Alternative Patterning Methods for Paper-based Analytical Devices Using Nail Polish as a Hydrophobic Reagent

Thiphol SATARPAI† and Atitaya SIRIPINYANOND

Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Bangkok 10400, Thailand

A rapid, easy, and cost effective fabrication method for paper-based analytical devices (PADs) is described. This newly developed method is based on the use of nail polish as an alternative hydrophobic reagent, and the nail polish was resistant to basic and organic solvents. Three approaches for fabrication of paper-based analytical devices (PADs) were investigated, namely writing, stamping, and spraying. The writing approach was carried out by drawing the hydrophobic area of a pre-designed pattern on filter paper with a simple lab-made pen filled with nail polish as the hydrophobic agent. The stamping and spraying approaches required the use of a designed mask, which was made by laser cutting of the magnet rubber sheet. With laser cutting, two types of templates were made, i.e., positive and negative counterparts. The positive counterpart was the inside pattern and the negative counterpart was the outside pattern of the magnet sheets. For the stamping approach, the negative counterpart of the magnet rubber mask was attached onto a simple rubber stamper that was then stamped onto filter paper after loading with nail polish solution. With the spraying method, the positive counterpart was used to cover the hydrophilic area on the paper. Then, the nail polish solution was used with an air brush and sprayed on the paper covered with the magnet rubber mask. All approaches were cost effective and required neither extra equipment nor any pretreatment step. Among all three methods, however, the spraying method was found most suitable for mass production and provided the best resolution when compared with the other two approaches. With this approach, the actual channel widths obtained were similar to the designed widths, with the narrowest possible channel width of 650 μm. Furthermore, a nail polish-treated PAD was prepared by soaking the paper in the nail polish solution. The ability of the nail polish-treated PAD was examined for its resistance to a strong basic solution and an organic solvent (up to 30% ethanol and dichloromethane). The nail polish-treated paper also showed the potential to be used as an organic-aqueous separator.

Keywords Paper-based analytical device, writing, stamping, spraying, nail polish

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Introduction

Paper-based analytical devices (PADs) have recently gained increasing interest as an analytical tool because they are cost effective, easy to use, disposable and biodegradable. To confine water flow within the hydrophilic nature of cellulose, some parts of paper were modified to become hydrophobic, creating the channels, reservoirs and detection zones on the paper. Several methods have been reported for paper patterning including photolithography, poly(dimethylsiloxane) or PDMS plotting/printing, plasma treatment (plasma etching), paper cutting (knife/cutter, laser), inkjet etching or inkjet printing, and wax printing or wax screen-printing as have been recently reviewed by Sriram et al. Each method has its own advantages and limitations depending on the type of material used, the complexity and the modification required for the application.

Various types of hydrophobic agents with various fabrication approaches were used for PAD fabrication. A UV curable photoresist, SU-8 polymer, was used in the photolithography. This method shows disadvantages because it requires organic solvents and expensive equipment, and the entire substrate and the hydrophilic areas are exposed to photoresist. PDMS was used in the plotting or printing method but this approach requires a plotter/printer device and a curing step. Wax material as hydrophobic agent shows some limitations due to its instability at high temperatures and the need of a heating source for wax melting and a wax printer. The use of alkyl ketene dimer (AKD), another type of wax material for paper sizing/hydrophobizing agent, was also reported by using a thermal inkjet printer for patterning the filter paper. This technique requires a heating cycle after printing. Other approaches for fabrication of PADs included a lacquer spraying method or a printing method using a hydrophobic UV curable acrylate. The aim of this work was to search for an alternative approach for simple and rapid fabrication without the need of expensive equipment for use in a resource limited laboratory.

Nail polish (or nail enamel, or nail varnish) is used as a beauty product for painting on the human fingernails or toenails. The main components of basic nail polish formulation are volatile organic solvent, film forming agents, film modifiers, resins, plasticizers, and various additives. After the nail polish is

† To whom correspondence should be addressed.
E-mail: hikarub13@hotmail.com
applied, the solvent component evaporates, leaving the film forming polymer coated over the fingernail. Previously, the use of nail polish for analytical device fabrication was reported.21–23 This included the use of nail polish coated filter paper to confine gold nanoparticle inks that were applied as a working electrode.21 Nail polish was applied on the paper-based screen-printed electrodes to insulate the carbon screen-printed connections.22 Moreover, nail polish was used in a thread-based device to block the hole after sewing thread on the substrate.23 Therefore, the applications of nail polish as a barrier material have been reported and well recognized. Nonetheless, the fabrication approach by using nail polish to completely pattern the hydrophobic contrast on the paper still remains unexplored. This work reports the use of nail polish as a hydrophobic agent for the low cost fabrication of PADs. Three fabrication methods were examined. These were writing or drawing, stamping, and spraying. These methods are cost effective without the need of expensive equipment or any extra pretreatment step. The combined use of nail polish and spraying method is reported here for the first time. The proposed technique was compared with the previously reported AKD printing method.17,24 The applicability of nail polish patterning paper for various types of solvent is also described.

**Experimental**

**Reagents and chemicals**

All chemicals used were of analytical reagent grade. Ethyl acetate was purchased from Fisons FSA Laboratory Supplies (Loughborough, England). Dichloromethane was purchased from JT Baker (NJ, USA). Acetone and sodium hydroxide were obtained from Merck (Darmstadt, Germany). Solution preparation was conducted in deionized water with resistivity of not less than 18 MΩ cm (Easypure® II Model D7031, Barnstead, Iowa, USA). Nitric acid and n-heptane were purchased from RCI Labscan Co., Ltd. (Bangkok, Thailand). All glasswares and plastic bottles were soaked in diluted HNO₃ and then rinsed with deionized water before use. Clear nail polish products were purchased from cosmetic shops in Thailand. The appropriate percentage of nail polish with solvent was prepared as hydrophobic solution. The filter paper Whatman® No. 41 and No. 4 were purchased from GE (Buckinghamshire, UK). A patterned magnet rubber sheet (0.8 mm thick) was made at a laser cutting shop in Bangkok.

**Apparatus**

The inkjet printer (PIXMA iP3680, Canon®) was used to print the designed pattern. An optical microscope (Olympus IX71, Japan) was used to observe the roughness of the filter papers and capture microscopic images. A stereo microscope (Meiji Techno EMT-2, Japan) with digital camera (Dino camera AM-423X, Taiwan) was used for capturing the image through the eyepiece of the microscope for measuring the contact angle of a water droplet on the surface. The contact angle was calculated by using drop shape analysis (DropSnake 2.1), a java plug-in for ImageJ software (NIH, USA).

**PAD fabrication by using writing method**

The writing method using nail polish as the hydrophobic agent was used to construct the pattern onto Whatman No. 4 filter paper. The pattern was designed by using Microsoft Powerpoint® software and printed using ink-jet printer on the filter paper (Fig. 1a). After printing, hand drawing of the designed pattern on the pink color zone was performed for creating the hydrophobic zone on the PAD. Hand drawing was carried out by using a simple lab-made pen filled with hydrophobic agent (100% nail polish without solvent dilution) and connected with an air pump, which was used to continuously load the nail polish to the tip (Fig. 1b). The viscosities of nail polish products in the market vary depending on degree of polymerization or manufacturing formulation. In the case of nail polish with low viscosity, the pump was not used.

**PAD fabrication by using stamping and spraying method**

The stamping and spraying approaches required the use of the designed mask that was made by laser cutting of the magnet rubber sheet. The magnet rubber mask was designed using Adobe Illustrator and made by laser cutting technique. After cutting, two types of magnet rubber pieces were obtained: one was the positive imprint pattern and the other was the negative imprint pattern, which was the openwork pattern type. The positive imprint pattern was used as a mask for the spraying method, whereas the negative imprint pattern was used as a
mask for the stamping method (Fig. 2). The positive counterpart was used for covering the hydrophilic part of the PAD and allows spraying on the other parts of the paper to create the hydrophobic zone. The negative counterpart was used for stamping the hydrophobic reagent on the PAD so that the hydrophobic boundary would exhibit a similar pattern as the stamp.

For the stamping method, the rubber stamper was made by using a drinking bottle cap as a handle and magnet rubber mask (the negative pattern) was attached to the cap. To reduce viscosity before use, the nail polish solution was diluted with ethyl acetate in the volume ratio of 1:4. The hydrophobic nail polish solution was loaded on the rubber mask surface by using a dropper or nail brush and then stamped onto Whatman® No. 41 filter paper (20 – 25 μm pore size, 220 μm thick). The hydrophobic area was then created on the filter paper as shown in Fig. 2.

For the spraying method, the magnet rubber mask (the positive pattern) on the iron plate holder was placed on the top of Whatman® No. 4 filter paper (20 – 25 μm pore size, 205 μm thick). The positive pattern magnet rubber mask was used for covering the paper from the nail polish spray and therefore to retain those areas as hydrophilic zones. The nail polish solution was diluted to 5 – 10% (v/v) with acetone because acetone not only provides good solubility of nail polish but it also evaporates rapidly, allowing for a fast fabrication process. The hydrophobic nail polish solution was loaded in the air brush (nozzle diameter: 0.2 – 0.3 mm) with air pump system (Puma MA1000GA, Taiwan) and sprayed on the mask (Fig. 2). As the hydrophilic area was protected by the magnet rubber mask, only the outside around the mask became hydrophobic. After spraying, acetone (normally used in nail polish cleanser) was loaded in the air brush to clean the nozzle to prevent clogging.

Results and Discussion

Effect of nail polish concentration on its hydrophobicity

In this study, clear nail polish products with resins/plasticizers, such as top coat, nail hardener, and gel, of varying formulas for different cosmetic applications were tested for their suitability to be used as a hydrophobic reagent. Various concentrations of nail polish products from 0 to 100% were prepared and dropped onto the filter paper. After drying at room temperature, the modified filter papers were tested by dropping water on the surface to see the penetration of water. The results in Table 1 show that at 100% concentration, nail polish products of all types can be effectively used as a hydrophobic agent. Depending on the type and manufacturer, the concentrations of the polymers in each nail polish formula were different and affected their viscosity. For nail polish products having a formula with high viscosity e.g. gel, the nail polish was diluted to 5 to 10% concentration, whereas it was diluted to 15 to 20% for those with low viscosity, such as top coat. Before use, the optimum concentration of nail polish should therefore be tested by dropping water on the paper surface after treatment with nail polish. The results illustrated in Table 1 clearly indicate that nail polish can be used as hydrophobic agent because it can turn cellulose fibers of the filter paper to become hydrophobic and therefore it was used for fabrication of PADs.

Three fabrication approaches by using nail polish as a hydrophobic agent

In order to develop a simple fabrication approach without...
using specific equipment, three approaches for fabrication of PADS were examined. The methods studied were writing, stamping, and spraying. With the writing method, a physical mask is not required. Bromophenol blue was dropped onto the hydrophilic area to test the confined hydrophilic zone obtained from this method. The hydrophilic area was well confined within the designed pattern without any leakage to the hydrophobic area, both at the front and the back sides, as illustrated in Fig. 1c. Despite the drawback of low throughput and poor resolution with the hand drawing method, this method was cost effective. The head pen is easily changed to allow appropriate patterning of the hydrophobic area. Therefore, this approach should be of interest in the resource limited laboratory for screening purposes or applied in the classroom for educational purposes. With the stamping method, lateral spreading or dispersion of the hydrophobic solution on the PAD was observed slightly after the stamper was lifted up, as shown in Fig. 3a. Thus, the channel width and the size of the reservoir were not well confined. Despite the poor channel resolution and consistency obtained by the stamping method, this fabrication method is simple and low cost, making this approach quite attractive. With the spraying method, dispersion of the hydrophobic nail polish solution into the hydrophilic zone was not observed as shown in Fig. 3b. Considering the contrast between hydrophobic and hydrophilic areas, writing and spraying methods are appropriate. Nonetheless, for large scale production, writing and stamping methods were not suitable. Therefore, the spraying method was selected for further study.

Characterization of hydrophilic and hydrophobic areas on PADS fabricated by nail polish spraying approach

The surface morphologies of the filter paper before and after spraying with the hydrophobic solution were observed by an optical microscope as illustrated in Figs. 4a and 4b, respectively. The optical contact angle of the filter paper after spraying was measured with a small drop of water (ca. 5 μL) on the hydrophobic area of the filter paper and was found to be approximately 120° (θ at the left side of the drop = 122.6 ± 4.1, at the right side of the drop = 124.6 ± 4.6, n = 3) as shown in the inset photograph in Fig. 4b. Clearly, the contact angle results indicate the low surface energy of the paper substrate or the hydrophobicity of the patterned paper. From Washburn’s equation as shown in Eq. (1), liquid penetration cannot occur if the contact angle is greater than 90°.17

\[ l = \sqrt{\frac{r \gamma \cos \theta}{2\eta t}} \]  

where \( l \) is the liquid penetration distance in paper, \( \gamma \) is the surface tension of the liquid-vapor, \( r \) is the equivalent capillary pore radius of paper, \( \eta \) is viscosity of the liquid, \( \theta \) is the contact angle between the liquid and capillary wall and \( t \) is the penetration time.

The proposed method of making hydrophobic contrast by the spraying method with nail polish was then compared with other widely available techniques, such as the AKD ink-jet printing method, which we have used in our previous work, after dropping the blue dye in the hydrophilic area, as shown in Figs. 4c (AKD) and 4d (nail polish). With nail polish hydrophobic patterning, a clear boundary was observed. Although AKD printing also provided a clear boundary between the hydrophilic and hydrophobic zones, heat treatment after AKD printing is required, whereas the nail polish spraying does not need any further treatment.

Moreover, the resolution was evaluated as a function of channel width. The narrowest possible widths of the channel created by the magnet rubber mask and spraying method were investigated. The nominal channel width was varied in the range of 650 to 1450 μm. The widths obtained on the PAD

| Nail polish #1 | 100% | 50% | 25% | 15% | 10% | 5% | 3% |
|---------------|------|-----|-----|-----|-----|-----|-----|
| Nail polish #2 | —    | —   | —   | —   | —   | —   | —   |
| Nail polish #3 | —    | —   | —   | —   | —   | —   | —   |

Table 1 Effect of nail polish concentration on hydrophobic property of filter paper (n = 3)

![Photographs of a) the magnet rubber mask for stamping and PAD after stamping, b) a comparison of the patterned PADS by stamping and spraying tested by the blue dye.](image_url)
were similar to the widths of the masks, as shown in Fig. 5. The photographs of the masks and the designed PAD with water drop are also illustrated in Fig. 5. The actual width of the PAD channel was measured after dropping water onto the channel. The actual channel width is linearly related to the nominal mask width as described by the equation, \( y = 1.1049x - 121.2 \), and a correlation coefficient of 0.9838 \( (n = 3) \). The slope close to unity implies that the actual and the obtained widths are equal. The channel width of narrower than 650 \( \mu \)m was not possible as the flow was obstructed.

Applicability of nail polish-treated PADs with strong basic solution and organic solvent (ethanol)

To test the applicability of PADs with a strong basic solution (\( ca. 2.5 \) M NaOH), PADs were fabricated by two hydrophobic agents for comparison purposes. These included the AKD inkjet printing and nail polish spraying method. As shown in Fig. 6, using nail polish as the hydrophobic agent can prevent the diffusion of the alkaline solution from the hydrophilic zone to hydrophobic area. Therefore, with nail polish as the agent, a better hydrophobic barrier was obtained compared to the AKD agent. This is due to the hydrolysis of the AKD reagent in the alkaline condition.25

Additionally, these PADs were tested with ethanol of varying concentrations from 10 to 50%, as illustrated in Fig. 7a. It is clearly seen from Fig. 7a that the filter papers soaked with nail polish as a hydrophobic barrier could resist ethanol better than the filter papers soaked with AKD reagent. A yellow dye was utilized for improving the visualization of ethanol leakage as shown in Fig. 7b. The results showed that the nail polish-
patterned PADs were tolerable to ethanol concentrations as high as 30% whereas the AKD-patterned PADs could be used at ethanol concentrations of less than 30%. Thus, the nail polish patterning was able to resist ethanol concentrations of 30% and still allowed desirable flows as shown in Fig. 7b. The AKD-patterned PAD is not applicable to a high concentration of alcohol; it is the wax material that is not compatible with some organic solvents as the solvents cause dissolution, solvent diffusion, or swelling. Even if the nail polish-patterned PAD is not resistant to 100% ethanol or a wide variety of organic solvents, when compared with PDMS-patterned PAD, it is still attractive as this approach is easy to fabricate, and requires no sophisticated instrument.

Feasibility of using nail polish-treated filter paper as an organic-aqueous separator

The resistibility of nail polish-patterned PADs to ethanol has inspired us to prepare nail polish-treated filter paper to be used as a permeable paper for organic-water separation. Three types of filter paper were examined; they were an untreated filter paper, AKD-treated filter paper, and nail polish-treated filter paper. The circular filter paper was soaked in diluted nail polish solution (5–10%) as used in the spraying method for 10 s and allowed to dry before use. Water was dropped on each type of paper to test for the hydrophobicity before further study (see red box in Fig. 8). A mixture of 10 mL dichloromethane (organic phase) and 10 mL water containing red dye (aqueous phase) was prepared and poured into these filter papers (dry filter papers) as illustrated in Fig. 8. Dichloromethane can freely permeate through the nail polish-treated filter paper while water containing the red dye color was retained on the filter paper without passing through. The AKD-treated filter paper, on the other hand, cannot retain water containing red dye, similarly to the results from the untreated paper. This is due to the possible dissolution of AKD in solvent. After complete separation, the filter papers were tested again with a droplet of water to examine the hydrophobicity of the treated filter papers after use. As illustrated in Fig. 8, only the nail polish-treated filter paper still remained hydrophobic (see black box in Fig. 8) on both sides of the paper. This observation suggests the applicability of nail polish-treated paper as an organic-aqueous separator.

Conclusions

Various approaches for PAD fabrication with nail polish are possible and offer different pros and cons. The writing method offers the advantages of being simple and cost effective. However, it is quite tedious and not suitable for production on a large scale. The stamping method is rather difficult and the sharp boundary between the hydrophilic and hydrophobic zones is not obtained. The spraying method is very effective and suitable for mass production. These three proposed methods
require neither sophisticated devices nor skilled personnel to fabricate PADs and nail polish has shown to be an effective hydrophobic agent for patterning paper-based analytical devices. In comparison with the previously used AKD agent, nail polish is applicable to strongly basic solvents and tolerable to low concentrations of ethanol and dichloromethane. The use of nail polish-treated paper as an organic-aqueous separator should be further explored.

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