SUPPORTING INFORMATION

Selective visible light-driven CO_2 reduction on a *p*-type dye-sensitized NiO photocathode

Andreas Bachmeier,[†] Samuel Hall,[†] Stephen W. Ragsdale,[‡] and Fraser A. Armstrong[*,†]

[†]Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR, Oxfordshire, United Kingdom
[‡]Department of Biological Chemistry, University of Michigan, Ann Arbor, Michigan 48109-0606, United States

*To whom correspondence should be addressed: fraser.armstrong@chem.ox.ac.uk

Content

General Considerations

All chemicals were of the highest available quality and used as received without any further purification. All protein film electrochemistry experiments (PFE, see below for detailed experimental procedures) were carried out in 0.2 M MES buffer (pH 6 at 20 °C), which was prepared by dissolving 2-(*N*-morpholino)ethanesulfonic acid (MES, Melford) in purified H_2O (Milli-Q, 18 MΩ cm). The pH was adjusted using to the correct value using NaOH (Sigma-Aldrich). Samples of CODH I *Carboxydothermus hydrogenoformans* were prepared as described previously.[1] The activity of for CO oxidation was 1300 μmol min^{-1} mg^{-1} at 20 °C.

All manipulations involving CODH were performed in an anaerobic glove box (Belle Technologies, O_2 < 3 ppm) under a nitrogen gas atmosphere.

Synthesis of NiO particles

Nanocrystalline NiO particles were synthesized according to a previously published procedure.[2] Solutions of 4 mM oxalic acid (Sigma-Aldrich, 99+ %), 20 mM hexamethylenetetramine (Sigma-Aldrich, ACS reagent, ≥99%) and 20 mM $Ni(NO_3)_2$ (BDH Laboratory Supplies) were mixed and refluxed at 100 °C for 5 hours. The resulting green precipitate was then filtered and washed with ethanol and water before being dried under vacuum overnight and heated to 400°C for 2 hours. The powder XRD pattern is depicted in Figure S1.

Fabrication of electrodes from NiO particles

ITO slides (SPI Supplies, USA) of approximate dimensions 1 x 2 cm were cleaned by sonication for 15 min in deionised ethanol, followed by acetone, and finally in deionized H_2O. The cleaned slides were activated in a solution containing 1.9 mg $KMnO_4$ (Sigma-Aldrich ACS reagent, ≥99%) 30 μL butanol (Alfa Aesar, 99%) and 20 mL water for 30 min at 93 °C. These activated substrates were washed thoroughly with H_2O and dried. NiO powder (2.0 g) was suspended in a mixture of 10 μL acetylacetone (Sigma-Aldrich, ReagentPlus, ≥99%), 25 μL Triton X100 surfactant (Fisher Scientific), and 12 mL H_2O. The suspension was sonicated for 30 min and then centrifuged for 20 s at 4000 RPM to create an aggregate-free NiO suspension. This suspension was applied to the activated ITO sheets by the doctor's blade technique, with the electrode film thickness being controlled by a layer of Scotch tape. The resulting films were then calcined at 550 °C for 10 min (SEM image shown in Figure S2). The synthesized NiO films were converted into electrodes by making ohmic contact with copper wire using silver paint (Agar Scientific G3691) at an uncoated area of the transparent conducting oxide. The contact edges of the films were then covered by epoxy (Loctite Hysol 9462), leaving only NiO exposed. Typical geometric surface areas were 0.1 – 0.4 cm^2.

Synthesis of P1 and sensitization of NiO electrodes

P1 (4-[Bis(4-{5-[2,2-dicyanovinyl]-thiophene-2-yl}phenyl)amino]benzoic acid) was synthesized as previously described by Qin et al.[3] and characterized accordingly. ^1H NMR and ^{13}C NMR spectra of **P1** are shown in Figures S3 and S4, respectively. NiO electrodes were sensitized with P1 by soaking the electrodes in a 300 μM solution of P1 in ethanol overnight.

Attachment of CODH to electrode surfaces

To study the (photo-)electrochemistry of CODH on PGE, aliquots of enzyme (< 100 pmol) were drop cast onto the electrode and left for a few minutes until partially dry. PGE electrodes of geometric surface area 0.03 cm^2 were constructed in house as described previously,[4] and abraded using P400 Tufbak Durite sandpaper and sonicated to remove carbon debris before attachment of enzyme. In the case of NiO and NiO-P1 electrodes, in a typical experiment, 4 μL of 0.12 mM enzyme was applied to a NiO electrode with area 0.4 cm^2. The total coverage is therefore 1.2 $nmol/cm^2$.

Electrochemistry experiments

The electrodes prepared according to the above mentioned protocols were used as working electrodes in a single-compartment electrochemical cell, with a Pt (wire) counter electrode and a 3.5 M KCL Ag/AgCl reference electrode. All potentials are quoted vs the standard hydrogen electrode (SHE) using the conversion $E_{\mathrm{SHE}} = E_{\mathrm{Ag/AgCl}} + 205$ mV at 25 °C. The electrolyte was 0.2 M MES at pH 6.0, and all solutions were prepared using purified water (Milli-Q, 18 MΩ cm). Electrochemical measurements were made with an Autolab potentiostat (PGSTAT30) controlled by Nova software (EcoChemie). A Kodak light source (Kodak Carousel S-AV 1010 projector) fitted with a 250 W tungsten-halogen bulb and a 420 nm long-pass filter (UQG Optics) was used in the photoelectrochemistry experiments. At the position of the electrochemical cell, the light intensity was 45 mW cm^{-2}, measured using a Melles Griot Broadband Power/Energy Meter (13PEM001). An optical chopper, built in house, was used to measure transient photocurrents. Precise gas mixtures (BOC gases) were created using mass flow controllers (Sierra Instruments), and the electrochemical cell was constantly purged with the gas mixture throughout the experiments.

Inhibition experiments to establish the activity of CODH for CO_2 and CO reduction using the selective inhibitors KOCN (Sigma-Aldrich) and KCN (Fisher-Scientific) were conducted as follows: 1.0 mL of a stock solution of the respective inhibitor (dissolved in 0.2 M MES buffer, pH 6, and pre-saturated with the gas-mixture present in the electrochemical cell) was injected into the electrochemical cell containing 9.0 mL buffer.

Supplementary Figures

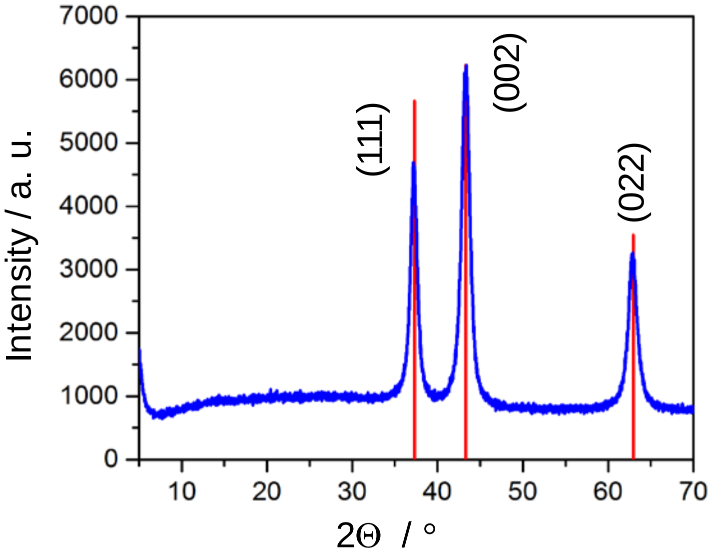

Figure S1. X-ray diffraction pattern of synthesized NiO powder.

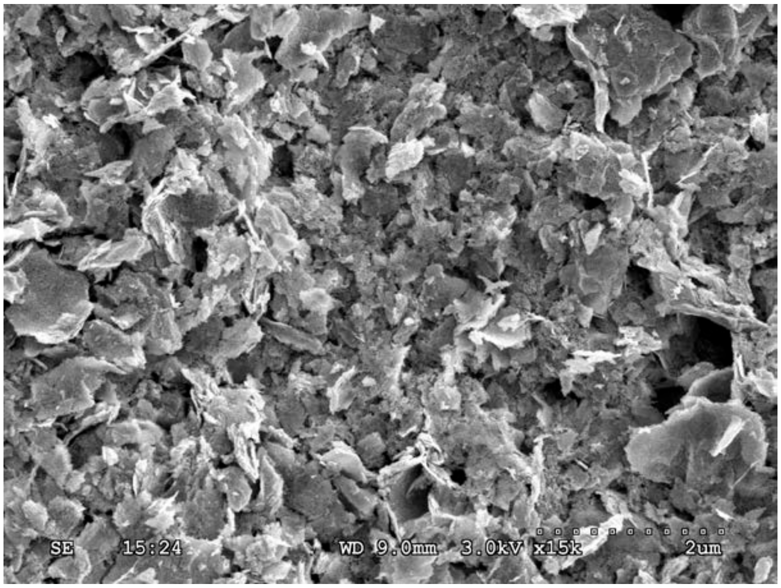

Figure S2. SEM image of a NiO film deposited on ITO.

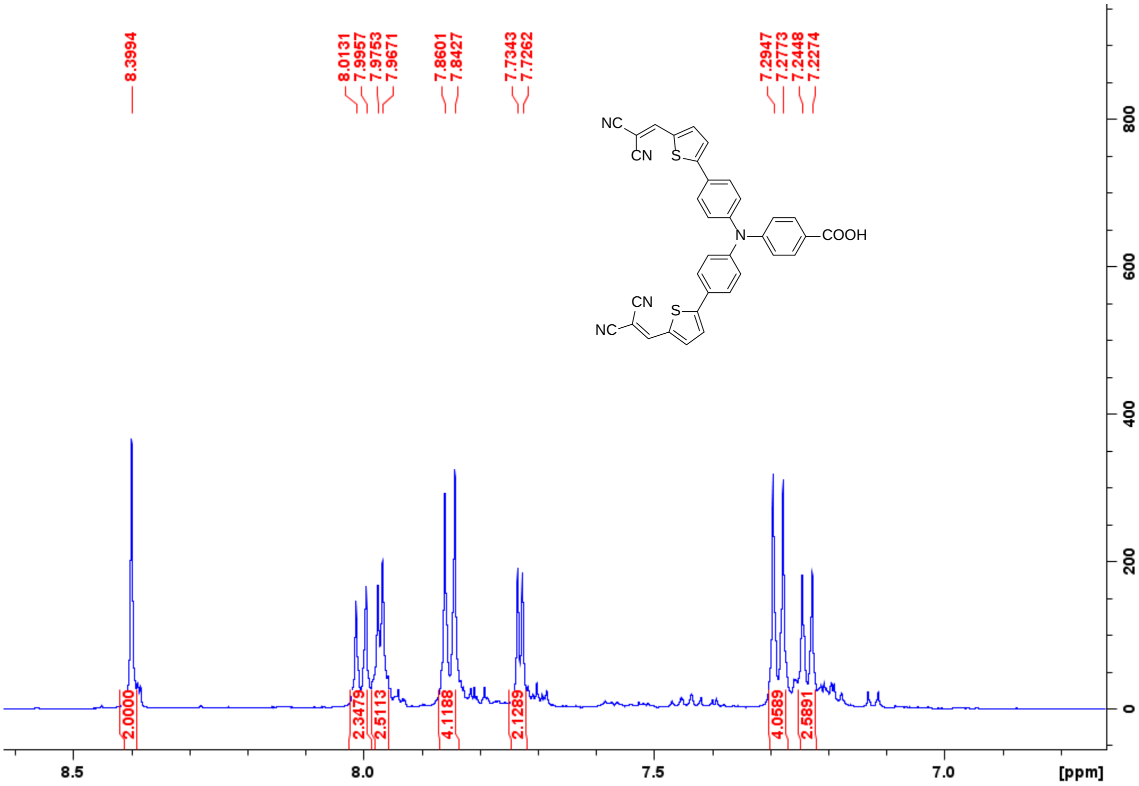

Figure S3. ^{1}H NMR spectrum of **P1**. δ_H (500 MHz, acetone-d_6) 7.23 (2H, d, J 8.72), 7.28 (4H, d, J 8.71), 7.73 (2H, d, J 4.10), 7.85 (4H, d, J 8.69), 7.97 (2H, d, J 4.10), 8.00 (2H, d, 8.70), 8.40 (2H, s).

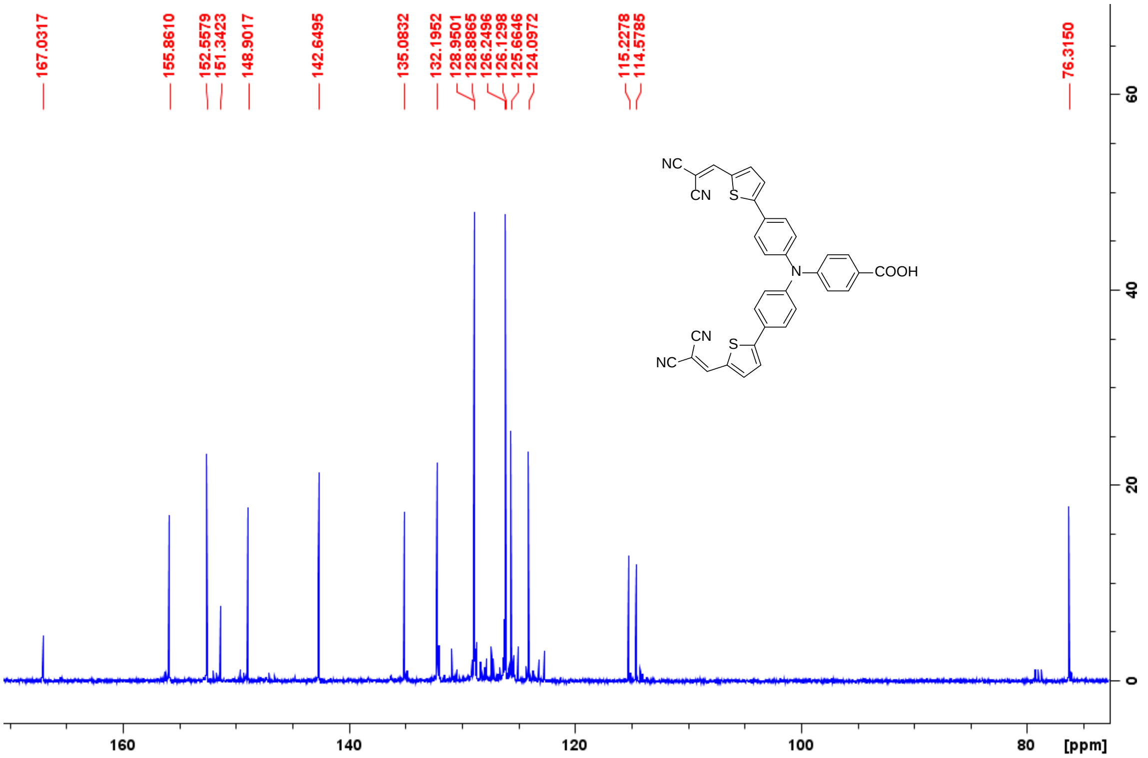

Figure S4. ^{13}C NMR spectrum of **P1**. δ_C (125 MHz, acetone-d_6) 76.3, 114.6, 115.2, 124.1, 125.7, 126.1, 126.2, 128.9, 129.0, 132.2, 135.1, 142.6, 148.9, 151.3, 152.6, 155.9, 167.0.

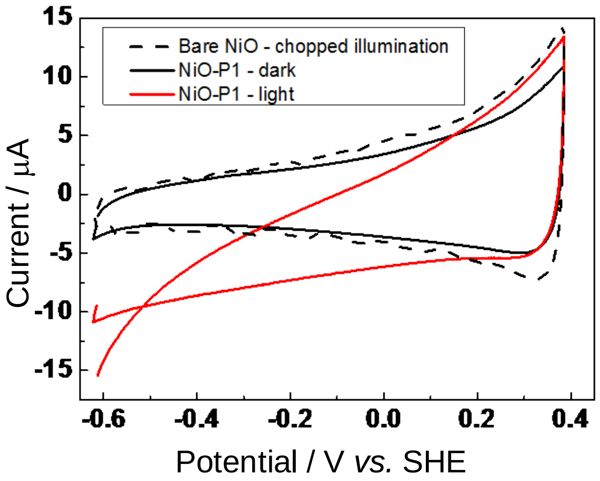

Figure S5. Cyclic voltammograms of a bare NiO electrode (dashed lined) and NiO-P1 in the dark (black) and under illumination (45 mW cm^{-2}, red). Scan rate 30 mV s^{-1}, 0.2 M MES buffer (pH 6), 25 °C.

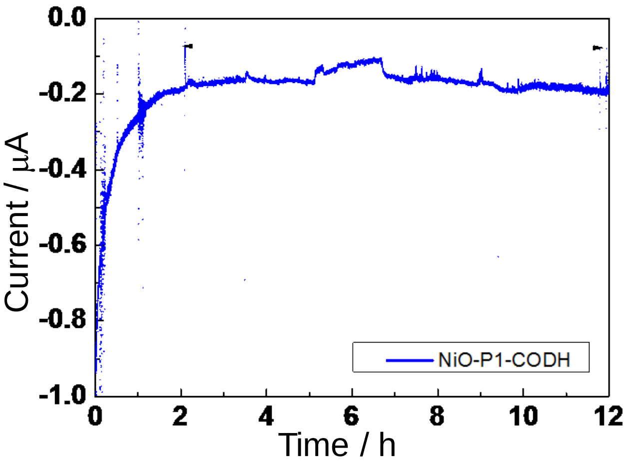

Figure S6. Typical long-term chronoamperometry experiment of NiO-P1-CODH under illumination (45 mW cm^{-2}) at -0.3 V vs. SHE; 0.2 M MES buffer (pH 6), 10 °C. The cell solution (7.5 mL buffer) and headspace were saturated with a mixture of 98% CO_2 and 2% CH_4 prior to the experiment (CH_4 served as internal standard in post-experimental gas chromatographic analysis). The black arrows indicate the capacitive dark current. No CO could be detected after the experiment. A total charge of 5.05 mC (after subtraction of the electrode capacitance) was passed through the system, which would, assuming 100% Faradaic efficiency for CO_2 reduction as the upper limit, correspond to the formation of a maximum of 26.2 nmol CO. Such a small amount could not be detected by GC, as it would still be dissolved in the cell solution and furthermore lie below the detection limit of the gas chromatograph employed.

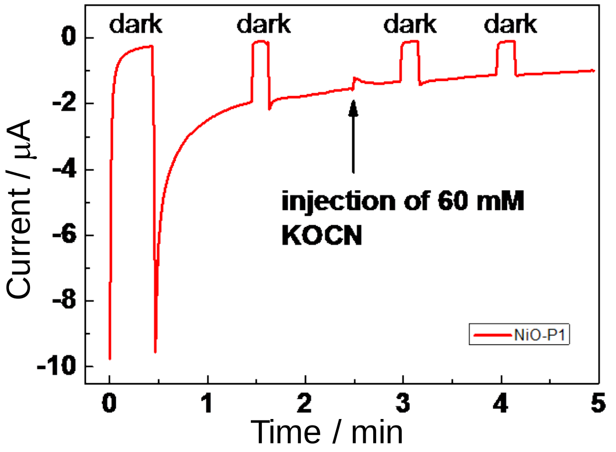

Figure S7. Chronoamperometry experiment of NiO-P1 (control experiment *without* CODH) under illumination (45 mW cm^{-2}) at -0.3 V vs SHE; 0.2 M MES buffer (pH 6), 25 °C, 50 scc/min CO_2 flow. At t = 2.5 min 60 mM KOCN solution was injected into the cell solution. KOCN did not affect the photocurrent, in contrast to NiO-P1-CODH.

References

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(3) Qin, P.; Zhu, H.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *J. Am. Chem. Soc.* **2008**, *130*, 8570.

(4) Sucheta, A.; Cammack, R.; Weiner, J.; Armstrong, F. A. *Biochemistry* **1993**, *32*, 5455.