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Alternatives to water oxidation in the photocatalytic water splitting reaction for solar hydrogen production

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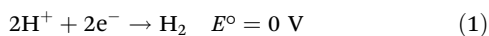
The photocatalytic water splitting process to produce H₂ is an attractive approach to meet energy demands while achieving carbon emission reduction targets. However, none of the current photocatalytic devices meets the criteria for practical sustainable H₂ production due to their insufficient efficiency and the resulting high H₂ cost. Economic viability may be achieved by simultaneously producing more valuable products than O₂ or integrating with reforming processes of real waste streams, such as plastic and food waste. Research over the past decade has begun to investigate the possibility of replacing water oxidation with more kinetically and thermodynamically facile oxidation reactions. We summarize how various alternative photo-oxidation reactions can be combined with proton reduction in photocatalysis to achieve chemical valorization with concurrent H₂ production. By examining the current advantages and challenges of these oxidation reactions, we intend to demonstrate that these technologies would contribute to providing H₂ energy, while also producing high-value chemicals for a sustainable chemical industry and eliminating waste.

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As humanity moves forward into the 21st century, the supplementation of clean and sustainable energy is one of our greatest scientific and technical challenges. The photocatalytic water splitting process using nanoparticulate photocatalysts and solar energy is a leading candidate to achieve low-carbon production of H₂ as a clean and sustainable energy carrier. In this process, water is split into H₂ and O₂ via the following redox reactions (eqn (1) and (2); pH 0 in aqueous solution versus (normal hydrogen electrode) NHE, 25 °C, 1 atm gas pressure, and 1 M for other solutes):



Water splitting is a non-spontaneous chemical reaction involving water oxidation to O₂, which requires four electrons to simultaneously transfer from at least two water molecules. Photocatalysis is a light-driven chemical process that involves oxidation and reduction reactions by the photogenerated electrons and holes. To achieve the photocatalytic water splitting reaction, the conduction band minimum must be more negative

than the H⁺ to H₂ reduction potential, while the valence band maximum must be more positive than the H₂O to O₂ oxidation potential. Consequently, the minimum theoretical energy required to initiate the water-splitting reaction is 1.23 eV. However, O₂ evolution from water leads to sluggish kinetics and high additional kinetic overpotentials,^{1,2} making photocatalytic H₂ evolution need the use of sacrificial reagents to provide an electron source.^{3–5} Specifically, the overpotential losses of the oxygen evolution reaction (OER) can reach up to 30%, resulting in a significant amount of wasted energy.⁶ In addition, the lack of effective methods to separate the produced O₂ and H₂ gases is a key problem for the practical application of photocatalytic water splitting.⁷ As a result of these challenges, increasing attention is being focused on emerging replacements for the OER that may support an expanding H₂ economy globally.

In this minireview, we highlight a variety of key reactions that are well suited as potential replacements for the OER, focusing on the recent developments in the study of photoreforming and photochemical oxidation reactions to produce value-added organic and inorganic products that have received considerable attention in the literature, such as formic acid (~1.1 \$ per kg) production from waste PET (≤0 \$ per kg) and H₂O₂ (~0.7 \$ per kg) formation by water (~2.9 × 10^{−4} \$ per kg) oxidation.^{8,9} These reactions are appealing because they would enable (1) the production of more valuable chemicals than O₂ (~0.1 \$ per kg) alongside the production of H₂; (2) the elimin-

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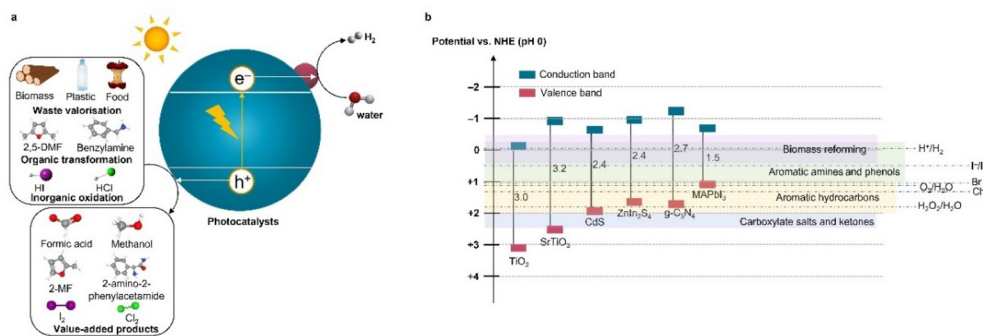
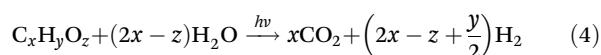
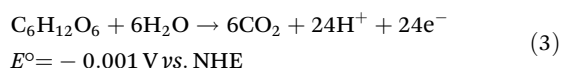


Fig. 1 (a) Diagram of the photooxidation reactions rather than water-to-O₂ oxidation combining with solar H₂ production. (b) Band structures of representative photocatalysts and standard redox potentials for some common oxidation reactions. Data were obtained from ref. 6.

ation of the need for a H₂ and O₂ mixture separation unit, thereby lowering the cost, improving the safety, and simplifying the design of photocatalytic processes; and (3) reduced overpotential due to the simpler 1 or 2 electron net oxidation mechanisms, which would result in an increased conversion efficiency and reaction rate.⁶ Under light irradiation, an inorganic or organic substrate is oxidized by the photoexcited holes at the valence band, which subsequently generated valuable chemicals or CO₂ or intermediate products and protons (Fig. 1a). The protons are reduced by electrons at the conduction band to produce H₂. While the direct oxidation of alternative substrates combined with the production of clean H₂ can be feasibly carried out using various technologies including electrolysis, photoelectrochemical and photocatalytic systems,^{6,7,10} we have targeted cases that have been demonstrated using nanoparticulate photocatalysts due to their potential for large-scale operations.

Photoreforming

Photocatalytic reforming that harnesses solar energy to convert sustainable or waste feedstocks for H₂ generation has become one of the most rapidly evolving applications in the field due to its ability to valorize a range of feedstocks especially biomass, food and plastics (≤ 0 \$ per kg) to both energy and value-added products (such as formic acid (~1.1 \$ per kg), methanol (~0.6 \$ per kg), acetaldehyde (~2 \$ per kg) and lactic acid (~3 \$ per kg)), as listed in Table 1.⁹ Research trends highlight the shift from the early work which focused on simple model substrates such as ethanol, glycerol, and cellulose to more recent work that utilizes real waste, making the process more complex but more economically and environmentally sustainable.¹¹ The energetics of coupling the oxidation of a variety of common organic waste substrates with H₂ evolution are nearly neutral (Fig. 1b), for example, glucose oxidation (eqn (3)), making it more favorable than water splitting, although these oxidation reactions involve multiple electron transfer steps.¹² Theoretically, coupling photoreforming with H₂ production would no longer restrict the use of semiconductors with deep valence bands, allowing the application of those with a smaller bandgap. The photocatalytic reforming could therefore be driven by a large portion of incident sunlight including visible and IR parts.



Initially, photocatalytic reforming research centered on the production of H₂ from a variety of lignocellulose biomass-derived feedstocks, the most abundant and non-edible biomass resource, including monosaccharides, such as pentoses (ribose and arabinose) and hexoses (glucose, fructose, galactose, and mannose), alcohols (methanol, propanol, ethanol, and butanol) and organic acids (formic acid and acetic acid).^{12–19} Theoretically, in the proposed biomass photoreforming process, photoexcited holes lead to the oxidation of biomass components and derivatives (denoted as C_xH_yO_z),



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University of Cambridge. She joined Nagoya University as an Associate Professor in May 2021 and established her research group, which is currently developing new materials, approaches, and technologies for solar energy storage in the form of renewable fuels via artificial photosynthesis.



Table 1 Performance metrics for some recent representative solar fuel production systems using alternative photooxidation reactions to the OER

Substrates	Photocatalysts	Reaction conditions	Products	Efficiency	Reaction time	Ref.
Glucose	Pt/C ₃ N ₄ (~1 µm)	40 W blue LED (λ = 427 nm) 10 M KOH	H ₂ : 3.39 mmol g ⁻¹ h ⁻¹ Lactic acid	Glucose conversion: 100% Selectivity (lactic acid): 86% QE: 42.8% at 365 nm	16 hours	28
Microcrystalline cellulose	Pt/TiO ₂	16 W UV-A lamp (λ = 365 nm)	H ₂ : 13.3 µmol h ⁻¹		5 hours	25
Cellulose	Pt/S- and N-doped graphene oxide dots (2–7 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) pH 12.5	H ₂ : 100 µmol h ⁻¹	QE: 23.3% at 420 nm	6 days	108
Glucose	TiO ₂ /Co(terpyridine) ₂ (~20 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) Aqueous sodium acetate and MeCN purged with CO ₂	Acetaldehyde, methanol, formate, etc. H ₂ : ~0.43 mmol per g _{catalyst} per 24 h CO: ~0.43 mmol per g _{catalyst} per 24 h	Glucose conversion efficiency: 20% QE: 0.22–0.41% at 360 nm for CO; 1.05–1.45% at 360 nm for formate	24 hours	48
Cellobiose	TiO ₂ /Co(terpyridine) ₂ (~20 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) Aqueous sodium acetate and MeCN purged with CO ₂	Formate: ~1.18 mmol per g _{catalyst} per 24 h H ₂ : ~0.72 mmol per g _{catalyst} per 24 h CO: ~0.92 mmol per g _{catalyst} per 24 h Formate: ~1.03 mmol per g _{catalyst} per 24 h	Cellobiose conversion efficiency: 8.6%	24 hours	48
Glycerol	Cu/TiO ₂ nanorods	LED irradiation (λ = 365 nm) MeCN–water solution	H ₂ : 22 mmol per g _{catalyst} per 12 h Methanol, CO, and CO ₂	QE: 3.4% at 365 nm	12 hours	49
Cellulose	Pt/ ^N CN ₄ CN _x	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) LiBr and LiOH in 0.1 M H ₂ SO ₄ solution	H ₂ : ~190 mmol g _{catalyst} ⁻¹ h ⁻¹ Formic acid, lactic acid, arabinose, erythrose, etc.		24 hours	50
Cellulose	NiP/carbon dots (<10 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~5 µmol per 24 h C ₆ H ₁₂ O ₆ and C ₆ H ₁₀ O ₅ compounds		24 hours	26
Glucose	NiP/carbon dots (<10 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~6 µmol per 24 h C ₆ H ₁₂ O ₆ and C ₆ H ₁₀ O ₅ compounds		24 hours	26
Cellulose	Pt/P25 TiO ₂ (20–30 nm)	UV–vis light (250 W iron doped halide lamp) 0.6 M H ₂ SO ₄ solution 403 K; 3.0 bar	H ₂ : ~170 µmol per 10 h HMF, erythrose, and arabinose		10 hours	35
α-Cellulose	Cds/CdO _x quantum dots (diameter ~5 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) 10 M KOH	H ₂ : ~2.57 mmol g _{catalyst} ⁻¹ h ⁻¹ Formate, carboxylic acid, CO ₂ , etc.	QE: 2.73% at 430 nm	6 days	24
Fructose	Cds/CdO _x quantum dots	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~1070 mmol per g _{substrate} per 20 h		20 hours	45
Starch	Cds/CdO _x quantum dots	10 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	Formate, etc. H ₂ : ~462 mmol per g _{substrate} per 20 h		20 hours	45
Apple	Cds/CdO _x quantum dots	10 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	Formate, etc. H ₂ : ~6070 mmol g _{catalyst} ⁻¹ h ⁻¹		20 hours	45
Cheese	Cds/CdO _x quantum dots	10 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~9350 mmol g _{catalyst} ⁻¹ h ⁻¹		20 hours	45
Artificial mixed waste	Cds/CdO _x quantum dots	10 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~9900 mmol g _{catalyst} ⁻¹ h ⁻¹		20 hours	45
Municipal waste	Cds/CdO _x quantum dots	10 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~5920 mmol g _{catalyst} ⁻¹ h ⁻¹		20 hours	45
Wooden branch	Cds/CdO _x quantum dots (diameter ~5 nm)	10 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	H ₂ : ~5.59 mmol g _{catalyst} ⁻¹ h ⁻¹		24 hours	24
Municipal solid waste PLA	CN _x /Ni ₂ P Cds/CdO _x quantum dots (diameter ~5 nm)	Simulated sunlight (100 mW cm ⁻²) 0.5 M KOH Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) 10 M NaOH	Formate, carbonate, etc. H ₂ : 130 mmol h ⁻¹ m ⁻² H ₂ : ~64.3 mmol g _{catalyst} ⁻¹ h ⁻¹ Pyruvate, etc.	QE: 15.0% at 430 nm	20 hours 4 hours	39 37





Table 1 (Contd.)

Substrates	Photocatalysts	Reaction conditions	Products	Efficiency	Reaction time	Ref.
PET	CdS/CdO _x quantum dots (diameter ~5 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) 10 M NaOH	H ₂ : ~3.42 mmol g _{catalyst} ⁻¹ h ⁻¹	QE: 3.74% at 430 nm	4 hours	37
PUR	CdS/CdO _x quantum dots (diameter ~5 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) 10 M NaOH	Formate, glycolate, ethanol, acetate, and lactate H ₂ : ~0.85 mmol g _{catalyst} ⁻¹ h ⁻¹	QE: 0.14% at 430 nm	4 hours	37
PET water bottle	CdS/CdO _x quantum dots(diameter ~5 nm)	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²) 10 M NaOH	Formate, acetate, pyruvate, and lactate H ₂ : ~4.13 mmol g _{catalyst} ⁻¹ h ⁻¹	QE: 2.17% at 430 nm	24 hours	37
			Formate, glycolate, ethanol, acetate, lactate, glyoxylate, methylglyoxal, and methanol	Conversion: 5.15%		
Methanol	CoP/Zn ₂ In ₂ S ₅ nanosheets	Simulated sunlight (AM 1.5G)	H ₂ : ~21 mmol g _{catalyst} ⁻¹ h ⁻¹ Ethylene glycol: 18.9 mmol g _{catalyst} ⁻¹ h ⁻¹ HCHO: ~4 mmol g _{catalyst} ⁻¹ h ⁻¹		12 hours	67
Ethanol	CoP/Zn ₂ In ₂ S ₅ nanosheets	300 W Xe lamp (λ = 400–780 nm)	H ₂ : ~8.5 mmol g _{catalyst} ⁻¹ h ⁻¹ 2,3-Butanediol: 3.2 mmol g _{catalyst} ⁻¹ h ⁻¹ CH ₃ CHO: ~5 mmol g _{catalyst} ⁻¹ h ⁻¹		12 hours	67
Benzyl alcohol	Zn _{0.3} In ₂ S _{3.2}	6 W LED (λ = 365 ± 5 nm)	H ₂ yield: 172% Benzoin yield: 61% Deoxybenzoin yield: 30% Benzaldehyde yield: 9%		12 hours	58
Furfural alcohol	Ti ₃ C ₂ T _x /CdS nanosheets (~60 nm)	300 W Xe lamp (λ ≥ 420 nm)	H ₂ : 773 μmol per g _{catalyst} per 4 h Furfural: 777 μmol per g _{catalyst} per 4 h		4 hours	54
Cetophenone	Pd/TiO ₂	6 W LED (λ = 365 ± 5 nm) Ethanol	H ₂ : ~0.25 mmol per 3 h Phenethanol: ~0.55 mmol per 3 h Ethylbenzene: ~0.05 mmol per 3 h		3 hours	109
DMF	Ni/CdS nanosheets	300 W Xe lamp (λ ≥ 420 nm)	Acetaldehyde: ~0.4 mmol per 3 h H ₂ : ~1 mmol per 3 h	QE: ~44% at 420 nm	3 hours	69
Benzyl alcohol	Zn ₃ In ₂ S ₆ (1–3 μm)	300 W Xe lamp (λ > 380 nm)	N-Benzylidenbenzylamine: ~2 mmol per 5 h H ₂ : 708.8 μmol per 4 h Benzaldehyde: 732 μmol per 4 h	QE: 6.48% at 380 nm 5.46% at 400 nm 4.02% at 420 nm 1.03% at 450 nm	4 hours	64
DMA	Pt/CN _x	14.4 W blue LED (λ _{max} = 470 nm)	H ₂ : ~12 μmol per 10 h		10 hours	59
THF	Pt/CN _x	14.4 W blue LED (λ _{max} = 470 nm)	Minisci oxidation products: ~15 μmol per 10 h H ₂ : ~9 μmol per 10 h		10 hours	59
2,5-DMF	Ru-ZnIn ₂ S ₄ (0.6–1.6 μm)	9 W blue LED (λ = 455 nm)	Minisci oxidation products: ~9.5 μmol per 10 h H ₂ : ~6.0 mmol g _{catalyst} ⁻¹ h ⁻¹ DFPS: ~1.04 g g _{catalyst} ⁻¹ h ⁻¹	QE: 15.2% at 452 nm	6 hours	68
2-MF	Ru-ZnIn ₂ S ₄ (0.6–1.6 μm)	9 W blue LED (λ = 455 nm)	H ₂ : ~1.2 mmol g _{catalyst} ⁻¹ h ⁻¹ DFPS: ~0.1 g g _{catalyst} ⁻¹ h ⁻¹	QE: 1.9% at 452 nm	12 hours	68
HMF	Pt/porous carbon nitride	Simulated sunlight (λ > 400 nm, 100 mW cm ⁻²)	H ₂ : 12 μmol m ⁻² h ⁻¹ DFE: 1.3 μmol m ⁻² h ⁻¹	DFE yield: 13.8% after 6 h Selectivity >99%	6 hours	53
Benzylamine	Ni/CdS nanoparticles	1.85 W Xe lamp (λ > 420 nm)	H ₂ : 21.4 mmol g _{catalyst} ⁻¹ h ⁻¹ Imine	Conversion: 99% Selectivity for imine: 97%	45 minutes	60
Benzyl mercaptane	PtS/ZnIn ₂ S ₄ nanocomposites	5 W LED (λ = 450 nm)	H ₂ yield: 100% Dibenzyl disulfide	QE: 11.2% at 450 nm Conversion: ~100% after 6 h Selectivity of dibenzyl disulfide: ~100%	6 hours	61
Methanol	MoS ₂ foam/CdS nanorods	300 W Xe lamp (λ = 420–780 nm)	H ₂ : 12 mmol g _{catalyst} ⁻¹ h ⁻¹ Ethylene glycol, etc.	QE: 0.28% at 400 nm	12 hours	66
MBA	RuCat/Pt-g-C ₃ N ₄	300 W Xe lamp (λ > 400 nm)	H ₂ : 56 μmol per 10 h MBAd		10 hours	65
Furfural alcohol	Ni/CdS nanosheets (thickness ~1 nm)	8 W blue LED (λ = 450 nm)	H ₂ : ~5 mL per 8 h		8 hours	52
HMF	Ni/CdS nanosheets (thickness ~1 nm)	8 W blue LED (λ = 450 nm)	Furfural H ₂ : ~0.5 mL per 8 h		8 hours	52
4-MBA	NiP/ ¹⁸ CN _x	Simulated sunlight (AM 1.5G, 100 mW cm ⁻²)	DFE H ₂ : ~21.3 μmol per 24 h 4-MBAd: ~19.8 μmol per 24 h	QE: 15% at 360 nm	24 hours	57
H ₂ O	CdS/ZnIn ₂ S ₄ nanosheets	300 W Xe lamp (λ > 400 nm)	H ₂ : ~0.5 mmol g _{catalyst} ⁻¹ h ⁻¹ H ₂ O ₂ : ~0.6 mmol g _{catalyst} ⁻¹ h ⁻¹	QE: 1.63% at 400 nm	12 hours	86
HI	MoS ₂ /MAPbI ₃	280 W Xe lamp (λ ≥ 420 nm)	H ₂ : ~29.4 mmol g _{catalyst} ⁻¹ h ⁻¹ I ₃ ⁻	QE: 13–22% in the range of 420–850 nm STH: 7.55%	90 hours	102

accompanied by hydrogen generation through the reduction of protons by electrons (eqn (4)). The irreversible reaction of $C_xH_yO_z$ with photogenerated holes results in the concomitant suppression of electron-hole recombination and back reactions involving the produced H_2 , thereby increasing the quantum efficiency and the rate of H_2 evolution.¹³

Nevertheless, lignocellulose refining is costly and inefficient, typically necessitating acid hydrolysis, enzymatic hydrolysis, or pyrolysis to produce more manageable substrates.²⁰ Therefore, viable H_2 production systems should directly reform lignocellulose. The main components of lignocellulosic biomass are cellulose (35–50%), hemicellulose (25–30%), and lignin (15–30%).^{21,22} Cellulose,^{23–28} hemicellulose^{24,29,30} and lignin^{24,26,31,32} have been reported to produce H_2 using various photocatalysts such as TiO_2 , CdS/CdO_x quantum dots, carbon dots, carbon nitride, and CdS (Table 1). Metallic nanoparticulate cocatalysts (e.g., Pt, Au, and Pd) and non-precious cocatalysts (e.g., NiP and NiS) are frequently loaded on photosensitizers by wet impregnation and photodeposition methods, with Pt the most commonly studied.³³ As an example, CdS/CdO_x quantum dots loaded Co species as cocatalysts were reported to perform photoreforming of cellulose, hemicellulose and lignin to H_2 in alkaline solution under simulated sunlight irradiation (H_2 evolution rates for cellulose, hemicellulose, and lignin were 2.57, 2.32, and 0.53 $mmol\ g_{catalyst}^{-1}\ h^{-1}$, respectively).²⁴

Reports on using raw biomass as the substrate for photoreforming are limited. Although direct H_2 production from unprocessed biomass has the advantage of lower production costs, it is limited by low substrate solubility. Additionally, light is scattered and absorbed by insoluble biomass and colored components, lowering the light absorption efficiency. The recalcitrance of raw biomass may lead to a large overpotential for biomass oxidation.¹² TiO_2 is frequently used as a photocatalyst for raw biomass reforming, despite its large bandgap (around 3.2 eV) and limited sunlight utilization ability. The H_2 evolution rates of TiO_2 for the photoreforming

of raw biomass, such as poplar wood chips,²⁷ rice husk,³⁴ paper pulp,³⁵ chlorella algae,³⁶ and turf,³⁶ are in the range of 0.01–0.1 $mmol\ g_{catalyst}^{-1}\ h^{-1}$, which are typically lower than those obtained using carbon nitride and CdS with narrower bandgaps (carbon nitride: ~ 2.7 eV; CdS : ~ 2.4 eV) (Table 1).^{24,29} For instance, a rate of over 5 $mmol\ H_2\ g_{catalyst}^{-1}\ h^{-1}$ was reported through photoreforming a wooden branch on $Co/CdS/CdO_x$, as shown in Fig. 2. The system was stable for more than 6 days and was capable of reforming unprocessed lignocellulose, demonstrating a cost-effective approach to produce H_2 from waste biomass. The high H_2 evolution rate may also be attributed to the alkaline conditions that not only provide an *in situ* pretreatment of lignocellulose by dissolving hemicellulose, lignin, cellulose, and other saccharides but also facilitate CdO_x deposition on CdS , thereby producing a photocatalyst that is active and resistant to corrosion.²⁴

The ideal feedstock for photoreforming comes from waste streams that cannot be recycled or reused in any other way.¹¹ To this end, the photooxidation of food waste and nonrecycled plastics has recently become an emerging topic in the field.^{11,37–44} The chemical composition of food waste varies greatly. Due to their hydrophobicity and typically chemically inert hydrocarbon chain, photoreforming fats in an aqueous solution is more difficult than photoreforming proteins composed of long chains of amino acid residues (Table 1).¹¹ Under simulated solar irradiation, simultaneous production of H_2 and the oxidation of a variety of carbohydrates, proteins and fats as well as real-world waste (apples, bread, and cheese) to generate formate and CO_2 or carbonate was observed over CdS/CdO_x quantum dots and Ni_2P/CN_x .⁴⁵ The carbon footprints of these processes were estimated to be 44 600–68 800 g_{CO_2} per kWh H_2 with a conversion efficiency of 1.9–22% after 3 days, which were still high due to the need for alkaline solutions as well as energy for stirring, and pre-treatment (accounts for more than 90% of the values).⁴⁵ The carbon footprint can be reduced to a negative value of $-3200\ g_{CO_2}$ per kWh H_2 if the waste in the water is 100% converted to H_2 and formate.

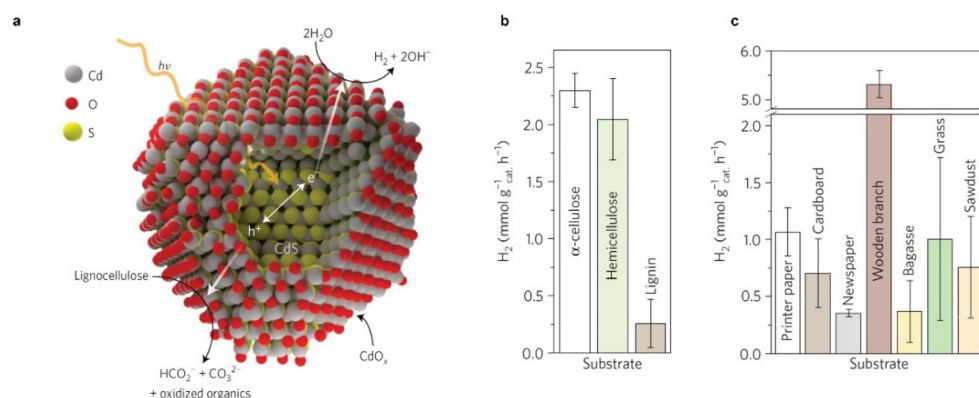
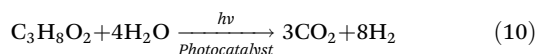


Fig. 2 (a) Diagram of the photoreforming of lignocellulose to H_2 on CdS/CdO_x . (b and c) Photocatalytic production rates of H_2 from α -cellulose, hemicellulose and lignin (b), and raw and waste biomass substrates (c) using $Co/CdS/CdO_x$ quantum dots in 10 M KOH aqueous solution under simulated solar light (AM 1.5G, 100 $mW\ cm^{-2}$). Reproduced with permission from ref. 24. Copyright 2017 Macmillan Publishers Limited, part of Springer Nature.



It is suggested that a theoretical maximum of 310–650 Mt of H₂ could be produced each year (the equivalent of ~6–13% of annual global energy consumption) if the above biomass, food and plastic components were all utilized for photoreforming.¹¹ The preliminary techno-economic and life cycle assessment of photoreforming has shown that it has a lower carbon footprint than or is comparable to existing methods for producing H₂, converting waste to fuel, and managing waste, but the improvement in production costs and energy balance is still required before industrial applications can be envisaged. Although the product of the oxidation reaction in photoreforming is typically CO₂, it is preferred that valuable organic chemicals can be produced instead of CO₂ to improve the sustainability and overall process value of the system.^{26,28,37,46,48–50} For example, Cu dispersed on titanium oxide nanorods was reported to be effective for the conversion of polyols and sugars into syngas and methanol under UV light irradiation and ambient conditions.⁴⁹ Decreased water content inhibited the formation of CO₂, whereas the copper loading amount controlled the decomposition way of the formic acid intermediate. Controlling the oxidation half-reaction is essential to produce



The reforming of plastics conjugating with proton reduction to H_2 is also nearly energy neutral.⁴⁰ For instance, the Gibbs free energy changes for the reforming of ethylene glycol (a monomer of PET) and lactic acid (a monomer of PLA) are $+9.2 \text{ kJ mol}^{-1}$ and $+27 \text{ kJ mol}^{-1}$, respectively. A variety of plastics including PLA, PET, PUR, and a PET water bottle were

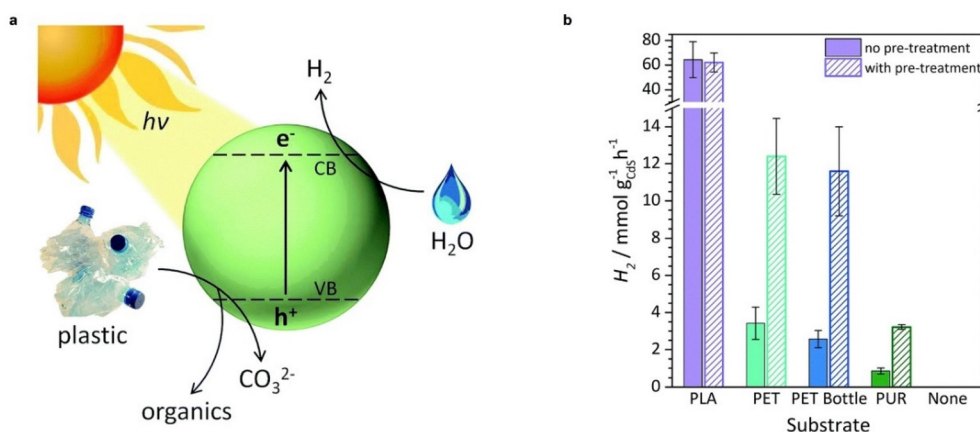


Fig. 3 (a) Diagram of the photoreforming of plastic waste using a CdS/CdO_x quantum dot photocatalyst. (b) Photoreforming of polymers to H₂ using CdS/CdO_x quantum dots under simulated solar light (AM 1.5G, 100 mW cm⁻²). Reproduced with permission from ref. 37. Copyright 2018 The Royal Society of Chemistry.

high-value organic products instead of CO_2 .^{21,41} In addition, pre-treatment, including physical pre-treatment (such as crushing, shredding, and grinding) and chemical pre-treatment (such as hydrolysis and solubilization under highly alkaline or acidic conditions), is one of the most critical barriers to the practical application of the current photocatalytic reforming systems, adding significant cost and time to the overall process. Recently, it was demonstrated that metal salt hydrate solutions allowed for the complete solubilization of biomass and could be used as a reaction medium for the photocatalytic reforming of lignocellulose to produce H_2 and organic products under more benign conditions than the typically required extremely alkaline aqueous solutions, though the photocatalysts suffered from partial deactivation due to metal salt hydrate adsorption, necessitating future development.⁵⁰

Organic transformation

Since the pioneering work of Kolbe that reported the electrochemical oxidation of organic molecules with the goal of developing new methods for synthesizing organic small molecules,⁵¹ a larger body of research has grown around this topic in the ensuing decades. Over the past decade, photocatalytic processes that use light as the energy input have emerged as a new alternative approach in the repertoire of the organic synthesis toolbox. In particular, interest has been aroused in

waste biomass valorization in order to produce high-value commodity chemicals instead of CO_2 . Researchers have succeeded in converting biomass-derived small molecules such as 5-hydroxymethylfurfural (HMF) and furfural alcohol into higher-value materials (*e.g.*, aldehydes and acids) (Fig. 4a).^{52–54} For example, photocatalytic H_2 evolution coupled with HMF (7110 \$ per kg) oxidation to 2,5-diformylfuran (DFF) (198 000 \$ per kg)⁵⁵ using porous carbon nitride was reported to reach a DFF yield of 13.8% with >99% selectivity after 6 h under visible light.⁵³

Recent research has revealed a wide range of photocatalysts for oxidizing alcohols in conjunction with H_2 production.^{57,58,62–65} Alcohols such as methanol have been widely used as sacrificial reagents for photocatalytic H_2 generation from water due to the lower thermodynamic requirements, and alcohols are oxidized to CO_2 .^{3–5} We will not discuss these examples because the focus of this work is on the co-production of high-value chemicals with H_2 . For instance, under visible light irradiation, the coupling of H_2 generation with the oxidation of benzyl alcohol (273 \$ per kg) yielded deoxybenzoin (57 200 \$ per kg) over ZnIn sulfides,^{55,58} and 4-methylbenzyl alcohol (2110 \$ per kg) was converted into an aldehyde (4-methylbenzaldehyde; 3440 \$ per kg) over a cyanamide surface functionalized with melon-type carbon nitride.^{55,57} Multi-carbon alcohols and polyalcohols have been reported to be photocatalytically produced by selectively activating the inert sp^3 α -C–H bonds of alcohols and directly forming C–C bonds with the

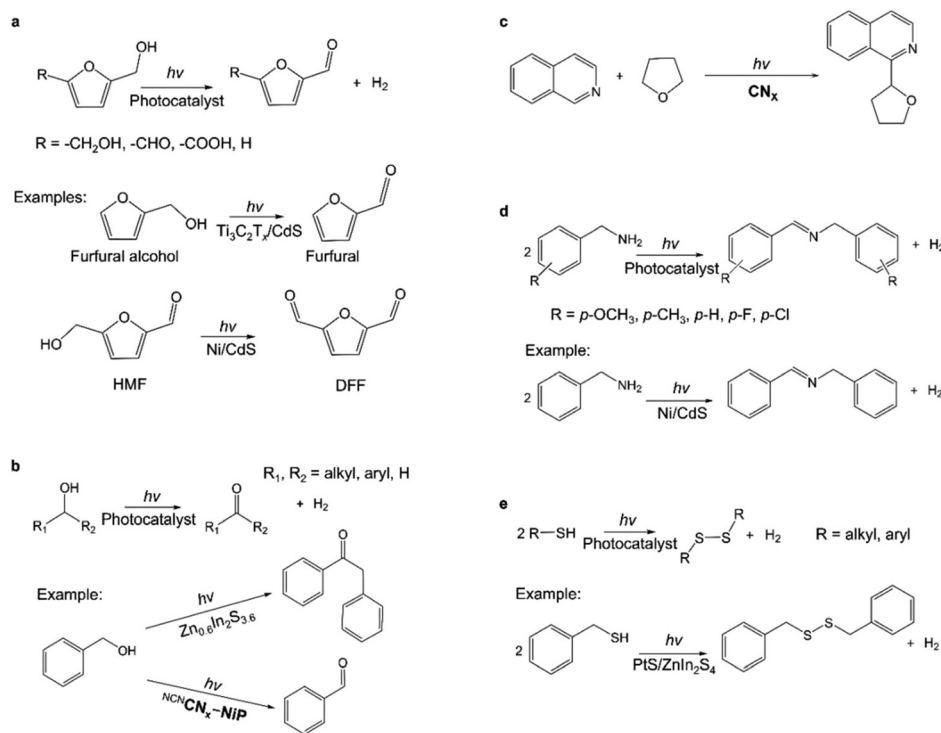


Fig. 4 (a) Photocatalytic oxidation of biomass-derived intermediate compounds.^{52,54,56} HMF: 5-hydroxymethylfurfural; DFF: 2,5-diformylfuran. (b) Photocatalytic oxidation of alcohols.^{57,58} (c) Photocatalytic Minisci coupling.⁵⁹ (d) Photocatalytic C–N coupling reactions.^{56,60} (e) Photocatalytic S–S coupling reactions.^{56,61}



coupling partners (Fig. 4b).⁶² For instance, $\text{Zn}_2\text{In}_2\text{S}_5$ and CdS were reported as visible-light-responsive photocatalysts for the selective activation of the $\alpha\text{-C-H}$ bond of methanol to generate ethylene glycol with a selectivity of as high as 90%.^{66,67} The CdS-based photocatalytic system was beneficial for the activation of the C-H bond in methanol without affecting the O-H group, forming ethylene glycol *via* a $\cdot\text{CH}_2\text{OH}$ radical intermediate with a yield of 16% and a quantum efficiency (QE) of above 5.0% at wavelengths ≤ 450 nm.⁶⁶ The high ethylene glycol selectivity (90%) was maintained throughout the 100-hour reaction, with a yield of 16% after 100 hours, demonstrating an alternative nonpetroleum strategy for ethylene glycol synthesis. The $\text{CoP}/\text{Zn}_2\text{In}_2\text{S}_5$ photocatalyst also was

demonstrated to be the first example of the visible-light-driven dehydrogenative coupling of ethanol to 2,3-butanediol with a selectivity of 53%.⁶⁷ The α -C-H bond of ethanol was selectively activated to form $\cdot\text{CH}(\text{OH})\text{CH}_3$ radicals for subsequent coupling to 2,3-butanediol, presenting that the α -C-H bond can be preferentially activated in the presence of the O-H group under mild conditions.

Aside from alcohols, the C–H bonds in furanics can also be activated for C–C coupling reactions through photocatalysis. The production of diesel fuel precursors from 2,5-dimethylfuran (2,5-DMF) and 2-methylfuran (2-MF), with concurrent H₂ production, over a Ru–ZnIn₂S₄ photocatalyst was demonstrated under visible light irradiation (Fig. 5).⁶⁸ Dehydrocoupling of

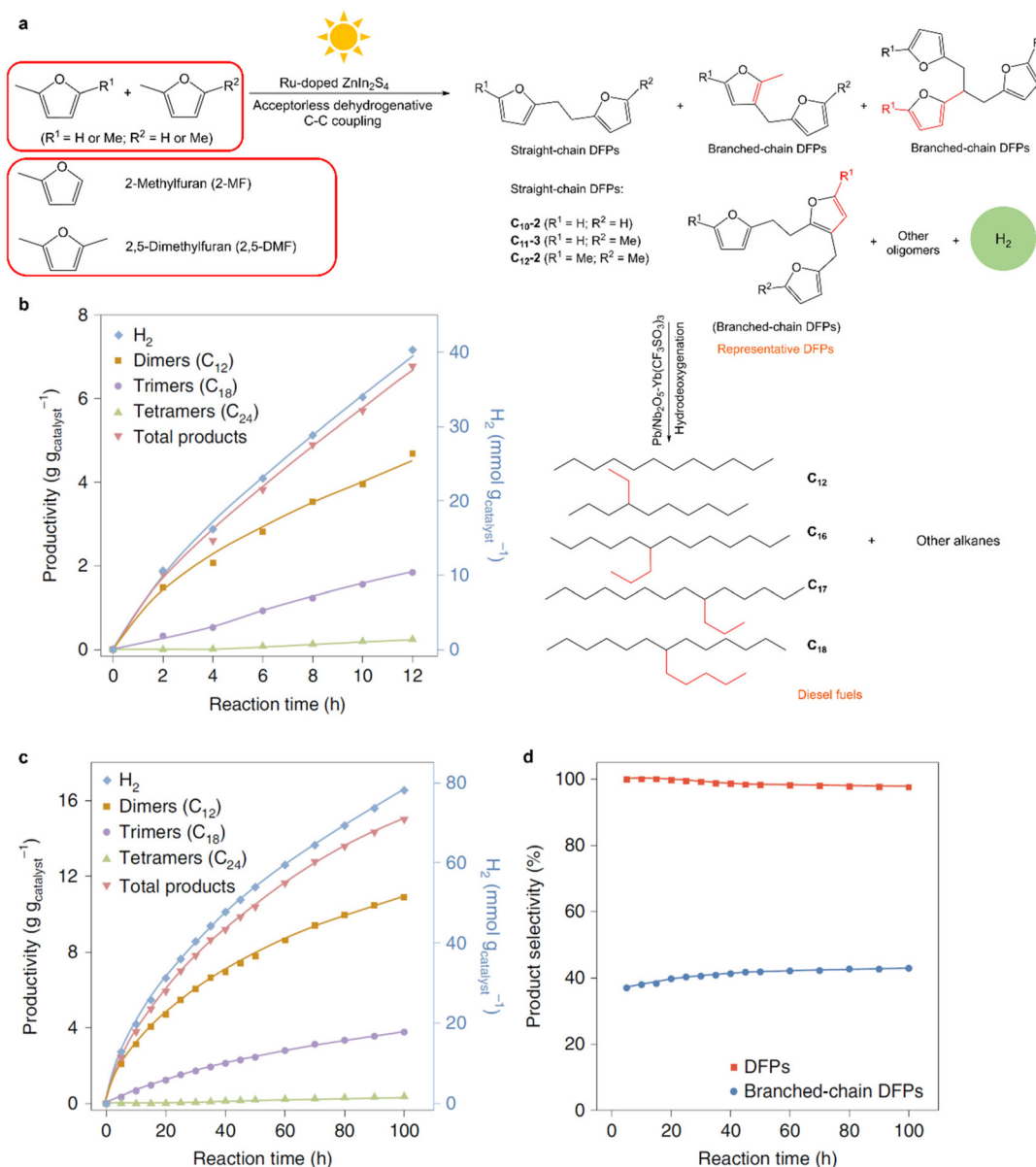


Fig. 5 (a) Schematic representation of the photocatalytic transformation of 2,5-DMF/2-MF into diesel fuel. (b–d) Photocatalytic dehydrocoupling of 2,5-DMF as a substrate: standard experiment (b), catalyst lifetime evaluation (c), and selectivity to oxygenated DFPs and branched-chain DFPs (d). Reproduced with permission from ref. 68. Copyright 2019 Springer Nature Limited.

2,5-DMF and 2-MF yielded mainly H₂, dimers and trimers as products with a small number of tetramers produced in 12 h. Photogenerated holes oxidized the furfuryl C–H bond of 2,5-DMF/2-MF, delivering protons and furfuryl radicals that, through C–C coupling, form the desired DFPs. Over Ru–ZnIn₂S₄, the QE for the dehydrocoupling of 2,5-DMF was 15.2% at 452 nm, which was approximately double that of ZnIn₂S₄ because Ru dopants substituted for indium ions in the ZnIn₂S₄ matrix facilitated charge separation efficiency and thus accelerated C–H activation. Diesel fuel precursors were produced with selectivities of more than 96% in conjunction with H₂ generation and were subsequently transformed into diesel fuels composed of straight- and branched-chain alkanes that were comparable to petroleum diesel in terms of alkane constituents. Future work should focus on improving the yields of C–C coupling products and the QE by the use of more efficient catalysts.

Lately, it has been demonstrated that H₂ production could be coupled with more complex organic synthesis. The Minisci reaction is a known strategy for the direct functionalization of C–H bonds in heteroarenes, involving the radical coupling of electron-deficient heteroarenes with oxidatively-generated nucleophilic radicals.⁵⁹ A visible light-mediated Minisci coupling of N-heteroarenes with ethers, alcohols, and amides in the presence of aerobic oxygen as an oxidant was reported to conjugate with proton reduction to H₂ using a cyanamide functionalized carbon nitride photocatalyst (Fig. 4c).⁵⁹

Photocatalytic C–N coupling of amines for the efficient synthesis of imines may have important applications in pharmaceutical and agricultural chemistry research (Fig. 4d).⁵⁶ Ni/CdS was reported to photocatalyze the non-oxygen coupling of amines to yield their corresponding imines under visible light irradiation, concurrent with H₂ generation.^{60,69} In particular, the photocatalyst showed a high conversion of benzylamine (99%) with 97% selectivity for imines, associated with a QE of 11.2% at 450 nm for simultaneous H₂ evolution.⁶⁰ By constructing *in situ* photoimmobilized Ni clusters on two-dimensional ultrathin CdS nanosheets, the generation of imines was dramatically improved with a QE of ~44% at 420 nm for the conversion of 4-methoxybenzylamine.⁶⁹ It was proposed that photogenerated holes initiated the oxidation of amines *via* the deprotonation process with the creation of C-centered α -amine radicals to form aldimine intermediates and release protons. The protons were reduced by the photogenerated electrons and produced H₂ with the assistance of a Ni cocatalyst. Additionally, the photocatalytic system converted a wide range of primary and secondary amines (*i.e.*, heterocyclic, aliphatic, and N-heterocycles) to form their corresponding imines with high yields ($\geq 84\%$) and selectivity ($\geq 95\%$), thereby offering a promising and versatile pathway for organic chemical synthesis.

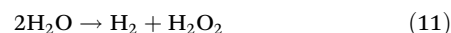
The photocatalytic synthesis of disulfides through the coupling of thiols is also of interest because disulfides function as protecting groups in synthetic applications and as vulcanizing agents for rubber (Fig. 4e). One of the examples is the visible-

light irradiation of CdSe quantum dots to result in virtually quantitative coupling of a variety of thiols, exemplified by 3-mercaptopropionic acid (MPA), to produce disulfides and H₂ in aqueous solution.⁷⁰ The conversion of MPA reached 99% in 1.5 hours and the yield of 3,3'-dithiodipropionic acid was near 100%. Likewise, PtS/ZnIn₂S₄ completely transformed benzyl mercaptan to produce dibenzyl disulfide in 6 h with a selectivity of ~100% under optimal conditions.⁶¹ These examples demonstrated an attractive alternative to existing procedures for synthesizing disulfides from thiols.

Controlling the selectivity of products is the most important issue of organic synthesis, as well as the existence of various potential reactive oxygen species in photocatalysis, including superoxide radicals (O_2^-), hydrogen peroxide (H₂O₂), hydroxyl radicals ($\text{OH}^\bullet$) and singlet oxygen ($^1\text{O}_2$).⁷¹ For selective oxidation, the reactive oxygen species and adsorption-desorption behavior must be carefully controlled.

Inorganic oxidation

Photocatalytic H₂ production along with more valuable inorganic products rather than O₂ *via* a two-electron oxidation pathway represents an alternatively appealing way. For instance, hydrogen peroxide (H₂O₂) production from water *via* the two-electron oxidation process is kinetically more favorable than the water-splitting reaction, which requires four electrons to produce O₂, despite the O₂ generation (1.23 eV *vs.* NHE) showing a thermodynamic advantage over the H₂O₂ production (1.78 eV *vs.* NHE). The photocatalytic reaction to simultaneously produce H₂ and H₂O₂ from water (eqn (11)) has attracted increasing attention in recent years because it obtains clean H₂ energy by utilizing abundant water resources and inexhaustible sunlight,^{72,73} as well as being environmentally friendly for producing the value-added H₂O₂ (~0.7 \$ per kg),⁹ which was widely utilized in the chemical industry, and disinfection, energy, and environmental fields.^{74–77} In addition, this reaction not only realizes the automatic separation of the oxidation product with gaseous H₂ but also effectively avoids the reverse reaction of generated H₂ and O₂ existing in the thoroughly overall water splitting reaction.^{78,79}

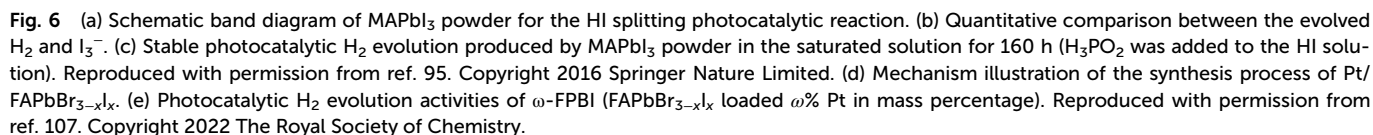


Recent efforts, including optimizing reaction conditions, doping, heterojunctions, cocatalyst loading, and using biological hybrids, have been made to enhance the carrier utilization efficiency of the photocatalyst and increase the selectivity for H₂O₂ production, thereby advancing this technology. Graphitic carbon nitride (g-C₃N₄), for example, as a notable photocatalyst with advantageous features of low cost and tunable optical and electronic properties was widely employed in this field. A sulfur doping treatment was performed on thin g-C₃N₄ nanosheets to compensate for the light absorption loss caused by the exfoliation process while improving the charge transfer efficiency.⁸⁰ Moreover, Co_xNi_yP nanoclusters were loaded onto



Though some promising progress has been made, photocatalytic H_2O_2 production is still far from the market requirement for practical applications, and the industrial production of H_2O_2 still mainly relies on the anthraquinone oxidation process (accounting for over 95% of production).⁸⁸ Facing the same problems with other semiconductor photocatalysis, photocatalytic H_2O_2 production also suffers from the drawbacks of low light utilization ability and the high recombination of photogenerated carriers. Another tricky problem is the rapid decomposition of the generated H_2O_2 occurs at the surface of the photocatalyst/cocatalyst, which can be caused by UV irradiation. More efforts should be devoted to the surface modification and fine control of the photocatalyst/cocatalyst and new cocatalyst development to promote H_2O_2 evolution and inhibit its decomposition process. For example, the combination of common inorganic semiconductor photocatalysts with bacteria, biomaterials, and organic semiconductors may have some positive effects. Additionally, a deeper understanding of the photocatalytic mechanism and H_2O_2 evolution

Photocatalytic HBr and HI splitting to produce H₂ based on halide perovskites has aroused a new research upsurge in recent years since the first report about the hydrogen generation from hydriodic acid using MAPbI₃ as a photocatalyst in 2016 (Fig. 6a–c).⁹⁵ Subsequently, material compositing and heterojunction construction were extensively employed to boost hydrohalic acid splitting. Reduced graphene oxide (rGO) was first used to composite with MAPbI₃ perovskites for the photocatalytic hydrogen evolution reaction, resulting in a hydrogen evolution rate (93.9 μmol h^{−1} under visible-light irradiation) 67 times higher than that of pure MAPbI₃.⁹⁶ Afterwards, various materials such as TiO₂, Ni₃C, carbon dots, black phosphorus, MoS₂, and CoP were used as cocatalysts or heterojunction counterparts to promote carrier separation.^{97–103} In particular, a MoS₂/MAPbI₃ composite exhibited a remarkable photocatalytic hydrogen evolution activity of 29.4 μmol g_{catalyst}^{−1} h^{−1} under visible light and an H₂ production of 103 mL day^{−1} under outdoor natural sunlight irradiation.¹⁰³ In addition to the heterostructures, composition regulation is also a feasible way. For instance, a graded and gradient halide ion distribution was realized in both organometal and all-inorganic mixed halide perovskites,^{104,105} and a resulting bandgap funneling was constructed for efficient carrier transfer, causing an enhanced photocatalytic activity and a solar-to-H₂ conversion efficiency (STH) of 1.05% for MAPbBr_{3−x}I_x/Pt.¹⁰⁴ In addition, single-atom decoration is also an effective strategy to improve the perovskite photocatalytic HI splitting efficiency,^{106,107} an excellent photocatalytic H₂



Halide perovskites possess several excellent material properties, such as a wide light absorption range, a high absorption coefficient, and a long carrier diffusion length, allowing them to be ideal photocatalysts. However, satisfactory performance of this kind of material for photocatalytic H_2 production has not been achieved. More efforts should be devoted to the investigation of the mechanism and fundamental principles of the physical/chemical process during photocatalysis for this special system, where exists a dynamic equilibrium of dissolution-crystallization between the catalyst and the corresponding saturated solution.

In any proton-to-H₂ generation, the availability of substrates at the scale required for the process is a key consideration. Biomass, food, and plastic wastes are abundant, inexpensive, and carbon- and hydrogen-rich feedstocks. Photocatalytic methods offer upcycling routes that yield higher-value products, as opposed to conventional mechanical strategies that typically downcycle to lower-quality products.^{11,40} In recent

For inorganic reactions, the H_2O -to- H_2O_2 conversion and halide oxidation present themselves as an attractive alternative to O_2 evolution due to the higher value of the products and the simpler mechanism resulting from the lower electron demand.

Table 2 Summary of the developed alternative photooxidation reactions to the OER

Oxidation reaction	Substrates	Main products	Challenges
Reforming	Lignocellulose biomass-derived feedstocks (pentoses, hexoses, alcohols, and organic acids)	CO ₂	• Costly and inefficient lignocellulose refining processes required • Low-value products
	Cellulose, hemicellulose, and lignin	CO ₂	• Low substrate solubility • Low-value products
	Raw biomass	CO ₂	• Low substrate solubility • Costly and environmentally unfriendly pre-treatment processes required • Low-value products
	Waste streams (biomass, food, and plastic)	CO ₂ , formate	• Low substrate solubility • Costly and environmentally unfriendly pre-treatment processes required • Competition with water reduction and plastic dehydrogenation to H ₂ • Low selectivity
Organics	Alcohols Furans	Dimers and trimers Imine Disulfides	• Low selectivity
Inorganics	Amines Thiols		
	Water HX (X = Cl ⁻ , Br ⁻ , I ⁻)	H ₂ O ₂ X ₂	

Nonetheless, the reaction efficiency of these reactions must be enhanced.

The H₂ production cost for a waste photoreforming pilot plant (400 m², 200 kg_{waste} per day, 14.4 kg_{H₂} per day) was estimated to be £11.80 per kg, which is more than H₂ sale targets of £3–5 per kg and predictions for H₂ produced by photocatalytic water splitting (£1–3 per kg).^{1,11} It can, however, be reduced by increasing the plant scale and photoreforming efficiency. If the plant scale is enlarged 30 times, the cost of producing H₂ can be decreased to £3 per kg. Furthermore, economic gains can be realized by producing high-value compounds such as pharmaceutical components at the same time. As an example, oxidizing biomass to 3-hydroxybutyrolactone (3-HBL), a precursor for chiral drugs, could cut H₂ production costs to £3 per kg even if the photoreforming conversion efficiency is as low as 0.2% per day. However, although 3-HBL and its hydrolyzed form 3,4-dihydroxybutyric acid (3,4-DHBA) have been reported to be produced from biomass (glucose, glycolic acid, and xylose) *via* biological synthesis using bacteria (*Escherichia coli*), enzymes and yeast, its production *via* a photocatalytic process has not yet been realized.^{110–112} Future efforts would combine photocatalysts with microbes to create abiotic–biotic hybrids capable of producing photocatalytic H₂ while oxidizing biomass to 3-HBL. Likewise, the H₂ production costs can be reduced by photocatalytic transformations to produce value-added organic and inorganic chemicals. For instance, a recent techno-economic analysis suggested that by oxidizing water to produce H₂O₂ instead of O₂ using the photoelectrochemical technique, a leveled cost of hydrogen of \$6.19 per kg can be obtained with an STH of 10.1% and an H₂O₂ price of \$0.85 per kg, which is a significant improvement over the values found in an analogy of the photoelectrochemical water splitting system.¹¹³ Aside from producing cost-effective H₂, the procedures would also reduce the cost of

organic and inorganic products. A minimal selling price of glucaric acid was predicted to be \$6.94 per kg under a base case scenario employing a potential photo-biorefinery approach for sunlight-driven electro-oxidation of glucose, which was 70% lower than the current market price.¹¹⁴

In spite of the obstacles listed in Table 2, significant progress has been made in the study of coupling H₂ production with diverse oxidation chemistry and will continue. With continued material and technological advancements, these technologies have the potential to produce fuels and chemicals with added value, while also reducing waste.

Conflicts of interest

There are no conflicts to declare.

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