STUDY OF MICROSTRUCTURE, MORPHOLOGY AND FUNCTIONAL GROUPS OF TITANIUM DIOXIDE (TiO$_2$) IMPREGNATED WITH COPPER (Cu)

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Abstract

This research aims to determine the differences in the microstructure, morphology, and functional groups of TiO$_2$ (P-25) after being impregnated with Cu. Cu-impregnated TiO$_2$ samples are synthesized using the impregnation method with TiO$_2$ (P-25) and copper sulfate as precursors. The microstructure and functional groups of TiO$_2$ (P-25) and Cu-TiO$_2$ were investigated using X-ray diffraction (XRD), scanning electron microscope-energy dispersive x-ray (SEM-EDX), and Fourier transform infrared (FTIR) analysis. The lattice parameters (a, b, and c) of the TiO$_2$ sample were found to be $a = b = 0.3778$ nm, $c = 0.9494$ nm, and these values increased to $a = b = 0.3779$ nm, $c = 0.9496$ nm after the addition of Cu. The distance between the lattices of the TiO$_2$ sample was measured at 0.3505 nm and increased to 0.3509 nm after Cu addition. The average crystallite size of the TiO$_2$ sample was 33 nm, which increased to 43 nm after Cu impregnation. The strain value decreased from $2.76 \times 10^{-3}$ to $1.82 \times 10^{-3}$ after Cu addition. SEM results revealed that the morphology of the particles from the Cu-doped synthesis showed agglomeration. The success of Cu doping was confirmed by EDX mapping, which showed the presence of Ti, O, and Cu evenly distributed on the TiO$_2$ surface. The FTIR spectrum indicated that TiO$_2$ (P-25) and Cu-TiO$_2$ particles had absorption peaks at similar wave numbers. However, in the absorption area of 1000 cm$^{-1}$ to 1250 cm$^{-1}$, new absorption bands affiliated with Cu-O bonds appeared in the Cu-TiO$_2$ sample, resulting from TiO$_2$ vibrations after Cu addition.

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INTRODUCTION

Among semiconductor oxides, titanium dioxide (TiO$_2$) nanomaterials have been widely studied in the last two decades [1]. TiO$_2$ is interesting to research because of its unique properties and applications in various fields. Among the properties of TiO$_2$ are good optical transmittance, high refractive index, and stability. Due to its properties, TiO$_2$ nanomaterial is used in many applications, including paint, toothpaste, UV protection, photocatalysis, photovoltaic, electrochromic, and photochromic [2]. TiO$_2$ exists in three phases, namely anatase, brookite, and rutile [3].

In recent years, research related to TiO$_2$ doping with transition metals has been routinely carried out. Doping TiO$_2$ with metal can change the physical properties of TiO$_2$ [4]. In practice, TiO$_2$
can only respond to photons in the wavelength range of ultraviolet light, which accounts for only 5% of sunlight. So, it is effective to expand the wavelength range to the visible light region, which covers 45% of the sun. An effective strategy to increase the visible light sensitivity of TiO₂ is doping with elements [5]. This will make TiO₂ work more efficiently as a photocatalyst. Several literatures have reported the synthesis and characterization process of TiO₂ powder doped with transition metals including iron (Fe)[6], nickel (Ni)[7], manganese (Mn)[8], magnesium (Mg) [9], and copper (Cu).

Among the doping elements, copper (Cu) is one of the dopants that can increase visible light absorption and photocatalytic efficiency [10]. Apart from that, copper (Cu) has an ionic radius that is not much different, namely Cu²⁺ (0.72 Å) is almost identical to Ti⁴⁺ (0.68 Å) [11]. In its application, the Cu atom is an antibacterial element [12]. So doping TiO₂ with Cu can expand its application area.

Many methods have been used for the preparation of Cu-TiO₂ including coprecipitation [4], liquid phase deposition techniques [13], impregnation [14], [15], and sol-gel [16]. Kaya and Türkten, [17] synthesized TiO₂ doped with non-metals (C, N, Se), metals (Cu, Fe), and co-doping (N/S) using the wet impregnation method and obtained changes in optical properties. TiO₂ shifts its band gap energy from 3.2 eV to lower, namely 2.55-2.90 eV. Leong et al [18] also reported the use of different methods to synthesize Cu-TiO₂, namely sonochemical, impregnation, and physical mixing methods. The result is that the sample forms a rutile phase with high crystallinity, smaller particle size with a larger sample surface area. In addition, there is a decrease in the band gap energy in the sample, so it is active in the visible light wavelength range.

In this research, the synthesis of Cu-TiO₂ was carried out using the impregnation method, because it is fast and cheap. In addition, the impregnation method can control the configuration, crystallography, and morphology of the sample [19]. X-ray diffraction (XRD), scanning electron microscope-energy dispersive x-ray (SEM-EDX), and Fourier transform infrared (FTIR) were used to characterize the resulting samples. In addition, the lattice strain values were also investigated.

**RESEARCH METHODS**

**Synthesis of Cu-TiO₂**

Cu-TiO₂ nanoparticles were synthesized using the impregnation method with CuSO₄.5H₂O precursor and Degusa TiO₂ (P-25) (Merck). A total of 0.21 grams of CuSO₄.5H₂O was dissolved in 50 ml of distilled water and stirred for 30 minutes at room temperature (solution X) at a speed of 120 rpm. Next, 3 grams of TiO₂ were added to solution X. The mixed solution was then stirred for 120 minutes at a temperature of 90°C with a speed of 500 rpm. Next, the sample was dried in an oven at 110°C for 30 minutes and ground until smooth. The Cu-TiO₂ powder sample was calcined at 500°C for 180 minutes.

**Characterization**

The Cu-TiO₂ sample was characterized for analysis of the structure and phases formed using X-ray diffraction (XRD) Merck PANalytical, Type: Cu metal target material. Crystal size, lattice spacing, lattice parameters, and cell volume were calculated using equations (1)-(4) respectively.

\[
t = \frac{k\lambda}{\beta \cos \theta}
\]

(1)

\[
d = \frac{n\lambda}{2 \sin \theta}
\]

(2)

\[
\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}
\]

(3)

\[
V = a^2c
\]

(4)

where \(t\) is the crystal grain size, \(k\) is Scherrer's constant (0.9), \(\lambda\) is the X-ray wavelength (in Å), \(\beta\) is the half-peak width (in radians), and \(\theta\) is the Bragg diffraction angle (in radians), \(d\) is the interplanar distance, \(a\) and \(c\) are lattice parameters, \(h\), \(k\), and \(l\) are miller index notation.

Analysis of surface morphology and elements using Scanning Electron Microscopy/Energy Dispersive X-Ray (SEM/EDX) spectroscopy (mapping) HITACHI SU-3500 brand, EDX detector HORIBA brand. Measurement conditions were carried out at room temperature (18-
RESULT AND DISCUSSION

X-ray diffraction

Figure 1 shows the XRD patterns of TiO$_2$ (P-25) and Cu-doped TiO$_2$ nanoparticles classed at 500°C for 3 hours. The sample shows peaks corresponding to the anatase phase with a tetragonal system affiliated to the miller indices (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), and (215) (JCPDS No. 21–1272). The XRD diffraction pattern of anatase has a maximum peak at an angle of $2\theta = 25.888^0$ for TiO$_2$ (P-25) and $2\theta = 25.361^0$ for Cu-TiO$_2$. Garg et al., 2017 also observed the anatase phase at the angle $2\theta = 25.3685^0$ which is affiliated with the Miller index (101) [20].

![XRD pattern of TiO$_2$ P-25 and Cu-TiO$_2$](image)

Gambar 1. XRD pattern of TiO$_2$ P-25 and Cu-TiO$_2$

The presence of a Cu peak was not observed, which indicates that Cu has been doped into the TiO$_2$ lattice. It also indicates that Cu is in amorphous or small crystalline form, which cannot be detected by XRD devices [21]–[23]. In addition, the absence of metal oxide diffraction peaks indicates good metal dispersion on the catalyst surface, in this case, TiO$_2$ [20], [24]. These results are supported by observations reported by Sahoo and Gupta, 2015 [25]. Another thing that causes the Cu metal diffraction peak to not be detected is the very low metal ion content [10].

Table 1. Cell volume and intensity of TiO$_2$ and Cu-TiO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average FWHM</th>
<th>Volume (nm$^3$)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.291</td>
<td>0.1355</td>
<td>862.283</td>
</tr>
<tr>
<td>Cu-TiO$_2$</td>
<td>0.188</td>
<td>0.1356</td>
<td>893.706</td>
</tr>
</tbody>
</table>

Based on Table 1, it appears that the cell volume increases after adding Cu. The level of nanoparticle crystallinity can be identified by looking at the diffraction peak profile that appears and the phase composition that appears in the resulting sample. Compared to pure TiO$_2$ (P-25), the Cu-TiO$_2$ sample shows an increase in intensity which indicates that the quality of the
crystallites is getting better. In addition, the average FWHM obtained decreased from 0.291 for TiO$_2$ (P-25) to 0.188 for Cu-TiO$_2$, respectively. Based on the diffraction peaks that appear, the (101) peak on TiO$_2$ and Cu-TiO$_2$ has a greater intensity than the other peaks. This indicates that the crystallite grains that appear have a preference for the (101) direction.

**Microstructural and Morphological Analysis**

Based on the X-ray diffraction pattern (Figure 1), estimates of the lattice parameters $a$ and $c$, the crystallite size ($t$), the distance between planes ($d_{hkl}$), and strain ($\varepsilon$) can be obtained. Table 2 is the value of the lattice parameters $a$ and $c$, calculated from the diffraction peak values (200) and (004), using equation (3) (with Miller indices for tetragonal systems).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter $a = b$ (nm)</th>
<th>$c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.3778</td>
<td>0.9494</td>
</tr>
<tr>
<td>Cu-TiO$_2$</td>
<td>0.3779</td>
<td>0.9496</td>
</tr>
</tbody>
</table>

Based on Table 2, it appears that the lattice parameters $a$ and $c$ of the TiO$_2$ sample experienced an insignificant increase after the addition of Cu. This is caused by the ion radius of Cu$^{2+}$ (0.72 Å) being greater than Ti$^{4+}$ (0.68 Å) [11]. This result is supported by observations made by Garg et al, 2017 and Jacoski, 2022, where TiO$_2$ doped with Cu experienced an increase [20][27].

Apart from knowing the crystal structure, from the results of characterization using XRD, the full width at half maximum (FWHM) value is also known. The smaller the FWHM value, the better the crystal quality, so the smaller the strain that occurs. A smaller FWHM value indicates that it is easier for adjacent atoms to adjust direction. The lattice strain value was obtained using the tangent formula (5) [28], the results of which are presented in Table 2.

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$

<table>
<thead>
<tr>
<th>Sample</th>
<th>2-theta ($2\theta^0$)</th>
<th>d-spacing (nm)</th>
<th>Crystallite Size, $t$ (nm)</th>
<th>Lattice Strain ($\varepsilon$)</th>
<th>2-theta ($2\theta^0$)</th>
<th>d-spacing (nm)</th>
<th>Crystallite Size, $t$ (nm)</th>
<th>Lattice Strain ($\varepsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>25.388</td>
<td>0.3505</td>
<td>39</td>
<td>0.00419</td>
<td>25.361</td>
<td>0.35092</td>
<td>47</td>
<td>0.00352</td>
</tr>
<tr>
<td></td>
<td>37.003</td>
<td>0.2427</td>
<td>53</td>
<td>0.00202</td>
<td>37.013</td>
<td>0.24268</td>
<td>52</td>
<td>0.00207</td>
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<tr>
<td></td>
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<td>43</td>
<td>0.00243</td>
</tr>
<tr>
<td></td>
<td>38.593</td>
<td>0.2331</td>
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<td>38.706</td>
<td>0.23245</td>
<td>45</td>
<td>0.00224</td>
</tr>
<tr>
<td></td>
<td>48.127</td>
<td>0.1889</td>
<td>11</td>
<td>0.00699</td>
<td>48.118</td>
<td>0.18895</td>
<td>37</td>
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<tr>
<td></td>
<td>53.954</td>
<td>0.1698</td>
<td>17</td>
<td>0.00390</td>
<td>53.973</td>
<td>0.16975</td>
<td>31</td>
<td>0.00210</td>
</tr>
<tr>
<td></td>
<td>55.127</td>
<td>0.1665</td>
<td>17</td>
<td>0.00368</td>
<td>55.146</td>
<td>0.16642</td>
<td>32</td>
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<tr>
<td></td>
<td>62.656</td>
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<td>31</td>
<td>0.00129</td>
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<td>0.14791</td>
<td>31</td>
<td>0.00170</td>
</tr>
<tr>
<td></td>
<td>68.823</td>
<td>0.1363</td>
<td>20</td>
<td>0.00226</td>
<td>68.601</td>
<td>0.13669</td>
<td>49</td>
<td>0.00093</td>
</tr>
<tr>
<td></td>
<td>70.375</td>
<td>0.1337</td>
<td>34</td>
<td>0.00130</td>
<td>70.366</td>
<td>0.13369</td>
<td>29</td>
<td>0.00149</td>
</tr>
<tr>
<td></td>
<td>75.104</td>
<td>0.1264</td>
<td>57</td>
<td>0.00069</td>
<td>75.101</td>
<td>0.12639</td>
<td>57</td>
<td>0.00068</td>
</tr>
<tr>
<td></td>
<td>76.050</td>
<td>0.1250</td>
<td>36</td>
<td>0.00106</td>
<td>76.071</td>
<td>0.12502</td>
<td>62</td>
<td>0.00061</td>
</tr>
</tbody>
</table>

The peak position corresponding to the Miller index (101) experiences a small shift to a lower angle. This indicates that the crystal is distorted by the incorporation of Cu dopant because the ionic radius of Cu$^{2+}$ is greater than Ti$^{4+}$. Cu substitution in Ti in the TiO$_2$ crystal lattice results in an increase in the interplanar distance. The distance between the lattices is almost the same, namely 0.3505 nm (TiO$_2$) and 0.3509 nm (Cu-TiO$_2$). This value is almost the same as the value
of the inter-lattice distance for the (101) diffraction peak given by JCPDS-21-1272 for anatase, namely 0.352 nm.

The average crystallite size of the samples was calculated from the full width at half maximum (FWHM) with the Debye-Scherer formula and obtained 33 nm for pure TiO$_2$ (P-25) and 43 nm for Cu-TiO$_2$. These results indicate that the size of TiO$_2$ crystallites increases after the addition of Cu. This increase in crystallite size shows that Cu doping affects the growth of TiO$_2$ crystallites in the synthesis process. Based on the results of research conducted by [29] [30], the size of Cu-TiO$_2$ crystallites slightly increased due to the presence of Cu$^{2+}$ and CuO species. Different radii of Cu and Ti ions cause lattice distortion and strain fields thereby changing the size of Cu-TiO$_2$ crystallites [31]. When Cu ions replace Ti, the lattice parameters will increase and become larger resulting in the average size of the crystallites becoming larger. Replacement of Ti ions by Cu ions will affect the distribution of cations in the nanoparticles.

The average lattice strain values for TiO$_2$ (P-25) and Cu-TiO$_2$ were obtained as 2.76 × 10$^{-3}$ and 1.82 × 10$^{-3}$, respectively. These results show that the strain decreased after adding Cu. Lattice strain measures the distribution of lattice constants that arise from crystal imperfections. Like lattice dislocations, as a result of changes in cation distribution. Crystal size and lattice strain influence peak broadening [32].

Figure 2(a) shows the SEM image of Cu-doped TiO$_2$ and 2(b-d) is the EDX mapping.
SEM results show that the samples obtained tend to clump. Distribution of Cu elements on the TiO₂ surface. Analyzed by X-ray elemental mapping, as shown in Figure 2(b)-(d). From energy-dispersive X-ray spectroscopy (EDX) and elemental mapping patterns. We can see the presence of Ti, O, and Cu. The mapped elements are shown as coloured spots. The Cu element is evenly distributed on the TiO₂ surface. These results indicate that the synthesis method has succeeded in doping Cu onto the TiO₂ surface. This observation shows the formation of a Cu–TiO₂ composite material.

**Functional Group Analysis**

Fourier transform infrared (FTIR) spectroscopy shows the presence of TiO₂ (P-25) and Cu-TiO₂ functional groups. The FTIR transmission spectrum of TiO₂(P-25) and Cu-TiO₂ in the range 400 cm⁻¹-4000 cm⁻¹ is shown in Figure 3. The peaks observed in TiO₂ (P-25) and Cu-TiO₂ show some of the same peaks. But there is also a new peak that appears when doped with Cu.

In the absorption peak range of 500 cm⁻¹ to 1000 cm⁻¹, it is related to the vibration absorption of the Ti-O-Ti bond. Based on Figure 3, the Ti-O-Ti structure appears in the absorption area of 501.49 cm⁻¹ and 669.30 cm⁻¹ for the TiO₂ anatase sample and 516.92 cm⁻¹ and 686.66 cm⁻¹ for Cu-TiO₂, which is the vibration characteristic of Ti-O. This result was also reported by Aritonang et al., [33] who stated that the absorption area of 450-600 cm⁻¹ was Ti-O
vibration. These results show that the absorption peak of TiO2 has shifted to a higher wavelength region after doping. The TiO2 spectrum also shows absorption at the wave number 3444.72 cm\(^{-1}\) which is the -OH stretching absorption area of Ti-OH on the TiO2 surface. This result is based on research conducted by Dong et al. [34] stated that the wave number range of 3200-3500 cm\(^{-1}\) is the area of absorption of hydroxyl groups (-OH). Meanwhile, in the Cu-TiO2 spectrum, it appears in the wave number absorption area of 3562.52 cm\(^{-1}\). These results indicate a shift in the -OH absorption peak of TiO2 after Cu was added to a higher wave number region. This shows that the shift in vibration absorption indicates that the Cu dopant has successfully entered the TiO2 structure. At 1658.78 cm\(^{-1}\) is related to the -OH bending of Ti-OH on the TiO2 surface [33]. However, the -OH absorption area obtained was at a wave number of 3446 cm\(^{-1}\), slightly larger than the results of this study. Meanwhile, the Ti-OH absorption area was found to be smaller, namely at a wave number of 1635 cm\(^{-1}\).

Besides that. Bond vibrations were also observed in the wave number range of 1000-1250 cm\(^{-1}\) after the addition of Cu, which was identified as a Cu-O bond resulting from TiO2 lattice vibrations as a result of the presence of the Cu element [31]. The same results were also reported by [35]. The peak around 1622.13 cm\(^{-1}\) is C=C and 2357.01 cm\(^{-1}\) is the C=O absorption peak [31]. Here is a fundamental difference in the FTIR transmission spectrum for TiO2 and Cu-TiO2, namely in the wave number range of 3300 cm\(^{-1}\) to 3800 cm\(^{-1}\). Besides that. A new absorption area appears in the Cu-TiO2 sample at the absorption peak from 2800 cm\(^{-1}\) to 3300 cm\(^{-1}\) as also reported by Yan et al. [36]. Namely in the 2850 cm\(^{-1}\) and 2920 cm\(^{-1}\) areas which are C-H stretching vibrations. This indicates that Cu doping on TiO2 was successfully carried out using the impregnation method.

**CONCLUSION**

TiO2 (P-25) samples and Cu-TiO2 nanoparticles have been synthesized using the impregnation method. Microstructure, morphology, and the functional groups of TiO2 (P-25) and Cu-TiO2 nanoparticles have been studied based on data from characterization using XRD, SEM-EDX, and FTIR. Based on XRD results, the crystal structure shows the anatase phase. The lattice parameters (a, b, and c) of the TiO2 sample were obtained a = b = 0.3778 nm, c = 0.9494 nm and increases after adding Cu, namely a = b = 0.3779 nm, c = 0.9496 nm. The cell volume and diffraction peak intensity of the TiO2 sample increased after the addition of Cu. The distance between the lattices of the TiO2 sample was found to be 0.3505 nm and increased after adding Cu to 0.3509 nm. The TiO2 sample has an average crystallite size of 33 nm and increases after adding Cu to 43 nm (Cu-TiO2). Meanwhile, the strain value decreased after adding Cu from \(2.76 \times 10^{-3}\) to \(1.82 \times 10^{-3}\). Based on the SEM test results, the morphology of the particles resulting from the synthesis of agglomerated Cu doping was obtained. The success of Cu doping is demonstrated by the EDX mapping results. This indicates the presence of Ti, O, and Cu are evenly distributed on the TiO2 surface. The FTIR spectrum shows that TiO2 (P-25) and Cu-TiO2 particles tend to have absorption peaks at the same wave number. However, in the absorption area of 1000 cm\(^{-1}\) to 1250 cm\(^{-1}\), new absorption appears in the Cu-TiO2 sample which is affiliated with Cu-O bonds as a result of TiO2 vibrations after the addition of Cu.

**REFERENCES**


