

Review

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Glucose photorefinery for sustainable hydrogen and value-added chemicals coproduction

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Abstract

As a naturally occurring and stable energy supply, biomass will be the leading renewable energy in the future, and its high-value application will help promote the realization of carbon neutrality. Glucose, as the basic unit of lignocellulosic biomass, has been widely investigated as the feedstock to produce various value-added chemicals. Compared to the traditional glucose valorization platforms, such as thermal catalysis and biological fermentation, solar-driven photocatalysis holds the advantages in mild reaction conditions and controllable reaction kinetics, and it is emerging as a sustainable and efficient technology for glucose conversion. With the rational design of the photocatalysts, glucose could be selectively converted into specified chemicals via oriented bond cleavage along with the sustainable generation of hydrogen at the same time, which is the so-called glucose photorefinery process. This present review introduces the general principles and latest progress in glucose photorefinery. The rational design of bifunctional photocatalysts to achieve extended light absorption, efficient charge separation, and favorable surface reaction is also introduced. The oriented breakage of the chemical bonds in glucose molecules to produce different chemicals on different active sites is highlighted. Finally, challenges and perspectives on glucose photorefinery to achieve further efficiency and more fruitful reaction pathways are proposed. This present review is believed to provide guidance for the biomass valorization by mild photocatalysis to simultaneously produce sustainable fuels and chemicals with the rational design of dually functional photocatalysts.

Keywords: Glucose, photorefinery, selective bond cleavage, hydrogen, value-added chemicals



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INTRODUCTION

Biomass is the most abundant natural renewable resource on Earth, and its high-value application plays a vital role in ensuring the stable development of human civilization^[1]. A large amount of agricultural and forestry waste biomass is produced in the world every year. If converted and utilized in a green and sustainable way, it can substantially contribute to economic development, facilitate energy structure adjustment, and aid in reducing carbon dioxide emissions^[2]. Traditional strategies for biomass valorization mainly include direct incineration, pyrolysis, biocatalytic conversion, *etc.*^[3]. These methods always suffer from high energy consumption, environmental pollution, and low efficiency. Relatively, biomass utilization by solar-driven photocatalysis holds great advantages in green sustainability, mild reaction conditions, controllable reaction pathways, and pollution-free properties^[4-7]. Biomass photorefinery is a newly proposed concept that involves the hydrogen generation and value-added chemicals coproduction. This concept is refined from the traditional photocatalytic hydrogen production from water, in which additives as the sacrificial agents are always involved in replacing the oxygen evolution reaction (OER)^[5]. Because the OER process needs huge energy input and is the rate-determining step of photocatalytic water splitting^[8]. However, the addition of traditional sacrificial agents, such as methanol and triethanolamine, greatly increases the process cost of photocatalytic hydrogen production. At the same time, the carbon dioxide emitted by the over-oxidation of sacrificial agents during the photocatalytic reaction is not environmentally feasible, making the application of photocatalytic hydrogen production in industrial settings notably difficult. A large number of reducing groups in biomass components, such as hydroxyl groups, can theoretically be used as electron donors for photocatalytic hydrogen production reactions to replace traditional sacrificial agents^[9-11]. It is believed that through the rational design of bifunctional photocatalysts, realizing the biomass photorefinery process to simultaneously produce sustainable hydrogen and value-added chemicals is a promising technology for future fuel and chemical production [Figure 1]^[12-15].

Natural biomass mainly exists in the form of lignocellulose, and its components are mainly composed of cellulose, hemicellulose, and lignin. Its basic composition structure is shown in Figure 2^[16-18]. Among them, cellulose is composed of glucose as a component unit through β -1,4 glycosidic bonds, intramolecular and intermolecular hydrogen bonds, and it accounts for 40%-60% of lignocellulose by mass. Hemicellulose is another polysaccharide, which is mainly composed of five-carbon sugars (xylose, arabinose, *etc.*) and six-carbon sugars (glucose, mannose, *etc.*). The specific components of hemicelluloses are closely related to the source of lignocellulose, and the mass proportion of hemicellulose in lignocellulose is 20%-25%. Different from cellulose and hemicellulose, lignin is a polymer formed by three-dimensional crosslinking of aromatic allyl alcohol. The spatial distribution relationship of the three major components in lignocellulose is that cellulose is in the core of lignocellulose, hemicellulose covers the surface of cellulose by forming tight hydrogen bonds, and lignin, such as the resin, fills in the space between the cellulose and hemicellulose. The lignocellulose constructed through the above interactions has a complex structure and stable physical and chemical properties. In order to realize the efficient conversion and utilization of lignocellulose, it is necessary to combine certain pretreatment strategies to destroy its inherent inertia^[19-21].

Glucose is the component unit of cellulose in lignocellulosic biomass and could be easily obtained after the hydrolysis of cellulose by inorganic acids or enzymes^[22,23]. Similar to the biomass as the sacrificial agent, glucose with hydroxyl groups could serve as the electron donor to boost the photocatalytic hydrogen production. Compared to the complex biomass, glucose as the sacrificial agent could improve the reaction kinetics. Besides, the reaction thermodynamics is also favorable as the oxidation of glucose requires negligible energy input ($\Delta E^0 = +0.001 \text{ V}$)^[24]. The energy barrier diagram of photocatalytic water splitting and photocatalytic glucose oxidation reaction process is shown in Figure 3.

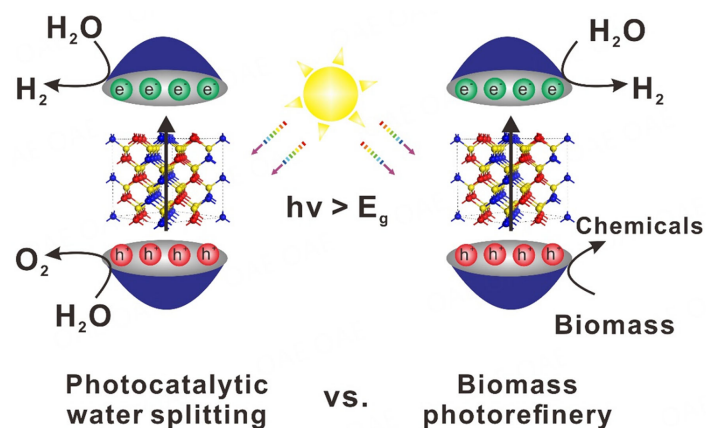


Figure 1. Schematic illustration of photocatalytic water splitting and biomass photorefinery.

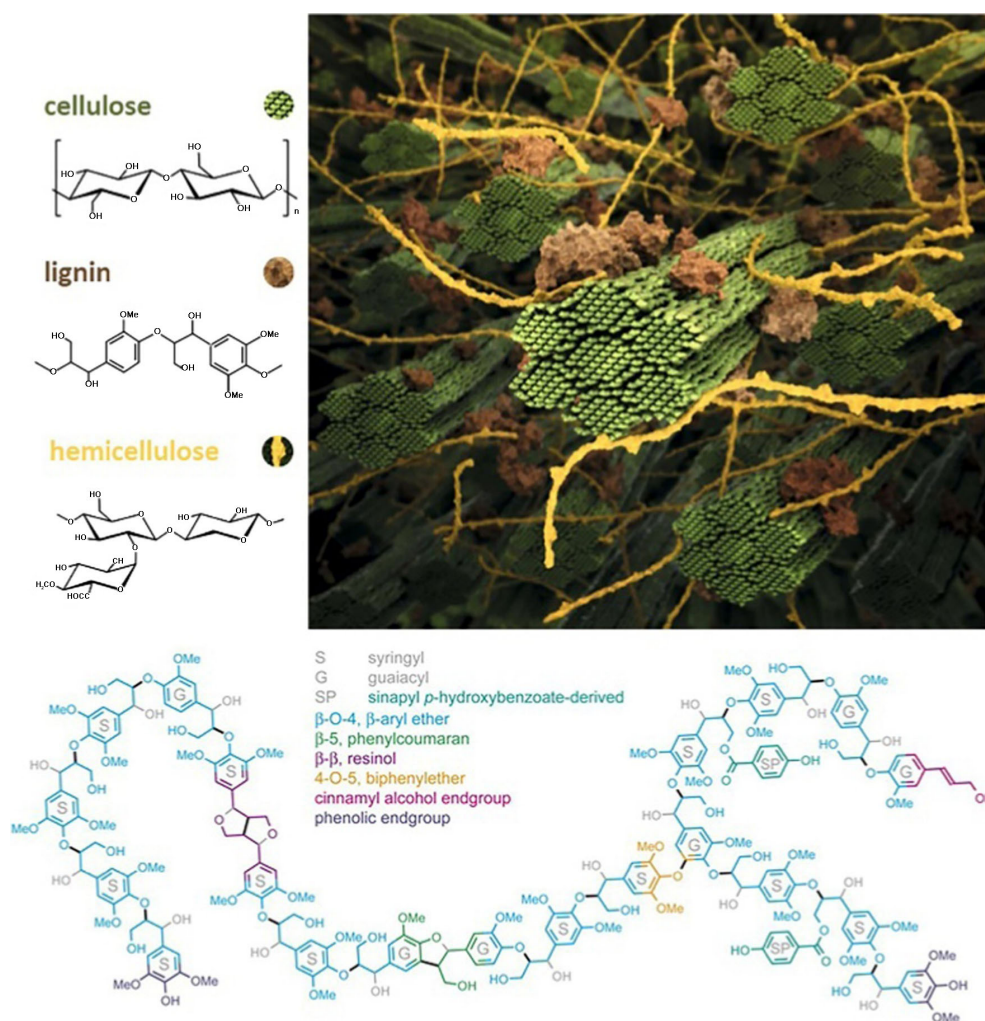


Figure 2. Schematic illustration of the component and spatial distribution of lignocellulosic biomass. Reproduced with permission^[17]. Copyright 2021, Springer Nature Ltd.

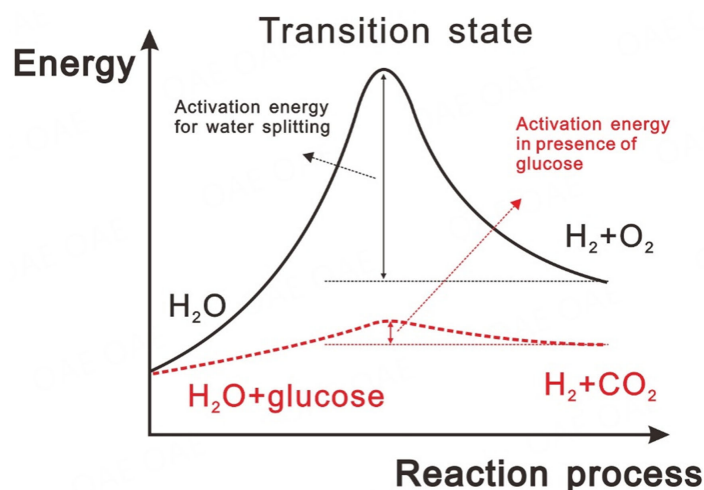


Figure 3. Schematic illustration of reaction barriers of photocatalytic water splitting and biomass photorefinery.

Currently, the research on glucose photorefinery is mainly divided into two aspects. One is the non-selective reaction process, that is, only using glucose as a sacrificial agent for photocatalytic hydrogen production, in which glucose conversion is not investigated or overoxidized into water and CO_2 . The second is the selective reaction process, in which glucose will be selectively converted into value-added chemicals along with photocatalytic hydrogen production^[5]. The comparison of these two reaction processes is shown in [Figure 4](#). From the aspect of photocatalyst design, the non-selective glucose photorefinery process only needs to consider the reaction efficiency of photogenerated electrons, while the selective glucose photorefinery process puts high demands on the photocatalysts, which could not only produce hydrogen but also realize the selective oxidation of glucose to produce value-added chemicals instead of CO_2 .

NON-SELECTIVE GLUCOSE PHOTOREFINERY

In the process of non-selective glucose photorefinery process, glucose only acts as electron donors to consume the photogenerated holes by semiconductor photocatalysts or free radical species induced by holes so as to improve the survival life of photogenerated electrons and promote the activity of photocatalytic hydrogen production. Iergolino *et al.* reported a series of works about using glucose as the sacrificial agent to improve the photocatalytic hydrogen production efficiency of modified TiO_2 , ZnO , and LaFeO_3 ^[25-28]. Although it holds the novelty of using glucose to replace the traditional methanol as the sacrificial agent and considerable hydrogen was also obtained, there are still some intrinsic drawbacks. All the used photocatalysts have wide bandgap structures, making them only respond to ultraviolet light. Besides, the modification by noble metals, such as Ru and Pt, greatly increased the cost of the photocatalytic hydrogen production. Due to the wide bandgap structure and the strong oxidation ability of these semiconductors, glucose was reported to be totally mineralized into CO_2 and H_2O . Moreover, the absence of labeling experiments using D_2O as the solvent, along with the corresponding mass spectrum, poses a limitation in revealing the origin of the protons in produced hydrogen.

Considering the large energy ratio of visible light in the whole solar spectrum, some semiconductors responsible for visible light have been developed as photocatalysts to produce hydrogen from glucose. For example, flower-like CdS/MoS_2 composites were designed for photocatalytic hydrogen production from glucose solution under visible light irradiation [[Figure 5A](#)]^[29]. The bandgap alignment of CdS and MoS_2 realized the significant promotion of charge separation efficiency while also achieving enhanced absorption

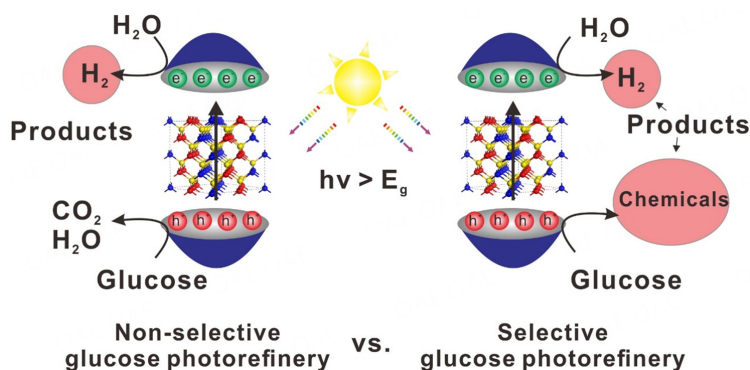


Figure 4. Schematic illustration of non-selective and selective glucose photorefinery.

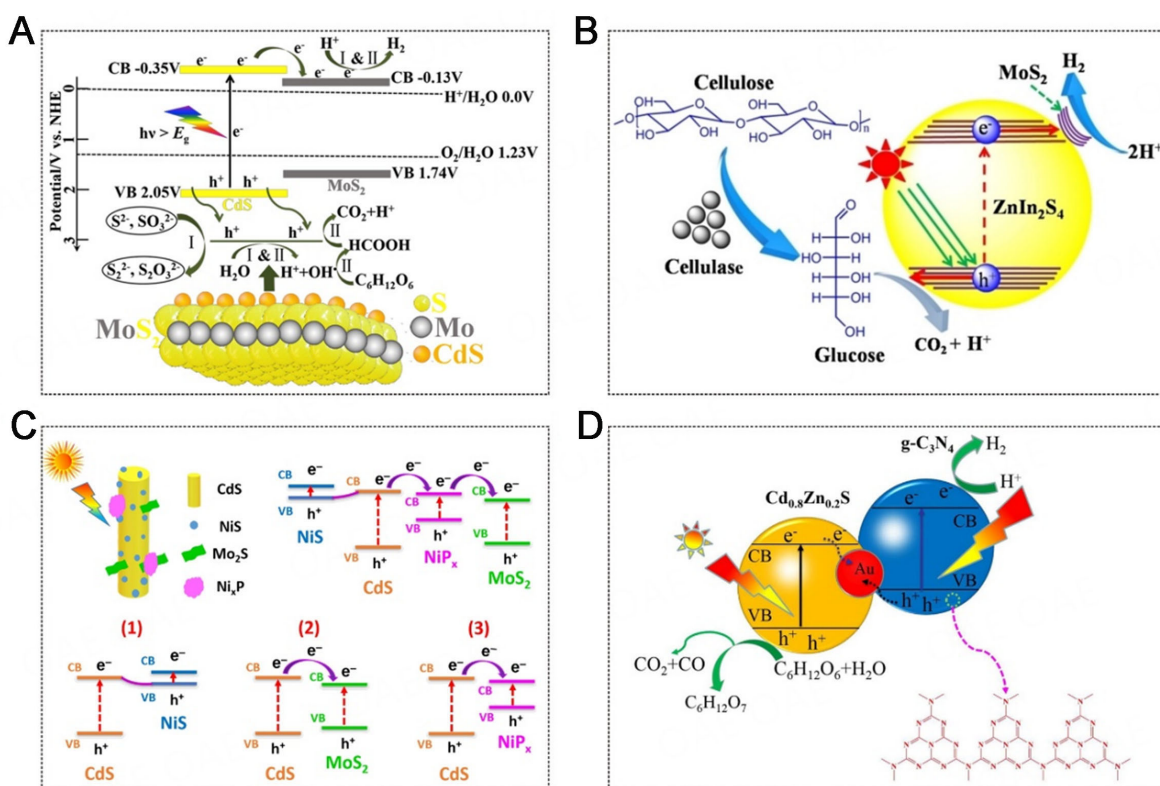


Figure 5. Schematic illustrations of photocatalytic hydrogen production by (A) CdS/MoS₂. Reproduced with permission^[29]. Copyright 2017, Elsevier; (B) MoS₂/ZnIn₂S₄ with assistance of cellulase. Reproduced with permission^[33]. Copyright 2022, Wiley; (C) NiP_x/MoS₂/NiS/CdS composite. Reproduced with permission^[34]. Copyright 2021, American Ceramic Society; (D) Cd_{0.8}Zn_{0.2}S/Au/g-C₃N₄. Reproduced with permission^[39]. Copyright 2017, Elsevier.

of visible light. As a result, the optimized composite exhibited excellent photocatalytic hydrogen production and stability from glucose solution (55.0 mmol·h⁻¹·g⁻¹), which was even higher than that from Na₂S/Na₂SO₃ as a sacrificial agent. ZnIn₂S₄ is another metal sulfide photocatalyst, and its unique layered structure endows it with excellent charge separation efficiency, making it one of the popular candidates for different photocatalytic applications^[30,31]. ZnS-coated ZnIn₂S₄ was prepared through a solvothermal process and used for the photocatalytic hydrogen production from glucose solution^[32]. The composition of the photocatalysts and concentrations of glucose and NaOH were optimized to achieve the highest hydrogen production. As a

result, the optimized photocatalyst with Pt as the cocatalyst exhibited much better hydrogen production from glucose compared to the pristine ZnIn_2S_4 . Some cascade reactions were also developed by directly using cellulose as the initial substrate. With the assistance of hydrolysis enzymes, ZnIn_2S_4 modified by MoS_2 was also fabricated and used for the photocatalytic hydrogen production from cellulose^[33]. In the presence of cellulase, the added cellulose was first converted into glucose, and then, the produced glucose acted as the sacrificial agent for photocatalytic hydrogen production [Figure 5B].

To improve the photocatalytic hydrogen production from glucose solution by the non-selective reaction process, it is essential to improve the charge separation by constructing the transfer channels for the photogenerated electrons. Multiple components were combined to realize the efficient and spatial immigration of the photogenerated electrons. $\text{NiP}_x/\text{MoS}_2/\text{NiS}/\text{CdS}$ composites in nanorod morphology were designed and fabricated through solvothermal processes^[34]. The presence of NiP_x and MoS_2 as the cocatalyst significantly improved the photocatalytic hydrogen production compared to the pristine NiS/CdS composite from a glucose solution. The immigration pathway of photogenerated electrons in this $\text{NiP}_x/\text{MoS}_2/\text{NiS}/\text{CdS}$ composite was also proposed [Figure 5C].

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is another typical photocatalyst with narrow bandgap structures to absorb visible light. The proper bandgap configuration of $\text{g-C}_3\text{N}_4$ makes it suitable for different photocatalytic applications^[35-37]. Compared to metal oxides, $\text{g-C}_3\text{N}_4$ may suffer from low efficiency in charge transfer due to its weak conductivity. With different modifications, the modified $\text{g-C}_3\text{N}_4$ -based photocatalysts showed excellent photocatalytic hydrogen production^[38]. In particular, the introduction of gold nanoparticles and $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ to $\text{g-C}_3\text{N}_4$ to construct the Z-scheme heterojunction endowed the composite with promising hydrogen production from a glucose solution [Figure 5D]^[39]. In a similar binary component system of $\text{TiO}_2\text{-Au-CdS}$, the presence of gold nanoparticles with the localized surface plasmon resonance (LSPR) effect played dual roles: light absorption enhancement and charge separation improvement^[10]. These binary component systems with the formation of Z-scheme heterojunction could efficiently increase the spatial separation of photogenerated electrons and holes^[40,41].

Although the presence of glucose as the sacrificial agent could realize the photocatalytic hydrogen production by the rational design of photocatalysts, the achieved hydrogen generation efficiency is still not comparable to the state-of-the-art ones from traditional sacrificial agents such as methanol, triethanolamine, lactic acid, *etc.* More importantly, the non-selective conversion of glucose into CO_2 greatly reduces the sustainability of photocatalytic hydrogen production and has a potential impact on climate change. Herein, more rational photocatalyst design and/or reaction system optimization are desired to realize the selective glucose photorefinery process to simultaneously produce hydrogen and value-added chemicals.

SELECTIVE GLUCOSE PHOTOREFINERY

Biomass photoreforming, including using glucose as the substrate, has been investigated in recent years. Despite this, the simultaneous coproduction of hydrogen and value-added chemicals in this process remains challenging^[5,11,13,42]. For the first time, we propose achieving the goal of “killing two birds with one stone” by designing photocatalysts with dual functions. These catalysts not only produce hydrogen but also selectively convert biomass substrates to produce high-value-added chemicals, that is, the selective biomass photorefinery process^[40,43]. Particularly noteworthy is the rational design of bifunctional photocatalysts, enabling the conversion of glucose into numerous chemicals alongside hydrogen production, such as fructose, gluconic acid, glucaric acid, arabinose, and lactic acid. The basic principle of this process is to use photocatalysts to generate electrons under light irradiation to produce hydrogen. Additionally, it aims to

oxidize glucose through photogenerated holes or produce free radicals to generate high-value-added chemicals. To realize this process, excellent separation efficiency of photogenerated electrons and holes is first required. At the same time, photocatalysts need to have specific catalytic reaction active sites to realize the selective conversion of biomass substrates. Besides, the oxidation stability of photocatalysts should be carefully modulated to avoid the over-oxidation of glucose.

From the molecular structure of glucose, the oriented breakage of different chemical bonds induces the selective production of different chemicals^[44]. With various catalysis, fermentation, and pyrolysis methods, glucose has been successfully converted into different chemicals [Figure 6A]^[45]. However, using photocatalysis to selectively convert glucose into a specific chemical along with hydrogen production is rarely reported. In the past few years, our team worked on the rational design of functional photocatalysts to realize the selective breakage of the chemical bonds in glucose to produce value-added chemicals and gas fuels, such as H₂ and CO, at the same time [Figure 6B].

Glucose isomerization to fructose

Fructose is another essential chemical in the industry to produce platform chemicals such as 5-hydroxymethylfurfural (HMF) and levulinic acid^[46]. Producing fructose from glucose isomerization processes by catalysts with Lewis acid or Brønsted base sites has been extensively documented^[47-50]. However, reports on photocatalytic glucose isomerization for fructose production are relatively scarce. Herein, we have, for the first time, realized this process by rationally designing photocatalysts with transient Lewis acid-base sites. A carbon nitride-based photocatalyst prepared through supramolecular preorganization-assisted molten-salt methods showed excellent activity for the photocatalytic glucose isomerization into fructose (> 60% selectivity)^[51]. The material characterizations revealed the presence of nitrogen vacancies and cyano groups in the as-fabricated photocatalyst, which induced the transient arrangement of the electron cloud under visible light irradiation, thus resulting in the activation of the oxygen atoms connected to the C1 and C1 in glucose. The deprotonation of O2-H and the following proton transfer process finally realized the glucose isomerization into fructose [Figure 7].

To realize the simultaneous generation of hydrogen along with fructose production from photocatalytic glucose isomerization processes, platinum (Pt) nanoparticles were loaded on the polymeric red carbon nitride (PRCN) as the cocatalyst to accumulate the residual photogenerated electrons to produce hydrogen^[52]. The as-fabricated photocatalyst exhibited much enhanced visible light absorption and charge separation efficiency. Besides, the carbon incorporation and potassium insertion induced the transient charge redistribution under visible light irradiation, which is different from the defect-induced Lewis acid-base sites. Specifically, the incorporated carbon atoms accumulated the π - π conjugated electrons as the Lewis base sites while inserted potassium ions attracted positive charges as the Lewis acid sites. The formation of Lewis acid-base sites under light irradiation synergistically promoted the process of glucose isomerization to fructose. More importantly, the decorated Pt nanoparticles gathered the residual electrons to realize photocatalytic hydrogen production at the same time [Figure 8].

Glucose oxidation to gluconic acid

Among the chemicals produced from glucose, gluconic acid has been widely used in the food and pharmaceutical industries. Gluconic acid is commercially generated from glucose fermentation by fungi, which suffers from long-time consumption and high costs^[53]. In order to improve the process of gluconic acid production, chemical catalysis has been developed^[54-57]. The widely investigated mechanism comes from the generation of active oxygen species (AOS) by noble metals in the presence of an oxygen atmosphere. From this aspect, photocatalysis is a potential approach to produce gluconic acid from glucose, as AOS could be selectively produced by the rational design of photocatalysts^[58]. Bai *et al.* reported the

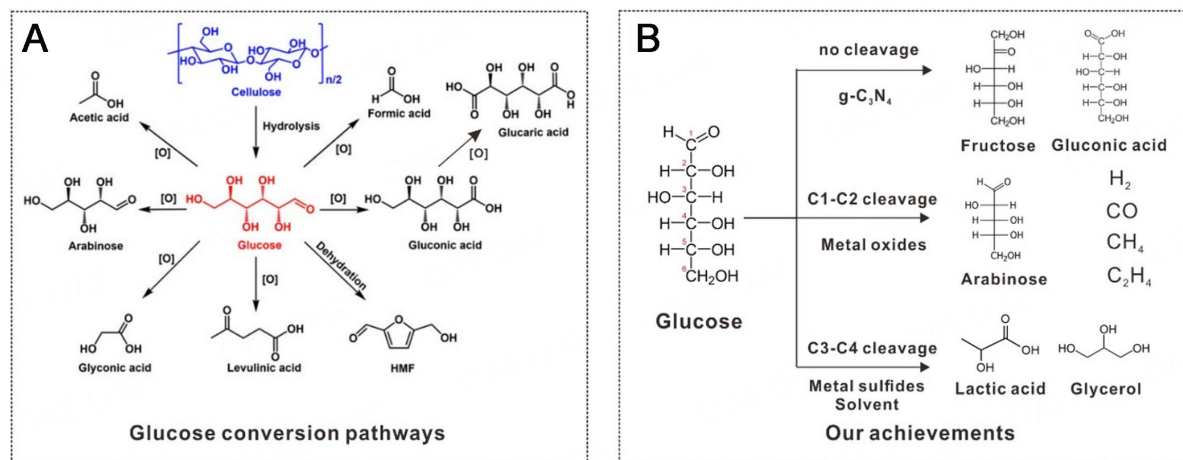


Figure 6. Schematic illustrations of selective glucose conversion in the (A) literature. Reproduced with permission^[45]. Copyright 2023, Frontiers Media S.A.; (B) The achievements in selective glucose conversion by our research work.

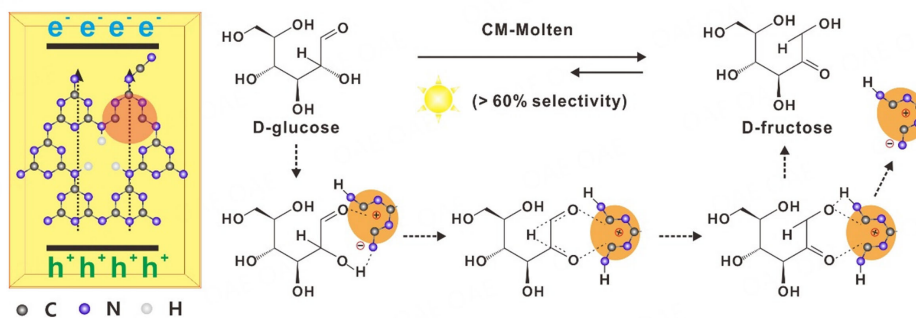


Figure 7. Schematic illustrations of photocatalytic glucose isomerization into fructose by CM-Molten. Reproduced with permission^[51]. Copyright 2021, American Chemical Society.

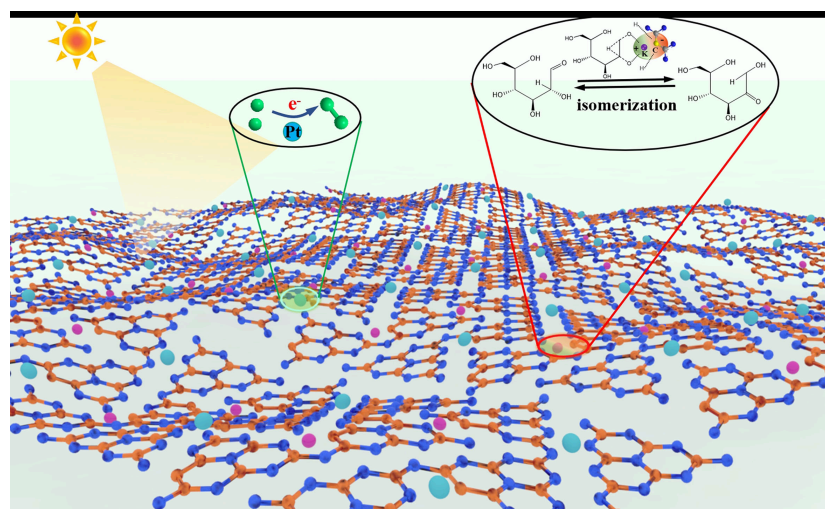


Figure 8. Schematic illustrations of photocatalytic glucose isomerization into fructose along with hydrogen production. Reproduced with permission^[52]. Copyright 2022, Elsevier.

synthesis of hierarchically porous CaTiO₃ coupling Zn_{0.3}Cd_{0.7}S quantum dots as the dually functional photocatalyst to realize photocatalytic H₂ production and glucose oxidation into gluconic acid^[59]. With the assistance of the hierarchically porous structure in light harvesting and beneficial mass diffusion and the Zn_{0.3}Cd_{0.7}S quantum dots in constructing heterojunction structures for charge separation, the as-fabricated composite exhibited 2.81 mmol·h⁻¹·g⁻¹ of H₂ with the AQY at 5.56%. More importantly, considerable yield of gluconic acid was also achieved at the same time.

Due to the presence of hydroxyl groups at the C6 position, gluconic acid could be further oxidized into glucaric acid with two carboxylic groups [Figure 9A]^[60]. Each of the oxidation steps involves two electrons. Notably, g-C₃N₄ is one of the typical photocatalysts with the unique two-electron reaction property, which could selectively produce AOS for the in-situ glucose oxidation. Herein, g-C₃N₄-based photocatalysts have been investigated for selective glucose conversion into gluconic acid. Bai *et al.* reported the chlorine e6 modified carbon nitride (Ce6@BNCN) as the metal-free photocatalyst for glucose oxidation. This process resulted in the production of both gluconic acid and glucaric acid, achieving a 62.3% glucose conversion rate [Figure 9B]^[61]. However, the detection of other products, such as arabinose, indicated the overoxidation of the produced gluconic acid and glucaric acid. With the modification of cobalt thioporphyrazine (CoPz) onto g-C₃N₄ [Figure 9C], the overoxidation of gluconic acid and glucaric acid was inhibited^[62]. Wang *et al.* reported the synthesis of potassium and oxygen co-doped g-C₃N₄ (RCN) as the photocatalyst to selectively produce gluconic acid from glucose oxidation^[63]. This process was realized by the intrinsic two-electron reaction pathway of RCN, which could selectively generate H₂O₂ and •O₂⁻ as the oxidation species for gluconic acid production [Figure 9D].

Glucose to arabinose with C1–C2 breakage

The processes of glucose isomerization and glucose oxidation into gluconic acid do not involve the breakage of the chemical bonds in glucose molecules. The selective cleavage of different C–C bonds will produce different chemicals. For example, the C1–C2 cleavage will generate arabinose from glucose. Arabinose has been regarded as a low-caloric aldopentose with a great market in biological and medical industries^[64]. Photocatalytic glucose conversion into arabinose has also been investigated in recent years^[43]. Chong *et al.* demonstrated the selective conversion of glucose to arabinose and other sugar aldose on TiO₂-based photocatalysts [Figure 10A]^[65]. The effects of the crystal phase of TiO₂ and active species on glucose degradation pathway in water conditions were first revealed. Apart from the liquid phase products, gaseous H₂, CO, and CO₂ were also detected during the photocatalytic process. Zhao *et al.* adopted the colloid template method to prepare 3DOM TiO₂-Au as the photocatalyst for glucose conversion into arabinose, and a similar reaction pathway was also observed in this work [Figure 10B]^[66]. The detailed reaction mechanism was investigated by the C18 labeling experiment. The presence of hierarchically porous structures and gold nanoparticles endowed the photocatalyst with another ability to produce methane. The reaction pathway of glucose to arabinose seems to follow the Ruff degradation mechanism [Figure 10C]. As glucose and arabinose have similar functional groups, the used photocatalysts could also further convert arabinose with the formation of erythrose and formic acid. Herein, in order to obtain higher selectivity and yield of arabinose from photocatalytic glucose conversion, the minor differences between glucose and arabinose in the aspects of chemical and physical properties should be fully considered. Apart from TiO₂-based photocatalysts, some other photocatalysts have also been applied for the photocatalytic glucose conversion into arabinose. For example, Wang *et al.* reported the synthesis of gold nanoparticle-modified carbon nitride (ACN), which regulated the two-electron reaction of pristine carbon nitride into a single-electron reaction pathway to selectively produce •O₂⁻ as the active species for arabinose production^[67]. Some other reduction reactions instead of photocatalytic hydrogen production, along with glucose oxidation into arabinose, have also been achieved. For example, Zhou *et al.* designed mesoporous CdS supported with Pd nanoparticles as the visible light photocatalyst, and it showed excellent performance for photocatalytic

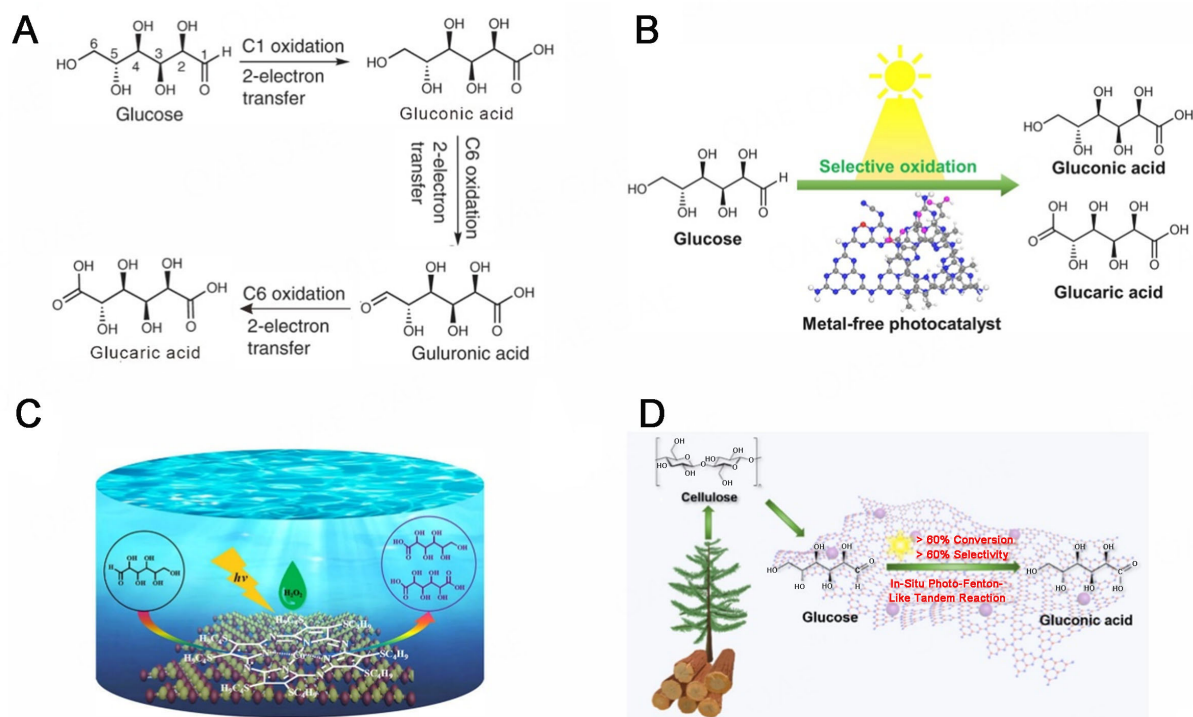


Figure 9. Schematic illustrations of (A) glucose oxidation into gluconic acid, glucuronic acid, and glucuronic acid. Reproduced with permission^[60]. Copyright 2020, Springer Nature Ltd; (B) glucose oxidation over Ce6@BNCN. Reproduced with permission^[61]. Copyright 2021, Elsevier; (C) CoPz/g-C₃N₄. Reproduced with permission^[62]. Copyright 2020, Elsevier; (D) RCN. Reproduced with permission^[63]. Copyright 2023, American Chemical Society.

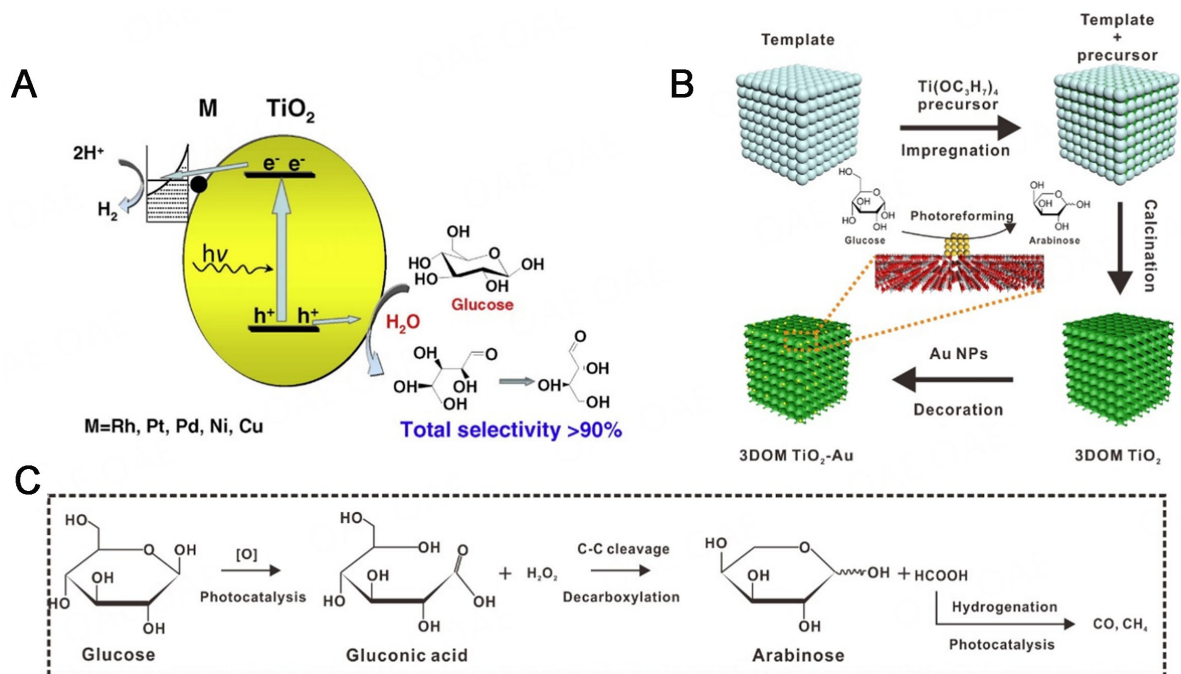


Figure 10. Schematic illustrations of the photocatalytic glucose conversion into arabinose of (A) M-TiO₂ (M = Rh, Pt, Ni, Cu). Reproduced with permission^[65]. Copyright 2014, Elsevier; (B) 3DOM TiO₂-Au and (C) proposed a reaction pathway for the selective conversion of glucose. Reproduced with permission^[66]. Copyright 2021, Elsevier.

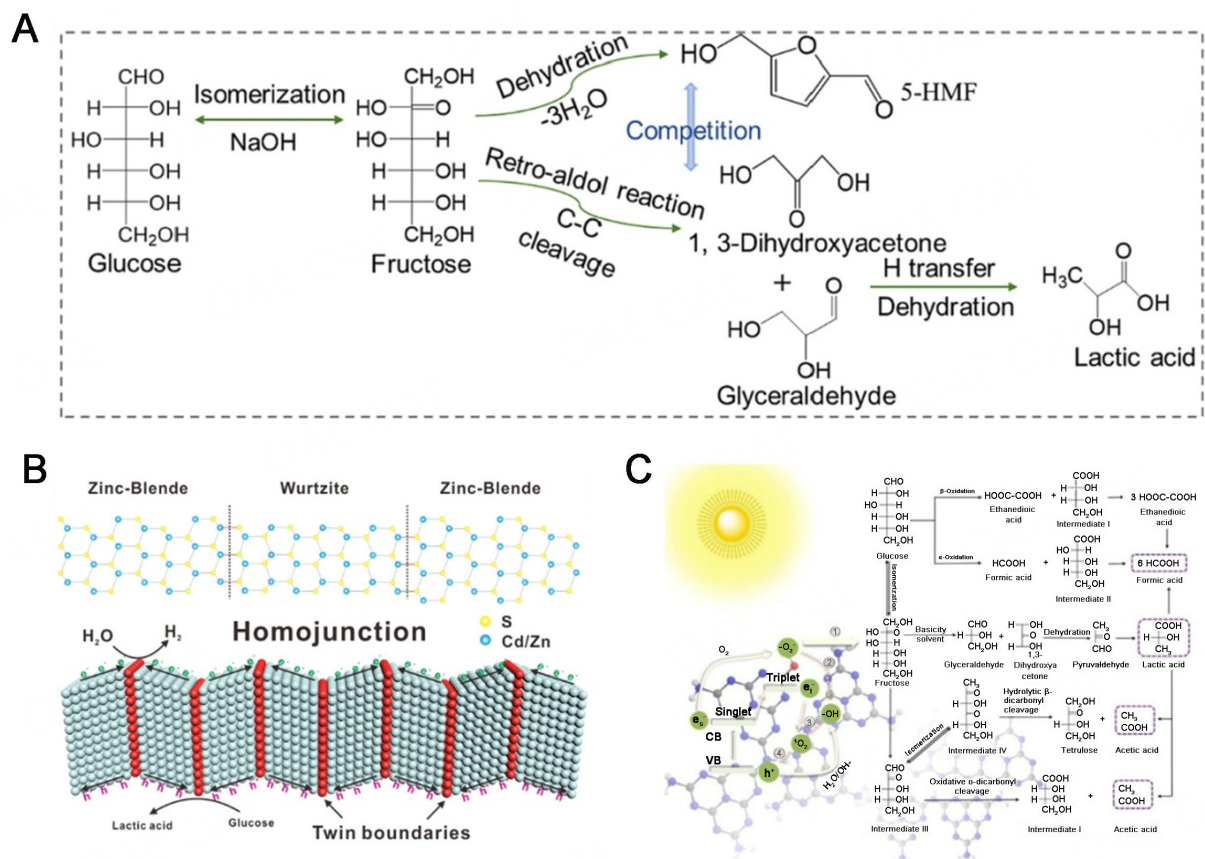


Figure 11. Schematic illustrations of (A) lactic acid production from glucose. Reproduced with permission^[71]. Copyright 2022, Elsevier; (B) Atomic illustration of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution with charge separation. Reproduced with permission^[72]. Copyright 2021, Elsevier; (C) Photocatalytic glucose conversion to lactic acid on carbon nitride-based materials. Reproduced with permission^[74]. Copyright 2020, Elsevier.

glucose conversion to arabinose. More importantly, the as-fabricated photocatalyst also exhibited dual functionality. The photogenerated holes oxidized glucose to arabinose with 70% selectivity, while the photogenerated electrons reduced nitrosobenzene into azoxybenzene with 92% selectivity^[68].

Glucose to lactic acid with C3–C4 breakage

Glucose could be artificially synthesized through aldol condensation reactions^[69]. Herein, it is reasonable to decompose glucose via retro-aldol reactions into glyceraldehyde and dihydroxyacetone. It has been widely reported that glucose could be converted via C3–C4 breakage by photocatalysis and finally produce lactic acid in an alkaline solution. The most widely acknowledged reaction pathway involves the glucose isomerization into fructose followed by retro-aldol reactions to produce glyceraldehyde and dihydroxyacetone. Pyruvaldehyde is then generated through the release of water from dihydroxyacetone. Finally, the stable lactic acid will be produced after a series of reactions, such as rearrangements and dehydration reactions [Figure 11A]^[70,71]. As photocatalysis could produce AOS to boost the retro-aldol process, a high yield of lactic acid has been achieved via glucose photorefinery. Zhao *et al.* synthesized a series of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solutions as the photocatalyst and 1 M of NaOH solution as the media. Besides of lactic acid production with 87% selectivity, considerable hydrogen was also evolved under the optimized condition [Figure 11B]. The rationally designed $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution was endowed with homojunction structures that were constituted by zinc blende and wurtzite twinning superlattice. The formed homojunction structure benefited the spatial separation of photogenerated electrons and holes and

facilitated the production of plenty of active species for glucose to lactic acid processes^[72]. Further investigations by using dual-functional marigold-like $Zn_{1-x}Cd_xS$ solid solutions revealed the active sites for photocatalytic hydrogen generation and lactic acid production^[71]. Ma *et al.* reported a series of photocatalysts, including carbon nitride, copper oxides, and bismuth oxide-based materials, which showed excellent performance for the photocatalytic lactic acid production from pentoses and hexoses^[73-77]. All the developed photocatalysts seem to produce AOS that are believed to play a vital role in the conversion of glucose to lactic acid via C3–C4 cleavage [Figure 11C]. However, all the achievements are realized in alkaline conditions, and it is still challenging to directly generate lactic acid from glucose in neutral conditions by photocatalysis^[78]. Noticeably, lactic acid may not be the only product from the C3–C4 cleavage of glucose or fructose via the retro-aldol reaction, as the direct liquid products are the glyceraldehyde and dihydroxyacetone, which may generate glycerol with the hydrogenation reaction. With the rational design of photocatalyst and solvent optimization, glycerol has been successfully prepared from glucose photorefinery processes^[79] [Table 1].

The principle for selective glucose photorefinery varies from the production of different value-added chemicals. In general, Lewis acid-base sites are essential for glucose isomerization into fructose. Active oxygen radicals play a crucial role in oxidizing glucose into gluconic acid or glucaric acid or breaking C–C bonds within glucose. Specifically, alkaline conditions, along with AOS, are necessary for the C3–C4 cleavage to produce glycerol or lactic acid.

CONCLUSION AND OUTLOOK

In summary, biomass and biomass derivatives have been developed as the sacrificial agent to overcome the reaction kinetics of photocatalytic water splitting to improve the hydrogen generation efficiency. With the rational design of photocatalysts, it is feasible to realize both non-selective and selective glucose photorefinery to produce hydrogen and/or value-added chemicals. Besides, the optimization of the photocatalyst, reaction solvent, and atmosphere could regulate the selective breakage of the chemical bonds in glucose molecules to produce different valuable chemicals. Challenges in the selective glucose photorefinery come from the following aspects. Firstly, highly efficient photocatalysts with bifunctionality are still desired. Compared to the traditional sacrificial agent, glucose is in more complex and larger molecular structures. The achieved photocatalytic hydrogen production is still far from state-of-the-art efficiency in the presence of traditional sacrificial agents, such as methanol, triethanolamine, lactic acid, *etc.*^[82]. Photocatalysts with more favorable bandgap structures and proton activation energy should be considered for the photocatalytic hydrogen production from biomass or biomass derivatives; Secondly, for the selective glucose photorefinery, the achieved glucose conversion and product yield should also be further improved. Compared to the traditional platforms for glucose conversion, such as biocatalysis and thermocatalysis, the photocatalytic activity for selective glucose conversion needs further improvement. Because most of the products from glucose, such as arabinose, gluconic acid, fructose, *etc.*, have similar functional groups with glucose, there is a possibility that these compounds could serve as reactants and be consumed by the photocatalysts, thus reducing the product yields. Herein, apart from the rational photocatalyst design, the reaction system, including solvents, reactors, atmospheres, *etc.*, should be taken into consideration to achieve better yield of liquid products^[12]. Thirdly, some other reaction pathways should be developed to produce other valuable chemicals. For example, the C2–C3 breakage induces the selective generation of erythrose^[83]. HMF was also observed to be produced from glucose photorefinery, but the achieved efficiency needs to be improved^[84]. Finally, beyond the glucose photorefinery, cellulose or biomass photorefinery to produce sustainable hydrogen and value-added chemicals holds a more promising perspective for natural biomass valorization, which also puts much higher demands on the photocatalyst design and reaction system optimization due to the presence of strong intermolecular and intramolecular

Table 1. Comparison of lactic acid production from glucose photorefinery

Entry	Photocatalyst	Reactant	H ₂ production (mmol·g ⁻¹ ·h ⁻¹)	Glucose conversion (%)	Lactic acid yield (%)	Ref.
1	ZnCdS	20 g/L glucose, 1 M NaOH	0.69	90	78	[72]
2	Ut-OCN	10 g/L fructose, 3 M KOH	-	98	70	[74]
3	s-TCS-4	20 g/L glucose, 1 M NaOH	0.56	96	90	[80]
4	CuO@CS-H	10 g/L glucose, 5 M KOH	-	98	54	[76]
5	CC ₁ @mCN ₁₀	10 g/L glucose, 2 M KOH	-	100	70	[77]
6	BiOBr/Zn _{0.2} @SnO _{2-n}	10 g/L glucose, 1 M NaOH	-	80	61	[81]
7	g-C ₃ N ₄	0.5 g/L glucose, 1 M NaOH	-	100	100	[78]

hydrogen bonding and some inevitable condensation of lignin in lignocellulosic biomass. Apart from photocatalysis, newly emerging technologies by electrocatalysis and/or photoelectrocatalysis would also be attributed to the biomass valorization to simultaneously produce sustainable hydrogen and valuable chemicals. In recent years, explosive reports on biomass or biomass-derived glucose photorefinery to produce hydrogen and value-added chemicals indicate a bright future for this research direction^[85,86]. We hope this present review could stimulate the development of a rational design of photocatalysts and reaction systems to better valorize biomass into fuels and chemicals.

DECLARATIONS

Authors' contributions

Prepared the manuscript: Sun Z, Yu X

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Availability of data and materials

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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