Electrowetting-on-dielectrics for manipulation of oil drops and gas bubbles in aqueous-shell compound drops†

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We present the manipulation of oil, organic and gaseous chemicals by electrowetting-on-dielectric (EWOD) technology using aqueous-shell compound drops. We demonstrate that the transport and coalescence of viscous oil drops, the reaction of bromine with styrene in benzene solution, and the reaction of red blood cells with carbon monoxide bubbles can be accomplished using this method.

Schematics of EWOD for aqueous-shell compound drops

The oil-in-water compound drops were generated in a microfluidic device, the schematic of which is shown in Fig. 1(a). A cylindrical glass capillary with an inner diameter of 0.3 mm was tapered by a pipette puller (P-97, Sutter Instrument Company) and was then fed into another tapered capillary with an inner diameter of 0.7 mm and an outer diameter of 1 mm. The two tapered capillaries were then inserted into a square glass capillary with an inner size of 1.05 mm. Air was injected into the outermost capillary as the outer phase, while the water phase was injected into the middle capillary as the middle phase, and the oil or gas phase was injected into the innermost capillary as the inner phase. By adjusting the flow rate ratios of the three phases, oil-in-water or gas-in-water compound drops separated by air bubbles were generated, and the size of the oil/gas cores was controlled. The video of the generation of the compound drops is available as Videos S1 and S2 in the ESI†.

Manipulation and coalescence of the compound drops using EWOD were performed on a dielectric substrate fabricated based on a standard process of printed circuit board (PCB).† The copper layer was etched into electrodes with a designed pattern on the substrate using the PCB process and...
was then coated with a thin layer of polydimethylsiloxane (PDMS, SYLGARD® 184 Silicone Elastomer Kit, Dow Corning) using a spin coater, where the weight ratio of the base to the crosslinker is 10 : 1. After heating at 70 °C for 72 hours, a 10 μm thick PDMS layer was formed, and then it was further coated with a 100 nm layer of Teflon AF (DuPont Co.). The whole processing procedure of the EWOD substrate is shown in Fig. 1(b).

The electrodes formed a T-shaped rail for manipulating the aqueous-shell compound drops, as shown in Fig. 1(c).

Manipulation of viscous oil cores

The contact angles of an oil-in-water compound drop were measured under different voltages between 0 V and 500 V. The inner oil drop is liquid paraffin (Sinopharm Chemical Reagent Beijing Co.) with 0.1% ABIL® EM90 (Evonik Industries), which is dyed red, and the aqueous shell is 8% polyvinyl alcohol (PVA, Sigma-Aldrich) solution. We found that the contact angles of the compound drop decreased from 93° to 57° with the increase in the applied voltage from 0 V to 500 V, and the contact angle returned to 78° when the voltage was decreased to 0 V, as shown in Fig. 2(a1). The returned contact angle was smaller than its initial contact angle, which is attributed to the occurrence of trapping of charge in or on the insulating layer under such a high voltage. The oil core in the compound drop did not affect the contact angles of the aqueous shell under different voltages, because the oil core had a lower density, such that it floats in the aqueous shell without contacting the solid surface, as shown in Fig. 2(a2)–(a3). Thus, the aqueous shell can be used as the carrier to move viscous oil cores on the electrodes, as shown in Fig. 2(b1)–(b3), where the viscosities of the oil phase and the water phase are 29.0 mPa s and 16.6 mPa s, respectively. The oil cores moved with the compound drops and finally coalesced on the EWOD substrate under the controlled voltage pulses on the patterned electrodes.

In addition, oil cores with higher viscosity were also successfully manipulated by EWOD of the compound drops, for example, the oil core in the compound drop was silicone oil with a viscosity of 100 mPa s (Sigma-Aldrich), as shown in Video S5 in the ESI. The viscosity of the oil cores will not increase the friction force between the drop and the substrate of the EWOD board. In contrast, an individual oil drop and the water-in-oil compound drops were not moved by EWOD. The case of an oil drop of liquid paraffin, dyed in blue, had a viscosity of 29.0 mPa s, as shown in Video S6 in the ESI.
red, is shown in Fig. 2(c1)–(c2), and the case of a water-in-oil compound drop is shown in Fig. 2(d1)–(d2), where the inner drop is 8% PVA solution, dyed in blue, and the outer oil phase is silicone oil with a viscosity of 100 mPa s.

It should be noted that the core–shell structure of the compound drop may break when the applied voltage to the control electrodes is higher than a specific value. For example, the oil-in-water compound drop in Fig. 2(a) broke when the voltage was increased to 600 V, and the oil core flew out of the aqueous shell and became a thin layer coating outside the aqueous drop.

**Reaction of organic cores**

The bromination of an alkene\(^{16}\) is demonstrated here to show the application of EWOD to compound drops with organic cores. Two compound drops with different organic cores in the aqueous shells of 8% PVA solution were manipulated in the experiment. One has a yellow core of the solution of 0.2 M bromine in benzene, while the other has a grey core of the solution of 0.85 M styrene in benzene. The two compound drops were placed on each end of the T-shaped rail and then manipulated to collide. The aqueous shells fused first with the two individual cores inside, as shown in Fig. 3(a1)–(a3). To induce the coalescence of the two organic cores, the fused compound drop was moved to the four electrodes on the vertical rail, and then the voltage pulses were applied periodically to the two pairs of the diagonal electrodes to stretch and relax the compound drop in the orthogonal directions. The stretch-to-relax motion of the compound drop causes a compression-to-separation motion of the two organic cores, which helps the coalescence of the two cores.\(^{17,18}\) After the periodical stretches, the two cores inside the compound drop coalesced, as shown in Fig. 3(a4)–(a6). The colour of the coalesced core changed from yellow to clear, indicating the completion of the reaction. In addition, the two toxic organic cores and the products of the reaction were all encapsulated in the aqueous shells, which reduced the cross contamination between the products and the environment.

**Reaction of gas cores**

Gaseous chemicals in the cores of compound drops with aqueous shells can also be manipulated by EWOD and react with other chemicals. Here we demonstrate the reaction between red blood cells (RBCs) and carbon monoxide (CO) bubbles and then evaluate the CO poisoning of the RBCs using the sodium hydroxide (NaOH) test.\(^{19}\)

A drop of whole blood from a healthy adult was washed with phosphate buffered saline (PBS) and then centrifuged for the separation of RBCs.\(^{20}\) The resulting RBCs were diluted to 10% in physiological salt solution (PSS). For comparison, two drops of the diluted RBCs were driven to coalesce with a simple drop of 8% PVA aqueous solution (Fig. 4(a1)–(a2))
and a gas-in-water compound drop with a CO bubble in 8% PVA aqueous solution (Fig. 4(b1)–(b2)). The compound drop was generated using the same method presented in Fig. 1. The two coalesced drops were left on the substrate for 150 s before another drop of 1 M NaOH was added (Fig. 4(a3)–(a4) and (b3)–(b4)). Consequently, in the compound drop (Fig. 4(b4)), CO bound to haemoglobin (Hb) in the RBCs, instead of oxygen, and formed carboxyhemoglobin (COHb), which caused the CO poisoning of the RBCs.21

After the drop of normal RBCs was mixed with the drop of NaOH solution (Fig. 4(a5)–(a7)), the initial red color (Fig. 4(a4) and (c)) turned to straw color quickly (Fig. 4(a5)–(a7) and (d)). For example, the color change was obviously observed within 4 s (Fig. 4(a5)) and the color of the entire drop changed within 76 s (Fig. 4(a6)). In contrast, for the CO-poisoned RBCs, the compound drop maintained the red color with a slight color change at the edge within 76 s (Fig. 4(b6)) and the color change of the entire drop (Fig. 4(b8)) was observed 330 s later after the reaction with NaOH. The significantly delayed color change of the compound drop (Fig. 4(b5)–(b8)) due to the COHb-saturated RBCs19 indicated that the reaction of the RBCs and the CO gas was effectively realized by EWOD of the compound drop.

Conclusions

The oil, organic and gaseous chemicals in the aqueous shell can be manipulated by EWOD. This EWOD technology for aqueous-shell compound drops was demonstrated to realize the transportation of high viscous oil drops, the mixture of organic chemicals, and the reaction with bubbles, which are usually difficult to realize by the traditional EWOD. Thus, the EWOD can be used for more complex fluids besides water drops and it would be a helpful tool in droplet microfluidics. Additionally, the aqueous shell also provides protection preventing the reaction products that are confined in the drops from releasing into the surrounding environment.

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Notes and references