

Photocatalysis for Water Splitting Capabilities

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Water could be used as the main source of hydrogen production. By definition, the dissociation of the water molecules into their constituents (hydrogen and oxygen) is known as water splitting. Rapid population growth and ever-increasing energy consumption have resulted in increased environmental pollution and energy demands. Accordingly, studies and research on innovative and efficient ways of wastewater clean-up and exploiting eco-friendly and renewable energy sources such as sunlight have become a necessity.

Keywords: photochemical ; hydrogen ; water

1. Photocatalytic Water Splitting

Photocatalytic water splitting uses sunlight, water, and a semiconducting photocatalyst to dissociate water molecules through the two redox reactions mentioned above. The breakthrough study was started in 1972 by Fujishima and Honda ^[1] in a photoelectrochemical cell using TiO_2 as their photocatalyst. Afterwards, photocatalytic water splitting received an enormous amount of attention due to its potential. During the past 40 years, various photocatalyst materials and systems were used to split water under ultraviolet light or visible light. Photocatalytic water splitting could be categorized into either photochemical water splitting or photoelectrochemical (PEC) water splitting ^[2].

Both types include three basic steps: a semiconductor photocatalyst absorbs more photon energy than the band gap energy of the photocatalyst and excites the electron-hole pairs; the photogenerated charge carriers are then separated out and move toward different sites of the photocatalyst's surface; finally, at these sites water reacts with the charge carriers in two separate redox reactions and therefore is reduced by electrons to produce H_2 in the same time its oxidized by holes to produce O_2 ^[3].

Even though the general concept of photochemical and PEC systems is the same, the setup is different. In photochemical reactions, the water-splitting reaction takes place at the semiconductor-electrolyte junction, whereas in a PEC setup the reaction takes place at two different sites. In this method, illuminating the cathode or anode would provide the required potential ^[4].

In order to understand the difference between these two setups, an important characteristic of the semiconductor should be taken into consideration. This characteristic is the band edge position of the semiconductor ^[4]. A suitable semiconductor for water splitting has a valance band position that is more positive than the $\text{O}_2/\text{H}_2\text{O}$ energy level (1.23–0.059 pH, V versus NHE) and a conduction band position that is more negative than the H^+/H_2 energy level (0–0.059 pH, V versus NHE). In other words, in the ideal case, a single semiconductor material should have a band gap that is large enough to split water, so the conduction band energy and valance band energy should straddle the electrochemical potentials $E^0(\text{H}^+/\text{H}_2)$ and $E^0(\text{O}_2/\text{H}_2\text{O})$ ^[5]. However, in the case of a single semiconducting material, the second requirement is not satisfied in most of the material systems (as will be discussed in depth in further sections). Scaife ^[6] mentioned in 1980 that it is exceptionally difficult to find a single semiconductor photocatalyst with both characteristics. This difficulty is why many studies focus on two semiconductor photocatalytic systems (PEC water splitting). By using two different materials, each one will act as either a photoanode or photocathode, which when used in tandem, satisfies the band gap requirement.

A two-step PEC system involves water splitting in two parts: one for the hydrogen evolution using a semiconductor that satisfies the conduction band position for that reaction, and the other for the O_2 evolution. In this method, a semiconductor that only partially satisfies the band edge position for the redox reaction could still be used in conjunction with another semiconductor to facilitate a water-splitting reaction ^[7]. However, there are many drawbacks to and critics of this method.

First, it requires the number of photons to be double that for the one-step system to achieve overall water splitting. The number of photons required in two-step photocatalytic water splitting is eight, whereas in one-step overall water splitting it

is four. This difference causes the amount of hydrogen and oxygen produced in a two-step process to be half that of the one-step process at light absorption values and apparent quantum yield of unity [8].

Second, there are still some drawbacks that involve promoting electron transfer between two semiconductors and opposing and suppressing the possible backward reactions that involve shuttle redox mediators [9]. Therefore, since the number of backward electron-transfer routes increases, which is the result of an increase in the number of elementary steps, this route is kinetically unfavorable. Overall, two different studies summarized the techno-economic analyses which determined that a high capital cost prevents PEC devices from being implemented into solar hydrogen production. For these reasons, authors will focus on one-step photochemical water-splitting systems.

2. Photochemical Water Splitting

In order to understand the photocatalytic process in photochemical water splitting, which is a quite complicated process, a simple step-by-step description of the process will be discussed in this section. Overall, the following steps occur:

- Photon absorption: Photocatalysts absorb photons and generate electrons and holes at the surface. When the material absorbs the photons with an energy that is equal to or more than the band gap energy of the semiconductor, an electron jumps from the valence band to the conduction band, leaving a hole in the valence band. Electrons and holes release energy (heat) and move the conduction and valence bands to the minimum and the maximum positions, respectively [10].
- Charge transport: After the charge carriers have been excited, there are different scenarios that could occur. The first scenario, which is highly unfavorable, is that excited-state conduction band electrons and valence band holes recombine. In the case where there is not a suitable force to separate these charged carriers, the energy stored in them will dissipate in a very short time (typically a couple of nanoseconds) in the form of heat. In the event that there is a defect state, a trap on the surface of the material, or a suitable scavenger, the recombination is potentially avoided. Another scenario is that the excited electrons and holes will move to the respective reaction sites [11]. In bulk, if the carriers do not recombine, it is only possible for either an electron or hole to be accumulated at the anode or cathode, whereas in a nanostructured semiconductor both of the photogenerated charge carriers could be present at the same surface. Low dimensionality, few numbers of defects, and a high surface area in nanostructured materials result in key differences in electron transport compared to their bulk counterparts [12][13].
- After the charges have moved to the reaction sites in the material/water interface, they can participate in the surface chemical reactions between these carriers and the compounds (e.g., water) [2].

3. Criteria for Selection and Synthesis of an Ideal Photocatalytic Material

As mentioned in the previous section, there are many different factors and steps in the photochemical water-splitting process. Therefore, the development of photocatalytic materials that can maximize the conversion of solar energy to solar fuel demands significant consideration. At the molecular level, several physicochemical functions need to be integrated into one stable chemical system that can set the criteria, which must be satisfied simultaneously.

3.1. Chemical and Electronic Properties of the Materials

- The band gap of the semiconducting material should lie between 1.6 eV (1.23 eV + overpotential) and 2.7 eV (larger than 2.43 eV). It is known that only 4% of the sunlight on earth is UV. Thus, in order to achieve maximum efficiency, the material should be able to harvest within the visible light spectrum [14].
- Band edge positions mean that band edges must straddle between the redox potentials of H₂O (0.00 eV and 1.23 eV). Semiconductor materials must satisfy the minimum band gap requirement (~1.4 eV) [15]. Although recently a couple of different ways of determining the valence band edge position of new material systems have been proposed, the task of predicting the exact band position of a new photocatalyst is arduous. For this reason, the applicability of a specific photocatalyst material for overall water splitting is unknown in advance [16][17].
- Charge transfer is necessary at the photocatalytic surface and must be fast enough to prevent photo-corrosion and shifting of the band edges. This prevention avoids the recombination of the charge carriers and can further provide efficient oxidation and reduction sites on the surface of the material. A prevalent approach to hinder the recombination process is the use of a cocatalyst. Cocatalysts have been used in many investigations on hydrogen generation;

however, some cocatalysts are highly active and induce a reverse reaction, i.e., the generation of water from molecular oxygen and hydrogen, which must be reduced [4].

- The stability of the material in an aqueous medium is an essential requirement (at least for 20 years). Many investigated material systems are susceptible to photo-corrosion such as CdS. Although high efficiencies are reported in the early stages of experiments, due to oxidation of the material the process deteriorates over time before eventually stopping [18].

3.2. Physical and Crystal Structure Properties of the Material

Aside from the electronic and chemical properties that were mentioned above, there are structural factors of semiconductors that play a significant role in the final efficiency of the photochemical water-splitting process. Recent capabilities in advanced characterization enabled material scientists to investigate these factors, some of which are briefly discussed below:

- Crystalline phases: Semiconductors with different polymorphs have been shown to have different photocatalytic overall water-splitting features. One famous example of this is TiO_2 , which has the three main polymorphs, anatase, rutile, and brookite [19][20]. Initially, it was proposed that overall water splitting could only occur using the rutile phase [21][22]. However, it was later discovered that the reaction is also feasible when anatase or brookite are treated with continued UV irradiation [23]. Early studies using infrared absorption–excitation energy scanning spectroscopy revealed that there are numerous trapped states close to the valance bands of anatase and brookite but not rutile. Later, it was concluded that the elongated emission of UV on these two phases promotes the phase transformation to a quasi-rutile structure that elevates water-splitting reactions. On the other hand, a recent experiment by the Akira group in 2017 [24] illustrated the opposite conclusion, that brookite should have better photocatalytic activities, by studying the depth of electron traps in the three different polymorphs. The group concluded that brookite has moderate trap levels that both preserves the reactivity of electrons and hinders the recombination process of the charge carriers. These inconsistent results and conclusions show that there is a lack of fundamental understanding of the different behavior of the photocatalytic activity of a semiconductor with different polymorphs.
- Crystallinity: A semiconductor with a high degree of crystallization has fewer structural imperfections such as vacancies and dislocations. These defects are known to be recombination sites for photogenerated charge carriers. Therefore, it is commonly suggested that a highly crystalline semiconductor has a lower electron–hole pair recombination rate [25]. However, in two distinct studies in 2019 published in the *Nature Materials* journal, two different conclusions have been derived. Wang et al. [26] studied the overall water splitting of single-crystal Ta_3N_5 nanorods with no surface defects and grain boundaries and compared the water-splitting efficiency of the same material system with different nanorods with relatively more defects. Their result demonstrates that the hydrogen production rate is almost three times higher in the case of nanowires with no defects. In another study by Li et al. in 2019 [27], N-doped titania samples with differing amounts of oxygen vacancies on the surface were studied. From this experiment, it was demonstrated that by increasing the oxygen vacancies on the surface by close to 13 times, these oxygen vacancies acted as electron traps and increased the final efficiency of hydrogen evolution by nearly two times. These two different conclusions show that, although it is known that defects act as recombination sites, it is possible that different types of defects could have different effects in the lifetime of photogenerated carriers that needs further investigation.
- Particle size and morphology: As one might expect, the particle size and morphology of the photocatalyst can have profound effects on the performance of the material [28]. In the case of particle size, the literature suggests that there is a degree of compromise that occurs [29]. That is, small particle sizes facilitate the diffusion of electron and hole pairs to the surface of the semiconductor, which results in a lower recombination rate. However, when the particle is too small, insufficient absorption of light can occur due to a lower surface area [30]. Therefore, for any particular material system, it is critical to optimize the effect of particle size. Morphology has a significant effect on determining the anisotropic distribution of charge within a semiconductor and the overall efficiency of the water-splitting process. For example, La-doped NaTaO_3 demonstrated the presence of different spatially resolved reaction sites where the edges and grooves acted as reduction and oxidation sites, respectively [31]. Unfortunately, there still exists a number of studies which do not specifically address the effect of morphology on the performance, such as of ultra-aspect ratio nanofibers and nanoribbons.
- Heterostructures and cocatalysts: As mentioned previously, the cocatalyst is another important component that is widely used in most of the literature on overall water splitting in a single system. The literature states that the main purpose of the cocatalyst is to provide redox reaction sites. Theoretically, a cocatalyst should allow the photoexcited electrons and holes to have a smooth migration towards the surface and the reaction sites. This theory comes from the

model of semiconductor and conductor interfaces that generate a built-in electric field, which should promote interfacial charge transfer [32][33][34]. However, this understanding and model is not experimentally supported, and the results do not align with the current understanding of the system. Even so, since an increased efficiency of overall water splitting in most of the material system has been reported, it is now used in ongoing research in this field [4]. On the other hand, these active sites could also promote the reverse reaction of the hydrogen evolution reaction and oxygen evolution reaction, and these reverse reactions are usually preferred to the forward reaction on a thermodynamic basis. Therefore, the use of cocatalysts in studies that require a fundamental understanding of this research area should be carried out with care. Ultimately, due to the nature of the nanostructures, uniform deposition of the cocatalysts on the materials is not usually achieved, which makes systematic studies difficult.

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