Electronic Supplementary Information (ESI)

Using Cellulose Polymorphs for Enhanced Hydrogen Production from Photocatalytic Reforming

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Supplementary Information

Methods

Cellulose preparation

Cellulose II was prepared from cellulose I using the following method. Briefly, a required quantity of cellulose I (microcrystalline cellulose procured from Acros organics) was separated into different size fractions using sieves with a pore size ranging from 110 to 425 µm (Sigma Aldrich). A predetermined quantity of cellulose I within the size range of 106 – 212 µm was added slowly to a glass vial containing TBAH (55 wt% TBAH in water procured from Alfa Aesar, used as received) and a magnetic stirrer bar to achieve a final concentration of 50 g L^{-1}. The mixture was stirred at room temperature until cellulose I was fully dissolved. Upon complete dissolution, excess anti-solvent (distilled water, at least 300 ml) was added to the mixture with continuous stirring. Cellulose II started to precipitate from solution instantly, however stirring was continued for at least 30 minutes to displace all cellulose. Precipitated cellulose II was filtered using filter paper and then washed with distilled water to remove any bound TBAH and to achieve a neutral pH. Images of the cellulose I and II in suspension (before and after agitation) are shown in Figure S1. Cellulose II was stored in its hydrate form for further experiments. Cellulose II was characterised using XRD to confirm the complete conversion of cellulose I to cellulose II. Crystallinity and lattice distance of both the feedstock were also calculated from the XRD results. The XRD measurements in this work were carried out on a PANanalytical X'Pert Pro X-ray diffractometer. The X-ray source was copper with a wavelength of 1.5405 Å. All measurements were carried out ex-situ using a spinning stage. The diffractograms were recorded from 4° to 50° with a step size of 0.017°. Particle size analysis was performed on cellulose 2 samples using a Malvern Zetasizer (Nanoseries, Nano-ZS) for unwashed and washed filtered samples. Unwashed samples were diluted with H_2O where required prior to analysis, while filtered samples were passed through a 0.22 µm syringe filter.

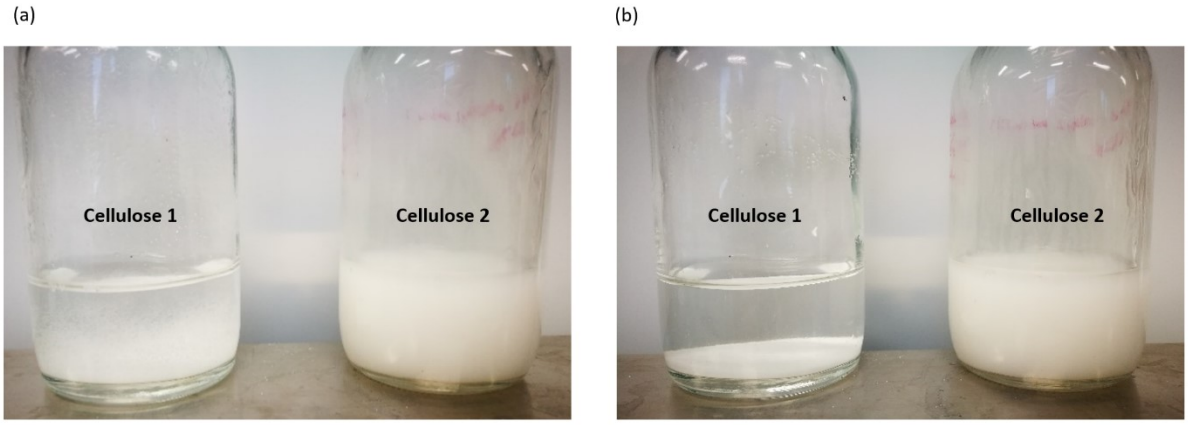

Figure S1**.** images of cellulose I and II agitated suspensions (a) and after 30 seconds of settling

Reactor concept and photocatalytic procedure

The reaction was performed in the PFPR, which is an annular glass bodied reactor that uses a stainless steel 4-blade propeller to create fluidisation. Full details of the reactor can be found elsewhere[1], however in general, the PFPR was operated as a sealed batch unit, with a propeller rotation speed of 1200 rpm. The reaction was performed under a N_2 atmosphere, with the PFPR being purged for 15 mins (150 mL min^{-1}) prior to any irradiation being switched on. Irradiation was provided by a novel spiral jacket array constructed from UV-LEDs (Lighting Will), which provided 360° irradiation of the PFPR. The LEDs had a peak wavelength in the range of 365 – 370 nm and were operated at V_F = 12.0 dcV and I_F = 1.1 A, which gave an overall electrical power of 13.2 W. Figure S2 (a) shows the PFPR under irradiation from the UV-LED cylindrical jacket while Figure S2 (b) and (c) shows the thermal imaging of the PFPR and LED array (Model TG165, FLIR). The LED jacket had a temperature of 39.5°C when operating, while the reaction solution inside the PFPR was at 28.5°C.

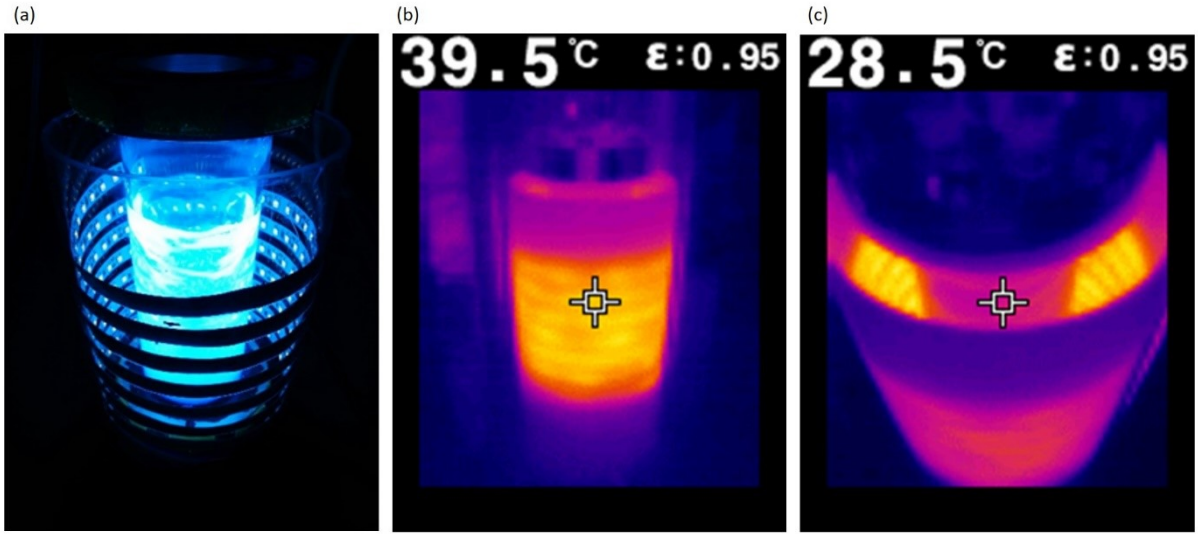

Figure S2. (a) image of the PFPR under irradiation (quinine was used for illustration purposes only) from the UV-LED cylindrical jacket array, (b) thermal image of the PFPR under irradiation and (c) thermal image of the reaction solution inside the PFFR while under irradiation

The intensity of the array was measured using actinometry and the potassium ferrioxalate method, which gave a value of 2.81 x 10^{-6} moles of photons min^{-1} (Equation S1 and S2). The array was also measured used a radiometer (UV-X) and gave an intensity of 5 mW cm^{-2} when the probe was positioned at the centre of the cylindrical array (4.5 cm away from the LED jacket array).

Equation S1 $$Photon\ flux = \frac{Moles\ of\ Fe^{2+}}{\sigma Fe^{2+} x\ t}$$

Where 'moles of Fe^{2+}' were determined based on the potassium ferrioxalate method (7.68 x 10^{-6}), 'σFe^{2+}' was set at 0.97 and 't' was the time (min) the actinometry solution was irradiated for. The photonic efficiency was then determined based on the calculated photon flux (2.81 x 10^{-6} mole of photons min^{-1}) and Equation S2.

Equation S2 $$\eta_{photon}(\%) = \frac{2\ x\ rH_2\ (moles\ of\ H_2\ min^{-1})}{photon\ flux\ (mole\ of\ photons\ min^{-1})} x\ 100$$

Where, 'η_{photon} (%)' is the photonic efficiency, 'rH_2' is the H_2 formation rate as moles per min and 'photon flux' is the mole of photons entering the reactor per min, as determined by actinometry. As H_2 formation is a 2-electron step, the $_rH_2$ was multiplied by 2.

In a typical experiment, 100 mL of distilled water was used as the reaction solvent with a set loading of cellulose and catalyst added. Cellulose in the range of 0.5 - 4 g L^{-1} was used while the catalyst remained constant at 0.75 g L^{-1}. The catalyst used throughout the investigation was TiO_2 (Hombikat) with a 0.5 % wt. Pt co-catalyst loading (herein referred to as 0.5 % Pt-TiO_2), synthesised via wet impregnation. Briefly, platinum nitrate was mixed with distilled water to match the number of pores of TiO_2. This was then added to TiO_2 in three portions and mixed until the catalyst was homogeneous. The catalyst was then dried over a period of 4 hours at 120 °C and finally calcined for a further 4 hours at 500 °C.

Washed Cellulose Samples

In addition to using cellulose I and II as starting feedstocks, experiments using washed and recovered filtrate samples were also performed. To obtain washed samples, cellulose I and II particles were washed in typically 100 mL volumes of distilled H_2O for a predetermined amount of time. These were performed under dark conditions in clean glass beakers with no presence of TBAH and/or any photocatalyst. The reaction suspension was then filtered to separate the suspended cellulose particles and the filtrate. The cellulose particles were resuspended in fresh H_2O (referred to as *'washed cellulose'*) and run under photocatalytic conditions (addition of Pt-TiO_2). The filtrate (referred to as *'recovered filtrate'*) was also run under photocatalytic conditions, by the addition of only Pt-TiO_2 (no

added cellulose). Experiments were also performed where the above procedure was repeated, which was referred to as a 2nd wash.

Analysis

Samples (0.1 mL) were taken at dedicated time intervals from the PFPR gas headspace (100 mL) and analysed using a gas chromatography (GC) system equipped with a thermal conductivity detector (TCD). An Agilent Technologies 7280 A GC system, hosting a packed column (RESTEK, 2 mm ID) was used. The injector was operated at a temperature of 150 °C, pressure of 26.1 psi and a flow rate of 22.9 mL min^{-1}. The flow rate in the column was 20 mL min-1 with an oven temperature of 50 °C, while the detector was maintained at 200 °C with a flow rate of 5 mL min^{-1}. Ar was used as the carrier gas. H_2 was determined by comparison to a standard injection of pure H_2, while quantification was determined form a calibration of known concentrations.

Liquid phase sample were analysed using an Agilent 1260 infinity high performance liquid chromatography system equipped with a refractive index detector (HPLC-RI) and hosting a Rezex ROA-Organic acid H+ column (300 × 7.8 mm). The mobile phase (5 mM H_2SO_4) flow rate was set at 0.5 mL min^{-1} and a sample volume of 10 µl was withdrawn to analyse for products. RI and column temperatures were set to 40 °C. HPLC profiles of the various commercial standards (including oligo and monosaccharides and a range of sugar oxidation products) were obtained and a calibration curve was prepared against which the unknown samples were measured.

Equation S3 $\quad CrI \text{ for cellulose I} = \frac{(I_{(200)} - I_{amI})}{I_{(200)}} \times 100$

Equation S4 $\quad CrI \text{ for cellulose II} = \frac{(I_{(1-10)} - I_{amII})}{I_{(1-10)}} \times 100$

Where CrI (%) is the crystallinity index (%) of cellulose, $I_{(200)}$ is the intensity of cellulose I at 2θ = 22.5°, I_{amI} is the intensity of cellulose I at 2θ = 18°, $I_{(1\text{-}10)}$ is the intensity of cellulose II at 2θ = 19.8° and I_{amII} is the intensity of cellulose II at 2θ = 16°.

Supplementary Information Results

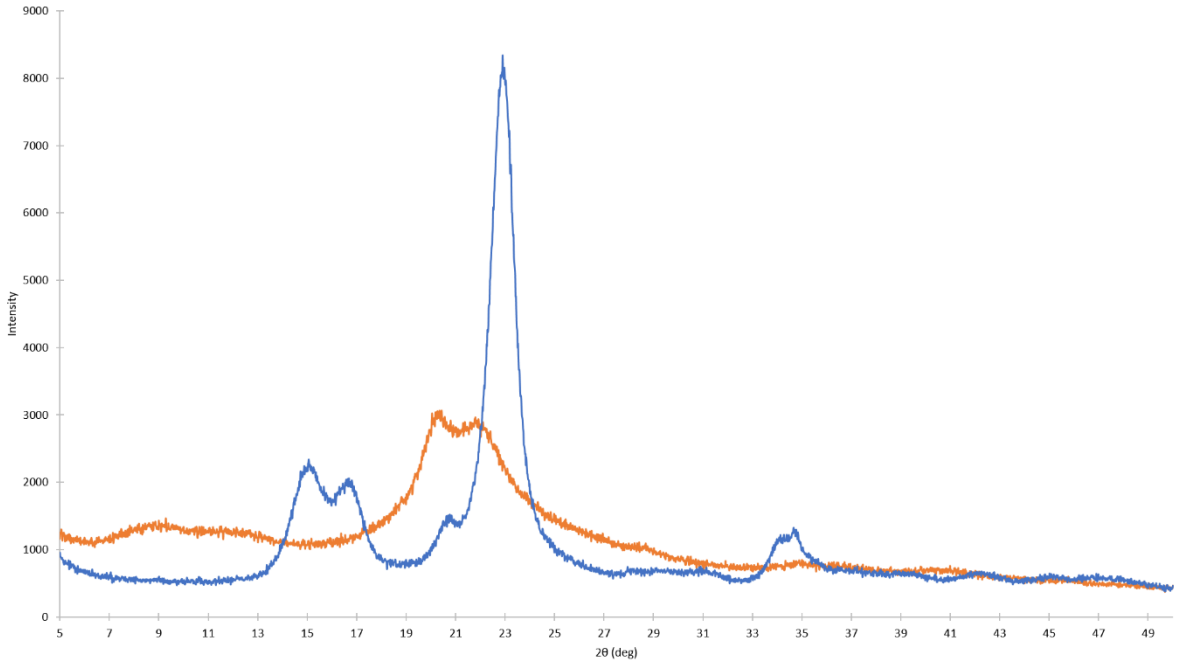

Figure S3**.** XRD pattern of cellulose I (•) and II (•) samples

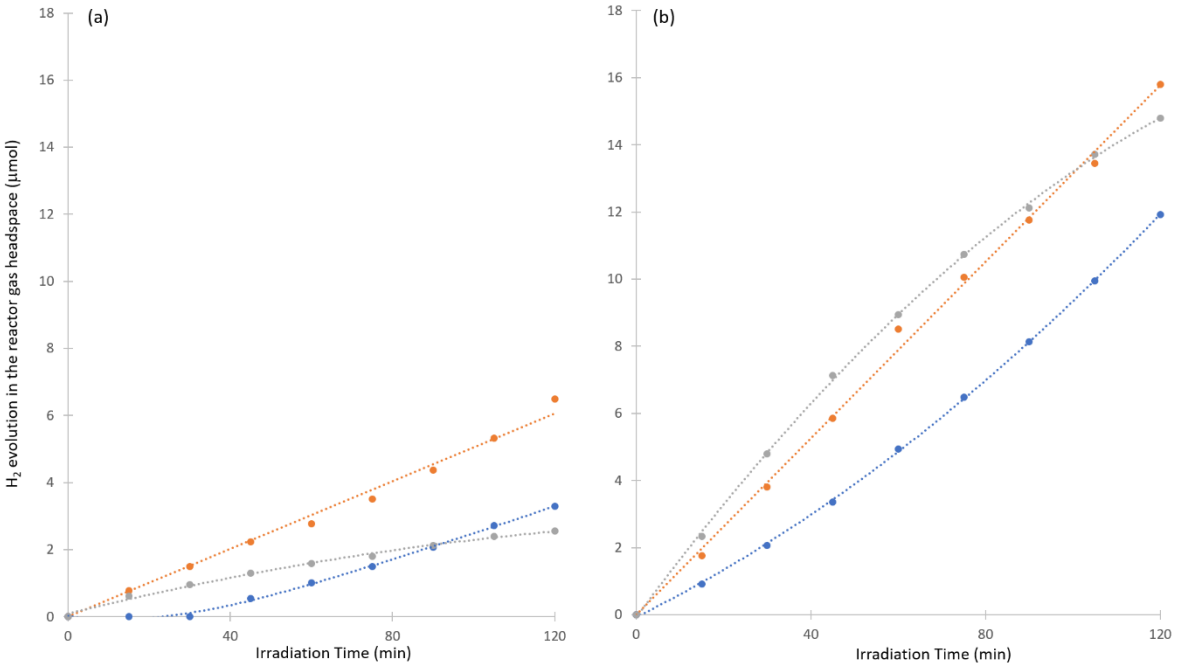

Figure S4. H_2 formation as a function of irradiation time from (a) cellulose I and (b) cellulose II where (•) is unwashed cellulose, (•) is washed cellulose and (•) is the recovered filtrate from washing

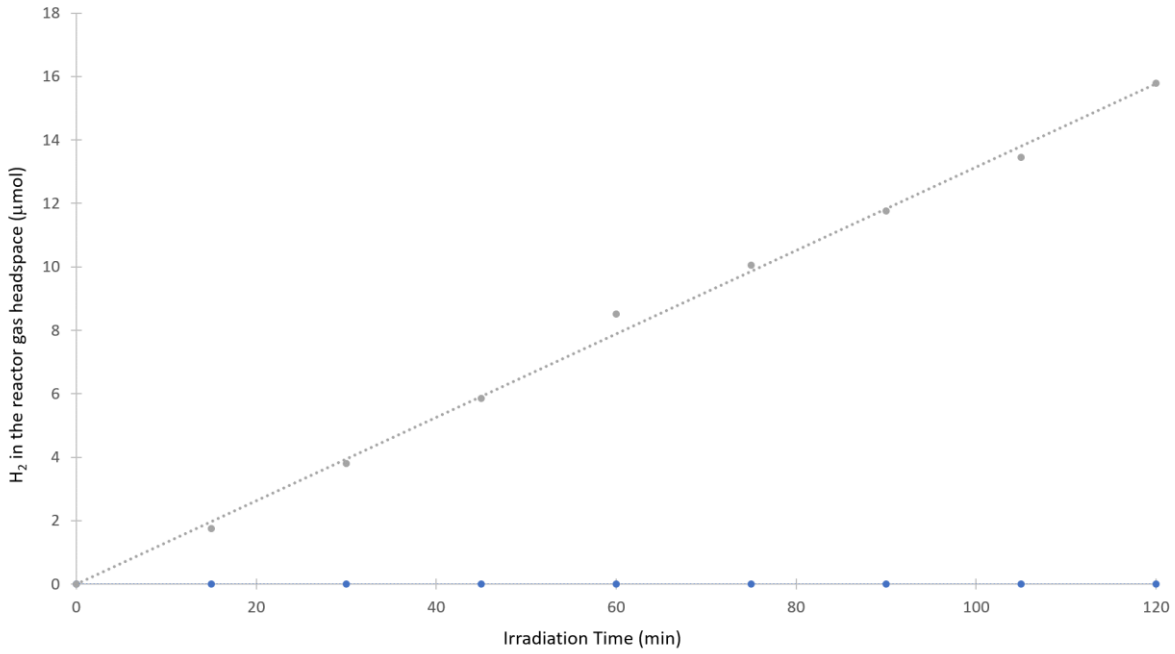

Figure S5. H_2 formation as a function of irradiation time from cellulose II at 1 g L^{-1} (•) and glucose at 1 x 10^{-4} g L^{-1} (•)

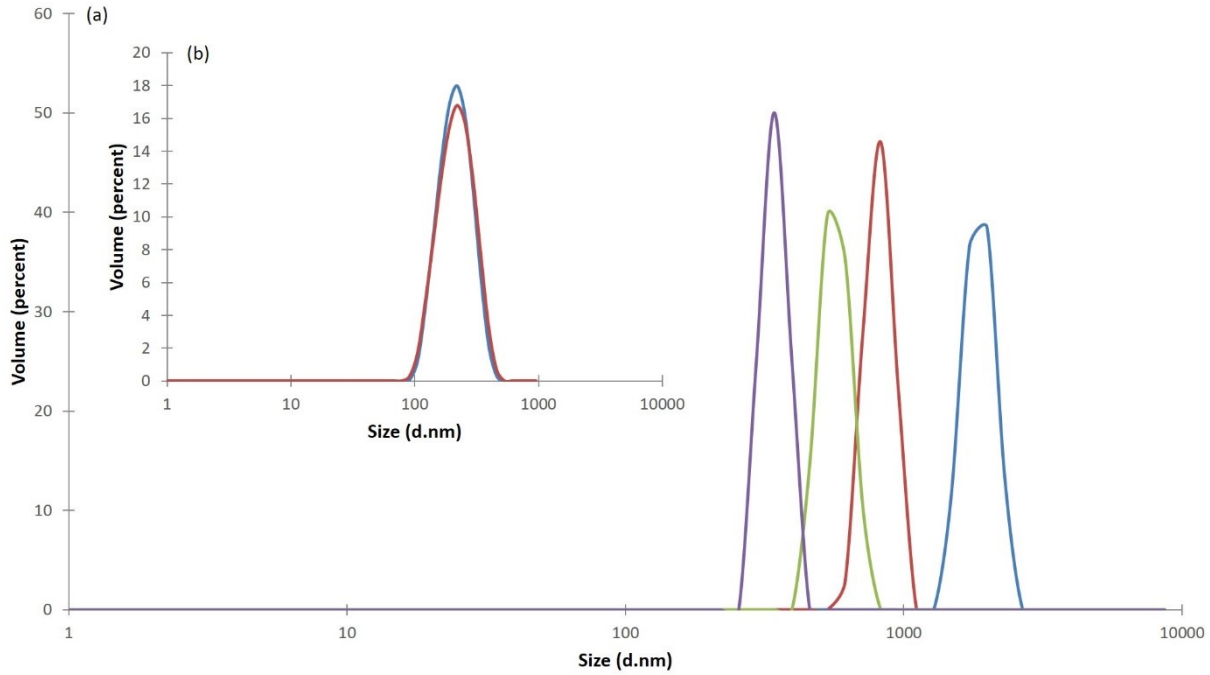

Figure S6**.** Particle size analysis of cellulose II samples where (a) is unfiltered samples for a 1:2 dilution (•), 1:4 dilution (•), 1:8 dilution (•) and 1:16 dilution (•) from a concentrated stock solution and (b) is filtered samples through a 0.22 μm filter for two replicate samples (replicate 1 (•) and replicate 2 (•))

Cellulose Sample	**Mean Particle size (nm)**
Cellulose II (unfiltered) – 1:2 dilution	*1847*
Cellulose II (unfiltered) – 1:4 dilution	*808.9*
Cellulose II (unfiltered) – 1:8 dilution	*562.1*
Cellulose II (unfiltered) – 1:16 dilution	*342*
Cellulose II (0.22 μm filtered) - replicate 1	*215.3*
Cellulose II (0.22 μm filtered) - replicate 2	*219.1*

Table S1**.** Particle size analysis of cellulose 2 samples unfiltered and 0.22 μm filtered. Unfiltered samples were diluted with water to provide an accurate reading for the instrument

References

[1] N. Skillen, M. Adams, C. McCullagh, S. Y. Ryu, F. Fina, M. R. Hoffmann, J. T. S. Irvine and P. K. J. Robertson, *Chemical Engineering Journal*. 286 (2016) 610-621.