Electric field assisted manipulation of microdroplets on a superhydrophobic surface

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The efficient manipulation of low-volume droplets offers many potential applications in relation to chemical and biomedical tests and protocols. A novel approach to the manipulation of a microdroplet on a superhydrophobic surface is introduced in the present communication. The microdroplet was first picked up onto a hydrophilic needle, transported from one location to another, and finally released under the action of an electric field force. Three key parameters in this process, the radius of the droplet, the distance between the two electrodes, and the required voltage, were investigated. This study should be helpful for the design of microfluidic devices. © 2010 American Institute of Physics. [doi:10.1063/1.3523472]

Advances in the technology of manipulation of low-volume droplets, and for automation of these processes, offer the potential to accelerate complex chemical and biochemical protocols while saving reagents. Many techniques have been developed for controlling and manipulating microfluidic flow,^{1–4} e.g., pressure, capillary effects, electric fields, and magnetic fields. However, a simple and efficient method for the management of tiny droplets, from the microliter down to the picoliter scale, is still in great demand for applications in chemical and biological analysis and in clinical diagnosis.^{5–7} Two methods are commonly available for manipulation of droplet flow: two phase flows in microchannels and sessile droplet displacement on surfaces.^{7,8} However, a frequent problem for microchannel flow is that the delivered sample is absorbed onto the internal surface of the channel, causing either clogging or sample loss.⁷ Consequently, the technology of sessile droplet displacement on surfaces has been used to avoid these difficulties. Although there have been a number of reports concerning the technology of actuating droplets using mechanical vibrations,⁸ electrowetting,⁹ and electromagnetic techniques,¹⁰ the movement of a sessile droplet on a hydrophobic surface still meets some problems, particularly the electrowetting driven technique supplies a very small force on the droplet and therefore heavy or sticky biological objects cannot be displaced on the surface.

Recently, the technology of manipulating droplets on a superhydrophobic surface of low adhesive force has been proposed as a solution to the problem of droplet-substrate adhesion.^{7,11–13} So-called “liquid marbles”¹¹ or superparamagnetic microdroplets⁷ conjugated with specific functional powders may be manipulated under a magnetic field. However, these powders could also contaminate the microdroplet. A slightly adhesive superhydrophobic surface can also be used to transport a droplet away from a superhydrophobic surface with lower adhesive force. However, with this method it is only possible to manipulate the droplet from a superhydrophobic surface to a hydrophilic surface.^{12,13} To the best of our knowledge, the transport of droplets between two superhydrophobic surfaces, each having a low adhesive force, has not been investigated.

Electrohydrodynamic technology has been investigated in relation to microdroplet spraying,^{14,15} single microdroplet dripping,¹⁶ drop-on-demand printing,¹⁷ and in the assembly of

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biosensors and nanomaterials.¹⁸ In this communication, a novel method of transporting microdroplets on a superhydrophobic surface with the help of an electric field, is introduced. This technology is able to move a droplet rapidly across a superhydrophobic surface or mix several microdroplets together on a superhydrophobic surface.

Figure 1 presents a schematic diagram of the microdroplet transporting system designed in our laboratory. A conductive microrod connected to an insulated holder, served as a “mechanical hand.” A charge-coupled device (CCD) connected to the computer was focused on the bottom of the microrod. The CCD was helpful for finding samples of interest and for capturing the images of the microdroplet sample while it was being raised and moved. The substrate (a conductive plate coated with a superhydrophobic surface), as shown in Fig. 1(c), was mounted on a three-axis (x , y , and z) stage to provide the relative motion between the superhydrophobic surface and the pendent microdroplet.

The superhydrophobic surface depicted in Fig. 1(c), prepared as described in Ref. 19 with a contact angle of $162 \pm 2^\circ$, served as the superhydrophobic substrate. The droplets (de-ionized water, specific conductivity of $0.061 \mu\text{S}/\text{cm}$ at 25°C , measured using DDS-307A, Shanghai REX Instrument, Inc., China) were placed onto the superhydrophobic substrate at a temperature of $20 \pm 2^\circ\text{C}$ and relative humidity of $45 \pm 5\%$.

The process of transporting the microdroplet consisted of three steps [Fig. 1(d)]. The first step was to find the microdroplet sample using the CCD and to move it to a position just below the microrod. Then, the supporting stage was moved upward until the droplet touched and adhered to the microrod. In the second step, the supporting stage was moved in the x and y directions to find the predetermined position where the droplet was to be set down. This is referred to as “picking-up mode.” Finally, the power supply was turned on to drip the microdroplet sample down onto the superhydrophobic surface. This is termed “dripping mode.” This transporting process used the relative motion between the microrod and the superhydrophobic surface. Alternatively, the microrod could be moved above the surface to the microdroplet.

The transfer process of a microdroplet from one location to another on a superhydrophobic surface using the steel microrod ($D=250 \mu\text{m}$) with the assistance of an electric field is shown in Fig. 2. The CCD was first focused on the microdroplet ($R=0.58 \text{ mm}$). Then, the microrod was used to touch and adhere to the microdroplet sample [Fig. 2(b)] and lift it by 0.634 mm [Fig. 2(c)]. Finally, after moving the sample to another location, the power supply was switched on and the voltage was adjusted to a high level causing the droplet to be dripped down [Figs. 2(d)–2(f)]. When the applied voltage reached 1200 V , the droplet was deformed into an ellipsoidal shape [Fig. 2(d)]. The moment when the microdroplet was dripped down onto the surface is displayed in Fig. 2(e). It should be noted that no liquid appeared to have adhered to the microrod. This is a very important feature in relation to the transport of microdroplet samples.

To understand the process of transport of the microdroplet samples, the forces acting on the sample are shown in Fig. 3. In the picking-up mode shown in Fig. 3(a), the forces acting on the droplet are gravity force F_g , superhydrophobic surface adhesive force F_s , and microrod adhesive force F_r . If F_r is greater than the sum of F_s and F_g , the droplet is raised. When the sample is detached from the surface, F_s disappears in this system (ignoring the universal gravitation between the droplet and the surface). In the dripping mode as shown in Fig. 3(b), when the power supply is switched on, the electric field force F_e acts on the droplet. With increase in the voltage, the droplet is dripped down from the microrod onto the superhydrophobic surface when the sum of F_e and F_g is greater than F_r .

In the picking-up mode, it is easy to pick up a microdroplet from a superhydrophobic surface using a hydrophilic steel microrod (contact angle is $\sim 60^\circ$), but in the dripping mode, the situation is more complex when an applied electric field is applied.

To gain further understanding of effect of the distance H between the droplet and superhydrophobic surface in dripping mode, the dependence of the required voltage (direct current) on the distance H is depicted in Fig. 4(a) for two sizes of microrods (diameters $D=450 \mu\text{m}$ and $D=140 \mu\text{m}$), respectively. It is seen that the required voltage is approximately proportional to distance H . The microrod with diameter $450 \mu\text{m}$ required a much higher voltage because of the

FIG. 1. Schematic diagrams of a microdroplet transporting system. (a) Schematic of the operational system. A stainless steel microrod (diameter $D=140\ \mu\text{m}$) is fixed onto an insulated holder and is set in the field of view of a CCD. A power supply connects the microrod and the conductive plate under the superhydrophobic surface. The substrate surface is mounted on a three-axis (x , y , and z) stage. (b) SEM images of the microrod used in the experiment. (c) SEM images of the superhydrophobic surface, which is prepared as described in Ref. 19 with an apparent contact angle of $162 \pm 2^\circ$. (d) Steps in the process of transporting a microdroplet on a superhydrophobic surface.

FIG. 2. Process of transfer of a droplet ($R=0.58$ mm) from one location to another on a superhydrophobic surface using the steel microrod (diameter $D=250$ μm) with the assistance of an applied electric field. [(a) The microrod was moved above the microdroplet. [(b) and (c)] The microdroplet was then touched by the microrod, picked up, and moved to another position. [(d)–(f)] The power supply was turned on and adjusted to drip the microdroplet onto the superhydrophobic surface. The droplet was elongated with increasing applied field until it dropped onto the solid surface. The precise moment when the microdroplet was dripped onto the surface is shown in Fig. 2(e). The images were taken using an optical microscope equipped with CCD camera at 25 frames/s.

FIG. 3. Schematic of the forces acting on the microdroplet sample in (a) picking-up mode and (b) dripping mode.

FIG. 4. Required voltage in the dripping mode. (a) The supplied dc voltage vs the distance H between the droplet and superhydrophobic surface for the same volume of droplet: $R=0.57$ mm (DI water); here, H denotes the original distance between the droplet and the solid surface when the no electric field is supplied as shown in the inset. (b) The supplied dc voltage vs the droplet radius for several heights of the droplets suspended above the superhydrophobic surface.

higher F_r . This indicates that the selection of a suitable microrod diameter represents a balance between the required voltage for microdroplet dripping and the diameter needed for efficient picking-up.

Figure 4(b) shows the required voltage for droplet dripping versus the radius of the droplet samples for different values of H . As the radius of the droplet samples was increased, the voltage required for droplet dripping decreased. It was observed that the greater the height and the smaller the size of the droplet, the higher was the required voltage.

There is a question if the technique described in the present communication can be applied to a droplet containing living cells under high voltage. The study of Jayasinghe *et al.*^{20,21} on electric field driven jetting shows that there are no apparent damaging effects of high voltage (ranging from 10 to 30 kV) on living cells. Eagles *et al.*²² reported the experiments of mouse neuronal cells subjected to electrohydrodynamic jetting at an electric field strength of 0.47–0.67 kV/mm, corresponding to an applied voltage of 7–10 kV. Their experiment indicates that the process of jetting does not significantly perturb the neuronal cells.

Many researchers^{23–27} have studied the process of microdroplet dripping. The process of the dripping mode is mainly controlled by two dimensionless numbers:^{23,24} the gravitational Bond number $B_o^G = \rho g R^2 / \gamma$ and the electrical Bond number $B_o^E = \epsilon R E^2 / \gamma$, where ρ is the sample liquid density, g is the gravitational acceleration, R is the microdroplet radius, γ is the interfacial tension of the liquid, ϵ is the permittivity of the sample liquid, and E is the applied electric field. In our experiment, the radius of the sample microdroplet is less than 750 μm , the applied electric field is less than 15 kV/cm. The value of B_o^G is on the order of $O(10^{-2})$, which is much smaller than B_o^E , which is on the order of $O(1-10)$. Therefore, the electric force is the most important factor to control the dripping process of a small droplet. A high voltage is required to supply a force large enough to overcome the adhesive force.

The droplet dripping is a key step for transferring microdroplets. More physical insights on the derivation of forces analyzed above in dripping mode would be helpful for understanding the process of the microdroplet dripping. Kim *et al.*²⁷ studied the mechanism of electrostatic microdroplet formation and the ejection of the droplet from a microtube. Although the dripping mechanism may be different from the case as studied here, the function of electric field is similar. Kim *et al.*²⁷ gave the adhesive force of microtube, $F_r = \pi D \gamma$, the gravitational force, $F_g = 4/3 \pi \rho g R^3$, and the electrical force, $F_e = 1/2 S \epsilon_o E^2$. Here, D is the outer diameter of the microtube, S is the surface area of the microdroplet, and ϵ_o is the permittivity of air. For a ball shape of microdroplet, the applied electric field E can be expressed by $E = \sqrt{2V/r' \ln(4H/r')}$,²⁷ where V is the applied voltage, $r' = K(R - D/2) + D/2$ is the modified radius of the droplet, and $K = 1.2$ is a correction factor. For the case studied by Kim *et al.*,²⁷ the distance H is much greater than the diameter ($2R$) of the droplet. However, in our case, H is of the same order as R , and the shape changes (elongation) of the droplet may affect the dripping mode. Also, the adhesive mechanism of a solid microrod to a droplet might differ from that of a microtube. However, we still use those equations to estimate the voltage required for dripping in our experiment in order to get a basic understanding of the dripping process. The estimated voltages required for the droplet dripping are $\sim 60-80\%$ of the experimental measurements. The main reason for this may be that we left out of consideration of the adhesive force on the end surface of the microrod, which is totally different from the adhesive force on the micro-tube end surface.

In summary, we introduce a technique to transport microdroplets on a superhydrophobic surface, which does not need any special preparation. With this method, it is possible to manipulate a single microdroplet on a superhydrophobic surface with an electric field. This finding may be helpful for designing new microfluidic devices, especially in applications that involve localized chemical and biological reactions.

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