# Chapter 1
# Cellulose Photocatalysis for Renewable Energy Production

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## Contents

**Abstract** Renewable energy, especially biofuels, has the potential to supplement a part of the existing fossil-based transportation fuels. Biofuels such as bioethanol can be produced from established glucose fermentation processes; however, cheap and efficient glucose production is a hindering factor. Cellulose, the world's most abundant organic material, is a polymer of glucose and is locked within the lignocellulosic framework of plants. Pre-treatment is required to facilitate effective cellulose saccharification. Semiconductor photocatalysis, an advanced oxidation process, is a potential method for cellulose breakdown and the focus of this chapter will be on harnessing photocatalysis for cellulose-based renewable energy production.

We reviewed over 100 publications along the lines of structural properties of cellulose polymorphs, current pre-treatment strategies, conversion methods from

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native cellulose I to an easily degradable polymorph cellulose II, and how semiconductor photocatalysis, an advanced oxidation process, can facilitate cellulose breakdown for saccharification and energy generation. Early reports in the 1980s utilized cellulose as sacrificial electron donor for the photocatalytic $H_2$ production over $TiO_2$ and noble metal co-catalysts; however, recently visible light activated photocatalysts have been used. An often-overlooked area with photocatalysis is cellulose saccharification. Only a handful of reports talk about saccharification over P25 $TiO_2$, which is predominantly due to the lack of control over process conditions leading to undesired products. Addressing the recalcitrance of cellulose, by converting native cellulose I to cellulose II using a simple dissolution and regeneration technique, can be advantageous for enhancing valorization via semiconductor photocatalysis. For example, ~1.5-fold increase in photocatalytic cellulose saccharification was observed with cellulose II compared to cellulose I over P25 $TiO_2$. A similar increase in photocatalytic $H_2$ production rate by over twofolds was also observed when cellulose II was used in suspension with $Pt/TiO_2$. With advances in the development of semiconductor photocatalytic materials, especially in visible light activated materials such as CdS, reactor design, light emitting diode technology, and a novel "simple to produce" feedstock such as cellulose II, vast possibilities have opened up in this novel area of photocatalytic cellulose saccharification and $H_2$ production. Overall, the chapter aims to instil interest in the readers that combining cellulose II and semiconductor photocatalysis can be a feasible way forward to contribute toward renewable energy production.

**Keywords** Cellulose II · Renewable energy · Cellulose photocatalysis

## 1.1 Introduction

Anthropogenic activities combined with increased exploitation of fossil fuel stock has led to an increase in greenhouse gas emissions. Moreover, global politics also influences the movement of fossil fuel stocks and determines the fluctuating price of fuels. Assessments reported during the late 1990s highlighted that the seriousness of fossil fuel depletion will be experienced by the start of 2030 (Wigley et al. 1996). Furthermore, the International Energy Agency's (IEA's) World Energy Outlook Report from 2018 estimated that by 2040, 40% of the global power generation will be contributed by renewables, which is ~1.5 times higher than the current share (International Energy Agency). Consequently, there is a rise in global investments to boost the renewable-energy-based power generation (van der Hoeven 2013). Therefore, to increase the possibility of alternative energy production and to achieve the energy targets set nationally and internationally, sustainable renewable energy production is crucial. Brundtland's commission defines sustainable development as "meeting the needs of the present without compromising the needs for the future" (Brundtland 1987). Although a variety of renewable energy alternatives in the form

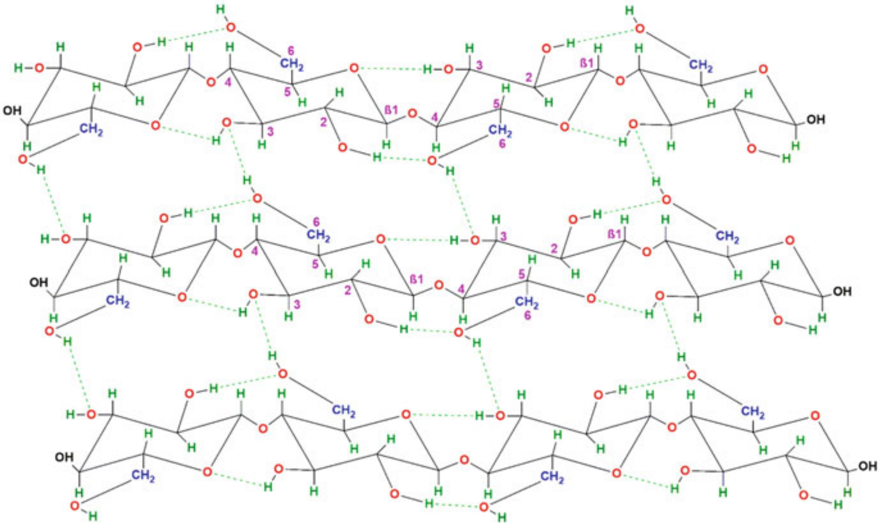


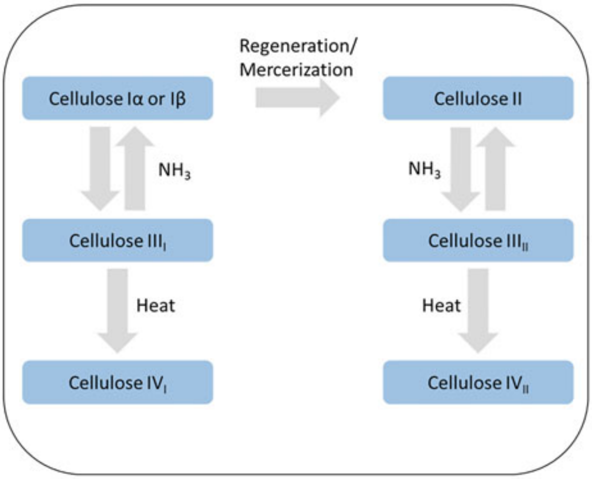
**Fig. 1.1** Structure of cellulose I with the intermolecular and intramolecular hydrogen bonds and β(1-4)-glycosidic bond between glucose monomers. (Reprinted with permission from Nagarajan et al. (2017a), Copyright (2017) Elsevier)

of solar, wind, geothermal, and tidal energies are available, sustainable renewable energy production is achievable via the utilization of waste biomass.

The primary component of waste biomass or lignocellulosic biomass in general is cellulose, which is the world's most abundant organic material (Lavoine et al. 2012). Cellulose is an amphiphilic homopolysaccharide compound (Lindman et al. 2010). β-D-glucose monomer units bonded by (1-4)-glycosidic bond as well as intermolecular and intramolecular hydrogen bonds present in the polymer leads to a rigid polymeric cellulose structure (Silverstein 2005). Highly ordered crystalline regions and disordered amorphous regions are found along the chain of cellulose (Sjöström 1993). Figure 1.1 represents the structure of cellulose with chair confirmation and equatorial orientation of the glucose molecules. Intramolecular and intermolecular hydrogen bonds are represented by the green dotted lines.

In higher plants, native cellulose naturally exists in the cellulose Iβ form, whereas microbes produce native cellulose Iα. The only similarity between cellulose Iα and Iβ is the occurrence of parallel strands, whereas the lattice arrangement is different with Iα exhibiting triclinic arrangement and Iβ having a monoclinic structure. In addition to the native polymorphs, due to a variety of physico-chemical treatments, various cellulose polymorphs can be produced (O'Sullivan 1997) as shown in Fig. 1.2. Cellulose II is the most commonly produced man-made polymorph from both cellulose Iα and Iβ via alkali treatment known as mercerization or solubilizing and recrystallizing or regeneration, respectively, and has been extensively characterized (Sjöström 1993; Silverstein 2005; O'Sullivan 1997; Klemm et al. 1998). Naturally occurring cellulose II has also been isolated from bacterial cultures in a

**Fig. 1.2** Production of various cellulose polymorphs, namely cellulose I, cellulose II, cellulose III, and cellulose IV via a range of physico-chemical treatment methods



few cases (O'Sullivan 1997; Shibazaki et al. 1998; Kuga et al. 1993). Cellulose II has an antiparallel strand arrangement and monoclinic lattice arrangement and therefore differs from cellulose I. Other polymorphs, namely cellulose III$_I$ and III$_{II}$, can be reversibly produced from cellulose I and II via ammonia treatment, respectively. Cellulose III polymorphs exhibit parallel strand arrangement and monoclinic crystal structure (Wada et al. 2004). Cellulose III$_I$ and III$_{II}$ materials, when further heat treated, give rise to cellulose IV$_I$ and IV$_{II}$. A detailed understanding of the polymorphs' properties is necessary for determining end use.

Among the characteristics possessed by cellulose, intermolecular and intramolecular hydrogen bonding plays a central role in determining the supramolecular structure of polymorphs. The hydrogen bonding networks for cellulose I and II are shown along the a-c axis in Fig. 1.3, where the irreversible transformation of cellulose I to cellulose II leads to the formation of antiparallel chains affecting the hydrogen bonding patterns. In addition to the differences observed in hydrogen bonding, cellulose II has a higher surface area and porous volume compared to cellulose I, increased interplanar spacing or d-spacing, decreased crystallinity, increased hydrophilicity, and weak hydrophobic van der Waals interactions that make cellulose II a superior polymorph for use in renewable energy production (Boissou et al. 2014; Dadi et al. 2006; Yamane et al. 2006; Wada et al. 2010; Sakurada and Hutino 1936; Medronho and Lindman 2014, 2015; Lindman et al. 2010; Alves et al. 2015; Behrens et al. 2016).

The chapter so far has emphasized on the ever-growing need for renewable energy production and also highlighted that cellulose in waste biomass must be utilized to fulfil the needs. In addition to mentioning about the characteristics of native cellulose, the possibility of a superior cellulose polymorph being a better starting material based on the structure and molecular arrangement was highlighted. With the feedstock now being established, effective utilization must follow. The first step in the effective utilization of any feedstock for renewable energy production is

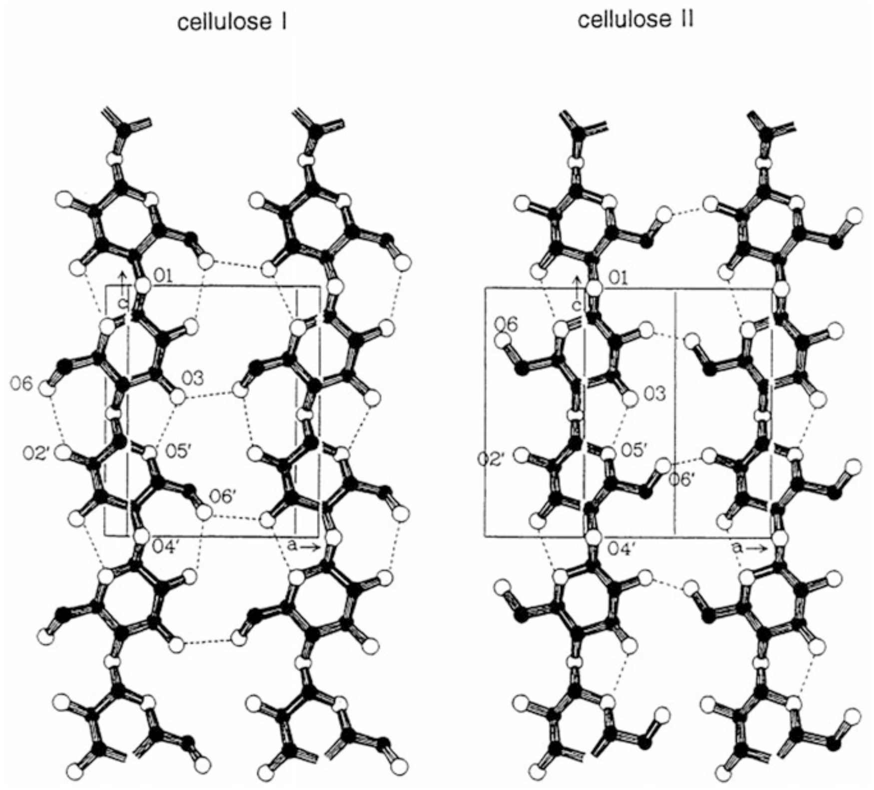


**Fig. 1.3** Intermolecular and intramolecular hydrogen bonding in cellulose I and II polymorphs. (Reprinted with permission from Klemm et al. (1998), Copyright (1998) Wiley-VCH Verlag GmbH)

pre-treatment. The following sections discuss the factors to consider when choosing a pre-treatment method and also briefly discuss the existing cellulose pre-treatment methods. The potential of heterogeneous photocatalysis as a novel pre-treatment alternative to produce fermentable sugars from cellulose as well as produce $H_2$ directly by using cellulose as the sacrificial electron donor (SED) based on the limited reported literature is also discussed. Comprehensive discussion on the production of superior cellulose II polymorph for biofuel production is also provided and the potential of combining cellulose II and heterogeneous photocatalysis as a way forward is also emphasized.

## 1.2 Cellulose Breakdown: Role of Potential of Advanced Oxidation Processes

Effective and complete utilization of cellulose is hindered usually due to its amphiphilic and water insoluble properties. To ensure effective cellulose exploitation, an appropriate pre-treatment method should be in place to enhance utilization. To classify a method as a suitable pre-treatment technique, majority of the following requirements must be met, namely (Silverstein 2005):

(i) Enable fermentable sugar release
(ii) Minimal loss of fermentable sugars
(iii) Minimal or no undesirable product formation
(iv) Cost-effectiveness
(v) Feasible scalability
(vi) Energy efficiency

Considering the above-mentioned criteria, a variety of methods can be used for pre-treatment. Among available methods, steam explosion with dilute acid is commonly used. During steam explosion, biomass is treated with high-temperature and high-pressure steam followed by rapid depressurization to physico-chemically pre-treat biomass. Although preferable, inevitable loss of fermentable sugars due to degradation and formation of undesirable inhibitory by-products is a limitation (Sun and Cheng 2002). An overview of conventional pre-treatment processes highlighting the advantages and disadvantages of each of the processes can be found in Table 1.1. Numerous review articles are also available in the area of biomass pre-treatment, so that the reader can refer to those if interested (Silveira et al. 2015; Kumar and Sharma 2017; Alvira et al. 2010; Chen et al. 2017; Sun and Cheng 2002).

Although numerous established pre-treatment methods are available, contemporary processes still continue to emerge. An example would be the emergence of advanced oxidation processes (AOPs) as pre-treatment methods. AOPs are methods that generate highly oxidizing hydroxyl radicals in-situ and are often deployed in wastewater treatment applications to oxidize and completely mineralize pollutants (Oturan and Aaron 2014). The target for AOPs in cellulose pre-treatment would be to however reduce the crystallinity index and facilitate efficient saccharification to mediate subsequent fermentation. The in-situ non-specific OH radicals produced by AOPs may lead to saccharification of cellulose without affecting the crystallinity, and further microbial inhibitors such as acetic acid or 5-hydroxymethylfufural may be formed in the highly oxidizing environment. Therefore, controlled AOPs are required for effective pre-treatment. The hypothesis behind AOPs as cellulose pre-treatment techniques has a firm base and therefore a range of AOPs have been identified to suit the purpose, namely degradation under ionizing radiation (von Sonntag and Schuchmann 2001; Ershov 1998), electrochemical saccharification (Meng et al. 2011; Wang et al. 2011), cavitation (Kojima et al. 2019; Zhang et al. 2016b), Fenton-based reactions (Hastrup et al. 2010, Arantes and Milagres 2006),

**Table 1.1** Advantages and disadvantage of conventional biomass pre-treatment methods

| Pre-treatment category | Method | Advantages | Disadvantages | References |
|---|---|---|---|---|
| Physical | Mechanical grinding | Ease of handling the raw materials | High energy requirement | Fan et al. (1981), Miao et al. (2011) and Hideno et al. (2009) |
| | Pyrolysis | Rapid decomposition | High temperature requirement | |
| Physico-chemical | Steam explosion along with dilute acids | Less energy requirement when compared to mechanical grinding; cost-effective | Decomposition of monosaccharides | Sassner et al. (2008), Kumar and Wyman (2009), Chen et al. (2011), da Costa Sousa et al. (2016), Li et al. (2015), Gao et al. (2010) and Alinia et al. (2010) |
| | Ammonia fiber explosion | Relatively higher yield of monosaccharides than steam explosion | Cost involved in ammonia recovery to make the process environmentally friendly | |
| | $CO_2$ explosion | Cost-effective | Low yield of monosaccharides when compared to steam or ammonia explosion | |
| | Ozonolysis | Environmentally friendly; room temperature and pressure reactions | Large quantities of ozone required | |
| Chemical | Acid hydrolysis | Higher yield of monosaccharides | Toxic and corrosive; cost involved in acid recovery to make the process environmentally friendly; downstream pH adjustment is required | Saha et al. (2005), Scordia et al. (2011), Yang et al. (2012a) and Wu et al. (2011) |
| | Alkaline hydrolysis | Works well to remove lignin and hemicellulose | Salt formation and downstream pH adjustment is required | |
| Biological | White-rot and brown-rot fungi | Low energy requirements | Slow rate of hydrolysis | Ray et al. (2010), Sindhu et al. (2016), Saha et al. (2016) and Wan and Li (2012) |
| Enzymatic | Cellulases | High specificity for cellulose | Large quantities of enzyme required; expensive | |

and photocatalysis (Kawai and Sakata 1980; Zhang et al. 2016a). Among the mentioned AOPs, heterogenous photocatalysis is least explored for cellulose pre-treatment due to the complexity involved. The limited literature available on photocatalytic cellulose conversion has predominantly focused on using cellulose as a sacrificial electron donor for $H_2$ production, which is understandable due to the non-specificity of the radicals. Recent articles have also started exploring the possibilities of saccharification alternatively. A detailed discussion on the photocatalytic cellulose breakdown for fermentable sugar and $H_2$ production can be found in later sections of the chapter. Owing to the complexities surrounding scale-up of photocatalytic processes, heterogeneity of cellulose photocatalytic systems, and effective separation technique of sugars, photocatalysis is often least explored. A recent thesis submitted by Nagarajan in 2017 has, however, attempted to overcome these complexities by coupling effective reactor design with the use of cellulose II polymorph as feedstock and dialysis membranes to separate fermentable sugars (Nagarajan 2017). The nature of the feedstock, namely cellulose itself, being a key parameter is discussed in the next section. Especially, routes of cellulose II production, current use of cellulose II in biofuel production and how cellulose polymorphs can be used in conjunction with photocatalysis for effective valorization are discussed.

## 1.3 Cellulose II for Energy Generation

Bioethanol is an attractive biofuel that has the potential to contribute toward transportation fuel requirements. The precursor for bioethanol production is glucose, whose polymer cellulose is abundantly available and locked within lignocellulosic biomass in a highly crystalline cellulose I form. As mentioned in the previous sections, cellulose I is recalcitrant to hydrolysis; however, converting cellulose I to cellulose II—a more easily accessible polymorph of cellulose—can help in exploiting the substrate fully. The following subsection will give an overview of cellulose II production; however, a detailed discussion on the importance of cellulose II as an alternative feedstock to cellulose I for bioethanol has been reviewed and reported by Nagarajan et al. (2017a).

### *1.3.1 Routes for Cellulose II Production*

The two oldest-known cellulose II production processes are the viscose process and mercerization (Guenet 2008; Mercer 1850; Klemm et al. 2005; Cross et al. 1893a, b). Aqueous NaOH is used in both these techniques to dissolve cellulose I and precipitate cellulose II. Many variants of these processes have also been reported since, including dissolution of cellulose I in cold alkali (Wang and Deng 2009; Mittal et al. 2011; Dinand et al. 2002; Sharma et al. 2015; Halonen et al. 2012; Revol et al. 1987; Yu et al. 2014; Jin et al. 2016). An overview of other routes of cellulose II production is shown in Fig. 1.4 and briefed in Table 1.2, while the limits of cellulose I solubility in various solvents for cellulose II production are shown in Fig. 1.5.

Although aqueous alkali has the capability to dissolve cellulose I, complete molecular dissolution is not possible (Alves et al. 2015). To achieve a molecular dissolution, either anhydrous ionic liquids or aqueous onium hydroxides have to be

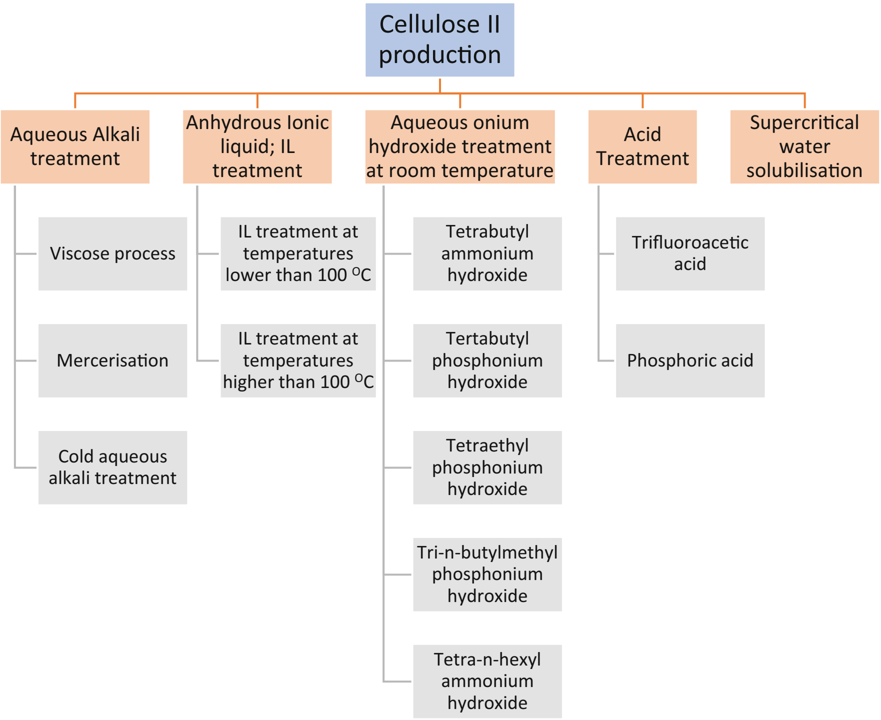


**Fig. 1.4** Various routes for cellulose II production from native cellulose or biomass. Note that ionic liquid or onium hydroxide treatments can achieve molecular dissolution and complete conversion to cellulose II and might be beneficial over other methods. (Figure based on Nagarajan et al. (2017a))

used (Abe et al. 2015). Salts with melting temperatures lower than 100 °C are known as ionic liquids. These are green solvents with negligible volatility and high flexibility. Due to the versatility possessed by ionic liquids, a range of cation–anion combinations could be made to effectively dissolve cellulose I. Swatloski et al. first reported a breakthrough research where methylimidazolium-based ionic liquid was used for the irreversible production of cellulose II from native cellulose (Swatloski et al. 2002). To date, methylimidazolium cations in combination with a variety of anions have been frequently reported as ionic liquids for cellulose dissolution (Dutta et al. 2012; Hou et al. 2012; Xiao et al. 2014; Park et al. 2012; Fu and Mazza 2011; Bokinsky et al. 2011; Cheng et al. 2011; Samayam et al. 2011; Dadi et al. 2006, 2007; Shafiei et al. 2013; Liu et al. 2015).

The nature of the constituting anion–cation mix determines the solubility of cellulose. Dissolution of cellulose II proceeds via the OH groups of $C_6$ and $C_3$ cellulose chains forming an electron acceptor–donor complex with the ionic liquids (Pinkert et al. 2009). Upon dissolution, water or alcohol can be used to precipitate cellulose II from the solution. Owing to high viscosity and anhydrous nature, the cellulose-dissolving capability of ionic liquids is limited. To overcome the limitation

**Table 1.2** Cellulose II production methods

| Treatment type | Solvent used | Temperature | Method synopsis | References |
|---|---|---|---|---|
| Alkali treatment | Aqueous NaOH solution | – | Cellulose xanthogenate prepared from pulp is dissolved in aqueous NaOH and precipitated out of solution (viscose process). | Klemm et al. (2005) and Cross et al. (1893a, b) |
| | 0–30% aqueous NaOH solution | 70 °C/85 °C | Cellulose I was dissolved in NaOH aqueous solution followed by precipitation and purification (Mercerization); 9–15% NaOH aqueous solution was found to produce better cellulose II yields than other concentrations at 85 °C. | Mercer (1850) and Yu et al. (2014) |
| | 6% aqueous NaOH solution | −8 °C to −20 °C | Cellulose I was dissolved at sub-zero temperatures and after 10 min of dissolution at −15 °C, cellulose II started to appear. | Wang and Deng (2009) |
| Ionic liquid treatment | 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) | 120 °C/ 160 °C | Avicel, switchgrass, eucalyptus, and pine samples were dissolved in EMIM-Ac at 120 °C/160 °C and upon dissolution, cellulose II was precipitated out using hot water. Higher rate of cellulose II formation was observed with higher temperature. | Cheng et al. (2011) |
| | 21 different ionic liquids | 50 °C/80 °C | Avicel, α-cellulose, spruce wood, silver fir, common beech, and chestnut wood of 1–5 wt % were dissolved in 21 different ionic liquids at 50 °C and upon dissolution cellulose II was precipitated. EMIM-Ac was found to dissolve standard cellulose samples and 1-allyl-3-methylimidazolium-chloride (AMIM-Cl) dissolved the wood samples. | Zavrel et al. (2009) |

| | | | | |
|---|---|---|---|---|
| | Imidazolium-based ionic liquids containing odd or even numbered alkyl side chains in combination with a range of anions | 100 °C | 8 wt% of Avicel PH 101 was dissolved in ionic liquids at 100 °C. Upon dissolution, excess methanol was used to precipitate cellulose II. It was determined that ionic liquids with shorter even-numbered side chains (2 or 4) combined with chloride anions showed good cellulose I dissolving properties. | Vitz et al. (2009) |
| Onium hydroxide treatment | Aqueous solutions of tetrabutylammonium hydroxide (TBAH) and tetrabutylphosphonium hydroxide (TBPH) | 25 °C | Cellulose I was dissolved in 40–70 wt% aqueous TBAH and TBPH solution. Hot ethanol was added to the solutions to precipitate cellulose II. It was determined that concentration ranges of 50–60% TBAH and 50–70% TBPH in water were required for complete cellulose I dissolution at room temperature. | Abe et al. (2012) |
| | TBAH | 16–28 °C | Cellulose I was dissolved in 40 and 60 wt% TBAH at different temperatures. Precipitation and regeneration of cellulose II were performed by the addition of hot water. It was determined that cellulose I dissolved better at 16 °C due to the stable ionic structure of TBAH at lower temperatures. | Wei et al. (2015) |
| | TBPH, tetraethylphosphonium hydroxide (TEPH), tri-n-hexylphosphine tetramethylammonium hydroxide (THTMAH), tetraethylammonium hydroxide (TEAH), TBAH, tri-n-butylmethylphosphonium hydroxide, and tetra-n-hexylammonium hydroxide | 25 °C | Cellulose I was dissolved in various 40 wt% onium hydroxide aqueous solutions. A concentration of 15 wt% cellulose was found to be dissolved in all the onium hydroxides, whereas TBPH and TBAH dissolved 20 wt% cellulose. THTMAH and TEAH did not dissolve any cellulose. | Abe et al. (2015) |

(continued)

**Table 1.2** (continued)

| Treatment type | Solvent used | Temperature | Method synopsis | References |
|---|---|---|---|---|
| Phosphoric acid treatment | 77–85 wt% phosphoric acid | 5–75 °C | 0.5–3% wt/v cellulose was dissolved in 77–85 wt% phosphoric acid in the temperature range of 5–75 °C. Regeneration was performed with the addition of water. The investigators determined that a higher concentration of phosphoric acid ($\geq$ 83 wt%) was required to completely dissolve cellulose. | Jia et al. (2013) |
| Trifluoroacetic acid (TFA) treatment | 99% trifluoroacetic acid | 0–65 °C | Cotton linters were mixed in 99% TFA in mass ratios of 1:15 at different temperatures ranging from 0 to 65 °C for 3 h. The swollen samples were washed with water to recover cellulose II. Complete conversion to cellulose II was only observed at 0 °C. | Zhao et al. (2007) |
| Supercritical water solubilization | Supercritical water | 320–400 °C | A 10 wt% cellulose I was mixed with water in a microreactor and rapidly heated for 0.02–0.6 s at 320–400 °C and 25–33 MPa pressure to obtain cellulose II. It was determined that at temperatures higher than 380 °C, cellulose conversion was constant and was independent of pressure. | Sasaki et al. (2003) |

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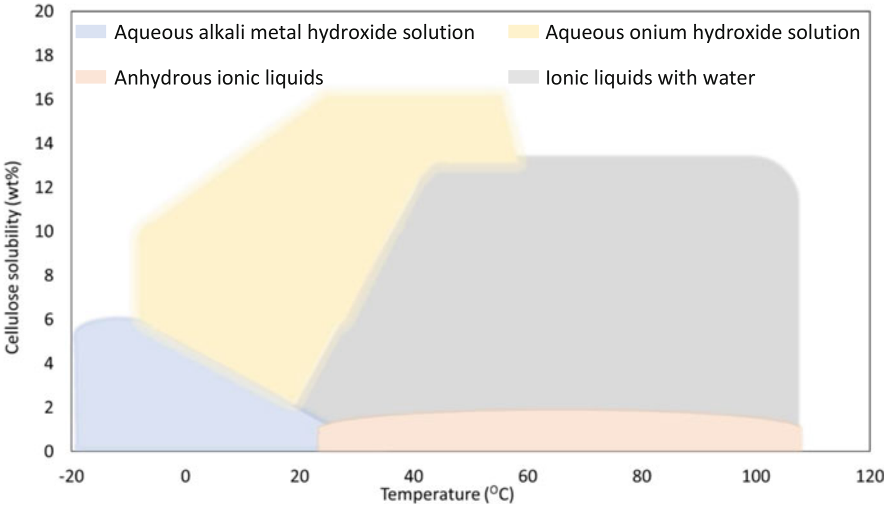

**Fig. 1.5** Representative solubilities of different cellulose I loading in various solvents such as alkali metal hydroxide aqueous solution in the blue-shaded region, ionic liquids with water in the orange-shaded region, anhydrous ionic liquids in the gray-shaded region, and aqueous onium hydroxide solution in the yellow-shaded region for cellulose II production. (Modified from Abe et al. (2015))

posed by the viscosity of ionic liquids, aqueous onium hydroxides can be used. Aqueous onium hydroxides are deep eutectic solvents and possess similar properties to ionic liquids and complement the amphiphilic property of cellulose thereby serving the purpose. Being an aqueous solution, onium hydroxides have a lower viscosity and higher cellulose-dissolving capability. The most commonly used onium hydroxides for cellulose II production are tetrabutylammonium hydroxide (TBAH) and tetrabutylphosphonium hydroxide (TBPH; Alves et al. 2015; Wei et al. 2015; Abe et al. 2012, 2015; Chang et al. 2019).

### 1.3.2 *Cellulose II as Feedstock for Biofuel Production*

There has been a lot of work lately on the use of cellulose II as feedstock for fermentable sugar and biofuel production. An overview of some of the reported work is shown in Table 1.3. As can be seen, when cellulose II was utilized as the feedstock, an enhanced yield of fermentable sugars or bioethanol was reported in all the cases. These reports established the importance of cellulose II as a renewable energy feedstock. Further sections in the chapter discuss the use of least-explored heterogeneous photocatalysis for fermentable sugar or $H_2$ production from cellulose polymorphs.

**Table 1.3** Use of cellulose II for fermentable sugar and biofuel production

| End use | Feedstock | Solvent used for cellulose II production | Key takeaway | References |
|---|---|---|---|---|
| Fermentable sugar production using Genencor GC220 cellulase enzyme preparation | Avicel PH-101, α-cellulose, cotton linters, and cellulose extracted from corn stover | 16.5 wt% aqueous NaOH at 25 °C under a nitrogen atmosphere | Enzymatic hydrolysis rate of cellulose II was twice higher than cellulose I | Mittal et al. (2011) |
| Fermentable sugar production using commercial *Aspergillus niger* cellulase | Corn stalk | Pyrrolidonium-based ionic liquids at 90 °C | Higher fermentable sugar yield with cellulose II | Ma et al. (2016) |
| Fermentable sugar production using mixture of cellulase and β-glucosidase enzymes and bioethanol production using *Saccharomyces cerevisiae* CCUG53310 | Spruce wood chips or powder | Methylimidazolium-based ionic liquids and *N*-methylmorpholine-*N*-oxide at 120 °C | Significantly higher fermentable sugar and bioethanol yield from cellulose II produced from ionic liquids compared to other feedstocks | Shafiei et al. (2013) |
| Fermentable sugar production using enzymatic hydrolysis | Triticale straw | Anhydrous and aqueous 1-ethyl-3-methylimidazolium acetate with varying amounts of water | Increase in fermentable sugar yield with decrease in water content in the aqueous ionic liquid mixture | Fu and Mazza (2011) |
| Fermentable sugar production using a mixture of cellulase and β-glucosidase | Microcrystalline cellulose | Aqueous TBPH and dimethyl sulfoxide (DMSO) mixture | Increasing rate of hydrolysis and fermentable sugar yield with decreasing crystallinity index of cellulose II | Pena et al. (2019) |
| Fermentable sugar and bioethanol production | Guinea grass | 1-ethyl-3-methylimidazolium acetate | Improved fermentable sugar and bioethanol yield with cellulose II | Odorico et al. (2018) |

## 1.4 Cellulose Photocatalysis and Renewable Energy

Photocatalysis and photocatalytic technology has developed significantly since the initial publications in the 1970s (Lyashenko and Gorokhovat-skii 1975; Inoue et al. 1979; Fujishima and Honda 1972) and, as a result, has now been deployed for a range of applications (Daghrir et al. 2013; Matsuoka et al. 2007; Van Gerven et al. 2007; Zhao and Yang 2003). The most commonly reported applications are in environmental remediation, reactor design, chemical and materials synthesis, and energy production. In particular, photocatalytic water and air treatments have developed rapidly over the past four decades and now represent the most commercial and industrial application in the field. In contrast, photocatalytic energy production is yet to achieve the same level of development; however, it remains as one of the most desirable applications, which is primarily due to two key reasons. Firstly, one of the initial publications on photocatalysis was by Fujishima and Honda in 1972, which demonstrated water splitting over an irradiated $TiO_2$ electrode (Fujishima and Honda 1972). In addition, achieving photocatalytic energy production could have significant impact on the global objective of increasing renewable fuel generation. As a result, photocatalytic research into energy conversion, renewable energy, and more recently bioenergy energy production has become extensive with the majority of publications focused on $H_2$ generation (Matsuoka et al. 2007; Bahruji et al. 2010; Colón 2016; Liu et al. 2019a).

Regardless of the application, photocatalysis efficiency is dictated by the absorption of light at a suitable wavelength and subsequent generation of electron–hole pairs. In an aerobic-water system, typically, hydroxyl and superoxide radicals are formed, which drive the efficiency of environmental remediation applications such as water and air treatments (Fig. 1.6a). Photocatalytic $H_2$ formation, however, is faced with several additional challenges in order to achieve the same level of efficiency. The primary challenges associated with a $H_2$ evolving system include the selectivity of the process, electron–hole pair recombination and competition between the back-reactions of $H_2$ and $O_2$. To discuss these further and to show how the field has evolved, photocatalytic $H_2$ systems can be broadly divided into either water splitting (Fig. 1.6b) or sacrificial electron donor (SED) systems (Fig. 1.6c). In addition, Fig. 1.6d shows the equations that summarize the typical reactions taking place in photocatalytic systems for both environmental remediation and energy producing systems.

In water splitting, the key objective is for simultaneous photo-oxidation and reduction reactions to take place, generating $H_2$ and $O_2$ under ambient conditions. These systems, however, are often limited by both the rate of recombination and the back-reaction of $H_2$ and $O_2$ to form $H_2O$. In an attempt to suppress these limitations, researchers will often operate in an inert atmosphere and deploy a photocatalyst loaded with a metal co-catalyst, for example, Pt, Pd, Au, or Ni, to act as an electron trap (Skillen et al. 2015). Even under these conditions, however, the unfavorable thermodynamics of water splitting, due to a large change in the Gibbs free energy with $\triangle G_o = -238\ \text{kJ mol}^{-1}$, restricts the overall efficiency of the process. In an attempt to overcome the stringent requirements associated with water splitting, SED systems are often used. In a photocatalytic system, an SED can undergo an irreversible oxidation reaction that prevents recombination from occurring while also supplying electrons and protons for the subsequent reduction reaction. While a range of SEDs have been shown to be suitable, for example, alcohols and acids (Chen et al. 2018; Skillen et al. 2016), the development of the field has seen a shift in

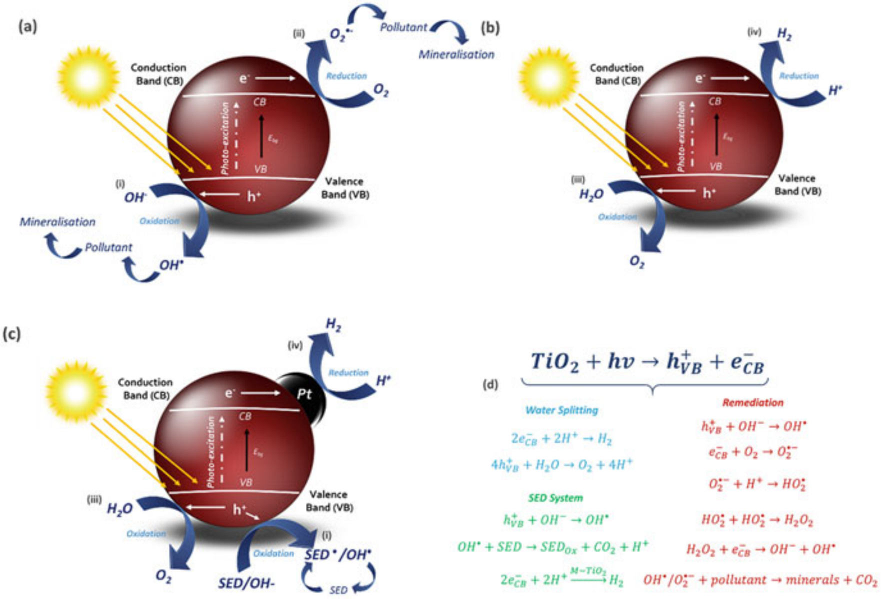

**Fig. 1.6** Typical photocatalytic mechanism that takes place in (**a**) environmental remediation, (**b**) water splitting, and (**c**) sacrificial electron donor (SED); SED-based systems along with (**d**) the equations that summarize the reactions. Processes shown include (i) formation of hydroxyl radicals (OH•) for both (**a**) pollutant and (**c**) SED oxidation, (ii) formation of superoxide radicals ($O_2^{\bullet -}$), (iii) $O_2$ formation from water splitting, and (iv) proton reduction to from $H_2$. VB denotes valence band and CB denotes conduction band

focus toward using more sustainable and *green* compounds. As a result, an increase in papers reporting glycerol reforming to $H_2$ has occurred (Luo et al. 2008; Slamet et al. 2017; Maurino et al. 2008; Bowker et al. 2008) and along with it, the use of biomass or biomass-derived substrates such as cellulose (Caravaca et al. 2016; Zhang et al. 2016a), lignin (Machado et al. 2000), and lignocellulose (Liu et al. 2019a; Kasap et al. 2018; Wakerley et al. 2017) has also increased. Recently, an extensive review was published by Liu et al., which highlighted the growth of photocatalytic conversion of lignocellulosic to $H_2$ and value-added products (Liu et al. 2019a). Discussed in the subsequent sections are, what the authors feel, some of the key publications within the field in relation to $H_2$ formation and biofuel generation. In addition, a more comprehensive overview of $H_2$ formation from cellulose, lignocellulose, and raw biomass photocatalytic conversion has been tabulated in Table 1.4.

**Table 1.4** Cellulose, lignocellulose, and biomass conversion to $H_2$ via photocatalysis (UV denotes ultraviolet)

| Substrate | Feedstock | Catalyst | Light source | Reaction solution | Hydrogen | Liquid phase products | References |
|---|---|---|---|---|---|---|---|
| Cellulose | Filter paper | $Ru/TiO_2/Pt$ | 500 W Hg ultra-high-pressure lamp | 6 M NaOH | 244 μmol | | Kawai and Sakata (1980) |
| | Micro crystalline cellulose | $Pt/TiO_2$ | 150 W Xe arc lamp | Water | ~2.8 mL | | Caravaca et al. (2016) |
| | Fibrous long cellulose | $Pt/TiO_2$ | 60 W UV-A lamps; natural irradiation | Water | 54 μmol; 33 μmol | | Speltini et al. (2014) |
| | Cellulose (bound to $TiO_2$) | $Pt/TiO_2$ | 250 W iron-doped halide lamp | Water | 195.2 μmol | Glucose, cellobiose, and formic acid | Zhang et al. (2016a) |
| | α-Cellulose | CdS/CdOx | 100 mW $cm^{-2}$ solar light simulator | 10 M KOH | ~2.25 mmol $g_{cat}^{-1}$ $h^{-1}$ | | Wakerley et al. (2017) |
| | Cellulose | $Pt/TiO_2$ | 250 W iron-doped halide lamp | 0.6 M $H_2SO_4$ | 123 μmol | 5-hydroxymethylfurfural | Zou et al. (2018) |
| | Cellulose | $TiO_2/NiO_X@C_g$ | 500 W Xe lamp | Water | ~270 μmol $g_{cat}^{-1}$ $h^{-1}$ | | Zhang et al. (2018) |
| | Cellulose | $TiO_2/Ni_XS_Y$ | 500 W Xe lamp | Water | 181.2 μmol | | Hao et al. (2018) |
| Lignocellulosic biomass | Wooden branch | $CdS/CdO_X$ | 100 mW $cm^{-2}$ solar light simulator | 10 M KOH | 5.3 mmol $g_{cat}^{-1}$ $h^{-1}$ | | Wakerley et al. (2017) |
| | Grass | $Pt/TiO_2$ | 150 W Xe arc lamp | Water | ~0.6 mL | | Caravaca et al. (2016) |
| | Sawdust | $^{NCN}CN_X$ | 100 mW $cm^{-2}$ solar light simulator | 0.1 M potassium phosphate | 202 μmol $g_{cat}^{-1}$ $h^{-1}$ | | Kasap et al. (2018) |
| | Rice husk | $Pt/TiO_2$ | Natural irradiation | Water | 16 μmol | | Speltini et al. (2014) |
| | Alfalfa stems | $Pt/TiO_2$ | 60 W UV-A lamps | Water | 24 μmol | | |

### *1.4.1 Photocatalysis of Cellulose I and Lignocellulosic Biomass*

While often described as an *emerging topic*, photocatalytic reforming of biomass to $H_2$ was reported along with some of the earliest publications in the field (Lyashenko and Gorokhovat-skii 1975; Inoue et al. 1979; Fujishima and Honda 1972). In 1980, Kawai and Sakata demonstrated for the first time the evolution of $H_2$ from sugar, starch, and cellulose using a $RuO_2/TiO_2/Pt$ photocatalyst in a suspension of water (Kawai and Sakata 1980). Interestingly, rather than producing a system that mimicked natural photosynthesis, as is often done with photocatalysis, the authors developed one aimed at operating alongside it. The photocatalytic conversion of sugar, starch, and cellulose to $H_2$ represented utilizing the carbohydrates produced during photosynthesis via $CO_2$ fixation for the generation of a fuel. Furthermore, the authors also suggested any $CO_2$ photocatalytically produced could be fed back into plants or alternatively captured by NaOH to form $Na_2CO_3$ or $NaHCO_3$. The authors referred to the process as *photoinduced fermentation*, which was considered an alternative to traditional methods of fermenting sugar. Under optimum conditions of 6 M NaOH and $\lambda = 380$ nm with a 500 W Xe lamp, quantum yields of 1.5%, 1.3%, and 1.0% were obtained for the photocatalytic conversion of sugar, starch, and cellulose to $H_2$, respectively. Moreover, a quantum yield of 0.02% was obtained when the photocatalyst was suspended in only water, to support that the formation of $H_2$ was primarily occurring from the carbohydrates. Kawai and Sakata suggested that the carbon chains of the carbohydrates were oxidized at the valence band leading to $H^+$ and $CO_2$ formation, with $H^+$ then being reduced by electrons to form $H_2$ at the conduction band. While the operating conditions could be considered to be unfavorable with respect to the use of harsh chemicals and poor energy efficiency, the paper did highlight the potential of photocatalysis for biomass conversion.

Despite the early report by Kawai and Sakata on photocatalytic reforming of poly- and monosaccharides, it was a number of years before additional papers on biomass reforming were published. Even though a lack of photocatalytic cellulose reforming/degradation based papers in the literature were not seen, there was significant interest in photocatalytic glucose conversion (Kim et al. 2015; Zhou et al. 2017; Colmenares et al. 2011; Iervolino et al. 2018; Jin et al. 2017; Fu et al. 2008; Chong et al. 2014; Da Vià et al. 2017; Iervolino et al. 2016). The majority of these papers focused on photocatalysts in combination with typical metals such as Pt, Au, Ni, and Ru (Zhou et al. 2017; Iervolino et al. 2018; Da Vià et al. 2017) to monitor $H_2$ formation, often as a comparison study to other SEDs. Given the structure of cellulose, there is obvious merit in investigating the photo-reforming of glucose as a model compound. Interestingly, however, very few of these papers looked at either the mechanism that may have occurred or a comparison between glucose, cellulose, and lignin. In this regard, Caravaca et al. (2016) looked at the formation of $H_2$ via photocatalytic reforming of cellulose, glucose, and raw biomass. Using a 0.2% $Pt\text{-}TiO_2$ catalyst, the paper demonstrated that the evolution of $H_2$ was occurring by initial in-situ hydrolysis via glucose. In a comparison study, the

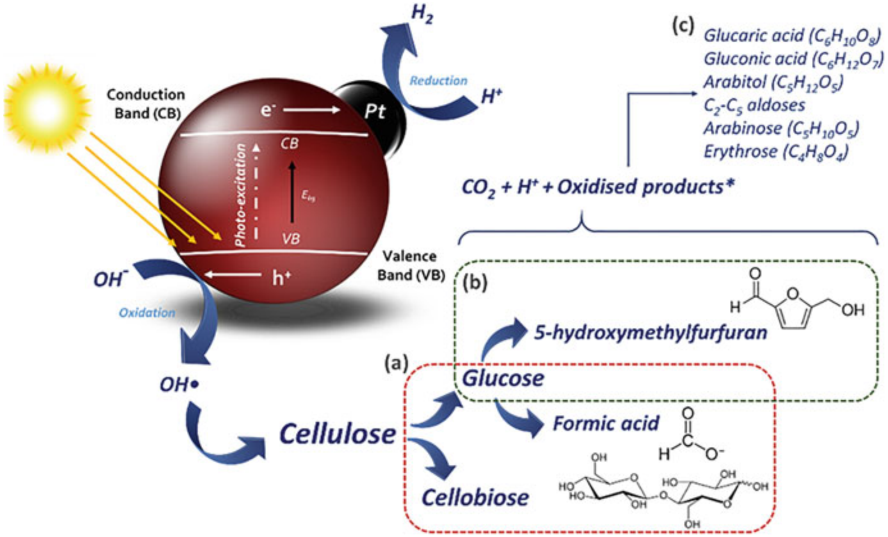

**Fig. 1.7** Proposed photocatalytic oxidation mechanism for cellulose conversion where (**a**) shows products such as glucose, cellobiose, and formic acid detected by Zhang et al. (2016a), (**b**) shows 5-hydroxymethylfuran from glucose as observed by Speltini et al. (2014), and (**c**) shows other typical oxidized products detected during glucose oxidation based on the literature (Kim et al. 2015; Zhou et al. 2017; Colmenares et al. 2011; Jin et al. 2017; Fu et al. 2008; Da Vià et al. 2017; Chong et al. 2014)

reaction orders for both glucose and cellulose were derived to be 0.24 and 0.2, respectively, which suggested that the initial stage of photocatalytic cellulose reforming was hydrolysis to glucose, which was followed by the reforming of glucose to eventually $H_2$ and a range of oxidation products. Similar findings were also reported by Zhang et al. (2016a) and Speltini et al. (2014) in 2015 and 2014, respectively, who performed a systematic study of $H_2$ evolution from cellulose. Speltini and colleagues confirmed that the initial stage in the conversion process was a $TiO_2$-mediated hydrolysis step followed by glucose reforming, which identified 5-hydroxymethylfurfural (5-HMF) as an intermediate in the mechanism. Figure 1.7 shows a potential mechanism and illustration for photocatalytic cellulose reforming based on the results obtained from literature.

Photocatalytic $H_2$ production has often been coupled with attempts to utilize solar irradiation as a means to drive the process and achieve a sustainable method of clean energy production. While challenging, a number of papers have reported solar-driven photocatalysis across a range of applications including water disinfection (Malato et al. 2009), air treatment (Giménez et al. 1999), $CO_2$ reduction (Varghese et al. 2009), and $H_2$ production (Skillen et al. 2016). Achieving solar photocatalytic reforming of biomass-based materials, however, represents an extremely favorable approach to renewable energy production. Despite papers on photocatalytic biomass conversion to $H_2$ being limited, many have already shown the potential to use solar light activated photocatalysts (Wakerley et al. 2017; Speltini et al. 2014; Zhang et al.

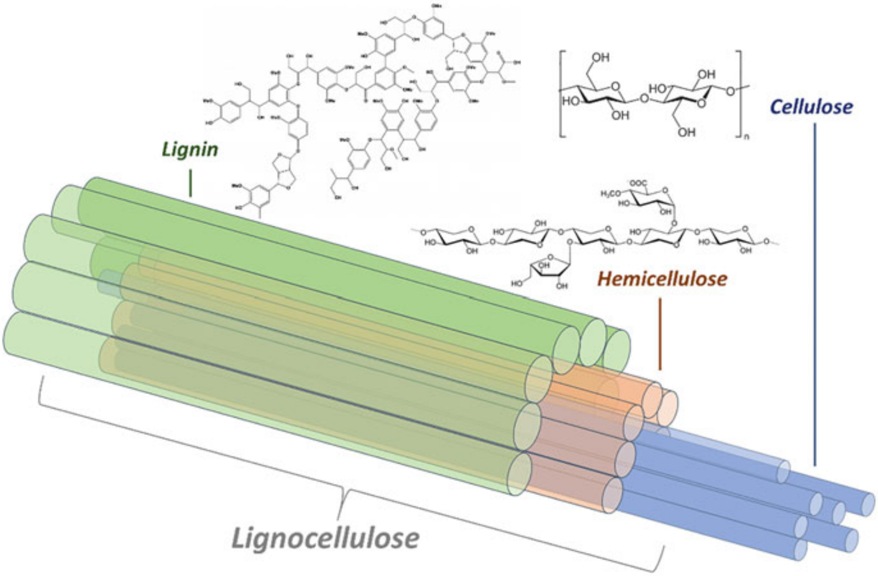

**Fig. 1.8** Simplified structure of lignocellulosic biomass with a cellulose core and subsequent layers of hemicellulose and lignin along with the representative chemical structure of each component

2016a). Work by Speltini et al. and Zhang et al. demonstrated the evolution of $H_2$ from cellulose using Pt-$TiO_2$ under natural sunlight in Pavia, Italy (45°11′N, 9°09′E), and St Andrews, Scotland (56°20′N, 2°48′W), respectively. Both investigations exposed reaction solutions containing cellulose and a catalyst to natural unconcentrated light to achieve ~16 μmole $H_2$ formation over 6 h (Zhang et al. 2016a) and 33 μmole $H_2$ formation over 4 h (Speltini et al. 2014).

While solar-driven conversion of cellulose to $H_2$ is a significant advancement, there is an argument to be made that using pure cellulose, that is, α-cellulose for photocatalysis, is not a true representation of typical biomass composition. Lignocellulose composed of lignin, hemicellulose, and cellulose (Fig. 1.8) is the most abundant form of biomass and as such represents a compound that, if valorized, could significantly contribute toward renewable energy production. Therefore, there are now papers that have focused on the conversion of lignocellulosic material to $H_2$ using typical visible light catalysts such as $C_3N_4$ with a Ni co-catalyst (Kasap et al. 2018) and CdS (Wakerley et al. 2017). Wakerley et al. reported the conversion of lignocellulose to $H_2$ using Cds/$CdO_x$, which promoted both visible photon absorption via CdS and proton reduction and lignocellulose oxidation via $CdO_x$ (Wakerley et al. 2017). Prior to Wakerley et al.'s publication, the majority of photocatalytic cellulose reforming work focused on the use of $TiO_2$ and standard cellulose substrates such as α-cellulose or microcrystalline cellulose, with only a few publications using alternative biomass substrates such as grass (Caravaca et al. 2016) and rice husks (Speltini et al. 2014; Lu et al. 2014). Alternatively, Wakerley and colleagues deployed CdS that was coated with CdOx as a photocatalyst along with α-cellulose,

**Table 1.5** Tabulated results obtained by Wakerley et al. (2017) in their study on the photocatalytic reforming of lignocellulosic material

| Substrate | Material | Substrate concentration | Hydrogen (mmol $g_{cat}^{-1}$ $h^{-1}$) |
|---|---|---|---|
| Standard feedstocks | α-Cellulose | 50 mg $mL^{-1}$ | ~ 2.25 |
| | Hemicellulose–xylan from beech wood | 25 mg $mL^{-1}$ | ~ 2.1 |
| | Lignin | 0.25 mg $mL^{-1}$ | ~ 0.25 |
| Biomass feedstocks | Printer paper | 50 mg $mL^{-1}$ | ~ 1.1 |
| | Cardboard | | ~ 0.75 |
| | Newspaper | | ~ 0.3 |
| | Wooden branch | | ~ 5.2 |
| | Bagasse | | ~ 0.3 |
| | Grass | | ~ 1.0 |
| | Sawdust | | ~ 0.75 |

All reactions were performed using 0.5 μM Cds/$CdO_x$ in 2 mL 10 M KOH at 25 °C in an anaerobic atmosphere and were irradiated for 24 h using a 100 mW $cm^{-2}$ solar light simulator

hemicellulose, and lignin as standard starting materials and also a range of biomass substrates such as a printer paper, a wooden branch, and sawdust. The $H_2$ yields from each substrate have been summarized and are tabulated in Table 1.5, which shows activity under simulated solar light. While relatively low yields of $H_2$ were achieved, the impressive study did, for the first time, achieve photocatalytic conversion of raw biomass substrates under solar irradiation.

The use of CdS as the photocatalyst by Wakerley et al. was an interesting material choice. In the first instance, CdS is a favorable compound with a natural bandgap, $E_{bg}$, of 2.4 eV suitable for visible light activation, and has been proven to be active for $H_2$ production (Yang et al. 2012b) and is relatively inexpensive. Moreover, as lignin absorbs strongly in the UV region, typically around 300–400 nm, therefore lignin is unlikely to “block” visible photons from reaching CdS. In contrast, $TiO_2$, which also absorbs strongly in the UV region, may have reduced activity due to competitive photon absorption. Incidentally, this is a limitation that has rarely been reported in the literature as to date there are limited examples of $TiO_2$ being used for photocatalytic lignin conversion. One of the few other examples, which used lignin as a feedstock, did so using a ZnO catalyst doped with C, N, and S to improve the visible light absorption properties of the material (Kadam et al. 2014). Kadam et al.’s study found that lignin degradation mildly enhanced the photocatalytic water splitting process. Despite the advantages of CdS, however, limitations associated with the stability and photo-corrosion of the compound have been well documented (Li et al. 2011; Fu et al. 2013). In addition, the valence band position of CdS , typically +1.9 V versus normal hydrogen electrode (NHE), does not support the formation of OH•. For OH• to be formed, the position of the valence band has to be more positive than +2.38 V versus NHE. OH• are important reactive oxygen species that have been suggested as the primary radicals responsible for cellulose oxidation. To overcome the limitations of CdS corrosion and valence band potentials,

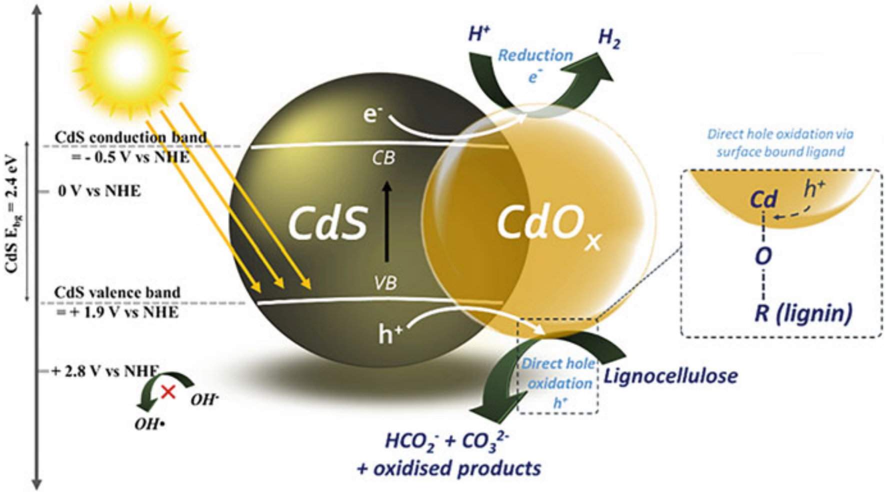

**Fig. 1.9** Mechanism suggested to be taking place in the work by Wakerley et al., which used $CdS/CdO_x$ to convert lignocellulose to both $H_2$ and oxidized product (Wakerley et al. 2017). (Illustration is based solely on information from the publication and is not a reprint)

Wakerley and colleagues performed reactions in a strong alkaline solution with 10 M KOH, which promoted the formation of $Cd(OH)_2/CdO$, referred to as $CdO_x$, on the CdS surface. The formation of $Cd(OH)_2/CdO$ structure suppressed photo-corrosion with the catalyst displaying activity for over 6 days of irradiation. Interestingly, however, the authors also suggested that in the absence of OH• production, the $CdO_x$ structure was responsible for the oxidation of lignocellulose material. An OH• probe molecule, namely terephthalic acid, was used to confirm that no OH radical formation occurred at pH 14 when $CdS/CdO_x$ was formed. Alternatively, direct hole oxidation at the surface of the catalyst was suggested as the dominant oxidation process. The presence of $CdO_x$ on the surface of CdS was suggested to promote effective binding between lignin and the catalyst via a Cd-O-R ligand, which would mirror the typical Ti-O-R bonds often reported during $TiO_2$ photocatalysis (Zhang et al. 2014, 2016a). Detection of products such as $CO_3^{2-}$ and $HCO_2^-$, which were expected to form from the continued oxidation of alcohol and aldehydes, released from lignocellulose confirmed the hypothesis. An illustrative representation of the proposed mechanism is shown in Fig. 1.9.

In $H_2$ evolving photocatalytic SED systems, the role of the donor molecule is to undergo an irreversible oxidation, which subsequently supplies electrons/protons for the reduction reaction while suppressing the rate of recombination. In the case of cellulose, however, platform chemicals and biofuel feedstocks can potentially be produced from the oxidation pathway. To date, the work by Zhang et al., which demonstrated cellulose conversion under natural light, is one of the few publications to report $H_2$ production coupled with liquid phase product formation (Zhang et al. 2016a). Following irradiation in an anaerobic environment, high-performance liquid

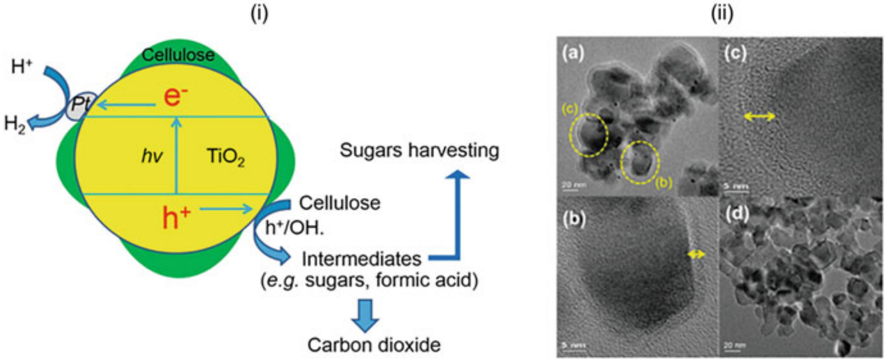

**Fig. 1.10** (**i**) Cellulose-$TiO_2$ composite material developed by Zhang et al. along with (**ii**) transmission electron microscopy (TEM) images showing a layer of cellulose around $TiO_2$ particles (*a*–*c*) and (*d*) bare Pt-$TiO_2$. (Reprinted with permission from Zhang et al. (2016a), copyright (2016), The Royal Society of Chemistry)

chromatography (HPLC) analysis of the liquid phase showed the presence of glucose, cellobiose, and formic acid within the concentration range of 0.25 to ~1.2 μmol. Furthermore, over seven experimental cycles, glucose was detected in each, while cellobiose was only present in cycles 1–3 and formic acid only present in cycles 4–7. The presence of liquid phase compounds could be attributed to the method of deployment of cellulose in the study by Zhang and colleagues. In contrast to previous work, which typically used a cellulose–catalyst suspension in water (Speltini et al. 2014; Caravaca et al. 2016), Zhang et al.'s study developed a composite material, which consisted of a thin layer of cellulose grafted to the surface of $TiO_2$ particles (Fig. 1.10). The authors described the immobilization process as a two-step procedure involving condensation of surface hydroxyl groups and formation of intramolecular H-bonds between cellulose strands and $TiO_2$. The approach of anchoring compounds to $TiO_2$ has been well documented and is ascribed to the formation of a "Ti-ligand" between the catalyst surface and compounds that have multiple hydroxyl groups (Zhang et al. 2014). The simultaneous production of $H_2$ and oxidation products by Zhang et al. was a significant achievement and demonstrated for the first time that photocatalytic cellulose reforming had a dual purpose—for renewable energy generation and as a pre-treatment method to release feedstocks for biofuel generation.

### *1.4.2 Photocatalysis of Cellulose II*

In a recent piece of work by Nagarajan, (via internal communication), cellulose II was produced from microcrystalline cellulose by dissolution in TBAH and precipitation with distilled water. Heterogeneous photocatalysis with suspended $TiO_2$ P25 photocatalyst and both cellulose I and II as feedstock was performed as a batch

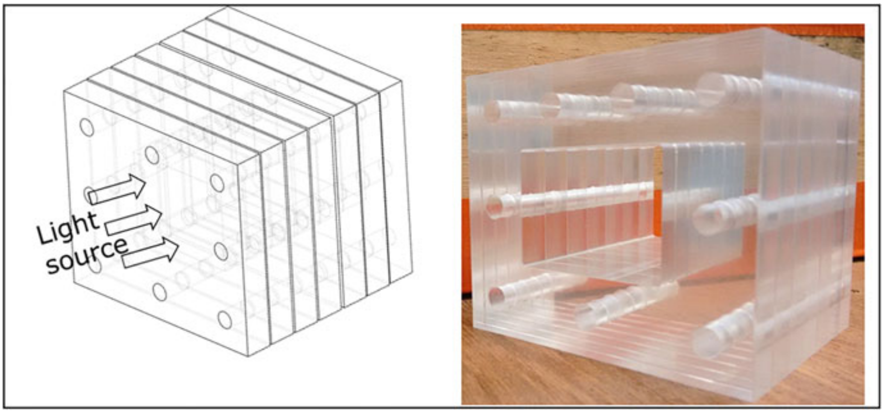

**Fig. 1.11** The stacked frame photocatalytic reactor used for fermentable sugar production from cellulose polymorphs

experiment in a beaker. In such a system, approximately fivefold increase in fermentable sugar production was observed upon photocatalysis of cellulose II when compared to cellulose I. With periodic separation of products using dialysis membrane bags, the cellulose II system produced 1.7 times higher fermentable sugars than the cellulose I system. Nagarajan's work was the first ever system to have observed and quantified fermentable sugars from cellulose II photocatalysis (Nagarajan 2017). The cellulose II production method used in the above process was similar to the one recently reported by Chang et al. (2019).

To further enhance the fermentable sugar yield, a stacked frame photocatalytic reactor (SFPR) was designed and used for the purpose. The design of the reactor has been reported by Nagarajan et al. (2017b). A schematic of the SFPR is shown in Fig. 1.11. With minor changes to the reported design, a separation chamber, separated by a dialysis membrane, was also included that aided in periodical removal of the produced fermentable sugars upon heterogeneous photocatalysis. The yield of fermentable sugars from cellulose II, upon photocatalysis, increased by ~3.5 times when compared to the aforementioned beaker system using the same feedstock. Similarly, when the SFPR was operated with cellulose I as the feedstock, approximately four times improvement in yield was observed when compared to the beaker system. Comparing sugar yields from cellulose II and I in SFPR, fermentable sugar yields with the former was found to be ~1.5 times higher than that observed with cellulose I feedstock. These results clearly indicate that cellulose II could be used as a superior feedstock for fermentable sugar production and thereby bioethanol production.

In the recent work by Chang et al., cellulose I and II were used as SEDs for photocatalytic $H_2$ production (Chang et al. 2019). Pt loaded $TiO_2$ was used as the photocatalyst and the reactions were performed in a novel propeller fluidized photo reactor (PFPR) irradiated with low power light emitting diodes (LEDs). The effect of type and concentration of starting cellulose polymorph, washed cellulose, and the respective filtrate on the rates and yields of $H_2$ production was determined. The rate of photocatalytic $H_2$ production from cellulose II was 0.13 mmol $\text{min}^{-1}$ and was over twofolds higher than that achieved with cellulose I at 0.05 mmol $\text{min}^{-1}$. The $H_2$ production with both the cases followed zero-order production kinetics. Lower crystallinity, particle size, and wettability possessed by cellulose II were established as reasons for higher $H_2$ yields. In addition to the previously mentioned study by Nagarajan in 2017, the study by Chang et al. has also shown that a novel process combining cellulose II and heterogeneous photocatalysis for fermentable sugars/energy production is possible. With further work focusing on photocatalytic reactor design and effective sugar separation, more exciting results could be achieved as well as new potentials could be unlocked to tweak the process toward sugar production or $H_2$ generation selectively.

## 1.5 Conclusion

While research on the utilization of cellulose as a feedstock for renewable fuel generation via photocatalysis has yielded some exciting and promising results, there are still some significant technical challenges that need to be overcome prior to the process being upscaled and commercially viable. While there has been much research on photoactive materials for photocatalysis for solar fuel generation, there has been significantly less activity on development of reactor technology for upscaling the process. Two of the key issues are the technical scalability and then the economic viability of the upscaled process.

To date, the photocatalytic yields of both $H_2$ and other fuel precursors have been low, at best in the μM range. For the first step in demonstrating a potentially viable process, a demonstrator unit capable of generating a minimum of between 1 and 5 $m^3h^{-1}$ would need to be achieved. In designing a process that is both technically and economically viable, the following key factors are deemed important:

- Mode of photocatalyst deployment
- Photocatalyst distribution within the reactor
- Irradiation sources to activate the photocatalyst and light distribution characteristics within the reactor
- Mass transfer of cellulose within the photocatalytic reactor
- Reaction kinetics of the photocatalytic cellulose breakdown process
- Separation of the “fuel” precursors

The issue about cellulose solubility is a particular problem as the effective interaction of cellulose with the surface of the photocatalyst prior to reaction is greatly hindered. As detailed above, approaches such as ball milling prior to reaction have enhanced reaction yields but these are still relatively small. Other solvent systems will need to be investigated in detail; however, organic solvents also have problems as the photocatalyst may start preferentially reacting with the solvent rather than the cellulose. Effective visible light activated photocatalysts would probably be a requirement for being economically viable. Over the past 25 years, there has been extensive research on visible light activated materials; however, to date the performance of visible light photocatalysts still falls short of UV-activated materials such as Evonik P25 $TiO_2$. If UV materials are to be utilized, significant advances happening in UV LED technology over the past decade have to be exploited, which of course would require less power. Once the technical challenges of producing a large-scale reactor have been overcome, there are still issues that need to be addressed to demonstrate that the process is also economically viable. Energy balance needs to be established to demonstrate that there is more energy being generated from the process than is being put in to generate the fuel. In addition, demonstration of the cost per kWh of the fuel produced must be competitive with alternative systems. Finally, a practical life cycle analysis (LCA) model will have to be established for the photocatalytic process to provide an effective understanding of the economic and environmental impacts of the complete process for photocatalytic valorization cellulose. This is also not an inconsiderable challenge as there are currently a lack of LCA models for photocatalytic renewable energy production.

Systems for generating fuels based on semiconductor photocatalysis for renewable energy generation not utilizing cellulose also face these challenges despite being extensively researched for over the past 40 years for the reduction of water to $H_2$. To date there are still no larger-scale commercial systems. One example of a larger-scale system that is being developed is the ARPChem project that involves Professor Domen's group at the University of Tokyo and a number of industrial partners including Mitsubishi Chemical, Mitsui Chemical, Sumitomo Chemical, Fuji Films, Inpex, and TOTO, which started in 2012 (Yamada and Domen 2018). The aim of the ARPChem project is to establish an artificial photosynthetic plant by 2030. Some further interesting examples of larger-scale applications of solar $H_2$ generation have been considered in a recent review by Liu and Xu (Liu et al. 2019b).

Overall, the chapter has emphasized on the growing interest within the research community on the utilization of cellulose and lignocellulosic materials as feedstock for photocatalytic fermentable sugar and $H_2$ generation. Furthermore, the authors believe that cellulose II utilization could provide a favorable way forward in combination with photocatalysis. The goal of the chapter is to instigate interest among the readers on the potential of heterogenous photocatalysis as a cellulose breakdown method. With huge gaps in the polymorph pre-processing, reactor design, challenges in light distribution, and product separation, there is scope for improvement in each of these areas with additional future research.

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# References

Abe M, Fukaya Y, Ohno H (2012) Fast and facile dissolution of cellulose with tetrabutylphosphonium hydroxide containing 40 wt% water. Chem Commun 48 (12):1808–1810. https://doi.org/10.1039/C2CC16203B

Abe M, Kuroda K, Ohno H (2015) Maintenance-free cellulose solvents based on onium hydroxides. ACS Sustain Chem Eng 3(8):1771–1776. https://doi.org/10.1021/acssuschemeng.5b00303

Alinia R, Zabihi S, Esmaeilzadeh F, Kalajahi JF (2010) Pretreatment of wheat straw by supercritical CO2 and its enzymatic hydrolysis for sugar production. Biosyst Eng 107(1):61–66. https://doi.org/10.1016/j.biosystemseng.2010.07.002

Alves L, Medronho BF, Antunes FE, Romano A, Miguel MG, Lindman B (2015) On the role of hydrophobic interactions in cellulose dissolution and regeneration: colloidal aggregates and molecular solutions. Colloids Surf A Physicochem Eng Asp 483:257–263. https://doi.org/10.1016/j.colsurfa.2015.03.011

Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ (2010) Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Bioresour Technol 101 (13):4851–4861. https://doi.org/10.1016/j.biortech.2009.11.093

Arantes V, Milagres AMF (2006) Degradation of cellulosic and hemicellulosic substrates using a chelator-mediated Fenton reaction. J Chem Technol Biotechnol 81(3):413–419. https://doi.org/10.1002/jctb.1417

Bahruji H, Bowker M, Davies PR, Al-Mazroai LS, Dickinson A, Greaves J, James D, Millard L, Pedrono F (2010) Sustainable $H_2$ gas production by photocatalysis. J Photochem Photobiol A Chem 216(2):115–118. https://doi.org/10.1016/j.jphotochem.2010.06.022

Behrens MA, Holdaway JA, Nosrati P, Olsson U (2016) On the dissolution state of cellulose in aqueous tetrabutylammonium hydroxide solutions. RSC Adv 6(36):30199–30204. https://doi.org/10.1039/C6RA03547G

Boissou F, Muhlbauer A, De OV, Leclercq L, Kunz W, Marinkovic S, Estrine B, Nardello-Rataj V, Jerome F (2014) Transition of cellulose crystalline structure in biodegradable mixtures of renewably-sourced levulinate alkyl ammonium ionic liquids, γ-valerolactone and water. Green Chem 16(5):2463–2471. https://doi.org/10.1039/C3GC42396D

Bokinsky G, Peralta-Yahya PP, George A, Holmes BM, Steen EJ, Dietrich J, Soon Lee T, Tullman-Ercek D, Voigt CA, Simmons BA, Keasling JD (2011) Synthesis of three advanced biofuels from ionic liquid-pretreated switchgrass using engineered Escherichia coli. Proc Natl Acad Sci U S A 108(50):19949–19954. https://doi.org/10.1073/pnas.1106958108

Bowker M, Davies PR, Al-Mazroai L (2008) Photocatalytic reforming of glycerol over gold and palladium as an alternative fuel source. Catal Lett 128(3):253. https://doi.org/10.1007/s10562-008-9781-1

Brundtland GH (1987) Our common future United Nations World Commission on Environment and Development. Available online at http://www.un-documents.net/our-common-future.pdf. Accessed Oct 2019

Caravaca A, Jones W, Hardacre C, Bowker M (2016) $H_2$ production by the photocatalytic reforming of cellulose and raw biomass using Ni, Pd, Pt and Au on titania. Proc R Soc A-Math Phys 472(2191):20160054. https://doi.org/10.1098/rspa.2016.0054

Chang C, Skillen N, Nagarajan S, Ralphs K, Irvine JTS, Lawton L, Robertson PKJ (2019) Using cellulose polymorphs for enhanced hydrogen production from photocatalytic reforming. Sustain Energy Fuels 3(8):1971–1975. https://doi.org/10.1039/C9SE00377K

Chen W, Pen B, Yu C, Hwang W (2011) Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bioethanol production. Bioresour Technol 102(3):2916–2924. https://doi.org/10.1016/j.biortech.2010.11.052

Chen H, Liu J, Chang X, Chen D, Xue Y, Liu P, Lin H, Han S (2017) A review on the pretreatment of lignocellulose for high-value chemicals. Fuel Process Technol 160:196–206. https://doi.org/10.1016/j.fuproc.2016.12.007

Chen W, Chan A, Sun-Waterhouse D, Llorca J, Idriss H, Waterhouse GIN (2018) Performance comparison of Ni/$TiO_2$ and Au/$TiO_2$ photocatalysts for $H_2$ production in different alcohol-water mixtures. J Catal 367:27–42. https://doi.org/10.1016/j.jcat.2018.08.015

Cheng G, Varanasi P, Li C, Liu H, Melnichenko YB, Simmons BA, Kent MS, Singh S (2011) Transition of cellulose crystalline structure and surface morphology of biomass as a function of ionic liquid pretreatment and its relation to enzymatic hydrolysis. Biomacromolecules 12 (4):933–941. https://doi.org/10.1021/bm101240z

Chong R, Li J, Ma Y, Zhang B, Han H, Li C (2014) Selective conversion of aqueous glucose to value-added sugar aldose on $TiO_2$-based photocatalysts. J Catal 314:101–108. https://doi.org/10.1016/j.jcat.2014.03.009

Colmenares JC, Magdziarz A, Bielejewska A (2011) High-value chemicals obtained from selective photo-oxidation of glucose in the presence of nanostructured titanium photocatalysts. Bioresour Technol 102(24):11254–11257. https://doi.org/10.1016/j.biortech.2011.09.101

Colón G (2016) Towards the hydrogen production by photocatalysis. Appl Catal A 518:48–59. https://doi.org/10.1016/j.apcata.2015.11.042

Cross CF, Bevan EJ, Beadle C (1893a) Die Chemie der Pflanzenfasern. Cellulosen, Oxycellulosen, Lignocellulosen. Ber Dtsch Chem Ges 26(3):2520–2533. https://doi.org/10.1002/cber.18930260348

Cross CF, Bevan ET, Beadle C (1893b) Thiokohlensäureester der Cellulose. Ber Dtsch Chem Ges 26(1):1090–1097. https://doi.org/10.1002/cber.189302601230

da Costa Sousa L, Jin M, Chundawat SPS, Bokade V, Tang X, Azarpira A, Lu F, Avci U, Humpula J, Uppugundla N, Gunawan C, Pattathil S, Cheh AM, Kothari N, Kumar R, Ralph J, Hahn MG, Wyman CE, Singh S, Simmons BA et al (2016) Next-generation ammonia pretreatment enhances cellulosic biofuel production. Energy Environ Sci 9(4):1215–1223. https://doi.org/10.1039/C5EE03051J

Da Vià L, Recchi C, Gonzalez-Yañez EO, Davies TE, Lopez-Sanchez JA (2017) Visible light selective photocatalytic conversion of glucose by TiO2. Appl Catal B Environ 202:281–288. https://doi.org/10.1016/j.apcatb.2016.08.035

Dadi AP, Varanasi S, Schall CA (2006) Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step. Biotechnol Bioeng 95(5):904–910. https://doi.org/10.1002/bit.21047

Dadi AP, Schall CA, Varanasi S (2007) Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment. Appl Biochem Biotechnol 137(1):407–421. https://doi.org/10.1007/s12010-007-9068-9

Daghrir R, Drogui P, Robert D (2013) Modified $TiO_2$ for environmental photocatalytic applications: a review. Ind Eng Chem Res 52(10):3581–3599. https://doi.org/10.1021/ie303468t

Dinand E, Vignon M, Chanzy H, Heux L (2002) Mercerization of primary wall cellulose and its implication for the conversion of cellulose I→cellulose II. Cellulose 9(1):7–18. https://doi.org/10.1023/A:1015877021688.

Dutta S, De S, Alam MI, Abu-Omar MM, Saha B (2012) Direct conversion of cellulose and lignocellulosic biomass into chemicals and biofuel with metal chloride catalysts. J Catal 288:8–15. https://doi.org/10.1016/j.jcat.2011.12.017

Ershov BG (1998) Radiation-chemical degradation of cellulose and other polysaccharides. Russ Chem Rev 67(4):315–334. https://doi.org/10.1070/RC1998v067n04ABEH000379

Fan LT, Lee Y, Beardmore DR (1981) The influence of major structural features of cellulose on rate of enzymatic hydrolysis. Biotechnol Bioeng 23(2):419–424. https://doi.org/10.1002/bit.260230215

Fu D, Mazza G (2011) Aqueous ionic liquid pretreatment of straw. Bioresour Technol 102 (13):7008–7011. https://doi.org/10.1016/j.biortech.2011.04.049

Fu X, Long J, Wang X, Leung DYC, Ding Z, Wu L, Zhang Z, Li Z, Fu X (2008) Photocatalytic reforming of biomass: a systematic study of hydrogen evolution from glucose solution. Int J Hydrog Energy 33(22):6484–6491. https://doi.org/10.1016/j.ijhydene.2008.07.068

Fu J, Chang B, Tian Y, Xi F, Dong X (2013) Novel $C_3N4$–CdS composite photocatalysts with organic–inorganic heterojunctions: in situ synthesis, exceptional activity, high stability and photocatalytic mechanism. J Mater Chem A 1(9):3083–3090. https://doi.org/10.1039/C2TA00672C

Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. Nature 238(5358):37–38. https://doi.org/10.1038/238037a0

Gao M, Xu F, Li S, Ji X, Chen S, Zhang D (2010) Effect of SC-CO2 pretreatment in increasing rice straw biomass conversion. Biosyst Eng 106(4):470–475. https://doi.org/10.1016/j.biosystemseng.2010.05.011

Giménez J, Curcó D, Queral MA (1999) Photocatalytic treatment of phenol and 2,4-dichlorophenol in a solar plant in the way to scaling-up. Catal Today 54(2):229–243. https://doi.org/10.1016/S0920-5861(99)00185-6

Guenet J (2008) Chapter 5 – cellulose. In: Guenet J (ed) Polymer-solvent molecular compounds. Elsevier, Amsterdam, pp 57–69

Halonen H, Larsson PT, Iversen T (2012) Mercerized cellulose biocomposites: a study of influence of mercerization on cellulose supramolecular structure, water retention value and tensile properties. Cellulose 20(1):57–65. https://doi.org/10.1007/s10570-012-9801-6

Hao H, Zhang L, Wang W, Zeng S (2018) Facile modification of titania with nickel sulfide and sulfate species for the photoreformation of cellulose into hydrogen. ChemSusChem 11 (16):2810–2817. https://doi.org/10.1002/cssc.201800743

Hastrup ACS, Jensen B, Green III F (2010) Chemical mediated depolymerization of cotton cellulose for the understanding of non-enzymatic fungal decay. In: Anonymous the International Research Group on Wood Protection, 9–13, May, Biarritz, France

Hideno A, Inoue H, Tsukahara K, Fujimoto S, Minowa T, Inoue S, Endo T, Sawayama S (2009) Wet disk milling pretreatment without sulfuric acid for enzymatic hydrolysis of rice straw. Bioresour Technol 100(10):2706–2711. https://doi.org/10.1016/j.biortech.2008.12.057

Hou X, Smith TJ, Li N, Zong M (2012) Novel renewable ionic liquids as highly effective solvents for pretreatment of rice straw biomass by selective removal of lignin. Biotechnol Bioeng 109 (10):2484–2493. https://doi.org/10.1002/bit.24522

Iervolino G, Vaiano V, Sannino D, Rizzo L, Ciambelli P (2016) Production of hydrogen from glucose by $LaFeO_3$ based photocatalytic process during water treatment. Int J Hydrog Energy 41 (2):959–966. https://doi.org/10.1016/j.ijhydene.2015.10.085

Iervolino G, Vaiano V, Sannino D, Rizzo L, Galluzzi A, Polichetti M, Pepe G, Campiglia P (2018) Hydrogen production from glucose degradation in water and wastewater treated by Ru-$LaFeO_3$/$Fe_2O_3$ magnetic particles photocatalysis and heterogeneous photo-Fenton. Int J Hydrog Energy 43(4):2184–2196. https://doi.org/10.1016/j.ijhydene.2017.12.071

Inoue T, Fujishima A, Konishi S, Honda K (1979) Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. Nature 277(5698):637–638. https://doi.org/10.1038/277637a0

International Energy Agency World Energy Outlook (2018) Available online at https://www.iea.org/weo2018/. Accessed Aug 2019

Jia X, Chen Y, Shi C, Ye Y, Wang P, Zeng X, Wu T (2013) Preparation and characterization of cellulose regenerated from phosphoric acid. J Agric Food Chem 61(50):12405–12414. https://doi.org/10.1021/jf4042358

Jin E, Guo J, Yang F, Zhu Y, Song J, Jin Y, Rojas OJ (2016) On the polymorphic and morphological changes of cellulose nanocrystals (CNC-I) upon mercerization and conversion to CNC-II. Carbohydr Polym 143:327–335. https://doi.org/10.1016/j.carbpol.2016.01.048

Jin B, Yao G, Wang X, Ding K, Jin F (2017) Photocatalytic oxidation of glucose into formate on nano $TiO_2$ catalyst. ACS Sustain Chem Eng 5(8):6377–6381. https://doi.org/10.1021/acssuschemeng.7b00364

Kadam SR, Mate VR, Panmand RP, Nikam LK, Kulkarni MV, Sonawane RS, Kale BB (2014) A green process for efficient lignin (biomass) degradation and hydrogen production via water splitting using nanostructured C, N, S-doped ZnO under solar light. RSC Adv 4 (105):60626–60635. https://doi.org/10.1039/C4RA10760H

Kasap H, Achilleos DS, Huang A, Reisner E (2018) Photoreforming of lignocellulose into $H_2$ using nanoengineered carbon nitride under benign conditions. J Am Chem Soc 140 (37):11604–11607. https://doi.org/10.1021/jacs.8b07853

Kawai T, Sakata T (1980) Conversion of carbohydrate into hydrogen fuel by a photocatalytic process. Nature 286(5772):474–476. https://doi.org/10.1038/286474a0

Kim G, Lee S, Choi W (2015) Glucose–$TiO_2$ charge transfer complex-mediated photocatalysis under visible light. Appl Catal B Environ 162:463–469. https://doi.org/10.1016/j.apcatb.2014.07.027

Klemm D, Philipp B, Heinze T, Heinze U, Wagenknecht W (1998) General considerations on structure and reactivity of cellulose: section 2.1–2.1.4. In: Anonymous comprehensive cellulose chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, pp 9–29

Klemm D, Heublein B, Fink H, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. Angew Chem Int Ed 44(22):3358–3393. https://doi.org/10.1002/anie.200460587

Kojima Y, Takayasu M, Toma M, Koda S (2019) Degradation of cellulose in NaOH and NaOH/urea aqueous solutions by ultrasonic irradiation. Ultrason Sonochem 51:419–423. https://doi.org/10.1016/j.ultsonch.2018.07.030

Kuga S, Takagi S, Brown RM (1993) Native folded-chain cellulose II. Polymer 34(15):3293–3297. https://doi.org/10.1016/0032-3861(93)90404-X

Kumar AK, Sharma S (2017) Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour Bioprocess 4(1):7. https://doi.org/10.1186/s40643-017-0137-9

Kumar R, Wyman CE (2009) Effects of cellulase and xylanase enzymes on the deconstruction of solids from pretreatment of poplar by leading technologies. Biotechnol Prog 25(2):302–314. https://doi.org/10.1002/btpr.102

Lavoine N, Desloges I, Dufresne A, Bras J (2012) Microfibrillated cellulose – its barrier properties and applications in cellulosic materials: a review. Carbohydr Polym 90(2):735–764. https://doi.org/10.1016/j.carbpol.2012.05.026

Li Q, Guo B, Yu J, Ran J, Zhang B, Yan H, Gong JR (2011) Highly efficient visible-light-driven photocatalytic hydrogen production of CdS-cluster-decorated graphene nanosheets. J Am Chem Soc 133(28):10878–10884. https://doi.org/10.1021/ja2025454

Li C, Wang L, Chen Z, Li Y, Wang R, Luo X, Cai G, Li Y, Yu Q, Lu J (2015) Ozonolysis pretreatment of maize stover: the interactive effect of sample particle size and moisture on ozonolysis process. Bioresour Technol 183:240–247

Lindman B, Karlström G, Stigsson L (2010) On the mechanism of dissolution of cellulose. J Mol Liq 156(1):76–81. https://doi.org/10.1016/j.molliq.2010.04.016

Liu W, Zhao S, Li L, Xin XZ (2015) Enhancement of cellulose reactivity using an ionic liquid pretreatment step. Cellul Chem Technol 49:397–403

Liu X, Duan X, Wei W, Wang S, Ni B (2019a) Photocatalytic conversion of lignocellulosic biomass to valuable products. Green Chem 21(16):4266–4289. https://doi.org/10.1039/C9GC01728C

Liu G, Sheng Y, Ager JW, Kraft M, Xu R (2019b) Research advances towards large-scale solar hydrogen production from water. EnergyChem 1(2):100014. https://doi.org/10.1016/j.enchem.2019.100014

Lu Y, Wei X, Wen Z, Chen H, Lu Y, Zong Z, Cao J, Qi S, Wang S, Yu L, Zhao W, Fan X, Zhao Y (2014) Photocatalytic depolymerization of rice husk over $TiO_2$ with $H_2O_2$. Fuel Process Technol 117:8–16. https://doi.org/10.1016/j.fuproc.2013.04.001

Luo N, Fu X, Cao F, Xiao T, Edwards PP (2008) Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst – Effect of catalyst composition and reaction conditions. Fuel 87 (17):3483–3489. https://doi.org/10.1016/j.fuel.2008.06.021

Lyashenko LV, Gorokhovat-skii Y (1975) Photocatalytic oxidation of carbon monoxide on metal oxides. Theor Exp Chem 10(2):138–142. https://doi.org/10.1007/BF00524461

Ma H, Zhang B, Zhang P, Li S, Gao Y, Hu X (2016) An efficient process for lignin extraction and enzymatic hydrolysis of corn stalk by pyrrolidonium ionic liquids. Fuel Process Technol 148:138–145. https://doi.org/10.1016/j.fuproc.2016.02.038

Machado AEH, Furuyama AM, Falone SZ, Ruggiero R, Perez DS, Castellan A (2000) Photocatalytic degradation of lignin and lignin models, using titanium dioxide: the role of the hydroxyl radical. Chemosphere 40(1):115–124. https://doi.org/10.1016/S0045-6535(99)00269-6

Malato S, Fernández-Ibáñez P, Maldonado MI, Blanco J, Gernjak W (2009) Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal Today 147 (1):1–59. https://doi.org/10.1016/j.cattod.2009.06.018

Matsuoka M, Kitano M, Takeuchi M, Tsujimaru K, Anpo M, Thomas JM (2007) Photocatalysis for new energy production: recent advances in photocatalytic water splitting reactions for hydrogen production. Catal Today 122(1):51–61. https://doi.org/10.1016/j.cattod.2007.01.042

Maurino V, Bedini A, Minella M, Rubertelli F, Pelizzetti E, Minero C (2008) Glycerol transformation through photocatalysis: a possible route to value added chemicals. J Adv Oxid Technol 11:184–192. https://doi.org/10.1515/jaots-2008-0201

Medronho B, Lindman B (2014) Competing forces during cellulose dissolution: from solvents to mechanisms. Curr Opin Colloid Interface Sci 19(1):32–40. https://doi.org/10.1016/j.cocis.2013.12.001

Medronho B, Lindman B (2015) Brief overview on cellulose dissolution/regeneration interactions and mechanisms. Adv Colloid Interf Sci 222:502–508. https://doi.org/10.1016/j.cis.2014.05.004

Meng D, Li G, Liu Z, Yang F (2011) Study of depolymerization of cotton cellulose by Pb/$PbO_2$ anode electrochemical catalysis in sulfuric acid solution. Polym Degrad Stab 96(7):1173–1178. https://doi.org/10.1016/j.polymdegradstab.2011.04.021

Mercer J (1850) Improvements in the preparation of cotton and other fabrics and other fibrous materials

Miao Z, Grift TE, Hansen AC, Ting KC (2011) Energy requirement for comminution of biomass in relation to particle physical properties. Ind Crop Prod 33(2):504–513. https://doi.org/10.1016/j.indcrop.2010.12.016

Mittal A, Katahira R, Himmel ME, Johnson DK (2011) Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: changes in crystalline structure and effects on enzymatic digestibility. Biotechnol Biofuels 4(1):1–16. https://doi.org/10.1186/1754-6834-4-41

Nagarajan S (2017) Development of photocatalytic reactor technology for the production of fermentable sugars. PhD, Queen's University Belfast. Available online at https://pure.qub.ac.uk/en/studentTheses/development-of-photocatalytic-reactor-technology-for-the-producti. Accessed Oct 2019

Nagarajan S, Skillen NC, Irvine JTS, Lawton LA, Robertson PKJ (2017a) Cellulose II as bioethanol feedstock and its advantages over native cellulose. Renew Sust Energ Rev 77(Suppl C):182–192. https://doi.org/10.1016/j.rser.2017.03.118

Nagarajan S, Stella L, Lawton LA, Irvine JTS, Robertson PKJ (2017b) Mixing regime simulation and cellulose particle tracing in a stacked frame photocatalytic reactor. Chem Eng J 313:301–308. https://doi.org/10.1016/j.cej.2016.12.016

O'Sullivan A (1997) Cellulose: the structure slowly unravels. Cellulose 4(3):173–207. https://doi.org/10.1023/A:1018431705579.

Odorico FH, Morandim-Giannetti A, Lucarini AC, Torres RB (2018) Pretreatment of Guinea grass (Panicum maximum) with the ionic liquid 1-ethyl-3-methyl imidazolium acetate for efficient hydrolysis and bioethanol production. Cellulose 25(5):2997–3009. https://doi.org/10.1007/s10570-018-1753-z

Oturan MA, Aaron J (2014) Advanced oxidation processes in water/wastewater treatment: principles and applications. A review. Crit Rev Environ Sci Technol 44(23):2577–2641. https://doi.org/10.1080/10643389.2013.829765

Park JI, Steen EJ, Burd H, Evans SS, Redding-Johnson A, Batth T, Benke PI, D'haeseleer P, Sun N, Sale KL, Keasling JD, Lee TS, Petzold CJ, Mukhopadhyay A, Singer SW, Simmons BA, Gladden JM (2012) A thermophilic ionic liquid-tolerant cellulase cocktail for the production of cellulosic biofuels. PLoS One 7(5):e37010. https://doi.org/10.1371/journal.pone.0037010

Pena CA, Soto A, King AWT, Rodríguez H (2019) Improved reactivity of cellulose via its crystallinity reduction by nondissolving pretreatment with an ionic liquid. ACS Sustain Chem Eng 7(10):9164–9171. https://doi.org/10.1021/acssuschemeng.8b06357

Pinkert A, Marsh KN, Pang S, Staiger MP (2009) Ionic liquids and their interaction with cellulose. Chem Rev 109(12):6712–6728. https://doi.org/10.1021/cr9001947

Ray MJ, Leak DJ, Spanu PD, Murphy RJ (2010) Brown rot fungal early stage decay mechanism as a biological pretreatment for softwood biomass in biofuel production. Biomass Bioenergy 34 (8):1257–1262. https://doi.org/10.1016/j.biombioe.2010.03.015

Revol JF, Dietrich A, Goring DAI (1987) Effect of mercerization on the crystallite size and crystallinity index in cellulose from different sources. Can J Chem 65(8):1724–1725. https://doi.org/10.1139/v87-288

Saha BC, Iten LB, Cotta MA, Wu YV (2005) Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol. Process Biochem 40(12):3693–3700. https://doi.org/10.1016/j.procbio.2005.04.006

Saha BC, Qureshi N, Kennedy GJ, Cotta MA (2016) Biological pretreatment of corn stover with white-rot fungus for improved enzymatic hydrolysis. Int Biodeterior Biodegradation 109:29–35. https://doi.org/10.1016/j.ibiod.2015.12.020

Sakurada I, Hutino K (1936) Über die intramizellare Quellung der Zellulose durch Wasser. Kolloid Z 77(3):346–351. https://doi.org/10.1007/BF01433526

Samayam IP, Hanson BL, Langan P, Schall CA (2011) Ionic-liquid induced changes in cellulose structure associated with enhanced biomass hydrolysis. Biomacromolecules 12(8):3091–3098. https://doi.org/10.1021/bm200736a

Sasaki M, Adschiri T, Arai K (2003) Production of cellulose II from native cellulose by near- and supercritical water solubilization. J Agric Food Chem 51(18):5376–5381. https://doi.org/10.1021/jf025989i

Sassner P, Mårtensson C, Galbe M, Zacchi G (2008) Steam pretreatment of H2SO4-impregnated Salix for the production of bioethanol. Bioresour Technol 99(1):137–145. https://doi.org/10.1016/j.biortech.2006.11.039

Scordia D, Cosentino SL, Lee J, Jeffries TW (2011) Dilute oxalic acid pretreatment for biorefining giant reed (Arundo donax L.). Biomass Bioenergy 35(7):3018–3024. https://doi.org/10.1016/j.biombioe.2011.03.046

Shafiei M, Zilouei H, Zamani A, Taherzadeh MJ, Karimi K (2013) Enhancement of ethanol production from spruce wood chips by ionic liquid pretreatment. Appl Energy 102:163–169. https://doi.org/10.1016/j.apenergy.2012.05.060

Sharma S, Nair SS, Zhang Z, Ragauskas AJ, Deng Y (2015) Characterization of micro fibrillation process of cellulose and mercerized cellulose pulp. RSC Adv 5(77):63111–63122. https://doi.org/10.1039/C5RA09068G

Shibazaki H, Saito M, Kuga S, Okano T (1998) Native cellulose II production by *Acetobacter Xylinum* under physical constraints. Cellulose 5(3):165–173. https://doi.org/10.1023/A:1009277122329.

Silveira MHL, Morais ARC, AMd L, Olekszyszen DN, Bogel-Łukasik R, Andreaus J, Ramos LP (2015) Current pretreatment technologies for the development of cellulosic ethanol and biorefineries. ChemSusChem 8(20):3366–3390. https://doi.org/10.1002/cssc.201500282

Silverstein RA (2005) A comparison of chemical pretreatment methods for converting cotton stalks to ethanol. Master of Science, North Carolina State University

Sindhu R, Binod P, Pandey A (2016) Biological pretreatment of lignocellulosic biomass – an overview. Bioresour Technol 199:76–82. https://doi.org/10.1016/j.biortech.2015.08.030

Sjöström E (1993) Wood chemistry: fundamentals and applications. Academic, London

Skillen N, McCullagh C, Adams M (2015) Photocatalytic splitting of water. In: Bahnemann DW, Robertson PKJ (eds) Environmental photochemistry part III. Springer Berlin Heidelberg, Berlin/Heidelberg, pp 45–86

Skillen N, Adams M, McCullagh C, Ryu SY, Fina F, Hoffmann MR, Irvine JTS, Robertson PKJ (2016) The application of a novel fluidised photo reactor under UV–visible and natural solar irradiation in the photocatalytic generation of hydrogen. Chem Eng J 286:610–621. https://doi.org/10.1016/j.cej.2015.10.101

Slamet, Ratnawati, Gunlazuardi J, Dewi EL (2017) Enhanced photocatalytic activity of Pt deposited on titania nanotube arrays for the hydrogen production with glycerol as a sacrificial agent. Int J Hydrog Energy 42(38):24014–24025. https://doi.org/10.1016/j.ijhydene.2017.07.208

Speltini A, Sturini M, Dondi D, Annovazzi E, Maraschi F, Caratto V, Profumo A, Buttafava A (2014) Sunlight-promoted photocatalytic hydrogen gas evolution from water-suspended cellulose: a systematic study. Photochem Photobiol Sci 13(10):1410–1419. https://doi.org/10.1039/C4PP00128A

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 83(1):1–11. https://doi.org/10.1016/S0960-8524(01)00212-7

Swatloski RP, Spear SK, Holbrey JD, Rogers RD (2002) Dissolution of cellulose with ionic liquids. J Am Chem Soc 124(18):4974–4975. https://doi.org/10.1021/ja025790m

van der Hoeven M (2013) World energy outlook report. Available online at http://www.worldenergyoutlook.org/media/weowebsite/factsheets/WEO2013_Factsheets.pdf. Accessed Oct 2019

Van Gerven T, Mul G, Moulijn J, Stankiewicz A (2007) A review of intensification of photocatalytic processes. Chem Eng Process 46(9):781–789. https://doi.org/10.1016/j.cep.2007.05.012

Varghese OK, Paulose M, LaTempa TJ, Grimes CA (2009) High-rate solar photocatalytic conversion of $CO_2$ and water vapor to hydrocarbon fuels. Nano Lett 9(2):731–737. https://doi.org/10.1021/nl803258p

Vitz J, Erdmenger T, Haensch C, Schubert US (2009) Extended dissolution studies of cellulose in imidazolium based ionic liquids. Green Chem 11(3):417–424. https://doi.org/10.1039/B818061J

von Sonntag C, Schuchmann HP (2001) Carbohydrates. In: Charles DJ, Madhava Rao BS (eds) Radiation chemistry present status and future trends, vol 87. Elsevier, Amsterdam/New York, pp 481–511

Wada M, Chanzy H, Nishiyama Y, Langan P (2004) Cellulose IIII crystal structure and hydrogen bonding by synchrotron X-ray and neutron fiber diffraction. Macromolecules 37(23):8548–8555. https://doi.org/10.1021/ma0485585

Wada M, Ike M, Tokuyasu K (2010) Enzymatic hydrolysis of cellulose I is greatly accelerated via its conversion to the cellulose II hydrate form. Polym Degrad Stab 95(4):543–548. https://doi.org/10.1016/j.polymdegradstab.2009.12.014

Wakerley DW, Kuehnel MF, Orchard KL, Ly KH, Rosser TE, Reisner E (2017) Solar-driven reforming of lignocellulose to $H_2$ with a $CdS/CdO_x$ photocatalyst. Nat Energy 2:17021. https://doi.org/10.1038/nenergy.2017.21

Wan C, Li Y (2012) Fungal pretreatment of lignocellulosic biomass. Biotechnol Adv 30(6):1447–1457. https://doi.org/10.1016/j.biotechadv.2012.03.003

Wang Y, Deng Y (2009) The kinetics of cellulose dissolution in sodium hydroxide solution at low temperatures. Biotechnol Bioeng 102(5):1398–1405. https://doi.org/10.1002/bit.22160

Wang Z, Li G, Yang F, Chen Y, Gao P (2011) Electro-Fenton degradation of cellulose using graphite/PTFE electrodes modified by 2-ethylanthraquinone. Carbohydr Polym 86(4):1807–1813. https://doi.org/10.1016/j.carbpol.2011.07.021

Wei W, Wei X, Gou G, Jiang M, Xu X, Wang Y, Hui D, Zhou Z (2015) Improved dissolution of cellulose in quaternary ammonium hydroxide by adjusting temperature. RSC Adv 5(49):39080–39083. https://doi.org/10.1039/C5RA04247J

Wigley TML, Richels R, Edmonds JA (1996) Economic and environmental choices in the stabilization of atmospheric $CO_2$ concentrations. Nature 379(6562):240–243. https://doi.org/10.1038/379240a0

Wu L, Arakane M, Ike M, Wada M, Takai T, Gau M, Tokuyasu K (2011) Low temperature alkali pretreatment for improving enzymatic digestibility of sweet sorghum bagasse for ethanol production. Bioresour Technol 102(7):4793–4799. https://doi.org/10.1016/j.biortech.2011.01.023

Xiao S, Liu B, Wang Y, Fang Z, Zhang Z (2014) Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures. Bioresour Technol 151:361–366. https://doi.org/10.1016/j.biortech.2013.10.095

Yamada T, Domen K (2018) Development of sunlight driven water splitting devices towards future artificial photosynthetic industry. ChemEngineering 2(3):36. https://doi.org/10.3390/chemengineering2030036

Yamane C, Aoyagi T, Ago M, Sato K, Okajima K, Takahashi T (2006) Two different surface properties of regenerated cellulose due to structural anisotropy. Polym J 38(8):819–826. https://doi.org/10.1295/polymj.PJ2005187

Yang L, Cao J, Jin Y, Chang H, Jameel H, Phillips R, Li Z (2012a) Effects of sodium carbonate pretreatment on the chemical compositions and enzymatic saccharification of rice straw. Bioresour Technol 124:283–291. https://doi.org/10.1016/j.biortech.2012.08.041

Yang J, Yan H, Wang X, Wen F, Wang Z, Fan D, Shi J, Li C (2012b) Roles of cocatalysts in Pt–PdS/CdS with exceptionally high quantum efficiency for photocatalytic hydrogen production. J Catal 290:151–157. https://doi.org/10.1016/j.jcat.2012.03.008

Yu L, Lin J, Tian F, Li X, Bian F, Wang J (2014) Cellulose nanofibrils generated from jute fibers with tunable polymorphs and crystallinity. J Mater Chem A 2(18):6402–6411. https://doi.org/10.1039/C4TA00004H

Zavrel M, Bross D, Funke M, Büchs J, Spiess AC (2009) High-throughput screening for ionic liquids dissolving (ligno-)cellulose. Bioresour Technol 100(9):2580–2587. https://doi.org/10.1016/j.biortech.2008.11.052

Zhang G, Kim G, Choi W (2014) Visible light driven photocatalysis mediated via ligand-to-metal charge transfer (LMCT): an alternative approach to solar activation of titania. Energy Environ Sci 7(3):954–966. https://doi.org/10.1039/C3EE43147A

Zhang G, Ni C, Huang X, Welgamage A, Lawton LA, Robertson PKJ, Irvine JTS (2016a) Simultaneous cellulose conversion and hydrogen production assisted by cellulose decomposition under UV-light photocatalysis. Chem Commun 52:1673–1676. https://doi.org/10.1039/C5CC09075J

Zhang M, Qin Y, Ma J, Yang L, Wu Z, Wang T, Wang W, Wang C (2016b) Depolymerization of microcrystalline cellulose by the combination of ultrasound and Fenton reagent. Ultrason Sonochem 31:404–408. https://doi.org/10.1016/j.ultsonch.2016.01.027

Zhang L, Wang W, Zeng S, Su Y, Hao H (2018) Enhanced $H_2$ evolution from photocatalytic cellulose conversion based on graphitic carbon layers on $TiO_2/NiO_x$. Green Chem 20(13):3008–3013. https://doi.org/10.1039/C8GC01398E

Zhao J, Yang X (2003) Photocatalytic oxidation for indoor air purification: a literature review. Build Environ 38(5):645–654. https://doi.org/10.1016/S0360-1323(02)00212-3

Zhao H, Holladay JE, Kwak JH, Zhang ZC (2007) Inverse temperature-dependent pathway of cellulose decrystallization in trifluoroacetic acid. J Phys Chem B 111(19):5295–5300. https://doi.org/10.1021/jp070253f

Zhou B, Song J, Zhang Z, Jiang Z, Zhang P, Han B (2017) Highly selective photocatalytic oxidation of biomass-derived chemicals to carboxyl compounds over $Au/TiO_2$. Green Chem 19(4):1075–1081. https://doi.org/10.1039/C6GC03022J

Zou J, Zhang G, Xu X (2018) One-pot photoreforming of cellulosic biomass waste to hydrogen by merging photocatalysis with acid hydrolysis. Appl Catal A 563:73–79. https://doi.org/10.1016/j.apcata.2018.06.030