Droplet manipulation on a liquid crystal and polymer composite film

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ABSTRACT

A droplet manipulation on a switchable surface using a liquid crystal and polymer composite film (LCPCF) based on phase separation is developed recently. The wettability of LCPCF is electrically tunable because of the orientation of liquid crystal directors anchored among the polymer grains. A droplet on LCPCF can be manipulated owning to the wettability gradient induced by spatially orientation of LC directors. We discuss the droplet manipulation on LCPCF and demonstrate several applications of LCPCF, such as polarizer-free displays, and human semen sensing.

Keywords: liquid crystal, polymeric film, droplet manipulation.

1. INTRODUCTION

Droplet manipulation on a switchable surface has many applications, such as tunable focusing liquid lenses, polarizer-free displays, biosensors and microfluidic devices. The switchable surfaces are usually realized based on self-assembled monolayers (SAMs) which can switch wettability of surfaces by changing the conformation of molecules under external stimuli.[1-3] When we properly control the distribution of wettability of the switchable surfaces, a droplet on the surfaces can be driven toward more hydrophilic region of the surface due to net Young's forces.[4-6] However, a fluid drop usually refuses to move because of the hysteresis. Many methods are published for manipulating droplets by obtaining gradient surfaces, such as thermal induced gradient,[7,8] vapor-phase diffusion,[9, 10] electrochemical method,[11] photoresponsive surface,[12] and photodegradation method.[13] Recently, we developed a switchable surface, a liquid crystal and polymer composite film (LCPCF), by phase separation between liquid crystals (LC) and polymers after the photopolymerization process.[16-19] The wettability of LCPCF is electrically tunable because of the orientation of liquid crystal directors anchored among the polymer grains. In this paper, a droplet manipulation on LCPCF is demonstrated and discussed. Two applications including polarizer-free displays and biosensing are introduced.

2. SAMPLE PREPARATION AND OPERATING PRINCIPLES

The structure of LCPCF and operating principles of a droplet manipulation of LCPCF are illustrated in Fig. 1. The structure consists of a LCPCF on a patterned ITO (indium tin oxide) glass substrate to provide in-plane electric fields. The ITO electrodes on the glass substrate were etched with interdigitated chevron patterns. The angle of the zigzag ITO stripes is 150°. The width and gap of the electrode stripes are 4 μm and 14 μm, respectively. To fabricate the LCPCF,[16]

we mixed a nematic LC mixture E7 (Merck) and a liquid crystalline monomer (4-(3-Acryloyloxypropyloxy)-benzoic acid 2-methyl-1, 4-phenylene ester) at 70:30 wt % ratios. The mixtures were then filled into an empty cell with a gap of 6 μm which consists of a glass substrate as a top substrate and a patterned ITO glass substrate as a bottom substrate. The top substrate of the cell was overcoated with a thin polyimide (PI) layer and then mechanically buffed at the direction of 20° with respect to the electrode stripes. After filling, the cell was exposed to a UV light with intensity I = 10 mW/cm^2 for ~30 min at 70 °C. After phase separation and photo-polymerization, the top glass substrate was peeled off by a thermal releases process. A solidified LCPCF was obtained with 6 μm thickness and 30 nm root-mean-squared roughnesses, as depicted in Fig. 1. At V=0, the LC directors are aligned along y-direction, parallel to the rubbing direction of the PI layer. Under an applied AC voltage (f = 1 kHz), LC directors are reoriented along the electric fields. The LCPCF is more hydrophobic at 0 V$_{rms}$ because the phenyl planes of LC molecules are more parallel to the surface of the LCPCF (x-y plane). On the contrary, the LCPCF is more hydrophilic at high AC voltage because of the field-induced uneven tilts of the terminal groups of LC molecules near the edges of the fringe electric fields on the LCPCF surface. Moreover, the hydrophile of the LCPCF is electrically tunable by changing the magnitude of the AC voltage. In order to manipulate a droplet, the droplet on LCPCF can be driven by an imbalanced Young's force, which arises from wettability gradient of LCPCF induced by orientation of LC molecules under a periodically applied inhomogeneous electric field, as shown in Fig. 1. The contact angle on the left is smaller when we apply AC electric field in the left region of electrodes because the left region of LCPCF is more hydrophilic. The droplet is then driven toward more hydrophilic region. The net Young's force (F) of the droplet owning to the difference of contact angles can be expressed as:

$$F = \pi \times r \times \gamma_{LV} (\cos(\theta_L) - \cos(\theta_R))$$

(1)

where γ_{LV} represents the surface tension (i.e., energy per unit surface) of the liquid–vapor interface, and r is the radius of the drop. θ_R and θ_L stand for the local contact angles on the right and on the left of the droplet, respectively.
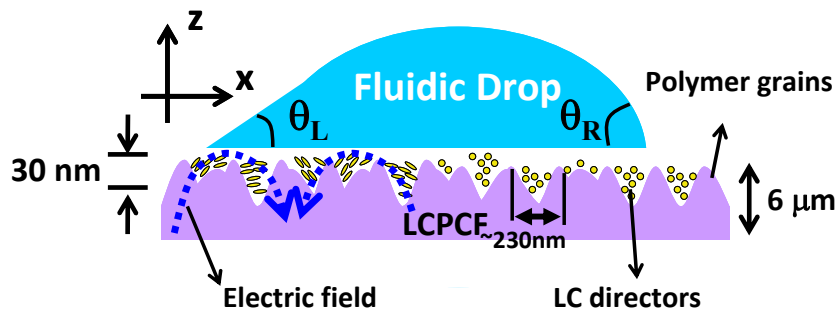

Fig. 1. Schematic structure and operating principles of LCPCF.

3. EXPERIMENTAL RESULTS

To observe the surface morphologies, the image of scanning emission microscopy of the surface of LCPCF after we removed the LC by hexane is shown in Fig. 2. The surface also shows elongated aggregation of polymer grains along the rubbing direction and void holes for LC molecules. The size of LC domains is around 100-300 nm. The averaged size of LC domains is around 230 nm and the averaged size of polymer grains is around 70 nm. The root-mean-square (RMS) roughness of the film surfaces was measured to be ~15 nm by an atomic force microscope (AFM) (Dimension 3100, Digital Instruments) at tapping mode at the room temperature (~23°C) in air. The surface morphologies depend on the phase separation process during fabrication, such as the temperature, concentration, and the intensity of UV light. Different morphologies affect the performance of droplet manipulation on LCPCF. The surface is smoother; the translation velocity of a droplet is larger.

In order to make sure that the fluid (or droplet) does not affect alignment of the LC anchored among the polymer grains, we placed a drop of DI water on LCPCF and observe the color under crossed polarizers when we rotated the LCPCF. The results are shown in Fig. 3. We found the colors under fluid and under the air are the same. That means the LC directors under fluids and air have same alignment. We also tested different fluids, such as ethylene glycol and glycerol, and we had the same results. The LC directors under fluids or air have same alignment because of the polymer grains provide a strong anchoring force to LC directors.
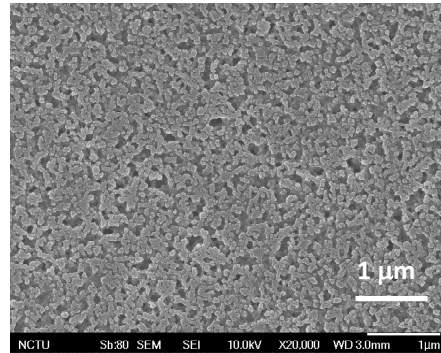

Fig. 2 The surface image of scanning emission microscopy of the LCPCF.
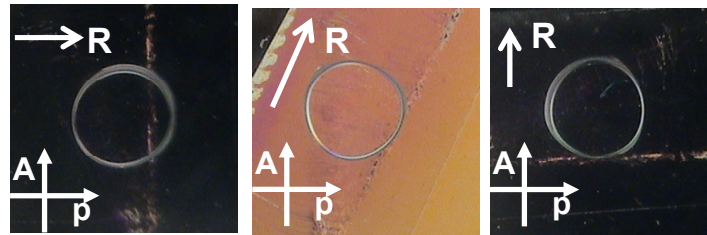

Fig.3. Observe the droplet on LCPCF under crossed polarizers and rotate the LCPCF. P represents the polarizer, A represents the analyzer, and R represents the reference direction of LCPCF.

To observe the droplet manipulation on LCPCF, we dropped a water droplet with 3μL on LCPCF, as shown in Fig. 4. When we turned on the pulsed voltage at 0.63 sec, the contact angle of the droplet on the left was 20 degree smaller than the contact angle on the right. The difference of the contact angle on the left and on the right resulted in a net force to drive the droplet toward left. Then the droplet run toward left after 0.633 sec. When we turned off the voltage at 1.6 sec, the droplet contracted to high contact angles because the LC orientation at V=0. The velocity of the droplet is around 1.12 mm/s. The droplet manipulation on LCPCF also depends on the amplitude of applied pulsed voltages. The Fig. 5(a) shows the translation distance of center of mass of the droplet as a function of time when we apply different amplitudes of applied pulsed voltages. The fluid we used in Fig. 5(a) was ethylene glycol. The pulsed voltage us turned on at 0.4 sec. When the amplitude of the pulsed voltages increases, the translated distance of the droplet increases. That means the droplet move faster with the amplitude of the pulsed voltages.
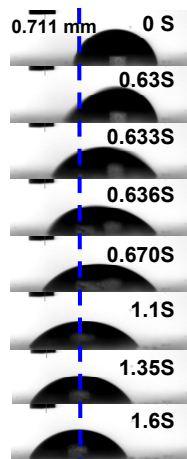
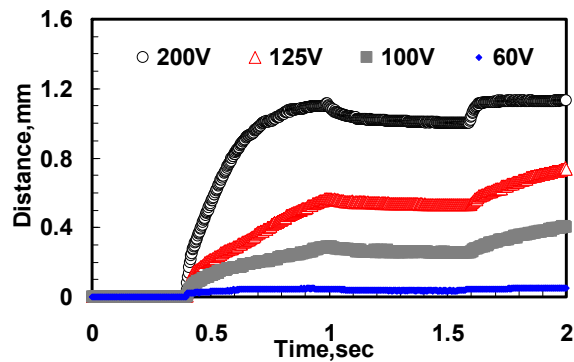Fig. 4 Side views of a water droplet manipulation on LCPCF at different times.

Fig. 5 The translated distance of the droplet as a function of time when we apply amplitudes of applied pulsed voltages of 60 V_{rms}, 100 V_{rms}, 125 V_{rms}, and 200 V_{rms}. The pulsed duration is 600 ms and the frequency is 1 kHz.

The droplet manipulation can be used to realize a single pixel of a polarizer-free, color-filter-free, reflective and bistable display using droplet manipulation on LCPCF, we used a color fluid on LCPCF, ethylene glycol, placed a black matrix on the top of a drop of ethylene glycol, and used a white paper as a reflective diffuser, as shown in Fig. 6(a), (b), and (c). When the droplet translates, the white aperture or opening of the black matrix turns out red gradually. We measured the percentage of white area as a function of time when we apply pulses voltages, as shown in Fig. 6(d). The response times are around 75 ms when the aperture is from full white color to full red color and 200 ms when the aperture is from full red color to full white color. As one can see, the color in the aperture remained even though we turned off the voltage. That means the display is bistable. The contrast ratio is around 8:1 in reflective mode for the white light. To improve the response time, we can reduce the thickness of LCPCF, reduce the roughness of LCPCF, and increase the amplitude of the pulsed voltage. To reduce the driving voltage, reducing the thickness of LCPCF is the best way. To improve the contrast ratio, the concentration of dye molecules can be increased.
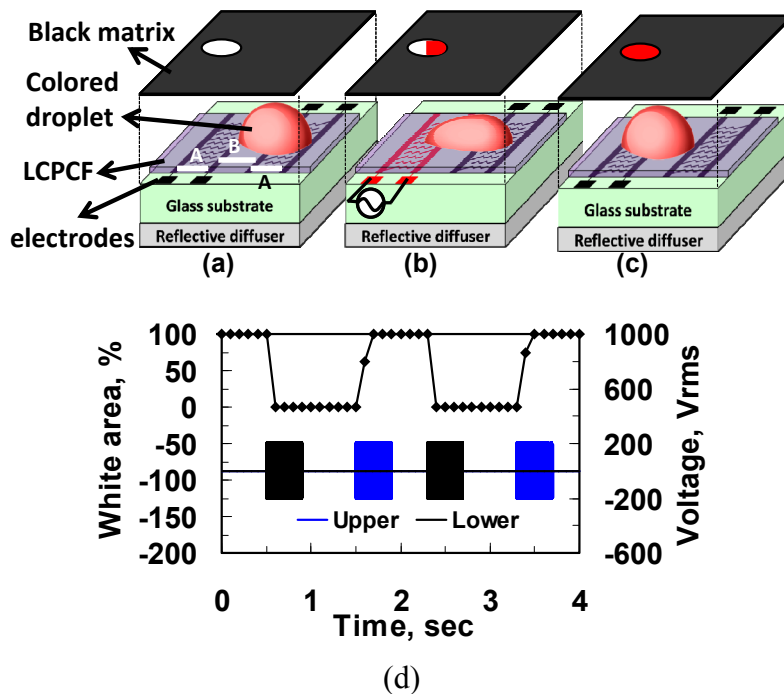
Fig.6 The structure and operating principles of a display using droplet manipulation on the LCPCF at (a) voltage-off state, (b) voltage-on state on the left electrode region. (c)After the voltage is turned off, the droplet contracts and then stops moving. A and B are 1.5 mm. (d)

We can also use droplet manipulation on LCPCF to realize human semen testing by replacing the water droplet with a human semen drop of 1.5 μL. A human semen drop consists of seminal plasma and sperms. Sperms are micro-sized particles with self motivated bio-forces. Because of high viscosity of human semen, the semen droplet can not translate. After testing 34 males, we observed two motions of semen droplets: collapse and back-and-forth stretch. The collapse of a droplet means the contact angle changes immediately when we turn on the voltage and then the contact angle does not recover when we turn off the voltage. And back-and-forth stretch of a droplet means the contact angles of a droplet changes periodically with pulsed voltages, but the droplet stay in the same location. According the experiments, the droplet stretches back and forth only when the semen concentration is larger than 100 million/mL, morphology is larger than 15 %, and motility is larger than 50%. Otherwise, the semen droplet collapses. Besides, the semen drop stretches only when larger than 30% of sperms moves straight forward and larger than 30% of sperms moves circularly. The reason why sperm droplet stretch is because the pull and drag between immotile and motile spermatozoa leads to the back-and-forth stretch of a semen droplet on LCPCF. The semen droplet collapse is not only because of flush of the seminal plasma induced by the wettability gradient, but also because of the attraction and traps of weak or immobile spermatozoa by the field of liquid crystals and weak fringing electric fields on the surface of LCPCF. The surface of LCPCF is then re-modified by the cover of the spermatozoa. Thus, the LCPCF can be used for testing the human semen by observing the motion of the human semen drop on LCPCF.

4. CONCLUSION

In conclusion, we have demonstrated the droplet manipulation on LCPCF. The droplet translates on LCPCF because the droplet experiences a net Young's force resulting from the wettability gradient of LCPCF. The wettability gradient of LCPCF is due to the orientation of LC directors anchored among the polymer grains. The increase of the amplitude of pulse voltages can boost the translation of the droplet. The applications based on the droplet manipulation

on LCPCF are introduced. First is the application of the display. We can realize a polarizer-free, color-filter-free, reflective and bistable display based on the droplet manipulation on LCPCF. The problems need to be overcome are the high driving voltage, slow response time, low aperture ratio and low resolution. The second application is biosensing. The droplet manipulation on LCPCF can be used in human semen sensing. By observing the motion of a semen drop, we can test the parameters of human semen. Other potential applications of LCPCFs are liquid lenses, and the microfluidic device in assisted reproductive technology and drug delivery.

Acknowledgments

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