

Supporting Information for *RSC Advances*

One-Step Microfluidic Approach for Controllable Production of Gas-in-Water-in-Oil (G/W/O) Double Emulsions and Hollow Hydrogel Microspheres

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Microfluidic device: Cross-junction channels are fabricated on a polymethyl methacrylate (PMMA) plate using a Computerized Numerical Control (CNC) machine tool with an end mill ($\Phi=1\text{mm}$). The plate is then similarly cut into several chips ($35\text{mm}\times 20\text{mm}\times 3\text{mm}$) each with a cross-junction channel. The channel for dispersed phase fluid is approximately $1.5\text{ mm wide}\times 1.5\text{ mm high}$, the channel for continuous phase is approximately $1.35\text{ mm wide}\times 1.35\text{ mm high}$. A circular glass capillary with inner-diameter of 0.70 mm and outer-diameter of 1.00 mm is tapered using a micropipet puller (P-97, SUTTER Co. Ltd., USA) for the injection of the gas phase fluid. The diameter of the tapered orifice is approximately $8\text{ }\mu\text{m}$. The first tapered capillary is inserted into another capillary with inner-diameter of 1.05 mm and outer-diameter of 1.5 mm for the middle phase and the orifice is also tapered to approximately $70\text{ }\mu\text{m}$. We make sure that both the orifices align in the same plate. Then, those compound capillaries are inserted into a third coaxially aligned capillary for the double emulsions. The inner-diameter of the third capillary is 0.86 mm and the outer-diameter is 1.5 mm . PTFE pipes are inserted into the channel and capillaries and microsyringe pumps (LSP01-1B, Baoding Longer Precision Pump Co., Ltd) are used to pump the gas phase and two liquid phases into the microfluidic device respectively.

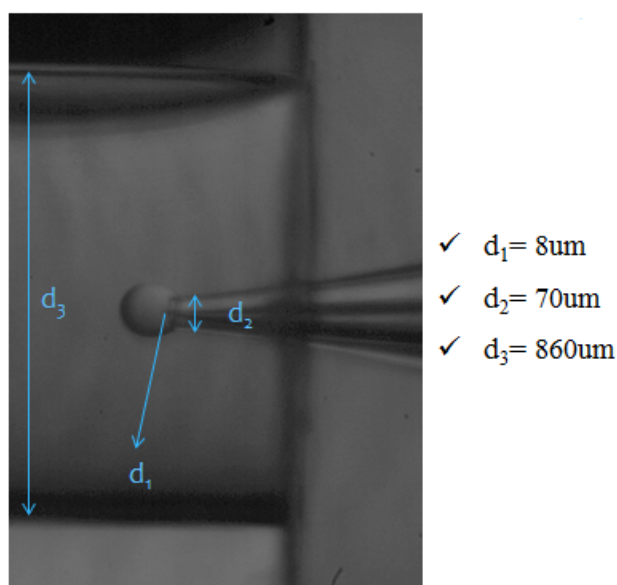


Fig. S1 The structure of the capillary microfluidic device.

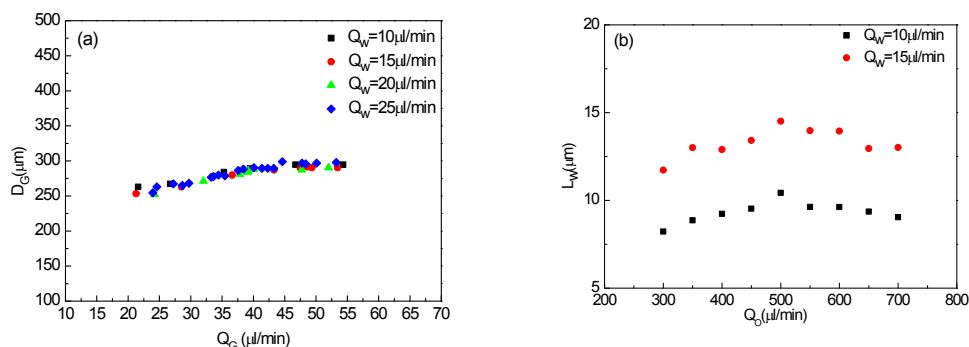


Fig. S2 (a) The effects of the inner and middle phase flow rates on microbubble size. $Q_i = 20 \sim 55 \mu\text{L}/\text{min}$, $Q_m = 10, 15, 20, 25 \mu\text{L}/\text{min}$, $Q_o = 400 \mu\text{L}/\text{min}$. (b) The effects of the outer phase flow rate on aqueous layers thickness. $Q_i = 50 \mu\text{L}/\text{min}$, $Q_m = 10, 15 \mu\text{L}/\text{min}$, $Q_o = 300 \sim 700 \mu\text{L}/\text{min}$.

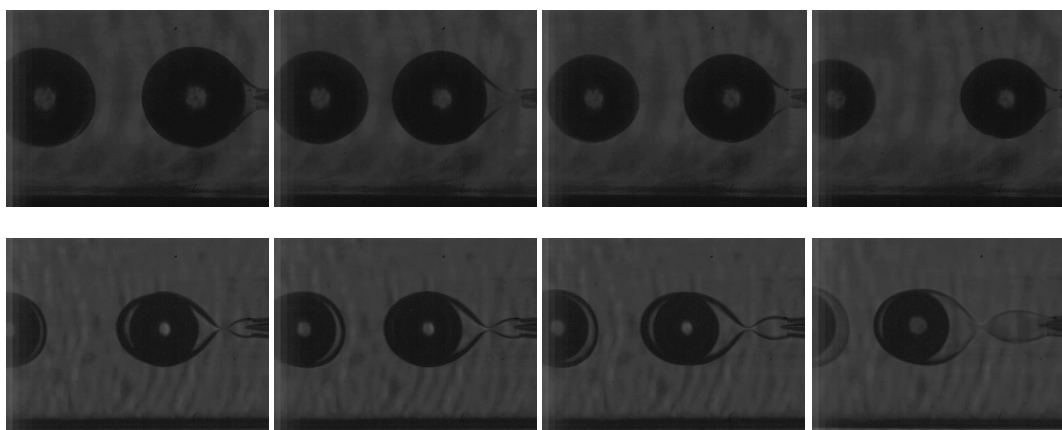


Fig. S3 The typical micrographs of G/W/O emulsion droplet with different dimensions of the encapsulated microbubble and aqueous layer.

Materials and Methods for Polymerization:

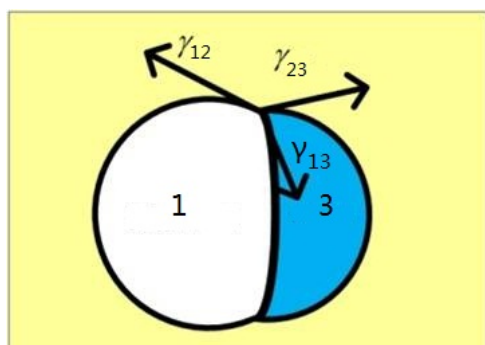
The system for the polymerization reactions is shown in Table S1. The hydrogel droplets encapsulating microbubble were polymerized by activating the photo-initiator using a UV spot light source (Hamamatsu, Model L9588-01). The formation of the droplets and bubbles was carried out with an optical microscope (BX61, Olympus, Japan) equipped with a high-speed camera with a frequency of 200 images per second (B742, Pixelink, Canada). More detailed structures were observed using scanning electron microscopy (SEM, FEI XL30).

Table S1. System for fabricating hollow hydrogel microspheres

Inner Phase	N_2
Middle Phase	72wt.% or 50wt.% Acrylamide + 3wt.% N_3N -methylenebisacrylamide + 3wt.% 2,2-diethoxyacetophenone + 2wt.% Triton X-100
Outer Phase	Silicon Oil (50cP) + 2wt.% Dow Corning 749 + 5wt.% 2,2-diethoxyacetophenone

The equilibrium structures of double emulsions are determined by the minimum interfacial energy

of three immiscible phases which formed a three-phase system. And there are three possible morphologies depending on the spreading coefficients related to the interfacial tension between every couple phases in a three-phase system, for which the mathematic relationship was derived by Torza et al.¹ The three possible equilibrium morphologies are completely engulfing structures, partial engulfing structure (Janus), and non-engulfing structure. If we measure the interfacial tension δ_{ij} between fluid i and j and calculate the spreading coefficient $S_i = \delta_{jk} - (\delta_{ij} + \delta_{ik})$ to predict the equilibrium morphology of the three-phase systems by using the prediction formula developed by Torza et al.¹ and Pannacci et al.², where : 1) $S_1 < 0, S_2 > 0, S_3 < 0$, results in the formation of non-engulfing structures; 2) $S_1 < 0, S_2 < 0, S_3 > 0$, results in the formation of completely engulfing structures, and 3) $S_1 < 0, S_2 < 0, S_3 < 0$, results in the formation of partial engulfing structures.



In our previous work, we successfully generated gas-in-oil-in-water (G/O/W) double emulsions. For this system, we measured the interfacial tension between three phases (Table S2) and calculated the spreading coefficients, and found it should be a thermodynamically stable system ($S_1 < 0, S_2 < 0, S_3 > 0$). So the G/O/W double emulsions could be stable for rather long time (several minutes). While for the G-W-O system used in this work, we calculated the spreading coefficients from Table S3 and found it is not thermodynamically stable ($S_1 < 0, S_2 > 0, S_3 < 0$). And the G-W-O emulsion would be broken in seconds, as shown in Movie S4 in ESI†.

Table S2. Data of interfacial tensions between the three phases of G/O/W system

	Oil-Water / δ_{23}	Oil-Gas/ δ_{13}	Water-Gas/ δ_{12}
Interfacial Tension (mN/m)	20.06	15.69	50.68

Table S3. Data of interfacial tensions between the three phases of G/W/O system

	Oil-water/ δ_{23}	Oil-gas/ δ_{12}	Water-gas/ δ_{13}
Interfacial tension (mN/m)	2.97	21.07	32.32

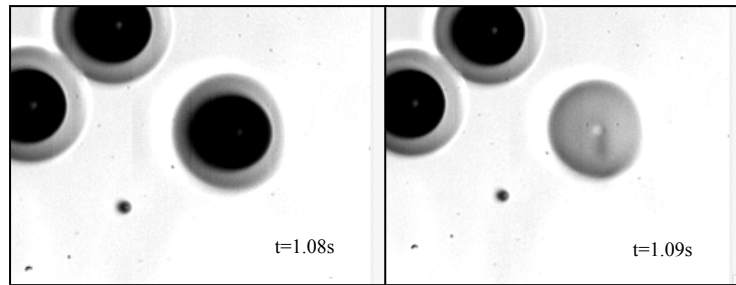


Fig. S4 Stability of G/W/O double emulsion. After flowing outside the device, the G/W/O double emulsion droplet breaks up in about one second as imaged by a fast camera.

References

1. Torza, S.; Mason, S. G. *Science* **1969**, *163* (3869), 813-814.
2. Pannacci, N.; Bruus, H.; Bartolo, D.; Etchart, I.; Lockhart, T.; Hennequin, Y.; Willaime, H.; Tabeling, P. *Phys. Rev. Lett.* **2008**, *101* (16), 164502-164505.