# **Supplementary Information**

## **Electrocoalescence of Liquid Marbles driven by Embedded**

# **Electrodes for Triggered Bio-reactions**

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#### The supporting information contains the following parts:

Calculation of the local electric field strength between two contacted liquid marbles.

Figure S1. Time sequence of liquid marbles coated with 6 μm silicone resin particles coalesced by direct charging of the immersed electrodes.

Figure S2. The curve of height over volume showing the similarity in effective surface tension of liquid marbles coated with nano-/microparticles used in this project.

Figure S3. Coalesced morphologies of multiple liquid marbles.

Figure S4. Optical image of a liquid marble coated with 75 µm lycopodium powder.

Figure S5. Circuit model of the liquid marble where the double-layer capacitance is taken into account.

Figure S6. SEM of the spheroid formed in liquid marbles after culture of 5 days.

Table S1. Effect of ramp rate on the critical voltage.

Table S2. Liquid marbles coated with different sized particles that can be coalesced by the non-contact electrostaticsdriven approach.

TableS3. Effective surface tension ( $\gamma_{eff}$ ) of liquid marbles formed in Figure S2 is calculated.

### Other Supplementary Material for this manuscript includes:

Video S1. Coalescence of R812 silica nanoparticle-coated liquid marbles triggered by electrostatics. Excess nanoparticles were injected from the interface.

Video S2. Coalescence of 6  $\mu$ m silicone resin microparticle-coated liquid marbles triggered by electrostatics. Particle jammed at the neck region where liquid bridge formed.

### Calculation of the local electric field strength between two contacted liquid marbles

To calculate the local electric field strength  $E_{loc}$ , we reconstruct the schematic of the platform by treating the air gap between the particle shell and the dielectric layer as a capacitor. We hypothesize there would be no electrical potential drop across the encapsulated droplet, and set the electrical potential at two droplet phases as  $U_1$  and  $U_2$ .  $E_{loc}$  is defined as the voltage difference between two bulk droplets across an air gap with a fixed distance around the particle diameter d.

$$E_{loc} = \frac{U_1 - U_2}{d} \#(1)$$

As the whole setup is symmetrical at the extension line of the point where two liquid marbles contact, which means in this system the sum of electrical potential at one half of the setup and of its conjugate point in the other half is equal to  $U_c$ . Therefore, we have  $U_1 + U_2 = U_c$ , and

$$E_{loc} = \frac{U_1 - U_2}{d} = \frac{2U_1 - U_c}{d} \#(2)$$

 $U_1$  can be resolved by simplifying the schematics into a circuit model (shown in Figure S4), where the dielectric layer and particle shells are treated as capacitors. Without loss of singularity, we assume  $U_1$  is higher than  $U_2$ , and the voltage at the extension line

of the point where two liquid marbles contact is  $\frac{U_c}{2}$ . By only considering the right part of this circuit model, we have

$$U_1 = U_1' + \frac{U_c}{2} \#(3)$$

 $U_1$  can be represented by simple voltage division applied to the total capacitance of the PDMS dielectric layer and the particle

shell contact to it which is  $\sim \frac{A\varepsilon_0\varepsilon_{air}\varepsilon_{PDMS}}{h\varepsilon_{air} + a\varepsilon_{PDMS}}$ , and we have  $U_1$ 

$$U_{1} = \frac{U_{c}}{2} \frac{\varepsilon_{PDMS}}{(1+\alpha)\varepsilon_{PDMS} + \frac{2\alpha h}{d}\varepsilon_{air}} \#(4)$$

where  $\alpha$  is defined as the ratio of contacting area of two liquid marbles over the contacting area between the liquid marble with the PDMS dielectric layer. Therefore

$$U_1 = \frac{U_c}{2} \left[ 1 + \frac{1}{(1+\alpha) + \frac{2\alpha h}{d} (\frac{\varepsilon_{air}}{\varepsilon_{PDMS}})} \right] \#(5)$$

We now get

$$U \sim 2 \sqrt{\frac{\gamma a}{\varepsilon_0 \varepsilon_r}} \left[ (1+\alpha) + \frac{2\alpha h}{d} \left( \frac{\varepsilon_r}{\varepsilon_{PDMS}} \right) \right] \#(6)$$

 $U_{theory}$  in Figure 4f in the manuscript is derived from Eq. (6), and is represented as a theoretical line.

Referring to eqn. (2) we could derive

$$E_{loc} = \frac{2U_1 - U_c}{d} = \frac{U_c}{dC_{PDMS}C_{P1} + C_{PDMS}C_{P2} + C_{P1}C_{P2}}{C_{PDMS}C_{P1} + C_{PDMS}C_{P2} + C_{P1}C_{P2}}$$
$$= \frac{U_c}{d}\beta, \qquad \beta = \frac{C_{PDMS}}{C_{PDMS} + C_{PDMS}C_{P2}} \#(7)$$

where	β	is	а	capacitive	voltage	dividing	parameter.
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**Figure S1.** Time sequence of (a) two liquid marbles coated with 6  $\mu$ m silicone resin particles coalescing by electrically charging electrodes immersed in them. Electrolysis happens once liquid marbles are coalesced, followed by bubble formation around the electrodes. Time sequence of (b) two liquid marbles coated with silica nanoparticles coalescing by charging embedded electrodes. Coalesced liquid marbles are left at critical voltage for 120s and no electrolysis is observed. Scale bars = 2 mm.

	1	2	3	4	5	6	7	8	9	10
20 Vs-1	520	470	310	440	580	460	230	420	460	460
40 Vs <sup>-1</sup>	440	450	460	440	340	270	400	330	430	440

**Table S1.** Effect of ramp rate on the critical voltage. Ramp rates of 20 V s<sup>-1</sup> and 40 Vs<sup>-1</sup> were tested for comparison. Each pairs of marbles were repeated for 10 times. The average critical voltage  $U_c$  for the ramp rates of 20 Vs<sup>-1</sup> and 40 Vs<sup>-1</sup> are 435±99.58 V and 400±64.29 V respectively. Hence, the difference is not statistically significant within this range of values.

Particle type	Material	Diameter	Air-water contact angle (θ)
Nai	noparticles		
R812	Silica	Primary: 7 nm	118° <sup>1</sup>
R972	Silica	Primary: 16 nm	105° <sup>2</sup>
R974	Silica	Primary: 12 nm	117° <sup>1</sup>
Micropa	urticles/Powder		
430935	Poly(tetrafluoroethylene)	1 μm	110° <sup>3</sup>
FG012	Fluorinated graphene	Lateral size: 0.1-5 μm Particulate thickness: < 5 nm	130° - 150° *
XF079	Fluorinated graphite	Lateral size: 0.5-10 μm Particulate thickness: < 10 nm	140° *
Tospearl 120	Silicone resin	2 µm	91° <sup>4</sup>
Tospearl 145	Silicone resin	4.5 μm	91° <sup>4</sup>
Tospearl 2000B*	Silicone resin	6 µm	91° <sup>4</sup>
Tospearl 3120	Silicone resin	8-16 µm (average 12µm)	91° <sup>4</sup>
NMBK 050	Silicone	5 µm	120° *
468096	Poly(tetrafluoroethylene)	35 µm	110° <sup>3</sup>

 Table S2. Liquid marbles coated with different sized particles that can be coalesced by the non-contact electrostatics-driven approach.

 $^{\ast}$  Contact angle is provided by the manufacturer.



**Figure S2.** (left) A typical liquid marble coated with 6  $\mu$ m silicone resin particles. (right) The curve of height against volume. Diamonds - liquid marbles coated with R812 silica nanoparticles, circles - liquid marbles coated with 6  $\mu$ m silicone resin particles. The similarity in effective surface tension ( $\gamma_{eff}$ ) could be proved by the good overlap of the two curves (the inset photos demonstrate the morphology transition of liquid marble from spherical to puddle). The effective surface tension ( $\gamma_{eff}$ ) can also be estimated by the puddle height method in the literature and the value is shown in Table S2.<sup>5</sup>

Particle type	Effective surface tension, $\gamma_{eff}$ (mN/m)			
R812 silica nanoparticles	63.60			
6 μm silicone resin particles	66.01			

**Table S3.** Effective surface tension ( $\gamma_{eff}$ ) of liquid marbles coated with two different particle types.



**Figure S3.** Coalesced morphologies of multiple liquid marbles coated with (a) R812 silica nanoparticles and (b) 6 µm silicone resin particles. Upper row – before coalescence, lower row – after coalescence. The morphology of the liquid marble after coalescence for 6 µm silicone resin-coated liquid marbles becomes more irregular as the number of marbles increases.



Figure S4. An optical image of a liquid marble coated with 75 µm lycopodium powder. The defects pointed by yellow arrows are at the same scale as the particle diameter.



**Figure S5.** (a) Schematic of the two liquid marble coalescence system when encapsulated droplets are highly electrically conductive. As the system is symmetrical, the electrical potential at the contact interface of two liquid marbles is considered to be half of the critical voltage Uc, and the effect of the electrical double layer can be reflected by only considering half of the system. (b) Corresponding circuit model of the liquid marble where electropotential  $U_1$  across the droplets and double-layer capacitance is considered.  $C_{P1}$  is equivalent to the capacitance of the particle shell  $C_{P1}$  in series

with the electric double-layer capacitance  $C_{EDL}$ .



FigureS6. A cell spheroid formed inside a liquid marble micro-reactor after five days of culturing. The cell spheroid has a size of 40  $\mu$ m \* 100  $\mu$ m.

### References

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