Improving preparation method of TiO$_2$-NiO composite materials for self-cleaning glass

I Farichah$^1$, 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. TiO$_2$-NiO Composite have been synthesized as self-cleaning material on glass. TiO$_2$ was prepared using titanium tetraisopropoxide (TTIP) by sol gel method, while TiO$_2$-NiO composite was prepared from TiO$_2$ synthesized with additional Ni(NO$_3$)$_2$·6H$_2$O precursor. TiO$_2$ synthesized powder was added to Ni$^{2+}$ concentrated solution in aquadest so it formed crystalline layer on TiO$_2$ powder. Core shell composite of TiO$_2$-NiO was obtained through the drying process at 110 °C and calcined at 700 °C. Identification and characterization of NiO-TiO$_2$ composite were carried out using X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF). XRD diffractograms show the appearance of TiO$_2$ and NiO peaks. Another analysis with XRF showed that composition of TiO$_2$-NiO composite are 2:1; 1:1 and 1:2 (w/w). The electronic spectrum from TiO$_2$-NiO core shell result showed an increasing response in visible light so it can be applied as coating material in manufacturing technology of self cleaning glass.

1. Introduction

Glass is a non-crystalline solid object that is usually transparent and has a variety of practical, technological and decorative uses in things like window panels, cutting tools, optoelectronics and others. Scientifically, the term "glass" is often defined in a broader sense, including every solid object which has a non-crystalline structure (amorphous) on the atomic scale and shows the transition from glass when heated to a liquid state [1]. Along with the development of the times, there have been many researches on the modification of glass substrate to have several advantages, including anti-bacterial, anti-fungal, anti-UV, not easily dirty and easy to clean. Glass is often installed in locations that are difficult to reach so there are obstacles to clean glass. In skyscraper buildings, there is a high risk of accidents in the process of cleaning the outer glass of the building. Therefore, self-cleaning glass is needed in order to reduce the risk of workplace accidents during glass cleaning.

Titanium dioxide (TiO$_2$) has been widely used in various fields of application especially as photocatalytic for self-cleaning [2], water treatment [3], antibacterial [4], and air purification [5]. In addition TiO$_2$ has been used for sensors [6], solar energy conversion [7], and as an antiultraviolet (UV) agent [8]. TiO$_2$ also has the ability of photocatalysts to absorb UV light (200-380 nm) with a band gap energy of 3-3.2 eV but the effectiveness of TiO$_2$ in photocatalysts is still low, this is due to the high band gap energy that can only absorb ultra violet light, 4 % of all sunlight energy reaches the earth's surface [9].

TiO$_2$ photocatalytic activity can be increased through the process of doping metal ions. The use of doping methods is more beneficial than the impregnation method. This is due to the use of
impregnation method on dopant insertion does not change the electronic structure of photocatalysts. Dopants function as electron trapping which can increase photocatalytic activity [10].

Nickel oxide (NiO) is one of the active catalysts for photocatalytic reactions. The addition of NiO into the photocatalyst can increase the decomposition of water, where hydrogen gas is formed on the surface of nickel oxide while oxygen gas is released from the photocatalyst surface [11]. In the study, Nickel metal was tested as a dopant to increase the efficiency of TiO₂ photocatalysts in visible light regions and reduction of band gap on TiO₂[12]. The anatase transformation to rutile due to the addition of dopants depends not only on the nature of the metal dopant (ionic radius), but also by the concentration of dopants [13]. In this paper, the addition of NiO to TiO₂ is expected to increase TiO₂ photocatalytic activity so that it can be better for self-cleaning applications.

2. Experimental

2.1. Materials

The materials used in this study were titanium tetraisopropoxide (TTIP) (E Merck), Ni(NO₃)₂.6H₂O (E Merck). Calcination of TiO₂ and TiO₂-NiO was performed by Furnace Thermo. Meanwhile, the analysis and characterization of materials were done by XRD (Bruker D8 Advantage), XRF (Bruker S2 Ranger), and UV Vis Spectrophotometer (Pelkin Elmer Lambda 25).

2.2. Methods

2.2.1. Synthesis of TiO₂

The titanium (IV) isopropoxide solution was hydrolyzed using a glacial acetic acid solution (temperature 10-14 °C) at a ratio of 1: 10 (v/v) and then stirred continuously using a magnetic stirrer until a white solid gel was obtained, then stirred and heated at 90 °C until white gel (sol gel TiO₂) obtained [14]. And then, sol gel TiO₂ was roasted at 150 °C for 24 hours until formed the xerogel TiO₂. Xerogel TiO₂ was further treated by calcined at 400 °C for 2 hours with a speed of 10 °C / minute. The resulting TiO₂ crystalline powder was analyzed by XRD.

2.2.2. Synthesis of TiO₂ – NiO

1.145 grams of xerogel TiO₂ was added to Ni²⁺ concentrated solution from Ni(NO₃)₂.6H₂O precusore until obtained a stoichiometric ratio of TiO₂: NiO = 2:1; 1:1; and 1:2 (mol/mol), then stirred for 60 minutes and heated at 90 °C until obtained green gel (sol gel TiO₂-NiO). The resulting sol gel of TiO₂-NiO was roasted at 110 °C for 3 hours. The obtained xerogel TiO₂-NiO was calcined at 700 °C for 2 hours [15]. The resulting TiO₂-NiO crystalline powder was analyzed by XRD, XRF, and UV-Vis spectrophotometer.

3. Results and Discussion

Synthesis of TiO₂ with the addition of NiO metal was carried out using the sol-gel method [14]. The addition of metal is expected to replace several positions of Ti atoms in TiO₂. The calcination process was carried out at 700 °C for 2 hours. X-ray diffractograms of TiO₂ and TiO₂-NiO are shown in Figure 1. Figure 1. (A) shows the diffraction pattern of the synthesized TiO₂ is indicated by the presence of characteristic peaks that appear at a certain diffraction angle (2θ). The peaks include (2θ) = 25.46° (d₁₀₁ = 3.498 Å), (2θ) = 37.432° (d₀₀₄ = 2.402 Å), (2θ) = 48.196° (d₂₀₀ = 1.888 Å), (2θ) = 54° (d₁₀₅ = 1.698 Å), and (2θ) = 62.807° (d₂₁₁ = 1.478 Å) which is the characterization area of anatase TiO₂ in accordance with JCPDS standard No.78-2486. XRD analysis of TiO₂-NiO composite be shown in Figure 1. (B)–(D). Figure 1. (B)–(D) shows a comparison of the TiO₂-NiO composite diffractogram with variations in the addition of NiO from the XRD result. The data has shown the significant differences with the TiO₂ yield spectra and changes in crystalline phase occurred due to changes in the increasing mass of NiO. From the Figure 1. (B) – (D) it is known that new peaks appear indicating the presence of NiO indicated by the peak (2θ) = 43° (d₂₀₀ = 2.08Å) in accordance with the JCPDS standard No.471-049. Besides the appearance of NiO,
NiTiO$_3$ also appeared in the region $(2\theta) = 24^\circ$ $(d_{012} = 3.682 \text{Å})$, $(2\theta) = 33^\circ$ $(d_{110} = 2.697 \text{Å})$, $(2\theta) = 49^\circ$ $(d_{024} = 1.838 \text{Å})$, and $(2\theta) = 57^\circ$ $(d_{018} = 1.599 \text{Å})$ in accordance with JCPDS standard No. 753-757.

Figure 1. Diffractogram of (A) TiO$_2$ (B) TiO$_2$-NiO (2:1) (C) TiO$_2$-NiO (1:1) (D) TiO$_2$:NiO (1:2)

Figure 2. Composition of TiO$_2$ and NiO in TiO$_2$–NiO Composite

The result of XRF analysis shown the ratio of TiO$_2$:NiO is 1:1 ; 1:1.5 ; and 1:2. Photocatalytic activity test of TiO$_2$-NiO composites was carried out by applying it to degradation of Methylene Blue for a period time. About 0.02 g of composite was put into 10 mL of 10 ppm Methylene Blue under halogen lamps illuminations in a reactor with varying time. Variations in the time used are: 0 minutes, 5 minutes, 10 minutes, 15 minutes and 20 minutes.
Methylene Blue concentration decreased due to photocatalytic degradation reaction by TiO$_2$-NiO composite. The results can be seen in Figure 3 by using composites (A) TiO$_2$ (B) TiO$_2$-NiO (2:1) (C) TiO$_2$-NiO (1:1) (D) TiO$_2$:NiO (1:2).

Based on the Figure 3 (A) – (D), generally the longer irradiation time, the more of Methylene Blue have degraded. From the figure 3 it can be seen that the decrease in absorbance of Methylene Blue is greater as the irradiation time increases from 0 minutes to 20 minutes. These results indicate that the longer the visible irradiation time, the greater the decrease in absorbance of Methylene Blue.

From the table 1 shows the percentage of degradation of Methylene Blue, in TiO$_2$ the degradation of Methylene Blue in the 5 minutes was 31.76962% while in the 20 minute it was 45.44908%. In TiO$_2$-NiO composite the highest degradation of methylene blue was 64.01827% within 20 minutes on TiO$_2$-NiO composite (1:1). This is consistent with research [16] which explains the duration of irradiation affects the degradation of Methylene Blue 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 radiation, the more electrons continue to be excited and play a role in the photodegradation activity of Methylene Blue.
Table 1. Degradation of Methylene Blue on TiO₂ and TiO₂–NiO Composite

| Composite          | Percentage of Degradation of Methylene Blue Based on Time Variation (%) |
|--------------------|-------------------------------------------------------------------------|
|                    | 5 Minutes | 10 Minutes | 15 Minutes | 20 Minutes |
| TiO₂               | 31.76962  | 37.39551   | 40.05956   | 45.44908   |
| TiO₂-NiO (2:1)     | 13.27231  | 18.04149   | 53.98603   | 57.59598   |
| TiO₂-NiO (1:1)     | 47.04096  | 48.40889   | 54.53982   | 64.01827   |
| TiO₂-NiO (1:2)     | 33.96763  | 37.55842   | 56.21077   | 61.61098   |

Figure 4. The image of contact angle calculation (A) No-coated glass before UV irradiation; (B) glass/TiO₂ before UV irradiation; (C) glass/TiO₂-NiO before UV irradiation

Figure 5. The image of contact angle calculation (A) No-coated glass after UV irradiation; (B) glass/TiO₂ after UV irradiation; (C) glass/TiO₂-NiO after UV irradiation

The contact angle measurements were carried out by using water droplets. The contact angle between water and the material was analyzed using ImageJ software. Small contact angles can reach stable hydroxyl forms grouped on the surface. Therefore, it can be done with this hydroxyl group. The results obtained from this process are shown in Figure 4-5. Based on measurements of TiO₂-NiO composite contact angles obtained contact angle on glass without coating before irradiation was obtained 59.8° (Figure 4A) and after irradiation 58.9° (Figure 5A) almost no change in this indicates the absence of photocatalytic activity on glass without coating so that the glass does not have self-cleaning properties. In glass/TiO₂, the contact angle before irradiation was 81.56° (Figure 4B) and after irradiation 63.59° (Figure 5B), whereas in glass/TiO₂-NiO the contact angle before irradiation was 68.65° (Figure 4C) and after irradiation 58.31° (Figure 5C). In glass/TiO and glass/TiO₂-NiO the decrease in contact angle increases the hydrophilic properties of the glass which indicates photocatalytic activity so that the glass has self-cleaning properties.
4. Conclusion

TiO\textsubscript{2}-NiO composite was successfully synthesized and applied for self-cleaning glass. The longer irradiation time, so that the greatest of decrease in absorbance of Methylene Blue, which shows that the photocatalytic activity of the composite TiO\textsubscript{2}-NiO is increasing. The maximum dye degradation of Methylene blue achieved was 64.01827\% for 20 minutes. In the hydrophobicity test, the contact angle of glass/TiO\textsubscript{2} after UV irradiation was obtained 63.59 °C and glass/TiO\textsubscript{2}-NiO 58.31 °C.

References

[1] Karasu B and Ay N2000 Ministry of Education Publication 3525. Ankara (in Turkish).
[2] Carneiro J O, Teixeira V and Portinha A 2007 Materials Science and Engineering B. 138 144–150
[3] Lachheb H, Puzenat E and Houas A 2002 Applied Catalysis B. 39 75–90
[4] Zhang H, Liu H, Mu C, Qiu C and Wu D 2006 Proceedings of 1st IEEE International Conference on Nano Micro Engineered and Molecular Systems. 955–958
[5] Yu H, Zhang K and Rossi C 2007 Indoor and Built Environment. 16 529–537
[6] Rella R, Spadavecchia J and Manera M G 2007 Sensors and Actuators B. 127 426–431
[7] Jung H S, Lee J K and Nastasi M 2005 Langmuir. 21 10332–10335
[8] Hoffmann M R, Martin S T, Choi W and Bahnemann D W 1995 Chemical Reviews. 95 69–96
[9] Qi K, Cheng B, Yu J and Ho W 2017 Chinese Journal of Catalysis. 38 1936–1955
[10] Liu H and Gao L 2006 Journal of the American Ceramic Society. 89 370–373
[11] Motahari F, Mozdianfard M R, Soofivand F and Niasari M S 2013 RSC advances. 4 27654–27660
[12] Takashi H, Y Sunagawa, S Myagmarjav, K Yamamoto, N Sato and A Muramatsu 2003. Materials Transactions. 44
[13] Choi J, Hyunwoong P and Michael R 2010 J. Phys.Chem.114 783-792
[14] Wahyuningsih S, C Purnawan, T E Saraswati, E Pramono, A H Ramelan, A Wisnugroho and S Pramono 2014 Journal of Enviromental Protection. 5 1630-1640
[15] Riyas S, Yasir V A and Das P N 2002 Bull. Mater. Sci. 25 267-273
[16] Alfina Bulan Tahta 2015 Chemistry Student Journal. 1 599-605