

# PREPARATION AND STRUCTURAL CHARACTERIZATION OF BINARY CATALYST FOR DYE WASTEWATER

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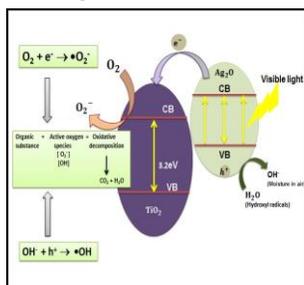
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## Graphical abstract



## Abstract

Synthetic dyes used in most industries have persistence chemical compounds which cannot be degraded by conventional method. To overcome this problem, researchers utilize photocatalytic oxidation and  $\text{TiO}_2$  has become favourite photocatalyst. However,  $\text{TiO}_2$  has wide band gap and needs modification. One of the modifications is binary catalyst which found to be more effective as it commonly binds another photocatalyst that is readily exist in visible region to  $\text{TiO}_2$ . Over the past 5 years  $\text{Ag}_2\text{O}$  has been a chosen catalyst due to its low band gap. However,  $\text{Ag}_2\text{O}$  often experiences self-aggregation. Thus, the optimum doping ratio of  $\text{TiO}_2/\text{Ag}_2\text{O}$  was determine by physical blend of  $\text{TiO}_2$  and  $\text{Ag}_2\text{O}$  into 2 ratios, which were 1%  $\text{Ag}_2\text{O}$  and 5%  $\text{Ag}_2\text{O}$ .  $\text{TiO}_2$  was synthesized using sol gel method and  $\text{Ag}_2\text{O}$  was synthesized using co-precipitation method. Both catalysts were blended physically and characterized using FESEM-EDX and XRD analysis. EDX mapping analysis showed  $\text{TiO}_2/\text{Ag}_2\text{O}$  -5% exhibit better distribution of  $\text{Ag}_2\text{O}$ . In addition, XRD analysis shows  $\text{TiO}_2/\text{Ag}_2\text{O}$  -5% has more intense  $\text{Ag}_2\text{O}$  peaks compare to  $\text{TiO}_2/\text{Ag}_2\text{O}$  -1%. Based on the characterization results,  $\text{TiO}_2/\text{Ag}_2\text{O}$ -5% showed promising ratio loading for dye wastewater photocatalytic degradation.

Keywords: Photocatalytic, binary catalyst,  $\text{TiO}_2$ ,  $\text{Ag}_2\text{O}$ , wastewater

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## 1.0 INTRODUCTION

Companies in most fields (e.g textile, food coloring, paintings etc) nowadays prefer to use synthetic dyes since it is cheaper and easier to get. The dyes, however, contain various chemicals that are not be degraded easily. In Malaysia, the acceptable concentration of colours or dyes must be less than 100mg/L or 200mg/L depends on the standard A or B respectively. Standard A is applicable to discharges into any inland waters within catchment areas listed in the Third Schedule and standard B is applicable to any other inland waters or Malaysian waters [1]. Thus, researchers have attempted various studies in order to find an effective solution. Many have tried to degrade it in various ways, which include coagulation, which is effective for treatment of

insoluble dye stuff wastewater but not for soluble dye type wastewater [2], [3], [4]. Biological approach also has been used to remove insoluble dyes but it creates other problems such as sludge drawback [5] although biological treatment is considered as environmental friendly treatment. Currently, the available water treatment technologies such as adsorption or coagulation merely concentrate the pollutants present by transferring them to other phases, these pollutants still remain. They are not being completely "eliminated" or "destroyed"[6]. Thus, it is important to find the best method in order to eliminate the pollutant.

AOPs can be broadly defined as Advanced Oxidation Processes based on the intermediacy of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms

leading to the destruction of the target pollutant [7]. There are four types of method in AOP, which are Fenton oxidations, photocatalysis, plasma oxidation and ozonation. Photocatalysis, can be described as the acceleration of photoreaction in the presence of a catalyst [8]. It uses semiconductors, usually metal oxides which is illuminated with light sources (e.g solar light, UV light, sunlight etc) in order to convert pollutant into harmless final product that can be discharge into river. It gradually breaks down the contaminant molecules with no residue of the original molecule remains and therefore no sludge disposal to landfill is produced [8]. The catalyst, which is usually a semiconductor metal, remains the same throughout the process and no consumable chemicals are required. The process result is considerably more able to save water production cost and keep the environment clean.

A semiconductor that is most significant with photocatalysis method is Titanium dioxide ( $\text{TiO}_2$ ).  $\text{TiO}_2$  has become the chosen compound as it a very useful non-toxic, environmentally friendly, corrosion-resistant material [9]. In addition,  $\text{TiO}_2$  is biologically inert, uses low operation temperature, has low energy consumption, high photocatalytic activity, suitable flat band potential, relatively high chemical stability, water insolubility under most environmental conditions and prevents the formation of undesirable by-products [10]. Nevertheless,  $\text{TiO}_2$  has wide band gap issue, which makes it unable to absorb visible light to be functional as photocatalyst. It has to be modified in order to fully absorb the light source. Modification of doping with another photocatalyst to become a heterojunction photocatalyst becomes the chosen option. Since it will not just lower the band gap, the doping will increase the efficiency of photocatalytic degradation.

There are many previous studies that have attempted multiple ways of including doping with non-metal[11] and even combine the photocatalyst with another photocatalyst metal, such as with Zinc[12]–[14], and Cobalt[15], as stated in Table 1. The problem with these metals is that they do not have the band gap as low as Silver oxide ( $\text{Ag}_2\text{O}$ ).  $\text{Ag}_2\text{O}$  band gap is 1.2eV-1.46eV [16], [17] which is the lowest among them. Nevertheless,  $\text{Ag}_2\text{O}$  is very oxidative and needs complementary metal to reduce its oxidative behaviour. Thus, it is interesting to study the compatibility and performance of  $\text{Ag}_2\text{O}$  with  $\text{TiO}_2$  as  $\text{TiO}_2$  is much more stable than  $\text{Ag}_2\text{O}$ .

**Table 1** Band gap of different photocatalyst

Photocatalyst	Band gap
$\text{TiO}_2$	3.2eV
$\text{Ag}_2\text{O}$	1.3eV
ZnO	3.1eV
CoO	2.4eV

Since  $\text{TiO}_2/\text{Ag}_2\text{O}$  have succeeded to give many positive results in past studies, it is interesting to study the rate of degradation of this heterojunction photocatalyst in dye wastewater. Thus, in this study the  $\text{TiO}_2$  and  $\text{Ag}_2\text{O}$  was combined together, physically, to determine the optimum doping ratio of  $\text{TiO}_2/\text{Ag}_2\text{O}$  for dye wastewater degradation based on physical characterization.

## 2.0 METHODOLOGY

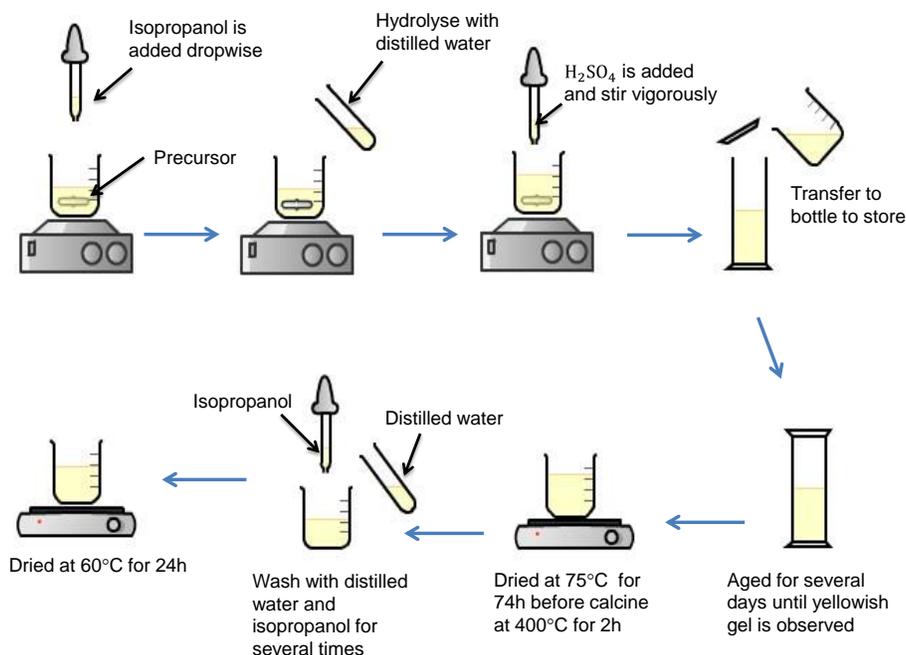
### 2.1 Chemical and Materials

In this study, the precursors for the catalysts are Titanium Butoxide ( $\text{TiOBu}_4$ ) from Sigma Aldrich and Silver Nitrate ( $\text{AgNO}_3$ ) from VChem, The dispersing medium was distilled water and isopropanol. Sodium hydroxide ( $\text{NaOH}$ ) (99%) and Nitric Acid ( $\text{HNO}_3$ ) (65%) and Polyethylglycol (PEG) (MW= 6000g/mol) from sigma Aldrich were also used as reagent in this study.

### 2.2 Synthesis of $\text{TiO}_2$

To obtain sol gel formation, the  $\text{TiOBu}_4$  as precursor of  $\text{TiO}_2$  was subjected in two processes, hydrolysis and peptidization [18].

The synthesis begun with the mix of 25mL  $\text{TiOBu}_4$  with 8mL isopropanol until homogenous solution was obtained. After that, the solution was hydrolysed using 200mL of water and was stirred for 30 minutes before adding 3mL of  $\text{HNO}_3$ . This mixture was stirred vigorously for another 30 minutes. It was then transferred to an air-tight container to be aged for five to seven days until a yellowish gelatin was obtained. The gel was then dried at 75°C for 74 hours in a vacuum oven to obtained a yellowish powder before calcined at 400°C with 5°Cmin<sup>-1</sup> for 2 hours. The subsequent powder was washed with distilled water followed by isopropanol and dried at 60°C for 24 hours. The synthesis is illustrated in Figure 1 below.



**Figure 1** Synthesis of  $\text{TiO}_2$  from precursor via sol gel method.

### 2.3 Synthesis of $\text{Ag}_2\text{O}$

Synthesis of  $\text{Ag}_2\text{O}$  was carried out using co-precipitation method. 20g PEG was added into 1 liter of RO water and heated up at  $50^\circ\text{C}$  to get homogenous solution. Next, 0.5g of  $\text{AgNO}_3$  was added into the solution and stirred for an hour. The pH solution was adjusted to pH 14 by adding NaOH solution 0.1M to complete the reaction. Black precipitate was observed in the end of the synthesis and was washed with distilled water before being rinsed with ethanol. It was dried in oven at  $60^\circ\text{C}$ .

### 2.4 Formation of $\text{TiO}_2/\text{Ag}_2\text{O}$

Both catalysts were physically combined via weight ratio without further treatment. The ratios are compiled in Table 2 below.

**Table 2** Weight Percent ratio between  $\text{TiO}_2$  and  $\text{Ag}_2\text{O}$ .

	$\text{TiO}_2$	$\text{Ag}_2\text{O}$
Weight	100	0
percent	99	1
(%)	95	5

### 2.5 Characterization of Binary Catalyst

#### 2.5.1 FESEM-EDX

The morphology of the  $\text{TiO}_2/\text{Ag}_2\text{O}$  was analyzed using field electron scanning electron microscope (FESEM,

JEOL, JAPAN) coupled with elementary dispersive xray (EDX). The sample was placed on carbon tape and coated with gold dust under vacuum about 5 minutes before analysis was carried out. The result of FESEM is coupled with EDX analysis by using line scan and mapping spectra.

#### 2.5.2 XRD Analysis

The  $\text{TiO}_2/\text{Ag}_2\text{O}$  was identified by XRD Data collection was carried out in the  $2\theta$  range  $10-90^\circ$ , with a scanning step of  $0.02^\circ$ .  $\text{TiO}_2/\text{Ag}_2\text{O}$  was crushed with agate mortar and pestle, ground to powder form, with particle size less than  $5\mu\text{m}$ . The samples were mounted on plate sample holders with a volume of  $0.1\text{ cm}^3$ . All X-ray experiments were carried out at room temperature. After the scanning process was completed, the crystalline patterns were compared with the standard line patterns from the powder diffraction file database supplied by International Centre for Diffraction Data (ICDD).

## 3.0 RESULTS AND DISCUSSION

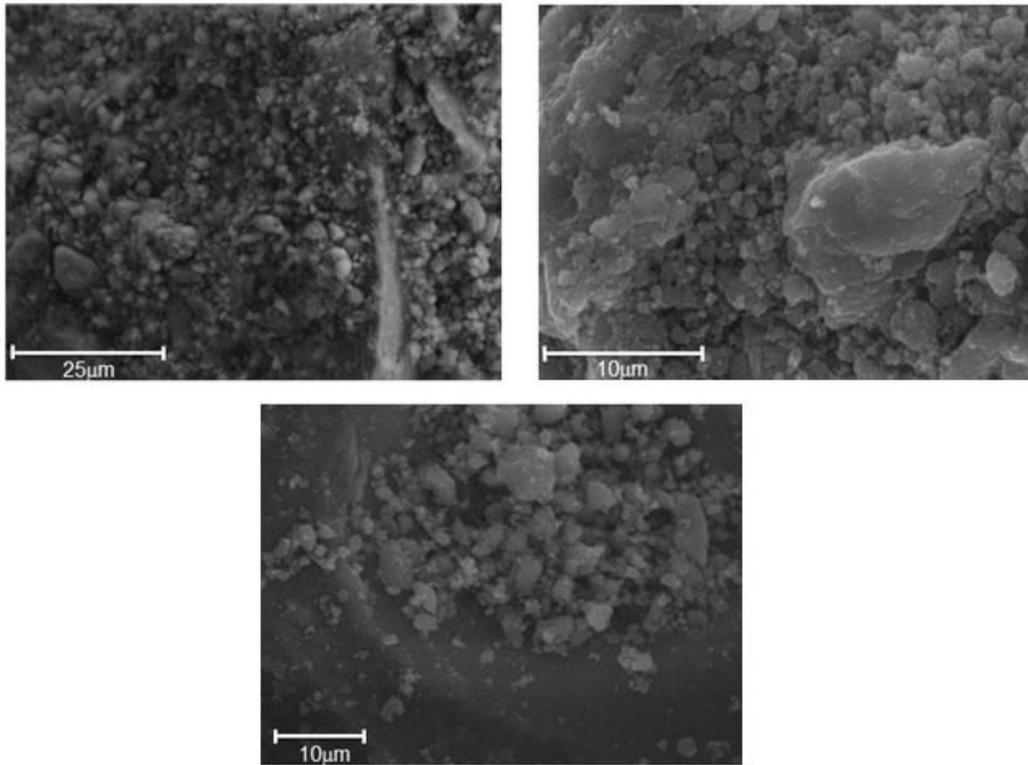
### 3.1 Morphology Analysis Using FESEM-EDX

Figure 2 showed the images from FESEM analysis of pure  $\text{TiO}_2$ , doped  $\text{TiO}_2/\text{Ag}_2\text{O}$ , with 2 different compositions, which are 1% percent  $\text{Ag}_2\text{O}$  and 5% percent  $\text{Ag}_2\text{O}$ .

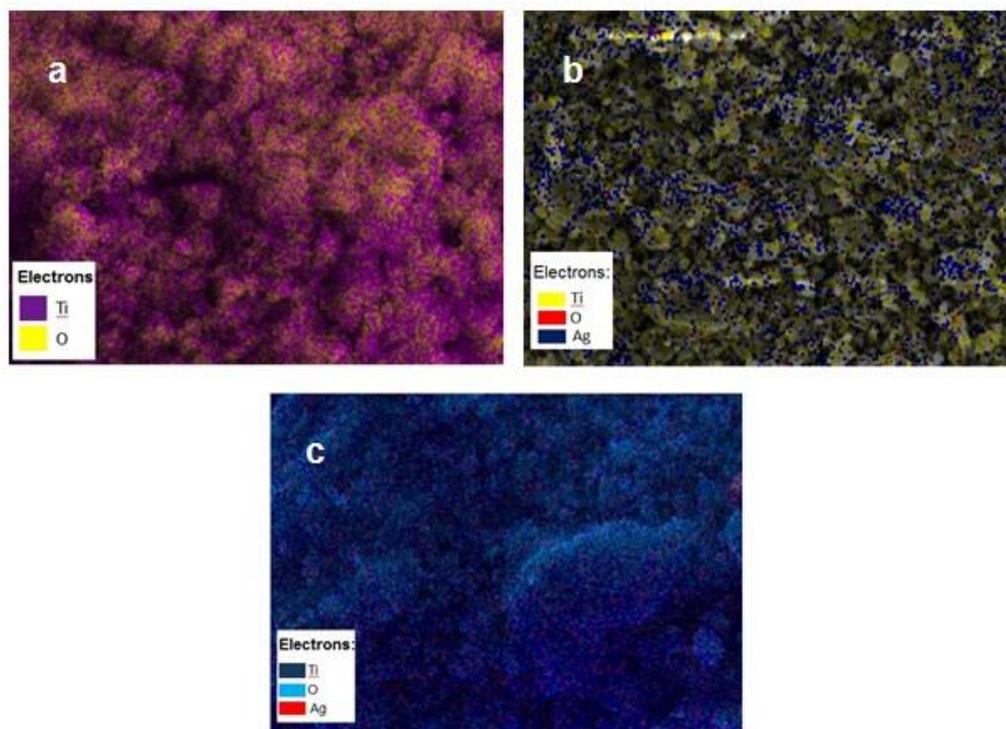
From Figure 2a, the synthesized  $\text{TiO}_2$  was able to produce fine particles, ranging from 19nm to 35nm. However, when  $\text{TiO}_2$  was combined with  $\text{Ag}_2\text{O}$ ,  $\text{TiO}_2$  can be seen to agglomerate with  $\text{Ag}_2\text{O}$  on Figure 4b and 4c. The rate of agglomeration becomes increased when the amount of  $\text{Ag}_2\text{O}$  is increased to 5%.  $\text{TiO}_2/\text{Ag}_2\text{O}$  have agglomeration is due to several

factors, such as high surface area of  $\text{TiO}_2$  [19], mixing time[20] and error during sample preparation.

Apart from agglomeration of  $\text{TiO}_2$ , both catalysts  $\text{TiO}_2$  and  $\text{Ag}_2\text{O}$  have uniform distribution. This fact is supported by the mapping analysis from EDX in Figure 3 below.



**Figure 2** FESEM images a). Pure synthesized  $\text{TiO}_2$  b).  $\text{TiO}_2/\text{Ag}_2\text{O}$ -1% c).  $\text{TiO}_2/\text{Ag}_2\text{O}$ -5%



**Figure 3** Mapping distribution of catalyst a). Pure synthesized TiO<sub>2</sub> b). TiO<sub>2</sub>/ Ag<sub>2</sub>O -1% c). TiO<sub>2</sub>/ Ag<sub>2</sub>O -5%

From Figure 3b and 3c, Ag<sub>2</sub>O can be seen is blend well with TiO<sub>2</sub> as it has scattered around TiO<sub>2</sub> nanoparticles. This is good indication as during photocatalytic degradation of dye, the dye can be degraded by both catalysts simultaneously. Furthermore, with the low band gap of Ag<sub>2</sub>O enabling both these binary catalysts to use low energy sources of light, this will reduce the cost of photocatalytic process. Figure 3c showed better distribution of Ag<sub>2</sub>O among TiO<sub>2</sub> nanoparticles compare to Figure 3b. This shows that ratio Ag<sub>2</sub>O 5% is more likely to be apply in photocatalytic degradation compare to Ag<sub>2</sub>O 1%.

### 3.2 XRD Analysis

One of the instrumental analyses that is commonly used to distinguish the different crystals of TiO<sub>2</sub>, which are anatase, rutile and brokite. Figure 4 shows the XRD pattern of TiO<sub>2</sub> 100% and binary catalyst TiO<sub>2</sub>/Ag<sub>2</sub>O. The average crystallite size of TiO<sub>2</sub> was approximated by using Scherrer's equation as follows:

$$D = K \lambda / \beta \cos \theta$$

Where K is the Scherer constant,  $\lambda$  is the X-ray wavelength,  $\beta$  is the peak width of half maximum, and  $\theta$  is the Bragg diffraction angle. The composition of anatase and rutile exist in TiO<sub>2</sub> samples were calculated using the stated equation below:

$$X_A = 100 / (1 + 1.265 I_R / I_A)$$

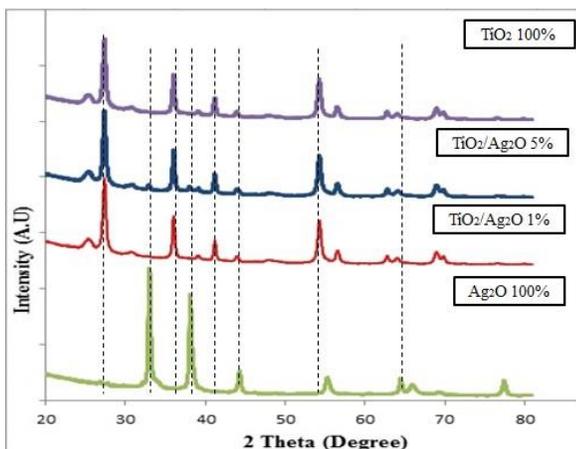
Where  $X_A$  the weight fraction of anatase in the mixture,  $I_A$  is intensity of anatase diffraction and  $I_R$  is intensity of rutile diffraction. The calculation of the crystallite size and fraction of anatase and rutile is showed below at Table 3.

**Table 3** Crystallite TiO<sub>2</sub> at different ratio loading

	$X_A$	$X_R$	Crystallite Size, nm	
			Anatase	Rutile
TiO <sub>2</sub>	83.84	16.16	23.169	18.98
TiO <sub>2</sub> /Ag <sub>2</sub> O 1%	29.92	70.07	21.11	18.9
TiO <sub>2</sub> /Ag <sub>2</sub> O 5%	28.17	71.82	26.21	19.03

From the XRD pattern in Figure 4, the existence of peaks at 25° and 48° confirmed the synthesized TiO<sub>2</sub> consist of anatase. Anatase TiO<sub>2</sub> is well known to have photocatalytic performance due to large crystallite size. Therefore it have better photocatalytic performance [21], compare to rutile and brokite. Nevertheless, the synthesized TiO<sub>2</sub> has mix peaks of anatase and rutile. From the previous study, TiO<sub>2</sub> can degrade contaminant more efficiently when the composition of its crystal is mixed phase of anatase and rutile [22]. This is because anatase possessed higher conduction band edge than rutile. Thus, electron photogeneration from anatase can be

passed to rutile, whereas the positive hole owned by rutile can be transferred to anatase[23].



**Figure 4** XRD pattern for a). Ag<sub>2</sub>O 100% b). TiO<sub>2</sub>/ Ag<sub>2</sub>O 0.01 c). Ag<sub>2</sub>O 0.05 d). TiO<sub>2</sub> 100%

Typically, high crystallinity of TiO<sub>2</sub> would demonstrate good intensity of XRD peaks. From the XRD patterns, both TiO<sub>2</sub> and Ag<sub>2</sub>O have intense peaks which indicate high crystallinity of the catalysts. Other than that, both binary catalysts also show peaks from TiO<sub>2</sub> and Ag<sub>2</sub>O. However, Ag<sub>2</sub>O 5% shows more intense peaks of Ag<sub>2</sub>O, compare to Ag<sub>2</sub>O 1%. Thus, TiO<sub>2</sub>/Ag<sub>2</sub>O 5% will not require high energy source light due to the presence of more Ag<sub>2</sub>O in the binary catalyst.

#### 4.0 CONCLUSION

From the characterization of TiO<sub>2</sub>/Ag<sub>2</sub>O by using FESEM-EDX and XRD, it can be conclude that ratio Ag<sub>2</sub>O 5% is the optimum ratio loading as it has better Ag<sub>2</sub>O and TiO<sub>2</sub> distribution. The binary catalyst also possessed more intense peaks of Ag<sub>2</sub>O which confirmed the existence Ag<sub>2</sub>O. Ag<sub>2</sub>O has lower band gap compare to TiO<sub>2</sub>, which is 1.3eV whereas TiO<sub>2</sub> has 3.2eV. By combine TiO<sub>2</sub> with Ag<sub>2</sub>O, low energy light can be use as well as this will reduce the cost of operation.

As stated in previous study [24], the doping ratio of TiO<sub>2</sub> and Ag<sub>2</sub>O is 10:4, which is also the same this study ratio where it manage to show good photocatalytic activity.

Nevertheless, fesem-edx was not able to determine the particle size of Ag<sub>2</sub>O due to the energy required to bombard Ag<sub>2</sub>O nanoparticles surface is higher. Thus, it is recommended to use TEM for more precise analysis. From the fesem-edx images, TiO<sub>2</sub> can be seen to undergo agglomeration. TiO<sub>2</sub> may need to be mix with Ag<sub>2</sub>O in vacuum condition or modify with chemical, such as  $\gamma$ -aminopropyltriethoxysilane as this chemical is able to reduce agglomeration of TiO<sub>2</sub>[25].

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