Supplementary Information

Enzymatically Triggered Rupture of Polymersomes

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1. Hydrogen Peroxide Control Experiments

To confirm that rupture of polymersomes was due to the enzymatic reaction cascade rather than the hydrogen peroxide (H_2O_2) intermediate, we performed thorough H_2O_2 control experiments. Catalase-free polymersomes were dispersed in the D-glucose solution and 0.2 ml of 2, 3, 5, 10, and 20 vol. % H_2O_2 were added in place of GOx solution. The resulting H_2O_2 concentration for the addition of 0.2 ml of 2, 3, 5, 10, and 20 vol. % H_2O_2 are 0.28, 0.43, 0.78, 1.43, and 2.86 vol. %, respectively. Figure S1 shows the surviving fraction (S_V) at 300 minutes. Interestingly, polymersomes made of poly(ethylene oxide$_{1300}$-b-butadiene$_{2500}$) amphiphilic diblock copolymer exhibit more than 90 % surviving fraction after 300 minutes with 0.78 vol. % of H_2O_2.

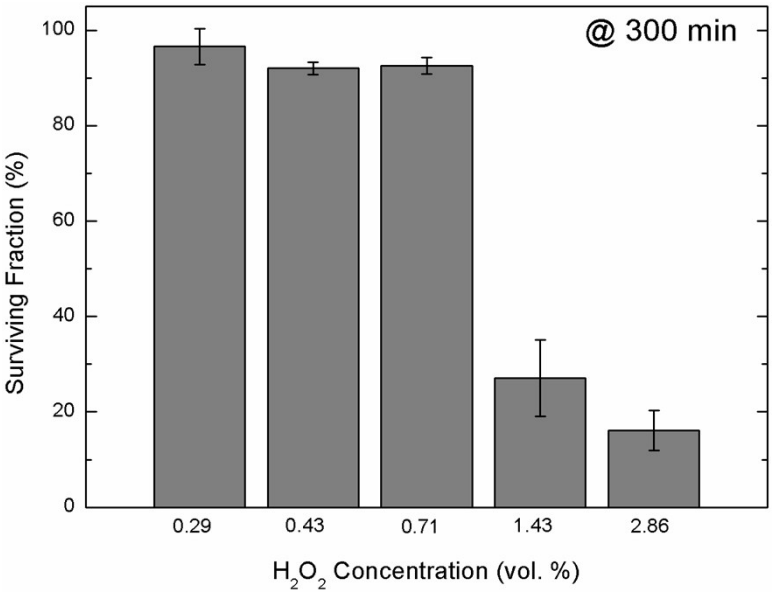
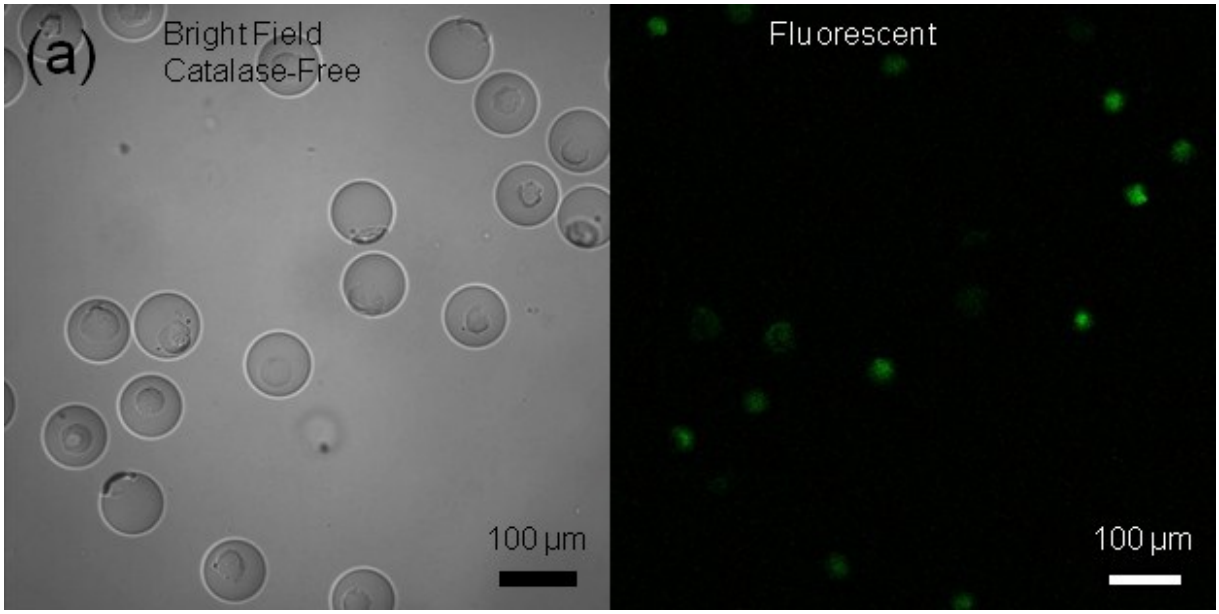


Figure S1. S_V (t = 300 minutes) for H_2O_2(−) controls. Interestingly, results for 0.29, 0.43, and 0.71 vol. % of H_2O_2 are above 90 %. On the other hand, S_V drops dramatically for 1.43 vol. % of H_2O_2.

2. Bright Field and Fluorescent Micrographs of Catalase-Free and Catalase-Loaded Polymersomes

When the organic solvent of double emulsion is completely removed, the extra polymer forms the bumpy polymer patch on the membrane which is an inevitable feature of microfluidic double emulsion-templated polymersomes. Figure S2(a) and S2(b) show the shape of patch on catalase-free and catalase-loaded polymersomes, respectively. Right and left images are taken in bright field and fluorescence, respectively. The focal plane of these images illustrate polymersome patches. Interestingly, we observed relatively strong auto-fluorescent signal from polymersome patches. However, Figure 4(b) shows strong local concentration of fluorescent signal which differentiates itself from auto-fluorescence.



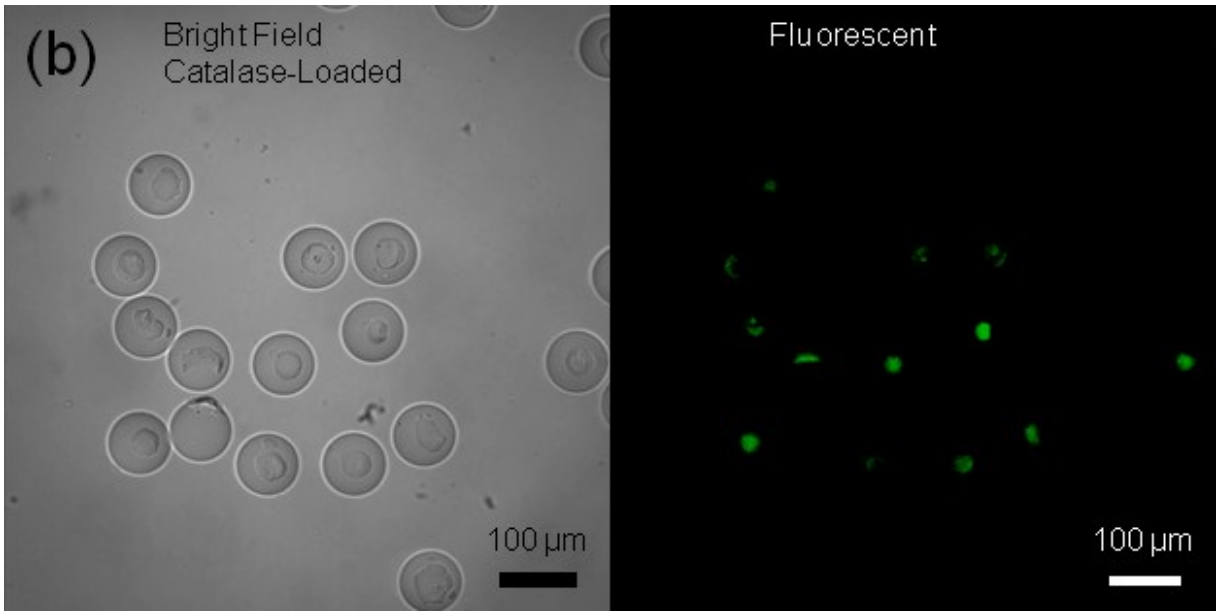


Figure S2. (a) Catalase-Free and (b) Catalase-Loaded Polymersomes.

3. Microfluidic Device

The size of double emulsion is directly influenced by the flow rates of the three fluid phases as well as the dimensions of the microfluidic device. For this work, typical device configuration and flow rates are:

Diameter of narrow capillary ≈ 20 μm

Diameter of wide capillary ≈ 140 μm

Inner Phase Flow Rate ≈ 1.0 ml/hour

Middle Phase Flow Rate ≈ 6.5 ~ 7 ml/hour

Outer Phase Flow Rate ≈ 20 ~ 25 ml/hour

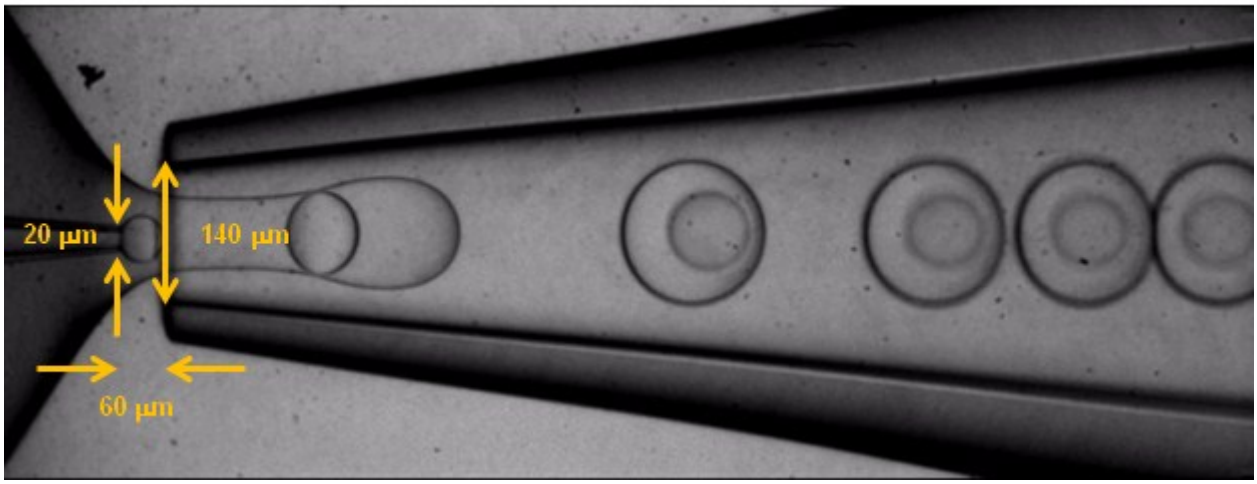


Figure S3. Representative device configuration.