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Electronic Supplementary Information

Electrochemistry in an optical fiber microcavity - optical monitoring of electrochemical processes in picoliter volumes

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1. Numerical analysis of the electrochemical response

Simulations of the electrochemical (EC) response were performed using the Comsol 5.6 software with the Electrochemistry module. The simulation volume is shown in **Figure S1.** The electrode reaction was modeled using the Butler-Volmer equation with the exchange current density following the mass action law. The electrode current density i is given by Equation (S1), where k_0 is the reaction rate constant, c_{ref} the reference concentration, c_{Eed} and c_{Ox} are the local concentrations of the reduced and oxidized forms of the redox probe, respectively, α_{a} the anodic transfer coefficient, $\alpha_c = 1 - \alpha_a$, F, R and T have their normal meanings. E_0, is the equilibrium potential and E is the electrode potential.

$$i = k_0 F c_{ref}\left(\left(\frac{c_{Red}}{c_{ref}}\right)\exp\left[\frac{\alpha_a F(E - E_0)}{RT}\right] - \left(\frac{c_{Ox}}{c_{ref}}\right)\exp\left[-\frac{\alpha_c F(E - E_0)}{RT}\right]\right) \tag{S1}$$

Calculations were performed using both cyclic voltammetry (CV) and chronoamperometry (CA). The parameters used are found in **Table S1**. Results of simulations of CVs are shown in **Figure S2**.

3D simulations were performed using the same EC model, but with a cavity inserted into a model of the optical fiber to reproduce the shape in Figure 1A. The sampling volume was a cylinder along the axis of the optical fiber, selected to match the calculations shown in Figure 4. The results of those calculations are shown in **Figure S3**. The 3D model was used only to verify the validity of the 2D calculation, since a single run took > 18 h to perform.

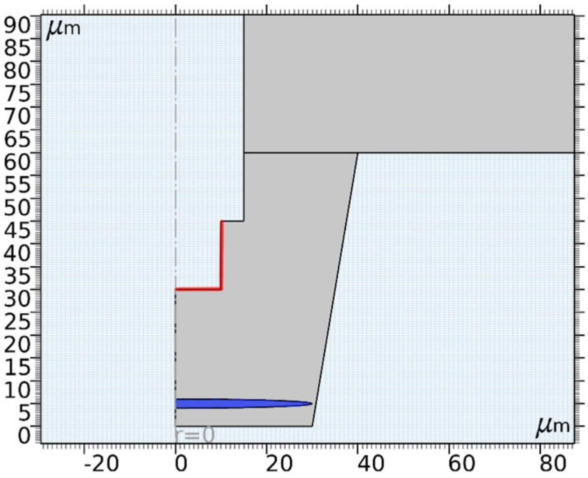

Figure S1. Simulation volume for the 2D rotational symmetrical geometry. The electrode surface is marked in red, and the sampling volume in blue. A constant concentration surface closes the volume as a quarter circle with 500 µm radius (well outside the depletion zone) outside the top-right corner.

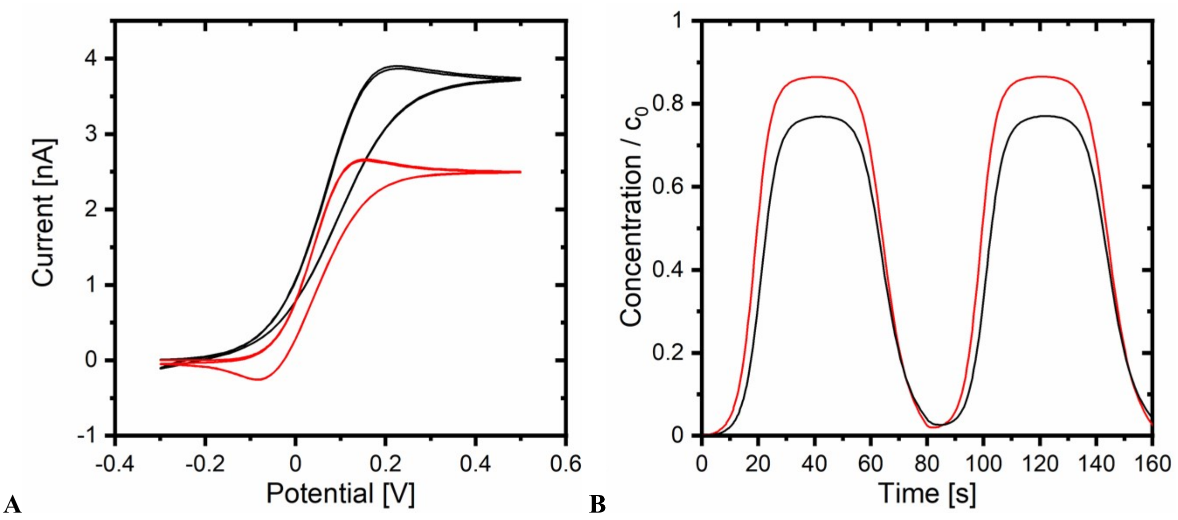

Figure S2. (A) Simulated cyclic voltammograms and (B) the corresponding changes in concentration of the oxidized form of the redox probe. Black lines are for the electrode in the middle of the cavity (h=30 µm) and brown with the electrode close to the bottom (h=7 µm). CV parameters same as in experiments.

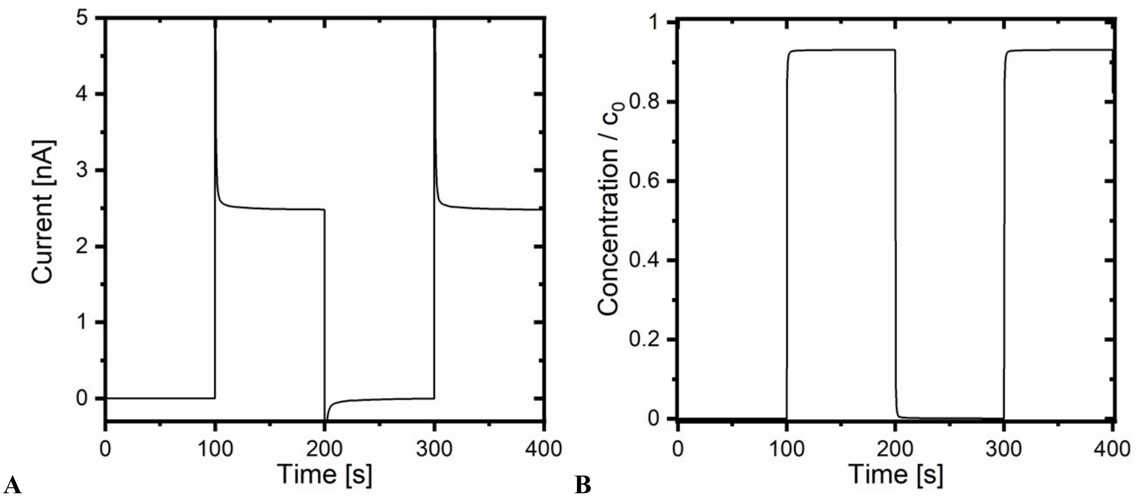

Figure S3. (A) Simulated CA and (B) the corresponding changes in concentration of the oxidized form of the redox probe. Simulations performed in the 3D model with the electrode close to the bottom of the cavity (h = 7 µm).

Table S1. Parameters used in the simulations.

Name	Value	Comment
Cavitybottom	60[um]/2	radius of cavity at bottom
Cavityopening	80[um]/2	radius of cavity at top
ID	20[um]/2	Electrode radius
OD	30[um]/2	glass radius
ElHeight	30[um]	height of electrode over bottom
C0	1[mM]	Initial concentraton
StickingOut	15[um]	Distance electrode is sticking out from glass sheat
k0	0.1 [cm/s]	
SquareTime	100	Time for each SW
LowerPot	-0.3[V]	CA lower limit
UpperPot	0.4[V]	CA upper limit
E0	0[V]	Redox potential
alpha	0.5	transfer coefficient

2. Identification of shift in wavelength during the CA experiment

On top of tracking transmission minimum discussed in the paper, changes in wavelength have also been identified during the CA measurements. The transmission spectrum in range of 1500-1600 nm was measured during CA, **Figure S4.** Then the wavelength values were analyzed at the fixed transmission level: -23 dB (the point was marked with a circle at Figure S4). The wavelength shift in wavelength of the rising slope at fixed transmission is shown in **Figure S5.**

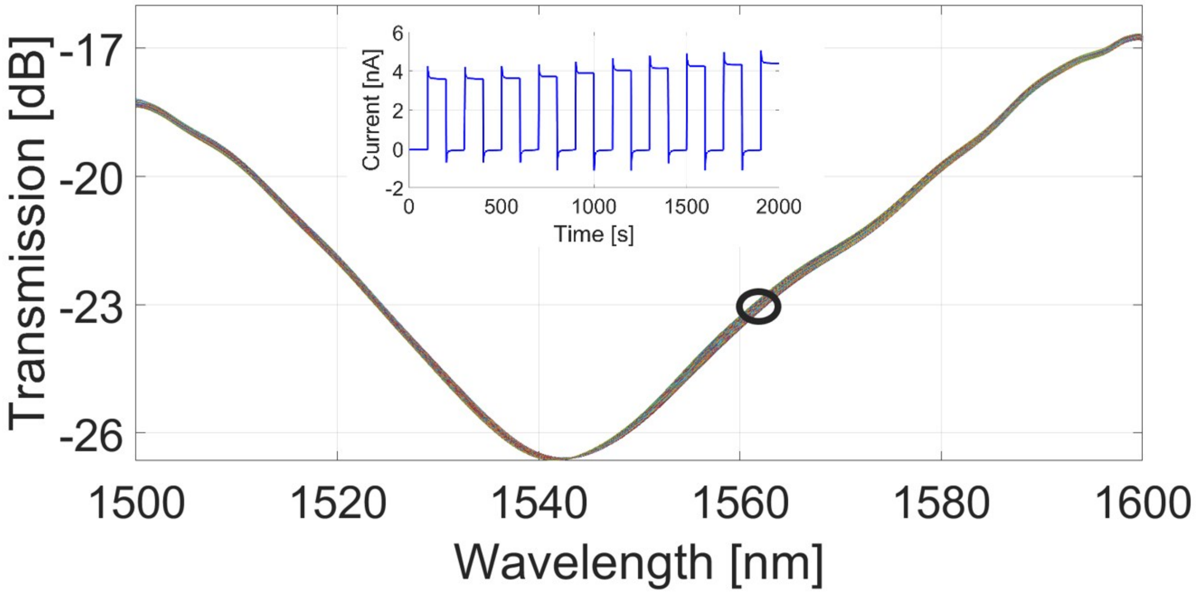

Figure S4. Optical and EC (inset) response during CA measurements for the microelectrode tip located in the microcavity.

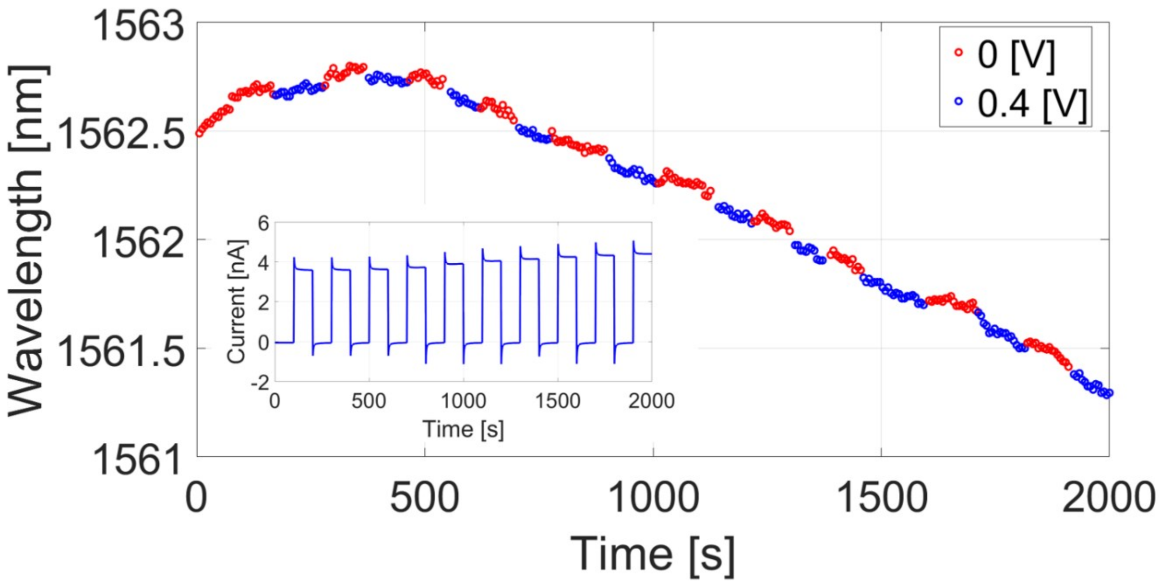

Figure S5. Optical and EC (inset) response during CA measurements for the microelectrode tip located in the microcavity. Blue and red shapes correspond to 0.4 V and 0.0 V potential, respectively. The wavelength values correspond to constant transmission of -23 dB at the rising slope of the spectrum.

3. Drift of the HBM system readout in time

To identify power drift of the HBM system, its input and output ports were connected with a patchcord. The transmission spectrum was measured in the range of 1500 – 1600 nm every 5 seconds for 3 hours. The values recorded at 1550 nm are shown in **Figure S6.**

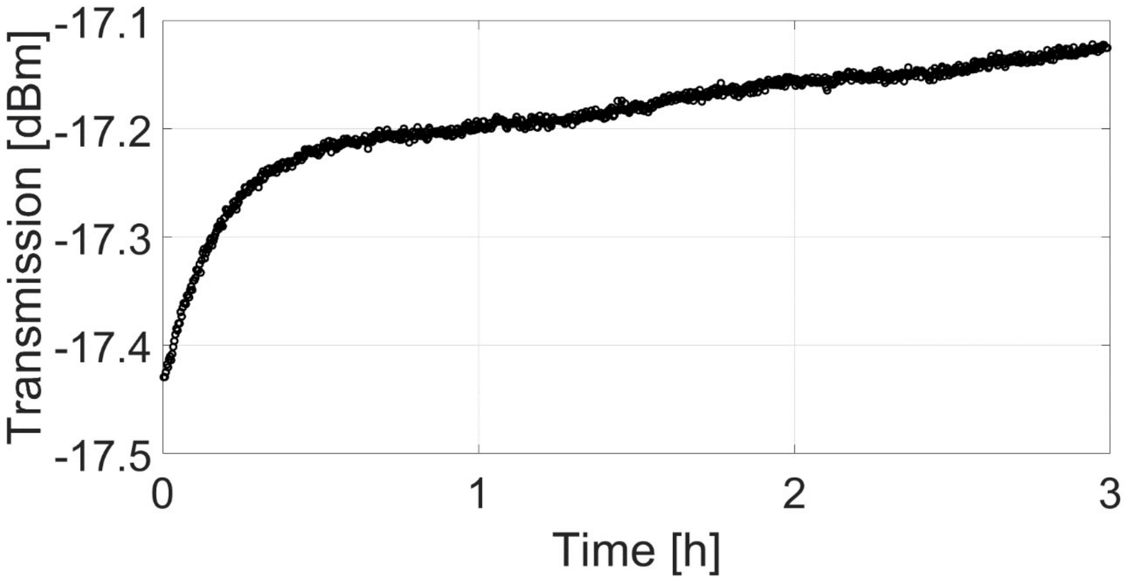

Figure S6. HBM light source power drift in time at 1550 nm verified using directly connected reference SMF patchcord.

4. Reference analysis of optical properties of the electrolyte solution

4.1. Refractive index

Additional experiments have been conducted to determine the change in refractive index (RI) of 1 mM 1,1'-ferrocenedimethanol (FcDM) in 0.1M KCl during the CV. Thus, a 1.2 μL droplet of the solution was measured using Rudolph J57 automatic refractometer first.

Operating wavelength of refractometer was 589.3 nm, accuracy was $2 \cdot 10^{-5}$ RIU, and the RI measurements were done at temperature of 20°C. Obtained average value of RI was 1.33407 RIU. Next, directly in the refractometer analyzing spot a CV was done with the scan rate of 20 mV/s using portable potentiostat PalmSens4 and Au as a working electrode and Pt wire as a pseudoreference electrode. The experimental setup is shown in **Figure S7**. After 10 cycles (approx. 10 minutes) the RI was measured again, and it reached 1.33414 RIU. The change in RI during EC experiments is relatively small (0.00007 RIU), what proves our hypothesis that the main cause of the shifts at optical spectra can be associated with changes in geometry of the system (distribution of the solution) rather than changes in the composition of the solution.

To spot differences between the RI of other redox probe available directly in oxidized and reduced form, i.e. $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ in the 1.2 µL droplet of 10mM $Fe(CN)_6^{3-}$ in 0.1M KCl and 10mM $Fe(CN)_6^{4-}$ in 0.1M KCl, were also measured using a Rudolph J57 automatic refractometer. The RI values were 1.33454 RIU and 1.33467 RIU for $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, respectively (the difference reaching 0.00013 RIU).

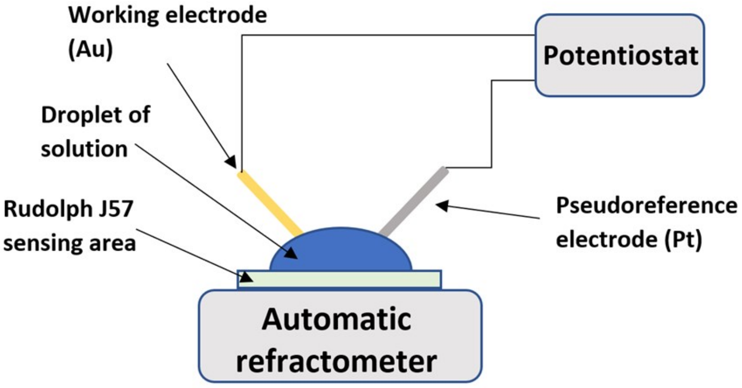

Figure S7. Schematically shown an experimental setup for RI measurements before and after electrochemistry.

4.2. Absorbance

Changes in absorbance of the KCl solution when FcDM was added are shown in **Figure S8.** The measurements were performed with a Shimadzu UV-3101PC spectrophotometer using quartz cuvettes with a 1 mm optical path length.

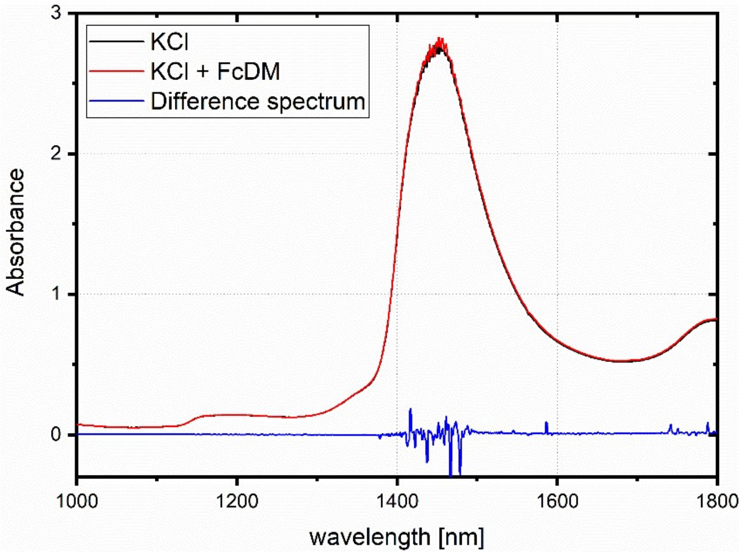

Figure S8. Comparison of absorbance of the used KCl solution and the solution with FcDM.