Chapter

New Strategy to Improve Photocatalytic Activity and Mechanistic Aspect for Water Splitting

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Abstract

Photocatalytic water splitting under irradiation of light is an ultimate system to make available renewable energy sources. However, significant efforts have been made to fabricate advanced nanocomposites; the major challenge persists, which is low efficiency and selectivity towards hydrogen evolution under the illumination of solar energy. In this chapter, the recent developments in photocatalysts, and heterojunction fabrication factors influencing the photocatalytic process for the dynamic production of hydrogen have been discussed. The improvements in photocatalyst systems have been classified as strategies to improve different factors of photocatalytic splitting such as Z-scheme systems and the influence of operating parameters such as band gap, morphology, temperature, oxygen vacancies, intensity, and pH. In addition, the thermodynamics of selective photocatalysts is conferred critically. The future research aspect of photocatalytic water splitting has been also discussed.

Keywords: water splitting, nanocomposite, photocatalyst

1. Introduction

Global energy consumption has remarkably increased due to the continual increase in world population and lifestyle standards [1]. Transportation and industrial sectors lead to high emissions of greenhouse gases including carbon monoxide, and carbon dioxide, 90% of the global energy and fossil fuel supply amounting to substantial depletion of the environment [2, 3]. Eventual depletion of energy supplies, market uncertainty, and mitigating the consequences of fossil fuel burning demands the development of clean and renewable resources of energy [4–6]. There are several alternative energy sources, including geothermal energy, hydropower, wind power, and solar energy, which are relatively cleaner and more sustainable than fossil fuels. However, the substitution of natural resources with alternative resources is much more challenging due to the limitations of each resource. Such as we cannot store the electricity which is produced by wind turbines. Hydropower undergoes dam construction limitations due to possible adverse environmental effects and high

costs. Geothermal energy is a costly operation because it is a continuous source and is limited in its lifetime [7]. Renewable and free solar energy is unlimited and capable of producing electricity without any maintenance or requirement of having turbines. Half an hour of solar radiation on the earth's surface can be used for 1 year [8].

Though, sunlight is an intermittent energy source that limits the ratio of solar radiation due to its dependence on the geographical season, day, time, and position [9, 10]. Another major disadvantage of solar energy is its low density per unit area of the earth's surface [11]. Therefore, to meet the global energy demand it is very necessary to develop a source of energy that is continuous, storable, and renewable. In this line of research, hydrogen is a profitable fuel for being profuse from different sustainable sources of water and biomass, high energy yield and efficiency, eco-friendly and capable of storage, thus it is considered an ideal alternative source of energy for nonrenewable energy source [12, 13]. Photocatalytic water splitting has attracted considerable attention as a potential renewable energy resource with limited use of fossil fuel and no CO_2 emission [1–4, 14]. Recent development in photocatalytic systems for photocatalytic water splitting can be divided into two main approaches. In the first approach, water is split into hydrogen and oxygen by visible light irradiation on the photocatalyst. In this type of system, the photocatalyst should have the suitable thermodynamic potential for photocatalytic water splitting. The narrow band gap of the photocatalyst system harvests visible light photons and provides stability against photo corrosion. Due to the rigorous requirement of photocatalyst, one-step water splitting is limited [5, 6]. The second approach is to apply a two-way mechanism by using two different types of photocatalysts [7]. These mechanisms were inspired by the natural photosynthesis phenomenon in green plants and are called the Z-scheme. The advantage of water splitting under the Z scheme is that a wider range of visible light is available because a change in Gibbs free energy is required for the one-step water splitting for the separation of water molecules and oxygen. Use of semiconductors used for either reduction or oxidation potential for one side of the system. For example, use of metal oxides such as WO_3 & $BiVO_4$ act as good oxygen evolution photocatalysts in two-way water splitting systems by using a suitable redox mediator, even though they are unable to reduce water [8, 9]. Overall water splitting via two-step photoexitation by the use of visible light and with different combinations of photo catalysts has been successfully reported [8–13, 15, 16]. However, there are several challenges in the promotion of electron transfer between two semiconductors. In addition, the photocatalytic activity of water splitting is strongly dependent on the physiochemical properties of photocatalysts such as the nature of active sites and the reaction conditions [2, 3, 14]. In past decade there are a number of material have been reported as a visible light active photocatalyst, which produces both oxygen and hydrogen under visible light irradiations [1, 4–17]. However, a number of photocatalysts have successfully achieved water splitting without any reagent. Significant progress has been made in the development of cocatalysts and the interpretation of reaction mechanisms. This perception of the mechanism highlights some important aspects of the recent development in water-splitting research.

2. Mechanistic aspect for water splitting

In the development of overall photocatalytic water splitting under visible light a number of photocatalytic materials and preparation methods have been studied. A number of studies have focused on the material development of materials that

are suitable for overall water splitting and their visible light absorption properties, crystallographic quality, phase purity, band edge position, and particle morphology. However, it is very challenging to identify the factor which dominates the net photocatalytic activity based on physical properties. Photocatalytic reactions proceed through an intricate sequence of competing for multistep processes. This multistep process establishes the kinetics and dynamics of photocatalytic water-splitting reactions for future applications [18]. The rate of water splitting with the modified photocatalyst was proportional to light intensity under solar irradiations. Excess loading of the co-catalyst did not improve the photocatalytic water splitting rate. The experimental results define the shortage of photo-exited carriers available for surface redox reactions under visible irradiations, this indicates that the balance between the rates of redox reactions on the surface of photocatalyst and charge carrier recombination in the bulk photocatalyst determines the charge concentration in the photocatalyst. The kinetic model of photocatalytic water splitting also determines the rate of reaction and probability of photoexcited holes for oxygen evolution and recombination. It was easy to assume two different co-catalyst distinctly facilitate hydrogen and oxygen evolution thereby stimulating overall water splitting in harmony. As stated earlier, visible light-responsive photocatalyst has been devoted to the development of active sites on photocatalyst and elucidating reaction mechanisms, which leads to significant progress in the field of heterogeneous photocatalytic water splitting [18–31]. Conversion of solar energy most efficiently can achieve overall water splitting under longer wavelength irradiation; this is because the number of accessible photons in the solar spectrum increased with an increased wavelength of the solar spectrum.

In this line of research, the development of a photocatalyst having a wider absorption band is highly desirable for overall water splitting. Although, a photocatalyst with an absorption edge of 600 nm would be optimal for the activation of the surface barrier and so surface reactions that can produce hydrogen and oxygen. The most promising candidates in this category have already developed, such as $LaTiO_2$, Ta_3N_5, and $Ti_2S_2O_5$ with a band gap of 2 eV which means they have an absorption edge near 600 nm [2]. However, the photocatalytic activities of these materials are not sufficient to achieve overall water splitting. Recent progress has been also made in material chemistry towards reducing the density defects [13, 31]. Consequently, it is very important to study the nature of defects, which can facilitate the undesirable electron–hole pair recombination in the photocatalytic system. In a two-step, a water-splitting system for $BaTaO_2N_{12}$ and Ta_3N_5 the absorption, the wavelength has been increased to 660 nm [16]. The research in this area is underway in direction of both photo catalyst preparations and mechanistic aspects of water splitting processing in harmony.

3. Band structure and surface properties for photocatalytic water splitting

Photocatalytic activity of water splitting reactions has been affected by various factors such as surface structure chemical functionality deactivating destructive surface state, band edge position, and extract of carriers to improve catalytic activity [32, 33]. In spite of surface area properties responsible for the photocatalytic activity, there is an adjustment between charge diffusion length and light absorption. An increase in surface area may lead to a decrease in photovoltage and an increase in the surface recombination process. Therefore, before surface modification, it is necessary to study the loss mechanism. It can be observed that sheet-like structures

exhibited higher light absorption capacity in comparison with spherical morphologies. The band gap shift towards lower energies with the reduction in crystallite size [34]. The most important example of this is $BiVO_4$ with a narrow band gap of 2.4 eV with control and desirable structure and morphology which is mandatory for the photocatalytic activity [35, 36]. Photocatalytic activity if $BiVO_4$ depends upon the facets which are exposed to irradiations [37]. Improved photocatalytic activity due to charge separation is reported for CdS/ZnO and CDs/TiO_2 heterostructure [38–41]. The incorporation of cations and anions into UV-active materials turned into visible light-active materials.

4. Photocatalytic water splitting modeling

Theoretical modeling studies of water splitting concern a number of aspects such as electron–hole transport/recombination, photocatalytic reaction, semiconductor band edge alignment, and photo redox chemistry [27–34]. DFT has been used extensively for the theoretical modeling of water splitting to predict the electronic structure of materials due to the modest cost and high accuracy reproducibility [35, 36, 42, 43]. However, the inaccurate predictions of band gaps are the major drawback of DFT. Hybrid materials have better performance for the prediction of band gap and the exited state position [44]. The band gap drawback and problems is tackled by perturbation theory which has a long-standing record of success [45, 46]. Computational methods are very helpful, especially in the prediction of impurities in photocatalysts induced by dopants in tuning with band gap for example TiO_2. Theoretical and computational tools are given an understanding and idea about various aspects of material and its state. For example, $BiVO_4$ in the band structures and density of states, migration energy profile of surface reactions, band structure, and density state, electron/hole pair generation comprehensive study. Also, electron–hole pairs driven to different crystal facets [47, 48]. All of these findings can obtain from comprehensive computational studies that are related to or compared with facet (011), (010) have lower absorption at 420 nm, better transport of electron–hole pair, and lower potential energy surfaces [49]. Theoretical studies are related to the improvement of band structure and morphology of the photocatalytic material.

5. Photocatalytic material description and design

As per earlier studies, a suitable photocatalyst should have a band gap of at least 1.23 eV for overall water splitting. High crystallinity and small particle size are major requirements to minimize the recombination of photo-generated electrons and holes. Metal oxide, nitrides, sulfides, phosphates, Groups I and II metals along with their lanthanides can also be used as photocatalytic material for overall water splitting. For the improvement of the efficiency of the photocatalyst, modification of material by doping some transition metal cations can help to increase the visible light response of the photocatalyst. Also, to exclude the energy backward reaction of water splitting and to increase the hydrogen production yields co-catalyst such as RuO_2, Au, Pt, and NiO can be used. This section of the chapter has focused on the heterogeneous photocatalyst including TiO_2 and metal oxides.

Fujishima and Honda first confirmed that TiO_2 was a potential photo-anode for UV light active photocatalytic water splitting. TiO_2 has been widely studied in

a number of photocatalytic reactions due to its low cost, environmentally friendly nature, chemical stability, and tunable energy band gap [50–54]. A number of alternative methods have been reported to extend the photocatalytic activity of TiO_2 into the visible light region, such as by doping with metal ions e.g. Carbon nanotubes [55, 56]. However, altered mechanistic methodologies have been proposed to explain this enhancement of activity. There are three mechanisms that have been reported to describe the synergistic effect of carbon nanotubes on TiO_2, the first prospective mechanism is that carbon can act as an electron sink, which can effectively prevent the recombination process [57]. In another mechanism, carbon acts as a photosensitizer, which can pump electrons into the TiO_2 conduction band [58]. In addition to proposed mechanisms, carbon can also act as a template for the dispersion of TiO_2 nanoparticles to avoid agglomeration [59]. Further nonmetal ion doping and metallic dopants usually add additional energetic levels in the band gap, which will reduce the energy barrier and introduce a new absorption band gap [58, 59]. Doping of TiO_2 with other elements can help to change the optical properties of nanomaterial and reduce the charge carrier recombination sufficiently s. Piskunov et al. suggested improvement in water splitting of TiO_2 doped with Fe, where Fe^{2+} and Fe^{3+} act as centers for electron trapping and Fe^{3+} & Fe^{4+} act as a center for hole trapping. Lu0 et al. confirmed the doping of vanadium into the crystal lattice of TiO_2 that shifts the absorption band to the visible range and V^{4+} V^{5+} efficiently traps the holes and electrons. Further, anionic doping has been extensively reported for TiO_2 by different dopant materials such as C, N, F, S, B, and sCl [58, 59].

Further, other than TiO_2 a number of metal Oxides such as Cu_2O, Al_2O_3, CoO and ZrO_2, Fe_2O_3, and Ta_2O_2 have been widely studied due to their low cost and stability. However, metal oxides suffer from limitations due to their large band gaps which limit their absorption of visible light. Ionic bonded materials have a large band gap because, in a typical metal oxide, the valence band and the conduction band have O_2p. To overcome this shortcoming transition metal cation has been used with dn configuration for example Fe_2O_3 with the band gap value (2.0 eV) and Co_3O_4 91.3 eV [31]. This may lead to an increase in light absorption but a decrease inefficient charge carrier transport due to high resistivity. Using post-transition metals such as PbO (2.1 eV), SnO_2 (2.4 eV), and Bi_2O_3 (2.5 eV) leads to better charge carrier generation however they are indirect semiconductors; so the optical absorption band edge varies with the square root of photon energy and gives less efficient charge carrier extraction process Therefore ternary metal oxides have been suggested to overcome these issues, for example, $Bi_{20}TiO_{32}$, $SnNb_2O_6$ and $BiVO_4$ [31, 35]. Properties of n and p-type semiconductor properties have been found in BiO_4 and high photon to current conversion efficiency [59]. In addition, Fe_2O_3 as photocatalytic material has a band gap of 2.2 eV which allows photon absorption under the irradiation of visible light. Morales-Guio et al. have proposed a photocatalyst of amorphous iron-nickel oxide (FeNiOx) for the oxygen evolution reaction. Similarly, WO_3 has been considered a good photo anode material due to its suitable valance band position, which favors a high water oxidation potential.

In addition, Amer et al. have suggested ZrO_2 modification with the deposition of ZrN on ZrO_2 thin layers for the preparation of core-shell structures which are visible light active. However, Moniz et al. stated that the main drawback of WO_3 is its instability towards corrosion. Due to the low e.g. of these materials, these can be modified with doping with metal cations or by combining with other semiconductors to form heterojunctions. Sivula et al. have confirmed a WO_3/Fe_2O_3 heterojunction for better water oxidation due to its suitable band gap and proper alignment between WO_3

and Fe_2O_3 metal oxide which leads to better electron transfer at the host and guest interface. Ta_2O_3 (Tantalum Oxide) has been considering an attractive semiconductor for overall photocatalytic water splitting because of its wide band gap value (4 eV), further it is required to narrow the band gap by doping with some doping ions. It is also mentioned by Lu et al. that Ta_2O_5 nanowires as an active photocatalyst with a high rate of hydrogen generation. Recently, Zhu et al. reported Ta_2O_3 nanowires that were modified by an aluminum reduction for the improvement of electron density and photoelectrochemical overall water splitting of the material.

6. Conclusions

One of the most promising steps towards generating clean and renewable alternatives to fossil fuels is hydrogen production from solar energy by using photocatalytic materials. Different approaches have been employed in order to use solar energy more efficiently and to shift the photocatalytic activity in the visible range with stability and efficiency. TiO_2 has been used most widely as a photocatalyst however it has also some limitations such as:

- high hydrogen overpotential, wide band gap, and increased recombination of electron–hole pairs. Other metal oxides such as copper oxide, zinc oxide, and iron oxide have been also discussed as photocatalytic materials.

- Nitrides and composite materials have been also reviewed. Efficient water splitting depends on the innovative design of photocatalytic material. In addition, recent studies on heterojunction photocatalysts have also studied the nature of charge transfer.

- Carbon-based material heterojunctions are feasible future routes for the efficient design of photocatalysts. The architecture of the heterojunction influences photocatalytic activity and could potentially lead to great improvements.

- The future development in direction of photocatalytic water splitting is focused on the development of an efficient photoanode with a band edge with a redox potential of water and increased charge transfer under visible light with stability.

- Computational and theoretical modeling could help to understand the electronic density state and band structure. Therefore, the rational design of the photocatalyst leads to better overall water splitting's. Computational screening is an emerging field that will be used in the selection of material and design of junctions to yield optimized band structures.

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