eProceedings Chemistry 3 (2018) 64-72

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

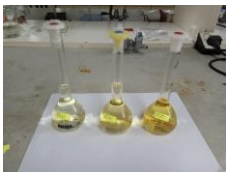
Preparation of Titania Photocatalyst Inks for Inkjet Printing onto Indium Tin Oxide Substrate

Mohamad Fadhli Mohamed Amin @ Azmin 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: 4 Oct 2018
Accepted: 15 Nov 2018

GRAPHICAL ABSTRACT



Prepared TiO_2 photocatalyst precursor inks with different concentrations; 0.10 M, 0.15 M and 0.20 M

ABSTRACT

Researchers have been taking great interest in titania (TiO_2) due to its potential in many applications, such as self-cleaning and antifogging surfaces. Two common forms of TiO_2 that have been widely used are nanopowdered-form and TiO_2 thin film supported on substrate. Among these two, TiO_2 supported thin films reduce the requirement for any further post-treatment filtering of the decontaminated fluid, although the surface area is more limited compared to the nanopowdered-form. Many methods can be used to prepare TiO_2 thin films onto substrates, such as sputtering technique, sol-gel method, electrochemical process, chemical vapour deposition (CVD) and spray pyrolysis. However, the methods mentioned above involve multiple steps, require long processing time, the usage of high temperature is necessary and many more. One way to solve these problems would be by using the inkjet printing method, which is an economical and cost-effective technique used for the deposition of thin layers on a substrate that provide selective and precise deposition of materials with a low waste of materials. In this work, stable TiO_2 photocatalyst precursor inks were prepared with different concentrations for inkjet printing method. The prepared TiO_2 photocatalyst precursor inks were then converted to the powdered form in order to determine the physicochemical properties. The field emission scanning electron microscopy (FESEM) images showed the TiO_2 particles were almost spherical in shape, with concentration of 0.15 M showing the most uniform size and the least agglomeration. Energy dispersive X-ray spectroscopy (EDX) results confirmed the presence of Ti and O elements in all of the samples, proving the successful synthesis of TiO_2. X-ray diffraction (XRD) patterns confirmed the synthesized TiO_2 samples are in the anatase phase. Results from diffuse-reflectance ultraviolet-visible spectroscopy (DR-UV-Vis) showed that the band gap energy of all samples was in the range of 3.42 and 3.46 eV, higher than the theoretical value, which might have been caused by the indirect transition of the synthesized TiO_2.

Keywords: titania, inkjet printing, anatase, photocatalyst

1. INTRODUCTION

Titanium dioxide or titania (TiO_2) is the most commonly used photocatalyst in various reactions due to its attractive characteristics such as nontoxicity, chemical stability to acidic and/or basic conditions, long term stability, good oxidizing ability, biocompatibility and cost effectiveness [1-4]. Among the popular uses of TiO_2 are in the purification of air and water, self-cleaning and antifogging surfaces, antibacterial photocatalyst, selective synthesis of organic compounds, lithium batteries, solar power system and pigments in paints, tiles and food [2,5,6]. These reactions involve both oxidation and reduction while also removing pollutants and bacteria. The photoinduced electrons produced in the redox process can then reduce an acceptor molecule, while the photoinduced holes can oxidize a donor molecule [2]. The electron and hole pair will convert the surrounding oxygen and water molecule into OH hydroxyl radical, photodegradation and decomposition of harmful organic substances [3].

TiO_2 has three different crystallographic phases; anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [2]. The electronic structure and properties of solids are related to the crystals structure. Among all these phases, anatase has the best photocatalytic activity resulting in the highest photocatalytic efficiency [4].

Two common forms of TiO_2 that have been widely used are nanopowdered-form and TiO_2 thin film supported on substrate [7]. Among these two, the more popular system used is TiO_2 in nanopowdered-form, which provides high surface area. However, at the end of the reaction, it requires filtration, thus complicates the whole process [8]. On the other hand, TiO_2 supported thin films reduce the requirement for any further post-treatment filtering of the decontaminated fluid, although the surface area are more limited compared to the nanopowdered-form [7]. In this work, the supporting material (substrate) used is indium tin oxide (ITO). Many methods can be used to prepare TiO_2 thin films onto substrates, such as sputtering technique, sol-gel method, electrochemical process, chemical vapour deposition (CVD) and spray pyrolysis [5].

However, the methods mentioned above involve multiple steps and require a very long processing time [8]. Apart from that, these methods may also exhibit incompatibility with selected substrate material, which may cause the active material's surface to be prone to cracking or pulverization due to mechanical strains [9]. Some of these methods also require the usage of high temperature, must be carried out in vacuum condition, and high cost. For the sputtering method, the density of sputtered layers is important as the adhesion of coating depends on it [5]. Lower density will cause bad adhesion. The deposition coating of material by sputtering method also require a long processing time [9]. As for CVD, the main weakness is that the films' quality depend on the size of droplet and the spray nozzle may become cluttered after a long processing time [10]. Meanwhile, for the popular sol-gel method, it requires the usage of alkoxide as its precursor to form TiO_2 and the pH value needs to be controlled regularly [11].

One of the possible methods that can be applied in the coating of substrate, namely ITO with TiO_2, is by using inkjet printing method. Inkjet printing is an economical and cost-effective microfabrication technique used for the deposition of thin layers on a target surface [12]. Inkjet printing is a promising method for direct deposition of functional materials for electronic devices, which will not damage or contaminate the substrate surface and deposit material only where it is required, resulting in little or no wastage [11]. The fast development of this method is mainly due to its unique advantage of providing selective and precise deposition of materials with a low waste of material but very high resolution [12].

In the present work, stable TiO_2 inks with different concentrations were prepared in order to be printed onto the ITO substrate by the inkjet printing method. A good printing can only be obtained if the inks are stable. In order to forecast the physicochemical properties of the printed TiO_2, the TiO_2 inks were dried and calcined in order to obtain TiO_2 in the form of powder. The physicochemical properties of the resulting TiO_2 were then determined by various methods.

2. EXPERIMENTAL

The experimental work was divided into four main stages. Firstly, TiO_2-based photocatalyst precursor ink was prepared with different concentration which were 0.10 M, 0.15 M and 0.20 M. The second stage was TiO_2 particle was synthesized from the TiO_2 photocatalyst precursor inks. For the third stage, the TiO_2 particle prepared was characterized by using FESEM equipped with EDX, XRD and DR-UV-Vis spectroscopy in order to determine the physicochemical properties of the ink. For the last stage, the stability of the ink prepared was determined.

3. RESULTS AND DISCUSSION

3.1 Stability of TiO_2 Photocatalyst Precursor Inks

The synthesized TiO_2 ink must be stable in order to not affect the system of the inkjet printer. There are two parameters that were observed during the study of the inks' stability, which were colour changes and presence of precipitates. The samples were wrapped by aluminium foil to prevent exposure to sunlight. Figure 1 shows the images of synthesized TiO_2 precursor ink samples that were taken from time to time. The colour of all samples became darker over time, but the most notable change was sample C with concentration of 0.20 M. After 9 weeks, there is were still no presence of precipitate in all the samples. This shows that the inks prepared were stable, even after a long period of time.

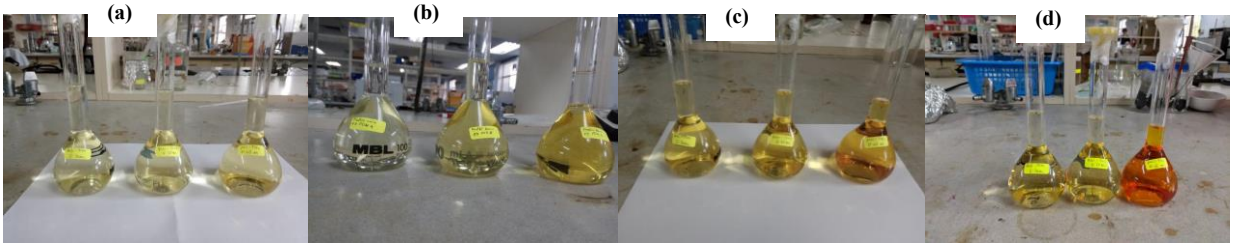


Figure 1 Images of the synthesized TiO_2 inks after (a) 1 week, (b) 3 weeks, (c) 6 weeks and (d) 9 weeks.

3.2 Characterization of TiO_2 Particles

The TiO_2 powders obtained from the inks were characterized using field emission scanning electron microscopy equipped with energy dispersive x-ray (FESEM-EDX). The surface morphology, particle size and elemental composition on the surface of the photocatalysts were determined using this analysis. The other instruments used to analyse the powder from the inks are XRD, DR-UV-Vis, FTIR and N_2 Sorption.

3.2.1 Morphology Studies by FESEM and Elemental Composition by EDX Analyses

The FESEM images in Figure 2 show the morphology of all the prepared TiO_2-based powdered photocatalysts in with different concentrations. All scanning was made with magnification of 80,000 times and 2.0 kV of scanning voltage. From the FESEM images, it can be clearly seen that the TiO_2 particles were almost spherical in shape. Based on the images, TiO_2 with concentration 0.10 M have particle size of 40 to 60 nm. TiO_2 with concentration of 0.15 M have particle size of 20 to 30 nm. For TiO_2 with concentration 0.20 M have particle size in range 40 to 70 nm. TiO_2 0.15 M shows the most uniform size and the least agglomeration compared to 0.10 M and 0.20 M.

Apart from that, EDX analysis was carried out to find out the distribution of elements present on the surface of the TiO_2 photocatalysts. Based on the EDX spectra shown in Figure 3, Figure 4 and Figure 5, the samples consist of titanium (Ti), oxygen (O) and carbon (C). No other element can be observed in the compound. The carbon might be due to the carbon tape used to mount the sample.

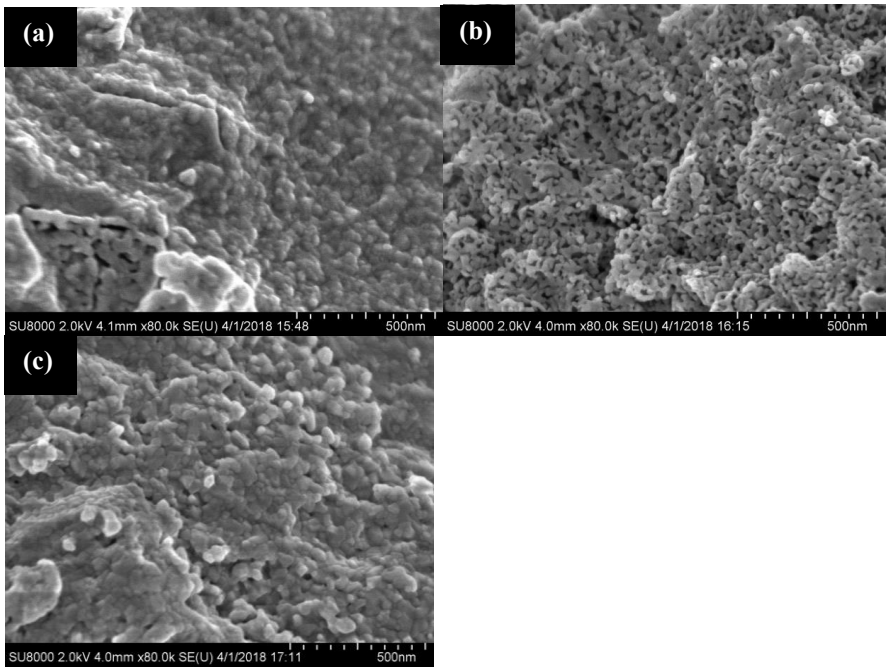


Figure 2 FESEM images of TiO_2 powders with different concentrations; (a) 0.10 M, (b) 0.15 M and (c) 0.20 M.

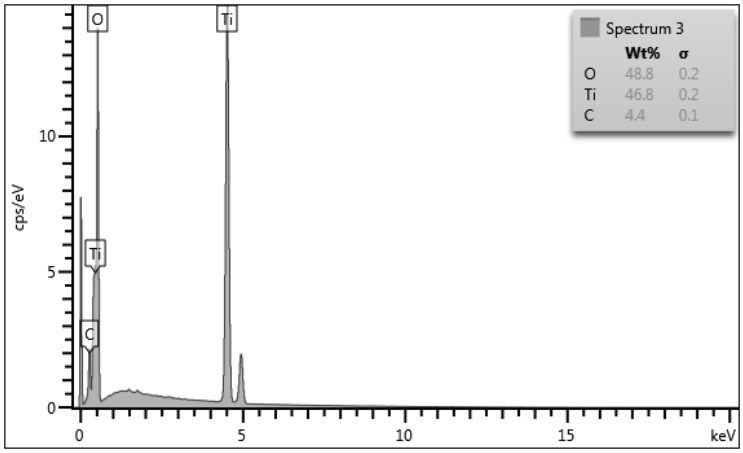


Figure 3 EDX spectrum of 0.10 M TiO_2 powder.

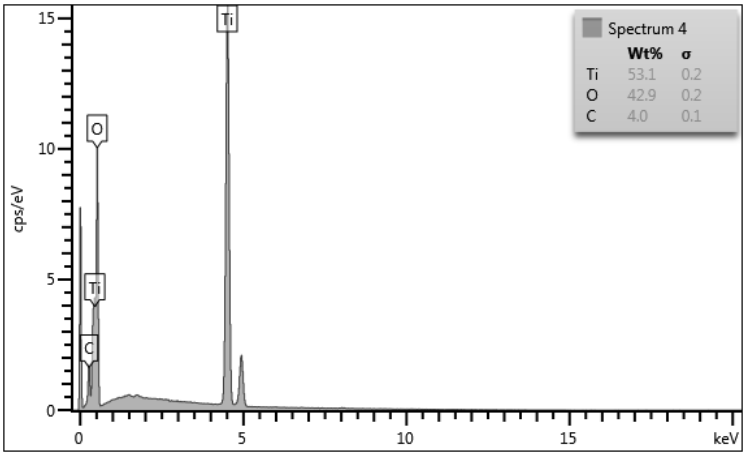


Figure 4 EDX spectrum of 0.15 M of TiO_2 powder.

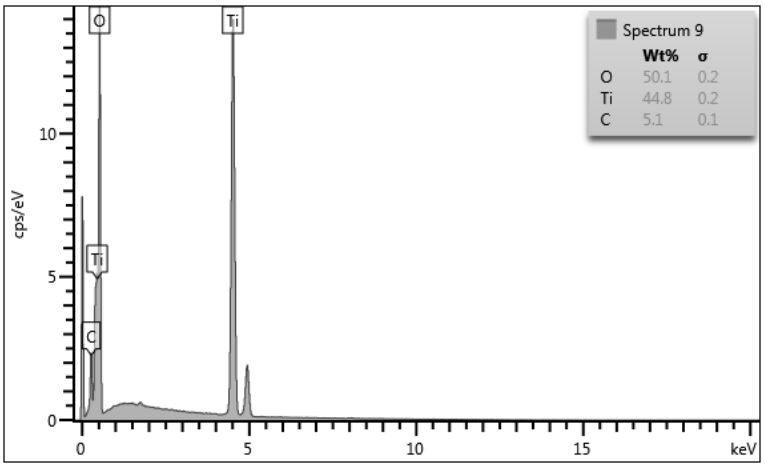


Figure 5 EDX spectrum of 0.20 M of TiO_2 powder.

Table 1 shows the atomic composition of the elements present in the synthesized TiO_2 powders. All of the samples show the highest percentage of Ti species compared to O and C elements. Although the results of the EDX analysis can be really useful, it only analyzes the specific area that was scanned and does not represent the whole sample.

Table 1 The atomic composition of elements present in the synthesized TiO_2 powders with different concentration

Sample	Concentration	Atomic Ratio (%)		
		Ti	O	C
A	0.10M	48.8	46.8	4.4
B	0.15M	53.1	42.9	4.0
C	0.20M	50.1	44.8	5.1

3.2.2 Crystallinity by XRD

The crystallinity and phase of the samples were determined by X-ray diffraction (XRD). Figure 6 shows the XRD patterns of the samples of TiO_2 with different concentrations, which were (a) 0.10 M , (b) 0.15 M and (c) 0.20 M. Based on the patterns, the existence of anatase phase is confirmed with the presence of the sharp diffraction peaks located at 2θ = 25.37 ° , 37.05 °, 37.90 °, 38.67 °, 48.16 °, 54.05 °, 55.20 °, 62.87 °, 68.98 °, 70.48 ° and 75.30 ° which correspond to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) respectively in all three of the TiO_2 samples. These findings were in accordance with previous researches [13].

The XRD patterns of all three concentration shows peak at 2θ = 25.37 ° corresponding to the (101) reflection of anatase TiO_2. There is no presence of rutile or brookite phases in the samples.

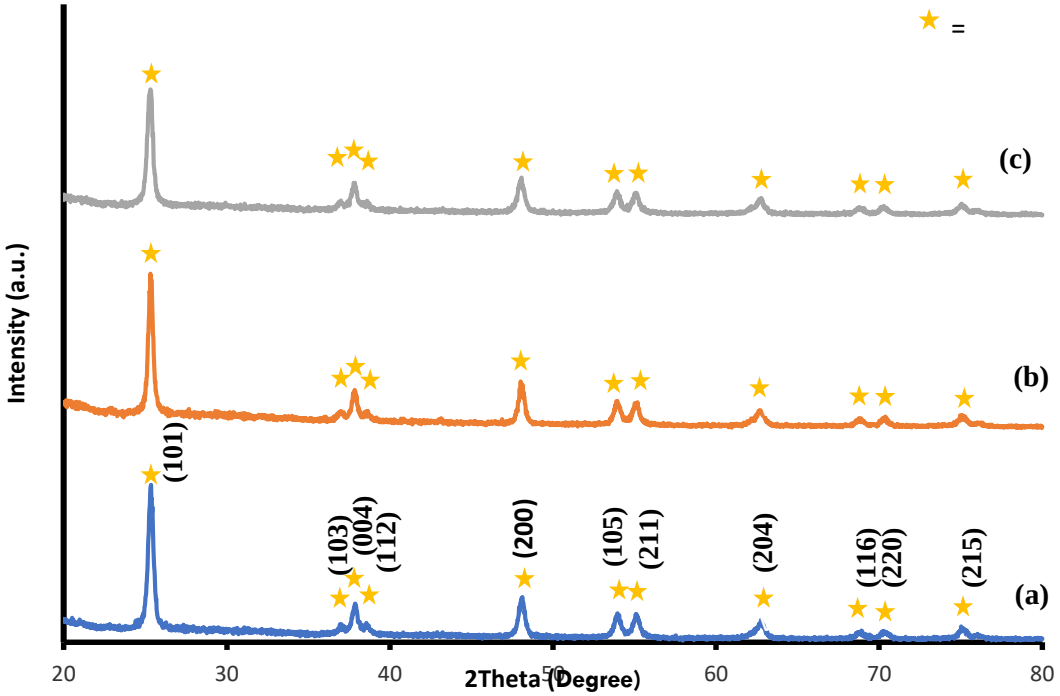


Figure 6 XRD patterns of the TiO_2 powders with different concentrations; (a) 0.10 M, (b) 0.15 M and (c) 0.20 M.

3.2.3 Band Gap Energy by Diffuse Reflectance Ultraviolet Visible (DR-UV-Vis) Spectroscopy

The diffuse reflectance UV-Vis spectra of the samples expressed in terms of Kubelka-Munk function are presented in Figure 7. Based on the spectra, there was one major peak at around 320 nm for all the prepared TiO_2 photocatalysts. The absorption peak of TiO_2 at around 320nm is due to the creation of octahedral polymeric Ti species. All samples of TiO_2 exhibited this major peak at around 320 nm although different concentrations of TiO_2 were used.

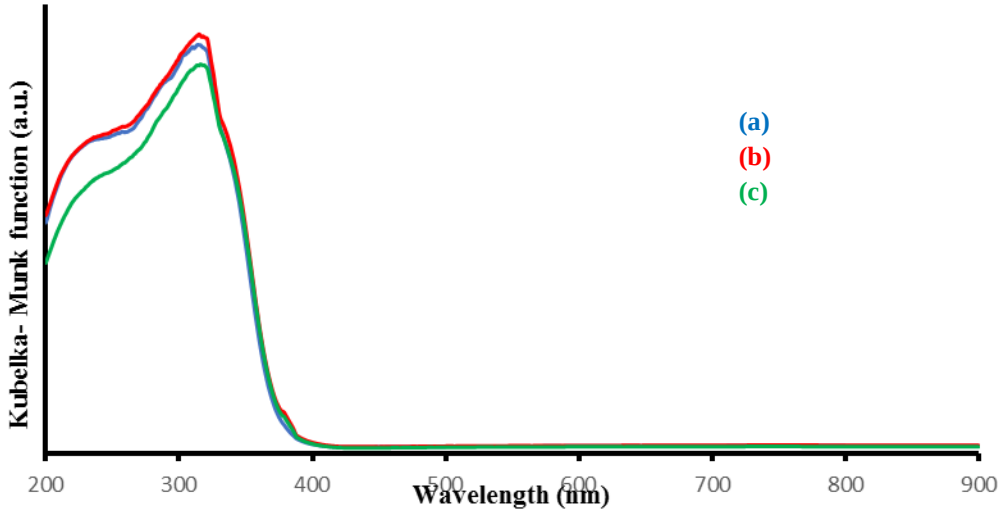


Figure 7 UV-Vis Diffuse reflectance spectra of TiO_2 powders with different concentrations; (a) 0.10 M, (b) 0.15 M and (c) 0.20 M.

Based on the UV-Vis absorption spectra, the effect of TiO_2 on the band gap energy (E_g) of the TiO_2 compound was then studied. Tauc Plot can be used to determine the E_g by plotting $(\alpha h\upsilon)^{2/n}$ versus $h\upsilon$. Anatase phase TiO_2 has been reported to prefer indirect transition, implying that n value should be 4. The E_g of the TiO_2 photocatalysts prepared was estimated based on the value of x-intercept by taking the linear extrapolation in the plot of $(\alpha h\upsilon)^{2/n}$ versus $h\upsilon$, as shown in Figure 8.

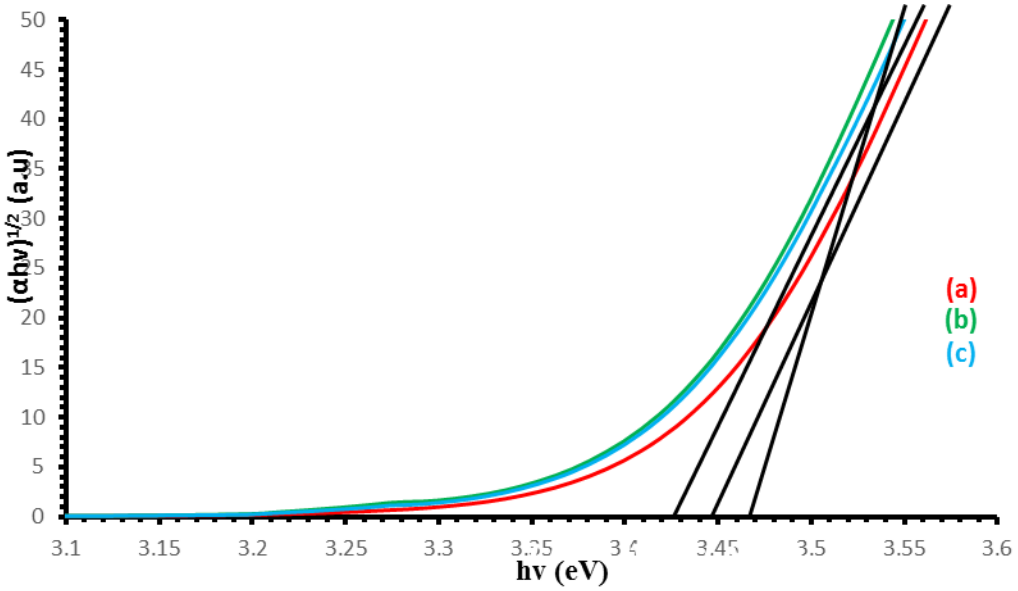


Figure 8 Tauc Plots of the samples with the TiO_2 concentrations of (a) 0.10 M, (b) 0.15 M and (c) 0.20 M.

Table 2 shows the E_g of the samples synthesized with different concentrations of TiO_2. The indirect band gap energies of the prepared TiO_2 photocatalysts for 0.10 M, 0.15 M and 0.20 M were estimated to be 3.42 eV, 3.46 eV and 3.44 eV, respectively. Based on these results, the band gap of the prepared photocatalysts were higher than that of pure TiO_2, which has band gap of 3.23 eV based on the literature. This might have been caused by the indirect transition of the synthesized TiO_2.

Table 2 E_g of the samples synthesized with different concentrations of TiO_2

Composition of TiO_2 composition	Band Gap Energy (eV)
Sample A with 0.10 M of TiO_2	3.42
Sample B with 0.15 M of TiO_2	3.46
Sample C with 0.20 M of TiO_2	3.44

3.2.4 Functional Groups by FTIR spectroscopy

Figure 9 shows the FTIR spectra of the TiO_2 powder photocatalyst samples with different concentration. All the spectra showed a band at 3208.14 cm^{-1} which correspond to the stretching of hydroxyl group. These hydroxyl groups and adsorbed water are usually present on the surface of TiO_2 [14]. Another peak was observed in the spectra at 1640.12 cm^{-1} which corresponded to the C=C groups. Peaks at 2341.65 cm^{-1} refer to the C-H stretching. The carbon might be the residue from the alkoxide precursor solution. The characteristic vibration of the inorganic Ti-O stretch was also observed in range of 650-690 cm^{-1}.

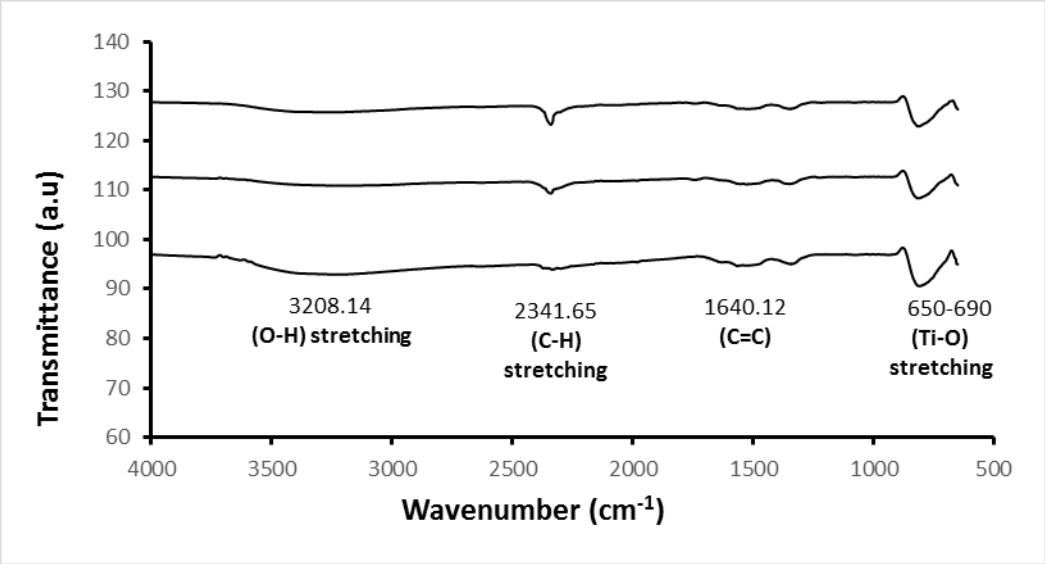


Figure 9 FTIR spectra of TiO_2 powder in different concentration (a) 0.10 M, (b) 0.15 M and (c) 0.20 M.

3.2.5 Surface Area and Pore Volume Analysis by N_2 Sorption

Figure 10 shows the nitrogen adsorption-desorption isotherm of TiO_2 powder. Based on the IUPAC classification, the isotherm for TiO_2 powder with concentration of 0.15 M can be classified as type V [15]. The hysteresis loop for this sample is type H3. According to IUPAC classification, type H3 hysteresis loop does not exhibit any limiting adsorption at high P/P_o, is observed with aggregates of plate-like particles giving rise to slit-shaped pores. The BET surface area obtained was 24.74 m²/g. The pore size was calculated using Barret-Joyner-Halenda (BJH) method. The total pore volume and pore size were 0.21 cm^3 g^{-1} and 30.4 nm respectively.

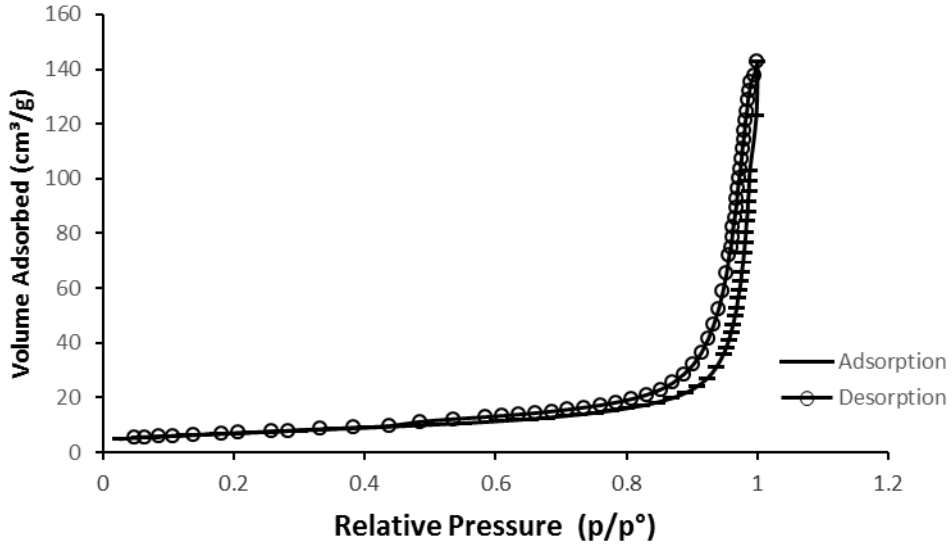


Figure 10 Adsorption isotherms for TiO_2 powder with concentration of 0.15 M.

4. CONCLUSION

In this study, TiO_2 photocatalyst precursor inks had been successfully prepared with three different concentrations, which were 0.10 M, 0.15 M and 0.20 M. The colour of the synthesized solution was transparent yellow. TiO_2 particles in powdered-form were then synthesized from the prepared inks. The solvent was removed from the ink solutions, dried in an oven and the resulting solid was grinded to powder form. The powder was yellow in colour. After being calcined in a furnace, pure white coloured TiO_2 photocatalyst were yielded. The physicochemical properties of the prepared TiO_2 powder has been successfully determined by using FESEM-EDX, XRD and DR-UV-Vis. Characterization by using FESEM showed that agglomeration took place among the TiO_2 particles. The most uniform particle size of TiO_2 and the least agglomeration was obtained with concentration of 0.15 M. Apart from that, the EDX results confirmed the presence of Ti and O elements in all the samples, proving the successful synthesis of TiO_2. Furthermore, the crystallinity of the TiO_2 powder by the XRD analysis shows that the titania was in anatase form, which is the best crystallographic phase for photocatalytic activity. Meanwhile, the UV-Vis spectroscopy identified the band gap energy of TiO_2 photocatalysts at the range of 3.42 to 3.46 eV. Based on these analyses, TiO_2 with concentration of 0.15 M showed the best physicochemical properties among all three samples. It can be concluded that the inks were stable and can be used for the next step. The best concentration for the TiO_2 precursor ink determined was 0.15 M. However, the printing of the prepared photocatalyst precursor ink cannot be carried out as the accommodation for small substrates in the modified printer has yet to be successful.

ACKNOWLEDGEMENT

The authors gratefully acknowledge funding from Ministry of Science, Technology and Information, Malaysia under Fundamental Research Grant Scheme (R.J130000.7826.4F923) and Ministry of Education, Malaysia, Universiti Teknologi Malaysia under Research University Grant (Q.J130000.2526.18H69).

REFERENCES

[1] Zhang, Y., Xu, Q., Lamson, J.J., Zhao, R. (2009) Photocatalytic purification of volatile organic compounds in indoor air: A literature review. Atmos. Environ. 43, 2229–2246.
[2] Carp, O.; Huisman, C.L.; Reller, A. (2004) Photoinduced reactivity of titanium dioxide. Prog. SolidState Chem. 32, 33–177.
[3] Lin, H., Deng, W., Zhou, T., Ning, S., Long, J., Wang, X. (2015). Iodine-modified nanocrystalline titania for photo-catalytic antibacterial application under visible light illumination. Applied Catalysis B: Environmental, 176-177, 36-43.
[4] Chen, Z., Zhong, W., Liang, Z., Li, W., He, G., Wang, Y., Li, W., Xie, Y., He, Q. (2013). Photocatalytic Activity Enhancement of Anatase TiO2 by Using TiO. Journal of Nanomaterials, 1-9.
[5] Nur, H., Chandren, S., & Yuan, L. S. (2014). Synthesis of titania with different shapes. In Proceedings of 2014 International Renewable and Sustainable Energy Conference, IRSEC , 531-535.
[6] Deng, X., Zhou, S., Wu, L., Gu, G., Yang, J. (2010). Formation of supra-amphiphilic self-cleaning surface through sun-illumination of titania-based nanocomposite coatings. Surface and Coating Technology, 205, 2556-2561.
[7] Bestetti, M.; Sacco, D.; Brunella, M.F.; Franz, S.; Amadelli, R.; Samiolo, L. (2010). Photocatalytic degradation activity of titanium dioxide sol-gel coatings on stainless steel wire meshes. Mater. Chem. Phys. 124, 1225–1231.
[8] Chandren, S., Ismail, K., Nur, H., & Ohtani, B. (2017). Preparation of titania on stainless steel by the Spray-ILGAR technique as active photocatalyst under UV light irradiation for the decomposition of acetaldehyde. Applied Sciences (Switzerland), 7(7), 698.
[9] Yao, H.C., Wu, W.T., Chiu, M.C., and Shieu, F.S. (2002). Characterization and microstructure of titanium dioxide prepared frequency magnetron sputtering. Journal of Non-Crystalline Solids, 303, 134.
[10] Maruyama, T., and Arai, S. (1992). Titanium dioxide thin films prepared by chemical vapor deposition. Solar Energy Materials and Solar Cells, 26, 323-329.
[11] Gadea, C., Marani, D., and Esposito, V. (2017). Nucleophilic stabilization of water-based reactive ink for titania-based thin film inkjet printing. Journal of Physics and Chemistry of Solids, 101, 10-17.
[12] Cherrington, R., Wood, B.M., Salaoru, I., Goodship, V. Digital Printing of Titanium Dioxide for Dye Sensitized Solar Cells. J. Vis. Exp. (111).
[13] Bagheri, S., Shameli, K., and Hamid, S, B. (2013). Synthesis and Characterization of Anatase Titanium Dioxide Nanoparticles Using Egg White Solution via Sol-Gel Method. Journal of Chemistry. Vol. 2013, Article ID 848205, 5 pages.
[14] Behnajady, M.A,. Li, Z., and Sogaard, E.G. (2008). Influence of OH groups on the photocatalytic acticity and photoinduced hydrophilicity of microwave assisted sol-gel TiO_2 film. Applied Surface Science, 255, 8054-8062.
[15] Sing, K.S W., Everett, D.H., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquerol, J., & Siemieniewska, T. (2008). Reporting Physisorption Data for Gas/Solid Systems Handbook of Heterogeneous Catalysis: Wiley-VCH Verlag GmbH & Co.KGaA.