The Influence of NiO Addition in TiO$_2$ Structure and Its Photoactivity

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Abstract. The synthesis of TiO$_2$ together with the TiO$_2$-NiO composite using various annealing temperatures has been studied. The synthesis of TiO$_2$ was performed by sol gel method using Titanium Tetra Isopropoxide (TTIP) precursor, whereas the synthesis of TiO$_2$-NiO composite was done by wet impregnation method using NiNO$_3$.6H$_2$O precursor. This study aims to determine the influence of NiO addition in its structure and photoactivity. The diffraction of synthesized TiO$_2$ at 400 °C temperature shows anatase TiO$_2$ peak at 2θ = 25.35 °. The addition of NiO dopant to the synthesis of TiO$_2$ process is carried out by annealing at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C, respectively. The TiO$_2$-NiO composite has been prepared and shows the diffraction peak of NiO at 2θ = 43° about 33.08 to 36.68%. The optimum result of Rhodamine B photodegradation with TiO$_2$ was 43.15%, while the optimum result of Rhodamine B degradation with TiO$_2$-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 (TiO$_2$) 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 TiO$_2$ 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 TiO$_2$ exists in three forms that are rutile, anatase, and brookite. Rutile is a stable form of TiO$_2$, 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 TiO$_2$ crystal structure a doping modification was conducted that inhibiting the electron-hole recombination process on the surface of TiO$_2$ 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 TiO$_2$. 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. 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 NiNO$_3$.6H$_2$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 20 = 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 TiO2 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.
The X-Ray diffraction in Figure 1 (a) and Figure 1 (b) shows the peak of TiO₂ 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 TiO₂ 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 2θ = 25,35˚ (d₁₀₁ = 3,5091Å), 2θ = 37,95˚ (d₀₀₄ = 2,3679 Å), 2θ = 48,15˚ (d₂₀₀ = 1,8874 Å ), 2θ = 54.11˚ (d₁₀₅ = 1,6931 Å) And 2θ = 55.01˚ (d₂₁₁ = 1,6674 Å) which is a characteristic of TiO₂ in accordance with JCPDS 782-486.

Based on XRD results, TiO₂ 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 TiO₂ crystal synthesized in various annealing temperature |
|-------------------|-------------------|-------------------|-------------------|-------------------|
| Ratios A:R        | 400°C             | 500°C             | 600°C             | 700°C             |
| A:R               | 1:0.0             | 1:0.064           | 1:0.716           | 1:9.929           |

These ratios show that at temperature 400 °C was formed TiO₂ pure anatase phase while increasing the annealing temperature caused the transformation of anatase to rutile.

TiO₂-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 TiO₂ due to the amorphous phase. The presence of new peaks in Figure 2 (c) - Figure 2(f) represented NiO at 2θ = 43˚ (d₂₀₀ = 2.08 Å) according to JCPDS No. 471-049. That is also produced NiTiO₃ which appears at 600 and 700 °C along with NiO formation in high temperature. The peaks of NiTiO₃ represented at 2θ = 24˚ (d₀₁₂ = 3.6584 Å), 2θ = 33˚ (d₁₁₀ = 2.6911 Å), 2θ = 49˚ (d₀₂₄ = 1.8356 Å), and 2θ = 57˚ (d₀₁₈ = 1.5969 Å) in according with JCPDS number 753-757.
Figure 2. The X-ray Diffractogram of the composite TiO$_2$-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 TiO$_2$, further information be explained in the activation of TiO$_2$-NiO composite degrade the Rhodamine B.

| Ratio A:R | 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 TiO$_2$ and TiO$_2$-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 TiO$_2$ and Figure 7, Figure 8, Figure 9 and Figure 10 for TiO$_2$-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.

| 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 TiO$_2$-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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ 700 at irradiation time of (a) 0 (b) 30 (c) 120 (d) 240 (f) 360 minutes
From this evidence, it can be assumed that the presence of NiO in TiO$_2$-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 TiO$_2$-NiO composite was able to improve the highest photodatal photodegradation of Rhodamol B. Material photocatalyst was a TiO$_2$-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 vacuo 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