

The Influence of NiO Addition in TiO₂ Structure and Its Photoactivity

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Abstract. The synthesis of TiO₂ together with the TiO₂-NiO composite using various annealing temperatures has been studied. The synthesis of TiO₂ was performed by sol gel method using Titanium Tetra Isopropoxide (TTIP) precursor, whereas the synthesis of TiO₂-NiO composite was done by wet impregnation method using NiNO₃.6H₂O precursor. This study aims to determine the influence of NiO addition in its structure and photoactivity. The diffraction of synthesized TiO₂ at 400 °C temperature shows anatase TiO₂ peak at $2\theta = 25.35^\circ$. The addition of NiO dopant to the synthesis of TiO₂ process is carried out by annealing at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, respectively. The TiO₂-NiO composite has been prepared and shows the diffraction peak of NiO at $2\theta=43^\circ$ about 33.08 to 36.68%. The optimum result of Rhodamine B photodegradation with TiO₂ was 43.15%, while the optimum result of Rhodamine B degradation with TiO₂-NiO composite was 92.85%.

1. Introduction

The utilization of inorganic materials as catalyst has grown quite rapidly. The catalyst that has been used in photochemical processes, or better known as photocatalysts. Photocatalyst is a mixture of photochemical processes and a catalyst to carry out a reaction chemistry that takes place on the surface of the charged semiconductor catalyst light. Titanium dioxide (TiO₂) is one of the catalysts that have been applied as a photocatalyst semiconductor that has photoactivity and high chemical stability is commercially available. The advantages of TiO₂ include: inert, capable of absorbing ultraviolet light well, high chemical stability, large pH intervals (0 to 4), resistant to photodegradation, insoluble in reaction either biologically or chemically, non-toxic, has redox properties, has a wide band gap of 3.2 eV and relative cheap [1, 9, 12]. The structure of TiO₂ exists in three forms that are rutile, anatase, and brookite. Rutile is a stable form of TiO₂, whereas the form of anatase and brookite is a stable meta structure [2]. Anatase has been shown to have good photocatalytic activity for degradation of various organic compounds, including dyes [3,8]. Anatase was formed at temperature 120-500 °C while after 700 °C it changed into rutile formed with a highly decreasing of photocatalytic activity [4].

In order to improve the TiO₂ crystal structure a doping modification was conducted that inhibiting the electron-hole recombination process on the surface of TiO₂ during the catalytic process. According to Ezema et al. (2008) [5] microstructure, surface area, particle size distribution, and dopant distribution may affect the photocatalytic activity of TiO₂. The transition metal oxide has a character can be used as a catalyst, since the transition metal oxide has *d* orbitals on its partially filled metal ion. It can capture electrons from reactants and forming a strong bond, to activate the reacting species.



Metal oxides often used as catalysts include oxides V, Cr, Mn, Fe, Co, Ni and Cu. Ni^{2+} is transition metal ion that has high crystallinity, low valence and can enhance photocatalytic activity of photocatalyst semiconductors [6, 11].

Nickel oxide (NiO) is a semiconductor material formed from transition metal ions Ni^{2+} in the form of metal oxide. NiO has been used as a sensor material with an energy band gap of 2.1-3.2 eV and showing the photoelectrochemical response at visible region. This material was combined with TiO_2 will produce a composite TiO_2 -NiO which can degrade organic compounds when subjected to light. The photocatalytic composites were irradiated for photocatalytic activity by visible light sources to activate the catalyst. Several studies have used photocatalysts on dye waste treatment. Rhodamine B is one of synthetic dye which is used for textile, paint, and paper industries. This dye can causing irritation and is a carcinogenic substance [7].

In this study have been composite TiO_2 semiconductors and NiO metal oxides to improving activity of TiO_2 at visible light and maintain the structure of TiO_2 anatase to transform a rutile when annealing in order to degrade the Rhodamine B dye effectively.

2. Experimental

2.1. Preparation of TiO_2

TiO_2 was synthesis by sol gel method from titanium tetra-iso-propoxide (TTIP) precursor. Firstly TTIP solution was hydrolyzed with excess acetic acid to maintain suspension of particles against agglomeration. The TTIP was mixed with glacial acetic acid at pH 2 in low temperature at least 30 minutes to form TiO_2 transparent at 90 °C to formed TiO_2 sol. TiO_2 sol was heated at 150 °C for 24 hours (overnight) to formed xerogel TiO_2 colored white as a standard TiO_2 .

2.2. Preparation of TiO_2 -NiO composite

1.145 grams of xerogel TiO_2 was added to 0.81 gram of $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ which has been dissolved in 25 ml of distilled water and mixed by stirrer about an hour to form a homogeneous solution. The mixture was heated at 110 °C for 3 hours in oven. Then, the precipitated was annealed at a temperature of 150 °C, 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, respectively.

2.3. Characterization of TiO_2 and TiO_2 -NiO composite

Sample of TiO_2 (150, 300, 400, 500, 600, and 700 °C) and TiO_2 -NiO (150, 300, 400, 500, 600, and 700 °C) composite were analyzed by using X-ray Diffraction (Shimadzu XRD-6000) to determine the crystal phase at $2\theta = 20$ -60 degree.

2.4. Photodegradation of Rhodamine B

Samples of TiO_2 and TiO_2 -NiO composite were placed to an erlenmeyer, each 0.01 gram of TiO_2 and TiO_2 -NiO composite was added 25 ml of Rhodamine B 5 ppm. Further, the solution was irradiated using visible light source lamp in the reactor for 0, 30, 120, 240, and 360 minutes. After irradiation process, each sample was decanted to obtain clear solutions. The remaining Rhodamine B solutions were analyzed with a UV-Vis spectrophotometer at wavelength between 500-600 nm.

3. Results and Discussions

TiO_2 is relatively fine grain or white powder, with good crystallinity which has three phases: rutile, anatase and brookite. The synthesized TiO_2 have been prepared using TTIP as a precursor into excess glacial acetic acid solution (pH=2) under below room temperature. Addition of TTIP into 98.5% of glacial acetic acid was performed at low temperatures of about 10 -15 °C, it was proposed to restrain the fast agglomeration of TTIP produced a white gel. Sol gel formation was conducted by evaporate the glacial acetic acid at a temperature of 90 °C. In order to find the annealing temperature optimum to form TiO_2 anatase phase, annealing was conducted in a temperature of 150 °C, 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, respectively. The diffraction pattern in Figure 1 have been determined the TiO_2 anatase at various annealing treatment.

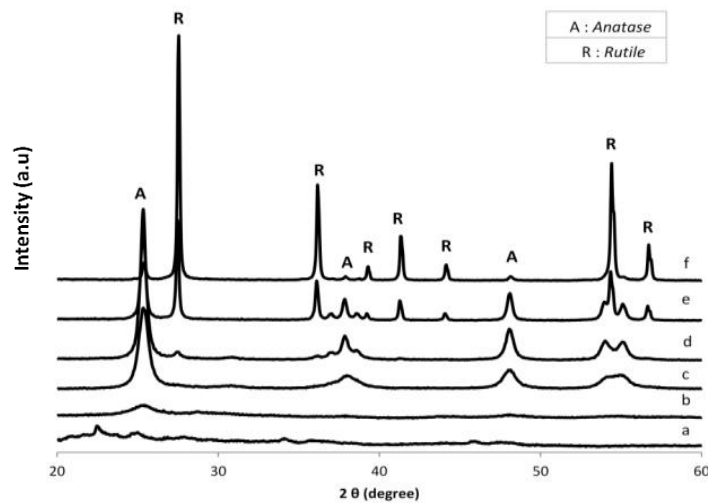


Figure 1. X-Ray Diffractogram of TiO_2 annealed at temperature of (a) 150 °C (b) 300 °C (c) 400 °C (d) 500 °C (e) 600 °C (f) 700 °C

The X-Ray diffraction in Figure 1 (a) and Figure 1 (b) shows the peak of TiO_2 at an annealing temperature of 150 °C and 300 °C, which is still in the amorphous phase, only small crystals have been formed. Figure 1 (c) further shows the TiO_2 diffractogram at a temperature of 400 °C so that the annealing temperature produces the highest anatase phase and no rutile phase occurs. This conclusion is supported by the diffraction peak at $2\theta = 25.35^\circ$ ($d_{101} = 3.5091 \text{ \AA}$), $2\theta = 37.95^\circ$ ($d_{004} = 2.3679 \text{ \AA}$), $2\theta = 48.15^\circ$ ($d_{200} = 1.8874 \text{ \AA}$), $2\theta = 54.11^\circ$ ($d_{105} = 1.6931 \text{ \AA}$) And $2\theta = 55.01^\circ$ ($d_{211} = 1.6674 \text{ \AA}$) which is a characteristic of TiO_2 in accordance with JCPDS 782-486.

Based on XRD results, TiO_2 anatase 100% will be produced by annealing treatment at 400 °C. A/R ratio calculation have been resumed in Table 1.

Table 1. Anatase rutile ratio (A/R) of TiO_2 crystal synthesized in various annealing temperature

Ratio	Annealing of TiO_2 (°C)			
	400	500	600	700
A:R	1:0.0	1:0.064	1:0.716	1:9.929

These ratios show that at temperature 400 °C was formed TiO_2 pure anatase phase while increasing the annealing temperature caused the transformation of anatase to rutile.

TiO_2 -NiO composites with various annealing can be seen in Figure 2. In Figure 2 (a) and Figure 2 (b), the overall spectra of XRD did not show the existence of TiO_2 due to the amorphous phase. The presence of new peaks in Figure 2 (c) - Figure 2(f) represented NiO at $2\theta = 43^\circ$ ($d_{200} = 2.08 \text{ \AA}$) according to JCPDS No. 471-049. That is also produced NiTiO_3 which appears at 600 and 700 °C along with NiO formation in high temperature. The peaks of NiTiO_3 represented at $2\theta = 24^\circ$ ($d_{012} = 3.6584 \text{ \AA}$), $2\theta = 33^\circ$ ($d_{110} = 2.6911 \text{ \AA}$), $2\theta = 49^\circ$ ($d_{024} = 1.8356 \text{ \AA}$), and $2\theta = 57^\circ$ ($d_{018} = 1.5969 \text{ \AA}$) in according with JCPDS number 753-757.

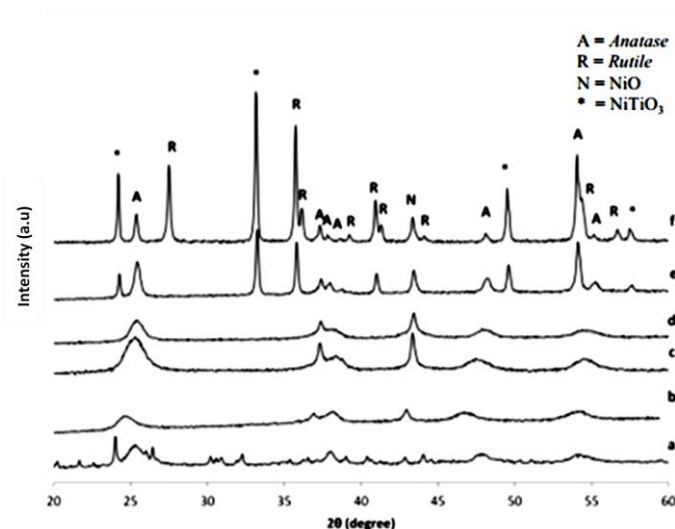


Figure 2. The X-ray Diffractogram of the composite TiO₂-NiO (a) 150 °C (b) 300 °C (c) 400 °C (d) 500 °C (e) 600 °C (f) 700 °C

The results of various annealing temperatures obtained that the ratio of anatase has been smaller due to increasing temperatures and it is mean the ratio of rutile has been greater (Table 2). While the additions of NiO dopant were inhibited anatase transform into rutile. It can explain by comparing the results without the addition of dopants (Table 1). The occurrence of such structural changes influenced the photoactivity of TiO₂, further information be explained in the activation of TiO₂-NiO composite degrade the Rhodamine B.

Table 2. Anatase ratios: rutile (A/R) on TiO₂-NiO composite result with various annealing.

Ratio	Annealing of TiO ₂ -NiO (°C)			
	400	500	600	700
A:R	1:0.20	1:0.21	1:0.41	1:1.75

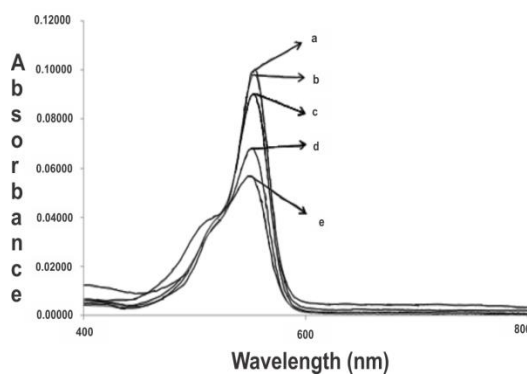
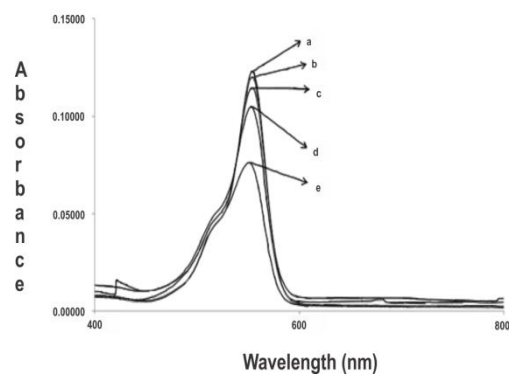
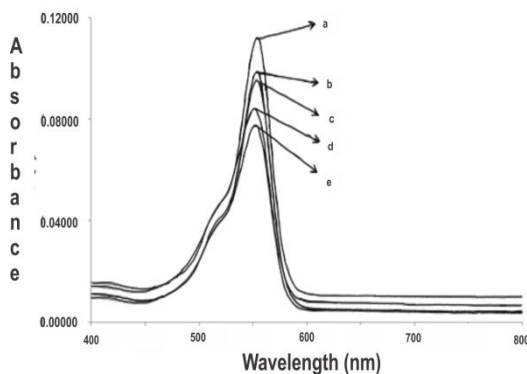
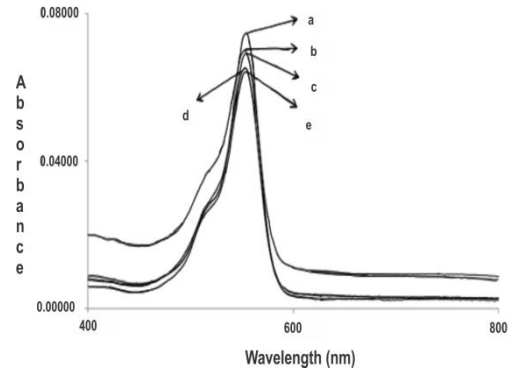
The activity of TiO₂ and TiO₂-NiO composites for Rhodamine B photodegradation was performed by experiments at various temperatures and annealing times. Rhodamine B degradation results have shown in Figure 3, Figure 4, Figure 5 and Figure 6 for TiO₂ and Figure 7, Figure 8, Figure 9 and Figure 10 for TiO₂-NiO composites. Each of samples was irradiated by Halogen lamps for 30, 120, 240, and 360 minutes, respectively. Rhodamine B has been degraded by TiO₂ at different time points and shows that the increase in irradiation time has further decreased Rhodamine B due to increasing electron excitation as an initiator in photodegradation process.

Table 3. Degradation result of Rhodamine B using TiO₂ in various irradiation times.

TiO ₂ sample	Percentage of degradation (%)			
	30 min	120 min	240 min	360 min
TiO ₂ 400	1.88	9.72	31.91	43.15
TiO ₂ 500	2.46	6.73	14.53	37.97
TiO ₂ 600	12.03	14.87	24.95	30.73
TiO ₂ 700	6.20	7.40	12.65	14.04

Table 4. Degradation result of Rhodamine B using TiO₂-NiO in various irradiation times.

TiO ₂ -NiO sample	Percentage of degradation (%)			
	30 min	120 min	240 min	360 min
TiO ₂ -NiO 400	2.32	4.95	5.45	11.32
TiO ₂ -NiO 500	2.82	4.86	5.32	8.60
TiO ₂ -NiO 600	0.80	6.64	8.94	28.99
TiO ₂ -NiO 700	90.63	90.86	91.58	92.85

**Figure 3.** The UV Vis absorption spectrum of Rhodamine B degraded by TiO₂ 400 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes**Figure 4.** The UV Vis absorption spectrum of Rhodamine B degraded by TiO₂ 500 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes**Figure 5.** The UV Vis absorption spectrum of Rhodamine B degraded by TiO₂ 600 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes**Figure 6.** The UV Vis absorption spectrum of Rhodamine B degraded by TiO₂ 700 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes

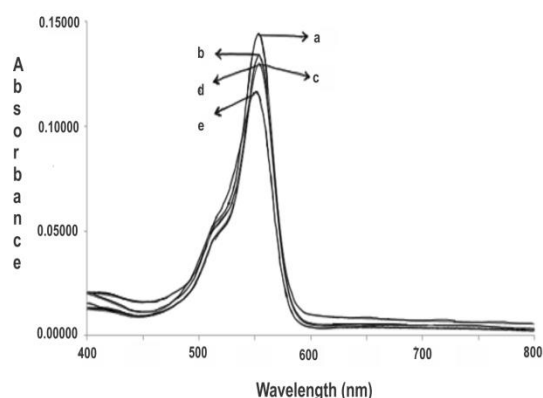


Figure 7. The UV Vis absorption spectrum of Rhodamine B degraded by $\text{TiO}_2\text{-NiO}$ 400 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes

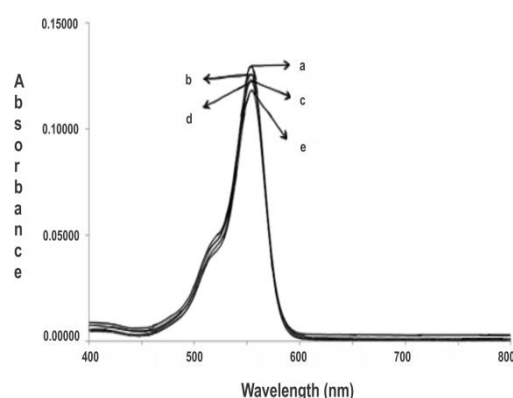


Figure 8. The UV Vis absorption spectrum of Rhodamine B degraded by $\text{TiO}_2\text{-NiO}$ 500 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes

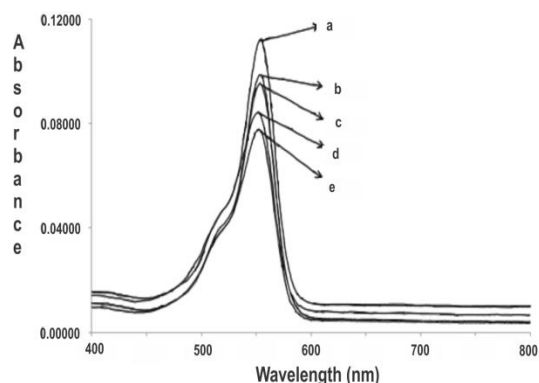


Figure 9. The UV Vis absorption spectrum of Rhodamine B degraded by $\text{TiO}_2\text{-NiO}$ 600 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes

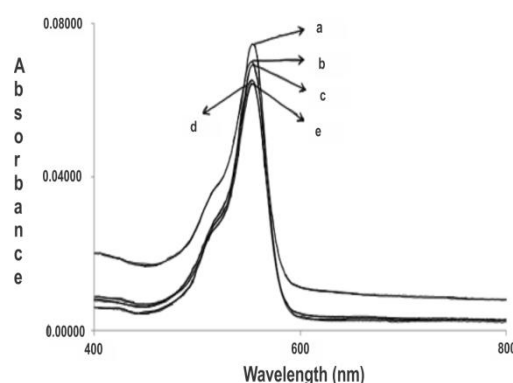


Figure 10. The UV Vis absorption spectrum of Rhodamine B degraded by $\text{TiO}_2\text{-NiO}$ 700 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes

From this evidences, it can be assumed that the presence of NiO in $\text{TiO}_2\text{-NiO}$ composite influenced the Rhodamine B degradation as shown in Table 4. Degradation increases with increasing time of irradiation.

4. Conclusion

In conclusion, the presence of NiO in the $\text{TiO}_2\text{-NiO}$ composite was able to improve the highest photodatal photodegradation of Rhodamol B. Material photocatalyst was a $\text{TiO}_2\text{-NiO}$ 600 composite with the result of Rhodamine B degradation reaching 92.85% at 360 minutes irradiation time.

References

- [1] Riyas S, Yasir V A, and Das P N M 2002 *Bull. Mater. Sci.* **25** 267-273
- [2] Riyas S, Krishnan G, and Das P N M 2008 *J. Braz. Chem. Soc.* **19** 1023-1032
- [3] Linsebigler A L, Lu G, and Yates J T Jr 1995 *Chemical Reviews.* **95** 735-758
- [4] Begum N S, Ahmed H M F, and Gunashekar K R 2008 *Bull. Mater. Sci.* **31** 747-751
- [5] Ezema F I, Ekwealor A B C, and Osuji R U 2008 *Superficies y vacto* **21** 6-10
- [6] Karami A 2010 *J. Iran. Chem. Soc.* **7** 154-160
- [7] Di Li, Hanedaa H, Hishita S, Ohashi N, and Labhsetwar N K 2005 *J. Fluor. Chem.* **126** 69-77

- [8] Ruslimie C A, Razali H, and Khairul W M 2011 *Sains Malaysia* **40** 897-902
- [9] Traistaru G A, Covaliu C I, Matei V, Cursaru D, and Jitaru I 2011 *Digest J. Nanomat. Biostruct.* **6** 1257-1263
- [10] Wang P, Wang D, Li H, Xie T, Wang H, and Du Z 2007 *J. Coll. Interface Sci.* **314** 337-340
- [11] Wei Y L and Chen K W 2009 *J. Vac. Sci. Techno* **23** 1385-1387
- [12] Reddy K, Reddy C, and Manorama S 2001 *J. Sol. State Chem.* **158** 180-186