

Inkjet Printing of a Highly Loaded Palladium Ink for Integrated, Low-Cost pH Sensors

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An inkjet printing process for depositing palladium (Pd) thin films from a highly loaded ink (>14 wt%) is reported. The viscosity and surface tension of a Pd-organic precursor solution is adjusted using toluene to form a printable and stable ink. A two-step thermolysis process is developed to convert the printed ink to continuous and uniform Pd films with good adhesion to different substrates. Using only one printing pass, a low electrical resistivity of $2.6 \mu\Omega \text{ m}$ of the Pd film is obtained. To demonstrate the electrochemical pH sensing application, the surfaces of the printed Pd films are oxidized for ion-to-electron transduction and the underlying layer is left for electron conduction. Then, solid-state reference electrodes are integrated beside the bifunctional Pd electrodes by inkjet printing. These potentiometric sensors have sensitivities of 60.6 ± 0.1 and $57 \pm 0.6 \text{ mV pH}^{-1}$ on glass and polyimide substrates, and short response times of 11 and 6 s, respectively. Also, accurate pH values of real water samples are obtained by using the printed sensors with a low-cost multimeter. These results indicate that the facile and cost-effective inkjet printing and integration techniques may be applied in fabricating future electrochemical monitoring systems for environmental parameters and human health conditions.

applications, metal nanoparticles, oxides, polymers, and many other materials were inkjet-printed.^[1] However, the inkjet printing of an essential material for electrochemical applications, palladium (Pd), is less commonly reported.

Pd is of significant importance for electrochemical applications due to its high electrocatalytic activity and affinity for hydrogen.^[9] Pd and Pd-based materials have been used as electrocatalysts in power sources,^[9,10] absorbers in hydrogen purification and storage devices,^[9,11] and sensing materials in gas/bio/chemical sensors.^[9,12,13] Previously, we demonstrated that the reversible redox reactions between palladium/palladium oxide (Pd/PdO) and hydronium ions (H_3O^+) could be used for highly sensitive pH monitoring.^[13] Besides, Pd can be used for electrical interconnections in electronic devices. For instance, Pd provided good ohmic contacts in carbon nanotube-based field-effect transistors because of its high

work function.^[14–16] Also, Pd was used for inter-chip interconnections due to its high electrical conductivity and resistance to chemicals.^[17] Thus, Pd and Pd-based materials have the potential to play a dual role as active sensing materials and electrical interconnections in future electrochemical sensing/monitoring systems.

One important challenge of applying Pd and Pd-based materials in low-cost electrochemical systems is related to its deposition techniques. Usually, Pd and Pd-based materials are deposited via hydrothermal growth, electrochemical deposition, thermal oxidation, and physical vapor deposition.^[9,18,19] These processing techniques require a large amount of chemicals, high-pressure chambers, high temperatures, and vacuum equipment. Also, additional patterning steps are needed to integrate the deposited materials into functional systems. These processing and patterning steps result in costly manufacturing. Therefore, the less complicated and more cost-efficient inkjet printing technique for Pd deposition should be developed.

To the best of our knowledge, inkjet printing of Pd has been used to deposit and pattern seed layers for electroless deposition,^[20–22] and also as the contact electrodes for thin-film resistors.^[15] The Pd inks used in these studies had low metal content (normally <5 wt%), which resulted in very thin, discontinuous, and high-resistance Pd films. Such Pd films were undesirable for electrochemical sensing because the inefficient

1. Introduction

Inkjet printing is an easy-to-use and low-cost approach to simultaneously deposit and pattern thin film materials from solutions. This technology can produce structures with fine patterns, consumes a small amount of materials, does not need complicated equipment, and is compatible with large-area processing lines for flexible and non-planar substrates.^[1] Numerous applications, for example, high-resolution electrodes,^[2,3] field-effect transistors,^[4] solar cells,^[5] light-emitting devices,^[6] bio/chemical sensors,^[7] and bio-printed tissues,^[8] were enabled by using inkjet printing technology. In these

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electron transfer in the high-resistance films results in a poor sensing performance.^[23] One method to reduce the resistance is to print the lightly loaded ink using multiple passes, but this is time-consuming.^[15] Alternatively, highly loaded Pd inks and their inkjet printing processes can be developed to deposit continuous, homogenous, and conductive Pd films using a single print pass, thus making it a fast film deposition technique.

In this work, we developed an ink loaded with >14 wt% Pd for inkjet printing. The inkjet printing process for such ink is optimized for the deposition of continuous, uniform and low-resistivity thin films with good adhesion to the underlying substrates. Utilizing this ink and printing process, we demonstrate the practical and cost-effective fabrication of an integrated pH sensing platform on both rigid and flexible substrates. Bifunctional sensing electrodes are fabricated by oxidizing the printed Pd. The PdO-rich surfaces function as pH sensing layers and the conductive portion beneath the surfaces are electron conduction paths. Solid-state reference electrodes are inkjet-printed besides the sensing electrodes to form potentiometric sensors. The integrated sensors exhibit high sensitivity, fast response, good stability, and are highly accurate in measuring real water samples. These low-cost printed sensors have the potential to be implemented in future wearable and portable electrochemical systems for ubiquitous monitoring of environmental parameters and human health conditions.^[23–26]

2. Results and Discussions

2.1. Inkjet Printing of Pd Inks

2.1.1. Pd Ink Formulation and Properties

The as-received Pd precursor solution contains a Pd-organoamine complex. Since the specific amine ligand significantly increases the solubility of the Pd complex in toluene (PhMe), the metal load for this precursor solution can be as high as ≈18.5 wt% (Table S1, Supporting Information). In addition, the organoamine ligand can prevent crystalline of the precursor upon solvent evaporation. Therefore, it is possible to use this Pd precursor solution for thin film deposition.

Two important parameters, viscosity and surface tension, must be considered when developing inks for inkjet printing. For the printhead used in this study, the ink's viscosity <9 cP and surface tensions of ≈30 mN m⁻¹ is preferred. Regarding the as-received Pd precursor solution, its viscosity was 31.54 cP and its surface tension was 33 mN m⁻¹, as listed in Table S1 in the Supporting Information. Although the surface tension was in the suitable range, its high viscosity made jetting difficult even at the maximum firing voltage (40 V) and a printhead temperature of 50 °C (higher temperature was not desired due to fast solvent evaporation). Thus, the viscosity of the Pd precursor solution was reduced by dilution.

Several criteria should be considered when formulating low-viscosity Pd inks.

- (1) The dilution solvent should be miscible with the precursor solution.
- (2) The Pd content should stay high to attain a thick and conductive layer after one printing pass.

- (3) The dilution solvent should have a surface tension of ≈30 mN m⁻¹ and a viscosity <9 cP.
- (4) Low jetting voltages should be applied to avoid the formation of satellite droplets.
- (5) Printhead temperatures <50 °C should be used to prevent nozzle clogging caused by fast solvent evaporation.
- (6) The dilution solvent should have a boiling point (BP) >100 °C to avoid rapid ink drying during storage.

Based on the 6 criteria, Pd-IBB and Pd-PhMe, as low-viscosity Pd inks, were prepared by mixing 80 wt% precursor solution with 20 wt% isobutylbenzene (IBB) and 20 wt% PhMe, respectively. Thermogravimetric analysis (TGA) test results in **Figure 1** show that the Pd contents of both Pd-IBB and Pd-PhMe were greater than 14 wt%, ≈3 times higher than other Pd precursor solutions.^[27] After dilution, the viscosities of Pd inks reduced to 12–13 cP at 25 °C while their surface tensions were kept ≈30 mN m⁻¹ (Table S1, Supporting Information). At 40 °C, the viscosity of Pd-IBB and Pd-PhMe was 8.50 and 8.93 cP, respectively. Consequently, using a peak firing voltage of 26 V at 40 °C nozzle temperature, both inks could be jetted stably at a droplet velocity of ≈10 m s⁻¹ without forming satellite droplets. Also, cleaning cycles for unclogging nozzles were not required for 1 h printing job. To study storage stability, newly prepared Pd inks were kept in capped cartridges at 23 ± 2 °C in ambient air. After 2 weeks, both inks could be jetted using the same parameters shown in Table S1 in the Supporting Information.

2.1.2. Formation of Pd Thin Films on Different Substrates

The wetting behaviors of as-received Pd precursor, Pd-IBB, and Pd-PhMe were studied on glass and polyimide (PI) surfaces. Before inkjet printing, all glass and PI substrates were cleaned by rinsing with isopropanol (IPA) and deionized (DI) water, followed by drying under compressed dry air. On glass substrates, all three types of inks showed good wetting. Figure S1a in the Supporting Information displays the printed Pd-PhMe on a glass

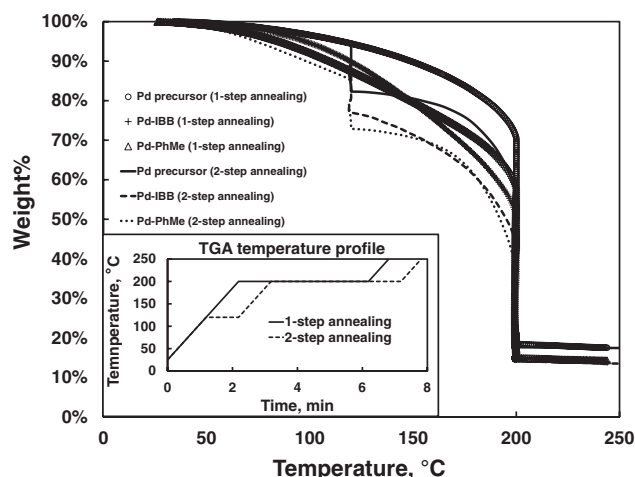


Figure 1. TGA test results of as-received Pd precursor solution, Pd-PhMe, and Pd-IBB using one-step and two-step thermolysis methods; inset: temperature profiles of one-step and two-step thermolysis.

substrate. As shown, a continuous and uniform ink layer was obtained. The measured line width of a printed Pd-PhMe layer was 547 μm , close to the designed values of 520 μm . The surfaces of some glass substrates were also treated using air plasma for 2 min. However, the Pd inks printed on plasma-treated glass substrates showed poor wettability. Therefore, we only focus on using the glass substrates cleaned by IPA and DI water here. More investigation is needed to study the mechanism for the dewetting of the Pd inks, but it is out of the scope of this study. On the as-received PI substrates, the Pd inks showed a poor wetting behavior due to the low surface energy of PI. Thus, the surface of PI was treated using air plasma for 2 min to increase its surface energy for better pattern definition (treatment for longer times had no significant effect). Figure S1b shows a printed Pd-PhMe layer on a treated PI substrate with a well-defined line of 547 μm wide (close to the designed value of 520 μm).

Printed Pd-PhMe were converted to metallic Pd using thermolysis. Two thermolysis temperature profiles (Figure 1) were compared to optimize the morphology of the printed Pd films. On the one hand, Pd inks were heated up to 200 $^{\circ}\text{C}$ on a hot-plate in air for 4 min (one-step thermolysis). During this period, the solvent of the ink evaporated, the precursor decomposed to palladium nanoparticles (PdNPs), and metallic Pd films formed. Figure 2a is a scanning electron microscope (SEM) image showing the morphology of a Pd film prepared by one-step

thermolysis of printed Pd-PhMe (30 μm droplet pitch) on a glass substrate. Pinholes with diameters <100 nm and a non-uniform film can be observed. Such surface morphology was caused by the decomposition of organic compounds in the Pd precursor and the unevenly distributed agglomeration of PdNPs. When the ink was heated up to 200 $^{\circ}\text{C}$ in one step, the solvent evaporation and the generation of PdNPs happened simultaneously. When the ink was not fully dried, PdNPs were surrounded by residual solvent. PdNPs in the liquid phase could move and aggregate with nucleation centers more easily than in the solid phase. Since the PdNPs were transported unevenly, thicker and thinner regions were formed once the solvent evaporation and precursor thermolysis were completed. The thicker regions were denser while the thinner regions consisted of pinholes or cracks.

Based on the one-step thermolysis discussed above, a two-step thermolysis was used to improve the film morphology. In the first step, the printed Pd ink was heated up to 120 $^{\circ}\text{C}$ in air for 1 min to evaporate most of the solvent. Then, the temperature was increased to 200 $^{\circ}\text{C}$ to decompose the precursor and produce a uniform Pd layer ≈ 100 nm in thickness. In the second step, PdNPs were generated in solid phase and immobilized on the substrate to coalesce into a uniform film. Figure 2b is the SEM image of a homogeneous Pd film prepared by the two-step thermolysis of printed Pd-PhMe on a glass substrate. Pd printed on PI (2 min plasma treatment, two-step thermolysis)

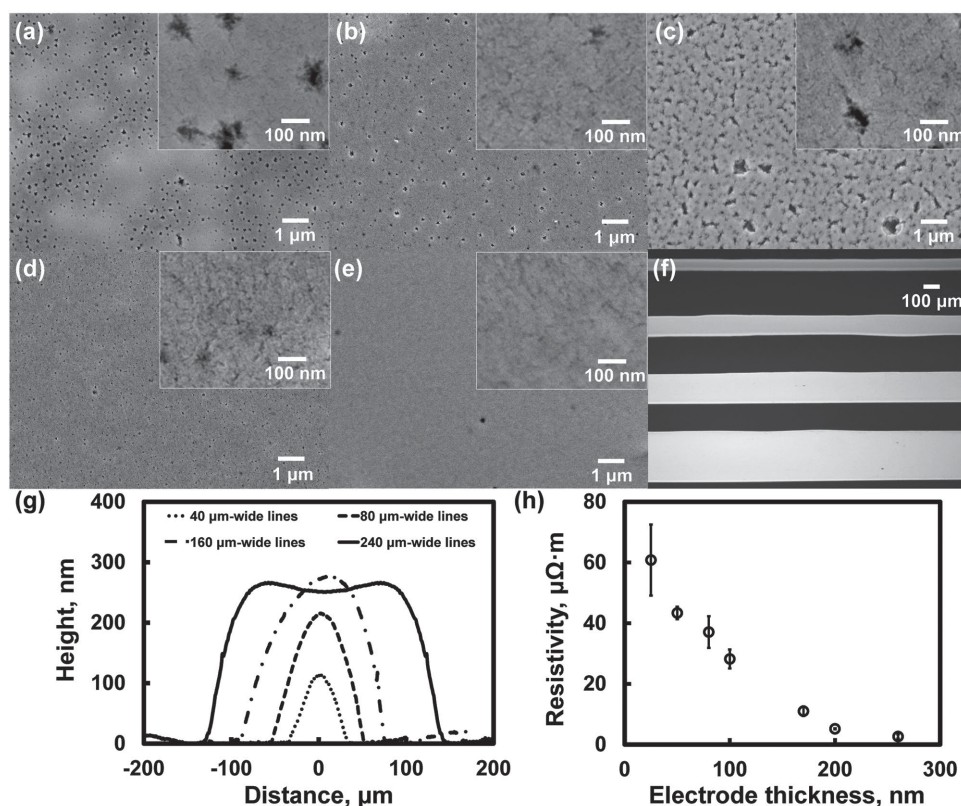


Figure 2. a–e) SEM images of surface morphologies of Pd films printed using Pd-PhMe ink. a) 30 μm droplet pitch, glass substrate, one-step thermolysis; b) 30 μm droplet pitch, glass substrate, two-step thermolysis; c) 40 μm droplet pitch, glass substrate, two-step thermolysis; d) 20 μm droplet pitch, glass substrate, two-step thermolysis; e) 30 μm droplet pitch, PI substrate, two-step thermolysis; f) optical microscopy image of two-step thermolyzed Pd lines printed using Pd-PhMe ink with 20 μm droplet pitch on a glass substrate. g) Thickness profiles of printed Pd lines shown in (f). h) Thickness dependence of the resistivity of printed Pd.

exhibited a dense morphology with few pinholes (Figure 2e). During plasma treatment, nitrogen moieties (such as $-\text{N}=\text{C}<$) were generated on the surface of PI and served as bonding sites for Pd atoms.^[28] The bonded Pd atoms behaved as nucleation centers and were uniformly distributed, resulting in a homogeneous Pd film of ≈ 80 nm thick.

Regarding Pd-IBB, a two-step thermolysis was also performed. However, a rough film was obtained after thermolysis at 170°C (170°C was selected due to the higher BP of IBB) for 1 min and 200°C for 4 min (Figure S2, Supporting Information). The rough surface indicated that a large amount of residual solvent (IBB) existed on the substrate when PdNPs were generated. IBB evaporated slowly because of its low vapor pressure (≈ 1.8 hPa, comparing to ≈ 29 hPa of PhMe and ≈ 23 hPa of water at 20°C). Since a 15 min evaporation step was needed to remove the IBB in the ink, the process was inefficient and not used in following studies.

The surface morphology of printed Pd was also a function of film thickness. Pd films of 50 (Figure 2c), 100 (Figure 2b), and 200 (Figure 2d) nm thick were obtained by printing Pd-PhMe on a glass substrate with a droplet pitch of 40, 30, and 20 μm , respectively. In the 50 nm thick film, pinholes were larger (comparing to the 100 nm thick film) and multiple pinholes connected to form cracks. In the 200 nm thick film, the pinholes were smaller. This result indicates the importance of having a high metal content in the ink to attain a thick Pd film free of pinholes and cracks.

The “coffee-stain” effect also reduces the uniformity of inkjet-printed films and is not desired for many applications.^[29] To reduce this effect, increasing the solid content in the inks, adding co-solvents with high BPs to the inks, and increasing the substrate temperature were shown to be effective.^[29] In our study, Figure 2f shows the optical microscopy image of printed Pd lines using Pd-PhMe with 20 μm droplet pitch on a glass substrate. The thickness profiles of these lines are shown in Figure 2g. As the designed line width increased from 40 to 240 μm , the thickness of Pd film increased from ≈ 100 to ≈ 260 nm. Due to the high metal content (≈ 14 wt%) of the ink, the “coffee-stain” effect was not apparent although the ink was single-solvent-based and the substrate was at $23 \pm 2^\circ\text{C}$.

2.1.3. Electrical Resistivity of Printed Pd Thin Films

A low resistance of the printed metal layer is required for electrical interconnections and low-impedance electrochemical sensing electrodes. From Section 2.1.2, we qualitatively observed that a thicker printed Pd film consists of less pinholes and cracks. The elimination of pinholes and cracks would result in a low electrical resistance of the films. From Section 2.1.2 and Figure 2b–d, one can observe that the morphology of the printed

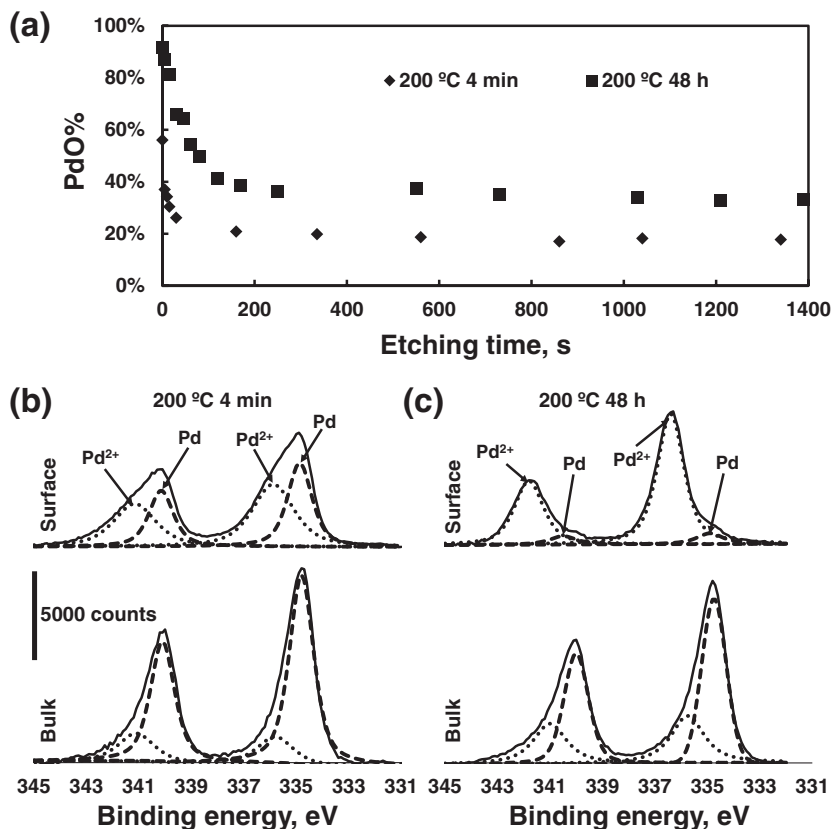


Figure 3. a) Depth-dependent chemical compositions of printed Pd films thermalized at 200°C for 4 min and 48 h obtained by XPS depth profiling. b) Pd 3d XPS spectra and curve fitting of the surface and bulk of printed Pd thermalized at 200°C for 4 min. c) Pd 3d XPS spectra and curve fitting of the surface and bulk of printed Pd annealed at 200°C for 48 h.

Pd film strongly depends on the film thickness. Also, the film morphology is not affected by the width or length of the film (Figure 2f). Thus, the effective resistivity of the printed Pd films was measured and calculated quantitatively as a function of film thickness (Figure 2h). Pd lines with different thicknesses were printed on glass (Pd-PhMe, two-step thermolysis) by varying the designed line width and the droplet pitch. From the resistance (R) measurement, the effective resistivity (ρ) was calculated using $\rho = Rt(W/L)$, where t , W , and L are the measured thickness, width and length of the printed Pd lines, respectively.

For a 25 nm thick Pd film, its effective resistivity was $60 \mu\Omega\text{m}$, much higher than that of bulk Pd ($\approx 0.1 \mu\Omega\text{m}$). When the Pd thickness increased, the effective resistivity decreased as expected, since the films became denser (Figure 2b–e). A printed Pd film of 260 nm thick had a low effective resistivity of $2.6 \mu\Omega\text{m}$, which is close to a previous result obtained by printing 5 passes of a lightly loaded ink.^[15] Here, we take advantage of the highly loaded Pd ink to get a low-resistance film by using only 1 printing pass. However, this effective resistivity is still higher than that of metallic Pd. This higher effective resistivity suggested a dependence on factors other than the film morphology. Therefore, the chemical composition of the printed Pd films was investigated.

Figure 3a shows the depth profiles of PdO percentage for 100 nm thick Pd films based on X-ray photoelectron

spectroscopy (XPS) analyses. For the film obtained right after thermolysis (200 °C, 4 min), its surface contained ≈56% PdO (curve fitting is shown in Figure 3b) while its bulk contained ≈17% PdO. The PdO was formed by the oxidation of Pd by oxygen in air during the thermolysis at 200 °C.^[18] Therefore, the presence of PdO limited the equivalent resistivity of the printed film to be higher than metallic Pd. When the film thickness decreased, the effect of surface PdO and pinholes were more pronounced. As a result, the effective resistivity of thinner films was higher than that of thicker films. In summary, the effective electrical resistivity of a printed Pd film was dominated by two factors: film morphology and chemical composition.

Besides, because the oxidation of Pd during thermolysis is primarily supported by oxygen in air, the distribution of PdO shows a diffusion-limited profile in the XPS depth profiling results. This process forms a bilayer structure with higher PdO concentration close to the surface and a more conductive layer underneath. In order to obtain a highly conductive Pd film, the concentration of PdO should be low. We propose that the amount of PdO in the films could be reduced by carrying out the thermolysis step in an inert atmosphere, for example, in an oven filled with argon gas.

2.1.4. Adhesion of Printed Pd Thin Films on Different Substrates

In printed flexible devices, adhesion between the printed structures and the underlying substrates is critical for the devices' stability and reliability. Film adhesion is especially important when it is used in a severe environment such as in a liquid.^[30] The adhesion test results of printed Pd films on glass and PI substrates are listed in Table S2 in the Supporting Information. On glass substrates, thin Pd films could pass the water rinse and scotch tape tests, but thick Pd films could be peeled off with the tape. The better adhesion of the thinner Pd films may be attributed to two reasons: the larger amount of pinholes/cracks in the films and the smaller film thickness. First, in thin Pd films, pinholes and cracks (Figure 2b–d) created many inter-domain boundaries. The Pd atoms at the boundaries had a less ordered structure, hence a higher surface energy.^[31] A thin film with a higher surface energy has a stronger tendency to attract to another surface, which results in a higher adhesive force between deposited films and substrates.^[32,33] Thus, the adhesion between thin Pd films and the substrates were better. Second, the stress in thin films promotes their delamination.^[34] The adhesion between a thin film and a substrate can be quantitated by strain energy release rate (G). The strain energy release rate is proportional to the film thickness (h) according to $G = Z\sigma_f^2 h/E_f$,^[35] where Z is a dimensionless cracking parameter, σ_f is the stress in the film, and E_f is the modulus of elasticity. A thicker film has a larger strain energy release rate, indicating the film delaminates from the substrate more easily for stress releasing. In addition to this theoretical explanation, our observation also agrees well with previous experimental results.^[33,36,37]

In contrast, on the PI substrates treated by air plasma for 2 min, thick Pd films exhibited a good adhesion. Although the plasma-introduced oxygen-containing groups are reactive to the deposited Pd, we believe the improved adhesion was mainly

attributed to the generation of nitrogen-containing groups at the surface of PI during the plasma treatment.^[28] The presence of the nitrogen-containing groups has been proved in previous studies by using XPS and Fourier transform infrared spectroscopy.^[28,38] The nitrogen atoms in the nitrogen-containing groups have unbonded electron pairs, which can serve as ligands for Pd.^[28,39] Therefore, the improved adhesion of Pd on PI was due to the higher affinity of nitrogen towards Pd than that of oxygen towards Pd. Figure S3 in the Supporting Information shows the atomic force microscopy (AFM) images of glass and PI surfaces. After the 2 min plasma treatment, the PI surface had a root-mean-square (RMS) roughness of 0.83 nm, which was about a half of the roughness of the glass substrate. The smooth PI surface indicated insignificant mechanical interlocking between Pd and PI. Thus, chemical bonding was the major factor for a strong adhesion between the printed Pd and PI substrates.

2.2. Inkjet-Printed Pd/PdO for Integrated pH Sensors

2.2.1. Design of Pd/PdO Sensing Electrodes

In a Pd/PdO electrochemical pH sensor, the sensing electrode should possess the following characteristics.

- (1). An oxide-rich surface for the ion-to-electron transduction based on the following redox reaction^[13]



The redox potential of this reaction can be described by Nernst equation

$$E = E^0 - \frac{2.303 RT}{F} \text{pH} = E^0 - 0.05916 \text{ pH},$$

where E^0 is the standard electrode potential, R is the gas constant, T is the absolute temperature, and F is the Faraday constant. At 25 °C, the theoretical pH sensitivity is 59.16 mV pH^{−1}.

- (2). A low-resistance bottom layer for electron conduction.
- (3). A good adhesion with the substrate for stable operation in the aqueous environment.

To demonstrate the usability of the printed Pd films, Pd/PdO printed sensing electrodes (PSEs) were fabricated by annealing the printed Pd at 200 °C for 48 h.^[13] After annealing, the PdO-rich surfaces (Figure 3a,c) functioned as the pH sensitive layers. The bulk of the electrodes had less PdO and a higher conductivity, functioning as the electron conducting layers. Thus, even though the PSEs were deposited using only one material, they played a dual role. This makes our fabrication process simpler than that in other studies where the sensing and electron conduction layers were deposited separately.^[23]

The size effect on the sensing performance of the PSEs on glass substrates was studied by keeping the electrode thickness constant (100 nm). According to previous theoretical studies,^[40] if the pH of a solution changes by 1, the potential of the pH

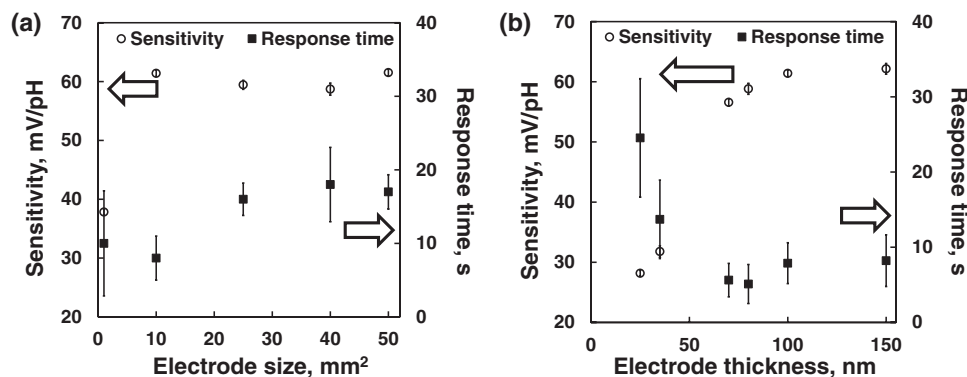


Figure 4. a) Effect of Pd/PdO electrode size on pH sensitivity and response time. b) Effect of Pd/PdO electrode thickness on pH sensitivity and response time.

sensing electrode will change by $\Delta V_{\text{Nernst}} \times [C_m / (C_m + C_c)]$. In this equation, ΔV_{Nernst} is the theoretical Nernstian response (≈ 59 mV),^[23] C_m is the lumped capacitance of the electrode, and C_c is the input capacitance of the readout circuit. Therefore, to approach a near-Nernstian pH response, a large double-layer capacitance at the electrode–solution interface is required. This large capacitance can be obtained by increasing the surface area of the sensing electrode. In **Figure 4a**, we find near-Nernstian sensitivities were obtained when the PSEs were larger than 10 mm². If the PSEs were smaller than 10 mm², a sensitivity drop could be observed. Also, an increase of response time with the increase of electrode size is shown in **Figure 4a**. When the morphological and chemical properties of the PSEs are similar, the response time is determined by the resistance and capacitance of the electrode.^[41] Here, all electrodes had similar width-to-length ratios and resistance values. Thus, a larger electrode provided a larger capacitance that resulted in a longer response time.

The thickness effect on the sensing performance of the PSEs of constant area (10 mm²) and on glass substrates was studied. **Figure 4b** shows that a thicker PSE had a higher sensitivity, which saturated at the Nernst limit for PSEs over 100 nm thick. The low sensitivity of thin PSEs was caused by the poor morphologies of the Pd films. On the one hand, pinholes and cracks exposed the substrates and reduced the effective surface area (**Figure 2b–d**), resulting in a reduced sensitivity. On the other hand, the redox reactions between PdO and H₃O⁺ ions generated electrons,^[23] which had to be transferred to external circuits for potentiometric sensing. The pinholes and cracks in the PSEs increased the electrode resistance (**Figure 2h**) and hindered the conduction of electrons, thus lowering the pH sensitivity. In terms of response time, fast responses (≈ 8 s) were found for the PSEs thicker 80 nm. Below this thickness, the response time increased significantly. The slow response for thin PSEs was attributed to the loosely packed films that increased the migration path for H₃O⁺.^[42] PSEs thicker than 150 nm were not studied here because of their poor adhesion to the glass substrate when immersed in solutions. Finally, an optimal PSE had a size of 10 mm² and a thickness of 100 nm.

2.2.2. Fabrication of Integrated pH Sensors

To prove the potential application of the PSEs in future compact, low-cost electrochemical monitoring systems, potentiometric

pH sensors were integrated on glass and PI substrates using Pd/PdO PSEs and silver/silver chloride/potassium chloride (Ag/AgCl/KCl) printed reference electrodes (PREs). The integration process is shown in **Figure 5**.

First, glass and PI substrates were cleaned by rinsing with IPA and DI water and dried under compressed dry air (**Figure 5a1**). For PI substrates, a 2 min air plasma treatment was performed before the printing processes (**Figure 5a2**). Next, one layer of Pd-PhMe ink was inkjet-printed onto the substrates (**Figure 5b**). The printed Pd-PhMe was converted to a PSE (100 nm thick and 10 mm² large) using two-step thermolysis and annealed at 200 °C for 48 h (**Figure 5c**). Afterwards, an SU-8 ink was prepared by diluting the as-received SU-8 3035 photoresist to 7.4 wt% using propylene glycol monomethyl ether acetate (PGMEA) (**Table S1**, Supporting Information). The SU-8 ink was inkjet-printed beside the PSE and cured to form an 8 mm × 25 mm block with a thickness of ≈ 100 nm (**Figure 5d**). The printed SU-8 layer adhered to glass and PI substrates well, and could be used as an interfacial layer between Ag (to be printed in the next step) and the substrates (**Table S2**, Supporting Information).^[4] Then, the PRE was fabricated based on previous reports with modifications,^[43,44] as explained below.

Figure 5e shows a Ag nanoparticle (AgNP) ink (**Table S1**, Supporting Information) that was inkjet-printed on the SU-8 layer and annealed at 120 °C for 10 min to form a 300 nm thick Ag layer (5 mm × 10 mm). Subsequently, a sodium hypochlorite (NaOCl) ink was prepared by diluting the as-received NaOCl solution to 0.4 wt% using DI water. The high surface tension (≈ 72 cP) of the aqueous solution was reduced to ≈ 31 cP by adding 2 vol% Triton X-100 surfactant so that the ink was printable (**Table S1**, Supporting Information). To chlorinate the top part of the printed Ag, ≈ 0.1 mL NaOCl ink was required. This amount of ink could not be deposited within 100 layers of printing because the jetting capability of the printhead was ≈ 10 pL per droplet. Therefore, to improve the process efficiency, ≈ 0.1 mL NaOCl ink was printed from a pipette to the Ag surface and allowed to chlorinate the Ag for ≈ 30 s before rinsing with DI water (**Figure 5f**). The SEM images of the printed Ag layer before and after chlorination is shown in **Figure S4a** and **b** in the Supporting Information. XPS analyses shown in **Figure S4c** in the Supporting Information confirmed the formation of AgCl on top of Ag.

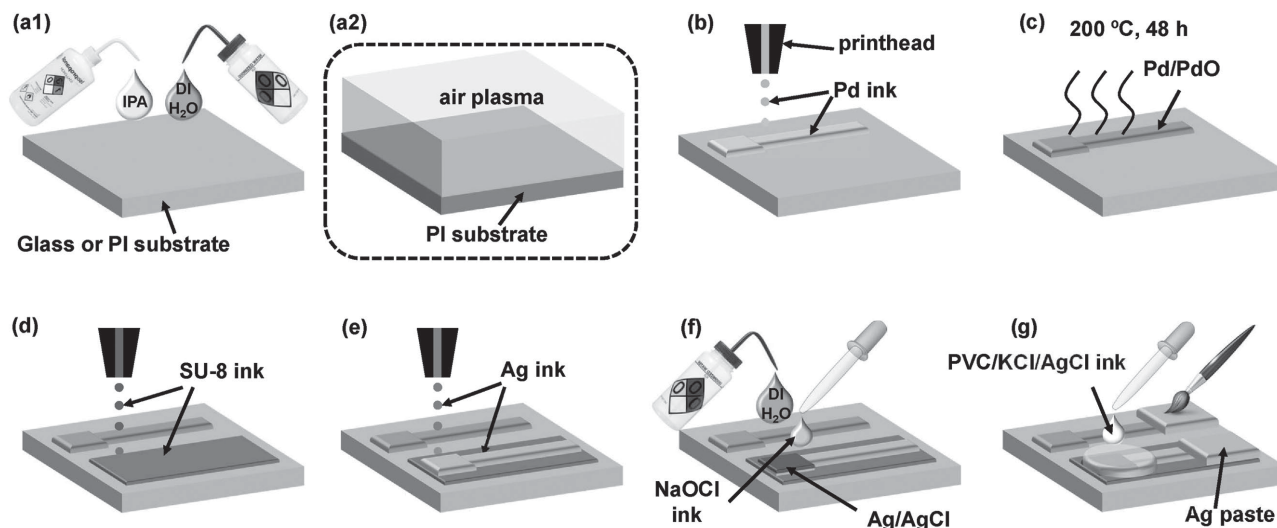


Figure 5. Integration process of a pH sensor using printing techniques. a1) Substrate cleaning. a2) Air plasma treatment of PI substrate. b) Inkjet printing of Pd ink. c) Thermolysis and annealing of printed Pd to form Pd/PdO sensing electrode. d) Inkjet printing of SU-8 ink as adhesion between Ag and the substrate. e) Inkjet printing of AgNP ink for the reference electrode. f) Pipette printing of NaOCl ink for the chlorination of the surface of Ag. g) Pipette printing of PVC/KCl/AgCl ink to form the solid electrolyte of the reference electrode, and painting of Ag paste for electrical contacts.

A printable ink for the solid electrolyte was formulated by dissolving 2 wt% poly(vinyl chloride) (PVC) in KCl- and AgCl-saturated cyclohexanone (Table S1, Supporting Information). Also due to the limited jetting capability of the printhead, ≈ 0.2 mL PVC/KCl/AgCl ink was printed from a pipette on top of Ag/AgCl (Figure 5g) to form a thick (≈ 1 μm) solid electrolyte layer. Finally, Ag paste was manually painted and annealed at 160 $^{\circ}\text{C}$ for 10 min to form electrical connections. The pH sensors with integrated PSE and PRE were conditioned in 1 M KCl solution for 12 h before testing.

2.2.3. Characterization of Integrated pH Sensors

The temporal pH response of the printed sensors on glass and PI were measured after 12 h conditioning in 1 M KCl. The results are shown in Figure 6a,b. The PREs exhibited negligible response between pH = 4 and 10 (referenced to a commercial reference electrode, CRE), suggesting that the PREs could replace CREs in integrated sensors. Also, fast responses of the PSE were observed upon pH variations, which is important for real-time measurements. The response time is determined by the transportation speed of H_3O^+ from the bulk solution to the PSE surface, as well as the rate of reactions between H_3O^+ and the surface sites of the PSE.^[23] The integrated sensor displayed a response time of 11 and 6 s on a glass and on a PI substrate, respectively. The difference in response time was mainly due to the different film morphologies on the two types of substrates. The 100 nm thick Pd films on glass contained pinholes and cracks (Figure 2b), which increased the migration path for H_3O^+ and slowed down the response.^[42] On PI substrates, the redox reactions (see Section 2.2.1) were limited at the surface of the closely packed films, which resulted in a fast response.

Another important factor limiting the sensors' accuracy is hysteresis, which is difficult to avoid. It is a combined effect of buried and slow-reaction sites in the PSEs, and is also affected

by the mechanical stability of the sensing material.^[23] In our study, the hysteresis was 8.9 mV for the sensor on glass, and was 5.3 mV for the sensor on PI. These response time and hysteresis values are comparable with other studies.^[13,19,23]

Figure 6c displays the sensitivity of an integrated sensor on a glass substrate. Due to the constant PRE potential (standard deviation, SD = 1.5 mV), the sensitivity of the integrated sensor (60.6 ± 0.1 mV pH^{-1}) was almost identical to that of a PSE (60.6 mV pH^{-1} , referenced to a CRE). On PI (Figure 6d), the SD of the PRE potential was 2.4 mV and the sensitivity of the integrated sensor was 57 ± 0.6 mV pH^{-1} . Because the thermal conductivity of PI (0.12 W m^{-1} K^{-1}) was lower than that of glass (0.8 W m^{-1} K^{-1}),^[45] it took a longer time for the Pd ink on PI to reach its decomposition temperature. A longer time before precursor decomposition resulted in more spreading and a thinner ink layer. Hence, the thinner PSE on PI (≈ 80 nm comparing to ≈ 100 nm on glass) was the main reason for this lower sensitivity.

The drift behavior of the integrated sensors was studied in 1 M KCl solution at 23 ± 2 $^{\circ}\text{C}$ in the dark for 16 h. On glass (Figure 6e), the drift of the PSE was 1 mV h^{-1} , and for the PRE, -0.6 mV h^{-1} . The drift of both electrodes resulted in the integrated sensor's drift of 1.6 mV h^{-1} , which is similar to previous studies.^[23] On PI (Figure 6f), due to the better adhesion of Pd, a lower drift rate of 0.6 mV h^{-1} was obtained for the integrated sensor.

A very important parameter for practical sensors is stability which specifies how the sensor's characteristics change with time. Therefore, we studied the stability of the integrated sensors stored in 1 M KCl solution at 23 ± 2 $^{\circ}\text{C}$ and in dark over a period of 70 d. Figure 7 shows the changing of sensitivity with storage time. After sensor fabrication (day 0, before being stored in 1 M KCl), the sensitivities of the PSEs were measured against a CRE because the PREs must be conditioned before use (the triangle and diamond at day 0). The PSEs on glass and PI had a high sensitivity of 63.6 mV pH^{-1} (triangle at day 0) and

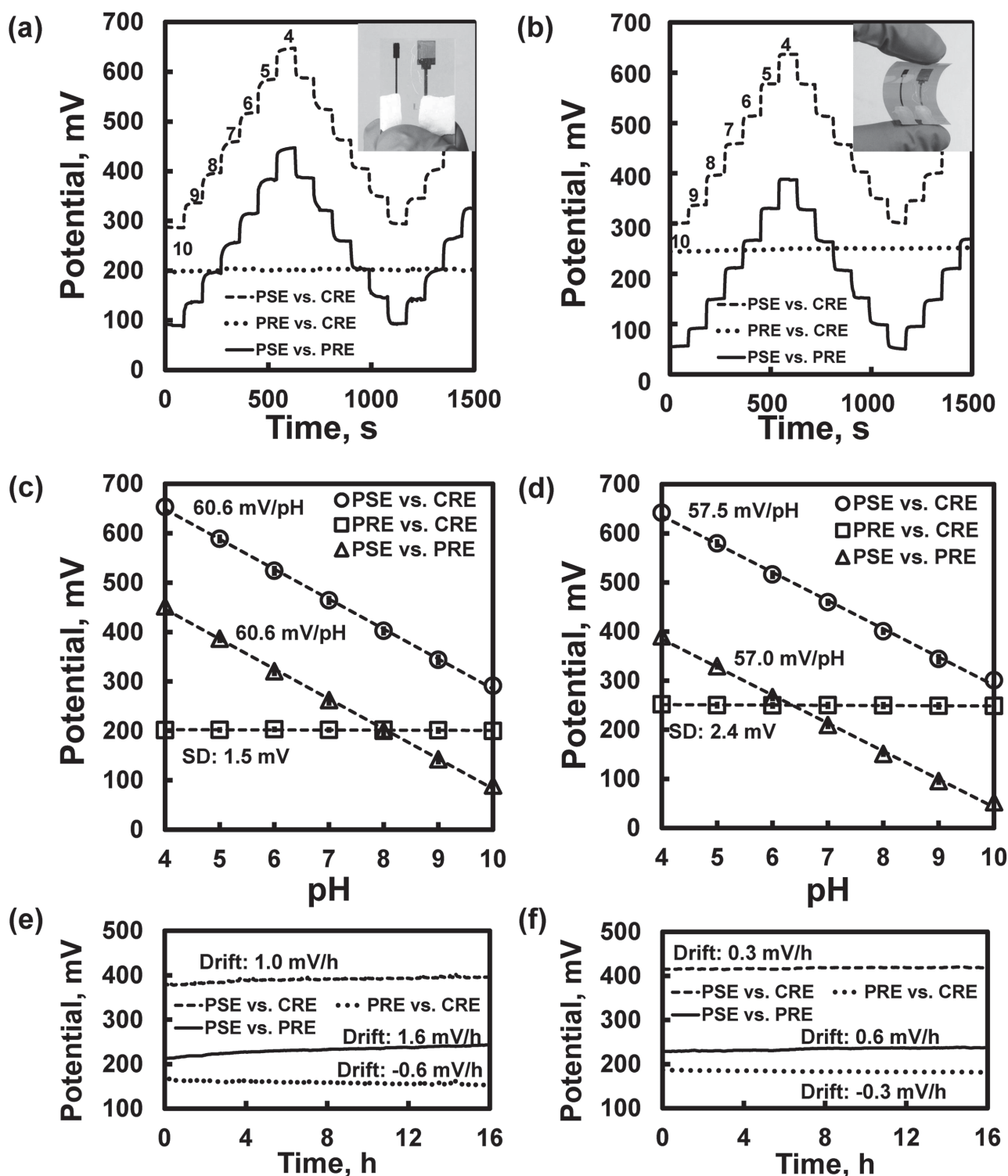


Figure 6. a) Temporal response of an integrated sensor on glass when the pH of buffer solutions cycles between 4 and 10; inset: photograph of an integrated sensor on glass. b) Temporal response of an integrated sensor on PI when the pH of buffer solutions cycles between 4 and 10; inset: photograph of an integrated sensor on PI. c) Open circuit potential versus pH values for an integrated sensor on glass. d) Open circuit potential versus pH values for an integrated sensor on PI. e) Drift behavior an integrated sensor on glass. f) Drift behavior an integrated sensor on PI.

60.2 mV pH⁻¹ (diamond at day 0), respectively. The difference in sensitivity may be due to the different PSE thicknesses, as discussed above. After storage in 1 M KCl, the sensor on PI had

a slightly lower but stable sensitivity of ≈57 mV pH⁻¹ (squares between day 1 and 31). The sensitivity drop was due to the rearrangement of surface Pd and oxygen atoms, the formation of

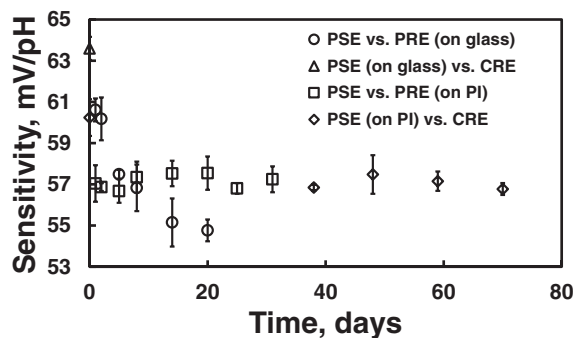


Figure 7. Stability of integrated sensors on glass and PI.

surface —OH groups, and the relief of stress in the Pd/PdO film.^[46] After 35 d of storage, the PRE delaminated from the substrate. The sensitivity of the PSE between day 38 and 70 was then assessed using a CRE, and was found to be stable during this period (diamonds between day 38 and 70). In contrast, the sensitivity of the sensor on glass kept decreasing (circles between day 1 and 20) until the PSE delaminated after 23 d of storage. The low stability of such sensors was primarily due to the poor adhesion between the printed Pd film and glass.

To prove the practical usability of the integrated sensors, the PSE and PRE (stored in 1 M KCl for 12 h) were connected to a multimeter to measure the pH values of real water samples. Figure 8 is the summary of the test results for nine types of water samples. In all cases, the differences between the calculated pH values (using measured potential) for the printed sensors and the pH readings for a commercial pH meter were less than 2%. In addition, these accurate results were obtained using a simple test setup without using complicated instruments. This indicated the possibility of building highly

accurate, easy-to-use, low-cost pH sensing systems that incorporate the printed sensors developed in this study.

3. Conclusion

We have developed an inkjet printing process for a highly loaded Pd ink to deposit Pd thin films. The viscosity and surface tension of as-received Pd precursor solution was adjusted by 20 wt% PhMe to form a printable ink. The printed ink was converted to continuous, homogenous, low-resistivity Pd films using a two-step thermolysis. The printed Pd films exhibited good adhesion to air-plasma-treated PI substrates. To demonstrate the electrochemical application of the printed Pd films, an annealing step was carried out at 200 °C in air. The resulted PdO-rich surface served as a pH sensing layer while the underlying conductive layer provided a path for electrons. The bifunctional Pd/PdO PSEs were designed with a size of 10 mm² and a thickness of 100 nm for an optimal sensitivity and response time. These PSEs were then integrated with solid-state PREs to form potentiometric sensors. The integrated sensors on glass and PI showed a fast and repeatable pH response with a sensitivity of 60.6 ± 0.1 and 57 ± 0.6 mV pH⁻¹, respectively. Also, accurate pH values of real water samples were obtained with the printed sensors. Because the drop-on-demand inkjet printing process consumes a small amount of functional materials and can be easily scaled up, these printed sensors can be very cost-effective for large-scale manufacturing. Finally, since the developed sensors are of high sensitivity and with a fast response, stable, low-cost, and easy-to-use, then an electrochemical sensing platform based on such sensors can be built for monitoring water quality and human health conditions.

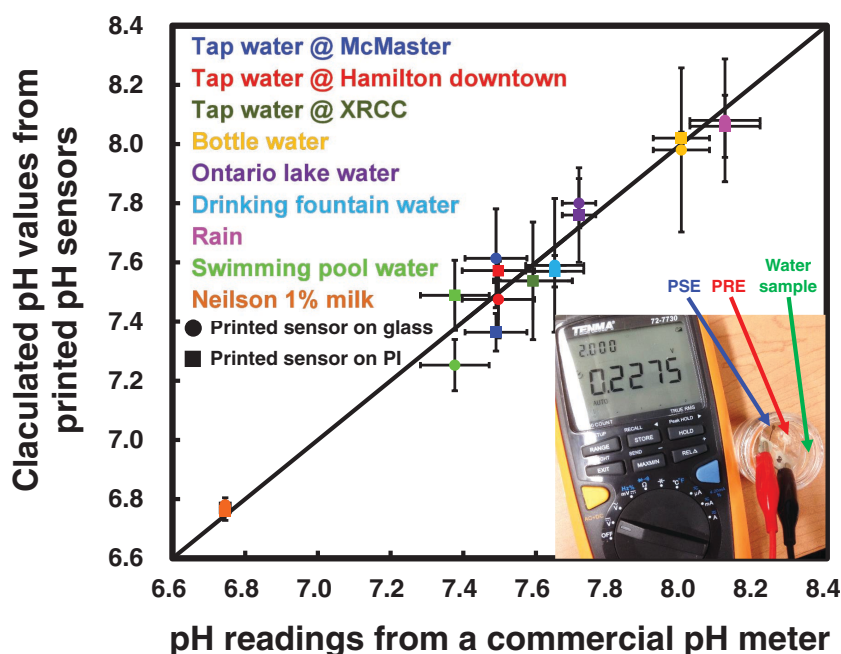


Figure 8. pH measurement results of real water samples and milk using integrated sensors on glass and on PI.

4. Experimental Section

Chemicals and Reagents: IPA ($\geq 99.5\%$, product No. 8600-1), acetic acid (HOAc , $\geq 99.7\%$, product No. 1000-1), and PhMe ($\geq 99.5\%$, product No. 9200-1) were purchased from Caledon Laboratory Chemicals. IBB (99% , product No. 113166), PGMEA ($\geq 99.5\%$, product No. 484431), NaOCl solution ($4.00\text{--}4.99\%$, product No. 239305), AgCl powder (99% , product No. 227927), PVC (average M_n 22 000, average M_w 43 000, product No. 389293), phosphoric acid (H_3PO_4 , ≥ 85 wt%, product No. 695017), boric acid (H_3BO_3 , 99.97% , product No. 339067), sodium hydroxide (NaOH) pellets ($\geq 98\%$, product No. S5881), and Triton X-100 (laboratory grade, product No. X-100) were purchased from Sigma-Aldrich. Pd precursor solution (≈ 20 wt% metal load, product No. Pd-25c) and AgNP ink (≈ 50 wt% metal load, product No. xcm-ns1) were obtained from Xerox Research Centre of Canada. SU-8 3035 photoresist was purchased from MicroChem. KCl ($>99\%$, product No. PX1405) was purchased from EMD Millipore. Conductive Ag paste (product No. CI-1001) was purchased from Engineered Materials Systems Inc.

Characterization of Inks: The surface tension of Pd inks was measured using a tensiometer (K100, Krüss) at 22 °C in ambient conditions. The measurement was based on Wilhelmy plate

method, and the viscosity data was averaged from 30 to 60 s after immersion of the Wilhelmy plate. The viscosity of Pd inks was measured using a rheometer (RFS3, TA Instruments). The viscosity was obtained by performing shear rate sweeps (between 1 and 400 s⁻¹) clockwise and anticlockwise at 25 °C. Before shear rate sweeping, the ink was equilibrated for 120 s. The solid contents of different inks were measured using a thermogravimetric analyzer (Q5000 IR, TA Instruments) with platinum pans as ink carriers. The temperature profiles are shown in Figure 1. All measurements were done under nitrogen purge (25 mL min⁻¹)

Inkjet Printing: Before inkjet printing, glass (7525M, J. Melvin Freed Brand microscope slides) and PI (Kapton 200HN, DuPont) substrates were rinsed with IPA and DI water, followed by drying under compressed dry air. The PI substrates were treated by air plasma for different durations using a plasma cleaner (PDC-32G, Harrick Plasma) with a background pressure of 200 mTorr and an RF power of 18W. The inkjet printer used in this study was a Dimatix DMP-2831 materials printer (Fujifilm), equipped with DMC-11610 Dimatix materials cartridges (Fujifilm). The cartridge was accompanied with a 16-nozzle piezoelectric printhead, which could jet ≈10 µL ink per droplet. All inks (≈1.5 mL each) were filtered through Whatman GD/X syringe filters (polytetrafluoroethylene membrane, pore size 0.2 µm, product No. WHA68741302, Sigma-Aldrich) before loading to the cartridges. The jetting waveforms for Pd and SU-8 inks were identical, and other inks were jetted using another waveform, as shown in Figure S5 in the Supporting Information. Other jetting parameters included the firing frequency of 2 kHz and the meniscus vacuum of 0.18 psi.

Characterization of Printed Thin Films: AFM (Dimension Icon, Bruker) was used to measure the surface roughness of different substrates. The AFM measurements were based on tapping mode with 2 µm × 2 µm scanning areas using a 1 Hz scan rate. The film thickness was measured using a stylus profiler (Dektak XT, Bruker). The stylus was scanned at 50 µm s⁻¹ with 3 mg applied force. A stereo microscope (AZ100, Nikon) and a field-emission SEM (JSM-7001F, JEOL) were used to observe the surface morphologies of printed films. The SEM was operated at an acceleration voltage of 10 kV and emission current of ≈80 µA. XPS (JPS-9200, JEOL) was used to analyze the chemical compositions of printed films. Narrow-scan spectra (0.1 eV resolution) were obtained using a magnesium X-ray source (10 keV, 15 mA). Depth profiling spectra for Pd/PdO were acquired using argon ion etching (3 keV, 20 mA) at 0.04 Pa with an etch rate of ≈0.1 nm s⁻¹. The resistance of printed Pd layers was measured by a semiconductor analyzer (4200-SCS, Keithley) equipped with a probe station (S-1160, Signatone). To check the adhesion between printed films and substrates, water rinse tests were performed by rinsing the printed films under tap water (flow rate ≈3 m s⁻¹) for 60 s. Scotch tape test was performed manually by pressing transparent scotch tapes (S-9782, 3M) onto printed films firmly and pulling off slowly. The delamination of printed films in both cases was visually observed.

pH Sensing Test: Britton-Robinson pH buffer solutions (pH = 4, 5, 6, 7, 8, 9, 10) were prepared by mixing a solution comprising 0.04 M H₃PO₄, 0.04 M HOAc, 0.04 M H₃BO₃ with an appropriate amount of 0.2 M NaOH solution. The pH levels of buffer solutions were monitored by a commercial pH meter (PHB-600R, OMEGA) with a glass electrode (PHE1311, OMEGA). The performance of PSEs was characterized based on a potentiometric configuration against a CRE (Ag/AgCl/1 M KCl, CHI111, CH Instruments). Both PSE and CRE were connected to a semiconductor analyzer (4200-SCS, Keithley). The open-circuit potential between the electrodes was recorded every 2 for 90 s when the electrodes were immersed in pH buffer solutions (without stirring). The electrodes were transferred into the next pH buffer solution without cleaning or drying. For characterization of the integrated sensors, a PSE, a PRE, and a CRE were connected to the semiconductor analyzer with the PRE grounded. Open circuit potentials between the PSE and PRE, as well as between the PRE and CRE were measured using the same method described above. For real water sample tests, a commercial multimeter (72-7730, TENNA) was connected to the PSE and PRE for recording the open-circuit potential. Single-point calibration using the pH = 7 buffer solution was done prior to the measurements to convert

the recorded potential differences to pH values. All pH sensing tests were performed at 23 ± 2 °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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