The Influence of Cr\(^{3+}\) on TiO\(_2\) Crystal Growth and Photoactivity Properties

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Abstract: The photocatalyst technology is an integrated combination of photochemical processes and catalysis in order to carry out a chemical transformation reaction. One of the semiconductor materials that have good photocatalytic activity is TiO\(_2\) anatase. This study aim to determine the effect of the Cr\(^{3+}\) addition on the growth of TiO\(_2\) rutile crystal and the increasing of TiO\(_2\) photoactivity. Diffractogram X-Ray of the samples showed that the synthesized TiO\(_2\) at 400 °C has been produced 100% TiO\(_2\) anatase. Synthesis of TiO\(_2\) doped Cr\(^{3+}\)composite was using wet impregnation method. The TiO\(_2\) doped Cr\(^{3+}\)composites have been grown by annealed at a temperature of 300, 400, 500, 600 and 700 °C, respectively. Annealing process have capabiled to gain to the TiO\(_2\) doped Cr\(^{3+}\)nanocomposite. The result product annealed at 500 °C only appear anatase phase due to the Cr\(^{3+}\) addition influence that was able to suppress the growth of rutile. Identification of TiO\(_2\) doped Cr\(^{3+}\)composite using Fourier Transform Infra-Red (FT-IR) showed O-Cr vibration at 2283.72 cm\(^{-1}\). The TiO\(_2\) doped Cr\(^{3+}\)photoactivity was studied to degrade Rhodamin B. The best result on photodegradation of Rhodamin B was performed by using TiO\(_2\) doped Cr\(^{3+}\)composite which was annealed at 700 °C i.e. 74.71%.

1. Introduction
The photocatalyst technology is a combination of integrated photochemical methods and catalysts in order to carry out a chemical transformation reaction. Titanium dioxide (TiO\(_2\)) is widely reported as an active semiconductor material as a photocatalyst. How to improve the photocatalytic activity of TiO\(_2\) in the visible region is the main focus of the recent TiO\(_2\) photocatalysis research. Many efforts have been made to achieve the utilization of visible light for TiO\(_2\) material, such as transitional metal ion doping [1–3], nonmetal element doping [4,5] and dye sensitization [6,7]. Nanomaterial TiO\(_2\) anatase phase has photocatalytic activity higher than rutile phase [2,4,5].

The TiO\(_2\) is one of the widely use photocatalyst because it has high photocatalytic efficiency, low cost, inert biologically and chemically [2,4,5]. Degradation photocatalytic is a technique used to water and air pollutants treatment. The degradation process is known to have two of compounds are added to accelerate the process of organic compounds degradation, namely chemical oxidants and photocatalyst. Photocatalyst can be utilized in the processing of dye waste [8–9]. The color quantity caused by Rhodamin B is very sharp, this is due to the presence of two auxochrome groups. Rhodamin
B is a synthetic dye waste used for textile, paint and paper industries. This dye can cause pollution, irritation, and carcinogen [4 10].

In previous study, TiO$_2$ doped Cr$^{3+}$ electrode have driven visible light response, and confirmed that the impurity band is formed near the $\pi^*$ conduction band of the TiO$_2$ [10]. In this study, the addition of Cr$^{3+}$ to TiO$_2$ semiconductors was conducted to suppress the growth of TiO$_2$ phase crystal rutile thus yield more anatase phase. This controlled crystal phase has an effect in increasing photocatalytic activity on the TiO$_2$ degradation of Rhodamine B.

2. Experimental
2.1. The Preparation of TiO$_2$
10 mL of TTIP (Titanium Tetra Iso Propoxide) was hydrolyzed with 100 mL acetic acid. After that, the temperature of the solution was maintained to 10-15 °C. The mixture was heated to a temperature of 90 °C until a TiO$_2$ sol gel was formed. Then the TiO$_2$ gel was heated to 150 °C for 24 h to assemble a white TiO$_2$ xerogel. Xerogel TiO$_2$ was calcinated for 4 h at 150, 300, 400, 500, 600, and 700 °C. The resulted TiO$_2$ was characterized with XRD and FTIR.

2.2. The Preparation of TiO$_2$ doped Cr$^{3+}$ Composites
0.8 gram of TiO$_2$ was added with 4 gram of Cr(NO$_3$)$_3$.9H$_2$O and 3 gram of urea dissolved in 100 mL of aquades. The mixture was then heated at 110 °C for 2 days. After the powders were obtained, it was calcined at 300°C, 400°C, 500°C, 600°C, and 700°C for 4 hours, respectively. Furthermore, The resulted TiO$_2$ doped Cr$^{3+}$ was characterized using XRD and FTIR.

2.3. Photodegradation of Rhodamine B
0.01 grams of TiO$_2$ and TiO$_2$ doped Cr$^{3+}$ samples were added to 25 mL of 5 ppm Rhodamin B then stirred. Samples were irradiated with visible light for 0, 30, 60, 120, and 180 min. Subsequently, the solution containing Rhodamine B were analyzed with UV-Vis spectrophotometer at a wavelength region of 400-600 nm.

3. Result and Discussion
The synthesis of TiO$_2$ material was carried out by sol-gel process. Figure 1 shows that pure TiO$_2$ diffractogram from annealing results. TiO$_2$ 400 crystals show as anatase phase, in accordance with JCPDS No. 78-486 ie peak at 20 = 25.35° (d$_{101}$ = 3.5091 Å), 20 = 37.95° (d$_{004}$ = 2.3679 Å), and 20 = 48.15° (d$_{200}$ = 1.8874 Å), 20 = 54.86° (d$_{211}$ = 1.6716 Å) and 20 = 55.01° (d$_{211}$ = 1.6674). While on TiO$_2$ 500, rutile TiO$_2$ was found with a peak at 20 = 27.50° (d$_{110}$ = 3.2394 Å) in accordance with JCPDS No. 870-710, this rutile peak at TiO$_2$ 600 and on TiO$_2$ 700 found more. At an annealing temperature of 700 °C, the peak intensity of anatase TiO$_2$ was decreased. Some of the anatase peaks of TiO$_2$ disappear while the peaks represented as a rutile TiO$_2$ was increased.
The synthesis of TiO$_2$ doped Cr$^{3+}$ composite was conducted with wet impregnation method. The growth mechanism can be explained by the reaction as follows:

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\begin{align*}
\text{Cr}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Cr(OH)}_3 + 3\text{H}^+ \\
\text{(NH}_2\text{)}_2\text{CO} + 3\text{H}_2\text{O} & \rightarrow 2\text{NH}_4^+ + 2\text{OH}^- + \text{CO}_2 \\
\text{Cr(OH)}_3 & \rightarrow \text{CrOOH} \\
\text{Cr}_2\text{O}_3 + \text{Xerogel TiO}_2 & \rightarrow \text{Xerogel composite TiO}_2\text{-Cr}_2\text{O}_3 \\
\text{Xerogel composite TiO}_2\text{-Cr}_2\text{O}_3 & \rightarrow \text{Powder composite TiO}_2\text{-Cr}_2\text{O}_3
\end{align*}
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**Figure 1.** X-Ray Diffractogram of TiO$_2$ annealed at temperature of (a) 150 °C (b) 300 °C (c) 400 °C (d) 500 °C (e) 600 °C (f) 700 °C

**Figure 2.** Diffractogram of TiO$_2$ doped Cr$^{3+}$ composite annealed at temperature of (a) 150 °C (b) 300 °C (c) 400 °C (d) 500 °C (e) 600 °C (f) 700 °C
The XRD diffractogram of TiO$_2$ doped Cr$^{3+}$ composite with various annealing can be seen in Figure 2. The presence of new peaks in Figure 2 represented Cr$_2$O$_3$ peak at $2\theta = 24.60^\circ$ (d$_{102} = 3.6144$ Å), $2\theta = 36.30^\circ$ (d$_{110} = 2.4717$ Å), $2\theta = 41.55^\circ$ (d$_{113} = 2.1707$ Å), $2\theta = 54.80^\circ$ (d$_{116} = 1.6730$ Å) according to JCPDS No. 381-479. That is also produced TiCrO$_3$ which appears at $2\theta = 33.50^\circ$ (d$_{104} = 2.6716$ Å), $2\theta = 50.15^\circ$ (d$_{024} = 1.8911$ Å) according to JCPDS No. 820-211. From the diffractogram in Figure 2 (d), a new peak indicates the presence of TiO$_2$ anatase shown with a peak at $2\theta = 25.30^\circ$ (d$_{101} = 3.5159$ Å) in according with JCPDS No. 782-486. The result on diffractogram in Figure 2 (e) was indicated two peaks of TiO$_2$ anatase at $2\theta = 25.35^\circ$ (d$_{101} = 3.5091$ Å) dan $2\theta = 48.05^\circ$ (d$_{200} = 1.8911$ Å) according to JCPDS No. 782-486. Annealing at 700 °C the peak of TiO$_2$ anatase begins to decrease in intensity.

When the diffractograms were compared to the diffractogram of pure TiO$_2$, we conclude that TiO$_2$ doped Cr$^{3+}$ have increasing in crystallinity, because TiO$_2$ annealed at 300 °C exhibit more pointed peaks whereas pure TiO$_2$ only shows a broad peak shown in Fig. 1 and Fig. 2. TiO$_2$ doped Cr$^{3+}$ be able to inhibit the rutile growth at high temperatures, supported by the absence of rutile peaks at 500 °C in XRD data. At temperatures of 600 °C until 700 °C, peaks intensity of TiO$_2$ rutile was increased and the peaks of TiO$_2$ anatase was decreased in intensity. Therefore, TiO$_2$ doped Cr$^{3+}$ can built thermal resistance at high temperatures compared with pure TiO$_2$ by mean no rutile peaks present in the composite. The result of FT-IR analyzes TiO$_2$ and TiO$_2$-Cr$_2$O$_3$ composite shown in Fig. 3 and Table 1.

![Figure 3. FT-IR spectra at 400 °C (a) pure TiO$_2$ (b) TiO$_2$- doped Cr$^{3+}$ composite](image)

| Wavelength | Function Group |
|------------|----------------|
| 459.06     | Ti-O-Ti        |
| 536.21     | Ti-O           |
| 1531.78    | -OH            |
| 3406.72    | Ti-OH          |
| 549.71     | Ti-O           |
| 1625.99    | -OH            |
| 3404.36    | Ti-OH          |
| 2283.72    | O-Cr           |

The photoactivity test of TiO$_2$-doped Cr$^{3+}$ composite for the degradation of Rhodamine B was performed in several temperatures (400 °C-700 °C), and was measured at certain times. The result of Rhodamine B degradation is shown in Fig. 4. The longer of irradiation time the greater decreasing of Rhodamine B absorbance. Degradation percentage of Rhodamine B is shown in Table 2.
**Figure 4.** The spectra represented of decreasing Rhodamin B concentration by expose the visible light along (a) 0 minute (b) 30 minute, (c) 60 minute (d) 120 minute and (e) 180 minute. The TiO$_2$-doped Cr$^{3+}$ were annealed at (A) 400 °C (B) 500 °C (C) 600 °C (D) 700 °C

**Table 2.** Degradation result of Rhodamine B using TiO$_2$ doped Cr$^{3+}$ composite in radiation time various.

| Annealing | Percentage of degradation (%)* |
|-----------|--------------------------------|
| 400 °C    | 2.99 3.80 10.59 18.13          |
| 500 °C    | 6.73 8.41 11.16 24.02           |
| 600 °C    | 19.34 25.01 28.31 29.49         |
| 700 °C    | 15.00 32.92 57.34 74.71         |

* percentage of degradation was calculate by $\frac{A_0-A_t}{A_0} \times 100%$

The Cr$^{3+}$ in TiO2 photocatalys act as photosensitizer so it can be used to overcome the limitations of the spectral sensitivity of the TiO$_2$ semiconductor with a high energy gap of 3.2 eV. The TiO$_2$ surface have been modified using color sensitizer molecules which lead to improvement of TiO$_2$ properties. The exposure of visible light in a certain time will have an effect on the increasing composite photocatalytic activity (Table 5). This because of the longer of visible light irradiation the more
Electrons are continuously excited. Electron generated in semiconductor material is importance step in the photocatalytic degradation process of Rhodamine B. The best result on photodegradation of Rhodamine B was achieved when TiO$_2$ doped Cr$^{3+}$ composite was annealed at 700 °C amount 74.71%.

4. Conclusion

The TiO$_2$-Cr$_2$O$_3$ composite can be synthesized using wet impregnation method. The addition of Cr$^{3+}$ prevents the growth of the TiO$_2$ crystal rutile phase. Influence of Cr$^{3+}$ increases the TiO$_2$ photoactivity on photocatalytic degradation process of Rhodamine B.

References

[1] Choi W, Termin A, Hoffmann M R 1994 J. Phys. Chem. 98 13669
[2] Zhu J, Deng Z, Chen F, Zhang J, Chen H, Anpo H, Huang J, Zhang L 2006 Appl. Catal. B 62 329
[3] Yuan S, Sheng Q, Zhang J, Chen F, Anpo M, Zhang Q 2005 Micropor. Mesopor. Mater 79-93
[4] Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y 2001 Science 293-269
[5] Cong Y, Zhang J, Chen F, Anpo M 2007 J. Phys. Chem. C 111 69-76
[6] Bae E, Choi W, Park J, Shin H S, Kim S B, Lee J S 2004 J. Phys. Chem. B 108 14093
[7] Bae E, Choi W 2003 Environ. Sci. Technol. 37 147
[8] Wahyuningsih S, Purnawan C, Kartikasari P, Praistia N 2014 Chemical Papers 68 1-9
[9] Wahyuningsih S, Ramelan A H, Hidayat R, Fadillah G, Munawaroh H, Saputri L N M Z, Hanif Q A 2015 Proc. Biophotonics Japan 97921E
[10] Matsumoto Y, Kurimoto J, Shimizu T, Sata E 1981 J. Electrochem. Soc. 1040-1044