Review

Photocatalytic Reforming for Hydrogen Evolution: A Review

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Abstract: Hydrogen is considered to be an ideal energy carrier to achieve low-carbon economy and sustainable energy supply. Production of hydrogen by catalytic reforming of organic compounds is one of the most important commercial processes. With the rapid development of photocatalysis in recent years, the applications of photocatalysis have been extended to the area of reforming hydrogen evolution. This research area has attracted extensive attention and exhibited potential for wide application in practice. Photocatalytic reforming for hydrogen evolution is a sustainable process to convert the solar energy stored in hydrogen into chemical energy. This review comprehensively summarized the reported works in relevant areas, categorized by the reforming precursor (organic compound) such as methanol, ethanol and biomass. Mechanisms and characteristics for each category were deeply discussed. In addition, recommendations for future work were suggested.

Keywords: photocatalysis; reforming; hydrogen; water splitting; solar energy

1. Introduction

Approximately 3×10^{24} J of solar energy is irradiated on the surface of earth annually, which is over 10^4 -fold the global energy consumption annually [1]. Effective restoration or transfer of solar energy is of great significance to human society. The photocatalytic process, one of the most promising techniques in solar energy conversion, has increasingly attracted attention since 1972 [2]. Applications of this advanced technology have been implemented in various areas, such as water/air purification, water splitting, chemical conversions, disinfection, reduction of CO_2 and N_2 fixation, etc. [3–6]. Hydrogen can be evolved through either photocatalytic water splitting or reforming [7,8]. Through these processes, solar energy can be converted to chemical energy, and stored in hydrogen. Considering the depletion of fossil fuel reserves and increasing environmental problems, hydrogen is an attractive alternative energy source with the following merits [9–12]:

- (i) Hydrogen atom is the most abundant element in the universe;
- (ii) The heating value of hydrogen (141.8×10^6 J/kg at 298 K) is much higher than that of most fuels (e.g., gasoline: 44×10^6 J/kg at 298 K);
- (iii) Water (H_2O) is the only exhaust product when hydrogen is converted into energy, which is more environmentally-friendly compared to fossil fuels.

Hydrogen is currently derived from non-renewable resources (such as natural gas and petroleum) through thermal catalytic reforming in industry. Compared with the industrial process for hydrogen evolution, photocatalysis can be realized in mild conditions, and induced by light energy instead of thermal energy. As a promising process, a large amount of work have been reported on photocatalytic reforming for hydrogen evolution. In this review, typical photocatalytic reforming processes

were categorized based on the precursor, and comprehensively discussed. Future development of photocatalytic reforming for hydrogen production has been proposed at the end.

2. Industrial Hydrogen Production

In industry, hydrogen is typically derived from fossil fuels. Specifically, the distribution of fossil fuel feedstock for hydrogen production is shown in Figure 1 [13]. Hydrogen is extracted from natural gas, coal and oil, in the ratio of 48%, 18% and 30%, respectively. The rest (4%) of hydrogen is produced from electrocatalysis.

Figure 1. Distribution of feedstock for hydrogen production (Adapted from ref. [13]).

Most of the hydrogen is produced from natural gas through steam reforming. Typically, methane is primarily applied, as steam reforming of methane is the most efficient route for hydrogen evolution. This process is carried out at the temperature of 970–1100 K and pressure of around 3.5 Mpa, and nickel is widely applied as the catalyst [14]. The basic reactions for steam reforming of natural gas are shown as Reactions 1 and 2.

The target for the second step is converting CO to CO₂, and utilizes the thermal energy left from the first step [15]. Even though steam reforming of natural gas is currently the primary process for hydrogen evolution, the disadvantages of this process are typical, such as large requirement of energy and large emission of CO₂.

Coal is also widely applied to produce hydrogen through a gasification process; the reactions are shown in Reaction 3. Alkali metal (such as potassium) salts are utilized as the catalysts for this process [16]. Disadvantages of this process include not only the emission of large quantities of CO₂, but also critical reaction conditions (1673 K and 2–7 MPa) are required to obtain a high conversion rate [17].

Due to the low cost of heavy oil or petroleum refinery residual oil, they are also widely applied as the feedstock for hydrogen production. The basic reaction is shown in Reaction 4. This process can occur with or without catalyst. Similar to the other above-mentioned processes, this process also emits a massive amount of both CO₂ and CO.

Despite hydrogen being currently derived from fossil fuels is the primary industrial process, explorations of new technologies and renewable energy sources have become more and more promising, especially in the background of severe energy shortage and environmental pollution. Water (H_2O) is regarded as a promising source for hydrogen production, as it is carbon-free [18–20]. Electrolysis is capable of dissociating water to evolve hydrogen in ambient conditions. Theoretically, the applied voltage for water electrolysis is 1.23 V. However, the hydrogen evolution reaction (HER) at the cathode requires high over-potential to yield enough current density. Hence, the energy consumption for water electrolysis in practice is about 1.5–2.2 times higher than that in principle. Currently, the energy-conversion efficiency in practical use is only 48%–70%. To improve the efficiency, noble metal-based catalysts were applied. Hindrances for electrolysis on a large scale include not only the high energy demand for electricity, but also the high cost of the catalysts [12,21].

Currently, global industrial hydrogen production is approximately 7.2×10^{18} J per year. Most of the hydrogen were derived from fossil fuels, resulting in approximately 5×10^{11} kg CO_2 emitted yearly. Such a large amount of CO_2 emissions is inconsistent with the IEA's (International Energy Agency) forecast of reducing CO_2 emissions by 60% of the world by 2050, aiming to slow down the global warming [22]. Therefore, the research on photocatalytic hydrogen production is of great significance.

3. Photocatalysis for Hydrogen Evolution

Since 1972, photocatalytic water splitting for hydrogen evolution has been widely reported and regarded as one of the most promising methods for solar energy storage [23–25]. Theoretically, semiconductor-based photocatalysis can be described based on the band structure. When the energy of the irradiated light photon is larger than the band-gap energy of the semiconductor, electrons on the valence band (VB) may be activated and jump to the conduction band (CB) with positive holes left behind. The electrons on CB may either return the VB to recombine with the positive holes, or react with adsorbed species on the surface of the semiconductor [1,3,5,26,27]. When the potential of electrons on CB is more negative than the redox potential of $\text{H}_2/\text{H}_2\text{O}$, the separated electrons are capable of reducing water to hydrogen (Figure 2). It has been comprehensively reviewed and discussed in reported works [28–32]. Photocatalytic production of hydrogen has been realized not only by water splitting, but also by reforming. As shown in Figure 2, the minimum requirements for photocatalytic production of H_2 are 1) the electrons on the conduction band of the semiconductor were capable reduce protons to form hydrogen and 2) the holes on the valence band of the semiconductor were capable of oxidizing water or R-OH to release protons. As reported in works on photocatalytic reforming for hydrogen evolution, it can be divided into three primary categories on the basis of the reforming precursor, which will be discussed in the following pages.

Figure 2. Photocatalytic production of H_2 .

3.1. Photocatalytic Reforming of Methanol

Methanol is the most widely used compound in photocatalytic reforming [33,34]. Unlike photocatalytic water splitting, the products of photocatalytic reforming of organic compound were H_2 and CO_2 , instead of H_2 and O_2 (Reaction 5) [35].

Reaction pathways for photocatalytic reforming of methanol on Au-TiO₂ involve the following processes (Figure 3) [36]:

- Photogeneration of charge carriers (electrons and holes);
- Adsorbed species on the surface of photocatalyst react with separated charge carriers: i.e., adsorbed H_2O and CH_3OH are oxidized by holes with the formation of $\cdot OH$ and various fragments including $CH_3O^\cdot$, $CH_2O^\cdot$, $CHO^\cdot$, $HCOO^\cdot$ and $HCOOH$;
- As-formed $HCOOH$ is further oxidized to CO_2 ;
- A large quantity of protons formed from the last steps, and are reduced by the electrons either on the CB of TiO₂ or Au to form H_2 .

Figure 3. Reaction pathways of photocatalytic reforming of methanol on Au/TiO₂ catalyst (Adapted from Ref. [36]).

The presence of methanol in the system acts as a scavenger for photo-generated holes on the VB of TiO₂, which was in favor of improving the separation of photo-generated charge carriers. To further improve the photocatalytic activity, modifications on the photocatalyst are still required. Nanocrystalline TiO₂ has paid attention throughout the past 50 years. Due to its strong oxidizing capacity under ultraviolet irradiation, high chemical stability, low cost, and environment-friendly, TiO₂ is the most widely studied photocatalyst, and has been applied for reforming of methanol [37,38]. However, as for the intrinsic properties of TiO₂, especially the large band gap (>3.2 eV) restricts its utilization of the visible light and the high electron–hole recombination rate, its photocatalytic activity is significantly limited [39–41]. Michael et al. reported on metal-modified TiO₂ applied in photocatalytic reforming of methanol [42]. Four different metals (Pt, Pd, Au and Ag) were selected to be combined with TiO₂. The products including H_2 , CO_2 and CO were detected for photocatalytic reforming of methanol on different photocatalysts, the result of which is depicted in Figure 4. For pure TiO₂, a small amount of H_2 was formed. With the metal modification, the production rate of H_2 was greatly improved. And Pt- modified TiO₂ exhibited the highest activity, with a H_2 production rate of $0.24 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. The loading of the metals on the surface not only facilitated the separation of photogenerated charge carriers, but also provided more reactive sites, resulting in the enhanced photocatalytic activity of TiO₂ in reforming of methanol. E. Tálas et al. further explored the Sn and Pt

co-modified TiO₂ in photocatalytic reforming of methanol [43]. It was found that the formation rate of H₂ was further improved to 2 mmol h^{−1} g_{cat}^{−1}. Carbon nanotubes (CNT) had been proven to be an excellent co-catalyst for improving photocatalytic activity. G. Silva et al. prepared CNT-TiO₂ using a hydration-dehydration method, and further loaded Pt on CNT-TiO₂ through impregnation process [44]. It was found that CNT provided more reactive sites and further improved the photocatalytic activity of TiO₂ in reforming methanol.

Figure 4. Products of photocatalytic reforming of methanol on different photocatalyst (no shading: H₂, diagonal shading: CO₂ and vertical shading: CO, adapted from Ref. [42]).

In order to reduce the cost of photocatalytic materials, research on improving the photoactivity of TiO₂ modified by non-noble metals (for example, Ni, Cu, Co) was also conducted [45]. Bernareggi et al. investigated Cu and Pt commodified TiO₂ on photocatalytic reforming of methanol [46]. The ternary composite, Cu-Pt-TiO₂ exhibited excellent production rate of H₂, which was 23.6 mmol h^{−1} g_{cat}^{−1}. Takuya Miwa et al. deposited CuO and Al₂O₃ onto TiO₂, to improve the photocatalytic activity towards hydrogen production from methanol reforming [47]. With the formation of ternary structure, heterojunctions were fabricated, which favored improving the lifetime of photogenerated charge carriers. The prolonged lifetime can further improve the photocatalytic activity of TiO₂. The results suggested that with the increase in the lifetime of photogenerated charge carriers, the photocatalytic activity of TiO₂ in methanol reforming was significantly improved, with H₂ production rate of 1.2 mmol h^{−1} g_{cat}^{−1} [48,49]. Graphene oxide (GO) has been widely applied to improve the photocatalytic activity [50–53]. Majrik et al. prepared GO modified TiO₂ by a hetero-coagulation method and evaluated its photocatalytic activity of methanol reforming [54]. It was found that with 2% of GO in the composite (GO-TiO₂), the photocatalytic production rate of H₂ was more than 5 times higher than pure TiO₂.

3.2. Photocatalytic Reforming of Ethanol

Ethanol is an attractive source of hydrogen, due to its non-toxic and capable of being stored, transported and handled safely [55–59]. There are two main processes for the production of H₂ from ethanol, which are steam reforming and thermal reforming [60,61]. Both processes are required to occur under high temperatures with noble metals as catalysts. Comparatively, photocatalytic reforming of ethanol for H₂ production can be conducted at ambient conditions under irradiation. Kawai et al. reported on photocatalytic reforming of ethanol on TiO₂ in 1981 [62]. Theoretically, the overall reaction for photocatalytic reforming of ethanol is shown in Reaction 6.

For the reaction pathways, ethanol may be first photocatalytically converted to acetaldehyde with H₂ released (Reaction 7). As-formed acetaldehyde may either reacts with water to form CO₂ and H₂

(Reaction 8), or be further converted to acetic acid (Reaction 9), which further reacts with water to form CO_2 and H_2 (Reaction 10) [63,64].

Photocatalytic reforming of ethanol has been widely studied on TiO_2 [65–67]. The photoactivity was pretty low for pure TiO_2 , and should be improved further [68,69]. Owing to multiphasic TiO_2 , materials demonstrate higher performance with respect to the correspondent monophasic systems in many photocatalytic processes [70,71]. The crystal structure of TiO_2 plays an important role in catalytic activity. There are three types crystal: anatase, rutile, brookite. The brookite is unstable, and the anatase-type TiO_2 lattice contains more defects and vacancies, which results in more oxygen vacancies to capture electrons. Rutile TiO_2 is the most stable crystalline structure, but has few defects, which makes electrons and holes easy to recombine. Montini et al. prepared anatase/brookite TiO_2 nano-composites by hydrothermal treatment of $\text{Na}_2\text{Ti}_2\text{O}_5$ precursor [72]. Compared with TiO_2 with single phase, the composite exhibited higher photocatalytic activity in ethanol reforming. Further, the authors loaded Pt onto this composite, and the production rate of H_2 in photocatalytic reforming of ethanol improved to $1.2 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. Yin et al. prepared Au onto TiO_2 to form a core-shell structure [73]. The preparation procedures are shown in Figure 5. TiO_2 as the shell can absorb light energy, and Au as the core acts as the electron acceptor and narrow the band gap. They found that controllable morphology of TiO_2 nanocrystals facilitates electron-hole separation and can expose more active surfaces. With the fabrication, the photocatalytic activity of TiO_2 in ethanol reforming improved to $1.07 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$.

Figure 5. Scheme for preparation of Au @ TiO_2 core-shell composite. (Adapted from Ref. [73]).

Other than TiO_2 , Wang et al. investigated on ZnO applied for photocatalytic reforming of ethanol [74]. ZnO with various morphologies including needle-like (ZnO-n), flower-like (ZnO-f) and rods (ZnO-r), were prepared. It was found that ZnO-f exhibited the highest photocatalytic activity with the H_2 production rate of $0.305 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. That might be due to its flower-like morphology that may scatter the incoming light, enhancing light absorption efficiency and increasing the photocatalytic

efficiency. With further surface modification with Au onto ZnO-f, the photocatalytic activity was further improved, and the H_2 production rate was $0.427 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. Fu et al. prepared $ZnSn(OH)_6$ nanocubes (ZHS) by a solvothermal method [75]. The photocatalyst obtained in the autoclave with a longer reaction time has higher crystallinity and better photocatalytic efficiency. The H_2 production rate was measured at as high as $16 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. ZHS with moderate longer reaction time has higher crystallinity, because amorphous materials with low crystallinity usually comprise numerous defects. These defects may act as recombination centers for the electrons and holes and result in the low photocatalytic efficiency.

3.3. Photocatalytic Reforming of Biomass

Biomass, as a promising renewable energy source, is a possible alternative to fossil fuels. The reforming of biomass is an effective way to convert biofuels to chemical fuels [76]. Production of hydrogen from biomass is feasible and very promising for future energy development [77,78]. Conventional processes for H_2 derived from biomass require critical reaction conditions [79–84]. Photocatalysis applied for reforming of biomass not only overcomes the problem of critical conditions required by thermal catalysis, but also combines the solar energy with biofuels [85].

The mechanism of photocatalytic reforming of biomass is similar to the photocatalytic reforming of other organics [35]. When the substrates are biomass, the substances consumed in this process are renewable [86,87]. Taking glucose as an example, the reaction pathways for photocatalytic reforming of glucose are described in Figure 6. It can be found that the photogenerated electrons and holes separately react with adsorbed species on the surface of photocatalyst, and trigger a series of redox reactions. Overall, 1 mol of glucose can be dissociated and produce 12 mol of H_2 [85]. Typical examples of photocatalytic reforming of biomass are summarized in Table 1.

Figure 6. Pathways of glucose in photocatalytic reforming (Adapted from Ref. [85]).

Table 1. Summary of photocatalytic reforming of biomass for hydrogen evolution.

Catalyst	Biomass	Efficiency	Light	Ref
Pt-TiO ₂ -W	1.25 mmol/L glucose	1.0 mmol h ⁻¹ g _{cat} ⁻¹	sunlight	[88]
Pt/P25	20 vol% methanol, 20 vol.% propanetriol, 1.3 mmol/L glucose	0.749, 7.094, 7.784 mmol h ⁻¹ g _{cat} ⁻¹	300 W Xe lamp	[89]
Pd/TiO ₂	250 mg/L glucose	5.7 mmol h ⁻¹ g _{cat} ⁻¹	125 W high-pressure mercury lamp	[85]
Rh/TiO ₂	1.25 mmol/L glucose	1.5 mmol h ⁻¹ g _{cat} ⁻¹	300 W Hg lamp	[90]
NiS/CdS	0.10 g/L lignin & 2.0 vol.% lactic acid	1.5 (both lignin and lactic acid) & 1.086 (only lactic acid) mmol h ⁻¹ g _{cat} ⁻¹	300 W Xe lamp	[91]
CdS/MoS ₂	0.1 mol/L glucose	55.0 mmol h ⁻¹ g _{cat} ⁻¹	300 W Xe lamp	[92]
O-g-C ₃ N ₄	1 mol/L glucose	1.37 mmol h ⁻¹ g _{cat} ⁻¹	simulated solar light	[93]
ZnS-g-C ₃ N ₄	50ppm glucose	69.8 μmol h ⁻¹ g _{cat} ⁻¹	300 W Xe lamp	[94]
S, N-GO	0.35 mol/L Sugar & 0.35 mol/L glucose	12.5 & 8.75 μmol h ⁻¹ g _{cat} ⁻¹	300 W Xe lamp	[95]
Bi _{0.5} Y _{0.5} VO ₄	1 mol/L glucose	50 μmol h ⁻¹ g _{cat} ⁻¹	350 W Xe lamp	[96]

3.3.1. TiO₂

In previous discussions, Pt/TiO₂ exhibited photocatalytic activity in reforming. Xu et al. investigated the effect of crystals on photocatalytic hydrogen production. It was found that compared with Pt/P25, the finely adjusted anatase-rutile Pt/TiO₂ photocatalyst improved the overall photocatalytic activity by 3 to 5 times, and greatly reduced the CO concentration in the hydrogen product, which can meet the fuel application requirements for battery technology. They believe that this result can be attributed to the adjustment of the crystal form in favor of light-induced charge separation, as well as the adjustment of the acidity and basicity of the interface surface. [89,97]. Bellardita et al. doped N and W into the lattice of TiO₂ using a hydrothermal method and further surface modified by Pt [88]. It was found that hydrogen production rate on Pt/(N and W)-TiO₂ in photocatalytic reforming of glucose under natural solar light was as high as 1.0 mmol h⁻¹ g_{cat}⁻¹. This activity under sunlight proves the applicability of such materials under realistic conditions. Yasuda et al. further studied Pt/TiO₂ in photocatalytic reforming of Italian ryegrass and Napier grass [98]. They used a combination of biological treatment and light reforming to first enzymatically saccharify the two alkali-treated grasses, and then used Pt/TiO₂ to perform phototransformation under UV light irradiation. Through this process, they can convert two natural plants into ethanol and hydrogen with recovery rates of 82.7% and 77.2%, respectively. However, the photocatalysts they used are still poorly responsive to visible light, which limits the application of this technology in real-life conditions.

Wu et al. investigated Pt, Rh, Ru, Cu, Ni Au and Ir modified TiO₂ in photocatalytic reforming of glucose for hydrogen production [90]. It was found that the supported metal exhibited the property of trapping electrons at the Schottky barrier of metal in contact with TiO₂ surface, which greatly improved the hydrogen generation rate and also reduced the CO selectivity. The specific impact depends on the type of metal, the generation rate of H₂ on these metal- modified TiO₂ followed the order: Ir < Ru < Au < Ni ≈ Cu ≈ Pt < Rh. Fu et al. [85] tested the photocatalytic reforming activity of another group of metals/TiO₂ photocatalysts, and the test results are shown in Figure 7. It can be found that Pd/TiO₂ exhibited the highest activity in photocatalytic reforming of glucose. In the research, they also found that the rate of hydrogen production using glucose depends on the initial pH of the solution, and the hydrogen production rate was highest at pH 11 in their system.

Figure 7. Effect of the kinds of noble-metal-loaded TiO_2 on hydrogen evolution. (Adapted from Ref. [85]).

3.3.2. Metal Sulfide

Even though TiO_2 has been widely investigated in photocatalytic reforming of biomass, it is necessary to explore other visible light-responsive materials applied in this field. Metal sulfides such as cadmium sulfide (CdS) and molybdenum disulfide (MoS_2) exhibited excellent activity in both photocatalytic water splitting and reforming to evolve H_2 [92]. Li et al. successfully prepared CdS/MoS_2 composites and tested their performance in photocatalytic reforming of glucose [92]. It was found that the composite containing 40 wt% of CdS exhibited the highest activity with a hydrogen production rate of $55.0 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$. They speculate that the heterojunction formed between MoS_2 and CdS promotes the interface charge transfer, inhibits the recombination of photogenerated electron-hole pairs, and then promotes the hydrogen evolution reaction. At the same time, due to the good matching characteristics of the conduction band edges of the two materials, the electrons in the CdS conduction band can be transferred to MoS_2 with higher efficiency, preventing the accumulation of electrons in the CdS conduction band, inhibiting the photocorrosion of the catalyst itself, and greatly improving stability. Then, Li et al. synthesized $\text{NiS}-\text{CdS}$ composite through a two-pot solvothermal process [91]. This composite exhibited excellent visible light-induced activity. The apparent quantum efficiency (AQE) of H_2 in photocatalytic reforming of lactic acid and lignin acid in the presence of different $\text{NiS}-\text{CdS}$ composites was shown in Figure 8. It was found that the 0.2- NiS/CdS exhibited the highest activity with the AQE as high as 29.33% for lactic acid and 44.9% for lignin acid, and the high stability was also showed. However, the potential toxicity of this photocatalyst has limited its application to some extent.

Figure 8. AQE for photocatalytic reforming of biomass on NiS-CdS composites (black column: lactic acid; red column: lignin acid) (Adapted from Ref. [91]).

3.3.3. Graphene Analog Photocatalyst

Photocatalysts commonly used in the past are usually metal and its derivatives. They all have more or less economic and environmental problems and are difficult to scale up. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has attracted wide attention as an advanced non-metal photocatalyst [26,99]. Xu et al. improved the photocatalytic activity of $g\text{-C}_3\text{N}_4$ in reforming of biomass with modification of ZnS. After examining the performance of carbon nitride derived from different raw materials as photocatalysts, they believed that the rate of reaction hydrogen evolution was affected by various factors such as the specific surface area of the catalyst, the band width, and the particle size of the doped material [94]. Nguyen et al. combined graphene with $g\text{-C}_3\text{N}_4$. Due to the vacancy defects of graphene oxide itself are not conducive to photocatalytic reactions, they synthesized sulfur and nitrogen co-doped graphene oxide dots (SNGODs). And found that the photocatalytic activity of SNGODs in reforming of sugar and glucose were both improved significantly [95]. Speltini et al. treated $g\text{-C}_3\text{N}_4$ in hot HNO_3 aqueous solution to obtain oxidized $g\text{-C}_3\text{N}_4$ (O- $g\text{-C}_3\text{N}_4$) [93]. After treatment, the production rate of H_2 in photocatalytic reforming of glucose was about 26 times higher than pure $g\text{-C}_3\text{N}_4$. Further, when the O- $g\text{-C}_3\text{N}_4$ were treated through ultrasonication, the production rate further improved to $1370 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. These studies have confirmed the possibility of hydrogen production with non-metal photocatalysts. But $g\text{-C}_3\text{N}_4$ catalysts doped with no metal elements still exhibited low activity and did not exhibit sufficient stability. These problems hinder its application in actual production.

3.3.4. Oxide Solid Solution Photocatalyst

From the aspect of thermodynamics, Jing et al. proposed that oxide photocatalysts were generally more stable and exhibited more positive valence band positions than sulfides and nitrides, which are more suitable for the oxidation of biomass [96]. They found that doping a certain amount of Y can promote the transformation of the crystal phase of BiVO_4 from a monoclinic phase to a tetragonal phase, which is beneficial to the improvement of catalytic activity. Therefore, an oxide solid solution, $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$ (BYV) was prepared and tested in photocatalytic reforming of glucose under visible light. The test results are shown in Figure 9. It was found that when the solution pH was at 3, the production rate of H_2 was the highest at $50 \text{ } \mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$. The results also showed that the CO_2 gas produced by the hydrogen evolution may inhibit the efficiency of the hydrogen evolution

reaction. How to transfer gas products in time is obviously an important issue in the actual production of photocatalytic reforming.

Figure 9. The time courses of photocatalytic hydrogen production over BYV ($x = 0.5$) under visible light at different pH. (Adapted from Ref. [96]).

4. Future Work and Concluding Remarks

Photocatalytic reforming is very promising for hydrogen evolution at ambient conditions. Through this process, solar energy can be converted and stored in the form of chemical energy. To date, various chemical compounds, especially alcohols and biomass, have been widely applied as the feedstock for photocatalytic reforming. Typical works on this research subject have been comprehensively discussed in this review. Albeit photocatalysis exhibited superiorities in reforming for H_2 production, the hindrances were also obvious and need to be overcome before its wide application. Possible approaches to overcome these hindrances and recommendations for future work are suggested below:

1. **Low photocatalytic efficiency.** Currently, the photocatalytic activity is too low to use on a large scale, which is also the most significant problem for not only photocatalytic reforming, but also all other photocatalytic applications. With the rapid development of material science, design and synthesis of novel materials are one of the most effective approaches. Meanwhile, exploration of effective modification methods to improve the photocatalytic activity is of the essence, as well.
2. **Low visible light-responsivity.** When we aim to utilize solar light as the energy source, it is essential to expand the utilization of the solar spectrum, especially the visible-light part. Feasible approaches include the modifications of existing photocatalyst to narrow its band gap, and preparation of new materials with narrow band gap. These effective modification methods include doping, noble metal nanoparticles loading and fabrication of heterojunction. Recently, with the rapid development of material science and preparation technologies, many advanced semiconductors exhibited excellent visible-light-induced photoactivity, including g-C₃N₄ and bismuth-based semiconductors (BiOBr, Bi₂WO₆, BiVO₄ etc.). All those materials are of promise to be applied in photocatalytic reforming for H_2 production, whereas were rarely been reported in this research field.
3. **Ambiguous mechanism for photocatalytic processes.** Most of the mechanism studies on photocatalysis were on the basis of band structures. However, some phenomena were difficult

to explain, based on the electrical band structures. Instead, advanced material characterization techniques, as well as simulation methodologies should be adopted to acquire an insight into the photocatalytic process.

4. **Rare studies on photoreactor design.** In the process of scaling-up photocatalysis, photoreactor design plays significant role. Photocatalytic activity can also be improved with rational photoreactor design. However, most of studies on photocatalytic reforming were still in lab scale. More contributions on the exploration of photoreactor design should be made to upscale this process.
5. **No standard platform.** So far, there has been no standard platform that can be used to compare photoactivity for either different materials or the same material tested from a different lab. There is an urgent need to establish a standard to evaluate different materials, and guide the direction of future work.

Aiming to provide an alternative approach for thermal reforming of hydrocarbons for hydrogen production, photocatalytic process is of promise with superiorities such as renewable energy resource applied and mild conditions required. However, due to the low activity which is still far below the requirements if applied in practice. More contributions should be made to further develop this advanced technology via breaking the bottleneck.

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