

Print-and-Peel Fabrication of Microelectrodes

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We describe a facile and expedient approach for the fabrication of arrays of microelectrodes on smooth substrates. A sequence of print-and-peel procedures allowed for the microfabrication of capacitance microsensors using office equipment and relatively simple wet chemistry. Microfluidic assemblies with reversibly adhered elastomer components allowed for the transfer of patterns of metallic silver, deposited via Tollens' reaction, onto the substrate surfaces. Electroplating of the silver patterns produced an array of micrometer-thick copper electrodes. Capacitance sensors were assembled by placing nonlithographically fabricated flow chambers over the microelectrode arrays. Triangular-waveform current-voltage (I/V) measurements showed a linear correlation between the capacitance of the print-and-peel fabricated devices and the dielectric constant of the samples injected into their flow chambers.

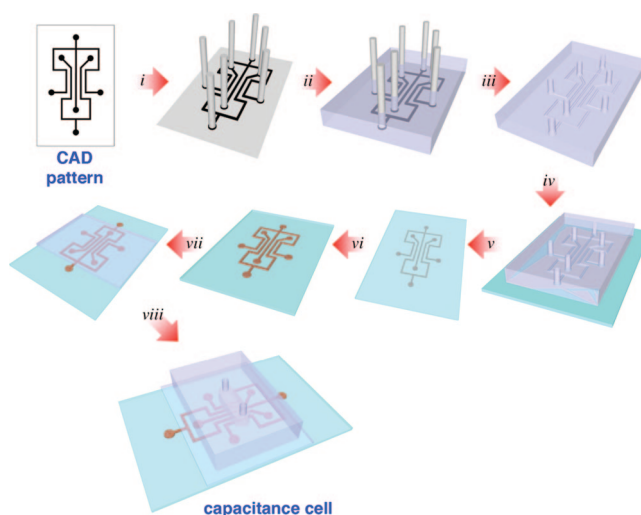
This letter describes a facile approach for fabrication of arrays of microelectrodes on smooth substrates. Microfluidic assemblies with reversibly adhered components allow for the transfer of patterns of conducting materials onto the substrate surface. Using this microfabrication approach, we prepared capacitance sensors and characterized their performance.

Nonlithographic, or print-and-peel (PAP), fabrication allows for facile and expedient prototyping of microfluidic devices.^{1–3} Unlike other fabrication techniques, PAP consists of direct printing of the masters, using regular office equipment, and attaching 3D elements to their surfaces.¹ Due to its simplicity and low cost, PAP offers valuable venues for research and development in an environment where microfabrication facilities are not readily available.

Impedance spectroscopy (IS) is an invaluable analytical tool for investigation of a broad variety of systems, such as complex liquids and biological samples.^{4–6} Electric interfaces are essential for microfluidic IS devices. A range of techniques, such as photolithography,⁷ sputtering,⁸ and microtransfer printing,⁹ are employed for the fabrication of microelectrodes for IS sensors. These fabrication methods, however, require specialized equipment and/or a clean-room environment.

Herein, we demonstrate the utilization of PAP for the microfabrication of IS sensors using an office printer and relatively simple wet chemistry. Direct printing of the computer-aided-design (CAD) pattern of microelectrodes to a polyester transparency film produced a master, to which we attached 3D elements for the inlet and outlet channels (Scheme 1i). To obtain

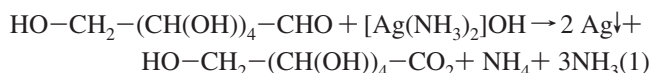
Scheme 1. Print-and-Peel Fabrication of a Capacitance Cell^a



^a (i) Master preparation; (ii) casting PDMS; (iii) curing of the PDMS “stamp”; (iv) reversible adhesion to glass; (v) consecutive flows of aqueous solutions of dextrose and $[\text{Ag}(\text{NH}_3)_2]^+$; (vi) electroplating with Cu; (vii) coating with PDMS; (viii) PDMS-to-PDMS permanent adhesion.

microchannels with improved contour smoothness, we utilized a solid-ink printer, instead of LaserJet printers, which we previously used for the PAP fabrication of microfluidic devices.¹ Casting polydimethylsiloxane (PDMS) over the master (Scheme 1ii) produced elastomer components with negative-relief imprints (Scheme 1iii). Reversible adhesion of the PDMS components to glass surfaces formed microfluidic assemblies (Scheme 1iv).

We used the Tollens' reaction to generate silver patterns on the glass surfaces. This process was named after Bernhard Tollens¹⁰ and involves the formation of metallic silver from an aqueous solution of diamminesilver(I) hydroxide, $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, via a two-electron oxidation of aldehydes, such as dextrose (open form), $\text{HO}-\text{CH}_2-(\text{CH}(\text{OH}))_4-\text{CHO}$:¹¹



The reaction between the aqueous solutions of the reducing agent, dextrose, and of the Tollens' reagent, which were

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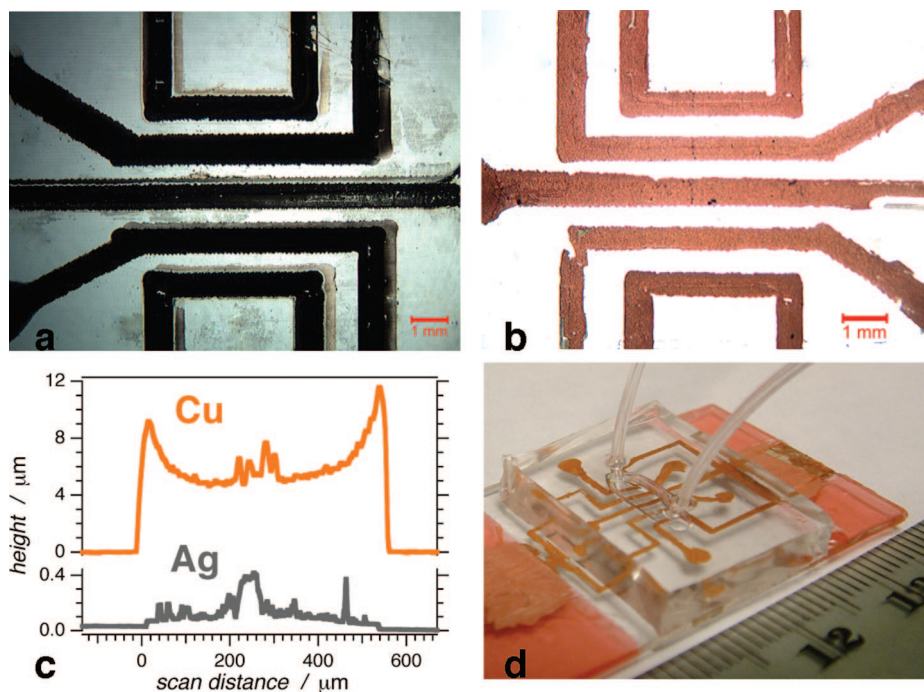


Figure 1. Print-and-peel fabricated capacitance cell. Reflection/transmission optical microscopy images of (a) silver and (b) copper electrode arrays. (c) Profilometry traces across silver (three consecutive dextrose/[Ag(NH₃)₂]⁺ treatments) and copper electrodes. (d) Photograph of a cell with a 1.5 mm center-to-center electrode separation.

consecutively flown through the microchannels, resulted in the deposition of silver metal onto the channel walls. To ensure continuous coverage with conductive material, the procedure of passing [Ag(NH₃)₂]⁺ solution through the microchannels prewet with dextrose mixture was repeated three to five times (Figure 1a).

Detachment of the PDMS components left patterns of electroconducting silver layers on the glass surfaces (Scheme 1v, Figure 1a). The silver patterns, however, were rough and prone to mechanical scratching (Figure 1c). Therefore, using electroplating, we deposited a 10- μ m-thick copper layers over the silver patterns, producing microelectrodes with improved mechanical stability (Scheme 1vi, Figure 1b,c).

In the middle of the patterns, the copper strips formed arrays of five parallel electrodes, which we utilized for impedance measurements. Electrical connections between every other electrode resulted in a “multilayer” capacitor, the characteristics of which were dependent on the dielectric properties of the surrounding media. IS allowed us to obtain information about the frequency dependence of the complex impedance, Z , of the microelectrode assemblies¹²

$$Z = Z_0 e^{i\varphi} = Z_S + Z_P + (R^{-1} + i2\pi fC)^{-1} \quad (2)$$

where Z_0 and φ are the amplitude and the phase of Z , respectively; f is the frequency of the sinusoidal wave of the applied voltage; Z_S and Z_P are the source (e.g., cable) and polarization impedance, respectively; and R and C are the resistance and the capacitance, respectively, of the microelectrode assembly. The capacitance, C , is directly dependent on the dielectric properties of the media surrounding the electrodes.

Placing water and other electroconductive samples directly into contact with the electrodes causes a considerable decrease in the resistance, R , of the capacitance cells. Hence, it results in an overwhelming contribution from R^{-1} in the last term of eq

2, making the contribution from C in the measured signals negligible. To prevent direct electrical contact between the microelectrodes and the samples, we coated the electrode arrays with 70 (± 10) μ m PDMS layers (Scheme 1vii). Over the coated electrodes we placed PDMS flow chambers, which were also fabricated using PAP techniques (Scheme 1viii). We prepared capacitance flow cells with 1 and 1.5 mm center-to-center electrode separations that correspond, respectively, to about 450 and 950 μ m separations between the edges of neighboring electrodes.

Because we are interested in the properties of the media in the flow chambers above the electrodes, we modeled each cell as two capacitors connected in parallel with total capacitance, C , of

$$C = C_C + C_S = C_C + \alpha\epsilon \quad (3)$$

The representation of the cells as parallel-connected capacitors is the simplest model that allows for a linear relation between the measured capacitance, C , and the dielectric constant of the sample, ϵ . C_S accounts for capacitance resulting from the penetration of the electric field through the sample flow chambers. Through C_S , therefore, C is linearly dependent on the dielectric constant of the sample. The proportionality parameter, α , depends on the shape, the size, and the position of the flow chamber over the electrodes. C_C accounts for the capacitance of the rest of the device and remains independent of the properties of the sample flown through the chamber of the capacitance cell.

For the PAP-fabricated capacitance cells, IS revealed phase values close to -90° and a nearly linear dependence of the amplitude on the frequency on a double logarithmic scale (Figure 2). These features indicate that the capacitance of the cells comprises most of the measured impedance. Fitting the impedance spectra with the $Z(f)$ function (eq 2) yielded the total capacitance, C , of the cells filled with different fluids. Consecutive linear fits of C versus the dielectric constant of the fluid (eq 3) produced the characteristics of the PAP-fabricated microelectrode capaci-

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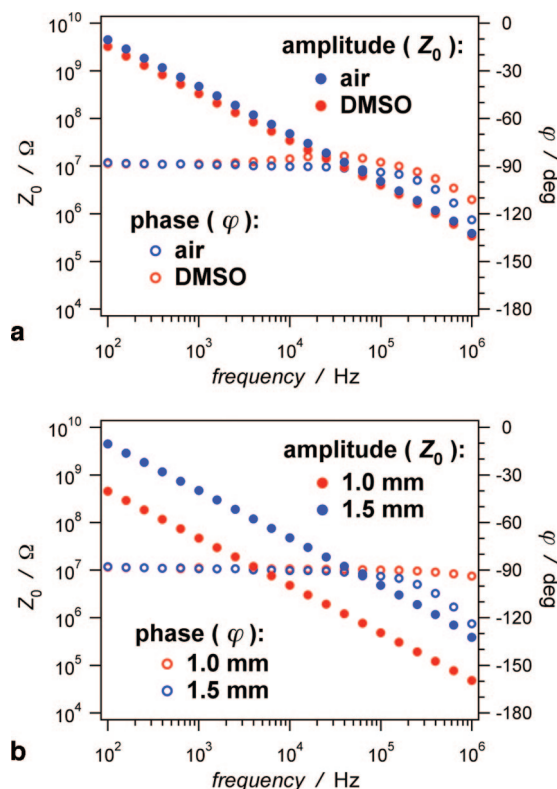


Figure 2. Comparison between impedance spectra for capacitance cells with different electrode separation filled with fluids with different dielectric constants, represented as the frequency dependence of the amplitude, Z_0 , and the phase, ϕ , of the measured complex impedance, $Z = Z_0 e^{i\phi}$ (eq 2). (a) Spectra for air and DMSO measured with a capacitance cell with a 1.5 mm center-to-center electrode separation. The capacitance values for air and DMSO are 0.34 and 0.48 pF, respectively. (b) Spectra for air measured with cells with 1.0 and 1.5 mm center-to-center electrode separations. The capacitance values for 1.0 and 1.5 mm electrode separations are 3.5 and 0.34 pF, respectively.

tance cells. From the intercept of the C versus ϵ linear fits, we determined that $C_C = 3.4$ and 0.34 pF for cells with 1 and 1.5 mm center-to-center electrode separations, respectively. The slopes of the linear fits gave values of 60 and 3.0 fF for the parameter α (eq 3) for cells with 1 and 1.5 mm center-to-center electrode separations, respectively.

Despite the successful application of IS for sensing, the relative complexity of the impedance model (eq 2) and the relatively long time required to collect a spectrum (seconds to minutes) pose a demand for an analytical technique in which the capacitance, modulated by the examined samples, can be directly and reliably extracted from the measured signals in an expedient manner. Triangular waveform (TW) dielectric measurements (i.e., application of TW voltage bias to the capacitance cells) yield current signals that are superpositions of two waves: (1) a triangular waveform resulting from the resistance component of the impedance, R , in eq 2 and (2) a rectangular waveform (RW) resulting from the capacitance component of the impedance, C , in eq 2.^{13,14} The height, h , of RW is linearly proportional to the capacitance, C , of the cell, and hence, to the dielectric constant, ϵ , of the sample. (The height, h , represents plateau-to-plateau current difference for RW; i.e., h is twice the value of the RW amplitude.) The lower limits of the duration of the measurement of TW dielectric response signals are compatible to the periods

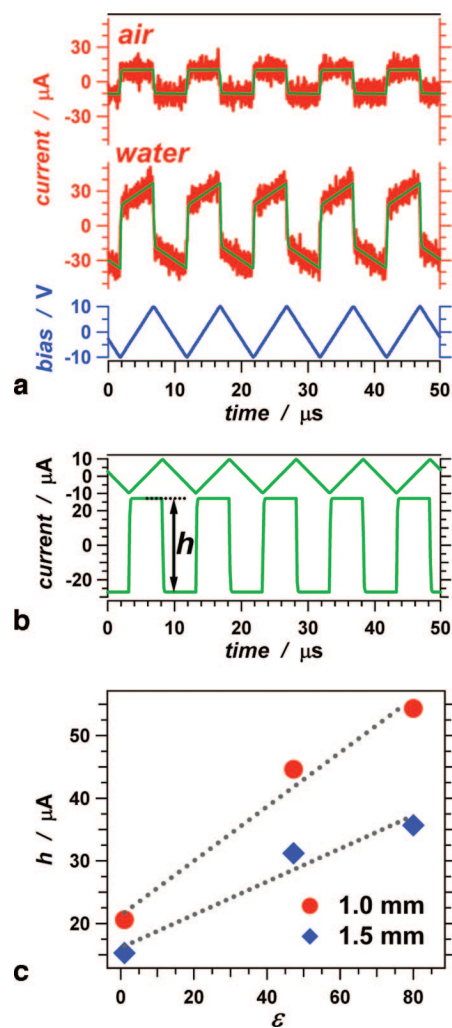


Figure 3. Triangular waveform (TW) current-voltage measurements. (a) Applied voltage (in blue) and current signals (in red) for air and water in a capacitance cell with a 1 mm center-to-center electrode separation. The data fits are shown in green. (b) Deconvolution of the current signal for water (from b) into triangular and rectangular waves. (c) Linear correlation between the height of the rectangular current waveforms and the dielectric constant of the fluid (air, DMSO, and water) in the sample chambers, measured with devices with 1 and 1.5 mm center-to-center electrode separations.

(i.e., f^{-1}) of the waves used (e.g., 10 μs for measurements using 100 kHz TW). This relatively high temporal resolution makes the TW technique an excellent choice for analytical and sensing applications, especially if real-time monitoring is required.

Using the TW technique, we characterized the performance of PAP-fabricated capacitance sensors. Measurements of air, dimethyl sulfoxide (DMSO), and water (i.e., fluids that do not swell PDMS)¹⁵ produced current waves that we deconvoluted into TW and RW components (Figure 3a,b). We observed a linear correlation between h and ϵ (Figure 3c), supporting our hypothesis that, despite its simplicity, the two-parallel-wired capacitor model (eq 3) adequately represents the investigated PAP-fabricated capacitance cells.

The described PAP technique offers a facile and inexpensive alternative for the fabrication of components for electrical interfaces of microfluidic devices. In addition to silver and copper, the procedure can be readily expanded to utilize the electroless deposition of other conducting and semiconducting materials, followed by electroplating of a wide range of metals.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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