

Electronic Supplementary Material

Porous ultrathin-shell microcapsules designed by microfluidics for selective permeation and stimuli-triggered release

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Calculation of the gyration radius of PEG

The gyration radius R_g of PEG chains ($\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$) in a good solvent is empirically calculated by

$$R_g = 0.181 * n^{0.58} \text{ nm},$$

where n is the number of EG monomers in each PEG chain.

For PEG chains with a molecular weight of 6000 g/mol in water, the number of EG monomers in each PEG chain is

$$n = (6000 - 18) / 44 = 135.95 \approx 136,$$

and the radius of gyration is

$$R_g = 0.181 * n^{0.58} \approx 0.181 * 136^{0.58} \approx 3.13 \text{ nm}.$$

Calculation of the thickness of ultrathin-shell double emulsions

The shell thickness L of the ultrathin-shell double emulsion is calculated by using the method reported in the literature (ChemPhysChem 2017, 18, 1). When a W/O/W double emulsion ruptures and becomes a O/W single emulsion, the volume of oil in

the O/W single emulsion is equal to the volume of oil in the shell of the double emulsion. Therefore, the relation between the size of single emulsion R_s , the size of double emulsion R_d and the shell thickness L of double emulsion is

$$4\pi R_d^3/3 - 4\pi(R_d-L)^3/3 = 4\pi R_s^3/3,$$

and thus

$$L = R_d - (R_d^3 - R_s^3)^{1/3}.$$

For ultrathin-shell double emulsions generated at constant flow rates of 200 $\mu\text{L/h}$, 400 $\mu\text{L/h}$ and 10000 $\mu\text{L/h}$ for the inner, middle and outer phases, respectively, the size of W/O/W double emulsions is $R_d \sim 325 \mu\text{m}$, as shown in **Fig. S1**. When W/O/W double emulsions rupture due to shaking, they become O/W single emulsions, and the size of O/W single emulsions is $R_s \sim 52 \mu\text{m}$. Therefore, the shell thickness of the ultrathin-shell double emulsion is $L \sim 383 \text{ nm}$.

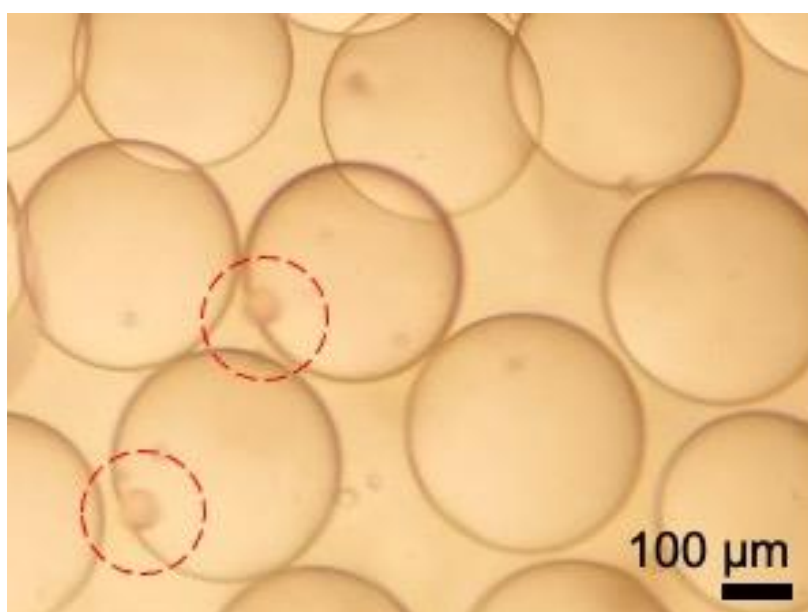


Fig. S1 Ultrathin-shell double emulsions generated at constant flow rates of 200 $\mu\text{L/h}$, 400 $\mu\text{L/h}$ and 10000 $\mu\text{L/h}$ for the inner, middle and outer phases, respectively. The size of W/O/W double emulsions is $R_d \sim 325 \mu\text{m}$. When W/O/W double emulsions rupture due to shaking, they become O/W single emulsions (marked by red dotted circles). The size of O/W single emulsions is $R_s \sim 52 \mu\text{m}$. The volume of oil in the O/W single emulsions is equal to the volume of oil in the shell of the double emulsions. Therefore, the shell thickness of the ultrathin-shell double emulsion is $L \sim 383 \text{ nm}$.