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Efficient and Clean Photoreduction of CO_2 to CO by Enzyme-Modified TiO_2 Nanoparticles Using Visible Light

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There is wide interest in converting the greenhouse gas CO_2 into organic molecules by chemical routes,[1,2] and a highly desirable goal is to use solar energy to reduce CO_2 to CO, efficiently and cleanly. Carbon monoxide is the feedstock for various synthetic processes, such as the d-metal catalyzed Fischer−Tropsch (production of hydrocarbons), Monsanto, and Cativa (both acetic acid) processes. Carbon monoxide also has significant fuel value ($\Delta_c H° = -283.0$ kJ mol^{-1}) and can readily be converted into methanol (*e.g.*, by the $CuO/ZnO/Al_2O_3$-catalyzed ICI-process) for use as a liquid fuel.[3] Here, we present a prototype enzyme-based system for rapid CO_2 reduction to CO, driven by visible light.

The core design of a highly efficient CO_2 photoreducing system features a catalyst linked electronically to a light-capturing moiety. Since the first report of CO_2 photoreduction by a semiconductor particle suspension by Inoue *et al.*,[4] many efforts have focused on TiO_2. These systems use either high-energy irradiation (UV) for band gap excitation[5,6] or visible light following sensitization with a dye complex, for injecting electrons into the conduction band.[7,8] Direct reduction of CO_2 at the TiO_2 surface proceeds via a thermodynamically uphill one-electron transfer to form $CO_2^{\bullet-}$ ($E = -1.90$ V vs SHE in water, corrected to pH 7).[9] This high energy pathway typically leads to mixtures of products, including methane and methanol. A metallic cluster (often Cu or Pt) on the TiO_2 surface can serve as the reaction center by acting as a trap for excited electrons, thereby forming a reducing site on the particle to minimize electron−hole recombination.[10,11] We now report that TiO_2 nanoparticles (NPs) modified with a photosensitizer and the CO_2-reducing enzyme CODH I from the anaerobic microbe *Carboxydothermus hydrogenoformans* (*Ch*) provide an extraordinary catalyst for CO_2 photoreduction. The enzyme bypasses the one-electron radical pathway, instead catalyzing a controlled, *two-electron* reduction giving CO ($E = -0.46$ V vs SHE at pH 6) as a clean product. The system is represented schematically in Figure 1.

CODH I is one of five CODH complexes expressed by *Ch*, with an unusual [Ni4Fe-4S] active site that catalyzes the reversible oxidation of CO to CO_2.[12] Turnover frequencies of up to 40 000 s^{-1} have been reported for CO oxidation by *Ch* CODHs (pH 8, 70 °C),[13] and we recently harnessed some of this activity to catalyze the water-gas shift reaction by coupling CODH I to a hydrogenase on a conducting graphite microplatelet.[14] Importantly, CODH I is a highly active catalyst in both directions (oxidation *and* reduction), requiring little overpotential.[15]

All stages of preparation of our photocatalytic system were carried out at room temperature in an anaerobic glovebox. TiO_2 NPs (5 mg, Evonik Aeroxide P25; 21 nm diameter) were dispersed for 15 min by sonication in 2-(*N*-morpholino)ethanesulfonic acid (MES, 5 mL of 200 mM solution) buffer in a Pyrex pressure vessel (total volume = 9 mL). Then, *Ch* CODH I (20 μL of 117 μM solution) was adsorbed on the TiO_2 particles by gently stirring for 20 min, whereupon the enzyme-modified TiO_2 NPs were sensitized by adding a solution of 0.05 mg of $[Ru^{II}(bipy)_2(4,4'-(PO_3H_2)_2\text{-}bipy)]Br_2$ (RuP; bipy = 2,2′-bipyridine) in MES buffer (0.1 mL) to the dispersion and stirring for a further 20 min for adsorption of the dye. The vessel was then sealed tightly with a rubber septum, and the headspace purged with 2% CH_4 in CO_2. The stirred dispersion was subsequently irradiated with visible light (tungsten-halogen lamp fitted with a 420 nm UV-light filter; light intensity 45 mW cm^{-2}). The temperature of the suspension was controlled by immersion of the reaction vessel in a water bath. The headspace gas composition was regularly monitored by GC analysis, with the amount of produced CO quantified against the internal CH_4 standard.

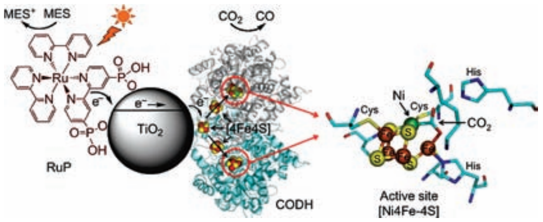

Figure 1. Cartoon representation of the CO_2 photoreduction system using *Ch* CODH I attached to RuP-modified TiO_2 NPs. A catalytic intermediate of the active site of the closely related enzyme CODH II with bound substrate (CO_2, indicated with an arrow)[16] is also shown. The oxidized photosensitizer is recovered by the sacrificial electron donor MES. The enzyme structure used in the cartoon is CODH II, created using PyMOL.

Figure 2 shows CO production at RuP-sensitized TiO_2 NPs functionalized with *Ch* CODH I. Panel A shows several different experiments overlaid in which the suspension (pH 6, 20 °C) was irradiated with visible light ($\lambda > 420$ nm) over a period of 4 h. Control experiments in which photosensitizer, NPs, enzyme, or light were excluded yielded negligible amounts of CO. Possible gaseous byproducts, *e.g.* methane (in the absence of CH_4 as internal standard), were not detected upon photoreduction of CO_2 in the fully assembled RuP−TiO_2−CODH system, indicating clean CO_2 to CO conversion. Panel A also shows photoreduction of CO_2 using UV band gap irradiation (UVL-28 EL Series UV lamp, 365 nm, 2 mW cm^{-2}) with CODH I attached to TiO_2 in the absence of RuP. The CO formation confirms the essential role of the TiO_2 NP as an electron relay between RuP and CODH I, rather than simply acting as a common support to bring the photosensitizer and enzyme into close proximity for direct electron transfer. In all cases rates

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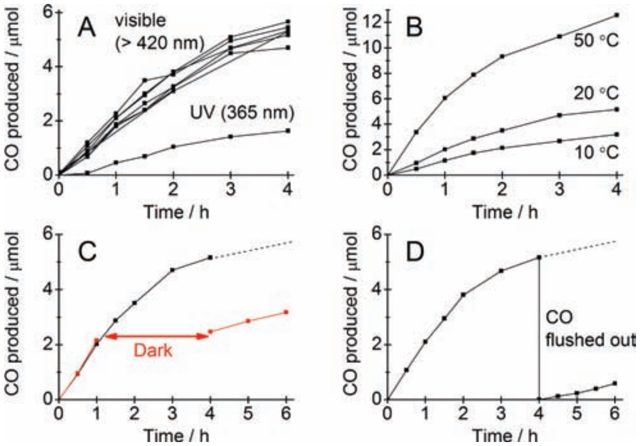

Figure 2. (A) Photoreduction of CO_2; top: at dye-sensitized, CODH I-modified TiO_2 NPs using visible light (20 °C, pH 6.0, $\lambda > 420$ nm); bottom: at nonsensitized, CODH I-modified NPs using band gap UV irradiation (20 °C, pH 6.0, $\lambda = 365$ nm). (B) Effect of temperature on the photoreduction rate of the dye-sensitized system (20 °C, pH 6.0, $\lambda > 420$ nm). (C) Black trace: photoreduction of CO_2 at dye-sensitized, CODH I-modified NPs with continuous visible light irradiation (20 °C, pH 6.0, $\lambda > 420$ nm); red trace: experiment in which visible light irradiation was interrupted for 3 h after 1 h of irradiation (same conditions as black trace). (D) Experiment in which CO was flushed out after 4 h of visible light irradiation (20 °C, pH 6.0, $\lambda > 420$ nm) and the CO_2 level was restored to the initial level (98%).

decrease with time (see below). Rates of catalysis scale with the amount of enzyme in the system (Supporting Information, SI), strongly indicating that the enzyme activity is limiting: this is supported by the results in Panel B which show how the CO production rate varies with temperature, again consistent with enzyme-controlled activation.

At pH 6 and 20 °C the visible light sensitized system produces ~5 μmol CO during 4 h of irradiation (Figure 2A). Evaluating this on a *per gram of TiO_2* basis gives an average turnover rate of 250 μmol of CO (g of TiO_2)$^{-1}$ h^{-1}, clean and superior to other sensitized TiO_2 systems, which usually produce a range of products.[17,18] On a *per mole of CODH I* basis, the turnover rate is ~530 h^{-1} (0.15 s^{-1}). An experiment using natural sunlight in which the temperature varied from 17 to 22 °C (Oxford sky, October, SI) performed photoreduction at a rate of ~0.09 s^{-1}, *i.e.* 60% of the rate we observe using the artificial visible light source.

The rates and stability (loss of activity with time) are low compared to a recently reported analogous H_2 production system (50 s^{-1}) using a *titaniaphilic* hydrogenase under comparable conditions (pH 7, 25 °C),[19] but several factors are likely to be influential, each of which are under further investigation. One factor is the smaller driving force (~0.1 V lower) for CO_2 reduction compared to H^+ reduction: at pH 6, the conduction band edge of TiO_2 is at ~ −0.52 V vs SHE,[20] which is only just sufficient for CO_2 reduction at CODH I. Another factor may be that CODH I molecules are only bound weakly to the TiO_2 or lie in electroinactive orientations: success depends upon efficient electron transfer from TiO_2 into the relay of iron−sulfur clusters leading to the active site (Figure 1) which will require a more specific linking mode. Weak binding is supported by the observation that centrifugation of the particles, followed by exchange of the buffer for fresh solution and resuspension, leads to a marked decrease in activity (SI). When the suspension was kept in darkness for 3 h after irradiating for 1 h, resumption of irradiation gave a rate approximately the same as that after 4 h of light exposure (Figure 2C), ruling out any significant photoinstability effect (*i.e.*, photodegradation of RuP or CODH I). Experiments were also carried out (Figure 2D) in which, after visible light irradiation for 4 h, the system was flushed with CO_2 to remove all CO and restore the CO_2 level to the initial concentration. After restarting, CO production continued at the same rate as measured after 4 h. In addition, the results were essentially unchanged when initial levels of 10, 20, and 30% CO were used (SI). Thus, neither substrate depletion nor product inhibition is responsible for the decrease in activity. The activity and stability of the system are not significantly affected by pH in the range 5.5−6.5 (SI) or by varying buffer concentration (50−200 mM). The lower rate of the UV system compared to the visible system is under investigation: explanations include inactivation of CODH by valence band holes and the lower power output of our UV source (2 mW cm^{-2} vs 45 mW cm^{-2} for the visible system).

In summary, we have demonstrated a heterogeneous catalyst for efficient and clean reduction of CO_2 to CO driven by visible light. The sensitized hybrid enzyme−nanoparticle system (even before important refinements are made) serves as a benchmark for what must be achievable using synthetic catalysts. The results provide a strong case for CO_2 activation catalysts to focus on a two-electron pathway to avoid the thermodynamically uphill step involved in one-electron activations.

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Supporting Information Available: Effect of lower enzyme concentration (Figure S1), CO_2 photoreduction using natural sunlight (Figure S2), effect of centrifuging particles and exchanging buffer solution (Figure S3), effect of pH (Figure S4), UV−visible study of CODH I adsorption onto TiO_2 NPs (Figure S5), effect of initial CO concentration (Figure S6), approximate calculation for CODH I loading on TiO_2 NPs, full ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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