Modification of morphology and optic properties of TiO$_2$ as photoreforming catalyst for H$_2$ production from biomass derivatives: a review

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Abstract. Hydrogen is one of the solutions to overcome the problems facing the world today, the energy crisis and a decrease in environmental quality. Its has high chemical energy per mass and its combustion only results water and does not emit greenhouse gas. Nevertheless, hydrogen doesn’t exist in nature as H$_2$ form. Hence, it requires a sustainable production methods. Biomass (lignocellulose) and its derivatives can be renewable feedstock for producing biohydrogen via clean process i.e photoreforming. One of the keys to the success of this technology is the development of suitable photocatalysts that are able to maximize light harvesting from solar and hydrogen production. TiO$_2$ is the establish material because of its high photocatalytic activity, not toxic, biologically and chemically inert. Its main drawback are its band gap value (ca. 3.2 eV) and fast recombination of electron–hole that detrimental to the photocatalytic activity. The alternative to overcome these problems are modification of TiO$_2$ by nanotubes structure and doping of metals. In this paper, we will review about TiO$_2$ nanotubes and its preparation strategies. Then, we will describe role of metal to enhance photocatalytic performance of TiO$_2$ nanotubes. The Impact of both modification to morphology and optic properties and enhancement of H$_2$ production from biomass and its derivatives will be study. The future direction for photoreforming of biomass and its derivatives were also suggested. Modification of Titania by nanotube structure and doping it with bi-metal consist of transition metal like Ni-Cu opens up opportunities and challenges for other researchers.

1. Introduction
Development of world population and industrialization has resulted increase in energy consumption. Based on BP Statistical review of world energy, the growth of primer energy consumption reached 1,3% in 2019. China, India and Indonesia are the three countries with the highest energy consumption in the world respectively. Among the existing energy source, fossil fuels reach 84% used as the primary source[1]. However, its hydrocarbon content give rise to
greenhouse gas (GHG) such as carbon oxide (CO\textsubscript{x}), nitrogen oxide (NO\textsubscript{x}) and methane. Its contribute to climate change and global warming. In the other hand, fossil fuels reserves have been decreases, its non-renewable energy source. Energy crisis, depletion of fossil fuel and environmental quality are major global issue that must be solve. One of the solutions is turn to renewable non-fossil fuel (like water and biomass) and sustainable energy source such as wind, solar, hydro, nuclear, geothermal and so on. Hydrogen have great potential to be an alternative energy source.[2–4]

Hydrogen will be clean energy source and carrier. Its use has two main advantages: i) a high chemical energy per mass (122 KJ/g), superior to that of many fossil fuels [5] ii) and ii) its combustion only results in water, therefore, it does not emit any toxic substance or greenhouse gas into the atmosphere [2,6,7]. Nevertheless, hydrogen does not exist in nature in its molecular H\textsubscript{2} form but combined to other elements or compound form both in organic (fossil and biomass) that contain hydrocarbon (C\textsubscript{x}H\textsubscript{y}) or organic compounds (C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}). This element also involves in inorganic compounds such as water (H\textsubscript{2}O), acid (HX) and others [8]. Hence, it requires dedicated methods for its production.

Hydrogen can be produced via several pathways i.e. thermochemical, electrolysis and biochemistry process. Thermochemical processes held by heating chemical reaction of fossil fuel or biomass at high temperature. Typical thermochemical processes for H\textsubscript{2} evolution include coal/biomass gasification, natural gas reforming, biomass-based liquid reforming, and solar thermochemical hydrogen. Currently, H\textsubscript{2} mostly produces via reforming process fossils fuel or natural gas. This process not fulfil renewable and sustainable resources and processes cause its harsh thermodynamic reaction. Electrolysis would be a cleaner technology than thermochemical. But it needed great electricity source to produce H\textsubscript{2}. In other hand, biochemistry process can produce H\textsubscript{2} form renewable source such as waste water but it difficult to applied at large scale[2,5,8–13]. Development of sustainable in feedstock and production process for H\textsubscript{2} production are challenge and need further research so all of the benefit of hydrogen can be obtained.

The photocatalytic is a sustainable process that can be applied for H\textsubscript{2} production. Sustainable in this case means sustainable both in raw materials feedstock and also the production process as well as the products so that future generations will continue to benefit from current development [12]. The photocatalytic is a combination process between photochemical and catalyst, namely a chemical transformation process involving light as a trigger and a catalyst as an accelerator of the transformation process [9,14–17]. Sunlight is a renewable energy source that is always available all over the world and is cheap. The use of solar energy is expected to reduce the use of energy from electricity or high temperature reaction [18,19]. Since Fujishima and Honda (1972) first investigated the production of H\textsubscript{2} by photocatalytic splitting of water molecules, research around the photocatalytic process for H\textsubscript{2} production expand greatly. Number of publication subjected to H\textsubscript{2} production via photocatalytic in last decade (Science Direct database) shown in Fig.1.
Photocatalytic water splitting is a clean process cause its produce hydrogen and oxygen so zero carbon emission. Unfortunately, it has drawback i.e low efficiency in H₂ production. Thermodynamically, water splitting is highly endothermic reaction (ΔGᵪₒ=+237 kJ/mol ≈ 1.23 eV). Kinetically, water molecule is a stable molecules when it irradiated by photon with energy close to 1.23 eV. So that, it needed a more kinetic requirement for water splitting. The activation energy for H-O-H bond cleavage is about 500 kJ mol⁻¹, which corresponds to a maximum wavelength of 250 nm (UV-C radiation) [15],[20]. All about research in photocatalysts water splitting subjected to overcome that’s drawback such as added sacrificial agent with organic molecules and/or by modification to photocatalyst materials. Several organics have been examined to be electron donor or hole scavenger in photoreforming. Nanotechnology in catalyst also plays vital role in research and development of novel photocatalyst material.

One of the keys to the success of this satisfy technology is the development of suitable catalysts that are able to maximize light harvesting from solar. This article review will focus on modification of TiO₂ as photocatalyis material to enhance H₂ production via photocatalytic reforming (phoreforming) of organic molecules that derived from biomass. First, basic concept of photoreforming process will be discuss earlier. Then, nanostructured of TiO₂ photocatalyst material via design one dimension nanotubes to get Titanium oxide nanotube (TiNT) will be explain. The further modification can be continue by doping metal as co-catalyst into TiNT. Furthermore, the modification will affect on properties of material, but in this review will examine on morphology and optic properties of material. Finally, the recommendation for future research about H₂ production via photoreforming biomass derived will be propose.

2. Basic Mechanism of Photoreforming of Biomass Derivatives to H₂ Production
Photoreforming is development of photosplitting of pure water process in H₂ evolution. Water photosplitting occurs through anaerobic photoreduction and photooxidation processes. The photoreduction process will reduce H⁺ to H₂ (E₄₋₅ <Eₖ₃ (H₂ / H₊)). The photooxidation process is the process of forming O₂ because the H₂O molecule is oxidized by h⁺ (Eᵥ₆ > E₅ (O₂ / H₂O))[21][22]. That’s process occurs according this reaction:
\[ \begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^{(\text{ads})} \\
\text{hv} & \rightarrow \text{e}^{-}\text{CB} + \text{h}^{+}\text{VB} \\
4\text{H}^{+} + 4\text{e}^{-} & \rightarrow 2\text{H}_2 \\
2\text{H}_2\text{O} + 4\text{h}^{+} & \rightarrow \text{O}_2 + 4\text{H}^{+} \\
\text{So net reaction will be} & \\
2\text{H}_2\text{O}(\text{l}) & \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) 
\end{align*} \]

Besides thermodynamic and kinetic requirement as discuss earlier, photosplitting have same drawback such as (i) rapid recombination of e\(^{-}\) - h\(^{+}\) pairs in bulk. In addition, (ii) the reverse reaction from H\(_2\) and O\(_2\) to H\(_2\)O is possible and the process is so fast (iii) the low efficiency of harvesting photons from sunlight in the visible region so that provides low efficiency H\(_2\) production. On the other hand, (iv) the reaction is using clean water, while its availability and sustainability is still limited, especially in developing countries.

Photoreforming realize by added organic molecule to water. It serve as electron donor or hole scavenger that can enhance H\(_2\) production. This process can avoid the photosplitting limitation[23]. Organic molecule can be alcohol group such as methanol[24,25], [26]; ethanol [26][27], ethylene glycol[28,29]; glycerol[25][26][30–39]; aldehyde group such as formaldehyde [40,41]) and carboxylic acid group such as butyric acid[42], acetic acid [43], formic acid[44–46], etc.). Carbohydrate that contain saccharide (glucose, fructose) also serve as sacrificial agent.

The mechanism of organic molecule photoreforming on semiconductor materials take place at several reaction steps that shown in figure 2. However, Photoreforming of specific organic molecule was more complicated than water photosplitting [17][18][47][48]. Reaction step that occur in photoreforming process are:

- **First**, the absorption of photons (hv) which has an energy equal to or higher than the bandgap energy of semiconductor. The absorbed energy is used to excite electrons (e\(^{-}\)) from the valence band (VB) to the conduction band (CB) leaving a hole (h\(^{+}\)) in the valence band. At this stage an electron-hole pair is formed.

- **Second**, the separation and migration of electrons or holes from the bulk to the surface. This process is known as e\(^{-}\) - h\(^{+}\) pair recombination in the bulk of the material. In this step, organic molecule will capture h\(^{+}\) and the oxidize C\(_x\)H\(_y\)O\(_z\) into CO\(_2\) and H\(_2\)O. Hence, rapid recombination of e\(^{-}\) - h\(^{+}\) can be avoided.

- **Third**, the breakdown of water molecules (water splitting) into H\(_2\) and O\(_2\) through anaerobic photoreduction and photooxidation processes. The photoreduction process will reduce H\(^{+}\) to H\(_2\) (E\(_\text{CB}\) < E\(_{\text{O}}\) (H\(_2\) / H\(_2\)O)). The photooxidation process is the process of forming O\(_2\) because H\(_2\)O molecules (result from oxygenated C\(_x\)H\(_y\)O\(_z\)) are oxidized by h\(^{+}\) (E\(_\text{VB}\) > E\(_{\text{O}}\) (O\(_2\) / H\(_2\)O)).
Figure 2. The mechanism of water photosplitting and organic molecule photoreforming on semiconductor materials. (Adapted from reference [17])

The production of H₂ by photoreforming of organic compounds has several advantages, namely (I) the reaction is slightly endothermic so thermodynamically more profitable than photosplitting of water (highly endothermic). Photoreforming a methanol has $\Delta G^0 = +9.3 \text{ kJ/mol}$, while photoreforming an ethanol has $\Delta G^0 = +97.4 \text{ kJ/mol}$. The longer the alkyl chain, the greater the $\Delta G^0$ value of the reaction. When the alcohol group is more than one site (namely poly-ol), the $\Delta G^0$ value is even smaller, for example glycerol photoreforming has $\Delta G^0 = 5.3 \text{ kJ/mol}$. The more complex the structure of the electron donor compound, the greater the $\Delta G^0$[17]. The other (2) advantage i.e. when photoreforming is carried out under the same conditions with photosplitting, it turns out that the amount of H₂ produced from photoreforming organic compounds increases significantly.

Electron donor can also be obtained from biomass which is abundant in nature and biomass derived. The main contain of biomass is cellulose $(C_{6}H_{10}O_{5})_n$, $n=3000-4000$, renewable and sustainable feedstock of H₂[47–50]. Therefore, more advantage is (3) increasing the added value of biomass. World biomass production reaches 100 million tons per year[17,51–54]. Hydrogen produced from biomass and/or with the help of microorganisms is known as "biohydrogen". The use of biomass can reduce biofuel production costs by up to 70%. Biomass photoreforming begins with hydrolysis and oxidation of cellulose to form organics (hydrolysate/sacrificial agent) and is followed by photoreduction hydrolysate which are formed into H₂ and CO$_2$[17,53]. In addition, photoreforming also use industrial wastewater as organics [11]. Industrial waste come from pulp and paper industry, food or fruit canning manufacture [4,11,55,56]. So that, photocatalysts plays dual function, produce H₂ and reduce waste[57]. However, if biomass or its derivatives are to be used as a feedstock for hydrogen production, a pre-treatment is required so that biomass is more easily converted.

3. TiO$_2$ as Photocatalyst

In the photocatalytic process, the choice of material for the photocatalyst is an important thing. Selection of the appropriate photocatalyst material is based on the following: (i) suppresses the H$_2$-O$_2$ reverse reaction, (ii) prevents the $e^- - h^+$ recombination process (timescale: c.10$^{-9}$s), and (iii) promotes the charge formed from bulk to the surface of the photocatalyst cause the water molecules and others react at the interface (timescale: 10$^{-8}$–10$^{-1}$s) (iv) the photoreforming is both reduction and oxidation reaction, so the value of the gap energy and the energy levels of the valence and conduction bands must correspond.
to the standard reduction potential value of each half the redox reaction involved [20]. In addition, the material must be light stable, inert and non-toxic [14].

The semiconductor material that is widely used as a photocatalyst is titanium oxide (TiO$_2$). It has the highest photocatalytic activity among other materials [22,58–60]. TiO$_2$ also has good photostability, high photocatalytic efficiency, has a band gap of $\sim 3.2$ eV, is biocompatible and non-toxic [60–64]. Other compounds that can be used include Graphitic Carbon Nitride (g-nitride), Zinc Oxide (ZnO), Cadmium Sulfide (CdS) [14], Copper oxide (CuO and Cu$_2$O), Strontium Titanate (SrTiO$_3$), Sodium tantalate (NaTaO$_3$), Indium tantalate (InTaO$_4$), tantalum nitride (Ta$_3$N$_5$), tantalum oxidantitrile (TaON), graphene [18], Fe$_2$O$_3$, WO$_3$, CeO$_2$, SnO$_2$, MoO$_3$, and ZrO$_2$ [16]. However, ZnO, CuO, Fe$_2$O$_3$, SnO and CdS have low photochemical stability in solution [19] while other materials are relatively expensive and difficult to obtain.

Although it has various advantages, the performance of TiO$_2$ as a photocatalyst still needs to be improved especially in the production of biohydrogen from biomass and its derivative. One of the way to enhance photocatalytic performance of TiO$_2$ is make it nanosized particle (1-100 nm). The properties of nanoscale materials different significantly from their atoms as well as from large particles. The advantages of particles with nanoscale dimensions are that they have a high interaction surface area and the more surface area of the interacting particles, more photocatalytic reaction take place. Nanomaterial also give quantum confinement effect so that fast bulk recombination can be avoided [63,65–67]. It can be used in powder or film form. However, the random nanoparticle morphology causes the efficiency of photon absorption and the speed of electron transport as a result of photon induction to be less than optimal and when used in powder form, there will be difficulties in separating the catalyst from the suspension and tends to clump, especially at high concentration [65]. Then, morphological modification to TiO$_2$ nanoparticle is an effective strategy to increase its photocatalytic. This surface modification can be done by making zero-dimension (0-D) of TiO$_2$ nanoparticles into one-dimensional (1-D) structures such as nanowire, nanorods or nanotubes [65,68–70]. Meanwhile, TiO$_2$ nanotube activity is better than TiO$_2$ nanowire in H$_2$ production [38,65,71,72], [66].

3.1. TiO$_2$ nanotubes (TiNT)
Titania nanotubes are TiO$_2$ with the morphology consists of a tubes. Hence, it have a diameter (D), thickness (t) and length (L) with a certain nanosized. This size can be controlled by adjusting the process variables. With its unique nanostructure, light (photon) adsorption rate and photoinduced that produce e‘-h‘ pairs can enhanced. The difference of TiO$_2$ nanosphere and nanotube morphology can be observed in Figure 3.

![HER TEM analysis for TiO$_2$ nanosphere (a) and TiO$_2$ nanotube (b)](image)

Figure 3. HER TEM analysis for TiO$_2$ nanosphere (a) and TiO$_2$ nanotube (b) (Picture capture with permission from reference [73] for a and [63] for b.)
Development of nanotube material was so fast after Iijima for the first time discover Carbon nanotube (CNT) in 1991. Nanotube make more efficiently in photocatalytic efficiency as shown in Figure 4. Formation e⁻-h⁺ is a crucial step in photocatalysis. This charge will interact with reactant so that compounds can photoreduced or photooxidized. Unfortunately, these two charge pairs are very easy to interact with and neutralize each other. This is well known as charge recombination. The recombination process can consist of volume recombination, bulk recombination and surface recombination. If recombination of pairs occurs, all photocatalytic capabilities disappear and all advantages from nanostructure modification are cancelled out [38,58,63,65,74,75]. Yet, with nanosized particles, current methods of preventing recombination, this fast recombination mostly possible in nanosphere structure (Fig 4.left). But, by a little effort, namely changing the shape of the nanosphere to the form of nanotubes, the recombination can be better handled. In nanotube, electrons and holes will flow uniaxially along the tube reducing the chance of the two charges meeting. (Fig 4.right)[66]. If recombination can be cancelled out thus surface reaction namely photoreduction of H⁺ to H2 and photooxidation of organics can be improve. Finally, photocatalytic process, especially in H₂ production will be more effective and efficient.

![Figure 4. Nanosphere (left) and nanotube (right) TiO₂ with their electron-hole pairs (adapted with permission form reference [66])](image)

3.2. Preparation Techniques of TiNT

Development in nanoscience and technology brings positive developments to novel catalyst materials. Currently, numerous novel catalyst have been discovered to overcome various problems faced by modern society today around the energy crisis, environmental quality depletion, food and health (medicine). In addition, various preparation techniques also to develop by scientists and engineers to enhance catalytic performance of materials.

TiNT can be synthesis by several methods namely hydrothermal, solvothermal, electrochemical anodization and template method. That’s different preparation methods result different unique structure, morphology and properties of materials [60],[68]. Among them, have advantages and disadvantages each other that it resumed in Table 1. Different structure of TiNT can be show in Figure 5.
Table 1. Comparison of several preparation techniques of TiNT*

| Preparation Techniques | Operation Conditions | Internal Diameter/Length (nm/μm) | Advantages | Disadvantages |
|------------------------|----------------------|----------------------------------|------------|---------------|
| Hydrothermal           | High temperature and pressure • Aqueous based solvent. | 3-10/50-500 | High nanotube production rate • Easy to enhance the features of titanium nanotubes. • Large scale preparation | Long reaction time • Not uniform size. |
| Solvothermal           | High temperature and pressure | | Better control of the nanosized, crystal phase and narrow size distribution. • Varieties of chosen organic solvent | Critical reaction conditions. |
| Electrochemical anodization | Organic solvent • 5–50 V and 0.2–10 h under ambient conditions. • F−-based buffered electrolytes and organic electrolytes, F−-free electrolytes. | 20-110/0.1-2.4 | Uniform structure • Dimension of nanotubes can be controlled by varying the voltage, electrolyte, pH and anodizing time. • Uniform size of nanotubes | Long reaction time. • Small scale preparation. • Length distribution and separation of nanotubes over a large surface area is not well-developed |
| Template               | AAO, ZnO etc. as sacrificial template under specific conditions | 2.5-6000/0.05-200 | Controllable scale of nanotube by applied template • Uniform size of nanotubes | Complicated fabrication process • Contamination or destroy of tubes may occur during fabrication process |

*summary from reference [68][76].
Figure 5. Different structure of TiO\textsubscript{2} nanotube result from different preparation methods a. Hydrothermal b. Solvothermal c. Electrochemical anodized d. template (collected form [66])

3.2.1. Hydrothermal Method. Hydrothermal synthesis involve water that heated at high temperature and pressure. Commonly, temperature for this method is slightly above boiling point of water. In sub-microscopic point of view, the process that occurs includes the growth of crystal, crystal transformation, phase equilibrium, and final ultrafine crystals formation [68]. TiO\textsubscript{2} nanotube mostly synthesized in this way cause it simplicity, not required sacrificial agent and can applied in large scale.

Practically, TiO\textsubscript{2} powders as precursor are mixed with concentrated NaOH. Then, the resulting mixture enclosed in a autoclave under controlled temperature and pressure. If the reaction is complete, rinse with deionized water and acidic solution is needed to remove the impurities. The synthesis process illustrated in Figure 6. There are several synthesis variable to control morphology, size and length of TiNT. That’s variable such as structure of TiO\textsubscript{2} feedstock, reacting solutions concentration, hydrothermal temperature and time, and even post treatment by acid washing and calcination [60][68][77].
Figure 6. Hydrothermal Method of Producing Nanotube TiO\textsubscript{2} (adapted from reference[77]).

TiNT resulted with this method reach 100% conversion. But, hydrothermal methods have some drawback i.e. kinetically, its slow reaction rate so it need long reaction duration and short nanotube length. The tubes in hydrothermal are in non-uniform[60][63][68][78] But it can be modified by control operation condition (synthesis variables) as written early. Time of reaction can be reduce by applied (ultra)sonication method[79], microwave assisted [80] and pre mixing of prior hydrothermal[81].

3.2.2. Solvothermal Method. Solvothermal synthesis basically same with hydrothermal method. One of distinct of both method is the solvent used. If in hydrothermal use water as solvent, in solvothermal use organics such as ethanol and glycerol. Selection of solvent plays important role to determine morphology of crystal. Physical and chemical properties of the solvent influence the solubility, reactivity, diffusion of reactant and crystallization of final product. Solvothermal technique produce bilayer and multilayer [68].

3.2.3. Electrochemical Anodization Method. TiO\textsubscript{2} nanotubes are of two types, namely nanotube arrays (abbreviated as TiNTA) and non-arrays (abbreviated as TiNT). TiNTA have highly ordered and orientated tube. These forms result from different synthesis methods. TiNT generated from hydrothermal and solvothermal synthesis methods as described earlier. Meanwhile, TiNTA was obtained from anodizing and template methods[68],[82].

Anodization technique attempt in electrochemical cell (Figure 7). Pt film serve as cathode and Ti film as anode. At the cathode there is a reduction reaction and H\textsubscript{2} gas will be produced, while at the anode, Titanium will be oxidized to TiO\textsubscript{2}.[82]There are some solvent used as electrolyte i.e fluoride-based electrolyte (HF, NaF, and KF), buffer neutral electrolyte contains various fluoride slat (NaF or NH\textsubscript{4}F) aquous organic solvent non-containing F- (glycerol, ethylene glycol, and dimethyl sulfoxide (DMSO)), electrolyte solution that fluoride-free (HClO\textsubscript{4}-containing electrolyte). The electrolyte will affect length of the tubes[68]. Anodization process was influenced by several factors i.e. applied potential, kind of electrolyte and its concentration, pH and temperature. Commonly, acetic acid, citric acid, nitric acid, phosphoric acid and sulfuric acid are used to control the acidity[68].
Anodization process was influenced by several factors i.e. applied potential, kind of electrolyte and its concentration, pH and temperature. Commonly, acetic acid, citric acid, nitric acid, phosphoric acid and sulfuric acid are used to control the acidity [68]. Although can produce TiNT with uniform tube, this method only applied in small scale and complicated condition of process.

3.2.4. Template Method. Template method is a commonly used synthesis technique that produce nanostructured material with a morphology follows the known and characterized templates. Typically, the templates that used are anodic aluminium membranes (AAM), ZnO, and silica etc. They can be easily removed via chemical etching or combustion, leaving the resultants with a pre-set porosity and reversely duplicated morphology. Among them, ZnO nanorod commonly used because its low cost, easy fabrication and easily remove by acid in mild condition [68], [83]. The template technique can be illustrated in Figure 8.

Figure 8. Step of TiNT formation via ZnO nanorod template methods (Adapted from reference [68]).
Template method gives a uniform tube and several kind of tube form. But, that disadvantages are template removed after synthesis generate waste, the cost of preparation was added and dissolution process might destroy Titania nanostructure[68].

4. Metal Doped TiO₂

Titanium oxide’s drawback as a photocatalyst not only fast recombination of charge pair (electron-hole) and possibility of reverse reaction of H₂ and O₂ result H₂O. The other limitation is photocatalyst performance of TiO₂ only at UV region. Even thought, photocatalyst active region on only in UV but also in Visible as shown in Figure 9. When, TiO₂ applied at that region, only 5% of solar energy can be absorbed by that photocatalyst. In other hand, if TiO₂ can be active in visible area, the solar energy can be harvest reach 40%.

Figure 9. Photocatalytic’s active region

Morphological modification by nanosized TiO₂ and convert it from nanosphere to nanotube can not overcome that’s problem. Further modification must be held to Titania. One of the solution of that limitation is doped TiO₂ with others compound such as metal (noble metal or transition metal and non-metal) or dye sensitizer. However, a more effective modification is by doping the metal to the TiO₂ surface. The presence of metals will directly affect the electronic properties of the photocatalyst surface[16],[22]. Metal doping in TiO₂ is one way to manipulate the band gap energy value or (Eg) which is still relatively high, namely 3.2 eV (anatase phase), 3.0 eV (rutile phase) and 2.96 eV (brookite phase) [70]. With this band gap engineering, the transition / migration of electrons from the valence band to the conduction band will occur more effective. The number of electrons that migrate will determine the value of the production efficiency of H₂.

4.1. Role of Metal in Photocatalytic

Sub-microscopically, enhancement of photocatalytic activity by metal doping occurs in several ways, including electron trapping by formation of a Schottky barrier, Surface Plasmon Resonance (SPR) effect and the formation of new energy levels[22].
Electron trapping can occur due to the formation of the Schottky barrier. This barrier appears in the metal-photocatalyst/ semiconductor interface region of TiO$_2$. This barrier is basically the energy level. This barrier will make it easier for electrons to migrate to the metal surface. This electron migration will continue until thermodynamic equilibrium is reached, which is when the fermi energy level of TiO$_2$ is parallel to the fermi energy of the metal. The migration of electrons to the metal surface will reduce the tendency for e- h + recombination or the return of electrons from the conduction band to the valence band. The more electrons there are on the metal surface, the more H$^+$ is reduced to H$_2$[17][22][49][58][84]. Electron trapping mechanism is shown in Figure 10.

![Electron trapping mechanism](image)

Figure 10. An overview of the process of forming the Schottky barrier and transfer of electrons from the conduction band to the metal surface. Adapted from reference [22]

Metal doping causes new energy levels in the TiO$_2$ photocatalyst. This new energy level could result from a crystal defect in TiO$_2$. Crystal Defects represent deviations from the proper crystal shape. With this new energy level, the migration of electrons from the valence band to the conduction band will take place better and more e-h formation will occur[85]. The energy level after doping electron is shown Figure 11.
Figure 11. Illustration of the formation of new energy levels in the TiO$_2$ band structure due to metal doping.

In TiO$_2$, Titanium metal has a +4 (Ti$^{4+}$) oxidation state. The doping of vanadium metal with the +5 (V$^{5+}$) oxidation state causes an electron deficiency and forms a vacancy. According to band theory, this deficiency of electrons will occupy a new energy level that lies slightly above the valence band. With the adsorption of photons (from sunlight), the electrons at the acceptor energy level will experience excitation to the conduction band. This new energy level has a smaller $E_g$ compared to $E_g$ TiO$_2$ ($\approx 3.2$ eV).

Meanwhile, if TiO$_2$ is doped with copper metal which has a valence of 2+ (Cu$^{2+}$) then one Ti$^{4+}$ ion will be replaced by 2 Cu$^{2+}$ ions (to neutralize the charge) and there will be an excess of Cu$^{2+}$ ions. This excess Cu$^{2+}$ ion will occupy a new energy level at the donor energy level. Its energy level lies slightly above the valence band. With the adsorption of photons (from sunlight), the electrons at the energy level of the donor will experience excitation to the conduction band with $E_g$ much smaller than $E_g$ TiO$_2$.

Surface Plasmon Resonance (SPR) is a collective oscillation of electrons in the conduction band caused by electromagnetic radiation. With phenomena SPR due to metal doping can change the optical properties of semiconductors and increase the absorption of visible light in TiO$_2$[86] SPR occurs when the electromagnetic field has an oscillation frequency in phase with free electrons on the metal. These plasmon-induced electrons can transfer to an electron-acceptor such as Titania[87]. Hence, metal particles (nanosized) doped to TiO$_2$ (i) act as antennas by promoting absorption in visible area and (ii) sensitize Titania by favouring the flux of charge carriers on to the conduction band of the semiconductor.
This process also called “Process of Plasmon-Induced Resonance Energy Transfer” (PIRET)[19][88]. SPR process is shown in Figure 12.

![Figure 12. Schematic SPR process in Ag-Pd/TiO2 (reproduce with permission from reference [22])](image)

4.2. Metal Screening
Various types of metals and non-metals which are often used to modify the photocatalytic properties of TiO2 can be observed in Figure 13. It is important to select the right metal for doping in TiO2. The choice of metal is based on several things, including the metal must have good photocatalytic activity, good photostability and resistance to corrosion when it comes into contact with a solution. This good photostability can be done by using double metal doping, one of which is inert and corrosion resistant[70]. In addition, the photocatalyst must be easily recovered from the solution mixture after the photoreforming process is complete and the metal is cheap [19]. For this reason, it is necessary to consider several quantities such as the work function (Φm) of the metal and also the standard reduction potential (E°red) of the process that occurs considering that photoreforming involves reduction and oxidation reactions [89][90]. Table 2 presents these important data.

Based on the work function data in Table 2, it can be seen that the value of Φm in metal is greater than that of Eg in TiO2 (3.2 eV). This means that the interaction between the metal and semiconductor TiO2 interface is getting better with the formation of the Schottky Barrier. Metals with a larger work function can produce a stronger Schottky barrier effect and the number of electrons migrating from TiO2 to the metal surface (surface recombination) will increase. As a result, the amount of H2 that is produced photocatalytically will be more. Pt metal has the highest Φm compared to other metals with a Φm value of 5.65 eV so that this metal is the most active in the photoreforming co-catalyst for H2 production biomass [70][90]. With more electrons moving from TiO2 to Pt metal, the metal surface becomes more negatively charged (excess negative charge) so that the photoreduction of H+ to H2 becomes easier. The surface of TiO2 (after electron migration) becomes more positively charged (excess positive charge) so that more biomass or biomass derivatives undergo photooxidation to form H2 and CO2 as well as more valuable chemicals (added value chemicals)[91,92].
Figure 13. The elements are used as dopants to modify the photocatalytic properties of TiO$_2$. (Adapted from reference [22])

| Metal | Work function ($\Phi_m$) | Reaction |
|-------|--------------------------|----------|
| Co    | 5                        | Co$^{2+}$ +2e $\rightarrow$ Co   |
| Ni    | 5.15                     | Ni$^{2+}$ +2e $\rightarrow$ Ni   |
| Cu    | 4.65                     | Cu$^{2+}$ +2e $\rightarrow$ Cu   |
| Ru    | 4.71                     | Ru$^{2+}$ +2e $\rightarrow$ Ru   |
| Rh    | 4.98                     | Rh$^{3+}$ +3e $\rightarrow$ Rh   |
| Ag    | 4.26                     | Ag$^+ +$e $\rightarrow$ Ag       |
| Pd    | 5.12                     | Pd$^{2+}$ +2e $\rightarrow$ Pd   |
| Ir    | 5.27                     | Ir$^{3+}$ +3e $\rightarrow$ Ir   |
| Pt    | 5.65                     | Pt$^{2+}$ +2e $\rightarrow$ Pt   |
| Au    | 5.1                      | Au$^{3+}$ +3e $\rightarrow$ Au   |

5. Morphology and Optic Properties of Modified TiO$_2$ and the Effect in H$_2$ Production

5.1. Relationship between morphology and optic properties of materials

The photocatalytic reaction of H$_2$ production through reforming of biomass or its derivatives is influenced by several variables such as raw material, photocatalyst material and operating conditions. However, this paper is devoted to carefully studying the photocatalyst material and the modifications that can be made to increase hydrogen production.

The molecular design of photocatalyst materials plays an important role in increasing H$_2$ production. It includes regulating the morphology of TiO$_2$ so that it can absorb solar energy maximally and the photocatalytic process runs effectively and efficiently. The response of a material to light/photons irradiated in a material is known as optical properties. Light can be absorbed or reflected or transmitted.
by a material. In the case of photocatalytic reactions, sunlight is expected to be absorbed as much as possible by the material. The absorbed solar energy will be used by electrons to migrate from the valence band to the conduction band of the semiconductor. During this migration, charge pairs (electrons and holes) are formed which play a role in the process of reducing $\text{H}^+$ to $\text{H}_2$ or the oxidation of organic molecules from biomass or its derivatives. Therefore, there is a close relationship between the morphology and optical properties of the photocatalyst material, especially TiO$_2$. The relationship among them is described in Figure 14.

![Figure 14. Adsorption of photon and electron transport in TiO$_2$ with different morphology. a. TiO$_2$ nanosphere and b. TiO$_2$ nanotube. (Reproduce with permission form reference [82])](image)

Based on Figure 14 the process of light absorption and electron transport in spherical and tubular materials will be different. In figure 14a, the light absorbed by the spherical TiO$_2$ material is used for the migration of electrons but they cannot move into the inside cause collides with the atomic lattice. Meanwhile, Figure 14b shows that the light absorbed by TiNT will be able to migrate to the inside without any obstruction[82]. The more electrons that can migrate, the better the photocatalyst reaction runs. This also corresponds to Figure 4 as previous.

Morphology of metal doped to TiO$_2$ also influence on optic properties. Metal that doped to TiO$_2$ can be monometallic or bimetallic. Their morphology and structure can be exist in several form commonly alloys, core-shell and Janus type. Specifically in bimetallic, it can be illustrated in Figure 15[87][93]. It can be shown in Figure 15 and effect of morphology in photoreforming process shown in Figure 16. The researchers assessed that the core shell structure was superior to the non-core types. Apart from increasing the performance of the metal, it can also increase the photostability of the catalyst especially in the solution system. These two properties are considered when choosing a photocatalyst material. In alloy and Janus structure, Material photocatalyst directly contact with solution or light. It might be cause of corrosion of material. If it happens, material will be inactive catalyst[66][94].
Figure 15. Bimetallic nanoparticles structure: (a) mixed alloys; (b) random alloys; (c) subclusters with two interfaces (d) subclusters with three interfaces; (e) subclusters with small number of A–B bonds; (f) core–shell nanoparticles; (g) multi shell core–shell nanoparticles; (h) multiple small core material coated by single shell material, (i) movable core within hollow shell material (reproduce with permission from reference [93]).

Figure 16. Photocatalytic process in non-core–shell and core–shell catalysts under solar light irradiation (based on reference [66]).
5.2. Effect of morphology and optic properties of materials on H2 production
The proper morphology can affect optic properties of material and then enhance Photocatalytic performance in H2 production [67,84,95]. It can be shown in Figure 17. As discuss previously nanotube morphology make will increase the absorbed amount of solar energy so that electron migration will be possible. More migration electron, more H+ can be reduced to H2. More hole that can be formed form migration electron, more organics (CₓHᵧOᵦ)will be oxidized to CO₂ and H₂O and then H₂. Nanotube structure enhance H₂ production twice or even three times than nanoparticle[72][61,65,68,96][67,77]

Figure 17. Influence of nanotube structure to H₂ production (based on reference [118])

Figure 18. Schematic overview H2 production in Cu doped TiNT (adapted from reference [66])
Metal doping to TiO$_2$ both nanoparticle or nanotube will enhance dramatically H$_2$ production. This effect illustrated in Figure 18. As explain in previous section, metal can enhance photocatalytic activity by electron trapped, LPSR and form a new level energy. In monometallic each of these effects can be observed. But in bimetallic effect synergetic effect among electron trapped, LPSR and form a new level energy can be observed.[93,97–103]. Morphology both metal doped and TiO$_2$ significantly influence the photocatalytic activity in H$_2$ production [38,87,93,104,105]. Influence of morphology and optical properties to H$_2$ production via photoreforming biomass and its derivatives by modified TiO$_2$ summarize in Table 3.

**Table 3. Literature review on modified TiO$_2$ as a photoreforming photocatalyst**

| Photocatalyst | Sacrificial agent | Reaction condition | H$_2$ production | Ref |
|---------------|-------------------|--------------------|------------------|-----|
| TiO$_2$ Nanotube | Glyserol | V solution: 400 mL, glycerol concentration: 10% vol catalyst amount: 0.4 g | 534.0 μmol | [118] |
| TiO$_2$ nanosphere | | Hg lamp | 224.5 μmol |
| Mono-metal doped to TiO$_2$ | | V solution: 50 mL UV-Vis Fe-X lamp T: 293-313 K catalyst amount: 15 mg | 0 μmol |
| 0,5% (Pt)TiO$_2$ | Cellulose | | – TiO$_2$ (Pt): 45 μmol |
| | | | – Cellulose +TiO$_2$: 0 μmol |
| | | | – Cellulose @TiO$_2$: 0 μmol |
| | | | – Cellulose +TiO$_2$(Pt): 45 μmol |
| | | | – Cellulose @TiO$_2$(Pt): 75 μmol |
| 0,01M Pt/TiO$_2$ | Sucrose | -closed vessel reactor -V sucrose 67mL involve TiO$_2$/Pt NPs -V aquades 67 mL -T: 281.1 K. Xe arc lamp (150 W dan 360 W) in outside reactor | 40 μmol | [49] |
| | | | – Conventional preparation method: 4.26 mmol.h$^{-1}$.g$^{-1}$ |
| | | | – Nanocomposite: 4.92 mmol.h$^{-1}$.g$^{-1}$ |
| Pt/TiO$_2$ | Glucose | -Glucose (aq., 5% w/v, 25 mL) -suspended M/TiO$_2$ (25 mg) -simulated sunlight irradiation (AM1.5G, 1.0 kW m$^{-2}$) -Ar atmosphere (1.4 bar) -T 25 °C t = 2 jam | Metal doping technique -Impregnation: < 300 μmol.g$^{-1}$ | [53] |
| Au/ TiO$_2$ | | | Photodeposition: Pt/TiO$_2$: 1.812.5 μmol.g$^{-1}$ |
| Ag/ TiO$_2$ | | | Au/TiO$_2$: 879.6 μmol.g$^{-1}$ |
| Cu/ TiO$_2$ | | | Ag/TiO$_2$:400 μmol.g$^{-1}$ |
| (% M=1-1.25%) | | | Cu/TiO$_2$:872.6 μmol.g$^{-1}$ |
| Catalyst       | Precipitation                  | Glucose (aq., 5% w/v, 25 mL) | Suspended M/TiO₂ (25 mg) | Simulated sunlight irradiation (AM1.5G, 1.0 kW m⁻²) | Ar atmosphere (1.4 bar) | T:25°C | t: 2 h | α-cellulose (2.5~12.5 mg) | TiO₂(Pt) (0~25 mg) | H₂SO₄ 0.6 M 50 mL | t:10 h | T: 403 K | Fe-Halide lamp 250 W |
|----------------|--------------------------------|-----------------------------|--------------------------|------------------------------------------------|--------------------------|--------|--------|-----------------------------|------------------|-------------------|--------|----------|-------------------|
| Pt/TiO₂        | ±1500 μmol.g⁻¹.cat⁻¹            |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| Au/TiO₂        | ±600 μmol.g⁻¹.cat⁻¹             |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| Cu/TiO₂        | 400 μmol.g⁻¹.cat⁻¹              |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| Cu₂O/TiO₂      | 500 μmol.g⁻¹.cat⁻¹              |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| 0.5%Pt/TiO₂    | ±108 μmol/g                   |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| 0.25%Pt/TiO₂   | ±108 μmol/g                   |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| 0.25%Au/TiO₂   | 8000 μmol.g⁻¹.cat⁻¹.h⁻¹        |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| 0.5%Pd/TiO₂    | 12 mL H₂ (glycerol)            |                             | 2 g/L catalyst           |                                                |                          |        |        |                             |                  |                   |        |          |                   |
| Cu₂O/TiO₂      | Production H₂ form Photocatalyst |                             |                          |                                                |                          |        |        |                             |                  |                   |        |          |                   |

Notes:
- Precipitation: H₂ Production not significant amount CO₂ and other organics hydrolized [53]
- Pt/TiO₂: 8000 μmol.g⁻¹.cat⁻¹.h⁻¹ [107]
- If only UV lamp, H₂ reduction not significant

References:
- [108]
bubbling and sampling. Photocatalyst 0.1 g
UV Xe lamp 150 W prepared by chemical
reduction better than wet impregnation
methods

| CuO_x/TiO_2 | Glycerol | Glass reactor 150 mL V solution : 50 mL Catalyst 22 mount: 100 mg Glycerol 5%. Solar simulator dan UV-Hg lamp 400 W |
| CuO_x/TiO_2 | Ethanol | Cu loading 1% dan 2,5% UV/Vis and solar simulator lamp |
| CuO_x/TiO_2 | Ethanol (from lignocellulos e) | - Ethanol : ±1700 μmol.g_cat^{-1}.h^{-1} (UV-Vis lamp) |
| CuO_x/TiO_2 | Ethanol (biodiesel side product) | - Ethanol : ±800 μmol.g_cat^{-1}.h^{-1} (solar simulator) |
| CuO_x/TiO_2 | Ethanol (biodiesel side product) | - Glycerol: ±1500 μmol.g_cat^{-1}.h^{-1} (UV-Vis lamp) |
| CuO_x/TiO_2 | Ethanol (biodiesel side product) | - Glycerol : ±600 μmol.g_cat^{-1}.h^{-1} (solar simulator) |

| Cu/FTiO_2 | Methanol | batch reactor with external cooling jacket. 500 mg of photocatalyst (2,5%) -V ethanol dan glycerol (1M) 240 mL T: 20 °C UV-Vis Hg lam 125 W |
| Cu/FTiO_2 | Methanol | - Ethanol CuO_x@TiO_2: 1300 μmol.g_cat^{-1}.h^{-1} |
| Cu/FTiO_2 | Methanol | - CuO_x/TiO_2: 700 μmol.g_cat^{-1}.h^{-1} |
| Cu/FTiO_2 | Methanol | - Glycerol CuO_x@TiO_2: 1000 μmol.g_cat^{-1}.h^{-1} |
| Cu/FTiO_2 | Methanol | - CuO_x/TiO_2: 600 μmol.g_cat^{-1}.h^{-1} |

| Cu/FTiO_2 | Methanol | pilot plant scale - Stainless steel reactor 27 L - Centrifuge flow rate 20 L min^{-1} - solar simulator - pH: 3, 5,6,7,8,9 - catalyst 22 mount 0.2 g.L^{-1} - Methanol and 22 mount 221 : 0,05M |
| Cu/FTiO_2 | Methanol | - Methanol: 377 μmol.L^{-1} at pH 6-7. Accumulation of energy 71,6 kJ.L^{-1} |
| Cu/FTiO_2 | Methanol | - Glycerol: 1240 μmol.L^{-1} at pH 5-6 Accumulation of energy 63 kJ.L^{-1} |
| Cu/FTiO_2 | Methanol | - Urban waste water: 43 μmol.L^{-1} at pH 7-8 Accumulation of energy 5 kJ.L^{-1} |
| Catalyst | Sacrificial agent | Reaction conditions | H₂ production | Notes |
|----------|-------------------|---------------------|--------------|-------|
| Ni/TiO₂ Glycerol | Catalyst 23 mg mount | 5 mg glycerol/water (10% v/v) mixing, 800 rpm, T 20°C, UV (Xe lamp) and solar simulator | H₂ activation | [112] |
| Ni, Pd, Pt dan Au on TiO₂ | Cellulose Glucose | Catalyst amount: 150 mg cellulose/water: 0.2 g/200 mL, T 60°C, UV-Vis: Xe lamp 150W, t: 180 min | H₂ production | [113] |
| 1.5%CuₓO/TiO₂ nanoparticle (CuTNP) | Propanol Ethanol Methanol Ethylene Glycol | Catalyst amount: 5 mg V solution: 50 mL, T: 4 h, T: 70°C, Natural solar light I: 1.15 x 10⁵ lx | H₂ production with EG | [114] |
| 1.5%CuₓO/TiO₂ Nanotube (CuTNT) | Ethylene glycol | Reactor: electrochemical cell, Solar simulator (110 mW cm⁻²) | H₂ production: 19 μmol.h⁻¹.cm² | [96] |
| Pt/TNTA | Acetone Ethanol Acetic acid Formaldehyde Ethylene glycol | Reactor glass 500 mL, UV lamp, T: 4 h | Ethylene glycol (best sacrificial agent) | [32] |

Notes:
- Ni, Pd, Pt dan Au on TiO₂
- 1.5%CuₓO/TiO₂ nanoparticle (CuTNP)
- 1.5%CuₓO/TiO₂ Nanotube (CuTNT)
Bimetallic doped to TiO$_2$

| System                  | Component                        | Mass/Amount                  | H$_2$ Production                          |
|-------------------------|----------------------------------|------------------------------|-------------------------------------------|
| RuO$_2$/TiO$_2$/Pt       | Sugar                            | Mass of sugar (600 mg)       | H$_2$ at 5% EG                           |
|                         | Amylose                          | Massa of Amylose (210 mg)    | 3 x 10$^{-4}$ – 6,4 x 10$^{-4}$ mol.g$_{cat}$^{-1}.min$^{-1}$ |
|                         | Cellulose form paper pulp        | Mass of cellulose (120 mg)   | H$_2$ at 0.5% EG                         |
|                         | Catalyst 24mount (300 mg)        |                              | 1 x 10$^{-6}$ – 2,66 x 10$^{-4}$ mol.g$_{cat}$^{-1}.min$^{-1}$ |
|                         | V H$_2$O 40 ML                    |                              |                                            |
|                         | NaOH 6M (40 mL)                   |                              |                                            |
|                         | Xe lamp 500W                      |                              |                                            |
| 0.1%Ag-0.3%Pd/TiO$_2$    | Ethylene glycol                  | P O$_2$: 0.001-0.2 atm       |                                            |
|                         |                                  | Ethylene glycol: 0.5 %vol (0.067 M) dan 0.5 % vol (0.0067 M) |                                            |
|                         |                                  | Catalyst 24mount:5 mg        |                                            |
|                         |                                  | UV light 100 W               |                                            |
| 0.5%Au-0.5%Pt/TiO$_2$    | Ethanol                          | Sacrificial agent: EtOH/ H2O (1:1 by volume) or glycerol (1M). | H$_2$ production                          |
|                         | Glycerol                         | UV-A lamp                    | UV A lamp                                 |
|                         |                                  | Photocatalyst mass (500 mg)  | Ethanol: 8000μmol.g$_{cat}$^{-1}.h$^{-1}$ |
|                         |                                  | V solution (240 mL)          | Glycerol: 4000 μmol.g$_{cat}$^{-1}.h$^{-1}$ |
|                         |                                  | Hg lamp 125 W                | Solar Simulator                           |
|                         |                                  | Solar Simulator, photocatalyst (125 mg), V solution (80 mL), Xe 150 W lamp | Ethanol: 1700μmol.g$_{cat}$^{-1}.h$^{-1}$ |
|                         |                                  | T 20ºC (UV-A experiments) or 25ºC (simulated sunlight experiments) | Glycerol: 1400 μmol.g$_{cat}$^{-1}.h$^{-1}$ |
| 5%Ni-5%Cu/TiO$_2$       | Ethanol                          | Photoelectrochemical cell photoanode (synthesized photocatalyst), working electrode (WE), electrode holder (Pt) Ag/AgCl/ KCl as standard electrode. Glycerol 10 v/v% | H$_2$ production: |
|                         |                                  | catalyst amount:5 mg         | TiO$_2$: 1.8 mL                           |
|                         |                                  | ethanol 5%.                  | 10%Cu/TiO$_2$:4,5 mL                      |
|                         |                                  | UV lamp 100 Watt             | 10%Ni/TiO$_2$: 3,1 mL                     |
|                         |                                  |                               | 5%Cu-5%Ni/TiO$_2$: 5,3 mL                 |
| Au-Pd/TiO$_2$            | Ethanol                          | Ethanol amount:5 mg          | H$_2$ production:                          |
|                         |                                  | UV lamp 100 Watt             | TiO$_2$: 1.8 mL                           |
|                         |                                  |                               | 10%Cu/TiO$_2$:4,5 mL                      |
|                         |                                  |                               | 10%Ni/TiO$_2$: 3,1 mL                     |
|                         |                                  |                               | 5%Cu-5%Ni/TiO$_2$: 5,3 mL                 |

**References:**

[115], [116], [103], [101], [27]
Cu-Ag/TiO$_2$ nanotube | Glycerol | Solar simulator | H$_2$ production: $4800 \mu$mol.g$_{cat}^{-1}.h^{-1}$

6. Conclusion and Future Direction
Sustainable production of H$_2$ from renewable raw materials, namely biomass and its derivatives, is one of the solutions to overcome the problems facing the world today, the energy crisis due to depletion of petroleum reserves and a decrease in environmental quality. This can be accomplished by a biomass photoreforming that uses sunlight as a renewable energy source to induce photocatalyst material in order to direct the reaction to H$_2$ formation. Nanoscience and technology are well developed and can be applied in fulfilling H$_2$ as environmentally friendly energy source and carrier. Nanosized photocatalyst materials have been shown to improve the performance of photocatalysts compared to microparticle sizes or larger materials. However, the performance of the photocatalyst can be improved by modification of the morphology and optical properties of the photocatalyst. Photocatalysts in nanoscale that have a morphology in the form of tubes (nanotubes) can be applied because they can increase the amount of solar energy absorbed by the photocatalyst material. The tube shape also reduces the rapid recombination of electron-holes due to the movement of electrons and holes along the tube axis. If recombination occurs, photocatalytic activity will not appear. Further modification of the morphology and optical properties can be applied by metal doping of TiO$_2$. By addition of metal to the surface of the TiO$_2$, there are three advantages that can be obtained at the same time, namely that the fast recombination of the electron-hole pairs can be reduced maximally, rapidly of reverse reaction of H$_2$O to H$_2$O can also be avoided and enlarge/ board solar energy absorption in UV-Vis region. These three things are the main limitations of TiO$_2$ as a photocatalyst material.

Biomass photoreforming is one complicated reaction because the stages of reaction are longer than water photosplitting. For this reason, the development of photocatalyst materials that can be applied to this process is a challenge and an opportunity for future research. In the development of materials, the appropriate synthesis method is vital role that must be an attention. TiO$_2$ nanotube synthesis using the hydrothermal method can be applied because it can produce TiO$_2$ nanotubes with high purity, no need organic solvents that have the potential to produce new waste, the tube structure is not easily damaged during washing so the method is relatively simple and can be applied on a large scale. To improve the photocatalytic performance of Titania nonotube, this material can be doped with metals. Although Pt is the most active metal as a co-catalyst, its price is relatively expensive, so it can be replaced with a transition metal which is cheap and easy to obtain. Among the existing transition metals, Cu metal is the most active compared to other metals. However, its activity can be reduced because the metal is prone to corrosion in solution. To prevent this, another transition metal can be added, namely Ni. Bimetallic Ni-Cu have been investigated to have the potential to increase H$_2$ production from organics as biomass derivatives. In the preparation methods of that catalyst is necessary to consider so that the core shell structure of Ni-Cu can be obtained. The core shell structure has been studied to have good photocatalytic activity and can increase the photostability of the material. As summarized in Table 3, there have not been many studies examining bimetal doping in TiO$_2$ nanotubes. This opens up opportunities for other researchers to study bimetallic potential doping of transition metal in Titania nanotubes. The obtained photocatalyst can be apply in the production of H$_2$ through photoreforming biomass or its derivatives.
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