Supplementary Information

Fabrication of pH-Responsive Monodisperse Microcapsules Using Interfacial Tension of Immiscible Phases

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I. Conversion of Single Emulsion Templates to Microcapsules

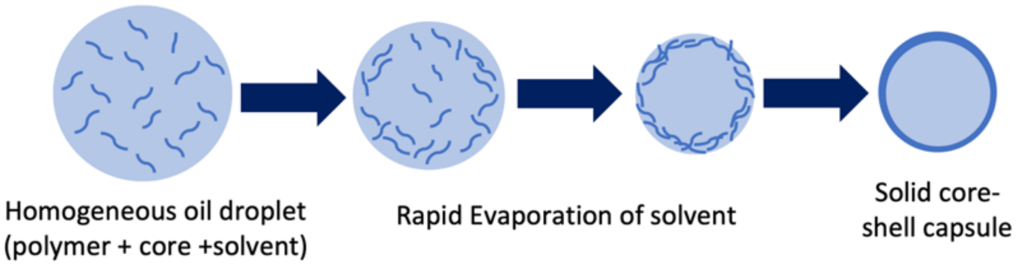


Figure S1. Schematic illustrating the formation of single-emulsion templated microcapsule.

II. Conversion of Double Emulsion Templates to Microcapsules

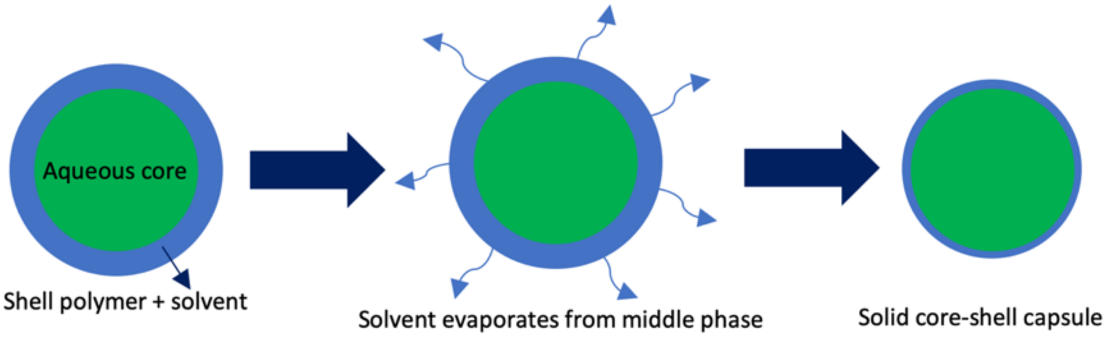
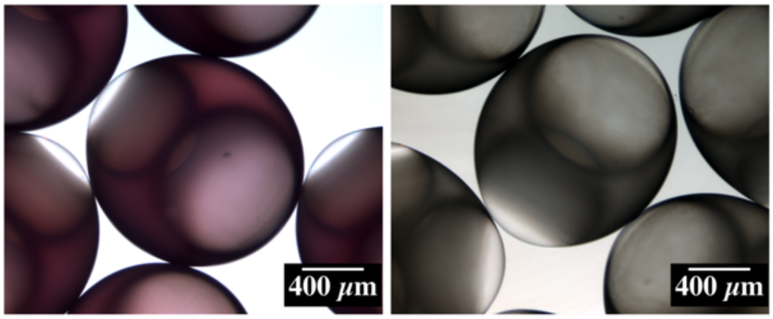


Figure S2. Schematic illustrating the formation of double-emulsion templated microcapsules

III. Eliminating the Role of Reciprocation Forces in Interfacial Emulsification



$Q_i = 1575\ \mu L\ h^{-1}$
$Q_o = 1575\ \mu L\ h^{-1}$

$Q_i = 1650\ \mu L\ h^{-1}$
$Q_o = 2400\ \mu L\ h^{-1}$

Figure S3. Confirmation of reciprocation forces playing no role in emulsification. Double emulsions generated by reciprocating at 7 Hz within the bulk of the continuous phase instead of the interface at two combinations of inner and outer flow rates.

In our proposed technique, generation of monodisperse droplets relies on the separation of the dispersed phase from the nozzle tip at the air-water interface upon the removal of nozzle from the continuous aqueous phase. The interfacial tension present at the air-continuous phase interface plays a key role on the separation of droplets with every cycle of reciprocation. However, at the lowest and highest positions of the reciprocation, a jerking force (referred to as reciprocation force) is applied on the droplet due to the sudden change in the direction of motion. This force may result in premature droplet separation at the lowest point of reciprocation if the reciprocation force and the weight of the droplet are higher than the attachment force exerted by the nozzle tip.

For elucidating the role of interfacial tension, we fixed the reciprocating nozzle in the aqueous phase without crossing the interface, while injecting the dispersed phases at a constant rate. In this case, the forces acting on the droplet remain the same, except we eliminate the interfacial tension of the air-continuous phase interface. Double emulsion templates were formed using the coaxial capillary nozzle by reciprocation at 7 Hz (Q_i/Q_o = 1575/1575 μL h^{-1} and Q_i/Q_o = 1650/2400 μL h^{-1}) within the bulk of the continuous phase without crossing the interface. The chemical composition of the emulsion phases and the flow rate combinations employed here remained the same as used for size tuning of double emulsion templates in the paper. The emulsions formed were optically imaged and are shown in Figure S2. The emulsions have a significantly higher size compared to emulsions achieved while reciprocating across the interface (Figure 5). This indicates that the reciprocation forces were not high enough to detach the droplet in one cycle and required multiple cycles to achieve a high enough weight to aid the reciprocation force in detachment. Additionally, all of the emulsions formed have multiple cores instead of a single inner core. It is important to note that these limits are true only for the experimental system used in the present work and would thus vary if any of the dispensing nozzle tip or the properties of the dispersed phase are changed.

IV. Formation and Size Estimation of Thin Shell-walled Double Emulsions

Figure S4a demonstrates an example of thin shell walled double emulsion formed at an outer flowrate of 30 μL h^{-1}, inner flowrate of 420 μL h^{-1} and frequency of 1 Hz. The measured outer diameter is 610 μm ± 8 μm (COV =1.3%, n = 50) which is in good agreement with the theoretically predicted diameter of 620 μm according to Equation 2. However, as it is evident from Figure S2a, the shell wall is too thin to optically determine the inner diameter. Thus, the double emulsions were manually ruptured to invert them to single emulsions composing of only the middle phase as shown in Figure S4b. The measured size of single emulsions is 246.3 ± 5 μm (COV = 2%, n = 50). Subtracting the volume of the resulting single emulsion from the total volume of the double emulsion as estimated by the outer diameter yields an inner diameter of 595 μm which is in good agreement with the theoretically predicted diameter of 606 μm. A representative fluorescence microscopic image of the produced double emulsions shown in Figure S4c also confirms the formation of double emulsions since only the middle phase is dyed with Nile Red and the dye is insoluble in the water (inner) phase.

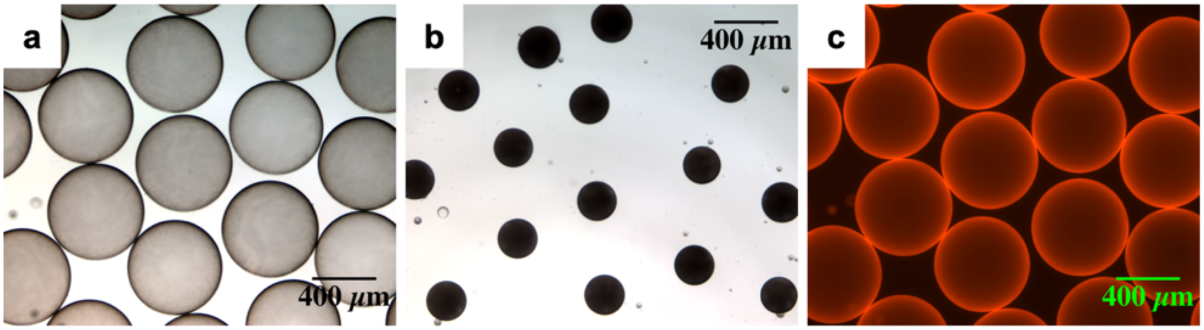


Figure S4. Size estimation of thin shell wall double emulsion. The double emulsions shown in (a) are ruptured manually to yield (b) single emulsions of only the middle phase. (c) Fluorescence microscopic images confirms the formation of double emulsions as only the middle phase is dyed.

V. Generation of Smaller Sized Emulsions

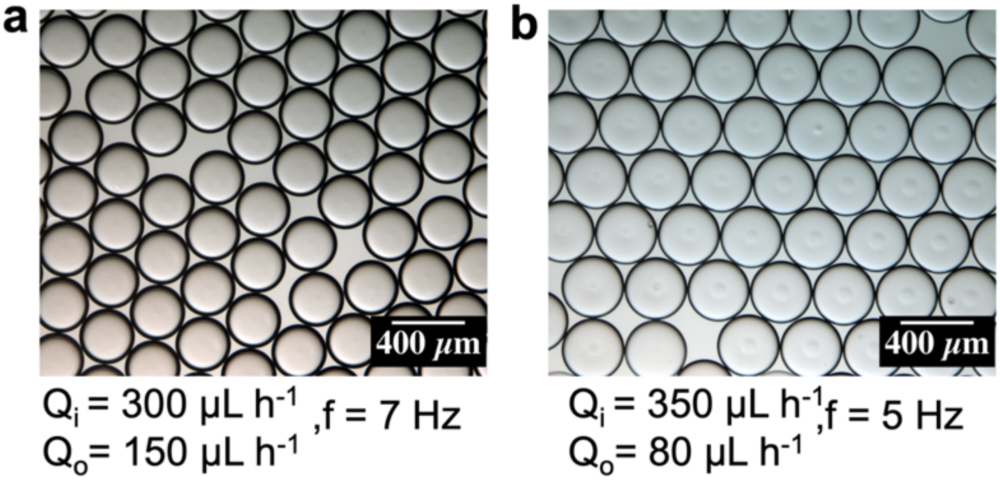


Figure S5. (a) Representative optical image of monodisperse double emulsions generated using the smaller sized coaxial capillary nozzle. (b) An example of double emulsions with thin middle layer of the order of tens of micrometers formed using the smaller coaxial nozzle with a middle phase of photocurable acrylate (NOA 89) and inner phase of 5wt% PVA in DI water.

The minimum diameter of double emulsions achieved using this technique are primarily limited by the dimensions of the coaxial nozzle. It is not theoretically possible to achieve emulsions smaller than the inner diameter of the capillaries in the nozzle. Further reduction in size requires a nozzle with smaller capillaries. In order to illustrate this, a smaller delivery device was fabricated having the following components:

- Outer capillary with OD of 400 μm and ID of 300 μm
- A square capillary of length 200 μm and thickness 50 μm and
- Inner capillary with OD 80 μm and ID of 50 μm.

The fabrication procedure is the same as reported in the paper. Two instances of double emulsions that were generated using the smaller nozzle are shown in Figure S5 along with their respective experimental conditions. The dimensions of the double emulsions are tabulated in Table S1. The inner diameter of the emulsions generated at 5 Hz were estimated using the procedure outlined in Section I of the Supplementary Information.

Table S1. Dimensions of double emulsions generated using the smaller coaxial capillary nozzle.

Q_i (μL h^{-1})	Q_o (μL h^{-1})	*f* (Hz)	Experimental		Theoretical	
			D_i (μm)	D_o (μm)	D_i (μm)	D_o (μm)
300	150	7	273 (COV=0.7%)*	312 (COV=0.9%)*	283	324
350	80	5	325 (COV=1.2%)*	348 (COV=0.9%)*	333	356

**n = 50*

VI. Generation of Thin Shell-walled Double Emulsion Templated Microcapsules

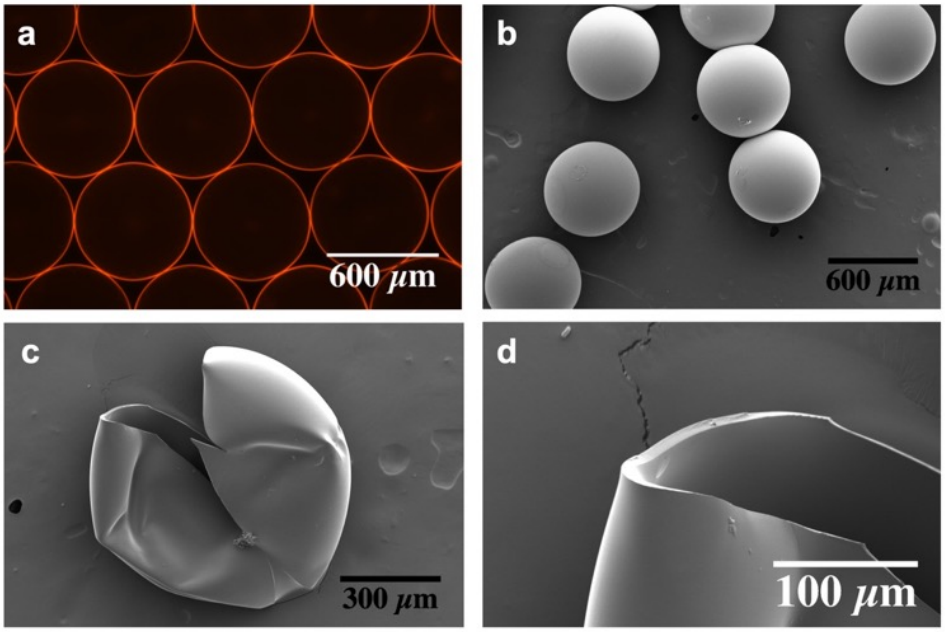


Figure S6. Formation of thin shell-walled photocured double emulsion-templated microcapsules. (a) Double emulsion templates formed at f = 1 Hz, Q_i = 450 μL h^{-1}, Q_o = 40 μL h^{-1}. Scanning electron micrographs showing the (b) size distribution (size of 630 μm, COV = 1.5%, n = 30) and (c, d) core-shell microstructure of the photocured polyisocyanurate microcapsules with 5wt% PVA in DI water as the core.

Double emulsion templates with a thin middle layer (order of micrometers) were formed at inner flow-rate of 450 µL h^{-1}, outer flow-rate of 40 µL h^{-1} and reciprocation frequency of 1 Hz as shown in Figure S6a. NOA 61 (diluted with acetone, 85:15 w/w) served as the inner phase and 5wt% PVA aqueous solution mixed with glycerol (40:60 w/w) served as the middle phase. The templates possessed an inner diameter of 625 µm (COV = 0.7%, n = 50) and outer diameter of 642 µm (COV = 0.8%, n = 50) which are in good agreement with the theoretically predicted inner diameter of 620 µm and outer diameter of 638 µm, respectively. The templates were photocured according to the procedure outlined in the paper to form microcapsules shown in Figure S6b and its core-shell structure is confirmed in Figure S6c and S6d. The microcapsules formed were of size 630 µm (COV = 1.5%, n = 30) which is in good agreement with the theoretically predicted size of 634 µm.

VII. Generation of Smaller Sized Double Emulsion Templated Microcapsules

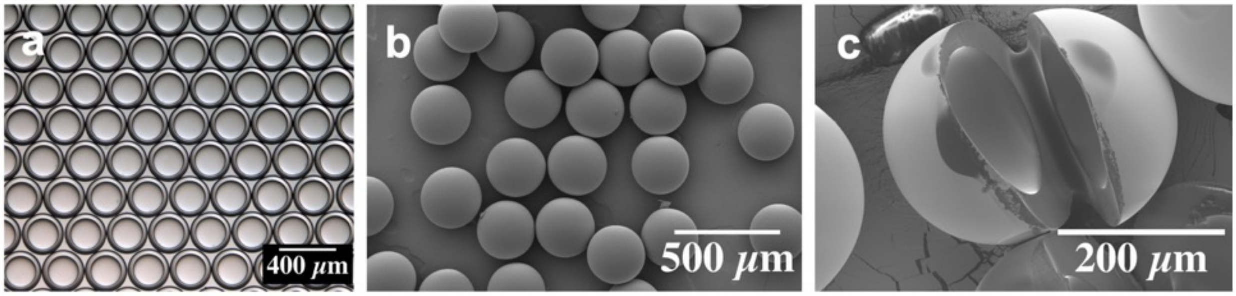


Figure S7. Formation of double emulsion-templated microcapsules using a smaller sized coaxial capillary nozzle. (a) Optical images of double emulsion templates (f = 3 Hz, Q_i = 60 µL h^{-1}, Q_o = 90 µL h^{-1}) that were subsequently converted to photocured polyisocyanurate microcapsules. Scanning electron micrographs showing the (b) size distribution (Size of 284 µm, COV = 1.8%, n = 50) and (c) core-shell microstructure of the microcapsules.

Double Emulsion-templated microcapsules were fabricated using a smaller sized coaxial capillary nozzle. The small coaxial nozzle was fabricated using the procedure outlined in Section S-III. Double emulsion templates shown in Figure S7a were formed at an inner flow-rate of 60 µL h^{-1}, outer flow-rate of 90 µL h^{-1} and frequency of 3 Hz. NOA 61 (diluted with acetone, 85:15 w/w) served as the inner phase and 5wt% PVA aqueous solution mixed with glycerol (40:60 w/w) served as the middle phase. The templates possessed an inner diameter of 224 µm (COV = 0.6%, n = 50) and outer diameter of 295 µm (COV = 0.9%, n = 50) which are in good agreement with the theoretically predicted inner diameter of 220 µm and outer diameter of 298 µm, respectively. Figure S7b shows the microcapsules formed by photocuring the above double emulsion templates according to the procedure outlined in the paper. The core-shell structure of the microcapsules was confirmed using scanning electron microscopy as shown in Figure S7c. The microcapsules possessed a diameter of 284 µm (COV = 1.8%, n = 50) and was in good agreement with the theoretically expected diameter of 283 µm.

VIII. Generation of cPPA Double Emulsion Templates

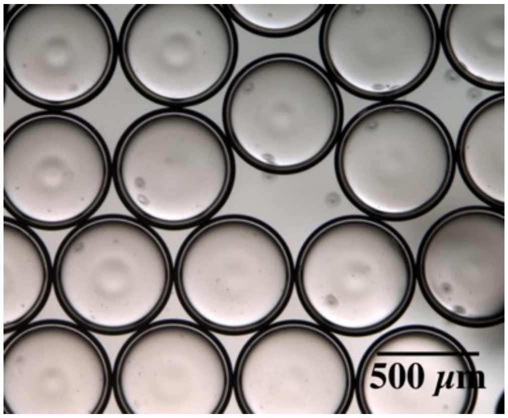


Figure S8. A representative optical image of cPPA double emulsion templates (f = 1 Hz, Q_i = 300 µL h^{-1}, Q_o = 150 µL h^{-1}) used to form acid-responsive cPPA microcapsules by solvent evaporation.

cPPA double emulsion templates shown in Figure S8 were formed at an inner flow-rate of 300 µL h^{-1}, outer flow-rate of 150 µL h^{-1} and frequency of 1 Hz. The templates possessed an inner diameter of 540 µm (COV = 0.9%, n = 50) and outer diameter of 622 µm (COV = 0.9%, n = 50) which are in good agreement with the theoretically predicted inner diameter of 542 µm and outer diameter of 620 µm, respectively.

IX. Double Emulsion Templated Polylactide Microcapsules

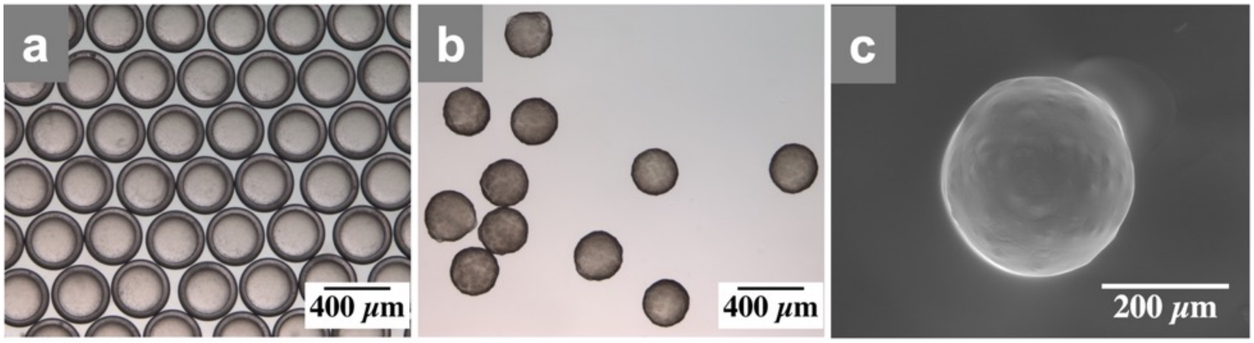


Figure S9. Formation of double emulsion templated polylactide microcapsules. (a) Optical images of double emulsion templates (f = 3 Hz, Q_i = 300 μL h^{-1}, Q_o = 150 μL h^{-1}) that were subsequently converted to (b) polylactide microcapsules with an aqueous core using solvent evaporation (Size of 320 μm, COV = 1.2%, n = 50). (c) Scanning electron micrograph showing the surface morphology of the polylactide microcapsule.

Double emulsion templates (Figure S9a) were formed with an inner phase of 5wt% PVA in DI water and a middle phase of 10wt % polylactide (Ingeo 4043D, M_n = 100,000 g mol^{-1}, Natureworks LLC) in dichloroethane. The templates were formed using the smaller sized coaxial capillary nozzle at a frequency of 3 Hz, inner flow rate of 300 μL h^{-1} and outer flow rate of 150 μL h^{-1}. Solvent evaporation of the templates at room temperature for 24 hours resulted in solid microcapsules shown in Figure S9b, c.