

**Photocatalysis**

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# 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  $50\,000\ mol\ H_2\ (mol\ H_2ase)^{-1}$  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 ( $\lambda > 420\ nm$ ).

**E**fficient and noble metal-free water photolysis using sunlight is a primary focus of research to advance sustainable solar energy generation.<sup>[1]</sup> 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.<sup>[2]</sup> 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.<sup>[3]</sup> 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,<sup>[4]</sup> and semiheterogeneous systems, in which the  $H_2ase$  is immobi-

lized on Ru dye-sensitized  $TiO_2$  nanoparticles,<sup>[5]</sup> and on Cd-containing quantum dots,<sup>[6]</sup> 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.<sup>[7]</sup> They possess a Ni bis(diphosphine) ligand core bearing pendant amino groups, which, much like those found in the active site of [FeFe]- $H_2ases$ ,<sup>[8]</sup> 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.<sup>[9]</sup>

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.<sup>[10]</sup> 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.<sup>[10b]</sup> 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.<sup>[10a,b]</sup> Cocatalyst integration of non-noble metals,<sup>[11]</sup> Pt,<sup>[10b,12]</sup> Ni-(TEOA)<sub>3</sub><sup>2+</sup> (TEOA = triethanolamine),<sup>[13]</sup> and cobaloximes<sup>[14]</sup> 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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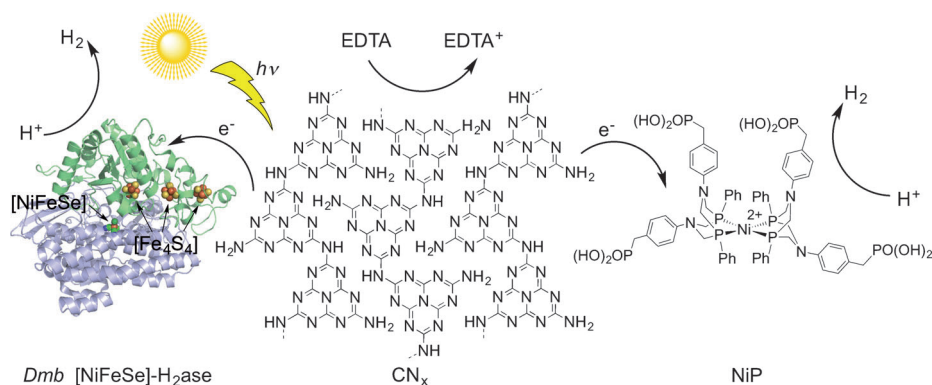
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**Figure 1.** Representation of the photo- $\text{H}_2$  production with  $\text{CN}_x$  and *Dmb* [NiFeSe]- $\text{H}_2$ ase (PDB ID: 1CC1)<sup>[15a]</sup> or  $\text{CN}_x$  and NiP (counterions omitted) in aqueous EDTA solution. Irradiation of  $\text{CN}_x$  results in the photoinduced direct electron transfer to the catalysts with  $\text{H}_2$  formation and hole quenching in  $\text{CN}_x$  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  $\text{H}_2$ ase-based systems. We selected *Desulfomicrobium baculatum* (*Dmb*) [NiFeSe]- $\text{H}_2$ ase because of its well-known<sup>[15]</sup> and excellent  $\text{H}_2$  evolution rate as well as tolerance toward  $\text{H}_2$  and  $\text{O}_2$ , allowing for the accumulation of  $\text{H}_2$  during irradiation and the handling of the enzyme in the absence of strictly anaerobic conditions.<sup>[4,5,15b]</sup>

The photocatalytic  $\text{H}_2$  generation systems were assembled in a photoreactor (total volume 7.74 mL) by dispersing  $\text{CN}_x$  (5 mg, approx.  $1 \mu\text{m}$ -sized particles with a Brunauer–Emmett–Teller surface area of  $9 \text{ m}^2 \text{ g}^{-1}$ ; see Figures S1–S4 for FTIR, XRD, SEM, and zeta-potential measurements) in an aqueous solution of the electron donor (0.1 M, 3 mL). The catalyst ( $\text{H}_2$ ase or NiP, see below) was added to the suspension and the light-protected reactor was sealed and purged with 2%  $\text{CH}_4$  (as an internal gas chromatography standard) in  $\text{N}_2$  before irradiating the stirred mixture at  $25^\circ\text{C}$ . Irradiation was provided by a solar light simulator (air mass 1.5 G,  $100 \text{ mW cm}^{-2}$ ) and headspace  $\text{H}_2$  was quantified at regular time intervals by gas chromatography. The reaction conditions were optimized for a high rate of  $\text{H}_2$  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).

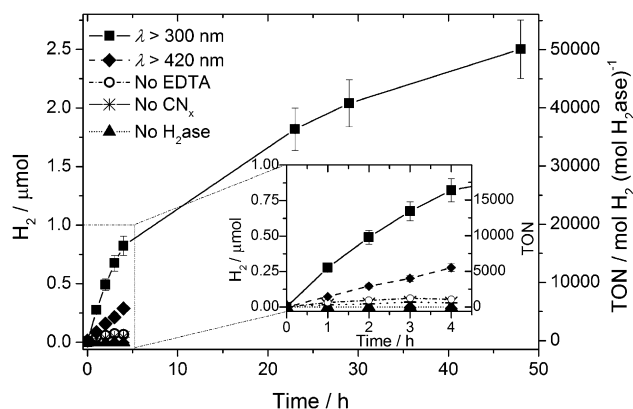
The optimized standard system for  $\text{CN}_x$ - $\text{H}_2$ ase comprises 50 pmol  $\text{H}_2$ ase with 5 mg melon in 3 mL ethylenediamine tetraacetic acid (EDTA, 0.1 M) at pH 6 under simulated solar irradiation at  $\lambda > 300 \text{ nm}$  (Figure 2). Under these conditions, a  $\text{TOF}_{\text{H}_2\text{ase}}$  of  $(5532 \pm 553) \text{ mol H}_2 (\text{mol H}_2\text{ase})^{-1} \text{ h}^{-1}$  and  $(55.3 \pm 5.5) \mu\text{mol H}_2 (\text{g CN}_x)^{-1} \text{ h}^{-1}$  are photogenerated with almost linear  $\text{H}_2$  evolution, producing  $(0.82 \pm 0.08) \mu\text{mol H}_2$  during the first four hours. Photoinduced direct electron transfer from  $\text{CN}_x$  to the  $\text{H}_2$ ase was therefore observed, making a soluble redox mediator unnecessary. The  $\text{CN}_x$ - $\text{H}_2$ ase suspension was photoactive for 48 h, whereupon  $(2.5 \pm 0.2) \mu\text{mol}$  of  $\text{H}_2$  was produced with a  $\text{TON}_{\text{H}_2\text{ase}}$  of  $> 50000$ . Control experiments in the dark and in the absence of  $\text{CN}_x$  or  $\text{H}_2$ ase showed no  $\text{H}_2$  formation. Only minimal

amounts of  $\text{H}_2$  were produced when the electron donor buffer EDTA was replaced by potassium phosphate buffer ( $\text{KP}_i$ ; 41 mM, pH 7, Table S1).

The amount of  $\text{H}_2$ ase per mg of  $\text{CN}_x$  and the light intensity were varied to gain insight into the performance-limiting factors of the  $\text{CN}_x$ - $\text{H}_2$ ase hybrid. Increasing the  $\text{H}_2$ ase loading from 50 to 200 pmol per 5 mg  $\text{CN}_x$  resulted in a linear increase in overall  $\text{H}_2$  generation with an unchanged  $\text{TOF}_{\text{H}_2\text{ase}}$  (Table S1, Figure S6). Decreasing the solar light intensity with neutral density filters from 100 to  $50 \text{ mW cm}^{-2}$  did not result in a significant reduction of the

photoactivity, although a further reduction to  $20 \text{ mW cm}^{-2}$  resulted in approximately 40% decreased activity (Table S2; Figure S7). These experiments suggest that the optimized  $\text{CN}_x$ - $\text{H}_2$ ase system is not limited by light absorption at  $\text{CN}_x$ , and support that enzyme adsorption and interaction with the  $\text{CN}_x$  is performance limiting (see below).

The  $\text{CN}_x$ - $\text{H}_2$ ase system was also studied under visible light irradiation ( $\lambda > 420 \text{ nm}$ ). A decrease in photoactivity was observed giving rise to a  $\text{TOF}_{\text{H}_2\text{ase}}$  of  $(768 \pm 77) \text{ h}^{-1}$ , which corresponds to 14% of the activity under UV/Vis irradiation (Figure 2). This can be attributed to the significantly reduced light absorption of  $\text{CN}_x$  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 ( $\lambda = 365 \text{ nm}$ ,  $I = 3.5 \text{ mW cm}^{-2}$  and  $\lambda = 460 \text{ nm}$ ,  $I = 47 \text{ mW cm}^{-2}$ ). UV-irradiation gave an unoptimized EQE of approximately  $7 \times 10^{-2}\%$ , whereas an EQE of  $5 \times 10^{-3}\%$  was obtained at  $\lambda = 465 \text{ nm}$  (Figure S8).



**Figure 2.**  $\text{H}_2$  production under optimized conditions using *Dmb* [NiFeSe]- $\text{H}_2$ ase (50 pmol) in EDTA (pH 6, 0.1 M, 3 mL) and  $\text{CN}_x$  (5 mg) under 1 sun irradiation in the absence ( $\lambda > 300 \text{ nm}$ ) and presence of a 420 nm UV filter. Control experiments without EDTA,  $\text{CN}_x$ , or  $\text{H}_2$ ase 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  $CN_x$ - $H_2$ ase 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 (0.1M, 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  $H_2$ ase. Physical adsorption of the  $H_2$ ase on the  $CN_x$  surface can be expected and we speculate that the  $H_2$ ase<sup>[16]</sup> may form hydrogen bonds with the  $-NH-$ , terminal  $-NH_2$  or Lewis basic heptazine edge nitrogens in  $CN_x$ .<sup>[10a,17]</sup> The isoelectric point of  $CN_x$  was determined by zeta potential measurements as 3.3<sup>[18]</sup> and, at pH 6, the surface of  $CN_x$  is therefore negatively charged ( $\approx -15$  mV) (Figure S4).

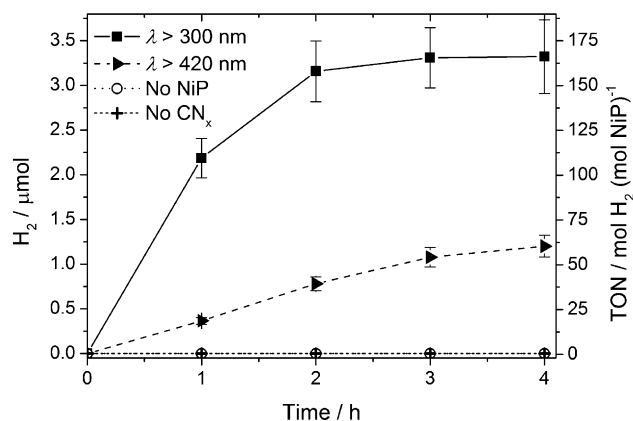
Although the direct electron transfer was observed from the photoexcited  $CN_x$  to the  $H_2$ ase, the  $CN_x$ - $H_2$ ase system displayed a significantly increased photoactivity under standard conditions upon addition of an excess of the redox mediator, methyl viologen (MV),<sup>[19]</sup> producing up to 18.7  $\mu\text{mol } H_2$  after 4 h (Figure S9). A long-term experiment with  $H_2$ ase (50 pmol),  $CN_x$  (5 mg), and added MV (5  $\mu\text{mol}$ ) in aqueous EDTA (0.1M) 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  $\mu\text{mol}$ ) was added at the same time intervals. After 69 h, the  $CN_x$ -MV- $H_2$ ase system produced 77  $\mu\text{mol } H_2$  with a TON of  $1.5 \times 10^6$  and an initial TOF of  $12.3 \text{ s}^{-1}$  (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  $H_2$ ase is not yet fully optimized, presumably due to weak and nonspecific interactions at the  $CN_x$ - $H_2$ ase 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  $\text{g mL}^{-1}$  in 0.1M EDTA pH 6) is more strongly quenched upon addition of 50 pmol MV compared to 50 pmol  $H_2$ ase. These results further support that the photoinduced electron transfer from  $CN_x$  to MV is more efficient than that to the  $H_2$ ase.

The reported semibiological hybrid system provides a novel “per active site” activity benchmark for a cocatalyst on a  $CN_x$  material.<sup>[7g,11a,b,20]</sup> Photocatalytic  $H_2$  generation schemes previously reported with  $H_2$ ases and other light absorbers show a high TOF <sub>$H_2$ ase</sub> (approximately  $10^6 \text{ h}^{-1}$ ), but these systems rely on an expensive (Ru dye), toxic (Cd-based quantum dot), and/or fragile (organic dye) visible light absorber.<sup>[4,5b,6c]</sup> 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  $H_2$ ase, the photoactivity will be further enhanced.

Successful  $H_2$  production with  $CN_x$ - $H_2$ ase prompted us to investigate a water-soluble and functional synthetic  $H_2$ ase-mimic,  $[Ni^{II}(P^{Ph}_2[NPhCH_2P(O)(OH)_2]_2)]Br_2$  (NiP;

Figure 1),<sup>[9]</sup> for comparison. Ni bis(diphosphine)<sup>[7a-c]</sup> 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.<sup>[9]</sup> The purely synthetic  $CN_x$ -NiP assembly is photoactive and conditions were optimized for the highest TOF<sub>NiP</sub>. Aqueous EDTA solutions (0.1M) 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  $(437.1 \pm 43.7) \mu\text{mol } H_2 (\text{g } CN_x)^{-1} \text{ h}^{-1}$  producing  $(2.2 \pm 0.2) \mu\text{mol } H_2$  in the first hour and giving a TOF<sub>NiP</sub> of  $(109.3 \pm 10.9) \text{ mol } H_2 (\text{mol NiP})^{-1} \text{ h}^{-1}$ .  $CN_x$ -NiP was photoactive for three hours, whereupon  $(3.3 \pm 0.4) \mu\text{mol}$  of  $H_2$  with a TON of  $(166.1 \pm 20.6) \text{ mol } H_2 (\text{mol NiP})^{-1}$  was produced (Figure 3). A 64% decrease in photocatalytic  $H_2$



**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.

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).

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  $< 0.5 \text{ h}^{-1}$  and a TON of 4 was reported for a cobaloxime,  $[\text{CoCl}(\text{dimethylglyoximate})_2(\text{pyridine})]$ , after 8 h irradiation with  $CN_x$  in aqueous TEOA at pH 10.4.<sup>[14a]</sup> Other systems comprising a cobaloxime with a pyrene-functionalized pyridine<sup>[14c]</sup> and  $NiCl_2$  with TEOA and  $CN_x$ <sup>[13]</sup> showed TONs of 160 and 281 and TOFs of approximately 40 and  $6.7 \text{ h}^{-1}$ , 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<sub>NiP</sub> of up to  $460 \text{ h}^{-1}$  and a TON<sub>NiP</sub> of up to 723 in pH 4.5 ascorbic acid solution were reported.<sup>[9]</sup>

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  $(71.1 \pm 7.1) \text{ h}^{-1}$  ( $I=100\%$ ) to  $(32.4 \pm 3.2)$  ( $I=50\%$ ) and  $(13.1 \pm 1.4) \text{ h}^{-1}$  ( $I=20\%$ ; Table S4; Figure S16). The purely synthetic system is therefore limited both by catalyst concentration and light absorption. The unoptimized EQE for the  $\text{CN}_x$ -NiP system was determined to be  $(0.37 \pm 0.02)\%$  under UV light ( $\lambda = 365 \text{ nm}$ ) and  $(0.04 \pm 0.01)\%$  under blue light irradiation ( $\lambda = 460 \text{ nm}$ ) after 2 h. The wavelength-dependent EQE is consistent with the decrease in light absorption by  $\text{CN}_x$  at higher wavelengths (Figure S17).

Centrifugation experiments in analogy to the enzyme system were performed to examine the strength of the interaction between  $\text{CN}_x$  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  $\text{CN}_x$  and NiP (Figure S18). Electronic absorption spectrophotometry was used to quantify the amount of NiP adsorbed to  $\text{CN}_x$ . By comparing UV-visible spectra of NiP ( $6.7 \mu\text{M}$ ;  $\lambda_{\text{max}} = 320$  and  $450 \text{ nm}$ ) in aqueous EDTA solution ( $3 \text{ mL}$ ;  $0.1 \text{ M}$ ,  $\text{pH } 4.5$ ) before and after the addition of  $\text{CN}_x$  and centrifugation, an estimate of approximately 20% NiP was adsorbed on  $\text{CN}_x$  (Figure S19). The physical adsorption and H-bonding between the phosphonic acid groups in NiP and the terminal  $-\text{NH}_2$  and  $-\text{NH}-$  groups in  $\text{CN}_x$  are possible modes of interaction.<sup>[10a,17]</sup>

The addition of MV ( $20 \mu\text{mol}$ ) to a standard photocatalytic experiment showed an approximately 20% decreased  $\text{H}_2$  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  $\text{CN}_x$ , but was unable to transfer them to NiP (Figure S20).

The comparison of the  $\text{CN}_x$ - $\text{H}_2$ ase with the  $\text{CN}_x$ -NiP hybrid system shows the expected higher “per active site” activity of the enzymatic system, whereas the purely synthetic system shows an overall higher  $\text{H}_2$  production rate due to the larger amount of NiP ( $20 \text{ nmol}$ ) used compared to  $\text{H}_2$ ase ( $50 \text{ pmol}$ ). Thus, we also studied the  $\text{CN}_x$  catalyst systems with the same amount of NiP and  $\text{H}_2$ ase ( $200 \text{ pmol}$ ) on  $\text{CN}_x$  ( $5 \text{ mg}$ ) in aqueous EDTA solution ( $\text{pH } 4.5$  and  $\text{pH } 7.0$ , respectively). At the same concentration, the enzyme ( $\text{TOF} = 2528 \text{ h}^{-1}$ ) greatly outperforms the NiP cocatalyst ( $\text{TOF} = 64 \text{ h}^{-1}$ ), 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  $\text{CN}_x$  ( $5 \text{ mg}$ ) for a direct comparison of this benchmark system with  $\text{CN}_x$ - $\text{H}_2$ ase and  $\text{CN}_x$ -NiP. Following a standard procedure,<sup>[12]</sup> the platinumized  $\text{CN}_x$  system was irradiated with visible light ( $\lambda > 420 \text{ nm}$ ) in an aqueous 10 vol% TEOA solution, generating  $94 \mu\text{mol H}_2(\text{g CN}_x)^{-1} \text{ h}^{-1}$ , which corresponds to a  $\text{TOF}_{\text{Pt}}$  of  $4.3 \text{ mol H}_2(\text{mol Pt})^{-1} \text{ h}^{-1}$ . Thus, the  $\text{CN}_x$ - $\text{H}_2$ ase and  $\text{CN}_x$ -NiP systems compare favorably when using TOF as the metrics of system performance.

In summary, solar-light-driven  $\text{H}_2$  production with hybrid systems consisting of polymeric  $\text{CN}_x$  with  $\text{H}_2$ ase 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  $\text{CN}_x$ - $\text{H}_2$ ase assembly achieved a record TOF of  $5532 \text{ h}^{-1}$  and TON of  $> 50000$  after two days as a cocatalyst with  $\text{CN}_x$ . The additional use of the redox mediator MV allowed for the photogeneration of  $\text{H}_2$  with a TOF of  $12.3 \text{ s}^{-1}$  and a TON of  $> 1 \times 10^6$ , which displays the further potential of the hybrid assembly after optimization of the biomaterial interface.  $\text{CN}_x$ - $\text{H}_2$ ase also maintains respectable activity under visible light irradiation for more than 48 h. Recent investigations into improving the absorption profile of  $\text{CN}_x$  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.<sup>[21]</sup> The entirely synthetic  $\text{CN}_x$ -NiP system displays an unprecedentedly high TOF ( $109 \text{ h}^{-1}$ ) and TON (166) for a hybrid system made of a molecular cocatalyst with  $\text{CN}_x$  in purely aqueous solution. This work advances the use of hybrid photocatalytic schemes by integrating highly active electrocatalysts with the photostable and inexpensive  $\text{CN}_x$ , which is shown to be compatible with biological and bioinspired electrocatalysts, namely hydrogenases and their mimics in aqueous solution.

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