Efficient Electrocatalytic CO₂ Fixation by Nanoconfined Enzymes via a C3-to-C4 Reaction That Is Favored over H₂ Production

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Supporting Information

ABSTRACT: Reduction of CO₂ and its direct entry into organic chemistry is achieved efficiently and in a highly visible way using a metal oxide electrode in which two enzyme catalysts, one for electrochemically regenerating reduced nicotinamide adenine dinucleotide phosphate and the other for assimilating CO₂ and converting pyruvate (C3) to malate (C4), are entrapped within its nanopores. The resulting reversible electrocatalysis is exploited to construct a solar CO₂ reduction/water-splitting device producing O₂ and C₄ with high faradaic efficiency.

KEYWORDS: artificial photosynthesis, CO₂ reduction, cofactor recycling, nanoconfinemen, biocatalysis

Nanoconfinement and compartmentalization are essential characteristics of living cells. A key feature ensuring that multistep catalytic processes are fast and efficient is that enzymes along a cascade are highly concentrated at a local level, and diffusion distances of intermediates are very short. For instance, in biological photosynthesis — in plants and algae — the reactions of the Calvin cycle along with NADP⁺ reduction and adenosine 5'-triphosphate generation occur in the chloroplast stroma over distances < 100 nm. The inspiration obtained by biological nanoconfinement thus suggests unique advantages to help drive the development of artificial photosynthesis. Recently, we reported that the ubiquitous photosynthetic enzyme ferredoxin NADP⁺ reductase (FNR) trapped within the nanopores of a porous indium tin oxide (ITO) layer deposited on a conducting support is highly active and stable for NAD(H) recycling and coupling to a second enzyme (E2) that is also nanoconfined (Figure 1). Crucially, regeneration of NAD(P)H is a subject of intense research, as hundreds of oxidoreductases catalyzing important reactions require stoichiometric amounts of NAD(P)H as a mobile redox cofactor. Recycling continuously is essential to make any biocatalytic process economically feasible. Cofactor recycling has been extensively reviewed. Several protocols most relevant to this paper are also mentioned later.

The electrode system we are developing is denoted (FNR + E2)@ITO/support. When trapped alone at ITO, FNR displays diagnostic reversible electrochemistry of its flavin adenine dinucleotide active site and of NADP⁺ when the latter is introduced. The highly efficient nanoconfined electrochemical recycling of NADP⁺/reduced nicotinamide adenine dinucleotide phosphate (NADPH) both drives catalysis and allows continuous monitoring of the overall catalytic rate as the electrical current.

Electrochemical CO₂ reduction exploiting the efficiency of enzymes as reversible electrocatalysts has long focused on C1 transformations using CO dehydrogenase or formate dehydrogenase. By introducing, as E2, the enzyme L-malate:NADP⁺ oxidoreductase (oxaloacetate-decarboxylating), EC 1.1.1.40 (MaeB from Escherichia coli: hereafter abbreviated as ME), the electrode offers an instructive way to drive CO₂ reduction with a very low overpotential, by incorporating it into pyruvate (C3) to form malate (C4) (Figure 1). The small ΔG (∼7 kJ mol⁻¹) at 25 °C, pH 7.5) for decarboxylation of malate by NADP⁺ allows the reaction to be run in reverse, so it presents an ideal system by which to achieve specific CO₂ reduction, provided a continuous supply of NADPH cofactor is available. Use of ME to incorporate CO₂ into pyruvate was first reported over 30 years ago and featured photoelectrochemical cofactor regeneration by FNR using methyl viologen as a low-potential electron mediator. Here, we show how nanoconfinement is exploited to perform C3-to-C4 CO₂ incorporation with ease, electrochemical clarity, and high efficiency with regard to overpotential and competition with H₂ evolution.

The stationary cyclic voltammograms (CVs) shown in Figure 2 demonstrate the reversibility of the electrocatalytic incorporation of CO₂ into pyruvate and the inhibitory effect of malate. A (FNR + ME)@ITO/Ti electrode (1 cm²) was prepared by placing a ITO/Ti foil electrode, preloaded with FNR (see Supporting Information for details) into a CO₂-saturated solution of pyruvate (50 mM) then adding ME to give a total concentration of 2.5 μM ME. The solution was

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buffered at pH 7.5 (25 °C) using 0.20 M N-(2-hydroxyethyl)-piperazine-N’-ethanesulfonic acid (HEPES) and 0.10 M KHCO₃ (see Supporting Information for details), and contained 4 mM MgCl₂ (required for activity of ME) and 20 μM NADP⁺. The voltammogram labeled as “pyruvate + CO₂” (black trace) was recorded after 6 cycles at 1 mV s⁻¹ (approx. 100 min after introducing ME): it reveals a large reductive current (reaching a limit at approximately −0.4 V) due to the incorporation of CO₂ into pyruvate. At a much more negative potential (below −0.55 V), the current increases again, because of H⁺ reduction. After adding malate (final concentration 50 mM) and stirring briefly, a new voltammogram (blue trace) is obtained, in which the reduction current is suppressed and a sizeable oxidation current has appeared. Under the conditions of equal concentrations of C₃ and C₄, the trace cuts through the zero-current axis at the formal potential for the C₃–C₄ interconversion (taking an average for scans in both directions): the markers that signify the potentials of relevance for this work include this value. Notably, CO₂ reduction commences at a significantly more positive electrode potential than the thermodynamic value for H₂ evolution: the C₃-to-C₄ potential is approximately +0.1 V versus the reversible 2H⁺/H₂ potential (RHE). High Faradaic efficiency for aqueous CO₂ reduction is therefore predicted. No catalysis is observed when NADP⁺ or ME are not included (see Supporting Information, Figure S1) and the electrode remains stable for several days without any significant loss.

Figure 3A shows a timecourse (chronoamperogram) for electrochemical CO₂ fixation [−0.45 V vs standard hydrogen electrode (SHE) at 25 °C, pH 7.5, stirring] with a constant flow of CO₂ through the cell headspace. A larger ITO/Ti electrode (16 cm²) preloaded with FNR was used for this experiment to increase the amount of the product formed in the reaction—the solution now containing 20 mM pyruvate, 50 mM phosphate as buffer (to clarify product analysis by 1H NMR), 0.10 M KHCO₃, and 4 mM MgCl₂. After injecting NADP⁺ (to 20 μM) which results immediately in a small catalytic current, introduction of ME (final concentration 2.5 μM) initiates the growth of a large catalytic current, which reaches a maximum after 2 h before slowly decreasing over the course of 24 h. The current increase, commencing from zero, corresponds to the rate at which ME enters the electrode nanopores to couple with the NADP(H) recycling as it occurs at FNR molecules. (At this stage, we do not know the optimum FNR/ME ratio that will be active at a local level, and further experiments must be devised to answer this question.) After 14 h, the quantity of malate formed (17.6 mM = 88% conversion) was confirmed by 1H NMR (Figure S2), the resulting total turnover number (TTN, moles malate formed/moles NADP⁺ present) being 880. The current decreases slowly over the course of time, which could be related to various factors, such as instability of the FNR/ME catalytic zones and/or product inhibition. To identify the origins of current decrease, we performed a series of interventions. In panel A, the reaction was recharged with pyruvate after 15 h, the injection of which (to give a further 20 mM) increased the current. Notably, the concentration of the unconverted substrate after 14 h of reaction had dropped well below Kₘ (6.21 mM for pyruvate). To investigate the effect of product inhibition a solution exchange was performed after 18.3 h. The injection of which (to give a further 20 mM) increased the result is shown in an enlarged form in panel B. Briefly, the cell compartment was washed 10 times with purified H₂O₂, then fresh buffer solution (without NADP⁺) was introduced: consequently, the new solution did not contain any enzyme and any product that had accumulated was removed. Re-injection of NADP⁺ (to 20 μM) caused an increase in current, 100 μA higher than the current (rate) before buffer exchange. This result demonstrated that product inhibition is an important contributor to the current decrease with time.

An electrode was also prepared by placing it in a stirred solution of FNR (15.7 μM) and ME (7 μM) in borate-buffered solution. Figure 2 shows the result of the chronoamperometry (−0.45 V vs SHE, stirring, 25 °C) with the resulting electrode. NADP⁺ was added to a final concentration of 20 μM and a sizeable reduction current (current density: 20 μA/cm²) was obtained. The amount of FNR adsorbed in this experiment, obtained by peak integration, was 9.9 pmol/cm²: this quantity allowed us to determine an absolute rate on a per-FNR basis of

(pH 8) for 2 h, then thoroughly rinsing with ultrapure H₂O (Milli-Q Millipore) to remove unbound proteins. The (FNR + ME)@ITO/Ti stationary electrode (area 1 cm²) in CO₂-saturated buffer (0.2 M HEPES, 0.1 M KHCO₃, 4 mM MgCl₂, 20 μM NADP⁺, pH 7.5 at 25 °C, under 100% CO₂), with 50 mM pyruvate (black), and after addition of 50 mM malate (blue). Scan rate = 1 mV s⁻¹.
approximately 7 s⁻¹, which is instructive, although we lack information on what local FNR/ME ratio is optimal. The result obtained using a much lower cofactor concentration is shown in panel D. Chronoamperometry (−0.45 V vs SHE, stirring, 25 °C) of a (FNR + ME)@ITO/Ti electrode (16 cm²) prepared as for panel A was carried out in 50 mM phosphate, 0.10 M KHCO₃, 4 mM MgCl₂, and 20 mM pyruvate (pH 7.5, volume 4 mL). In this experiment, NADP⁺ was injected to a final concentration of 1 μM. The current trace differs from panel A in that it only starts to decrease after 7 h, and more than 60% of the maximum current is retained after 24 h when, based on coulometry, a conversion of 31% (6210 TTN) has been achieved. The lower conversion/current decrease is again consistent with lower product inhibition. The fact that a reasonable rate is still achieved with such a low NADP⁺ concentration highlights the practical possibilities for a (FNR + E2)@ITO/Ti electrode technology in cofactor recycling for organic synthesis.8

Investigations were made to gauge the affinity of the two-enzyme system for CO₂, noting that natural photosynthesis occurs in air containing approximately 0.04% CO₂. Results are shown in Figure 4. Panel A shows a chronoamperometry
experiment (stirred), conducted at −0.45 V versus SHE, 25 °C, pH 7.5, in which a FNR@ITO/Ti electrode (62.3 pmol/cm²) was placed in a cell containing 0.20 M HEPES, 4 mM MgCl₂, 80 mM pyruvate. Initially, 100% argon was bubbled into the solution. After introducing NADP⁺ (final concentration 20 μM), ME was added to a final concentration of 2.5 μM. After about 80 min, small aliquots of a saturated CO₂ stock solution were injected to increase the CO₂ concentration in stages, from 0.4 to 100%. Each addition resulted in a sharp increase in reduction current which decreased to a new steady level. The area under the initial current burst was similar in all cases and attributable to the reduction of trace O₂ in the stock solution. An experiment was also carried out using cyclic voltammetry, allowing time for removal of O₂, and similar results were obtained. A titration curve was prepared by plotting the normalized current increase against % CO₂ (Figure 4B). The results showed that 50% of the maximum catalytic rate was attained with 4.0 ± 0.5% CO₂ (see Supporting Information and Figure S3).

The low overpotential needed to drive CO₂ reduction suggested the feasibility of constructing a device mimicking the essential features of photosynthesis by using H₂O as the...
electron donor. We chose Mo-doped BiVO₄ as a photoanode because of its high light absorption, high photocurrent, and straightforward synthesis. A fluorine-tin oxide electrode (1 cm²) was coated with Mo-doped BiVO₄ (Mo 2%) and a layer of O₂ evolution catalyst, FeOOH (goethite), was added by photo-electrodeposition (ESI). Although the band gap of BiVO₄ (2.4 eV) is suited for visible light excitation, the conduction band potential is too positive to reduce NADP⁺. This situation is clarified in Figure 5 which compares two voltammograms—the reductive carboxylation of pyruvate to malate by the (FNR + ME)@ITO/Ti electrode (blue trace, using Pt as the counter) and water oxidation by the 2%Mo:BiVO₄/FeOOH photoanode (using Pt as the counter) in the dark (black trace) and during illumination (red trace). It is clear that an additional bias of at least 0.4 V is required in order to drive the C3-C4 reaction. The situation resembles that of oxygenic photosynthesis in which two photosystems are required. Here, the problem was solved by adding a 1 V Si-solar cell (Figure S4A), the output voltage of which could be attenuated. Panel B of Figure 5 shows the result obtained when water photo-oxidation is driven by the photoanode coupled to the 1 V silicon solar cell (purple trace). Given the low overpotential requirement expected, the voltage was cut to 0.5 V by including an additional resistance (Figures S4B and 5B blue trace). In both cases, the (FNR + ME)@ITO/Ti electrode could be driven using visible light and water as a...
electrode (see Supporting Information and Figure S5). The result obtained with a FNR@ITO/Ti cathode was due to H2 evolution. After the illumination a background current was observed, which was expected, no current was detected in the dark, whereas upon auxiliary solar cell with the output capped at 0.5 V. As systems (Table 1). The Faradaic efficiency (charge used to produce malate/total charge passed) was approximately 70% after 24 h. In another experiment (see Supporting Information, Figures S6 and 6B) were 0 mM (0 h), 3.4 mM (8 h), and 14.8 mM (24 h) thus resulting in 18.5% conversion and a TTN of approximately 300. The latter value is 1–2 orders of magnitude higher than other light-driven cofactor regeneration systems (Table 1). The Faradaic efficiency (charge used to produce malate/total charge passed) was approximately 70% after 24 h. In another experiment (see Supporting Information, Figure S7), the full 1 V of the solar cell was used: this resulted in 34% conversion and a TTN of 544. Tests carried out in different experiments showed that the decrease in photocurrent was due at least in part to the accumulation of H2 evolution. Addition of NADP+ (to 50 μM) produced a small increase in current (accompanied by an O2 spike); ME was then added (to give 2.5 μM) and a large increase in current was observed for several minutes. Three interventions were made over a 6 h period, each signified with a blue square. In the first of these interventions (3 h after commencing the experiment), the light was switched off, the cathode compartment was washed with H2O, fresh buffer was added (without pyruvate, NADP+, ME), and a bias of 0.8 V was applied. Restoring illumination revealed a much larger background current, as expected because H2 can now be produced at a high rate. Re-addition of NADP+ and pyruvate (N’ and P) to achieve the same concentrations as before resulted in an increase in photocurrent. The procedure was repeated with applied biases of 1 and 0.4 V: for each condition, the faradaic efficiency was calculated from the total photocurrent and that observed without NADP+ and pyruvate. Values were: 75 ± 8% at 0.5 V, 50 ± 6% at 0.8 V, 33 ± 10% at 1 V. No significant current increase was observed when 0.4 V was applied.

In conclusion, direct, reductive CO2 incorporation into organic molecules becomes highly efficient when two cooperating catalysts, one recycling transferable “hydride” using electrons and the other using the hydride to perform carboxylation, are confined within the nanopores of an electrode. While the system uses enzymes and has little or no practical use, enzymes provide the ultimate benchmarks for rates, efficiencies, and selectivities, and their inspirational values cannot be ignored. Cyclic voltammetry demonstrates that the two enzymes function in unison as a reversible electrocatalyst for the C3-to-C4 interconversion and the reaction is easily detectable at low (<1%) CO2 levels. The thermodynamics are favorable with respect to H2 evolution and a biomimetic artificial photosynthesis device based on the (FNR + ME)@ITO/Ti electrode evolves O2 and reduces CO2 with 70% Faradaic efficiency at minimal (0.5 V) bias.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b03532.

Material and methods, control CV of a FNR@ITO/Ti electrode with no ME, spectra (1H-NMR) for CO2 reduction, CV of (FNR+ME)@ITO/Ti at different CO2 percentages (0.4% to 100%), current/voltage (i/V) curve of the 1 V silicon solar cell and chronopotentiometry of the solar cell, continuous detection of photogenic O2, 1H-NMR spectra obtained for light-driven CO2 reduction, light-driven pyruvate reductive carboxylation to malate, and addition of malic enzyme and ferredoxin NADP+-reductase after 20 hours of light-driven reductive carboxylation of pyruvate to malate (PDF).

#### Table 1. Comparison of Light-Driven NADH/NADPH Regeneration Systems

| Substrate | Product | [NADP(H)]/[mM] | Absorber | Mediator | TTN | References |
|-----------|---------|----------------|----------|----------|-----|------------|
| pyruvate  | malate  | 0.18           | Ru(bpy)32+ | MV2+     | 64  | 14         |
| 2-oxoglutarate | l-glutamate | 2          | BiVO4,FeOOH/perovskite | [Cp*Rh(bpy)H2O]2+ | 20.3 | 31         |
| isobutyraldehyde | isobutanol | 0.25        | CdS      | no mediator | 3.6  | 33         |
| pyruvate  | malate  | 0.05           | 2%Mo:BiVO4/FeOOH-solar cell | no mediator | 300  | this work |

*The TTN is defined as moles of product formed/moles of cofactor added at the beginning of the experiment.*
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