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Efficient and clean photo-reduction of CO₂ to CO by enzyme-modified TiO₂ nanoparticles using visible light

Thomas W. Woolerton^a, Sally Sheard^a, Erwin Reisner^{a,#}, Elizabeth Pierce^b, Stephen W. Ragsdale^b, and Fraser A. Armstrong^a

Fraser A. Armstrong: fraser.armstrong@chem.ox.ac.uk

^aDepartment of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

^bDepartment of Biological Chemistry, University of Michigan, Ann Arbor, MI 48109-0606, U.S.A.

Abstract

A hybrid enzyme-nanoparticle system is described for achieving clean reduction of CO₂ to CO using visible light as the energy source. An aqueous dispersion of TiO₂ nanoparticles modified by attachment of carbon monoxide dehydrogenase (CODH) and a Ru photosensitizer produces CO at a rate of 250 μmol CO (g TiO₂)⁻¹ h⁻¹ when illuminated with visible light at pH 6 and 20 °C.

There is wide interest in converting the greenhouse gas CO₂ into organic molecules by chemical routes^{1,2} and a highly desirable goal is to use solar energy to reduce CO₂ 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 ($\Delta_c H^\circ = -283.0$ kJ mol⁻¹), and can readily be converted into methanol (*e.g.*, by the CuO/ZnO/Al₂O₃-catalyzed

Correspondence to: Fraser A. Armstrong, fraser.armstrong@chem.ox.ac.uk.

[#]Current address: School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, U.K.

Supporting Information **Available:** Effect of lower enzyme concentration (Fig. S1), CO₂ photo-reduction using natural sunlight (Fig. S2), effect of centrifuging particles and exchanging buffer solution (Fig. S3), effect of pH (Fig. S4), UV-visible study of CODH I adsorption onto TiO₂ nanoparticles (Fig. S5), effect of initial CO concentration (Fig. S6), approximate calculation for CODH I loading on TiO₂ nanoparticles, full list of authors for ref. 12. This material is available free of charge via the Internet at <http://pubs.acs.org>.

ICI-process) for use as a liquid fuel.³ Here, we present a prototype enzyme-based system for rapid CO₂ reduction to CO, driven by visible light.

The core design of a highly efficient CO₂ photo-reducing system features a catalyst linked electronically to a light-capturing moiety. Since the first report of CO₂ photo-reduction by a semiconductor particle suspension by Inoue *et al.*,⁴ many efforts have focussed on TiO₂. 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 CO₂ at the TiO₂ surface proceeds via a thermodynamically uphill one-electron transfer to form CO₂^{•-} ($E = -1.90$ 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 TiO₂ 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 TiO₂ nanoparticles modified with a photosensitizer and the CO₂-reducing enzyme CODH I from the anaerobic microbe *Carboxydotherrmus hydrogenoformans* (*Ch*) provide an extraordinary catalyst for CO₂ photo-reduction. 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 CO₂.¹² 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 micro-platelet.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. TiO₂ nanoparticles (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 TiO₂ particles by gently stirring for 20 min, whereupon the enzyme-modified TiO₂ nanoparticles were sensitized by adding a solution of 0.05 mg of [Ru^{II}(bipy)₂(4,4'-(PO₃H₂)₂-bipy)]Br₂ (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% CH₄ in CO₂. 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 CH₄ standard.

Figure 2 shows CO production at RuP-sensitized TiO₂ nanoparticles 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, nanoparticles, enzyme or light were excluded yielded negligible amounts of CO. Possible by-products, *e.g.* methane (in the absence of CH₄ as internal standard), were not detected upon photo-reduction of CO₂ in the fully assembled RuP-TiO₂-CODH system, indicating clean CO₂ to CO conversion. Panel A also shows photo-reduction of CO₂ using UV band gap irradiation (UVL-28 EL Series UV lamp, 365 nm, 2 mW cm⁻²) with CODH I attached to TiO₂ in the absence of RuP. The CO formation confirms the essential role of the TiO₂ nanoparticle 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 decrease with time (see below). Rates of catalysis scale with the amount of enzyme in the system (Supporting Information), 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 approximately 5 $\mu\text{mol CO}$ during 4 h irradiation (Figure 2A). Evaluating this on a *per-gram TiO₂* basis gives an average turnover rate of 250 $\mu\text{mol CO (g TiO}_2\text{)}^{-1} \text{ h}^{-1}$ – clean, and superior to other sensitized TiO₂ systems, which usually produce a range of products.^{17,18} On a *per-mole CODH I* basis, the turnover rate is approximately 530 h^{-1} (0.15 s^{-1}). An experiment using natural sunlight in which the temperature varied from 17 °C to 22 °C (Oxford sky, October, Supporting Information) performed photo-reduction at a rate of approximately 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 H₂ 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 (about 0.1 V lower) for CO₂ reduction compared to H⁺ reduction: at pH 6, the conduction band edge of TiO₂ is at approximately -0.52 V *vs SHE*,²⁰ which is only just sufficient for CO₂ reduction at CODH I. Another factor may be that CODH I molecules are only bound weakly to the TiO₂, or lie in electro-inactive orientations: success depends upon efficient electron transfer from TiO₂ 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 re-suspension leads to a marked decrease in activity (Supporting Information). 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 after 4 h light exposure (Figure 2C), ruling out any significant photoinstability effect (*i.e.* photo-degradation 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 CO₂ to remove all CO and restore the CO₂ level to the initial concentration. After re-starting, 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 (Supporting Information). 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 (Supporting Information) 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 CO₂ 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 CO₂ activation catalysts to focus on a two-electron pathway in order to avoid the thermodynamically uphill step involved in one-electron activations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Cartoon representation of the CO₂ photo-reduction system using *Ch* CODH I attached to RuP-modified TiO₂ nanoparticles. A catalytic intermediate of the active site of the closely related enzyme CODH II with bound substrate (CO₂, 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.

A. Photo-reduction of CO₂; top: at dye-sensitized, CODH I-modified TiO₂ nanoparticles using visible light (20 °C, pH 6.0, $\lambda > 420$ nm); bottom: at non-sensitized, CODH I-modified nanoparticles using band gap UV irradiation (20 °C, pH 6.0, $\lambda = 365$ nm). **B.** Effect of temperature on the photo-reduction rate of the dye-sensitized system (20 °C, pH 6, $\lambda > 420$ nm). **C.** Black trace: photo-reduction of CO₂ at dye-sensitized, CODH I-modified nanoparticles 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 CO₂ level was restored to the initial level (98%).