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**Review Article**

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# A Concept: Improved Hydrogen Production using Pt-N-$TiO_2$ under Visible Light via Photocatalysis Process

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**Abstract** The demand of energy in Indonesia is still dominated by the use of fossil fuels. In 2013, fossil fuels contributed 94.3 percent of the total energy. However, production of fossil fuels: coal, oil, and gas has been decreasing very significantly. Additionally, high energy requirements has not been matched with an equitable electrification ratio throughout Indonesia. To overcome the above energy problems, hence hydrogen ($H_2$) can be used as an alternative and potential energy supplier because it is an environmentally friendly energy source. An effort to produce $H_2$ is by utilizing water. Water can be converted into $H_2$ through photocatalyst process applying photon energy and using $TiO_2$ semiconductor. The other alternative method to extend the photocatalytic activity of $TiO_2$ to visible light region is to dope this material with zink dioxide. A variety of metals and non-metals have been doped into $TiO_2$ materials. Nowadays special interest has been focused on the preparation of titania mixed Pt and N because they show important photocatalytic properties as well as potential applications in the water splitting. The main of the obtained has been related to the creation of oxygen vacancies in the $TiO_2$ crystalline structure which improve the photocatalytic activity. It is clear that production of hydrogen increases with the increase of Pt and N contents.

**Keywords** Water splitting, Hydrogen production, Photocatalysts

## Introduction

Nowadays energy demands in Indonesia have dominated by fossil fuels. In 2013, fossil fuels contributed 94,3% of total energy (1,357 million barrel of oils), the rest 5,7% fulfilled by EBT. From that amount, oil contributes around 49.7%, 20.1% natural gas, and coal 24.5% [1]. Conventional energy sources such as coal, oil, and gas which those are frequently use for supplying the requirement of the world's energy production that it has decreased significantly. It triggers challenge to produce a new alternative fuel.

Hydrogen is one of the potential options to answer this challenge and can become the future main energy source because it is friendly for environment [2]. In nature, hydrogen is not available or can be obtained as free as fossil energy sources but hydrogen must be produced. Many attempts have been made to produce hydrogen, there are the steam reforming process [3] and produce through renewable sources, one of them is process trough electrolysis of water [4]. The process hydrogen produced by steam reforming of this is costly and requires a high-temperature atmospheric pressure [5]. Electrolysis of water is also a technology to produce hydrogen that requires a huge amount

of electricity and less economical. Therefore, an alternative process that is required as well as environmentally friendly. One of the alternatives offered to produce hydrogen is by using sunlight and water photocatalyst [6]. Research on hydrogen production based on renewable natural materials had been made, both based on electrical work (electrolysis), photocatalyst, and electro fotocatalyst [7].

The photocatalytic decomposition of water is an ideal method to produce hydrogen using water as the renewable source. The use of semiconductor photo catalysts for this reaction to be a promising technique and has many advantages, such as: a solid phase, relatively inexpensive, safe for operation, and resistant to deactivation. Photocatalyst process that utilizes photon energy (not thermal energy) and a photo catalytic $TiO_2$ potential applied to convert water into hydrogen effectively. Titanium Dioxide ($TiO_2$) is frequently used because of its properties which are inert, stable, and relatively inexpensive [8]. $TiO_2$ photocatalytic reaction on the surface can produce pairs of electrons ($e^-$) and holes ($h^+$). Nonetheless, the process of using $TiO_2$ photocatalyst has a low function due to the band gap which is large thus less responsive to visible light. To that end, there should be some efforts to improve the performance of photocatalysts in producing hydrogen from water. Attempts to manipulate $TiO_2$ is by adding metal dopants on $TiO_2$ catalyst. Dopant has function which is as an electron trapping that can enhance the photocatalytic activity [9]. Huang (2007) has shown that photocatalytic $TiO_2$ didopan N can be synthesized and managed to degrade organic pollutants in water under visible light effectively [10]. Zhang (2010) reported that further modifications to the N-$TiO_2$ can be done with the addition of metal ions [11]. The presence of metal such as Pt on TiO2 surface can prevent recombination thus improving the photocatalytic reaction efficiency. In addition, Li et al (2009) stated that photocatalytic Pt-$TiO_2$ showed very good results for $H_2$ production from a mixture of water and glycerol. In this paper will do the review with the catalyst Pt-N-$TiO_2$ for hydrogen production applications [12].

**Discussion**

The photocatalytic process is a combination of photochemical processes and catalysis. The catalyst in this process is referred to as a photocatalyst because it has the ability to absorb the photon energy. A material can be used as a photocatalyst if it has an empty area called the energy band gap energy (energy band gap). The photocatalytic process that usually used is a heterogeneous photocatalytic process. In this process takes semiconductors. Semiconductors can be used as a photocatalyst because it has an empty area of energy, called the energy band gap that lies between the limit of the conduction band and valence band does not provide the energy levels to promote the recombination of electrons and holes produced by a photoactivation in the semiconductor. In photochemical reactions, there is a semiconductor-electrolyte junction at which the water splitting reaction takes place (Figure1). The required potential for water splitting is generated at the semiconductor-liquid interface. The semiconductor should be stable in the electrolyte to prevent any corrosion. Depending on the band edge position of the semiconductor as discussed previously, they can be active in hydrogen production, oxygen production, or overall water splitting [13].

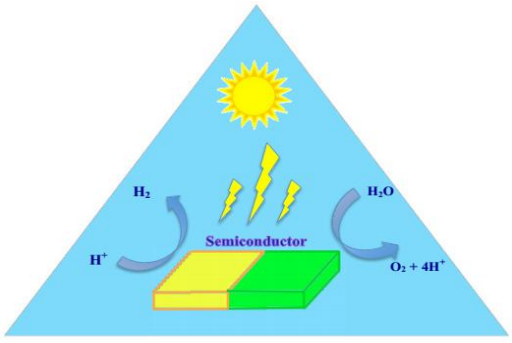



*Figure 1: Schematic representation of photochemical water splitting. Figure adapted from reference of Currao work [14].*

**Photocatalyst Materials**

**Titanium Dioxide ($TiO_2$)**

Titanium dioxide ($TiO_2$) is a transition metal oxide which includes the Group IV B of the periodic table, it also known as titanium anhydride, an acid anhydride, titanium oxide or titania are typically available in white powder. Materials have many advantages over other semiconductor materials. The properties include: Having chemical stability in the interval wide pH (0 to 14). Resistant to photodegradation, Characteristically inert and insoluble in the reaction, both biologically and chemically, Non-toxic, has the ability in high oxidation and relatively inexpensive.

In addition, $TiO_2$ is considered environmentally friendly because it supports a unique textural property, including activity at a low temperature (280-300°C), high thermal stability (rutile temperature is 900°C) and excellent mechanical properties (strength presses (16 N / mm). the catalyst $TiO_2$ has 3 types of crystal structure that are anatase, rutile, and brookite. the structure of rutile and anatase fairly stable existence than the structure of brookite and is used as a photocatalyst [15]. The difference in these two structures leads to differences in the density of (3,9 g / mL for anatase and 4.2 g / mL for rutile), energy gap, and the light absorption capability.

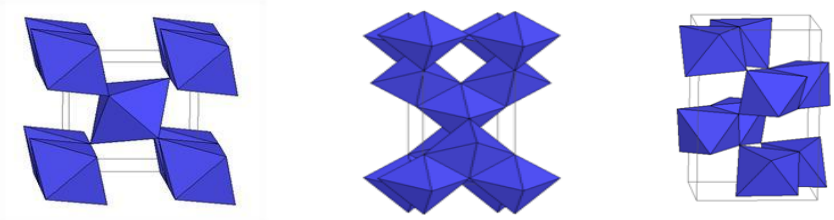


*Figure 2: $TiO_2$ Crystall Structure a) Rutile; b) Anatase; c) Brookite [15].*

Since Fujishima and Honda first demonstrated that $TiO_2$ was a promising photo-anode for UV light-driven photocatalytic water splitting which has been widely studied in many photocatalytic reactions due to its chemical stability, low cost, environmentally friendly nature, and tunable electronic energy band gap [12, 16-19]. Figure 3 shows a band gap illustration of $TiO_2$.

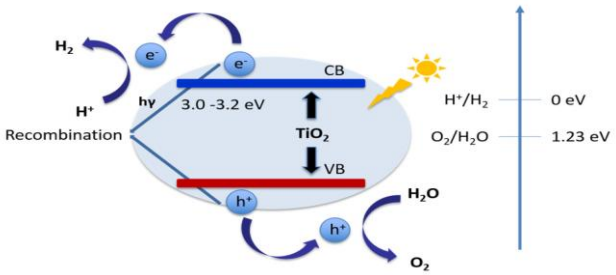



*Figure 3: Schematic band gap diagram of $TiO_2$. Figure adapted from references of Moniz et al and Miao et al. works respectively [20-21].*

The other alternative method to extend the photocatalytic activity of $TiO_2$ to visible light region is to dope this material with zink dioxide. A variety of metals and non-metals have been doped into $TiO_2$ materials. Nowadays special interest has been focused on the preparation of titania mixed oxides like CuO, ZnO, NiO and CeO [2, 22] because they show important photocatalytic properties as well as potential applications in the water splitting. The main of the obtained metallic oxide has been related to the creation of oxygen vacancies in the $TiO_2$ crystalline structure [23-24] which improve the photocatalytic activity.

**Mechanism of water splitting using titanium dioxide**

The basic principle of photocatalytic decomposition of water, based on the change of light energy into electrical energy in a semiconductor exposure to light. The light causes the ionized n-type semiconductor material on energy gap that causes the formation of an electron in the conduction band and holes in the valence band. The hole will split

water molecules into oxygen and hydrogen ions. Simultaneously, the electrons that are generated in the equation will reduce the hydrogen ions into hydrogen gas [2].

$$2hv \longrightarrow 2e^- + 2h^+ \quad (1)$$

$$H_2O + 2h^+ \longrightarrow \frac{1}{2} O_{2(g)} + 2H^+ \quad (2)$$

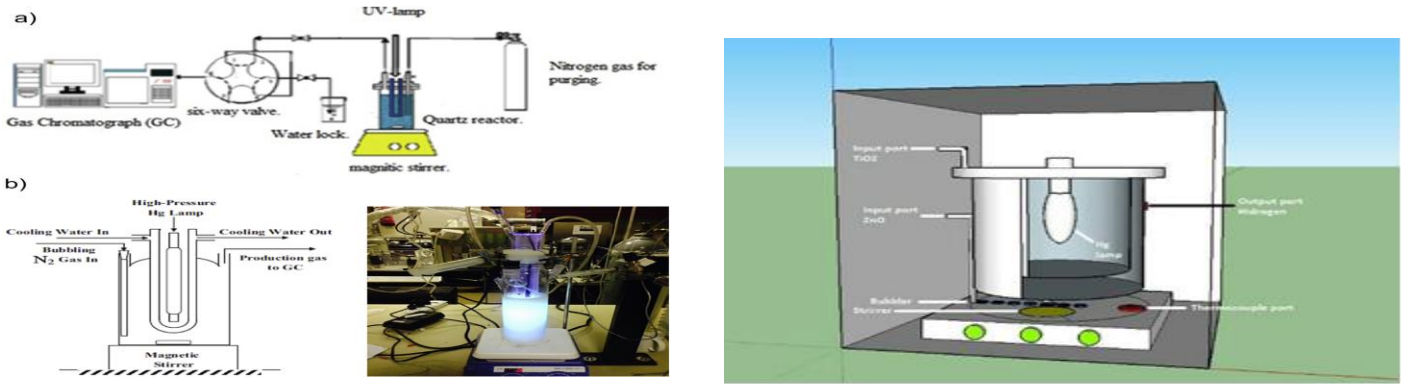
$$2H^+ + 2e \longrightarrow H_2 \quad (3)$$

Overall, the above equation can be simplified to,

$$2hv + H_2O_{(l)} \longrightarrow \frac{1}{2} O_{2(g)} + H_{2\,(g)} \quad (4)$$

There are several possibilities in electron-hole pairs, there are:

Some pairs recombine inside the particles (volume recombination). The electron-hole pair recombines on the surface (surface recombination) or in bulk particles in just a few nanoseconds.The electron pair of each species can react with the donor (D) and acceptor (A) are adsorbed on the particle surface.




(a) (b)

*Figure 4: a) Schematic diagram of experimental setup for photocatalyst hydrogen production [25] (b) $H_2$ production schema (author design).*

The photocatalytic hydrogen evolution over pure $TiO_2$, N-$TiO_2$, Pt-N-$TiO_2$ was investigated in an aqueous media in the presence of ethanol as an electron donor under UV-light irradiation. The presence of an electron donor other than water is crucial for photocatalytic $H_2$ production. In this set-up, ethanol functions primarily as hole traps to prevent the rapid electronehole recombination. The reaction assembly consists of a tank for suspension (distilled water, photo-catalyst powders and sacrificial reagent) and an inner chamber placed inside the reactor for the lamp and jacket around the lamp for controlling temperature of the lamp [25]. In this set-up, the photo-reactor is design by Fig 4.

**Activity $H_2$ production for the Pt-N-$TiO_2$**

To determine the extent of the influence of a dopant to the performance of the catalyst, it was ordered to review the performance of hydrogen production from Pt-N-$TiO_2$ catalyst.

**Table 1:** Recent visible light active photocatalysts for water splitting.

| Samples | $H_2$ production ($\mu$mol/h) | Source |
|---|---|---|
| $TiO_2$ P25 Degussa | 224 | [26] |
| $TiO_2$ Nanotubes | 534 | [26] |
| N-$TiO_2$ Nanotubes | 676 | [26] |
| Pt (1%)- $TiO_2$ Nanotubes | 2492 | [26] |
| Pt (1%)- N-$TiO_2$ Nanotubes | 3017 | [26] |
| $TiO_2$ | 0 | [27] |
| N-$TiO_2$ | 54.8 | [27] |
| 0.05% wt% Pt/N-$TiO_2$ | 376 | [27] |

Performance photocatalyst Pt-N-$TiO_2$ nanotubes are high is the synergism of the three treatment terhdap photocatalyst $TiO_2$ Degussa P-25, namely the formation of nanotubes, giving dopant N, as well as the provision of Pt dopant. The influence of each of these treatments, theoretically is:

1. The morphology of nanotubes increases the surface area of photocatalyst [28-29] thereby increasing the interaction between the reactants with the photocatalyst. In addition, the morphology of the nanotubes also increases the concentration of the dopant can be provided in the photocatalyst.
2. Dopants N can increase the photocatalytic activity under visible light [10, 30] due to lower energy band gap of the photocatalyst [31].
3. Dopants Pt on $TiO_2$ surface to prevent recombination reaction thereby increasing the efficiency of photocatalysts [8, 10]. In addition, Pt can also improve the stability of N in the photocatalyst [11]. Metals Pt also found a catalyst in the steam reforming process using glycerol [12].

**Conclusion**

Modification photocatalyst Pt-N-$TiO_2$ provides an increase in total production of hydrogen compared to the material $TiO_2$ Degussa P-25 and N-$TiO_2$.

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