A review of recent advance studies of synthesizing novel material for enhancing photo driven hydrogen evolution

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Abstract: Solar light-driven water splitting provides a promising way to store and use abundant solar energy in the form of gaseous hydrogen which is the cleanest chemical fuel for mankind; therefore, this field has been attracting increasing attention over the past decades. The fundamental steps for efficient photocatalyst for water splitting include uptake of photons of targeted energy range by appropriate electronic band structure, excited electrons and holes (excitons) migration, as well as recombination and selective conversion excited electrons for H^+ reduction to H_2 and holes and OH^- to O_2 on catalyst surface. Each step if not efficiently taken place could hamper the overall photocatalytic activity. Numerous semiconductors with appropriate bandgaps have mainly been developed as candidates for effective solar energy capture, whereas at present, their low quantum efficiency remains as the major obstacle in further applications. In this minireview, we will disentangle the progress to develop photocatalysts with good photon uptake from photocatalytic water splitting performance. In accordance with the thermodynamic and kinetic considerations of the photocatalytic water splitting reaction, different strategies for improving the fundamental processes have been briefly reviewed. Some recent advances in facilitating charge carrier's separation have also been presented. Photocatalytic water splitting at elevated temperatures is emphasized as a novel approach to suppress photo-excitons recombination on catalyst surface owing to adsorption of enhanced concentration of ionic species including H^+ and OH^- to create their local polarization to the excitons. Stronger polarization to hinder the excitons recombination can also be obtained by using polar-faceted support materials to the active phase of semiconductor. It is clearly demonstrated in this minireview that such high temperature promoted photocatalytic water splitting systems could open a new direction and provide an innovation to this field.

Keywords: Photocatalytic activity, Semiconductor, Water splitting, Hydrogen

1. Introduction

Energy and environmental issues have been of increasingly importance in recent decades, owing to the subtle global climate change arising from the use of fossil fuels. Thus, renewable and carbon emission free energy sources are in great demand [1-3]. Solar energy is attracting considerably interest as a sustainable and clean energy source, but

for practical application, the solar energy is required to be converted to other forms of energy such as chemical fuels, so that it can be stored and transported more efficiently [4-6]. Hydrogen (H_2) is considered as an ideal chemical fuel because of its highest energy capacity of 143MJ kg^{-1} for all matters in the universe and its emission-free advantage with the only byproduct water from combustion energy [7-9]. Therefore, solar light driven photocatalytic water splitting has become a promising method to convert solar energy into hydrogen. Since the first photoelectrochemical water splitting system was demonstrated by Fujishima and Honda [10] in 1972, photocatalytic water splitting has been persistently studied and significant progresses have been achieved since then. Visible light driven oxygen and hydrogen evolutions from water have been extensively explored separately, with the help of various sacrificial reagents [11-15]. For example, Han and Hu [15] have recently reported an enhanced hydrogen production using input of methanol as hole-scavenger at elevated temperatures. Apparently, the methanol molecules contribute to the overall hydrogen production via their decomposition. The additional capital cost for the methanol input and the unwanted hydrocarbon/alcohols by-products would largely hinder any practical application. Before further discussion, it should be clarified in this review that water splitting reaction is mainly focused upon. This refers to the overall splitting of water, where water molecule is the only required reactant and with the help of photocatalyst and sunlight, stoichiometric hydrogen and oxygen are produced. Therefore, sacrificial oxygen and hydrogen evolutions are not hereby considered as water splitting. Semiconductors such as TiO_2, $SrTiO_3$, GaN, CdS, MoS_2, and some conjugated semiconductors have been extensively studied as photocatalysts [3-5,14-22]. In general, photocatalytic water splitting reaction over semiconductors mainly involves the following fundamental processes (as shown in Fig. 1a) [23,24]: (1) formation of electron-hole pairs (excitons) by photon absorption; (2) charge separation and migration to trapping sites on catalyst surface; (3) construction of surface chemical reactions for H_2 and O_2 evolutions. In the process (3), protons in water are reduced by the excited electrons in the conduction band (CB) to produce H_2, and simultaneously, oxygen evolution happens from the water oxidation by the excited holes in valence band (VB). Therefore, to achieve the stoichiometric H_2 and O_2 evolution, the valence band maximum (VBM) should be more positive than E^0 $O_{2/}H_2O$ =1.23 V (vs. normal hydrogen electrode, NHE) and CB conduction band minimum (CBM) is more negative than $E^0 H + H_2$ 0.00 V (vs. NHE) to make oxygen and hydrogen evolutions to happen at the same time to sustain the catalysis (Fig. 1b). Obviously, the minimum bandgap of the semiconductor photocatalyst is 1.23 eV, corresponding to a wavelength of around 1000 nm. Despite the wide range of solar emission spectrum, the most intense solar radiation lies in the regime of visible light, which contributes nearly 43% of the solar energy [23]. Thus, an ideal photocatalyst for water splitting reaction should possess a corresponding bandgap to best use the visible light, bearing in mind that the bandgap should be at least 1.23 eV to drive the water splitting reaction. Apart from capturing photons from solar radiation with corresponding bandgap, photocatalytic activity and quantum efficiency (QE) are important aspects to evaluate the performance of a photocatalyst in gauging the effectiveness in conversion of capture energy to chemical

products. Typically, TiO_2-based materials have attracted most attention in the recent decades, and various methods have been applied to reduce the wide bandgap of TiO_2 (3.2eV), resulting in modified TiO_2 in different [16,25-27]. Although high activity and QE can be easily obtained over colored TiO2 under the UV light irradiation, the QE does not sustain but drops dramatically when it switches to visible light irradiation. This means that good degree of visible light absorption by the photocatalyst does not necessarily lead to good photocatalytic performance [12,17,28]. Perovskite also shows promising results in the field of solar energy applications, such as for solar cell and photocatalytic water splitting [29-32]. Doped perovskites show promising QE of 56% at 365 nm [31]. Narrow bandgap materials such as $(Ga_{1-x}Zn_x)$ $(N_{1-x}O_x)$, CdS and C_3N_4 exhibit promising photocatalytic activity under the visible light irradiation [5,33,34]. Besides, it has been reported recently a Z scheme photocatalytic water splitting system consisting of $BiVO_4$ and $SrTiO_3$ shows a QE of 30% at 419 nm with the help of cocatalysts [35]. Despite the exploration of different materials and efforts made on the enhancement of visible light absorption, low H_2 evolution rate and low QE under visible light and ambient conditions still hinder the current water splitting systems from practical applications. This is due to the rapid recombination of excitons to dissipate the captured solar energy to heat to environment. On the other hand, recent reports show that polarization plays an important role in the separation of these photogenerated electrons and holes from rapid recombination, which prolongs the exciton lifetime, therefore leading to enhanced photocatalytic performance [36-38]. Cocatalyst deposition is an effective approach to facilitate the surface reactions and suppresses the backward reactions [39-41]. There have been some good review articles published focusing from theoretical study to feasibility of largescale applications and economics [1-4,8,23,24]: Emphasis on photon absorption [1,2], materials synthesis and characterizations [3,4,24], and strategies to optimize the photocatalytic systems [8,23] can be found. Obviously, novel strategies are urgently required, and new approaches have been emerged recently. Therefore, we will focus on some recently reported progresses in this field to highlight on the fundamental underlying principles and current research trends. Over the recent decades, different strategies have been explored to enhance the photocatalytic water splitting performance and will also be briefly discussed. Based on our recent work, it is reported that elevated temperatures can lead to much enhanced photocatalytic water splitting performance owing to local polarization of the excitons on the catalyst by enhanced concentrations of H^+ and OH^- at saturated water vapor pressure at high temperatures. It is also demonstrated that the strong local electric field (LEF) can also be introduced by using polar-faceted support materials which show an extraordinary effect on promoting the separation of photogenerated electron and hole pairs from rapid recombination, which is considered as a facile and versatile approach for photocatalytic water splitting reaction and also for other systems.
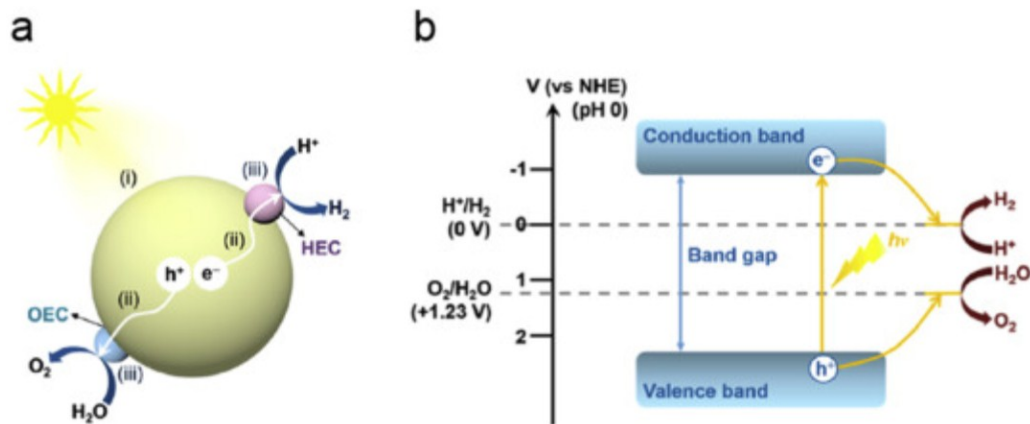
Fig. 1.   (a) Fundamental steps during photocatalytic water splitting on a semiconductor photocatalyst: (i) photoexcitation, (ii) charge separation and transport, and (iii) surface chemical reactions; (b) Schematic band structure and energy levels for photocatalytic water splitting based on one-step excitation.

Photocatalytic water splitting is adapted from the process of photosynthesis, which can be described as a chemical reaction stimulated by photo-irradiation in the presence of a photocatalyst. In plants, photosynthesis is an important process, which include two photochemical reactions and several intermediate enzymatic redox reactions as demonstrated in Fig. 2 (a). When sunlight strikes over the plant, chlorophyll (P680) in a photocatalyst two (PS II) is excited to P680* (PSII). In the next step, electrons from P680* are transmitted to Chlorophyll P700 (PS I), with the involvement of cytochrome and protease. Eventually, electrons in P700* combines with NADP+ to produce NADP, which finally reduces CO_2 into carbohydrate, whereas O_2 is formed by the oxidation of water in P680 (PS II) [37]. In a photocatalysis process, when light strikes over the semiconductor photocatalyst, electrons and holes involve in redox reaction for the hydrogen production through several steps as demonstrated in Fig. 2 (b). A semiconductor consists of valence band (VB), conduction band (CB) and an energy band gap i.e., energy difference between VB and CB. Upon exposure of semiconductor to light irradiation of photons with energy equal or higher than the band gap energy, electrons and holes are generated in the VB of semiconductor. Next, charge separation takes place and electrons jump from VB to CB of the semiconductor. This is a significant phenomenon in photocatalysis, playing vital role towards selection of suitable photocatalyst for enhanced H_2 evolution. Generally, following steps are involved in photocatalysis; 1) light harvesting, 2) charges separation, 3) transportation of electrons and holes to the surface of the photocatalyst and 4) redox reaction. Working principle of photocatalytic water splitting consists of three elements; photocatalyst, source of light and water. Photo-generated holes oxidize the water into O_2 and H^+, while photo-generated electrons reduce H^+ to H_2. However, if electrons and holes do not find the substrate immediately, they recombine with each other and release heat energy. In general, efficiency of photocatalytic water splitting for hydrogen production depends

on several factors as demonstrated in Fig. 3. In designing photocatalysts, it is important to understand all the steps involved during the photocatalytic process, which includes photon absorption, photo-excited charges separation, charge diffusion/transportation, mass transfer and catalytic reaction over the catalyst active sites. The photocatalytic water splitting process is highly dependent on the properties of the photocatalyst, the co-catalyst (nature of the active sites), the reaction conditions and adsorption of reactants. According to time scale, photoexcited charges relax immediately at their respective band positions in femto to pico seconds time and then transport towards catalyst surface in a nano-to-microsecond time to perform oxidation and reduction reactions.
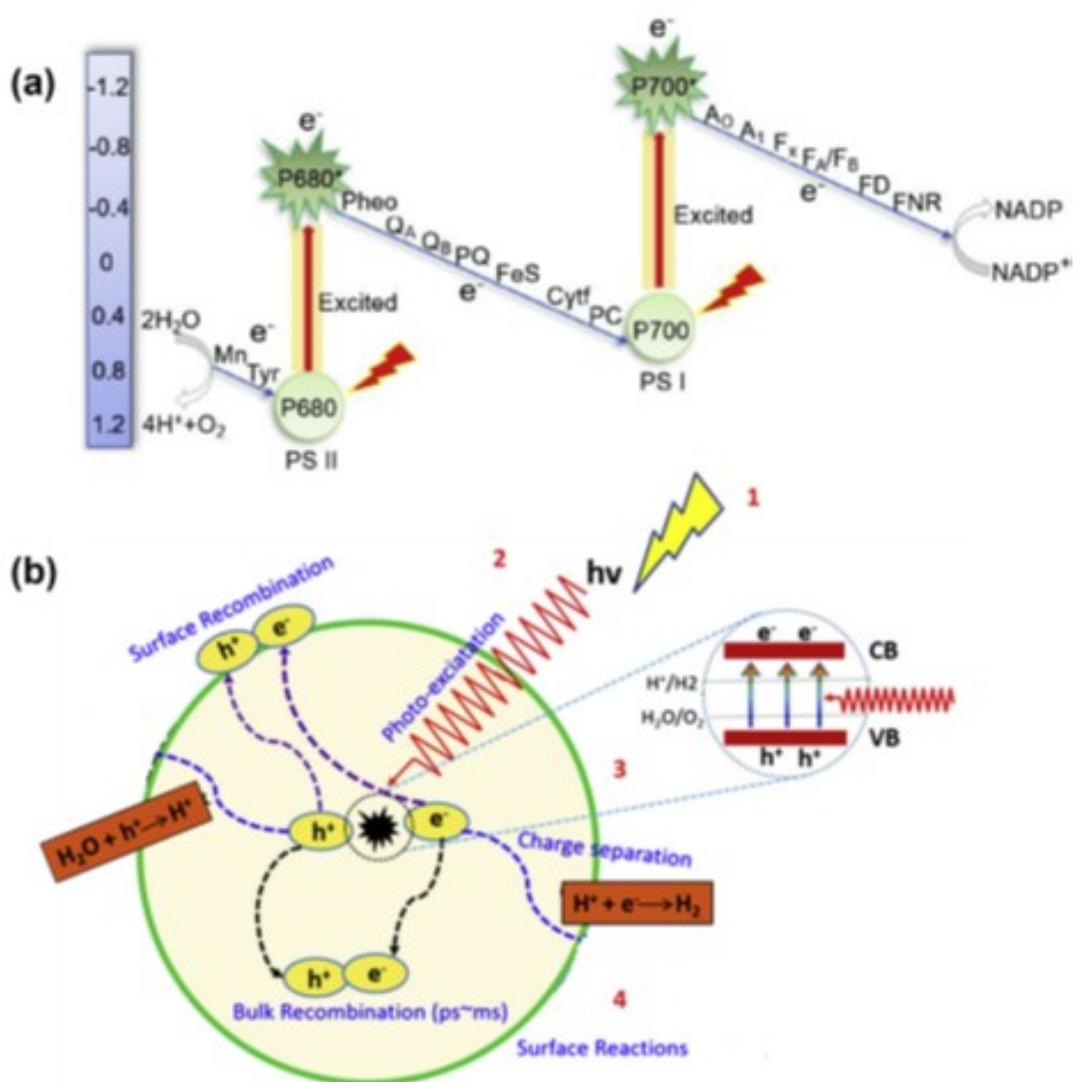

Fig. 2.   (a) Charge separation mechanism in natural photosynthesis, (b) Schematic diagram of steps involved in process of photocatalysis and phenomenon of charge recombination.
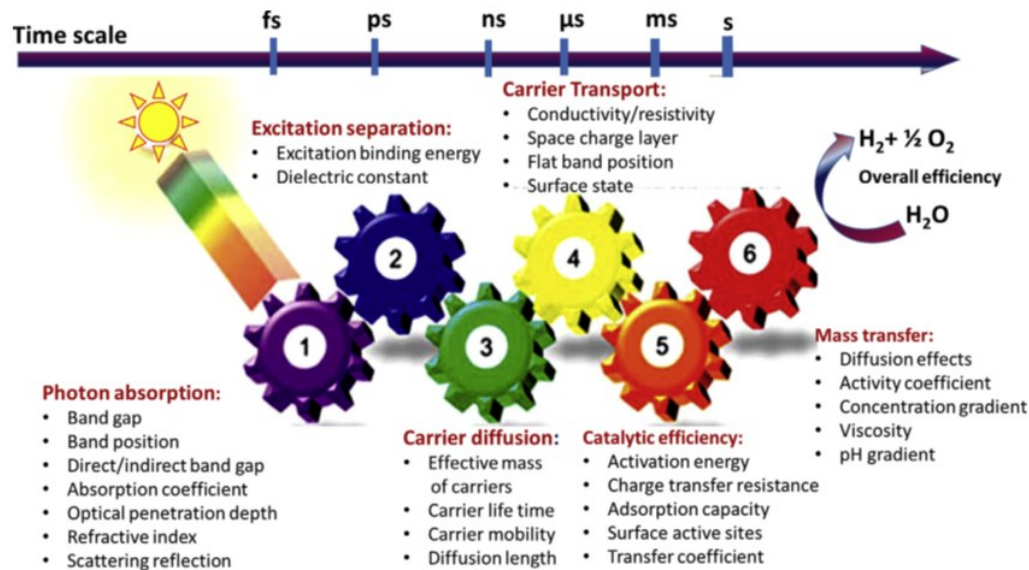
Fig. 3.   Schematic of major steps involved in photocatalytic water splitting process for hydrogen production

As discussed, the overall photocatalytic water splitting reaction performance is influenced by the efficiency of each of the three processes, therefore much effort has been made to gain their understanding, leading to different strategies developed to promote each step. Band structure engineering is a useful technique to narrow the wide bandgap materials down to the visible light region to maximize the energy capture [26,27,42-45]. Different methodologies have been used, such as sensitization with organic dyes, where the dye acts as a photosensitizer and injects electrons into the CB [43]. Another methodology is doping with anions or cations which inserts new band levels into the original bandgap of the semiconductors or facilitates a band shift to enhance light absorption properties [44,45]. Defects such as oxygen vacancies is also believed to provide intermediate band levels or extra states that can trap electrons and contribute to enhanced visible light absorption [46-53]. Cocatalysts such as noble metal and metal oxides are often engaged to facilitate the surface chemical reactions, lower the overpotentials for H_2 and O_2 evolution, and suppress the backward water-formation reaction [40,41,54-58]. Besides, methods have also been developed to promote the separation of the photogenerated electrons and holes on catalyst surface and suppress the recombination process, including shape and facet engineering, heterojunction formation and introduction of internal electric fields, and so on [37,59-61]. In this section, some prevalent strategies such as defect engineering and cocatalyst deposition will be discussed. The new promising approach to prolong the excitons lifetime by polarization will also be scrutinized in this section.

Materials and Experiment

1.1 g-C_3N_4 based photocatalyst

The binary g-C_3N_4/ZnO sample was constructed using an electrostatic self-assembly

assisted deposition technique. As follows, 0.1/ g of exfoliative g-C_3N_4 was firstly dispersed in 40/ ml of distilled water, after stirring for a while, 2.7/ g of $Zn(Ac)_2 \cdot 2H2O$ was added into the g-C_3N_4 solution, and further magnetic stirring was undertaken for 1/ h at room temperature to form a stable and homogenous suspension. Later, an appropriate amount of NaOH solution was added dropwise into the former suspension, and vigorously stirred for 2/ h at 60/ °C. The resulting product was collected through centrifuging, washing for several times and drying overnight, which is specified as 10CN/ ZO. Similarly, the other xCN/ZO samples (where x indicated different weight percentage of g-C3N4 relative to ZnO) were prepared by altering the amounts of g-C_3N_4, namely 5CN/ZO, 7CN/ZO and 12CN/ZO. For comparison, the bare ZnO was synthesized in the same manner without g-C_3N_4. The synthesis process of g-C_3N_4 nanosheets and g-C_3N_4/ZnO composites was illustrated in Fig. 4. Designing heterostructure photocatalysts by simple and efficient methods has attracted increasing attention nowadays, since the heterojunction between two different semiconductors would promote the separation of photogenerated electron-hole pairs and improve the photocatalytic activity. In this study, the efficient g-C_3N_4/ZnO nanocomposite photocatalysts with outstanding separation ability of photogenerated carriers were synthesized via a facile approach of electrostatic self-assembly combined with low-temperature precipitating method. The treatment of concentrated sulphuric acid endows g-C_3N_4 with more negative polarity and more active sites, which serves the deposition of ZnO nanoparticles. Besides, the in-situ growth way produces a tight and perfect heterojunction for speedy electron transfer between g-C_3N_4 and ZnO. The g-C_3N_4/ZnO composite samples exhibited much ehanced photocatalytic performance than single catalysts, and the degradation efficiency of the optimal product for decomposition of methylene blue (MB) reached to 60% within 120/ min, of which the total reaction rate constant was about 3.9 times higher than that of pure ZnO. The trapping experiments showed that the •OH radical was the major reactive oxygen species for degradation of MB, and it dropped approximate 50% of the degradation efficiency after the addition of the scavengers of ·OH. The Z-scheme mechanism is employed to explain the electron transfer pathway, which is a main reason for the enhancement of photocatalytic activity. This work provides a facile synthetic method and new sight for constructing heterojunctions for photocatalytic decomposition organic pollutants.
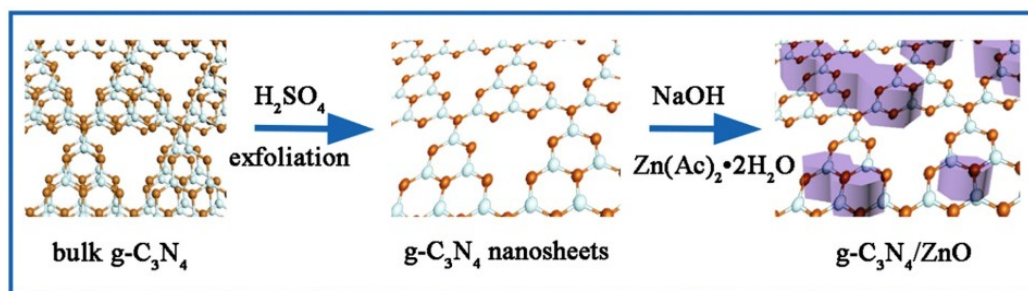

Fig. 4.   Schematic illustration of the synthesis of g-C_3N_4/ZnO photocatalysts.

3.2. Titanium dioxide (TiO$_2$) based photo-catalysts

The significant properties of the semiconductor of photocatalytic system are desired band gap, suitable morphology, high surface area and stability. Titanium dioxide (TiO$_2$) is the first semiconductor employed for photocatalytic activity by Fujishima and Honda [62]. Recently, TiO$_2$ has attracted much attention and is the most investigated photocatalyst credited to long-term stability, great absorption and photo-produced charge separation properties [63]. Anatase TiO$_2$ is more favorable than rutile and brookite as it has better performance for photocatalytic H2 production [64]. TiO$_2$ with anatase has appropriate band gap (3.2 eV) than brookite (3.4 eV), in addition of higher kinetic stability than rutile under ambient conditions [30]. It is also one of the most guaranteeing photocatalyst as a result of its excellent photocatalytic performance, easy accessibility, non-toxicity, and low price [65,66]. However, TiO$_2$ catalyst has limitation to maximize the photocatalytic activity due to faster charge recombination rate. Also, it can be mainly activated by UV light, which makes up only 4-5% of solar spectrum [67]. For water splitting under visible light, photo-catalysts must have narrow band gap, stable under photo irradiation and possess suitable CB and VB for H$_2$ generation using single photocatalyst [68]. The catalyst can exhibit stability when the photoelectron ready for the reduction reaction over the surface and the photo-generated transient electrons highly energetic with high reduction capability [46]. In order to enhance the performance of photocatalytic activities particularly for visible light irradiation, several methods on TiO$_2$ have recently been proposed and investigated. Recent developments on TiO$_2$ modifications include metal modified TiO$_2$, non-metal modified TiO$_2$, semiconductors coupling to TiO$_2$ and ternary TiO$_2$ photocatalysts.

2. Result and Discussion

Coupling TiO$_2$ with other semiconductors through type I, II and III hetero junctions, constructing Z-scheme and S-type photocatalytic system are important methods to maximize efficiency for photocatalytic hydrogen production under visible light irradiation [70]. The heterojunction of TiO$_2$ can be constructed using semiconductors with more negative CB values than TiO$_2$. For example, a type I heterojunction of g- C$_3$N$_4$/Fe$_2$O$_3$ with Pt as co-catalyst for enhanced photocatalytic H$_2$ evolution has been reported [71]. The enhanced photocatalytic activity was observed due to electrons and holes transporting towards Fe$_2$O$_3$ surface, resulting in 1150 times high H$_2$ evolution than using pristine TiO$_2$ due to faster charge carrier separation. In another development, type II heterojunction of NiO-TiO$_2$-x/C composites constructed for enhanced photo-catalytic hydrogen production as demonstrated in Fig. 5 (a). Carbon nanosheets improve dispersion of TiO$_2$, whereas NiO facilitates the separation of charge carrier and enhances the photo-activity under visible light irradiation, which is 18 folds higher than using TiO$_2$/C [71]. Likewise, Bi$_4$Ti$_3$O$_{12}$/TiO$_2$ composite formed type I heterojunction which enhanced photocatalytic performance because of effective charge carrier transfer and improved visible light utilization. Type I heterojunction promoted the activation of wider band gap TiO$_2$ under visible light and the H$^+$ to H$_2$ reaction took place on surface of Bi$_4$Ti$_3$O$_{12}$ [72]. In the development of type II heterojunction, g-C^{3}N^4/TiO$_2$ composite is famous,

where photo-excited electrons transferred to TiO_2 for oxidation and holes were transferred to g- C_3N_4 monolayer for redox reaction, resulting in inhibited charge carrier recombination. Moreover, extra electrons were provided for H_2 production reaction due to the synergic effect raised by the favorable CB positions of g-C_3N_4 and TiO_2 in heterojunction [73]. As another example, fabricated TiO/ $BiFeO_3$ nanocomposite showed improved H2 production due to the transfer of electrons generated in $BiFeO_3$ under visible light (l -500 nm) to TiO_2, which promotes photo-generated charge carriers' separation [74]. Umer et al., studied $SWCNTs/TiO_2$ heterojunction composite for dynamic H_2 generation. TiO_2 was not completely activated under visible-light irradiations leading to recombination, however; montmorillonite (Mt) and SWCNTs were capable of absorbing visible light, leading to TiO_2 activation [75].
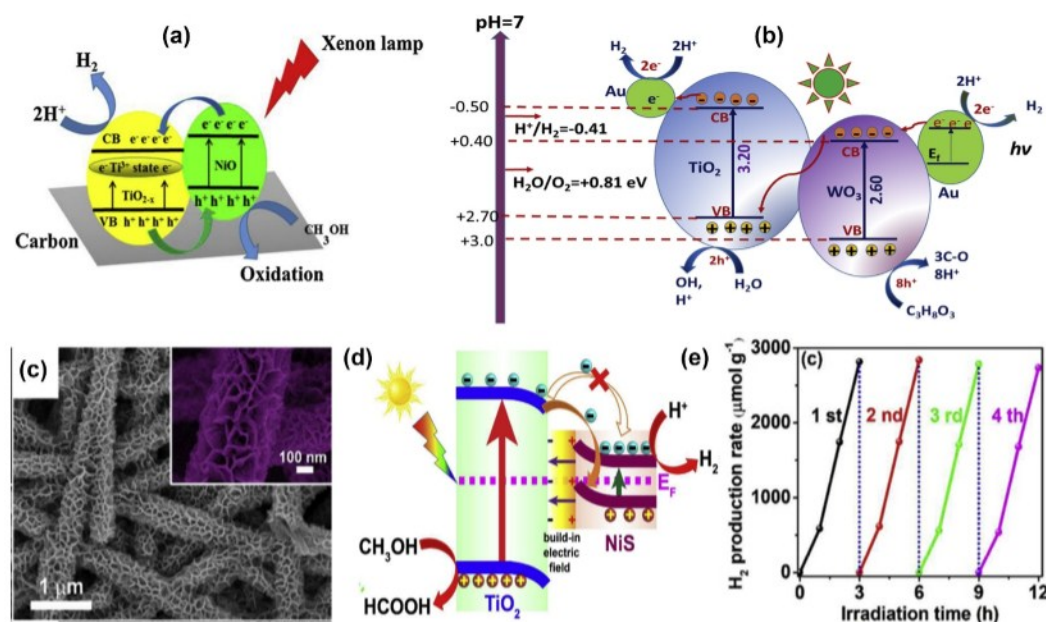

Fig. 5.   (a) Schematic illustration of type II heterojunction of NiO/TiO_2 for photocatalytic hydrogen production, (b) Direct Z-scheme mechanism of Au–TiO_2/WO_3 for H_2 production; (c–e) Schematic illustration of the mechanism for photocatalytic water splitting in core-shell NiS/TiO_2 heterojunction.

Visible light activity was observed for CdS/TiO_2 composite by formation of type II heterojunction in which the low band gap of CdS assisted the transfer of photo-generated excited electrons from CdS nanoparticles to crystalline TiO_2 [76]. Besides, for enhancement of activity by co-dopants, carbon nanotubes (CNTs) are also another alternative of potential hybrid for TiO_2 doping. Carbon could act as an electron sink, which prevents the recombination process. Thus, employing co-catalyst is a promising system to maximize photocatalytic hydrogen production under visible light. In the Z-scheme development, water splitting through photocatalysis was first introduced by Bart et al., [77] in 1979, since then this approach has gained much attention and is considered as an efficient method to enhance photocatalytic hydrogen production. This

method is inspired from the two-step photosystem in natural photosynthesis, where water and CO_2 react to form O_2 and carbohydrates. There are several reports available on water splitting through photocatalysis using Z-scheme approach. For instance, Z-scheme photocatalyst coupling of Pt/TiO_2 irradiated under UV with wavelength 300 nm in the presence of IO_3 redox mediator was studied for improved photocatalytic activity [78]. Furthermore, reduced charge recombination and efficient charge transfer was studied for Z-scheme heterojunction of TiO_2/NiO. This was due to the formation of mid-gap state by Ti^{3+} and oxygen vacancies, resulting in direct Z-scheme based transfer of charge carries transfer between the Ti^{3+}/oxygen vacancies state and NiO valence band (VB). Li et., [79] investigated in situ growth of $ZnIn_2S_4$ (ZIS) nanosheets on the surface of hollow sphere TiO_2 by hydrothermal method to form direct Z scheme heterojunction composite. This Z-scheme was observed to be efficient towards applications in photocatalytic systems attributing to the intimate contact and matched band edge positions of ZIS and TiO_2 Z-scheme heterojunction between $CuInS_2/TiO_2$ (CIS-TO) generated up to 785.4 mmol/g/h of H_2 due to improved charge transfer, narrow band gap of CuInS2 and inhibition of charge carrier recombination [80]. Likewise, redox mediator free Z-scheme for TiO_2/CdS binary hierarchical photocatalyst was discussed to show improved H_2 production efficiency based on the hierarchical structure [81]. Hu et al., [82] fabricated carbon-layer-coated TiO_2/WO_3 nanofibers (WTC) to study Z-scheme heterojunction and observed improved H_2 production as compared to pure TiO_2. The activity was attributed to improve charge-carrier heterojunction system and improved electron transport in C due to graphitization by WO_3.

$CuGaS_2/rGO/TiO_2$ as a Z scheme heterojunction supported by solid state electron meditator was studied for visible light photocatalytic activity. Upon illumination by visible light, the electrons in CB of TiO_2 and holes in VB of CuGaS2 were recombined by the rGO as mediator. Hence, the holes left in VB of TiO_2 and electrons in CB of leaving holes in TiO_2 and electrons in $CuGaS_2$ lead efficient water splitting [83]. Another technique for modification of semiconductors is cooping in which low band gap of one material induces photocatalytic activity in a wide band gap material [84]. Co-doping increases the charge separation and improves the range of photo-excitation energy in the process. For instance, in case of co-doping of TiO_2 andWO_3, the narrower band gap of WO_3 utilizes solar irradiation better than TiO_2, and underwent photoexcitation, creating electrons and holes. The photo-generated electrons were transferred to TiO_2 conduction band, leaving behind holes inWO_3 valence band. This long emigration time of electron transfer increases the charge separation leading to redox reaction [85,86]. For example, TiO_2 anatase is inactive under visible light because of 3.2 eV band energy, but $BiVO_4/TiO_2$ heterojunction induces visible light activity in TiO_2 and led to efficient charge separation and transfer [87]. Fig. 5 (b) depicts Z-scheme heterojunction system of WO_3/TiO_2 with plasmonic effect of Au for enhanced photocatalytic hydrogen under visible light irradiation. The H2 evolution rate over $Au-WO_3/TiO_2$ was increased by 6 folds due to SPR effect of Au and proficient charge carrier separation among the semiconductors [88]. Fig. 5(c-e) demonstrated core-shell Z-scheme heterojunction of TiO_2/NiS hybrid nanofibers with enhanced stability for photocatalytic hydrogen

production. The H_2 evolution rate of 14.6-fold higher over composite was achieved than using only pristine TiO_2. This enhanced photocatalytic activity was due to direct Z-scheme heterojunction formation, which greatly promotes the separation of electrons and holes [89]. A recent development in TiO_2 based heterojunction formation with binary semiconductors has been summarized in. Obviously, different types of semiconductors such as NiO, CdS, Ag_2O, Bi_2O_3, RuO_2, ZnO, CoO, ZrO_2, SnO_2 and WO_3 has been employed in the formation of TiO_2 heterojunction. According to all above discussion, type II and Z scheme heterojunction formations are effective methods to enhance visible light absorption and promotes charge carrier separation to get higher hydrogen production during photocatalytic water splitting under visible light irradiation. However, Z-scheme heterojunction is more promising due to getting more negative CB and more positive VB during band adjustment of semiconductors, which is favorable to get higher hydrogen production and can be employed in other solar energy applications.

3. Conclusion

In conclusion, regardless of the previous reports, the probability of TiO_2 and $g-C_3N_4$ modification for more efficient photocatalytic water splitting apparently has not been fully discovered. While the challenges in heterojunction have not been studied in detail, Z-scheme photocatalytic system is like the natural photosynthesis. It is recommended that full exploration of this can results in discovery in the efficiency of photocatalytic activity while using monolith photoreactor system. As a concluding remark, both opportunities and challenges are present in future development of this encouraging technology. Ideally, this review will enhance further advancement of TiO_2 and $g-C_3N_4$ modification for attaining its application for effective photocatalytic water splitting in the presence of sacrificial reagents with different types of photo reactors. Z-scheme coupling mechanism enables a wider band gap semiconductor photocatalyst to achieve stronger redox potential, while simultaneously makes it active for absorption of visible light. Doping increases the charge separation and improves the range of photoexcitation. Structural modifications lead to larger surface area, provides more active site and higher visible light absorption for maximizing photocatalytic activity.

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