Electronic Supplementary Material (ESI) for Chemical Science.

Transfer of Photosynthetic $NADP^+$/NADPH Recycling Activity to a Porous Metal Oxide for Highly Specific, Electrochemically-driven Organic Synthesis

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Electronic Supplementary Information

Scanning electron microscopy (SEM)

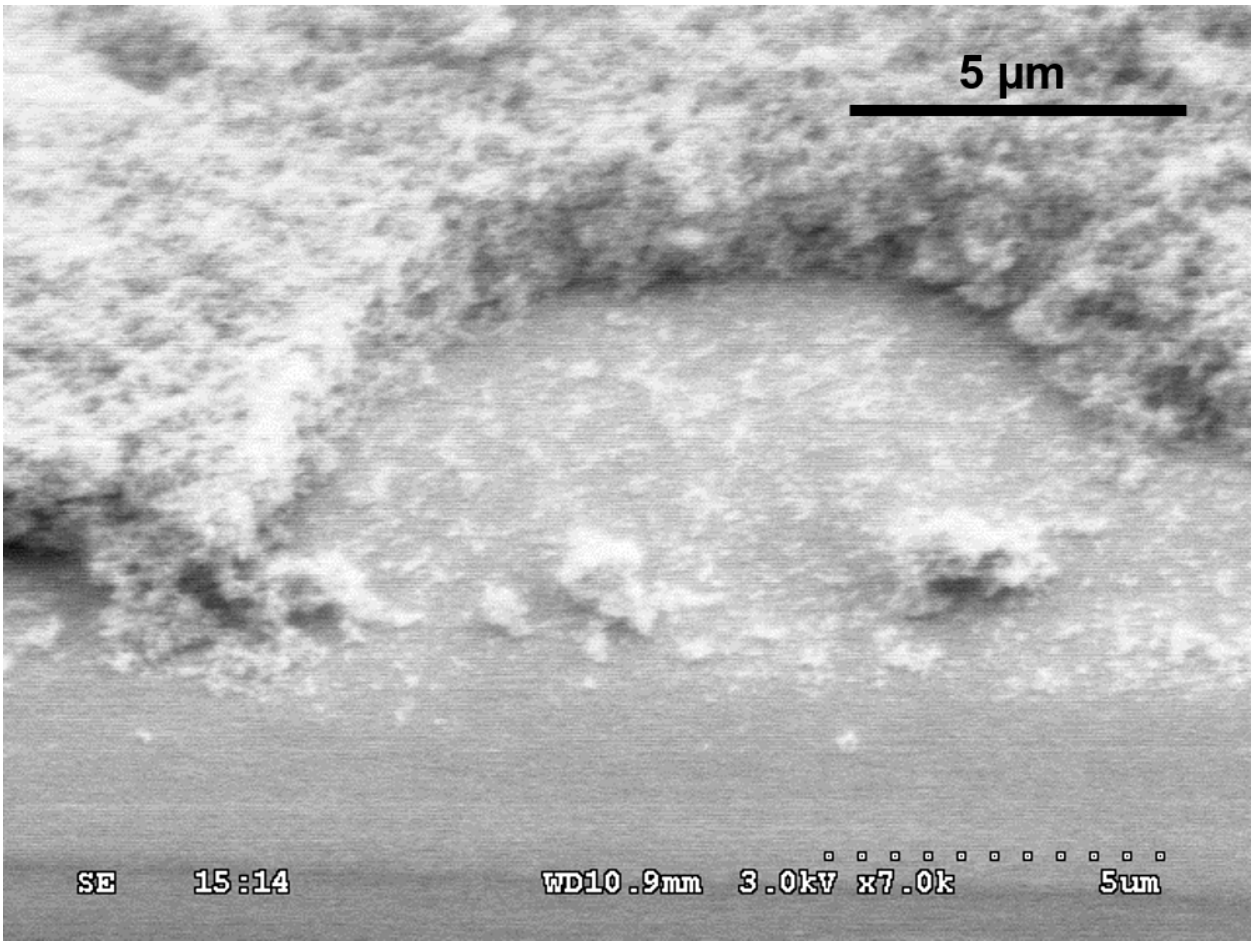

Figure S.1 SEM image of an ITO electrode made by electrophoretic deposition of ITO particles onto an ITO glass slide at 7000x magnification, with the sample tilted at 50 degrees. Scale bar: 5 µm

Scan rate dependence

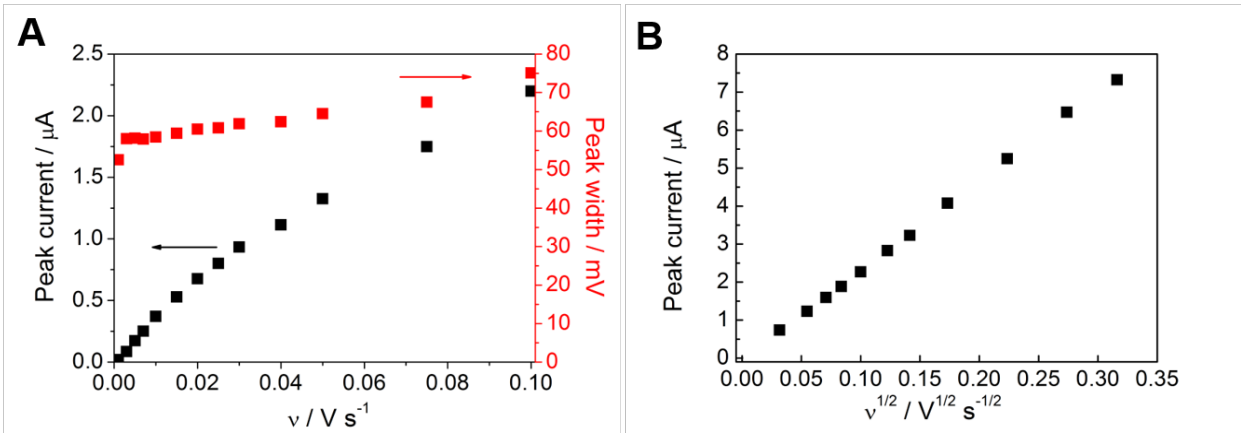

Figure S.2 Scan rate dependences for FNR immobilized in ITO pores (FNR@ITO/PGE) and reduction of $NADP^+$ in aqueous solution catalyzed at FNR@ITO/PGE electrode.

A) Peak current and peak width at half maximum of FNR against the scan rate. **B)** Peak $NADP^+$ reduction current due to $NADP^+$ (50 µM) against the square root of scan rate. The diffusion coefficient of $NADP^+$ was calculated from the slope using the Randles-Sevčik equation (Bard, A. J., Faulkner, L. R., Electrochemical Methods, Wiley, 2001.) Other conditions: MES 25 mM, TAPS 25 mM buffer solution pH 8.0, 20 °C, solution purged with Ar before measurement.

Observation of catalytically redundant FNR molecules on the oxidative scan

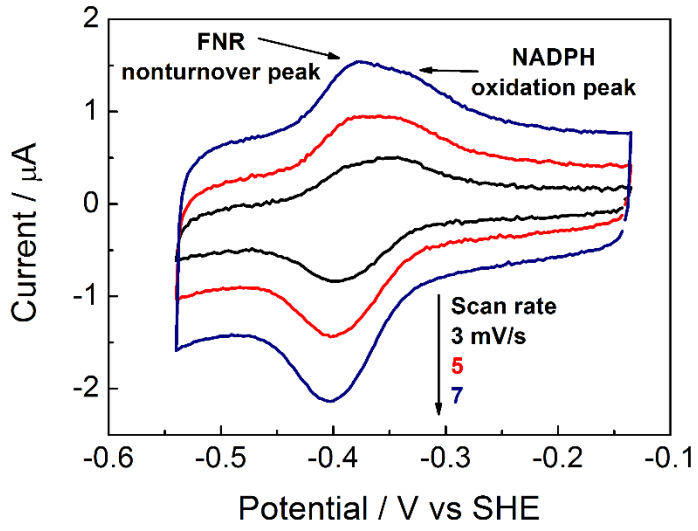

Figure S.3 Cyclic voltammograms with scan rate of v = 3 (black), 5 (red) and 7 (blue) mV s^{-1}. Non-turnover peak of FNR is observed on the left in the oxidative scan, and it increases more at higher scan rate compared to the NADPH oxidation peak on the right.

Other conditions: MES 25 mM, TAPS 25 mM buffer solution pH 8.0, 20 °C, solution purged with Ar before measurement.

pH changes and coverage

To observe FNR coverage changes with pH, a single film of FNR on ITO/PGE was made and voltammograms were recorded to measure the coverage in pH 9. Then a buffer exchange was conducted to change the cell solution to pH 8, keeping the same FNR film, and the coverage was again measured before changing the solution back to pH 9. This was repeated successively with lower pH values until pH 5, resulting in Figure S.3 which shows results of two separate experiments. After the first pH change, the FNR coverage always decreased when the film was taken to a lower pH, but partial recovery was observed when returning the film to higher pH. This indicates that the FNR binding to ITO is weaker at low pH, but the FNR molecules are not totally desorbed from the ITO layer. The recovery in the coverage at pH 9 can be interpreted as FNR molecules that became loosely bound or bound in the inactive configuration at low pH (thus not contributing to the non-turnover peak signal) were returned to the active bound state when the ITO surface is more negative.

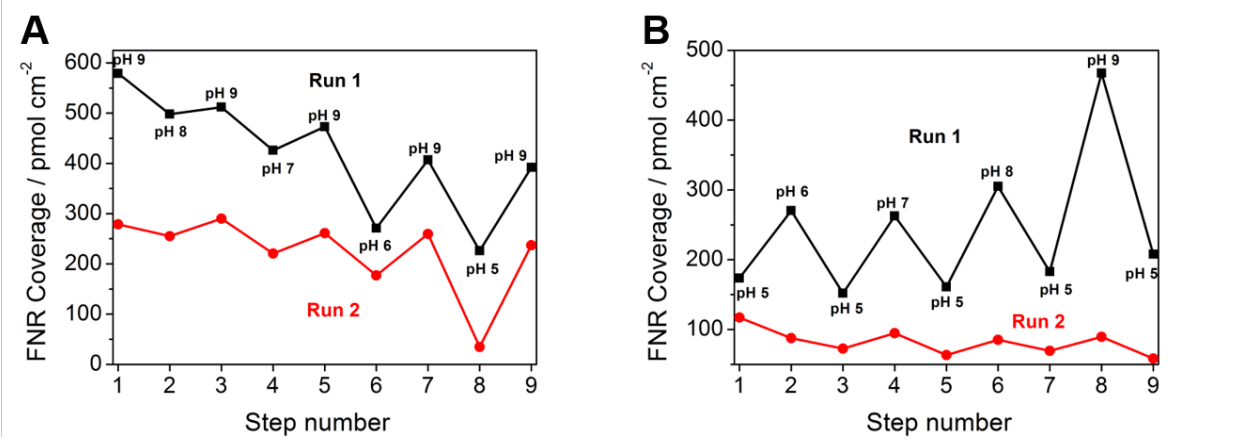

Figure S.4 Changes in FNR coverage with pH.

A) Starting at pH 9.

B) Starting at pH 5.

Other conditions: MES 25 mM, TAPS 25 mM buffer solution, 20 °C, solution purged with Ar before measurement.

NMR spectra

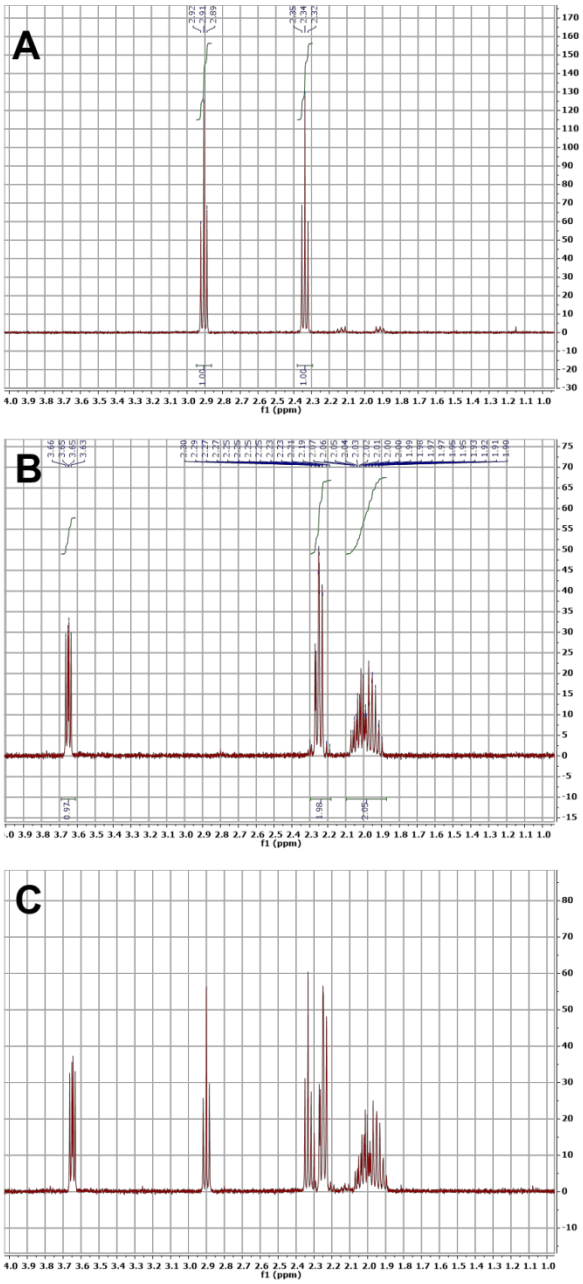

Figure S.5 NMR spectra of cell solutions for the experiment in Figure 4. **A)** Initial cell solution, showing integrals for 2-oxoglutarate (δ 2.34 (t, 2H), 2.91 (t, 2H)). **B)** After chronoamperometry for 20 h, showing integrals for L-glutamate (δ 1.99 (m, 2H), 2.25 (m, 2H), 3.65 (q, 1H)). **C)** After chronoamperometry for 40 h. The peaks for 2-oxoglutarate can be observed, because 2-oxoglutarate was replenished at 20 h and was not exhausted. The L-glutamate peaks correspond to the cumulative amount produced over 40 h.

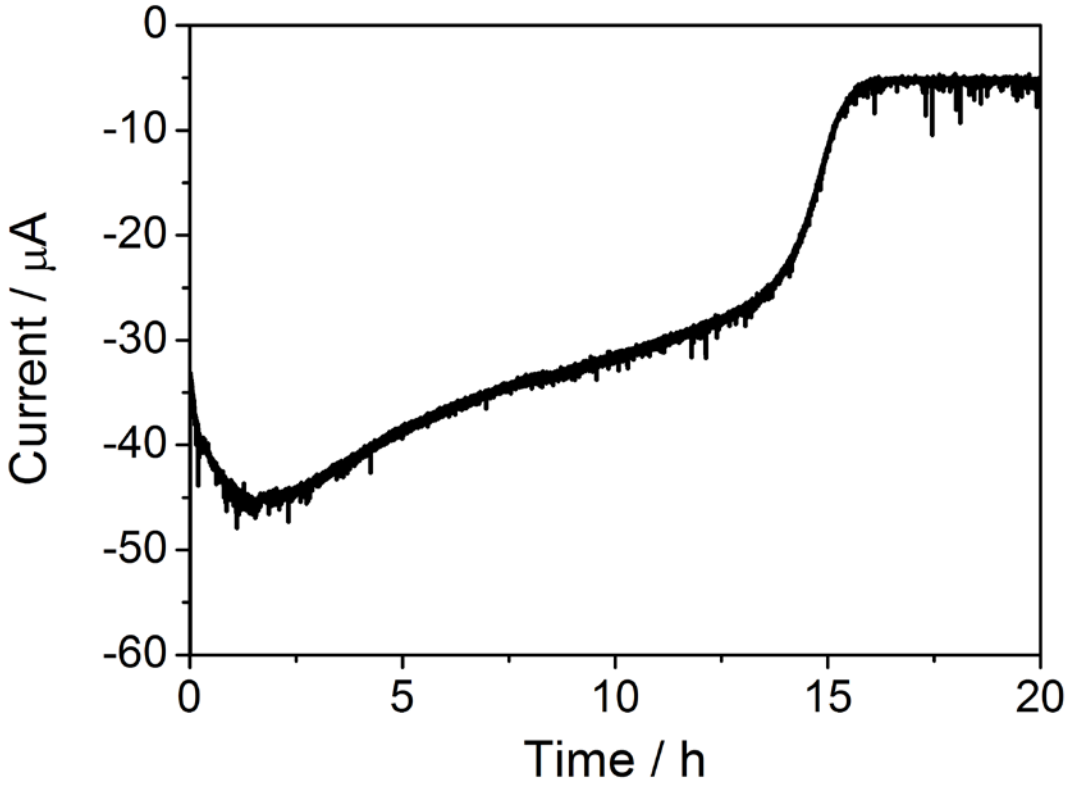

Figure S.6 Electrochemical monitoring of L-glutamate synthesis coupled to FNR@ITO/Ti foil. Electrode area 2.6 cm^2, double sided. Conditions: electrode potential -0.46 V vs SHE, 50 mM borate (pH 8.0), cell volume 2 mL, room temperature, constant Ar bubbling. Before starting the chronoamperometry experiment, $NADP^+$ 20 µM, NH_4^+ 20 mM, 2-oxoglutarate 5 mM, and GLDH 4 µM were present in the cell solution, and cyclic voltammograms were recorded to confirm current enhancement from coupling GLDH to FNR@ITO. After 20 h, NMR analysis of the cell solution showed the L-glutamate concentration to be 4.74 mM, yielding a TTN of 237.