanoparticles with variations in Cu content

Figure 5 is the result of UV-Vis Spectroscopy testing for a wavelength of 700-400 nm. From Figure 5 it can be observed that the maximum absorption value of the variation of the calcination temperature for the $TiO_2$-Standard sample is in the wavelength range of 500-400 nm with a value of about 0.42%.

Figure 6 is a conversion graph for the absorption fitting spectrum (AFS) method results of UV-Vis Spectroscopy testing of Cu-doped $TiO_2$ nanoparticles with variations in Cu content.

**Table 3.** Bandgap energy values of the AFS method for variations in Cu content

| Sample | $1/\lambda$ | $E_g$(eV) |
|---|---|---|
| Standard $TiO_2$ | 0.00250 | 3.099 |
| $TiO_2$-1 | 0.00370 | 4.587 |
| $TiO_2$-3 | 0.00265 | 3.285 |
| $TiO_2$-5 | 0.00245 | 3.037 |

Based on Table 3, it can be seen that the band gap energy value obtained is in accordance with the literature, which is around 3 eV to 3.4 eV. The difference in the band gap energy values of the synthesized Cu-doped $TiO_2$ nanoparticles may be due to differences in Cu elements, which also affect the crystallinity of the nanoparticles. The samples obtained from $TiO_2$-3, with a variation of Cu 3%, had the closest band gap energy compared to standard $TiO_2$-, $TiO_2$-1, and $TiO_2$-5. This is probably because $TiO_2$-3 nanoparticles have the highest crystallinity and structural regularity compared to other samples.

## 4 Conclusion

The effect of adding Cu on the structural properties of $TiO_2$ can be seen in the results of XRD analysis which shows the crystallite size is getting bigger when the Cu element is higher then the phase formed is anatase when the Cu element is higher and the shape of the nanoparticles is tetragonal. The effect of the addition of Cu on the optical functional properties of $TiO_2$ can be seen in the UV-Vis results, namely the addition of Cu causes the band gap energy of $TiO_2$ to increase. The effect of calcination temperature on the physical properties of TiO2 can be seen in the XRD results, namely the size of the crystallites increases when the calcination temperature is higher and the phase formed without Cu doping and temperatures below 500°C is brookite and the nanoparticles are tetragonal.

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