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 ºC 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 beed grown by annealed at a temperature of 300, 400, 500, 600 and 700 ºC, respectively Annealing process have capabled to gain to the TiO_2 doped Cr^{3+}nanocomposite. The result product annealed at 500 ºC 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 ºC 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

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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 π*conduction band of the TiO2 [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 $Cr(NO_3)_3.9H_2O$ and 3 gram of urea dissolved in 100 mL of aquadest. 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. 782-486 ie peak at $2\theta = 25.35^o$ (d_{101} = 3,5091 Å), $2\theta = 37.95^o$ (d_{004} = 2.3679 Å), and $2\theta = 48.15^o$ (d_{200} = 1.8874 Å), $2\theta = 54.86^o$ (d_{211} = 1.6716 Å) and $2\theta = 55.01^o$ (d_{211} = 1.6674). While on TiO_2 500, rutile TiO_2 was found with a peak at $2\theta = 27.50^o$ (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.

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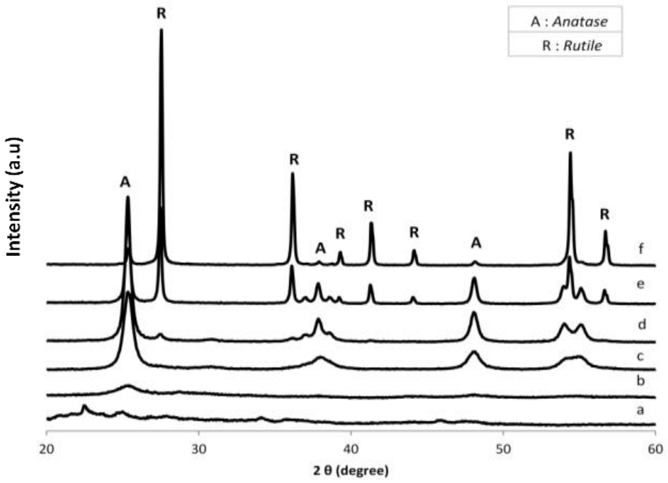


Figure 1. X-Ray Diffractogram of TiO_2 annealed at temperature of (a) 150 ˚C (b) 300 ˚C (c) 400 ˚C (d) 500 ˚C (e) 600 ˚C (f) 700 ˚C

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:

$Cr^{3+} + 3H_2O \longrightarrow Cr(OH)_3 + 3H^+$

$(NH_2)_2CO + 3H_2O \longrightarrow 2NH_4^+ + 2OH^- + CO_2$

$Cr(OH)_3 \longrightarrow CrOOH \longrightarrow Cr_2O_3$

Cr_2O_3 + Xerogel TiO_2 $\longrightarrow$ Xerogel composite TiO_2-Cr_2O_3

Xerogel composite TiO_2-Cr_2O_3 $\longrightarrow$ Powder composite TiO2-Cr_2O_3

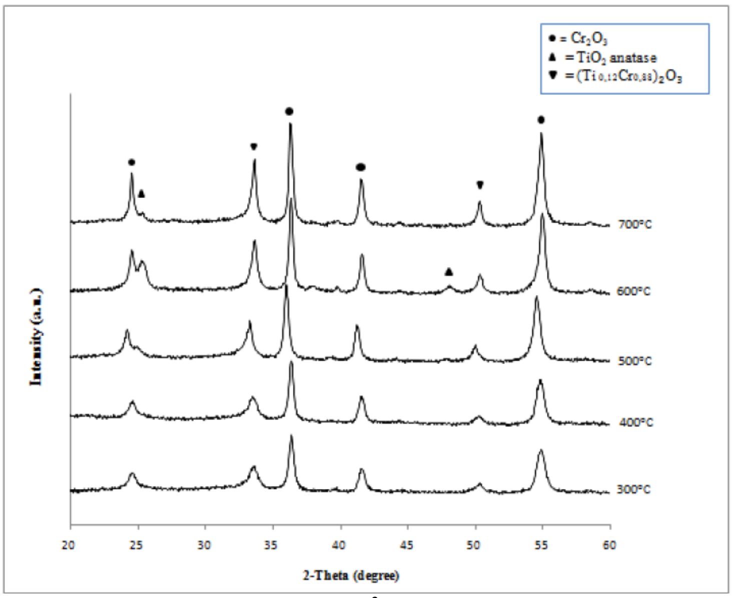


Figure 2. Diffractogram of TiO_2 doped Cr^{3+}composite annealed at temperature of (a) 150 ˚C (b) 300 ˚C (c) 400 ˚C (d) 500 ˚C (e) 600 ˚C (f) 700 ˚C

The XRD diffractogram of TiO_2 doped Cr^{3+}composite with various annealling can be seen in Figure 2. The presence of new peaks in Figure 2 represented Cr_2O_3 peak at 2θ = 24.60° (d_{102} = 3.6144 Å), 2θ = 36.30° (d_{110} =2.4717 Å), 2θ = 41.55° (d_{113} = 2.1707 Å), 2θ = 54.80° (d_{116} = 1.6730 Å) according to JCPDS No. 381-479. That is also produced $TiCrO_3$ which appears at 2θ = 33.50° (d_{104} = 2.6716 Å), 2θ = 50.15° (d_{024} = 1.8167 Å) in according with 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 2θ = 25.30° (d_{101} = 3.5159Å) in according with JCPDS No.782-486. The result on diffractogram in Figure 2 (e) was indicated two peaks of TiO_2 anatase at 2θ = 25.35° (d_{101} = 3,5091 Å) dan 2θ = 48.05° (d_{200} = 1,8911Å) according to JCPDS No. 782-486. Annealing at 700 °C the peak of TiO_2 anatase begins to decrease in intensity.

When the difractograms were compared to the difractogram 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_2O_3 composite shown in Fig. 3 and Table 1.

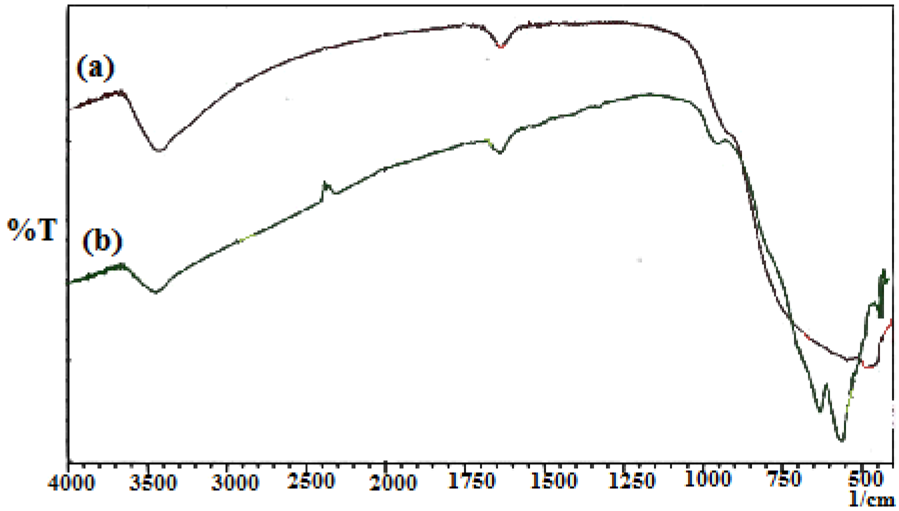
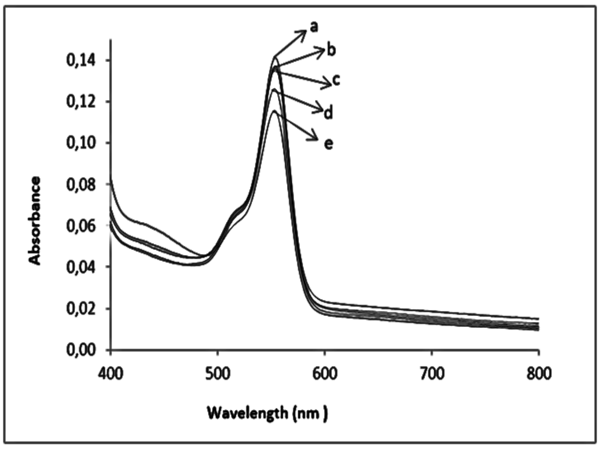


Figure 3. FT-IR spectra at 400 °C (a) pure TiO_2 (b) TiO_2- doped Cr^{3+} composite

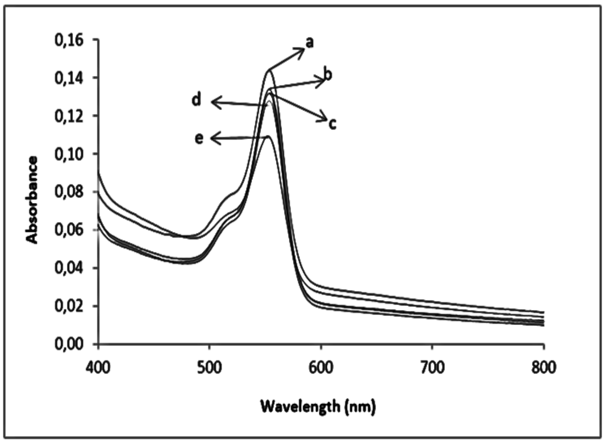
Table 1. Result of FTIR absorption in pure TiO_2 and TiO_2 doped Cr^{3+} composite

	Wavelength	Function Group
TiO_2	459.06	Ti-O-Ti
	536.21	Ti-O
	1531.78	-OH
	3406.72	Ti-OH
TiO_2-doped Cr^{3+} composite	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.



(A)



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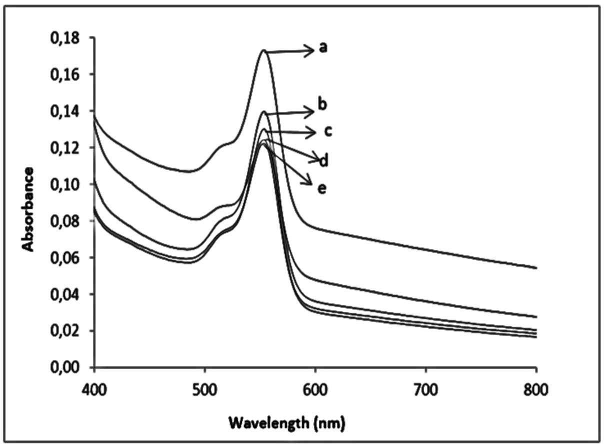
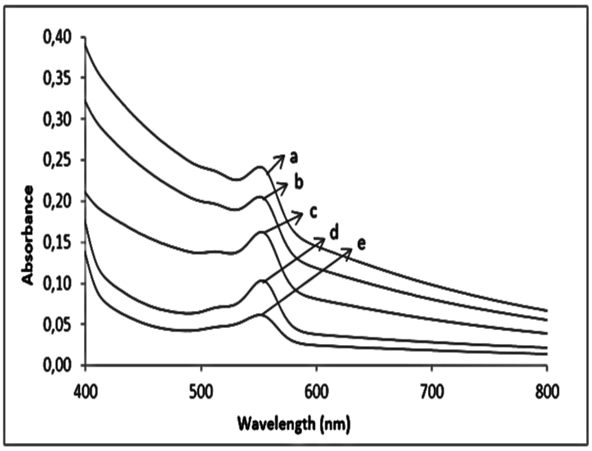


(C)



(D)

Figure 4. The spectras reprensented 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 º (B) 500 ºC (C) 600 ºC (D) 700 ºC

Table 2. Degradation result of Rhodamine B using TiO_2 doped Cr^{3+} composite in radiation time various.

Annealing	Percentage of degradation (%)*			
	30 min	60 min	120 min	180 min
400 ºC	2.99	3.80	10.59	18.13
500 ºC	6.73	8.41	11.16	24.02
600 ºC	19.34	25.01	28.31	29.49
700 ºC	15.00	32.92	57.34	74.71

* percentage of degradation was calculate by A_0-A_t/A_0 x100%

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_2O_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.

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