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*Published in:*  
Advanced Energy Materials

*DOI:*  
[10.1002/aenm.202300257](https://doi.org/10.1002/aenm.202300257)

*Publication date:*  
2023

*Document Version*  
Publisher's PDF, also known as Version of record

#### [Link to publication](#)

*Citation for published version (HARVARD):*  
Zhao, H, Liu, J, Zhong, N, Larter, S, Li, Y, Kibria, MG, Su, BL, Chen, Z & Hu, J 2023, 'Biomass Photoreforming for Hydrogen and Value-Added Chemicals Co-Production on Hierarchically Porous Photocatalysts', *Advanced Energy Materials*, vol. 13, no. 21, 2300257. <https://doi.org/10.1002/aenm.202300257>

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# Biomass Photoreforming for Hydrogen and Value-Added Chemicals Co-Production on Hierarchically Porous Photocatalysts

Heng Zhao, Jing Liu, Na Zhong, Steve Larter, Yu Li, Md Golam Kibria, Bao-Lian Su,\* Zhangxin Chen,\* and Jinguang Hu\*

Biomass, a naturally abundant, sustainable and clean resource has great potential as an alternative to replace the limited fossil feedstock for value-added chemicals and fuels. Biomass with abundant reductive functional groups could theoretically act as electron donor to consume photogenerated holes and/or active free radicals. Biomass photoreforming over semiconductor photocatalysts using solar light as energy input attracts much attention in this context. However, biomass photoreforming still suffers low conversion efficiency and product selectivity due to its structural complexity, poor solubility and unclear reaction mechanism. Owing to the advanced features of mass diffusion of biomass derivatives and adjustable surface properties, hierarchically porous photocatalysts with desired active sites at each length scale of porosity have shown their superiority in boosting the conversion efficiency and selectivity of biomass photoreforming. Herein, a critical review is presented on selective biomass photoreforming for simultaneous H<sub>2</sub> and value-added chemicals co-production on hierarchically porous photocatalysts. The fundamentals of biomass photoreforming and current bottleneck of biomass valorization by photocatalytic process are presented and analyzed. The rational photocatalyst design with hierarchically porous structure to improve the biomass conversion and product selectivity by boosting mass transfer is highlighted. Finally the challenges and opportunities for photocatalytic biomass valorization are presented in the perspective section.


technologies to utilize renewable energy sources such as wind, solar, geothermal, and biomass is highly desired to maintain the harmonious, sustained, and steady development of human civilization.<sup>[1–3]</sup> Biomass, a most widely abundant and easily accessible natural resource have already supported mankind for thousands of years.<sup>[4–6]</sup> Until now, biomass is still supplying ≈25% of global energy and it has been widely recognized as one of the most important energy source in the future.<sup>[7–10]</sup> The first-generation biofuels such as bioethanol generated from carbohydrates in corn and wheat have already made huge contribution to the global economies. However, drawbacks are from the huge consumption of food crops during the production procedure, which exacerbates food shortage problem.<sup>[11–13]</sup> The second-generation biofuels are derived from various types of non-food feedstocks such as lignocellulosic biomass and wastes, which holds great potential to sustainably produce fuels and value-added chemicals along with addressing environmental issues and without competing with food reserves.<sup>[14–16]</sup>

Lignocellulosic biomass consisting of polysaccharides (cellulose and hemicellulose) and aromatic polymers (lignin) comprises more than 50% of total organic matter on earth.<sup>[5]</sup> Developing efficient technologies to convert lignocellulosic biomass into high-intensity fuels and platform

## 1. Introduction

Along with depletion of traditional fossil fuels and growing environmental issues, developing advanced and sustainable

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DOI: 10.1002/aenm.202300257

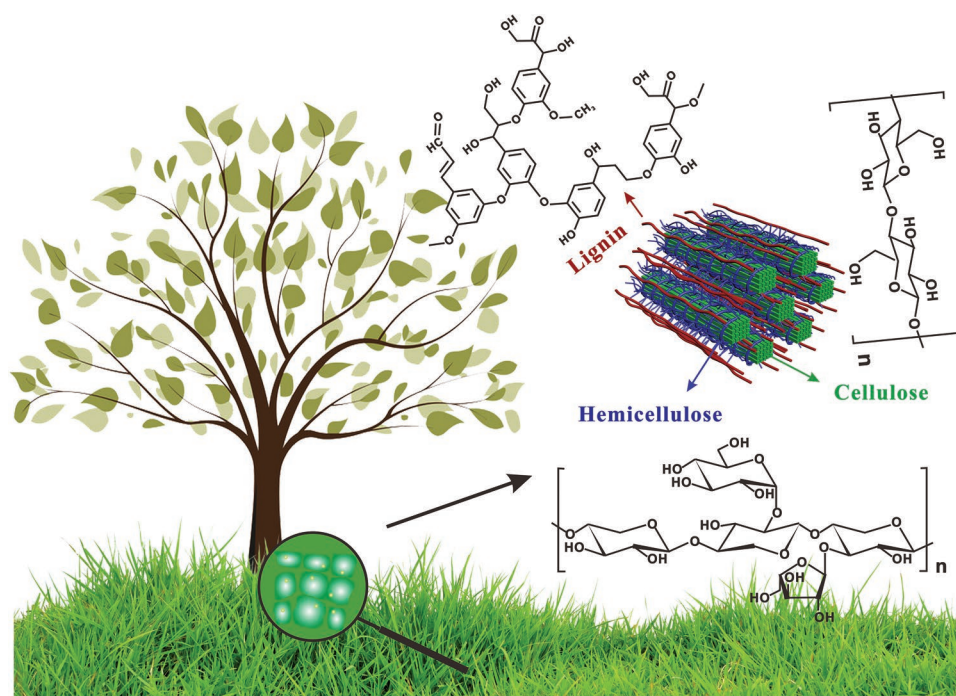
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chemicals are always pursued to realize carbon neutrality.<sup>[17,18]</sup> Cellulose is the most abundant polymer in lignocellulosic biomass with weight ratio of 40–60%, consisting with  $\text{D}$ -glucose as monomeric unit and cellobiose with  $\beta$ -1,4-glycosidic bonds as fundamental repeating unit.<sup>[19]</sup> The high degree of polymerization (800 to 1000) and complex inter- and intra-hydrogen bonds make cellulose with three levels: cellulose chains, supramolecular cellulose layer, and fibril layer, which endow cellulose with excellent advantages as materials in various applications.<sup>[20–23]</sup> Hemicellulose is another polysaccharide in lignocellulose with 20–25% weight ratio, which is composed of numerous pentoses (xylose, arabinose, and rhamnose) and hexoses (glucose, galactose, and mannose) as well as sugar acid (glucuronic acid).<sup>[24,25]</sup> Different from cellulose, the chemical formula of hemicellulose is not fixed but depends on the plant species. Four main types of hemicellulose exist according to the structure of the cell wall: xylan, mannan,  $\beta$ -glucan, xyloglucan, and xylan is the major component.<sup>[26,27]</sup> Distinct from cellulose and hemicellulose, lignin is a three-dimensionally cross-linked polymer of aromatic allylic alcohols.<sup>[28]</sup> Three monomers are recognized as the primary unit of lignin: *p*-coumaryl, coniferyl, and sinapyl alcohol, which correspond to three structural units of hydroxyphenyl (H), guaiacyl (G), and syringyl (S) respectively.<sup>[29,30]</sup> The monomers in lignin are connected by C–O ( $\beta$ -O-4,  $\alpha$ -O-4, etc.) and recalcitrant C–C ( $\beta$ -1',  $\beta$ -5', 5-5', etc.) linkages, and the  $\beta$ -O-4 linkage is in highest content (43–65%) in lignin of natural lignocellulosic biomass.<sup>[31,32]</sup> In term of the structural distribution of the whole lignocellulose, cellulose is located at the core of lignocellulosic matrix and it is packed into semi-crystalline microfibrils.<sup>[33,34]</sup> Inter- and intra-hydrogen bonds as well as van der Waals forces are the corresponding driving force between the cellulose microfibrils. Hemicellulose covers cellulose fibers by forming intimate hydrogen bond while lignin fills the spaces

of cellulose fibers like a resin to hold the lignocellulose matrix tight together.<sup>[35,36]</sup> The interaction between polymers in lignocellulose is illustrated in **Figure 1**. Considering the abundantly available and renewable properties of lignocellulose, the development of efficient technology to selectively produce biofuels and value-added chemicals from lignocellulosic biomass holds very promising foreground.<sup>[37–41]</sup>

In order to realize the conversion and valorization of lignocellulosic biomass, the complex structure formed by the assembly of different polymers via different interactions has to be first disintegrated by depolymerization and partial deoxygenation with high energy input.<sup>[42–45]</sup> Currently, there have already been a number of feasible processes and technologies to develop biomass valorization such as biological process and chemocatalytic methods.<sup>[46–52]</sup> Biochemical process such as fermentation and enzymatic hydrolysis involves the use of enzymes, bacteria, and microorganisms for biomass pretreatment under mild condition. However, the exploitation of this technology on large scale is still questionable due to the low efficiency because of the low accessibility of complex biomass and long pretreatment time.<sup>[53]</sup> Thermochemical processes such as pyrolysis, gasification, and direct combustion could improve the biomass conversion efficiency. These processes require high temperature and/or high pressure with intensive energy consumption to overcome the activation barrier for biomass conversion.<sup>[54,55]</sup> Besides, considering the plenty and multiple functional groups in lignocellulose, the rough thermocatalysis always leads to low product selectivity and less valuable humins.<sup>[56]</sup> Comparatively, photocatalytic biomass valorization provides the mild operation and high efficiency and selectivity.<sup>[57–64]</sup> Biomass utilization by photocatalytic process the so called photoreforming is a novel concept and emerging technology.<sup>[65–68]</sup> Both hydrogen and value-added chemicals are produced under solar light



**Figure 1.** Schematic illustration of chemical structure for lignocellulose biomass, including cellulose, hemicellulose, and lignin.

irradiation.<sup>[69]</sup> Such concept is derived from photocatalytic hydrogen production from solar-driven water splitting reaction.<sup>[70–72]</sup> The photocatalytic water splitting involves proton reduction reaction and oxygen evolution reaction (OER) from water. However, limited to the slow kinetics and high thermodynamics of OER, whole photocatalytic water splitting suffers from extremely low efficiency.<sup>[73,74]</sup> To boost the hydrogen production activity, electron donors such as alcohols, organic acids, inorganic salt, etc. as sacrificial agents are added into reaction solution to timely consume photogenerated holes or active radicals from holes.<sup>[75–78]</sup> Therefore, the photocatalytic hydrogen production could be significantly enhanced by inhibiting OER reaction. However, the addition of these sacrificial hole scavengers will not only definitely increase the cost of hydrogen production but also bring environmental issues. The generated hydrogen energy is far away to offset the energy required to produce the sacrificial agents.<sup>[79]</sup> Considering the presence of plenty reductive groups in lignocellulose such as hydroxyl and aldehyde, using biomass themselves as electron donor to scavenge photogenerated holes and/or free radicals generated from holes could be a good strategy to enhance hydrogen production. Meanwhile, value-added chemicals could also be obtained as fine designed photocatalysts can selectively break specific chemical bond and functionalize specific groups.<sup>[80–82]</sup> However, the current efficiency of the biomass and biomass derivatives photoreforming is still unsatisfied with the state-of-the-art energy production.<sup>[83]</sup> Challenges originate from the low accessibility of lignocellulosic biomass to photocatalysts and intrinsic drawbacks of current photocatalysts, which puts higher demands on the photocatalyst. Considering the macromolecular property and complex spatial structure, constructing hierarchically porous photocatalyst would improve the photocatalytic efficiency by increasing the substrate diffusion and enhance light harvesting.<sup>[84–87]</sup> From this perspective, rational design of hierarchically porous photocatalysts is one promising strategy to improve solar-driven biomass utilization to produce value-added chemicals along with hydrogen coproduction.

Due to the excellent enhancement in mass diffusion and light harvesting, materials with hierarchically porous structure have widely been used for biomass derivatives conversion.<sup>[88–95]</sup> The advantages of applying hierarchically porous photocatalyst to realize biomass valorization are 1) large surface area facilitates active site exposure and interaction with biomass; 2) different porosity combination will realize efficient diffusion of substrates and products; 3) inter-connected porous structure benefits for uniform formation of Schottky junction and/or heterojunction to improve the photocatalyst properties; 4) multiple scattering or slow photon effect originated from inter-connected porous structure increases the interaction of incident photons with photocatalyst; 5) tandem structure with multiple levels of pore sizes helps to improve product selectivity by confinement effect.

For the first time, we provide the insight in biomass valorization by using hierarchically porous photocatalysts. We introduce the fundamentals of biomass photoreforming in Section 2, including non-selective photoreforming for hydrogen production and selective photoreforming for hydrogen and value-added chemicals coproduction. In this section, photocatalyst design, biomass pretreatment and process conditions to

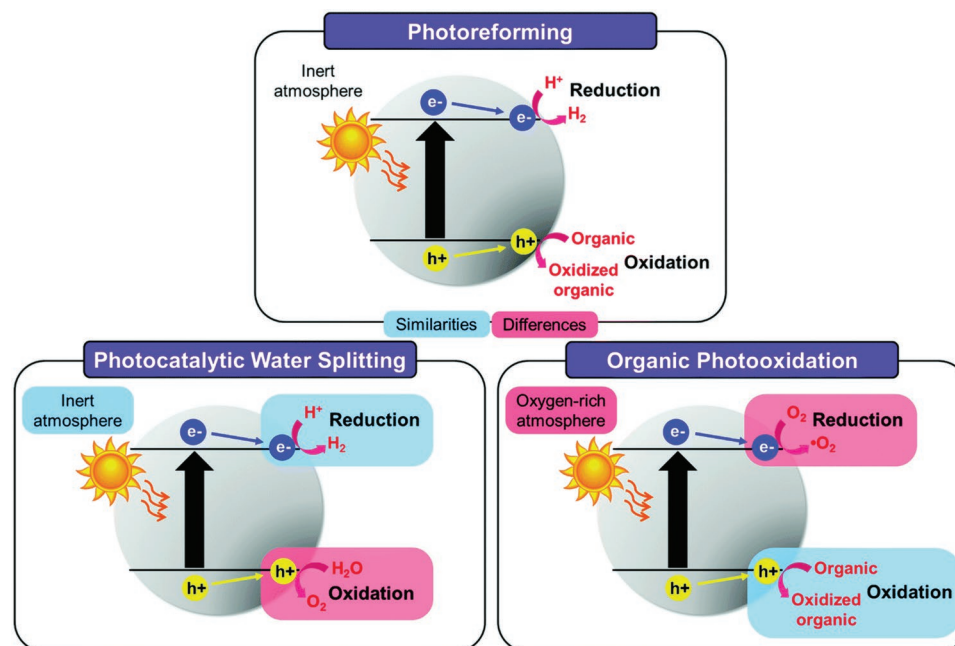
improve the selective biomass photoreforming are summarized and discussed. Major hinders in biomass photoreforming are raised in Section 3 based on the complex structure of biomass macromolecule and the inefficiency of photocatalyst. Then we emphasize the advantages and importance of hierarchically porous materials from both theoretical and practical point of view in Section 4, including the introduction of applying generalized Murray's law to design materials with maximum diffusion efficiency. The current application of hierarchically porous materials in biomass photoreforming is summarized in Section 5. A comprehensive summary and perspective are concluded and pointed out in Section 6. This review provides an overview of biomass photoreforming for both hydrogen and value-added chemicals production by using hierarchically porous materials. We believe this review will shed new light on promoting biomass valorization with mild photocatalytic technology.

## 2. Fundamentals of Biomass Photoreforming

### 2.1. Non-Selective Biomass Photoreforming for H<sub>2</sub> Production

The prototype of biomass photoreforming is the photocatalytic hydrogen production from water by using biomass-derived alcohols as sacrificial agent and this process is actually a non-selective photoreforming (Figure 2).<sup>[83]</sup> In this process, semiconductor photocatalysts are excited under light irradiation with certain wavelength to produce active electrons from valence band to conduction band, leaving corresponding holes at the valence band. The immigration of these produced electrons to the photocatalyst surface triggers proton reduction to H<sub>2</sub> while the photogenerated holes induce the oxidation of adsorbed H<sub>2</sub>O or electron donors. Inert atmosphere and sacrificial agents are the two necessary conditions for the non-selective photoreforming to produce H<sub>2</sub>. In presence of oxygen, the oxygen reduction reaction to form superoxide radicals ( $\blacksquare\text{O}_2^-$ ), H<sub>2</sub>O<sub>2</sub> or water competes with the proton reduction reaction and the produced  $\blacksquare\text{O}_2^-$  may also involve the oxidation reaction of sacrificial agents.<sup>[96–98]</sup> In absence of oxygen, the reduction reaction proceeds with H<sup>+</sup> reduction to H<sub>2</sub> while the oxidation reaction occurs through direct hole transfer or formation of hydroxyl radicals ( $\blacksquare\text{OH}$ ). Although the addition of sacrificial agents as electron donor could timely consume photogenerated holes or  $\blacksquare\text{OH}$  from the water oxidation by holes to improve the production efficiency of H<sub>2</sub> production, the H<sub>2</sub> generation cost by this approach far exceeds that of industrial steam reforming due to the high price of traditional sacrificial agents such as alcohols, organic acids, Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>, and triethanolamine.<sup>[99]</sup> The principle of adding sacrificial agents in the photocatalytic H<sub>2</sub> evolution system is that these chemicals with strong reducing properties can react with photogenerated holes. From this aspect, lignocellulosic biomass with plenty hydroxyl groups and unsaturated chemical bonds is also good candidate as electron donor. Besides, lignocellulose with abundant hydrogen atoms could act as the precursor for H<sub>2</sub> production.

Recently, many research works already demonstrate the feasibility of photocatalytic H<sub>2</sub> production by using lignocellulose and/or derivatives as electron donor. From the reaction kinetics,



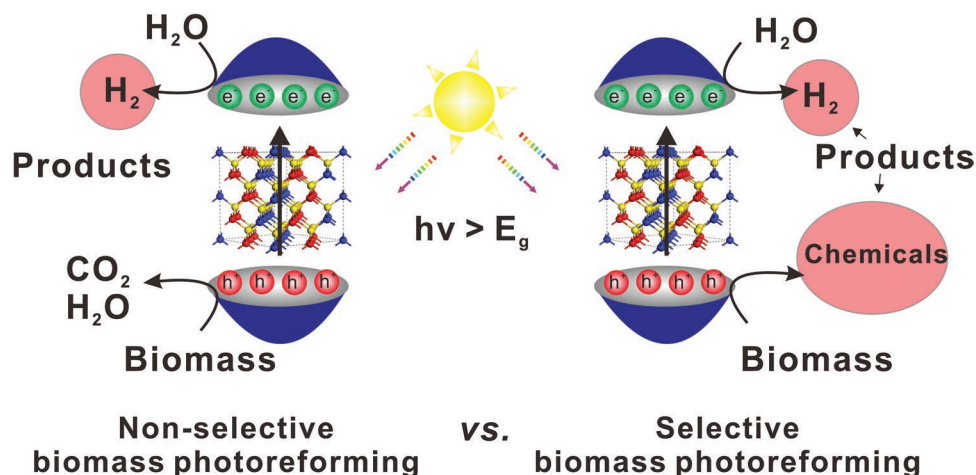
**Figure 2.** Comparison of photoreforming with photocatalytic water splitting and organic photooxidation processes, Reproduced with permission.<sup>[83]</sup> Copyright 2021, The Royal Society of Chemistry.

the usage of model components of biomass such as glucose, xylose shows high efficiency in  $H_2$  production compared to the more complexed substrates of cellulose, lignin, or raw biomass.<sup>[100,101]</sup> With the development in photocatalyst design and insight into reaction mechanism, photocatalytic  $H_2$  evolution from raw biomass or biomass derivatives with complexed structure and component is also achieved. Reisner's group reported the sustainable  $H_2$  generation from purified and raw lignocellulose samples by decorating different cocatalysts onto the cyanamide-functionalized carbon nitride.<sup>[67]</sup> They also demonstrated the light-driven photoreforming of cellulose, hemicellulose, and lignin to  $H_2$  by using cadmium sulfide quantum dots in alkaline condition.<sup>[102]</sup> Porous polymeric carbon nitride with Pt as cocatalyst also showed much higher  $H_2$  production efficiency than pristine carbon nitride from biomass derivatives photoreforming.<sup>[103]</sup> Wei et al. decorated Ni cocatalyst onto mesoporous  $TiO_2$  and realized photocatalytic  $H_2$  production by using soluble paper in alkaline solution.<sup>[104]</sup> Although a lot of recent works demonstrate the possibility of  $H_2$  evolution by using biomass or biomass derivatives as electron donor, two major scientific problems are still waiting to be solved. One is the change of complex lignocellulosic biomass after photocatalytic reaction and the other one is the source of produced  $H_2$ . Different from the model components of biomass which could directly be detected by high-performance liquid chromatography (HPLC)<sup>[105]</sup> or gas/liquid chromatography-mass spectrometry (GC/LC-MS), the lignocellulosic biomass or raw biomass is difficult to be directly measured to demonstrate the structural and chemical changes during the photoreforming process. Herein, most of the reported works only focus on non-selective photoreforming to produce  $H_2$  and the oxidation reaction of the added biomass is ignored or mineralized into  $CO_2$  and  $H_2O$ . The over-oxidation for  $CO_2$  formation is common as  $\blacksquare OH$  could be easily

produced by most UV responsible semiconductors, which has strong oxidation ability to realize the direct mineralization of the added organic sacrificial agents.<sup>[106,107]</sup> There is always controversy about the source of  $H_2$  in biomass photoreforming as the  $H_2$  could be generated from both water and biomass. Although  $D_2O$  was used as the solvent to clarify the source of produced hydrogen, it cannot represent to all the cases of biomass photoreforming.<sup>[67]</sup> It is undeniable that the dehydrogenative approach to produce  $H_2$  from biomass or biomass derivatives indeed holds more promising perspectives.<sup>[108–110]</sup> Apparently, non-selective biomass photoreforming for  $H_2$  production has much room for improvement if the added biomass could also be selectively converted into value-added chemicals rather than  $CO_2$ . In this aspect, selective photoreforming by simultaneously producing  $H_2$  and value-added chemicals holds more promising perspective by fine regulating the oxidation ability of photocatalyst.

## 2.2. Selective Biomass Photoreforming for $H_2$ and Value-Added Chemicals Coproduction

Comparatively, selective biomass photoreforming for the coproduction of  $H_2$  and valuable chemicals holds more promising features compared to non-selective biomass photoreforming process. The rational design of bifunctional photocatalysts facilitates to clarify the active sites and reaction mechanism. Biomass could also be well valorized by mild photocatalysis to produce platform chemicals. The photogenerated electrons and holes could be fully utilized to produce fuels and chemicals. More importantly, with the assistance of proper reactor, biomass pretreatment, and reaction condition regulation, cascade reactions could be realized to generate high-value chemicals



**Figure 3.** Schematic comparison of non-selective biomass photoreforming and selective biomass photoreforming.

such as glucaric acid (Figure 3).<sup>[111,112]</sup> Despite all the advantages of selective biomass photoreforming mentioned above, its practical application remains extremely challenging because of poor product selectivity currently. The intrinsic reasons for poor selectivity are: 1) the uncontrollable generation of active oxygen species (i.e.,  $\cdot\text{OH}$ ); 2) non-selective adsorption and desorption of reactants/products on the photocatalyst surface; 3) further spontaneous reactions such as decarboxylation and  $\text{CO}_2$  formation. The highlights of selective biomass photoreforming are to simultaneously utilize photogenerated electrons for hydrogen production (reduction reaction) and holes for value-added liquid products (oxidation reaction), the purity of gas fuel and selectivity of liquid chemicals decrease if over-oxidation of biomass into  $\text{CO}$  or  $\text{CO}_2$  happens without proper control of reaction process. Various strategies have been explored and investigated to improve the selectivity of biomass photoreforming, which includes photocatalyst design, biomass pretreatment and reaction system regulation.<sup>[83,113–115]</sup> As the core of photocatalysis, photocatalyst design is the preferred strategy to control the liquid- and gas-phase product distribution from biomass photoreforming. The approaches of photocatalyst design could be summarized into heterojunction/homojunction formation, defect engineering, morphology, and crystallization control. The following section will thoroughly review current strategies to improve the liquid product selectivity during the biomass or biomass-derivatives photoreforming with  $\text{H}_2$  production.

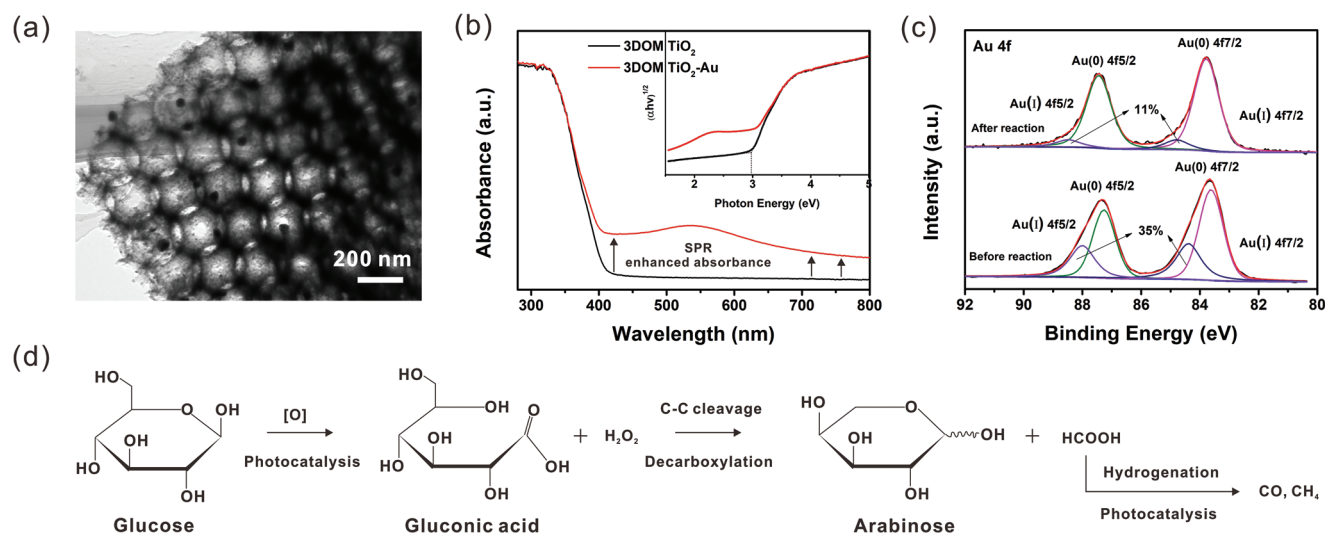
### 2.2.1. Photocatalyst Design

Proper photocatalyst design can not only improve solar-to-chemical energy conversion but also realize selective biomass photoreforming with high efficiency and product selectivity. Considering the drawbacks of pristine photocatalyst, such as light absorption limitation and high recombination of photogenerated electrons and holes, Heterojunction could be formed by decorating co-catalysts (such as metals, carbon materials, Mxene, etc.) or combining with another semiconductor on original semiconductor photocatalyst. The former is Schottky junction while the later tends to form type-II, Z-scheme or S-scheme

junction.<sup>[116–118]</sup> One of the factors that limits the photocatalytic performance is the recombination of photogenerated electrons and holes. Depositing metals or carbon-based materials as the co-catalysts is an efficient approach to improve the charge separation efficiency, thereby enhancing the photocatalytic activity.

**Co-Catalyst:** Platinum (Pt) has the largest work function (5.56 eV) and is the widely used co-catalyst in photocatalyst to boost the charge separation for  $\text{H}_2$  production. Recently, the deposition of Pt on semiconductor has also been used for biomass-derivates photoreforming along with  $\text{H}_2$  production. The formed Schottky junction introduces the up-bending of bandgap structure of semiconductors at the interface and induces the efficient electron spatial transfer from semiconductors to Pt under light irradiation.<sup>[119]</sup> The separated electrons trigger proton or water reduction to produce  $\text{H}_2$  while the photogenerated holes at the valence band induce substrate selective oxidation. For example, the Pt-decorated porous carbon nitride demonstrated simultaneous  $\text{H}_2$  and 2,5-diformylfuran (DFF) co-production from biomass derived 5-(hydroxymethyl) furfural (HMF) photoreforming.<sup>[120]</sup> Combined with Pt nanoparticles,  $\text{TiO}_2$  with different crystalline phase also exhibited the ability to achieve selective biomass photoreforming. Both liquid (arabiose, erythrose, gluconic acid, etc.) and gaseous ( $\text{H}_2$ ) products were obtained.<sup>[121]</sup>

In some cases, metal nanomaterials with high work function also have localized surface plasmon resonance (LSPR) effect, which could significantly improve light absorption.<sup>[122]</sup> Most of the plasmonic metals have the LSPR effect in visible light region, such as Au, Ag, Cu, which is beneficial for extending the light absorption region of semiconductors with wide band gap.<sup>[123]</sup> The LSPR absorption could be regulated by changing material shape, size, and surrounding environment.<sup>[124,125]</sup> Besides, the photogenerated hot electrons by LSPR also have the ability to trigger selective biomass photoreforming. Corresponding carboxyl compounds were selectively obtained from biomass-derived feedstocks by AuNPs/ $\text{TiO}_2$  composite under both UV and visible light in  $\text{Na}_2\text{CO}_3$  aqueous solution.<sup>[126]</sup> The Cu NPs encapsulated in few-layered carbon from pyrolysis of the HKUST-1 metal-organic framework exhibited good

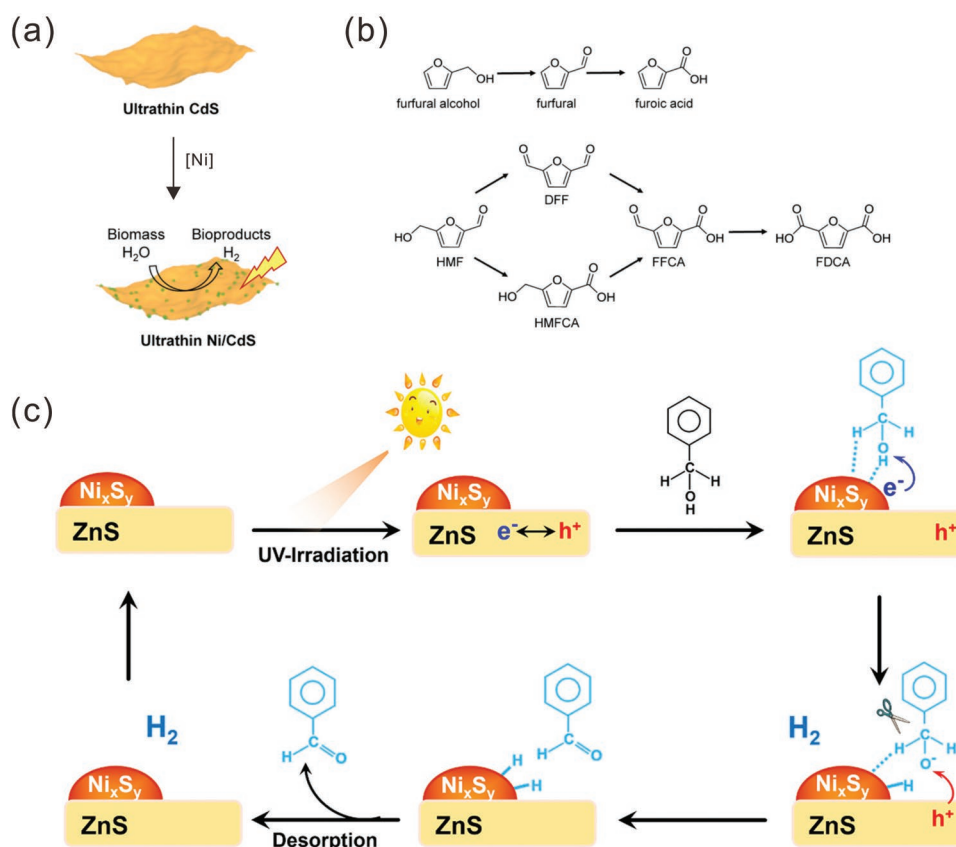


**Figure 4.** a) TEM image of 3DOM TiO<sub>2</sub>-Au, b) UV-vis absorption (inset is the corresponding plots of  $(\alpha h\nu)^{1/2}$  versus photon energy ( $h\nu$ )), c) XPS Au 4f spectra of 3DOM TiO<sub>2</sub>-Au before and after photocatalytic reaction. d) Proposed reaction pathway for arabinose production from glucose photoreforming. Reproduced with permission.<sup>[129]</sup> Copyright 2021, Elsevier.

photocatalytic hydrogenation of furfural to furfuryl alcohol.<sup>[127]</sup> Because the oxygen reduction reaction (ORR) also involves photogenerated electrons, the ORR is a competitive reaction with H<sub>2</sub> production under aerobic condition. The produced  $\blacksquare\text{O}_2^-$  from single-electron ORR could also improve the product selectivity. The well-designed Au/CeO<sub>2</sub>-TiO<sub>2</sub> NT photocatalyst as photocathode exhibited excellent aerobic oxidation of biomass alcohols to selectively produce benzaldehyde (>99% selectivity).<sup>[128]</sup> Apart from the high work function as electron relay and LSPR effect, the presence of partial oxidation state of these plasmonic metals sometimes show better photocatalytic performance. We recently demonstrated the presence of Au (I) on the surface of Au NPs improved the glucose photoreforming for arabinose and gas fuel co-production over hierarchically porous TiO<sub>2</sub>-Au photocatalyst.<sup>[129]</sup> The presence of hierarchically three dimensionally ordered macroporous (3DOM) structure benefits the uniform distribution of Au NPs in the framework (Figure 4a) and the introduced Au NPs improve visible light absorption due to the SPR effect (Figure 4b). The partial oxidation of Au to produce Au<sup>+δ</sup> was proved to have better performance than metal state of Au, but the produced Au<sup>+δ</sup> was not stable during the photocatalytic reaction (Figure 4c). Along with gas fuels (H<sub>2</sub>, CO, and CH<sub>4</sub>) production, glucose is simultaneously converted into high-value arabinose with C1–C2  $\alpha$ -scissions reaction pathway (Figure 4d). This provides an alternative to improve selective biomass photoreforming for both H<sub>2</sub> and value-added chemicals production by introducing stable Au<sup>+δ</sup> as co-catalyst.

Taking the high price and limited abundance of precious metals into account, using non-noble metals or carbon materials as co-catalyst holds more promising perspective in photocatalytic applications.<sup>[132–135]</sup> 2D Ni/CdS nanosheets exhibited value-added bioproducts (i.e., furoic acid, 2,5-diformylfuran (DFF), 2,5-furandicarboxylic acid (FDCA)) and H<sub>2</sub> from biomass-derived intermediate compounds photoreforming (Figure 5a,b).<sup>[130]</sup> In a similar Ni/CdS photocatalytic system, efficient conversion of biomass-derivatives (i.e., furfural alcohol

and 5-hydroxymethylfurfural (HMF)) into value-added platform chemicals (i.e., furfural and DFF) were also realized. Ni<sub>x</sub>S<sub>y</sub> loaded on ZnS nanorods as co-catalyst showed good performance for both H<sub>2</sub> and benzaldehyde production from benzyl alcohol selective oxidation (Figure 5c).<sup>[131]</sup> Detailed mechanism investigation indicated the presence of Ni<sub>x</sub>S<sub>y</sub> co-catalyst not only improved the charge separation under light irradiation by capturing photogenerated electrons, but also facilitated dehydrogenation of the OH group due to the strong adhesion of protons to Ni<sub>x</sub>S<sub>y</sub> for affording Ni<sub>x</sub>S<sub>y</sub>-H species. Afterward, the photogenerated holes located at nearby ZnS surface oxidized the alkoxide anion to form benzaldehyde and another Ni<sub>x</sub>S<sub>y</sub>-H hydride formed, which finally evolved into H<sub>2</sub>. Carbon materials such as graphene and carbon dots also have potential as co-catalyst to both enhance charge separation due to its fast charge transfer ability and improve biomass selective conversion because its functional surface modification.<sup>[136–143]</sup> Carbon quantum dots (CQDs) derived from citric acid and sodium citrate as co-catalyst on P25 TiO<sub>2</sub> showed excellent photocatalytic performance for glucose conversion to arabinose along with H<sub>2</sub> coproduction.<sup>[144]</sup> The different colors of CQDs was revealed to be ascribed to the size and content of heteroatomic nitrogen (Figure 6a). Glucose also proceeded with C1–C2  $\alpha$ -scissions reaction pathway triggered by produced active oxygen species to generate arabinose while H<sub>2</sub> was produced by proton reduction reaction by photogenerated electrons (Figure 6b). Graphene as the electron relay mediator in ternary heterostructure Ni<sub>2</sub>P-graphene-TiO<sub>2</sub> exhibited significantly photocatalytic performance toward cogeneration of benzaldehyde and H<sub>2</sub> from biomass-derived benzyl alcohol photoreforming.<sup>[145]</sup> Moreover, apart from the ability as co-catalyst, graphene oxide dot could also act as photocatalyst to realize selective biomass photoreforming.<sup>[146]</sup> Under alkaline condition, cellulose was decomposed into D-glucose units through piece-by-piece peeling process. Then, the S- and N-doped graphene oxide dots (SNGODs) showed ability to reform D-glucose units into formate and gaseous H<sub>2</sub> (Figure 6c).



**Figure 5.** a) Synthetic route of ultrathin Ni/CdS nanosheets for integrated H<sub>2</sub> production and biomass valorization. b) Oxidation reactions of furfural alcohol and HMF to their corresponding aldehydes and acids. Reproduced with permission.<sup>[130]</sup> Copyright 2017, American Chemical Society. c) Proposed reaction mechanism for the photocatalytic selective oxidation of benzyl alcohol and H<sub>2</sub> evolution over ZnS-Ni<sub>x</sub>S<sub>y</sub> composite in aqueous solution. Reproduced with permission.<sup>[131]</sup> Copyright 2019, American Chemical Society.

*Combination with another Semiconductor.* Heterojunctions formed by combining two separate semiconductor is derived from natural photosynthesis.<sup>[147–149]</sup> Two light responsible components (P700 as PS I and P680 as PS II) and electron transfer media (cytochrome) together construct Z-scheme electron transfer pathway in nature plant and algae.<sup>[150,151]</sup> Inspired by this natural photocatalyst, artificial photocatalysts with Z-scheme and/or type II heterojunctions have been developed and widely used in different photocatalytic applications since the first Z-scheme demonstration by Bard.<sup>[116,152–156]</sup> Combination with another semiconductor with proper band gap structure realizes the spatial and spontaneous charge separation.<sup>[157]</sup> Besides, by rationally choosing suitable band gap structure to selectively produce certain active radicals could regulate the selective biomass photoreforming.<sup>[98,158,159]</sup> As the generation of active oxygen species (AOS) always involves oxygen during the photocatalytic reaction, the oxygen reduction reaction (ORR) is the competitive reaction with hydrogen evolution reaction (HER). In this case, the selective biomass photoreforming leads to high substrate conversion as well as liquid chemical selectivity and yield, but low H<sub>2</sub> production. The TiO<sub>2</sub>-CdS is the most widely investigated heterojunction system because the widely and commercially used TiO<sub>2</sub> suffers limited light absorption (only UV light) and high recombination of photo-generated charge carriers, while the introduction of visible-light

responsible CdS not only extends the light absorption to visible light region, but also realizes the spatial charge separation to improve the quantum efficiency of pristine TiO<sub>2</sub>.<sup>[160–165]</sup> Due to the high electron resistance at the interface of CdS and TiO<sub>2</sub>, the charge separation and transfer are still limited in the TiO<sub>2</sub>-CdS binary system. To improve this case, metals or carbon materials with high electron conductivity are introduced between CdS and TiO<sub>2</sub> to mimic the natural photosynthesis.<sup>[93,166–172]</sup> Besides, the introduction of plasmonic metals also helps the photocatalytic improvement due to the presence of LSPR effect and hot electron injection.<sup>[168,173–175]</sup> Under visible light irradiation, only CdS is activated to generate electron–hole pairs. Due to the more negative conduction band (CB) position of CdS than that of TiO<sub>2</sub>, the photogenerated electrons tend to immigrate the CB of TiO<sub>2</sub>, leaving the photogenerated holes at the valence band (VB) of CdS and realizing the spatial separation of electrons and holes. This electron transfer pathway is defined as type II heterojunction (**Figure 7a**). While under UV–vis light irradiation, both CdS and TiO<sub>2</sub> are activated to generate electron–hole pairs. The electron transfer pathway has been revealed to be in Z-scheme type, in which the electrons at the CB of TiO<sub>2</sub> tend to recombine with the holes at the VB of CdS. The holes at the VB of TiO<sub>2</sub> trigger the oxidation reaction while the electrons at the CB of CdS induce the reduction reaction (**Figure 7b**). The efficient charge transfer not only improves the separation of



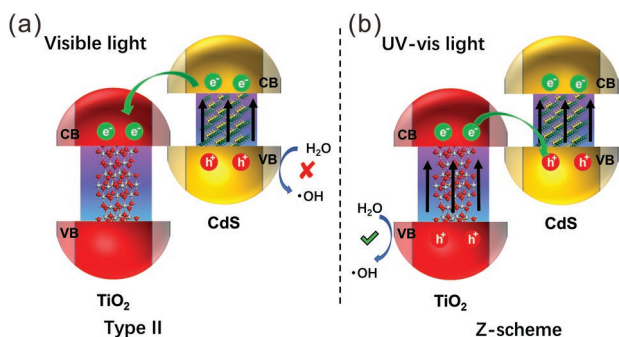


**Figure 6.** a) Photographs of carbon quantum dots with different colors prepared from sodium citrate and citric acid, b) proposed reaction mechanism for glucose photoreforming to produce arabinose and H<sub>2</sub> over CQDs-TiO<sub>2</sub> composite. Reproduced with permission.<sup>[144]</sup> Copyright 2017, Elsevier. c) Photocatalytic mechanism of cellulose reforming in alkaline condition over graphene oxide-dot catalysts. Reproduced with permission.<sup>[146]</sup> Copyright 2017, American Chemical Society.

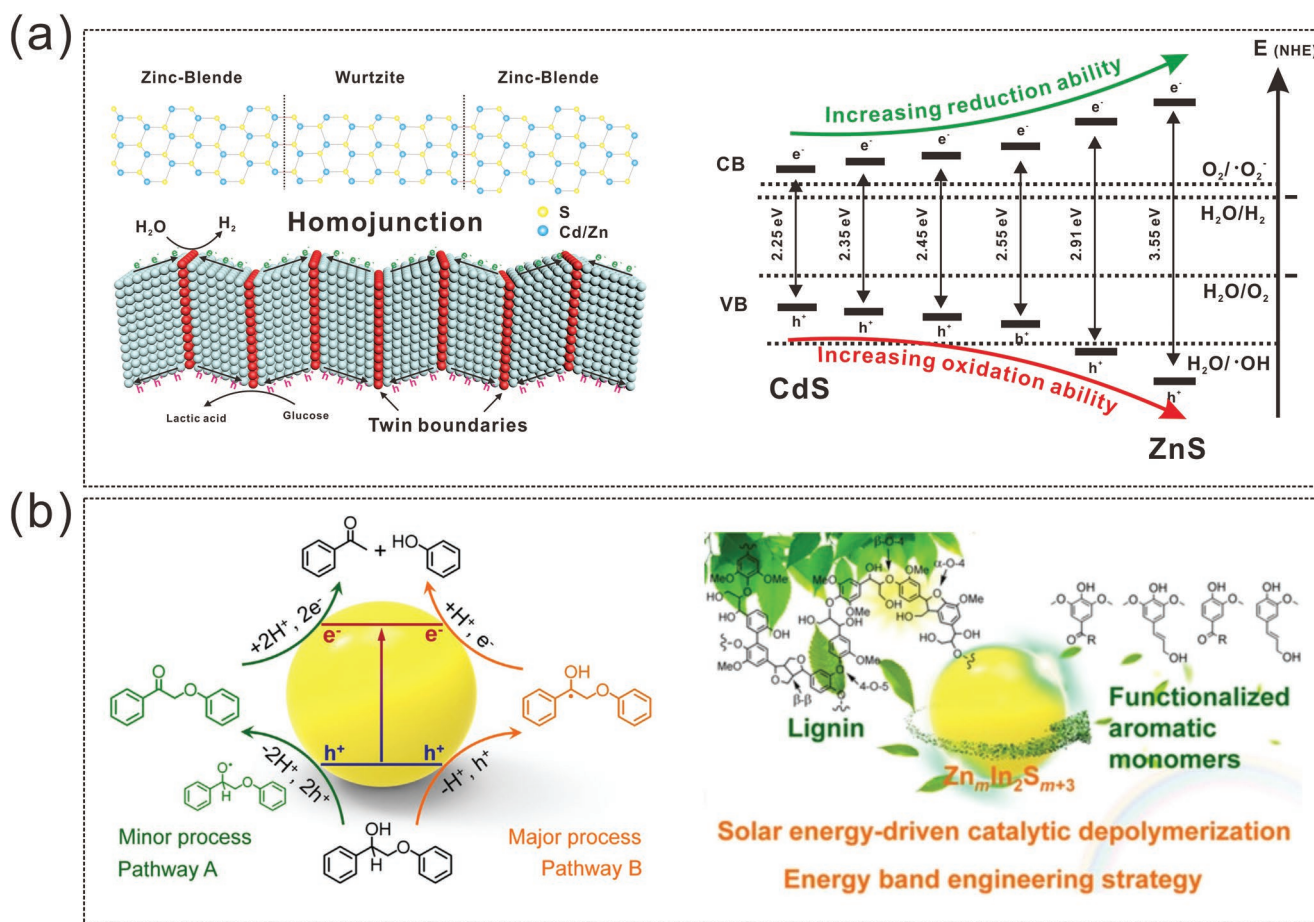
electrons and holes but also regulates the redox ability of charge carriers due to the different CB and VB positions. This system has been used to selectively oxidize alcohols to corresponding aldehydes.<sup>[176–178]</sup> Considering the strong oxidative ability and non-selective property of  $\bullet\text{OH}$  which would be produced from the water oxidation by holes at the VB of TiO<sub>2</sub> under UV light irradiation, the above selective conversion of alcohols is always conducted under visible light condition. In this case, the photogenerated holes of CdS have insufficient ability to produce  $\bullet\text{OH}$  while the photogenerated electrons transferred to the CB of TiO<sub>2</sub> via type II heterojunction have the ability to produce

$\bullet\text{O}_2^-$ , which helps to inhibit the over-oxidation reaction and improve product selectivity.

**Homojunction:** Different from the heterojunction which is formed by combining two individual materials together, homojunction is constructed by pure materials but with different crystalline structure.<sup>[179–181]</sup> Although the formed heterojunction has been revealed to be an efficient and common strategy to improve the charge separation efficiency in photocatalysis, it always shows problems such as lattice mismatch, phase separation, morphological defects, and interfacial impedance.<sup>[182–184]</sup> Homojunction stands out from this point and perfect lattice matching could be formed naturally. The most typical homojunction in photocatalytic applications is the commercial Degussa P25, which contains  $\approx 80\%$  anatase phase (3.2 eV) and  $\approx 20\%$  rutile phase (3.0 eV). The intrinsic bandgap alignment forms the internal electron transfer channel from anatase phase to rutile phase, boosting the photocatalytic activity by increasing the utilization of photogenerated electrons.<sup>[185,186]</sup> Arabinose was selectively produced from glucose photoreforming over carbon quantum dots modified P25 TiO<sub>2</sub>.<sup>[144]</sup> Another typical homojunction constructed by twinning superlattice (TSL) always exists in II–VI and III–V group semiconductors, such as CdS, CdSe, InP, GaN, etc.<sup>[187–189]</sup> The cubic zinc-blende (ZB) and hexagonal wurtzite (WZ) with different bandgap structure can spontaneously form the spatial channel for transferring photogenerated electrons and holes, realizing reduction reaction and oxidation reaction on different location



**Figure 7.** Transfer pathways of photogenerated electrons in TiO<sub>2</sub>-CdS binary system under a) visible light irradiation and b) UV-vis light irradiation.



**Figure 8.** a) Schematic atomic model of a zinc blende (ZB)-wurtzite (WZ) superlattice structure, twin boundaries in homojunction and bandgap structure of  $Zn_{1-x}Cd_x$  solid solutions. Reproduced with permission.<sup>[100]</sup> Copyright 2021, Elsevier. b) Proposed mechanism for  $\beta$ -O-4 bond cleavage in the photocatalytic conversion of lignin over the  $Zn_mIn_2S_{m+3}$  catalyst. Reproduced with permission.<sup>[190]</sup> Copyright 2019, Wiley.

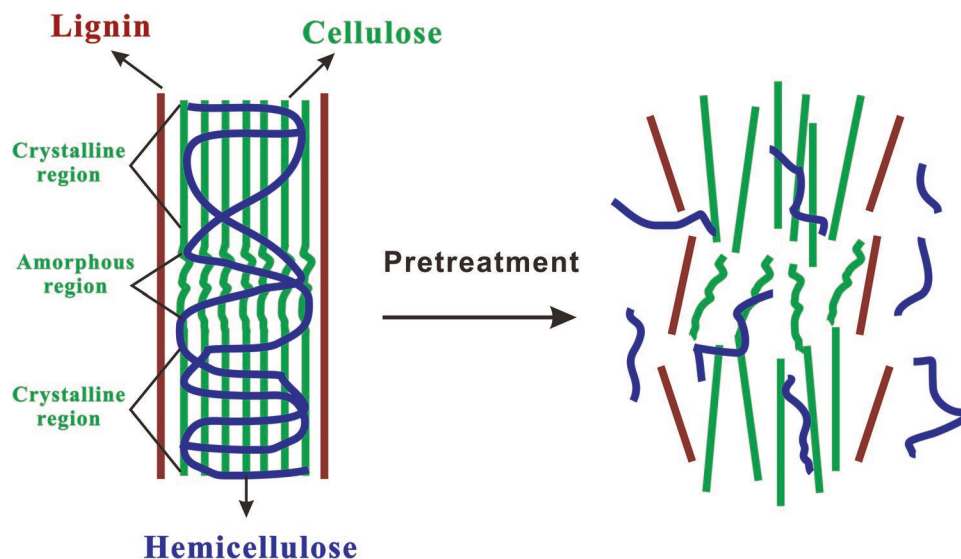
of the photocatalyst (Figure 8a). Metal sulfides with similar lattice parameters such as CdS and ZnS could easily form the solid solution semiconductors, which involve solute atoms dissolving in the solvent lattice while still maintaining the solvent type. This solid solution photocatalysts endow with synergistic effects of homojunction in charge separation and continuously adjustable bandgap structure. The bandgap engineering with different constituent ratio not only modulates redox ability but also realizes the control in incident light utilization (Figure 8b). The synergistic promotion of homojunction and bandgap engineering contributes to glucose photoreforming with hydrogen and lactic acid coproduction.<sup>[101]</sup> With the change of Zn/In ratio, the energy band can also be engineered for zinc-indium-sulfide ( $Zn_mIn_2S_{m+3}$ ) and appropriate energy band structure attributes to the selective cleavage of  $\beta$ -O-4 bond to produce functionalized aromatic monomers from lignin photoreforming under visible light irradiation (Figure 8c).<sup>[190]</sup>

### 2.2.2. Biomass Pretreatment

There have been quantities of research articles that have considered the catalysts factors which could influence the efficiency

of biomass photocatalytic conversion. However, it is apparent that not only the catalysts but also the substrates' physical and chemical characters are essential.<sup>[191,192]</sup> Biomass pretreatment is a required step in biomass bioconversion and thermal chemical conversion to weaken its recalcitrant structure and improve the biomass accessibility to hydrolytic enzymes and thermal conversion catalysts (Figure 9).<sup>[193]</sup> It has been widely reported that the enhanced biomass accessibility is crucial for the improved hydrolytic performance of hydrolytic enzymes thereby achieving the more efficient bioconversion.<sup>[194-196]</sup> Considering the crucial influence of the interaction between biomass and photocatalysts on the efficiency of photocatalytic conversion, it is beneficial for us to learn from the traditional biomass bioconversion process and employ a pretreatment step before the light-driven biomass conversion with the purpose of achieving a desirable photocatalytic conversion of various types of biomass.

Biomass pretreatment methods have generally been categorized into physical, chemical, and biological approaches or a combination of these.<sup>[197]</sup> Physical pretreatment refers to the increase of temperature or pressure to alter the structure of the biomass which leads to decreased biomass recalcitrance. The widely reported physical pretreatment methods include



**Figure 9.** Schematic illustration of lignocellulose pretreatment to reduce the structural recalcitrant.

mechanical, microwave and ultrasound pretreatment, etc. The chemical pretreatment is characterized by the leverage of inorganic or organic compounds to interact with interpolymer or intrapolymer bonds in cellulose, hemicellulose, and lignin which can cause the destruction of the lignocellulosic materials. Extensive research has been focused on the chemical pretreatment approach such as acid pretreatment, alkaline pretreatment, ionic liquids pretreatment, etc. Considering the advantages of both the physical and chemical pretreatments, the combination of these two has attracted widespread attention. An extensive number of the research papers concerning the physio-chemical pretreatment technologies have been published during the last two decades, such as acid or sulfite steam explosion, AFEX, SPROL, and DEL, to name a few.<sup>[198–200]</sup> The biological pretreatment is normally mediated with enzymes/microorganisms and capable of being performed under milder conditions. However, compared with the physical or chemical pretreatment, biological pretreatment is still lack of wide exploration due to its lower efficiency.<sup>[201]</sup> Another potential alternative for biomass pretreatment is to use photocatalysis. The rational design of photocatalyst to generate active radicals could realize the selective conversion of lignin in lignocellulose to achieve the goal of biomass pretreatment.<sup>[80,202,203]</sup>

As described above, learning from the traditional bioconversion where pretreatment is widely employed, the leverage of pretreatment approach to facilitate the biomass photorefinery is promising due to the improved biomass accessibility to the photocatalysts. In previous research, the authors of this paper have accessed the influence of various pretreatment technologies on the efficiency of biomass photoreforming (PR) of wheat straw biomass focusing on the co-production of hydrogen and lactic acid as well as the cellulose conversion.<sup>[114]</sup> A bottom-up approach was employed to systematically investigate the photoreforming performance of glucose, different model celluloses and raw biomass. Regarding the raw biomass photoreforming, several well-developed and more realistic biomass pretreatment strategies were accessed prior to the visible light illumination, including steam pretreatment, phosphoric acid pretreatment,

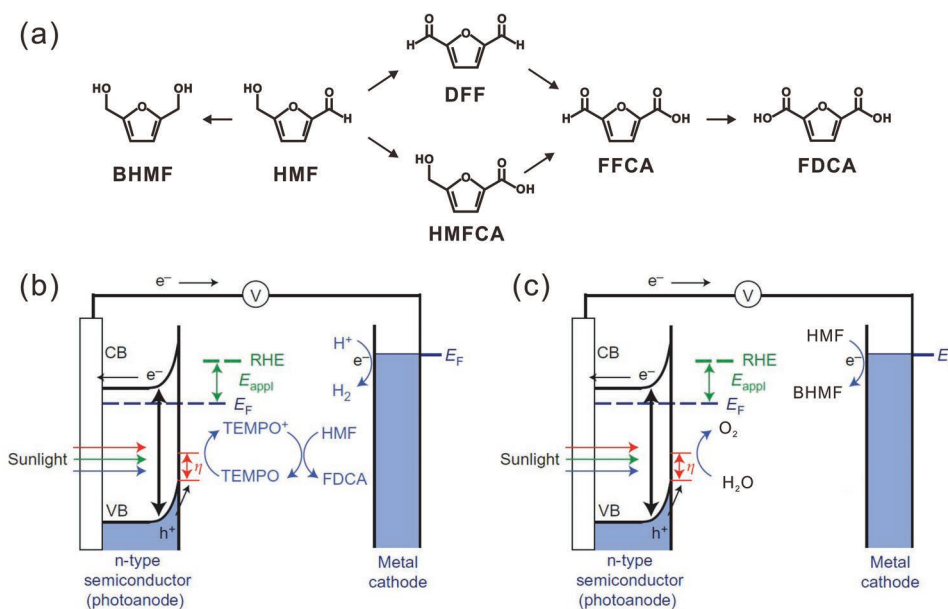
hot water pretreatment, and organosolv pretreatment. The results showed that compared with untreated raw biomass, the biomass subject to pretreatment showed much higher H<sub>2</sub> and lactic acid production as well as cellulose conversion, and the degree of improvement is highly dependent on pretreatment strategies. This paper successfully demonstrated the significant role of pretreatment in developing efficient biomass photoreforming approaches via improving the cellulose and photocatalyst interactions. Another piece of the research article published by Lan et al. claimed ball milling treatment was an effective pretreatment method to improve the photoreforming of cellulose for H<sub>2</sub> production, mainly caused by the decreased particle size. Meanwhile, the ball milling-induced formation of the cellulose II phase from the recrystallization of amorphous cellulose in aqueous media is a crucial factor for the activity of cellulose photoreforming as well.<sup>[204]</sup> Technical lignins were extracted from different biomasses and used as the substrates to evaluate the photocatalytic activity of CdS quantum dots.<sup>[205,206]</sup> The established lignin-first approach demonstrated a good example for monomeric aromatics production from biomass photoreforming.

Along with the rapid growth of people's living demands and the enlarged scale of industrial goods production, municipal solid waste (MSW), a new type of biomass comprising large amounts of lignocellulosic biomass waste (e.g., Packaging paper, tissues, woods, etc.) and starch biomass (e.g., food waste), becomes an emerging challenge for our society. Even though the improvement of industrial processes and changes in consumer behavior might be able to help reduce waste in the future, unlocking the value of waste biomass with clean technologies is also necessary. Photoreforming utilizes MSW as feedstock while producing H<sub>2</sub> production is a promising approach to address the waste and energy issues. Thus far, plenty of published research on MSW has claimed that before utilization in PR, MSW must undergo pretreatment such as crushing, shredding, or chemical pretreatment (e.g., alkaline or acid treatments) to facilitate contact between substrates and photocatalyst during PR thereby increasing the H<sub>2</sub> evolution rate.<sup>[207]</sup>

### 2.2.3. Processing Conditions

Apart from the photocatalyst design to improve the selective biomass photoreforming for both  $H_2$  and valuable chemicals production, the adopted processing conditions such as head-space, solvent, pH, and reactor also play vital effect on the photocatalytic activity.<sup>[208]</sup> Oxygen reduction reaction (ORR) is competitive to the proton reduction for  $H_2$  production. Herein, to achieve the better  $H_2$  generation, non-selective biomass photoreforming is always conducted under inert or vacuum condition. However, to realize the selective biomass photoreforming, the presence of oxygen seems to benefit the substrate conversion.<sup>[209]</sup> One possible reason is the generation of active oxygen species such as superoxide radicals, which facilitates the substrate conversion. It reveals the practical biomass photoreforming for  $H_2$  and value-added chemicals coproduction is a complicated process. The photogenerated electrons not only participate in the proton reduction for  $H_2$  production but also have effect on the substrate conversion in presence of oxygen atmosphere. Besides, some special photocatalysts with the ability to proceed two electron reaction, such as carbon nitride can continuously produce hydrogen peroxide ( $H_2O_2$ ) via 2e-ORR in oxygen atmosphere.<sup>[210,211]</sup> The further decomposition of generated  $H_2O_2$  in presence of reducible metal ions such as  $Fe^{2+}$  will produce  $\bullet OH$  to convert substrate, which is the Fenton reaction pathway.<sup>[212]</sup> Coupling photocatalysis with Fenton reaction is emerging as an alternative approach to realize biomass treatment and valorization.<sup>[213]</sup> Carbon nitride with K and O codopant showed the selective gluconic acid production from glucose photoreforming via the in-situ photo-Fenton-like tandem reaction pathway.<sup>[214]</sup> Apart from the reaction atmosphere, the reactor design is another important parameter to realize selective biomass photoreforming for both hydrogen and value-added chemical production.<sup>[215]</sup> The ideal

reaction pathway for selective biomass photoreforming is the hydrogen production from proton reduction by photogenerated electrons, while the photogenerated holes oxidize biomass substrate into value-added chemicals. From this point of view, one-pot reactor could theoretically achieve this coproduction without any further separation of gaseous and liquid products. However, one-pot reaction suffers from low liquid product selectivity as the photogenerated electron sometimes involves the conversion of liquid products by the formation of superoxide radicals. From this perspective, photoelectrochemical (PEC) reaction stands out in separating reduction reaction and oxidation reaction into two different electrodes.<sup>[216]</sup> By using PEC approach, the hydrogen could be formed at the cathode while biomass oxidation is proceeded at the anode, which is much beneficial for mechanism investigation. 5-hydroxymethylfurfural (HMF) is one of the platform chemicals, which has been regarded as the one of the top 30 chemicals. It could be used as the precursor to prepare many valuable chemicals via reduction or oxidation reactions (Figure 10a). Choi group demonstrated the PEC cell for hydrogen production and biomass valorization.<sup>[217,218]</sup> By using n-type  $BiVO_4$  as the working electrodes, 5-hydroxymethylfurfural (HMF) was oxidized into 2,5-furandicarboxylic acid (FDCA) with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a mediator at the anode and  $H_2$  was simultaneously produced at the metal cathode (Figure 10b). When the working electrode was changed to metal (Ag) cathode, 2,5-bis-(hydroxymethyl)furan (BHMF) could be produced from the HMF reduction reaction while the  $BiVO_4$  as the anode oxidized water into oxygen (Figure 9c). With a proton exchange membrane, the products of oxidation and reduction could be simultaneously separated at two different channels. Selectivity of liquid products is another issue to be considered for reactor design because the liquid products could also be further converted. A flow reactor can timely inhibit the further



**Figure 10.** a) Schematic illustration of HMF conversion into different chemicals. b) Photoelectrochemical TEMPO-mediated HMF oxidation with  $H_2$  coproduction. Reproduced with permission.<sup>[217]</sup> Copyright 2015, Macmillan Publishers. c) Photoelectrochemical HMF reduction with water oxidation. Reproduced with permission.<sup>[218]</sup> Copyright 2016, American Chemical Society.

reaction of intermediates, thus improve the selectivity of some intermediates.<sup>[219–221]</sup>

Besides, some other photocatalysis-based hybrid systems have also developed recently to achieve better performance for biomass valorization and H<sub>2</sub> evolution. Coupling photocatalysis with thermocatalysis has been widely demonstrated for H<sub>2</sub> generation and/or chemicals production from biomass or biomass derivatives.<sup>[222–224]</sup> The common limitation of photo-thermal biomass valorization comes from the low selectivity of liquid chemicals. From this aspect, photobiocatalysis by coupling photocatalysts with enzymes in one system would be an alternative approach to realize high selectivity for biomass conversion.<sup>[225–227]</sup> Lytic polysaccharide monoxygenases (LPMOs) with the copper species as the active sites could be activated by incident light or photocatalysts to degrade recalcitrant cellulose into high-value oligosaccharides and other chemicals.<sup>[228–230]</sup>

### 3. Major Hinders in Biomass Photoreforming

Although non-selective or selective biomass photoreforming shows various advantages in hydrogen and value-added chemicals production, the currently achieved efficiency is very limited due to the low accessibility of lignocellulosic biomass to photocatalyst and lack of dually functional photocatalysts. Lignocellulosic biomass is a multi-component structure that has evolved to provide mechanical and chemical stability to plants. For a typical catalysis process, the diffusion of substrates and products and interaction between substrate and catalyst play vital effect on reaction dynamics.<sup>[231–233]</sup> The complexity in structure and component hampers its solubility in most solvents, making it difficult to have strong interaction with photocatalyst surface. Biomass derivatives with specific molecular structure, functional groups, and smaller size have been extensively investigated by rationally design photocatalyst morphology to enhance the diffusion of substrates and products. In this aspect, hierarchically porous photocatalyst with great mass diffusion stands out in improving the reaction dynamics. Meanwhile, to achieve the photoreforming for raw biomass, pretreatment is also essential to destroy the recalcitrant nature of biomass such as reducing the degree of depolymerization, breaking inter- and intramolecular hydrogen bonds to improve the accessibility of biomass to photocatalysts.

The use of photocatalysts, especially in water, can generate highly reactive radical species leading to a low selectivity. Using biomass and biomass-derived substrates is even more problematic due to the multiple functional groups present. For example, although several works have demonstrated the glucose photoreforming to produce H<sub>2</sub> and arabinose, the selectivity of arabinose gradually decreased with reaction time due to the similarity of arabinose and glucose in structure and functional groups.<sup>[129,144,234,235]</sup> Electronic band structure and photochemical properties can be tuned to regulate the reaction pathway and selectively produce the desired chemicals while sustaining high rates of H<sub>2</sub> production. As the oxidation ability of photocatalyst is mostly related to the valence band position and charge mobility, the bandgap engineering of photocatalysts by changing the components and forming heterojunctions can theoretically realize high liquid product selectivity. Aside from

catalyst design, strategies to tailor reaction conditions have also been successfully applied to control the selectivity to the desired product.<sup>[57]</sup> In this aspect, further mechanistic studies are vital to guide strategies to tune physicochemical parameters of the catalysts and optimal reaction conditions that can improve the overall efficiency.

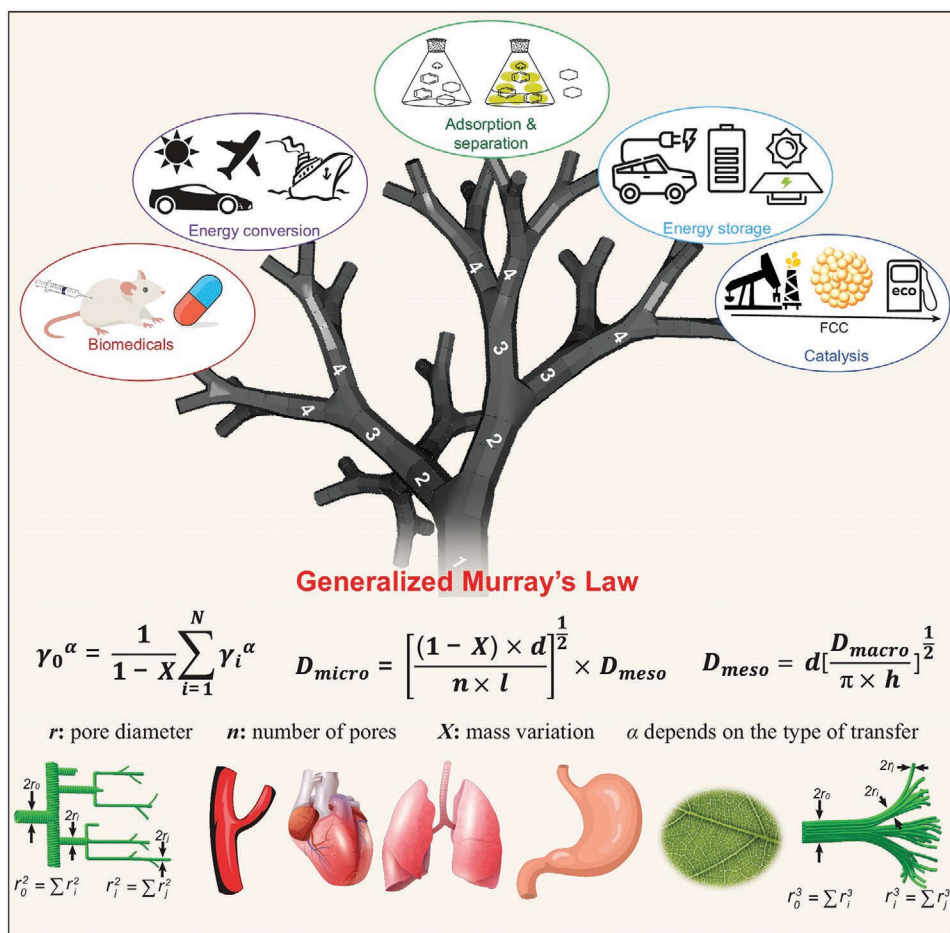
In face to the difficulties presented, we still have a lack of efficient photocatalyst for biomass photoreforming. Not to mention that most investigations on the selective biomass photoreforming toward valuable products and hydrogen production are still on a laboratory scale. To realize scale-up biomass photoreforming, efficient photocatalyst with dual functions for hydrogen production and high selectivity of liquid product is highly desired. Further studies investigating reactor configuration and downstream process are also essential for scaling up biomass photoreforming. Several demonstrations on scale-up biomass photoreforming have already investigated, in which self-designed reactor systems were built and natural solar energy was captured and utilized.<sup>[236–238]</sup> However, the achieved efficiency and product yields are still far from the industrial requirement. The evaluation of separation methods will play an essential role since even when high selectivity is achieved, a wide range of products is generated.<sup>[59]</sup> Concepts such as the lignin-first approach, where native lignin structure and polysaccharides preservation is considered upfront, are valuable strategies to promote integral use of biomass and to reduce separation cost.<sup>[206]</sup>

### 4. Advantages of Hierarchically Porous Materials

To address the reaction dynamics, adopting hierarchically porous materials with excellent mass diffusion ability and light harvesting is one of the best choices for photocatalyst design. Constructing photocatalysts with inter-connected porous structure based on the law of hierarchy can maximize the substrate and product diffusion. Combing this hierarchical porosity with dual functions can theoretically improve biomass photoreforming activity for coproduction of hydrogen and value-added chemicals. The obvious advantages of hierarchically porous photocatalysts are introduced and discussed accordingly in following section.

#### 4.1. Excellent Mass Diffusion to Boost Reaction Kinetics

Hierarchically porous materials with a highly inter-connected and well-organized porous architecture at different scales are endowed with excellent efficiency in mass transfer. The macropore benefits the easy diffusion of macromolecule and light harvesting.<sup>[93,239]</sup> The mesopore provides improved accessibility of substrate to active sites on the surface of photocatalysts.<sup>[240]</sup> The micropore allows for size/shape selectivity or confinement.<sup>[241]</sup> Considering the large size of biomass as substrate, designing photocatalysts with macro- and mesoporous structure facilitates photocatalytic activity. While for small biomass derivatives or model component such as glucose and furfural, the presence of micropore will have a major effect on providing active sites or confinement to selectively produce



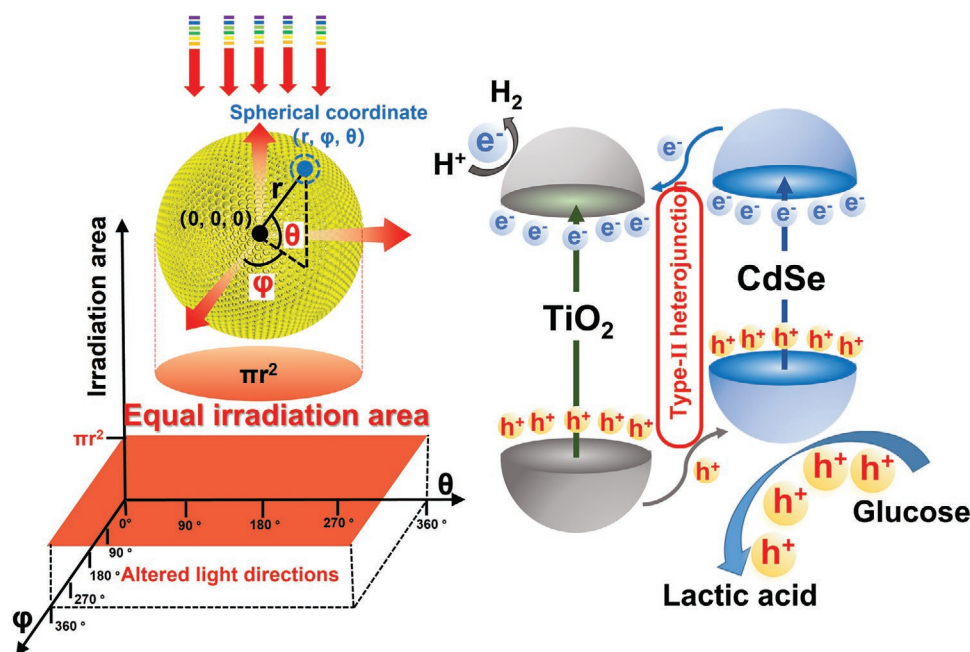
**Figure 11.** Schematic illustration of the applications of a model hierarchically porous Murray material. Reproduced with permission.<sup>[242]</sup> Copyright 2020, Oxford Academic.

liquid or gaseous products. The coordinated matching of porosity in different scales to maximize the mass diffusion performance is based on the generalized Murray's law by taking the substance exchange on surface and mass variation into consideration (Figure 11).<sup>[242,243]</sup> The quantitative relationship among different pore diameters can be established to realize the maximum efficiency in mass transportation. The well-defined microporous ZnO nanoparticles assembling into 3D architecture with enhanced mass transfer in heterogeneous reaction system successfully demonstrated the feasibility of this "learning from nature" strategy for efficient catalyst development.<sup>[244]</sup>

#### 4.2. Light Harvesting to Improve Solar Energy Utilization

Light absorbance as the first step of photocatalysis is crucial in the whole photocatalytic processes. Most of the pristine semiconductor photocatalysts suffer from low light absorbance efficiency due to the limited interaction time of incident photons and photocatalysts. Considering the slow reaction kinetics, biomass photoreforming process requires higher efficiency in light utilization to guarantee photocatalytic activity. From this

aspect, the natural advantage of hierarchically porous materials in light harvesting by multiple scattering effect is beneficial for both non-selective and selective biomass photoreforming.<sup>[245]</sup> More importantly, the presence of slow photon effect by finely designing and fabricating three-dimensionally ordered macroporous (3DOM) structure is another well-investigated approach to improve photon utilization by photocatalysts.<sup>[246–248]</sup> Colloid template method is the common strategy to prepare three dimensionally porous structure, especially for the 3DOM structure.<sup>[249]</sup> The disordered 3D structure improves light harvesting mainly by multiple scattering effect while the 3DOM structure facilitates light harvesting by both multiple scattering and slow photon effect, which has been systematically investigated by Su's group.<sup>[93,250–255]</sup> By changing the diameter of polymeric spheres, the edges of reflectance spectra match with the intrinsic bandgap absorption of semiconductors, realizing slow photon effect and enhancing photocatalytic performance. According to the reflectance spectra, there would be two types of slow photon effects. For the slow photons with lower energy (longer wavelength)-the case of red-edge slow photon effect, these photons interact with high dielectric constant part (skeleton components). While for the slow photons with higher energy (shorter wavelength)-the case of blue-edge slow photon



**Figure 12.** Schematic illustration of  $\text{TiO}_2\text{-CdSe}$  with holo-symmetrically spherical photonic crystal structure for photocatalytic conversion of glucose into lactic acid along with  $\text{H}_2$  coproduction. Reproduced with permission.<sup>[259]</sup> Copyright 2022, Chinese Chemical Society.

effect, the slow photons concentrate in the low dielectric constant part (air in most cases). Commonly thinking that the red-edge slow photon effect should endow photocatalyst with better activity as the photocatalyst material interacts with these slow photons. However, a series of experimental and theoretical investigations revealed the better photocatalytic performance was achieved for blue-edge slow photon effect rather than the red-slow photon effect.<sup>[93,255]</sup> Aside from the 3DOM structure in long-range order, a newly emerging photonic crystal-amorphous photonic crystal with short-range order also possesses photonic band gap and amplify the light harvesting by both slow photon effect and multiple reflectance.<sup>[256–258]</sup> Spherical photonic crystal with 3DOM structure has been recently developed to address the dependence on incident light angle of slow photon effect. The holo-symmetrically spherical photonic crystal structure is endowed with strong light trapping ability and uniform mass diffusion property. Combining the advantages of spherical photonic crystal structure and heterojunction, the well-designed materials exhibited excellent performance for glucose conversion into lactic acid along with sustainable  $\text{H}_2$  production (Figure 12).<sup>[259]</sup>

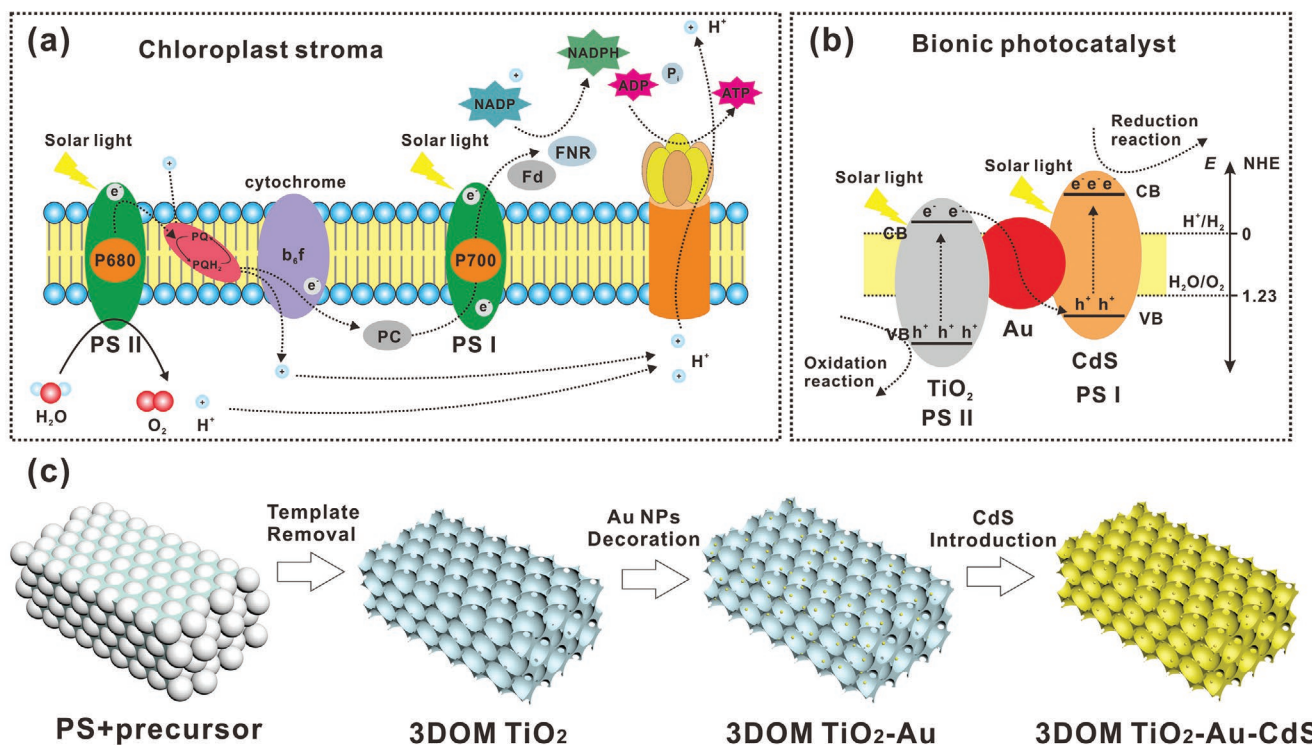
#### 4.3. Large Surface Area to Provide Abundant Active Sites

The exposure of active site is a key factor for the reaction and more active sites increase the possibility of molecular collision to boost the photocatalytic activity. Large surface area can provide more exposure of active site and another advantage of hierarchically porous structure is that it can endow materials with large surface area, especially when the hierarchically porous material is constructed by micro-mesopore. Although micropore is believed to have negligible contribution to convert

biomass or some biomass derivatives with large molecular size directly due to the mismatch in diameter, it greatly increases the photocatalytic hydrogen production from small model component of biomass such as glucose.<sup>[260,261]</sup> During the selective biomass photoreforming, some small molecules such as formic acid and  $\text{CO}_2$  are generated. The presence of microporous structure provides great catalytic sites for these small molecules' conversion. For example, the produced formic acid during the Ruff degradation process of monosaccharides could further be converted into  $\text{H}_2$  with the contribution of micropore. Considering the diameter of biomass, the photocatalyst design with hierarchical meso-macropore would be a choice in priority. The presence of macropore facilitates light harvesting and mass diffusion while the mesopore increases the exposure of reactive site, thus improves photocatalytic activity. Our group conducted a series of investigation about using hierarchically porous materials for selective biomass photoreforming.<sup>[129,209,262]</sup> Inspired by the natural photosynthesis, a hierarchically 3DOM  $\text{TiO}_2\text{-Au-CdS}$  ternary photocatalyst was well designed and fabricated (Figure 13). It possessed both ordered macropore and accumulated mesopore. The presence of 3DOM structure improved light absorption in visible light region and diffusion of cellobiose. The mesopore provided high specific surface area and reactive sites to produce more active oxygen species, leading to simultaneous production of hydrogen and valuable chemicals such as gluconic acid, glucaric acid, and arabinose.

#### 4.4. Confinement Effect for Fine Catalyst Preparation

The quantum size effect is an efficient strategy to tailor the redox ability of semiconductor photocatalysts.<sup>[263]</sup> However, it is challenging to directly prepare photocatalysts with desired



**Figure 13.** Schematic illustration of a) photosynthesis process in nature plant, b) spatial separation of photogenerated electrons and holes, c) preparation of 3DOM TiO<sub>2</sub>-Au-CdS ternary photocatalyst. Reproduced with permission.<sup>[209]</sup> Copyright 2021, Elsevier.

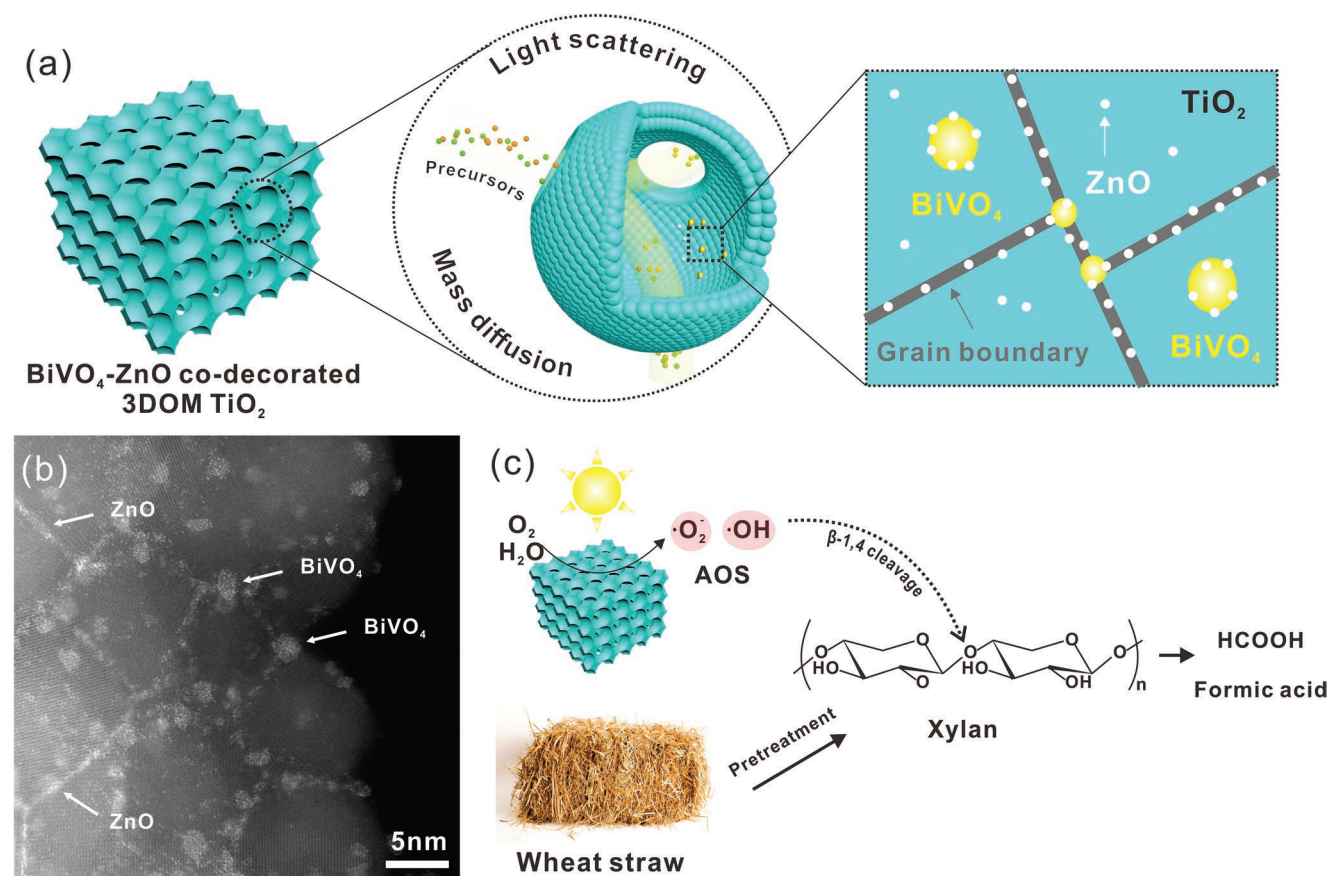
quantum size. The confinement effect of hierarchically porous structure provides an alternative idea to realize the fine regulation on the size of semiconductor photocatalysts. The confinement effect of hierarchically porous materials has well demonstrated in other applications aside from photocatalysis, such as lithium-sulfur batteries. Wang et al. revealed the construction of micro-macroporous carbon materials significantly enhanced the electrochemical properties. The presence of macropore offered plenty channels to improve the diffusion of sulfur and electrolyte to micropore while the micropore trapped the polysulfides to suppress the shuttle effect during the long-time cycling test, leading to the high stability of the samples.<sup>[264]</sup> We also revealed the confinement effect of 3DOM structure with accumulated mesopores. The well-fabricated TiO<sub>2</sub> with hierarchical 3DOM structure not only facilitated light harvesting but improved the fast diffusion of precursors of BiVO<sub>4</sub> and ZnO. The presence of accumulated mesopores at the grain boundaries trapped the precursors and formed BiVO<sub>4</sub> nano dots and ZnO clusters.<sup>[262]</sup> The quantum sized BiVO<sub>4</sub> along with the formation of heterojunction in the composites exhibited excellent activity to break  $\beta$ -1,4-glycosidic linkages of xylan in hemicellulose from wheat straw to produce xylose and formic acid (Figure 14). The confinement effect of hierarchically porous materials not only helps to prepare specific photocatalysts but also provides shape-selective catalysis. Microporous ZSM-5 zeolites showed high selectivity of phenol and propylene from lignin-derived 4-*n*-propylphenol with the synergistic effect of strong Lewis/Brønsted acid sites and transition state shape selectivity.<sup>[265]</sup> Another new type of hierarchically porous photocatalyst-covalent organic frameworks (COFs)

and/or metal-organic frameworks would show potential application on biomass photoreforming due the well-ordered structure and regulable apertures, leading to the easily tailorable for shape-selective catalytic reactions.<sup>[266]</sup> Carbazolic copolymers (CzCPs) with confined shape-selective property showed photocatalytic oxidation of  $\beta$ -O-4 linkage in lignin.<sup>[267]</sup> Although the confinement effect of hierarchically porous structure in biomass photoreforming has been demonstrated from photocatalyst preparation and shape-selective reaction, the application is still in the preliminary stage with great potential.

## 5. Current Applications of Biomass Photoreforming by Hierarchically Porous Materials

Hierarchically porous materials as photocatalysts possess some specific advantages for solar-driven reactions, which has been applied for different applications such as hydrogen production, CO<sub>2</sub> reduction, and wastewater treatment. However, as the newly emerging photocatalytic application, non-selective and/or selective biomass photoreforming by using hierarchically porous materials is still limited but with great potential. Our primary exploration revealed the feasibility of using hierarchically porous materials as photocatalysts for biomass valorization due to the synergistic promotion by light harvesting, mass diffusion, large surfaces, confinement effect, etc. The most important advantage of hierarchically porous structure in biomass photoreforming is the favorable mass diffusion, which





**Figure 14.** a) Schematic illustration of the confined synthesis of composite photocatalyst, b) HR-TEM image of the as-fabricated photocatalyst (dotted white circles represent  $\text{BiVO}_4$  nanodots and solid white circles represent  $\text{ZnO}$  clusters), c) proposed mechanism of wheat straw photoreforming into formic acid. Reproduced with permission.<sup>[262]</sup> Copyright 2021, The Royal Society of Chemistry.

greatly improves the transportation of biomass or biomass derivatives to the reactive sites of photocatalysts. Jin et al. developed a hierarchically porous  $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}/\text{CA}$  (CA: carbon aerogel) composite as efficient photocatalyst to selective production of lactic acid from pentoses and hexoses oxidation.<sup>[268]</sup> The carbon aerogel as the flexible framework provided inter-connected porous structure, which was beneficial for light harvesting and easy diffusion of substrates. Jin et al. fabricated a hierarchically hollow  $\text{WO}_3$  microspheres, which was constructed by self-interconnected nanosheets, for selective conversion of biomass-derived alcohols into carbonyl chemicals via photocatalytic process.<sup>[269]</sup> The enhanced photocatalytic performance was ascribed to the light harvesting via multiple light reflections by hierarchical spherical cavity and surface oxygen vacancies. Recently, semiconducting porous organic polymers including covalent organic frameworks (COFs), covalent triazine frameworks (CTFs) and conjugated microporous polymers (CMPs) as photocatalysts have also been applied to produce hydrogen from biomass photoreforming. Guan et al. reported the synthesis of a CTFs constructed by benzyl halide monomers, which exhibited considerable hydrogen evolution from glucose photoreforming.<sup>[261]</sup> Seadira et al. prepared a nanostructured  $\text{TiO}_2$  hollow spheres as the photocatalyst for hydrogen production from glycerol.<sup>[270]</sup> The improved hydrogen production activity was attributed to the high surface area and light harvesting due

to the hierarchically porous structure. Carbon nitride is another typical photocatalyst material, which has already been widely investigated for different applications including biomass photoreforming.<sup>[271,272]</sup> With the rational material design, carbon nitride based materials could be endowed with hierarchically porous structure and they exhibit potential application in selective biomass photoreforming.<sup>[108,109,273,274]</sup> Although few investigations on using hierarchically porous catalysts for biomass photoreforming have been reported, it is believed to have bright prospects considering the significant features of hierarchically porous photocatalysts for the valorization of complex biomass.

## 6. Conclusions and Perspectives

In summary, both non-selective biomass photoreforming for hydrogen production and selective biomass photoreforming for simultaneous production of hydrogen and value-added chemicals are highly attractive but challenging. This present article reviewed the recent progress of biomass photoreforming and summarized the rational design of photocatalyst to efficiently achieve biomass photoreforming process. For non-selective biomass photoreforming to produce hydrogen, major challenges come from the complex constitute and structure of biomass, leading to the slow reaction kinetics. Photocatalyst design to

realize efficient separation of photogenerated electrons and holes is in priority to boost hydrogen production efficiency. In this case, biomass is just the substitute of traditional sacrificial agent to provide electrons and protons. While for selective biomass photoreforming, the oxidation ability and specific reactive sites should be considered when designing dually functional photocatalysts to achieve selective production of value-added chemicals along with hydrogen production. In this case, more complex reaction system and functional photocatalysts are necessary to reduce recombination of photogenerated charge carriers and control reaction process. For both non-selective and selective biomass photoreforming, the light harvesting and mass diffusion of photocatalysts are the crucial to maintain photocatalytic activity. From this aspect, hierarchically porous materials stand out to improve light absorption efficiency via slow photon effect and multiple scattering of incident light, and improve reaction dynamics via easy transportation of substrate to active sites. Besides, other features of hierarchically porous materials such as large specific surface area and confinement effect also endow photocatalysts with enhanced activity. Although few investigations have been reported by using hierarchically porous photocatalysts for biomass photoreforming, rational design of photocatalysts to improve light absorption, charge separation, substrate diffusion based on hierarchically porous structure holds great potential in biomass photoreforming. Detailed directions of dually functional photocatalyst design could refer to following strategies. 1) Heterojunction or homojunction based on hierarchically porous structure. Although hierarchically porous structure can facilitate the substrate diffusion and improve light absorption efficiency, the total efficiency of biomass photoreforming is still mainly limited by the separation of photogenerated electrons and holes, which is the critical factor of internal quantum efficiency. Constructing channels for spatial separation of electrons and holes is preferable for photocatalyst design. Heterojunction and/or homojunction are still in high priority to boost the photocatalytic efficiency for biomass photoreforming. 2) Selective generation of active species. The presence of oxygen competes with hydrogen production as it also reacts with electrons via oxygen reduction reaction (ORR). However, many investigations have revealed the positive effects of oxygen on selective conversion of biomass or biomass derivatives. For example, the production of  $\blacksquare\text{O}_2^-$  is the key factor for glucose oxidation into gluconic acid. However, the derivatization of  $\blacksquare\text{O}_2^-$  into  $\blacksquare\text{OH}$  radicals and excess concentration of these active oxygen species will lead to the overoxidation of substrates into  $\text{CO}_2$ , thus reducing the selectivity of valuable chemicals. Bandgap engineering, oriented surface vacancies and heterojunctions are the preferred strategies to finely regulate the oxidation and reduction ability of photocatalyst to selectively produce required active species with proper concentration, which facilitates to maintain the liquid product selectivity. 3) Biomass pretreatment to improve the accessibility. Even with the help of hierarchically porous structure in mass diffusion, the recalcitrant nature of biomass greatly limits the interaction with photocatalyst. Destroying the inter- and intramolecular hydrogen bonds, and reducing the condensation via biomass pretreatment is an alternative to improve the activity of biomass photoreforming. 4) Synergistic promotion with other technology. Biomass photoreforming

holds promising prospect, but it is still in the early-stage investigation and most of the reported works are performed in a laboratory scale as the achieved efficiency is limited. Coupling photoreforming with other processes such as thermocatalysis, electrocatalysis and bioprocessing is one of best choices to improve the intrinsic activity for biomass valorization to produce hydrogen and valuable chemicals. Considering the significant advantages of hierarchically porous structure, photocatalyst design based on hierarchically porous structure is in high priority to boost the activity for biomass photoreforming. With the rational material design, it will also be feasible to realize the selective conversion of biomass or biomass derivatives by using the specific features of hierarchically porous structure, such as shape-selective catalysis. Last but not the least, theoretical models and principles are still lacking for the biomass photoreforming by hierarchically porous structure. More insight investigations should be performed to establish the theory on highly efficient conversion of biomass to fuels and chemicals by hierarchically porous photocatalysts.

## Acknowledgements

This work is financially supported by the Canada First Research Excellence Fund (CFREF), Major Program of the National Natural Science Foundation of China (22293020, 22293022).

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

biomass photoreforming, hierarchically porous photocatalysts, hydrogen, value-added chemicals

Received: January 25, 2023

Revised: March 8, 2023

Published online: April 7, 2023

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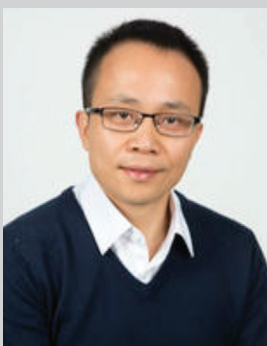
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