Dissociation of water into hydrogen and oxygen through a combination of electrolysis and photocatalyst

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Abstract. Hydrogen from water is an alternative energy source that can replace fossil fuels and is environmentally friendly. Various methods have been developed in producing hydrogen from water, including the process of photocatalysis and electrolysis. Photocatalysis is a water splitting event to produce hydrogen from water that utilizes photon energy. Most photocatalyst materials are made of semiconductor material because they have an energy gap that allows them to produce electron-holes if they are subjected to photon energy from a particular source that causes a water splitting event. Water electrolysis is the decomposition of water compounds (H₂O) into oxygen gas (O₂) and hydrogen gas (H₂) by using an electric current through the water. Some of the obstacles of the two methods above are 1) photocatalysis: most of the photocatalyst materials that have been developed to date only work efficiently in the ultra violet light range and the amount of hydrogen production has not been maximized, 2) electrolysis: to produce hydrogen on a large scale, requires electricity in large quantities as a trigger for a reaction, so it requires high production costs. In this paper, through a literature review, a method of separating hydrogen and oxygen from water through a photocatalysis process that utilizes the energy of photons from visible light is combined with the electrolysis process to increase hydrogen production with a fairly small current.

1. Introduction

Hydrogen in water is an alternative energy source that can replace fossil fuels, especially as a fuel cell. The hydrogen fuel cell is considered to be an environmentally friendly fuel, this is due to the combustion of hydrogen which does not cause carbon dioxide emissions (zero emissions). Hydrogen fuel cells also have very low pollution levels compared to fuel oil. The availability of hydrogen in nature is very abundant. Therefore various efforts have been made by researchers to produce hydrogen.

Photocatalysis is a water splitting event to produce hydrogen that uses photon energy. Most photocatalyst materials are made of semiconductor material because the semiconductor material has an energy gap that allows it to produce electron holes if it is to give the photon energy from a source particular. This electron-hole pair will later cause a water splitting event. So far, the most widely used semiconductor material as photocatalyst is TiO₂. Interest in TiO₂ to be used as photocatalyst compared to other semiconductor materials, TiO₂ is known to have various important advantages, in particular for applications of hydrogen production from water (fractionation of water), including having high stability, corrosion resistance, abundant availability in nature and relatively inexpensive prices.

In general, the TiO₂ photocatalyst which has been developed so far can only produce hydrogen optimally if it operates in an area under visible light. This is due to the band gap energy of the TiO₂ semiconductor material greater than the photonic energy produced by visible light. Efforts to design the TiO₂ catalyst in order to improve its performance in the water splitting, both in the ultraviolet (UV)
and visible light zones, have been made by giving doping from other materials (metallic or non-metallic) such as: TiO₂ / Pt -RuO₂ (Duonghong, D., et al. 1981), Rh-NaOH / TiO₂ (anatase) [1], TiO₂ (P25) / Pt [20], La₂TiO₅ en layers, loose LaTiO₃ / Ni [10] and SrTiO₃. Although some of these studies in the engineering of TiO₂ photocatalysts have been successful, the Rh-NaOH / TiO₂ (anatase) which produces the most hydrogen in the water splitting event is approximately 449 \( \mu \text{mol H}_2 / \text{h} \) using a lamp source of 500W-Hg (250 < \( \lambda \) <400 nm).

The separation of water into hydrogen and oxygen can also be carried out by the electrolysis process. Water electrolysis is the breakdown of water compounds (H₂O) into gaseous oxygen (O₂) and hydrogen gas (H₂) using an electric current through the water. At the cathode, two molecules of water react by capturing two electrons, reduced to gaseous H₂ and hydroxide ions (OH⁻). Meanwhile at the anode, two other molecules of water decompose into gaseous oxygen (O₂), releasing 4H⁺ ions and circulating electrons in the cathode. The H⁺ and OH⁻ ions are neutralized to form several molecules of water.

Several obstacles and problems encountered in the production of hydrogen using the two methods above, such as 1) Photocatalyst: the amount of hydrogen production which was not efficient and the maximum production of hydrogen only in areas under visible light, 2) Electrolysis: to produce hydrogen on a large scale, requires large amounts of electricity as a reaction trigger. In this article, through a review of the literature, developed a method of separating hydrogen and oxygen from water by the photocatalysis process uses the photonic energy of visible light and is combined with the process of electrolysis. The development of a combination of methods in this study, can make it possible to obtain a large production of hydrogen with a small electric current in the electrolysis process.

2. Hydrogen as a Fuel

Lately, global consumption of fossil fuels has started to worry both in terms of existence or sustainability and in terms of environmental damage. Sustainable community development in the future depends on renewable and environmentally friendly alternative energy sources. Because the sun is the largest and cheapest (free) energy source available, it can be considered a potential source of renewable energy. With various methods that have been carried out for the conversion and utilization of solar energy, water splitting by solar energy has been considered the most effective and cleanest way to produce hydrogen. The hydrogen produced can then be used by fuel cells to produce electricity, where water (H₂O) is the only emission produced.

![Figure 1. Economic diagrams of solar energy and hydrogen](image)

From the conversion of solar energy to the use of hydrogen, savings based on renewable energies can be successfully proposed and developed in the coming decades. Figure 1 shows the economic diagram of renewable energies (solar energy and hydrogen) based on several technologies selected for the conversion and use of renewable energies. For solar energy to be a major contributor to the production of clean fuel (hydrogen), the efficiency of solar water separation devices must be improved.
High-capacity hydrogen storage technology and high-performance fuel cells also need to be developed so that hydrogen becomes the main fuel of a renewable energy economy in the future [2].

Hydrogen is a light gas (lighter than air), colorless and odorless. If it burns, it does not show any flame but it produces a very high heat. Based on the results of research experts, determined the physical properties of the hydrogen element as summarized in Table 1.

**Table 1 Physical properties of hydrogen gas [3]**

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Color                           | Colorless                                  |
| Phase                           | gas                                        |
| Melting point                   | 13,99 K (-259,16 °C, -434,49 °F)           |
| Boiling point                   | 20,271 K (-252,879 °C, -423,182 °F)        |
| Density at sts (0 °C and 101,325 kPa) | 0.08988 g/L                              |
| Triple point                    | 13,803 K, 7,041 kPa                       |
| Critical point                  | 32,938 K, 1,2858 Mpa                      |
| Melting heat                    | (H₂) 0,117 kJ/mol                          |
| Evaporation heat                | (H₂) 0,904 kJ/mol                         |
| Molar heat capacity             | (H₂) 28,836 J/(mol·K)                     |

3. **Photocatalyst in Water Splitting**

Thermodynamically, the separation of water (H₂O) into hydrogen gas and oxygen gas is a separation reaction which requires an energy supply which can be determined with Gibss free energy as indicated in equation 1 below.

$$ H_2O \rightarrow H_2 + \frac{1}{2} O_2 \quad \Delta G^0 = 237.13 \text{ kJ mol}^{-1} $$ (1)

Photocatalytic is a process of chemical transformation involving the elements of light and catalyst as well as in carrying out and accelerating the transformation process that occurs. Photocatalytic reactions in the mechanism stages are the same as conventional catalytic reactions. It is just that in the photocatalytic reaction, the catalyst activation in the form of activation by photons, in contrast to conventional type catalytic reactions with catalyst activation is done thermally.

![Diagram of water splitting in semiconductor photocatalysts](image)

**Figure 2.** Diagram of water splitting in semiconductor photocatalysts: (i) light absorption, (ii) separation and transport of charges, and (iii) redox reactions [4].

Figure 2 presents a typical semiconductor particle diagram, which is filled with hydrogen evolutionary cocatalyst (HEC) and oxygen evolutionary cocatalyst (OEC) on its surface. These particles will be used as photocatalysts for the separation of water as a whole, generally these particles are semiconductor materials. Semiconductors have a reduction potential (valence band, VB) or oxidation potential (conduction band, CB). The reactions of photocatalysts or semiconductors during the water splitting, occur in three stages namely (i) the conversion of light energy into electrical
energy when light is absorbed by the semiconductor. (ii) Light having photons \((hv)\) causes intrinsic ionization of the n-type semiconductor material, then regenerates the electrons (-) in the conduction band and the holes (+) in the valence band (equation 2). (iii) Light drives the electrons (-) and the holes (+) to divide the water molecules into gaseous oxygen and hydrogen ions using cocatalysts (equations 3 and 4).

The stages of the photocatalytic reaction on water splitting to hydrogen in a photocatalyst are as follows:

\[
\text{Photocatal} \quad yst + 2h^+ \rightarrow 2e^- + 2h^+ \\
H_2O + h^+ \rightarrow H^+ + \cdot OH \\
\text{OH} + h^+ \rightarrow H^+ + \cdot OH \\
2H^+ + 2e^- \rightarrow H_2
\]

Total reaction:
\[
H_2O + 2hv \rightarrow H_2 + \cdot \cdot O_2
\]

At the same time, the electrons generated as a result of Equation 2 reduce hydrogen ions to hydrogen gas (Equation 5). In order to facilitate the reduction and oxidation of H2O by photoexcitation of electrons and holes, both the reduction and the oxidation potential must lie between the photocatalytic band gap. The band gage is the energy between the valence band and the semiconductor conduction band. In order to induce this reaction, the absorbed photon energy must be at least 1.23 eV. According to this equation, the optimal band gap for hydrogen production is less than 2.0 eV.

Electrons and holes can be joined (recombined) on the bulk or semiconductor surface in a very short time and release energy in the form of heat or photons [5], as shown in Figure 3. This should be avoided so that the reaction of H2 water formation can well occur.

![Figure 3. Events of electron and hole recombination in the photocatalytic water separation process (Copyright 1995 American Chemical Society).](image)

### 4. Semiconductor Materials as Photocatalysts

Materials that can be used as photocatalysts are materials that have energy band intervals like most transition metals and when exposed to light, light energy can excite the electrons in the valence band to the conduction strip. This occurs if the light energy supplied is equal to or greater than the energy band gap of the material. The photocatalysis process can be divided into two depending on the type of catalyst, namely homogeneous photocatalysts and heterogeneous photocatalysts. Homogeneous photocatalysis is a photocatalytic process that occurs in the same phase and using oxidants such as ozone and hydrogen peroxide, while heterogeneous photocatalytic processes are photocatalytic processes that occur between two phases or more and are generally assisted by light or solid catalysts. Heterogeneous photocatalytic processes are technologies based on the irradiation of semiconductor photocatalysts such as titanium dioxide (TiO2), zinc oxide (ZnO) or cadmium sulfide (CdS).
There are several factors that can influence the photocatalysis reaction in semiconductors regarding the structure of the band which is owned, namely the deviation of the energy band, the lowest position of the conduction band and the upper position of the valence band. The ability of a semiconductor to undergo photo-induced electron transfer to a material adsorbed on its surface is determined by the position of the band energy of the semiconductor and the redox potential of the adsorbate. Figure 4 shows that, to facilitate the reduction and oxidation of H₂O by electrons and holes, the position of the lowest level of the photocatalyst conduction band must be more negative than the reduction potential of H⁺ / H₂ (0 V), while the position of the upper level of the valence band must be more positive than the oxidation potential of O₂ / H₂O (1.23 V), [4].

The position of the edge bands of several semiconductors is shown in Figure 5. The internal energy scale is given on the left for comparison with the vacuum level and on the right for comparison with normal hydrogen electrodes (NHE). The position is obtained from the flat strip potential in the liquid electrolyte contact solution at pH = 1. The pH of the electrolyte solution affects the edge position of the various semiconductor strips with respect to the redox potential for the adsorbate.

5. TiO₂ photocatalyst
The TiO₂ catalyst has 3 types of crystal structure, namely anatase, rutile and brookite. Brookite crystal structures are difficult to prepare, so generally only rutile crystal structures and anatases are commonly used in photocatalytic reactions, with anatases having higher photocatalytic activity [7]. The structure of rutile and anatase can be explained in relation to the TiO₆ octahedron chain. The two crystal structures differ in the distortion of each octahedron and in the pattern of assembly of the octahedron chain. Figure 2.6 shows the structure of unit cells of rutile crystal and anatase. Each Ti⁴⁺ ion is surrounded by octahedra with six O²⁻ ions. The rutile octahedra are irregular and have a slight
orthorhombic distortion. The octahedra in the anatase are considerably distorted so that the symmetry is weaker than the orthorhombic. The distance from Ti-Ti in anatase is greater (3.79 and 3.04 Å vs 3.57 and 2.96 Å in rutile) while the distance from Ti-O is shorter than rutile (1934 Å and 1980 Å in anatase vs 1949 Å and 1980 Å in rutile). In the rutile structure, each octahedron is in contact with 10 neighboring octahedra (two oxygen pairs are on the side and eight oxygen atoms are at an angle) while in the anatase structure each octahedron is connected to eight neighbors (four are on the edge and four are on an angle). These differences in the network structure cause different mass densities and electronic band structures between the two forms of TiO₂, as shown in Figures 6 (a) and (b).

![Figure 6. Crystal form of TiO₂ (a) anatase structure, (b) rutile structure [7].](image)

The effect of the photocatalyst structure on the activity of the photocatalytic reaction rate depends very much on the photocatalytic structure itself. As we know that the energy gap of the two TiO₂ structures has a slightly different value, namely for the rutile TiO₂, the gap energy is 3.1 eV while the TiO₂ anatase is 3.3 eV. To obtain the structure of the anatase and rutile for photocatalyst, several factors such as the choice of starting material, the stage of preparation of the catalyst and the method used must be taken into account.

The photocatalysis process for water splitting applications can be classified according to the source of light energy it receives, namely UV light and visible light. Visible light is the most dominant light in the sun (50%), while UV light is only about 5% from the sun. Visible rays have wavelengths ranging from 400 to 800 nm, while UV rays have wavelengths <400 nm. Semiconductors with band gap energy (~ 3 eV) is not response to visible light / sunlight because they are only response to UV light which has a shorter wavelength than visible light (<400 nm). At present, the efficiency of energy conversion from solar to hydrogen is still low with the use of TiO₂ as photocatalyst in water splitting reactions. This can be concluded as follows [8]:

1) Recombination of electron-hole pairs; The electrons in the conduction band can combine very quickly with holes in the valence band and release energy in the form of heat or unnecessary photons.
2) Fast feedback reaction; Decomposing water into hydrogen and oxygen is a process that increases energy. Thus, feedback reactions (recombination of hydrogen and oxygen in water) will easily occur.
3) Inability to use visible light; The TiO₂ anatase band gap is 3.2 eV and only UV light can be used for the production of hydrogen. Since UV light accounts for only about 5% of the sun's radiant energy while visible light is about 50%, the inability to use visible light limits the efficiency of hydrogen production in photocatalytic reactions with solar energy.

6. Dopants on TiO₂ as Photocatalysts

Although so far TiO₂ has been known as the most potential material to use as a photocatalyst in water splitting reactions, but there are still various weaknesses and obstacles as discussed above. Likewise with other semiconductor materials. Therefore, various methods have been adopted to overcome these obstacles. These methods are divided into two main parts, namely by adding sacrificial agents and by
modifying photocatalysts. These two methods have done a lot of research and it has been proven that some of them increase the production of hydrogen. To increase the production of hydrogen, the TiO$_2$ photocatalysts must be added dopants in order to obtain optimal performance. The dopants added to the catalytic system are divided into two types: non-metallic and metallic dopants.

6.1. Addition of Non-Metallic Dopants

Metal dopants tend to have a recombination central property, so the use of non-metallic dopants has recently been developed. The use of non-metals is relatively more recent than dopants with metal ions. However, both have the same function, that is, TiO$_2$ photocatalysts can respond to visible light. The difference, unlike metal ions, is that anions are less likely to cause recombination central and, therefore, will be more effective at increasing photocatalytic activity. Asahi (2001) shows several substitution dopants such as C, N, F, P and S for O in TiO$_2$ anatase [9]. It has been found that the mixture of the states of N with 2p of O can increase the valence band in order to be able to reduce the forbidden band of TiO$_2$, while the position of the conduction band has remained. In the water splitting reaction, the TiO$_2$ conduction band is only slightly superior to its ability to reduce water to H$_2$, so that the conduction band does not have to be shifted.

Among the different uses of dopants studied, substitution with the N dopant is the most effective to achieve. Even if Dopan S has the same O substitution performance in the conduction band, substitution of the dopant S in the crystal structure of TiO$_2$ will be more difficult. This is due to the larger ionic radius S; it has been proven in experiments that the energy of formation for the substitution of the dopant S is higher than the dopant N [9]. As for the dopants other than N and S, their performances are lacking, because their states in the interval TiO$_2$ are less significant. To be able to improve the overall photocatalytic capacity, this method of adding ionic dopants must also be supported by other technologies, such as the deposition of precious metals or the addition of donor electrons (chemical additives).

6.2. Addition of Metal Dopants

The use of metals as photocatalyst dopants for the production of hydrogen has been widely practiced, both precious metal dopants and metal ions. Precious metals which are widely used as photocatalyst dopants include Pt, Au, Pd and Rh. Precious metals are widely used because they have lower Fermi energy levels than TiO$_2$, so that the excited electrons can be transferred from the conduction band to the metallic particles deposited on the surface of TiO$_2$, while the holes in the valence band remain with TiO$_2$.

The transfer of electrons from TiO$_2$ to Pt particles has been studied by Anpo and Takeuchi (2003) [10]. This can be seen with the increase in the Ti$^3+$ signal with the irradiation time and the deposition of Pt reducing the amount of Ti$^3+$. As the electrons accumulate in the precious metal particles, the Fermi level approaches the conduction band of TiO$_2$, which results in a more negative energy level [11]. The smaller metal particles deposited on the TiO$_2$ surface exhibit a more negative level shifted farm. The electrons that accumulate in the metal particles can then be transferred to the protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Thus, precious metals with proper working functions can help transfer electrons, which ultimately succeed in increasing photocatalytic activity.

Pt/TiO$_2$ catalysts prepared using the plasma method produce more hydrogen than impregnated Pt/TiO$_2$ catalysts [12]. In this study, the optimal charge for Pt dopants was 0.5% by weight [12]. However, this difference is not too large compared to the use of sacrificial agents. The influence of the method for preparing Pt dopants has also been realized by Yasuro, et al. (2007) [13]. The use of the formaldehyde method in the preparation of Pt dopane provides the best production of hydrogen compared to the H$_2$ reduction and photocatalysis methods. In this method, the donor electron used is 40% methanol. The addition of precious metals can reduce the recombination reaction to some extent, the production of hydrogen from the separation of pure water remains difficult to do because (1) recombination cannot be completely eliminated; (2) the reverse reaction of H$_2$ and O$_2$ to form H$_2$O is
easier thermodynamically. Therefore, donor electrons or carbonate salts are needed to avoid these problems. Due to the high cost of Pt, a lot of research has been done to find cheap metals that can increase the activity of photocatalysts.

7. Water electrolysis

Water can be broken down into hydrogen and oxygen using electricity in the electrolysis cell. The electrolysis of water is the event of decomposition of water molecules (H\textsubscript{2}O) into gaseous oxygen (O\textsubscript{2}) and hydrogen gas (H\textsubscript{2}) using an electric current through the water. At the cathode, two molecules of water react by capturing two electrons, reduced to gaseous H\textsubscript{2} and hydrocidal ion (OH\textsuperscript{-}). Meanwhile at the anode, two other water molecules decompose into gaseous oxygen (O\textsubscript{2}), releasing 4H\textsuperscript{+} ions and causing electrons to flow to the cathode. The H\textsuperscript{+} and OH\textsuperscript{-} ions are neutralized to form several molecules of water.

The factors which influence the electrolysis of water are the quality of the electrolyte, the temperature, the pressure, the electrolytic resistance, the material of the electrodes and the material of the separator. The hydrogen and oxygen produced from this reaction form bubbles on the electrodes and can be collected (Figure 7). This principle is then used to produce hydrogen which can be used as fuel for a hydrogen vehicle.

![Water Electrolysis Process](image)

**Figure 7.** Water Electrolysis Process [14].

The total reaction of water electrolysis during the decomposition of water into hydrogen and oxygen depends on the type of electrolyte used. The reaction of half cells to acidic or basic electrolytes is written in two different ways. Hydrogen is formed at the cathode, while oxygen is at the anode. The reaction is as follows:

\[
\text{Acid electrolytes, at the anode: } H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^- \quad E^{0}_{\text{anoda}} = 1,23 \text{ V} \quad (7)
\]

\[
\text{at the cathode: } 2H^+ + 2e^- \rightarrow H_2 \quad E^{0}_{\text{cathode}} = 0,00 \text{ V} \quad (8)
\]

\[
\text{Base electrolytes, at the cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^{0}_{\text{cathode}} = -0,83 \text{ V} \quad (9)
\]

\[
\text{at the anode: } 2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^- \quad E^{0}_{\text{anoda}} = 0,40 \text{ V} \quad (10)
\]

Then the total reaction is

\[
H_2O \rightarrow H_2 + \frac{1}{2} O_2 \quad E^{0}_{\text{cat}} = -1,23 \text{ V} \quad (11)
\]

The above calculation results can also be obtained using equation (12) below.

\[
E^{0}_{\text{sel}} = E^{0}_{\text{anoda}} - E^{0}_{\text{anoda}}
\]

\[
= 0,00 \text{ V} - 1,23 \text{ V} = -1,23 \text{ V} \quad \text{or} \quad = -0,83 \text{ V} - 0,40 \text{ V} = -1,23 \text{ V}
\]
The oxidation reaction at the anode will produce oxygen gas, while the reduction reaction at the cathode will produce hydrogen gas. The cell potential (\( E_{cell}^{0} \)) of the entire reaction is -1.23 V. The results of the calculation show that the value \( E_{cell}^{0} \) of the electrolysis reaction of water is 1.23 V. A negative sign on \( E_{cell}^{0} \) indicates that the reaction is not spontaneous. Therefore, to produce hydrogen gas and oxygen from water, theoretically a potential of -1.23 V.

### Table 2. Standard reduction and oxidation potentials of several cations and anions.

| Reduction Potential | (V) | Reduction Potential | (V) |
|---------------------|-----|---------------------|-----|
| Au\(^+\) + e \(\rightarrow\) Au | +1.69 | Ba\(^{2+}\) + 2e \(\rightarrow\) Ba | -2.90 |
| Mn\(^{2+}\) + 2e \(\rightarrow\) Mn | +1.51 | Ra\(^{2+}\) + 2e \(\rightarrow\) Ra | -2.91 |
| Au\(^{3+}\) + 3e \(\rightarrow\) Au | +0.15 | Cs\(^+\) + e \(\rightarrow\) Cs | -2.92 |
| Pt\(^{2+}\) + 2e \(\rightarrow\) Pt | +1.20 | Rb\(^+\) + e \(\rightarrow\) Rb | -2.93 |
| Cu\(^{2+}\) + 2e \(\rightarrow\) Cu | +0.34 | K\(^+\) + e \(\rightarrow\) K | -3.05 |
| Sn\(^{4+}\) + 4e \(\rightarrow\) Sn | +0.15 | Li\(^+\) + e \(\rightarrow\) Li | -3.40 |
| H\(^+\) + e \(\rightarrow\) H\(_2\)(g) | 0.00 | \(\text{Potential Oxidation}\) | (V) |
| Sn\(^{2+}\) + 2e \(\rightarrow\) Sn | -0.14 | Se\(^{2-}\) \(\leftrightarrow\) Se \(+\) 2e | +0.92 |
| Mo\(^{3+}\) + 3e \(\rightarrow\) Mo | -0.20 | S\(^2\) \(\leftrightarrow\) S \(+\) 2e | +0.45 |
| Ni\(^{2+}\) + 2e \(\rightarrow\) Ni | -0.25 | S\(_2\)O\(_3\)\(^2-\) \(\leftrightarrow\) S\(_2\)O\(_4\)\(^2-\) + 2e | -0.08 |
| Co\(^{2+}\) + 2e \(\rightarrow\) Co | -0.287 | 4OH\(^-\) \(\rightarrow\) O\(_2\) \(+\) 2H\(_2\)O \(+\) 4e | -0.401 |
| Cd\(^{2+}\) + 2e \(\rightarrow\) Cd | -0.40 | 2I\(^-\) \(\rightarrow\) I\(_2\) \(+\) 2e | -0.54 |
| Fe\(^{2+}\) + 2e \(\rightarrow\) Fe | -0.44 | MnO\(_2\)\(^\bullet\) \(\leftrightarrow\) MnO\(^-\) \(+\) e | -0.56 |
| Cr\(^{3+}\) + 3e \(\rightarrow\) Cr | -0.74 | 2CN\(^-\) \(\leftrightarrow\) (CNS\(_2\)) \(+\) 2e | -1.07 |
| Zn\(^{2+}\) + 2e \(\rightarrow\) Zn | -0.76 | 2Br\(^-\) \(\rightarrow\) Br\(_{2(aq)}\) \(+\) 2e | -1.087 |
| H\(_2\)O + 2e \(\rightarrow\) 2OH\(^-\) + H\(_2\) | -0.83 | ClO\(_2\) \(\leftrightarrow\) ClO\(_2\)(g) \(+\) e | -1.16 |
| Mn\(^{2+}\) + 2e \(\rightarrow\) Mn | -1.18 | H\(_2\)O\(_2\) \(\leftrightarrow\) 2H\(^+\) \(+\) 1/2O\(_2\) \(+\) 2e | -1.23 |
| Al\(^{3+}\) + 3e \(\rightarrow\) Al | -1.66 | 2Cl\(^-\) \(\rightarrow\) Cl\(_2\)(g) \(+\) 2e | -1.36 |
| Mg\(^{2+}\) + 2e \(\rightarrow\) Mg | -2.36 | 2SO\(_4\)\(^2-\) \(\leftrightarrow\) S\(_2\)O\(_4\)\(^2-\) \(+\) 2e | -2.01 |
| Na\(^+\) + e \(\rightarrow\) Na | -2.71 | 2F\(^-\) \(\rightarrow\) F\(_2\)(g) \(+\) 2e | -2.87 |
| Ca\(^{2+}\) + 2e \(\rightarrow\) Ca | -2.87 | Other acid oxidation anions: NO\(_3\), SO\(_4\)\(^2-\), PO\(_4\)\(^3-\) and so on | |
| Sr\(^{2+}\) + 2e \(\rightarrow\) Sr | -2.89 | have less oxidation potential than water. | |

If there are no other compounds or elements (electrolyte solutions) present in the water electrolysis process, an electrolysis event is difficult to occur. This is because the ions contained in the water molecules in the electrolytic cell are not able to supply the cell with an electrical current in the form of a closed circuit. If the electrolysis of water is done in the form of a solution (there is an electrolyte solution) where water is as solvent, there will be competition for cations and anions being oxidized with anode and reduction at the cathode. If in the electrolysis solution of water as solvent, the reduced cation at the cathode is the reduction potential greater than -0.83 V. Then, the anion oxidized at the anode is the greater oxidation potential at -1.23 V. Reduction of the potential value and the oxidation of certain cations and anions is indicated in table 2.

#### 7.1. Electrolysis Cells

Electrolysis is the event of the breakdown of electrolytes in an electrolytic cell by an electric current. In Volta / Galvani cells, the oxidation reduction reaction takes place spontaneously and the chemical energy produced by the chemical reaction is converted into electrical energy. Whereas electrolysis is the reverse reaction of Volta/Galvani cells with negative cell potential. Electrolysis cells are cells that use electrical current to carry out chemical reactions. In electrolytic cells, chemical reactions do not occur spontaneously but through potential differences which are triggered from outside the system in the form of a current source. The source of negative polar current leads to the cathode and the source
of positive polar current certainly leads to the anode. As a result, the anode functions as a positively charged electrode and a negatively charged cathode, so that an electric current flows from the anode to the cathode. Electrolysis cells generally consist of a direct current (DC) source, a conductive wire, two electrode rods (cathode and anode) and an electrolytic fluid.

The use of electrodes determines the reaction that takes place in the electrolysis cell. There are two types of electrodes used in electrolysis cells: inert electrodes and non-inert electrodes or active electrodes. Inert electrodes are electrodes that do not react either as a cathode or anode, so in electrolysis cells that experience a redox reaction are electroct as a solute and / or water as a solvent (for example C, Pt and Au). While the electrodes are not inert or active electrodes, those that react, especially if used as an anode, can undergo oxidation reactions (for example Fe, Al, Cu, Zn, Ag, and Au).

7.2. Catalysts in water electrolysis
One of the factors that influence the electrolysis of water is the use of catalysts. To facilitate the reaction of the H₂O molecules, a catalyst is necessary so that the reaction is faster. A catalyst is a substance that changes the speed of a chemical reaction but the substance does not change at the end of the reaction, based on this definition, the catalyst can speed up or slow down chemical reactions. Compounds such as acids, bases and salts which can conduct electric current can be used in the electrolysis process. The presence of ions in solution causes conduction events and when an electric current flows through the solution, electrons move between the ions. For example, for the bases of H₂SO₄ acid and NaOH, it works to simplify the process of decomposition of water into hydrogen and oxygen because the catalyst ions are capable of influencing the stability of water molecules in H⁺ ions and OH⁻ which are easier to electrolyze due to a decrease in activation energy.

8. Evaluation of Water Separation Techniques
In recent years, various researchers and scientists have made efforts to obtain hydrogen from water, which can then be used as a fuel to replace fossil fuels. Some methods that have been developed is photocatalysis and electrolysis. For photocatalyst itself, there have been many developments in research designs that have been made, both from the material of the photocatalyst as well as from the method used. In this review, we will present several general methods that have been implemented to produce hydrogen from water, particularly in the photocatalysis process. Based on the results of studies of several methods that have been done, at the end a new method will be considered which will be a suggestion for researchers to overcome some of the weaknesses of the method which has been carried out both in terms of the efficiency of the amount of hydrogen production and economically.

8.1. Photoelectrocatalysis (PEC) system
Honda and Fujishima (1972) were the first to introduce a photoelectrocatalysis (PEC) system to produce hydrogen from water as a whole with a diagram similar to that of Figure 8 [15].

![Figure 8. Schematic representation of a photoelectrochemical cell (PEC) [15]](image-url)
Photoelectrochemical cell (PEC) are composed of TiO$_2$ anodes and Pt cathodes for the production of oxygen and hydrogen. When the TiO$_2$ anode is irradiated by light with an energy higher than the forbidden band, electrons and holes are produced in the conduction band and the valence. As a result, water is oxidized through holes in the TiO$_2$ anode to produce oxygen, while the electrons are photogenerated in Pt electrodes and participate in the production of hydrogen [15]. In the PEC process, the production of oxygen in the photoanodes, which is involved in 4-electron reactions, is kinetic limited to the separation of water. As such, many research efforts have focused on the design of nanostructured photoanodes for the production of oxygen by the separation of PEC water.

8.2. Photoassisted Electrolysis cell system

In 1975, Wrighton et al. conducted a study on the separation of water, developing a new method, namely photoassisted electrolysis cells [16]. In their research, they carried out an experiment by comparing two methods, namely the method of cell PEC with photoassisted electrolysis cell. Figure 9 (a) is a PEC diagram while Figure 9 (b) is a photo-assisted electrolysis diagram.

![Figure 9. Photoassisted Electrolysis cell sistem [17].](image)

In this experiment, quantitative measurements were made at the voltage applied in the circuit as in Figure 9 (b) using the Hewlett-Packard 6214A power supply as an external voltage source with a positive tip attached to the TiO$_2$ electrode. As in the cell of figure 9 (a) PEC, the photocurrent is such that the electrons circulate from TiO$_2$ to Pt. In this experiment, it was shown that water can be separated into hydrogen and oxygen with an external tension 0.5 V or 0.25 V (less than that required for H$_2$O electrolysis is 1.23 V). This is believed to be the result of additional photonic radiation energy from an external source (a 150 W xenon lamp, the emission of which passes through a spectrometer excitation monochromator). In the experimental data show that the energy stored in the form of H$_2$(68 kcal / mol) is greater than the energy entered into the system by power supply.

8.3. Particulate photocatalysis (PC) system

In 1979, the concept of photoelectrochemical water separation was applied by Bard to design a photocatalytic water separation system using semiconductor particles or powder as photocatalysts [17]. In the photocatalytic systems illustrated in Figure 10, the electrons and holes are photographed (holes) in the generation of conduction bands and valence bands on the surface of the particulate photocatalysts, play a role in the redox reactions, each producing hydrogen and oxygen [3].

By examining the basic mechanisms and processes of photocatalytic water separation, it is known that an effective photocatalyst must have (1) a band gap and a suitable ribbon structure to absorb abundant sunlight and cause half the evolution reactions of hydrogen and oxygen; (2) good charge transfer capacity for the electrons and the holes which move towards the semiconductor / electrolyte interface with charge recombination, and finally; (3) high surface catalytic reactivity for half-reactions.
In recent decades, a great deal of effort has gone into meeting the important requirements of photocatalysts designed for the production of high-efficiency hydrogen from water.

![Diagram of a water particulate photocatalysis (PC) system separation](image10)

**Figure 10.** Schematic illustration of a water particulate photocatalysis (PC) system separation

8.4. **Photovoltaic–Electrochemical (PV–EC) System**

Solar-powered water electrolysis is an interesting way to store chemical energy and supply hydrogen to industry because hydrogen is produced using clean and unlimited solar energy [18]. This method of separating water with the PV-EC cell has the same operating principle as electrolysis of water using a PLN voltage source. For PV-EC cells, the voltage source used is a solar panel.

![Diagram of a Photovoltaic-Electrochemical (PV-EC) system](image11)

**Figure 11.** Schematic of Photovoltaic-Electrochemical (PV-EC) [19].

In general, the diagram of the PV-EC sales circuit in the water electrolysis process is illustrated in Figure 11. In an integrated PV-EC device, a charge carrier (eg electrons and holes) is generated in the PV section and transferred to the electrocatalyst to separate the water. Several PV-EC devices have been developed using different types of PV technology, such as crystalline silicon, hybrid organic-inorganic perovskite and multifunction solar cells [20-22]. Although the PV-EC cell is a method of electrolysis of renewable water, there are obstacles in the PV treatment system that require special attention.

8.5. **Photocatalyst-Electrolysis System**

In this diagram, we propose a new model of the method of dividing water into hydrogen and oxygen. Based on a review of the literature of various cell models that have been carried out by researchers as explained above, we propose a new method in the form of photocatalyst electrolysis cell. This method is a combination of an electrolysis method with a particulate photocatalyst.

Using a TiO$_2$ photocatalyst, a circuit diagram can be constructed based on Figure 12. The separation of water into hydrogen and oxygen can be carried out by the electrolysis process which is accelerated by the photocatalysis process. The hope is that with the help of photonic energy from certain sources, with a sufficiently low current in the electrolysis event, it will be able to produce a
water splitting event to produce more efficient hydrogen in large quantities. The next hope is that with the combination of these methods, the event of water splitting in photocatalysis can move into the region of visible light.

![Figure 12. Photocatalyst-electrolysis cell diagram](image)

9. Summary
Photocatalysis is a water splitting event to produce hydrogen from water that uses photonic energy. Most photocatalyst materials are made of semiconductor material because the semiconductor material has an energy gap that allows it to produce electron holes if it is charged with photonic energy from a source particular. This electron-hole pair will later cause a water splitting event. So far, the most widely used semiconductor material as photocatalyst is TiO₂. Interest in TiO₂ to be used as photocatalyst compared to other semiconductor materials, TiO₂ is known to have various important advantages, in particular for applications of hydrogen production from water (fractionation of water), including having high stability, corrosion resistance, abundant availability in nature and relatively inexpensive prices.

Water splitting into hydrogen and oxygen can also be carried out by the electrolysis process. Water electrolysis is the breakdown of water compounds (H₂O) into gaseous oxygen (O₂) and hydrogen gas (H₂) using an electric current through the water. At the cathode, two molecules of water react by capturing two electrons, reduced to gaseous H₂ and hydroxide ions (OH⁻). Meanwhile at the anode, two other molecules of water decompose into gaseous oxygen (O₂), releasing 4H⁺ ions and circulating electrons in the cathode. The H⁺ and OH⁻ ions are neutralized to form several molecules of water.

Several obstacles and problems encountered in the production of hydrogen using the two methods above, such as 1) Photocatalyst: the amount of hydrogen production which was not efficient and the maximum production of hydrogen only in areas under visible light, 2) Electrolysis: to produce hydrogen on a large scale, requires large amounts of electricity as a reaction trigger. In this article, through a review of the literature, will present a new method of separating hydrogen and oxygen from water by the photocatalysis process uses the photonic energy of visible light and is combined with the process of electrolysis. The development of a combination of methods in this study make it possible to obtain a large production of hydrogen with a fairly low current in the electrolysis process.

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