PERSPECTIVE

Photoreforming of lignocellulose into hydrogen

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The naturally plentiful, clean, and sustainable biomass resource has the ability to partially replace the limited supply of fossil fuels as a feedstock for the long-term, sustainable production of high-value chemicals and fuels. Meantime, the straightforward, gentle, and ecologically friendly photocatalytic technique seems to be a novel line of inquiry for the conversion of lignocellulose into hydrogen and other fuels. In this perspective, the photoreforming of lignocellulose into H_2 including their fundamentals, some typical examples, and significant scientific discussion are rigorously examined.

INTRODUCTION

The scientific community has an urgent need to find a sustainable energy source because of the rising CO_2 emissions and climate change. Lignocellulose, the most abundant renewable resource, offers the opportunity to produce value-added chemicals and meet rising energy demands in an environmentally friendly manner. An emerging method for producing clean and renewable H_2 from lignocellulose is photoreforming technology. This method combines photocatalytic H_2 production at room temperature and pressure with photooxidation of renewable biomass. Compared to water splitting, lignocellulose conversion uses less energy and produces high-purity H_2 without generating O_2. Direct photoreforming of unprocessed lignocellulose into H_2 offers the potential to produce high-value materials from inexpensive and renewable biomass. In this perspective, the photoreforming of lignocellulose into H_2 including their fundamentals, some typical examples, and significant scientific discussion are exhibited.

FUNDAMENTALS OF PHOTOREFORMING OF LIGNOCELLULOSE

Photocarriers can be produced by the semiconductor photocatalyst when it undergoes exposure to an appropriate light source that has photon energy higher than the associated bandgap energy (E_g) (Figure 1A), which can be used for the activation of photocatalytic reactions. Protons can be reduced to generate H_2 through the electrons in the conduction band (CB), and meantime lignocellulose acting as sacrificial agents can be oxidized through the holes on the valence band (VB) to obtain value-added fuels. Numerous oxygen-containing functional groups exist in lignocellulose, which possess abundant lone pair electrons in nonbonding orbitals, and can effectively eliminate holes in the VB to produce electron-deficient species. In aprotic or nitrate environments, these species can also lead to simultaneous oxidation and H_2 production. Besides, reactive oxygen species (ROS) including hydroxyl radicals (•OH) and superoxide anions ($O_2^{\bullet-}$) are also produced during the photocatalytic process, which causes the oxidation of lignocellulose. Nevertheless, lignocellulose is more likely to overoxidize into CO_2 than valuable compounds. Therefore, it is essential to restrict the overoxidation of lignocellulose intermediates to increase the selectivity of photooxidation products. Additionally, the lignocellulose molecules can be also oxidized by holes directly or indirectly through ROS produced by electrons and holes, e.g., $O_2^{\bullet-}$, O_3^-, •OH, etc. Therefore, adjusting the generation of ROS through tuning the structure of photocatalysts, reaction atmosphere, and solvent to obtain higher activity and selectivity is vital during the photoreforming of lignocellulose into H_2.

PHOTOREFORMING OF LIGNOCELLULOSE COMPONENTS

Research on photoreforming mainly concentrated on producing H_2 from lignocellulose feedstocks. A brief overview of the photoreforming of several lignocellulose components, such as sugars, cellulose, lignin, and oligo- and polysaccharides, will be provided in the section that follows.

Sugars

Sugars are commonly researched as exemplary substrates for the photoreforming of lignocellulose into H_2. For example, Teng and co-workers used sulfur and nitrogen codoped graphene oxide dots (SNGODs) to photoreform of glucose into H_2. In order to repair the vacancies in graphene, tetravalent nitrogen was introduced via codoping into the cardinal plane of the material. Similarly, steam sterilization produced a conjugation between nitrogen nonbonding states and the graphitic-p orbital through inserting periphery amide and amino groups. Consequently, under visible light illumination for over 80 hours, the produced SNGODs photocatalysts might catalyze the continuous production of H_2 from aqueous solutions of glucose.[1] Moreover, the produced SNGODs photocatalysts were also used for the reforming of xylose into C_5-C_1 species and H_2.[2] Hu and co-workers[3] reported the photoreforming of glucose into H_2 and arabinose with enhanced selectivity employing carbon quantum dots modified TiO_2 composites (CQDs/TiO_2). The prepared CQDs/TiO_2 composites with specific colored carbon quantum dots could significantly increase the selectivity of the glucose to arabinose conversion (~75%) and the H_2 production rate of 2430 μmol g^{-1} h^{-1} in water. Single atom catalysts (SACs) also displayed superior photoreforming of glucose into H_2 performance.[4]

Oligosaccharides and polysaccharides

Oligosaccharides and polysaccharides (i.e., cellobiose, maltose, sucrose, lactose, etc) typically exhibit lower photoreforming effectiveness than monosaccharides because of their larger molecular weights and stable hydrogen bonding structure. A H_2 production rate of 3096 μmol g^{-1} h^{-1} was achieved by photoreforming of sucrose over Pd/TiO_2.[5] Amazingly, when using xylan as substance, and an unprecedented H_2 production rate of 13533.8 μmol g^{-1} h^{-1} was achieved over atomically dispersed Zn atoms on carbon nitride (Zn-mCN).[6] Meantime, a large amount of lactic acid is also co-produced. When using monosaccharides including xylose and galactose as substance, H_2 production rate of 165.8 and 233.3 μmol were obtained, respectively over cyanamide-functionalized carbon nitride ($^{NCN}CN_x$).[7] The documented room-temperature photoreforming method functions in a safe aqueous environment (pH=2-15) devoid of hazardous substances.

Cellulose

Because of cellulose's compact tertiary structure, the kinetics of cellulose photoreforming are more difficult than those of oligosaccharides, although the thermodynamics are still similar. Reisner and co-workers[8] reported the photoreforming of cellulose to H_2 employing CdS/CdO_x in alkaline aqueous solution. The H_2 production rate could reach 2400 μmol g^{-1} h^{-1} using 50 mg/ml of *α*-cellulose. Huang and co-workers[9] reported a hollow structural S-scheme heterojunction of ZnSe and oxygen vacancy enriched TiO_2 (h-ZnSe/Pt@TiO_2), which was used for the effective photoreforming of cellulose for H_2 of 374 μmol g^{-1} h^{-1} in pure water for continuous 300 h irradiation. These noteworthy development raises the possibility that photoreforming of cellulose reforming will be used in the future as an economical and environmentally beneficial method of utilizing solar energy.

Lignin

Photoreforming of lignin is greatly limited by its high stability and brown color when compared to other lignocellulose components. Visible-light driven lignin photoreforming was achieved through utilizing CdS/CdO_x (260 μmol g^{-1} h^{-1})[8] and low-bandgap Si flakes/Ni-coordinated N-doped graphene quantum dots SiF/Ni-NQGDs (14200 μmol g^{-1} h^{-1}).[10] As shown in Figure 1B, the record-high H_2 production activity and excellent stability can be achieved

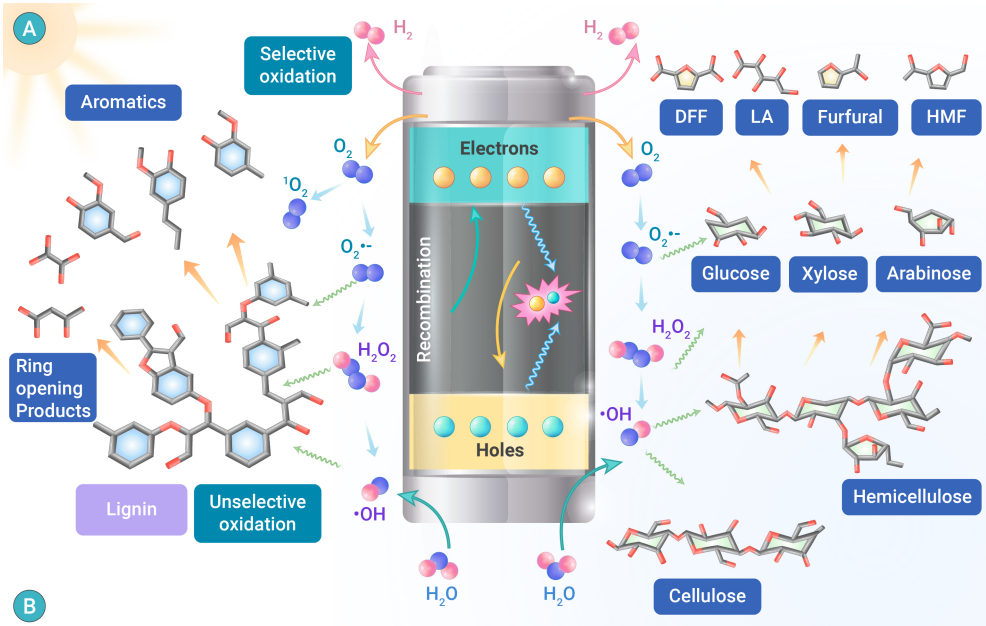

Figure 1. (A) Schematic illustration of photoreforming of lignocellulose. (B) Selected examples of photoreforming of lignocellulose into H_2.

Selected examples of photoreforming of lignocellulose into H_2

Substrate	Catalyst	H_2 production rate (μmol g^{-1} h^{-1})	Apparent quantum yield (%)	Conditions	Light source	Ref
Glucose	SNGODs	125	7.4 (420 nm)	0.35 mol L^{-1} of glucose	300 W Xe lamp	1
Xylose	SNGODs	58.3	6.8 (420 nm)	5 wt% of xylose	Solar simulator (100 mW cm^{-2})	2
Glucose	CQDs/TiO_2	2430	-	2 g/L of glucose solution	300 W Xe lamp	3
Glucose	Pt-MCNN	60	-	Glucose solution (96 ppm)	300 W Xe lamp	4
Sucrose	Pd/TiO_2	3096	-	-	Solar simulator	5
Xylan	Zn-mCN	13533.8	-	1 wt% of Xylan	10 W VLight	6
Xylose Galactose	$^{NCN}CN_x$	165.8 233.3	-	-	Xe lamp (100 mW cm^{-2})	7
α-Cellulose Lignin Paper Grass	CdS/CdO_x	2400 260 1340 1280	-	50 mg/ml of α-cellulose 0.25 mg/ml of lignin 50 mg/ml of printed paper 50 mg/ml of grass	Solar simulator (100 mW cm^{-2})	8
α-Cellulose	h-ZnSe/Pt@TiO_2	374	-	-	300 W Xe lamp	9
Lignin	SiF/ Ni-NQGDs	14200	-	1 mg/ml of kraft lignin	Solar simulator (100 mW cm^{-2})	10

by SiF/Ni-NQGDs. This method offers significant perspectives into the development of composite photocatalysts for lignocellulose photoreforming and effective H_2 generation.

CONCLUSION

A promising strategy for producing fuels and feedstock chemicals in a sustainable manner is photoreforming of lignocellulose. Although the efficiency of this room-temperature approach of producing clean H_2 is still not up to par with traditional procedures, it is still far simpler than thermochemical strategies. Future research should concentrate on developing photocatalysts with many active sites and narrow E_g that can effectively photoreform lignocellulose in the presence of sunlight. Meantime, in order to increase selectivity towards high-value compounds and reduce the needed driving force, customized biomass oxidation catalysts will be required. In addition, the researches regarding native lignocellulose are in their preliminary stage. Most of the current studies use model compounds such as sugar and furfural compounds instead of real lignocellulose. This is also a crucial point. The mechanism of the photoreforming of lignocellulose is also unclear, and it is urgently needed to be revealed by some advanced characterizations such as *in-situ* technologies and theoretical calculations. In eventually, the secret to turning photoreforming into a scalable and profitable process may lie in combining it with other solar fuel generation systems such as solar- driven H_2O_2 production, CO_2 conversion, N_2 fixation, etc and employing low-energy photons that are inappropriate for water splitting.

REFERENCES

1. Nguyen, V.-C., Ke, N.-J., Nam, L.D., et al. (2019). Photocatalytic reforming of sugar and glucose into H_2 over functionalized graphene dots. J. Mater. Chem. A **7**: 8384–8393. DOI: 10.1039/C8TA12123K.
2. Nguyen, V.-C., Sanoe, M., Putri, N.P., et al. (2024). Co-catalyst design to control charge transfer and product composition for photocatalytic H_2 production and biomass reforming. Sustain. Energy Fuels **8**: 1412–1423. DOI: 10.1039/D3SE01544K.
3. Zhao, H., Yu, X., Li, C.-F., et al. (2022). Carbon quantum dots modified TiO_2 composites for hydrogen production and selective glucose photoreforming. J. Energy Chem. **64**: 201–208. DOI: 10.1016/j.jechem.2021.04.033.
4. Zhang, J., Xu, X., Liu, Y., et al. (2023). Platinum single atoms anchored on ultra-thin carbon nitride nanosheets for photoreforming of glucose. Surf. Interfaces **42**: 103423. DOI: 10.1016/j.surfin.2023.103423.
5. Beasley, C., Gnanamani, M.K., Qian, D., et al. (2021). Photocatalytic reforming of sucrose and dextrose for hydrogen production on Pd/TiO_2. ChemistrySelect **6**: 6512–6524. DOI: 10.1002/slct.202101277.
6. Ma, J., Li, X., Li, Y., et al. (2022). Single-atom zinc catalyst for co-production of hydrogen and fine chemicals in soluble biomass solution. Adv. Powder Mater. **1**: 100058. DOI: 10.1016/j.apmate.2022.100058.
7. Kasap, H., Achilleos, D.S., Huang, A., et al. (2018). Photoreforming of lignocellulose into H_2 using nanoengineered carbon nitride under benign conditions. J. Am. Chem. Soc. **140**: 11604–11607. DOI: 10.1021/jacs.8b07853.
8. Wakerley, D.W., Kuehnel, M.F., Orchard, K.L., et al. (2017). Solar-driven reforming of lignocellulose to H_2 with a CdS/CdO_x photocatalyst. Nat. Energy **2**: 17021. DOI: 10.1038/nenergy.2017.21.
9. You, Y., Chen, S., Zhao, J., et al. (2024). Rational design of S-Scheme heterojunction toward efficient photocatalytic cellulose reforming for H_2 and formic acid in pure water. Adv. Mater. **36**: 2307962. DOI: 10.1002/adma.202307962.
10. Choi, Y., Choi, S., Lee, I., et al. (2023). Solar biomass reforming and hydrogen production with earth-abundant Si-based photocatalysts. Adv. Mater. **35**: 2301576. DOI: 10.1002/adma.202301576.

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Initiation and conceptualization: G.L. Methodology and experiment design: G.L. and M.W. Investigation: G.L. and M.W. Funding acquisition: G.L. and M.W. Project administration: G.L. and M.W. Supervision: G.L. Writing - original draft: G.L. Writing - review and editing: G.L. and M.W.

DECLARATION OF INTERESTS

The authors declare no competing interests.

ETHICAL STATEMENT AND PATIENT CONSENT

Not applicable.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.