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Abstract. The biochar/TiO_2 thin layer has been made by using the sol-gel method and the coating technique by Doctor Blade method. The variation of biochar on TiO_2 were 0%, 1%, 2%, 3% and 4%. The characterization was done by using XRD (X-Ray Diffractometer) to see the crystal structure of samples and UV-Vis spectrophotometer to obtain the value of *band gap energy*. Based on XRD data, it was obtained that the crystal structure of all samples is anatase TiO_2. The crystalline size of all samples has no significant difference by the increasing of doping percentage. The smallest crystal size was at the addition of 3% and 4% bio char which was 118.22 nm. The results of UV-Vis characterization showed the lowest value of *band gap energy* was at sample doping 1% bio char which was 3.25 eV. *Band gap energy* value for doping sample above 1% showed an increase of *band gap energy* of Biochar-TiO_2.

1. Introduction

Semiconductor material that has been observed by many researchers all over the world is TiO_2. These recent years, TiO_2 film has been extensively studied due to its interesting photocatalytic nature. TiO_2 thin film finds various applications in various fields such as photocatalysis, gas sensing, anti-reflective and protective layer, antibacterial layer and optic, dielectric film for new generation terrain effect of transistor, solar cell, etc [1].

If the thin layer of TiO_2 is applied to photocatalyst and solar cell, *band gap energy* that is wide enough from TiO_2 which is around 3,2 – 3,9 eV makes TiO_2 cannot work optimally. However, TiO_2 works effectively only at the UV wave length which means the solar energy that can be beneficial is only around 5%. Due to that reason, the modification of TiO_2 is necessary to increase the absorption of sunlight. It means, the *band gap energy* from TiO_2 must be minimized so the sunlight can be absorbed in maximum amount, and it is usually done through doping. Many doping materials that have been

used increase the TiO_2 photocatalyst performance, such as transition metal (Ti, Fe, Ru, Au, and Mo) [2-4] and non-metal (C, N, and S) [5-7].

But the problem is, those materials mentioned above are relatively expensive, non-renewable, and risky to be secondary pollutants. Getting inexpensive and eco-friendly doping that is also able to optimize TiO_2 performance need to be done. In the research, biochar made of organic waste / field waste is used as TiO_2 doping. Biochar is porous solid residue that contains rich carbon. Supported by the unique physicochemistry characteristic of biochar and its low cost, stable, eco-friendly, reachability and sustainability, biochar is the right choice as the doping for TiO_2 [8,9].

Previous research by Zhang, et al. [10] carried out photocatalyst test for TiO_2-biochar that is synthetized by using sol gel method. TiO_2-biochar showed better ability in sulfamethoxazole (SMX) than pure TiO_2. Lisowski, et al. [11] also has tested TiO_2-biochar as degradation in liquid phase and methanol selective oxidation in gas phase. The technique used in the process of Biochar/TiO_2 layer deposition is on glass substrate preparation by using *doctor blade. Doctor blade* is the technique used to make layers by depending on basting. This technique is used because of its simple process and low in budget.

This research is done by making layer of TiO_2 without biochar doping and with biochar doping in concentration vary between 1 to 4%. This doping is expected to be able to minimize *band gap energy* of TiO_2. The reduction of *band gap energy* can be known by using UV-Vis characterization. Based on the test of UV-Vis the value of maximum and minimum transmittance is obtained. The data are processed in *Swanepoel* equation and *Touch Plot* method to determine the *band gap energy*. And to know the structure and the size of crystal from Biochar/TiO_2, XRD (*X-ray diffraction*) analysis is executed.

2. Methods

This research took place in integrated laboratory of Science and Technology Faculty, Jambi University, Indonesia, which was started in May until August 2019. As the beginning, glass substrate preparation was cleaned in detergent solution to remove dirt like oil, dust and many more. Next, it was cleaned by using *Ultrasonic Cleaner* for 30 minutes in the alcohol 70% in order to get optimal cleaning. And the last step, glass substrate was dried by using hair drayer.

Biochar from empty bunches of palm oil, also known as *Tandan Kosong Kelapa Sawit* (TKKS) was washed, grilled, and pyrolysis by flowing it with nitrogen for 3 hours at 500 ºC temperature. After the biochar got pyrolysis, the washing was done by using dionizer water (DI) to remove ash left after pyrolysis, and then it was grilled again at 80 ºC temperature for two hours [12]. Next, biochar colloid/TiO_2 was made by dissolving 2 gram of pilivinil alcohol (PVA) into aquades, and then stirred by using magnetic stirrer. During the stirring process, the measuring cup was covered by using aluminium foil. The purpose is to reduce evaporation during the stirring process itself. TiO_2 powder then was added as much as 2 gram and stirred for 2 hours at 80°C temperature. At last, biochar was dissolved in 2 ml of aquades then mixed into TiO_2 colloid. It was stirred again by using magnetic stirrer for 1 hour at the same temperature [6].

TiO_2 colloid without doping and biochar/TiO_2 was deposited on preparation glass by using doctor blade technique. The colloid was dropped on the glass by using drop pipette then flattened by using glass rod until it cover up all glass surface evenly. The glass was heated up at 150°C temperature for 30 minutes to remove water vapour in the layer. Produced Biochar/TiO_2 layer was then characterized by using *ultraviolet visivel* (UV-Vis), after the maximum and the minimum transmittance values were gotten, the data were processed by using *Swanepoel* equation (equation 1) to determine the value of refractive index (equation 2), layer thickness (equation 3) and absorption coefficient (equation 4) of thin layer of Biochar/TiO_2 [13].

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{{n_s}^2 + 1}{2} \qquad (1)$$

$$n = \sqrt{N + \sqrt{N^2 - {n_s}^2}} \quad (2)$$

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (3)$$

$$a = -\frac{1}{d} \ln T \quad (4)$$

The next process is using *Tauc Plot* method by drawing extrapolation line at the linear area of the hv and $(\alpha hv)^n$ relationship chart until it cut energy axis by using software origin that is suitable with Touc equation (equation 5) [14].

$$(\alpha hv)n = B(hv - Eg) \quad (5)$$

Explanation; T_M = maximum transmittance value; T_m = minimum transmittance value ; n_s = refractive index of glass ; n = refractive index ; d = layer thickness ; λ_1 = wave length 1 λ_2 = wave length 2 ; a = layer absorption coefficient; T = transmittance

XRD characterization to recognize the structure and the crystal size of Biochar/TiO_2 was done by using *Scherrer* equation (equation 6) [15].

$$D = K \frac{\lambda}{B \cos\theta} \quad (6)$$

Explanation; D is crystalline (nm), K is constant (0,96), B is graph width (Rad), λ is wave length (1,506 Å) and θ is maximum angle (Rad).

3. Results and discussion

Biochar/TiO_2 layer can be grown in glass substrate by using doctor blade technique. The layer will be white in color and spread evenly on the glass substrate. The effect of biochar doping towards the optic nature of TiO_2 can be known by using UV-Vis characterization. It was done by obtaining the transmittance value from biochar/TiO_2 layer. The sample was transmitted with 200-800 nm wave length and 50 nm in range. The range of UV is 200-400 nm while the visible is 400-800 nm. The result of transmittance measurement of biochar/TiO_2 can be seen at figure 1.

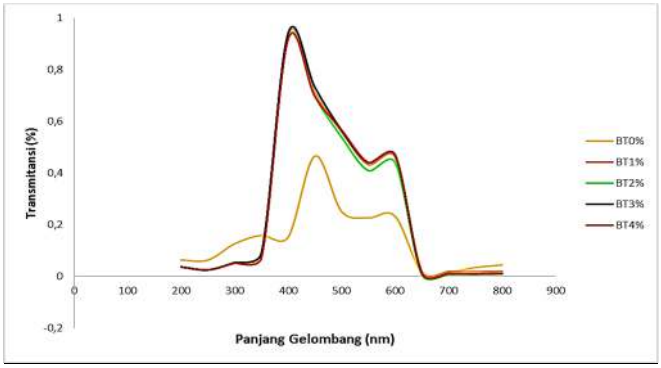

Figure 1. Transmittance of Biochar/TiO_2 layer.

From this image, it can be seen that the transmittance value of TiO_2 without biochar doping (BT0%) is lower than TiO_2 with biochar doping (BT1%, BT2%, BT3% dan BT4%), it indicates that the addition of biochar to TiO_2 increases its transmittance value. The enhancement of transmittance value shows

relatively high optical absorption at that wave length. In the other hand, the variation in biochar percentage (BT1%, BT2%, BT3% dan BT4%) did not change the transmittance value significantly. Optical transmittance value is affected by suitable doping percentage to make the bond of the structure to have fine quality, which means, biochar/TiO_2 was grown evenly and homogeny in the glass substrate. The fine quality thin layer is the layer that can transmit all visible light spectrums. In the figure 1, TiO_2 layer with biochar doping has optimal transmittance at the 400 nm wave length while without the doping, the optimal transmittance is in 450 nm wave length.

From the sample BT0%, TM_1, TM_2, Tm_1, Tm_2 obtained are 0,4653; 0,2323; 0,2263; 0,1517 with the wave length 1 λ_1 = 450 and wave length 2 λ_2 = 600. From the sample BT 1% the value of transmittance increased from 0,4653 to 0,9323 with the larger range of wave length which is from 400-800 nm. The wave length that is getting larger will increase the absorption of electron of UV and visible light. It gives good impact to photocatalyst application and solar cell.

Based on transmittance spectrum of UV-Vis, the calculation of *band gap energy* is begun by using Swanepoel equation to determine the value of refractive index, layer thickness, and absorbs coefficient from biochar/TiO_2 layer [13]. The process was continued by using Tauc Plot method which is pulling extrapolation at the linear area from hv dan $(\alpha hv)^n$ relationship graph until it cut energy axis [14] as shown in figure 2.

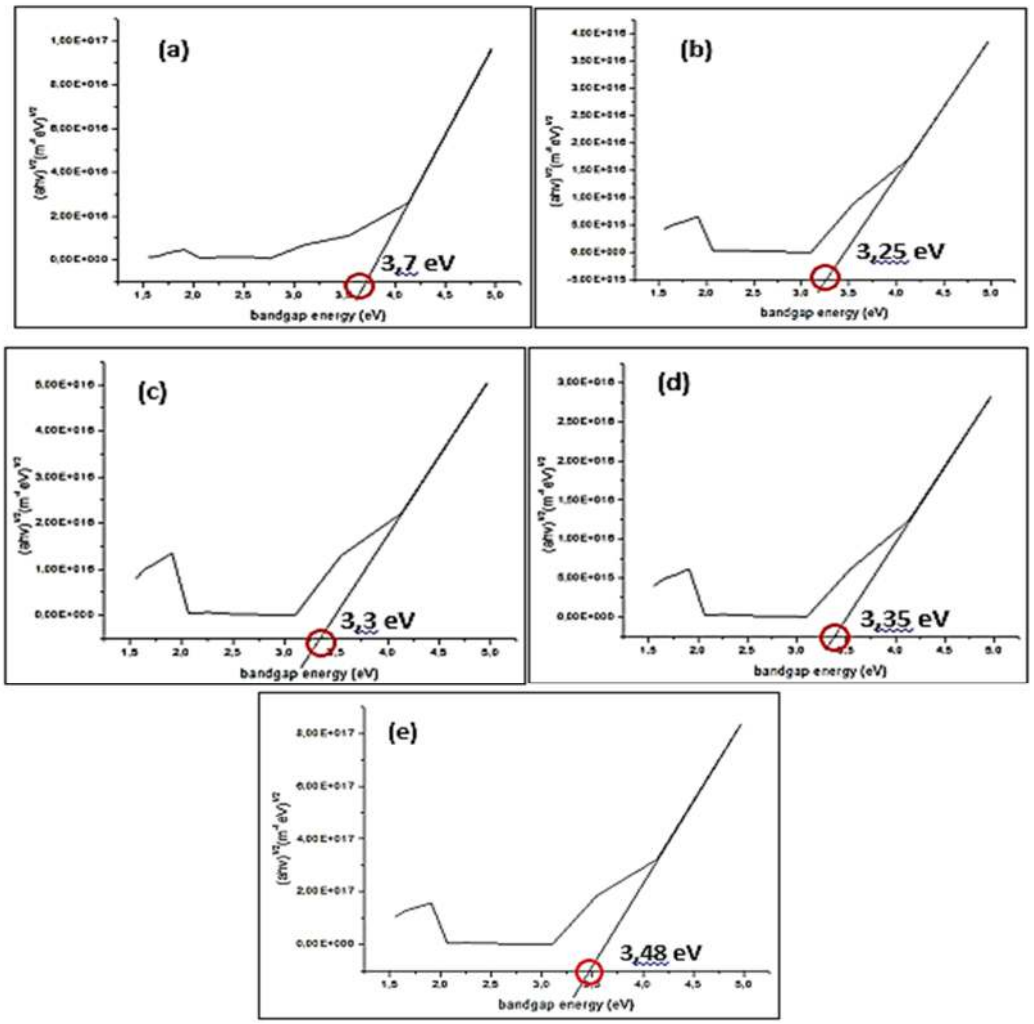

Figure 2. *Bandgap energy* (a) BT0% ; (b) BT1%% ; (c) BT2%% ; (d) BT3%% ; (e) BT4%.

The figure 2 shows the relationship between band gap energy (hv) and the coefficient it was absorbed at photon (αhv^2) as the ordinate until it cut energy axis, and as the result, *band gap energy* value can be gotten. The independent variable is showed as X-axis while Y-axis shows dependent variable. The changing of the αhv^2 value is caused by the value of obtained transmittance. The smaller the value of transmittance, the bigger αhv^2 value is. The value of hv at X-axis is affected by the wave length which is 200-800 nm. The value of *band gap energy* for all thin layers can be seen in the table 1.

Table 1. *Band gap energy* Biochar/TiO_2.

Biochar/TiO_2 Layers	***Band gap energy***
BT0%	3,70 eV
BT1%	3,25 eV
BT2%	3,30 eV
BT3%	3,35 eV
BT4%	3,48 eV

Table 1 shows the value of *band gap energy* with the variation of biochar doping started from 0%, 1%, 2%, 3% and 4% where each is as big as 3,7 eV; 3,25 eV; 3,3 eV ; 3,35 eV and 3,48 eV. *Band gap energy* in its highest is at BT0%, while the optimal reduction of *band gap energy* happens when the doping is added as much as 1% or 3,25eV. It is caused by narrowed energy band. The narrowing itself is caused by the appearance of new energy level between valence band and conduction band after the doping. The new energy level is just a little bit above the valence band [15].

Whilst for BT2%, BT3% and BT4%, *band gap energy* increases until 3,48 eV. The increasing of *band gap energy* at 2%, 3% and 4% doping is due to the addition of doping have reached the limit of maximum ability or called doping saturation. Even though the band gap energy increases with the doping as much as 2, 3 and 4%, Table 1 shows the addition of biochar doping to TiO_2 as a whole makes the value of band gap energy TiO_2, decrease, which are 3,70 eV for BT0%; 3,25 eV for BT1%; 3,30 eV for BT2%; 3,35 eV for BT3% and 3,48 eV for BT4%. By the reduction of band gap energy, photon needed for electron excitation from valence band to conduction band will be smaller, which means electron can be transported faster and hopefully the efficiency value from the solar cell DSSC will increase, so will the photocatalyst activity.

Next step is the XRD characterization to the sample of TiO_2 without doping and biochar/TiO_2 with variation of doping, the pattern of their diffraction can be seen in the figure 3.

From the figure, five layers of biochar/TiO_2 have the peaks at 2θ around 25°, 36°, 37°, 38°, 48°, 53°, 55°, 62° and 68°, the peaks are corresponding with the peaks owned by anatase phase based on the data from JCPDS No.211272. Those peaks correspond with crystal orientation in the sector (101), (103), (004), (112), (200), (105), (211), (204), and (116). Highest peak is owned by sector orientation (101). It is shown in the figure that all pure peaks owned by anatase phase with tetragonal crystal structure, and no rutile peak appears at all. The phase of anatase crystal indicates TiO_2 has high photo catalyst nature.

Apparent crystal size from all five samples of biochar/TiO_2 layers were obtained from the data of XRD result that can be counted by using *Debye Scheerer* method, by utilizing maximum peak owned by the peak of anatase at sector orientation (101).

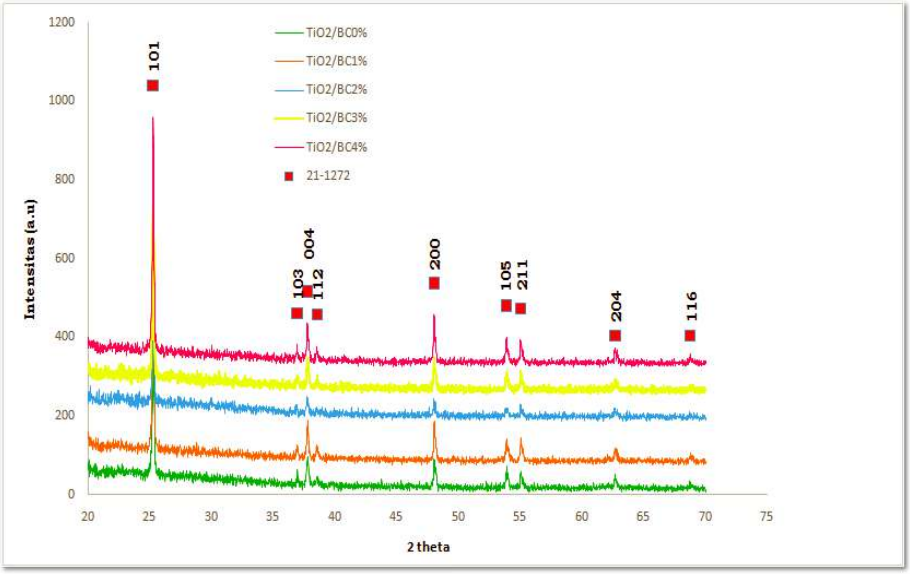

Figure 3. Diffraction pattern of Biochar//TiO2 layers.

From the shape of the produced XRD curve profile, it can be seen that all samples have relatively same peak width which indicates the size of crystal particle is at the same order. Through quantitative calculation by using equation (6), the data about the crystal size of all five samples were obtained as shown in table 2.

Table 2. Biochar/TiO2 crystal size.

Sample	Crystal Size (nm)
BT0%	137,95
BT1%	137,95
BT2%	137,94
BT3%	118,22
BT4%	118,22

It can be observed in the table 2 that BT0% sample produce the same crystal size as BT1% and BT2% sample which is 137,95 nm, meanwhile, BT3% sample has the same crystal size as BT4% which is 118,22 nm. Giving the right amount of doping can minimize the size of crystal of a material, but the temperature is more affecting towards the crystal size of a material. These five samples are not significantly different in size because the temperature given is same, which is 150 ºC.

Small crystal will have larger surface, and it is very advantageous to be applied to DSSC solar cell and photocatalyst. Besides, the degree of samples' crystalinity are quite good as the intensity of diffraction peak is quite high and firm (Figure 3).

The fine degree of crystalinity makes the process of electron diffusion in TiO_2 to be faster, and as the implication is, the process of electron transfer for DSSC as a whole will be higher and increase the solar cell efficiency. Besides, the crystal size obtained from all five samples of Biochar/TiO_2 approach nanometer scale, so they have larger surface that can collect more *dye* because the smaller the crystal size is, the more cavity formed and the more dye will be absorbed which means the more photon will be absorbed too. All of this cycle as a whole increase DSSC performance.

Furthermore, anatase phase owned by biochar/TiO_2 is very advantageous when it is applied to photocatalyst. The photocatalyst activity of anatase phase is more reactive than rutile phase. The effectiveness of photocatalyst at anatase phase is caused by its larger surface so that the active side of

anatase phase per unit is bigger than the other kind of TiO_2 phase. The TiO_2 crystal with anatase phase has larger activation area, that is why it is more reactive towards light [16].

4. Conclusion

Based on this complete research, the result of *band gap energy* calculation from biochar doping towards TiO_2 is; the smallest *band gap energy* is at BT1% sample which is 3,25 eV, the doping above 1% cause the *band gap energy* of Biochar-TiO_2 increase. Moreover, the analysis of biochar-TiO2 structure from XRD characterization shows all Biochar-TiO2 samples are in anatase phase with tetragonal structure and the smallest size of crystal is 118,22 nm for BT3% dan BT4% samples. As a whole, the addition of biochar doping to TiO2 can decrease the band gap energy of TiO2, and it indicates positively if the material is applied to DSSC solar cell and photocatalyst. Besides, the other supporting factor is the material of biochar/TiO2 is in a very stable anatase phase when it is applied to DSSC solar cell and photocatalyst.

Acknowledgments

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