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# Carbon nitride–TiO<sub>2</sub> hybrid modified with hydrogenase for visible light driven hydrogen production†

Christine A. Caputo,<sup>a</sup> Lidong Wang,<sup>b</sup> Radim Beranek<sup>b</sup> and Erwin Reisner<sup>\*a</sup>

A system consisting of a [NiFeSe]–hydrogenase (H<sub>2</sub>ase) grafted on the surface of a TiO<sub>2</sub> nanoparticle modified with polyheptazine carbon nitride polymer, melon (CN<sub>x</sub>) is reported. This semi-biological assembly shows a turnover number (TON) of more than  $5.8 \times 10^5$  mol H<sub>2</sub> (mol H<sub>2</sub>ase)<sup>−1</sup> after 72 h in a sacrificial electron donor solution at pH 6 during solar AM 1.5 G irradiation. An external quantum efficiency up to 4.8% for photon-to-hydrogen conversion was achieved under irradiation with monochromatic light. The CN<sub>x</sub>–TiO<sub>2</sub>–H<sub>2</sub>ase construct was also active under UV-free solar light irradiation ( $\lambda > 420$  nm), where it showed a substantially higher activity than TiO<sub>2</sub>–H<sub>2</sub>ase and CN<sub>x</sub>–H<sub>2</sub>ase due, in part, to the formation of a CN<sub>x</sub>–TiO<sub>2</sub> charge transfer complex and highly productive electron transfer to the H<sub>2</sub>ase. The CN<sub>x</sub>–TiO<sub>2</sub>–H<sub>2</sub>ase system sets a new benchmark for photocatalytic H<sub>2</sub> production with a H<sub>2</sub>ase immobilised on a noble- and toxic-metal free light absorber in terms of visible light utilisation and stability.

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## Introduction

The use of efficient electrocatalysts in artificial photocatalytic schemes has been an area of recent interest for the conversion of protons to hydrogen using sunlight. Specifically, the use of redox enzymes in photocatalytic schemes highlights the importance of investigating the compatibility of biological systems with light harvesting materials and testing the stability of the resultant bio-hybrid assemblies.<sup>1</sup> Hydrogenases (H<sub>2</sub>ases) are the most efficient noble-metal free electrocatalysts for H<sub>2</sub> production and achieve a turnover frequency (TOF) of more than 1000 s<sup>−1</sup> with a small overpotential.<sup>2</sup> H<sub>2</sub>ases also show impressive H<sub>2</sub> production rates and yields in sacrificial photocatalytic schemes in pH neutral aqueous solution.<sup>1a</sup> In these systems, a photoexcited light absorber provides electrons to the protein *via* an internal wire, the iron–sulfur electron relay, to the active site where proton reduction occurs. Examples are the immobilization of a H<sub>2</sub>ase on Ru-sensitised TiO<sub>2</sub>,<sup>3</sup> on Cd-based quantum dots<sup>4</sup> as well as homogeneous systems using the H<sub>2</sub>ase with a covalently linked photosystem I<sup>5</sup> or in combination with an organic dye,<sup>6</sup> and multi-component systems with a dye and a soluble redox mediator.<sup>7</sup>

Polymeric carbon nitride (polyheptazine or melon, herein CN<sub>x</sub>) is a promising visible-light absorber for the photocatalytic generation of H<sub>2</sub>.<sup>8</sup> We have recently reported the use of CN<sub>x</sub> as a light harvesting material in combination with a H<sub>2</sub>ase and a H<sub>2</sub>ase-inspired synthetic Ni catalyst for solar H<sub>2</sub> generation.<sup>9</sup> The CN<sub>x</sub>–H<sub>2</sub>ase system showed sustained catalysis with a turnover number (TON) of more than 50 000 after 70 h solar light irradiation. However, this hybrid system suffered from a weak interaction between the H<sub>2</sub>ase and the CN<sub>x</sub> surface, and consequently, poor electron transfer from CN<sub>x</sub> to the H<sub>2</sub>ase. Furthermore, CN<sub>x</sub>–H<sub>2</sub>ase only showed efficient H<sub>2</sub> production up to wavelengths of approximately 420 nm and therefore only limited visible light harvesting capabilities.

Here, we selected a hybrid material consisting of TiO<sub>2</sub> (Hombikat UV 100, anatase, BET surface area: 300 m<sup>2</sup> g<sup>−1</sup>, crystallite size < 10 nm) surface-modified with CN<sub>x</sub> polymer as a light absorbing hybrid material for the photocatalytic system with a H<sub>2</sub>ase for three main reasons (Fig. 1; see ESI and Fig. S1† for synthesis and characterisation). Firstly, CN<sub>x</sub>–TiO<sub>2</sub> can be readily prepared on a gram scale by heating TiO<sub>2</sub> nanoparticles in the presence of urea, an inexpensive and sustainable material.<sup>10</sup>

Secondly, CN<sub>x</sub>–TiO<sub>2</sub> provides us with substantially improved solar light harvesting performance compared to individual CN<sub>x</sub> and TiO<sub>2</sub>. *Band gap excitation* of TiO<sub>2</sub> (pathway 1; Fig. 1) efficiently utilises the UV spectrum (band gap of 3.2 eV for anatase TiO<sub>2</sub> with CB<sub>TiO<sub>2</sub></sub> at approximately −0.6 V vs. NHE at pH 6).<sup>11</sup> A significant portion of the visible spectrum is utilised with CN<sub>x</sub>–TiO<sub>2</sub> as it can, upon photo-excitation of CN<sub>x</sub>, perform *photoinduced electron transfer* from the LUMO<sub>CN<sub>x</sub></sub> to CB<sub>TiO<sub>2</sub></sub> (pathway 2).

<sup>a</sup>Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, Cambridge University, Lensfield Road, Cambridge CB2 1EW, UK. E-mail: reisner@ch.cam.ac.uk; Web: <http://www-reisner.ch.cam.ac.uk>

<sup>b</sup>Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany

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the contribution of intrinsic absorption by TiO<sub>2</sub> (pathway 1). A photoactivity with an initial TOF<sub>H<sub>2</sub>ase</sub> of 6353 ± 635 h<sup>-1</sup> was observed, which results in the generation of 1.31 ± 0.13 μmol H<sub>2</sub> after 4 h. After 72 h, 13 ± 1 μmol of H<sub>2</sub> were generated with a TON<sub>H<sub>2</sub>ase</sub> of more than (2.6 ± 0.3) × 10<sup>5</sup> (Fig. 2).

Subsequently, irradiation was carried out at λ > 455 nm to investigate the contribution of the direct charge-transfer from the HOMO<sub>CN<sub>x</sub></sub> to CB<sub>TiO<sub>2</sub></sub> to the photoactivity. A TOF<sub>H<sub>2</sub>ase</sub> of 1096 ± 175 h<sup>-1</sup> with the evolution of 0.26 ± 0.06 μmol H<sub>2</sub> after 4 h and 2.9 ± 1.6 μmol H<sub>2</sub> after 72 h was observed, which corresponds to 17% of the visible light activity. This suggests that all three pathways in Fig. 1B contribute to the UV-vis photoactivity, whereas pathways 2 and 3 are responsible for the visible-light response of CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase. Previous investigations of CN<sub>x</sub>-TiO<sub>2</sub> hybrids have shown that their activity is limited by the strong electronic coupling between CN<sub>x</sub> and TiO<sub>2</sub> leading not only to intense visible light absorption but also to fast back electron transfer (primary recombination).<sup>13,16</sup>

In order to study the role of TiO<sub>2</sub> as heterogeneous electron relay in CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase in more detail, a sample of CN<sub>x</sub>-ZrO<sub>2</sub> (15 mg) was also tested with the H<sub>2</sub>ase. The negative CB<sub>ZrO<sub>2</sub></sub> at approximately -1.35 V vs. NHE at pH 6, prevents electron injection from LUMO<sub>CN<sub>x</sub></sub> (approximately -1.25 V vs. NHE at pH 6).<sup>17</sup> This band level mismatch allowed us to demonstrate that spatial proximity of surface-bound H<sub>2</sub>ase to CN<sub>x</sub> alone cannot promote productive electron transfer as no H<sub>2</sub> was observed with CN<sub>x</sub>-ZrO<sub>2</sub>-H<sub>2</sub>ase (λ > 300 nm; Fig. S4†). Thus, charge transfer from the LUMO<sub>CN<sub>x</sub></sub> into CB<sub>ZrO<sub>2</sub></sub> (pathway 2) is not possible, nor is the direct electron transfer from HOMO<sub>CN<sub>x</sub></sub> to CB<sub>ZrO<sub>2</sub></sub> (pathway 3), which are crucial to the formation of H<sub>2</sub> with the hybrid material.

For comparison, H<sub>2</sub> production was also tested with CN<sub>x</sub> (5 mg) and H<sub>2</sub>ase (50 pmol) in the absence of metal oxide under standard conditions. A TON<sub>H<sub>2</sub>ase</sub> of 14852 ± 1485 was obtained after 4 h with an initial TOF of 6288 ± 649 h<sup>-1</sup> when irradiated with UV-visible light (λ > 300 nm, Table S1†). Under visible light irradiation (λ > 420 nm), a TON<sub>H<sub>2</sub>ase</sub> of 2375 ± 267 was observed after 4 h and no H<sub>2</sub> was produced at λ > 455 nm, demonstrating the substantially enhanced activity with CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase compared to CN<sub>x</sub>-H<sub>2</sub>ase at all wavelengths (Fig. S4†).

Experiments were also performed with TiO<sub>2</sub>-H<sub>2</sub>ase. While the system showed comparable activity under UV-visible irradiation due to efficient band gap excitation of TiO<sub>2</sub> (pathway 1), it showed significantly reduced activity under visible only irradiation at λ > 420 nm and displayed negligible H<sub>2</sub> yields at λ > 455 nm compared to CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase (Fig. S4†).<sup>9</sup> Thus, UV-band gap excitation of TiO<sub>2</sub> dominates the absorption of the CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase hybrid material under UV-light irradiation, which becomes less significant under visible irradiation.

The effect of light intensity on the photocatalytic activity (λ > 300 nm) was studied by employing neutral density filters. A photoactivity of approximately 90% remained when employing a 50% absorbance filter (50 mW cm<sup>-2</sup>) and 44% of activity remained with an 80% filter (20 mW cm<sup>-2</sup>; Fig. S5†). The initial non-linear decrease in activity implies that the system is not limited by light at 1 Sun intensity as has been observed

previously with synthetic H<sub>2</sub> evolution catalyst-modified Ru dye-sensitised TiO<sub>2</sub> systems.<sup>18</sup>

The CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase system sets a new benchmark for visible light driven and prolonged H<sub>2</sub> production with a heterogenised H<sub>2</sub>ase without the need for expensive or toxic materials.<sup>3,4,9</sup> A part of this improvement can be attributed to the direct optical electron transfer (pathway 3) within CN<sub>x</sub>-TiO<sub>2</sub>, which draws the absorption of solar light significantly into the visible spectrum.

The enzyme loading onto CN<sub>x</sub>-TiO<sub>2</sub> was calculated based on the BET surface area of 111 m<sup>2</sup> g<sup>-1</sup>, a crystallite surface area of ~314 nm<sup>2</sup> per particle and an estimation that approximately one-quarter of the surface area of TiO<sub>2</sub> is accessible for the enzyme to adsorb. This equates to ~0.1 H<sub>2</sub>ase per particle of CN<sub>x</sub>-TiO<sub>2</sub>. The approximate 1 : 10 enzyme : particle ratio allows the H<sub>2</sub>ase to function at the maximum rate (*i.e.*, TOF) as the maximum electron flux of conduction band electrons is directed towards a single enzyme. To qualitatively determine the amounts of surface-bound and solubilised H<sub>2</sub>ase in the optimised system, H<sub>2</sub>ase (50 pmol) was loaded onto CN<sub>x</sub>-TiO<sub>2</sub> (5 mg) in aqueous EDTA solution by stirring under N<sub>2</sub> for 15 min. The suspension was centrifuged and the supernatant decanted (see ESI† for experimental details). The CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase pellet was re-dispersed in fresh EDTA solution (3 mL, 0.1 M, pH 6) and the photocatalytic vessel purged with 2% CH<sub>4</sub> in N<sub>2</sub>. The suspension was then irradiated (λ > 420 nm) and H<sub>2</sub> production monitored (Fig. 3). The H<sub>2</sub> production activity was nearly identical to a sample that was not centrifuged, both in the presence and absence of methyl viologen (MV<sup>2+</sup>, see below), indicating that attachment of H<sub>2</sub>ase to CN<sub>x</sub>-TiO<sub>2</sub> is essentially quantitative. The substantially improved adsorption of the enzyme on the TiO<sub>2</sub> surface compared to the inert CN<sub>x</sub> polymer therefore also contributes to the increased activity of CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase compared to CN<sub>x</sub>-H<sub>2</sub>ase. Previously an 88% decrease in photoactivity was observed with the poorly interacting CN<sub>x</sub>-



Fig. 3 Photocatalytic H<sub>2</sub> production using *Dmb* [NiFeSe]-H<sub>2</sub>ase (50 pmol) in EDTA (pH 6, 0.1 M, 3 mL) with CN<sub>x</sub>-TiO<sub>2</sub> (5 mg) under optimised conditions before and after centrifugation and re-suspension in fresh EDTA buffer solution followed by 1 Sun irradiation (λ > 420 nm). Results are also shown in the presence and absence of redox mediator, methyl viologen (MV<sup>2+</sup>).





H<sub>2</sub>ase after centrifugation and re-dispersion in fresh electron donor buffer.<sup>9</sup>

The external quantum efficiency (EQE) of the CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase system was measured by applying narrow band pass filters ( $\lambda = 360 \pm 10$  nm;  $I = 2.49$  mW cm<sup>-2</sup> and  $400 \pm 10$  nm;  $I = 4.34$  mW cm<sup>-2</sup>; see ESI† for experimental details). UV-irradiation gave an EQE of approximately 4.8% and under visible irradiation an EQE of 0.51% was obtained. These values are more than a 10-fold improvement over the UV and visible EQE for the CN<sub>x</sub>-H<sub>2</sub>ase system,<sup>9</sup> which can be attributed to the improved light absorption (Fig. S6†) and increased electron transfer rate due to adsorption of the H<sub>2</sub>ase onto the particle surface.

We previously showed that a significantly increased photo-activity was observed under standard conditions using CN<sub>x</sub>-H<sub>2</sub>ase upon addition of an excess of the redox mediator MV<sup>2+</sup>, producing up to 77  $\mu$ mol H<sub>2</sub> after 69 h of UV-visible irradiation.<sup>9</sup> A long-term experiment with H<sub>2</sub>ase (50 pmol), CN<sub>x</sub>-TiO<sub>2</sub> (5 mg) and added MV<sup>2+</sup> (5  $\mu$ mol) in aqueous EDTA (0.1 M) at pH 6 was performed with both  $\lambda > 300$  nm light and with visible light only ( $\lambda > 420$  nm). Under UV-visible irradiation after 72 h, the CN<sub>x</sub>-TiO<sub>2</sub>-MV-H<sub>2</sub>ase system produced 193  $\mu$ mol H<sub>2</sub> with a TON<sub>H<sub>2</sub>ase</sub> of  $> 3.8 \times 10^6$  and an initial TOF<sub>H<sub>2</sub>ase</sub> of 35 s<sup>-1</sup> (Fig. S7†). Under visible-light only, 66  $\mu$ mol H<sub>2</sub> was produced with a TON<sub>H<sub>2</sub>ase</sub> of  $1.3 \times 10^6$  and an initial TOF<sub>H<sub>2</sub>ase</sub> of 9 s<sup>-1</sup> (Fig. S8†). The ratio of the amount of hydrogen produced in the presence and absence of MV<sup>2+</sup> can be used to estimate the relative efficiency of the charge transfer from material to H<sub>2</sub>ase. Under full spectrum irradiation ( $\lambda > 300$  nm) with CN<sub>x</sub>-H<sub>2</sub>ase the ratio was found to be 22, whereas for both TiO<sub>2</sub>-H<sub>2</sub>ase and CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase systems the ratio was 5. This strongly supports the fact that there is a significant improvement in the charge transfer from a TiO<sub>2</sub>-based material to H<sub>2</sub>ase. In addition, this ratio remains constant when the wavelength of light used is restricted to the visible region ( $\lambda > 420$  nm).

The H<sub>2</sub> production rates in the presence of MV<sup>2+</sup> are significantly higher than those obtained in the absence of MV<sup>2+</sup>. The blue colour of the vials containing MV<sup>2+</sup> is indicative of the formation of reduced MV<sup>+</sup> in solution (Fig. S9†). By comparison, addition of MV<sup>2+</sup> to the previously reported Ru-dye-sensitised TiO<sub>2</sub>-H<sub>2</sub>ase system caused a slight decrease in activity, which was attributed to the decreased availability of electrons for the H<sub>2</sub>ase and the absorption of incident photons by MV<sup>+</sup>.<sup>3a</sup> Here, solubilised MV<sup>+</sup> does not limit light absorption by CN<sub>x</sub>-TiO<sub>2</sub> significantly and is able to efficiently donate electrons to surface-bound H<sub>2</sub>ase, resulting in increased H<sub>2</sub> production. This result implies that interfacial electron transfer from CN<sub>x</sub>-TiO<sub>2</sub> to H<sub>2</sub>ase is still not fully optimised in this system, where the orientation of the H<sub>2</sub>ase is not fully 'directed'. Ideally, the distance from the CN<sub>x</sub>-TiO<sub>2</sub> surface to the [Fe<sub>4</sub>S<sub>4</sub>] electron transport chain should be minimised and an improved orientation of the enzyme would allow trapping of CB<sub>TiO<sub>2</sub></sub> electrons more efficiently for maximised turnover.<sup>19</sup>

Favourable electron transfer kinetics at the CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase interface can be assumed based on previous reports. Electron transfer in the order of 10<sup>7</sup> s<sup>-1</sup> was reported from CdS nanorods to an [FeFe]-H<sub>2</sub>ase isolated from *Clostridium*

*acetobutylicum*.<sup>4c</sup> In addition, a long lived photo-excited state lifetime of  $\tau_{1/2} \sim 0.8$  s was previously reported for TiO<sub>2</sub> conduction band electrons in a photocatalytic system with Ru dye-sensitised TiO<sub>2</sub> and electron transfer to co-immobilised molecular cobaloxime catalysts occurred with  $\tau_{1/2} \sim 5$  to 50  $\mu$ s.<sup>20</sup> Based on these reports, we can assume that a reasonably long-lived TiO<sub>2</sub> conduction band electron is generated and that H<sub>2</sub>ase is capable of readily collecting these electrons.

## Conclusions

In summary, solar light driven H<sub>2</sub> production with a semi-biological system consisting of TiO<sub>2</sub> modified with polymeric CN<sub>x</sub> and immobilised H<sub>2</sub>ase has been demonstrated. We have shown that by improving the surface interaction of the enzyme with the light harvesting CN<sub>x</sub> material, specifically by adsorption of the enzyme onto the TiO<sub>2</sub> surface, H<sub>2</sub> generation is drastically improved. Another important factor is the improved visible light absorption by direct CN<sub>x</sub> excitation (pathway 2) and CN<sub>x</sub>-TiO<sub>2</sub> charge transfer (pathway 3), which enables high photoactivity. The CN<sub>x</sub>-TiO<sub>2</sub>-H<sub>2</sub>ase assembly achieved a TOF of 8 s<sup>-1</sup> and TON of  $> 5.8 \times 10^5$  after 72 h in the absence of an external soluble redox mediator, thereby setting a new benchmark for photochemical architectures based on abundant and non-toxic materials and a heterogenised H<sub>2</sub>ase. The additional use of the redox mediator MV<sup>2+</sup> allowed for the photo-generation of H<sub>2</sub> with a TOF of 35 s<sup>-1</sup> and a TON of  $> 3.8 \times 10^6$ . This work advances the use of hybrid photocatalytic schemes by integrating highly active electrocatalysts with advanced light absorbing materials such as CN<sub>x</sub>-TiO<sub>2</sub>, which is shown to be compatible with H<sub>2</sub>ases in aqueous solution.

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