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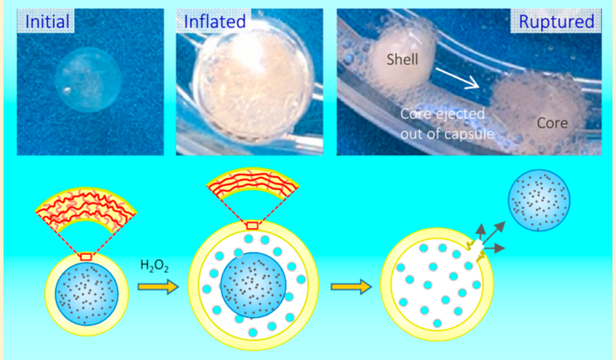
Catalyst-Loaded Capsules that Spontaneously Inflate and Violently Eject their Core

Kerry C. DeMella[†] and Srinivasa R. Raghavan*[,†,‡]

[†]Department of Chemistry & Biochemistry, University of Maryland, College Park, Maryland 20742, United States
[‡]Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States

Supporting Information

ABSTRACT: We present a design for polymer capsules that exhibit a range of unusual autonomous behaviors when exposed to a chemical fuel. The capsules have a physically gelled core (alginate-Ca^{2+}) loaded with catalytic (silver) particles and a shell composed of a chemically cross-linked gel. In the presence of the fuel (H_2O_2), a catalytic reaction occurs, which generates oxygen (O_2) gas. The gas collects in a zone between the core and the shell, and the resulting gas pressure causes the elastic shell to stretch. This makes the capsule inflate in a process reminiscent of a swelling pufferfish. As the capsule inflates, the polymer chains in the shell continue to stretch until a breaking point is reached, whereupon the shell ruptures. Three rupture modes are documented: gentle, moderate, and violent. The latter involves the gelled core being forcefully ejected out of the shell in a manner similar to the ejection of needles out of nematocysts on jellyfish. The extent and duration of inflation can be tuned by altering the core and shell composition; for example, shells that are more densely cross-linked swell less and rupture faster. Also, instead of a catalytic reaction, capsule inflation can be achieved by combining reactants, one in the capsule and the other in the external solution, that together generate a different gas (e.g., CO_2).



INTRODUCTION

In the field of soft matter, there has been much recent interest in developing materials that show autonomous behavior, such as the ability to spontaneously move,[1−3] change shape,[4−6] grip a target,[7] or destroy a target.[8] The inspiration for such "smart" or "active" soft materials frequently comes from nature.[9,10] Microscale examples of autonomous natural systems include the immune cells in our body, which can move through blood, identify foreign bodies, and selectively destroy them.[8,11] At the macroscale, autonomous behavior is exhibited by plants (folding of leaves),[6,12] terrestrial animals (color change of chameleons),[9,10] and aquatic creatures (swelling of pufferfish).[13,14] Autonomous systems are not generally dependent on an external field such as a magnetic field or light to provide the driving force for their behavior. Instead, they either have a built-in power source or use the resources in their environment as a source of power. Thus, in building autonomous devices such as self-propelling robots, researchers have sought to harness power from chemical fuels using catalysts. For example, a microscale "motor" containing a metallic catalyst (such as platinum, Pt) can harness a fuel such as hydrogen peroxide (H_2O_2) that is dissolved in the external aqueous medium.[1−3] The fuel is decomposed into oxygen (O_2) gas, and if bubbles of gas are ejected from the motor along a specific direction, the motor will be propelled in the opposite direction. In effect, by this process, chemical energy is converted to kinetic energy. This is a well-exploited principle for autonomous motion of small objects,[1,2] including soft microbeads or microcapsules.[3]

In this paper, we report a new kind of autonomous behavior for a class of soft capsules in water. Our capsules have a physically gelled core containing catalytic silver (Ag) particles and a shell composed of a chemically cross-linked hydrogel. When the capsules are placed in a chemical fuel (such as H_2O_2), they exhibit the unusual phenomena of inflation and explosion (bursting). The inflation (i.e., a rapid increase in capsule volume) is caused by gas evolved in the capsule core via a catalytic reaction;[1−3] thus, this phenomenon is somewhat like the gas-induced expansion of a balloon, albeit one that is initially filled with water. During inflation, the *gas stays within the capsule*, unlike in previous studies done with catalyst-bearing structures[1−3] where the gas was released into the solution. Thereby, the gas causes a buildup of internal pressure in the capsule, due to which the polymer shell of the capsule gets stretched. The stretching continues until a breaking point is reached, whereupon the shell finally ruptures. We show that the rupture can be gentle or violent; in the latter case, the explosion is powerful enough to eject the core contents with force. To our knowledge, the ability of an aqueous structure to rapidly inflate

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due to gas and forcefully expel its contents is yet to be demonstrated in the literature. The closest parallels to our work are recent examples of aqueous capsules that spontaneously swell and rupture after some time when placed in water, e.g., due to a buildup of osmotic pressure in the core[15−19] or due to the action of an enzyme on the capsule shell.[20] While these studies are interesting, the swelling in most cases was modest and gradual (in contrast to a rapid inflation) and the eventual rupture of the capsule was not violent, with the core contents being released gently into solution. More forceful rupture has been reported in capsules with an emulsified core and a temperature-responsive polymer shell.[21,22] There has also been a recent report of capsules with an oil core that rupture due to light-induced generation of a gas.[23]

Interestingly, there are examples in nature of aquatic creatures that, when perturbed, either rapidly inflate or eject a payload with force. Inflation is exhibited by the family Tetraodontidae that includes the pufferfish and balloonfish.[13,14] These fish have a highly elastic stomach, which they can fill with water or air, causing the creature to inflate to a larger size. The inflation is a defense mechanism for several reasons. First, predators that swallow the fish before inflation may die from choking. Second, in their inflated form, the fish expose pointed spines that ward off the predator. With regard to payload ejection, one instance of such behavior is by aquatic creatures from the phylum Cnidaria, such as jellyfish or sea anemones.[24−26] These creatures are able to inject submicron needles into the body of their predators. The jellyfish "sting" experienced by swimmers in the ocean is due to such needles piercing their skin. Needle injection is accomplished by specialized "cnidocyte" cells on jellyfish tentacles, which contain sacs called nematocysts,[24−26] and this is schematically shown in Figure 1A. Initially, the barbed needle is coiled up in the cell, but when the cell is perturbed, an osmotic gradient (up to 150 bar) rapidly builds up and causes the needle to rapidly eject out of the cell. This ejection is forceful enough to pierce through the body of predators.

Here, we show that it is possible to control the inflation and rupture of the capsules designed in this study, including their extent of inflation, the time until rupture, and the intensity of rupture. In the case of violent rupture (which results in core ejection), an analogy can be made to the ejection of needles from nematocysts, as indicated by the schematic in Figure 1B. Many plants also use an explosive burst of their seedpods to disperse seeds far from their original location.[12,21] The ability to emulate these naturally occurring autonomous phenomena in a synthetic system is one interesting aspect of this study. It is worth pointing out that our system is very simple and can be easily replicated in any lab; all precursors are commercially available, and the capsule synthesis can be completed in minutes, unlike those made by more complicated synthesis methods like the layer-by-layer (LbL) technique. Inflating/exploding capsules could also potentially have utility, for example, in delivery applications where a large payload of drugs[27,28] or other chemicals such as fragrances[23] has to be delivered in a single, large burst. Another application is the direct injection of drugs through skin for which nematocyst capsules isolated from aquatic creatures have already been explored.[29,30] Future designs of soft robots could also use the core ejection strategy to defend against predators.

■ RESULTS AND DISCUSSION

Synthesis of Inflating Capsules. The procedure for synthesizing capsules in this study is shown schematically in Figure 2.[31] First, we create core particles by contacting the anionic biopolymer, sodium alginate, with divalent cations like Ca^{2+}.[31,32] A 2 wt % alginate solution is mixed with 2 wt % of silver (Ag) microparticles (2 to 3.5 μm in diameter), and this slurry is added dropwise into a reservoir containing 0.5 M $CaCl_2$ (Figure 2A). The droplet is converted into a gelled bead due to cross-linking of alginate chains by Ca^{2+} ions. The Ag microparticles (μPs) are immobilized in the bead. We chose Ag for its ability to catalyze the decomposition of H_2O_2 (see below). Next, we employ the "inside-out" polymerization technique recently developed by our lab[31] to create a shell of chemically cross-linked polymer gel around the alginate core. For this, the bead is loaded with a free-radical initiator (ammonium persulfate, APS) and then transferred to a solution containing an acrylamide monomer and cross-linker (Figure 2B). The cross-linker used here is *N*,*N*′-methylene bis-acrylamide (BIS for short) in all cases, while the monomer can be acrylamide (AAm), *N*-isopropylacrylamide (NIPA), or *N*,*N*′-dimethylacrylamide (DMAA). Within a few minutes of immersion in the monomer solution, a polymer shell (chemical gel) grows outward from the core. The final result is a capsule with a distinct shell or layer (Figure 2C). Typically, our inflating capsules have a single polymer shell (~500 μm thick) surrounding the alginate core, as can be seen from the inset image in Figure 2C. Subsequently, we will also study capsules with multiple shells.

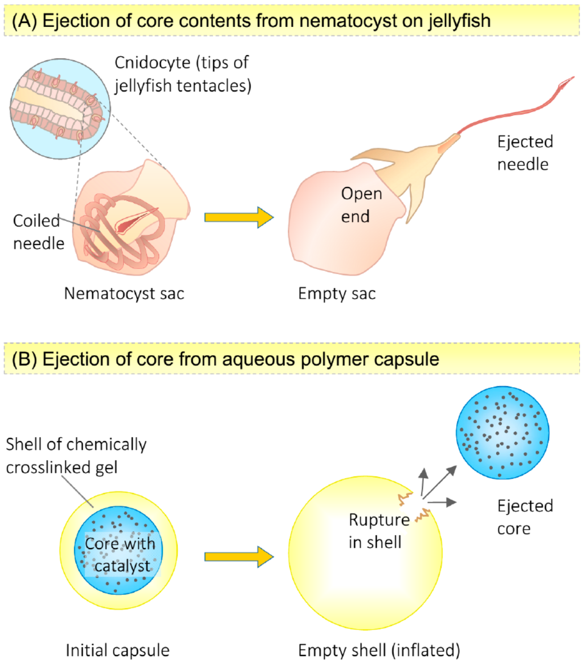

Figure 1. Analogy between the response of nematocysts and of the capsules in this study. (A) Nematocysts are sacs or capsules present in cnidocyte cells on the tips of jellyfish tentacles. When the end is opened, the coiled needle in the sac is ejected with force into a predator. (B) The capsules in this study have a gel core with catalyst particles and a polymeric shell. When gas is generated in the core by a reaction, the shell inflates and eventually ruptures. The rupture can be a violent explosion, inducing the core to be forcefully ejected out of the ruptured shell.

Cross-linked Polymer Shell Required for Inflation. When the above Ag-containing capsule is placed in an aqueous solution of H_2O_2, the H_2O_2 is able to diffuse through the capsule shell and contact the Ag μPs in the core. The Ag μPs catalyze the decomposition of H_2O_2 into water and oxygen (O_2) gas.[1−3] The

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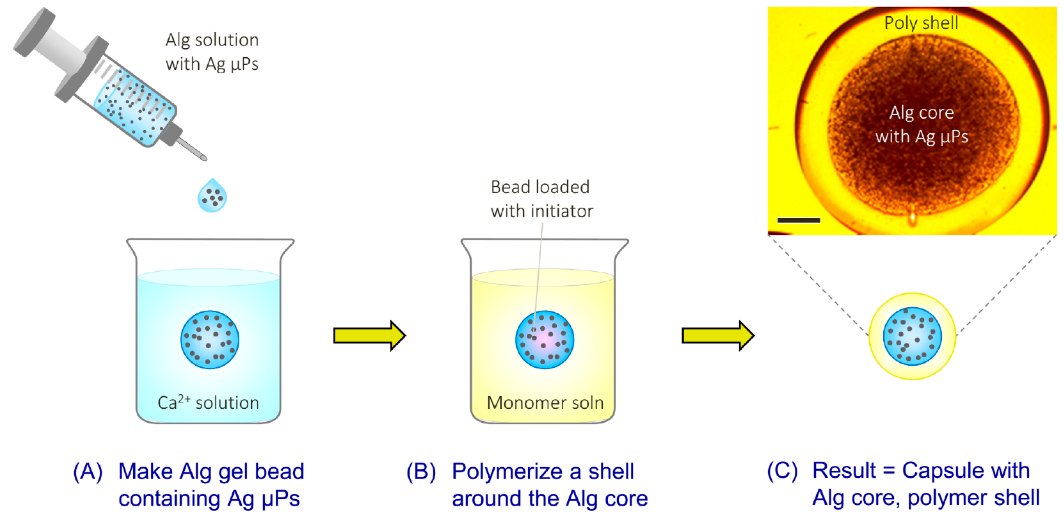

Figure 2. Synthesis of inflating capsules. (A) An alginate (Alg) solution with suspended Ag microparticles (μPs) is dropped out of a syringe into a $CaCl_2$ solution. The droplet is instantly converted into a gelled bead. (B) This bead is then removed, loaded with initiator, and then placed in a solution of monomer (acrylamide derivative), along with cross-linker and accelerant. (C) Upon polymerization, a shell of chemically cross-linked polymer gel is formed around the core. A microscope image of the resulting capsule is shown in the inset (scale bar: 1 mm).

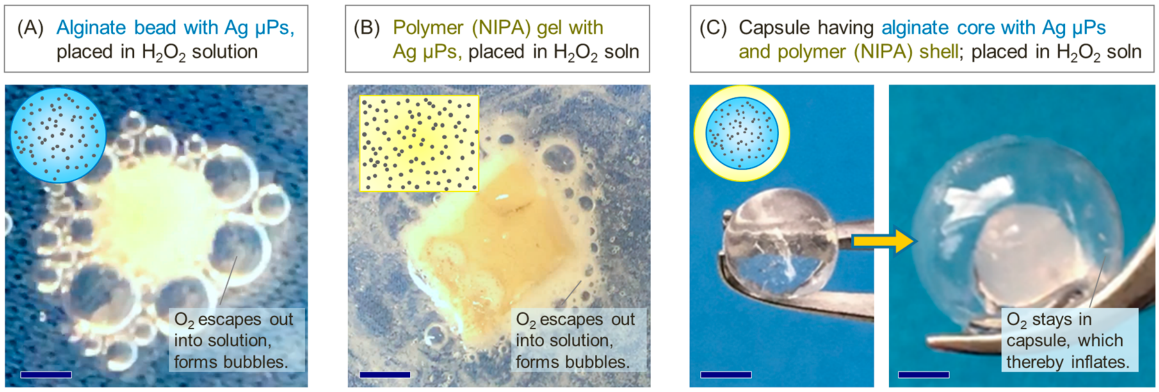

Figure 3. Images demonstrating that capsules inflate but beads and gels do not. In all cases, the structures have 2 wt % Ag μPs inside and are placed in a solution of 30% H_2O_2. The Ag catalyzes the decomposition of H_2O_2 into O_2 gas. (A) Alginate gel-beads give rise to O_2 bubbles in the external solution. No inflation is seen. (B) NIPA gels also produce O_2 bubbles in the surrounding solution. Again, no inflation is seen. (C) Capsules with an alginate core and a NIPA shell inflate due to the O_2 generated in the core. Scale bars: 3 mm.

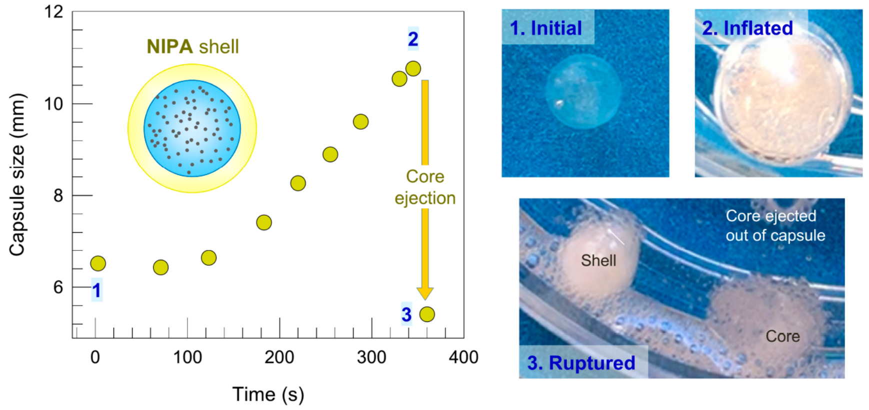

Figure 4. Inflation and rupture of a capsule with a shell of NIPA. The capsule has an Alg core with Ag μPs (2 wt %). At $t = 0$, the capsule is placed in 30% H_2O_2 and the subsequent behavior is revealed by Movie 1 (SI). Capsule size vs t is shown in the plot, and still images at discrete times are provided on the right. The capsule inflates by about 100% and then explodes, ejecting the core with some force.

interesting result we then observe is that the capsule inflates due to the gas generated. We will discuss the inflation in detail below. However, it is important to note that inflation is seen only for capsules that have the cross-linked polymer shell surrounding the alginate gel core. For comparison, the case of an alginate bead (lacking a shell) with Ag μPs in its core is illustrated in

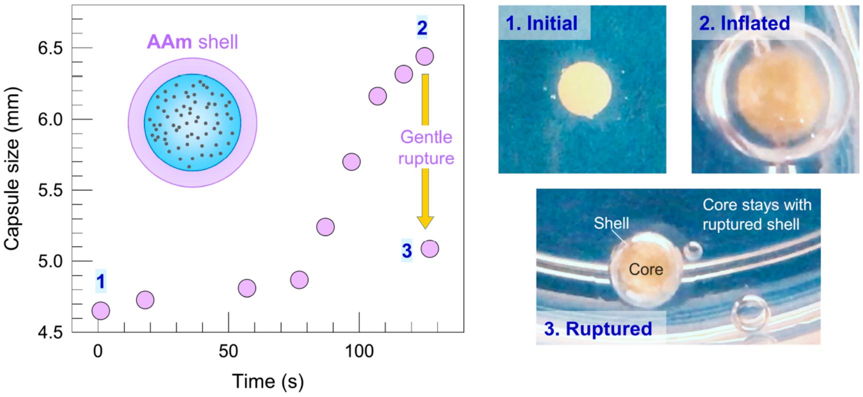

Figure 5. Inflation and rupture of a capsule with an AAm shell. The capsule has an Alg core with Ag μPs (2 wt %). At $t = 0$, the capsule is placed in 30% H_2O_2 and the subsequent behavior is revealed by Movie 2 (SI). Capsule size vs t is shown in the plot, and still images at discrete times are provided on the right. The capsule undergoes a gentle rupture, with the core remaining with the broken shell.

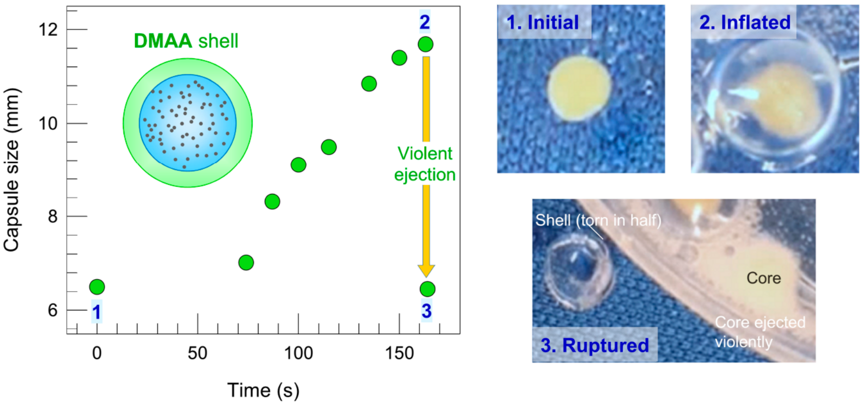

Figure 6. Inflation and rupture of a capsule with a DMAA shell. The capsule has an Alg core with Ag μPs (2 wt %). At $t = 0$, the capsule is placed in 30% H_2O_2 and the subsequent behavior is revealed by Movie 3 (SI). Capsule size vs t is shown in the plot, and still images at discrete times are provided on the right. The capsule inflates by about 100% and then ruptures violently, with the core being forcefully ejected far from the shell.

Figure 3A. When the bead is placed in H_2O_2, the O_2 produced is released into the surrounding solution in the form of bubbles. Thus, no inflation of the bead occurs. Likewise, a gel of NIPA containing the same Ag μPs also produces O_2 gas when placed in H_2O_2, but once again, the gas is released as bubbles into the solution (Figure 3B). Thus, the scenario of inflation is seen only when there is a catalyst-laden core (alginate gel containing Ag μPs) *and* a chemically cross-linked shell (Figure 3C). We will show that in this case, the generated gas occupies a space between the core and the shell, which is why it is able to cause inflation of the shell.

Capsule Inflation and Rupture: Different Modes. We studied capsule inflation using three different polymer shells: NIPA, AAm, and DMAA. These are three kinds of polymer gels that we have worked with in the past.[31] In all cases, the core was the same alginate gel containing Ag μPs (2 wt %) and all capsules were placed in 30% H_2O_2 unless otherwise stated. The core size was about 4 to 5 mm, and the shell thickness was about 0.5 mm. All shells were synthesized with 1 M monomer and 2.2 mol % BIS with respect to the monomer (other details are included in the Experimental Section). For these three cases, we find three different modes of behavior, which are shown in Figures 4 to 6. The data presented in all these figures is for the capsule diameter as a function of time.

The sequence of events in all cases is as follows. At $t = 0$, the capsule is placed in the H_2O_2 solution. For all experiments, a movie was recorded, and from still images, the capsule size at discrete time points was extracted. The data in Figures 4 to 6 show an initial lag period over the first 50 to 100 s where the capsule size is unaffected. During this time, H_2O_2 molecules diffuse into the capsule. Once the catalytic reaction begins, the capsule begins to inflate, i.e., it increases uniformly in size in all directions. This increase is roughly linear in time, which is especially evident in the case of the NIPA shell as shown in Figure 4. In all three cases, the inflation proceeds for 100 to 200 s, but ultimately the shell ruptures. Once the rupture occurs, the gas escapes out, and numerous bubbles are seen around the ruptured capsule. At this point, the capsule size drops to its original value. The data point for size after rupture in the figures is the size of the outer envelope (shell) that is left behind.

The key differences between the three shells is in the manner of rupture. The NIPA-shelled capsule ruptures rapidly with enough force that the core is ejected from the shell (Figure 4); see also the accompanying Movie 1 in the Supporting Information (SI) section. Conversely, the capsule with the AAm shell experiences a gentle rupture (Figure 5 and the accompanying Movie 2 in the SI). In this case, when the shell ruptures, the core remains inside the broken shell. Finally, the rupture of the DMAA-shell capsule is rather violent; in this case, the shell breaks into two halves and the core is ejected with force (Figure 6 and the accompanying Movie 3 in the SI). If the experiment is done in a Petri dish, the core typically shoots into the air and out of the Petri dish.

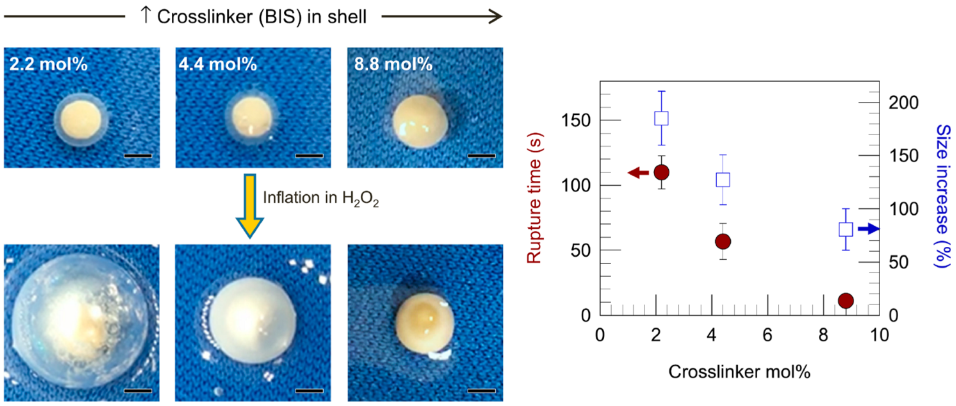

Figure 7. Effect of cross-linker concentration on capsule inflation and rupture. Capsules with NIPA shells and 15 wt % Ag μPs in the core were made with different mol % of BIS cross-linker relative to monomer. Photos of the different capsules, before and after inflation, are provided on the left (scale bars: 3 mm). Data for rupture time and size increase (%) against BIS mol % are plotted on the right; the error bars are standard deviations calculated from multiple measurements. The data show that as BIS mol % is increased, the capsules inflate less and rupture faster.

In the above cases, the shells were made using a monomer concentration of 1 M and a cross-linker/monomer ratio of 2.2 mol %. Thus, we expect the three shells to be polymer networks with similar cross-linking densities. Nevertheless, rheological studies on the three polymer gels corresponding to the shell compositions show appreciable differences. All these gels were prepared independently as disks (see Experimental Section) and tested on a rheometer. The gels showed the expected solid-like rheology (frequency-independent elastic G' and viscous G'' moduli with $G' \gg G''$).[33,34] Therefore, the gels can be characterized by their elastic modulus G' value, which is a measure of the gel stiffness.[33] The G' of the DMAA gel is 9800 Pa, which is about 10 times that of the AAm gel (1100 Pa), while the G' for the NIPA gel is intermediate at 7900 Pa. This means that the DMAA gel is the stiffest of the three, and thus, the violent-rupture mode occurs for the capsule with the stiffest polymer shell (DMAA).

Controlling Capsule Inflation and Rupture. We tested the effects of several variables on capsule inflation and rupture. To characterize inflation, we measured the maximum extent of inflation, i.e., the difference between the maximum size reached by the capsule upon inflation and its original size. To characterize rupture, we measured the rupture time, i.e., the time it takes for the capsule to rupture (with $t = 0$ being the instant when the capsule is contacted with H_2O_2).

One variable that has a significant effect on the above properties is the concentration of cross-linker (BIS) used during synthesis; the higher the BIS, the stiffer the shell. We tested the effect of BIS concentration keeping NIPA as the monomer at a constant level of 1 M. Photos of these capsules before and after inflation, and data for the size increase (%) and rupture time are shown in Figure 7. All capsules had 15 wt % Ag in the core and were studied in 30 wt % H_2O_2. The capsules with the lowest BIS (2.2 mol % with respect to the NIPA) inflate the most (140% size increase) and take the longest time (150 s) to rupture. Increasing the BIS causes a monotonic decrease in both these parameters. We also studied the rheology of NIPA gels corresponding to the three BIS concentrations tested. As expected, the elastic modulus G' increased monotonically with increasing BIS (from 7900 Pa for 2.2 mol % BIS to 11000 Pa for 8.8 mol % BIS). This confirms that increasing BIS makes the polymer gel stiffer due to the higher density of cross-links.[33,34] We therefore conclude that the stiffer the shell (meaning the less it will stretch), the less the capsule will inflate. Conversely, the stiffer the shell, the sooner the capsule will break.

Other important variables are the concentration of Ag μPs in the capsule core and the concentration of H_2O_2 in the solution. These were tested for capsules with a shell of NIPA (1 M) cross-linked with 2.2 mol % BIS, and the data are shown in Figure S1 in the SI section. The Ag μP and H_2O_2 concentrations had no discernible effect on the extent of inflation, but both caused a decrease in the rupture time. Both these variables increase the rate at which O_2 gas is produced and thereby the concentration of gas in the capsule at any instant of time. With increased gas in the capsule, the NIPA shell will be stretched to its breaking point in a shorter time, thus explaining the data.

One other aspect we have investigated is the capsule architecture itself, i.e., whether the capsule has a single shell or more shells. The procedure to create a capsule with more than one shell is very similar to that for making the first shell.[31] For this, a single-shell capsule, made as in Figure 2, is freshly loaded with initiator and then placed in a monomer solution. A second shell then forms outside the first one in a few minutes. This procedure can be repeated to create additional shells. Photos of 2-shell and 3-shell capsules with identical cores containing Ag μPs (2 wt %) are shown in Figure S2 (SI). Each shell is a NIPA-BIS gel of about 500 μm in thickness. We proceeded to try the inflation experiment with the 2-shell and 3-shell capsules in 30 wt % H_2O_2; the results are then compared with those for the 1-shell capsule from Figure 4. The data in Figure S2 show that as the number of shells increases, the capsule takes a longer time to rupture and its inflation is slightly reduced. With regard to the rupture, this is observed in every shell of the 2- and 3-shell capsules, not just the outer shell. However, while the 1-shell NIPA capsule ejects its core during rupture (Figure 4), the core of the 3-shell NIPA capsule remains together with the punctured shells.

Why Do Capsule Inflation and Rupture Occur? To further understand the phenomena of inflation and rupture, we examined the process using a high-speed camera. Stills from the corresponding movie (Movie 4, SI) at the onset of inflation are particularly revealing and are shown in Figure S3 in the SI. The key insight is regarding the nature of the interface between the core (alginate gel) and the shell (chemically cross-linked acrylamide gel) during the "inside-out" polymerization used to synthesize the capsule (Figure 2). We infer that the core and shell are *discrete layers* that are only adhered together by physical

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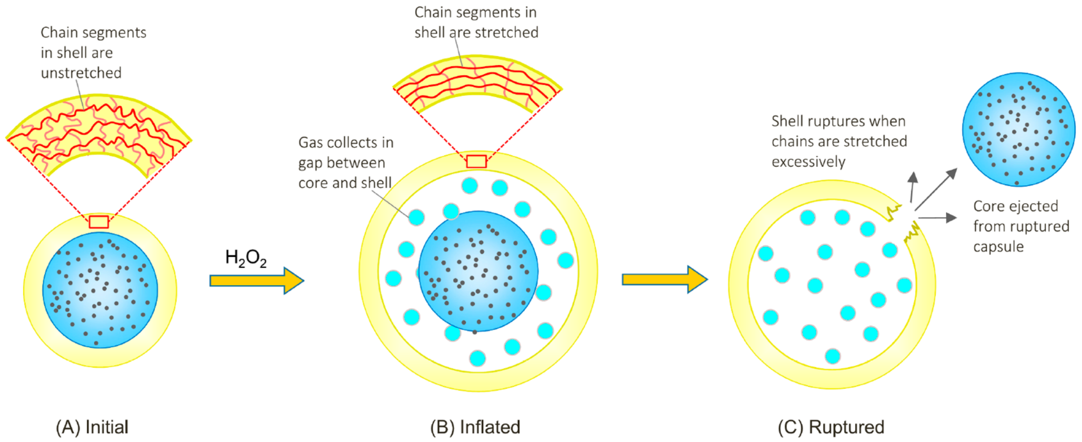

Figure 8. Mechanism for capsule inflation and rupture. (A) Before inflation, the capsule shell is a polymer network in which the segments between cross-links are loose and unstretched. The shell and core are weakly adhered. (B) When gas is produced, it collects in a gap between the core and shell. The gas pressure stretches the segments in the shell-network. (C) When the stress in the shell exceeds the breaking point of the network, the shell ruptures, causing the core to be ejected.

bonds.[31] Consequently, as the O_2 gas is produced, bubbles of the gas are able to collect between the core and the shell, creating a gap zone (Figure S3b). That is, the path of least resistance for the gas seems to be to move into the gap between the two aqueous layers (rather than diffusing through the outer shell and out into the external solution). One additional factor here is the low solubility of O_2 in water. The Henry's law constant for O_2 in water at 25 °C is 770 L·atm/mol from which we can calculate that under ambient conditions, only 0.27 mM of O_2 will be in dissolved form. Above this concentration, bubbles of the gas will nucleate and grow, and it will be these bubbles that collect in the gap. As shown by Figure S3c, the gap surrounds the core within 4 s after the onset of bubbles. As the gas continues to evolve, the gap between core and shell widens. In the process, the pressure exerted by the gas stretches the segments of the polymer network present in the shell, i.e., it inflates the capsule (Figure S 3d).

The gap between core and shell can also be clearly seen in Movie 5 (SI), stills from which are shown in Figure S4 in the SI. In this experiment, a capsule with an alginate core and a DMAA shell was placed in a H_2O_2 solution, whereupon it inflated. But before the inflation proceeded to the point of explosion, the capsule was removed from the H_2O_2 solution. Thus, the capsule is in a stable, but inflated state. In Movie 5, the inflated capsule is held with tweezers and twirled around. One can clearly see the core rolling inside the capsule, which implies that the core has separated from the shell and become free to move (also shown in Figure S4). No bubbles of gas are visible in the capsule; i.e., the bubbles seem to have dissipated, even though the capsule remains in an inflated state. Interestingly, this inflated capsule can be stored in water and it retains its size for at least a week.

The schematics in Figure 8 depict the sequence of events during inflation and explosion. Initially (Figure 8A), when the capsule is placed in H_2O_2, the core and shell are weakly adhered. The segments between adjacent cross-links in the shell-network are loose and unstretched. When O_2 gas is produced due to the catalytic reaction in the core, the gas creates a gap between the core and the shell (Figure 8B). As this gap widens, the segments in the shell-network become stretched significantly due to the gas pressure. This stretching cannot continue indefinitely. At some point, the stress in the shell becomes so high that it exceeds the yield stress or stress-at-break of the network. When this point is reached, the shell ruptures (Figure 8C). The retraction force when the stretching of the shell is suddenly released will be proportional to the elastic modulus of the network (much like the spring constant of a spring). This retraction force is responsible for core ejection. Thus, a stiffer network will experience a more violent ejection, which is consistent with our findings.

Other Ways to Inflate Capsules. So far, we have shown capsule inflation using O_2 produced by the Ag-catalyzed decomposition of H_2O_2. We have also examined whether other gas-producing reactions could be utilized for capsule inflation. First, instead of a catalyst, we introduced *insoluble particles* of calcium carbonate ($CaCO_3$) into the core of our capsules. The particles (10 μm in diameter, 5 wt %) were again added to the alginate solution in the first step of the capsule synthesis. When the resulting capsule (alginate core, NIPA shell) is placed in a solution of glacial acetic acid (CH_3COOH), a reaction occurs that generates carbon dioxide (CO_2) gas in the core. Figure 9A shows that this amount of gas is sufficient to inflate the capsule to a size that is 78% larger than the original size. In this case, 5 wt % $CaCO_3$ was not enough to make the capsule rupture after inflation. However, capsules with 10 wt % $CaCO_3$ produced enough CO_2 to not only inflate the capsule but also ultimately rupture the shell.

Next, we tried a *water-soluble reagent*, i.e., sodium bicarbonate ($NaHCO_3$) in the capsule core instead of insoluble $CaCO_3$ particles. For this case, 5 wt % $NaHCO_3$ was added to the alginate solution in the first step of the capsule synthesis. This concentration was above the solubility limit of $NaHCO_3$, and so the aqueous solution was turbid because some of the $NaHCO_3$ was suspended as particles. Nevertheless, the solution appeared homogeneous when stirred, and it was used to prepare alginate core gels and subsequently a capsule with a NIPA shell. When this capsule is placed in glacial acetic acid, the reaction between the soluble $NaHCO_3$ and CH_3COOH again generates CO_2 gas. The gas inflates the capsule to a size that is 24% larger than the original size (Figure 9B), and this amount of gas is insufficient to rupture the capsule. The lower extent of gas evolution and thereby inflation is likely because the molecules of $NaHCO_3$ can diffuse out of the core into the external solution while the reaction is going on. This is in contrast to the cases of Ag or $CaCO_3$ particles, which are both too large to diffuse out of the

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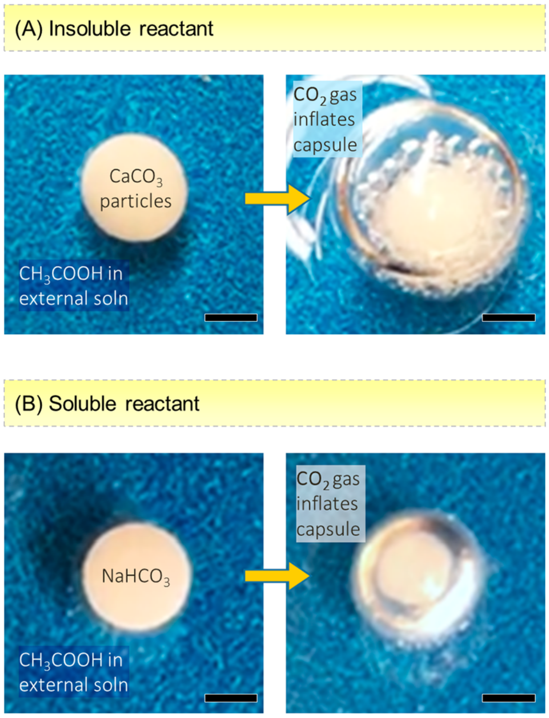

Figure 9. Capsule inflation by noncatalytic reactions. In both cases, the capsules have a NIPA shell. (A) The core has 5 wt % $CaCO_3$ particles (insoluble), and the capsule is placed in CH_3COOH. The capsule inflates by about 78% due to the formation of CO_2. (B) The core has 5 wt % $NaHCO_3$ (a soluble reagent), and the capsule is again placed in CH_3COOH. The capsule inflates by about 24%, again due to CO_2. Scale bars: 3 mm.

core.[31] One crucial point about the approaches in Figure 9A,B is that they both rely on a chemical reaction that is not catalytic. Thus, the reagents in the capsule core, whether $CaCO_3$ or $NaHCO_3$, will be used up by the reaction. That is, the core reagent is the limiting reactant, and the inflation will stop when this is completely consumed. In contrast, in the case of a catalytic core, inflation will occur as long as there is reagent in the external solution; hence, such inflation can continue for a much longer time.

■ CONCLUSIONS

In summary, we have designed capsules that spontaneously inflate due to the gas generated by a chemical reaction in the capsule core. This behavior seems to arise only for capsules made by an “inside-out” technique, where the capsule core is a physical gel whereas the shell is a chemically cross-linked gel. Inflation occurs for a variety of gas-generating reactions; the typical one we have used is the catalytic decomposition of a chemical fuel (H_2O_2) in the external solution to produce O_2. The reason why inflation occurs is that the gas remains contained in the capsule (between the core and the shell); thereby, the gas pressure causes the shell to stretch. If inflation is allowed to continue (and if there is sufficient fuel), the capsule shell eventually ruptures. Rupture occurs when the chain segments between cross-links in the capsule shell are stretched beyond their breaking point. This rupture can be gentle (e.g., for an AAm shell), in which case the core and shell stay together. Conversely, the rupture can be explosive, and in an extreme case (for a shell of DMAA), the core gets violently ejected out of the capsule.

We have highlighted the analogy between the behaviors exhibited by our capsules to naturally occurring phenomena such as the swelling of pufferfish and needle-ejection from jellyfish. The ability to tune the extent and duration of inflation, and also the intensity of the explosion, could make our capsules potentially useful. Attempts to use nematocysts isolated from sea anemones in topical drug delivery are already under way.[29,30] In those studies, the needles ejected out of nematocysts have been shown to penetrate the skin of mice. For skin-penetration to occur, the needle has to be discharged very rapidly (in <1 ms), and the pressure at the site of impact has to be >1 GPa. These will be some of the challenges for our system to be applicable in the same manner. In future studies, we will explore the ability of exploding capsules to deliver both needle-like objects as well as large doses of specific solutes.

■ EXPERIMENTAL SECTION

Materials. The monomers *N*,*N*′-dimethylacrylamide (DMAA), acrylamide (AAm), and *N*-isopropylacrylamide (NIPA) and the accelerant *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine (TEMED) were from TCI America. Hydrogen peroxide (30% solution) was purchased from BDH Chemicals and glacial acetic acid from Fisher Scientific. Sodium bicarbonate ($NaHCO_3$) and calcium carbonate ($CaCO_3$) particles (10 μm size) were from J.T. Baker. All other chemicals were from Sigma-Aldrich. Two biopolymers were used: alginate, i.e., medium viscosity alginic acid, sodium salt from brown algae, and xanthan gum (from *Xanthomonas campestris*). Other chemicals included *N*,*N*′-methylenebis(acrylamide) (BIS), calcium chloride dihydrate ($CaCl_2$) salt, ammonium persulfate (APS), and silver (Ag) microparticles (μPs) (average size of 2 to 3.5 μm). Deionized (DI) water was used in all experiments.

Preparation of Alginate Gel Beads. Alginate beads formed the core of the capsules developed in this study. The beads additionally contained either Ag μPs (Figures 2−7) or $CaCO_3$ or $NaHCO_3$ (Figure 9). To prepare the beads, first, a 2 wt % solution of alginate in DI water was made. Ag μPs were suspended in this solution at a typical concentration of 2 wt % (in some experiments, this was increased up to 15 wt %). In the case of $CaCO_3$ particles, the concentration used was 5 or 10 wt %. In the case of $NaHCO_3$, it was added at 5 wt %. At this concentration, the $NaHCO_3$ could not be fully solubilized in the alginate solution. Thus, all the three above samples appeared turbid due to the suspended particles. Samples were sonicated for a minute and then loaded into a syringe to which a 22-gauge needle was attached. Droplets of each sample were then added to a reservoir of 0.5 M $CaCl_2$ in DI water. The Ca^{2+} ions cross-link the alginate chains, thus converting the droplets into gelled beads. The size of the droplets, which was also the size of the beads, could be altered by changing the needle diameter. Typically, with the 22G needle, the bead size was 4−5 mm. After 20 min of incubation in the reservoir solution, the gelled beads were washed and stored in DI water.

Preparation of Capsules. The above gelled beads were used as the core templates for capsule synthesis, which followed the procedure reported by us in a previous paper.[31] First, the cores were soaked in a 15 mg/mL solution of the initiator APS for 2 min. The APS-loaded cores were then transferred to a second solution containing monomer, cross-linker (BIS), the accelerant (TEMED), and xanthan gum. Three different monomers were used: DMAA, NIPA, and AAm. The monomer concentration was kept at 1 M while the BIS concentration was typically 2.2 mol % with respect to the monomer. TEMED (1.5 mg/mL) was used, which allowed the polymerization to proceed at room temperature. The xanthan gum was added at 0.5−0.75 wt % to increase the solution viscosity; thereby, the cores remained suspended during the reaction. Polymerizations were conducted at room temperature for 15 min, and this resulted in a shell of chemically cross-linked polymer around the alginate cores. The capsules thus formed were washed and stored in DI water.

To make the 2-shell and 3-shell capsules studied in Figure S2, the above procedure was repeated using the single-shelled capsule as the template. That is, a capsule with a single NIPA shell was placed in the APS solution for 2 min then transferred to a NIPA solution. After polymerization at room temperature for 15 min, a 2-shell capsule was obtained. This was washed with DI water, and the same procedure was repeated to obtain a 3-shell capsule.

Preparation of Gels. Individual gels were synthesized, either for control experiments (Figure 3B) or for rheological studies. For each gel, two solutions were made: one with the monomer and the second with the initiator. The monomer solution contained 1 M monomer (NIPA, DMAA, or AAm), cross-linker (BIS, typically 2.2 mol % with respect to the monomer), 0.15 g of TEMED, 2 wt % Ag μPs, and 6 g of DI water. In the initiator solution was 0.15 g of APS in 3 g of DI water. Both solutions were cooled to 5 °C (this was done because the reaction is exothermic). The two cooled solutions were mixed together, and the mixture was left to sit in a Petri dish at room temperature. The polymerization occurred immediately and was completed within about 20 min. The final gel was washed and stored in DI water. For the experiment in Figure 3B, a piece of the gel ($10 \times 10 \times 4$ mm) was cut and placed in 30% H_2O_2. For rheological experiments, a disc of 20 mm diameter and 4 mm thickness was cut from the above gel and used.

Rheological Studies. All rheological experiments were run on an AR 2000 rheometer (TA Instruments) at 25 °C using a parallel plate geometry (20 mm in diameter). For the oscillatory shear (dynamic rheology) experiments, gel discs, synthesized as above, were used. The linear viscoelastic region of each sample was obtained by stress-sweep experiments, and a strain within this region (typically 1%) was used to run the frequency-sweep experiments.

Imaging of Capsules. Movies of capsule inflation were typically taken on an iPhone 5SE and edited using Windows MovieMaker. A homemade "light box" was used in some cases to set the lighting for these movies. In addition, a high-speed movie of capsule inflation (Movie 4 and Figure S3) was taken using a Vision Research Phantom Miro M110 camera at 600 fps (1666 μs exposure, f/2.8). Lighting of the scene was supplemented with an external LED source. Movies were limited to 30−45 s due to the high frame rate. Bright-field images of capsules were also captured with an optical microscope (Zeiss Axiovert 135 TV) using a 2.5× objective. In some cases, the microscopy was performed with slight under-focus, which helped to clearly define the outlines of the layers and/or the overall capsule.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b02174.

> Effects of AgμP and H_2O_2 concentrations on capsule rupture (Figure S1). Effect of the number of shells on capsule inflation and rupture (Figure S2). Stills from a high-speed movie of capsule inflation showing the core-shell gap (Figure S3). Stills from a movie of an inflated capsule removed from H_2O_2 solution showing the core-shell gap (Figure S4) (PDF)
>
> Inflation and rupture of a capsule with a shell of NIPA (Movie 1) (MP4)
>
> Inflation and rupture of a capsule with an AAm shell (Movie 2) (MP4)
>
> Inflation and rupture of a capsule with a DMAA shell (Movie 3) (MP4)
>
> High-speed movie of capsule inflation showing the core-shell gap (Movie 4) (MP4)
>
> Inflated capsule removed from H_2O_2 solution showing the core-shell gap (Movie 5) (MP4)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sraghava@umd.edu.

ORCID

Srinivasa R. Raghavan: 0000-0003-0710-9845

Notes

The authors declare no competing financial interest.

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Supporting Information for:

Catalyst-Loaded Capsules that Spontaneously Inflate and Violently Eject their Core

Kerry C. DeMella and Srinivasa R. Raghavan*
Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111
*Corresponding author. Email: sraghava@umd.edu

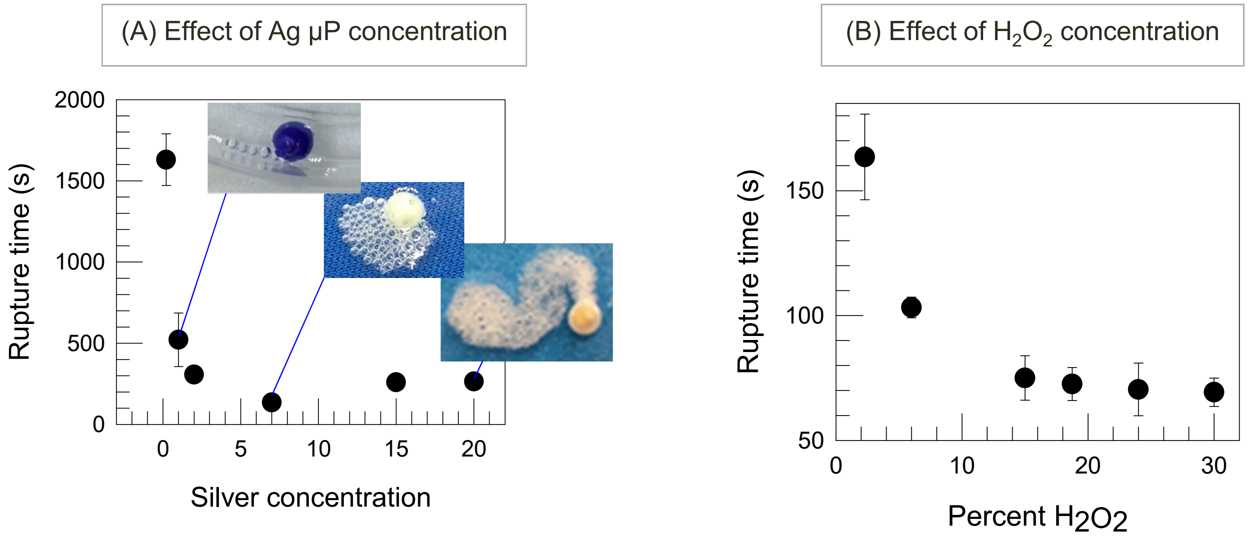

Figure S1. Effects of two parameters on capsule inflation and rupture. The capsules tested had an alginate core and a shell of NIPA crosslinked with 2.2 mol% BIS. (A) Silver microparticle (Ag µP) concentration in the alginate core. For these tests, capsules were placed in 30% H_2O_2 at $t = 0$. (B) H_2O_2 concentration. The capsules tested had 10 wt% of Ag µPs in their core. They were placed in solutions with different concentrations of H_2O_2 at $t = 0$. The plots show that the time to rupture decreases with increasing particle and H_2O_2 concentrations. The extent of inflation was unaffected. The inset images in (A) are for capsules right after rupture and reveal that, the higher the Ag µPs, the more the gas bubbles produced. The error bars in the plots are standard deviations calculated from multiple measurements.

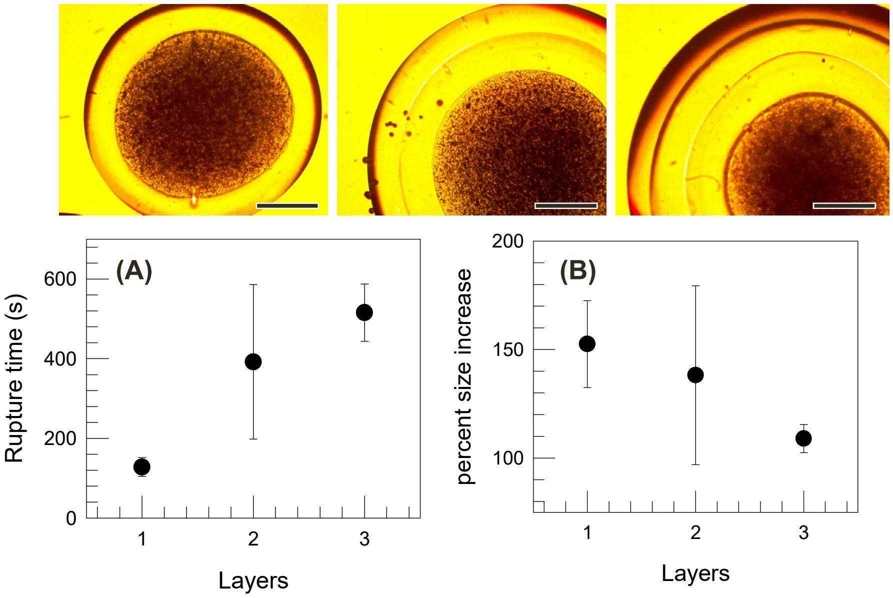

Figure S2. Effect of the number of shells on capsule inflation and rupture. Capsules were made with 1, 2, or 3 identical shells (see images, scale bars 1 mm) of NIPA crosslinked with 2.2 mol% of BIS. All capsules had 2 wt% Ag in the core and were placed in 30 wt% H_2O_2 for these measurements. Plots are shown for the rupture time (A) and size increase (%) (B) vs. the number of layers. The error bars are standard deviations calculated from multiple measurements.

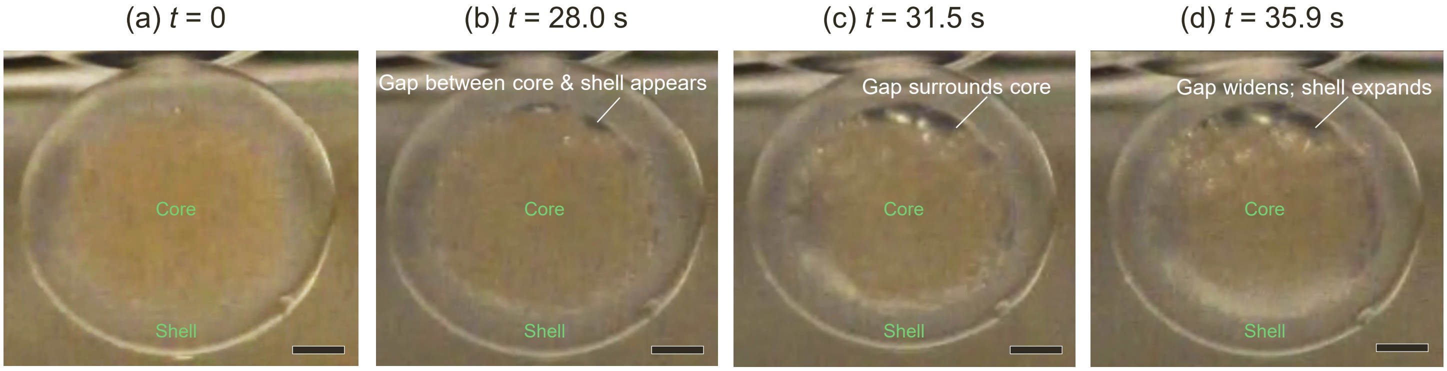

Figure S3. Stills from a high-speed movie of capsule inflation showing the formation of a gap between the core and shell. The experiment was designed for a 30-45 s time-frame due to camera limitations. The capsule was chosen for fast rupture and low inflation so that it remained in focus during the process. The capsule contains 7 wt% Ag µPs in its core and a shell of DMAA crosslinked with 8.8 mol% BIS. It is placed in 30% H_2O_2 at t = 0. **(a)** Initially, the shell and core of the capsule are in close contact. **(b) and (c)** Around the 28 s mark, bubbles of O_2 gas are seen to form, and these collect in a gap between the core and the shell. **(d)** As more gas is produced, this gap widens, and the shell is thereby stretched. This expansion (i.e., capsule inflation) continues until the shell ruptures. Scale bars: 1 mm. The corresponding movie (Movie 4) is provided in the SI.

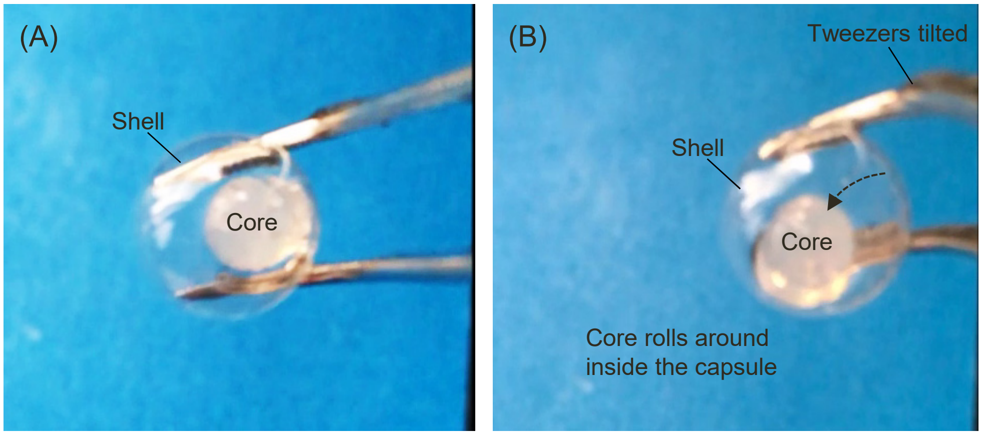

Figure S4. Stills from a movie showing an inflated capsule removed from H_2O_2 solution. The capsule has a NIPA shell and was inflated to about double its original size by placing in 30% H_2O_2. Before it ruptured, the capsule was removed from the H_2O_2 solution using tweezers. (A) In this inflated state, the capsule remains stable and there is a clear gap between the core and the shell, filled with O_2 gas. The core is roughly its original size (no inflation) while the shell has expanded. (B) Since the core is a spherical alginate gel, it can roll around inside the capsule when the tweezers are tilted. Scale bars: 3 mm. The corresponding movie (Movie 5) is provided in the SI.