Photoreforming of lignocellulose into H₂ using nano-engineered carbon nitride under benign conditions

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Supporting Information Placeholder

ABSTRACT: Photoreforming of lignocellulose is a promising approach toward sustainable H₂ generation, but this kinetically challenging reaction currently requires UV-absorbing or toxic light absorbers under harsh conditions. Here, we report a cyanamide-functionalized carbon nitride, N₅C₅Nₓ, which shows enhanced performance upon ultra-sonication. This activated N₅C₅Nₓ allows for the visible-light driven conversion of purified and raw lignocellulose samples into H₂ in the presence of various proton reduction co-catalysts. The reported room-temperature photoreforming process operates under benign aqueous conditions (pH ~2-15) without the need for toxic components.

Utilization of the most available form of biomass, lignocellulose, can provide sustainable and scalable H₂ fuel production, and its utilization does not impact on food production as it is an agricultural waste product.¹ The complex and energy-rich structure of lignocellulose is composed of cellulose, hemicellulose and lignin,¹ ² which have evolved to prevent degradation and are therefore kinetically challenging to utilize under ambient conditions.³ Gasification at high-temperature (≥750 °C) is a common method for H₂ production from lignocellulose, but energy-intensive and produces side products such as the fuel-cell inhibitor carbon monoxide.⁴ Enzymatic hydrolysis is another process for biomass utilization, but this multi-step conversion suffers from low overall yields.⁵ ⁶ Thus, there is substantial interest in developing novel approaches for the valorization of lignocellulose.⁵ ⁶⁻¹¹

Photoreforming of unprocessed biomass to H₂ has emerged as a clean alternative,¹² ¹³ and it requires only a photocatalyst that generates holes to oxidize lignocellulose and electrons to drive proton reduction upon photoexcitation.¹² This process is traditionally carried out using UV-light harvesting TiO₂ modified with noble-metal catalysts such as RuO₂ and Pt.¹⁴ ¹⁶ Visible-light absorbing CdS quantum dots were recently reported for biomass photoreforming, but the system required toxic Cd and alkaline conditions (10 M KOH).¹⁷ There is therefore a need to identify a photoreforming process that utilizes an inexpensive, non-toxic and visible-light absorbing photocatalyst, capable of operating under benign conditions.

Polymeric carbon nitride (CNₓ) is a non-toxic and inexpensive carbonaceous photocatalyst.¹⁸ ²⁰ The well-positioned band edges of CNₓ give enough driving force for many photocatalytic reactions including proton reduction,²⁰ ²² CO₂ reduction,²³ ²⁴ organic transformations (including alcohol oxidation),²⁵ ²⁶ redox catalysis²⁷ and water splitting.²⁸ ²⁹ Herein, we report a straightforward approach to enhance the photocatalytic performance of bulk cyanamide-functionalized carbon nitride (N₅C₅Nₓ) by ultrasonication. The activated N₅C₅Nₓ is subsequently used to photoreform lignocellulosic biomass and generate H₂, in the presence of a molecular Ni bis(diphasphine) catalyst (NiP), heterogeneous Pt or MoS₂ in aqueous media over a range of pH values (Figures 1 and S1).

Figure 1. Schematic representation of H₂ generation through photoreforming of lignocellulose with N₅C₅Nₓ and H₂ production co-catalysts.

Bulk N₅C₅Nₓ was prepared and characterized as previously reported (see SI).²² ³⁰ Activated N₅C₅Nₓ was obtained by ultra-sonication an aqueous suspension of bulk N₅C₅Nₓ (5 mg mL⁻¹) in a potassium phosphate (KP) solution for 10 min at 40 °C (Figure S2). UV-vis spectroscopy of the bulk and ultra-sonicated N₅C₅Nₓ reveals strong UV absorption, which tails into the visible region (λ₂₅₄ < 450 nm). A significant increase in absorbance is observed upon ultra-sonication of N₅C₅Nₓ, which may be due to disruption of aggregated N₅C₅Nₓ and subsequently reduced light scattering and enhanced light absorption.³¹ Photoluminescence studies (λₑₓ = 360 nm) also reveal an increased emission intensity for the ultra-sonicated N₅C₅Nₓ, possibly suggesting a higher density of photexcited states. Brunauer-Emmett-Teller measurements show a 60% increase in the surface area after ultra-sonication (97.4±0.6 m² g⁻¹).³²
and a smaller aggregate size following ultra-sonication is confirmed by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Nearly identical X-ray diffraction patterns and Fourier Transform Infrared spectra are observed, indicating that the characteristic functional group features of \( \text{NCN}_x \) are preserved after ultra-sonication (Figure S2).\(^{22,33}\)

A photocatalytic screening assay was carried out by dispersing \( \text{NCN}_x \) in KP (pH 4.5) solution containing a DuBois-type Ni proton reduction catalyst (NiP; Figure S1),\(^{34}\) with 4-methyl benzyl alcohol (4-MBA, 30 \( \mu \)mol).\(^{25}\) 4-MBA was selected as the electron donor as it is as an easily oxidized model cellulose substrate. The samples were irradiated under a N\(_2\) atmosphere with simulated solar light (100 mW cm\(^{-2}\), AM1.5G, 25 \( ^\circ\)C). The reaction conditions were optimized systematically with respect to \( \text{NCN}_x \)-based H\(_2\) production activity (specific activity; \( \text{mol H}_2 (g \ \text{NCN}_x)^{-1} h^{-1} \)). NiP-based activity represented by Ni-based turnover frequency (TOF\(_{\text{NiP}}\); mol H\(_2\) (mol NiP\(^{-1}\)) \( h^{-1} \)) and turnover number (TON\(_{\text{NiP}}\); mol H\(_2\) (mol NiP\(^{-1}\)), and overall proton reduction and alcohol oxidation rates (Tables S1-S7).

The results of photoreforming 4-MBA using 0.5 mg bulk and activated \( \text{NCN}_x \) with 300 nmol of NiP are shown in Figure 2. After 1 h of irradiation, activated \( \text{NCN}_x \) shows more than three times the photocatalytic activity of bulk \( \text{NCN}_x \), reaching 17.2±0.6 \( \mu \)mol H\(_2\) \( h^{-1} \), TOF\(_{\text{NiP}}\) of 57.5±2.1 \( h^{-1} \) and 34480±1240 \( \mu \)mol H\(_2\) (g \( \text{NCN}_x \))\(^{-1} h^{-1} \). Quantitative and selective oxidation of 4-MBA into 4-methyl benzaldehyde (4-MBAD) is observed in less than 6 h irradiation. A specific activity of 39310±1970 \( \mu \)mol H\(_2\) (g \( \text{NCN}_x \))\(^{-1} h^{-1} \) is reached with 0.5 mg activated \( \text{NCN}_x \) and 400 nmol of NiP (Figure S3 and S4), which represents a benchmark H\(_2\) evolution rate for a CN photocatalyst.\(^{35,36}\) Control experiments in the absence of \( \text{NCN}_x \), NiP, 4-MBA or light did not produce H\(_2\) (Table S6). The external quantum efficiencies (EQE; \( \lambda = 360\pm10 \) nm) yielded (22±1)% and (13±1)% for the activated and bulk systems, respectively.

![Figure 2](image)

**Figure 2.** Photocatalytic H\(_2\) and 4-MBAD formation using activated and bulk \( \text{NCN}_x \) (0.5 mg) with NiP (300 nmol) in KP (0.1 M, pH 4.5, 3 mL) with 4-MBA (30 \( \mu \)mol) under AM1.5G irradiation at 25 \( ^\circ\)C (hollow symbols refer to H\(_2\) generation; filled symbols to MBAD production).

We have previously shown that \( \text{NCN}_x \) can photo-charge and accumulate trapped electrons with a very long life-time in the presence of 4-MBA.\(^{25,37}\) The density of accumulated charges remain approximately the same for bulk and activated \( \text{NCN}_x \), but activated \( \text{NCN}_x \) shows a faster discharging behavior (Figure S5 and Table S7), indicating that the co-catalyst can more easily access electrons stored in \( \text{NCN}_x \).

4-MBA was subsequently replaced with purified lignocellulose components, \( \alpha \)-cellulose was initially selected as the most abundant form of wood-derived biomass and the most unreactive form of cellulose.\(^{38}\) The reaction conditions were optimized for the overall amount of H\(_2\) being produced by varying the amount of \( \alpha \)-cellulose, activated \( \text{NCN}_x \) and NiP loadings (Table S8, Figures S6-S7). The system containing 0.5 mg \( \text{NCN}_x \) and 50 nmol NiP photo-produced 1690±10 \( \mu \)mol H\(_2\) (g \( \text{NCN}_x \))\(^{-1} h^{-1} \) and TOF\(_{\text{NiP}}\) of 17.0±1.1 \( h^{-1} \). The highest overall H\(_2\) production yield of 2.62±0.09 \( \mu \)mol H\(_2\) was observed with 5 mg activated \( \text{NCN}_x \) and 50 nmol NiP in KP, (pH 4.5) after 4 h of AM 1.5G irradiation. UV-filtered simulated solar light (\( \lambda > 400 \) nm) produced 1.10±0.03 \( \mu \)mol of H\(_2\), indicating efficient utilization of visible light. The importance of surface-functionalization for cellulose photoreforming is highlighted by the negligible activity of unfunctionalized bulk \( \text{NCN}_x \) (only 0.13±0.04 \( \mu \)mol H\(_2\)) and reduced performance of bulk \( \text{NCN}_x \) (1.91±0.07 \( \mu \)mol H\(_2\) after 4 h of UV-vis irradiation (Figure S8).\(^{25}\) This significant difference in activity has been previously attributed to the superior oxidizing ability of \( \text{NCN}_x \) due to more positively positioned valence band (+2.2 V vs. NHE at pH 6; band gap of 2.7 eV),\(^{39}\) as well as improved hole transfer to the electron donor via the cyanamide moieties.\(^{25,30,40}\)

Photocatalytic biomass reforming into H\(_2\) was then expanded to xylan and lignin as well as the most common units found in their structures (Figure 3, Table S9). As the substrate size is reduced, solubility improves in pH 4.5 KP\(_r\), resulting in significantly enhanced photoactivity. After 24 h of irradiation, up to 32.1±4.8 \( \mu \)mol of H\(_2\) was produced from glucose at 1120±80 \( \mu \)mol H\(_2\) (g \( \text{NCN}_x \))\(^{-1} h^{-1} \) and TOF\(_{\text{NiP}}\) of 112±8 \( h^{-1} \). In the presence of xylene and galactose monosaccharides, 19.9±2.3 and 28.0±2.5 \( \mu \)mol of H\(_2\) were produced respectively after 24 h of irradiation. Photoreforming of polymeric xylan generated 4.92±0.17 \( \mu \)mol of H\(_2\). Despite the strong light absorbing nature and robustness of lignin, 0.20±0.03 \( \mu \)mol H\(_2\) production was achieved, with TOF\(_{\text{NiP}}\) of 4.0±0.7 \( h^{-1} \) and 40.8±6.8 \( \mu \)mol H\(_2\) (g \( \text{NCN}_x \))\(^{-1} h^{-1} \). The results demonstrate that the system photoreforms biomass under mildly acidic aqueous conditions, but is still limited by substrate availability to quench photogenerated holes in \( \text{NCN}_x \).

Replacement of purified lignocellulosic components with raw and unprocessed ‘real-world’ biomass samples (Figure S9, Table S10) resulted in H\(_2\) formation with a range of samples (including paper and cardboard). Sawdust produced 3.89±0.34 \( \mu \)mol of H\(_2\) with TOF\(_{\text{NiP}}\) of 20.2±0.4 \( h^{-1} \) and 202±4 \( \mu \)mol H\(_2\) (g \( \text{NCN}_x \))\(^{-1} h^{-1} \) upon irradiation using \( \text{NCN}_x \) in KP solution. The long-term performance of the system was investigated by comparing the activity of NiP with benchmark proton reduction co-catalysts, Pt and MoS\(_2\) (Figure 4a, Table S11) in the presence of \( \alpha \)-cellulose.\(^{22,41}\) NiP shows a superior initial rate, but the fragile molecular framework degrades after 24 h,\(^{42}\) producing 3.7±0.1 \( \mu \)mol of H\(_2\) with \( \text{NCN}_x\)-NiP. Instead, Pt and MoS\(_2\) display slower kinetics, but a much-enhanced stability while photocatalytic systems with Pt are still active after twelve days.
Mass spectrometry of the photocatalytic samples prepared in H₂O and D₂O confirms that H₂ production originates from the aqueous protons (Figure S10, Table S12). The oxidation products were characterized after photoreformation of uniformly 13C-labelled cellulose over activated NCN (5 mg) and Pt (4 wt.%) in pH 4.5 KP, solution prepared in D₂O using 13C-NMR spectroscopy. 13C-NMR spectroscopy of the filtered solution shows the formation of formate (δ = 171 ppm) and carboxylate groups (δ = 183 ppm) of presumably lower molecular weight polysaccharides (δ = 50-110 ppm; Figure S11).17,40 Other gaseous oxidation products in the headspace were monitored by gas chromatography and mass spectrometry after 6 days of irradiation (Figure S12, Table S13). Negligible amounts of CO and CO₂ were measured, which is in agreement with the insignificant quantities of carbonate detected by 13C-NMR spectroscopy. The oxidation is likely to occur directly via hole transfer due to strong binding between the lignocellulosic substrates and NCN, as photogenerated holes in NCN are not oxidizing enough to produce HO₂.17,25,30

The versatility of the system was investigated by suspending α-cellulose in 1, 5, 10 M KOH (pH 14-15), KP, solution (pH 4.5, pH 7) and H₂SO₄ (pH 2) during stirring for 24 h at 25 °C prior to addition of H₂PtCl₆ (4 wt.%) and activated NCN (Figure 4b, Table S14). After six days of irradiation under 10 M KOH conditions, 39.5±1.1 μmol of H₂ was produced, which is twice the H₂ production yield observed in 5 M KOH, H₂SO₄ and pH 7 KP, solution all resulted in H₂ production yields comparable to that of a pH 4.5 KP, solution. These activities are consistent with the higher solubility of cellulose under alkaline conditions (Figure S13, Table S15).14,45 The conversion yield determined with different α-cellulose loadings indicates that 22% conversion is reached after six days of irradiation in 10 M KOH solution (Table S16), more than twice the yield reported for Cds/CdO quantum dots under similar conditions (9.7%).17

In summary, we report a straightforward ultra-sonication approach to breakdown aggregates of NCN, which results in enhanced photocactivity. The activated NCN reaches 39310±1970 μmol H₂ (g NCN⁻¹)⁻¹ h⁻¹ for the photoreforming of 4-MBA. Both purified lignocellulose components and raw biomass substrates are photo-reformed to H₂ with activated NCN and NIP in KP (pH 4.5) at 25 °C, demonstrating precious metal-free, non-toxic and visible light-promoted photoreforming of biomass under benign conditions. Activated NCN functions with molecular and heterogeneous co-catalysts, with high stability and a range of pH values, although alkaline conditions still exhibit the best performance and highest conversion yield. The utilization of a carbon-based photocatalyst for photoreforming of biomass offers new perspectives for clean H₂ fuel production from waste sources, with prospects to extract valuable chemicals from the oxidation process in future development.
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