Solar Hydrogen Generation from Lignocellulose

Moritz F. Kuehnel* and Erwin Reisner*
Photocatalytic reforming of lignocellulosic biomass is an emerging approach to produce renewable \( H_2 \). This process combines photo-oxidation of aqueous biomass with photocatalytic hydrogen evolution at ambient temperature and pressure. Biomass conversion is less energy demanding than water splitting and generates high-purity \( H_2 \) without \( O_2 \) production. Direct photoreforming of raw, unprocessed biomass has the potential to provide affordable and clean energy from locally sourced materials and waste.

1. Introduction

Biomass is Earth’s most abundant renewable resource and has been a source of energy to mankind since the Stone Age. Today, our economy depends on fossil fuels, which are derived from ancient biomass. With the gradual consumption of these non-renewable resources and problems associated with CO\(_2\) emission, finding a sustainable source of energy is imperative.\(^1\) \( H_2 \) is a promising energy carrier for a post-fossil era, but current \( H_2 \) production relies on fossil fuel reforming and is thus not sustainable.\(^2\) Generating \( H_2 \) fuel directly from waste biomass without the timescales of fossilization has the potential to afford renewable energy at large scale and low cost, without competition with food production.

Lignocellulose is the most abundant form of biomass. It has a multi-component structure, evolved to provide mechanical and chemical stability (Figure 1).\(^3\) Its primary component, cellulose, forms strong, poorly soluble fibrils comprising linear glucose \( \beta-1,4 \)-homopolymer chains linked by hydrogen bonds. Cellulose fibrils are cross-linked by hemicellulose, a branched co-polymer of different pentose and hexose sugars. The major non-carbohydrate component, lignin, is a polymethoxy derived from different phenol monomers in varying compositions. It cross-links the fibril structure and protects it from UV damage.\(^4\) Lignocellulose utilization is therefore kinetically challenging, as it requires disruption of this robust structure.

A number of strategies have been developed to produce fuels directly from biomass.\(^5\) Alcohol production from combined cellulose saccharification and fermentation is a field of intense research,\(^6\) but cellulose hydrolysis is slow and...
separation of the resulting alcohol is uneconomical at low concentrations. Thermochemical processes such as biomass gasification and reforming require high temperatures and pressures, and the generated H₂ contains impurities that must be removed before use.[7]

2. Photocatalytic Reforming of Biomass

Photocatalytic reforming (PR) of biomass uses the photo-excited state of a semiconductor to drive reforming at ambient conditions (Figure 2A). When the semiconductor absorbs light of energies greater than its band gap, an electron is excited from the valence band (VB) to the conduction band (CB). CB electrons are highly reducing and can promote the fuel-forming hydrogen evolution reaction [HER, Eq. (1)], while the oxidizing holes left in the VB can drive the biomass oxidation reaction [BOR, shown for glucose in Eq. (2)].

H₂ generation from water splitting [Eqs. (3) and (4)] has a large thermodynamic barrier (ΔE° = −1.23 V) due to the energy-demanding oxygen evolution reaction [OER, Eq. (5)]. It also generates explosive mixtures of H₂ and O₂. In contrast, the overall biomass reforming reaction [Eq. (5)] is almost energy neutral (ΔE° = −0.001 V),[8] meaning energy is only needed to overcome activation barriers. In theory, biomass PR is therefore possible using low-energy photons (visible and IR light), which are highly abundant in the solar spectrum (Figure 2B).

3. PR of Lignocellulose Components

Photocatalytic conversion of biomass to CO₂ and H₂ was first reported in 1980 using TiO₂ modified with Pt and RuO₂ as hydrogen evolution and biomass oxidation co-catalysts, respectively.[9] The field has progressed significantly since then, but the majority of studies are still performed with TiO₂-based photocatalysts.[10] While these materials are robust and inexpensive, their large band gaps (3.2 eV) limit solar light utilization to the UV region (Figure 2B). PR studies initially focused on generating H₂ from biomass-derived feedstocks. The higher solubility and reactivity of these feedstocks facilitate reaction kinetics,[9] but they are valuable chemicals themselves, and thus biomass PR must focus on using inedible waste material without any additional processing.

3.1. Sugars

Sugars have been widely studied as model substrates for biomass photoreforming, since the majority of lignocellulose is based on saccharide monomers (cellulose and hemicellulose).

Glucose PR is most established using Pt/TiO₂.[11] These UV light-absorbing photocatalysts achieved performances up to 1.15 mmolH₂ gcat⁻¹ h⁻¹,[12] and 8.5% EQE.[13] Other co-catalysts (Rh,[14] Ru,[13b,14] Pd,[15] Au)[13b,15b,16] showed enhanced activity, with AuPd/TiO₂ reaching 8.8 mmolH₂ gcat⁻¹ h⁻¹ and 17.5% EQE.[17] Non-precious co-catalysts (Ni,[13b,18] Fe,[19] Cu)[13a] gave up to 2.0 mmolH₂ gcat⁻¹ h⁻¹ and 59 mmolH₂ gbio⁻¹ yield. Performing PR at elevated temperature (30–60°C)
improved activity\textsuperscript{[25]} and allowed quantitative \( \text{H}_2 \) yield\textsuperscript{[13b,20]}. Moreover, heteroatom doping (B/N\textsuperscript{[21]} \& \text{S} \& \text{F})\textsuperscript{[22]} or sensitization with upconverting Er\textsuperscript{3+}:YAlO\textsubscript{4} particles was employed to improve the light absorption of TiO\textsubscript{2}\textsuperscript{[24]} Pt/TiO\textsubscript{2} also demonstrated PR activity towards other sugars (fructose\textsuperscript{[12a,17,25]}, galactose\textsuperscript{[26]}, mannose\textsuperscript{[26a]}, sorbose\textsuperscript{[26a]}, arabinose\textsuperscript{[25]}, xylose\textsuperscript{[12d,24]}).

Visible-light driven glucose reforming was reported using Pt/CdZnS with rates up to 0.485 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}\textsuperscript{[28]} whereas a related ZnS/ZnIn\textsubscript{2}S\textsubscript{4} solid solution offered a lower performance\textsuperscript{[29]}. Non-precious co-catalysts were shown to be superior over Pt, with a MoS\textsubscript{2}/CdS composite\textsuperscript{[30]} achieving up to 55 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and 9.3 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} and 81 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} reported for Co/CdS/CdO\textsubscript{x} quantum dots\textsuperscript{[31]}.

3.2. Oligosaccharides and Polysaccharides

Disaccharides (celllobiose\textsuperscript{[25,26]} maltoose\textsuperscript{[28b,34b]} sucrose\textsuperscript{[9,11a,12a,b,13b,21,26a,39]} lactose\textsuperscript{[26b]} generally gave lower PR rates than monosaccharides, with a maximum activity of 3.69 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} reported for sucrose PR over Pt/B-N:TiO\textsubscript{2} and a maximum yield of 20 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} over Pd/TiO\textsubscript{2}\textsuperscript{[136]}. PR of soluble polysaccharides proceeded at even lower rates\textsuperscript{[9,12a,b,26b]} presumably due to their higher molecular weights and stable hydrogen-bonded structures. Soluble starch gave 3.14 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and 26 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} reported over Pd/TiO\textsubscript{2}\textsuperscript{[136]} over Pt/TiO\textsubscript{2} (1.8 % EQE)\textsuperscript{[11a]} Visible-light driven PR of polysaccharides has only been investigated for hemicellulose with Co/CdS/CdO\textsubscript{x}, with a rate of 2.04 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}\textsuperscript{[31]}.

3.3. Cellulose

Only a handful of examples have demonstrated cellulose PR. While the thermodynamics of cellulose reforming are similar to that of oligosaccharides,\textsuperscript{[9,10]} the kinetics are more challenging due to the compact tertiary structure of cellulose.

Direct cellulose PR was first demonstrated using Pt/TiO\textsubscript{2}/RuO\textsubscript{2} at low activities (0.012 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1})\textsuperscript{[26]} comparable performance was achieved with Pt/TiO\textsubscript{2}\textsuperscript{[116]}. Improved cellulose solubility at alkaline conditions led to enhanced activity (0.041 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and 1.3 % EQE)\textsuperscript{[9,11b]}. Optimization of catalyst loading, cellulose concentration, and pH further increased the performance of Pt/TiO\textsubscript{2} to 0.223 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}\textsuperscript{[41]}. Remarkably, cellulose photoreforming proceeded with comparable activity under natural sunlight, demonstrating real-world applicability. Immobilizing cellulose on the photocatalyst surface enhanced the rate of photocatalysis and produced 67 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} under UV light; 14 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} yield were produced under natural sunlight\textsuperscript{[42]}. Further enhancement was reported upon raising the reaction temperature (0.61 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} at 40°C)\textsuperscript{[26b]}. An inexpensive Ni/TiO\textsubscript{2} photocatalyst achieved a performance of 0.12 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} at 60°C\textsuperscript{[158]}. Visible-light driven cellulose PR was reported at Co/CdS/CdO\textsubscript{x} in alkaline solution with rates up to 4.9 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and 7.4 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1}\textsuperscript{[31]}.

3.4. Lignin

Although lignin is considered a promising renewable feedstock,\textsuperscript{[40]} it has received little attention as a PR substrate. Lignin PR is hampered by its redox stability and brown color, limiting light absorption by the photocatalyst. Pt/TiO\textsubscript{2} generated 0.026 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} from lignin under UV light (0.6 % EQE)\textsuperscript{[44]}.

4. Raw Biomass PR

Direct PR of unprocessed biomass is highly desirable to lower H\textsubscript{2} production cost, but is hampered by low substrate solubility. Light is scattered from insoluble biomass and absorbed by colored components. The recalcitrance of raw biomass causes a large overpotential for the BOR reaction, requiring strongly oxidizing VB holes.

PR of various plants (Table 1) was first shown over Pt/TiO\textsubscript{2} at rates comparable to pure cellulose (0.004–0.018 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1})\textsuperscript{[11a,h]}. Enhanced performance was achieved in alkaline solution, or upon addition of the OER catalyst RuO\textsubscript{2} (0.058 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}). Elevated temperatures (60°C) allowed PR of Fescue grass over Pt/TiO\textsubscript{2} at 0.061 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}, albeit only after removal of chlorophyll.\textsuperscript{[158]} Natural sunlight-driven PR of plant matter proceeds in neutral water at rates up to 0.095 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} over Pt/TiO\textsubscript{2}\textsuperscript{[42]} H\textsubscript{2} yields were found to vary widely across the different types of biomass (Table 1), with aquatic plants generally demonstrating higher rates and yields than terrestrial plants under similar conditions, presumably due to their lower lignin content. 3.5 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} were produced from laver with 3.3 % EQE.\textsuperscript{[11a]} A visible-light absorbing Co/CdS/CdO\textsubscript{x} photocatalyst showed high PR activity under simulated sunlight.\textsuperscript{[31]} Bagasse, wood, grass and sawdust gave H\textsubscript{2} production rates and yields of up to 5.3 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and 0.49 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1}. Strongly alkaline conditions enhanced biomass solubility and photocatalyst stability.

Biomass solubility is crucial for high PR performance. Adding detergents was shown to enhance the PR rate of castor oil at aqueous Pt/TiO\textsubscript{2}\textsuperscript{[46]} PR of cotton subjected to hydrothermal liquefaction (250°C, 40 bar)\textsuperscript{[77]} was 50 times faster than with untreated cotton under similar conditions\textsuperscript{[21b]}, but the overall H\textsubscript{2} yield was lower. Dilute acid hydrolysis of pine wood (160°C, 10 bar) gave a hydrolysate suitable for high-yield PR over Pt/TiO\textsubscript{2} (0.813 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1} h\textsuperscript{−1})\textsuperscript{[46]}. Alternatively, raw biomass can be digested at mild conditions using natural enzymes. PR of various cellulose/xylanase-treated grasses\textsuperscript{[27,49]} over Pt/TiO\textsubscript{2} achieved rates up to 1.9 mmol H\textsubscript{2} g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and a yield of 34.6 mmol H\textsubscript{2} g\textsubscript{bio}\textsuperscript{−1}. Protease
A-digested chlorella produced 30 mmol$_{H_2}$/g$_{bio}$ at rates up to 0.234 mmol$_{H_2}$/g$_{cat}$ h$^{-1}$ in neutral water (cf. 0.73 mmol$_{H_2}$/g$_{bio}$ and 0.024 mmol H$_2$/g$_{cat}$ h$^{-1}$ for untreated chlorella under these conditions). Although the yields and rates of pre-treated biomass compare favorably to PR without pre-treatment, pre-processing adds considerable cost and time to the overall process.

5. The PR Mechanism

Photoreforming consists of two separate half-reactions (see Section 2). HER is substrate-independent, and typically proceeds at metal co-catalysts such as Pt. This co-catalyst acts both as a Schottky barrier that suppresses charge recombination and as a HER catalyst. PR in D$_2$O has shown that the generated H$_2$ originates from the aqueous solvent rather than the biomass.$^{[11,31]}$ Infrared (IR) spectroscopy,$^{[31]}$ electron energy loss spectroscopy (EELS)$^{[31]}$ and X-ray absorption near edge structure (XANES)$^{[32]}$ measurements confirm that glucose chemisorbs on TiO$_2$. Improving this binding by changing the ionic strength,$^{[28b]}$ using α-glucose instead of β-glucose,$^{[53]}$ or immobilizing the substrate$^{[42]}$ enhances the PR rate. Chemisorption promotes electronic interactions such as substrate-photocatalyst charge transfer,$^{[51a]}$ shifting the flat band potential$^{[11c,12a]}$ and hole trapping at the substrate.$^{[54]}$ BOR is therefore believed to involve direct hole transfer to the chemisorbed substrate (Figure 3A)$^{[51b,52,54]}$ generating surface-bound radicals on the sub-ns timescale, as evidenced for glucose by transient absorption spectroscopy (TAS)$^{[52]}$ and electron paramagnetic resonance (EPR)$^{[55]}$ spectroscopy. Fragmentation of these radicals leads to C$_x$/C$_0$ bond cleavage starting from C$_1$, resulting in a step-wise degradation of glucose to arabinose, erythrose etc. with concomitant formic acid production.

Table 1: Selected examples of photocatalytic reforming of unprocessed lignocellulose.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>Rate [mmol$<em>{H_2}$/g$</em>{cat}$ h$^{-1}$]</th>
<th>Yield [mmol$<em>{H_2}$/g$</em>{bio}$]</th>
<th>EQE [%]</th>
<th>Conditions</th>
<th>Light source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cherry wood</td>
<td>4% Pt/TiO$_2$</td>
<td>0.049</td>
<td>0.296 (10 h)</td>
<td>1.1</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11b]</td>
</tr>
<tr>
<td>wooden branch</td>
<td>Co/CdS/CdO$_2$</td>
<td>0.31</td>
<td>0.49 (24 h)</td>
<td>n/a</td>
<td>10 M KOH, 25°C</td>
<td>AM 1.5</td>
<td>[31]</td>
</tr>
<tr>
<td>sawdust</td>
<td>Co/CdS/CdO$_2$</td>
<td>0.075</td>
<td>0.070 (24 h)</td>
<td>n/a</td>
<td>10 M KOH, 25°C</td>
<td>AM 1.5</td>
<td>[31]</td>
</tr>
<tr>
<td>Dutch clover</td>
<td>4% Pt/TiO$_2$</td>
<td>0.047</td>
<td>0.284 (10 h)</td>
<td>1.1</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11b]</td>
</tr>
<tr>
<td>goldenrod</td>
<td>4% Pt/TiO$_2$</td>
<td>0.018</td>
<td>0.11 (10 h)</td>
<td>0.1</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11b]</td>
</tr>
<tr>
<td>rice plant</td>
<td>5% Pt/TiO$_2$</td>
<td>0.058</td>
<td>1.75 (10 h)</td>
<td>1.3</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11a]</td>
</tr>
<tr>
<td>rice husk</td>
<td>0.5% Pt/TiO$_2$</td>
<td>0.095</td>
<td>n/a</td>
<td>n/a</td>
<td>H$_2$O</td>
<td>sunlight</td>
<td>[41]</td>
</tr>
<tr>
<td>alfalfa stems</td>
<td>0.5% Pt/TiO$_2$</td>
<td>0.100</td>
<td>n/a</td>
<td>n/a</td>
<td>H$_2$O</td>
<td>UV</td>
<td>[41]</td>
</tr>
<tr>
<td>turf</td>
<td>5% Pt/TiO$_2$</td>
<td>0.033</td>
<td>0.98 (10 h)</td>
<td>0.74</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11a]</td>
</tr>
<tr>
<td>fescue grass</td>
<td>0.2% Pt/TiO$_2$</td>
<td>0.061</td>
<td>0.076 (3 h)</td>
<td>n/a</td>
<td>H$_2$O, 60°C</td>
<td>Xe</td>
<td>[15b]</td>
</tr>
<tr>
<td>grass</td>
<td>Co/CdS/CdO$_2$</td>
<td>1.0</td>
<td>0.093 (24 h)</td>
<td>n/a</td>
<td>10 M KOH, 25°C</td>
<td>AM 1.5</td>
<td>[31]</td>
</tr>
<tr>
<td>bagasse</td>
<td>Co/CdS/CdO$_2$</td>
<td>0.37</td>
<td>0.034 (24 h)</td>
<td>n/a</td>
<td>10 M KOH, 25°C</td>
<td>AM 1.5</td>
<td>[31]</td>
</tr>
<tr>
<td>water hyacinth</td>
<td>4% Pt/TiO$_2$</td>
<td>0.034</td>
<td>0.202 (10 h)</td>
<td>0.7</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11b]</td>
</tr>
<tr>
<td>wakame seaweed</td>
<td>4% Pt/TiO$_2$</td>
<td>0.055</td>
<td>0.332 (10 h)</td>
<td>1.2</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11b]</td>
</tr>
<tr>
<td>chlorella algae</td>
<td>5% Pt/TiO$_2$</td>
<td>0.090</td>
<td>2.7 (10 h)</td>
<td>2.0</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11a]</td>
</tr>
<tr>
<td>laver</td>
<td>5% Pt/TiO$_2$</td>
<td>0.111</td>
<td>3.32 (10 h)</td>
<td>3.3</td>
<td>5 M KOH</td>
<td>Xe</td>
<td>[11a]</td>
</tr>
</tbody>
</table>

Figure 3. Mechanism of biomass PR on metal-oxide surfaces. A) Mechanistic pathway depending on the substrate reproduced from Ref.$^{[51b]}$ with permission from Elsevier. B) Mechanistic proposal for glucose reforming on TiO$_2$, reproduced from Ref.$^{[55]}$ with permission from the ACS.
acid formation (Figure 3B). Metal co-catalysts can be involved in BOR, presumably by interaction with chemisorbed intermediates.

Alternatively, involvement of OH- radicals has been suggested on the basis of spin-trapping EPR experiments in the absence of biomass. However, biomass PR is known to proceed on photocatalysts incapable of generating OH- radicals.

6. Biomass PR Beyond H2 Generation

The low market value of H2 renders alternative PR products desirable and, consequently, the selective photocatalytic transformation of renewable feedstocks into valuable organic products is a field of intense research. The radical nature of glucose PR over M/TiO2 gives rise to a number of trace by-products such as CO2, CH4, and other OH- radicals produced only H2 and gluconate, because further oxidation to CO2 was suppressed. Polymorph-dependent selectivity control was observed in glucose PR over Rh/TiO2. Rutile showed preferred decarboxylation of glucose to give arabinoose and erythrose, while further oxidation to CO2 was suppressed. LaFeO3 produced only H2 and gluconate because further oxidation was slow on the less oxidizing VB compared to TiO2. Impregnating Pt/TiO2 with cellulose promoted glucose, cellulose and formic acid formation during PR. The produced glucose could be further photoformed at Pt/TiO2 to hydroxymethyl furfural. Accumulation of formate was seen during cellulose PR at CdS/CdO2 as formic acid PR was slower than cellulose PR. Formic acid could be further photoformed at CdS to H2 or CO.

Alternatively, reducing equivalents generated upon biomass photo-oxidation can be used for organic transformations instead of H2 generation. Photocatalytic conversion of glucose to arabinoose and erythrose over Pd/TiO2 could be coupled with the reduction of nitroarenes and aldehydes to amines and alcohols, respectively, thus producing high-value products from both half-reactions. This approach was recently adapted using lignin as both reductant and oxidant. Photo-oxidation of lignin alcohol moieties to ketones with simultaneous reductive C–O bond cleavage in the lignin backbone resulted in an overall transfer hydrogenolysis of lignin to substituted phenols.

7. Conclusion and Outlook

Biomass PR is a promising approach to sustainably generate fuels and feedstock chemicals. The simplicity of this room-temperature process to produce clean H2 fuel is of considerable advantage over thermochemical methods, but efficiencies are yet to match conventional processes. This field has historically focused on materials and catalysts designed for solar water splitting, limiting photocatalytic activity to UV light. Future work should focus on designing narrow band-gap materials specifically for biomass PR to enhance the performance under natural sunlight. Tailor-made biomass oxidation catalysts will be needed to lower the required driving force and to improve the selectivity towards high-value products. Ultimately, integrating PR with other solar fuel production systems by utilizing low-energy photons unsuitable for water splitting may be the key to translate PR into a scalable and economically viable process.

Acknowledgements

This work was supported by the Christian Doppler Research Association (Austrian Federal Ministry of Science, Research and Economy and the National Foundation for Research, Technology and Development), the OMV Group and the EPSRC (IAA Follow-on fund). We thank Dr. David W. Wakerley, Taylor Uekert and Daniel Antón García for helpful discussions.

Conflict of interest

A patent covering biomass photoreforming has been filed by Cambridge Enterprise (PCT/EP2017/080371) that name M.F.K. and E.R. as inventors.

Photocatalytic reforming of lignocellulosic biomass is a promising approach to produce renewable H₂ at ambient temperature and pressure. Direct photocatalytic reforming of raw, unprocessed biomass is emerging as a potential technology to provide affordable, clean energy from abundant waste.