# **Electronic Supplementary Information**

# Photoreforming of biomass in metal salt hydrate solutions

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### Reagents

Melamine, chloroplatinic acid, trisodium citrate dihydrate, sodium borohydride, microcrystalline cellulose, sodium benzoate, salicylic acid, lithium bromide and glucose were purchased from Sigma Aldrich. Potassium thiocyanate was purchased from Fisher Scientific. TiO<sub>2</sub> nanoparticles (anatase and rutile, 10-30 nm diameter, surface area anatase:  $150 \text{ m}^2 \text{ g}^{-1}$ ; rutile:  $50 \text{ m}^2 \text{ g}^{-1}$ ) were obtained from SkySpring nanomaterials and TiO<sub>2</sub> P25 was a gift from Evonik (Surface area:  $50 \text{ m}^2 \text{ g}^{-1}$ ). All chemicals were used as received.

# **Catalyst Synthesis**

Carbon nitride (<sup>H2N</sup>CN<sub>x</sub>) was prepared following a literature procedure.<sup>1</sup> Briefly, 2 g melamine were heated in a covered crucible to 550 °C for 4 h (heating ramp 5 °C min<sup>-1</sup>). For post-synthetic modification the as-obtained <sup>H2N</sup>CN<sub>x</sub> was mixed and ground with KSCN (weight ratio 1:2 for <sup>H2N</sup>CN<sub>x</sub>:KSCN) using a mortar and pestle.<sup>2</sup> The mixture was heated under an argon atmosphere to 400 °C for 1 h followed by a temperature increase to 500 °C and holding at this temperature for 30 min (ramp rate 30 °C·min<sup>-1</sup>). This procedure converts the amine groups of the carbon nitride into cyanamide groups.<sup>3–5</sup> Characterisation and mechanistic details regarding the introduction of the cyanamide functionality can be found in reference 2.The resulting <sup>NCN</sup>CN<sub>x</sub> material was washed with water thoroughly and dried under vacuum at 60 °C.

For platinum loading a literature procedure was adapted:<sup>6</sup> 150 mg of support material [<sup>H2N</sup>CN<sub>x</sub>,  $^{NCN}CN_x$ ,  $TiO_2$  (P25, anatas or rutile nanoparticles)] were dispersed in 10 mL H<sub>2</sub>O with sonication for 30 min. Then 0.29 g trisodium citrate dihydrate were added and the dispersion was further sonicated for 30 min before 42 µL H<sub>2</sub>PtCl<sub>6</sub> solution (8 wt.% in H<sub>2</sub>O) were added. After further sonication for 30 min, the mixture was stirred with a magnetic stirrer and 5 mg NaBH<sub>4</sub> dissolved in 1 mL H<sub>2</sub>O were added. After stirring for 30 min the material was isolated via centrifugation, washed with H<sub>2</sub>O and dried at 80 °C overnight.

### Powder X-Ray Diffractometry (XRD)

XRD was conducted on a PANalytical Empyrean Series 2 instrument using Cu Kα irradiation.

### Transmission Electron Microscopy (TEM)

TEM was conducted on a Thermo Scientific (FEI) Talos F200X G2 TEM. All samples were drop-cast on carbon-coated Cu grids.

#### Gas Chromatography (GC)

The accumulated  $H_2$  was measured in the headspace by GC on an Agilent 7890A gas chromatograph equipped with a thermal conductivity detector and HP-5 molecular sieve column using  $N_2$  as the carrier gas. Methane (2% CH<sub>4</sub> in  $N_2$ ) was used as an internal standard after calibration with different mixtures of known amounts of  $H_2/N_2/CH_4$ .

### High Performance Liquid Chromatography (HPLC)

Chromatographic separations were conducted with a Pheomenex Rezex ROA organic acid 8% H<sup>+</sup> column at 75 °C column temperature. Samples were analysed in the isocratic flow mode (flow rate 0.025 M H<sub>2</sub>SO<sub>4</sub> in water, 0.5 mL min<sup>-1</sup>) using a Shimadzu LC 20 equipped with refractive index (RID-10A) and diode array UV-Vis ( $\lambda$  = 190 nm) detectors. To identify particular substances in the pre-treated or photoreformed samples, retention times were compared to those of authentic samples.

#### **Fluorescence Spectroscopy**

Emission spectra ( $\lambda_{ex}$  = 308 nm,  $\lambda_{em}$  = 350-550 nm) were recorded on an Edinburgh Instruments FS5 spectrofluorometer equipped with a Xe lamp and integrating sphere. For obtaining calibration solutions the desired amount of salicylic acid was dissolved in a water or a water-LiBr mixture (25 wt% LiBr) containing 0.24 mg mL<sup>-1</sup> sodium benzoate. To assess the ability of generating OH radicals of different catalysts (8 mg catalyst) were dispersed in 2.5 mL solution containing 0.24 mg mL<sup>-1</sup> sodium benzoate either in pure water or containing 25 wt% LiBr. The samples were irradiated in the solar simulator under stirring for 1 h and then the catalyst was removed by filtration with a syringe filter. The clear solution could then be used for the fluorescence measurements. The amount of salicylic acid can be calculated from the fluorescence intensity at 420 nm. An arbitrary index (OH index) is generated for H<sub>2</sub>O and LiBr containing samples, by dividing the amount of calculated salicylic acid of every sample (irrespective if in H<sub>2</sub>O or with LiBr) by the salicylic acid amount of the sample with the highest salicylic acid concentration (which value is therefore set 1).

#### **Cellulose and Wood Dissolution Experiments**

To obtain LiBr based metal salt hydrate solutions, literature procedures were followed.<sup>7,8</sup> LiBr (5 g) and 0.02 mL H<sub>2</sub>SO<sub>4</sub> (98%) were dissolved in 3.1 mL H<sub>2</sub>O. The solution is abbreviated as LiBr MSH and contains 62.5 wt% LiBr and 0.1 M H<sub>2</sub>SO<sub>4</sub>. cellulose (100 mg) or sawdust were dispersed in 2 mL LiBr MSH and heated to 90 °C. The cellulose or sawdust dissolved in less than 30 min and the mixture was stirred for at least 5 h before use in photoreforming tests. This solution is labelled as standard LiBr-MSH solution.

#### **Photoreforming Experiments**

The catalyst (4 mg TiO<sub>2</sub> or <sup>NCN</sup>CN<sub>x</sub>) was dispersed by sonication in 1.5 mL H<sub>2</sub>O (or 0.1 M LiOH for tests in alkaline reaction media). Then 1 mL of LiBr MSH (either with or without predissolved cellulose or biomass, LiBr concentration: 62.5 wt%) was added, giving a solution with 25 wt% LiBr. For some experiments without pre-dissolved cellulose, 50 mg of glucose were added to this solution to simulate the depolymerised cellulose. The ratio of H<sub>2</sub>O and LiBr MSH could be varied for different experiments, but the catalyst concentration was 1.6 mg mL<sup>-1</sup> in all experiments. The prepared samples were added to Pyrex glass photoreactor vials (internal volume 7.91 mL) and capped with rubber septa. After briefly vortexing, the samples were purged with  $N_2$  (containing 2% CH<sub>4</sub> for GC analysis) at ambient pressure for 10 min. The samples were then irradiated by a calibrated solar light simulator (Newport Oriel, 100 mW cm<sup>-2</sup>) equipped with an air mass 1.5 global (AM 1.5G) filter and a water filter to remove infrared radiation. All samples were stirred at 600 rpm and kept at a constant temperature of 25 °C during irradiation. H<sub>2</sub> generation was monitored by periodically analysing samples of the reactor head space gas (50 µL) by GC (see above). Overpressure within the vial is minimal (an increase of 0.03 atm per 10 µmol of H<sub>2</sub> produced). PR experiments exhibited a small blank activity, which may partially arise from bromide oxidation for the LiBr containing samples and/or minor water splitting activity. However, this contribution lies mostly below 5-10% compared to the overall hydrogen yield. The resulting hydrogen amount from the blank activity is subtracted from the amount obtained during substrate PR. The same PR procedure was employed in control experiments in the absence of MSH (using H<sub>2</sub>SO<sub>4</sub> or LiOH solutions). Control experiments with catalyst and reaction solution in the dark and without catalyst in light did not exhibit any hydrogen formation. Regarding photoreforming tests in LiOH it must be considered that glucose slowly degrades in alkaline media yielding several products, such as formate.<sup>9</sup> This was considered, as the amount of formate originating from alkaline degradation was determined in control experiments and subtracted from the values obtained during photoreforming.

**Table S1A:**  $H_2$  and product yields for alternative reaction conditions, LiBr conditions: 25 wt.% LiBr + 0.1M  $H_2SO_4$ . The considerable amount of lactic acid detected in 1M LiOH reaction solutions is not a direct reaction product from the photoreforming process. Instead, it derives alkaline decomposition of molecular sugars. For entries 6 and 7 the formed amount of product is so small that it is below the detection limit of the HPLC method.

Entry	Reaction Conditions			Reaction Products [µmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ] (mean (N=3))						
	Catalyst	LiBr	Other	Arabinose	Erythrose	Formic acid	H <sub>2</sub>	Lactic acid		
1	P25	-	2 M H <sub>2</sub> SO <sub>4</sub>	5.6	n.d.	n.d.	19.8 ± 1.8	n.d.		
2	P25	yes	-	45.4	14.6	46.6	124.0 ± 27.5	n.d.		
3	Anatase	-	2 M H <sub>2</sub> SO <sub>4</sub>	n.d.	n.d.	n.d.	14.6 ± 1.3	n.d.		
4	Anatase	yes	-	29.5	6.5	17.8	76.6 ± 2.4	n.d.		
7	Rutile	-	2 M H <sub>2</sub> SO <sub>4</sub>	n.d.	n.d.	n.d.	0.25 ± 0.1	n.d.		
8	Rutile	yes	-	92.8	32.4	123.0	180.0 ± 1.6	n.d.		
9	Rutile	yes	0.1 M LiOH	16.1	n.d.	12.5	16.7 ± 0.8	n.d.		
10	Rutile	yes	1 M LiOH	n.d.	n.d.	n.d.	32.2 ± 22.5	1049.8		
11	<sup>NCN</sup> CN <sub>x</sub>	-	2 M H <sub>2</sub> SO <sub>4</sub>	5.6	n.d.	6.6	57.1 ± 13.7	n.d.		
12	<sup>NCN</sup> CN <sub>x</sub>	yes	-	10.3	n.d.	n.d.	20.9 ± 9.3	n.d.		
13	<sup>NCN</sup> CN <sub>x</sub>	yes	0.1 M LiOH	74.5	18.2	97.6	112.8 ± 21.3	n.d.		
14	<sup>NCN</sup> CN <sub>x</sub>	yes	1 M LiOH	n.d.	n.d.	24.6	190.6 ± 36.2	930.9		
15	<sup>NCN</sup> CN <sub>x</sub>	-	0.1 M LiOH	n.d.	n.d.	n.d.	0.8 ± 0.3	n.d.		
Tests with Visible light (400 nm Filter used)										
16	<sup>NCN</sup> CN <sub>x</sub>	yes	-	n.d.	n.d.	n.d.	3.1 ± 0.7	n.d.		
17	<sup>NCN</sup> CN <sub>x</sub>	yes	0.1 M LiOH	47.3	19.9	12.8	49.0 ± 12.6	n.d.		
18	Rutile	yes	-	n.d.	n.d.	n.d.	n.d.	n.d.		
19	Rutile	yes	0.1 M LiOH	n.d.	n.d.	n.d.	n.d.	n.d.		

**Table S1B:** Results from Table S1, but product formation rates now normalised to catalyst surface area (m<sup>2</sup>) and not mass. Surface areas of the catalysts: P25: 50 m<sup>2</sup>/g, anatase: 150 m<sup>2</sup> g<sup>-1</sup>, rutile: 50 m<sup>2</sup> g<sup>-1</sup>, <sup>NCN</sup>CN<sub>x</sub>: 97 m<sup>2</sup> g<sup>-1</sup>.<sup>5</sup>

Entry	Reaction Conditions			Reaction Products [µmol m <sub>cat</sub> <sup>-2</sup> h <sup>-1</sup> ] (mean (N=3))						
	Catalyst	LiBr	Other	Arabinose	Erythrose	Formic acid	H <sub>2</sub>	Lactic acid		
1	P25	-	2 M H <sub>2</sub> SO <sub>4</sub>	0.11	n.d.	n.d.	0.39 ± 0.04	n.d.		
2	P25	yes	-	0.90	0.29	0.93	2.48 ± 0.55	n.d.		
3	Anatase	-	2 M H <sub>2</sub> SO <sub>4</sub>	n.d.	n.d.	n.d.	$0.09 \pm 0.008$	n.d.		
4	Anatase	yes	-	0.19	0.04	0.11	0.51 ± 0.02	n.d.		
7	Rutile	-	2 M H <sub>2</sub> SO <sub>4</sub>	n.d.	n.d.	n.d.	0.005 ± 0.001	n.d.		
8	Rutile	yes	-	1.85	0.64	2.46	3.60 ± 0.39	n.d.		
9	Rutile	yes	0.1 M LiOH	0.32	n.d.	0.25	0.33 ± 0.016	n.d.		
10	Rutile	yes	1 M LiOH	n.d.	n.d.	n.d.	0.64 ± 0.54	20.99		
11	<sup>NCN</sup> CN <sub>x</sub>	-	2 M H <sub>2</sub> SO <sub>4</sub>	0.05	n.d.	0.06	0.58 ± 0.14	n.d.		
12	<sup>NCN</sup> CN <sub>x</sub>	yes	-	0.11	n.d.	n.d.	0.21 ± 0.09	n.d.		
13	<sup>NCN</sup> CN <sub>x</sub>	yes	0.1 M LiOH	0.76	0.18	1.01	1.16 ± 0.21	n.d.		
14	<sup>NCN</sup> CN <sub>x</sub>	yes	1 M LiOH	n.d.	n.d.	2.72	1.96 ± 0.37	9.59		
15	<sup>NCN</sup> CN <sub>x</sub>	-	0.1 M LiOH	n.d.	n.d.	n.d.	0.007 ± 0.002	n.d.		
Tests with Visible light (400 nm Filter used)										
16	<sup>NCN</sup> CN <sub>x</sub>	yes	-	n.d.	n.d.	n.d.	0.03 ± 0.007	n.d.		
17	<sup>NCN</sup> CN <sub>x</sub>	yes	0.1 M LiOH	0.48	0.19	0.12	0.50 ± 0.12	n.d.		
18	Rutile	yes	-	n.d.	n.d.	n.d.	n.d.	n.d.		
19	Rutile	yes	0.1 M LiOH	n.d.	n.d.	n.d.	n.d.	n.d.		



**Figure S1.** Powder XRD patterns of Pt/P25, Pt/Anatase, Pt/Rutile, and Pt/<sup>NCN</sup>CN<sub>x</sub>. The diffractograms show the expected TiO<sub>2</sub> phases and  $CN_x$  peaks for all supports.



**Figure S2.** TEM images of platinised (A) P25, (B) anatase  $TiO_2$ , (C) rutile  $TiO_2$ , (D) <sup>NCN</sup>CN<sub>x</sub>. On the  $TiO_2$  supports, small Pt nanoparticles can be found with a size of around 5-15 nm. For the <sup>NCN</sup>CN<sub>x</sub> material the Pt particles are smaller with around 3-8 nm.



**Figure S3.** Estimation of OH radical formation. To investigate the role of the OH radicals, the amount of generated OH radicals was estimated using fluorescence spectroscopy experiments.<sup>10</sup> The substrate benzoic acid will be oxidised by OH radicals, generating salicylic acid during photocatalysis. The fluorescence intensity of the generated salicylic acid can then be used to estimate the amount of formed OH radicals. As expected,<sup>11</sup> the tests in water show that P25 yields the highest amount of OH radicals, followed by anatase, whereas rutile forms very few free radicals. The measurements in LiBr containing solutions are more challenging, as the presence of LiBr lowers the fluorescence intensity of salicylic acid dramatically. Nevertheless, it can be concluded that the presence of LiBr also clearly reduces the number of OH radicals reaching the benzoic acid substrate to oxidise it. But the order of the catalysts stays the same with P25 forming the most OH radicals.



**Figure S4.** Infrared spectra of <sup>NCN</sup>CN<sub>x</sub> catalysts after treatment for 24 h with standard (acid) and basic conditions. New peaks appear between 1400-1600 cm<sup>-1</sup> for the acid treated material, at the same time the characteristic peak for the cyanamide group at 2180 cm<sup>-1</sup> is reduced for the acid treated material, whereas it stays nearly constant for the base treated catalyst. These observations indicate that the cyanamide group is hydrolysed significantly faster under acid reaction conditions.<sup>12</sup>



**Figure S5.** Long-term PR of wood lysate over platinised rutile (left) and <sup>NCN</sup>CN<sub>x</sub> (right). Conditions: Catalyst (4 mg), 1.5 mL H<sub>2</sub>O for rutile or 1.5 mL 0.1 M LiOH for <sup>NCN</sup>CN<sub>x</sub>, + 1 mL LiBr MSH wood lysate, irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>, 25 °C).



**Figure S6.** PR experiments with different photocatalysts using glucose as substrate in  $H_2O$  or LiBr MSH based solution: 4 mg catalyst in 2.5 mL reaction solution (2.5 mL pure  $H_2O$ , blue bars) (1 mL MSH (62.5 wt% LiBr, 0.1 M  $H_2SO_4$ ) + 1.5 mL  $H_2O$ , giving 25 wt.% LiBr, green bars), 50 mg Glucose, irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>, 25 °C, 24 h), Glucose adsorption capability of the catalyst in pure  $H_2O$  or 25 wt% LiBr (black squares).



**Figure S7.** PR experiments with different amounts of LiBr and glucose as substrate with P25 and <sup>NCN</sup>CN<sub>x</sub> as catalysts. Photocatalysis conditions: 4 mg catalyst in 2.5 mL reaction solution (different concentrations of MSH (62.5 wt% LiBr in 0.1 M  $H_2SO_4$ ) in  $H_2O$ , resulting in different LiBr concentrations), 50 mg glucose, irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>, 25 °C, 24 h).

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