Supplementary Information

Device Fabrication

The y-channel electrochemical cell is comprised of a polydimethylsiloxane (PDMS) channel and metal electrodes deposited on a glass substrate. Below we describe the fabrication of these two parts and their assembly.

PDMS Channel

The PDMS channels were fabricated using standard soft-lithography techniques[1]. Initially, a 4 inch silicon wafer is spin coated with SU-8 2050 (MicroChem). The spin rate is chosen such that the SU-8 is about 200 μm thick (this is later verified by microscopy). Photo -lithography was used to define the channel features and the images were developed using PM Acetate. PDMS was molded on the SU-8 master and cured for 1.5 hours at 70 °C. After curing, the PDMS was removed from the mold and then cut and cleaned.

Electrodes

The electrodes were evaporated onto a Pyrex wafer and shaped using lithography and lift-off techniques. In addition to the electrodes, deposition included metal alignment marks. An image reversal photoresist, AZ 5214E, was spun onto a 6 inch Pyrex wafer, achieving a thickness of about 1.5 μm. Image reversal photo-lithography and development in AZ 422 defined the electrode features. 200 nm of gold was evaporated onto the wafer with a 20 nm titanium adhesion layer. After metal deposition, the wafers were submerged in acetone to remove the remaining resist, thereby lifting off the unwanted metal. The wafers were cleaned and cut into individual device pieces. The reference electrode was converted from gold to silver/silver chloride using a previously developed method[2]. Silver was electoplated onto the gold electrode and then chemically converted to silver chloride using aqueous $FeCl_3$.

Device Assembly

In order to bond the glass substrate to the PDMS channels, both pieces are placed in an oxygen plasma. After removing the glass and PDMS from the plasma they are immediately brought into contact with each other. To prevent irreversible bonding before proper alignment can take place, a few drops of ethanol are placed in between the glass and PDMS. This allows the pieces to move around while preserving the effects of the plasma. Using a microscope, the PDMS channels were aligned with the metal alignment marks on the glass substrate. After alignment, the device was left in a 70 °C oven over night. This ensured that the ethanol was completely evaporated, leading to an irreversible bond between the PDMS and glass substrate. After bonding, fluidic and electronic leads were glued in place.

Experimental Methods

Fluid was injected into the y-channel using Harvard Apparatus syringe pumps. Volumetric flow rates were chosen such that the analyte and reference fluids have the same average velocity. Before running experiments, $FeCl_3$ was injected over the reference electrode. The oxygen plasma used to bond the device has the potential to chemically alter the surface of the silver/silver chloride electrode. By flowing $FeCl_3$ over the reference electrode, the electrode returns to its previous state. The working, counter, and reference electrodes were connected to a potentiostat (Uniscan Bistat 3200) and potentiometery was conducted via a computer. Cyclic voltammmograms (scan rate 0.01-0.05 V/s) were taken at a variety of flow rates to determine the degree of contamination.

References

[1] Y. Xia and G. Whitesides, *Annual review of materials science*, 1998, **28**, 153–184.

[2] B. Polk, A. Stelzenmuller, G. Mijares, W. MacCrehan and M. Gaitan, *Sensors and Actuators B: Chemical*, 2006, **114**, 239–247.