Fabrication of microstructured electrodes via electroless metal deposition onto polydopamine-coated polystyrene substrates and thermal shrinking

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Abstract
The ability to provide high sensitivity with small footprints makes miniaturized electrodes key components of biosensing, wearable electronics and lab-on-a-chip devices. Recently, thin film deposition onto polystyrene films, followed by thermal shrinking has been used to produce microstructured electrodes (MSEs) with high electroactive surface area (ESA). Nevertheless, the high cost associated with film deposition through evaporation used in microfabrication and the variability in performance of screen-printed electrodes (SPEs) remain key barriers that limit their widespread deployment. Here, a simple and inexpensive method is developed for the solution-based patterning of high-quality metallic films on polystyrene substrates for MSE fabrication. The ESA of electrodes produced through this method is 2 × and 12 × larger than that of microstructured and planar electrodes produced through sputtering, respectively, and their cost is only 20% of sputtered ones. This methodology allows the fabrication of on-chip microstructured electrochemical cells (SMECs) with excellent analytical performance (3% RSD inter-day reproducibility and 0.3% RSD repeatability), superior to that of commercially available SPEs. In addition, the ESA of SMECs is significantly higher than that of SPEs, and they show excellent response toward dopamine detection. We anticipate that this solution-based fabrication approach will expedite the development of miniaturized sensing platforms for point-of-care applications.

KEYWORDS
cost-effective, dopamine detection, electroactive surface area, solution-based fabrication, solution-processed microstructured electrochemical cell
One of the main challenges to the real-time on-field electrochemical detection of target analytes is the miniaturization of sensing platforms. To achieve point-of-need analysis, it is necessary to develop on-chip solutions to replace the classical electrochemical cell approach. At the same time as the footprint of electrochemical cells is reduced, it is necessary to maintain the high sensitivity afforded by macroscale sensing platforms. In this sense, high surface area miniaturized electrodes have become increasingly attractive for applications in biosensing, electronic, and lab-on-a-chip devices.[1–5] Several approaches have been used to increase the electroactive surface area (ESA) of electrodes used for electrochemical sensing, with the majority of them focused on introducing roughness onto the electrode surface.[6] A recently developed method to increase the surface area uses the shrinking and wrinkling of a thin film, which produces miniaturized micro-structured electrodes (MSE).[7] In this technique, a pre-stressed polystyrene (PS) film is masked with vinyl and a gold film is deposited through vapour deposition techniques like sputtering. Then, the substrate containing the patterned film is placed in an oven at a temperature above the glass transition temperature of PS (~100 °C) and shrunken to 16% of its original area. Our group has shown that MSEs obtained through wrinkling present a 6–7-fold increase of the ESA compared to planar electrodes of the same geometrical footprint.[4] Enhancing the ESA of electrodes used in electrochemical sensing provides an important advantage because it decreases the limit of detection (LOD) and increases the sensitivity for a given application. However, the most expensive step in the fabrication of MSEs for on-chip platforms through this method is the deposition of the gold film through sputtering, which can prevent their use in resource-limited settings, calling for the exploration of alternative electrode fabrication methods.

Screen-printed electrodes (SPEs) have emerged as simple and inexpensive substitutes for electrodes fabricated through vapour deposition. SPEs are produced by spreading a thixotropic fluid or ink containing a mix of components (e.g., graphite, carbon black, solvents, and polymeric binder) evenly across a mesh screen that defines the shape and size of the electrode.[8] This allows them to be printed onto a variety of substrates, including plastic films, ceramics, paper sheets, garments, stretch thin films, and the epidermis.[9] SPEs have become common components of sensing devices used in the biomedical, environmental, and food industries, among others.[10–12] Despite these advantages and their widespread use, SPEs have some limitations; their fabrication remains a difficult and time-consuming process, the commercial inks used to produce SPEs are usually proprietary mixtures where the composition is not precisely known, and they typically do not present enhanced electrochemically active surfaces. This can limit their usefulness given that the materials used in SPE fabrication, pre-treatment procedures, and the temperature conditions during the curing of the printed layer can affect their sensitivity to redox processes and thus impact the performance of the electrode.[13] Furthermore, while the reproducibility and repeatability of SPEs have been improved in recent years, they remain major limitations for the use of SPEs.[10]

Electroless deposition is an alternative process to pattern films using solution-based processes, which has made it attractive for applications in surface-enhanced Raman scattering, catalysis, and stretchable electronics, microstructures electrodes, among others.[14–21] Although this process is amenable to the deposition of a variety of thin films, including metals, semiconductors, and even insulators, on a range of substrates,[22] its most common use is for the deposition of noble metal films. The electroless deposition method is simple, low cost, avoids the use of toxic solvents, and allows the conformal coating of three-dimensional structures, which is not possible with other methods like sputtering or vapor deposition.[17,23] Unlike electrodeposition, electroless plating does not require a conductive substrate, enabling the coating of several types of insulating materials.[24,25] The general process for metal electroless plating consists of submerging the substrate in a solution containing a salt of the metal of interest and a reducing agent. To obtain a homogenous and high quality film the substrate often needs to be treated, which can involve the use of intensive and complex techniques (e.g., lithography) to pattern catalytic nuclei, or multiple chemical steps like pre-treatment, sensitization or activation (e.g., through the use of plasma activation and silane layers).[23,26,27] In this sense, the discovery of polydopamine (PDA), a polymer that resembles mussel bio-adhesives, as a layer for substrate activation and metal film nucleation seems an ideal solution to overcome the drawbacks of traditional electroless deposition processes.

PDA coatings can be easily produced by dissolving dopamine hydrochloride (DA) in water and initiating the polymerization through the addition of base.[28] Due to the presence of conjugated rings, polar, and ionisable groups along the polymer chain, PDA has the unique ability of being able to coat almost any type of surface, regardless of whether it is conductive, insulating, hydrophobic, or hydrophilic.[29–31] While the exact polymerization mechanism is unclear, most authors in the literature agree that several mechanisms take place simultaneously in the process of converting DA into PDA.[32,33] A key advantage of PDA coatings is the presence of several chemical moieties (i.e., amino, hydroxyl, alkene) exposed to the environment,
which allow reactions with chemically active groups, or can act as reducing or complexing agents for electroless deposition processes. Most PDA coating in the literature is done through a dip coating method,\textsuperscript{[22,28,33–35]} where the substrate is submerged in a basic solution of DA and left to polymerize for a given period of time. This methodology is convenient when the whole substrate surface needs to be coated but can present some challenges when only specific parts of the substrate are targeted for deposition.

This work contributes a new simple and inexpensive solution-based method to pattern noble metal films and microstructure them to fabricate on-chip electrochemical cells with excellent analytical performance. In this workflow, we have developed and optimized a drop casting technique to deposit and pattern PDA coatings on PS substrates. The patterned coatings were used to optimize electroless processes for the deposition of high-quality copper, silver, and gold films, which upon shrinking of the thermoresponsive substrates result in microstructured electrodes (MSEs). Using this simple and inexpensive solution-based approach, we demonstrate the ability to fabricate on-chip microstructured electrochemical cells with analytical performance on par or superior to that of commercially available SPEs when sensing model redox probes or targeted analytes, like dopamine. We anticipate that these fabrication approaches will find use in the development of miniaturized sensing platforms for point-of-care applications.

2 RESULTS AND DISCUSSION

Noble metal films were plated onto commercial thermoresponsive polystyrene using a water-based electroless deposition methodology. In the general fabrication approach, PS substrates were cut to 15 × 45 mm rectangles and self-adhesive vinyl masks were affixed to the substrates to define the area where the metallic film electrodes were deposited (Figure 1). The electroless deposition of the films involved first laying down an adhesive PDA coating, followed by the formation of the metallic film by direct nucleation and growth from a metal ion solution (Cu\textsuperscript{2+} or Ag\textsuperscript{+}), or by adsorption of gold nanoparticles (AuNPs) as nucleation sites followed by growth from a solution containing Au\textsuperscript{3+} ions. Removal of the vinyl patterning mask revealed the patterned metal electrodes. The procedures to reliably deposit the metallic films were optimized as described in the following sections. Electrode microstructuring was next achieved through thermal shrinking of the PS substrates, which reduced the dimensions of the substrates to \( \sim 16\% \) of their original area and resulted in the concomitant wrinkling of the metallic films. Through this fabrication approach, copper, silver, and gold electrodes could be plated using aqueous electroless processes, free of organic solvents and using no equipment other than an orbital shaker. As described below, the combination of electroless plating and shrinking allowed us to fabricate solution-processed microstructured electrochemical cells (SMECs) with high surface areas in a simple and cost-efficient manner.

2.1 Polydopamine coating by drop casting

PDA is commonly used as a polymer coating to aid in the electroless deposition of metallic thin films, with most reports in the literature using a dip coating method. While highly effective, this method presents the disadvantage that a relatively large volume of the dopamine (DA) solution is used and that the coating is deposited over the whole immersed substrate, with no coating selectivity to a region of interest. In this work, we explored a simple alternative approach that allowed us to drop-cast a PDA coating within a region of interest by masking the PS substrate with a self-adhesive vinyl stencil and applying a small volume (250 \( \mu \)L) of DA solution in the unmasked area that defined the electrode. In this approach, we observed that the two key parameters affecting the quality of the drop-cast PDA coatings were the concentration of the DA solution and the polymerization time. Therefore, we performed a study to optimize the properties of the PDA coatings when these parameters were varied. The response variables we used to evaluate the quality of the PDA films were their thickness, their surface roughness, the number of aggregates per \( \mu \)m\(^2\), and the average size of the aggregates.

Qualitatively, AFM images (Figures S1 and S2) did not show striking differences between the films produced by varying the concentration of the DA solution from 1–5 mg mL\(^{-1}\), while keeping the polymerization time constant, or by varying the deposition time from 2–24 hour, while keeping the DA concentration constant. Although the qualitative analysis suggested that the small volume of DA solution applied to the PS template produced PDA coatings that did not change considerably in the parameter space explored, differences became evident when the response variables were quantitatively analyzed (Figure 2). From Figure 2A-B it can be observed that the thickness of the PDA film, as measured from AFM images of a masked film edge, increases linearly with DA concentration (\( R^2 = 0.99 \)), while keeping the polymerization time constant at 8 hours. In contrast, Figure 2C shows that for concentrations greater than 2 mg mL\(^{-1}\) the roughness of the films tends to plateau, with no statistical differences between the films made at higher concentrations (\( P < .05 \)). This indicates that the film obtained at a concentration of
1 mg mL\(^{-1}\) is the only one that does not completely coat the PS surface, and that at higher concentrations the PDA is deposited on an existing polymer layer, resulting in a constant surface roughness. We observed an increase in the number (Figure 2D) and size (Figure 2E) of aggregates as the concentration of DA was increased up to 4 mg mL\(^{-1}\), after which the number of aggregates decreased. This was attributed to the coalescence of aggregates in solution. The wettability of the films was also assessed through contact angle goniometry. We observed that when the PS film was coated with PDA, the surface became more hydrophilic due to the addition of amino and catechol polar surface groups. However, increasing the concentration of DA during deposition resulted in a slight increase of the contact angle (Figure 2F), due to the increased number of aggregates on the surface that impact the film’s nanoscale roughness. These results show that the thickness of the PDA film, its roughness and the number of aggregates can be controlled by the concentration of DA during the polymerization process, and that the most uniform films can be obtained when the polymerization is performed at a concentration to produce the thinnest film that ensures the complete coverage of the substrate. This was determined to be at a DA concentration of 2 mg mL\(^{-1}\).
Characterization of PDA films deposited through drop casting. A, Characteristic AFM image showing the edge of the PDA film on a substrate (PS) and highlighting an aggregate (red arrow). Dependence of the response variables (selected to represent film quality) on the concentration of dopamine and the polymerization time used during the deposition of PDA films. The response variables studied were: (B) PDA film thickness, (C) PDA film roughness, (D) number of aggregates per µm², (E) aggregate size, and (F) contact angle.

When comparing the films produced by varying the polymerization time, while keeping the DA concentration at 2 mg mL⁻¹, the trends we observed were similar to those from the concentration study. Increasing the polymerization time also resulted in an increase in PDA film thickness (Figure 2B), but the linear fit was slightly worse ($R^2 = 0.97$). The change in slope of the thickness versus time graph indicates that the initial adsorption of the polymer to the substrate is slow (< 4 hours), but that after an initial PDA layer is deposited over the whole substrate, the deposition accelerates (> 4 hours). It was also observed that the roughness of the films (Figure 2C) increases with increasing polymerization times and reaches, after 4 hours, a plateau similar to that observed in the concentration study. The number of aggregates were observed to decrease (Figure 2D), but their size increased with longer polymerization times (Figure 2E). This suggests that the aggregates diffuse in solution and over time grow by polymer adsorption or coalescence to produce larger aggregates that adsorb onto the substrate. This trend can be explained by the fact that larger spherical particles minimize the surface energy, making them more energetically favorable when present in solution. The reduced number of aggregates also impacted the wettability of the surface, where increasing the polymerization time slightly decreased the contact angle (Figure 2F). Altogether, these results show that in the polymerization process, varying the concentration of DA results in large changes in the film properties, while varying the polymerization time produces more moderate changes in the thickness and roughness but can be used to minimize the number and size of aggregates deposited on the film. Given that the purpose of the PDA film in this work is to serve as a substrate for electroless plating of metal films, a thin PDA coating with moderate roughness and the lowest number and size of aggregates is desired. Based on the results obtained in the studies to optimize PDA deposition, a DA concentration of 2 mg mL⁻¹ and a polymerization time of 8 hours were used to produce all PDA coatings for electroless deposition.

2.2 Electroless plating of metallic films onto PDA-coated surfaces

Metallic films consisting of copper, silver, or gold were successfully plated onto PDA coated PS substrates and structured via thermal shrinking of the substrate. Copper was used as a model film to test and troubleshoot the electroless plating process on PDA-PS substrates. Copper plating was done from a CuCl₂ solution, at pH 7, and using
FIGURE 3 SEM images of the planar (top) and microstructured (bottom) electrodes fabricated through electroless plating and thermal shrinking. Columns represent: (A) copper, (B) silver, and (C) gold electrodes. All images were taken at the same magnification.

DMAB as the reducing agent. To optimize the film plating process, we studied the effect of CuCl₂ concentrations between 30–70 mM on the metallization time and film quality. It was observed that at concentrations < 40 mM, there was no metallization even after 3 days, indicating that at low concentrations the electroless plating process is very inefficient. For higher concentrations, slow electroless deposition was observed, taking ∼24 hours to completely metalize the substrate. AFM images revealed that increasing the CuCl₂ concentration increased the grain size (Figure S3) and the thickness (from ∼70 nm at 40 mM to 170 nm at 70 mM, Figure S4) of the films. However, the films obtained at 60–70 mM exhibited poor structural integrity. The edges of all films at these concentrations delaminated, and for some samples most of the film lifted off. This could be attributed to poor adhesion between the film and the substrate and residual stress in the film that arises from a mismatch in the thermal expansion coefficient of the polymer and the copper film, which increases as the thickness of the film increases. With these observations, the spallation limit of the copper films deposited using electroless plating onto PDA-PS substrates was established to be ∼160 nm. Given their stability, films made at 40 and 50 mM CuCl₂ were structured via thermal shrinking of the PS substrate at 160 °C. At these concentrations, there was no significant difference observed in the metallization time (24 hours), but the thickness of the resulting films increased from 73 ± 5 to 88 ± 8 nm for 40 and 50 mM, respectively. Figure 3A shows SEM images of a copper film before and after structuring. Aggregates could be seen on the surface of the planar and structured films produced at either concentration. We speculate that these aggregates could be composed of copper oxide particles formed during the plating process, which was performed under ambient conditions. This is supported by four probe sheet resistance measurements that show that the resistivity of the flat and microstructured copper films is almost an order of magnitude larger than that of bulk copper (Figure S5). Nevertheless, copper thin film plating and structuring showed that MSEs could be fabricated through a simple benchtop solution-based processing approach.

As a next step, we optimized the process to fabricate structured silver metal electrodes through electroless plating and thermal shrinking. While silver possesses a higher reduction potential than copper and the amino group from the PDA layer could act as a reducing agent to create Ag nuclei, our attempts to deposit silver films by submerging a PDA coated substrate in a AgNO₃ solution (50 mM) without a reducing agent failed to produce conductive films. After 24 hours of plating, a yellow-tinted film was formed, which we attributed to the formation of a discontinuous coating of Ag nanoparticles (Figure S6). This would justify the lack of conductivity in the deposited film and is consistent with previous reports of Ag nanoparticle formation on PDA films. To overcome this, the concentration of AgNO₃ was increased to 150 mM and glucose was used as a reducing agent. This process resulted in the deposition of uniform silver tinted films, with a thickness of 131 ± 2 nm, which could be structured through thermal shrinking. Figure 3B shows the silver-plated films, before and after shrinking. It can be observed that the film’s surface shows large grains, but the film is continuous and homogeneous, with very few aggregates present. After the shrinking process, wrinkles were formed without cracking or delamination. Figure S5 shows that the resistivities of the flat electrodes (4.1 × 10⁻⁸ Ω·m) and structured electrodes (3.1 × 10⁻⁸ Ω·m) are close to the bulk resistivity of silver (1.6 × 10⁻⁸ Ω·m). A lower resistivity for MSEs is expected because
through the shrinking process some of the wrinkles come into contact, reducing the mean path that the electrons have to travel between the contacts, therefore increasing the conductivity. The ability to pattern and fabricate silver MSEs through solution processing provides a simple route for the fabrication of on-chip reference electrodes (REs), as is discussed below.

Gold electrodes could not be produced on PDA-coated PS substrates from solutions of gold salts alone, even in the presence of a reducing agent, but required the use of a seed layer of gold nanoparticles (AuNPs) to produce uniform films. A PDA-PS substrate that was submerged directly into a 1 mM solution of H[AuCl₄] with 4 mM of hydroxylamine as the reducing agent resulted in a very thin (almost transparent) inhomogeneous gold layer. Given the lack of nucleation and film growth, we decided to deposit AuNPs on the PDA-PS template as a seed layer for the film. The AuNPs used in this study were produced in-house through the Turkevich method[40] and presented spherical morphology with a diameter of 12 ± 1 nm (Figure S7).

Our hypothesis was that when a PDA-PS substrate was submerged in a suspension of AuNPs, these would interact with the hydroxyl and amino groups of the PDA and strongly adhere to the substrate, serving as nuclei for further adsorption and growth of a continuous gold film from a salt solution. We observed the successful deposition of a uniform layer of AuNPs after 24 hours incubation of a PDA-PS substrate with a nanoparticle suspension.

Given that AuNP deposition is the most time-consuming step in the electroless plating process, we optimized the incubation time to achieve a uniform nanoparticle coating. To this end, we followed the depletion of the AuNP solution during the first 12 hours of deposition via absorbance measurements at 450 nm and used the changes in absorbance to calculate the number of deposited AuNPs (Figure S8). It was observed that the majority of the AuNPs were deposited onto the substrate within the first 2 hours, after which the deposition plateaued. Using the geometrical area of the PS substrate coated with PDA (5 × 10¹⁴ nm²), the cross-sectional area of one AuNP (estimated from TEM data as 113 nm²), and the number of particles deposited, we calculated that the AuNPs covered 85% of the PDA-coated area within 30 minutes. This is remarkably close to the maximum packing possible of \(\pi \sqrt{12}\) or \(~90%\) for spherical particles on a surface, suggesting that 30 minutes is enough to cover the PS substrate with AuNPs and nucleate the growth of a continuous gold film. SEM images of PDA substrates after 12 hours of immersion in the AuNP solution show that the surface of the template is almost completely coated (Figure S9). AuNP-coated substrates were then placed in a solution containing 1 mM H[AuCl₄] and 100 mM mM H₂O₂ (reducing agent) for 30 minutes under constant agitation at room temperature. Through this approach, uniform and continuous 76 ± 6 nm-thick gold films were obtained, which presented uniform surfaces with no apparent defects or pinholes, even after structuring (Figure 3C). Furthermore, the films exhibited excellent conductivity, with resistivity values (3.6 × 10⁻⁸ Ω-m) that decreased as the films were structured through thermal shrinking (2.8 × 10⁻⁸ Ω-m), and were close to the reported value of bulk gold (2.5 × 10⁻⁸ Ω-m, Figure S5). Thus, high quality structured gold electrodes could be produced through AuNP adsorption and film growth using entirely solution-based processes, which are attractive for use as conductive elements in electronic circuits or as working and counter electrodes for on-chip electrochemical cells.

2.3 | ESA of plated gold electrodes

The most common methodologies to fabricate on-chip gold electrodes are via patterning through photolithography and thin film deposition by evaporation – processes that are time consuming and require expensive instrumentation and materials. The electroless plating and structuring method presented above could provide a simple and cost-effective way to fabricate on-chip high surface area gold films to be used as working electrodes (WEs) for electrochemical sensing. To test the suitability of the plated structured electrodes, their ESA – an important parameter to control in a WE, was measured and compared against electrodes of the same thickness made through sputter deposition and thermal shrinking. Cyclic voltammetry (CV) was performed in a dilute H₂SO₄ solution using the structured films as WEs. The area under the reduction peak in the voltammograms was used to calculate the total charge transferred, which was divided by the charge associated with an oxide monolayer formation in one square centimeter of gold (386 μC cm⁻²)[41] to obtain the electrode’s ESA. Figure 4A shows an overlay of the voltammograms obtained from the structured electrodes made through electroless plating and from those made by sputtering. The reduction current peak is noticeably higher for the electrodes made through plating, which is reflected in the ~2 × enhancement of the calculated ESA (Figure 4B). The differences in ESA can be explained by a difference in the surface topography of the electrodes (Figure 4C). Due to the deposition processes, the sputtered electrodes are smoother and have a finer grain than the electroless plated ones. The increased roughness of the plated electrodes results in a larger surface area available for oxide monolayer formation and therefore an increase in the ESA. Furthermore, after the shrinking process, the MSEs showed...
an enhancement in ESA of 5× compared with the planar electrodes with similar footprint fabricated using electroless deposition and 12× compared with ones fabricated via sputtering. It was also observed that the oxidation peaks in all the plated electrodes were very close to one another, which indicates that the electroless plating process yields gold films with reproducible crystalline structure; however, the crystalline structure of plated electrodes is noticeably different from that of the sputtered ones. Recent X-ray diffraction studies have shown that gold films produced through electroless deposition possess a different crystallographic orientation than those obtained by more conventional methods like E-beam evaporation, which also results in different oxidation signatures in CV. Submitting an amorphous gold electrode repeatedly to CV in sulfuric acid has been shown to uncover the main crystallographic planes (100), (110), and (111), which can be respectively indexed to peaks in the voltammograms at 1.14, 1.2, and 1.35 V. This indicates that the electrodes made through our electroless deposition process have surfaces where the gold is preferentially arranged towards the (111) and (100) crystalline planes, whereas the sputtered ones show preferential orientation towards the (110). This characteristic has important implications for applications that leverage the catalytic activity of the (111) facet, such as the enzyme-free sensing of glucose.

In an effort to further reduce the cost of fabrication of the plated structured electrodes and given that the most expensive reagent is the gold salt used to produce the AuNPs, we explored the possibility of re-using the AuNP solution three times in the seeding step. Substrates seeded with AuNPs using re-used solutions showed the formation of uniform gold films, similar to those produced with fresh solutions. Furthermore, the voltammograms obtained from MSEs fabricated using fresh AuNP solutions were no different from those obtained from ones made from the second or third use of the nanoparticle solution (Figure 4A). Similarly, a comparison of the ESA of MSEs made from the first three uses of the AuNP solution showed no significant differences (P < .05). This result indicates that the AuNP solution can be reused for the fabrication of a minimum of three gold electrodes, effectively reducing the cost per electrode to $0.80 for the electroless deposition approach, which presents a significant advantage when compared to the cost of $4.30 for electrodes made through sputtering.

2.4 Solution-based fabrication of on-chip electrochemical cells

Screen-printing has become one of the most widely used processes to fabricate on-chip electrodes for electrochemistry. Its low cost and the ability to customize the electrode shape is what makes this technique unique and broadly applicable. One of the main drawbacks of SPEs is their...
The performance of on-chip solution-processed microstructured electrochemical cells (SMECs) was tested via CV in a solution containing 2 mM KFeCy at a scan rate of 0.1 V s⁻¹. Voltammograms obtained from n = 6 independently fabricated electrochemical cells. Voltammograms obtained from a single electrochemical cell, taken at (B) three-minute and (C) daily intervals. D, Plot and linear fits of the peak cathodic current versus the square root of the scan rate for n = 6 replicate electrochemical cells. Inset: voltammograms obtained at the different scan rates from one representative electrochemical cell.

low reproducibility, repeatability, and interday precision (if they can be reused). The fabrication process can also be intensive and time-consuming. Using the solution-based metallization procedures optimized above, we fabricated an electrochemical cell with a layout similar to those previously reported for SPEs but incorporating microstructured gold and silver electrodes (Figure 1). To produce Ag/AgCl REs, silver electrodes were chlorinated through five cycles of CV (0.4 to -0.05 V) in a KCl solution (1 M), after which the electrochemical cells were stored in 18.2 MΩ cm water until further used. The performance of the solution-processed structured electrochemical cells (SMECs) was evaluated by obtaining CV curves in a 2 mM KFeCy solution and testing the reproducibility, repeatability, and interday precision of the measurements. To assess the reproducibility of the fabrication process, six SMECs were independently made and three each were used 4 hours and 7 days after the chlorination process. Figure 5A presents the voltammograms obtained from the replicate SMECs, which show reproducible reduction/oxidation peaks. The relative standard deviation (RSD) of the current intensity at the cathodic peak (i_pc) was calculated to be 3%, indicating excellent reproducibility in the fabrication. The repeatability of the measurements for each SMEC was tested by taking measurements every 3 minutes, with five total repetitions. Figure 5B shows sample measurements for a single SMEC displaying excellent repeatability, with RSD for i_pc of 0.1%. The average RSD obtained from three replicate electrochemical cells was 0.3%, highlighting the repeatability of measurements across a set of electrodes. The interday precision was evaluated for three SMECs over a span of 5 days (Figure 5C, Table S1), which yielded an average RSD of 2%. For comparison, a similar procedure was carried out for three commercially available screen-printed electrochemical cells (DropSens, model 61208210). The measurements of the i_pc for three electrodes yielded an average RSD value of 1.5% for repeatability, and 3% for the interday precision. This is consistent with results reported in the literature, where reproducibility measurements for gold SPEs, evaluated through CV of solutions of KFeCy, yielded an RSD of 3.8% for the best performing cell (n = 6).[44] Another study evaluating the reproducibility of commercially available graphite screen printed electrodes, using as standard redox probe KFeCy, found RSD
TABLE 1
Performance of different electrodes in 2 mM KFeCy

| Electrode type          | Manufacturer   | WE Material | ESA [cm²] | Geometric area [cm²] | Rf  |
|------------------------|----------------|-------------|-----------|----------------------|-----|
| SMECs                  | This work      | Gold        | 0.414     | 0.283                | 1.46|
| Flat sputtered         | This work      | Gold        | 0.152     | 0.196                | 0.78|
| Flat electroless       | This work      | Gold        | 0.162     | 0.196                | 0.83|
| Wrinkled Sputtered     | This work      | Gold        | 0.236     | 0.196                | 1.20|
| SPE                    | Homemadea      | Gold        | 0.096     | 0.126                | 0.76|
| SPE                    | DropSensb     | Gold        | 0.112     | 0.126                | 0.89|
| SPE                    | Homemadec      | Gold        | 0.126     | 0.126                | 1.00|
| SPE                    | DropSens      | Gold        | 0.080     | 0.126                | 0.63|
| SPE                    | DropSens      | Graphite    | 0.099     | 0.126                | 0.79|
| SPE                    | Kanichi       | Graphite    | 0.050     | 0.071                | 0.70|
| SPE                    | Zensor        | Graphite    | 0.035     | 0.071                | 0.45|

Values (n = 10) of 8%, 4.8%, and 3.6%, respectively, for DropSens, Zensor, and Kanichi electrochemical cells.[6]

Overall, these results demonstrate that the solution-based fabrication process developed yields excellent reproducibility and maintain excellent precision, even after repeated operation over a period of days.

We further compared the effective ESA of SMECs to that of commercial electrochemical cells when sensing KFeCy in solution (Table 1). The ESA calculated above from CV on dilute H₂SO₄ reflects the maximum available electroactive area. For a kinetically controlled process, like the formation of a gold oxide layer, most of the electroactive sites are accessible to the reagent molecule. In contrast, for a diffusion-controlled process, such as the oxidation-reduction of KFeCy, the redox process is so fast that not all of the electroactive sites are accessible to the molecule in the short time span of the CV scan. A more realistic value of the ESA for a diffusion-controlled process can be obtained using the Randles-Sevcik equation. To this end, CV was performed in 2 mM KFeCy solutions at scan rates ν = 25 – 300 mV s⁻¹ on six independently fabricated SMECs. Figure 5D presents the plots and linear fits of iₚc versus √ν for the data obtained from the replicate cells, where it can be seen that the linear fit adjusts very well to the data (R > 0.996). The inset in this figure shows that the position of the peak does not shift upon changing the scan rate, which indicates that a quasi-reversible process is occurring at the surface of the electrode. From this data, the SMEC ESA and roughening factor Rf (calculated as the ratio of the ESA to the WE footprint ~ 0.283 cm²) were calculated to be 0.41 ± 0.03 cm² and 1.46 ± 0.09 (n = 6), respectively. In comparison, our measurement of commercially available SPEs (DropSens, model 61208210, electrode footprint of 0.126 cm²) revealed an ESA and Rf of 0.0796 ± 0.0009 cm² and 0.634 ± 0.007 (n = 3), respectively. When these two electrochemical cells are compared, it can be seen that the electrochemical cells fabricated through the solvent-based process present a significant increase in Rf of ~220%, which could translate into enhanced sensitivity in electrochemical assays. Furthermore, when compared to several commercially available or homemade SPEs reported in the literature (Table 1), the SMECs fabricated in this work presented an improvement of 150%–320%. Altogether, this data shows that the electroless process developed in this work not only produces electrodes with an enhanced effective ESA for kinetically controlled processes (Figure 4) but also for diffusion-controlled probes, such as KFeCy.

2.5 SMECs for dopamine sensing

Having shown that the fabricated SMECs exhibit excellent analytical responses to model redox probes, we aimed to test their response to a targeted analyte of interest. Dopamine levels in the body are key to human response to stimuli, making this molecule possibly the most important neurotransmitter in the brain. Thus, we evaluated the direct sensing of dopamine using the fabricated cell through chronoamperometry, given that this technique is the most commonly applied in sensing. Figure 6A shows the increase in current in response to an increase in the concentration of dopamine in solution from 0 to 100 µM. Figure 6B shows the calibration curve generated through chronoamperometry for the same range of concentrations. The linearity of the calibration curve is excellent (R² = 0.998), and the LOD and limit of quantification (LOQ) were calculated as 6 and 18 µM, respectively. This is on par with reported LODs for nanocomposite electrodes.
and even slightly higher than such electrodes modified with electrocatalytic additives (e.g., BaMoO₄),[[45]] with the added advantage that the SMECs are fabricated using much simpler and inexpensive methodologies.

3 | CONCLUSIONS

In this work, we have developed and optimized a simple and inexpensive solution-based electroless plating methodology to pattern copper, silver, and gold electrodes, which could be further structured using thermal shrinking of a polystyrene substrate. The characterization of the solvent-processed gold electrodes showed that their ESA, as measured through the formation of a gold oxide layer, is 2× larger before shrinking and 12× larger after shrinking than comparable gold electrodes made through sputtering, which may translate into advantages in the sensitivity of on-chip electrochemical cells. The developed solution-based processes were used to fabricate on-chip microstructured electrochemical cells (or SMECs). SMECs showed excellent analytical performance (3% RSD reproducibility and 0.3% RSD repeatability), on par or superior to that of commercially available SPEs. For diffusion-controlled processes, SMECs also showed higher ESAs and roughening factors than commercially available on-chip cells. The suitability of SMECs for the reproducible sensing of targeted analytes was shown through the detection of dopamine, which led to LOD and LOQ that are competitive with previously published composite electrodes, but with the advantage of much simpler fabrication. We anticipate that the methodologies developed in this work will help accelerate the development of inexpensive and high sensitivity on-chip electrochemical sensors suitable for a wide variety of point-of-care applications.

4 | EXPERIMENTAL SECTION/METHODS

4.1 | Chemicals

Copper chloride (CuCl₂, 99.999%), silver nitrate (AgNO₃, 99.999%), gold (III) chloride trihydrate ([H[AuCl₄]3H₂O, 99.9 %), dopamine hydrochloride (DA), potassium ferri-cyanide (K₄[Fe(CN)₆]⋅3H₂O, borane dimethylamine complex (DMAB, 97 %), tris-acid, 99.0 %, ethylenediaminetetraacetic acid (EDTA, 99 %), boric acid (H₃BO₃, 99.5 %), glucose, 99.5 %, potassium chloride (KCl, 98 %), and sodium citrate dihydrate, 99 %, were purchased from Sigma-Aldrich (Oakville, ON, Canada). Tris-base, and phosphate buffered saline (PBS) 10x were acquired from BioShop (Burlington, ON, Canada). Hydrogen peroxide (H₂O₂, 30 %) and isopropanol (IPA, 99.5 %) were supplied by Fisher Scientific (Ottawa, ON, Canada). Sulfuric acid (H₂SO₄, 95%–98%), nitric acid (HNO₃, 68%–70%) and hydrochloric acid (HCl, 36.5%–38%) were obtained from Caledon Laboratories (Georgetown, ON, Canada) and ammonium hydroxide (NH₄OH, 28%–30%) from EMD Millipore (Etobicoke, ON, Canada). All materials were used as received without further treatment or purification.

4.2 | Substrate preparation

Patterned metal squares and electrodes were fabricated on pre-stressed polystyrene films (PS, Graphix Shrink Film, Graphix, Maple Heights, OH, USA). Adhesive vinyl sheets (FDC-4300, FDC graphic films, South Bend, IN, USA) were cut into stencils to define the electrode or square shapes using a Robo Pro CE5000–40-CRP blade cutter (Graphitec America Inc., Irvine, CA, USA) equipped with a CB09UA.
super-steel blade. After cutting the vinyl, it was peeled and transferred to the PS sheets. Before use, the PS electrodes were washed with isopropanol (IPA), 18.2MΩ-cm water (from a Reference A10+ Millipore System, Z00QSVC01 Millipore SAS, Molsheim, Bas-Rhône, France), nitrogen dried, and plasma-treated for 5 minutes (30 sccm airflow, 600 mTorr) in a PDC expanded oxygen plasma cleaner (Harrick, Ithaca, NY, USA) operated in high power setting (30 W).

### 4.3 PDA adhesion layer

A study was conducted to assess the impact of DA concentration on the formation of PDA films. The washed and plasma-treated masked PS substrates were placed in a plastic Petri dish. Solutions of DA with concentrations from 1–5 mg mL\(^{-1}\) in Tris buffer 8.5 were prepared in 1.5 mL microcentrifuge tubes. Then, 250 µL of each solution was drop cast onto masked PS substrates, the Petri dishes were sealed with Parafilm, and the DA was left to polymerize onto the substrates for 8 hours. After the polymerization time, the PS electrodes were removed from the Petri dish, rinsed with water, and nitrogen dried. This procedure was done in triplicate for each DA concentration.

A study of the effect of polymerization time on the formation of PDA films was also conducted, where a similar procedure was followed. A solution of 2 mg mL\(^{-1}\) of DA was prepared in a 15 mL conical tube. Then, 250 µL of the DA solution was drop cast onto masked PS substrates, the Petri dishes were sealed with Parafilm, and the DA was left to polymerize on the substrates for 2, 4, 8, 12, or 24 hours. After the polymerization time, the electrodes were removed from the Petri dish, rinsed with water, and nitrogen dried. This procedure was done in triplicate for each polymerization time. The optimized PDA deposition conditions (2 mg mL\(^{-1}\) of DA and 8 hours polymerization time) were used for all subsequent experiments.

### 4.4 Electroless copper plating

To study the impact of concentration on copper film plating, five different aqueous solutions containing CuCl\(_2\), EDTA, and H\(_2\)BO\(_3\) were prepared with CuCl\(_2\) concentrations of 30, 40, 50, 60, and 70 mM and EDTA: CuCl\(_2\), H\(_2\)BO\(_3\): CuCl\(_2\) concentration ratios of 1:2 in all cases. The solutions were placed under ultrasonication until complete dissolution of the EDTA and H\(_2\)BO\(_3\). The pH was adjusted to 7 with NaOH 2 M and 0.5 M. All the bottles were stored in the fridge until further use. 10 mL of the prepared solutions were placed in a 15 mL conical tube and DMAB for a final concentration ratio with CuCl\(_2\) of 1:1 was added. A substrate with a PDA drop cast coating was immersed face up in the solution and placed under orbital shaking (85 rpm) for 24 hours. The vinyl mask was then removed, the copper plated film rinsed with water and nitrogen dried. This procedure was done in triplicate for each concentration.

For all subsequent experiments, the optimized concentrations of 50 mM CuCl\(_2\), 100 mM EDTA, and 100 mM H\(_2\)BO\(_3\) were used for the copper plating solution. Then, 10 mL of the solution were placed in a conical tube and DMAB was added to a final concentration of 50 mM. A substrate with a PDA drop cast coating was immersed in the solution and placed under orbital shaking (85 rpm) for 24 hours. The vinyl mask was then removed, the copper plated film rinsed with water and nitrogen dried. Finally, the PS substrates containing copper films were shrunk in an oven at 160 °C to produce MSEs. For flat electrodes with a geometrical footprint equivalent to the MSEs, the procedure was the same but was performed in a glass vial containing 5 mL of the plating solution.

### 4.5 Electroless silver plating

NH\(_4\)OH (0.5 M) was added dropwise into a conical tube containing 5 mL of an aqueous solution of AgNO\(_3\) (0.15 M). Initially, a brown precipitate appeared, corresponding to the formation of Ag\(_2\)O. The addition of base continued until the precipitate completely disappeared. A PDA coated substrate was placed in the tube and 5 mL of glucose (2 M, prepared in 3:7 MeOH:H\(_2\)O) was added. The solution was placed under orbital shaking for 15 minutes at 120 rpm. The vinyl mask was then removed, the silver-plated film rinsed with water, and nitrogen dried. Finally, the PS substrates containing silver films were shrunk in an oven at 160 °C to produce MSEs. For flat electrodes with a geometrical footprint equivalent to the MSEs, the procedure was the same but was performed in a glass vial containing 5 mL of the plating solution.

### 4.6 Gold nanoparticle synthesis

Gold nanoparticles (AuNPs) were produced through the classic Turkevich method.\([40]\) Briefly, 80 mL of H[AuCl\(_4\)] (1 mM) were heated to 100 °C on a heating plate under magnetic stirring until the solution started to condense at the neck of the Erlenmeyer flask. Afterwards, 8 mL of 2 wt% sodium citrate were added and the solution was kept under stirring and heating until a reddish color appeared (approximately 5 minutes), indicating the formation of the AuNPs. The solution was removed from heating and kept under stirring until it cooled to room temperature.
Electroless gold plating

A PDA-coated substrate was immersed in a conical tube containing 10 mL of the previously obtained AuNP suspension and incubated under orbital shaking (120 rpm) overnight. The AuNP coated substrate was removed, rinsed with water, and nitrogen dried. Then, the substrate was placed in a conical tube containing 9.898 mL of H[AuCl₄] (1 mM), 102 µL of H₂O₂ (30 %) were added, and the sample was incubated under orbital shaking (120 rpm) for 30 minutes. After plating, the vinyl mask was removed, the gold electrode rinsed with water, and nitrogen dried. Finally, the substrates containing the plated gold electrodes were shrunk in an oven at 160 °C to produce gold MSEs. For flat electrodes with a geometrical footprint equivalent to the MSEs, the plating procedure was the same but performed in a glass vial containing 5 mL.

Kinetic behavior of AuNP coating

The absorbance of freshly synthesized AuNPs was determined between 400–800 nm with a Cary 100 Bio UV-Vis spectrophotometer (Varian Medical Systems of Palo Alto, California, USA). Then, in a 50 mL conical tube containing 10 mL of the AuNPs, a PS substrate with a drop-casted PDA coating was submerged face up and placed under orbital shaking. The absorbance of the solution was measured at 30 minutes, 1, 2, 3, 4, 5, 6, 7, 8, 10, and 12 hours. The number of particles in the solution at each time (Np(tₙ)) was determined according to Equation 1 and the number of particles on the electrode surface at each time (NPs(tₘ)) was obtained through Equation 2. All measurements were performed in triplicate and two batches of AuNPs were used.

\[
N_P (t_n) = \frac{A_{450}}{\epsilon b} \times N_a \times V
\]

\[
NPs (t_m) = N_P (t_0) - N_P (t_m)
\]

Resistivity measurement

For the resistivity measurement, PS squares of 2 × 2 cm were plated following the methodology established above for each metal. The 4-probe resistance measurements were performed using a source picoammeter (Model 2450, Keithley Instruments, Cleveland, OH). Then, the films were shrunk and the resistivity determined again. Previously, the thickness of each film was determined through AFM. The sheet resistance was determined by multiplying the resistivity by the thickness of the film. All the measurements were done in triplicate.

Solution-processed electrochemical cell fabrication

The RE was fabricated by drop-casting a PDA film, followed by silver plating (Figure 1) according to the methodologies described above (the stencil openings defining the working and auxiliary electrodes (AEs) were masked during these steps). Then, the plated silver electrode was masked with self-adhesive vinyl and the working and AE openings were unmasked. A PDA film was drop-cast and the electrodes were gold plated following the protocol described above. Afterward, the vinyl was removed and the electrochemical cell electrodes were rinsed with 18.2 MΩ cm water and nitrogen dried. The electrochemical cell was shrunk for 5 minutes at 160°C in an oven to produce MSE surfaces. Finally, to produce an Ag/AgCl RE, the silver-plated electrode was chlorinated in a solution of KCl (1 M) through five cycles of CV between 0.4 and -0.05 V at a scan rate of 0.1 V s⁻¹.

Dopamine detection

A stock solution of dopamine (1 mM PBS 1x) was prepared in a 50 mL conical tube. From there, the desired solutions of dopamine at different concentrations (0–100 µM) were prepared in PBS 1x. Then, the solutions were added to the electrochemical cell and chronoamperometry was performed. This procedure was repeated with three electrochemical cells for all the studied dopamine concentrations.

Thickness measurements

All thickness measurements (PDA coating, copper, silver, and gold plating) were done using an Atomic Force Microscopy (AFM) Asylum MFP-3D instrument (Asylum
Research, an Oxford Instrument Company, Santa Barbara, CA, USA) in AC mode. Images (10 × 10 µm) that included the edge of the film and the PS substrate were acquired (Figure 2F). The average height of the PDA film side and the PS side were calculated using Gwyddion 2.55 software. The film thickness was then obtained by subtracting the height of the film from the PS side. In all cases, the measurements were done on three independent samples. The same procedure was followed for the metal films.

4.13 Electrochemical measurements

All the electrochemical measurements were done using a CHI600E electrochemical workstation (CH Instruments, Austin, TX, USA) using a three-electrode electrochemical cell setup. The gold electrodes were used as the WE, a platinum wire was used as the AE, and an Ag/AgCl electrode as the RE. The ESA of the plated electrodes was determined by placing the gold electrode in the electrochemical cell containing H₂SO₄ (0.5 M) as a conductive medium. A voltage sweep between 0.3 and 1.6 V and a scan rate of 0.1 V s⁻¹ were applied during five cycles. The area under the reduction peak of the three last cycles was used to calculate the total charge transferred and dived by the charge associated with an oxidized monolayer formation in one square centimeter of gold (386 µC cm⁻²) to obtain the electrode’s ESA. All the measurements were done in triplicate. The chronoamperometry was performed by applying a 0 V potential for 2 seconds followed by 0.1 V for 2 seconds for five cycles. The oxidation current was obtained by averaging the values in the time intervals 1–2, 5–6, 9–10, 13–14, and 17–18 seconds for each sample. The reproducibility, repeatability and interday precision of the solution-processed microstructured cell (SMECs) were measured through CV in potassium ferricyanide (KFeCy – K₄[Fe(CN)₆], 2 mM in PBS1X). A voltage sweep between -0.05 and 0.4 V and a scan rate of 0.1 V s⁻¹ were applied during three cycles. For the reproducibility performance, the response of six independently fabricated electrodes was measured. The repeatability was assessed by measuring the response of one electrode every 3 minutes for five repetitions. Finally, the interday precision was determined by obtaining the CV of three independently fabricated electrodes every day for 5 days.

The Randles-Sevcik equation (Equation 1) was used to determine the ESA in KFeCy. In this case, the voltage sweep was between -0.05 and 0.4 V and the different scan speeds evaluated were 25, 50, 75, 100, 150, 200, 250 and 300 mV s⁻¹. The current of the cathodic peak was plotted versus the square root of the scan speed and the slope of this plot used to determine the ESA. The diffusion coefficient used for KFeCy was 2.88 × 10⁻³ cm² s⁻¹.

\[
i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C^{1/2} v^{1/2}
\]

\(i_p\) = peak current maximum (A)
\(n\) = number of electrons transferred
\(A\) = electrode area (cm²)
\(D\) = diffusion coefficient of redox probe (cm² s⁻¹)
\(C\) = concentration (mol cm⁻³)
\(v\) = scan rate (V s⁻¹)

4.14 Scanning and transmission electron microscopy

Scanning electron microscopy (SEM) imaging of the electrodes was performed on a JEOL 7000F SEM (JEOL, Tokyo, Japan). The samples were mounted on 1″ stainless steel stubs with carbon tape. SEM of the nanoparticle coated samples was performed in a Magellan 400 (FEI, Hillsboro, OR, USA). Transmission electron microscopy (TEM) imaging was done on a JEOL 1200EX TEMSCAN (JEOL, Tokyo, Japan). A 3 µL drop of the sample was deposited onto a 200 mesh Cu-Pd grid and left to dry for 4 hours before imaging.

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AUTHOR CONTRIBUTIONS

Eduardo Gonzalez-Martinez designed and performed the experiments, analyzed the data, and wrote the first draft of the manuscript. Sokunthearith (Kevin) Saem assisted with initial electrochemical and electron microscopy characterization, and Nadine E. Beganovic assisted with electrochemistry data acquisition. Jose Moran-Mirabal provided experimental guidance, verified consistency of data analysis and edited the manuscript. Eduardo Gonzalez-Martinez, Sokunthearith (Kevin) Saem, Nadine E. Beganovic and Jose Moran-Mirabal reviewed and approved the final manuscript.
CONFLICT OF INTEREST
The authors report no conflicts of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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