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RESEARCH ARTICLE

HYDROGEN PRODUCTION PHOTOCATALICALLY BY Pd-SUPPORTED TiO_2 IN THE PRESENCE OF AQUEOUS OXALIC ACID

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ABSTRACT

In this work palladium nanoparticles were supported on mixed mixture of 75 wt % anatase and 25 wt % rutile titanium oxide to create holes on the surface of titanium oxide and electrons on the surface of metal electrodes. The effects of different parameters were investigated namely, oxalic acid wt %, pH, Temperature, Irradiation time, and NaCl wt %. The formed particles were characterized by X-ray diffraction, high resolution transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy and diffuse reflectance UV-V is spectroscopy and nitrogen adsorption–desorption isotherms (BET). Hydrogen evolution was monitored by sampling at different intervals and measured using gas chromatography. Optimum conditions to obtain the highest hydrogen yields were; oxalic acid 2 wt % (2229 µmol g^{-1}), pH 2.2 (2229 µmol g^{-1}), Temperature 50 °C (2180 µmol g^{-1}) and NaCl 1 wt % (3530 µmol g^{-1}). No decreasing was observed when long term experiment was evaluated (154 hrs). This could be attributed to the fact when TiO_2 is irradiated with light having a wavelength of 380 nm or less, a pair of electron holes is formed. Using the electrons, Pd ions are reduced and precipitated on TiO_2. At this time, if Pd is reduced and precipitated on TiO_2, it is considered that the electrons photogenerated by TiO_2 move onto Pd, suppress the recombination of electrons and holes, and promote the hydrogen production reaction in other words photogeneration can proceed as long as there is irradiation.

KEYWORDS

Fuel cell, Hydrogen production, Clean Energy, Oxalic acid, Palladium nanoparticles (Pd), Titanium oxide (TiO_2)

1. INTRODUCTION

Hydrogen energy in combination with fuel cells are expected to be the most promising source of energy that can prevent global warming. Hydrogen is produced from water and organic compounds containing hydrogen that exist indefinitely on earth, and it is expected to be used widely in a variety of industrial applications. Hydrogen is a clean energy that easily returns to the original water during combustion in any process and does not disrupt the natural environment's circulation. As an energy medium, hydrogen is expected to play an important role in the development of clean energy and the resolution of environmental problems in the future, and it is anticipated that a hydrogen energy society will emerge. In recent years, there has been an increase in interest in the realization of a hydrogen energy society, and one of the fields of research and development is fuel cells.

Fuel cells have a high-power generation efficiency because electrochemical energy can be extracted directly as electrical energy without being converted into thermal energy. As hydrogen energy systems become more widespread in the future, the demand for hydrogen will naturally increase. How to produce the amount of hydrogen that meets this demand is a major issue for the spread of hydrogen energy systems, and it is thought that the method greatly affects the utility of introducing hydrogen energy systems. There are various hydrogen production methods, and it is possible to classify hydrogen from various viewpoints such as; raw materials, processes, and locations. Currently, the reforming of fossil resources and the electrolysis of water are in practical use (Hakki et al., 2018; Friehs et al., 2016; Alsalka et al., 2018).

Photocatlyitc looks promising approach to obtain clean energy however the main obstacle is when we use optical semiconductor alone such as TiO_2 low activity is produced due to the fast recombination of photoexcited electrons and holes (Rinaudo et al., 2020; Li et al., 2001; Franch et al., 2002; Bowker et al., 2015; Yamada et al., 2012). The activity as a photocatalyst can be improved by supporting a metal such as Pd on the surface of TiO_2 (Kim et al., 2014). Therefore, as one of the methods for increasing the photocatalytic efficiency, a method has been proposed in which metal fine particles such as micron-sized palladium are supported on titanium oxide powder to create holes on the surface of titanium oxide and electrons on the surface of metal electrodes (Xiaolan et al., 2019; Sakthivel et al., 2004).

This type of photocatalyst is equivalent to a smaller Schottky photochemical diode, also sometimes called a micro photoelectrochemical cell. Unlike photoelectrode cells, which require an electrolyte for the movement of ions between electrodes, this type of photocatalyst works without an electrolyte. This is because the distance between the metal and the semiconductor is extremely short, and ions can move without an electrolyte. Therefore, considered to be the cleanest source for fuel cell

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since no production of green house gases (Yang et al., 2007; Patsoura et al., 2006; Nada et al., 2005; Wu et al., 2008; Dawson et al., 2001; Park et al., 2007).

Based on the mentioned fact, in our previous work we investigated the influence of acid and co-catalyst on photocatalytic hydrogen production and choose the most suitable acid and co-catalyst to get the maximum amount of H_2 production. Pd and oxalic acid were chosen as the best among others (Bin et al., 2022). In this study, we investigated an inexpensive and simple hydrogen generation method using Pd ions that can be added to the reaction system, and Pd can be more easily supported on the surface of titanium oxide semiconductor photocatalyst (75% anatase type and 25% rutile type). Work was done in the presence of different ranges of Pd, oxalic acid, pH, temperature, and NaCl to get the maximum yield of the produced hydrogen (Table 1).

2. MATERIALS AND METHODS

2.1 Chemicals and Setting

Chemicals were purchased from different suppliers; P-25 TiO_2 (anatase 75%, rutile 25%, surface area 53m^2 g^{-1}, particle size 25 nm) from Degussa Japan Co. Ltd. NaCl; $(COOH_2)$, NaOH and Pd from Nacalai Co., Ltd; H_2, N_2, O_2, Ar from Kawase Co., Ltd, Pd^{2+} from Kanto Co., Ltd. Hydrogen generation experiment is shown in Figure 1. Begin by adding 40 mL of oxalic acid aqueous solution and 50 mg of TiO_2 photocatalyst to a 123 mL reactor and setting the temperature to 50°C. A fixed amount of Pd ion concentrations were added to the reactor. Silicon septum was used to seal the reactor after addition of the proper ingredients. While maintaining the temperature and stirring with a magnetic stirrer, it was irradiated with ultraviolet rays (wavelength: 357 nm) from the side, as shown in Figure 1. Following the reaction, the generated gas was extracted from the upper part of the reactor with a micro-syringe and measured using gas chromatography.

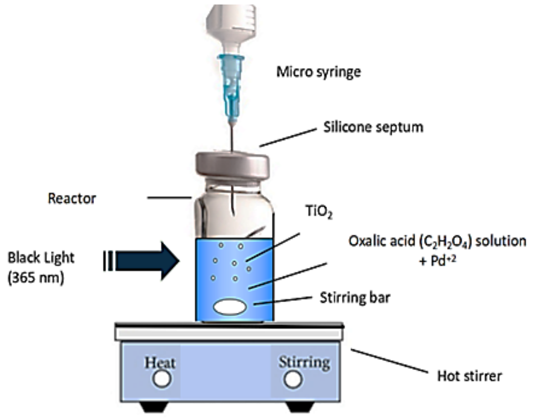

Figure 1: Hydrogen generation Apparatus

2.2 Characterization Methods

2.2.1 Spectrophotometry

The UV-VIS spectra of Pd sols were measured in 1 cm quartz cells in an Agilent 8453 diode array spectrophotometer (Agilent Technologies, Santa Clara, CA, USA), with Millipore MilliQ ultrapure water as blank reference.

2.2.2 SEM, TEM images and BET

photocatalyst after reaction was recovered was precipitated using a centrifuge. Then the supernatant was separated from the precipitates. The dried sample was pulverized with an agate mortar for 15 minutes to obtain a photocatalyst powder. The obtained photocatalyst powder was used for characterization using SEM, TEM, BET, X-ray diffraction, photoluminescence spectrum, diffuse reflectance spectrum.

2.3 H_2 Production Measurements

The suspension of the freshly prepared, washed catalyst in 50 mM oxalic acid solution was poured into a glass reactor (total volume: 150 mL), surrounded by ten 15 W UV lamps (λmax = 365 nm). The well-stirred suspension (co-catalyst = 1 g/L) was purged with N_2 at a flow rate of 50 mL/min (in the majority of experiments) to ensure O_2-free conditions. The reactor was connected through a PTFE tube to a Hewlett Packard 5890 gas chromatography fitted with 5Å molecular sieve column and a thermal conductivity detector. Gas samples were taken with a 2 mL micro-syringe every 10 min in the first hour of the experiment and every 20 min in the second hour. The rate of H_2 evolution was calculated with regard to the GC calibration (carried out with certified 5% H_2:N_2 gas) and the N_2 flow rate.

2.4 UV Decomposition of Oxalic Acid

These experiments were carried out under the same conditions as H_2 production measurements, but liquid samples were taken from the suspensions at predetermined intervals during the reaction, and the residual oxalic acid concentration was measured. After centrifugation and filtration with a Whatman Anotop 25 Syringe Filter (0.02 μm), the HPLC measurements were performed on a Merck Hitachi device fitted with an L-4250 UV-VIS detector and column of 8 μm (GROM Resin ZH).

2.5 Adsorption of Oxalic Acid on the Catalyst

Oxalic acid adsorption was investigated on bare and platinized TiO_2. The applied oxalic acid concentrations were in the range of 0.1–50 mM. The 1 g/L suspensions were thermostated instead of thermos stated at 25 °C and stirred for 4 h in the dark. Then the samples were filtered using a Whatman Anotop 25 (0.02 μm) syringe filter and the residual oxalic acid concentration was determined by HPLC.

2.6 Method of Measuring Diffuse Reflectance Spectrum

Barium sulphate (3g) was employed as a base in the sample stage. Then 500 mg of barium sulphate and 50 mg of sample powder were mixed for 20 minutes in an agate mortar before being packed from the top down. The background was assessed with a sample stage that was exclusively filled with barium sulphate. The sample was then placed on a sample stage and measured. A graph was produced using the measurement results' Kubelka-Munk transform.

Table 1: Experimental Conditions

Photocatalyst	TiO_2, 50 mg
Reactor	Pyrex glass vessel (volume 123 mL)
Volume	40 mL
Addition	Pd (0-2.25 ppm)
Medium	Oxalic acid solution (0-3.0 wt.%)
pH	1.5～9.5
Temperature	25-70°C
Irradiation time	1-154 hours
NaCl	0-3 wt %
Light source	Black Light (357 nm, 0.26 mW/cm^2)
Analysis	Gas chromatography (TCD), HPLC, UV-Vis Spectrophotometer

3. RESULTS AND DISCUSSION

3.1 Effect of Oxalic Acid Concentration on Photocatalytic H_2 Production

As depicted in Figure 2, maximum hydrogen was produced when concentration of oxalic acid 2 wt % and reached 2250 μmol g^{-1} after that reduced when 2.5 and 3 wt % were used.

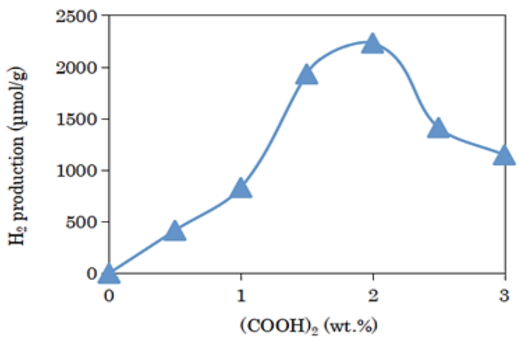

Figure 2. Effect of oxalic acid concentration on the photocatalytic H_2 production using TiO_2 with aid of simultaneous photo deposition for Pd.

Co-catalyst: Pd 0.1 wt.%.

Irradiation time: 5 hours.

3.2 Effect of Pd Concentration on Photocatalytic H_2 Production

The effect of palladium concentration was also investigated as shown in Figure 3, maximum hydrogen was produced when wt % reached 0.1 after that significant drop as much as 50% was noticed.

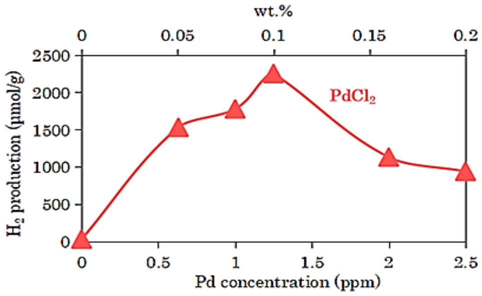

Figure 3: Effect of Pd concentration on the photocatalytic H_2 production using TiO_2 with aid of simultaneous photo deposition

Irradiation time: 5 hours.

3.3 Effect of pH on photocatalytic H_2 production

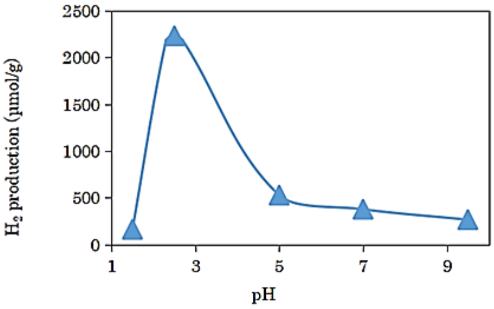

Figure 4: Effect of pH on the photocatalytic H_2 production from aqueous oxalic acid solution using TiO_2 with aid of simultaneous photo deposition for Pd

Co-catalyst: Pd 0.1 wt.%.

Irradiation time: 5 hours.

Alkalinity and acidity of the solution usually measured by the concatenation of hydrogen ions or in other words pH value. Even without the presence of solutes in the liquid water, the hydrogen ion, H^+ and hydroxide ion, OH^- able to be formed by breaking down few H_2O molecules. This dissociation process in chemical equilibrium condition can be written as H_2O (l) ↔ $H^+ + OH^-$. The pH measurement identified by the concentration H^+ ions in the water which pH = -log [H^+]. With high concentration of H^+ ions causing the water turns acidic, thus lowering the pH value and high concentration of OH^- leads to increasing of pH value (Abdul Hakim et al., 2019). The pH effect on H_2 production was investigated between 2-10 (i.e acidic and alkaline range) as shown in Figure 4. Results show that pH of 2 was the best to get the highest yield of hydrogen formation under the applied conditions. increasing pH values above 5 produce the lowest amount of hydrogen.

3.4 Effect of Temperature on Photocatalytic H_2 Production

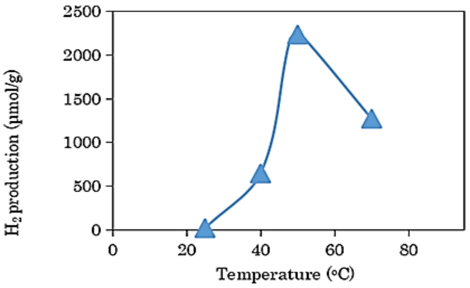

Figure 5: Effect of temperature on the photocatalytic H_2 production from aqueous oxalic acid solution using TiO_2 with aid of simultaneous photo deposition for Pd.

Co-catalyst: Pd 0.1 wt %

Figure 5, shows that, most hydrogen was produced when temperature was 50 °C at a Pd concentration of 0.1 % wt, after 50 to 80 °C the amount of hydrogen produced decreased. Moreover, in a separate experiment when comparing the cases where palladium chloride and palladium nitrate were used, it was confirmed that the amount of hydrogen produced was larger when palladium chloride was used. Therefore, the Pd concentration was set to 1.25 ppm (1 wt %), and other experiments were conducted using palladium chloride.

3.5 Effect of Nacl Concentration on Photocatalytic H_2 Production

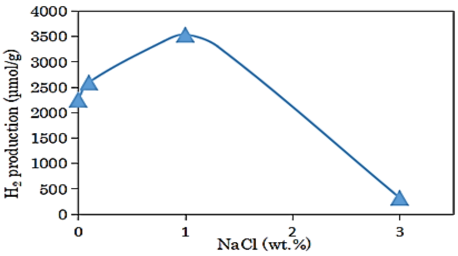

Figure 6: Effect of NaCl on the photocatalytic H_2 production with TiO_2

Since the effect of NaCl is crucial in the production of H_2, the wight percentage of NaCl was studied. Figure 6, summarized the obtained data. The produced H_2 was significantly increase from 2100 when no addition of NaCl to 3550 when 1 wt%. From this result, it is considered that the optimum concentration of NaCl to get the maximum yield should not exceed 1 wt %.

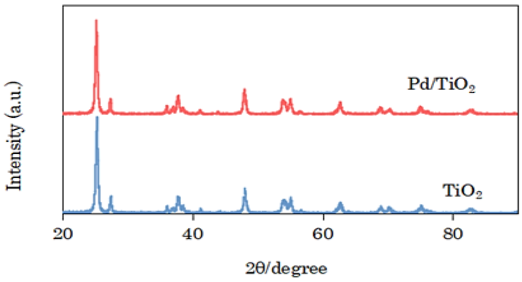

Figure 7: XRD patterns of TiO_2 and Pd/TiO_2

As shown in Figure 7, an X-ray diffraction analysis was performed to evaluate the crystalline structure of supported catalysts of Pd/TiO_2 and TiO_2. There was no significant difference, and the peaks were the same for pure titanium oxide and Pd/TiO_2. These findings suggested the presence of almost pure anatase phase in this catalyst, however the presence of small palladium crystalline deposits on this catalyst, was illustrated by further TEM analysis (Figure 10).

3.6 Effect of Irradiation Time on Photocatalytic H_2 Production

Long-term continuous hydrogen production experiment was carried out to assess the photocatalytic activity for the period of 6.7 days (160 hrs). Analysis was done by taking representative samples between different intervals assuming that the rest of the bulk solution has the same quality as the sample. Data are summarized in Figure 8. Obvious results show that even though long irradiation time was applied no reduction in the quantify of H_2 produced indicating that the longer time applied the more H_2 produced.

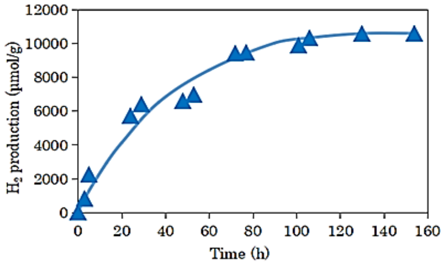

Figure 8: Effect of irradiation time the photocatalytic H_2 production from aqueous oxalic acid solution using TiO_2 with aid of simultaneous photo deposition for Pd.

Co-catalyst: Pd 0.1 wt.%.

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Figure 9 shows an SEM image of P-25 titanium oxide (a) and Pd/TiO_2 (b), and Figure 10, shows the TEM image for the same samples. According to SEM observation, the yield of Pd/TiO_2 (b) particles decreased in size compared to that of Pd/TiO_2. Moreover, when BET analysis was carried out for both samples, the BET surface area value of the Pd/TiO_2 catalyst was smaller and the total pore volume and average pore diameter values were larger than those of the P-25 TiO_2 catalyst as shown in Table 2. Same size observed (Matías et al., 2020). However, the preparation methods not the same.

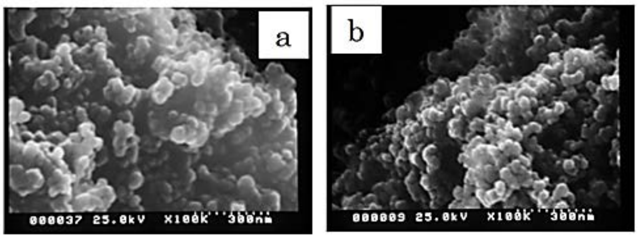

Figure 9: SEM images of P-25 TiO_2 (a), Pd/TiO_2 (b)

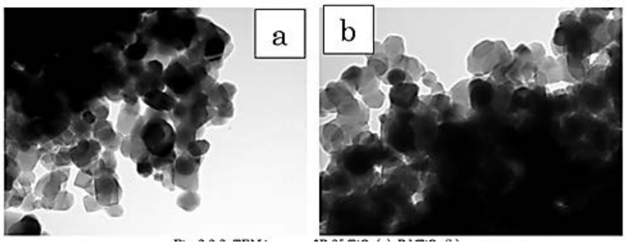

Figure10: TEM images of P-25 TiO_2 (a), Pd/TiO_2 (b)

Table 2: Textural Properties of TiO_2 And Pd/TiO_2.

	BET Surface Area [m^2 g^{-1}]	Total Pore Volume [cm^3 G^{-1}]	Average Pore Diameter [nm]
P-25 TiO_2	53	0.296	22.3
Pd/TiO_2	51	0.483	38.2

3.7 UV-Vis Diffuse Reflectance Spectra and TAUC plot

The band gap energy can be calculated from the diffuse reflection spectrum according to the following formulas.

$$\alpha h\nu = (h\nu - E_g)^n \qquad (1)$$

$$(\alpha h\nu)^{1/n} = h\nu - E_g \qquad (2)$$

Here, α is the absorption coefficient, h is Planck's constant, ν is the frequency, and E_g is the band gap energy. n is a value determined by the excitation between electron bands, and n = 1/2 in the case of direct transition and n = 2 in the case of indirect transition. In the case of anatase-type titanium oxide, the inter band excitation is indirect transition, so n = 2. From equation (2), the band gap energy can be obtained by plotting with (αhν) 1 / n on the vertical axis and hν on the horizontal axis and extrapolating the straight line as shown in Figure 11. In the same graph there is a slight shift towards the left side of x-axis. This mean possibility to enhance H_2 production with less energy (in the graph from 3.22 when TiO_2 only to 3.18 eV when Pd/TiO_2 was used).

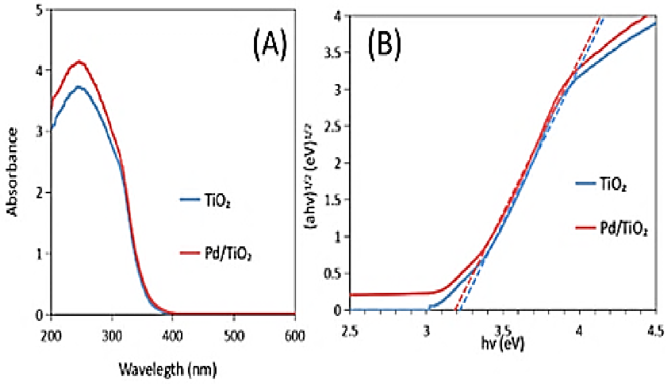

Figure 11: UV-Vis DRS (A) and tauc plot (B) for TiO_2 and Pd/TiO_2.

3.8 Hydrogen Formation Mechanism

When TiO_2 is irradiated with light having a wavelength of 380 nm or less, a pair of electron holes is formed. Using the electrons, Pd ions are reduced and precipitated on TiO_2 as Pd. At this time, if Pd is reduced and precipitated on TiO_2, it is considered that the electrons photogenerated by TiO_2 move onto Pd, suppress the recombination of electrons and holes, and promote the hydrogen production reaction. It is thought that the photogenerated holes oxidize water and oxalate ions to generate protons and carbon dioxide. Protons generated by the oxidation reaction of water and oxalate ions are reduced on the surface of Pd to generate hydrogen as shown in Figure12.

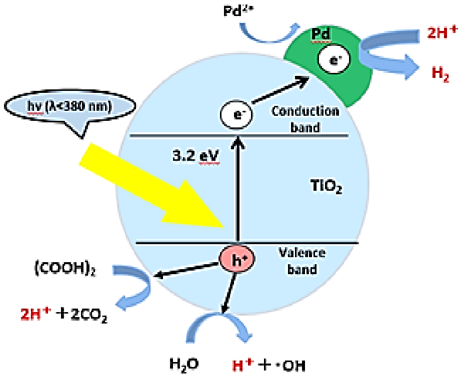

Figure 12: Mechanism for photocatalytic H_2 production.

There are two possible routes for promoting hydrogen production in this experiment. Here two ways are possible; first option, as the first action, promotion of hydrogen production on the surface of metal particles (Pd) can be considered. This is because the electrons that have moved to the conduction band move from the top of TiO_2 onto the surface of the metal particles (Pd), which promotes the reduction reaction and improves the ability to generate hydrogen. Second, it is considered that hydrogen production is increased by promoting the oxidation reaction. This is because the adsorption of oxalic acid on the surface of metal particles (Pd) promotes the oxidation reaction and at the same time promotes the reduction reaction.

It is considered that the two effects are occurring simultaneously, but the first effect is considered to be predominant. In the photocatalyst, a photocatalyst that is photoexcited acts on the reaction substrate to cause a reaction. When light with an energy larger than the band gap energy is irradiated, electrons in the valence band are photoexcited into the conduction band, free electrons are generated in the conduction band, and holes are generated in the valence band, which are reduction and oxidation reactions, respectively. If it can be caused, the photocatalytic reaction will proceed. At this time, if the electrons and holes are recombined, the reaction does not occur, but a mechanism for separating them exists on the semiconductor surface.

4. CONCLUSIONS

Unlike photoelectrode cells that require an electrolyte for the movement of ions between electrodes, our research however focused on photocatalytic reaction that does not require electrolyte. Occurrence of the reaction depends solely upon the distance between the metal and the semiconductor that extremely short, therefore ions can move freely without an electrolyte. Successful continuous production of hydrogen was achieved though long irradiation time and no reduction in the quantify of H_2 produced indicating that the production continues as long there is irradiation.

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