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Enabling Inkjet Printed Graphene for Ion Selective Electrodes with Postprint Thermal Annealing

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Supporting Information

ABSTRACT: Inkjet printed graphene (IPG) has recently shown tremendous promise in reducing the cost and complexity of graphene circuit fabrication. Here we demonstrate, for the first time, the fabrication of an ion selective electrode (ISE) with IPG. A thermal annealing process in a nitrogen ambient environment converts the IPG into a highly conductive electrode (sheet resistance changes from 52.8 ± 7.4 MΩ/□ for unannealed graphene to 172.7 ± 33.3 Ω/□ for graphene annealed at 950 °C). Raman spectroscopy and field emission scanning electron microscopy (FESEM) analysis reveals that the printed graphene flakes begin to smooth at an annealing temperature of 500 °C and then become more porous and more electrically conductive when annealed at temperatures of 650 °C and above. The resultant thermally annealed, IPG electrodes are converted into potassium ISEs via functionalization with a poly(vinyl chloride) (PVC) membrane and valinomycin ionophore. The developed potassium ISE displays a wide linear sensing range (0.01–100 mM), a low detection limit (7 μM), minimal drift (8.6 × 10⁻⁶ V/s), and a negligible interference during electrochemical potassium sensing against the backdrop of interfering ions [i.e., sodium (Na), magnesium (Mg), and calcium (Ca)] and artificial eccrine perspiration. Thus, the IPG ISE shows potential for potassium detection in a wide variety of human fluids including plasma, serum, and sweat.

KEYWORDS: graphene, inkjet printing, thermal annealing, ion selective electrode, potassium, potentiometry

INTRODUCTION

The incorporation of both single-layer and multilayer graphene into electrodes has significantly improved the sensitivity, detection limit, response time, and biocompatibility of electrochemical sensors and biosensors. The enhanced performance of graphene-based sensors/biosensors is attributed to the unique and advantageous material properties of graphene including high electron mobility of up to 200 000 cm² V⁻¹ s⁻¹, high nominal surface area of 2630 m² g⁻¹, and high tensile strength of 42 N m⁻¹ as well as the relative ease of functionalization. In addition to graphene agents, the electrochemical properties of graphene and other graphitic materials in general (e.g., highly ordered pyrolytic graphite (HOPG), graphene oxide (GO), carbon nanotubes (CNTs), and graphite) can be enhanced by inducing edge plane like-sites/defects and defect site functional groups onto the carbon surface through a variety of techniques (e.g., plasma etching, ion bombardment, and wet etching) to increase heterogeneous electron transfer rates and hence improve sensitivity/detection limits of electrochemical sensors. Additional graphene modification techniques such as nitrogen doping and metallic nanoparticle integration have also been developed to improve graphene sensor performance. Indeed, the use of graphene and “modified” graphene has shown tremendous promise for electrochemical sensing, but the high cost and complexity of graphene electrode fabrication (fabrication that often requires lithographic patterning and high temperature chemical vapor deposition in a vacuum chamber reactor) and subsequent chemical modification steps have impeded their implementation and commercialization in a wide variety of in-field and point-of-care applications.

IPG has recently shown tremendous promise in reducing the cost and complexity of graphene circuit fabrication. Graphene used in inkjet printing can be synthesized via low cost solvent-exfoliation processes to rapidly produce large batches of graphene or graphene oxide flakes that can be subsequently dispersed and formulated into a printable ink.
Furthermore, the ink jet printing process can be used to make microcircuits with line resolution of approximately 60 μm—thus eliminating the need for UV lithographic techniques that utilize a prefabricated photomask followed by dry etching of active materials or screen printing techniques that use a prefabricated metal stencil to pattern surfaces with defined circuit geometries. Subsequently, inkjet printing has been used for a wide variety of functional devices including thin film transistors,19,23 acoustic actuators,24 dipole antennas,25 interdigitated electrodes for electrically induced stem cell differentiation,26 and sensors such as a NO2, Clo2 vapor sensor,27 a digital temperature sensor,28 and a hydrogen peroxide sensor.28 and a hydrogen peroxide sensor. 34

**EXPERIMENTAL SECTION**

Reagents. Valinomycin (90%), bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis(4-chlorophenyl)borate (KTCIPB), poly(vinyl chloride) (PVC), tetrahydrofuran (THF, 99.8%), sodium chloride (NaCl), sodium sulfate (Na2SO4), sodium bicarbonate (NaHCO3), potassium chloride (KCl), magnesium chloride (MgCl2), sodium phosphate anhydrous monobasic (NaH2PO4), calcium carbonate (CaCO3), and ammonium hydroxide (NH4Cl) were procured from Sigma-Aldrich (St. Louis, MO). Spiked sweat containing potential interfering electrolytes including NaCl, Na2SO4, NaHCO3, KCl, MgCl2, NaH2PO4, CaCO3, and NH4Cl at physiological concentrations5 were used in the experiments and spiked with potassium concentrations as stated. Artificial eccrine perspiration (stabilized at pH 4.5) was purchased from Pickering Laboratory with a listed concentration of ~33 mM. The artificial perspiration contains the following metabolites (uric acid, lactic acid, urea, ammonia), minerals (sodium, iron, nitrate, calcium, copper, sulfate, magnesium, potassium, zinc, chloride), and amino acids (glucose, 1-histidine, l-serine, l-alanine, l-isoleucine, l-threonine, l-arginine, l-leucine, l-tyrosine, l-asparagine, l-lysine, l-valine, l-aspartic acid, l-methionine, taurine, l-citrulline, l-ornithine, l-glutamic, l-phenylalanine) in concentration levels found in real eccrine perspiration.

**Graphene Ink Formulation.** Inkjet printable, graphene-based ink was produced from exfoliated graphene powder, solvents, and the stabilizing polymer ethyl cellulose by modifying previously described methods. 20,22,34 Briefly, graphene ink batches (20 mL) were synthesized by vortex mixing single layer dispersible graphene (ACS Materials, “completely” reduced graphene oxide obtained via the Hummer’s methods) in a mixture of 85% cyclohexanone (Sigma-Aldrich 398241) with 15% terpineol (Sigma-Aldrich T3407) for 1 min at high speed in a 50 mL falcon vortex tube. The initial concentration of graphene to solvent was set to 3.5 mg/mL ratio. Ethyl cellulose (Sigma-Aldrich 433837) was added to the mixture at a ratio of 3.5 mg/mL, and the subsequent solution was vortex mixed for 5 min. The graphene ink was then poured into a 50 mL beaker and probe sonicated (Sonic’s Vibra-cell VCX-750 ultrasonic processor) at 50% amplitude for 30 minutes three times, bath sonicated for 6 h at high power, and finally filtered through a 0.45 μm syringe filter to break up and filter out large graphene particles and ensure a consistently jettable ink with a measured viscosity of 10 cP with a microVISC RheoSense viscometer.

**IPG Electrode Fabrication.** Graphene ink was inkjet printed via a Dimatix Materials Printer (Model DMP 2800, FujiFilm) while the electrode patterns were designed in AutoCAD (Auto- desk, San Rafael, CA). To print the ink, 5 mL of the formulated graphene ink was loaded into a Dimatix printer cartridge with 10 mL nominal drop volume nozzles. Printing was conducted on a 100 mm silicon wafer placed on the printer platform that was maintained at a temperature of 60 °C. The printing parameters were optimized by adjusting the droplets speed (8 m/s) using the temperature (60 °C), waveform, and
The IPG electrodes were subsequently annealed in a nitrogen environment at varying temperatures (200 °C, 350 °C, 500 °C, 650 °C, 800 °C, and 950 °C) within a 2 in. compact split tube furnace (MTI Corp.) for 1 h at the prescribed temperature and were left in the annealing furnace for an additional 30−60 mins during both the furnace temperature ramp up and ramp down periods. Subsequent Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and electrical sheet resistance data were acquired for unannealed and thermally annealed samples. Raman spectroscopy was acquired with a Renishaw spectrometer microscope using a 488 nm excitation source (argon ion laser), a total acquisition time of 30 s (i.e., three acquisition times of 10 s each), and a 200 μW laser power illumination. The spectrometer was calibrated using an internal silicon reference prior to the measurements. FESEM micrographs were obtained via a FEI Quanta 250 FE-SEM with an electron beam voltage of 10 kV. Electrical sheet resistance data were obtained from a signatone four-point probe. The measurements were taken at multiple spots (four different spots) on the sample surface, and the average values of these measurements were plotted. The XPS spectra were collected using a Kratos Amicus X-ray photoelectron spectrometer using an Al Kα excitation source (1486.7 eV). The corresponding photoelectron energies from the constituent elements were measured by subtracting the excitation energy from the scan and subsequently obtaining the binding energy survey scan. The N 1s spectrum was analyzed for each distinctly annealed IPG electrodes. A Shirley background fitting and Gaussian–Lorentzian line peak fitting on the N 1s peak spectrum was performed with a CasaXPS software package.

**Potassium ISE Synthesis.** IPG electrodes were converted into potassium ISEs by depositing a potassium selective membrane onto the circular section of the graphene electrode. The potassium selective membrane cocktail consisted of 1.0 wt % valinomycin, 66 wt % DOS, and 33 wt % PVC. The components were dissolved in 1 mL of THF with concentration of 15 wt %. Next, 10 μL of cocktail was drop-coated onto the IPG electrodes and subsequently dried in air for 6 h.

**Potentiometric Analysis.** The potentiometric measurements were performed using a CHI667E electrochemical workstation (CHI Instruments, USA). An Ag/AgCl electrode (saturated in 3 M KCl) was used as the reference electrode. The electrodes were conditioned in 0.01 M KCl solution for 24 h before electrochemical testing and dry stored at room temperature between testing experiments. The analytical performance of the potassium ISEs was analyzed in the concentration range of 10^−6−10^−2 M via a KCl salt solution. The interfering tests were conducted by following similar protocols29 where DI water was first spiked with 0.001 M KCl, next with 0.01 M KCl, and finally with artificial eccrine perspiration IPG ISE drift analysis was performed by constant current chronopotentiometry where the potential was recorded by applying a positive 1 nA current for 100 s followed by a negative current of 1 nA for 100 s in a test vial containing 0.1 M KCl solution. The drift of the IPG ISE was derived from the potential change during the recording time (ΔE/Δt) while a fixed current was applied to the IPG ISE.30

### RESULTS AND DISCUSSION

**Potassium IPG ISE Fabrication Strategy.** The potassium ISEs were developed on thermally annealed IPG per the process steps displayed in Figure 1. First, graphene ink was formulated with single-layer graphene dispersed in solvent (85% cyclohexanone/15% terpineol) and stabilized with an ethyl cellulose polymer by both bath and probe sonication as noted in the Experimental Section and by modifying existing graphene ink recipes (Figure 1a).20,22 The formulated graphene ink (viscosity of 10 cP) was inkjet printed via a Dimatrix Materials Printer onto a silicon wafer (with 300 nm silicon oxide) (Figure 1b−d and Experimental Section). Next, a split tube furnace was used to anneal the IPG at 200, 350, 500, 650, 800, and 950 °C in a nitrogen environment (i.e., without oxygen) to prevent graphene oxidation during the annealing process (Figure 1e). As shown in subsequent electrical and optical characterization experiments, this annealing process was conducted to improve the electrical conductivity of the printed graphene and improve its electrochemical sensing performance. Finally, a potassium ion-selective cocktail (see Experimental
Characterization of IPG Electrodes. Before potassium ISE immobilization, the IPG was thermally annealed and characterized via electrical measurements, Raman spectroscopy, and FESEM (Figure 2). First, the electrical sheet resistances of the IPG electrodes annealed at six distinct temperatures, viz., 200, 350, 500, 650, 800, and 950 °C, were compared with the sheet resistance of the unannealed graphene electrode (Figure 2a). Figure 2a displays an unannealed IPG sheet resistance of $52.8 \pm 7.4 \, \Omega / \square$ ($\pm\,\text{1 std dev}$; $n = 4$) that decreases with increasing annealing temperature until a plateau of approximately $147.7 \pm 14.9 \, \Omega / \square$ ($\pm\,\text{1 std dev}$; $n = 3$) at 800 °C is reached. The sheet resistance slightly increases to $172.7 \pm 33.3 \, \Omega / \square$ ($\pm\,\text{1 std dev}$; $n = 3$) when the annealing temperature is raised to 950 °C. Thus, there is more than 5 orders of magnitude increase in the electrical conductivity as the graphene is annealed to a temperature of 800 °C. This significant increase in electrical conductivity (equivalently, decrease in the sheet resistance) is most likely due to the further reduction of the reduced graphene oxide flakes, graphitic crystal formation, and nitrogen doping as verified in subsequent FESEM, Raman spectroscopy, and XPS analysis.

Raman spectroscopy was performed on both annealed and unannealed IPG samples (Figure 2b). Raman spectroscopy was employed to analyze the printed graphene as it is has been extensively used to characterize both graphene and graphitic materials. Single crystal micromechanically exfoliated graphene possesses two characteristic peaks, namely, a G peak and 2D peak that correspond to wavenumbers of approximately 1580 and 2700 cm$^{-1}$, respectively. Furthermore, edge defect, grain boundary, and/or topological defects in the graphene give rise to the D peak observed at $\sim 1350 \, \text{cm}^{-1}$ as often portrayed in jagged petal-like growth of CVD grown multilayered graphene. In the IPG presented here, the D, G, and 2D peaks are observed at wavenumbers of approximately 1350, 1590, and 2700 cm$^{-1}$, respectively. Overall, these three graphene characteristic peaks can be attributed to a defect-rich multilayer graphene stack (the reduced intensity of the 2D peak intensity compared to that of the G peak reveals a multilayer structure, while the D peak intensity reveals a high degree of defects). Also, the D and G peaks are red-shifted by several tens of wavenumbers (the D and G peaks red-shifts by $10-20 \, \text{cm}^{-1}$) as compared to the typical Raman spectrum for single-layer, single-crystal graphene. This red-shift can be attributed to the combination of defects and thermally induced tensile strain in the printed graphene structure as the red-shift...
of the D peak increases with increasing annealing temperature and the red-shift of the G and 2D peaks remains stable and temperature independent. Such increasing strain could originate from movement in the defect sites and edge/junctions of the printed graphene layers during thermal annealing. In addition to the one-phonon defect-assisted process, there were also multiphonon defect-assisted processes such as the D + D’ peak present in all the electrodes (Figure S1 in the Supporting Information).33

The microstructure of the IPG electrodes was also characterized via FESEM (Figure 2c) for both unannealed IPG and IPG annealed at distinct temperatures (200, 350, 500, 650, 800, and 950 °C). The FESEM micrographs reveal the relative roughness of the graphene microstructure of the unannealed IPG. This microstructure does not noticeably change during thermal annealing at 200 and 350 °C (Figure 2d,e). However, upon reaching an annealing temperature of 500 °C, the graphene microstructure is noticeably more smooth with less exposed graphene flake edges (Figure 2f). At these higher annealing temperatures (500 °C), the individual flakes appear to merge together, making a smooth microstructure. This “thermally induced smoothening” of the microstructure of the IPG electrode exhibits more than 4 orders of conductivity enhancement compared to the unannealed electrode as the physical boundaries between individual graphene flakes becomes “welded” together34 and the defects are minimized. Further increases in the annealing temperature (650 °C or greater, Figure 2g–i) displays a more porous microstructure in the electrode (see Figure S2). At these higher annealing temperatures, the D peak of the IPG Raman spectra increases and the sheet resistance further decreases. As the IPG annealing temperature is further increased (800 °C or greater), the IPG achieves both a relatively high electrical conductivity and a high number of defects that are necessary for fast heterogeneous charge transport which can subsequently lead to highly sensitive electrochemical sensing/biosensing. The presence of more defects at higher temperatures, relating to the porous micro/nano structure, is further evidenced from the Raman spectra at higher temperature (increasing trend of the ratio of D-peak intensity to G-peak intensity).

To further probe the local electronic structure, the N 1s photoelectron spectra of all the annealed electrodes under consideration were analyzed via XPS (Figure 3). Note that an unannealed sample does not have a nitrogen peak as shown previously.34 However, all the annealed electrodes, including the IPG annealed at 200 °C, contain nitrogen (Figure 3). Figure 3d shows the total nitrogen atomic percentage doped in graphene with minimum of 0.4 at. % at 200 °C and maximum of 1.1 at. % at 350 °C. Such N 1s peaks at 400 eV (blue lines/points in Figure 3) are consistent with nitrogen bonded to graphene lattice defects (nitrogen atom substitutional doped in the graphene lattice).35,36 It is interesting to note that the formation of nitrogen within the graphene lattice (alternatively called “quaternary nitrogen”) has been realized before in reduced graphene oxide matrices using ammonia annealing at a temperature of 900 °C;36 however, in this work the IPG electrodes exhibit nitrogen-doped graphene (NG) at much lower temperatures (200 °C) in a nitrogen annealed ambient. A higher binding energy N 1s component can also be found at 402 eV (red lines/points in Figure 3) in the thermally annealed IPG which is consistent with nitrogen that contains a higher coordination number. Such higher binding energy N 1s components are presumably formed via substitution with the carbon atoms in the graphene lattice (this type of coordination has been reported to be an “oxidized nitrogen” phase35,37). The higher binding energy component gains more intensity as annealing temperature increases; however, the relative nitrogen doping in graphene displays a decreasing graphitic coordination with increasing temperature (Figure 3c). Finally, to collectively understand the role of nitrogen annealing at various temperatures from a defect generation standpoint the $I_D/I_G$ intensity ratio from the Raman spectroscopy data originally displayed in Figure 2b was plotted versus total atomic nitrogen concentration (see Figure 3d). The IPG defects, as denoted in the $I_D/I_G$ ratio plot (greater $I_D/I_G$ signifies more defects and vice versa), continue to rise with an increasing rate according to annealing temperature while the total nitrogen doping increases to a maximum (350 °C) and then decreases with higher annealing temperatures. Thus, the concomitance of increasing superficial defects and a lower level of overall nitrogen composition, i.e., a more graphitic surface, may have led to higher electrical conductivity in high temperature annealed IPG (800 °C or higher) as well as to the higher electrochemical potassium sensing capability (see subsequent sections).

Electrochemical Analysis of Potassium ISE. The IPG was converted into a potassium ion selective electrode by drop-coating a potassium selective membrane cocktail (containing valinomycin as the potassium ionophore) onto the graphene electrodes that were thermally annealed at 200, 350, 500, 650, 800, and 950 °C (see Experimental Section; also note the unannealed IPG electrodes were not sufficiently conductive for electrochemical sensing and hence were not tested in these experiments). The electrochemical ionic response to potassium of the IPG ISE was measured in DI water with various concentrations of KCl solutions vs an Ag/AgCl reference electrode (Experimental Section). Experimental results show that with increasing annealing temperature, the IPG ISE sensors achieve lower detection limits (Figure 4a) and
increased sensitivity (Figure 4b and Table S1). More specifically, the detection limit of the IPG ISE sensor steadily decreases from 22 μM (log $K^+$ = 10$^{-4.6}$) to 7 μM (log $K^+$ = 10$^{-5.2}$) as the annealing temperature increases to 950 °C. The sensitivity values of IPG ISEs also increase and display less variability from 48.6 to 57.6 mV with increasing annealing temperature. Thus, when the annealing temperature of IPG electrodes reaches 800 °C, the ISE sensors begin to exhibit a sensitivity value close to that predicted by the Nernstian equation. Furthermore, the overall sensor drift (Figure 4c), as measured via chronopotentiometry, continued to decrease to 8.6 × 10$^{-8}$ V/s as the annealing temperature increased to 800 °C.

The decreases in the IPG ISE detection limit and drift with higher annealing temperature could be explained in part by the smoother thermal annealed IPG surface minimizing the spontaneous formation of a water layer between the ISE membrane and IPG electrode. Such a water layer acts as an electrolyte reservoir which re-equilibrates on each sample composition change, consequently introducing potential instability and higher detection limits. At annealing temperatures of 200 and 350 °C, the rough IPG microstructured surface is more conducive to water layer formation within the more rugged graphene flake topology. This water layer formation could explain the higher variation of sensitivity value for IPG ISEs annealed at the lower temperatures of 200 and 350 °C. However, as the annealing temperature increases, the microstructure of the graphene flakes becomes much more smooth, which in turn could reduce the formation of water layer buildup and hence lower the drift and detection limit of the ISE.

Based on the electrochemical characterization, the ISE based on IPG thermally annealed at 950 °C was chosen for further characterization. This graphene potassium ISE exhibited a Nernstian response to KCl corresponding to a sensitivity value of 57.6 mV per decade of $K^+$ concentration, a characteristic that is predicted by the theory for solvent polymeric membranes doped with valinomycin as the potassium ionophore. As shown in Figure 4a, the ISE displayed a linear response to $K^+$ concentration (in logarithmic scale) within the KCl concentration range of 0.01–10 mM. The small standard deviation even between the lowest concentrations of potassium (i.e., RSD 2.27%, n = 3; see Figure 4a) yielded a reliable and repeatable observable detection limit of 7 μM (log $K^+$ = −5.2). The potential versus log $K^+$ plot reveals that the sensing response is nearly instantaneous and reaches the stability within 10 s, a response time faster than that of a liquid-contact ion-selective electrode, especially at lower concentrations (Figure 5a inset). Such a fast response is important for the real-time monitoring of rapid changes in potassium concentration in the sweat that can fluctuate quickly according to perspiration rates.

Furthermore, the IPG ISE was also tested for repeatability by subjecting the sensor to successive changes in KCl solutions with potassium concentrations alternating from 1, 10, and 100 mM, using four oscillation cycles (see Figure S3). This improvement in potassium sensitivity and detection limit is most likely due to reduced water layer formation as previously described, but also do to the increasing porosity of the graphene with higher annealing temperatures (see Figure S2). Such higher porosity or edge defects in graphene render the surface more electroactive than pristine basal plane graphene and subsequently most likely led to improvements in the capacitance and charge storage capability of the electrodes and the near Nernstian slope/sensitivity.

The developed potassium ISE was also tested against the backdrop of common ion interferences that are typically found in sweat. These initial selectivity experiments were conducted by spiking DI water with said interferents (at concentration levels typically found in sweat) while the potassium concentration was varied over the sweat potassium physiological range of 1–63 mM (Figure 5b). The potassium ISE sensor showed a Nernstian response with the sensitivity value consistent with that of the membrane-based potassium ISE.
of 54.5 mV per decade of potassium ion concentration (RSD 0.91%, n = 3). The obtained potassium sensitivity was also similar to the sensitivity of K ions previously demonstrated in the KCl solution. The small standard deviation in sensor sensitivity for experiments conducted in both KCl solution (RSD 2.27%, n = 3; see Figure 5c) and KCl solution with multiple additive ions (RSD 0.91%, n = 3; see Figure 5d) demonstrates that the sensor is capable of detecting potassium concentrations in a repeatable fashion. The selectivity coefficients, log $K_{\text{IPG}i}$ [± standard deviation (n = 3)], of common interfering ions [i.e., sodium (Na), magnesium (Mg), and calcium (Ca)] were also obtained, according to previously reported protocols as follows: log $K_{\text{IPIPIG}}$ = 0.12, log $K_{\text{IPG.}}$ = 3.90 ± 0.08, and log $K_{\text{IPG.}}$ = 3.39 ± 0.21. The obtained selectivity coefficients are comparable to other carbon-based to solid-contact or solid-state ISEs.

Furthermore, the IPG ISE was capable of accurately detecting the amount of potassium found within artificial eccrine perspiration (Figure S3) where the measured potentiometric response correlated to a potassium concentration of 33.9 ± 2.4 mM—a potassium concentration that is close to the listed value of 33 mM (see Figure S4 and the Experimental Section). This result demonstrates that the IPG ISE is capable of selectively detecting potassium within a complex matrix containing a combination of 33 metabolites, minerals, and amino acids (see Experimental Section).

Finally, the potassium sensing results of the IPG ISE was compared with similar carbon-based electrodes that have been recently published in the research literature (Table 1). For example, the potassium detection limit of the IPG ISE reached log $K_{\text{IPG}}$ = 105.2, which is lower than similar ISEs comprised with nanostructured carbon fullerene (log $K_{\text{IPG}}$ = 105.0) and graphene on glassy carbon (log $K_{\text{IPG}}$ = 105.8). The recorded drift (8.6 × 10−6 V/s) of the IPG ISE is lower than similar ISEs nanostructured withCNTs (1.7 × 10−5 V/s) and graphene on glassy carbon (1.2 × 10−5 V/s). The linear sensing range (0.01–10 mM) of the developed IPG ISE is also on par with similar solid-state potassium ISEs that use nanocarbon-based materials as the transduction element.

### CONCLUSION

In summary, we have developed a scalable inkjet printing process for graphene-based ion selective electrodes or IPG ISEs. Before functionalization with a potassium detecting ionophore, the IPG was thermally annealed in a nitrogen environment to improve both the electrical conductivity and electrochemical sensing capability of the resultant IPG ISE. This annealing process improved the electrical sheet resistance of the IPG by several orders of magnitude from 52.8 ± 7.4 MΩ/□ for unannealed IPG to 147.7 ± 14.9 and 172.7 ± 33.3 MΩ/□ for annealed at temperatures of 800 and 950 °C, respectively. Furthermore, the thermal annealing process created a highly conductive graphene surface that is well-suited for electrochemical sensing as the “welded porous” surface is sufficiently “electroactive” without the need for graphene chemical modification steps such as metallic nanoparticle integration which is often used to increase the electroactive nature of carbon-based electrochemical electrodes. The IPG electrodes were subsequently converted into potassium ISEs by functionalizing the graphene surface with the potassium ionophore, valinomycin, drop-coated within a PVC matrix. The resultant IPG ISE, thermally annealed at 950 °C, displayed a wide linear sensing range (0.01–10 mM) and low detection limit (7 μM) that favored favorably to other potassium ISEs that used a nanocarbon-based transduction element (e.g., graphene on glassy carbon electrodes, carbon nanotubes and mesoporous carbon; see Table 1). Furthermore, the inkjet printing process developed herein presents a scalable nonmanufacturing route for nanostructured ISEs that eliminates the need for both the costly fabrication of graphene through chemical or physical vapor deposition, the need for costly electrode patterning through clean room process such as photolithography, and the need to fabricate metal stencils for each new pattern design such as performed in screen printing. The developed potassium IPG ISE was capable of measuring potassium in a complex artificial eccrine perspiration solution that contained a combination of 33 metabolites, minerals, and amino acids. The IPG ISE is also capable of sensing physiologically relevant concentrations of potassium including those found in plasma and serum where potassium concentrations can range between 3.1–4.6 and 0.3–0.4 mM, respectively. Also, the developed IPG ISE could potentially be used to detect plant available potassium levels in soil (1.1–2.2% of the 10–20 g of potassium found in a typical kg of soil is plant available) where a typical soil slurry dilution (1 kg of soil per 2 L of water) would yield a potassium concentration range from 1.4 to 5.7 mM. Because of the plastic to print graphene on flexible, curvilinear surfaces as well as the ability to detect concentrations of potassium found in sweat (~ 1 mM), the developed potassium ISEs may also be well-suited for wearable epidermal sensors that monitor potassium levels from eccrine sweat glands. Of course, in all of these potassium sensing examples, rigorous testing within field conditions will need to be conducted to prove the viability of the IPG ISE in these various environments where temperature, humidity, and interfering species may vary widely. Such rigorous testing is reserved for future work. In summary, the developed potassium IPG ISEs represent a potential scalable, low-cost manufacturing protocol for monitoring potassium in a variety of biomedical and environmental applications.

### Table 1. Performance Comparison Table of Nanocarbon-Based, Solid-State ISEs

<table>
<thead>
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<th>electrode*</th>
<th>detection limit (M)</th>
<th>slope (mV/decade)</th>
<th>linear range (M)</th>
<th>drift</th>
<th>ref</th>
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<td>57.2</td>
<td>10^{-3}–10^{-2}</td>
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<td>55</td>
<td>10^{-3}–10^{-2}</td>
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<td>14.9 × 10^{-6} μV/h^d</td>
<td>44, 49</td>
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*IPG inkjet printed graphene; CNT = carbon nanotube; GC = glassy carbon; CIM carbon = colloid-imprinted mesoporous carbon. ^Drift was obtained via chronopotentiometric means (see Experimental Section). ^Long-range drift test acquired by monitoring the open circuit potential over a time frame of 70 h. ^Long-range drift test acquired by monitoring the open circuit potential over a time frame of 20 h.
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## REFERENCES


(32) Shang, N. G.; Papakonstantinou, P.; McMullan, M.; Chu, M.; Stamboulis, A.; Potenza, A.; Dhesi, S. S.; Marchetto, H. Catalyst-Free Efficient Growth, Orientation and Biosensing Properties of Multilayer...


