

Supporting Information

Integrating Electronics and Microfluidics on Paper

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Background

In the integrated devices demonstrated to date, conductors and electrodes are printed on top of paper using a carbon or silver ink^[1]. These conductors are used as wires in electronics, or as electrodes for electrochemical applications. For example, we and others have demonstrated the integration of electronic and electroanalytical systems in paper by stencil printing of carbon and silver electrodes on top of the bare paper, for printed circuit boards^[2], and paper microfluidic systems. We have also shown stencil and ink-jet printing of carbon and silver inks on chemically modified hydrophobic paper – R^F paper – for electroanalysis^[3–5]. In other examples, Nie *et al.* printed a three-electrode system using a Ag/AgCl ink, and a carbon ink^[6], to build three layers on paper substrate, and then utilized a second layer of paper to carry a fluid on top of these three electrodes. They also prepared a “paper-based analytical device” where wax printing was used to create a fluidic path in paper. The carbon electrodes were stencil-printed on top of the wax-printed fluidic structure. The spontaneous wicking of liquid in paper carried the fluid to the edge of the printed carbon structures, where electrochemical processes occurred. Zhang *et al.* placed the working, counter, and reference electrodes on different layers of paper, and employed this device in electrochemiluminiscent analysis^[7]. Renault *et al.* designed “hollow channel devices”^[8,9], prepared by cutting channels in paper, and stacking these between wax printed hydrophobic layers to create all-paper hollow channels. Printing carbon inks on top of the paper, inside the hollow channel, allowed contact between liquid and the electrodes. Ge *et al.* designed a device that comprised four working electrodes surrounding the counter and reference electrodes. Folding one of them on the center created a complete electrochemical cell^[10].

Kinetics for Coulometric Glucose Assay

To understand the kinetics of the coulometry, we consider the following three relevant time constants: i) the maximum plausible diffusion time $t_{\text{diff_max}}$, which should be that of the passive diffusion of ferrocyanide ions across the electrode in the absence of capillary actions (*i.e.* 180 μm across the entire sheet of paper); ii) the minimum diffusion time $t_{\text{diff_min}}$, which occurs inside the pores of electrofluidic structures when they are filled; iii) the time for wicking t_{wick} across the sheet of paper. We estimated the diffusion times by using equation (2)

$$t = r^2 / 2D \quad (2)$$

We used a diffusion constant $D=5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for ferrocyanide^[11], and an average pore radius of $r=5 \mu\text{m}$ (based on data describing Whatman grade1 paper) to calculate $t_{\text{diff_min}} \sim 25 \text{ ms}$.

We used $r=180 \mu\text{m}$ to calculate $t_{\text{diff_max}} \sim 32 \text{ s}$. We estimated the time for wicking across the sheet of paper (assuming no viscous resistance), from the Washburn equation (3), where $L=180 \mu\text{m}$ is the length of wicking and K is a constant.

$$t_{\text{wick}} = KL^2 \quad (3)$$

We estimated the constant $K \sim 2.75 \times 10^5 \text{ sm}^{-2}$ (from previous experiments on Whatman paper^[12]), to calculate $t_{\text{wick}} \sim 10 \text{ ms}$.

Since the activity of GOx was 250 U/ml and 30 μl was employed, the maximum activity is 7.5 U per device. The sample volume added was 1.5 μl , so the number of moles of glucose that have to be converted is very small (0.03 μmol for the highest concentration $\sim 20 \text{ mM}$). If we assume that all the enzyme is active, accessible, well mixed (although convective mixing does not happen, diffusion distances are very short), and under optimal temperature/pH conditions, the conversion would take $0.03 \mu\text{mol} / 7.5 \mu\text{mol min}^{-1} = 0.004 \text{ min} = 0.24 \text{ s}$.

Figures

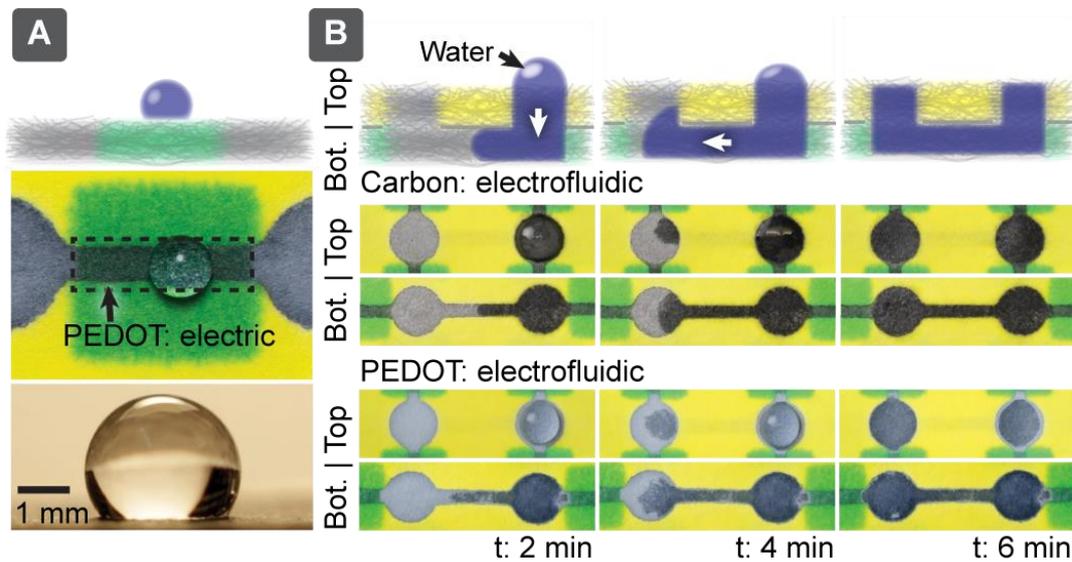


Figure S1 A) schematic diagram (top), and top (middle), and side (bottom) photos of a droplet of water on top of an electrical structure B) (top) Schematic diagram of water wicking through electrofluidic structure in two layers. Time laps photos showing spontaneous wicking of water through a two layer structures of MWNT (middle) and PEDOT electrofluidic structures (bottom).

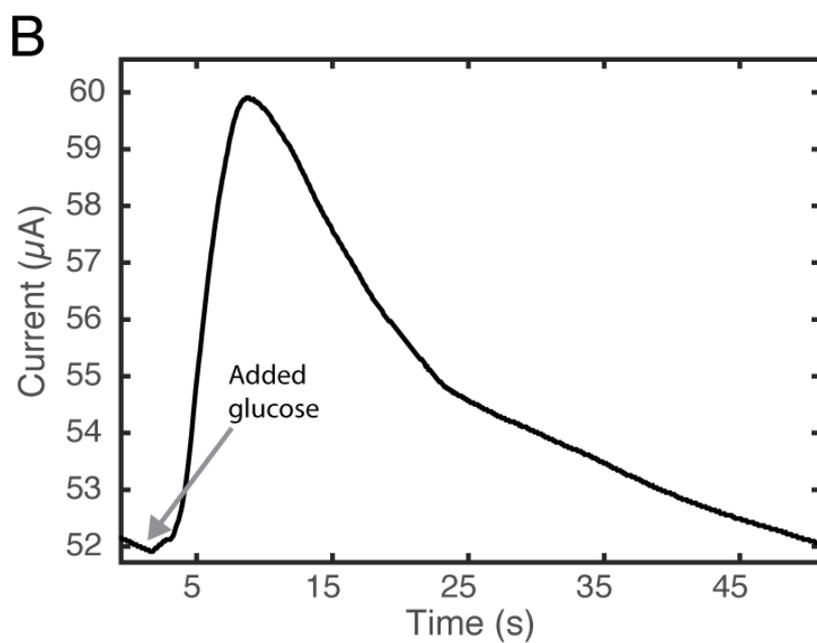
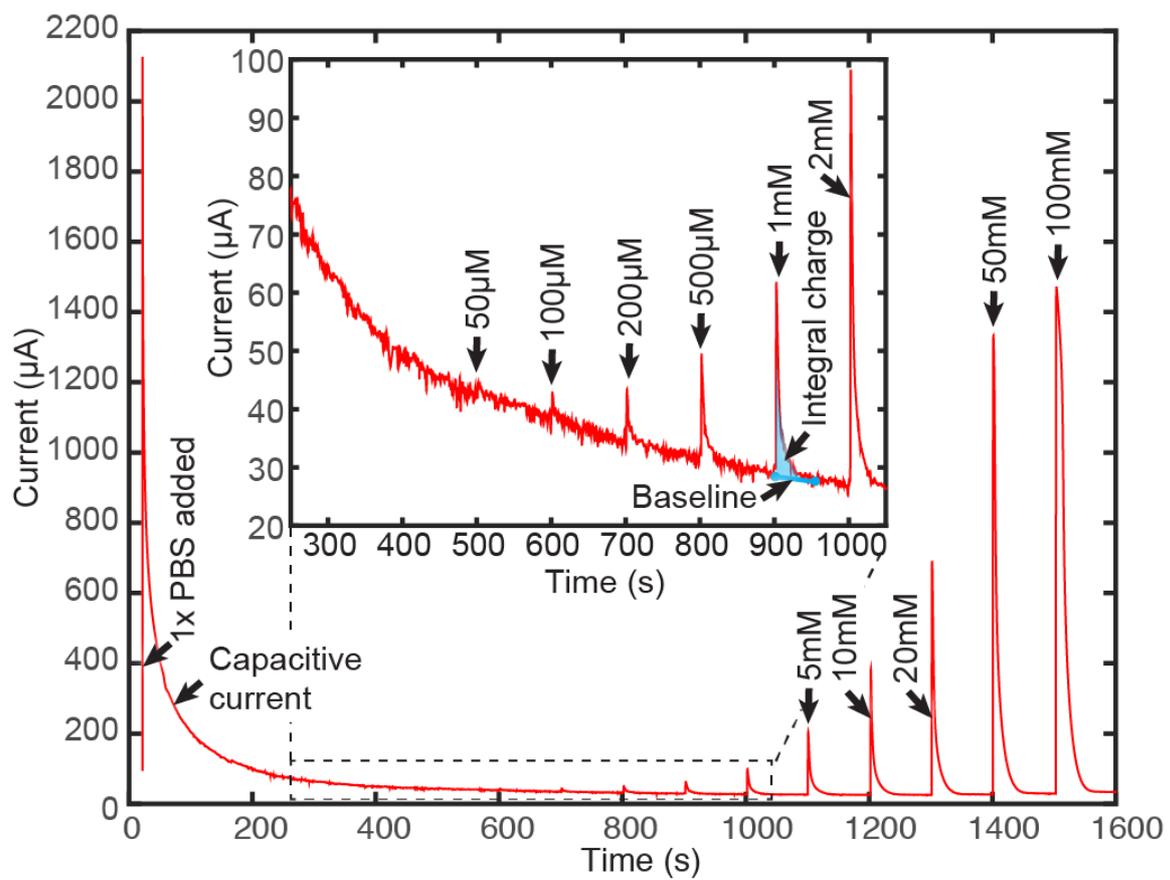


Figure S2. A) Potentiostatic amperometry (applied potential: +0.6V vs. Ag/AgCl) of a vertical flow device. At t=0 a solution of phosphate saline buffer 1XPBS was added to the device. Next, 2 μ L of ferrocyanide solutions was added in an increasing concentration (indicated by the numbers in the graph). **B)** Potentiostatic amperometry (applied potential: +0.6V vs. Ag/AgCl) of a vertical flow glucometer device. The device was preloaded with an enzyme and a mediator, at t=3 s, a glucose solution (1 mM, 1.5 μ L) was added to the device, and the current due to oxidation of ferrocyanide was recorded. The current reached a maximum at t=10 s, and decreased to a baseline as it was consumed in the measurement.

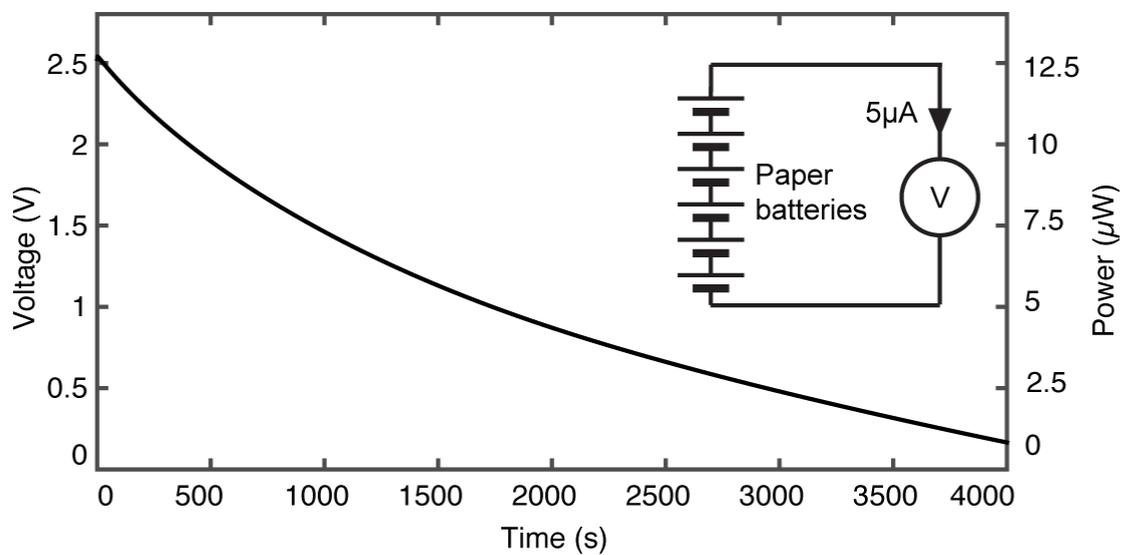


Figure S3. Discharge voltage/power measured using a constant current of $5\mu\text{A}$, across six parallel-connected paper batteries.

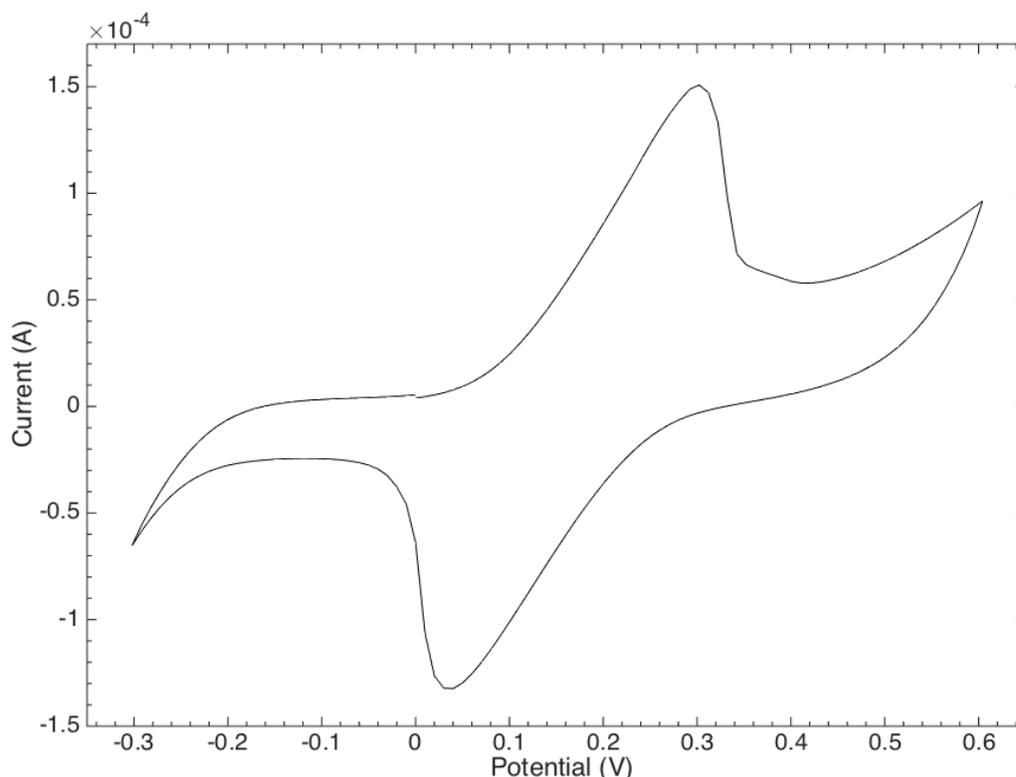


Figure S4. Cyclic voltammogram (5 mV/s) recorded on a solution of potassium ferrocyanide, (100-mM in 1xPBS). The large surface area of the electrodes, and the internal resistance of the cell requires that the sweep rate be slow. The reason that the difference between peak potentials is higher than 59 mV, may be due to a high cell resistance; This characteristic would also be compatible with the “tilted” shape of the cyclic voltammogram. The anodic peak potential however is ~0.3 V, which is in agreement with other data measured with conventional electrodes and with Ag/AgCl reference electrodes. The anodic and cathodic peak currents (i_{p_a} , i_{p_c}) are similar, with a calculated ratio i_{p_a}/i_{p_c} of 1.03; This value indicates almost complete reversibility.

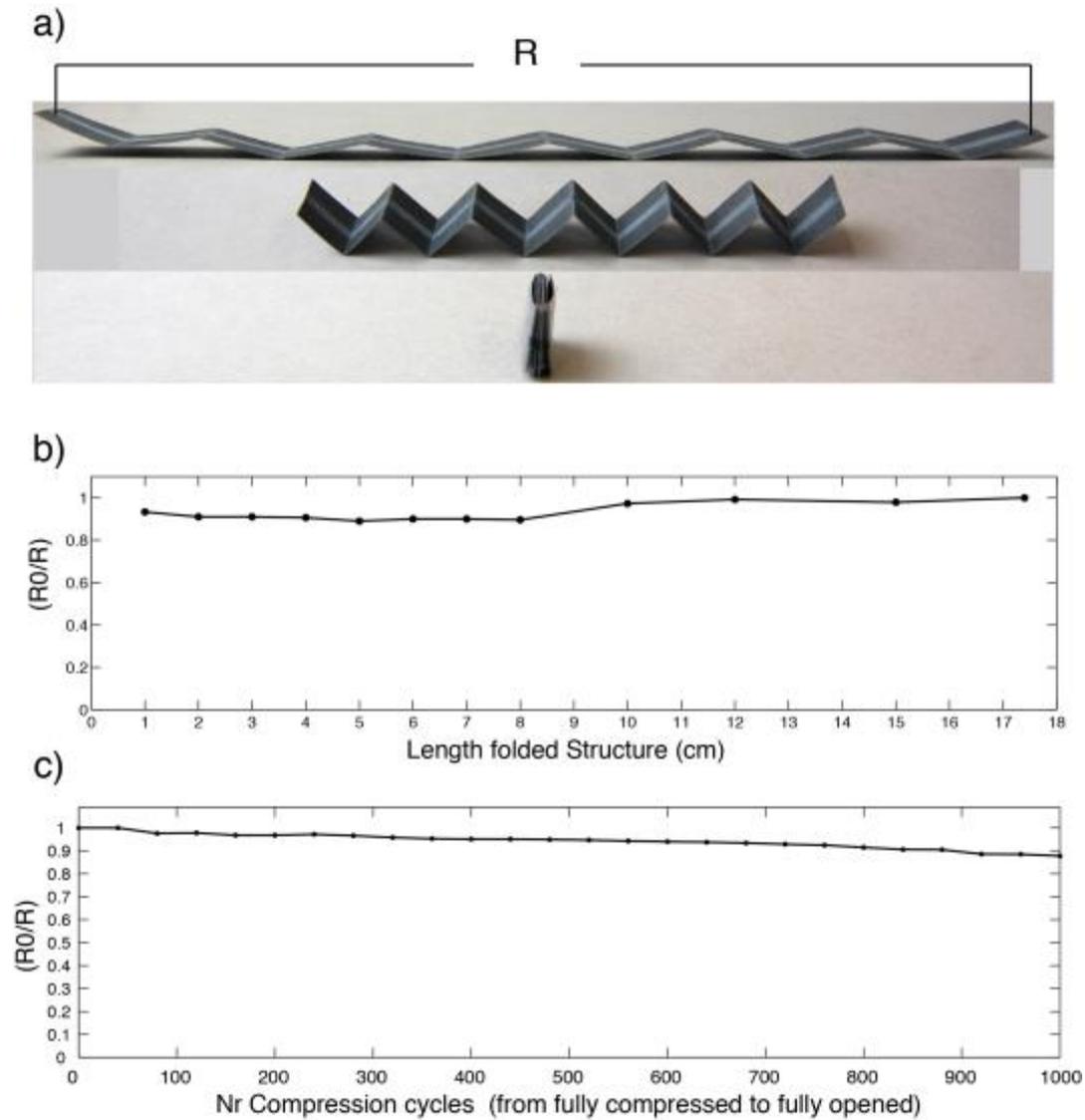


Figure S5. a) Photographs of an accordion shaped folded paper structure at different folding angles/total length.) b) Normalized resistance of the electrical wire (1mm wide, 18cm long), measured from one side of the folded paper to the other side, as a function of compressed length. c) Normalized resistance measured at the uncompressed state, as a function of number of cycles, where each cycle corresponds to a complete closing and opening of the folded structure (i.e. moving each crease from 180 to 0 degrees' angle).

References

- [1] E. J. Maxwell, A. D. Mazzeo, G. M. Whitesides, *MRS Bull.* **2013**, 38, 309.
- [2] A. C. Siegel, S. T. Phillips, M. D. Dickey, N. Lu, Z. Suo, G. M. Whitesides, *Adv. Funct. Mater.* **2010**, 20, 28.
- [3] A. C. Glavan, R. V. Martinez, A. B. Subramaniam, H. J. Yoon, R. M. D. Nunes, H. Lange, M. M. Thuo, G. M. Whitesides, *Adv. Funct. Mater.* **2014**, 24, 60.
- [4] A. C. Glavan, D. C. Christodouleas, B. Mosadegh, H. D. Yu, B. S. Smith, J. Lessing, M. T. Ferna, G. M. Whitesides, *Anal. Chem.* **2014**, 86, 11999.
- [5] J. Lessing, A. C. Glavan, S. B. Walker, C. Keplinger, J. a Lewis, G. M. Whitesides, *Adv. Mater.* **2014**, 26, 4677.
- [6] Z. Nie, C. a Nijhuis, J. Gong, X. Chen, A. Kumachev, A. W. Martinez, M. Narovlyansky, G. M. Whitesides, *Lab Chip* **2010**, 10, 477.
- [7] M. Zhang, L. Ge, S. Ge, M. Yan, J. Yu, J. Huang, S. Liu, *Biosens. Bioelectron.* **2013**, 41, 544.
- [8] C. Renault, M. J. Anderson, R. M. Crooks, *J. Am. Chem. Soc.* **2014**, 136, 4616.
- [9] C. Renault, X. Li, S. E. Fosdick, R. M. Crooks, *Anal. Chem.* **2013**, 85, 7976.
- [10] L. Ge, S. Wang, J. Yu, N. Li, S. Ge, M. Yan, *Adv. Funct. Mater.* **2013**, 23, 3115.
- [11] S. J. Konopka, B. McDuffie, *Anal. Chem.* **1970**, 42, 1741.
- [12] K. M. Schilling, A. L. Lepore, J. A. Kurian, A. W. Martinez, *Anal. Chem.* **2012**, 84, 1579.