

Supporting Information

Redox Cycling Without Reference Electrode

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1. Fabrication Methods

A nanogap sensor with two parallel planar electrodes, as sketched in Fig. 1a, was used for experiments. The method for microfabricating the devices is summarized here. The 20 nm thick platinum bottom electrode was deposited using electron beam evaporation using a Blazers BAK 600 system and patterned by photolithography and a lift off process using Arch Chemical OIR 907-17 as photoresist. A 60 ± 5 nm chromium sacrificial layer and a 100 nm platinum top electrode were subsequently deposited and patterned by the same procedure. The whole structure was buried in a passivation layer of 750 nm of silicon nitride using a Film PECVD Oxford 80 system. Using reactive ion etching (Etch RIE Plasma Therm 790), two access holes, $2 \times 2 \mu\text{m}$, were then etched through the passivation layer to allow the inflow of solution into the nanochannel. The top and cross sectional view of the device has been sketched as shown in Fig. S1.

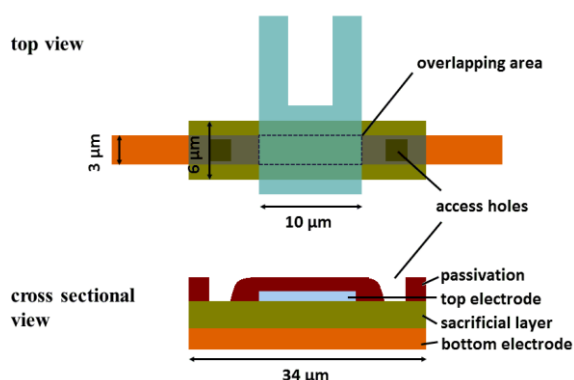


Figure S1: Top and cross sectional view of the device. The areas of the top and bottom electrodes are $60 \mu\text{m}^2$ and $102 \mu\text{m}^2$. The overlapping area is $30 \mu\text{m}^2$ and represents the active area during redox cycling.

2. Characterization of solution after exposure to device

1 mM solution of Ferrocenedimethanol ($\text{Fc}(\text{MeOH})_2$, Sigma-Aldrich, Catalog no. 372625, diffusion coefficient $D = 6.7 \times 10^{-10} \text{ m}^2/\text{s}$) nominally in the reduced form was prepared in Milli-Q water with 0.1 M KCl added as supporting electrolyte. Cyclic voltammetry was performed on this solution using a 10 μm diameter platinum ultramicroelectrode (BASi, MF-2005), as shown in Fig. S2 (blue curve). The sigmoidal oxidation wave confirmed that the $\text{Fc}(\text{MeOH})_2$ was predominantly in the reduced form. A small amount of reducing current was also observed, presumably due to some contamination and consistent with other reports in the literature¹. The crossing potential (V_{rp}) was found to be 0.17 V. A small volume of solution (ca. 80 μl) was then introduced in a Polydimethylsiloxane (PDMS) reservoir in contact with the device to perform measurements with the nanogap sensor. Prior to this, both the device and the reservoir had been exposed to a chromium etchant solution (BASF, Selectipur) which was used to etch the sacrificial layer of the nanochannel. Sulphuric acid had similarly been used to clean the electrodes. It is likely that residues from both the etchant and the acid were absorbed within the PDMS. After conducting the measurements with the nanogap device, the solution was extracted out

of the reservoir and cyclic voltammetry was performed again using the ultramicroelectrode, as shown in Fig. S2 (red curve). The voltammogram exhibits a much more pronounced reduction wave, leading to an increase in the value of the V_{rp} to 0.21 V. This indicates that the solution became oxidized when introduced in the reservoir due to contamination, consistent with the measurements performed with the nanogap device.

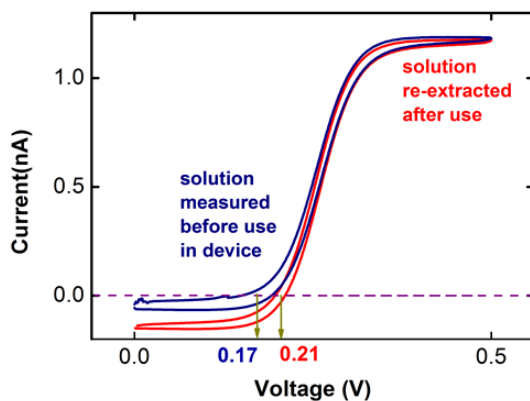


Figure S2: Cyclic voltammograms for 1mM $\text{Fc}(\text{MeOH})_2$ in 0.1M KCl before (blue curve) and after (red curve) being introduced in the nanodevice (scan rate 10 mV/s).

1. J. W. Xiong and H. S. White, *Journal of Electroanalytical Chemistry*, 2013, **688**, 354-359.