

Advanced Study on Novel Composite and Comparison with Carbon and Semiconductor-Based Materials for Efficient Hydrogen Evolution

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Abstract: Photocatalytic water splitting with solar light is one of the most promising technologies for solar hydrogen production. From a systematic point of view, whether it is photocatalyst and reaction system development or the reactor-related design, the essentials could be summarized as: photon transfer limitations and mass transfer limitations (in the case of liquid phase reactions). Optimization of these two issues is therefore given special attention throughout our study. In this review, the state of the art for the research of photocatalytic hydrogen production, both outcomes and challenges in this field, were briefly reviewed. Research progress of our lab, from fundamental study of photocatalyst preparation to reactor configuration and pilot level demonstration, were introduced, showing the complete process of our effort for this technology to be economic viable soon. Our systematic and continuous study in this field lead to the development of a Compound Parabolic Concentrator (CPC) based photocatalytic hydrogen production solar reactor for the first time. We have demonstrated the feasibility for efficient photocatalytic hydrogen production under direct solar light. The exiting challenges and difficulties for this technology to proceed from successful laboratory photocatalysis set-up up to an industrially relevant scale are also proposed. These issues have been the object of our research and would also be the direction of our study in future. 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 H₂ and holes and OH⁻ to O₂ 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.

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1. Introduction

Conventional energy resources, which are being used to meet most of the world's energy requirements, have been depleted to a great extent. It is therefore necessary to produce an alternative fuel that should in principle be pollution-free, storable, and economical. Hydrogen satisfies the first two conditions, and research has been focused on fulfilling the third requirement in the past decades [1,2]. To be an economical and sustainable pathway, hydrogen should be manufactured from a renewable energy source, i.e., solar energy. Photocatalytic water splitting is the most promising technology for the purpose, since H₂ could be obtained directly from abundant and renewable water and solar light from the process. If successfully developed with economic viability, this could be the ultimate technology that could solve both energy and environmental problems altogether in the future [3–9]. Water splitting using light energy has been studied for a long-time using powder systems since the Honda–Fujishima effect was reported [10,11]. Much progress has been made in the past decades. Thermodynamically, water splitting into H₂ and O₂ is an uphill reaction, accompanied by a large positive change in the Gibbs free energy (238 kJ/mol). The efficiency of water splitting is determined by the band gap and band structure of the semiconductor and the electron transfer process, as shown in Fig. 1 [12,13]. [Generally, for efficient H₂ production using a visible-light-driven semiconductor, the band gap should be less than 3.0 eV (420 nm), but larger than 1.23 eV, corresponding to the water splitting potential and a wavelength of ca. 1000 nm. Moreover, the conduction band (CB) and valence band (VB) levels should satisfy the energy requirements set by the reduction and oxidation potentials for H₂O, respectively. Band engineering is thus necessary for the design of semiconductors with these combined properties. In the past decades, efforts have been made to address the following two important issues. One issue is the development of efficient visible-light-driven photocatalyst which has undergone a rapid progress especially in the past decade. The other key issue concerns the efficient utilization of the solar energy itself. Two major drawbacks of solar energy must be considered: (1) the intermittent and variable manner in which it arrives at the earth's surface (2) efficient collection of solar light on a useful scale. The first drawback can be resolved by converting solar energy into storable hydrogen energy. For the second, the solution could be the use of solar concentrator. The strategies are schematically illustrated in Fig. 2. As can be found in Fig. 2, whether it is photocatalyst development or the reactor- and system-related design, the essentials could be summarized as: photon transfer limitations and mass transfer limitations (in the case of liquid phase reactions) [14]. For photon transfer optimization, it concerns the choice of photocatalyst, the reaction media and the reactor configuration. Here, reaction media is often the aqueous solution containing various sacrificial agents for the elimination of photo-generated holes and for further improvement of photocatalytic efficiency or simultaneous decomposition of toxic organics. The photocatalytic material should efficiently absorb photos and separate photo-generated charges. Fast transportation of the photo-generated carriers must be guaranteed to avoid bulk electron/hole recombination. The separated electrons and holes act as reducer and

oxidizer, respectively, in the water splitting reaction over semiconductors to produce hydrogen and oxygen. In the field of mass transfer optimization, many reactors and reactor configurations have been investigated for their use in photocatalysis. Gas-liquid two phase and gas-liquid-solid three phase flow study in various reactor configurations, especially tubular reactors, are important for mass transfer optimization. Research on photocatalytic hydrogen production in China has been initiated in nineties of the last century and we are among the groups conducting earliest work in the field. In 2003, the project of the Basic Research of Mass Hydrogen Production Using Solar Energy founded by National Basic Research Program of China (973 Plan) was initiated by SKMFPE with the participation of almost all the main teams conducting the related studies at the time. With the support of 973 Project and other financial support from the government, SKMFPE has set their research direction to the development of highly efficient, stable and low-cost visible-light-driven photocatalyst by various modification methods, such as doping, sensitization, supporting and coupling methods to extend the light responsive and performance of the photocatalyst. We have studied the photocatalytic materials as powders for photocatalytic reaction and as solid films for photoelectrochemical hydrogen production as well. Various photocatalytic reactors and relevant instruments have also been developed for photocatalytic hydrogen production, photocatalyst screening and evaluation, which formed a complete platform for further in-depth study. In particular, we have devoted to photocatalytic hydrogen under direct solar light and have also been successful. A series of significant results were obtained in the course of our continuous research. With all these accomplishments, we have been supported by the new 973 project of China which started in 2009. In this review, the state of the art for the research of photocatalytic hydrogen production, both outcomes and challenges in the field, were briefly reviewed. In general, efficiency of photocatalytic water splitting for hydrogen production depends A review of recent advance studies of synthesizing novel material for enhancing photo 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.

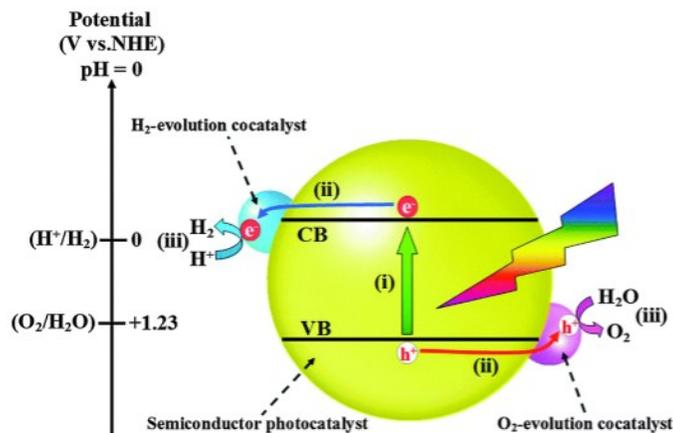


Fig. 1: Basic principle of overall water splitting on a cocatalyst- loaded semiconductor. [12,13]

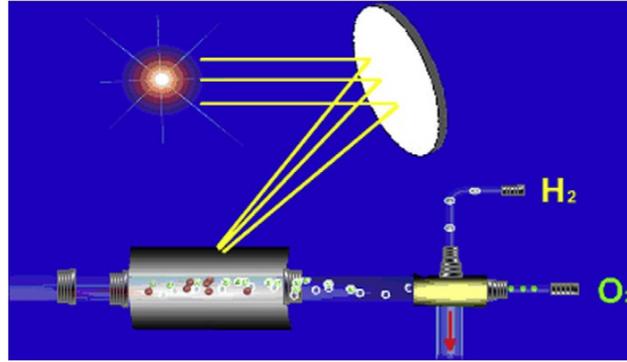


Fig. 2: Schematic illustration for the process of photocatalytic water splitting hydrogen production under solar light considered from a systematic point of view. [14]

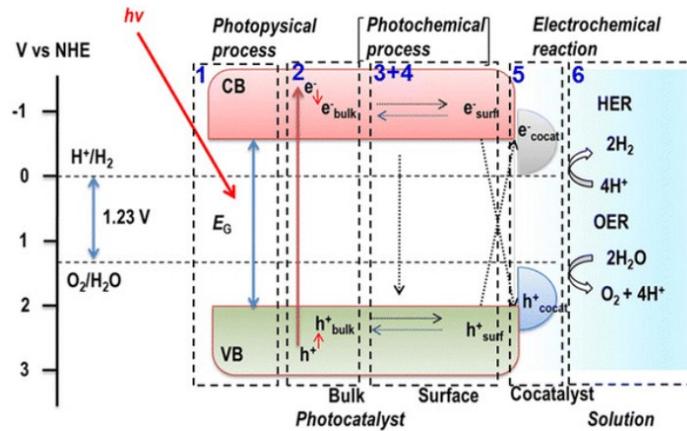


Fig. 3. Schematic of major steps involved in photocatalytic water splitting process for hydrogen Production. [15,16]

Research progress of our lab, from fundamental study of photocatalyst preparation to the issues related to reactor configuration and pilot level demonstration, were introduced, showing the complete process of our effort for this technology to be economic viable soon. 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 [15,16]. Different methodologies have been used, such as sensitization with organic dyes, where the dye acts as a photosensitizer and injects electrons into the CB. 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. 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 [17-24]. 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 [25-32]. 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 [33-37]. 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.

2. Materials and Experiment

2.1. $g-C_3N_4$ based photocatalyst [49]

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 $Zn(Ac)_2 \cdot 2H_2O$ 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 $g-C_3N_4$ 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, showed in Fig. 5 (a-e). 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 enhanced 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 $\cdot OH$ 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 $\cdot OH$. 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 of organic pollutants. Graphite phase $g\text{-C}_3\text{N}_4$ is a non-metallic organic semiconductor possessing a narrow bandgap of 2.7 eV. It has two chemical structures: triazine rings and 3-s-triazine rings. In addition, its conduction band is lower than the standard hydrogen electrode potential, which facilitates water splitting to produce H_2 . Although $g\text{-C}_3\text{N}_4$ is considered as an efficient photocatalyst, it still suffers from a low specific surface area, wide bandgap, and fast recombination of electron-hole pairs, which restrain its practical applications. Various modification methods such as morphology control, metal or non-metal element doping, and constructing heterojunctions are used to improve its photocatalytic properties. $\text{CuGaS}_2/\text{rGO}/\text{TiO}_2$ as a Z scheme heterojunction supported by solid state electron mediator was studied for visible light photocatalytic activity. Upon illumination by visible light, the electrons in CB of TiO_2 and holes in VB of CuGaS_2 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 and WO_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 in WO_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 $\text{BiVO}_4/\text{TiO}_2$ heterojunction induces visible light activity in TiO_2 and led to efficient charge separation and transfer [87]. Fig. 6 (a-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 H_2 evolution rate over $\text{Au-WO}_3/\text{TiO}_2$ was increased by 6 folds due to SPR effect of Au and proficient charge carrier separation among the semiconductors [88]. Fig. 6(a-e) demonstrated core-shell Z-scheme heterojunction of TiO_2/NiS hybrid nanofibers with enhanced stability for photocatalytic hydrogen.

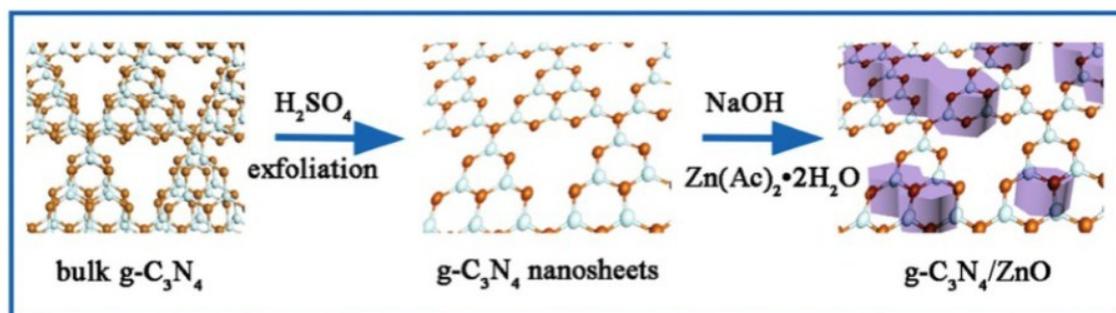


Fig. 4. Schematic illustration of the synthesis of $g\text{-C}_3\text{N}_4/\text{ZnO}$ photocatalysts. [49]

2.2. Other Photocatalysts

The application of metal oxynitride as a photocatalyst was firstly reported by the scientists from Nippon Institute of Technology. TaON, a metal oxynitride, has a small bandgap of 2.5 eV and can respond to visible light. Furthermore, its CB potential is slightly negative than the standard hydrogen electrode potential and its VB potential is 2.2 V, which is sufficient for water decomposition. Chen et al. used Ni(OH)₂ as the co-catalyst to modify TaON by loading Ni(OH)₂ on TaON via a precipitation method [38]. They found that the H₂ generation yield on Ni(OH)₂/TaON reached 3.15 μmol h⁻¹, which was greater than that obtained 0.5 wt% Pt/TaON (1.48 μmol h⁻¹). Qi et al. firstly prepared a 1-D Ta₃N₅/BaTaO₂N (BTON) heterostructure via a facile one-step ammonia thermal pathway by using single-phase KBa₂Ta₅O₁₅ (KBTO) as the precursor. This heterostructure showed an absorption edge at 600 nm. The special interface and increased surface area provided a large number of channels for electron transfer and charge separation, which remarkably improved the H₂ generation yield of Ta₃N₅/BaTaO₂N (4.8 μmol h⁻¹), higher than those of bare Ta₃N₅ and BTON nanoparticles). Li and co-authors summarized the recent advances in H₂ generation on nickel-based photocatalysts (noble co-catalysts are also included) [39]. Modification strategies such as enhancing the light capture rate, improving the charge separation/transport, and reinforcing the interfacial interaction of semiconductor/co-catalyst assemblies were discussed in detail, providing new pathways for designing high-activity and high-stability nickel-based photocatalysts for H₂ evolution. The methods used for enhancing the light trapping rate of photocatalysts include designing hierarchical photocatalysts, using surface sensitization, and developing broad-spectrum catalysts. For example, Zhang et al. used a solvothermal route to prepare core-shell TiO₂ nanothorns/C nanofiber photocatalysts, which exhibited 13.5 times higher H₂ generation rate than that of doped NiS. The separation of photogenerated carriers in photocatalysts can be improved by constructing Schottky junctions or semiconductor heterojunctions. Li et al. immobilized NiS on g-C₃N₄/C black Schottky junctions and achieved a H₂ generation efficiency of 992 μmol g⁻¹ h⁻¹ [40]. Strengthening the interfacial interactions (increase interface contact area or tightness) is another approach to improve the H₂ generation efficiency of photocatalysts. He et al. reported a g-C₃N₄ nanosheet/NiS heterojunction with a close-contact interface via one-step in-situ calcination of urea, thiourea, and nickel acetate. This heterojunction exhibited a maximum H₂ yield of 29.68 μmol h⁻¹ [41]. The significant properties of the semiconductor of photocatalytic system are desired band gap, suitable morphology, high surface area and stability. Titanium dioxide (TiO₂) is the first semiconductor employed for photocatalytic activity by Fujishima and Honda [42]. Recently, TiO₂ has attracted much attention and is the most investigated photocatalyst credited to long-term stability, great absorption and photo-produced charge separation properties [43]. Anatase TiO₂ is more favorable than rutile and brookite as it has better performance for photocatalytic H₂ production [44]. TiO₂ 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 [45,46]. However, TiO₂ 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 [47]. For water splitting under visible light, photo-catalysts must have narrow band gap, stable under photo irradiation and possess suitable CB and VB for H₂ generation using single photocatalyst [48]. 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 TiO₂ have recently been proposed and investigated. Recent developments on TiO₂ modifications include metal modified TiO₂, non-metal modified TiO₂, semiconductors coupling to TiO₂ and ternary TiO₂ photocatalysts.

3. Result and Discussion

The heterojunction of TiO₂ can be constructed using semiconductors with more negative CB values than TiO₂. For example, a type I heterojunction of g- C₃N₄/Fe₂O₃ with Pt as co-catalyst for enhanced photocatalytic H₂ evolution has been reported [49]. The enhanced photocatalytic activity was observed due to electrons and holes transporting towards Fe₂O₃ surface, resulting in 1150 times high H₂ evolution than using pristine TiO₂ 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 TiO₂, whereas NiO facilitates the separation of charge carrier and enhances the photoactivity under visible light irradiation, which is 18 folds higher than using TiO₂/C. Likewise, Bi₄Ti₃O₁₂/TiO₂ 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 TiO₂ under visible light and the H⁺ to H₂ reaction took place on surface of Bi₄Ti₃O₁₂ [50]. In the development of type II heterojunction, g-C₃N₄/TiO₂ composite is famous, where photo-excited electrons transferred to TiO₂ for oxidation and holes were transferred to g- C₃N₄ monolayer for redox reaction, resulting in inhibited charge carrier recombination. Moreover, extra electrons were provided for H₂ production reaction due to the synergic effect raised by the favorable CB positions of g-C₃N₄ and TiO₂ in heterojunction [51]. As another example, fabricated TiO/ BiFeO₃ nanocomposite showed improved H₂ production due to the transfer of electrons generated in BiFeO₃ under visible light (λ -500 nm) to TiO₂, which promotes photo-generated charge carriers' separation [52]. Umer et al., studied SWCNTs/TiO₂ heterojunction composite for dynamic H₂ generation. TiO₂ was not completely activated under visible-light irradiations leading to recombination, however; montmorillonite (Mt) and SWCNTs were capable of absorbing visible light, leading to TiO₂ activation [53]. Visible light activity was observed for CdS/TiO₂ 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 TiO₂ [54]. Besides, for enhancement of activity by co-dopants, carbon nanotubes (CNTs) are also another alternative of potential hybrid for

TiO₂ 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., [55] 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 CO₂ react to form O₂ and carbohydrates. There are several reports available on water splitting through photocatalysis using Z-scheme approach. For instance, Z-scheme photocatalyst coupling of Pt/TiO₂ irradiated under UV with wavelength 300 nm in the presence of IO₃ redox mediator was studied for improved photocatalytic activity [56]. Furthermore, reduced charge recombination and efficient charge transfer was studied for Z-scheme heterojunction of TiO₂/NiO. This was due to the formation of mid-gap state by Ti³⁺ and oxygen vacancies, resulting in direct Z-scheme based transfer of charge carriers between the Ti³⁺/oxygen vacancies state and NiO valence band (VB). Li et al., [57] investigated in situ growth of ZnIn₂S₄ (ZIS) nanosheets on the surface of hollow sphere TiO₂ 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. The band edge positions of ZIS and TiO₂ Z-scheme heterojunction between CuInS₂/TiO₂ (CIS-TO) generated up to 785.4 mmol/g/h of H₂ due to improved charge transfer, narrow band gap of CuInS₂ and inhibition of charge carrier recombination [58]. Likewise, redox mediator free Z-scheme for TiO₂/CdS binary hierarchical photocatalyst was discussed to show improved H₂ production efficiency based on the hierarchical structure [59]. Hu et al., [60] fabricated carbon-layer-coated TiO₂/WO₃ nanofibers (WTC) to study Z-scheme heterojunction and observed improved H₂ production as compared to pure TiO₂. The activity was attributed to improve charge-carrier heterojunction system and improved electron transport in C due to graphitization by WO₃. For example, TiO₂ anatase is inactive under visible light because of 3.2 eV band energy, but BiVO₄/TiO₂ heterojunction induces visible light activity in TiO₂ and led to efficient charge separation and transfer [68]. Fig. 5 (b) depicts Z-scheme heterojunction system of WO₃/TiO₂ with plasmonic effect of Au for enhanced photocatalytic hydrogen under visible light irradiation. The H₂ evolution rate over Au-WO₃/TiO₂ was increased by 6 folds due to SPR effect of Au and proficient charge carrier separation among the semiconductors [69]. Fig. 5(c-e) demonstrated core-shell Z-scheme heterojunction of TiO₂/NiS hybrid nanofibers with enhanced stability for photocatalytic hydrogen.

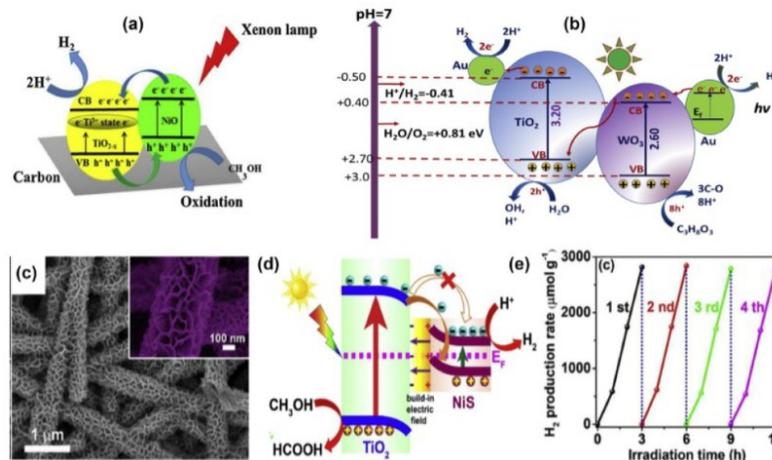


Fig. 5. (a) Schematic illustration of type II heterojunction of NiO/TiO₂ for photocatalytic hydrogen production, (b) Direct Z-scheme mechanism of Au-TiO₂/WO₃ for H₂ production; (c-e) Schematic illustration of the mechanism for photocatalytic water splitting in core-shell NiS/TiO₂ heterojunction. [68]

The introduction of additional components on ZnO to construct heterojunctions is a prominent approach to enhance its photocatalytic H₂ yield. Wang et al. fabricated core-shell *g*-C₃N₄/ZnO (CN/OD-ZnO) heterojunctions by coupling *g*-C₃N₄ nanosheets with oxygen-deficient ZnO nanorods (OD-ZnO) and proposed the Z-scheme mechanism of electron transport in the photocatalysts [61]. As shown from the electrochemical impedance spectroscopy (EIS) results, the composite photocatalyst with 10 wt% *g*-C₃N₄ (CN-10/OD-ZnO) had the smallest diameter i.e., the lowest electron-transfer resistance (Ret). On the other hand, pure *g*-C₃N₄ showed the largest diameter i.e., the highest Ret. The heterojunctions significantly improved the electroconductivity of the ZnO, as shown in Fig. 6A. EIS is generally used to analyze the photocurrent response of a material. Accordingly, CN-10/OD-ZnO demonstrated the maximum photocurrent response, which was nearly eight folds greater than that upon *g*-C₃N₄ (Fig. 6B), due to its minimum Ret. Among the three characteristic heterostructures shown in Fig. 6C, the Z-scheme showed highly improved separation of the photogenerated carriers and the highest charge lifetimes, and hence the highest H₂ yield [62]. Yuan et al. synthesized a new MoS₂ nanosheet-coated ZnO heterojunction using a hydrothermal method [63]. They found that 1 wt% MoS₂/ZnO had the maximum H₂ generation rate of 768 mmol g⁻¹ h⁻¹, which is 14.8 times greater than that on single ZnO. It may be mentioned that the HER photocatalytic activity of MoS₂ is greater than those on precious metals including Pt or Au, demonstrating its potential to replace noble-metal co-catalysts. Ma et al. prepared a new CdS/ZnO heterostructure by combining 0-D CdS quantum dots (QDs) with 2-D ZnO nanosheets (NSs). CdS/ZnO-12 (12 is the deposition number of the CdS QDs) showed the maximum H₂ generation yield about 22.12 mmol g⁻¹ h⁻¹, which is 138 folds greater than that upon ZnO (0.16 mmol g⁻¹ h⁻¹). CuGaS₂/rGO/TiO₂ as a Z scheme heterojunction supported by solid state electron mediator was studied for visible light photocatalytic activity. Upon illumination by visible light, the electrons in CB of TiO₂

and holes in VB of CuGaS_2 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 [64]. 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 [65]. 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 and WO_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 in WO_3 valence band. This long emigration time of electron transfer increases the charge separation leading to redox reaction [66,67].

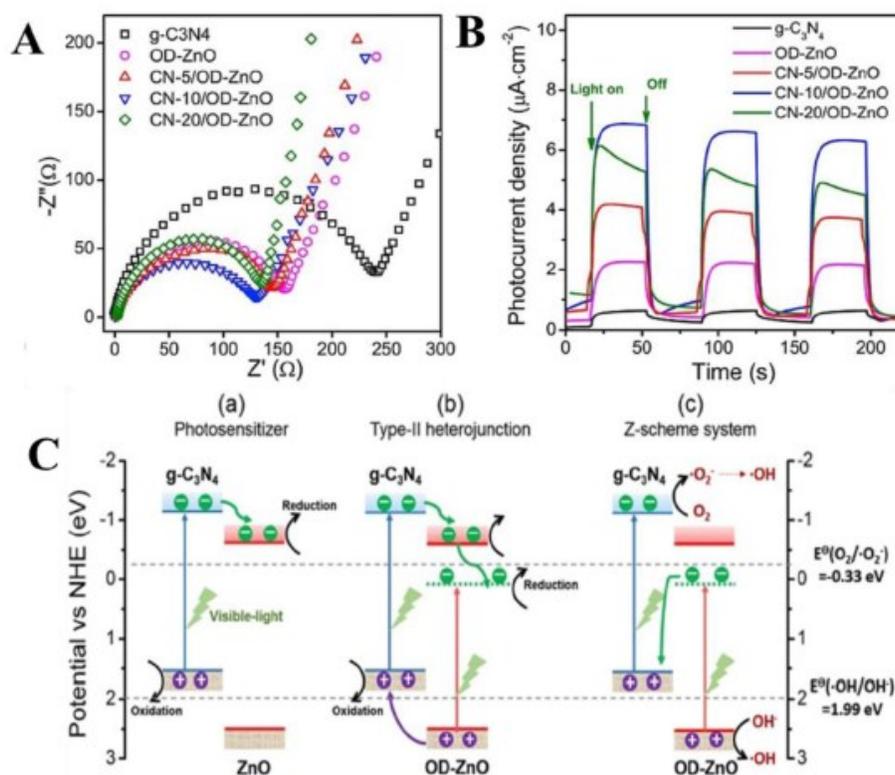


Fig. 6 (A) EIS results (B) photocurrent responses (C) $g\text{-C}_3\text{N}_4$ /defect-free ZnO (a), type II heterojunction of $g\text{-C}_3\text{N}_4$ /OD-ZnO (b), Z-scheme system of $g\text{-C}_3\text{N}_4$ /OD-ZnO (c) (Reproduced with the permission from the publisher. [35,64])

4. Conclusion

Photocatalytic water splitting is the simplest approach to robustly convert and utilize the abundant solar energy to produce H_2 , which is a promising and green alternative to fossil fuels. Intensive efforts have photocatalysts for practical applications. This review mainly focuses on the H_2 evolution of high-performance photocatalysts without precious

metals. Five types of non-noble metal photocatalysts including metal oxide-based, metal sulfide-based, metal phosphide-based, metal-free, and other non-precious metal photocatalysts have been comprehensively reviewed. Various strategies used for enhancing the photocatalytic H₂ generation from water splitting involving (1) metal or metalloid (non-metal) doping, (2) ion co-doping, (3) establishing heterojunctions (p-n type or Z-scheme), (4) constructing core-shell structures, (5) constructing ternary systems, (6) dye-sensitization, (7) controlling the morphology of the catalysts, and (8) increasing the contact area and strength of the interface have been discussed in detail. It should be noted that high H₂ evolution efficiency can be achieved on photocatalysts without noble metals (even greater than those on the photocatalysts containing precious metals). Unlike noble metal photocatalysts, which deactivate in the presence of contaminants, non-noble metal photocatalysts exhibit high stability even in the presence of contaminants. Considerable progress has been achieved in improving the H₂ evolution efficiency of photocatalysts. However, the photocatalysts developed till date are not suitable for large-scale practical applications. The challenges for large scale H₂ generation on photocatalysts without noble metals should not be ignored. (1) The long-term stability of the catalysts. The generally used photocatalysis loop tests are limited to several cycles, and long-term testing based on months or years is hardly reported. This makes it difficult to comment on the industrial applicability of presentday non-noble metal photocatalysts. (2) Low utilization of sunlight. Various approaches such as composition engineering have been used to expand the light absorption range. However, it is still a challenge to achieve solar-driven photocatalytic H₂ evolution. (3) Rapid annihilation of electron-hole pairs. Although approaches, for instance, the construction of the Schottky barrier, p-n junctions, and heterojunctions have been proposed to improve the charge separation of non-noble metal photocatalysts, significant progress has not been achieved in this regard. (4) The cost of the photocatalyst is always a challenge for its practical applications. (5) The low efficiency or deactivation of photocatalysts in the presence of contaminants.

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