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Photocatalysis

Photocatalytic Hydrogen Production using Polymeric Carbon Nitride with a Hydrogenase and a Bioinspired Synthetic Ni Catalyst**

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Abstract: *Solar-light-driven H_2 production in water with a [NiFeSe]-hydrogenase (H_2ase) and a bioinspired synthetic nickel catalyst (NiP) in combination with a heptazine carbon nitride polymer, melon (CN_x), is reported. The semibiological and purely synthetic systems show catalytic activity during solar light irradiation with turnover numbers (TONs) of more than 50000 mol H_2 (mol H_2ase)$^{-1}$ and approximately 155 mol H_2 (mol NiP)$^{-1}$ in redox-mediator-free aqueous solution at pH 6 and 4.5, respectively. Both systems maintained a reduced photoactivity under UV-free solar light irradiation ($\lambda > 420$ nm).*

Efficient and noble metal-free water photolysis using sunlight is a primary focus of research to advance sustainable solar energy generation.[1] Photocatalytic H_2 production can be achieved by employing hybrid systems with a solid-state light absorber such as an inorganic semiconductor assisted by a metallic, synthetic, or enzymatic electrocatalyst.[2] These systems typically contain expensive, inefficient, and/or unstable components, but high performance solar fuel devices need to be constructed from parts without these limitations.

Hydrogenases (H_2ases) are H_2-cycling enzymes and are by far the most efficient noble-metal-free electrocatalysts for H_2 generation with an unrivalled turnover frequency (TOF) benchmark of more than $10^3\,s^{-1}$ even at a modest overpotential.[3] This excellent electrocatalytic activity of H_2ases was exploited in photocatalytic schemes with a light absorber in the absence of a soluble redox mediator: a homogeneous photocatalytic system with a molecular organic dye,[4] and semiheterogeneous systems, in which the H_2ase is immobilized on Ru dye-sensitized TiO_2 nanoparticles,[5] and on Cd-containing quantum dots,[6] displaying excellent photocatalytic activity in sacrificial schemes.

An efficient class of H_2ase-inspired synthetic catalysts containing non-noble metal centers have been developed by DuBois and co-workers.[7] They possess a Ni bis(diphosphine) ligand core bearing pendant amino groups, which, much like those found in the active site of [FeFe]-H_2ases,[8] can act as catalytically active proton relays in the second coordination sphere of the 3d metal center. Photocatalytic H_2 generation with such Ni bis(diphosphine) catalysts has only been achieved in combination with a costly Ru dye in purely aqueous solution.[9]

Amorphous polymeric carbon nitride (CN_x) with a poly(tri-*s*-triazine) (polyheptazine) building block (often referred to as melon or g-C_3N_4) has recently emerged as an attractive visible-light absorber and can generate H_2 photocatalytically.[10] It can be easily synthesized by condensation of cyanamide, dicyandiamide, or melamine at elevated temperatures and displays high activities and photostability of more than 72 h.[10b] The material has well-suited band positions for water splitting and a band gap of approximately 2.7 eV with a conduction band potential at −0.8 V vs. RHE.[10a,b] Co-catalyst integration of non-noble metals,[11] Pt,[10b,12] Ni-$(TEOA)_3^{2+}$ (TEOA = triethanolamine),[13] and cobaloximes[14] with CN_x has previously been used as a strategy to enhance H_2 evolution rates.

In this study, we report a photocatalytic CN_x–enzyme hybrid system for visible-light-driven H_2 generation (Figure 1). This CN_x–H_2ase hybrid assembly operates in an

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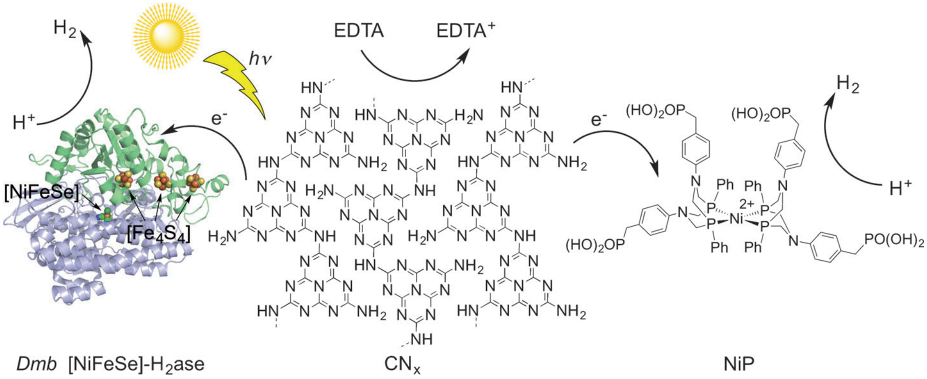

Figure 1. Representation of the photo-H_2 production with CN_x and *Dmb* [NiFeSe]-H_2ase (PDB ID: 1CC1)[15a] or CN_x and NiP (counterions omitted) in aqueous EDTA solution. Irradiation of CN_x results in the photoinduced direct electron transfer to the catalysts with H_2 formation and hole quenching in CN_x by EDTA.

aqueous sacrificial electron donor solution and does not require an expensive or fragile light absorber for visible light promoted photocatalysis as reported for the previous H_2ase-based systems. We selected *Desulfomicrobium baculatum* (*Dmb*) [NiFeSe]-H_2ase because of its well-known[15] and excellent H_2 evolution rate as well as tolerance toward H_2 and O_2, allowing for the accumulation of H_2 during irradiation and the handling of the enzyme in the absence of strictly anaerobic conditions.[4,5,15b]

The photocatalytic H_2 generation systems were assembled in a photoreactor (total volume 7.74 mL) by dispersing CN_x (5 mg, approx. 1 µm-sized particles with a Brunauer–Emmett–Teller surface area of $9\,m^2\,g^{-1}$; see Figures S1–S4 for FTIR, XRD, SEM, and zeta-potential measurements) in an aqueous solution of the electron donor (0.1M, 3 mL). The catalyst (H_2ase or NiP, see below) was added to the suspension and the light-protected reactor was sealed and purged with 2% CH_4 (as an internal gas chromatography standard) in N_2 before irradiating the stirred mixture at 25 °C. Irradiation was provided by a solar light simulator (air mass 1.5 G, $100\,mW\,cm^{-2}$) and headspace H_2 was quantified at regular time intervals by gas chromatography. The reaction conditions were optimized for a high rate of H_2 production per catalyst (as expressed by the TOF) by varying the pH of the solution, the amount of catalyst and by screening different electron donors (Table S1; Figures S5 and S6).

The optimized standard system for CN_x–H_2ase comprises 50 pmol H_2ase with 5 mg melon in 3 mL ethylenediamine tetraacetic acid (EDTA, 0.1M) at pH 6 under simulated solar irradiation at $\lambda > 300$ nm (Figure 2). Under these conditions, a TOF_{H_2ase} of $(5532 \pm 553)\,mol\,H_2\,(mol\,H_2ase)^{-1}\,h^{-1}$ and $(55.3 \pm 5.5)\,\mu mol\,H_2\,(g\,CN_x)^{-1}\,h^{-1}$ are photogenerated with almost linear H_2 evolution, producing $(0.82 \pm 0.08)\,\mu mol\,H_2$ during the first four hours. Photoinduced direct electron transfer from CN_x to the H_2ase was therefore observed, making a soluble redox mediator unnecessary. The CN_x–H_2ase suspension was photoactive for 48 h, whereupon (2.5 ± 0.2) µmol of H_2 was produced with a TON_{H_2ase} of $> 50\,000$. Control experiments in the dark and in the absence of CN_x or H_2ase showed no H_2 formation. Only minimal amounts of H_2 were produced when the electron donor buffer EDTA was replaced by potassium phosphate buffer (KP_i; 41 mM, pH 7, Table S1).

The amount of H_2ase per mg of CN_x and the light intensity were varied to gain insight into the performance-limiting factors of the CN_x–H_2ase hybrid. Increasing the H_2ase loading from 50 to 200 pmol per 5 mg CN_x resulted in a linear increase in overall H_2 generation with an unchanged TOF_{H_2ase} (Table S1, Figure S6). Decreasing the solar light intensity with neutral density filters from 100 to $50\,mW\,cm^{-2}$ did not result in a significant reduction of the photoactivity, although a further reduction to $20\,mW\,cm^{-2}$ resulted in approximately 40% decreased activity (Table S2; Figure S7). These experiments suggest that the optimized CN_x–H_2ase system is not limited by light absorption at CN_x, and support that enzyme adsorption and interaction with the CN_x is performance limiting (see below).

The CN_x–H_2ase system was also studied under visible light irradiation ($\lambda > 420$ nm). A decrease in photoactivity was observed giving rise to a TOF_{H_2ase} of $(768 \pm 77)\,h^{-1}$, which corresponds to 14% of the activity under UV/Vis irradiation (Figure 2). This can be attributed to the significantly reduced light absorption of CN_x above 420 nm (Figure S8). The external quantum efficiency (EQE) of the system was determined by irradiation of samples under standard conditions using a monochromatic LED light source at two wavelengths ($\lambda = 365$ nm, $I = 3.5\,mW\,cm^{-2}$ and $\lambda = 460$ nm, $I = 47\,mW\,cm^{-2}$). UV-irradiation gave an unoptimized EQE of approximately 7×10^{-2}%, whereas an EQE of 5×10^{-3}% was obtained at $\lambda = 465$ nm (Figure S8).

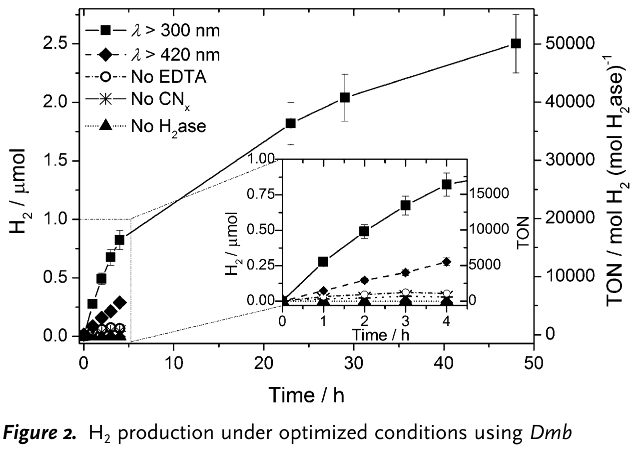

Figure 2. H_2 production under optimized conditions using *Dmb* [NiFeSe]-H_2ase (50 pmol) in EDTA (pH 6, 0.1 M, 3 mL) and CN_x (5 mg) under 1 sun irradiation in the absence ($\lambda > 300$ nm) and presence of a 420 nm UV filter. Control experiments without EDTA, CN_x, or H_2ase are also shown.

A centrifugation test was performed to gain insight into the strength of interaction between the enzyme and CN_x particles. First, H_2 production was monitored for 2 h with CN_x–H_2ase under standard conditions. The suspension was then centrifuged (5000 rpm, 5 min) followed by washing the pellet with water and redispersion of the particles in aqueous EDTA (0.1 M, pH 6). This suspension was then irradiated again after purging the headspace with 2% CH_4 in N_2. The remaining activity of this mixture was 12% relative to the activity prior to centrifugation, indicating that a relatively weak interaction suffices for electron transfer to occur from CN_x to the H_2ase. Physical adsorption of the H_2ase on the CN_x surface can be expected and we speculate that the H_2ase[16] may form hydrogen bonds with the −NH−, terminal $-NH_2$ or Lewis basic heptazine edge nitrogens in CN_x.[10a,17] The isoelectric point of CN_x was determined by zeta potential measurements as 3.3[18] and, at pH 6, the surface of CN_x is therefore negatively charged (≈ -15 mV) (Figure S4).

Although the direct electron transfer was observed from the photoexcited CN_x to the H_2ase, the CN_x–H_2ase system displayed a significantly increased photoactivity under standard conditions upon addition of an excess of the redox mediator, methyl viologen (MV),[19] producing up to 18.7 μmol H_2 after 4 h (Figure S9). A long-term experiment with H_2ase (50 pmol), CN_x (5 mg), and added MV (5 μmol) in aqueous EDTA (0.1 M) at pH 6 was also performed. The photoreactor was purged with 2% CH_4/N_2 after 24 and 48 h and additional MV (5 μmol) was added at the same time intervals. After 69 h, the CN_x–MV–H_2ase system produced 77 μmol H_2 with a TON of 1.5×10^6 and an initial TOF of 12.3 s^{-1} (Figure S10). Replenishment of MV was required due to decomposition of the organic mediator during irradiation. The substantially increased H_2 production activity in the presence of MV suggests that the electron transfer from CN_x to H_2ase is not yet fully optimized, presumably due to weak and nonspecific interactions at the CN_x–H_2ase interface.

Steady-state photoluminescence (PL) measurements were also performed with the CN_x in suspension upon photoexcitation at $\lambda = 365$ nm and following the PL emission at 450 nm (Figure S11). The PL emission of sonicated CN_x (0.22 g mL^{-1} in 0.1 M EDTA pH 6) is more strongly quenched upon addition of 50 pmol MV compared to 50 pmol H_2ase. These results further support that the photoinduced electron transfer from CN_x to MV is more efficient than that to the H_2ase.

The reported semibiological hybrid system provides a novel "per active site" activity benchmark for a cocatalyst on a CN_x material.[7g,11a,b,20] Photocatalytic H_2 generation schemes previously reported with H_2ases and other light absorbers show a high TOF_{H_2ase} (approximately 10^6 h^{-1}), but these systems rely on an expensive (Ru dye), toxic (Cd-based quantum dot), and/or fragile (organic dye) visible light absorber.[4,5b,6c] This study demonstrates that the biocompatibility of CN_x can be exploited to overcome these limitations and that by improving the coupling of CN_x to the H_2ase, the photoactivity will be further enhanced.

Successful H_2 production with CN_x–H_2ase prompted us to investigate a water-soluble and functional synthetic H_2ase-mimic, $[Ni^{II}(P^{Ph}_2\{NPhCH_2P(O)(OH)_2\}_2)_2]Br_2$ (NiP; Figure 1),[9] for comparison. Ni bis(diphosphine)[7a–e] complexes are among the most active H_2 generation electrocatalysts and, importantly, NiP has recently been shown to act as an excellent electrocatalyst in aqueous solution.[9] The purely synthetic CN_x–NiP assembly is photoactive and conditions were optimized for the highest TOF_{NiP}. Aqueous EDTA solutions (0.1 M) at pH 4.5 containing NiP (20 nmol) and suspended CN_x (5 mg) were studied under simulated solar irradiation at $\lambda > 300$ nm (Table S3, Figures S12–S14). Under these conditions, solar H_2 generation by CN_x–NiP gave an initial activity of (437.1 ± 43.7) μmol H_2 (g CN_x)$^{-1}$ h^{-1} producing (2.2 ± 0.2) μmol H_2 in the first hour and giving a TOF_{NiP} of (109.3 ± 10.9) mol H_2 (mol NiP)$^{-1}$ h^{-1}. CN_x-NiP was photoactive for three hours, whereupon (3.3 ± 0.4) μmol of H_2 with a TON of (166.1 ± 20.6) mol H_2 (mol NiP)$^{-1}$ was produced (Figure 3). A 64% decrease in photocatalytic H_2 generation yield was observed for CN_x–NiP when irradiating with $\lambda > 420$ nm instead of > 300 nm solar light. Decomposition of NiP is the likely reason for the ceased activity after three hours, because the photoactivity is fully regenerated if additional NiP is added (Figure S15).

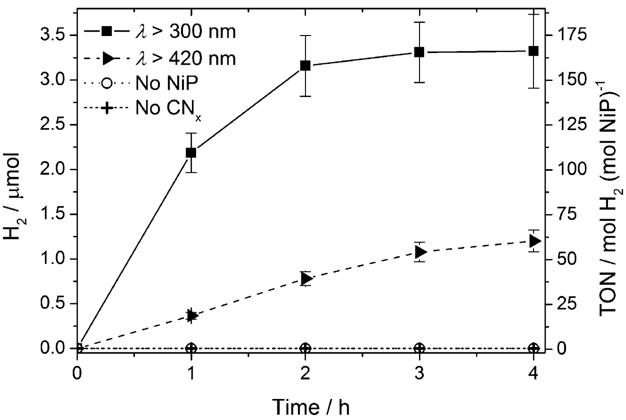

Figure 3. H_2 production under optimized conditions using NiP (20 nmol) in aqueous EDTA (0.1 M, pH 4.5, 3 mL) and CN_x (5 mg) under 1 sun irradiation. Data collected under standard conditions ($\lambda > 300$ nm), with UV-light-filtered irradiation ($\lambda > 420$ nm) and control experiments without NiP catalyst or CN_x are also shown.

Photo-H_2 generation with CN_x–NiP is thus significantly higher than for previously reported CN_x systems with immobilized noble-metal-free cocatalysts in aqueous solution. A TOF of < 0.5 h^{-1} and a TON of 4 was reported for a cobaloxime, $[CoCl(dimethylglyoximato)_2(pyridine)]$, after 8 h irradiation with CN_x in aqueous TEOA at pH 10.4.[14a] Other systems comprising a cobaloxime with a pyrene-functionalized pyridine[14c] and $NiCl_2$ with TEOA and CN_x[13] showed TONs of 160 and 281 and TOFs of approximately 40 and 6.7 h^{-1}, respectively, but required excess organic solvent. Previously, photo-H_2 generation with NiP was only reported with a molecular Ru dye, in which a TOF_{NiP} of up to 460 h^{-1} and a TON_{NiP} of up to 723 in pH 4.5 ascorbic acid solution were reported.[9]

The photo-H_2 generation activity of CN_x–NiP is dependent on the NiP concentration (Figures S13 and S14) and reduction of the light intensity (I) with neutral density filters has a substantial impact on the photoactivity. The NiP-based TOF decreases from $(71.1\pm7.1)\,h^{-1}$ ($I=100\,\%$) to (32.4 ± 3.2) ($I=50\,\%$) and $(13.1\pm1.4)\,h^{-1}$ ($I=20\,\%$; Table S4; Figure S16). The purely synthetic system is therefore limited both by catalyst concentration and light absorption. The unoptimized EQE for the CN_x–NiP system was determined to be $(0.37\pm0.02)\,\%$ under UV light ($\lambda=365$ nm) and $(0.04\pm0.01)\,\%$ under blue light irradiation ($\lambda=460$ nm) after 2 h. The wavelength-dependent EQE is consistent with the decrease in light absorption by CN_x at higher wavelengths (Figure S17).

Centrifugation experiments in analogy to the enzyme system were performed to examine the strength of the interaction between CN_x and NiP. After centrifugation, washing, and redispersion in fresh EDTA solution, 8% of the photoactivity remained for the synthetic system implying a weak interaction between the CN_x and NiP (Figure S18). Electronic absorption spectrophotometry was used to quantify the amount of NiP adsorbed to CN_x. By comparing UV-visible spectra of NiP (6.7 μM; $\lambda_{max}=320$ and 450 nm) in aqueous EDTA solution (3 mL; 0.1M, pH 4.5) before and after the addition of CN_x and centrifugation, an estimate of approximately 20% NiP was adsorbed on CN_x (Figure S19). The physical adsorption and H-bonding between the phosphonic acid groups in NiP and the terminal $-NH_2$ and $-NH-$ groups in CN_x are possible modes of interaction.[10a,17]

The addition of MV (20 μmol) to a standard photocatalytic experiment showed an approximately 20% decreased H_2 production activity. The reaction mixture turned dark blue upon irradiation, indicative of the presence of reduced MV, and implies that MV successfully scavenged electrons from the photoexcited CN_x, but was unable to transfer them to NiP (Figure S20).

The comparison of the CN_x–H_2ase with the CN_x–NiP hybrid system shows the expected higher "per active site" activity of the enzymatic system, whereas the purely synthetic system shows an overall higher H_2 production rate due to the larger amount of NiP (20 nmol) used compared to H_2ase (50 pmol). Thus, we also studied the CN_x catalyst systems with the same amount of NiP and H_2ase (200 pmol) on CN_x (5 mg) in aqueous EDTA solution (pH 4.5 and pH 7.0, respectively). At the same concentration, the enzyme ($TOF=2528\,h^{-1}$) greatly outperforms the NiP cocatalyst ($TOF=64\,h^{-1}$), demonstrating that substantial improvements are still required to develop synthetic catalysts with activities comparable to enzymes (Figure S21, Tables S1 and S3).

Finally, we photodeposited 1 wt% Pt onto CN_x (5 mg) for a direct comparison of this benchmark system with CN_x–H_2ase and CN_x–NiP. Following a standard procedure,[12] the platinized CN_x system was irradiated with visible light ($\lambda>$ 420 nm) in an aqueous 10 vol% TEOA solution, generating 94 $\mu mol\,H_2\,(g\,CN_x)^{-1}\,h^{-1}$, which corresponds to a TOF_{Pt} of 4.3 $mol\,H_2\,(mol\,Pt)^{-1}\,h^{-1}$. Thus, the CN_x–H_2ase and CN_x–NiP systems compare favorably when using TOF as the metrics of system performance.

In summary, solar-light-driven H_2 production with hybrid systems consisting of polymeric CN_x with H_2ase and the bioinspired synthetic catalyst, NiP, has been demonstrated. The systems operate without a soluble redox mediator and are not limited by a photo-unstable or expensive dye. The semibiological CN_x–H_2ase assembly achieved a record TOF of 5532 h^{-1} and TON of > 50000 after two days as a cocatalyst with CN_x. The additional use of the redox mediator MV allowed for the photogeneration of H_2 with a TOF of 12.3 s^{-1} and a TON of $>1\times10^6$, which displays the further potential of the hybrid assembly after optimization of the biomaterial interface. CN_x–H_2ase also maintains respectable activity under visible light irradiation for more than 48 h. Recent investigations into improving the absorption profile of CN_x in the visible range demonstrate the potential of this material and illustrate that its use as a light-harvesting material will continue to develop, as its absorption profile is further improved.[21] The entirely synthetic CN_x–NiP system displays an unprecedentedly high TOF (109 h^{-1}) and TON (166) for a hybrid system made of a molecular cocatalyst with CN_x in purely aqueous solution. This work advances the use of hybrid photocatalytic schemes by integrating highly active electrocatalysts with the photostable and inexpensive CN_x, which is shown to be compatible with biological and bioinspired electrocatalysts, namely hydrogenases and their mimics in aqueous solution.

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