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# Ionic–surfactant–mediated electro–dewetting for digital microfluidics

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**The ability to manipulate droplets on a substrate using electric signals<sup>1</sup>—known as digital microfluidics—is used in optical<sup>2,3</sup>, biomedical<sup>4,5</sup>, thermal<sup>6</sup> and electronic<sup>7</sup> applications and has led to commercially available liquid lenses<sup>8</sup> and diagnostics kits<sup>9,10</sup>. Such electrical actuation is mainly achieved by electrowetting, with droplets attracted towards and spreading on a conductive substrate in response to an applied voltage. To ensure strong and practical actuation, the substrate is covered with a dielectric layer and a hydrophobic topcoat for electrowetting-on-dielectric (EWOD)<sup>11–13</sup>; this increases the actuation voltage (to about 100 volts) and can compromise reliability owing to dielectric breakdown<sup>14</sup>, electric charging<sup>15</sup> and biofouling<sup>16</sup>. Here we demonstrate droplet manipulation that uses electrical signals to induce the liquid to dewet, rather than wet, a hydrophilic conductive substrate without the need for added layers. In this electro-dewetting mechanism, which is phenomenologically opposite to electrowetting, the liquid–substrate interaction is not controlled directly by electric field but instead by field-induced attachment and detachment of ionic surfactants to the substrate. We show that this actuation mechanism can perform all the basic fluidic operations of digital microfluidics using water on doped silicon wafers in air, with only  $\pm 2.5$  volts of driving voltage, a few microamperes of current and about 0.015 times the critical micelle concentration of an ionic surfactant. The system can also handle common buffers and organic solvents, promising a simple and reliable microfluidic platform for a broad range of applications.**

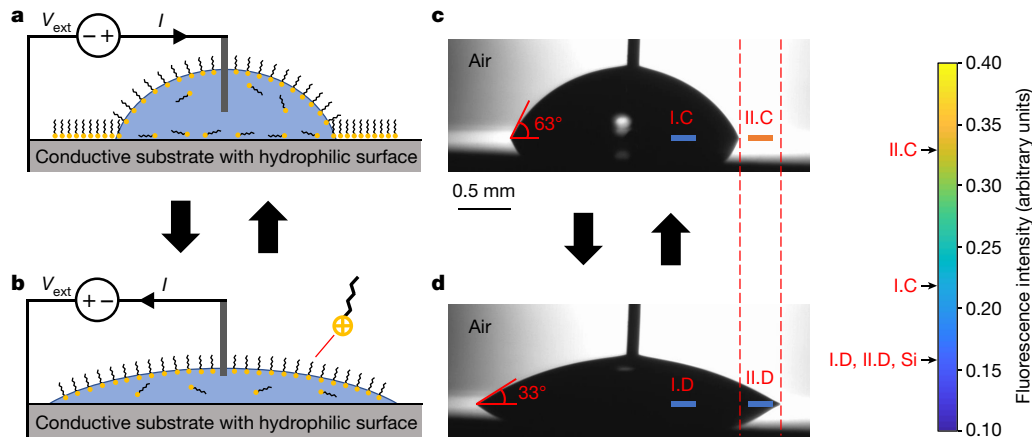
As a hydrophobic surface is desired for a liquid-attraction mechanism to work well, we recognize that a hydrophilic surface would be preferred for a liquid-repelling mechanism. Since most materials are hydrophilic, a dewetting actuation, if found to be effective, would enable digital microfluidics just as EWOD does, but without the requirement for the hydrophobic coating. Although most electrically induced dewetting phenomena are not effective for common microfluidics because they are based on irreversible processes<sup>17,18</sup> or special conditions<sup>19</sup>, studies involving surfactants have shown that reversibility may be possible. For example, electrically initiated dewetting of an aqueous film on derivatized gold electrodes has been demonstrated using redox-active surfactants<sup>20</sup>. Recently, by using ionic surfactants, the coefficient of a lubricated friction has been switched in a solid–liquid–solid configuration<sup>21</sup>, and boiling bubble nucleation has been modulated in a liquid–vapour–solid system<sup>22</sup>. Furthermore, an organic droplet has been moved on a conjugated polymer electrode in an aqueous electrolyte<sup>23</sup>. However, these methods have not led to a microfluidic platform technology, which would require an electric actuation that is reversible, repeatable, strong and easily applicable to a liquid–fluid–solid system<sup>24</sup>. In fact, we could not obtain effective actuations with aqueous droplets containing ionic surfactants on either bare metal electrodes<sup>21,22</sup> or on dielectric-coated electrodes. Instead, we have discovered that a bare silicon wafer works effectively, because its native oxide is hydrophilic enough to allow easy dewetting yet thin enough

(around 2 nm) not to insulate the conductive substrate. Requiring neither the added dielectric layer nor the hydrophobic topcoat, this system may avoid the reliability problems of EWOD, while benefiting from device simplification and cost reduction.

To study the underlying principle and basic characteristics of the proposed electro-dewetting mechanism, we adopted the test configuration that is usually used for electrowetting studies, as shown in Fig. 1. An elaborate setup was developed for accurate experimentation, as detailed in the Methods and Extended Data Fig. 1. The droplet contains an ionic surfactant, which consists of a charged hydrophilic ‘head’ group and a neutral hydrophobic ‘tail’ region, and is placed on an electrically conductive substrate, whose surface is highly hydrophilic. When direct-current (d.c.) voltage (or current) is applied, current flows through the conductive (or resistive) liquid and an electric field is established inside the droplet. A circuit analogy is given in the Methods and Extended Data Fig. 2. The ionic surfactant molecules migrate towards or away from the substrate under the electric field, making the drop dewet (Fig. 1a) or rewet (Fig. 1b) the surface, respectively. An exemplary result shown in Fig. 1c, d used a water droplet (pH  $\approx$  7) containing dodecyltrimethylammonium bromide (DTAB) on a highly doped silicon wafer, chosen for its smooth surface and native oxide. The proposed mechanism has been corroborated by three different experiments detailed in the Methods and Extended Data Fig. 3, including visualization with a fluorescent surfactant. The fluorescence intensity on two surface regions—region I (always inside droplet) and region II (outside droplet during electro-dewetting but inside during wetting)—are overlaid on Fig. 1c, d. The fluorescence level is slightly higher on I.C than on I.D, supporting the illustration of Fig. 1a, b for region I. For region II, the fluorescence level on II.C is much higher than II.D, confirming that the retraction of the liquid–solid contact line by electro-dewetting leaves a large amount of surfactant on the substrate immediately outside the droplet. Furthermore, the fluorescence level on II.D is as low as those on I.D and the fresh surface well outside the droplet (noted as Si), supporting the reversibility by which the adsorbed surfactant molecules are desorbed from the surface back to the droplet as the contact line advances during wetting.

All the characterization experiments were performed as described in the Methods, using aqueous droplets of three cationic surfactants and one anionic surfactant: DTAB, tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS), respectively. Observation of the ionic-surfactant-mediated dewetting may be complicated by the ‘autophobic’ effect<sup>25,26</sup> caused by the surface charges. To obtain the electro-dewetting effect in isolation, that is, at the isoelectric point with a negligible electric double layer and thus little autophobic effect, we used pH  $\approx$  2.3 (see the Methods and Supplementary Video 1) for all the characterization tests of Fig. 2, which shows only the average values for visual clarity. The complete data with error bars are presented in Extended Data Fig. 4. For surfactant concentration, Fig. 2a revealed that the four surfactants all follow a similar trend, exhibiting

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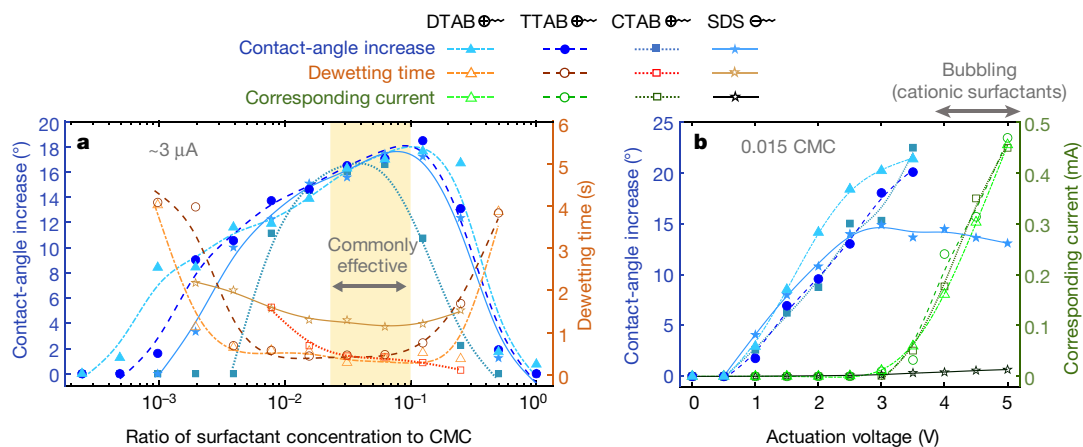
**Fig. 1 | The proposed ionic-surfactant-mediated electrode wetting mechanism, studied with a sessile drop on a conductive, hydrophilic substrate.** **a**, An electric field inside a droplet, formed by external voltage  $V_{\text{ext}}$  and current  $I$ , electrophoretically drives the ionic surfactant molecules (a cationic surfactant is shown) towards the hydrophilic substrate and deposits them on its surface (mostly near the contact line), rendering the surface hydrophobic and making the droplet dewet (that is, bead up on) the substrate. **b**, A reverse electric field formed inside a droplet removes the deposited ionic surfactant molecules from the surface and

electrophoretically drives them away from the substrate, returning the surface to its hydrophilic state and making the droplet rewet (that is, spread on) the substrate. **c, d**, Electrode wetting experiment corresponding to panels **a** and **b**, respectively, with a DTAB-containing aqueous droplet (about  $3\ \mu\text{l}$ ) on bare silicon (with native oxide) using a voltage of  $\pm 3\ \text{V}$  with a current of  $\pm 3\ \mu\text{A}$ . The surfactant concentrations on two different regions (I, II) of the substrate surface, obtained in a separate test using a fluorescent cationic surfactant, corroborate the proposed mechanism.

effective dewetting (that is, large change in contact angle and short dewetting time) in the same concentration range if the concentration is expressed with respect to critical micelle concentration (CMC). We hypothesize that when the surfactant concentration is too low, there are too few molecules to affect the surface wettability appreciably, whereas when it is too high, the contact angle is already large before actuation, leaving little room for further increase. In terms of actuation speed, Fig. 2a shows that the dewetting time was around 0.5 s, which is slower than EWOD (for example, 0.02 s)<sup>27</sup>. Probably this can be explained by the time needed for migration and assembly of surfactant molecules during the surfactant-mediated electrode wetting compared with the near-instantaneous polarization of the dielectric layer for EWOD. For electrical actuation, Fig. 2b shows the increase in contact angle and the corresponding current as functions of the actuation voltage for the four surfactants. The current for SDS is noticeably smaller than those for the cationic surfactants because its actuation polarity anodizes (passivates) the silicon surface. The trends found in Fig. 2 allowed us to assess other

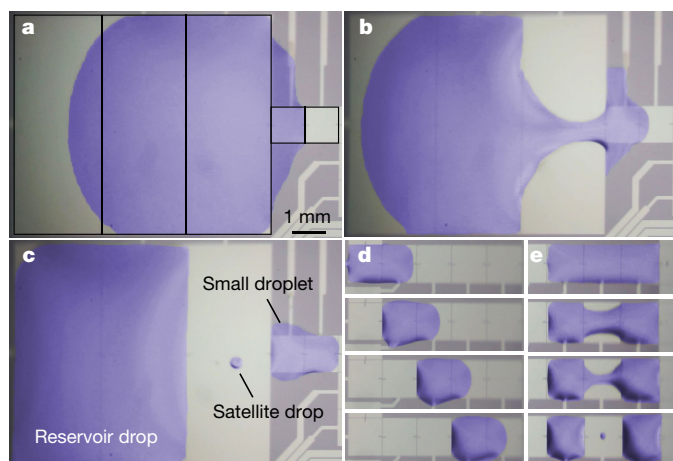
surfactants without full characterization. A variety of (13 in total) ionic surfactants have been tested, and all of them were found to facilitate the electrode wetting, as summarized in the Methods.

With the basic characteristics of the proposed electrode wetting established, we next examine its robustness and longevity—the two most critical reliability problems of EWOD. First, the robustness is evaluated by performing electrode wetting with excessive voltages and currents. For cationic surfactants, at around 4 V and around 0.2 mA (that is, approximately 100 times above the usual  $3\ \mu\text{A}$  or so; see Fig. 2b), bubbles began to appear inside the droplet on both the wire and the substrate, indicating that substantial electrolysis of water was occurring. However, dewetting and rewetting continued to repeat effectively while, and even after, bubbles were generated violently at about 10 V with a runaway current above 3 mA (beyond Fig. 2b), as shown in Supplementary Video 2. This strong resilience is in contrast to EWOD, for which even slight electrolysis by leakage current would lead to a device failure.



**Fig. 2 | Effect of surfactant concentration and actuation voltage on the electrode wetting.** **a**, Experiments using cationic (DTAB, TTAB, CTAB) and anionic (SDS) surfactants showed effective responses in a common range (yellow band) of concentration to CMC. The increase in contact angle was the increase from the unactuated (wetted) to the actuated (dewetted) state, where 2.5–3.0 V (corresponding to about  $3\ \mu\text{A}$ ) was applied between the wire and substrate. The dewetting time was the time

it took for the wetted state to reach the dewetted state upon actuation. **b**, Tests with the four surfactants at 0.015 CMC showed that the increase in contact angle grew with applied voltage until it reached about 3 V. For cationic surfactants, the electrolytic bubbling rendered the contact angle unmeasurable above 3.5 V. In the usual actuation range ( $< 3.0\ \text{V}$ ), the current remains below a few microamperes for all cases.

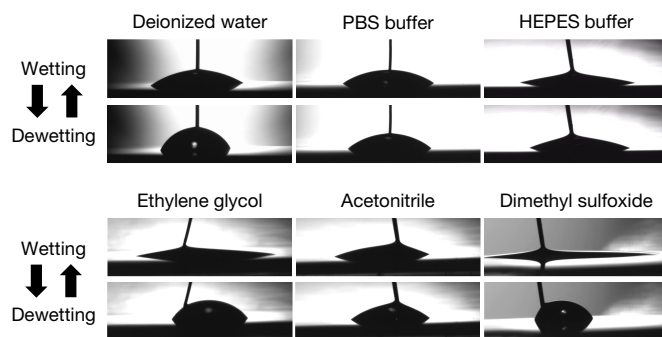


**Fig. 3 | Droplet generation, transportation and splitting realized by the proposed electrode wetting.** Water droplets are operated in air on a silicon device with no cover plate, using  $\pm 2.5$  V (or 0 V and 5 V). Images were captured from Supplementary Video 4 and enhanced by colouring the liquid portions. **a–c**, Sequential images of a small (about  $0.2 \mu\text{l}$ ) droplet generated from a reservoir droplet (about  $3 \mu\text{l}$ ). **a**, The black lines were added to indicate the large electrodes underneath the reservoir. **b**, Dewetting the third reservoir electrode from left results in necking of the reservoir droplet. **c**, A droplet is generated on the two small electrodes to the right of the reservoir. **d, e**, Sets of four sequential images showing droplet transportation (**d**) and splitting (**e**). Along with droplet generation (panels **a** to **c**) and merging (not shown), they establish the basic operations of digital microfluidics.

Second, the longevity is evaluated by testing how long the electrode wetting actuation can proceed without degradation (for example, a decrease in the change of contact angle). By minimizing droplet evaporation (Extended Data Fig. 5), electrode wetting could be switched for over  $10^4$  cycles, that is, the continuous 6 h that the droplet lasted without noticeable evaporation, with no hint of deterioration, as shown in Supplementary Video 3. In comparison, dielectric charging would degrade the performance of an EWOD device after just a few hundred cycles in air. Free from the reliability problems of EWOD, the surfactant-mediated electrode wetting has thus been shown to be extremely robust and highly durable.

To assess the potential for a platform technology, we have developed a digital microfluidic device, as detailed in the Methods and Extended Data Fig. 6. Using an aqueous solution with DTAB at 0.015 CMC, we have achieved droplet generation, transportation, splitting and merging, as shown in Fig. 3 and Supplementary Video 4. Building blocks for more complex microfluidic protocols for applications<sup>1</sup>, these key digital microfluidic operations were successfully obtained in air on an open device, that is, without the help of the frequently used filler oil and without using a cover plate. Interestingly, the droplets were transported (Fig. 3d) at a speed comparable to that in EWOD (see Supplementary Video 4) even though the observed actuation was 10–100 times slower during sessile drop tests (Fig. 2a). Although pH 2.3 was used for the demonstrations of Fig. 3 to be consistent with the characterization of Fig. 2, other pH levels can also be used. These results suggest that the proposed electrode wetting method is comparable to EWOD in performance while being inherently superior in reliability.

We now discuss the requirements of surfactant and electric current. Surfactant is rarely a concern for physical (for example, optical) applications, and the very low concentration used here (about 0.015 CMC) is acceptable even for many biochemical assays. This level is lower than the level usually found as a contaminant in environmental water (about 0.05 CMC)<sup>28</sup> and much lower than the level usually used in EWOD during biochemical assays, to combat fouling, for example ( $>1$  CMC)<sup>29</sup>. However, ionic surfactants, especially cationic surfactants, may pose a problem to cell viability and would require additional investigation. Regarding electric current, a few microamperes per droplet is negligibly



**Fig. 4 | The proposed electrode wetting confirmed for a variety of liquids on bare silicon.** Deionized water (Fig. 1) is included as a reference. DTAB was used for all, with different concentrations as described in the Methods. For PBS and HEPES, contact-angle changes of approximately  $9^\circ$  and  $6^\circ$  were obtained, respectively, using  $\pm 5$  V. For ethylene glycol, acetonitrile and DMSO, changes of approximately  $40^\circ$ ,  $15^\circ$  and  $60^\circ$  were obtained, respectively, using  $\pm 3$  V.

small for nearly all applications. Even for life science applications, this level is much smaller than that used to monitor cell culture<sup>30</sup>, and the associated power dissipation would be small enough for most biochemical assays.

Finally, we have explored the validity of the proposed electrode wetting for a variety of liquids: two buffer solutions widely used in biology (phosphate-buffered saline (PBS) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES)); two common organic solvents used in chemistry (acetonitrile and dimethyl sulfoxide (DMSO)); and a common coolant (ethylene glycol). Although the degree of effectiveness varied, as shown in Fig. 4, the electrode wetting was found to be effective for all the liquids tested. We studied the working liquids only under the conditions in which they are typically used, in order to assess their utility, leaving more complete characterizations for future studies. The successful results with these five additional liquids suggest that the proposed electrode wetting mechanism has practical utility and versatility, opening the door for broad application.

### Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-019-1491-x>.

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