

Supporting Information

Photoelectrochemical Water Oxidation by Cobalt Cytochrome C Integrated-ATO Photoanode

Carla Casadevall^{1,2,#,*}, Haojie Zhang¹, Shaojiang Chen¹, Dayn J. Sommer¹, Dong-Kyun Seo^{1,*}, Giovanna Ghirlanda^{1,*}

¹ School of Molecular Sciences, Arizona State University Tempe, AZ 85287-1604

² Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain

Present address: Yusuf Hamied Department of Chemistry University of Cambridge, Lensfield Road, CB21EW, Cambridge, United Kingdom

*Correspondence: ccasadevall@iciq.es; DSeo@asu.edu; Giovanna.Ghirlanda@asu.edu

1. Materials and Physical Methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise indicated.

UV-Vis spectra were recorded on a Varian Cary Bio Spectrophotometer. Concentration of Co-cyt c was measured using cyt C's extinction coefficient of $11580 \text{ M}^{-1}\text{cm}^{-1}$ at 280 nm. ICP-MS data were collected from a Thermo-Finnigan Neptune ICP-MS. FT-IR-ATR data were collected using a Bruker IFS 66v/S instrument equipped with a diamond ATR and KBr beam splitter. Gas analysis was performed in a SRI instruments, Model no. 310C GC with a 5 \AA molecular sieve column with a thermal conductivity detector and argon as carrier gas. Calibration curves for H_2 were made by injecting various volumes of a standard gas mixture containing 1 % H_2 and 99 % N_2 onto the GC. Calibration curve for O_2 was created using various volumes of air.

2. Electrochemical studies

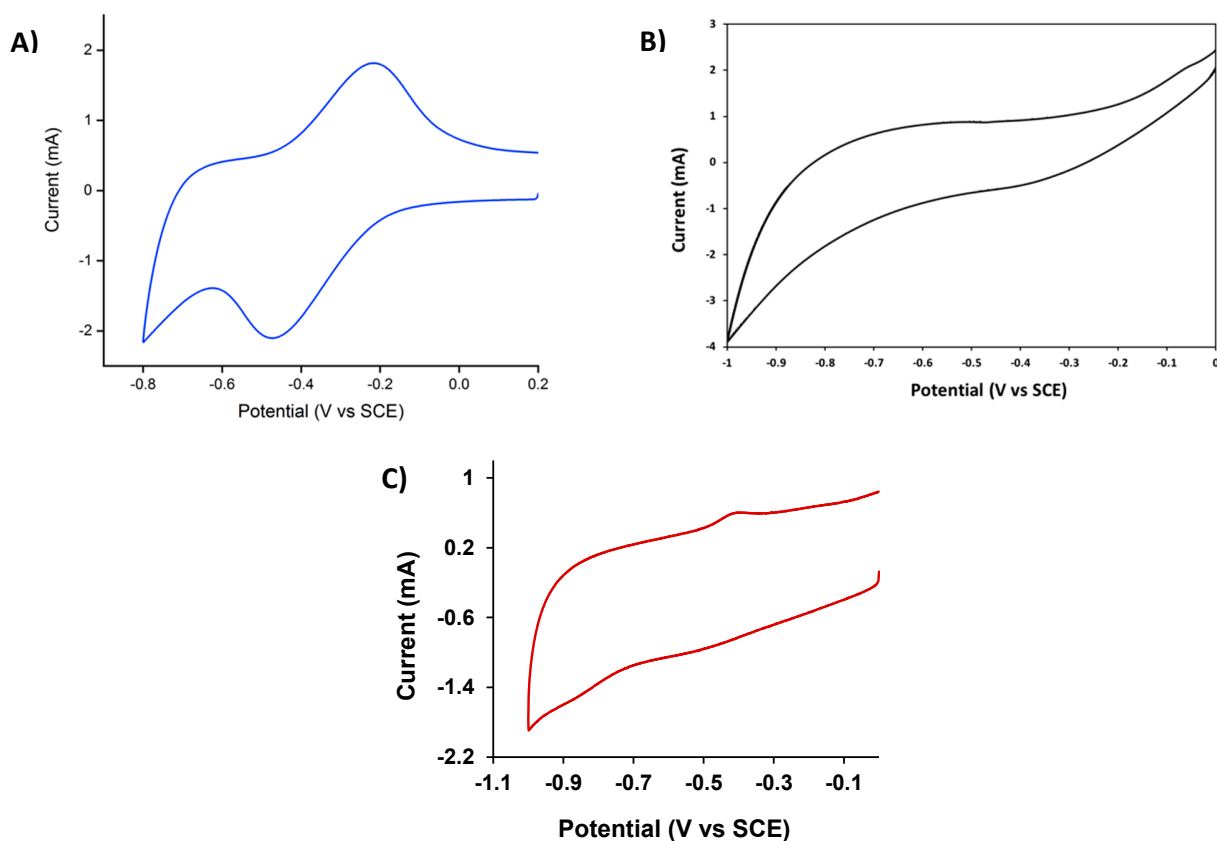


Figure S1. Cyclic voltammogram of (A) ATO-Co-cyt c, in 100 mM citrate buffer, 1M KNO_3 , pH 5.0 at scan rate of $100 \text{ mV}\cdot\text{S}^{-1}$, the redox wave at -0.34 V vs SCE (-0.39 V vs RHE) is assigned to Co (III) to Co(II); (B) blank ATO in the same buffer and scan rate; and (C) Co-cyt c in solution in the same buffer and scan rate, the redox wave at -0.43 V vs SCE (-0.48 V vs RHE) is assigned to Co (III) to Co(II).

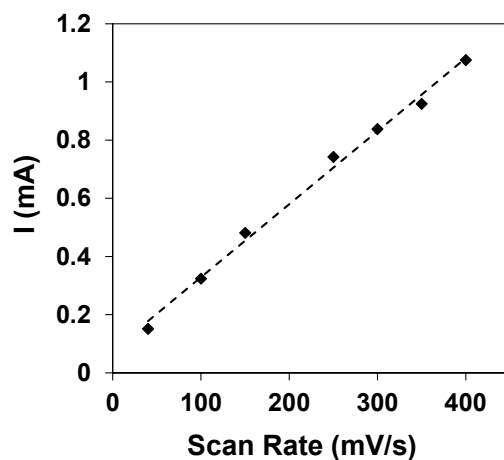


Figure S2. Anodic peak current dependence on scan rate for ATO-Co-cyt C, in 100 mM citrate buffer, 1M KNO₃, pH 5.0 at the following scan rates: 40, 100, 150, 200, 250, 300, 350 and 400 mV·s⁻¹.

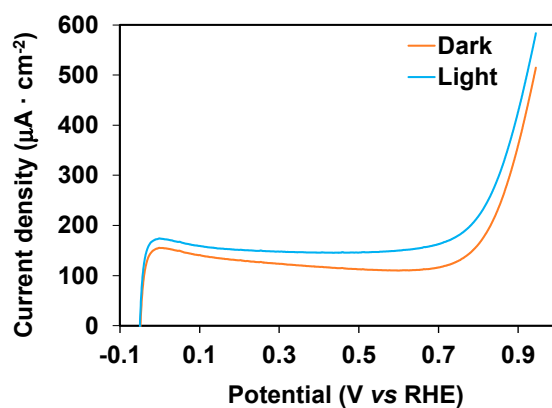


Figure S3. Linear sweep voltammograms of the working electrode ATO-Co-cyt c, in the dark (orange line) and under light illumination (blue line) in 100 mM citrate buffer at pH 5.0.

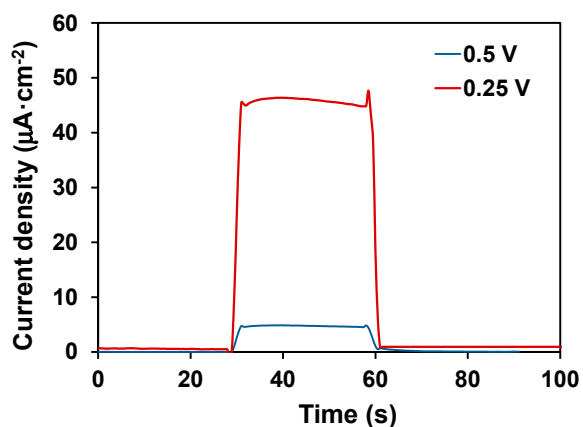


Figure S4. Chronoamperometry behavior of ATO-Co-cyt c at 0.5 (blue) and 0.25 V (red) *vs* RHE applied bias in 100 mM citrate buffer at pH 5.0.

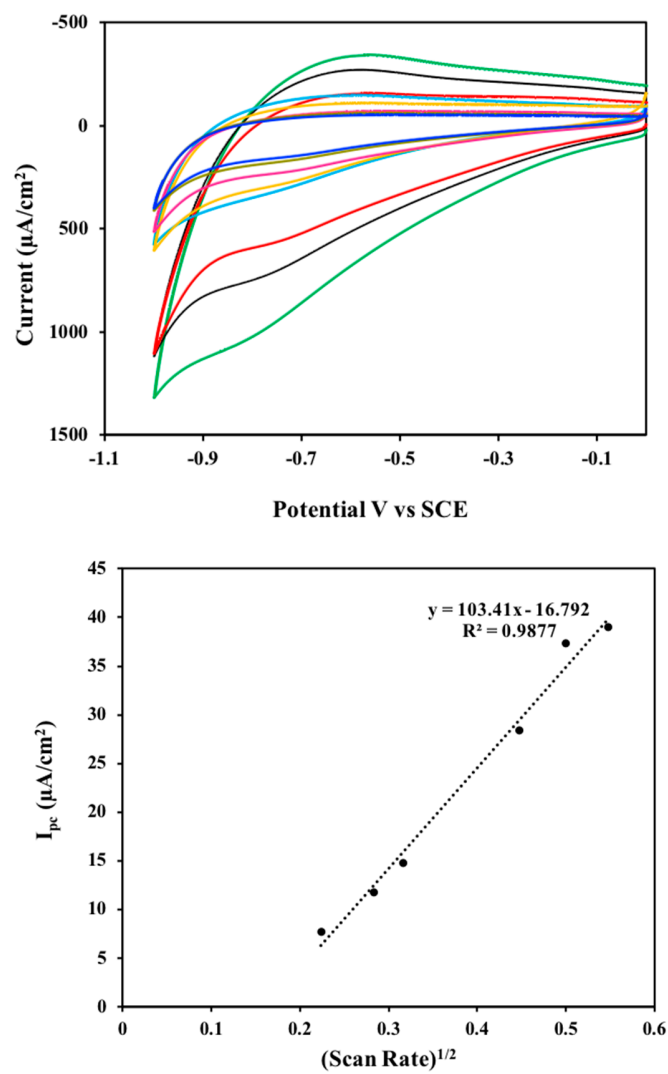


Figure S5. (A) Cyclic voltammograms of 5 μM Co-PPIX in 100 mM citrate buffer, 1M KNO_3 , pH 5.0, at varying scan rates: 50, 80, 100, 200, 250 and 300 $\text{mV}\cdot\text{s}^{-1}$, respectively. (B) The I_{pc} vs square root of scan rate obtained from the data in (A) was used to calculate the diffusion coefficient.

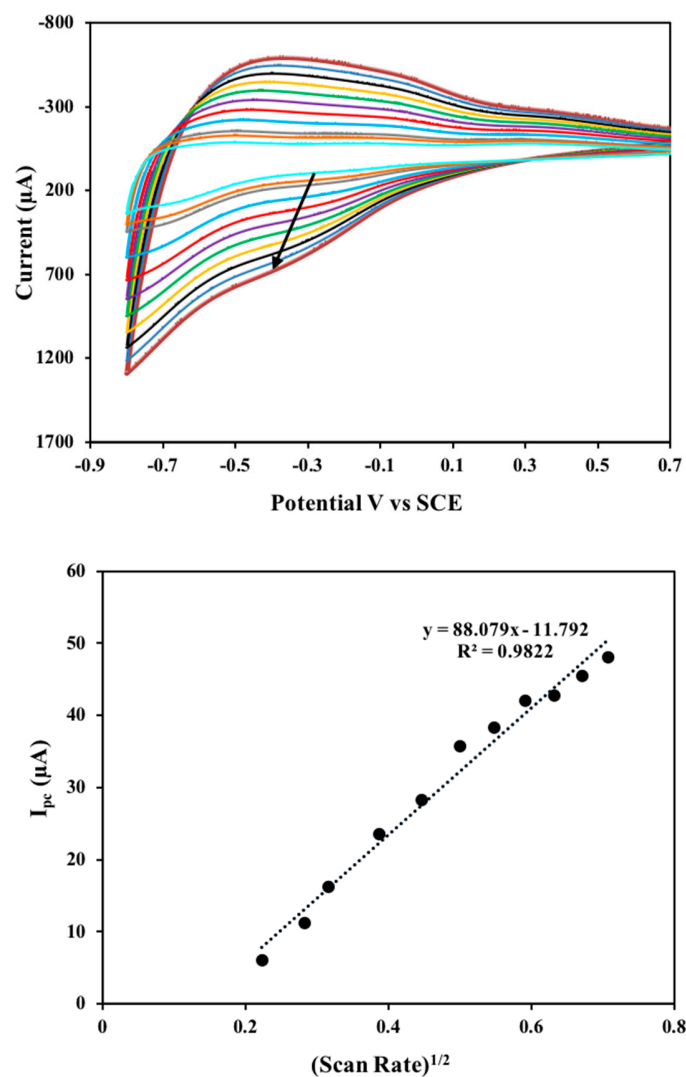


Figure S6. (A) Cyclic voltammograms of 5 μM Co-cyt c in 100 mM citrate buffer, 1 M KNO_3 , pH 5.0, at varying scan rates: 50, 80, 100, 150, 200, 250, 300, 350, 400, 450 and 500 $\text{mV}\cdot\text{s}^{-1}$, respectively. (B) The I_{pc} vs square root of scan rate obtained from A was used to calculate the diffusion coefficient.

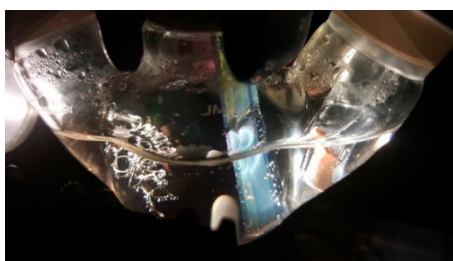


Figure S7. Evolution of gas bubbles on the ATO-CocytC working electrode and Pt counter electrode upon illumination

3. Calculation of the Faradic Efficiency

The passed charge carriers through the external circuit were measured with integrating the area under the i-t plot in a 6 h photoelectrochemical water splitting test. Simultaneously, amounts of produced H₂ and O₂ was detected by gas chromatography. The Faradic efficiency was calculated according to the following equation:

$$\eta_{\text{hydrogen}} = \frac{\text{amount of hydrogen (mol)}}{\text{amount of } e/2 \text{ (mol)}}$$

$$\eta_{\text{oxygen}} = \frac{\text{amount of oxygen (mol)}}{\text{amount of } e/4 \text{ (mol)}}$$

The following equation was used to calculate the Induced Photon to Current Efficiency (IPCE):

$$\text{IPCE(\%)} = \frac{\text{Number of electrons generated}}{\text{Number of incident photons}} \times 100$$

Ferrioxalate actinometry experiment was used to calculate the number of incident photons.^[1] The two solutions required for conducting actinometry are 0.15 M potassium ferrioxalate and 0.1% buffered phenanthroline solution. To prepare the 0.15 M potassium ferrioxalate, 1.3 g of potassium ferrioxalate was dissolved in 18mL of water with 2 mL of 1.0 N H₂SO₄. 0.1% buffered phenanthroline was prepared by dissolving 1.12 g of sodium acetate, and 5mg of phenanthroline in 5 mL of 1.0 N H₂SO₄.

To conduct the actinometry, 3 mL of potassium ferrioxalate were added in a 1 cm × 1 cm quartz cuvette and irradiated with the Kessil lamp for 1 minute while stirring, and another cuvette was left in the dark as a control. 500 uL of 0.1% buffered phenanthroline solution was added to both cuvettes upon completion of the irradiation, and they allowed to develop in dark for 5 minutes. The absorption for both samples were measured at 510 nm, and the amount of produced Fe²⁺ during irradiation was measured using the following equation:

$$[\text{Fe}^{2+}] = \frac{A_{\text{light}} - A_{\text{dark}}}{\epsilon_{510 \text{ nm}} l}$$

The photon flux absorbed by the sample then calculated as previously reported.^[1]

References:

[1] Scaiano, J. C.; Intermolecular photoreductions of ketones; *Journal of Photochemistry*, 2 (1973/74) 81-118.

