eProceedings Chemistry 2 (2017) 255-261

eISSN2550-1453 http://eproceedings.chemistry.utm.my/

Synthesis and characterization of carbon-doped titanium dioxide driven visible light photocatalyst

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Article history :
Received 20 June 2017
Accepted 21 July 2017

The as-synthesized C-doped TiO_2

ABSTRACT

The carbon-doped titanium dioxide (C-doped TiO_2) photocatalysts were synthesized by a sol-gel method without the addition of external carbon sources. Titanium (IV) butoxide and ethanol were used as the starting materials in which the titanium (IV) butoxide act as a titanium precursor and also a carbon sources. The physical properties of the C-doped TiO_2 synthesized at different calcination temperatures were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), diffuse reflectance UV-Vis spectroscopy (DR UV-Vis), and photoluminescence (PL). The peak of carbon at about 1376 to 1538 cm^{-1} from FTIR spectra of carbon-doped TiO_2 showed the decrease in intensity as the calcination temperature increases to 300 ºC and disappears when calcined at 400 ºC. The C-doped TiO_2 which calcined at 200 and 300 ºC have the ability to absorb visible light as demonstrated in DR UV-Vis spectra while PL analysis gives a result of very small emission intensity at 465 nm. The photocatalytic activity of synthesized photocatalyst was examined by degradation of methylene blue as a model pollutant for 240 min reactions under visible light irradiation. The C-doped TiO_2 which calcined at 300 ºC was found to be an active photocatalyst under visible light irradiation which exhibits 10 percent degradation of methylene blue. It can be deduced that the carbon doping with a controlled calcination temperature have contribute to the photocatalytic activity of the photocatalysts.

Keywords: Photocatalysis, carbon-doped titanium dioxide, self-doping, sol-gel method.

INTRODUCTION

Through the years, the development of various chemical technologies are become the major interest where involving the interaction of light with molecules such as photocatalysis. The term photocatalysis itself consists of two combinations of photochemistry and catalysis. Photocatalysis can be defined as acceleration of the rate of chemical reaction, induced by the absorption of light by a catalyst or co-existing molecule [1]. In another word, the catalyst may accelerate or speeding up the rate of chemical reaction by its interaction with the substrate depending on the mechanism of the photoreaction.

A photocatalyst can be chemically activated by light irradiation. One of the excellent photocatalyst nowadays is titanium dioxide (TiO_2) which also called titanium (IV) oxide or titania due to its properties such as high photo-oxidation power, excellent stability, non-toxicity and cost effective material [2]. TiO_2 exists in amorphous and crystalline phase. The crystalline phases include anatase, rutile and brookite. Although both anatase and rutile having the tetragonal crystal structures, they have different chemical and physical properties as well as their applications. The technology of titanium dioxide photocatalyst has developed rapidly since its properties are the main advantages for it to contribute in various applications such as environmental purification, decomposition of organic compound, self-cleaning coating and white pigment for paint [3, 4].

Even though titanium dioxide is one of the most promising catalysts, yet, the current situation is far from being satisfactory. As the solar energy contains only 5% ultraviolet radiation, there are limited environmental applications of pure titanium dioxide, whereby the titanium dioxide cannot fully utilize the solar energy. Photocatalytic treatment of pollutants by semiconductor photocatalyst titanium dioxide needs to be improved by enhancing the absorption to the visible region. Thus, numerous study towards the modification of titanium dioxide has been developed for fully utilize the visible light which will be used in photocatalytic reaction [1, 5]

The performance of the titanium dioxide can be improved by modifying the physicochemical properties of photocatalyst. There are many forms of modification that can be applied to the photocatalyst material in order to enhance the activity of that material towards the photoreaction. The three main forms of modification are bulk modification, surface modification, and the use of composite materials [5]. Doping method in bulk modification refers to controlling its electronic properties by adding guest chemical species with metals like Ag and Fe or nonmetal such as C, F, S and N elements without altering its crystalline structure [3].

Doping titanium dioxide with carbon is currently a large interest as many recent publications have reported the results of visible light absorption by carbon-doped titanium dioxide [2, 3] Hence, in this study, the carbon-doped titanium dioxide with high visible light photocatalytic activity was prepared and the degradation of methylene blue was employed to investigate the performance of the synthesized carbon-doped titanium dioxide.

EXPERIMENTAL

The experiment was divided into three main stages. The first stage was on the synthesized of C-doped TiO_2 by self-doping sol gel method at different calcination temperatures. Titanium (IV) butoxide and ethanol were used as the starting materials without the addition of any other carbon sources since the titanium (IV) butoxide is a dual function material which acts as titanium precursors and also as a carbon sources. The sol-gel synthesis involves the hydrolysis and condensation process. The formation of homogeneous white sol of the mixture was allowed to age before drying it in oven at 105 ºC.

$$Ti(OBu)_4 + 2H_2O \rightarrow TiO_2 + 4BuOH$$

The synthesized C-doped TiO_2 were calcined at different calcination temperatures of 200, 300 and 400 ºC for 6 hours.

The second stage was the characterization of as-synthesized C-doped TiO_2 by using attenuated total reflectance-Fourier transform infrared (ATR-FTIR), diffuse reflectance ultraviolet visible (DR UV-Vis) and photoluminescence (PL).

The last stage was the photocatalytic degradation of methylene blue as the model pollutant under visible light. The degradation of methylene blue was monitored using ultraviolet-visible spectroscopy (UV-Vis). A 150 W halogen fiber optic light illuminator (BOTE) lamp was used as visible light source.

RESULTS AND DISCUSSION

3.1. The Effect of Various Calcination Temperature

The as-prepared carbon-doped titanium dioxide was in the form of crystal powder. The effect of calcination temperature can be seen from the colour changes of the samples. The uncalcined sample denoted as CT-1 has creamy white coloured powder. Dark brown sample of CT-2 obtained after the sample being calcined at 200 ºC. For CT-3, grey colour formed which was calcined 300 ºC while at 400 ºC calcination, white powder was formed and labelled as CT-4. The colour of the samples is shown as in Figure 1. The change of colour was much related to the carbon content in the TiO_2 [6]. The decrease in colour intensity from dark colour to white might have resulted from the gasification of carbon at higher temperature, where desorption of carbon from the surface of photocatalyst occurred [7]. The effects of calcination temperature was further analysed using the instrumental analysis.

Figure 1: Photograph of synthesized carbon-doped TiO_2

Characterization

3.2.1 Fourier Transform Infrared (FTIR)

The FTIR spectra carbon-doped TiO_2 with various calcination temperatures at 200, 300, 400 ºC and uncalcined sample are presented in Figure 2. The intensity of each band related to certain functional group indicates its amount exist in the particular sample. The broad absorption band around 3244 cm^{-1} is assigned to the O-H stretching vibration mode of adsorbed water molecule and the surface hydroxyl groups on TiO_2 while peak located at around 1634 cm^{-1} is attributed to the corresponding O-H bending vibration [3, 8]. The intensity of the O-H bands at 1634 cm^{-1} showed a decrease as the calcination temperature increases. The presence of hydroxyl groups inhibit the recombination of photogeneration of electrons and holes [6]. Also, hydroxyl groups could promote the formation of hydroxyl radical ($^{\bullet}OH$). Thus, the presence of hydroxyl groups could enhance the photocatalytic activity of the photocatalysts.

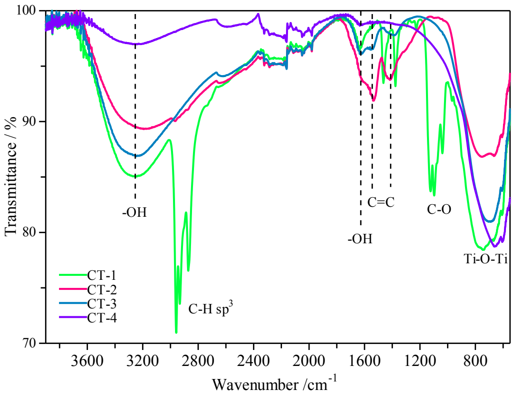

Figure 2: The FT-IR spectra of (a) CT-1, (b) CT-2, (c) CT-3 and (d) CT-4

For the peak around 2958 cm^{-1}, 2933 cm^{-1} and 2872 cm^{-1} are probably belonged to C-H sp^3 bond which is only appeared in CT-1 spectrum. The absence of this peak in CT-2, CT-3 and CT-4 is due to the decomposition of that organics at the high temperature. The bands appear at about 1376 to 1538 cm^{-1} in the FTIR spectra of CT-1, CT-2 and CT-3 indicating the presence of carbon-related substrate. The band intensity of carbon related substrate decreases as the calcination temperature increases to 300ºC. While at 400 ºC, these peaks are no longer appear in FTIR profile due to complete decomposition of carbonaceous materials [8]. The broad band in the range of 400-800 cm^{-1} is attributed to the stretching vibrations of the Ti-O and this broad band is shown in all synthesized carbon-doped titanium dioxide. As the calcination temperature increases from 200 to 400 ºC, the intensities of Ti-O vibration band increases. This is due to the rearrangement of Ti-O network in the formation of titanium dioxide crystal.

3.2.2 Diffuse Reflectance UV Visible (DR UV-Vis)

DR UV-Vis analysis was performed to study the optical properties of C-doped TiO_2 that was synthesized at different calcination temperatures. The diffuse reflectance spectra and the corresponding Kubelka-Munk plots of CT-1, CT-2, CT-3 and CT-4 are illustrated in Figure 3.

Based on the Kubelka-Munk plot, it clearly show that the C-doped TiO_2 prepared exhibit a significant shift of the absorption edge of where the absorption are slightly shifted towards the visible region as compared to the uncalcined C-doped TiO_2. This phenomenon is called red shift in which the absorption edge is at higher wavelength. It can be suggested that the C-doped TiO_2 with higher calcination temperature up 400 ºC exhibit a significant absorption at higher wavelength.

The band gap of each samples was obtained from the x-intercept of the $(F(R)h\,v)^2$ against hv plot as shown in Figure 4. The uncalcined C-doped TiO_2 synthesized has the highest band gap energy with 3.60 eV followed by CT-4 with 3.25 eV and the lowest band gap energy is CT-3 which is 3.20 eV. The band gap energy of CT-2 cannot be determined.

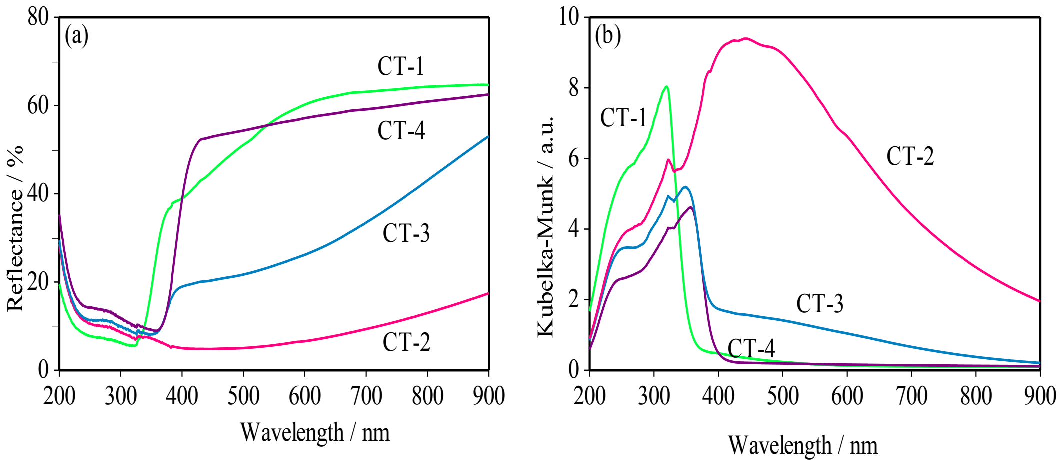

Figure 0: (a) Diffuse reflectance spectra and (b) the Kubelka-Munk plots for the carbon-doped TiO_2 samples

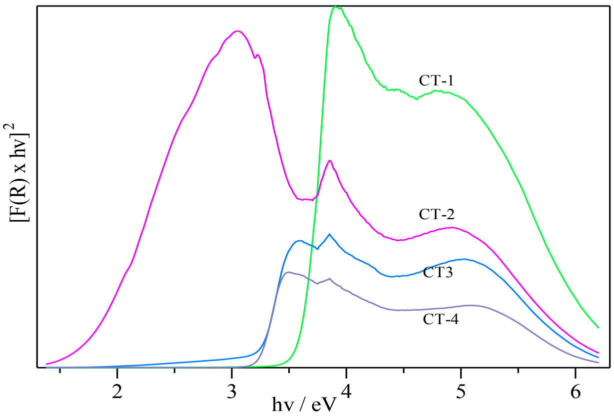

Figure 4: The plot of (F(*R*)*h v*)2 against hv

3.2.3 Characterization by Photoluminescence (PL)

The effect of calcination temperatures was further studied using photoluminescence (PL) spectra. The PL signal generated from the radiative recombination of photogenerated charge carriers that are produced under an excitation of the light source. This technique is very sensitive to the surface and bulk defects where these defects play an important role in the performance of the photocatalysts [9]. Figure 5 depicts the PL spectra of C-doped TiO_2 samples which calcined at 200, 300 and 400 ºC and the uncalcined C-doped TiO_2 in the range of 325 to 600 nm wavelength excitation source.

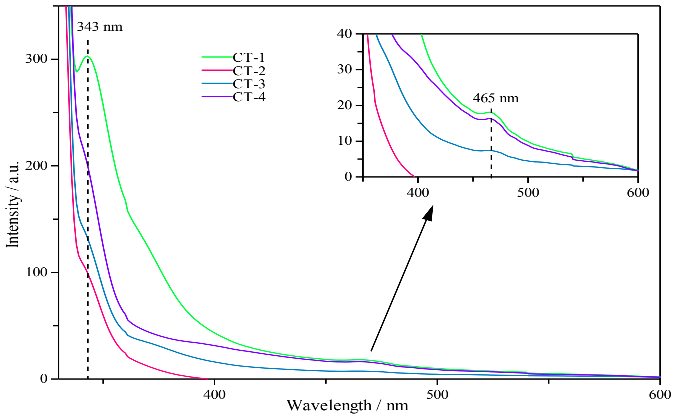

Figure 5: Emission of C-doped TiO_2 series

The as-synthesized C-doped TiO_2 photocatalyst exhibits a visible emission peak at 465 nm when excited with the light of photon energy higher than 325 nm. The presence of PL bands at the long wavelength side of anatase TiO_2 much related to oxygen vacancies attribution. Generally, the oxygen defects associated with shallow traps were illustrated at 465 nm below the conduction band [10]. Thus, the 465 nm bands shown in Figure 5 can assigned as the oxygen vacancy states. The intensity of the PL band increases with the increase the calcination temperature up to 400 ºC.

The carbon doping has created the oxygen defects with associated with the formation of F and F^{2+} trap centers. F center is the site where there are the two electrons are being trapped in oxygen vacancy while F^{2+} center is the oxygen vacancy site without electron trapped [10]. These charged sites of oxygen vacancy able to delay the rate of recombination of electrons and holes. The mobility of the free electrons is reduced by the carbon doping to slow down the recombination e^-/h^+ phenomenon [11].

Photocatalytic Activity

3.3.1 Calibration Curve

The calibration curve was plotted by considering the λ max of MB at about 664 nm in UV-Vis spectra where this calibration giving a linear graph of absorbance against concentration with R^2 =0.9936. In this case, Beer's Law was applied in which under the ideal conditions, the concentration of solution and its absorbance is directly proportional where at a high concentration of solution, there will be high absorbance as the solution absorbs more light. Based on this law, it is possible to determine the unknown concentration by considering its absorbance [12]. Thus, it is quite important to determine the concentration of the degraded MB solution.

3.3.2 Adsorption-Desorption Equilibrium throughout Degradation

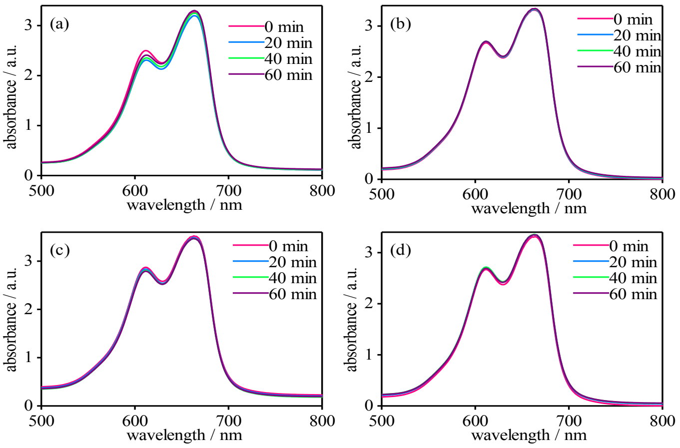

Figure 6: UV-Vis spectra MB solution under dark reaction containing (a) CT-1, (b) CT-2, (c) CT-3 and (d) CT-4

The preliminary studies of MB adsorption by the same amounts of CT-1, CT-2, CT-3 and CT-4 at room temperature were conducted for the confirmation of the complete adsorption before being irradiated. This reaction is performed in the dark condition for about 1 hour in which the adsorption is determined for every 20 minutes. Based on the Figure 6, it can be seen that most of the adsorption occurred within 40 min. However, Matos *et al.,* (2010) [13] have reported that the complete adsorption achieved at the first 30 min of the dark reaction in the presence of photocatalyst. The extension period of dark reaction to 60 min was done to ensure a proper equilibrium of adsorption.

3.3.3 Photocatalytic Activity under Visible Light

After the complete adsorption in the dark reaction, the MB solution containing prepared sample was irradiated by visible lamp. The concentration of MB solution for every 30 min were recorded until 4 hours (240 min) reaction and the temperature of the MB solution slightly increases to 40-45 ºC after 30 min being irradiated with visible light source. Figure 7 represents the photocatalytic activity of C-doped TiO_2 corresponds to the concentration of the MB solution. Blank is the MB solution without the presence of any photocatalysts sample.

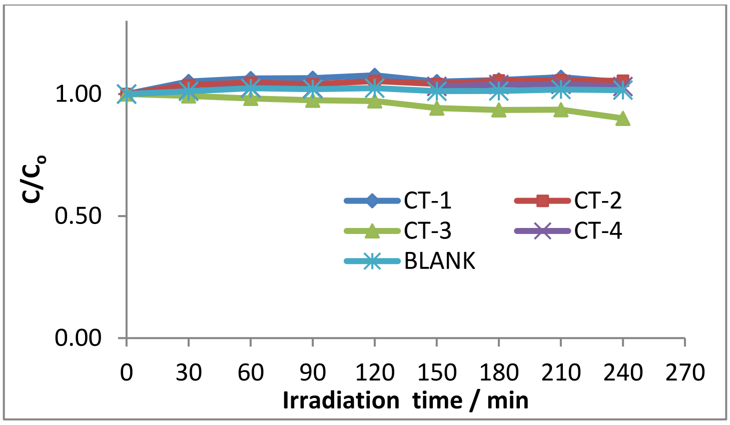

Figure 7: The photocatalytic activity for methylene blue degradation of C-doped TiO_2

The degradation (D) percentage was measured using the formula:

$$\%D = \frac{Co - C}{Co} \times 100\%$$

where,
Co = Initial concentration of sample
C = Concentration of sample after irradiation under visible light

Based on the Figure 7 above, there is no degradation of MB solution upon irradiation with visible light. This shows the MB solution is very stable towards photolysis. The MB solution that are treated with the prepared CT-1, CT-2 and CT-4 also shows no photocatalytic activity in which can be deduced that these three samples are not active in degradation of MB under light irradiation for 4 hours reaction. Differ with CT-3 sample, the MB solution shows decreasing in concentration. It was observed that C-doped TiO_2 which was calcined at 300 ºC able to degrade MB with 10% degradation after 4 hours reaction under visible light irradiation.

CT-1 shows no photocatalytic activity towards MB degradation is due to its high band gap energy which is about 3.60 eV. CT-1 is unable to absorb visible light in order to degrade MB. CT-2 which was calcined at 200 ºC also shows no photocatalytic activity. This might due to its dark colour which represents the abundance of carbon content in TiO_2. This carbon might cover the photocatalyst surface where the active site on the surface is not available for the reaction to take place.

Besides that, CT-4 is also unable to degrade MB. According to FTIR spectrum of CT-4, the carbon-related substrates is no longer appears due to the complete decomposition at 400 ºC. Although it has almost same band gap energy with CT-3, CT-4 does not show the higher absorption towards the visible region. In contrast, the absorption of CT-3 is slightly higher up to 700 nm. This absorption feature indicates that CT-3 can be activated by visible light. Thus, CT-3 is able to degrade MB in the presence of visible light. Since the percentage degradation of CT-3 is low, the factors such as temperature and visible light intensity must be monitored. These parameters should be constant throughout the reaction to reduce the errors that could affect the results of the reaction.

4. CONCLUSION

In this research, carbon-doped TiO_2 photocatalysts have been successfully synthesized by self-doping of sol gel method. The synthesized C-doped TiO_2 were calcined at different calcination temperatures of 200, 300 and 400 ºC for 6 hours. From the analyses conducted, the ATR-FTIR has proven the presence of carbon-related substrate in TiO_2 samples at about 1376 to 1538 cm^{-1}. The peak of the carbon-related substrate showed a decrease in intensity from the uncalcined sample to the higher calcination temperature of 200 and 300 ºC, while at 400 ºC, the carbon peak start to disappear indicates the decomposition of carbon at high temperature. For DR UV-Vis, the C-doped TiO_2 synthesized that was undergo calcination process shows red shift absorption compared to the uncalcined C-doped TiO_2 where the sample that was calcined at 200 and 300 ºC shows a significant absorption at visible region while the sample that was calcined at 400 ºC shows almost no absorption at visible region. While, PL analysis depicts emission intensity at 465 nm which related to oxygen vacancy state associated with the formation of F and F^{2+} trap centers for the reducing of recombination e^-/h^+ phenomenon. The degradation percentage of methylene blue as a model of pollutant by photocatalyst under visible light irradiation represents the effectiveness of the photocatalyst. Based on the results obtained, C-doped TiO_2 synthesized that was calcined at 200 and 400 ºC and the uncalcined one shows no degradation towards the methylene blue solution while the sample that was calcined at 300 ºC shows small percentage of degradation which is about 10 percent degradation.

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