eProceedings Chemistry 5 (2020) 26-32

eISSN 2550-1453 **http://eproceedings.chemistry.utm.my/**

Synthesis of Hydrogenated Titania and Its Photocatalytic Activity in Photodegradation of Phenol

Nurfarhana Shukri and Sheela Chandren*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
**Corresponding Author: sheela@kimia.fs.utm.my*

Article history:
Received 3 Sept 2020
Accepted 30 Sept 2020

GRAPHICAL ABSTRACT

Titanium Dioxide

ABSTRACT

TiO_2 is widely utilized in many applications, such as self-cleaning, antifogging properties and a favorable photocatalyst in solving environmental problem. However, TiO_2 has a large bandgap of 3.0 – 3.3 eV that limits its optical absorption to ultraviolet (UV) spectrum, resulting in low photocatalytic efficiency. One way to solve these problems would be by synthesizing hydrogenated TiO_2 using a simple hydrogenation method, which is a surface modification phenomenon and does not perturb the crystalline core of TiO_2. Therefore, this study reports on the preparation of hydrogenated TiO_2 from commercial TiO_2 at different hydrogen gas pressure and hydrogenation duration, that give a bluish-grey colour of hydrogenated TiO_2. The physicochemical properties of the synthesized hydrogenated TiO_2 were characterized by TPR, FESEM-EDX, XRD, NIR UV-Vis and FTIR. TPR analysis measured the reducibility of commercial TiO_2 is at 400 to 600 °C. FESEM images of hydrogenated TiO_2 showed that the particles size of hydrogenated TiO_2 is bigger than the commercial TiO_2. EDX analysis confirmed the presence of titanium (Ti) and oxygen (O) element, while XRD patterns confirmed the synthesized hydrogenated TiO_2 samples are in anatase phase. NIR-UV-Vis showed that the band gap energy of all samples was in the range of 3.23 – 3.26 eV, higher than the expected value. Most probably due to insufficient hydrogen gas supplied to the TiO_2. The photocatalytic activity of the synthesized hydrogenated TiO_2 was tested out in photodegradation of phenol under UV and visible light irradiations for 7 hours. It was found that the hydrogenated TiO_2 were able to decompose phenol, although at lower degradation percentage of less than 50%.

Keywords: Hydrogenated TiO_2, TiO_2, photodegradation of phenol.

1. INTRODUCTION

Titania (TiO_2) is extremely well-known for its outstanding properties such as good photocatalytic activity, low in cost, non-toxicity and high stability, which makes it a favourable semiconductor photocatalyst in solving environmental problem, especially to remove organic pollutants [1]. Titania consists of three main polymorphic crystal phase, which are anatase, rutile and brookite [2]. These three polymorphic types have the same chemical formula but different structure of crystal as shown in Figure 1. Efficiency of TiO_2's photocatalytic activity is highly dependent on the ability to generate electron-hole pairs and effective charge separation. In general, as the amount of light absorbed by TiO_2 increases, TiO_2's photocatalytic efficiency also improved [3]. Although TiO_2 is widely utilized, TiO_2 has a large electronic band gap of 3.0 3.2 eV that limits its optical absorption to ultraviolet (UV) spectrum, resulting in low photocatalytic efficiency [1]. Due to its low photocatalytic efficiency, structural modification of TiO_2 has been at research frontier to expand the utilization of TiO_2 as a favourable photocatalyst. Hydrogenated TiO_2, which is commonly black in colour, is able to enhance the photocatalytic activity towards pollutant removal and hydrogen generation from water. Hydrogenated TiO_2 consists of a narrow band gap with wider light harvesting efficiency in the visible and infrared region [2]. The enhancements in photocatalytic activity using hydrogenated TiO_2 are mainly due to its superior light absorption and presence of surface disorders as additional active sites [4].

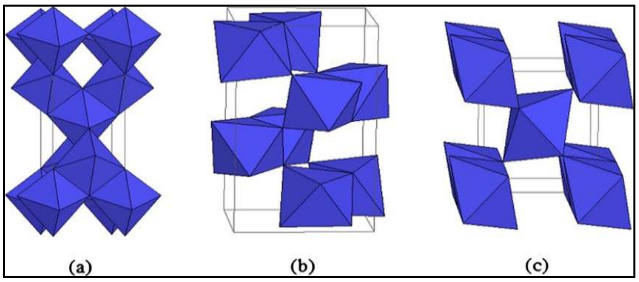

Figure 1. Crystal structure of TiO_2; (anatase), (b) brookite and (c) rutile.

This research will emphasize on synthesizing and characterizing hydrogenated TiO_2. In this case, hydrogenated TiO_2 was prepared from commercial TiO_2 by using hydrogenation method. The physicochemical properties of the synthesized hydrogenated TiO_2 have been carried out using various instrumental analysis. Following that, the hydrogenated TiO_2 was used as the photocatalyst in photodegradation of phenol under UV and visible light irradiations.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage was focused on the synthesized of hydrogenated TiO_2. The second stage was the characterization of the physicochemical properties of hydrogenated TiO_2. The last stage is photocatalytic testing of hydrogenated TiO_2 by photodegradation of phenol. In order to synthesize the hydrogenated TiO_2, the hydrogenation process of TiO_2 was conducted in a tube furnace at 600 °C. Figure 2 shows the set-up of tube furnace and gas line of the hydrogenation process of commercial TiO_2. Next, the synthesized hydrogenated TiO_2 were characterized to study their physicochemical properties by using TPR, FESEM-EDX, XRD, NIR UV-Vis and FTIR. Later, in stage three, the resulting hydrogenated TiO_2 underwent a photocatalytic testing in photodegradation of phenol. The synthesized hydrogenated TiO_2 were denoted as H24-200 and H24-400 for hydrogenated TiO_2 at 200 and 400 kPa respectively, for hydrogenation duration of 24 hours. Meanwhile, H10-200 and H10-400 were for hydrogenated TiO_2 that underwent hydrogenation for 10 days at 200 and 400 kPa, respectively.

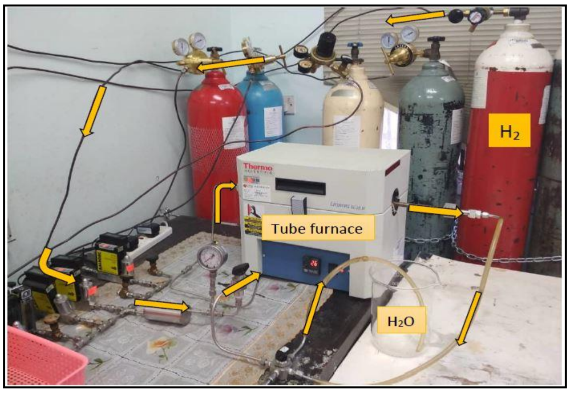

Figure 2 Set-up of tube furnace and gas line of the hydrogenation process.

3. RESULTS AND DISCUSSION

3.1. Synthesis of hydrogenated TiO_2

Hydrogenated TiO_2 in powder form was carried out by the hydrogenation method with both different pressure; 200 kPa and 400 kPa of hydrogen gas and different duration; 24 hours and 10 days of hydrogenation process. A bluish-grey colour of hydrogenated TiO_2 was obtained from the white commercial TiO_2 for all 4 samples. In this work, an increased in hydrogenation duration and hydrogen gas pressure give no distinctive difference between the colours of the synthesized hydrogenated TiO_2. It is evident that hydrogenation affects the colour of TiO_2 and thus alters its optical properties. The change in colour for the hydrogenated TiO_2 may indicate successful level of hydride-titanium bond formation in O-Ti-H linkage and also formation of Ti^{3+} in TiO_2 lattice [2]. The colour of the hydrogenated TiO_2 could also vary depending on the conditions of the hydrogenation process. Darker colour of the hydrogenated TiO_2 could be obtained with increasing formation of O-Ti-H bonds and Ti^{3+} in the lattice.

3.2. Characterization of the synthesized hydrogenated TiO_2

The reducibility of the commercial TiO_2 has been determined by H_2-TPR analysis. Figure 3 shows the H_2 consumption profiles of the commercial TiO_2 at different temperatures. It can be seen that one significant broad peak, which started from 400 to 600 °C, with maximum peak at the approximate temperature of above 480 ºC with total H_2 consumption of 9.8668 mmol/g. The results indicated that all Ti^{4+} species present in the commercial TiO_2 were reduced to lower oxidation number of Ti^{3+} at reduction temperature of below 600 °C. However, hydrogenation of commercial TiO_2 at 500 °C and below showed minimal changes in the colour of the commercial TiO_2. Therefore, the temperature for the hydrogenation process of the commercial TiO_2 was set at 600 ºC, which produced bluish-grey colour of hydrogenated TiO_2.

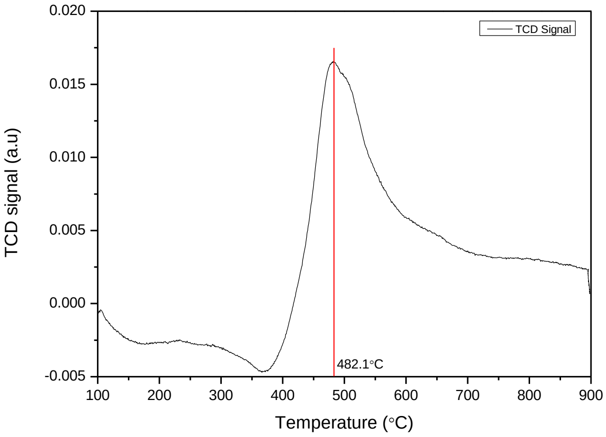

Figure 3. H_2 consumption profile of commercial TiO_2.

The morphologies of the commercial TiO_2 and hydrogenated TiO_2 were analysed using field emission scanning electron microscope (FESEM) at magnification of 200,000 times and showed significant differences in terms of shape and size uniformity as shown in Figure 4. Well distributed and uniform particles size of 8 – 11 nm were observed for commercial TiO_2. For 24 hours hydrogenation at 400 kPa, the particle size of H24-400 increased significantly to 23 – 25 nm with mixture of smaller particle of particle size and inhomogeneity are observed for longer hydrogenation period. The hydrogenated TiO_2 consists of mixed morphology of irregular spheres and sub rounded particles shapes. There is no definite explanation for such irregular shape of sphere particles but could be the result of prolonged exposure of hydrogen under intense heat, which perturb the growth, orientation and kinetics of the TiO_2 crystal [5].

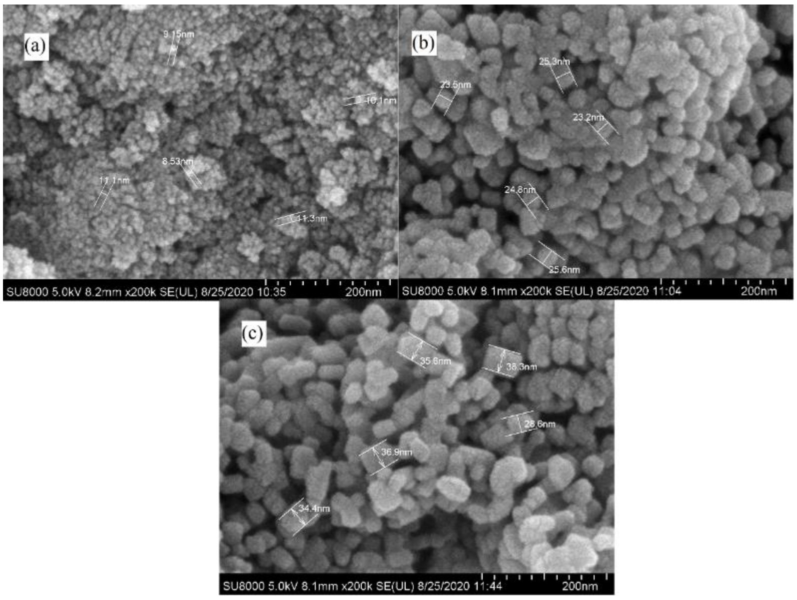

Figure 4. FESEM images of (a) commercial TiO_2, (b) H24-400 and (c) H10-200 with magnification of 200000 time and accelerating voltage of 5.0 kV

Based on electron dispersive X-rays (EDX) analysis, the percentage of atomic composition of titanium and oxygen atoms in hydrogenated TiO_2, H10-200 shows a decrease in oxygen amount at longer duration of hydrogenation, which indicate higher oxygen vacancies due to high pressure used during the hydrogenation process, that may have induced more oxygen vacancies in the lattice of TiO_2 [6]. From the XRD peaks, synthesized hydrogenated TiO_2 were assigned anatase crystal phase of TiO_2 according to the Joint Committee on Powder Diffraction Standard (JCPDS) card number 21-1272, with crystallite size increases with longer hydrogenation duration. However, at increased hydrogen gas pressure, the synthesized hydrogenated TiO_2 shows irregularity in crystallite size The band gap energy obtained from NIR Uv-vis analysis is in accordance to XRD results obtained, where the range band gap energy is in anatase phase (3.20 eV). Based from the results obtained, even though the difference of band gap energy between commercial and hydrogenated TiO_2 is minimal, it shows that the band gap energy can be reduced slightly at higher pressure of hydrogen gas in the hydrogenation process. The wide band gap energy of hydrogenated TiO_2 explains the absence of peak at the visible region at range 400 – 800 nm in the absorption spectrum shown in Figure 5.

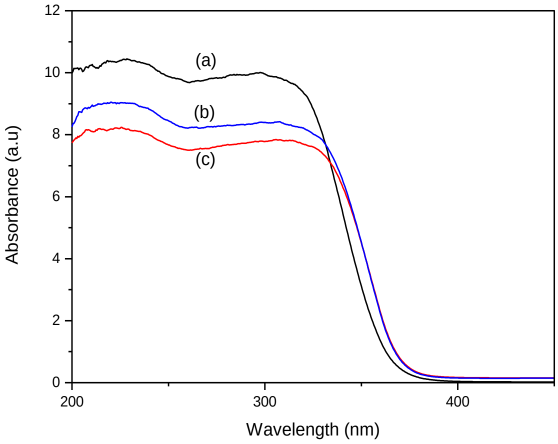

Figure 5 NIR-Vis spectra of TiO_2; (a) commercial TiO_2, (b) H10-200 and (c) H24-400.

The FTIR spectra of commercial TiO_2 and hydrogenated TiO_2 are shown in Figure 6, where all of the spectra showed a band at 3320 cm^{-1} which correspond to the stretching of hydroxyl group. Another peak was observed in the spectra at 1638 cm^{-1} which corresponded to the Ti-OH bond. These peaks confirmed the presence of hydroxyl ions in the structure of TiO_2. A significant difference in the broad peak of surface hydroxyl group of commercial TiO_2 as compared to hydrogenated TiO_2 at 3320 cm^{-1}, whereby the corresponding peak area decreases gradually as hydrogenation duration and pressure of hydrogen gas increases as continuous hydrogenation process would eliminate more oxygen atoms, forming a Ti-H bond which lead to surface disorders [7].

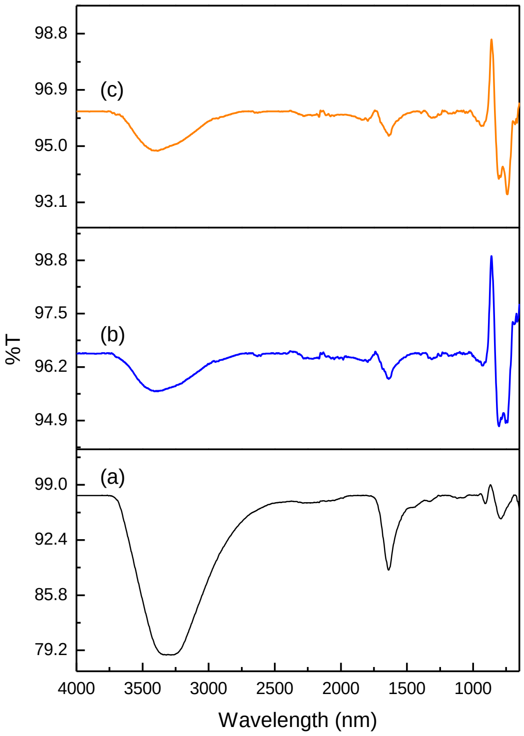

Figure 6 FTIR spectra of TiO_2; (a) commercial TiO_2, (b) H24-400 and (c) H10-200.

3.3. Photocatalytic testing of hydrogenated TiO_2 in photodegradation of phenol

The photocatalytic activity of the hydrogenated TiO_2 was tested out in the photodegradation of 50 ppm phenol solution under UV and visible light irradiation for 7 hours. It was found that the intensity of phenol's peak decreased gradually after the 7 hours of light irradiation for both commercial TiO_2 and hydrogenated TiO_2 as shown in Figure 7 and Figure 8. However, an apparent new peak formed at approximately 240 nm after 7 hour of irradiation with commercial TiO_2 and hydrogenated TiO_2. This implies that phenol has been degraded into intermediate compounds during the photocatalytic reaction as reported in [8]. Based on the results, it can be seen that the time need to complete degradation of phenol may take more than 7 hours, as the slow rate of degradation is caused by highly stable benzene rings present in phenol, which are resistant to decomposition reaction [8].

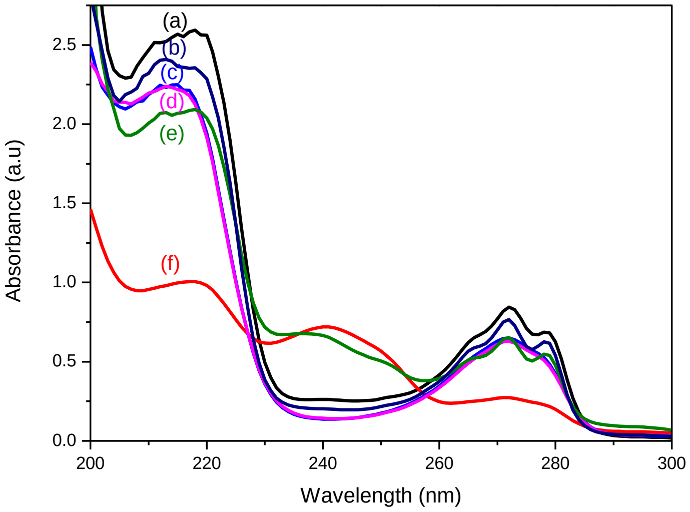

Figure 7. UV-vis spectra of degradation of phenol under UV light irradiation; (a) Initial, (b) H10-400, (c) H24-200, (d) H24-400, (e) H10-200 and (f) commercial TiO_2.

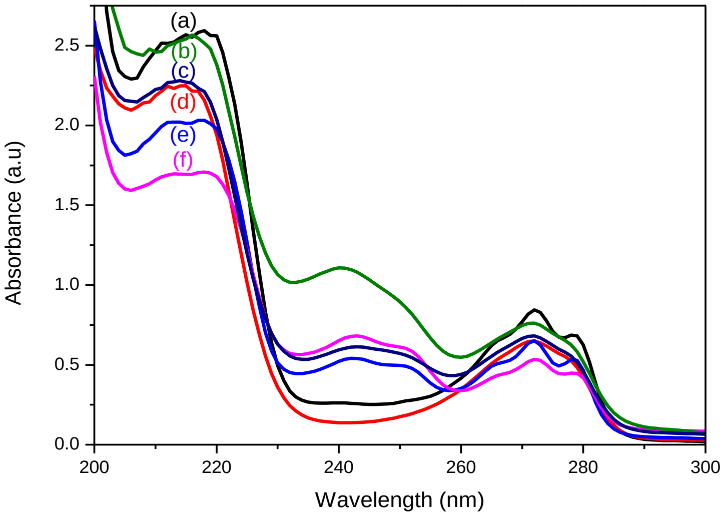

Figure 8. UV-vis spectra of degradation of phenol under visible light irradiation; (a) Initial, (b) H10-200, (c) H10-400, (d) commercial TiO_2, (e) H24-200 and (f) H24-400.

Table 1. The degradation percentage of phenol by commercial TiO_2 and hydrogenated TiO_2 after 7 hours under UV and visible light irradiations.

SAMPLE	**% Degradation**	
	UV	**Vis**
Commercial TiO2	62.8	84
H24-200	25.6	23.9
H24-400	24.12	35.8
H10-200	24.07	14.89
H10-400	12.23	22.45

From Table 1, it is shown that hydrogenated TiO_2 are able to decompose phenol under UV and visible light irradiations, although at a lower percentage. It can also be observed that commercial TiO_2 has higher percentage of degradation under both UV and visible light irradiations, with 62.8% and 84% respectively, compared to hydrogenated TiO_2 with degradation percentage of less than 50%. From the table 4.4, it can be seen that percentage degradation of phenol decreases as the hydrogenation duration increases under both UV and visible light irradiation. However, at increasing H_2 pressure, there were irregularity in the degradation percentage of phenol under UV and visible light irradiations, where for UV light irradiation, the hydrogenated TiO_2 at 200 kPa has a higher percentage of phenol degradation as compared to that of 400 kPa. Meanwhile, for visible light irradiation, the hydrogenated TiO_2 at 400 kPa has higher degradation percentage to that of 200 kPa.

It was expected that the photocatalytic activity of hydrogenated TiO_2 will be lower than that of commercial TiO_2, due to lack and excess of oxygen vacancies in the lattice. Based on the EDX analysis of H24-400, the atomic composition of oxygen atom is higher which indicates lack of oxygen vacancies in the lattice. Oxygen vacancies are unable to act as an electron donor and to enhance the photocatalytic activity of the hydrogenated TiO_2. However, overexposed of H_2 due to long duration of hydrogenation may lead to excessive amount of oxygen vacancies, such as H10-200, where its atomic composition of oxygen atom is very low with only10.82%, indicating high amount of oxygen vacancies. The excessive amount of oxygen vacancies may also serve as a charge traps centres that decrease the photocatalytic activity of H10-200 [4]. Furthermore, based on the band gap energy value of commercial and hydrogenated TiO_2 (3.23 – 3.26 eV), it is not possible for both commercial and hydrogenated TiO_2 to be active in visible light irradiation. In order for the hydrogenated TiO_2 to be able to absorb visible light, the band gap energy value need to be reduced to approximately 2.8 eV. However, degradation percentage shown in Table 1 indicates differently. Comparing the photocatalytic activity of commercial TiO_2 and hydrogenated TiO_2 (H24-400 and H10-200) under UV and visible light, it can be seen that for commercial TiO_2 and H24-400, the degradation percentage of phenol is higher under visible light irradiations with 84% and 35.8%, compared to UV light. Meanwhile, H10-200 shows only 14.89% of degradation percentage under visible light, lower than that of under UV light irradiation. This irregularity would probably due to other factors that may directly or indirectly affect the photocatalytic activity of the commercial TiO_2 and hydrogenated TiO_2.

Some of the factors that can be put into account is the intensity of visible light and presence of UV light in the visible light source. In this study, the intensity of visible light could not be measured due to the absence of visible light intensity meter, higher intensity of visible light compared to UV light cause more heat to be released in the photocatalytic reaction box, higher temperature may lead to degradation of phenol. Besides that, the probability of both commercial and hydrogenated TiO_2 are to be active under visible light may be due to the presence of UV light in the visible light source as no UV light filter were used during the photocatalytic testing. The presence of UV light from the light source may have caused the commercial TiO_2 and hydrogenated to be active even under visible light source. Based on the high degradation percentage of phenol under visible light, the intensity of UV light from the visible light source could be high.

4. CONCLUSION

The attempts to synthesize hydrogenated TiO_2 at different duration and hydrogen gas pressure of hydrogenation process. Hydrogenated TiO_2 has been prepared at 24 hours and 10 days with hydrogen gas pressure of 400 kPa and 200 kPa, respectively. The colour of the synthesized hydrogenated TiO_2 is bluish-grey with increasing particles size from 9 nm of commercial TiO_2 to the range of 23 - 36 nm of hydrogenated TiO_2. The physicochemical properties of the synthesized hydrogenated TiO_2 has been successfully determined by using TPR, FESEM-EDX. XRD, NIR UV-Vis and ATR-FTIR. Characterization by using TPR showed the reducibility of commercial TiO_2 started from 400 till 600 °C, with maximum peak at 482.1 ºC. FESEM showed that hydrogenated TiO_2 were in irregular spheres and sub-rounded shape. EDX confirmed that the presence and atomic composition of Ti and O element in the hydrogenated TiO_2, where it was shown that H24-400 has low oxygen vacancies compared to H10-200. XRD analysis showed that the synthesized hydrogenated TiO_2 is in anatase phase, with the corresponding band gap energies in the range of 3.23 – 3.26 eV determined by NIR UV-Vis spectroscopy. The functional groups of hydroxyl (-OH), and Ti-O of hydrogenated TiO_2 were successfully determined using ATR - FTIR. From the photocatalytic testing, it was found that both hydrogenated TiO_2 were able to decompose phenol under UV and visible light irradiations, although at a lower percentage. It can also be seen that hydrogenated TiO_2 shows lower photocatalytic activity as compared to commercial TiO_2, probably due to the higher amount of oxygen vacancies and value of band gap energy that are not ideal for the photodegradation of phenol.

ACKNOWLEDGEMENT

The authors gratefully acknowledge funding from Ministry of Higher Education (MOHE) under the Collaborative Research Grant (R.J130000.7354.4B502), and Research Grant from Nippon Sheet Glass Foundation for Materials Science and Engineering (R.J130000.7354.4B515).

REFERENCES

[1] Yan, X., Li, Y., & Xia, T. (2017). Black Titanium Dioxide Nanomaterials in Photocatalysis. *International Journal of Photoenergy*.

[2] Chen, X, Liu, L. and Huang, F. (2015). Black titanium dioxide (TiO_2) nanomaterials', *Chemical Society Reviews*, 44(7), 1861-1885

[3] Chen, S., Xiao, Y., Wang, Y., Hu, Z., Zhao, H., & Xie, W. (2018). A facile approach to prepare black TiO_2 with oxygen vacancy for enhancing photocatalytic activity. *Nanomaterials*, *8*(4), 1–16.

[4] Naldoni, A., Altomare, M., Zoppellaro, G., Liu, N., Kment, Š., Zbořil, R. and Schmuki, P. (2019) 'Photocatalysis with reduced TiO_2 : From Black TiO 2 to cocatalyst-free hydrogen production', *ACS Catalysis*, 9(1), 345–364.

[5] Teng, F., Li, M., Gao, C., Zhang, G., Zhang, P., Wang, Y., … Xie, E. (2014). Preparation of black TiO_2 by hydrogen plasma assisted chemical vapor deposition and its photocatalytic activity. *Applied Catalysis B: Environmental*, *148–149*, 339–343.

[6] Samsudin, E. M., Hamid, S. B. A., Juan, J. C., Basirun, W. J., & Kandjani, A. E. (2015). Surface modification of mixed-phase hydrogenated TiO_2 and corresponding photocatalytic response. *Applied Surface Science*, *359*, 883–896.

[7] Chen, X., Liu, L., Yu, P. Y., & Mao, S. S. (2011). Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science*, *331*(6018), 746–750.

[8] Dang, T. T. T., Le, S. T. T., Channei, D., Khanitchaidecha, W., & Nakaruk, A. (2016). Photodegradation mechanisms of phenol in the photocatalytic process. *Research on Chemical Intermediates*, *42*(6), 5961–5974.