Literature review of the development of ZnO and TiO$_2$ as photocatalytic material in water splitting processes

Istiroyah, Y Engge, F Maulana and M Nurhuda

Physics Department, Faculty of Natural Science, Brawijaya University

E-mail: istie@ub.ac.id

Abstract. Water with hydrogen content is a source of renewable fuels that are available in abundance. However, the main constraint of the process of water splitting or hydrolysis is the amount of energy needed in the process. Photocatalysis material is a material that can function as a catalyst that helps the water-splitting process. The characteristics of photocatalytic material are mainly determined by the energy gap or bandgap that will allow the excitation of electrons and holes. This paper will discuss the literature review on the development of ZnO and TiO$_2$ semiconductors as photocatalysis materials.

1. The problem of sustainable energy

Energy consumption in human life rises significantly as technology develops. It is even predicted that in 2035 world energy consumption will reach 739 million quadrillion BTUs [1]. So energy sustainability becomes a very important central issue in the world today. Various investigations, research, and exploration of renewable energy sources have become a priority step in various parts of the world. Hydrogen from water is an alternative source of energy that is environmentally friendly. Available water is quite abundant on Earth and can support the sustainability of energy in the future.

Hydrogen from water sources can be obtained through the process of splitting water molecules or better known as water splitting. The concept of hydrogen production from the water separation process was first investigated and demonstrated by Fujishima and Honda in 1972 [2], and Khaselev and Turner in 1998 [3]. In general, this water-splitting process can be grouped into photoelectrochemical and photocatalytic methods. However, the photoelectrochemical method is more complicated and expensive, so the photocatalytic method is widely developed by researchers. This photocatalytic method utilizes the abundantly available sunlight on Earth. Solar radiation exposure reaches 120,000 TW. [4-5]. The process requires the help of catalyst material in the form of semiconductor material. The driving energy in the photocatalytic process is closely related to the gap energy and surface properties of the catalyst material used in the process. This paper will discuss the development of ZnO and TiO$_2$ as catalysts in the process of separating water by photocatalysis.

2. Photocatalysis

Photocatalysis is a combination of photochemical and catalysis processes. This process combines the chemical transformation process by involving light as a trigger and the use of a substance (material) which functions to speed up the course of the reaction by changing the reaction mechanism without the material reacting in the process. Material that can be used as a photocatalyst is material that has an energy bandgap (bandgap energy) so that when exposed to light energy there will be excitation of electrons from the valence band to the conduction band. Excited electrons in the conduction band and
holes in the valence band will trigger oxidation and reduction reactions in the form of hydrogen evolution (HER) and oxygen evolution (OER) reactions.

Photocatalysis can be categorized into two types of homogeneous and heterogeneous photocatalysis. Homogeneous photocatalysis occurs in processes that have the same phases and are triggered by oxidizing agents. Whereas heterogeneous photocatalysis occurs in processes that have two or more phases involved in it and are triggered by light and solid catalysts.

3. Photocatalysis of semiconductor materials

The semiconductor material can be used as a photocatalyst because it has an empty energy region called the energy bandgap (bandgap energy), which is between the boundary of the conduction band and its valence. The energy band gap is the distance between the lowest position of the conduction band and the top position of the valence band. Figure 1 shows the magnitude of the energy band gap of various semiconductor materials when in contact with an electrolyte solution at pH 1.

![Figure 1. Position the potential energy of some semiconductor material when with an electrolyte solution at pH 1.][6]

The energy of the valence band and the conduction band will control the charge transfer capability that is triggered by light exposure to molecules on the semiconductor surface. So, it can be likened to a semiconductor having a reduction potential (valence band, VB) and oxidation potential (conduction band, CB). The process of heterogeneous photocatalysis in semiconductor material begins with photoexcitation due to exposure to light in the semiconductor. Light energy will be absorbed and used for the excitation of electrons in the valence band to the conduction band. So, in this photoexcitation process electrons are generated in the conduction band and holes in the valence band. The photo-excited reaction is:

$$\text{Semiconductor} + \text{hv} \rightarrow e_{CB}^- + h_{VB}^+ \quad (1)$$

Electron-hole pairs can experience several possibilities, namely: recombination in particles (volume recombination), recombination on the surface (surface recombination), or reacting with Donor (D) or Acceptor (A) species that are adsorbed on the particle surface and produce oxidation reactions and reduction. The equation of the oxidation and reduction reaction is [7]:

$$\text{hv + semiconductor} \rightarrow e^- + h^+ \quad (2)$$

$$\text{A (ads) + e}^- \rightarrow \text{A}^- \text{ (ads)} \quad (3)$$

$$\text{D (ads) + h}^+ \rightarrow \text{D}^+ \text{ (ads)} \quad (4)$$
Some of the reactions that can occur in the radical ions formed (A- and D +) are reacting between fellow radical ions, combining through reverse electron transfer, diffusing from the surface of the semiconductor, and participating in chemical reactions that occur in the solution. The efficiency of the photocatalysis process can be improved by inhibiting the rate of electron-hole recombination [8].

4. Application of photocatalysis in the water-splitting process

The phenomenon of water splitting or decomposition of water into oxygen and hydrogen through the photocatalysis process was first observed by Fujishima and Honda in 1972. This process was observed through photoelectrochemical cells (PEC) with n-type TiO2 semiconductor photoanodes. Water splitting reaction in semiconductors occurs through three steps, namely (1) absorption of light photons and converted to electrochemical energy by semiconductors. (2) Light having photons (hv) causes intrinsic ionization of n-type semiconductor materials, then regenerates electrons (-) in the conduction band and hole (+) in the valence band. (iii) Light pushes electrons (-) and holes (+) to split water molecules into oxygen gas and hydrogen ions. This water splitting reaction can be written as:

\[
\text{Reduction : } 2\text{H}^+ + 2e \rightarrow \text{H}_2 \quad \text{(HER)}
\]

\[
\text{Oxidation : } 2\text{H}_2\text{O} + 2\text{h}^+ \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+
\]

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2
\]

In its development, powder (particulate) systems are more widely used because they are more economically and design feasible [9].

5. ZnO and TiO2 as photocatalytic materials

The reaction in the water-splitting process is an uphill reaction with the value of the positive Gibbs ΔG free energy change. The uphill reaction is not spontaneous but must be triggered by a catalyst. So that in this water-splitting process the semiconductor material will act as a catalyst to trigger spontaneous reactions. The spontaneous reaction of the water-splitting process triggered by this semiconductor catalyst must meet the minimum bandgap requirements of the semiconductor material must be 1.23 eV. The minimum conduction band position, Ec, must be above the electrochemical potential level of water reduction, H2O / H2, or Ec> EH2O / H2. While the minimum position of the valence band must be below the level of the electrochemical potential of water oxidation, O2 / H2O, or Ev <EO2 / H2O. Therefore, the challenges related to the semiconductor photocatalytic bandgap material are [10] first, the material stability requirements in the photocatalytic process, this can be met by the oxide semiconductor material, but the bandgap of the semiconductor oxide material is in the range of 3 eV so that it does not match the length of the photocatalytic process. visible light waves. Second, the efficiency requirement, so that the energy absorption of solar visible light photons is efficient, the bandgap of this semiconductor catalyst should be around 2.2 eV, but materials that have a bandgap in that range are photochemically inclined to be unstable in water. Third, the energetic position, so that the water-splitting reaction runs spontaneously, the position of the conduction band and the valence band must stretch.

While from the kinetics aspect, 2 things should be considered in the process of water splitting, namely: electron-hole recombination and back reaction between hydrogen and oxygen products to form water again [11]. The electron-hole recombination will be closely related to the size of the bandgap of the semiconductor material. The smaller the bandgap of the semiconductor material, the electrons from the conduction band will more easily combine with holes from the valence band. This will inhibit the activity of photocatalysis and reduce the efficiency of the water-splitting process.

The process of water splitting with the application of photocatalysis in visible light requires modification of the semiconductor oxide catalyst materials such as TiO2 or ZnO. The development of photocatalysts began in the 1970s and early 1980s using TiO2 and SrTiO3 [8]. In the early 1990s,
modification of active catalysts such as the Ag + doped WO3 began to be developed. Also, investigations and explorations of the crystal structure and microstructure of photocatalysis materials were developed. TiO2 itself has 3 crystal structures: rutile, anastase, and brookite. Among these three crystal structures, the structure of the Anastasia has best met the requirements of photocatalysis materials. So that in the following decades many TiO2 anastase modifications were developed as photocatalysts [12]. Also, TiO2 anastase also has higher photocatalytic activity than other structures [13]. However, the efficiency of converting solar energy to hydrogen is still low [11] so efforts have been re-developed to improve its efficiency.

The techniques used in photocatalytic modification can be classified into two groups, namely doping techniques and photocatalyst microstructural modification techniques. Doping or the addition of sacrificial agents aims to prevent the recombination of electron-holes and back reactions. The mechanism is like the addition of a donor electron that functions as a hole scavenger. The compounds used as hole scavenger include Pt [14], S2- / S4O62- , Ce4+ / Ce3+ [15]. While microstructure modification can be done by modifying particle size and shape. The smaller the particle size of the catalyst, the active surface will expand to react so that the better catalyst performance [16]. The methods used to modify particle size and shape include sol-gel and co-precipitation.

6. Conclusion
Water splitting is one of the promising techniques for harvesting hydrogen from water as a renewable energy source. Photocatalytic is one method of water splitting which is widely applied by utilizing solar radiation and catalytic materials. Oxide semiconductors are the best choice of catalytic material in the photocatalytic process. The effectiveness of the photocatalytic process can be enhanced by modifying semiconductor catalytic materials by microstructural and doping modifications.

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