Spectroelectrochemical Characterization of a Penta-Heme Cytochrome in Solution and as Electrocatalytically Active Films on Nanocrystalline Metal-Oxide Electrodes.

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Supporting Information:

Experimental Procedures.

NrfA concentrations were determined from electronic absorption spectra of the air equilibrated (oxidized form) using ε_{410nm} = 497,650 M^{-1} cm^{-1}. The MCD monitored titer was performed in the presence of the following mediators at 40 μM each; dichlorophenolindophenol, 2,3,5,6-tetramethyl-1,4-phenylenediamine, ruthenium hexamine chloride, trimethyl hydroxyquinone, 5-hydroxynathpthoquinone, menadione, nile blue, phenosafranine, neutral red and 9,10-anthraquinone-2,6- disulfonate, together with 10 μM each of benzyl viologen, sulfonyl viologen and methyl viologen.

Cyclic voltammetry with SnO_2 electrodes (1 × 0.7 cm^2) was performed inside a 1 cm path length quartz cuvette. A platinum wire formed the counter electrode and a AgCl coated Ag wire formed the reference electrode. The SnO_2 electrode was positioned at 90° to the light path and the cuvette flushed with argon during experiments. Faradaic currents were obtained by baseline subtraction using baselines constructed with The Utilities for Data Analysis 010716 Program kindly provided by Dr Dirk Heering. The reference electrode was calibrated daily by cyclic voltammetry of a solution of potassium ferricyanide in 50 mM Hepes, 2 mM $CaCl_2$, pH 7. The reduction potential of this sample was then measured in a conventional three-electrode cell with an Ag/AgCl saturated KCl reference electrode (Radiometer) to allow potentials in the cuvette to be converted to values versus standard hydrogen electrode (SHE).

For fitting the Faradaic currents and dA/dE plots, an n = 1 Nernstian component was described by

$$i = \frac{F^2 \upsilon A \Gamma \exp\left(\frac{F\left(E-E^o\right)}{RT}\right)}{RT\left(1+\exp\left(\frac{F\left(E-E^o\right)}{RT}\right)\right)^2}$$

where F is the Faraday constant, υ scan rate, A electrode area, Γ electroactive coverage, E electrode potential, E^o reduction potential, R the gas constant and T the temperature. (Bard & Faulkner, Electrochemical Methods: Fundamentals and Applications, Second Edition (2001) page 590).

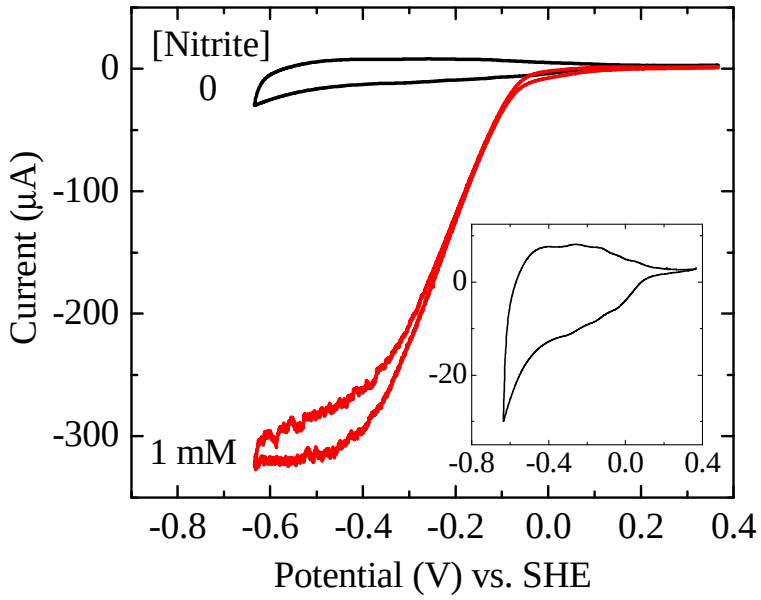

Figure S1. Cyclic voltammetry of a NrfA coated mesoporous SnO_2 electrode in 0 and 1 mM nitrite. Inset shows the voltammetry in 0 mM nitrite in greater detail. Scan rate 5 mV s^{-1} in a stirred solution containing 50 mM Hepes, 2 mM $CaCl_2$, pH 7 at 24 ^{o}C.

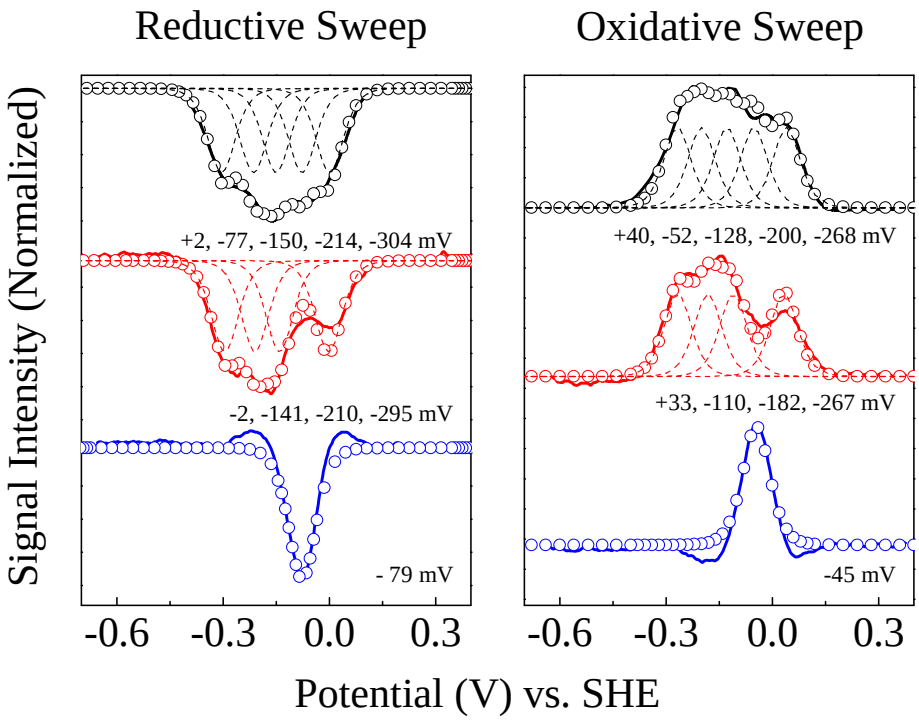

Figure S2. Representative spectroelectrochemical characterization of NrfA adsorbed on mesoporous SnO_2. Faradaic current (black), dA_{552nm}/dE (red) and dA_{442nm}/dE (blue) for experimental data (solid lines), fits (circles) and n = 1 Nernstian contributions (broken lines). Reduction potentials are indicated for each fitted component. Buffer-electrolyte: 2 mM $CaCl_2$, 50 mM Hepes, pH 7, 24 ^{o}C. Scan rate 5 mV s^{-1}.