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Electric Conductive Pattern Element Fabricated Using Commercial Inkjet Printer for Paper-Based Analytical Devices

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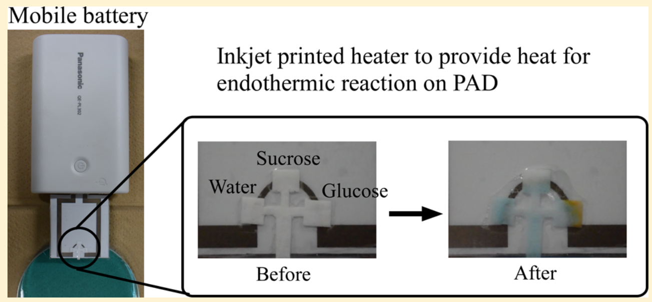
Supporting Information



ABSTRACT: Herein, we proposed the addition of an inkjet-printed conductive pattern to paper-based analytical devices (PADs) in order to expand their applications. An electric conductive pattern was easily, quickly, and inexpensively fabricated using a *commercial inkjet printer*. The addition of a printed electric element will enhance the applications of PADs without the loss of properties such as cost efficiency, disposability, and portability. In this study, we applied an inkjet-printed heater to a piece of paper and investigated its characteristics. The use of the heater as a valve, concentrator, and heat source for chemical reactions on PADs was investigated. Previously, these functions were difficult to realize with PADs. The inkjet-printed heater was used as a valve and concentrator through evaporation of the working fluid and solvent, and was also found to be useful for providing heat for chemical reactions. Thus, the combination of printed electric circuits and PADs has many potential applications.

In recent years, paper-based analytical devices (PADs) have received much attention, as they are cost efficient, disposable, and portable.[1] Though there have been many studies developing new design prototype devices and fabrication techniques, there have been minimal studies developing new thermofluid control techniques due to limited PAD resources. In PADs, test fluid is transported by capillary action through the paper; thus, control methods of thermofluid flow are limited. For example, the fluid motion is controlled by varying the wettability of the paper,[2] placing a buffer pad on a fluid channel,[3] or using a dissolvable sugar barrier as a valve.[4] These passive methods lack versatility and are only applicable in special situations. There have been some studies on flow control by mechanical means; however, these techniques make the geometry and operation complex. While there have been many studies developing PADs based on colorimetric detection,[5−9] assays based on chemical reaction which require heat have been difficult to accomplish.

On the basis of these shortcomings, we propose the use of inkjet-printed electronic circuits as heaters for valves, concentrators, and heat sources for chemical reactions on PADs. Recently, inkjet-printed electrically conductive patterns have been developed.[10−14] In these studies, an electronic circuit was made from silver nanoparticle ink or carbon ink and printed by an industrial, research, or scientific grade inkjet printers or screen printed. Since these techniques are expensive, their application decreases the cost efficiency of PADs. Conductive patterns can also be fabricated by conductive pens such as the Bare conductive electric pen (Bare Conductive, U.K.), CircuitWriter (CAIG Laboratories, U.S.A.), Circuit Scribe conductive ink pen (Electroninks Writeables, U.S.A.), etc. The conductive line, however, is painted by hand, resulting in low reproducibility; thus, this is not feasible for the application to PADs. Electronic circuit fabrication techniques using a commercial inkjet printer were proposed by some researchers.[15−17] In these techniques, the high temperature of annealing (several hundreds of degrees Celsius) is necessary to activate the conductive property of printed patterns. Moreover, electrically conductive patterns are achieved by multiple prints of conductive patterns (minimum 30 repetitions). The printing of a precise pattern with multiple prints is very difficult, because the paper-feeding mechanism of a commercial inkjet printer is inaccurate. This inaccuracy of paper-feeding mechanism misaligns printed patterns with multiple printing. Therefore, these conductive pattern fabrication techniques have low reproducibility and are not feasible for the fabrication of an electric circuit. For example, the printed pattern was not used as an electric circuit but an electrode for H_2O_2 sensor in Huang et al.[15]

Kawahara et al.[18,19] and Shen et al.[20] proposed instant electronic circuit fabrication techniques using a commercial inkjet printer. Since commercial inkjet printers are inexpensive (∼$100 USD), these circuit fabrication techniques are suitable for combination with PADs. This technique enables us to easily, quickly, and inexpensively fabricate electronic circuits on flexible substrates, allowing for on demand production in less-industrialized areas with limited resources, because an annealing

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is not necessary and electric circuits are fabricated by printing once. We believed that this technique enhances the applications of PADs without the loss of properties such as cost efficiency, disposability, and portability. In this study, we have first applied this technique to PADs in order to fabricate an electric element whose power is supplied by a USB port allowing it to be useful in various situations. Through this method, we were able to fabricate an inkjet-printed heater on a piece of paper and investigate its characteristics.

INKJET PRINTING OF ELECTRONIC CIRCUIT

Method of Electric Conductive Pattern Printing. Silver nanoparticle ink (NBSIJ-MU01, Mitsubishi Paper Mill, Japan) was printed on resin-coated paper (NB-WF-3GF100, Mitsubishi Paper Mill, Japan) using a commercial inkjet printer (DCP-J540N, Brother, Japan). The inkjet printer had four independent color cartridges: black, cyan, magenta, and yellow. The inkjet printer was carefully cleaned before use by filling the four empty cartridges of the inkjet printer with ethanol, which was then printed on paper to rinse the nozzles and tubes. This cleaning procedure is important as there is residual ink in the nozzles and tubes even in a brand new inkjet printer. The silver nanoparticle ink was then filled into an empty cartridge using a syringe and filtering through an attached disposable syringe filter with pore size of 5 μm. The cartridge of silver nanoparticle ink was in the black ink cartridge position. Operation of the inkjet printer was controlled by the attached driver software (DCP-J540N printer driver ver. 1.11.01). Customized software was not required as one can print an electric conductive pattern as they print documents and photos, which is an advantage of using a commercial inkjet printer. The detailed printer mode is given in Supporting Information. The printing pattern was drawn by illustration software, CANVAS X.

Under these conditions, we printed straight conductive lines (length, 50.0 mm; width, 0.25, 0.5, 0.75, 1.0, 2.0, and 3.0 mm), and measured their electric resistance with a digital multimeter (VOAC7521A, Iwatsu, Japan) as shown in Figure 1 with error bars representing the standard deviation of five independent printed conductive lines. The sheet resistances are also shown in Figure 1. The electric resistance decreases with increasing width of the conductive line. The sheet resistance approaches at constant value of 0.36 ± 0.02 Ω/sq when the width of the conductive line was larger than 1.0 mm. However, the sheet resistance increased when the line width was less than 1.0 mm. The conductive line was formed by drops of silver nanoparticle; thus, an electric current flows only through the connected drops and clusters. Since there are not enough clusters in thinner lines to connect both ends of the conductive line, the sheet resistance is high. Conversely, when the conductive lines are wider, there are enough clusters to connect both ends of the conductive line. An error of 5.6% in the sheet resistance shows the high reproducibility of this printing method.

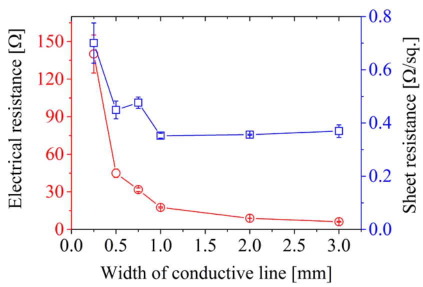

Figure 1. Relationship between resistance and conductive line width. Red circles represent electrical resistance. Blue squares represent sheet resistance.

Properties of the Inkjet-Printed Heater. In the present study, we printed a conductive pattern that functioned as a heater due to Joule heating. The inkjet-printed conductive pattern (Figure 2) consisted of two types of lines whose widths were 0.75 and 2.5 mm. The electronic resistance of the thin line was high, allowing it to function as a heater. The pattern of connector was printed as in Figure 2 and was then able to be connected directly to the USB receptacle of a PC, which is a type A connector. In this study, the power of the inkjet-printed heater was supplied by a 5 V and 1.5 A mobile battery (QE-PL302, Panasonic, Japan).

Figure 3 shows the temperature versus heating time in a 25 °C room temperature. The surface temperature was measured with a type K thermocouple and recorded by a data logger (GL220, Graphtec, Japan). As shown in Figure 3, the surface temperature increased to 60 °C in 40 s. The temperature decreased by 1 °C/s after heating was stopped at 300 s. The temperature response of this heater is quick enough to our following demonstration. The temperature continuously increased from 50 to 300 s, because the electric resistance of the heater increased with increasing temperature and the supplied power was constant (5 V and 1.5 A).

RESULTS AND DISCUSSION

Stop Valve Using the Inkjet-Printed Heater. We believed that the inkjet-printed heater could be used as a stop valve for PADs. For this purpose, the heater would be used to evaporate the working fluid, causing the flow to stop upon complete evaporation at the location of the heater.

To demonstrate this, we prepared two pieces of 30 mm long and 3.0 mm wide cellulose filter paper (Whatmann grade 1 filter paper, pore size 11 μm, GE Healthcare, U.S.A.). One was placed on the heater and the other was placed directly on a base plate as a control. A glass plate was placed on the filter paper to hold them on the base plate. The glass plate had a gap of 1 mm in order to allow evaporation of the test fluid. Ethanol (special grade, Kanto Chemical, Japan) was used as the test fluid, dyed with 0.2 g/L rhodamine B (special grade, Wako, Japan).

The test fluid was introduced at one end of filter paper and flowed to the other end due to capillary force. When the heater was turned on, the test fluid evaporated at the location of the heater, effectively stopping the flow, as shown in Figure 4. The distance traveled by the fluid front was measured every 10 s (Figure 5) with the accuracy of 1 mm by the images taken by an 8-bit CMOS camera (Nikon 1 S2, Nikon, Japan). Though the spatial resolution of image was 0.04 mm, the shape of the fluid front was not always flat and the averaged distance was measured with 1 mm accuracy. The slopes of both data sets (with and without valve tests) were identical from 0 to 70 s;

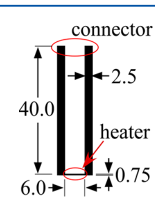

Figure 2. Inkjet-printed heater pattern (unit: mm).

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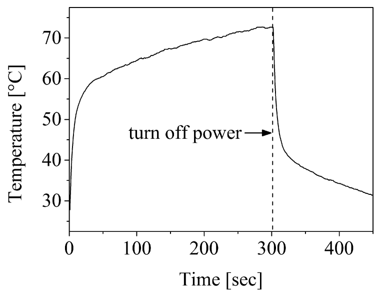

Figure 3. Temperature vs heating time.

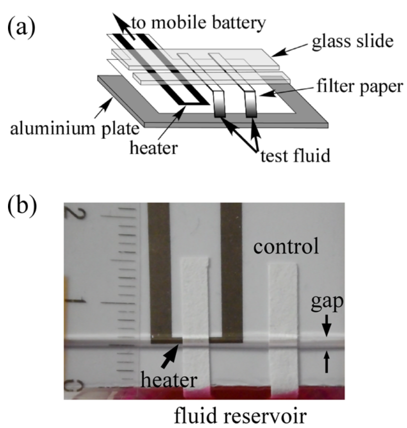

Figure 4. Experimental setup for valve test: (a) schematic diagram of valve experiment; (b) close-up of experimental setup (filter paper and valve).

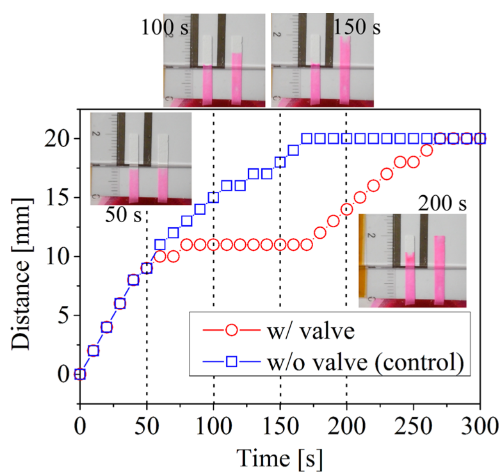

Figure 5. Distance traveled by fluid front vs time. The distance was measured with ±1 mm.

thus, both flow rates of the fluid were identical. The fluid front reached the heater at 70 s and remained at that location between 70 and 170 s. The fluid continued flowing once the heater was turned off at 170 s. This showed that the inkjet-printed heater worked well as an active valve.

Concentrator Using the Inkjet-Printed Heater. In the previous section, a stop valve using the inkjet-printed heater was realized by the evaporation of the working fluid (solvent); thus, prolonged heating time would lead to concentration of the solute. The relationship of the solute concentration and heating time was investigated. An ethanol solution containing rhodamine B (6.45×10^{-2} g/L) was used as the test fluid. The experimental setup was similar to that of the previous section, with the exception of a piece of filter paper used. Images were taken with an 8-bit color CMOS camera (Nikon 1 S2, Nikon, Japan).

The relationship of the concentration of the solute, rhodamine B, and heating time was investigated, as shown in Figure 6. The working fluid arrived at the heater position at 0 min. As the concentration of rhodamine B increased, the color of the filter paper became darker, as shown in the pictures in Figure 6. The time-series images with red−green−blue (RGB) color map were then converted to grayscale images using the "rgb2color" function in the Image Processing Toolbox of MATLAB R2014B. The concentration of rhodamine B was evaluated by the average grayscale intensity of the region of interest (85 × 15 pixels at the heater position). The vertical axis of Figure 6 shows "256/(grayscale intensity)", as the intensity decreased inversely with increasing concentration. The inverse of the intensity rapidly increased before heating for 10 min. This is because the filter paper was white (high grayscale intensity) prior to solute concentration and suddenly changed color upon evaporation of the working fluid. The inverse of the intensity proportionally increased after heating for 10 min, with the solute concentration being proportional to the heating time. This shows that the proposed method is feasible for increasing solute concentration on PADs.

Providing Heat for Chemical Reactions Using the Inkjet-Printed Heater. Endothermic chemical reactions cannot be realized using conventional PADs. Therefore, we attempted to use the inkjet-printed heater to provide heat for endothermic reactions. To demonstrate this, we performed Benedict's test for reducing sugars using Benedict's regent. When the mixture of reducing sugar and Benedict's reagent is heated, copper(I) oxide (Cu_2O) is precipitated as a brick-red powder, indicating a positive Benedict's test, i.e., presence of a reducing sugar.

A piece of filter paper was cut into a pattern having three detection zones as shown in Figure 7. A drop of aqueous glucose solution (20 g/L), aqueous sucrose solution (20 g/L), and pure water were spotted in each detection zone and dried. The filter paper was then placed on the inkjet-printed heater and attached with tape (3842N, Scotch, U.S.A.) as shown in Figure 7. The pattern of the inkjet-printed heater was changed from that of the previous sections in order to heat all three detection zones simultaneously. Benedict's reagent was then absorbed by capillary action from one end of the filter paper and the heater was turned on. The results of the experiment are shown in Figure 8. The Benedict's reagent penetrated to the position of the heater 3 min after the start of the experiment, at

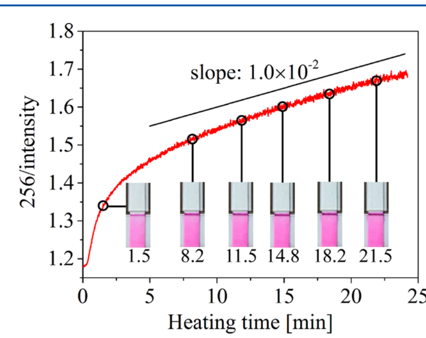

Figure 6. Relationship between concentration of the solute and heating time.

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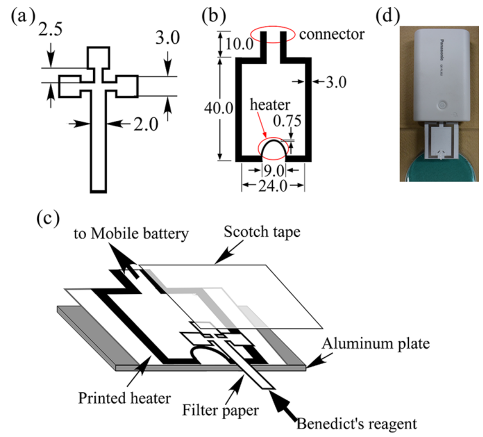

Figure 7. Schematic diagram of Benedict's test on PAD: (a) filter paper pattern, (b) inkjet-printed heater pattern, (c) configuration of experimental setup, and (d) picture of experimental setup (unit: mm).

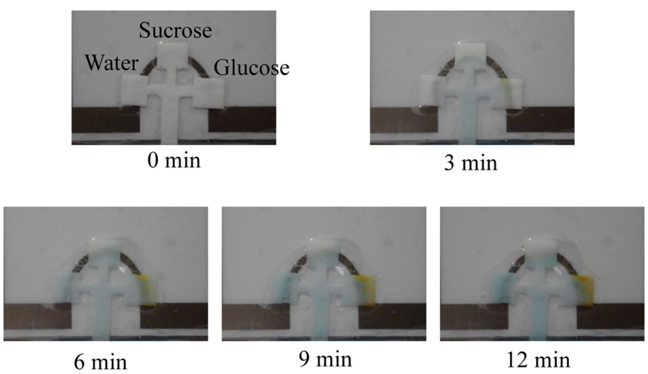

Figure 8. Results of Benedict's test on PAD.

which point, the color of the glucose zone began to turn orange. The color of the glucose zone became clearly orange after 9 min, while the color of the other two detection zones remained unchanged. This color change indicated a positive Benedict's test. The color of the sucrose and pure water detection zones became blue at 9 min due to concentration of the Benedict's reagent by the heater. This shows that the proposed method is feasible for conducting a test based on endothermic chemical reactions on PADs.

■ CONCLUSIONS

We proposed the application of an electric conductive pattern printed by a commercial inkjet printer to PADs. The electric resistance of printed conductive lines with several line widths was investigated. The sheet resistance of conductive lines of 0.36 ± 0.02 Ω/sq for line widths larger than 1.0 mm was low enough to fabricate an electric circuit. An inkjet-printed heater was then fabricated and operated by a mobile battery. The temperature of the heater reached 60 °C at a rate of 1.5 °C/s, allowing it to efficiently be applied as a valve, concentrator, and heat source for chemical reactions on PADs.

In the future, printing method of conductive patterns using a commercial inkjet printer will be applied to electrowetting, electroosmosis, and electrocapillarity on PADs, further increasing their applications.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b01568.

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Notes

The authors declare no competing financial interest.

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