Electrochemical sensing in paper-based microfluidic devices

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Supplementary Information

Geometry of the hydrodynamic μPED for the analysis of metals

The dimension of the blotting paper was 2.5 cm by 2.5 cm. The dimension of the paper channel was approximately 3.5 cm in length and 4 mm in width. The arrangement of electrodes is shown in Figure S1. A typical working and counter electrode had dimensions of 8 mm in length and 6 mm in width, and a typical reference electrode had dimensions of 1.0 cm in length and 3 mm in width. WE: working electrode; CE: counter electrode; RE: reference electrode.

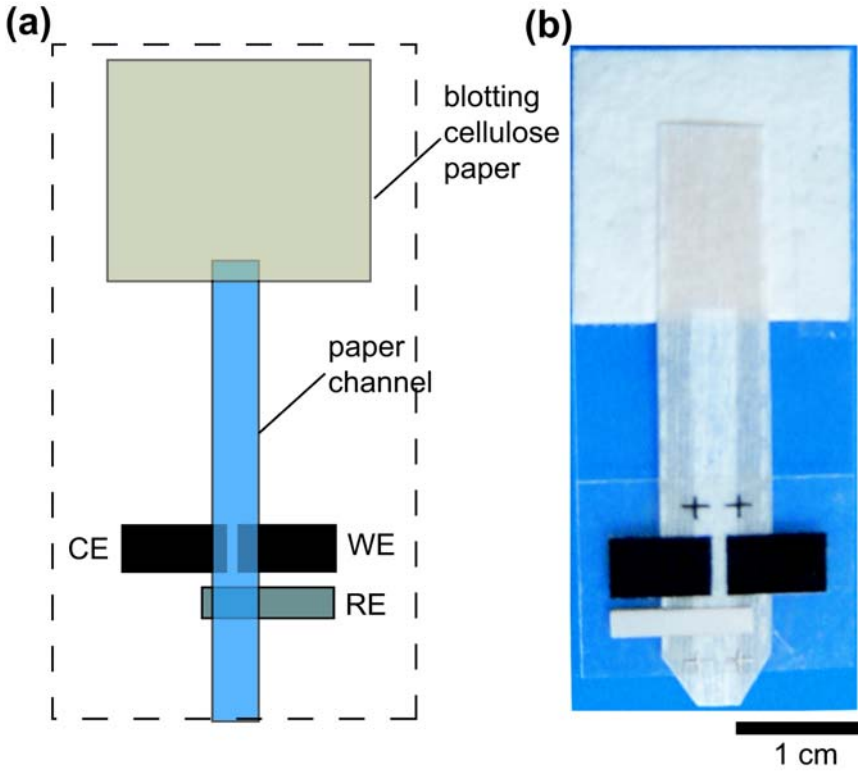

Figure S1. Schematic (a) and photography (b) of the hydrodynamic μPED for analysis of heavy metal ions.

Artificial urine

An artificial urine solution was prepared according to the recipe reported by Brooks and Keevil[1]. The artificial urine solution contained 1.1 mM lactic acid, 2.0 mM citric acid, 25 mM sodium bicarbonate, 170 mM urea, 2.5 mM calcium chloride, 90 mM sodium chloride, 2.0 mM magnesium sulfate, 10 mM sodium sulfate, 7.0 mM potassium dihydrogen phosphate, 7.0 mM dipotassium hydrogen phosphate, and 25 mM ammonium chloride and all mixed in Millipore-purified water. The pH of the solution was adjusted to 6.0 by the addition of 1.0 M hydrochloric acid.

Estimation of diffusion coefficient

We calculated the diffusion coefficient of ferrocene carboxylic acid based on the Randles-Sevcik Equation (eq 1, 2) where *n* is the number of electrons appearing in half-reaction for the redox couple, ν is the rate at which the potential is swept, *F* is Faraday's constant, *A* is the electrode area (cm^2), *D* is the diffusion coefficient of the analyte, and *K* is the slope of the $i_p \sim \nu^{1/2}$ plot.

$$i_p = (2.69 \times 10^5) n^{2/3} A D^{1/2} C \nu^{1/2} \qquad (1)$$

$$i_p = K \nu^{1/2} \qquad (2)$$

Combining equation (1) and (2) yields eq 3.

$$D = \left(\frac{K}{(2.69 \times 10^5) n^{2/3} A C} \right)^2 \qquad (3)$$

We plotted i_p as a function of $\nu^{1/2}$ (Figure 2b), obtained the *K* value from the plot, and calculated the diffusion coefficient of ferrocene carboxylic acid based on eq 3.

Cottrell plot for the analysis of glucose

We plotted the current as a function of $t^{-1/2}$ for glucose solutions over a range of concentrations from 0 to 22.2 mM. The representative curves (Figure S2) indicate that two seconds ($t^{-1/2}$ = 0.707 $s^{-1/2}$) after the potential step the current becomes mass transport limited.

Figure S2.

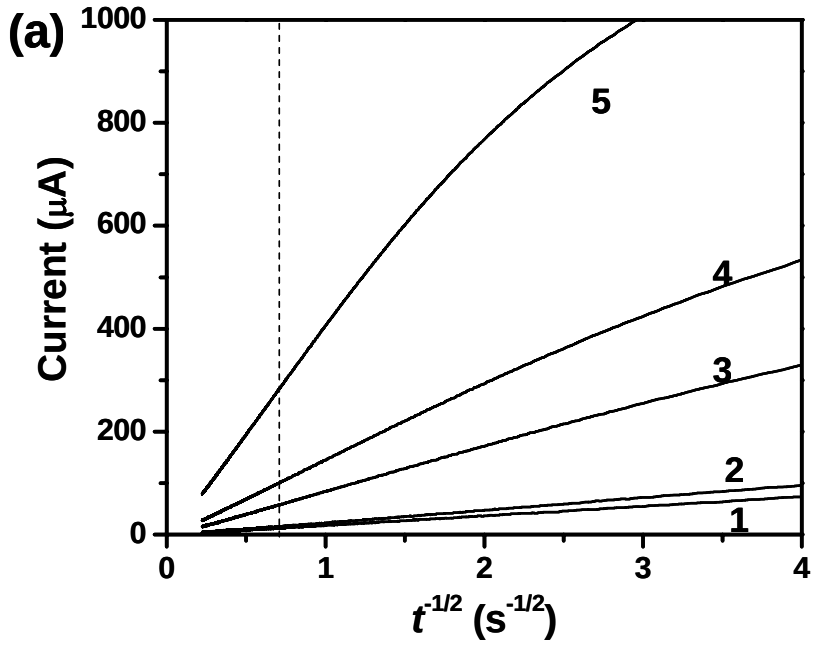

Figure S2. (a) Representative Cottrell plot for the analysis of glucose at +500 mV potential step (*vs* a carbon pseudo-reference electrode) for glucose concentrations: 0 (1), 0.22 (2), 2.78 (3), 5.56 (4), and 16.67 (5). The vertically dashed line positions $t^{-1/2}$ = 0.707 $s^{-1/2}$.

Chronoamperometric analysis of glucose in blood plasma and bovine blood

We also demonstrated the analysis of glucose in an artificial blood plasma solution and whole bovine blood (Rockland, Bovine/calf Blood) (Figure S3). The artificial blood plasma solution was prepared according to the recipe reported previously.[2]

Figure S3.

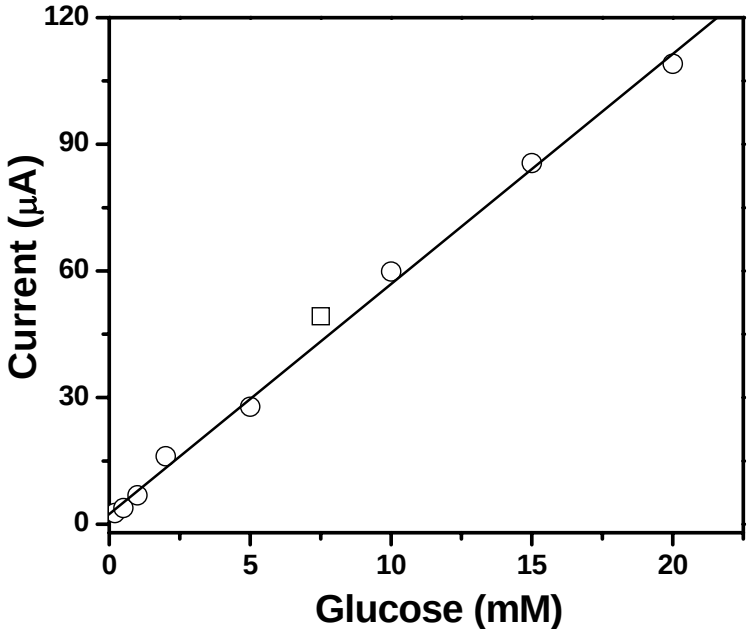

Figure S3. Calibration plots of current as a function of the concentration of glucose in blood plasma for the analysis of glucose in the μPEDs. Experimental conditions are the same as described in Figure 3. The point (□) indicates a measurement of an unknown sample with 7.5 mM glucose in bovine blood. The solid line represents a linear fit to (○) with regression equation: y= 2.4+ 5.5x (R^2 = 0.997, n=3).

Performance of carbon electrodes in a μPED (*vs* carbon pseudo-reference electrode)

Figure S4.

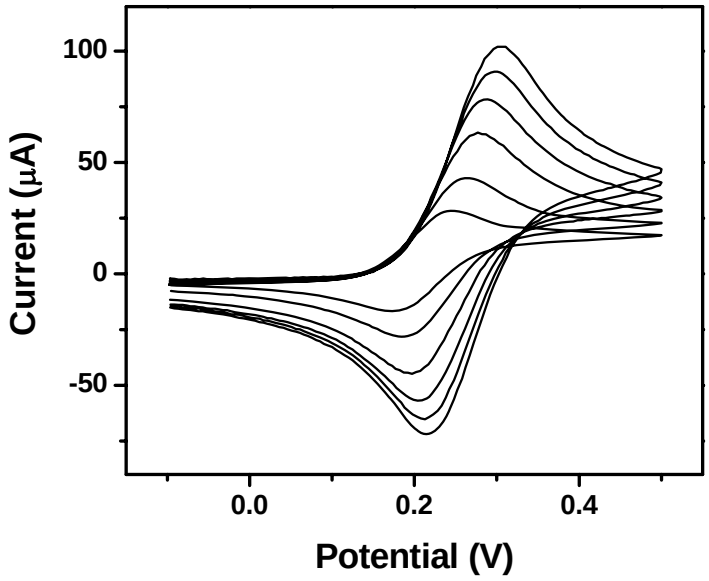

Figure S4. Cyclic voltammograms of 2.0 mM ferrocene carboxylic acid in 0.5 M KCl aqueous solution (pH=7.0) in a μPED at various scanning rates (ascending along y-axis): 50, 100, 200, 300, 400, and 500 mV/s. We used a 4 mm by 4 mm carbon-printed electrode as the working electrode, and a printed carbon electrode as the pseudo-reference electrode.

Performance of carbon electrodes in bulk solution (*vs* Ag/AgCl electrode)

Figure S5.

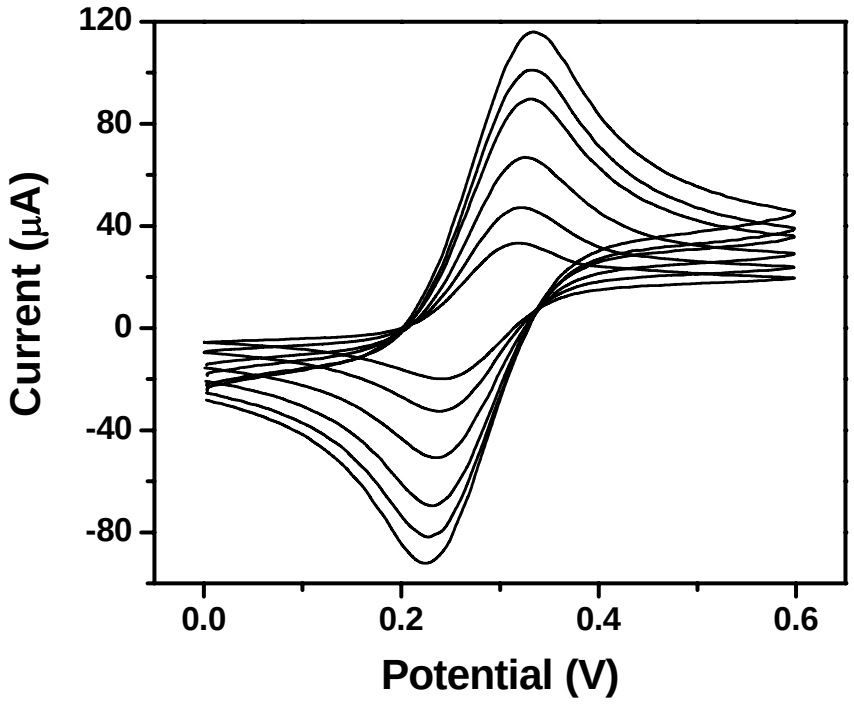

Figure S5. Cyclic voltammograms of a bulk solution of 2.0 mM ferrocene carboxylic acid with 0.5 M KCl at varying scan rate (ascending along y-axis): 50, 100, 200, 300, 400, and 500 mV/s. We used a carbon-printed electrode as the working electrode, and a printed Ag/AgCl electrode as the reference electrode. The three electrodes placed side-by-side on a plastic film were immersed in the solution (approximately with an area of 4 mm by 4 mm working electrode in the solution).

Performance of gold electrodes in the paper-based devices

Figure S6 shows that the electrochemical reactions are reversible on Au electrodes in the μPEDs. However, considering the robustness and the price of the device (which is tightly relevant to its potential commercialization in the future), we chose carbon-based electrodes for the fabrication of the proof-of-concept devices presented in the article.

Figure S6.

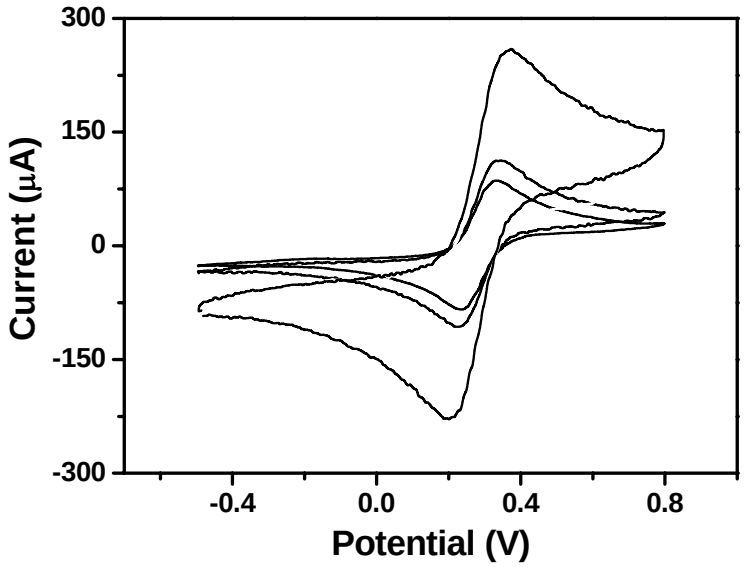

Figure S6. Cyclic voltammograms of 8.0 mM ferricyanide in 1.0 M KCl aqueous solution on a paper device at varying scan rates (ascending along y-axis): 50, 100, 500, and 1000 mV/s. A paper microfluidic channel was sandwiched between two gold strips, which were served as working and counter electrodes. The contact area between working electrode and paper channel was about 16 mm^2. An Ag/AgCl electrode was used as the reference electrode.

Chronoamperometric analysis of glucose in bulk solution

Figure S7.

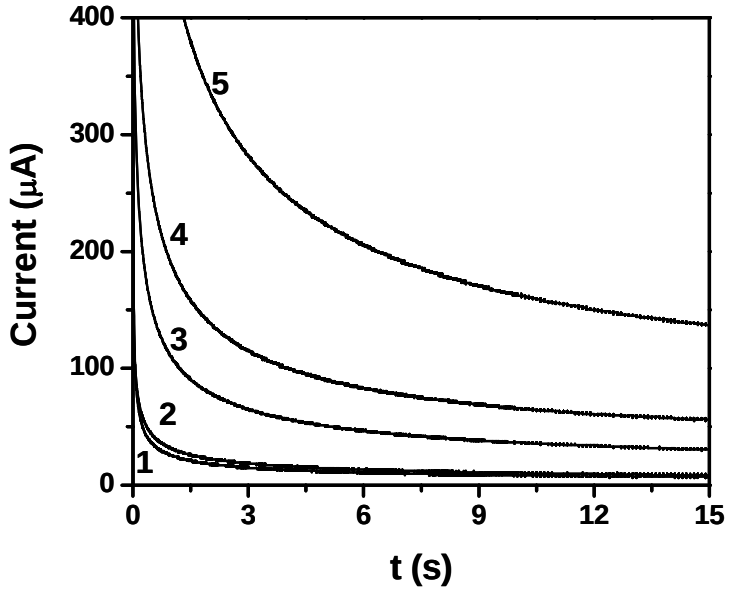

Figure S7. Representative chronoamperometric curves at +500 mV step potential (*vs* a carbon pseudo-reference electrode) for glucose concentrations (mM): 0 (1), 0.22 (2), 2.78 (3), 5.56 (4), and 16.67 (5) in the bulk solution. We used three carbon electrodes as the working, counter, and pseudo-reference electrodes, respectively. The working electrodes had a surface area of 16 mm^2 in contact with the solution.

Reference

1. T. Brooks and C. W. Keevil, *Letters in Applied Microbiology*, 1997, **24**, 203-206.
2. L. Liu, C. L. Qiu, Q. Chen and S. M. Zhang, *J. Alloys Compd.*, 2006, **425**, 268-273.