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Using Cellulose Polymorphs for Enhanced Hydrogen Production from Photocatalytic Reforming

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Efficient energy production and waste valorisation are the most challenging fields in photocatalysis. Reported here is enhanced hydrogen production from cellulose, achieved through the conversion of cellulose I to II via a simple pretreatment step.

Photocatalytic conversion of waste material to sustainable fuels is a highly desirable yet challenging process. Specifically, the formation of H₂ over a semiconductor using either water or a sacrificial electron donor (SED) remains one of the biggest challenges in the field of photocatalysis since the initial publication by Fujishima and Honda¹. Ever since, focus has primarily been on material synthesis to produce a highly active and preferably solar activated catalyst. Alongside this, research into the use of SEDs to facilitate the production of H₂ has also increased. SEDs have been frequently used to supply electrons and reduce recombination by undergoing an irreversible oxidation reaction. SEDs such as methanol, oxalic acid and trimethylamine are among the most commonly reported in the literature^{2–4}. More recently, with the increase in bioenergy applications, focus has shifted to cheaper alternative SEDs such as glycerol⁵ and lignocellulosic biomass⁶. Both compounds are abundant and have low commercial value making them ideal for photocatalytic applications.

While glycerol has been shown to be readily oxidised and reduced to H₂ via favourable stoichiometry^{5,7,8}, lignocellulosic biomass is a far more challenging starting material. The primary challenge in utilising lignocellulosic biomass is its recalcitrance possessed due to the interlinked cellulose, hemicellulose and lignin. Resourceful cellulose locked within the biomass, when

extracted could however be utilised as the feedstock for a variety of purposes including photocatalytic H₂ production. While limited, there are a number of excellent papers that have shown the potential of directly converting cellulose and cellulose based materials to H₂^{6,9–12}.

While these papers have shown the potential of the application, the crystallinity and insolubility of cellulose remain an issue. These issues could be eliminated by using a pre-treatment step to form a more favourable starting material. Existing methods however, often include harsh conditions and are energy intensive such as steam explosion and acid hydrolysis. An alternative approach is to convert native cellulose (cellulose I) to one of its polymorphs which often have a smaller particle size, increased lattice distance and reduced crystallinity. The literature has reported a number of ways this can be done^{13–16} and recently Nagarajan *et al.* reviewed the conversion of cellulose I to II using tetrabutylammonium hydroxide (TBAH) as an energy efficient and environmentally friendly approach¹⁶.

Therefore, reported in this article is the use of TBAH as a pre-treatment step to convert cellulose I to cellulose II for improved photocatalytic reforming to H₂. To date, this is yet to be reported in the literature with previous publications focusing on direct conversion or liquid phase oxidation products. Furthermore, a novel propeller fluidised photo reactor (PFPR) was used to perform the reaction using low power Light Emitting Diodes (LED) to produce an energy efficient method of generating H₂ from cellulose.

The effect of starting feedstock for photocatalytic H₂ production is shown in Figure 1 along with H₂ production from different batches of cellulose II in the inset (Figure 1 (b)). The conversion of cellulose I to cellulose II via TBAH treatment resulted in over a 2-fold increase in H₂ yield; *r*H₂ increased from 0.05 to 0.13 μmol min^{−1}. Under pure water splitting conditions, no H₂ was detected, suggesting it was the reforming of cellulose that was generating H₂. Furthermore, no H₂ was produced in the absence of Pt, TiO₂ and/or light, confirming that the reaction was due to firstly TiO₂ acting as a semiconductor to generate an electron-

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hole pair and secondly, Pt acting as an electron trap for proton reduction to H₂.

Under photocatalytic conditions, the evolution of H₂ from both cellulose I and II was linear with increasing irradiation time suggesting zero order kinetics. Furthermore, good reproducibility was seen for cellulose II conversion to H₂ as indicated by the replicates shown in Figure 1 (a). In contrast, a slightly larger increase between replicates was seen for cellulose I, which may have been due to the varied range of particles present when in suspension. Comparable H₂ production was also achieved when using different batches of cellulose II to demonstrate the reproducibility of the conversion method (Figure 1 (b)). Batches 1, 2 and 3 were all prepared separately from individual batches of cellulose I (particle range of 106 – 212 μm) and fresh TBAH.

Figure 1. Effect of starting feedstock on photocatalytic H₂ production where (a) shows H₂ from cellulose I (replicate 1 (•) and 2 (•)) and cellulose II (replicate 1 (•) and 2 (•)) while (b) is H₂ formation from cellulose II from individually synthesised batches (batch 1 (•), 2 (•) and 3 (•))

The improved activity when using cellulose II was also reflected in the overall reaction rates (r_{H_2}) and photonic efficiencies (η_{photon}), Table 1. The data shows over a 2-fold increase for both r_{H_2} per gram of photocatalyst per hour of irradiation and η_{photon} .

Irradiation Source	r_{H_2} ($\mu\text{mol g}_{\text{cat}}^{-1} \text{hr}^{-1}$)	$r_{\text{H}_2} \text{ max}$ (moles min^{-1})	η_{photon} (%)
Cellulose I	40	1.09×10^{-7}	3.9
Cellulose II	104	2.64×10^{-7}	9.4

Table 1. Calculated H₂ evolution rates per gram of photocatalyst and hour of irradiation and as $r_{\text{H}_2} \text{ max}$ and η_{photon} (%) for cellulose I and II.

The significantly improved yield when using cellulose II can primarily be attributed to decreased crystallinity, a lower degree of polymerisation, a smaller particle size (see ESI) and an increase in H₂O uptake as a result of increased lattice spacing¹⁶. The crystallinity of both starting materials was determined from XRD analysis (see ESI)¹⁷. The X-ray diffractograms showed cellulose I to have typical peaks at 15°, 16.5° and 22.8° while cellulose II was found to have peaks centred around 19.8° and 21.8°, which agreed with the literature^{16,17}. The crystallinity of

both materials was a crucial factor in the photocatalytic conversion process. The crystallinity of cellulose II was found to be 60 %, which was significantly lower than cellulose I at 85 % (see ESI for calculation). As was also discussed by Caravaca *et al.*, a higher degree of crystallinity results in restricted interaction between the photocatalyst surface and cellulose particles, which is a particular challenge given that both particles were present as a suspension⁹. The cellulose-catalyst interaction was likely the primary parameter which dictated the efficiency of the system. To overcome this limitation, a previous report had used a TiO₂-cellulose composite, which created a thin layer of cellulose around TiO₂ particles, which ensured interaction between the two materials¹⁰. Reported here however, is increased interaction achieved through pre-treatment to decrease the crystallinity of cellulose. Therefore, the observed decrease in crystallinity and rearranged H-bonding network were likely to facilitate an increased interaction between the catalyst particle and the interior sites of cellulose. Furthermore, the increased lattice spacing improved radical diffusion between the planes which broke the glycosidic and hydrogen bonds and accelerated photocatalytic oxidation.

The relationship between cellulose II starting concentration and H₂ production is shown in Figure 2. It was found that increasing the starting concentration in the range of 0.5 – 4 g L⁻¹, resulted in an increase in H₂ while increasing further to 10 g L⁻¹ resulted in a 28.5 % drop, Figure 2 (a). As cellulose II was a suspension in the PFPR, increasing to higher loadings had a significant impact on light penetration and at concentration greater than 4 g L⁻¹, the system became saturated. Figure 2 (b) also shows that after 45 – 60 mins of irradiation, steady state H₂ production was achieved for all starting concentrations of cellulose II. A starting concentration of 4 g L⁻¹ produced the highest rate of production at $\sim 2.4 \mu\text{mol hr}^{-1} \text{g}_{\text{cat}}^{-1}$. A plot of cellulose II starting concentration versus r_{H_2} (Figure 2 (c)) and the corresponding natural logarithm plot (Figure 2 (d)) shows that despite an 8-fold increase in cellulose concentration, only a 1.7 fold increase in r_{H_2} was recorded. This would suggest that the reaction was near zero-order, which was also reported by Caravaca *et al.* when using cellulose I⁹.

If a pre-treatment step is used in any photocatalytic application, it is paramount to understand its impact on the overall system. Therefore, to investigate this, cellulose I and II were first washed with distilled H₂O, centrifuged and then filtered (see ESI). The recovered filtrate and 'washed' cellulose were then used as starting feedstocks for photocatalysis. Figure 3 shows the overall effect of the washing steps on H₂ production, which highlights a number of interesting observations (supported by Figure S4 and S5). Firstly, Figure 3 shows the recovered filtrate from both cellulose I and II produced a significant amount of H₂. In particular, cellulose II showed a comparable r_{H_2} of 0.13 and 0.12 $\mu\text{mol min}^{-1}$ for unwashed cellulose and the recovered filtrate respectively. Furthermore, upon resuspending the washed cellulose, a r_{H_2} of 0.03 and 0.09 $\mu\text{mol min}^{-1}$ was recorded for cellulose I and II respectively. These findings would suggest that H₂ was forming from both the cellulose particles

and what was potentially being 'washed' off into the recovered filtrate.

Figure 2. The relationship between cellulose II starting concentration and H_2 production where (a) is the effect of cellulose II starting concentration on H_2 production showing 0.5 (•), 1 (•), 2 (•), 4 (•) and 10 $g L^{-1}$ (•) starting cellulose concentrations, (b) is rH_2 at different starting concentrations, (c) is the plot of rH_2 as a function of cellulose II concentration and (d) is a kinetic plot of $\ln(\text{cellulose II})$ versus $\ln(rH_2)$

Figure 3. Effect of washing on H_2 production from cellulose; the comparison of cellulose I (■) and II (■) rH_2 when using unwashed cellulose, recovered filtrate (after 1st wash) and washed cellulose (after 1st wash) as a starting feedstock.

In the case of H_2 from cellulose (both washed or unwashed), the likely mechanism was *via* $OH^\bullet$ attack which would produce a range of sugars and smaller organic compounds. These compounds would subsequently be readily oxidised in a photocatalytic system, which would also lead to H_2 formation. In the case of the filtrate however, the H_2 may have been coming from either smaller cellulose particles (which passed through the filtering step) or alternatively from smaller

dissolved compounds (such as sugars) that had been released during treatment with TBAH. In this instance it would be undesirable to have compounds being released during the pre-treatment stage. To determine if the H_2 formed from the recovered filtrate was due to dissolved organic compounds, HPLC-RI analysis was performed. Samples of the filtrate and of water taken directly from the cellulose II suspension (prior to photocatalysis) showed no products were present in the liquid phase. This confirmed that the pre-treatment step (using TBAH) wasn't releasing any sugars and was facilitating conversion and not hydrolysis. Furthermore, H_2 production was tested using a lower concentration glucose feedstock that corresponded to the limit of detection (LOD) of the HPLC ($\sim 1 \times 10^{-4} g L^{-1}$) (Figure S5). Under these conditions, no H_2 was detected which suggests that if any compounds had been released *via* TBAH pre-treatment (that were beyond the LOD of the HPLC), they weren't contributing towards H_2 formation. Based upon these results, the H_2 observed from the washed filtrate was likely forming from smaller cellulose particles that had been released from the washing step and passed through a filtering step (0.22 μm). Particle size analysis (Figure S6 & Table S1) confirmed the presence of smaller particles after filtration in the range of ~ 200 nm, while unfiltered samples showed cellulose II particles to range between 300 and 1842 nm. It was the presence of smaller particles that was thought to contribute towards the formation of H_2 .

These observations are further supported by Figure 4 (a) and (b) which show the impact of a second washing step on H_2 production. Figure 4 (a) shows that a second washing step decreased H_2 formation from the recovered filtrate by 65 %, suggesting that the presence of smaller cellulose particles had been reduced. In contrast however, Figure 4 (b) shows that the overall rH_2 from the washed cellulose remained comparable. It is interesting to note that a small induction period occurred when using the washed cellulose II that had been resuspended in H_2O , with linear production occurring after 45 and 60 mins for the 1st and 2nd wash respectively. This was to be expected if the mechanism of H_2 formation is considered to proceed *via* conversion to oxidation products first. As cellulose was present as a suspension, the interaction at the catalyst surface was expected to be low which would reduce initial oxidation and therefore H_2 . During the induction period it was likely that cellulose oxidation occurred first, resulting in a build-up of sugars and smaller compounds which subsequently leads to linear H_2 formation (Figure 4 (b)).

The exact mechanism of H_2 formation from cellulose as a SED is yet to be confirmed in the literature. While the mechanism remains elusive, it seems likely that formic acid is expected to be the final intermediate product before conversion to H_2 ⁹. The pathway from cellulose to formic acid however can proceed *via* multiple mechanisms including OH radical attack of oxidised products¹⁸ as well as the formation of glucose radicals¹¹. In the present work the mechanism of formation is still under investigation, with focus now on the determination of various liquid phase products using HPLC analysis. In general, the authors believe the mechanism would follow the pathway detailed in Equations 1-5 and Figure 5, in which cellulose is first

oxidised to glucose and oligosaccharides and a range of glucose oxidation products. Following this, the products are expected to subsequently undergo further OH radical attack leading eventually to mineralisation to H₂ and CO₂.

Figure 4. Effect of washing steps on H₂ production from cellulose where (a) shows the effect of the 1st (■) and 2nd (■) wash on H₂ production using the recovered filtrate and (b) the washed cellulose II.

Figure 5. Illustration of the proposed mechanism of cellulose II photocatalytic reforming to H₂

Conclusion

The conversion of cellulose I to cellulose II via a TBAH pre-treatment step has been found to be favourable for photocatalytic reforming to H₂. Using cellulose II, a 2-fold increase in *r*H₂ over cellulose I was recorded along with an increase in photonic efficiency from 3.9 to 9.4 % in an LED irradiated PFPR. Pre-washing both cellulose materials also showed that smaller particles were released that could primarily contribute towards H₂ formation. Upon resuspending washed cellulose particles into water, an induction period was noted before linear H₂ production occurred. This suggests the mechanism was proceeding via initial oxidation to

oligosaccharides, smaller sugars and organic compounds before reduction to H₂. These findings are key to further show the potential of photocatalytic technology for the conversion of cellulose to H₂ along with applications in the wider field of bioenergy.

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Conflicts of interest

There are no conflicts to declare.