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Selective superhydrophilic/phobic coating using capillary pressure for positive-displacement nanoliter dispensing

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A R T I C L E I N F O

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A B S T R A C T

Owing to the fact that liquid-dispensing devices are used in a wide variety of scientific fields, including chemistry, biology, pharmacology, and mechanics, droplet dispensing has come to be regarded as a key technology with respect to micro/nanoengineering. Positive-placement dispensing technology is being used widely because it allows for a high degree of controllability without requiring a complex dispensing system; however, adhesion and slip-related issues limit the performance of this technology. In this letter, we report a technique for the fabrication of selective superhydrophilic/phobic coatings in syringe-type positive-displacement dispensing nozzle tips. The superhydrophilic capillary in the nozzle tip was coated selectively with superhydrophobic materials by exploiting the difference in the capillary pressure. The surface of the front part of the capillary was made superhydrophobic; it thus allowed the liquid to flow without adhesion. In contrast, the back part was made superhydrophilic; it retarded the flow of the liquid, holding it in place. Together, the two surfaces minimized the volume of the dispensed droplets. High-speed images of the dispensed liquid were taken to compare the two droplet-dispensation processes. It was found that the volume of the water droplets dispensed from the selectively coated nozzle tip was as low as 27 nL and much smaller than that of the droplets dispensed from the superhydrophobic nozzle tip.

1. Introduction

Liquid-dispensing technology has become very important in the fields of chemistry, bioengineering, medicine, and mechanical engineering. For instance, high-throughput screening analysis [1–5] allows for millions of chemical, genetic, or pharmacological tests to be performed rapidly. Liquid-dispensing technology plays a critical role in this process. Further, labs-on-a-chip also use a variety of liquid-dispensing platforms. In addition, DNA microarray chip [6–8] and microfluidic systems such as those involving electrowetting-on-dielectric [9–11] or liquid dielectrophoresis [12–14] also make use of droplet-based dispensing.

Liquid-dispensing systems can be divided into two types: contact-type systems and noncontact-type systems. Noncontact-type systems are used more widely for dispensing liquids, owing to the disadvantages associated with contact-type systems. For example, when contact-type systems are used, there is a risk of contamination of the liquid, because the dispensing nozzle (i.e., the pin tool or the syringe) touches the target surface. Problems with adhesion between the dispensing nozzle and the liquid being dispensed also make contact-type systems less attractive. In the case of noncontact-type systems, the liquid is ejected from the dispensing nozzle with force; thus, there are no issues related to contamination and adhesion. Noncontact-type systems also have the advantage that they allow for the volume of liquid dispensed to be low. Droplets with volumes in the nanoliter to the picoliter range can be dispensed using noncontact-type systems. Volume minimization can reduce reagent use, decrease analysis time, lower costs, and reduce exposure to toxic chemicals.

Ink jet and acoustic ejection technologies are usually used for dispensing droplets with volumes lower than 1 nL. These technologies allow for accurate droplet volume control but require an additional pulse device to exert pressure or an acoustic signal. Valve-based dispensing systems composed of a high-pressure chamber, pump, and valve controller are commonly used in noncontact-type systems. The liquid inside the chamber is subjected to a high pressure, and the valve is opened or closed in a short time by a piezoelectric device [15,16] or a solenoid [17,18] in order to dispense the droplets. This technology can dispense small volumes with precision; however, the dispensing process is affected by the experimental environment, including the temperature. Positive-displacement dispensing systems, which dispense droplets based on the movement of a motor, are simple and allow for greater control over the dispensing process. However, since a positive displacement of the plunger pushes the liquid in such systems, these systems also experience adhesion-related problems similar to those seen in contact-type systems. To avoid these adhesion-related problems, the dispensing speed is increased or a low-surface-tension

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agent is used; however, volume control and the precision of dispensing become worse, owing to the slipping of the liquid. Thus, the adhesion- and slip-related problems need to be solved simultaneously.

In this paper, we describe a technique for selectively fabricating superhydrophilic/phobic coatings on positive-displacement dispensing nozzle tips. The nozzle tips coated using this method did not exhibit any adhesion-related (because of the superhydrophobic part) or slip-related problems (because of the superhydrophilic part). The phenomena of selectively coating the nozzle tip and liquid movement in the coated nozzle tip are discussed. The coated nozzle tip exhibited better performance than did a completely superhydrophobic nozzle tip with respect to droplet volume minimization. Images of the droplets dispensed from both nozzle tips were obtained using a high-speed camera, in order to compare the dispensing performances of the two tips. In the case of the selectively coated nozzle tip with a diameter of 150 μm, the minimum volume of the dispensed droplets was as low as 27 nL.

2. Experimental section

Capillary pressure is the difference in the pressures at the interface between two immiscible fluids such as water and air. This pressure depends on the liquid/vapor interfacial tension (γ), the contact angle (θ) of the material, and the radius of capillary (*a*), as shown in Eq. (1).

$$\Delta P = \frac{2\gamma}{R} = \frac{2\gamma\cos\theta}{a} \tag{1}$$

In the case of small capillaries, the capillary pressure can either induce or prevent a liquid from entering the capillary. In a hydrophilic capillary, the liquid spreads within the capillary because of positive pressure, while in a hydrophobic capillary, an additional pressure greater than the negative pressure determined by Eq. (1) needs to be exerted to force the liquid into the capillary.

For materials with the same wetting properties, the capillary pressure only depends on the diameter of the capillary and is inversely proportional to it. The two connected capillaries shown in Fig. 1 have different diameters, and each experiences a capillary pressure, which induces the liquid within the capillary to move. As shown in Fig. 1, the capillary pressure can be divided into two ranges. P_{cap1} is the capillary pressure for the small-diameter capillary 1 (300 μm), while P_{cap2} is the capillary pressure for large-diameter capillary 2 (5 mm). In the case of the hexane solution in the superhydrophilic capillaries, the capillary pressure is 0.123 MPa for the 300-μm capillary and 0.007 MPa for the 5-mm capillary.

If a pressure ranging between P_{cap1} and P_{cap2} is applied within the large-diameter capillary (0.01 MPa in this case), liquid will enter the capillary and rise until the end of the small-diameter capillary, because P_{cap1} would be higher than the applied pressure but P_{cap2} would not. This phenomenon can be exploited for selectively depositing coatings on the capillaries of liquid dispenser nozzle tips. A nozzle tip with a small superhydrophobic capillary (such as capillary 1 in Fig. 1) and a large superhydrophilic capillary (capillary 2 in Fig. 1) can be fabricated by injecting gas through the capillaries during the hydrophobic dip coating of the nozzle tip.

A copper cylinder (diameter of 10 mm, width of 5 mm) was used to fabricate the nozzle tip. The cylinder was machined to a depth of 4.5 (diameter of 5 mm) from the top surface and to a depth of 500 μm at a distance of 300 μm from the first machined surface. The nozzle tip was selectively coated as per the following two steps. First, the hydrophilic coating was deposited by chemically treating the surface of the copper cylinder. This was done using the process described by Chen et al. [19]. The copper nozzle tip was cleaned in 200 ml of 17% hydrochloric acid for 15 s and in ethanol for 5 min using an ultrasonicator. The cleaned copper nozzle tip was immersed in 200 ml of a mixture of 2.5 M NaOH and 0.1 M $(NH_4)_2S_2O_8$; the temperature was maintained at 4 °C for 30 min. The copper surface turned light blue, because of the formation of copper hydroxide in the solution. The thus-treated copper nozzle tip was then dried at 30 °C in air for 3 h to allow for stabilization. Nanorod-like structures several hundreds of nanometer in width and several micrometers in length appeared on the thus-formed copper hydroxide surface. This surface was superhydrophilic and had a contact angle of 0°. The second step was to selectively form a hydrophobic coating on the copper nozzle tip by gas injection. The system used for this purpose consisted of a gas injector, a pressure controller (Musashi ML-5000XII), and a syringe. A polytetrafluoroethylene connector and silicon adhesive were used to connect the nozzle tip to the syringe. The syringe was connected to a gas pressure controller, which helped maintain the gas pressure within the copper nozzle tip during the coating process. 200 ml of a mixture of hexane and HDFS (heptadeca-fluoro-1,1,2,2-tetra-hydrodecyltrichlorosilane) (ratio 1000:1) was prepared, and the copper nozzle tip was immersed in this mixture to form the hydrophobic coating. Nitrogen gas was supplied to the controller, and the injection pressure was controlled throughout the formation of the hydrophobic coating, which was applied for 10 min. Finally, the copper nozzle tip was removed and dried at room temperature for 24 h.

To ensure precise control over the volume of liquid dispensed, a syringe pump (NE-1000) was used. This pump was set vertically and a syringe attached to the nozzle tip was installed. The system used, which also consisted of a syringe, a Teflon connector, and a nozzle tip, was same as the one employed for the dispensing experiments. A schematic of the droplet-dispensing setup is shown in Fig. 2. During the droplet-dispensing process, the syringe pump pushed the liquid inside the nozzle tip constantly. A high-speed camera (Phantom Miro m320s) was used to capture images of the dispensing moments at intervals of 1/1000 s. The dispensed volume was calculated from the captured images.

3. Results and discussion

Fig. 3 shows the water droplets dispensed from the two nozzle tips. The first nozzle tip (Nozzle Tip A) was completely coated with a

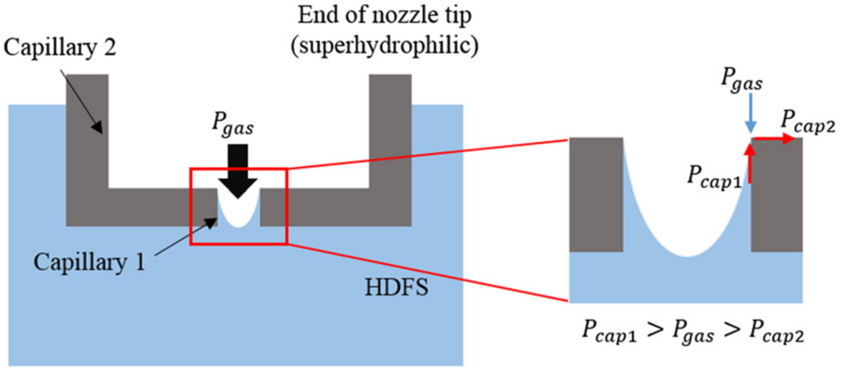

Fig. 1. Gas injection to avoid penetration inside the nozzle during HDFS coating.