

## Studies on Photoelectrocatalytic Water Splitting by Titanium Dioxide

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### Abstract

This research aimed to produce hydrogen gas from Photoelectrocatalytic Water Splitting (PWS) by TiO<sub>2</sub> photocatalyst prepared from Titanium (IV) isopropoxide (TTIP) by sol-gel method. The catalysts' preparation involved the calcination at 500°C for 3 hours. Then, the chemical and physical properties were characterized by X-Ray diffraction, Laser Particle size analysis, scanning electron microscopy and Nitrogen gas adsorption, respectively. The electrolysis, electrocatalysis and PWS were applied to test the hydrogen production with dark as the controlling experiment. The results of TiO<sub>2</sub> photocatalyst, it showed only anatase phase with the particle size of 47.5 micron and surface area of 54.7m<sup>2</sup>/g. After varying the weight of TiO<sub>2</sub> for hydrogen production in Lab, it was found that 0.25 g TiO<sub>2</sub> photocatalyst provided the best hydrogen production for 77.9 μmol/g-cat. Compared among triethanolamine (TEA), diethanolamine (DEA) and ethanol (EtOH) in this order, TEA improved the highest hydrogen production and then DEA and the lowest from EtOH, respectively. From the types of light, it was found that the UVA light produced the highest hydrogen production of 455.1 μmol/g-cat. But the efficiency of hydrogen production decreased when using UVC, visible light and sunlight respectively. This contributes to the energy band gap of TiO<sub>2</sub> corresponding to that of the UVA light. In summary, TiO<sub>2</sub> photocatalyst prepared by sol-gel method, it could produce the highest hydrogen from photoelectrocatalytic water splitting.

**Keywords:** Photoelectrocatalytic Water Splitting, Titanium Dioxide, Hydrogen Gas production, Photocatalysis, Heterogeneous catalysis

### Introduction

The increasing demand of hydrogen energy will reach 20 million metric ton (MMT) H<sub>2</sub> for Fuel cell Electric vehicles (FCEV) in USA by 2040 which was reported by M. Ball and Wietschel [1]. The supply of hydrogen will be 4-10 MMT H<sub>2</sub> so it has to increase the production to fill the gap. While EU with hydrogen energy, it estimates 35% of new cars by zero-carbon hydrogen system and average CO<sub>2</sub> reduction about 44.8 g/km. The driving force for EU community to use H<sub>2</sub> energy is due to the reduction of air pollution from fossil fuel combustion engine and it increases the energy security. Among EU members, Germany as the highest producer, it has 37% of chemical hydrogen production and Finland as the lowest one with that of 7.5% to meet the demand [2]. Hydrogen sources or its supply can be classified into 3 methods- thermal, electrolytic and photonics methods [3-4]. Among them, photonics method as Photoelectrocatalytic water splitting (PEC-WS) is comprised of electrolysis with photocatalyst and light irradiation. Meanwhile, the challenging point for PEC-WS for research worldwide, it needs the selection of reactive photocatalysts, cost minimization, and reliability with safety. So this research mainly conducted on PEC-WS for hydrogen production in lab scale using TiO<sub>2</sub> suspension and the variation of light irradiation with the addition of electron donor.

Titanium dioxide classified as semiconductor oxide, it has the versatile application in wastewater treatment reported by Fujishima et al. [5] and air purification by Mak et al. [6] in combination with UV light or sunlight. Another role of TiO<sub>2</sub> photocatalyst for hydrogen clean energy [7], it generated hydrogen with sunlight by water photosplitting. The mechanism on TiO<sub>2</sub> active surface during reactions, it involves electron-hole during light irradiation with 3.2 eV energy bandgap and charge separation [8] with light absorption [9] on TiO<sub>2</sub> surface. For

examples, Yan attempted to use TiO<sub>2</sub> microsphere for production of H<sub>2</sub> by water splitting from sunlight. Its advantage of TiO<sub>2</sub> microsphere gave the large surface areas and tunable pore size so it allowed light absorption with the excellent electronic properties as well [10]. Afterwards, the modified photocatalysts with electron behavior to improve the solar hydrogen evolution was examined by Yang et al. [11].

The objectives of this research aimed to prepare TiO<sub>2</sub> from sol-gel method by using titanium tetraisopropoxide (TTIP) as the precursor. Afterward, the TiO<sub>2</sub> photocatalysts were suspended in photoelectrochemical system (PEC) to produce hydrogen. The important factors controlling hydrogen production to examine, it consisted of TiO<sub>2</sub> mass, addition of electron donor and type of light irradiation. The evaluation of each system conducted by Hydrogen production during 120 min and the graphs plotted were discussed. The experimental procedure and the results were described in the next section, consecutively.

## Materials and methods

The experiment consisted of 3 sections: photocatalysts' preparation, characterization and the tests of hydrogen production in laboratory scale. The hydrogen production probably depended on the type and mass of photocatalysts, type of light applied, and type of electron donor. The details were described in this part.

### Materials

Titanium tetraisopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, TTIP) and Titanium dioxide (TiO<sub>2</sub>) were supplied by Sigma-Aldrich in AR grade. They became TiO<sub>2</sub> precursor. P-25 was the commercial grade of TiO<sub>2</sub> produced from Degussa Co. Ltd. For sol-gel preparation, nitric acid and sodium hydroxide were provided by RCI Labscan Ltd. in AR grade in the same as isopropanol. Ethanol was in AR grade from RCI Labscan Ltd, and methanol was from Scharlau Co., respectively. Triethanolamine (TEA) and diethanolamine (DEA) in AR grade, they were purchased from Carlo-Erba Reagent Co. Ltd. There were 3 types of the electron donors. All of the reagents were used as derived without purification.

### Methods

The mixture of TTIP and isopropanol with the molar ratio of 1.6 was prepared and reacted with nitric acid solution with the molar ratio of HNO<sub>3</sub>: TTIP= 1:1. After mixing and it kept stirring for 1 hr, then the white precipitate formed. The sol-gel involved in this step. The volumetric ratio of H<sub>2</sub>O: TTIP of 5:1 was added and it took 1 hr for stirring. Next, the pH adjustment by NaOH solution for the mixture, it was carried out to reach pH9 and stirring 1 hr. After pH adjustment, the suspension was in saturated condition for 24 hr. Then, the white precipitate was collected from the filtration. The drying of white precipitate and the calcination were conducted at 100°C for 24 hr., and 500°C for 3 hr., respectively. The white precipitate was TiO<sub>2</sub> photocatalysts and they were carefully kept in a desiccator before the test of hydrogen production. They were characterized by Laser particle sizer and N<sub>2</sub> adsorption as the BET method. For the morphological analysis and phase determination were carried out by SEM and XRD, respectively. Particle size analysis from SEM images was carried out directly by Image J software. All of the TiO<sub>2</sub> samples had to be dried and kept in a desiccator before characterization.

The hydrogen production experiment was carried out in the same way as electrolysis of water (EC). The direct current with 10V and 2 hr was applied with 200 mL H<sub>2</sub>O and light irradiation as Photoelectrochemical method (PEC). For the effect TiO<sub>2</sub> mass, the addition of TiO<sub>2</sub> photocatalysts was varied from 0, 0.25, to 2.0 g in the system with UVA irradiation. The effect of electron donor was examined by the addition of 0.3 molar of ethanol, TEA and DEA solution with UVA irradiation. For the effect of irradiation, the 0.01 molar NaSO<sub>4</sub> electrolyte with the selected solution of electron donor was carried out with dark as the controlling experiment and UVA, UVC, sunlight and visible light or white light. All of the experiments were compared on the basis of hydrogen production from the electrolysis and PEC system, consecutively.

## Results and discussion

The results of TiO<sub>2</sub> photocatalysts characterization consisted of particle size, surface area by N<sub>2</sub> adsorption, XRD diffraction and SEM for morphological studies. Then, TiO<sub>2</sub> photocatalysts from TTIP sol-gel method, from

TiO<sub>2</sub> Bottle and P-25 were tested for H<sub>2</sub> production to find out the best condition. The variation of TiO<sub>2</sub> photocatalysts' mass, type of electron donor and the light irradiation were conducted. All of the results would be described consecutively.

### Characterization of TiO<sub>2</sub> Photocatalysts

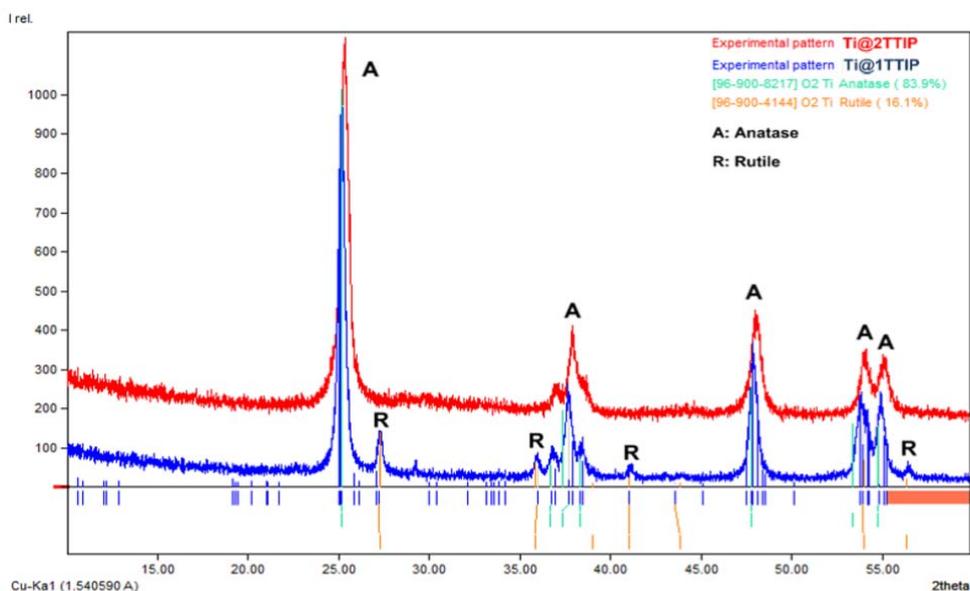
All of the TiO<sub>2</sub> from 3 sources, they came out in white powder. The color did not change after calcination either. Table 1 showed the values of particle size of TiO<sub>2</sub> samples by Laser particle sizer. Based on D(3,2) results, TiO<sub>2</sub> photocatalyst from TTIP sol-gel method had 4.95 micrometer which was the largest particle, and TiO<sub>2</sub> from the bottle and the P-25 had 3.13 and 0.32 micrometer, respectively. Likewise for surface area, the order of surface area showed that TiO<sub>2</sub> from sol-gel method had the largest surface area of 54.76 m<sup>2</sup>/g, and then, TiO<sub>2</sub> from the bottle and the P-25 with 48.29 and 10.13 m<sup>2</sup>/g. It indicated that TiO<sub>2</sub> photocatalyst from TTIP sol-gel method gave the largest agglomeration particle about 15.5 times compared to that from the bottle and P-25 samples. The larger particle came from the small particle agglomeration during suspension in the real behavior. And it was likely to provide the large surface area for hydrogen production from Photoelectrochemical Water Splitting (PWS), as well. Compared TiO<sub>2</sub> nanoparticle prepared by glycolated precursor, it had 50-683 nm as the size-controlled synthesis which was in the same range of the result in Table 1 [12].

**Table 1** Particle size and surface area of TiO<sub>2</sub> photocatalysts

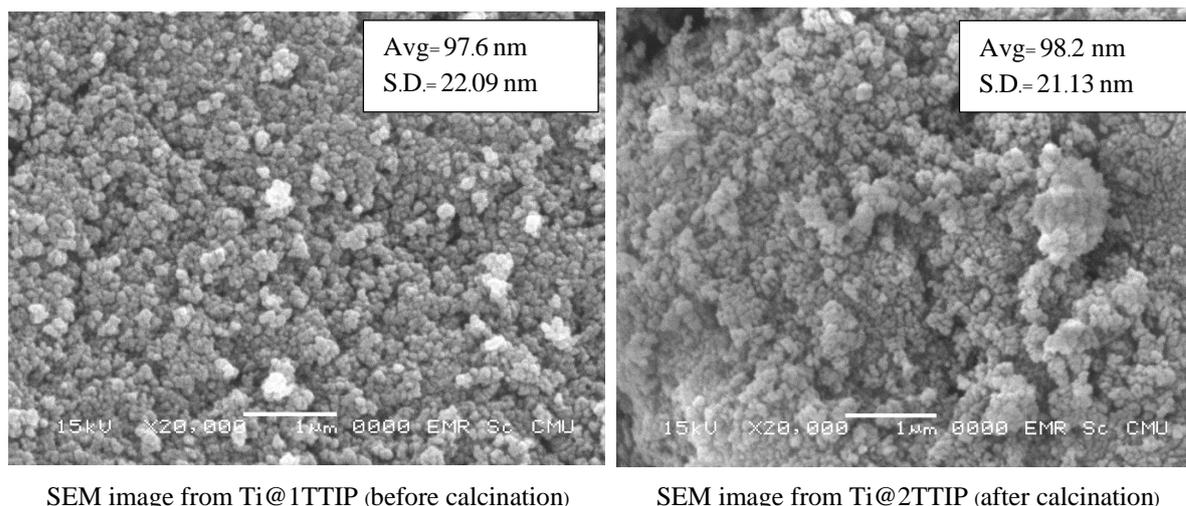
TiO <sub>2</sub>	D(3,2), micrometer	Particle Image J, nm	Surface area, m <sup>2</sup> /g
B	0.32	205.5	10.13
P-25	3.13	110.2	48.29
TTIP	4.95	98.2	54.76

**Note** All TiO<sub>2</sub> photocatalysts after the calcination at 500 °C for 3 hr in the ambient atmosphere and B stood for bottle.

Phase characterization by XRD method and morphological studies by SEM method, they both gave more information for TiO<sub>2</sub> photocatalysts from sol-gel method as shown in Fig.1-2. There were peaks located at 25, 38, 48, 54 and 55 degrees which followed anatase phase for both TiO<sub>2</sub> before and after calcination. But the disappearing peaks of rutile phase at 27, 36, 42, 57 degree were found after calcination. In case of TiO<sub>2</sub> from the bottle(B) and P-25, they had the relevant XRD results to these peaks of TiO<sub>2</sub> from TTIP sol-gel method. Therefore, the main phases were anatase and the minor phases belonged to rutile of TiO<sub>2</sub> photocatalysts. The anatase phase followed JCPDS no. 04-0477 and rutile for JCPDS no. 73-1765, as well.

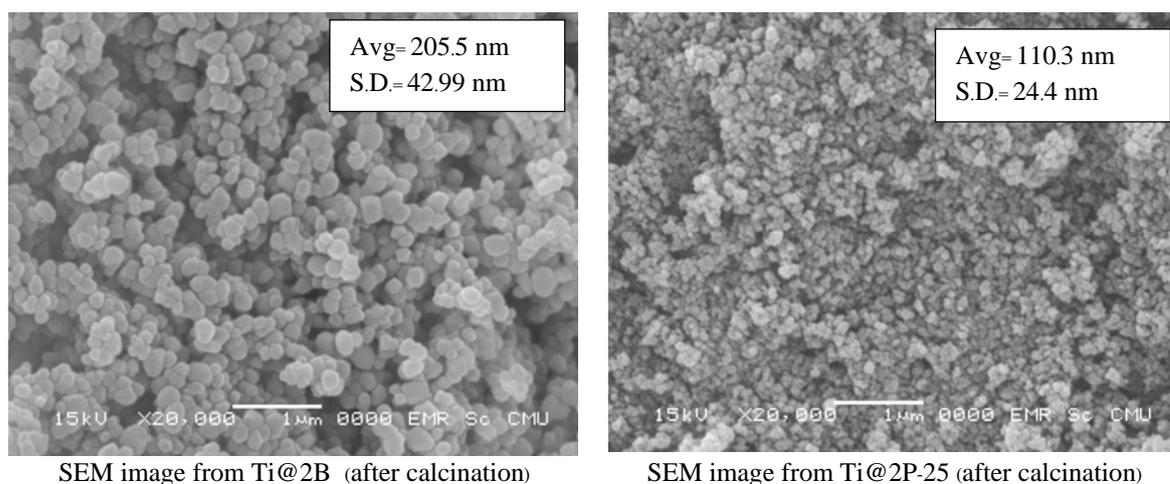


**Figure 1** XRD diffractograms of Ti@1TTIP(before calcination) and Ti@2TTIP (after calcination)



**Figure 2** SEM images of TiO<sub>2</sub> where Ti@1TTIP(before calcination) and Ti@2TTIP (after calcination)

The similarity of SEM images, Fig. 2, with 20,000 magnification, the particles from TiO<sub>2</sub> before and after calcination showed the spherical particles with some agglomeration. After calcination, the more agglomeration was found. Using ImageJ to analyze the particle size, it was found that Ti@1TTIP and Ti@2TTIP had 97.6 nm and 98.2 nm. While, TiO<sub>2</sub> from the bottle and P-25 had 205.5 and 110.3 nm by Image J on SEM images shown in Fig. 3, respectively. Ti@2B from the bottle gave the largest size and the smallest from Ti@2TTIP.



**Figure 3** SEM images of TiO<sub>2</sub> where Ti@2B( after calcination) and Ti@2P-25 (after calcination)

The calcination of TiO<sub>2</sub> from TTIP sol-gel method, it did not change the particle size of TiO<sub>2</sub> photocatalysts. Pal et al. work [12] reported the TiO<sub>2</sub> size ranging from 0.1 micron or 100 nm, it followed with these work for Ti@2TTIP and Ti@2P-25 but not for Ti@2B. The difference likely came from the preparation. It meant that SEM + Image J, they gave the real particle size unlike Laser particle size in Table 1. The characterization of XRD and SEM methods, the calcination eliminated rutile phase and the particle size slightly changed with the morphology. Meanwhile, surface area of TiO<sub>2</sub> from sol-gel method and P-25 had larger surface area compared to that of TiO<sub>2</sub> from the bottle. The smaller particle size gave the larger surface area. It indicated that the TiO<sub>2</sub> from sol-gel method possibly gave higher photoreactivity for H<sub>2</sub> production by Photoelectrochemical Water Splitting (PWS). The next part could clarify the result of PWS from the variation of TiO<sub>2</sub> mass, type of irradiation and type of electron donor.

### Hydrogen production by Photoelectrochemical method

The comparison of hydrogen production by EC and PEC methods was tabulated in Table 2 with the controlling experiment as electrolysis without photocatalyst (E). And the mass of TiO<sub>2</sub> photocatalysts varying from 0.25 to 2.0g was conducted to find out the optimum mass including the variation of light irradiation and various type of electron donor. The PEC method was applied for PWS (Photoelectrochemical Water Splitting) in this experiment.

**Table 2** Comparison of Electrolysis (E) , Electrochemical (EC) and Photoelectrochemical (PEC) methods

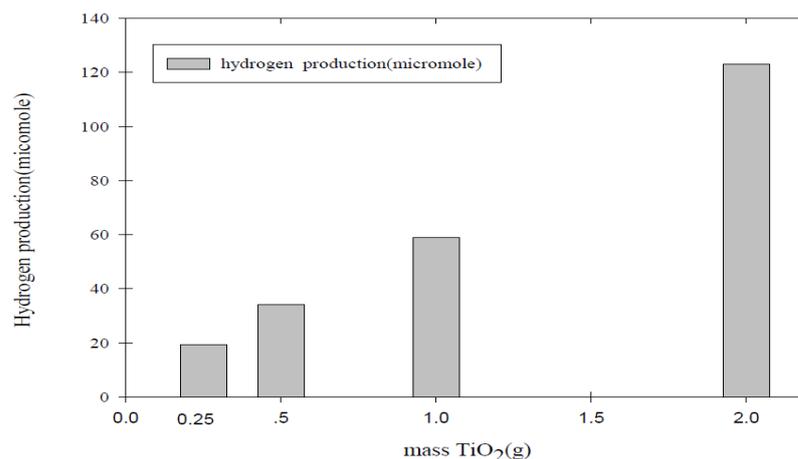
Time (min.)	Hydrogen production( micromole/g-cat)						
	E	Electrochemical method(EC)			Photoelectrochemical method (PEC)		
		Ti@2B	Ti@2P-25	Ti@2TTIP	Ti@2B	Ti@2P-25	Ti@2TTIP
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	2.4	6.4	6.4	7.9
40	0.0	0.0	0.7	5.5	7.8	12.8	21.3
60	0.0	0.8	0.7	7.7	9.3	14.2	36.0
80	0.0	2.4	1.6	9.4	12.4	14.9	45.9
100	0.0	4.8	2.3	11.7	13.8	16.3	52.5
120	0.4	8.0	3.1	14.9	15.3	20.1	68.4

**Note** Using 10 Volt, constant weight of 0.5 g TiO<sub>2</sub> photocatalyst after calcination with UVA light irradiation.

Electrolysis as the controlling system, it could not produce H<sub>2</sub> but EC and PEC produced H<sub>2</sub> during 120 min. Both EC and PEC gave the increasing H<sub>2</sub> as the time increased directly. Testing of Ti@2B, Ti@2P-25 and Ti@2TTIP, they generated H<sub>2</sub> of 8.0, 3.1 and 14.9 micromol/ g-cat by electrocatalytic method. After applying UVA as the light irradiation to EC method, it was found that at Ti@2TTIP had the highest hydrogen of 68.4 micromole/g-cat or 4.6 times higher than that of EC method by Ti@2TTIP. The second one for hydrogen production was Ti@2P-25 provided 20.1 micromole/g-cat or 6.5 times higher than EC method. The last one was Ti@2B from PEC method had 1.9 times higher than EC method. The clear evidence of Ti@2TTIP with PEC method gave the best result due UVA and the smallest particle with large surface area including its photoreactivity. The PEC system also convinced the system that it could generate hydrogen for further studies. The doubtful point was to find the optimum mass of TiO<sub>2</sub> photocatalyst.

#### Effect of TiO<sub>2</sub> mass for PWS system

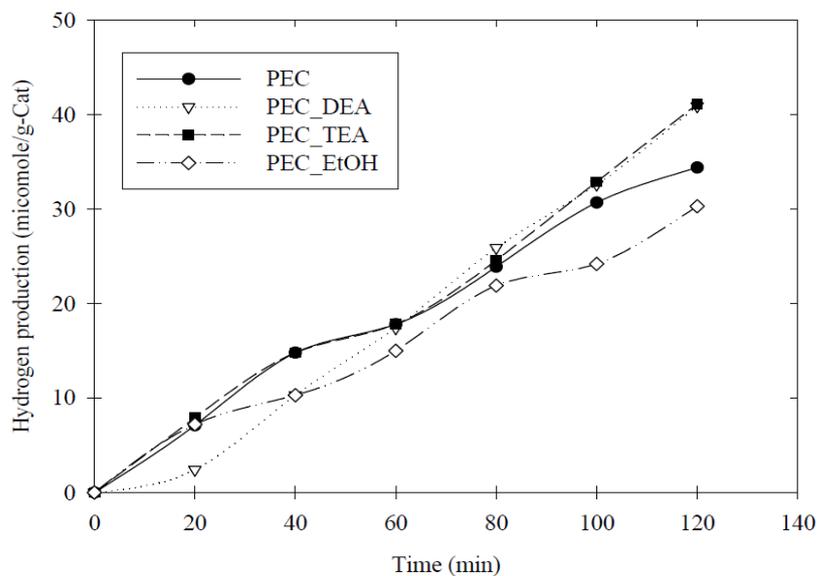
In Fig. 4, the optimum mass of TiO<sub>2</sub> mass for Hydrogen production was the main factor to find out by varying the TiO<sub>2</sub> mass from 0.25 to 2.0 g in 200 mL water. During 120 min., it was found that 2.0 g TiO<sub>2</sub> gave the highest amount of Hydrogen production at 123.2 micromol whereas 0.25g TiO<sub>2</sub> provided the lowest one of 19.4 micromol. The increasing of TiO<sub>2</sub> mass also gave the increasing Hydrogen production conversely. To compare among them, the effectiveness of weight was applied. It showed the best effectiveness mass of TiO<sub>2</sub> came from 0.25 g TiO<sub>2</sub> with 77.9 micromole/g-Cat. And the worst one came from 1.0 g TiO<sub>2</sub> with 58.8 micromole/g-Cat. This clarified that the excess TiO<sub>2</sub> mass hindered the light impingement on TiO<sub>2</sub> surface and it also blocked the irradiation among themselves during Photoelectrochemical Water Splitting. The optimum mass of TiO<sub>2</sub> enhanced the particle moved freely during the suspension. Then, they all could expose the reactive surface to light irradiation, as well. The effect of TiO<sub>2</sub> increasing weight, it followed the similar report from Liangpeng group's investigation [13]. The excess TiO<sub>2</sub> mass had the adverse effect on hydrogen generation.



**Figure 4** The effect of mass of TiO<sub>2</sub> photocatalyst on H<sub>2</sub> production by PEC system.

#### Effect of Electron Donor on Hydrogen production

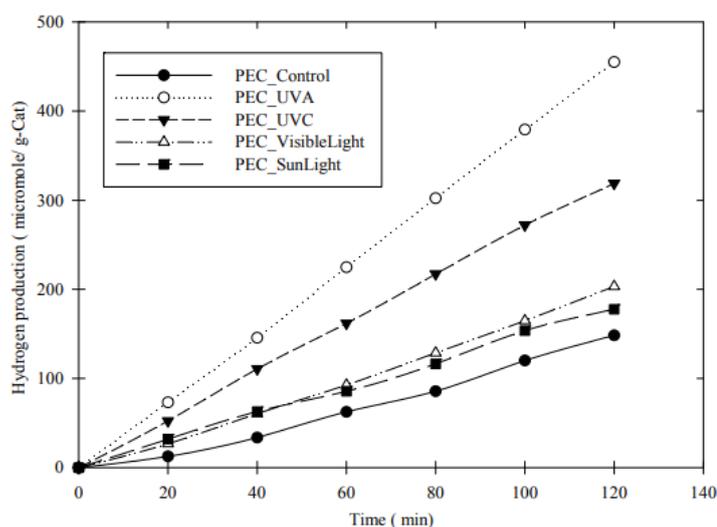
As TiO<sub>2</sub> surface with electron-hole interaction, various electron donors were applied toward these experiments to examine the hydrogen production. There were DEA, TEA and ethanol at the constant concentration of 0.3 molar using UVA irradiation. In Fig. 5, hydrogen production gradually generated and it reached the highest values at 120 min. Based on PEC as the control experiment, DEA and TEA showed 40.9 and 41.1 micromole/ g-cat compared to that of 34.4 micromole/ g-cat from PEC system. With the addition of ethanol or PEC-EtOH, it had 30.3 micromole/ g-cat. The contribution of DEA and TEA possibly came from the presence of amine group which it increased H<sup>+</sup> reduction to hydrogen formation. On the other hand, ethanol had the opposite result because the OH group decreased electron-hole formation on the surface and it obstructed hydrogen formation. Ethanol acted as sacrificing agent and it depleted the adsorbed species on TiO<sub>2</sub> surface so hydrogen desorbed easily [14]. This is opposite from our results. And no report on TEA effect is clarified.



**Figure 5** The effect of electron donor on Hydrogen production by TiO<sub>2</sub> photocatalysts in PWS system.

## Effect of Light Irradiation on PWS system

The variation of light irradiation from UVA, UVC, visible light and sunlight in Figure 6, it gave the hydrogen production of 455.1, 318.8, 203.2 and 177.6 micromole/ g-cat. In case of the PEC\_ control, it had hydrogen only 148.3 micromole/ g-cat as the lowest value. Among light irradiation, the highest value came from PEC\_UVA with 3.06 times higher than PEC-Control. And UVC showed 2.2 times higher than PEC\_Control. PEC\_VisibleLight and PEC\_SunLight, they both provided Hydrogen production slightly higher than that of PEC\_Control. According to Planck's equation, the photon energy of each light irradiation from UVC, UVA, visible light, sunlight was 6.2- 4.2 eV, 3.8- 3.1 eV, 3.1- 1.77eV and 6.2-0.5 eV, respectively. Energy bandgap( $E_g$ ) equal to 3.2 eV of  $TiO_2$ , only UVA irradiation had the corresponding  $E_g$  with the highest Hydrogen production. While, UVC had excessive energy and it did not match with  $E_g$  or did not quantized. On the other hand, visible light had less energy for  $TiO_2$ . And sunlight had much wide spectrum of light wavelength and infrared with heat. This finding supported that UVA with  $E_g$  was suitable for PWS with  $TiO_2$  photocatalysts [15]. Compared to the report of Diaz et al. [14], our result was 303 micromole/  $h^{-1}$  about one-third less than that which required further studies.



**Figure 6** The effect of Light irradiation on Hydrogen production by PWS system

## Conclusion

Titanium dioxide prepared from sol-gel method of Titanium isopropoxide and calcination, it had 100% anatase while those from the bottle(B) and P-25 had 100% and 83.9%, respectively. The surface areas had 54.7, and 48.3 and 10.1 m<sup>2</sup>/g. varying from TTIP, B and P-25 types. Using electrolysis system to produce hydrogen for 120 min., it was found that TTIP photocatalyst gave 68.4 micromol/ g-cat compared to B and P-25 with 20.10 and 15.43 micromol/ g-cat. Increasing the mass of photocatalysts, the hydrogen production increased conversely with the maximum mass of 2 g  $TiO_2$  for 123.2 micromol  $H_2$ . Based on the effectiveness, it was found that 0.25g  $TiO_2$  produced 77.9 micromol/ g-cat. The excess  $TiO_2$  hindered hydrogen production because it blocked the impingement of irradiation. Among TEA, DEA and ethanol as the electron donor, the maximum hydrogen production reached 41.1 micromol/ g-cat using TEA in the system. The comparison of irradiation type, UVA gave 455.1 micromole/g-cat as the highest value among UVC, sunlight, visible light and the dark as the controlled experiment.  $TiO_2$  could perform PWS with UVA and TEA to generate hydrogen gas and it will be the solution for Power generation or some hydrogenation reaction, as well. The improvement should focus on the cocatalyst and electrolyte in the system for the better result.

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