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Electroanalytical Devices with Pins and Thread

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This work describes the adaptive use of conventional stainless steel pins—used in unmodified form or coated with carbon paste—as working, counter and quasi-reference electrodes in electrochemical devices fabricated using cotton thread or embossed omniphobic R^F paper to contain the electrolyte and sample. For some applications these pin electrodes may be easier to modify and use than printed electrodes; their position and orientation can be changed as needed, and the electrodes can be washed and reused between multiple devices. Electroanalytical devices capable of multiplex analysis (thread-based arrays or 96-well plates) can easily be fabricated using pins as electrodes in either thread or omniphobic R^F paper.

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Introduction

The most widely used methods for fabrication of electrodes in paper-based [1-10] and thread-based[11, 12] electroanalytical devices (e.g. screen printing, stencil printing, gravure, chemical vapor deposition with shadow masking) require custom-patterned components such as screens, stencils or masks to deposit conductive materials on the surface of a substrate. [13-18] The fabrication of these custom-patterned components is time-consuming, and can be expensive. In the finished device, the position of the electrode cannot be altered after the fabrication process has been completed.

Existing strategies for the fabrication of electrodes are particularly challenging on non-planar substrates such as embossed hydrophobic[19, 20] and omniphobic paper,[20, 21] and thread.[11, 12, 22-25] The deposition of conductive materials on porous media such as paper or thread can alter its interfacial energy, porosity, tortuosity, and wicking. Inhomogeneity in the distribution of fluid can also affect the stability of the liquid electrode interface and influence the performance of the electroanalytical devices.[26] These effects are most significant in the case of thread, where the fluid flow is confined to one dimension, and might be among the reasons behind the few examples of electroanalytical devices that utilize thread[11, 12] (in contrast to the widespread interest in those that utilize paper [1-10]).

We wished to develop a new class of electrodes that could expand the versatility of the paper and thread-based analytical systems developed by our group[27, 28] and by others.[29-34] Adaptive use of prefabricated stainless steel pins—either unmodified, or coated with a thin layer of graphite ink—provides a simple solution to the problems of fabrication and integration of electrodes in a low-cost analytical device. We show that these pins can be used as electrodes in systems fabricated using either

omniphobic R^F paper or thread; as electrodes, pins are sensitive and can be used to quantify metabolites (e.g., lactate in human plasma). Surprisingly, because they offer readily accessible connection points to electrochemical readers and easily modifiable configurations, pin electrodes allow the fabrication of devices suitable for multiplexed analysis. We demonstrate the fabrication of thread-based arrays that can be used to detect different analytes in the same array, or to perform multiple measurements of the same analyte simultaneously, or in close succession. We also describe the fabrication of a 96-well plate in omniphobic R^F paper that can be used to perform independent measurements in each well.

Henry,[1, 4, 10] we[2, 5] and others[3, 7-9] have described the development of microfluidic paper-based electroanalytical devices (EμPADs), and used this methodology to detect a wide variety of analytes, including small-molecule metabolites, [1, 2, 6] metal ions,[2] nucleic acids,[9] and serum proteins.[5] EμPADs use capillary-driven flow to transport aqueous solutions of analyte through the hydrophilic matrix of cellulose paper, or through "hollow" channels in hydrophilic paper,[26] to the surface of an integrated electrode. In EμPADs and related systems, screen-printing is the most common method used for the fabrication of electrodes.

Recently, we have reported the development of a new class of paper-based electroanalytical devices in which liquids do not wick through the cellulose matrix, but rather rest on the surface of electrodes printed on the surface of omniphobic[21] or hydrophobic paper;[19, 21] in these reports, the electrodes were printed on the surface of the embossed, silanized hydrophobic paper using inkjet printing[21] or a pen-on-paper approach.[19]

Shen[23], and we [24] have described the fabrication of thread-based microfluidic analytical devices (μTADs); thread has since been used as a matrix for several bioassays with colorimetric detection.[22, 23, 25, 35, 36] Hamedi et al. reported the use of fibers for the fabrication of electrochemical transistors.[37] Very

few thread-based analytical devices have so far been integrated with electrochemical detection. Sekar et al. [12] describe one use of thread in voltammetric analysis; this demonstration more closely resembles a conventional electrochemical cell than a μTAD. Individual pieces of thread were first coated with screen-printing pastes (carbon paste for the working and counter electrodes, and Ag/AgCl for the reference electrode), then coated with a thick layer of candle wax; one end of the thread was connected to a potentiostat, while the other end was immersed in a beaker containing a large volume (several milliliters) of a solution of analyte. Wei et al. [11] also reported the use of a microfluidic chip based on thread for electrophoretic separation and detection of electroactive ions. The electrodes are fabricated by sequentially sputtering platinum and gold, using an aluminum mask, on protruding features hot-embossed in a PMMA substrate. Choudhary et al. have described a system based on woven fibers to form fabrics that can serve as electrochemical sensors.[38]

Small-diameter metal electrodes—wires, microwires, needles, and hollow microcylinders—and non-metal fibers—graphite fibers or coated yarns—have been used as electrodes in a variety of electrochemical applications. Wojclechowski et al. used a graphite fiber as working electrode for anodic stripping voltammetry.[39] Suarez-Fernandez et al. used graphite fibers as electrode for square-wave voltammetry analysis.[40] Nuwer and Osteryoung used a carbon-fiber microcylinder electrode for square-wave voltammetry analysis.[41] Choudhary et al. used silk yarns, coated with conductive inks and woven into large-area fabrics to fabricate industrial quantities of electrochemical sensors.[38] Liu et al. and Castano-Diaz et al. used platinum, gold, and copper microwires as working electrodes for post-separation amperometric detection in capillary electrophoresis.[42, 43] Fosdick et al. have reported the use of gold and carbon microwires as electrodes, and showed that they can be integrated with microfluidic paper-based analytical devices. [7] Stainless steel has been used as a material for auxiliary and quasi-reference electrodes in electroanalytical flow systems and other electrochemical applications. [39]

Fernández-Abedul et al. reported a flow system in which a hollow stainless-steel cylinder acted as both the outlet of the flow and the auxillary electrode.[44] Wojclechowski et al. used stainless-steel syringe needle as reference and auxiliary electrode for anodic stripping voltammetry.[39]

Results and Discussion

Design of the R^F paper-based and thread-based devices incorporating pins as 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. We shaped the paper by embossing [45] and rendered it omniphobic using a gas-phase treatment with a fluorinated organosilane. [20]

Stainless-steel pins have several characteristics that make them attractive as candidates for adaptive use as electrodes in electrochemical devices. Stainless steel pins are inexpensive (less than $0.001/per pin when purchased from commercial retailers, and much less if purchased wholesale) and available nearly all over the globe. Stainless steel is highly conductive and stable electrochemically in neutral or mildly acidic or basic aqueous solutions.[46, 47] Different parts of a pin (the head, the shaft and the sharp tip) can be used for different purposes: the head can serve as an electrode in omniphobic paper-based devices, part of the stem can serve as an electrode in thread-based devices, the stem can be used for connection to the potentiostat, and the sharp tip can be used to anchor the pins in a mechanical support. To generate an electroactive surface area of the working electrode that is sufficiently large to be useful for analysis, we coated a stainless-steel pin with carbon ink prepared by mixing graphite paste and solvent thinner with a multi-walled carbon nanotube powder[48] (details in the Supporting Information).

We show in **Figure 1**A the strategy used for the fabrication of an R^F paper-based electrochemical cell in which the pins–serving as working electrode (WE), reference electrode (RE), and counter

electrode (CE)—were inserted in an embossed well. The electrodes were placed 0.1 in (~2.53 mm) away from one another, using a transparency with precut holes as an alignment tool. Figure 1B shows the design of an electrochemical cell, in which pins (WE, RE, CE) are surrounded by helical turns of thread. To allow the solution of analyte to contact the electrodes, we used a micropipette to add a drop of liquid either to the embossed omniphobic well or to the thread.

In the omniphobic paper-based device, the liquid rests on the surface of the well, and forms an interface with the surfaces of the heads of the pins (Figure 2 A1, A2). On thread, the liquid wicks along the thread and forms a cylindrical interface with the shaft of each pin (Figure 2C). The approximate geometrical areas of the two interfaces are 5 mm^2 and 4 mm^2, respectively.

Evaluation

We evaluated the performance of the pins as electrodes in thread-based and omniphobic R^F paper-based electrochemical cells by recording the cyclic voltammograms (CVs) at a scan rate of 100 mV s^{-1} of a solution of a redox probe with well-characterized electrochemical behavior (ferrocene carboxylic acid, $FcCO_2H$). Figures **2B** and **2D** show the variation in the CVs of the solution of $FcCO_2H$ (at 100 μM in 1x PBS, pH 7.6) for paper-based and thread-based cells, each recorded using seven different devices. The device-to-device variation in the performance of the electrodes was, in both cases, less than 10% as indicated by the relative standard deviation (RSD, defined as the percentage ratio of the standard deviation to the mean of the distribution) of 6.3 % (σ = 2.2 μA) and 9.4 % (σ = 1.6 μA) in the anodic peak current, i_{pa}, for paper and thread-based cells, respectively.

To determine whether the electrochemical processes at the pin electrode-liquid interface in R^F paper and thread-based devices are diffusion-controlled, we recorded cyclic voltammograms of 500 μmol L^{-1} $FcCO_2H$ in PBS, pH 7.6, at scan rates between 10 and 300 mV s^{-1}. The anodic and cathodic peak

currents (i_{pa} and i_{pc}) were linearly proportional to the square root of the scan rate in both R^F paper (R^2=0.991 and 0.992, respectively) and thread-based cells (R^2=0.986 and 0.989, respectively) (see Figure 3C). These results indicate that, in both cases, the rate of the electrochemical reaction at the surface of the pin electrode is governed by the diffusion of $FcCO_2H$ to the surface of the electrode.

These results are in agreement with results of finite-element simulations confirming that, for short diffusion distances and high scan rates, the geometry of the electrode (cylindrical or hemispherical, depending on whether the shaft or the head of the pin forms an interface with the solution of analyte) does not influence the process. Thus, under our experimental conditions, the electrochemical cells fabricated using pin electrodes and either thread or R^F paper can reproduce the classical diffusion-limited electrochemical processes reported in EμPADs incorporating screen-printed electrodes.

Applications in clinical diagnostics: analysis of L-lactate in human serum

We evaluated the feasibility of using R^F paper-based and thread-based devices to measure the concentration of a clinically relevant analyte, L-lactate, in human serum. The range of L-lactate concentrations relevant for diagnosis is between 0.5 and 15–20 mM in serum.

We used chronoamperometry to perform this demonstration of principle because it is a simple and frequently used technique that provides a quantitative result. Cyclic voltammetry (CV) is less useful for accurate quantitation of electroactive species than chronoamperometric or pulse voltammetric techniques, because the correction for the capacitive current in CV is typically ambiguous.[49] Chronoamperometry measures current as a function of time at constant applied voltages, and starts with a large capacitive current that decays within the first few seconds. Faradaic current, which is proportional to the concentration of the analyte, becomes dominant, and decays according to the Cottrell equation (eq 1), where n is the number of electrons, F is Faraday's constant, A is the area of

the electrode, D is the diffusion coefficient of analyte, C is the concentration of analyte, and t is time.

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad (1)$$

In the lactate assay, potassium ferricyanide, $K_3[Fe(CN)_6]$, served as a mediator (eq 2-4):

$$\text{Lactate} + 2[Fe(CN)_6]^{3-} \xrightarrow{\text{Lactate oxidase}} \text{Pyruvate} + 2[Fe(CN)_6]^{4-} \quad (2)$$

$$2[Fe(CN)_6]^{4-} \xrightarrow{\text{Anode}} 2[Fe(CN)_6]^{3-} + 2e^- \quad (3)$$

$$2[Fe(CN)_6]^{3-} + 2e^- \xrightarrow{\text{Cathode}} 2[Fe(CN)_6]^{4-} \quad (4)$$

For each mole of lactate that is oxidized, two moles of $[Fe(CN)_6]^{3-}$ are reduced to $[Fe(CN)_6]^{4-}$; the latter can be quantified using chronoamperometry at an applied voltage of 0.4 V *vs.* a stainless-steel quasi-reference electrode. **Figure 4** shows the calibration curves for the measurement of L-lactate, for values between 1.1 mM (the value initially present in the serum) and 20 mM (with additional lactate spiked in the serum). The sensitivity is 0.08 μA mM^{-1} for the R^F paper- and 0.06 μA mM^{-1} for the thread-based device.

Approaches to multiplexing: Electrochemical 96 well plate.

We prepared a 96-well plate capable of carrying out parallel analyses of different analytes, using embossed omniphobic R^F paper as a substrate, and pins as electrodes. **Figure 5** shows that different wells can be used to perform independent analyses—cyclic voltammetry for the analysis of solutions of $FcCO_2H$ and hydroquinone, respectively.

Approaches to multiplexing: Thread-based arrays of pin electrodes

We produced linear arrays of electrodes (carbon-coated stainless steel pins as working electrodes, and

stainless steel pins as either counter or quasi-reference electrodes) that form interfaces with the liquid wicking along the same thread. The electrochemical cells within the thread-based arrays can be either linked or independent, such that each cell in a multiplex device can be used to perform, in rapid succession or simultaneously, independent measurements for one or several solutions of analyte along the same thread.

Figure 6 shows chronoamperograms for the same solution of analyte, recorded, in succession, using each of the seven WEs positioned along a single thread. In each measurement, the two adjacent stainless steel pins served as CE and RE, such as each two successive cells share one stainless steel pin that serves as a counter electrode in the former and as reference electrode in the latter.

By introducing hydrophobic barriers along the thread, we can form independent electrochemical cells capable of performing different analyses along the same thread. **Figure 7** shows square-wave voltammograms recorded with each of the three electrochemical cells along a single thread, for three solutions with different concentrations of analyte: 10 μM $FcCO_2H$ in PBS, pH 7.6; buffer only, PBS, pH 7.6; and 100 μM $FcCO_2H$ in PBS, pH 7.6. There is no observable interference between neighboring cells.

Conclusion

One unmet need in the development of low-cost electroanalytical devices is a method to assemble and reconfigure devices "on-the fly", to meet the needs of specific applications and settings. The strategy we describe in this paper is based on electrodes that are by themselves nearly as ubiquitous, portable, inexpensive, and easily storable as are paper and thread. The combination of stainless-steel pins—untreated or coated with a thin layer of carbon ink—and embossed omniphobic R^F paper or cotton thread, provides the basis for the fabrication of simple, versatile and low-cost electroanalytical devices.

Like the familiar screen printed EμPADs, these devices are inexpensive and lightweight, exhibit diffusion-controlled electrochemical behaviours, and can be used with biological samples. With further development, the paper and thread-based devices fabricated using this method have the potential to provide new functional options in clinical diagnostics, environmental monitoring, and microfluidic and electronic systems.

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The supporting information is available free of charge via the Internet at http://pubs.acs.org/ or from the website of the Whitesides group (http://gmwgroup.harvard.edu/pubs).

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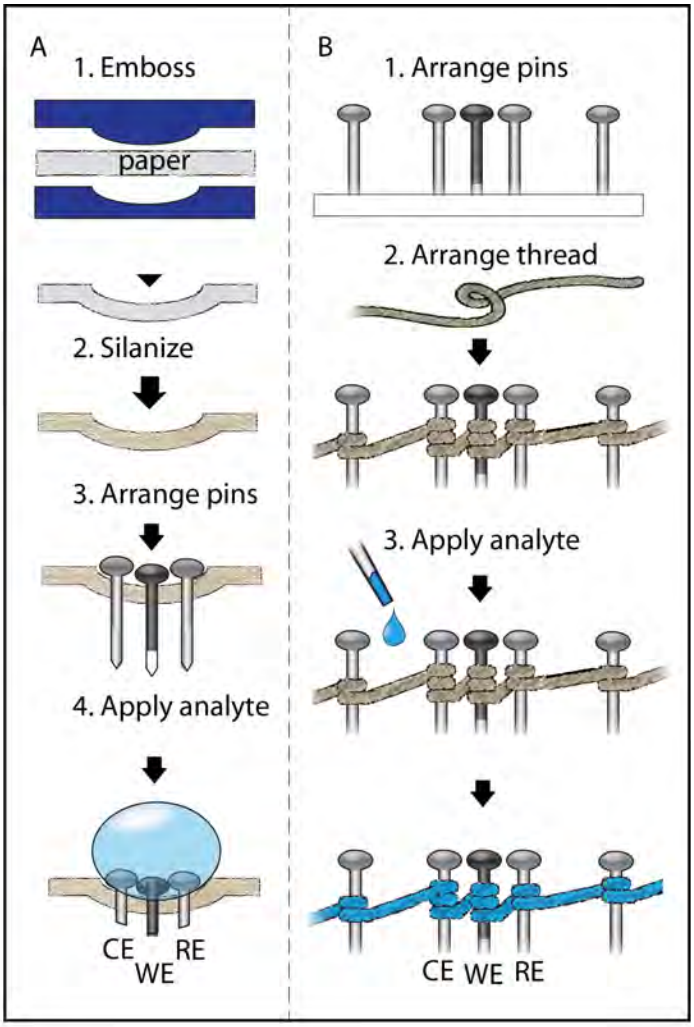
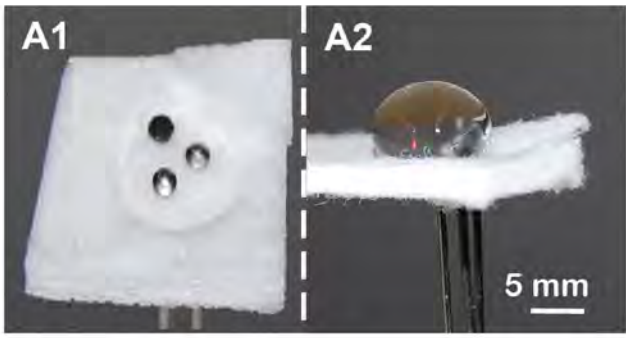


Figure 1. A) Schematic representation of the process used for the fabrication of electrochemical cells in embossed omniphobic R^F paper. B) Schematic representation of the process used for the fabrication of an electrochemical cell with cotton thread. In both cases we use stainless steel pins as reference and counter electrodes (RE and CE), and a stainless steel pin coated with a graphite and carbon nanotube ink as working electrode (WE).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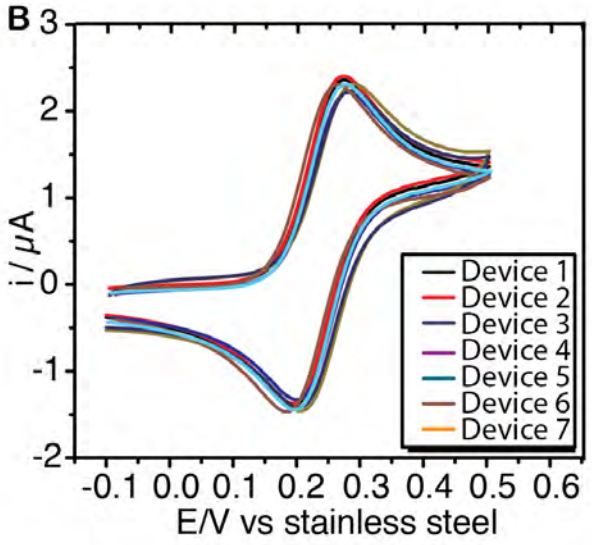
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E/V vs stainless steel
Device 1
Device 2
Device 3
Device 4
Device 5
Device 6
Device 7


C
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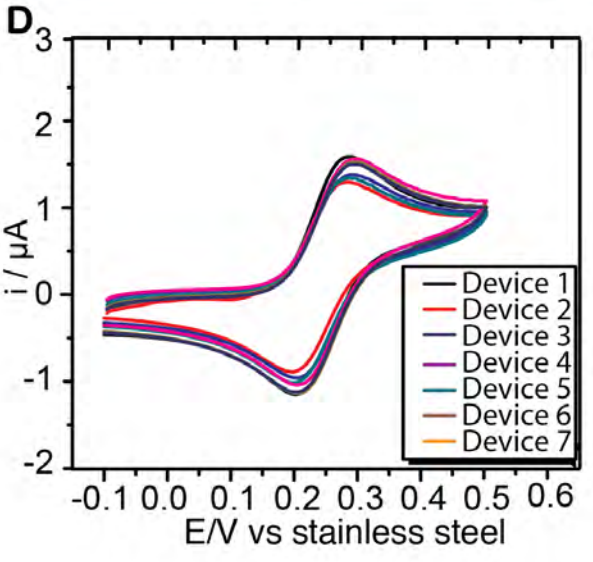
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0
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i / μA
-0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6
E/V vs stainless steel
Device 1
Device 2
Device 3
Device 4
Device 5
Device 6
Device 7

Figure 2. (A1, A2) photographs of an electrochemical cell fabricated using embossed omniphobic R^F paper and stainless steel pins as reference and counter electrodes (RE and CE), and a stainless steel pin coated with a graphite and carbon nanotube ink as working electrode (WE). The electrodes are placed at a distance of ~ 0.1 inch (2.53 mm) away from one another. (C) Photograph of an electrochemical cell fabricated using cotton thread and stainless steel pins as reference and counter electrodes, and a stainless steel pin coated with a graphite and carbon nanotube ink as working electrode. The electrodes are placed at a distance of ~ 0.1 inch (2.53 mm) away from one another. Cyclic voltammograms recorded in a 500 μM solution of $FcCO_2H$ in 1x PBS, pH 7.6 at a scan rate of 100 mVs^{-1} using: (B) seven independent embossed omniphobic R^F paper devices, and (D) seven independent thread-and-pin arrays.

Figure 3: Cyclic voltammograms of 500 μM $FcCO_2H$ in 1x PBS (pH 7.6) in electrochemical cells fabricated using (A) embossed omniphobic R^F paper and (B) thread, at various scan rates ascending along y-axis: 10, 20, 50, 100, 200, 300 mV s^{-1}. (C) The plot of anodic and cathodic peak currents *vs.* the square root of the scan rate ($\nu^{1/2}$). CV experiments conducted on an omniphobic R^F paper device (up-pointing triangle ▲: anodic peak current, down-pointing triangle ▼: cathodic peak current) and in a thread device (circles ○ : anodic peak current, squares □ : cathodic peak current). The dashed lines represent linear regressions with equations:

$y_1 = 6\,x\ \mu A\,V^{-1/2}s^{1/2} + 0.1\,\mu A$ [$R^2 = 0.991$], $y_2 = 5\,x\ \mu A\,V^{-1/2}s^{1/2} - 0.05\,\mu A$ [$R^2 = 0.986$],

$y_3 = -4x\ \mu A\,V^{-1/2}s^{1/2} + 0.05\,\mu A$ [$R^2 = 0.989$], $y_3 = -6x\ \mu A\,V^{-1/2}s^{1/2} - 0.05\,\mu A$ [$R^2 = 0.992$].

Error bars correspond to standard deviation of measurements performed using seven independent devices.

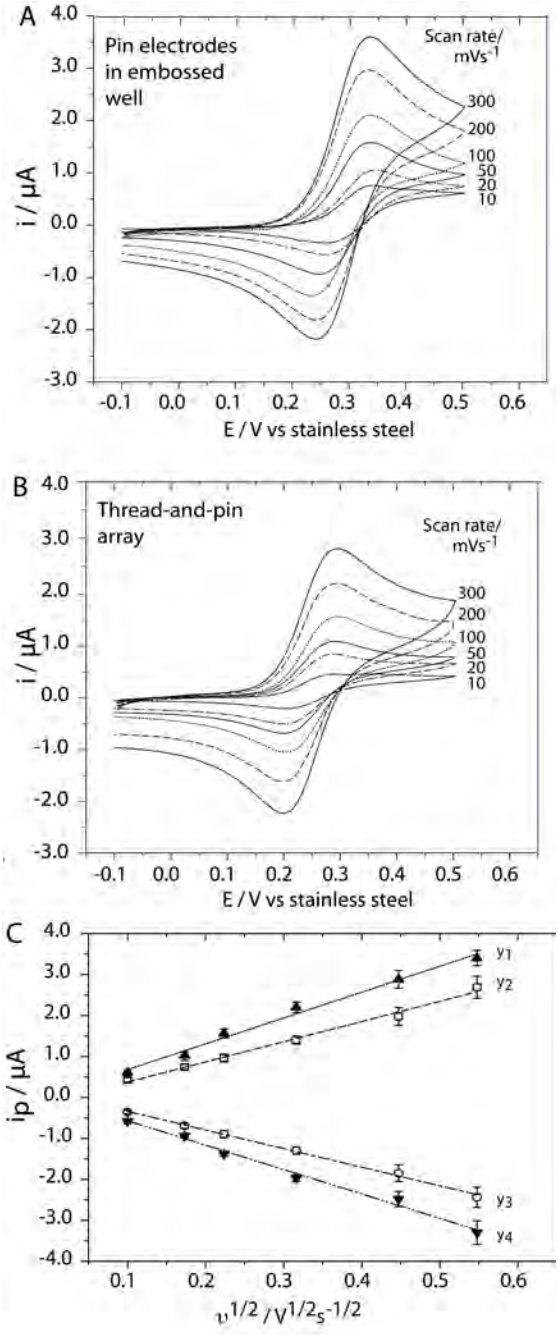

A
Pin electrodes
in embossed
well
Scan rate/
mVs-1
300
200
100
50
20
10
i / µA
E / V vs stainless steel
B
Thread-and-pin
array
Scan rate/
mVs-1
300
200
100
50
20
10
i / µA
E / V vs stainless steel
C
y1
y2
y3
y4
ip / µA
υ1/2 /V1/2s-1/2

Figure 4: (A) Chronoamperograms recorded on thread for the mixture of the enzymatic assay for the determination of lactate, at concentrations between 1.1-20 mM. The chronoamperograms were recorded at 0.4 V *versus* a stainless steel quasi-reference pin electrode. (B) The calibration plots of the currents recorded after 40s as a function of concentration of lactate on thread-and-pins arrays and in wells embossed in omniphobic R^F paper. The dashed black line represents a fit to the equation: $y=0.08x +1.13$ ($R^2= 0.994$) whereas the red line represents a fit to the equation: $y=0.06x +0.91$ ($R^2= 0.987$), for concentrations of lactate between 1.1-20 mM. Error bars correspond to standard deviation of measurements performed using 7 independent devices.

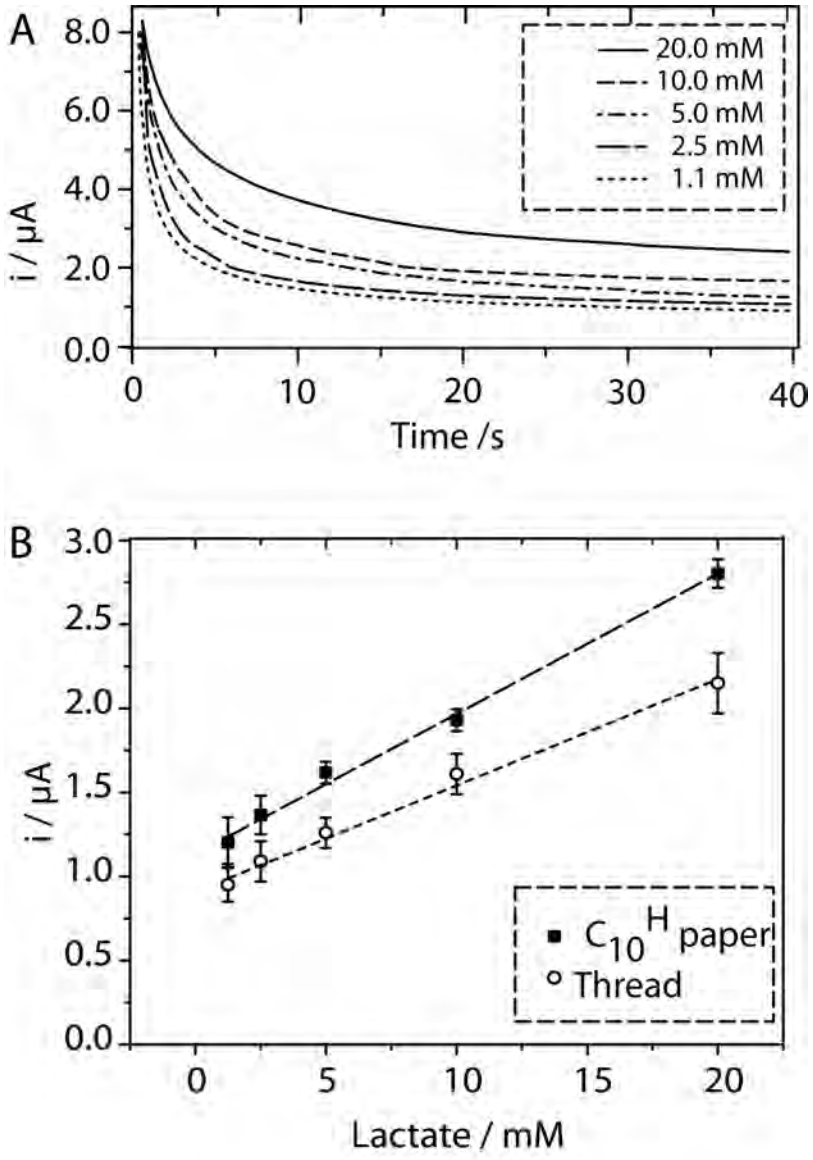

A
8.0
6.0
4.0
2.0
0.0
i / µA
0
10
20
30
40
Time /s
20.0 mM
10.0 mM
5.0 mM
2.5 mM
1.1 mM
B
3.0
2.5
2.0
1.5
1.0
0.5
0.0
i / µA
0
5
10
15
20
Lactate / mM
C10H paper
Thread

Figure 5: Photography of a 96 well plate fabricated using embossed omniphobic R^F paper and pin electrodes. (A) before and (B) after 50 µL drops of an aqueous solution are added to each well. (C) Independent voltammograms recorded in different wells (a1 and a2) of the plate: a 100 µM solution of hydroquinone (HQ), and a 250 µM solution of FCA, both in 1x PBS, pH 7.6, recorded at a scan rate of 100 mV s^{-1}; the presence of a different analyte in a neighboring well does not interfere with measurements.

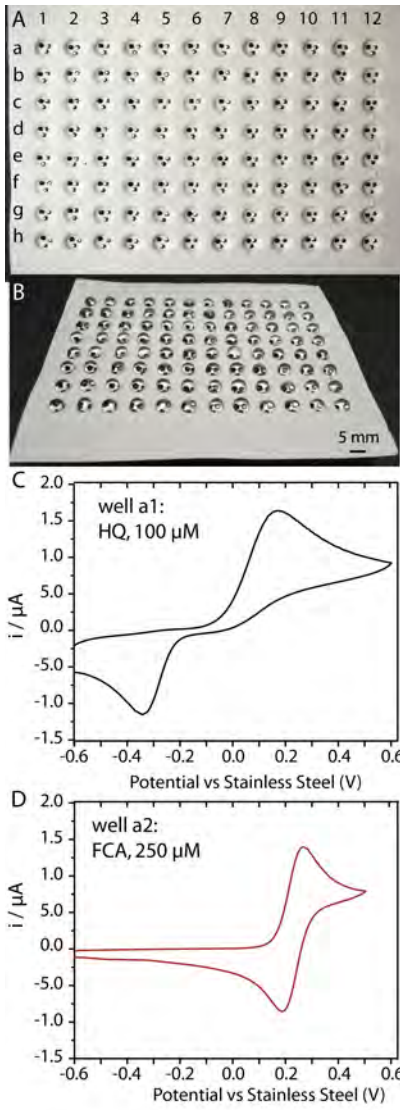

A
1 2 3 4 5 6 7 8 9 10 11 12
a
b
c
d
e
f
g
h
B
5 mm
C
well a1:
HQ, 100 µM
i / µA
2.0
1.5
1.0
5.0
0.0
-5.0
-1.0
-1.5
-0.6 -0.4 -0.2 0.0 0.2 0.4
Potential vs Stainless Steel (V)
D
well a2:
FCA, 250 µM
i / µA
2.0
1.5
1.0
5.0
0.0
-5.0
-1.0
-1.5
-0.6 -0.4 -0.2 0.0 0.2 0.4
Potential vs Stainless Steel (V)

Figure 6: (A) Schematic and (B) photograph of a device comprising multiple alternating stainless steel pins and carbon-coated stainless steel pins and a single thread that forms three helical turns around each pin. The device can be used for multiple measurements (in rapid succession) of the same analyte on thread. (B) Chronoamperograms at 0.4 V recorded with each of the seven cells along the thread, using in each case the two adjacent stainless steel pins as CE and RE. Solution: 100 mM potassium ferricyanide in 1x PBS pH 7.6.

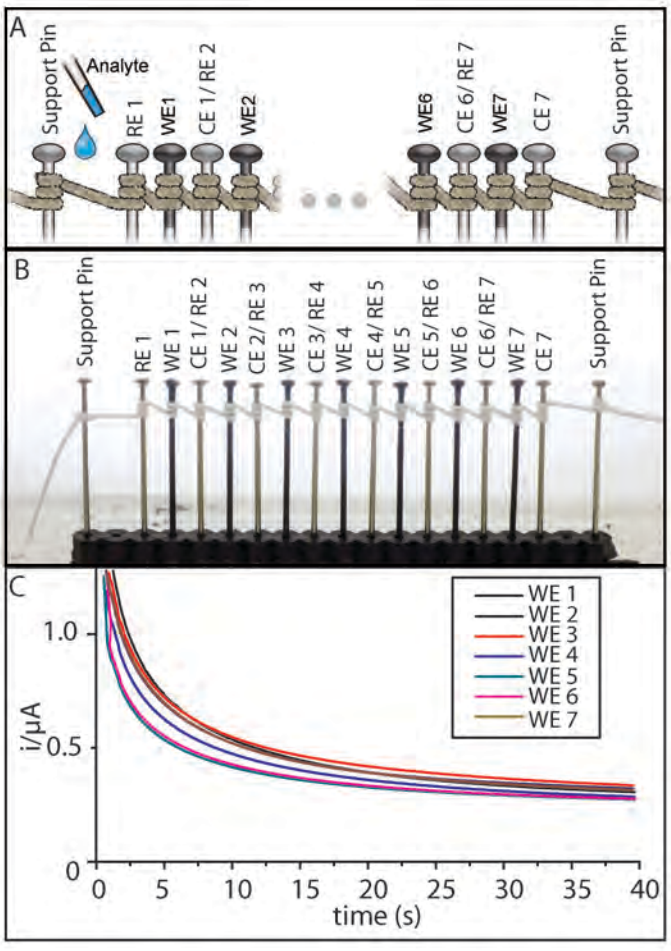
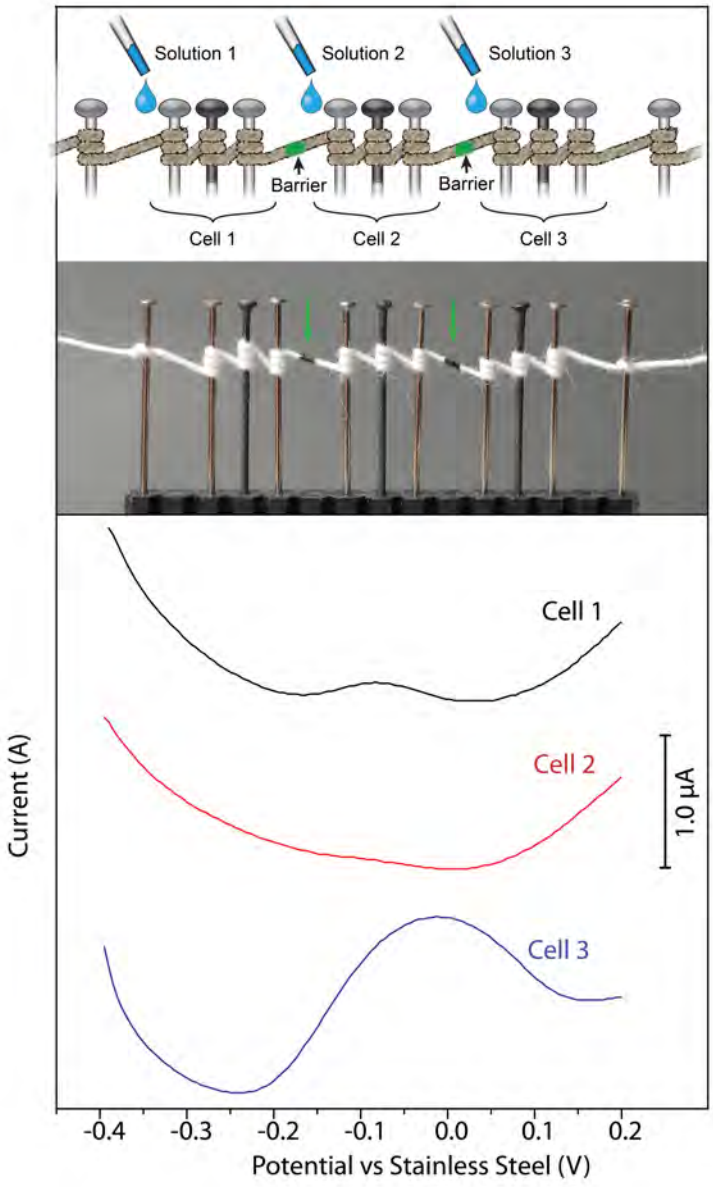


Figure 7: (A) A schematic and (B) a photograph of a device comprising three distinct electrochemical cells formed from a single thread; arrows indicate the presence of a small amount of polymer (cyanoacrylate) that serves as a boundary between consecutive cells. The device can be used for measurement of three different analytes (in rapid succession or simultaneously) (C) Square-wave voltammograms recorded with each electrochemical cell, for: (1) left: 10 μM FCA in PBS, pH 7.6; (2) middle: buffer only, PBS, pH 7.6; (3) right: 100 μM FCA in PBS, pH 7.6. The center cell, where the thread is wet with buffer only, has no observable interference with neighboring cells.


Solution 1
Solution 2
Solution 3
Barrier
Barrier
Cell 1
Cell 2
Cell 3
Cell 1
Cell 2
Cell 3
1.0 µA
Current (A)
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
Potential vs Stainless Steel (V)