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Characterization of Nitrogen and Magnesium-Doped With Titanium Dioxide (TiO_2) Using TGA/ DTA Analysis for Wastewater Treatment Applications

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Abstract
Water is an important raw material for most of the industries and it is necessary to find a good wastewater treatment at industrial level in order to sustain and protect the water resource. An efficient and applicable wastewater treatment method need to be identified. Wastewater released from these industries may contain about 15% to 20% dyes. These dyes have complex chemical structures which cannot be treated easily. The objectives of this research is to synthesis theTiO2 then will doped with nitrogen (N) and magnesium (Mg). From that, the N-TiO2and Mg-TiO2will characterized using Thermogravimetric and Differential Thermal (TGA/ DTA) analysis. Results found that for 0.5% of N-TiO2and Mg-TiO2shows different phase and characteristics of sample at different calcination temperature (300oC, 500oC and 700oC).

Keywords: *N-TiO2and Mg-TiO2, TGA/ DTA, wastewater, treatment*

1. Introduction

Water is a precious commodity to living things and environment which cannot be replaced by man for his daily requirement, development and industrialization. The quality of water is decreasing due to the growth of industrialization and increasing of population of living things. The environmental problems created by the textile industry have received much attention because contaminated and polluted effluent mainly generated by this industry. Dye adsorbs and reflects the sunlight entering water, which will interferes the growing process of aquatic species and hindering photosynthesis to occur. Hence, as the photosynthesis is disturbed the oxygen level will be decreasing. Many treatment methods are available for the wastewater treatment, but they are unable to remove completely the dyes and pigments from the wastewater. Some of the wastewater treatment methods depend on the formation of the secondary pollutants and these methods are not suitable and applicable methods in preserving the environment. In addition, these methods are involving high-cost, difficult to perform and not a sustainable way for wastewater treatment (Shivaraju *et al*, 2017; Ghani *et al*, 2019).

The wastewater discharged from industries consist several of harmful chemicals. These chemicals will affect the water resource and it is necessary to maintaining the water quality. Hence, this study is significant in order to improve the present method of photocatalysis in treating the wastewater treatment. In effort to find the viable and reliable ways for wastewater treatment, it is necessary to conduct research and study on this issue. The photocataytic of TiO_2 is effective in dye removing and phenolics from aqueous solutions that the conventional techniques. However, the limitations of this technique have been identified and it can affect the photocatalytic effectiveness which are large bandgap, high aggregation tendency and difficult to separate and recover after the treatment process. Thus, this study is carried out to improve the present photocatalytic process using TiO_2. In order to achieve the objectives of the study, the method that has been chosen is by using sol-gel method. Sol-gel is one of the most exploited methods and it is used mainly to produce thin films and fine powder catalyst. Sol-gel method is easy, low cost and can be conducted at low temperature. Nitrogen and magnesium will be used as dopants because doping of TiO_2 generally found will enhance the photocatalytic activity of the catalyst as the band gap of TiO_2 can be narrowed by introducing metal and non-metal ion into TiO_2 (Etacheri *et al*, 2015). In addition, due to small atomic radius of nitrogen and magnesium, the particle size of photocatalyst could be produced in smaller size, hence larger surface area will be available for adsorption of pollutants (Akpan & Hameed, 2009). Parameters that involved in the research are including the amount of doping which is 0.5 wt.%, type of dopant used (nitrogen and magnesium) and also the calcination temperature. Therefore, doping with another species either metal or non-metal is one of the proposed methods in order to promote the separation of the electron-hole pair, improving the photocatalytic efficiency and at the same time reducing the possibility for the recombination of electron charge carriers to occur (Palaez*et al*, 2012; Islam *et al* 2017). When doping technique is applied, the band gap of titanium dioxide can be narrowed and new energy level will be produced. This is the reason why visible light can be applied to the photocatalytic process despite of using UV light when doping technique is use to modified the semiconductors (Benerjee, *et al*, 2015).

2. Methodology

TGA (Thermogravimetric Analysis) measured the weight loss or gain as a function of temperature, the TGA trace appear as steps, one can deal with the derivative of TGA with respect to time or temperature and this trace consist from peaks. DTA (differential thermal analysis) is a technique for recording the difference in temperature between a substance and a reference material as a function of time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The samples were prepared by put the sample into the crucible provided at 1/3 volume of the crucible. The weight of prepared sample was recorded. In this study, nitrogen-doped TiO_2 and magnesium-doped TiO_2 were prepared using sol-gel method with tetraisopropoxide (TTIP) as the precursor. 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. %)type of dopants (nitrogen and magnesium) and calcination temperature (300°C, 500°Cand 700°C).

In this research, several chemicals were used and bought from Sigma-Aldrich. Titanium (IV) isopropoxide (TTIP) 97% bought from Sigma-Aldrich was used as the precursor in the process of photocatalyst preparation. Magnesium chloride-6-hydrate from Bendosen and ammonium nitrate 99 % from Emory were bought from Saintifik Bersatu (M) Sdn, Bhd. Company. Ethanol, 95 %, a laboratory grade from HmbG chemical was used as solvent. Acetic acid glacial, 100 %, AR from Emory was used. The refrigerator centrifuge was used in order to obtain the sol gel from the solution. At 9000 rpm for 10 minutes, the samples were centrifuged, excess liquid was removed and sol gel was collected. Next, for the heat treatment process, a furnace box (model 524120-P) was used. Different calcination temperature of 300 °C, 500 °C, and 700 °C were applied on the sample for 1 hour.

3. Results and Discussions

The thermal behavior was investigated by a simultaneous TG-DTA analysis on samples with a heating rate of 10°C/min, up to 800°C.The TGA/DTA analysis of 0.5wt. % Mg-$TiO_2$and 0.5 wt. % N-TiO_2 calcinated at 300°C can be observed by referring to Fig. 1 and Fig2. From the Fig.1 and 2, it can be seen that at 94 °C and 101°C for each figure respectively, there is slightly mass loss due to the loss of organic solvents which are ethanol and acetic acid. There is also occur a further weight loss up to 700°C may be due to the condensation of free hydroxyl groups from ethanol. The weight loss above 700°C can be seen as negligible signifying that TiO_2 has undergone complete crystallization to form a stable anatase phase. The weight loss of the sample from the analysis were observed about 9mg and 14 mg for 0.5wt. % Mg-$TiO_2$and 0.5 wt. % N-TiO_2 respectively. The loss of water and decomposition of organic residues are reciprocated by the appearance of an exothermic peak from room temperature to 150°C in the DTA curve. Another exothermic peak can be observed at 350 °C, without any weight loss, which indicates that a phase transformation has occurred. Endothermic peak also can be observed at 380 °C and the weight loss found nearly stabilized after 400 °C, it can be assumed that the additional small amount of weight loss above 400 °C was probably caused by a residual decomposition product that formed by the heating process of TiO_2 particles.

Fig. 3 showed the TGA/DTA analysis for TGA/DTA of 0.5wt. % Mg-TiO_2 calcinated at 500°C. In the studied temperature range, sample showed slightly changed in weight which is about 2.92mg from the TGA curve. At 84 °C, there is exothermic peak which there is noticeable weight loss which is related to the loss of physically absorbed moisture and/or of remaining solvent still present within the sample. The TGA curve showed a continuous of weight loss up to 800°C, however the weight loss after 750°C is negligible as the sample have reached the stable state. The DTA curve showed exothermic peak at 84°C which implies the loss of water and excess ethanol, the peak also can be attributed to the crystallization of amorphous TiO_2 to anatase phase. Four exothermic peaks can be observed from 390 °C to 490°C showing the further crystallization process without any weight loss. The process end at 500 °C showed complete crystallization of stable anatase phase.

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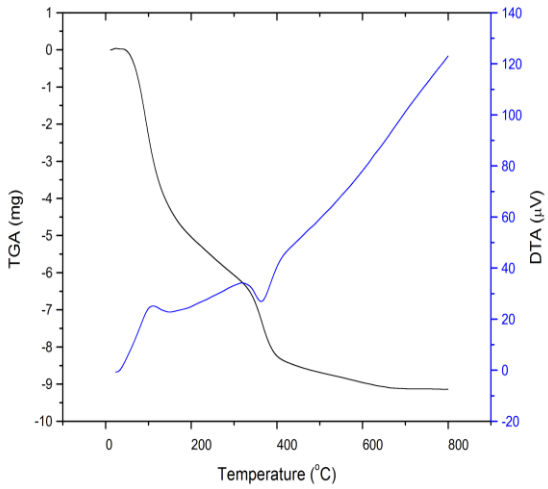

Figure 1: TGA/DTA of 0.5wt. % Mg-TiO_2 calcine at 300°C

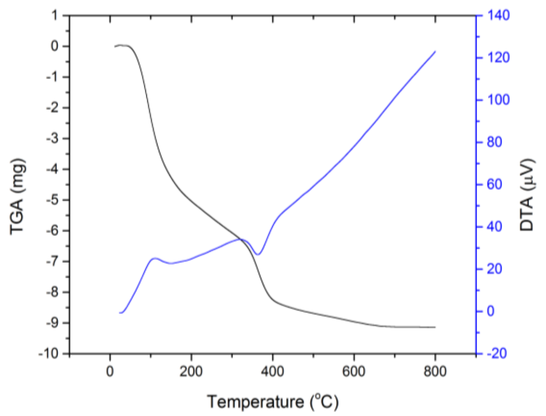

Figure 2: TGA/DTA of 0.5wt. %N-TiO_2 calcine at 300°C

Fig. 4 showed the TGA/DTA curve for 0.5wt. % N-TiO_2 calcine at 500°C. Weight loss can be observed from the room temperature up to 500°C because of the loss of water and organic solvents. In the end of the analysis, it can be observed from the graph, that the weight loss was about 4.13mg. The weight above 700°C is negligible as the TiO_2 has reached a stable phase of anatase. The first peak of exothermic in DTA curve showing that water loss and decomposition of organic residues has occurred at 81 °C. A broad endothermic curve from 140 °C showed that the samples has undergone crystallization from amorphous to anatase phase.

The TGA/DTA curve of 0.5wt. % Mg-TiO_2 calcine at 700°C is shown in Fig.5. From the TGA curve, it can be observed that there is weight loss from room temperature up to 100°C as there is water and solvents loss. At 400°C and above the sample is observed to have a maintain and stable weight, this may due to the complete heat treatment have been applied during the preparation of the sample with calcination temperature of 700°C. 1.57mg weight in change were found at the end of the analysis. DTA curve showed there is an exothermic peak at 55°C showing there is loss of organic solvent and at temperature of 400°C and above, there is no more peak were found as may be the sample has been completely undergo the crystallization phase.

Fig.6 showed the TGA/DTA analysis for TGA/DTA of 0.5wt.% N-TiO_2 calcine at 700°C.In the studied temperature range, sample showed only slight changed in weight about 0.11mg. TGA curve at 30 °C indicating weight loss attributed to the evaporation water and residual organic solvents. There is significant weight loss in the 95–345 °C range is attributed to combustion of the organic compounds. The DTA curve showed slightly exothermic peak at 100°C which implies formation of anatase phase and the curve seem to stable until the end of the analysis showing there is no crystallization process occur as the sample already in rutile form synchronize with the XRD analysis result showing that the rutile phase presence in the sample.

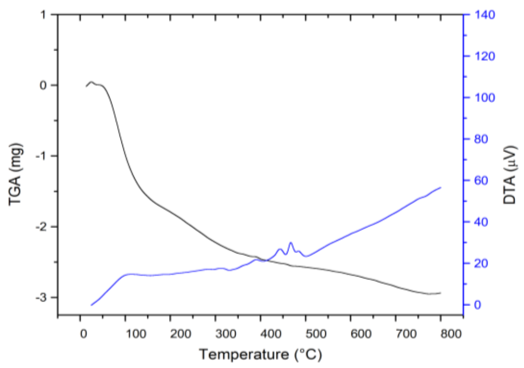

Figure 3: TGA/DTA of 0.5wt. % Mg-TiO_2 calcine at 500°C

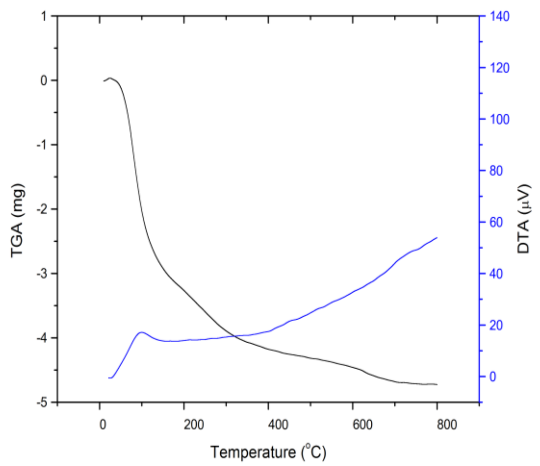

Figure 4: TGA/DTA of 0.5wt. %N-TiO_2calcine at 500°C

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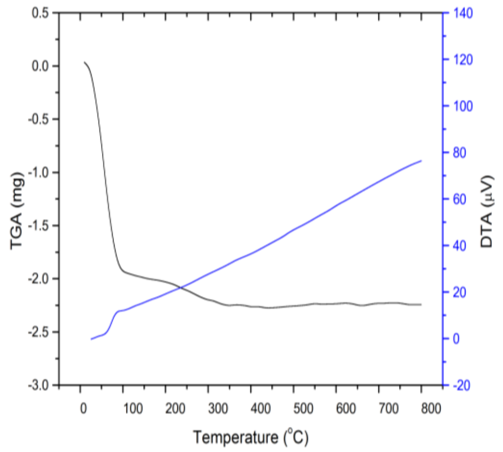

Figure 5: TGA/DTA of 0.5 wt. % Mg-TiO_2 calcine at 700°C

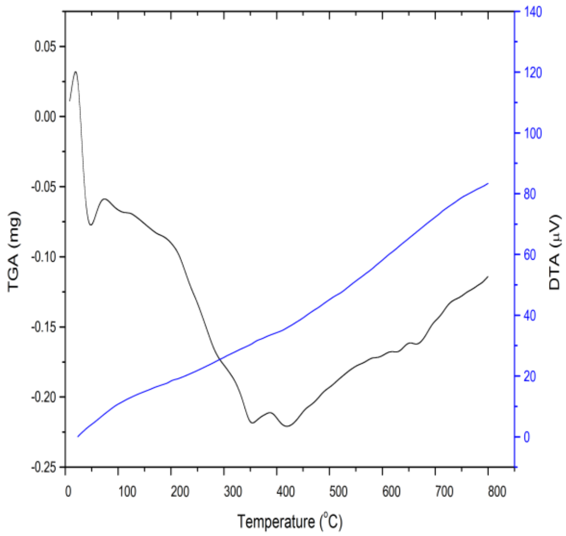

Figure 6: TGA/DTA of 0.5 wt. % N-TiO_2 calcine at 700°C

4. Conclusion

Many treatment methods are available for the wastewater treatment, but they are unable to remove completely the dyes and pigments from the wastewater. From the results of TGA/ DTA, different characteristics of particles size can be produced by controlling the calcination temperature. This indirectly enhanced the properties of N-TiO_2 and Mg-TiO_2in treating the wastewater.

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