Supporting Information

Electroanalytical Devices with Pins and Thread

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Materials and Methods

Pin Electrodes.

We chose stainless steel pins as electrodes because these pins are produced in large quantity for the clothing manufacturing industry and hobby use, and are available at a low cost (less than $0.001/per pin when purchased from commercial retailers, and much less if purchased wholesale).

The pins were cleaned by sonication in isopropyl alcohol for 20 min, and used without further modification as reference and counter electrodes.

The working electrode was a stainless-steel pin coated with freshly prepared carbon ink. The carbon ink was prepared using graphite ink (C10903P14, from Gwent Electronic Materials Ltd, Montypool, UK), multi-walled carbon nanotube powder (# 724769, from Sigma-Aldrich) and ET160 solvent thinner (Ercon Inc., Wareham, MA). These components were mixed in mass ratio 49.9 % : 0.2 % : 49.9 %, respectively. We sonicated the mixture for 15 min using a high power tip sonicator (Branson Sonifier 450, with a Micro 3/16 tip), with 50% duty cycle at 50% power (total power 400W). This procedure yielded homogeneous ink, with no particles or phase separation.

The stainless steel pins were immersed in the solution, removed and allowed to dry for 5 min at room temperature, then dried for 5 min in an oven at 110° C. The process was repeated 3 times. The process resulted in a coating thickness around the shaft of the pin of ~30 μm, and around the head of the pin ~100 μm. All macroscopic geometrical properties of electrodes were measured either directly with micrometer (resolution: 0.0001") or from image analysis of macro photographs.

Assembly of a 96-well plate embossed in omniphobic R^F paper with integrated pin electrodes

We have chosen paper and thread as a substrate for the fabrication of the electrochemical cells because they are widely available, inexpensive, lightweight, and flexible.

Embossing was chosen to shape the paper into a microplate because it is simple, fast and requires simple equipment (only reusable molds generated easily using a 3D printer, printed molds costing ~$0.32 per gram of material, or about $8 for a mold used to emboss the 96-well plate).

We rendered paper hydrophobic using a fast (five minute in the process we use), vapor-phase treatment with organosilanes. The treatment with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) trichlorosilane ($CF_3(CF_2)_7CH_2CH_2SiCl_3$, "$C_{10}^F$") transformed paper in an omniphobic substrate.[43] To keep the pins in stable position, we used a 1-mm thick paper (Whatman Gel Blot paper, GE Healthcare).

We approximated the diameter of the head of the pin to be an oblate spheroid with diameter 1.5 mm and height 0.68 mm for the uncoated pin, and 1.5 mm and 0.77 mm for coated pin, respectively. From these parameters, we estimate that the macroscopic surface area of the WE in an omniphobic R^F-paper electrochemical cell is ~5 mm^2.

Pins were inserted in wells embossed in omniphobic paper such that the heads of the WE, CE, and RE pin were equally spaced, with a 0.1 in (2.53 mm) distance among them. A transparency sheet with precut holes served as alignment tool for the insertion of the pins. Single devices were separated from the 96-well plate by cutting, or individual wells were used while part of the intact 96-well plate.

Assembly of threaded pin-electrode arrays.

Cotton thread (YLI Fiberactive Organic Cotton Thread, 24/3 ply TEX 60) was washed with a solution of 0.05% Span 60, rinsed and air dried, then plasma oxidized for 30 min to increase its hydrophilicity.

The plastic, empty housing of a 2.53 mm male PCB single row strip connector was used to guide the insertion of the pins in a mechanical support (here, PDMS) and maintain constant spacing between them.

For the formation of a three electrode array, we used ~70 mm-long pieces of thread. To control the tension in the thread, two knots were placed 1.5 inch (~38 mm) apart from each other; after the first knot was fixed with a support stainless steel pin, the thread was sequentially wrapped around each electrode: two helical turns around the RE pin (apparent contact area 3 mm^2), 3 helical turns around the WE pin (apparent contact area 4 mm^2), 3 helical turns around the CE pin (apparent contact area 4 mm^2). After the array is complete, the second knot was fixed with a support stainless steel pin.

L-lactate assay.

For the measurement of L-lactate, we mixed a solution of L-lactate in human plasma with a solution containing lactate oxidase and ferricyanide in a centrifuge tube. We prepared solution A containing 200 units/mL of lactate oxidase and 250 mM potassium ferricyanide in PBS buffer (pH 7.6). Solution B was prepared by diluting a 100-mM

lactate standard (Biovision, Lactate Assay kit) in human serum (Innovative Research, Inc.; the plasma as received contained 1.1 mM L-lactate). A 45-µL volume of solution A was then mixed with 5 µL of solution B, and the reaction was allowed to proceed for 60 s. The solution was then applied either to an embossed well or a threaded array using a micropipette.

Electrochemical Analysis.

We performed cyclic voltammetry (CV), chronoamperometry (CA), and square-wave voltammetry (SWV) with our electrochemical device using a commercial potentiostat (Autolab PGSTAT12, Metrohm). We connected the paper device to the potentiostat by anchoring a mini test clip leads, (x100w mini hook to banana socket, TestPath.com)**,** to the stem of each pin electrode. All the electrochemical measurements were carried out at room temperature (23 ± 2 °C).

To evaluate the performance of the electrodes, we used cyclic voltammetry (CV). We performed this analysis using cyclic voltammetry using a solution of FCA (100 µM in PBS, pH 7.6) at different scan rates (10, 20, 50, 100, 200, and 300 mV s^{-1}).

For SWV, the parameters were: scan potential between −0.4 V and 0.2 V; amplitude=0.10 V; square wave frequency =25 Hz; step height = 0.005 V.
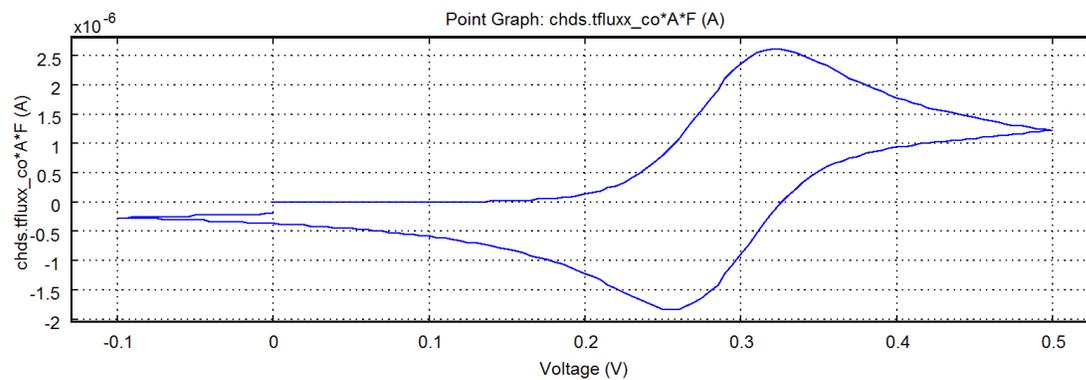
Finite-element simulation.

The finite element simulation was performed on COMSOL Multiphysics 4.1 (COMSOL AB, Stockholm, Sweden). The model considered one-dimensional time

dependent convection diffusion for two species (C_R and C_O, corresponding to reduced and oxidized state of the mediator respectively). The electrochemical process was described with a reaction term at one of the boundaries converting C_R to C_O and the reverse, with a reaction rate determined by the current i. In eq. 3, n is the number of electrons transferred per reaction (n=1 for FcCO$_2$H), F is Faraday's constant, A is electrode area (here 5 mm^2), k is electron transfer efficiency (here assumed to be 1 $cm\ s^{-1}$), E^O is oxidation potential of for FcCO$_2$H (0.29V), α is the symmetry parameter of the reaction (0.5 for symmetric reactions, as assumed here) and E is the potential, scanned a at rate 100 mVs^{-1}, completing one full cycle with nodes 0V, +0.5V, -0.1V and 0V. For simplicity, the convection and migration terms were neglected; the diffusion constant was assumed to be $1.7 \cdot 10^{-10}\ m^2\ s^{-1}$.

$$i(t) = nFAk\left(C_O(0,t)e^{-\alpha nF(E-E^O)/RT} - C_R(0,t)e^{(1-\alpha)nF(E-E^O)/RT}\right) \qquad (3)$$

Mass transport occurs over less than 100 μm, a small distance compared to the diameter of the pin (about 550 μm). Therefore we can neglect the curved geometry of the pin and consider it equal to planar electrode described by abovementioned 1D model. Simulation reproduced the shape of voltammogram, as well as peak current (~2 μA), but experimental peaks appeared at slightly lower voltages than in the simulation (0.27 V and 0.33 V in simulation, *vs.* 0.2 V and 0.27 V in experiments), while the peak potential difference is the same and close to theoretical expectation of 59 mV.

Supplementary figure S1. Finite-element simulation of a cyclic voltammogram for a solution of FcCO$_2$H.