Study of the Properties of TiO$_2$ Doped with Nitrogen and Magnesium using DR-UV Vis Analysis as Catalyst in Wastewater Treatment

Nur ‘Aliaa Razali$^1$ and Siti Amira Othman$^1$

$^1$Department of Physics and Chemistry, Universiti Tun Hussein Onn Malaysia, Johor, Malaysia

E-mail: sitiamira@uthm.edu.my

Abstract. Due to the environmental issue that have become serious each day, many researchers interested to solve the problem with few method of water treatment including carbon adsorption, ultrafiltration, coagulation using chemical method, biodegradation using microbes, ozonation and also advanced oxidation process. One of the popular methods is using doping method. The photocatalytic activity is said to be directly proportional to the dopant concentration based on previously study. The optimum photocatalytic activity will occur at optimum dopant concentration, but at certain level of dopant concentration, the photocatalytic efficiency will be decreasing. DR-UV Vis analysis shows that the nitrogen and magnesium doped caused the formation of new mid-gap energy state and make the band gap shifted.

1. Introduction

Recently, the water pollution has become a critical issue globally as 70% of untreated wastewater is released from the industry without any filtering and processing. The amount of drinkable water is believed to be run out each day due to the few factors including natural disasters, increasing in population and water pollution [1]. Nowadays, the textiles industries use the complex synthetic organic dyes extensively as the coloring agents to obtain the bright and vibrant colors. However, this type of dyes is not completely absorbed by the fabrics and the excess dye will be released without proper treatment to the environment.

The traditional treatment applied such as coagulation, membrane separation and adsorption using activated carbon cannot completely treat the wastewater. Water treatment using TiO$_2$ photocatalyst is no longer a new method in the industries, many researchers have been carried out including doping technique with a particular materials including metals and non-metals doping [2]. However, there are few limitations in this technique which need to be improved. Disadvantages on having agglomerated particles, inefficient exploitation of visible light, and post-recovery of the TiO$_2$ particles after water treatment have become limitations for the photocatalytic process to perform the higher rate of decolourization of pollutants [3]. Hence, many studies have been conducted with the objective to improve or eliminate the limitations.

Semiconductors are substance with electronic structure characterized by a filled valence band and an empty conduction band. The energy difference between the conduction and valence band is called the band gap energy. Titanium dioxide is not only chemically stable, but also inexpensive, non-toxic and capable to induce reductive and oxidative reactions on its surface have made TiO$_2$ widely applied as photocatalyst [4]. Doping technique has been applied in photocatalytic reaction in order to
overcome the limitations of using pure TiO₂. Among these dopants, nitrogen and magnesium showed a great result in achieving the efficient photocatalysis process. In this paper, the properties of TiO₂ doped with nitrogen and magnesium using DR-UV Vis analysis will be discussed.

2. Experimental

2.1. Materials
In this study, nitrogen-doped TiO₂ and magnesium-doped TiO₂ were prepared using sol-gel method with tetraisopropoxide (TTIP) as the precursor. All chemicals are bought from Sigma- Aldrich. The samples will be varied at different weight. % (0.5 wt. %, 0.7 wt. % and 0.9 wt. %) for each dopant. Parameters that involved in this experiment are weight concentration of dopants (0.5 wt. %, 0.7 wt. % and 0.9 wt.%), type of dopants (nitrogen and magnesium), calcination temperature (300°C, 500°C and 700°C) and initial concentration of RB5 at 70 ppm.

2.2. Sample Characterizations
The band gap study of photocatalyst were study using diffuse reflective spectrophotometer. The analysis was done using Perkin Elmer spectrophotometer (model Lambda 35).

3. Results and Discussion
Titanium dioxide is well known with their capability as photocatalyst in photodegradation in polluted wastewater stream, have strong oxidize power, non-toxic substance and also have long term in photostability. However, despite of all the benefits, titanium dioxide only could be activated with UV light (λ <380 nm) due to the wide band gap (3.2eV) [5]. Therefore, some efforts have been done in order to narrow the band gap of titanium dioxide such as doping with metal and non-metal substances, sensitzations by using organic dyes and also by using transition metals doping method [6].

In this study, nitrogen and magnesium have been used for doping process with TiO₂. Basically, from the analysis using DR-UV Vis, the band gap for all samples are shifted to the visible region which are all the band gap below 3.2 eV. As for nitrogen doped, the incorporation of nitrogen into the TiO₂ lattice caused the formation of new mid-gap energy state which is known as N 2p that is located higher than the O 2p valence band. This process decreases the band gap of TiO₂ and shifted to the visible light region from the UV light state [6].

The samples analyzed for DR-UV Vis are 0.5wt. % Mg-TiO₂ (calcined at 300°C), 0.5wt. % N-TiO₂ (calcined at 300°C), 0.5wt. % Mg-TiO₂ (calcined at 500°C), 0.5wt. % N-TiO₂ (calcined at 500°C), 0.5wt. % Mg-TiO₂ (calcined at 700°C), and 0.5wt. % N-TiO₂ (calcined at 700°C). In order to find the band gap, the band gap energy formula is based on equation (1),

\[
\text{Band gap energy } E = h \left( \frac{C}{\lambda} \right)
\]  

Where,

\( h = \text{Plank constant } = 6.626 \times 10^{-34} \text{ Joules sec} \)
\( C = \text{Speed of light } = 3.0 \times 10^8 \text{ meter/sec} \)
\( \lambda = \text{Cut off wavelength (m)} \)

Where 1eV = 1.6 X 10⁻¹⁹ Joules (conversion factor)
Figure 1. The plot of $(ahv)^{1/2}$ against the energy (eV).

Figure 1 showed the plot of $(ahv)^{1/2}$ against the band gap energy which is constructed based on the formula of energy band gap as shown in equation 1. In order to find the band gap of the samples, based on the graph plotted in figure 1, a line tangent is plotted as figure 2, 3, 4, 5, 6 and 7. From the figures, it can be observed, the energy band gap have been shifted to the lower value compared to the theory value of pure TiO$_2$ which is 3.2 eV. Sheena et al. [7] reported that the shifted of energy band gap may be due to the dopants or vacancies present in the samples producing a new energy level and reduced the band gap energy. However, the band gap is found to decrease with an increase in the calcination temperature due to the crystallite growth. A study conducted by Devi and Panigrahi [8], found that the band gap of Mg-TiO$_2$ reduced to 1.64 eV when the annealing temperature is at 350 °C and 2.56 eV when no heat treatment is applied on the sample. This shown that even without heat treatment, as there is a present of dopant, the band gap energy still can be reduced.
Figure 2. The plot of (ahv)^{1/2} against the energy (eV) for 0.5 wt. % Mg-TiO$_2$ calcined at 300°C.

Figure 3. The plot of (ahv)^{1/2} against the energy (eV) for 0.5 wt. % N-TiO$_2$ calcined at 300°C.

Figure 4. The plot of (ahv)^{1/2} against the energy (eV) for 0.5 wt. % Mg-TiO$_2$ calcined at 500°C.

Figure 5. The plot of (ahv)^{1/2} against the energy (eV) for 0.5 wt. % N-TiO$_2$ calcined at 500°C.

Figure 6. The plot of (ahv)^{1/2} against the energy (eV) for 0.5 wt. % Mg-TiO$_2$ calcined at 700°C.

Figure 7. The plot of (ahv)^{1/2} against the energy (eV) for 0.5 wt. % N-TiO$_2$ calcined at 700°C.
Table 1 showed energy band gap of samples which has been found by plotting a tangent line on the graph of (ahv)½ against energy band gap. It can be seen that the energy band gap of all samples are lower than 3.0 eV which means that the doping technique helps in shifting the band gap to the lower value. 2. As the band gap value is lower, the photocatalyst can be activated by using visible light, which is economical compared to the UV light. From this DR-UV analysis, it can be concluded that the objectives of the research to undergo the experiment under the visible light is achieved and it is proven by applying the doping technique, the band gap of TiO₂ can be shifted to the lower value.

| Photocatalysts | Mg-TiO₂, at 300°C | N-TiO₂, at 300°C | Mg-TiO₂, at 500°C | N-TiO₂, at 500°C | Mg-TiO₂, at 700°C | N-TiO₂, at 700°C |
|---------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| λ (m)         | 435 x 10⁻⁹        | 411 x 10⁻⁹        | 395 x 10⁻⁹        | 404 x 10⁻⁹        | 424 x 10⁻⁹        | 424 x 10⁻⁹        |
| E (eV)        | 2.86              | 2.98              | 2.98              | 2.98              | 2.75              | 2.75              |

4. Conclusions
As conclusion, the band gap study showed that all samples calcinated at 300°C, 500°C and 700°C have shifted from UV region to the visible region. This result analysis showed that the weakness of TiO₂ can be overcome by using doping technique.

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