



ISSN 1823-626X

# Journal of Fundamental Sciences

available online at <http://jfs.ibnusina.utm.my>

## Synthesis of Tungsten Oxide as Visible Light-Driven Photocatalyst for Removal of Salicylic Acid

Leny Yuliaty<sup>1\*</sup>, Maisarah Mazalan<sup>2</sup> and Hendrik O. Lintang<sup>1</sup><sup>1</sup>Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia<sup>2</sup>Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Received 22 April 2011, Revised 2 May 2011, Accepted 10 May 2011, Available online 28 June 2011.

### ABSTRACT

In the present study, tungsten oxide ( $\text{WO}_3$ ) was prepared using mesoporous carbon nitride ( $\text{m-C}_3\text{N}_4$ ) as a template. Based on the results obtained from X-ray diffraction (XRD) and diffuse reflectance (DR) UV-Visible spectroscopy, it was confirmed that  $\text{WO}_3$  can be successfully prepared at all investigated calcination temperatures, even at low temperature of  $200^\circ\text{C}$ . It was found that the  $\text{WO}_3$  prepared at  $700^\circ\text{C}$  using  $\text{m-C}_3\text{N}_4$  showed higher photocatalytic activity than the commercial  $\text{WO}_3$  for salicylic acid removal under visible light irradiation. With the optimum loading amount of platinum as cocatalyst, 80.6% of salicylic acid removal was obtained on the prepared  $\text{WO}_3$ . It was suggested that the small particle size and the high crystallinity of the prepared  $\text{WO}_3$  played important role in giving high photocatalytic activity.

|  $\text{WO}_3$  |  $\text{m-C}_3\text{N}_4$  | photocatalyst | visible light | salicylic acid |© 2011 Ibnu Sina Institute. All rights reserved.  
<http://dx.doi.org/10.11113/mjfas.v7n1.221>

## 1. INTRODUCTION

Among the carboxylic acids, salicylic acid has been recognized as one of the most found water pollutants, which arises from various industries, such as paper milling, cosmetic industries, and land fill leachate [1]. Therefore, the removal of salicylic acid is highly required in order to reduce the effect of salicylic acid as a water pollutant in the waste water. In the point of view of green technology, photocatalytic degradation of salicylic acid would be one alternative method to solve this problem. Some photocatalysts have been reported to be active for degradation of salicylic acid, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{Ga}_2\text{O}_3$  [1-4]. However, these photocatalysts can work only under UV light irradiation. Due to the fact that visible light has larger part than UV light in the sunlight spectrum, the utilization of visible light has become one important issue in the development of photocatalytic systems.

On the other hand, it is known that tungsten oxide ( $\text{WO}_3$ ) has a suitable band gap for visible light absorption. In addition to its visible light absorption,  $\text{WO}_3$  also has high stability in aqueous solution and shows no photocorrosion. These properties strongly indicate that  $\text{WO}_3$  can act as a potential photocatalyst. Its photocatalytic activity has been reported for degradation of some organic compounds, such as phenol, acetaldehyde, acetic acid, formic acid, hexane, acetyl acetate, and also acetone [5-7].

However, the potential photocatalytic activity of  $\text{WO}_3$  has still not been investigated for removal of salicylic acid.

There are some methods reported for preparation of  $\text{WO}_3$ , such as hydrothermal, pyrolysis, and sol-gel process [8-10]. In the present study, new approach to synthesize  $\text{WO}_3$  using a removable template, *i.e.*, mesoporous carbon nitride ( $\text{m-C}_3\text{N}_4$ ) is proposed. The  $\text{m-C}_3\text{N}_4$  has been used as a template to produce metal nitride materials [11, 12], but has never been reported as a template for preparation of metal oxide.

## 2. EXPERIMENTAL

### 2.1 Sample Preparation

As a template,  $\text{m-C}_3\text{N}_4$  was synthesized in the similar way to the previous studies [11-13]. The used silica template has particle size of 7 nm. The silica template was then removed with ammonium hydrogen difluoride ( $\text{NH}_4\text{HF}_2$ , Acros) solution. For preparation of  $\text{WO}_3$ , tungstic acid ( $\text{H}_2\text{WO}_4$ , Acros) was dissolved in ammonia solution ( $\text{NH}_4\text{OH}$ , QR&C). After tungstic acid was dissolved, the solution was mixed with  $\text{m-C}_3\text{N}_4$  and stirred at room temperature for 1 h. The mixture was filtered, and then dried at  $90^\circ\text{C}$  overnight. After drying, the product was ground and calcined in a furnace at different temperatures, which were 200, 300, 600, and  $700^\circ\text{C}$  for 3 hours. The samples were labelled to as W200, W300, W600, and W700, respectively. As a reference sample, commercial  $\text{WO}_3$  (Acros) was used without any treatments.

Corresponding author at: Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia  
E-mail addresses: leny@ibnusina.utm.my (Leny Yuliaty)

## 2.2 Characterizations

Nitrogen adsorption-desorption isotherm analysis was carried out on a BELSORP-Mini instrument, BEL Japan. A Perkin-Elmer diffuse reflectance (DR) UV-visible spectroscopy (Lambda 900) was used to determine absorption spectra of the samples. The barium sulphate ( $\text{BaSO}_4$ ) was used as reference for the measurement. X-ray diffraction patterns of the samples were recorded at room temperature (Bruker AXS Diffrac plus release 2000). Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM) images were measured on a JEOL JSM-6390LV microscope with an accelerating voltage of 15 kV and JEOL JSM-6701F microscope with an accelerating voltage of 2.0 kV, respectively.

## 2.3 Photocatalytic Reactions

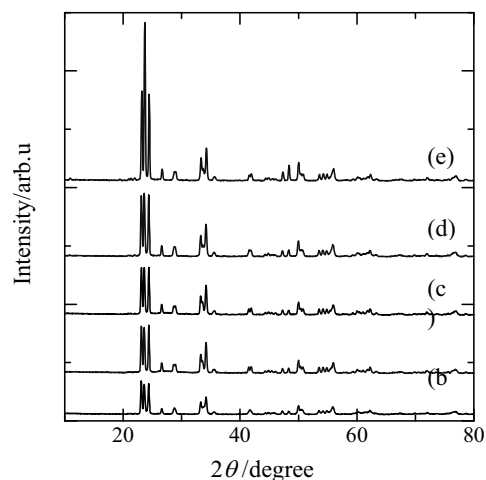
The photocatalytic reaction experiments were carried out at room temperature. The photocatalyst sample (0.05 g) was dispersed into 50 mL aqueous of salicylic acid (0.2  $\mu\text{M}$ ). The mixed solution was stirred for 30 min in the dark condition in order to reach the absorption equilibrium prior to the irradiation. The platinum with various amounts (in wt%) were added into the solution as cocatalyst by *insitu* photodeposition method. The light source was turned on and the solution was stirred under visible light at various irradiation times. After the reaction was completed at each given time, the solution was filtered to remove the photocatalyst. The absorbance of salicylic acid after the photocatalytic removal process was monitored at 295 nm on a Perkin-Elmer UV-Vis spectrophotometer (Lambda 25).

## 3. RESULTS & DISCUSSION

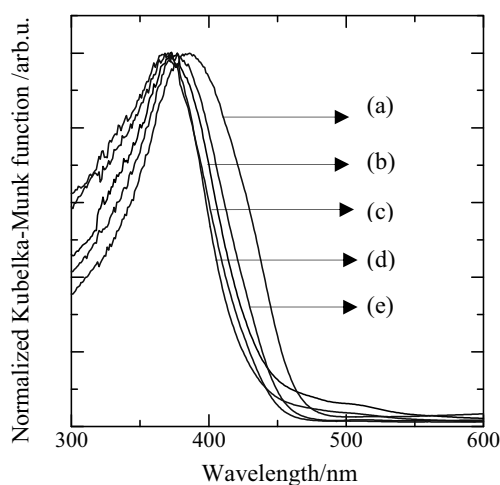
### 3.1 Preparation and Characterizations

It was confirmed that from nitrogen adsorption-desorption isotherm measurement, the prepared  $\text{m-C}_3\text{N}_4$  showed the characteristic of mesoporous material with pore size of 7 nm, in good agreement with other literature [11]. From XRD pattern and DR UV-visible spectroscopy, the successful formation of amorphous  $\text{m-C}_3\text{N}_4$  having absorption band up to 450 nm was confirmed.

Figure 1 shows XRD patterns of synthesized samples using  $\text{m-C}_3\text{N}_4$  after calcination at various temperatures, which were 200, 300, 600, or 700°C. As can be seen in Figure 1, all samples showed similar diffraction peaks to each other, suggesting that they have similar structure to each other. Since the diffraction peaks are similar to that of commercial  $\text{WO}_3$  (Figure 1(a)), it can be concluded that all synthesized samples are  $\text{WO}_3$ . There was no other peak observed, suggesting that there was no other phase that was formed during the calcination process. From this result, it is clear that  $\text{WO}_3$  can be formed even at low



**Figure 1:** XRD patterns of synthesized samples: (a) commercial  $\text{WO}_3$ , (b) W200, (c) W300, (d) W600, and (e) W700



**Figure 2:** Normalized DR UV-Visible spectra of synthesized samples: (a) commercial  $\text{WO}_3$ , (b) W200, (c) W300, (d) W600, and (e) W700

temperature such as 200°C. When the calcination temperature increased from 200 to 600°C, the intensity of the diffraction peak was not remarkably changed, suggesting that crystallinity was almost similar to each other. However, when the sample was calcined at 700°C, the peak intensity increased, might be due to the increase in the crystallinity and/or the particle size. It is worthy noted here that compared to the commercial  $\text{WO}_3$ , all  $\text{WO}_3$  samples prepared by the present method showed higher diffraction peak intensity. This result suggests that the present prepared samples may have higher crystallinity and/or larger particle size than the commercial  $\text{WO}_3$ , which will be discussed later from the results of FESEM and SEM images.

Figure 2 shows the DR UV-visible spectra of all prepared samples and the commercial WO<sub>3</sub>. All samples have similar characteristic of absorption band to that of commercial WO<sub>3</sub> (Fig. 2(a)). Samples prepared at low temperatures, *i.e.*, W200 and W300, showed absorption band up to 600 nm (Figs. 2(b) and (c)). On the other hand, samples prepared at high temperatures, *i.e.*, W600 and W700, showed absorption band up to 480 nm (Figs. (d) and (e)) that was much similar to the absorption spectrum of commercial WO<sub>3</sub> (Fig. 2(a)). The difference in the absorption band level would be due to the possibility that the m-C<sub>3</sub>N<sub>4</sub> was still remained on W200 and W300 samples. This is in good agreement with the fact that the colour of W200 and W300 are light yellow, which is similar to the colour of m-C<sub>3</sub>N<sub>4</sub>. On the other hand, the W600 and W700 samples have light green colour, which is similar to the colour of commercial WO<sub>3</sub>. Thus, from DR UV-Visible spectroscopy, it is also clear that the formation of WO<sub>3</sub> was confirmed by using the present method.

### 3.2 Photocatalytic Activity

The commercial WO<sub>3</sub> without cocatalyst showed low photocatalytic activity (Table 1, Entries 1 and 2). Since it is known that Pt can be used as cocatalyst to prevent the recombination of electron and holes during photocatalytic reactions, in the present study, Pt was also used as cocatalyst to increase the activity of WO<sub>3</sub> for photocatalytic

removal of salicylic acid. There was no increase in the activity with the addition of small amount of Pt, such as 0.1 wt% (Table 1, Entry 3). However, when Pt amount was 0.5 wt%, the activity of WO<sub>3</sub> increased from 1.9% to 10.5% after 18-h irradiation (Table 1, Entries 2 and 5).

Using the same amount of Pt (0.5 wt%) as cocatalyst, the prepared m-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> samples were tested for photocatalytic removal of salicylic acid. It was obtained that Pt (0.1)/m-C<sub>3</sub>N<sub>4</sub> has low activity, *i.e.*, 0.3% (Table 1, Entry 6). For the prepared WO<sub>3</sub> samples, the highest percentage removal of salicylic acid was 18.2%, which was obtained on Pt (0.5)/W700 after 18-h irradiation (Table 1, Entry 7). The activity of W700 was found to be higher than that of commercial WO<sub>3</sub>. Very low activity was obtained on Pt (0.5)/W600 (Table 1, Entry 8) while almost no activity was observed on other samples (Table 1, Entries 9, 10). At present, the reason why these samples did not show any activity is still unclear. Further investigations should be required to answer the problem. Since only W700 showed photocatalytic activity for salicylic acid removal, further discussion will be focused on W700.

In order to increase the photocatalytic activity of W700, the effect of the Pt loading amount was investigated. When the amount of Pt was too small or too high, no photocatalytic activity was observed (Table 1, Entries 7, 11-14). The highest photocatalytic activity (80.6%) was obtained when the amount of Pt was 1.5 wt% (Table 1, Entry 13).

**Table 1:** Photocatalytic removal of salicylic acid over various WO<sub>3</sub> samples

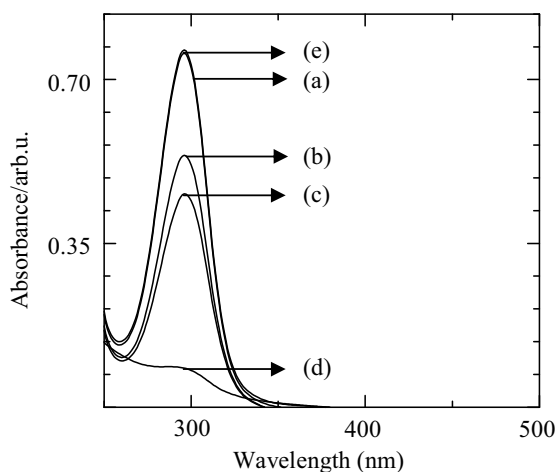
Entry	Sample <sup>b</sup>	Percentage removal of salicylic acid (%) <sup>c</sup>	Irradiation time (h)
1	WO <sub>3</sub>	0.0	3
2	WO <sub>3</sub>	1.9	18
3	Pt(0.1)/WO <sub>3</sub>	0.0	3
4	Pt(0.5)/WO <sub>3</sub>	3.7	3
5	Pt(0.5)/WO <sub>3</sub>	10.5	18
6	Pt(0.1)/m-C <sub>3</sub> N <sub>4</sub>	0.3	18
7	Pt(0.5)/W700	18.2	18
8	Pt(0.5)/W600	0.2	18
9	Pt(0.5)/W300	0.0	18
10	Pt(0.5)/W200	0.0	18
11	Pt(0.1)/W700	0.0	18
12	Pt(1.0)/W700	26.4	18
13	Pt(1.5)/W700	80.6	18
14	Pt(2.0)/W700	0.0	18

<sup>a</sup>Sample was 0.05 g, salicylic acid was 0.2 μM (50 mL), the dark absorption was carried out for 30 min prior to the irradiation, light source was halogen lamp, 150 W.

<sup>b</sup>Pt(x)/WO<sub>3</sub> was prepared by photodeposition method of Pt on WO<sub>3</sub>, with x was the weight percentage of Pt to the WO<sub>3</sub>.

<sup>c</sup>The percentage removal of salicylic acid was calculated from  $\frac{C_0 - C}{C} \times 100\%$ , where

$C_0$  was initial absorbance and  $C$  was the absorbance measured after irradiation.



**Figure 3:** The decrease of salicylic acid absorbance on W700 with different amounts of platinum loading: (a) 0.1, (b) 0.5, (c) 1.0, (d) 1.5, and (e) 2.0 wt%.

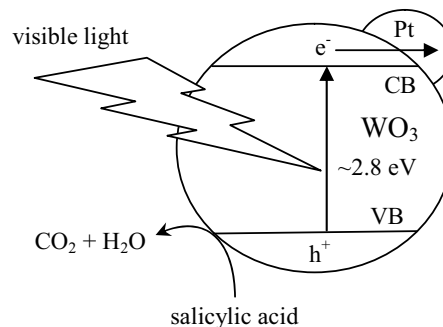
As can be seen in Figure 3, the absorbance peak of salicylic acid was almost disappeared on Pt(1.5)/W700. The absorption peak of salicylic acid was remained high that was similar to the initial one when using Pt(0.1)/W700 and Pt(2.0)/W700 as the photocatalyst. This phenomenon can be explained since when the amount of platinum loading was too low, the surface of  $\text{WO}_3$  was not activated effectively. On the other hand, when the amount of platinum loading was too high, the surface of  $\text{WO}_3$  was covered by platinum and the light could not reach the surface. In this case, the  $\text{WO}_3$  became inactive.

The role of Pt cocatalyst in increasing the photocatalytic activity can be explained further as shown in Figure 4. When  $\text{WO}_3$  absorbed visible light radiation, the electron was excited from the valence band to the conduction band of  $\text{WO}_3$ . Therefore, the negative electron ( $e^-$ ) and positive hole ( $h^+$ ) pairs were created. In the presence of platinum, electron will be trapped by platinum, thus the electron-hole separation will be more effective and the electron-hole recombination can be prevented. If the recombination between electron and hole can be prevented, holes and electrons can react with reactants to oxidize and reduce them to specific products. In the case of salicylic acid, it was expected that the oxidation of salicylic acid by holes will produce water and carbon dioxide.

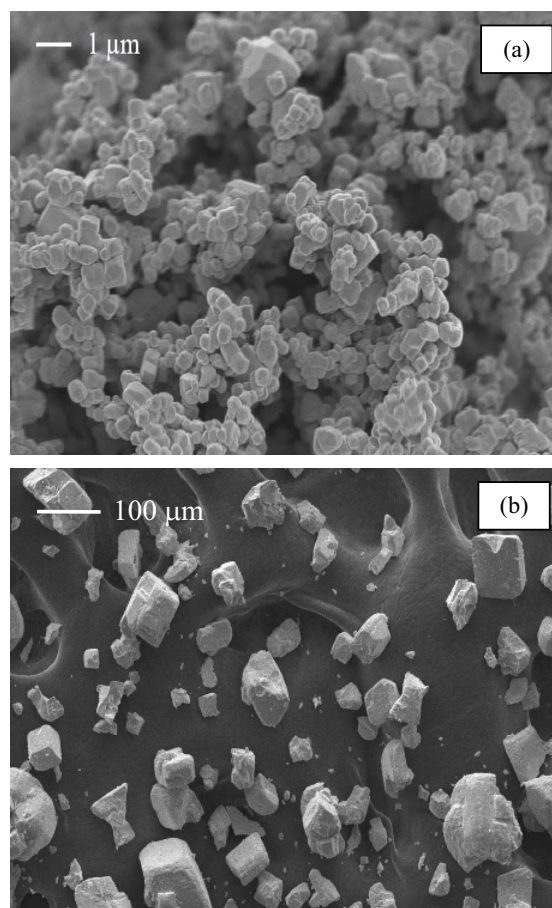
In order to study the effect of photocatalyst properties on the activity, further characterizations on W700 and commercial  $\text{WO}_3$  were carried out. The difference between W700 and commercial  $\text{WO}_3$  was clarified by studying the morphology and particle size, which were characterized by FESEM and SEM for W700 and commercial  $\text{WO}_3$ , respectively.

Figure 5(a) shows the FESEM image of W700 sample. It was clarified that all the particles are mostly uniform and have the same range of size about 200 nm. The particle size obtained was much higher than the template

size, suggesting that there was a sintering effect during the calcination process. In the present study, the effects of heating time and condition parameters were not investigated. It can be considered that once the  $m\text{-C}_3\text{N}_4$  template was removed, the growth of the crystal could not be controlled.



**Figure 4:** Role of Pt as cocatalyst on  $\text{WO}_3$  for photocatalytic removal of salicylic acid. VB and CB are valence band and conduction band, respectively.



**Figure 5:** FESEM and SEM images of (a) W700 and (b) commercial  $\text{WO}_3$ , respectively.

Figure 5(b) shows the SEM image of commercial WO<sub>3</sub>. Different from W700, the particle of the commercial WO<sub>3</sub> was not uniform and the particle size was much larger than the W700, in the range of 20-100 μm. It is believed that the smaller particle size would result in the shorter diffusion length for photogenerated electron-hole pairs, which would reduce the possibility for electron-hole recombination. Therefore, the photocatalytic activity was higher on smaller particle. It is noted that even though the particle size of W700 was much smaller, the intensity of diffraction pattern was much higher than that of the commercial WO<sub>3</sub>. Therefore, it can be proposed that the higher intensity of the diffraction peak would be due to the higher crystallinity of the W700 sample than that of the commercial WO<sub>3</sub>. Thus, the higher photocatalytic activity on the W700 compared to the commercial WO<sub>3</sub> might be due to the higher crystallinity as well as the uniform particle size on the W700.

#### 4. CONCLUSION

WO<sub>3</sub> was successfully synthesized using m-C<sub>3</sub>N<sub>4</sub> as a template. The percentage removal of salicylic acid as high as 80.6% was achieved on the prepared Pt(1.5)/W700 sample after 18-h irradiation under visible light irradiation. Even though the removal rate was low, this result showed the potential ability of WO<sub>3</sub> to remove salicylic acid under visible light irradiation. It was suggested that the low particle size and high crystallinity would be the important parameters to obtain high photocatalytic activity.

#### ACKNOWLEDGEMENT

The authors thank to Universiti Teknologi Malaysia for financial support through Institutional Research Grant Scheme, Universiti Teknologi Malaysia (Vote Number: 77549)

#### REFERENCES

- [1] A. Mills, C. E. Holland, R. H. Davies, and D. Worsley, *J. Photochem. Photobiol. A: Chem.*, 83 (1994) 257-263 and references therein.
- [2] S. Vilhunen, M. Bosund, M.-L. Kääriäinen, D. Cameron, and M. Sillanpää, *Sep. Purif. Technol.*, 66 (2009) 130-134.
- [3] A. N. Rao, B. Sivasankar, and V. Sadasivam, *J. Hazard. Mater.*, 166 (2009), 1357-1361.
- [4] Y. Hou, J. Zhang, Z. Ding, and L. Wu, *Powder Technol.*, 203 (2010), 440-446.
- [5] A. Sclafani, L. Palmisano, G. Marci, and A. M. Venezia, *Sol. Energ. Mater. Sol. Cells*, 51 (1998), 203-219.
- [6] T. Arai, M. Yanagida, Y. Konishi, Y. Iwasaki, H. Sugihara, and K. Sayama, *Catal. Commun.*, 9 (2008), 1254-1258.
- [7] R. Abe, H. Takami, N. Murakami, and B. Ohtani, *J. Am. Chem. Soc.*, 130 (2008) 7780-7781.
- [8] B. Yan, Y. Xu, N. K. Goh, and L. S. Chia, *Chem. Commun.*, (2000), 2169-2170.
- [9] M. Regragui, M. Addou, A. Outzourhit, E. E. Idrissi, A. Kachouane, and A. Bougrine, *Sol. Energ. Mater. Sol. Cells*, 77 (2003), 341-350.
- [10] B. Yang, P. R. F. Barnes, W. Bertram, and V. Luca, *J. Mater. Chem.*, 17 (2007), 2722-2729.
- [11] L. Yuliati, J.-H. Yang, X. Wang, K. Maeda, T. Takata, M. Antonietti, and K. Domen, *J. Mater. Chem.*, 20 (2010), 4295-4298.
- [12] A. Fischer, M. Antonietti, and A. Thomas, *Adv. Mater.*, 19 (2007) 264-267.
- [13] F. Goettmann, A. Fischer, M. Antonietti, and A. Thomas, *Angew. Chem. Int. Ed.*, 45 (2006), 4467-4471.