Supporting Information

AWE-somes: All Water Emulsion Bodies with Permeable Shells and Selective Compartments

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The information included in this document is meant to supplement details presented in the main text. Included here are SEM images of shell thicknesses, an analogous hanging drop experiment to Figure 2, with the complexing agents' initial positions swapped, a more extensive set of data describing the PEG permeation graph in Figure 4, and a confocal image of a lysozyme-incorporated AWE-some.

PE/NP AWE-somes imaged with SEM after washing with water and dried on a surface (Figure S1). These data were collected on an FEI Strata® DB235 instrument at an accelerating voltage of 5 kV, a working distance of 5 mm, and a tilt of 52°. From these images, the shell thicknesses range from 2-4 μm.

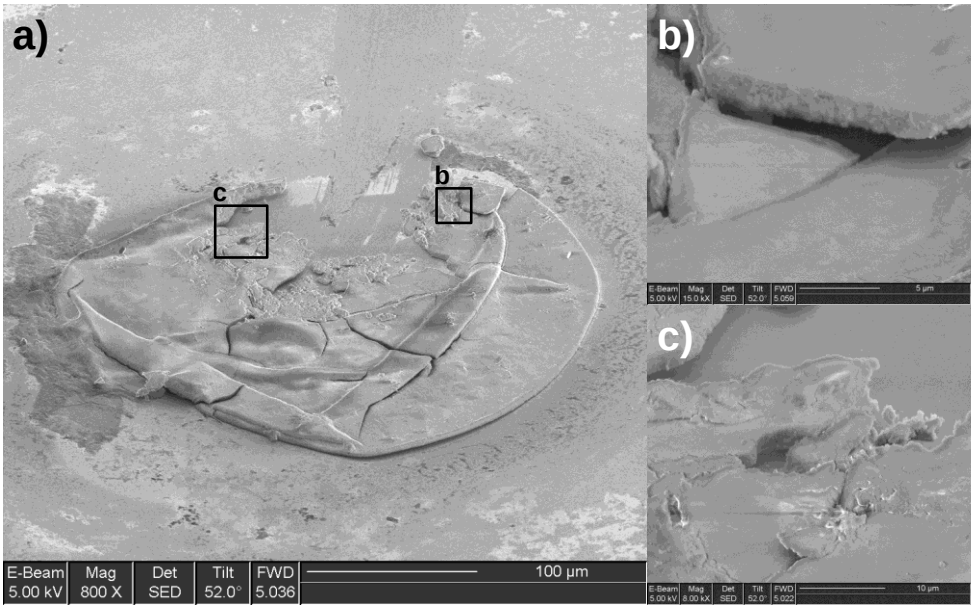

Figure S1. SEM micrograph of 0.5% PDADMAC/4.5% NP microcapsule. (a) Scale bar 100 μm, insets indicated by boxes. (b) Inset of cracked wall, shell thickness 2.1 μm, scale bar 5 μm. (c) Inset of cracked wall, shell thickness 2.0 μm. Scale bar 10 μm.

When the NPs are initially included in the dextran phase, as depicted in Figure S2a, the final structure, as illustrated in Figure S2d, is a NP-PDADMAC membrane included within the dextran phase. The extent to which the dextran phase is extracted through the membrane is a function of PDADMAC concentration in the PEG phase, as seen in the video snapshots shown in Figure S2b compared to Figure S2c. Notably, in Figure S2c, there is an apparent complexation front that makes its way toward the center of the drop through Figure S2c (iii) until the entire droplet phase becomes a coacervate phase in which NP-PDADMAC is also complexed within the dextran phase.

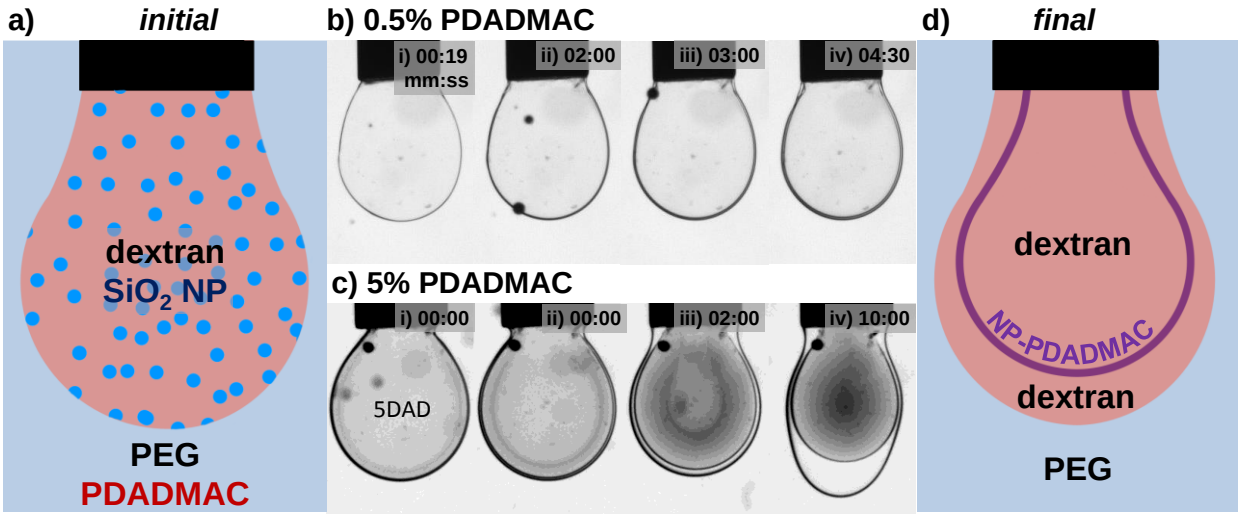

Figure S2. Injection of 0.5 uL 15% dextran/4% 22 nm silica NPs at a rate of 1 uL/s into 10% PEG and PDADMAC. (a) Schematic of initial state. (b) Time evolution of hanging drop with 0.5% PDADMAC post injection. (c) Time evolution of hanging drop with 5% PDADMAC up to 10 min post injection. (d) Schematic of final state of hanging drops. Needle diameter = 0.85 mm.

This series of videos supports the mechanism that relies on an osmotic driving force as presented in Figure 3 in the main text. In Figure S2, however, it is $\Pi_{dex} > \Pi_{PEG}$, which flips the sign of the water flux. Thus, water is driven into the dextran droplet through the rigid shell, causing the dextran phase to swell, and concomitantly moving the PEG-dextran interface to the other side of the NP/PE shell, Figure S3.

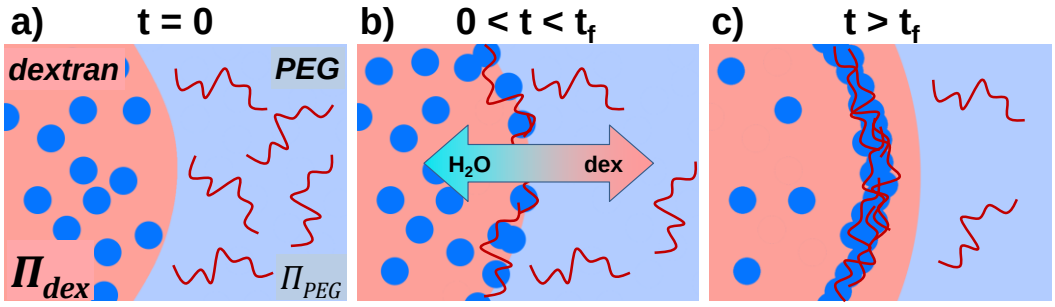

Figure S3. Schematic of osmotic driving force for NP/PE microcapsules. a) At t = 0, there is an osmotic pressure imbalance, $\Pi_{dex} > \Pi_{PEG}$, due to the presence of NP in the dextran phase. b) After the initial templating of NP/PE at the PEG-dextran interface, water and dextran are exchanged through the pores for a characteristic time t_f, after which (c) the NP/PE shell is impermeable to dextran transport.

The PEG permeability behavior presented in the main text (Figure 4) is consistent for different size PEG drops, capsules of different ages, and different NP sizes. Furthermore, the discrete value represented

on the y-axis of Figure 4 is seen to be a function of the amount of f-PEG added to the solution and can be normalized for all data to superpose onto the same curve, Figure S4. This superposition suggests that the permeability of the membrane is very similar for all cases studied here.

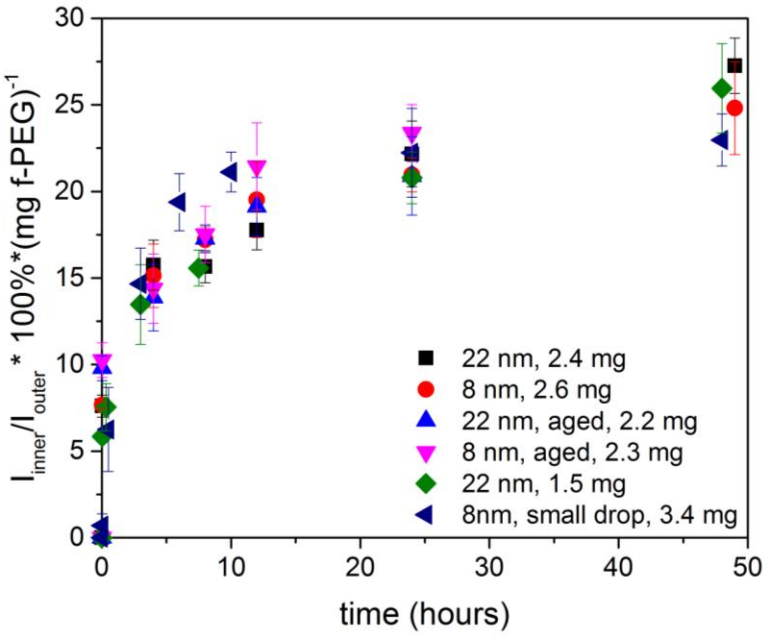

Figure S4. Additional data to Figure 4; measurement of PEG permeation into capsules by adding f-PEG to 5 mL continuous PEG phase and normalized by the mass of f-PEG. Legend descriptions indicate the size of silica NP used to form the capsule (nm) and the amount of f-PEG added to the 5 mL solution (mg). All capsules were made for inner PEG drop fractions of 0.25 except (◀), which is made to a fraction of 0.05. Data designated as 'aged' (▲,▼) are capsules that were made 1 week prior to adding f-PEG.

Lysozyme is easily incorporated into the shell, as it is known to complex with charged silica.[1] Figure S5 shows a lysozyme, PE/NP shell; lysozyme, originally added to the inner phase, is incorporated into the shell. Additionally, due to the strong complexation, we do not observed apparent phase separation of the lysozyme within the shell, as seen in previously reported systems.[2]

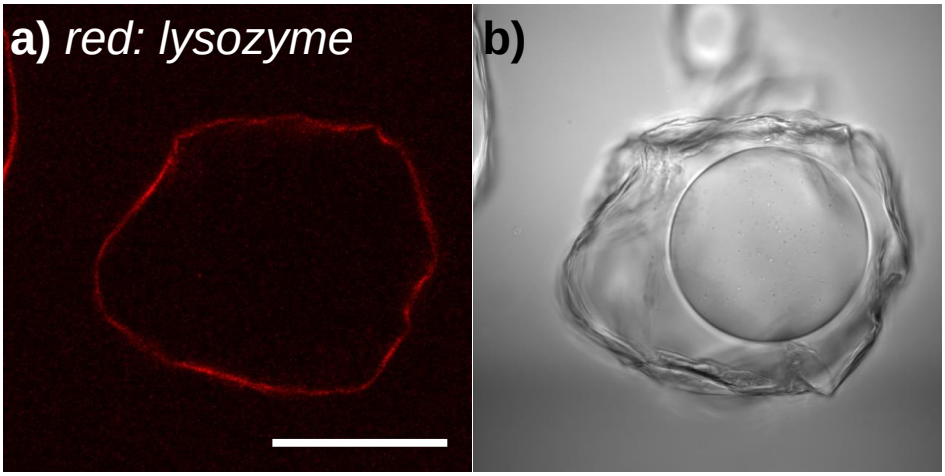

Figure S5. Confocal image of microcapsule fabricated with 15% dextran/0.5% PDADMAC/1μM rhodamine tagged lysozyme into 10%PEG/4.5% 22 nm silica NPs. (a) Fluorescent image, where red is the rhodamine tagged lysozyme. (b) Corresponding bright field image. Scale bar is 100 μm.

References

(1) Vertegel, A. A.; Siegel, R. W.; Dordick, J. S. Silica Nanoparticle Size Influences the Structure and Enzymatic Activity of Adsorbed Lysozyme. *Langmuir* **2004**, *20* (16), 6800–6807.

(2) Forciniti, D.; Hall, C. K.; Kula, M. R. Electrostatic Effects on Protein Partitioning: Simultaneous Effect of pH and Polymer Molecular Weight. *Chem. Eng. Sci.* **1992**, *47* (1), 165–175.