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Recent Developments on Photocatalytic water Splitting using Semiconductors for Hydrogen Production

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Abstract: Hydrogen fuel has gained heed in the recent years as fossil fuels and other non-renewable sources of fuels are fast depleting. Hydrogen has been contemplated to be a prospective source of an alternative fuel, predominantly if it can be produced from a renewable and sustainable source such as water. Methods such as photocatalytic water splitting are arguably one of the simple methods to produce clean, green and renewable energy by disassociating water into H_2 (hydrogen) and O_2 (oxygen) using catalyst and sunlight. Numerous techniques have been developed to improve photocatalytic activity in materials such as TiO_2. This paper describes the recent progress, state of art and the future challenges in photocatalytic water-splitting.

Keywords: Photocatalytic, Semiconductors, Hydrogen Production.

INTRODUCTION

With growing awareness of adverse effects of conventional fuels to the environment and the fast depletion of conventional fossil fuels, the need for sustainable and environment friendly, an alternate source of energy has gained importance in recent years. Moreover, conventional energy sources are well known for polluting air and water by emissions of oxides of sulphur, oxides of nitrogen, carbon dioxides, particulate matter and other gases and the pressure and focus on mitigating them is growing. On the other hand, reaching energy needs is vital as human development index depends on per capita energy consumption but the predominant source is dwindling. Thus, not only fossil fuel utilisation for energy requirements needs to be reduced but also be replaced by cleaner, greener, and sustainable fuels.

Hydrogen as an energy source

Hydrogen is an ideal clean fuel of the future because it can be produced from renewable energy sources and causes no pollution and thus, its life cycle is clean, green and renewable. Renewable energy sources such as solar, wind, and hydropower, though affluent, are sporadic, non-storable, non-portable, and inconvenient for practical uses. However, presently, renewable energy contributes only about 5% of the commercial hydrogen production primarily via water electrolysis, while other 95% hydrogen is mainly derived from fossil fuels [1]. Hydrogen economy has already been set in the progress.

Photoelectrolysis

Basic research is being carried out to use sunlight directly to produce hydrogen in a photolectro-chemical cell. The feasibility of producing H_2 using UV light in a phtoelectro-cehemical cell was first illustrated by Fujishima and Honda in the year 1972 using the semiconductor material titanium dioxide (TiO2) [2]. Since then, a large number of semiconductor materials have been investigated for photoelectrocatalytic electrodes for H_2 production.

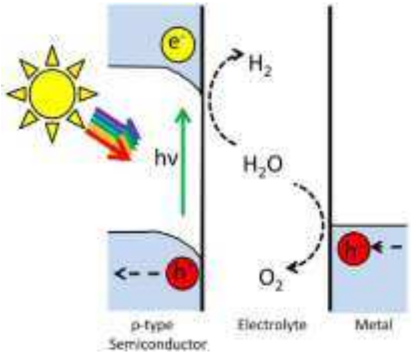


Figure 1: Schematic Representation of Phototelectrolysis Process

As shown in figure 1, hydrogen is produced from water using sunlight and specialized semiconductors called photoelectrochemical materials, which use light energy to directly dissociate water molecules into hydrogen and oxygen. Water splitting essentially refers to electrolysis of water i.e. reduction of water to hydrogen at cathode and oxidation to oxygen at the anode. This process is also known as artificial photosynthesis, process with photocatalysis in a photoelectrochemical cell.

$$OH^- + h^+ \rightarrow O_2$$

$$H^+ + e^- \rightarrow H_2$$

Irradiation of light with energy greater than or equivalent to the band gap of semiconductor photo catalyst can generate electrons and holes in the conduction band and the valence band of photo catalyst. This causes reduction and oxidation of adsorbed species on the semiconducting material. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production. State-of-the-art photoelectrochemical systems report solar to hydrogen conversion (STH) efficiencies of 2 to 3%.

Photocatalytic processes such as light absorption, which induces a charge separation process with the formation of positive holes that are able to oxidize organic substrates [4–6]. In this process, a metal oxide is activated with either UV light, visible light or a combination of both, and photoexcited electrons are promoted from the valence band to the conduction band, forming an electron/hole pair (e-/h+). The photogenerated pair (e-/h+) is able to reduce and/or oxidize a compound adsorbed on the photocatalyst surface. The photocatalytic activity of metal oxide comes from two sources:

(i) Generation of OH radicals by oxidation of OH anions,
(ii) Generation of O2 radicals by reduction of O2.

Although many semiconductor materials have shown photocatalytic activity, most of them suffer from limitations including photocorrosion, poor catalytic activity, poor solar spectrum absorption, etc. TiO_2 is one of the most studied oxide semiconductor materials in this regard because of its high chemical stability in electrolytes as well as strong catalytic activity.

TiO_2 has a band gap of 3.2 eV, which limits the absorption of sunlight to the high-energy portion (UV) of the solar spectrum. Earlier, it has been reported that attempts have been made to improve the absorption of visible light of TiO2 by incorporation of substitutional atoms into the lattice. The discovery of photo electrolysis of water directly into oxygen at a titania electrode and hydrogen at a Pt electrode by the illumination of light with energy greater than the band gap of titania is attributed to Fujishima and Honda through photocatalysis by titania. Since then, extensive work has been carried out to produce hydrogen from water by oxidation and reduction reactions using a variety of semiconductors such as ZnO, SnO_2, and CeO_2. Water splitting into H_2 and O_2 is accompanied by a large positive change in the Gibbs free energy i.e., it is an uphill reaction and on the other hand, degradation reactions such as the photo-oxidation of organic compounds using oxygen molecules are usually downhill reactions. [4,5,6,7]

METHODS AND MATERIALS

BASIC PRINCIPLE OF WATER SPLITTING BY PHOTOCATALYSIS

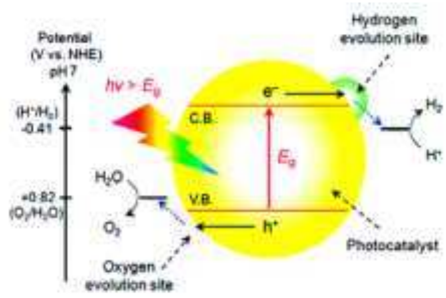
The electronic structure of a semiconductor plays a critical role in semiconductor photocatalysis. A semiconductor consists of Valance Band (VB) and Conduction Band (CB). The energy difference between these two levels is said to be the band gap (E_g).Semiconductors photocatalyst used for water splitting should possess a band gap energy (Eg) over 1.23 eV. Moreover, in order to achieve overall water splitting, its conduction band (CB) has to be located at a more negative potential than the reduction potential of H+/H2, while the valence band (VB) be located at a more positive position than the oxidation potential of O_2/H_2O. Under illumination with photon energy equal to or higher than the band gap energy (Eg) of a semiconductor photocatalyst, electrons are excited from the VB to the CB, leaving holes in the VB. Then, the electrons reduce water to H_2 and the holes simultaneously oxidize water to O_2, leading to the overall water splitting as shown in Figure 3.

MECHANISM

Both the electrons and holes are present in the valence band. When semiconductors are excited by light, (photons) with energy equal to or higher than their band gap energy level, electrons receive energy from the photons and are thus promoted from valance band to conduction band if the energy gain is higher than the band gap energy level.

Electrons and holes that migrate to the surface of the semiconductor without recombination reduce and oxidizes the reactants adsorbed by the semiconductor. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production. For hydrogen production, the conduction level should be more negative than hydrogen production level $E_{H2/H20}$ while the Valance Band should be more positive than water oxidation level $E_{O2/H2O}$ for efficient oxygen production from water by photocatalysis.

The schematic representation of water splitting reaction by photo catalytic materials is shown in Fig4.



Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactants adsorbed by the semiconductor. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production.

$$\begin{aligned}
& & TiO_2 &\xrightarrow{hv} \overset{+}{h} + \overset{-}{e} \\
&\text{Oxidation:} & H_2O + 2\overset{+}{h} &\longrightarrow 2\overset{+}{H} + 1/2\,O_2 \\
&\text{Reduction:} & 2\overset{+}{H} + 2\overset{-}{e} &\longrightarrow H_2 \\
&\text{Over all:} & H_2O &\xrightarrow{TiO_2/hv} H_2 + 1/2\,O_2
\end{aligned}$$

For hydrogen production, the CB level should be more negative than hydrogen production level ($E_{H2/H20}$) while the VB should be more positive than water oxidation level $E_{O2/H2O}$ for efficient oxygen production from water by photocatalysis.

Most of the semiconductors, such as CdS and SiC, that cause photocorrosion, are not suitable for water-splitting. TiO_2 having a strong catalytic activity, high chemical stability and long lifetime of electron/hole pairs, it is the most widely used photocatalyst. Currently, the energy conversion efficiency from solar to hydrogen by TiO2 photocatalytic water-splitting is still low, mainly due to the following reasons:

(1)Recombination of photo-generated electron/hole pairs: CB electrons can recombine
with VB holes very quickly and release energy in the form of unproductive heat or photons;

(2) Fast backward reaction: Decomposition of water into hydrogen and oxygen is an energy increasing process, thus backward reaction (recombination of hydrogen and oxygen into water) easily proceeds.

(3) Inability to utilize visible light: The band gap of TiO2 is about 3.2 eV and only UV light can be utilized for hydrogen production. Since the UV light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, the inability to utilize visible light limits the

efficiency of solar photocatalytic hydrogen production.

For TiO_2, the reaction is expressed as:

$$TiO_2 hv \rightarrow e^-_{TiO2} + h^+_{TiO2}$$

In order to overcome the above listed limitations and make solar photocatalytic hydrogen production feasible, many modification techniques have been studied as listed below:

1. Noble metal loading
2. Metal Ion Doping
3. Composite Semiconductors

These methods have been investigated and some of them have been proven to enhance the production of hydrogen. The fundamental mechanisms, current development and potential of these methods for hydrogen production are discussed in the following sections.

1. Noble Metal Loading

Noble metals such as Pt, Au, Pd, Rh, Ni, Cu, and Ag, have been studied and reported to be very effective for improvement of TiO2 photocatalysis [8, 9,10].

When the Fermi levels of these noble metals are lower than that of TiO2, photo excited electrons can be transferred from the conduction band to metal particles deposited on the surface of TiO2, while photo-generated valance band holes remain on the TiO2. Fermi levels give us the information about the velocities of electrons which participate in ordinary conduction. Such activities greatly reduce the possibility of electron-hole recombination, which results in efficient separation and stronger photocatalytic reactions. As electrons accumulate on the noble metal particles, their Fermi levels shift closer to the conduction band of TiO2 [11, 12, 13, 14], resulting in more negative energy levels. This is helpful for water-splitting hydrogen production. Furthermore, smaller metal particles deposited on TiO2 surface exhibit more negative Fermi level shift [11]. Accumulated electrons on metal particles can then be transferred to protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Therefore, noble metals with suitable work function can help electron transfer, leading to higher photocatalytic activity. However, Pt-loaded TiO2 was found to be less reactive to the preparation methods. Sakthivel et al. [15] investigated photooxidation of acid green 16 using Pt, Au and Pd-loaded TiO2 as photocatalysts. Optimal loading was observed in their experiments. Because of too much metal particle deposition might reduce photon absorption by TiO2 and might also become electron-hole recombination centres, resulting in lower efficiency. Loadings of Pt and Au were more effective than loading of Pd because of suitable electron affinity and the work function of Pt and Au [15].

Therefore, hydrogen production from pure water-splitting is difficult to achieve, because of the following:
(i)Recombination cannot be completely eliminated;
(ii) the backward reaction of H2 and O_2 to form H_2O is thermodynamically commendable.
Since Pt is very expensive, much research is required to identify low-cost metals with shows improvement of photocatalytic activity. For example, Dhanalakshimi et al. [17] investigated dye sensitised hydrogen production. When Pt/TiO2 and Cu/TiO2 were used as photocatalysts, enhanced hydrogen production was observed and the effect of Cu loading was almost comparable to Pt loading. Other low-cost metals, namely, Ni and Ag [16], were also found to be effective for photocatalytic activity enhancement. These low cost but effective metals are anticipated to be proving materials to improve photocatalytic activities of TiO2 for practical applications.

2. Metal Ion Doping

Metal ion doping and rare earth metal ion doping have been extensively investigated for enhancing the TiO2 photocatalytic activities in water splitting. [19-34]. Choi et al. [19] carried out a systematic investigation to study the photoreactivity of 21 metal ions doped into TiO2. It was found that doping of metal ions could expand the photo-response of TiO2 into the visible spectrum. As metal ions are incorporated into the TiO2 lattice, impurity levels in the energy band gap of TiO2 are formed which is given below:

$$M^{n+} + hv \rightarrow M^{(n+1)+} + e^-_{ch}$$

$$M^{n+} + hv \rightarrow M^{(n-1)+} + h^-_{vb}$$

Where, M and $M^{(n+1)}$ represent metal and the metal ion doping agent, respectively.

The energy level of Mnþ=Mðn_1Þþ should be less negative than that of the CB edge of TiO2, while the energy level of Mnþ=Mðnþ1Þþ should be less positive than that of the VB edge of TiO2. For photocatalytic reactions, carrier transferring is as important as carrier trapping. Only if the trapped electron and hole are transferred to the surface, photocatalytic reactions can occur. Therefore, metal ions should be doped near the surface of TiO2 particles for a better charge transferring. In case of deep doping, metal ions likely behave as recombination centres, since electron/hole transferring to the interface is more difficult.

Furthermore, there exists an optimum concentration of a doped metal ion, above which the photocatalytic activity decreases due to the increase in recombination. Among the 21 metal ions which were studied, Fe, Mo, Ru, Os, Re, V, and Rh ions can increase photocatalytic activity, while doping agents Co and Al ions cause harmful effects. [19]

An analysis in finding the effects of doping transitional metal ions (Cr, Mn, Fe, Co, Ni, and Cu) on photocatalytic activity of TiO2 was carried out by Wu et al. [25]. Acetic acid photocatalytic oxidation was employed to evaluate the effects of different metal ion doping. As Cu, Mn and Fe ions can trap both electrons and holes, doping of these metal ions may work better than doping of Cr, Co and Ni ions, as the latter metal ions can only trap one type of charge carrier. Xu et al. [23] compared photocatalytic activities of different rare earth metal ions such as (La, Ce, Er, Pr, Gd, Nd, and Sm) doped into TiO2. Enhanced photocatalytic activities and red shift of photo-response were observed at certain doping content. Dopant Gd ions were found to be most effective in enhancing the photocatalytic activity due to its highest ability to transfer charge carriers to the surface of TiO_2.

Hameed et al. [22, 35] studied photocatalytic water-splitting for hydrogen production using transitional metal ions (Fe, Co, Ni, Cu, and Zn) doped WO_3 under UV laser irradiation. The Conduction Band edge of WO_3 was less negative than EH_2/H_2O. Therefore, WO3 under irradiation in water could not reduce protons to hydrogen molecules. However, when transitional metal ions were on the surface of WO_3, transitional metal oxides were formed, which could further act as composite semiconductor photocatalysts. As FeO, CoO, NiO, and Cu_2O had more negative conduction band levels than EH_2/H_2O, the conduction band electrons were able to reduce protons. Unlike the above four metal oxides, ZnO could not capture electrons from the conduction band of WO_3. Therefore, doping of Zn was found to be less effective than other metal ions. Doping of 1% and 10% Ni ions exhibited the highest hydrogen production rate, which might be partially credited to mechanical - catalytic water-splitting hydrogen production since magnetic stirrer was employed [35]. It was reported that when NiO or Cu2O was used with a magnetic stirrer, hydrogen could be produced by water-splitting even in the dark, known as a mechanocatalytic reaction [36-47]. Unlike the above study, Wu et al. [25] reported that doping of Cu and Fe ions in TiO_2 was more effective for acetic acid oxidation degradation than doping of Ni ions. The discrepancy could be explained by different forms of doping. In Wu et al.'s study, metal ions were doped in the lattice of TiO_2 particles, while in Hameed et al.'s study, metal ions were deposited on the surface of WO_3 in a form of metal oxide, resulting in composite semiconductors.

3. Composite Semiconductors

Semiconductor composition (coupling) is another method to utilize visible light for hydrogen production. When a large band gap semiconductor is coupled with a small band gap semiconductor with a more negative CB level, CB electrons can be injected from the small band gap semiconductor to the large band gap semiconductor. Thus, a wide electron hole separation is achieved. It can be successful if it meets the following conditions:
(i) Semiconductors should be photo corrosion free,
(ii) The small band gap semiconductor should be able to be excited by visible light,
(iii) The conduction band of the small band gap semiconductor should be more negative than that of the large band gap semiconductor,
(iv) The conduction band of the large band gap semiconductor should be more negative than EH_2/H_2O and
(v) Electron injection should be fast as well as efficient. [48]

So et al. [49] conducted photocatalytic hydrogen production using CdS-TiO_2 composite semiconductors. Photocorrosion of CdS was prevented by addition of Na_2S. Optical absorption spectra analysis showed that CdS-TiO_2 could absorb photons with wavelength up to 520 nm. Under visible light illumination CdSTiO_2 composite semiconductors produced hydrogen at a higher rate than CdS and TiO_2 used separately.

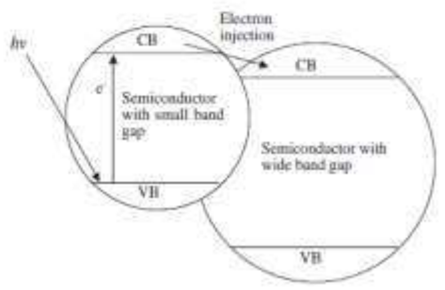

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Figure 5: Schematic Representation of Electronic injection in Composite Semiconductor

De et al. [50] conducted solar photocatalytic hydrogen production using CdS-ZnS composite semiconductor. Photo corrosion was inhibited by addition of Na_2S/Na_2SO_3 solution. Under solar irradiation, the addition of n-Si enhanced hydrogen production. This was due to the smaller band gap of n-Si together with its more negative conduction band. When exposed to solar radiation with a wavelength longer than 520 nm, electrons were excited from the valance band of n-Si to the conduction band of n-Si and then transferred to the conduction band of CdS sequentially, resulting in a higher solar radiation utilization.

Besides coupling with small band gap semiconductors, TiO_2 coupled with a large band gap semiconductor has also been investigated and proven to be more efficient under UV irradiation. Keller and Garin [51] observed that photocatalytic oxidation of methylethylketone (MEK) was increased by coupling TiO_2 with WO_3 (2.7 eV band gap) and SiC (3.0 eV band gap). As the conduction band of SiC was more negative, electron transfer to the conduction band of TiO2 could be more efficient. On the other hand, the conduction band of WO_3 was less negative than that of TiO_2, and thus electrons were transferred from the conduction band of TiO_2 to WO_3, resulting in a wide electron-hole separation. These composite semiconductors were found to be more effective than TiO_2 for MEK oxidation due to efficient charge separation. However, although WO3 coupling with TiO_2 could enhance photocatalytic oxidation, it could not reduce protons, since the conduction band of WO_3 was not negative enough. Comparatively, the electrons transferred from the conduction band of SiC to the conduction band of TiO_2 were more negative than EH_2/H_2O; therefore, SiC coupling was suitable for hydrogen production under UV illumination. Meanwhile, Nguyen et al. [52] studied the effect of electronic characteristics of TiO_2-SiO_2 and RuS_2/TiO_2-SiO_2 on hydrogen production. They observed that the coupled TiO_2-SiO_2 semiconductor showed more negative CB than TiO_2. When further coupled with RuS_2, electrons could be transferred to the conduction band of RuS_2 (-0.6 eV), accomplishing reduction of
Protons to hydrogen molecules.

CONCLUSION

Numerous modification techniques and chemical additives have been developed in the recent years to improve photocatalytic activity of TiO2 under visible light irradiation. These applications provide a promising capability for enhancing photocatalytic water splitting.

Currently, the hydrogen production rate obtained is low due to quick charge recombination, quick backward reaction and inability to utilize visible light efficiently.

It is anticipated that the low cost, environmentally friendly photocatalytic water-splitting for hydrogen production will play an important role in the hydrogen production and contribute much to the coming hydrogen economy as per the above mentioned techniques.

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