

Supplementary Information:

Expansion and rupture of charged microcapsules

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1 Supporting movies

Movie S1: Optical micrographs of a hybrid microcapsule expanding when exposed to $c_{NaOH} = 500$ mM.

Movie S2: Optical micrographs of a hybrid microcapsule first disintegrating, then expanding into a wrinkled jellyfish-like structure, when exposed to $c_{NaOH} = 1.6$ mM.

2 Double emulsion-templated fabrication of pH-responsive microcapsules

We use a glass capillary microfluidic device to prepare monodisperse W/O/W double emulsion drops as templates to form microcapsules.¹ The innermost aqueous phase is a 6 wt% aqueous solution of polyvinyl alcohol (PVA) of molecular weight 13,000-23,000. The middle oil phase is a mixture of 20 wt% base-responsive PAA-b-PMMA, suspended in tetrahydrofuran (THF), with 80 wt% pH-unresponsive ethylene glycol phenyl ether methacrylate monomer, 0.5 wt% 1,6-hexanediol dimethacrylate crosslinker, and 0.2 wt% 2-hydroxy-2-methylpropiophenone photoinitiator. The outermost aqueous phase is a 10 wt% aqueous solution of PVA containing 15 wt% THF. After the double emulsion drops are formed, we collect them, and the solvent in the middle oil phase slowly diffuses into the outer continuous phase; this forces the PAA-b-PMMA to precipitate. Within one hour, this forms a uniform solid shell of radius $\approx 69 \mu\text{m}$ and thickness $\approx 3 \mu\text{m}$. We wash the monodisperse microcapsules thus formed with water, adjusted to have pH = 6, three times to remove any surfactant from the continuous phase. When exposed to NaOH, the carboxyl groups in pH-responsive PAA-b-PMMA polymer chains at the microcapsule exteriors become deprotonated and thus highly charged, as schematized in Figure 1(a) of the main text. Our estimate of the microcapsule surface charge density, integrated over the shell thickness, is $\sigma \approx 300 e/\text{nm}^2$, as described in the main text. We perform our experiments using a microcapsule volume fraction $< 10\%$ within a sample volume $\sim 1 \text{ cm}^3$; thus, the concentration of NaOH required to fully charge the microcapsule shells is < 1 mM, well below the concentrations used in the experiments reported here. We therefore assume that the vast majority of the NaOH ions act as counterions that screen the repulsive interactions between the charges on the microcapsule shells, and thus the counterion concentration is $\approx c_{NaOH}$.

It is not clear whether the Na^+ or OH^- can diffuse into the shell *during* the expansion process, and this may very well be the case; however, in the simple model we present here, we only consider the charging of

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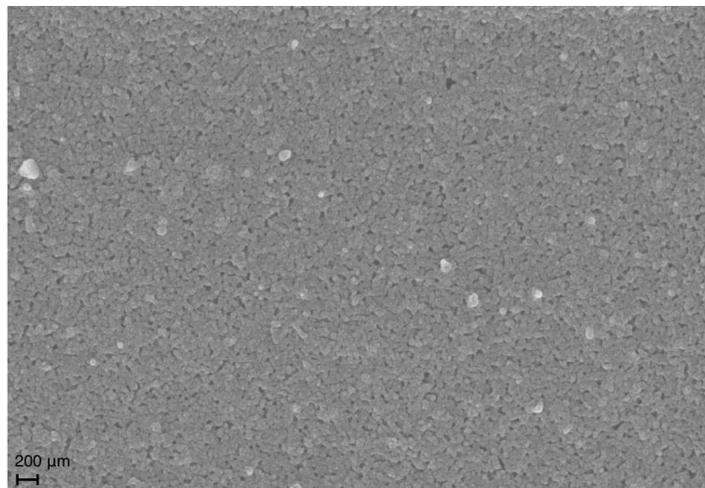


Figure 1: SEM micrograph of zoomed-in region on the surface of a microcapsule with a shell containing 5 wt% pH-responsive polymer, after it is exposed to a pH stimulus (pH=9).

the microcapsule surface, and thus, our interpretation of the results does not depend on whether or not the ions diffuse into the shell. We do believe that the PVA remains in the core during the expansion process; we estimate that the characteristic size of the PVA molecules (~ 50 nm) is significantly larger than the characteristic mesh size of the cross-linked polymer network making up the microcapsule shell ($\sim 1 - 10$ nm), and we thus do not expect the PVA molecules to diffuse through the shell.

To elucidate the origin of the opacity that develops when the microcapsules are exposed to a pH stimulus, we use scanning electron microscopy (SEM) to directly visualize the structure of the microcapsule shell after exposure to a pH stimulus. We find that small heterogeneities develop in the shell, although these do not appear to form pores that span the entire radial extent of the shell [exemplified by Figure S1].

Intriguingly, we do not observe any strong effect of the core osmotic pressure. Indeed, the osmotic pressure of the core, which we estimate at $\Pi_{in} N_A k_B T \sim 10^4$ Pa, is much smaller than the typical pressure [see Ref. 4 of the main text] required to deform the shell, $E(h/R_0)^2 \sim 10^6$ Pa; $\Pi_{in} \approx 60$ mOsm/L is the osmolarity of 6 wt% PVA, N_A is Avogadro's number, k_B is Boltzmann's constant, $T = 300$ K is temperature, $E \approx 600$ MPa is the Young's modulus of the shell material, $h \approx 3$ μ m is the shell thickness, and $R_0 \approx 60$ μ m is the microcapsule radius. We thus do not expect the osmotic pressure of the core to play a significant role, consistent with our observations.

3 Estimate of electrostatic pressure

The thickness-integrated charge on a microcapsule shell is given by $Q = \sigma \cdot 4\pi R^2$. Using the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory for screened electrostatics, we approximate the electrostatic potential at the microcapsule surface as $\psi_0 \approx \sigma/\epsilon\epsilon_0\kappa$, where ϵ , ϵ_0 , and κ are as defined in the main text. We thus calculate the potential energy of the shell, $U = \int \psi_0 dQ$, and use this to calculate the electrostatic pressure $p_e = -dU/dV$, where V is the shell volume. This yields $p_e \approx \sigma^2 \kappa^{-1}/\epsilon\epsilon_0 R$, as noted in the main text. A detailed discussion of this result can be found in Ref.².

References

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- [2] A. Siber and R. Podgornik. *Phys. Rev. E*, 76:061906, 2007.