Improving method of TiO$_2$-Fe$_2$O$_3$ composite materials for self-cleaning glass preparation

J P Ramadhani$^1$, S Wahyuningsih$^1$, A H Ramelan$^1$

$^1$Inorganic Material Research Group, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Jalan Ir. Sutami No.36A Kentingan Surakarta

E-mail: sayekti@mipa.uns.ac.id

Abstract. Fe$_2$O$_3$-TiO$_2$ composite have been synthesized as a self-cleaning material on glass. TiO$_2$ was prepared from titanium tetraisopropoxide (TTIP) by sol gel method. Meanwhile, Fe$_2$O$_3$-TiO$_2$ composite was prepared from TiO$_2$ synthesized with additional precursor Fe(NO$_3$)$_3$•9H$_2$O. TiO$_2$ synthesized powder was added to Fe$^{3+}$ solution in aquadest so it formed crystalline layer on TiO$_2$ powder. Core shell composite of Fe$_2$O$_3$-TiO$_2$ was obtained after calcination on temperature 600 °C. Identification and characterization of composite by X-Ray Diffraction (XRD) showed that there are diffractogram peaks of TiO$_2$ and Fe$_2$O$_3$. Another analysis by X-Ray Fluorescence (XRF) showed that composition of Fe$_2$O$_3$-TiO$_2$ composite are 1:1, 1:1.5, 1:2, and 1:3 (w/w). The morphology of composite shown by Scanning Electron Microscope (SEM) that explained coverage character of TiO$_2$ with Fe$_2$O$_3$ formed core shell type. The electronic spectrum of Fe$_2$O$_3$-TiO$_2$ core shell result showed an increasing response in visible light so it can be aplicated as a coating material in manufacturing technology of self cleaning glass.

1. Introduction

Glass is a transparent material that also has some disadvantages, such as being contaminated with dirt if it is not gradually cleaned which will cause lighting reduction in the room and can even damage the surface of the material. The use of glass remains an option for buildings in the 21st century [1]. In addition to the growing knowledge of the nature of transparent materials [2], glass also beautifies property and becomes an alternative to save energy because of its benefits in relation to room lighting and heating of a building. The development of glass production processes has led to the widespread use of this material in almost all parts of the building [3].

In recently years, the research about photocatalyst has been developed. One of the important application of TiO$_2$. Photo-oxidation using TiO$_2$ photocatalysts is widely studied as a new alternative to pollution reduction techniques such as dust, mold, bacteria, and other organic compounds [4]. However, the practical application seems limited. Some reasons include low photon utilization efficiency. Another reason is the need for ultraviolet (UV) use as a source of excitation. To overcome this problem, modification of this catalyst has also been tried by doping with various other metal oxides, including Fe$_2$O$_3$.

Iron metal oxide (Fe$_2$O$_3$) has been shown to increase the catalytic activity of TiO$_2$ against oxidation of organic pollutants. This result is quite satisfactory because the nature of TiO$_2$ photocatalyst is very suitable for the construction of photochemical energy conversion systems and treatment of pollutants [5]. Several studies have claimed that TiO$_2$ as anatase coexists with metallic iron at acidic pH or in
situations where iron doping levels are less than 1 % (m/m) which increases the photocatalytic properties of TiO$_2$. The higher the doping level or the higher pH, the α-Fe$_2$O$_3$ phase has a greater probability to form, the cause is TiO$_2$ transformation from anatase to rutile [6]. Therefore, to overcome some of these problems, it is necessary to modify the surface of the TiO$_2$ thin layer by adding Fe$_2$O$_3$ metal oxide as a dopant.

2. Experimental

2.1. Materials

The materials used in this study were titanium tetraisopropoxide (TTIP) (E Merck), Fe$_2$O$_3$.9H$_2$O (E merck), glacial acetic acid, aquades, and 98% ethanol (E Merck). Calcination of TiO$_2$ and TiO$_2$-Fe$_2$O$_3$ was performed by Furnace Thermo. Meanwhile, the analysis and characterization of materials were done by XRD (Bruker D8 Advantage), XRF (Bruker S2 Ranger), SEM-EDX (SEM 250 Quanta). The degradation result of rhodamine B was calculated using UV Vis Spectrophotometer Pelkin Elmer Lambda 25.

2.2. Methods

The titanium (IV) isopropoxide solution was hydrolyzed using a glacial acetic acid solution (temperature 15 °C) at a ratio of 1: 10 (v/v) and then stirred continuously using a magnetic stirrer until a white sol gel was obtained, then stirred and heated at 90 °C until obtained white gel [7]. Then Fe$^{3+}$ solution from precursor Fe$_2$O$_3$.9H$_2$O was added into white gel. The mass variation of Fe$_2$O$_3$.9H$_2$O precursor are 0.625 gram; 1.25 gram; 2.5 gram; and 5 gram(s). The mixing solution was stirred using a magnetic stirrer and was heated at temperature 100 °C for ± 2 hours to improve crystal phase of α-Fe$_2$O$_3$ until obtained red-copper gel. Then red-copper gel has been calcined in oven at temperature 150 °C for 12 hours followed by roasted in furnace at temperature 600 °C for 2 hours [8]. The resulting TiO$_2$-Fe$_2$O$_3$ crystalline powder was then analyzed by XRD, XRF, spectrophotometer and SEM.

TiO$_2$-Fe$_2$O$_3$ composites then has been coated on a glass to prove the self-cleaning ability. The test is using Rhodamine B that will be degraded by coated-glass under visible light. The degradation result of Rhodamine B was calculated using UV-Vis spectrophotometer.

3. Results and Discussion

3.1. Characterization of TiO$_2$-Fe$_2$O$_3$ by XRD and XRF

Synthesis of TiO$_2$ with the addition of Fe$_2$O$_3$ was carried out using the sol-gel method according to Wahyuningsih et al. [7]. The addition of metal is expected to replace several positions of Ti atoms in TiO$_2$. The calcination process was carried out at 400 °C for 2 hours to obtain the anatase phase TiO$_2$ crystal. X-ray diffractograms of TiO$_2$ and TiO$_2$-Fe$_2$O$_3$ are shown in Figure 1.

The XRD analysis results for TiO$_2$-Fe$_2$O$_3$ composites can be shown in Figure 1. (b)-(e), in this figure shows the diffractogram comparison of TiO$_2$-Fe$_2$O$_3$ composites with variations in Fe$_2$O$_3$ addition. In Figure 1 (b) overall XRD spectra results have not shown significant differences with pure TiO$_2$ XRD results spectra, this is because the addition of Fe$_2$O$_3$ is slightly so that the TiO$_2$ is still dominant. From Figure 1 (c) - (e) it is known that new peaks appear indicating the presence of Fe$_2$O$_3$ which is indicated by a peak of 2θ = 35° (d$_{110}$ = 2.5176 Å) and 2θ = 48° (d$_{104}$ = 2.6995 Å) in accordance with the JCPDS No.871-165 standard. In addition to the appearance of Fe$_2$O$_3$, FeOOH is produced which usually does appear together with Fe$_2$O$_3$ due to alkaline conditions at the time of synthesis. The peak that characterizes the FeOOH phase is the peak of 2θ = 21° (d$_{110}$ = 4.1896 Å) and 2θ = 35° (d$_{101}$ = 2.5297 Å) according to JCPDS No. 810-462.

The results of the analysis using XRD can also be used as a semi-quantitative analysis, and can be applied to calculate the phase ratio material contained. Identified TiO$_2$ material is the phase anatase and rutile. Each variation of the anatase and rutile ratio of TiO$_2$-Fe$_2$O$_3$ composites can be compared by looking at the bar diagram Figure 1. In other words, the addition of Fe$_2$O$_3$ dopant turned out to affect TiO$_2$ crystal structure changes. The addition of dopant was able to improve anatase transformation to
rutile as shown in Figure 8. The occurrence of these structural changes will change the photoactivity of TiO$_2$ and further explained in the activation of TiO$_2$-Fe$_2$O$_3$ composites in degrading Rhodamin B.

![Diffractogram](image)

**Figure 1.** Diffractogram of (a) TiO$_2$, (b) TiO$_2$-Fe$_2$O$_3$ A (1:1), (c) TiO$_2$-Fe$_2$O$_3$ B (1:1,5), (d) TiO$_2$-Fe$_2$O$_3$ C (1:2), (e) TiO$_2$-Fe$_2$O$_3$ D (1:3)

**Table 1.** Relative Percentages of Fe$_2$O$_3$ in TiO$_2$ Synthesis Composite Results of TiO$_2$-Fe$_2$O$_3$ A (1:1), B (1:1,5), C (1:2), and D (1:3) based on XRF result

| Compound       | A    | B    | C    | D    |
|----------------|------|------|------|------|
| TiO$_2$        | 49.22% | 41.38% | 33.62% | 23.96% |
| Fe$_2$O$_3$    | 48.71% | 56.67% | 65.11% | 74.95% |
| P$_2$O$_5$     | 0.53%  | 0.47%  | 0.42%  | 0.37%  |
| SO$_3$         | 0.33%  | 0.28%  | 0.27%  | 0.25%  |
| K$_2$O         | 0.23%  | 0.29%  | 0.26%  | 0.23%  |
| Others         | 0.98%  | 0.91%  | 0.32%  | 0.24%  |

From the XRF data (Table 1) shows that the composite material TiO$_2$-Fe$_2$O$_3$ contains the main components of TiO$_2$ and Fe$_2$O$_3$. Fe$_2$O$_3$ produced in the XRF analysis (Table 1) also included FeOOH which was characterized by XRD. XRF analysis shows that the main composition of the composites is Ti, O, and Fe. The presence of Fe ensures the formation of metal oxides on the surface of TiO$_2$ and the appearance of O elements as chemical bonds between elements to form oxide compounds. This indicates that the composite material TiO$_2$-Fe$_2$O$_3$ has been successfully synthesized correctly.
Synthesis of TiO$_2$-Fe$_2$O$_3$ composites also contains other components which are impurities such as Cl, P$_2$O$_5$, SO$_3$, and K$_2$O with relatively small levels of less than 1%. The impurity can come from the remainder of the solvent which has not completely disappeared during calcination, and can also be due to contact with air.

3.2. Photocatalytic Activity Test
Activity test of TiO$_2$-Fe$_2$O$_3$ composites for degradation of Rhodamine B with time variation was carried out on compositions of TiO$_2$-Fe$_2$O$_3$ variation 1 to variation 4 and pure TiO$_2$. The results of degradation of Rhodamine B are shown in Figure 3-7. A total of 0.02 grams of composite was put into 10 mL of 10 ppm Rhodamine B which was conditioned illuminated by halogen lamps in a reactor with various time. The time variation used are: 0 minutes, 5 minutes, 10 minutes, 20 minutes and 40 minutes.

![Figure 2](image1)

**Figure 2.** Rhodamine B Degradation Curve by TiO$_2$ photocatalyst for a period (a) 0 minutes, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes, (e) 40 minutes

![Figure 3](image2)

**Figure 3.** Rhodamine B Degradation Curve by TiO$_2$-Fe$_2$O$_3$ A (1:1) (a) 0 minutes, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes, (e) 40 minutes
Figure 4. Rhodamin B Degradation Curve by TiO$_2$-Fe$_2$O$_3$ B (1:1.5) for a period (a) 0 minutes, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes, (e) 40 minutes

Figure 5. Rhodamin B Degradation Curve by TiO$_2$-Fe$_2$O$_3$ C (1:2) for a period (a) 0 minutes, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes, (e) 40 minutes
Figure 6. Rhodamin B Degradation Curve by TiO$_2$-Fe$_2$O$_3$ D (1:3) for a period (a) 0 minutes, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes, (e) 40 minutes

Figure 2-6 shows a decrease in absorbance of Rhodamin B with variations in irradiation time for: 0 minutes, 5 minutes, 10 minutes, 20 minutes and 40 minutes by each variation of TiO$_2$-Fe$_2$O$_3$ composites. From the figure it can be seen that the decrease in absorbance of Rhodamin B is greater as the irradiation time increases from 0 minutes to 40 minutes. These results indicate that the longer the visible irradiation time, the greater the decrease in absorbance of rhodamine B.

This result is consistent with the research conducted by [9] and [10] which proves that the longer the visible light irradiation time will have an increasing effect on composite photocatalytic activity. This is because the longer the visible light irradiation, the more electrons will continue to be excited and play a role in the photodegradation activity of Rhodamin B. From the absorbance reduction data obtained (Figure 6) the effectiveness percentage can be determined. The percentage of degradation can show optimization of photocatalytic-based self-cleaning activities of TiO$_2$-Fe$_2$O$_3$ composites. The results of the percent degradation calculation can be shown in Table 2.

Table 2. Self-cleaning Rhodamin B uses a glass test sample at the time of contact exposure of 40 minutes

| Sample               | η (%) |
|----------------------|-------|
| TiO$_2$              | 38.45 |
| Composite TiO$_2$-Fe$_2$O$_3$ A (1:1) | 43.86 |
| Composite TiO$_2$-Fe$_2$O$_3$ B (1:1,5) | 42.72 |
| Composite TiO$_2$-Fe$_2$O$_3$ C (1:2) | 31.45 |
| Composite TiO$_2$-Fe$_2$O$_3$ D (1:3) | 20.99 |

The data obtained in Table 2 shows that the optimal results were obtained in TiO$_2$-Fe$_2$O$_3$ A (1:1) composites which were able to degrade Rhodamin B as much as 43.86%. These results indicate that the composition of Fe$_2$O$_3$ will affect composite self-cleaning activities. In a composite variation with a higher ratio of Fe$_2$O$_3$, it will reduce self-cleaning activity. This is due to the presence of the FeOOH crystalline phase which normally appears with Fe$_2$O$_3$ because of the synthesis process under alkaline conditions, where FeOOH has a photocatalytic activity that is not good at degrading Rhodamin B.
3.3. Hydrophobicity Test

![Contact angle measurements](image)

**Figure 7.** Contact angle before sun-drenched of (a) Non-coated glass, (c) TiO$_2$-Fe$_2$O$_3$-coated glass, and after sun-drenched (b) non-coated glass, (d) TiO$_2$-Fe$_2$O$_3$-coated glass

The contact angle measurement was performed by using water droplets. Small contact angle could be achieved when a stable form hydroxyl grouped on the surface. Hence, when the water appeared, it could be directly bound to these hydroxyl groups. The results obtained from this process are shown in Figure 5. The contact angle of coated glass shows a decrease after it’s irradiated by visible light means that self-cleaning process based on photocatalytic is occured so the characteristic of glass surface change from hydrophobic into hydrophilic.

4. Conclusion

TiO$_2$-Fe$_2$O$_3$ composites was successfully synthesized and applied for self-cleaning glass. The longer irradiation time, the more decrease of concentration of Rhodamine B, which shows that the photocatalytic activity of the composite TiO$_2$-Fe$_2$O$_3$ is increasing. The maximum degradation of Rhodamin B reached 43.86% for 40 minutes by TiO$_2$-Fe$_2$O$_3$ A (1:1). In the hydrophobicity test, the contact angle of TiO$_2$-Fe$_2$O$_3$ coated glass after UV irradiation is 58.4º.

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