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Multi-Layered Marble for Hydrogel Encapsulation

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ABSTRACT: Hydrophobic skins on fruits play a crucial role in preventing dehydration and shielding against environmental stress. Inspired by this natural structure, hydrophobic encapsulation is widely employed to preserve the functionality and long-term stability of hydrogels. However, instability at the interface between hydrophobic shell and hydrogel remains a critical challenge. Here, we present a hydrogel encapsulation strategy to stabilize the incompatible interface using a concept of liquid marble, where liquid droplet is covered with hydrophobic particles. A uniform nonpolar liquid layer is first formed on the hydrogel surface through interfacial bridges with hydrophobic particles. A secondary hydrophobic particle layer is then deposited onto this liquid layer to prevent leakage, yielding a multi-layered marble (MLM) structure. This MLM-encapsulation is highly versatile, accommodating various hydrogels, liquids, and structural configurations. By maintaining hydrogel performance and functionality across diverse applications, MLM-encapsulation provides a universal and robust solution for overcoming the long-standing interfacial instability problem.

Introduction

Analogous to biological cells and tissues that constitute living organisms, hydrogels possess distinctive properties with a three-dimensional polymeric network structure predominantly filled with water, typically exceeding 50% of their weight.^{1, 2, 3, 4, 5, 6} The solid phase generally consists of hydrophilic polymers crosslinked into a network capable of retaining large amounts of water or aqueous solutions. This architecture enables hydrogels to be applied in diverse fields, including soft robotics,^{7, 8, 9} drug delivery,^{10, 11, 12} tissue engineering,^{13, 14, 15} water harvesting,^{16, 17, 18} and cosmetics.^{19, 20} However, when hydrogels are directly exposed to external environments, their practical applications become severely limited due to rapid dehydration and susceptibility to environmental stress.²¹ Effective encapsulation on hydrogels promises long-term stability by preventing dehydration and protecting against undesirable environmental conditions.

Nature addresses these vulnerabilities through adaptive strategies. For example, mammalian skin is a hydrophobic composite of polymers and oily substances, where intercellular lipids form an essential barrier against environmental stress.^{22, 23, 24} Similarly, many fruits develop a hydrophobic epicarp (skin) consisting of multiple cellular layers to safeguard the hydrophilic mesocarp (flesh), which is rich in water and nutrients.^{25, 26, 27} Typically, the epicarp includes an outer cuticle composed of fatty acids and hydrophobic waxes, and an inner hypodermis that interfaces directly with the flesh, together providing robust protection. Inspired by these natural passivation strategies, hydrophobic encapsulation using oily substances presents a promising

pathway to protect hydrogels under diverse environmental conditions, thereby extending their practical applicability.

Despite this promise, achieving effective hydrophobic encapsulation of hydrogels remains challenging due to their inherently superhydrophilic nature, characterized by high water content and extensively hydrated surfaces. Previous attempts have largely focused on solidified polymer-based coatings, including direct chemical bonding of polymeric layers to hydrogel surfaces, elastomer adhesion,^{22, 28, 29, 30} organogel coating,^{6, 31, 32} and polymer-brush grafting^{23, 24, 27} (**Table 1**). However, such approaches often lead to undesirable side effects, including mechanical alterations,^{33, 34} free radical generation,^{6, 24} and local pH changes.^{23, 27} More recently, oil-swollen polymer encapsulation methods have been explored, but their applicability is restricted by harsh processing conditions, such as prolonged reaction times (>1 h) and high temperatures (up to 120 °C).^{23, 24} Thus, the development of a versatile and facile encapsulation method remains an unresolved challenge for expanding hydrogel applications.

Here, we propose a hydrogel encapsulation strategy for creating uniform, highly stable hydrophobic shells around hydrogels by stabilizing the hydrogel/oil interface through the concept of liquid marble—a liquid droplet coated with hydrophobic particles.^{35, 36, 37, 38, 39, 40, 41} Building on this idea, we introduce a multi-layered marble (MLM) structure consisting of three layers: i) a primary particle layer, ii) an oil layer, and iii) a secondary particle layer. The primary particle layer first covers the hydrogel surface, forming interfacial bridges that enable stable oil deposition. This stabilized interface facilitates the formation of a uniform oil layer on the hydrogel. Subsequently, a secondary particle layer coats the outer liquid layer, effectively suppressing leakage. In this way, the MLM structure stabilizes the oil/water interface, forming a robust oil film on water and

providing a solution to long-standing interfacial mismatching issues in general.

The MLM shell effectively prevents water evaporation, thereby preserving the intrinsic properties of hydrogels over extended periods in air. Notably, although the hydrogel is almost completely encapsulated, the fluidic MLM shell allows reversible opening and closing, enabling additional control even after encapsulation. Furthermore, the oil phase within the MLM can be tuned between liquid and solid states, depending on mechanical requirements. Owing to these features, the MLM shell significantly broadens the scope of hydrogel-based applications, including actuators, microreactors, and cell storage systems, by providing long-term stability and functional adaptability.

Results

Fabrication of the MLM shell on hydrogels

The MLM shell was designed as a hydrogel coating composed of an intermediate oil layer stabilized between two distinct particle-assembled layers (**Figure 1**). In principle, particles ranging in size from the sub-micrometer to millimeter scale, consistent with those typically used in liquid marble fabrication, can be applied. However, to form stable marble structures, both size of particles and the ratio of particle to hydrogel diameter should be carefully considered.^{42, 43} To achieve the required hydrophobicity and/or oleophobicity, these particles must possess low surface energies.^{44, 45, 46, 47} In this study, we primarily employed glass microparticles with two distinct size ranges (diameters: 200–300 μm and 0–50 μm) to fabricate the MLM shells with good performance. Specifically, larger particles were used for primary particle layer to ensure high interfacial stability,

while smaller particles were utilized for secondary particle layer to achieve high mechanical durability. The particle size distributions were determined by optical microscope images (**Figure S1**). The diameters of the larger glass beads ranged from 200 to 300 μm (average: $225 \pm 18.8 \mu\text{m}$), whereas those of the smaller beads ranged from 7 to 50 μm (average: $11.7 \pm 9.2 \mu\text{m}$).

For the primary particle layer, the particle surfaces were modified with a hydrocarbon self-assembled monolayer (HSAM), enabling their assembly onto the hydrogel surface. Water wettability test on HSAM-treated particles (hereafter referred to as HSAM particles) revealed that the water droplet maintained a spherical shape and formed stable liquid marble structure driven by the minimization of interfacial energy associated with particles adsorption at the water/air interface, analogous to the principles governing liquid marble formation,^{36, 38} while the water immediately fully wetted on bare particles (**Figure S2**). Taking advantage of the inherently hydrated layer on hydrogel surfaces, the primary particle layer was prepared by gently rolling the hydrogel over a bed of HSAM particles. The HSAM particles readily adhered to and assembled on the hydrogel surface like as Cheerios effect⁴⁸, forming a hydrogel marble.^{49, 50} As shown in the bottom images of **Figure 1**, the hydrogel marble perfectly confines hydrogel, preventing direct contact with solid substrates. By contrast, bare hydrogels placed on glass surfaces exhibited water leakage. To enhance visual clarity, red dye was incorporated into the hydrogel. When oil (dyed blue) was subsequently deposited onto the hydrogel marble, it coated the primary particle layer but quickly drained to the underlying glass substrate, indicating that oil stabilization by the primary layer alone was insufficient. Meanwhile, the oil was readily dewetted from the bare hydrogel surface (**Figure S3**). To address this, we introduced a secondary particle layer treated with a fluorinated self-assembled monolayer (FSAM), which possesses a lower surface energy than oil. This secondary particle layer successfully stabilized the oil layer and yielded a sandwich-like MLM shell with a

solid outer surface.

Importantly, bare hydrogels resist oil spreading because of their highly hydrated surfaces, making hydrophobic coating particularly challenging. The introduction of the primary particle layer solved this issue. The interstitial spaces between particles facilitated oil film formation via capillary-driven imbibition (**Figure 2a**).^{51, 52} During this process, a curvature gradient develops between the upstream (where oil initially contacts particles) and the downstream (as oil advanced through the interstices). This gradient generated a Laplace pressure difference, which in turn induced a “meniscus pumping” effect that further accelerates oil spreading between adjacent particles (**Figure 2b**).^{53, 54, 55, 56} This effect was clearly demonstrated when oil was dropped onto the HSAM particle coated hydrogel surface by snapshots of optical microscopy (**Figure 2c**). Owing to meniscus pumping, oil spontaneously spread across the entire hydrogel surface. A comparison of different hydrogel surfaces (**Figure 2d**) showed that oil remained as a droplet on bare hydrogels, whereas on HSAM particle coated hydrogel it spread uniformly to form a continuous film. Although FSAM-treated particles (hereafter referred to as FSAM particles), could also form a particle layer on the hydrogel, oil spreading was less effective compared to the HSAM particle layer. This reduced performance is attributed to the lower surface energy of FSAM relative to oil, which decreases wettability.^{57, 58} For this reason, the HSAM particle layer was selected as the primary particle layer of the MLM, serving as an interfacial bridge that enables the formation of a uniform and stable oil layer.

In contrast, the secondary particle layer required low wettability toward oil to prevent oil leakage, as shown in **Figure 1**. Based on principles established for liquid marbles, the outer stabilizing particles should have oleophobicity.^{59, 60} For this reason, FSAM-treated particles were

chosen for the secondary particle layer. The oleophobicity of FSAM particles were evaluated through the wettability test of oil (**Figure S2**). Deposited castor oil droplet maintained spherical shape on FSAM particles and formed stable liquid marble structure upon particle coating. As shown in **Figure 2e**, the oil-coated hydrogel marble without the secondary layer moved sluggishly across a glass slide and left oil traces due to leakage. In contrast, the secondary particle layer produced a solidified outer shell that allowed the MLM-encapsulated hydrogel to slide freely on glass without oil residues (**Figure 2f**).

We evaluated the surface chemistries of the particles in each layer using Pickering emulsion theory. The key parameters governing particle stability at the water/oil interface are the spreading coefficient of water in oil, $S(w/o)$, and the particle attachment energy (E_{att}) by employing the **Equation 1** and **2** as various oils from the theory of Pickering emulsion (water in oil).^{61, 62, 63} The spreading coefficient quantifies how the water spread over the particle surface in oil; a negative value of spreading coefficient indicates that water does not spontaneously spread over the surface of particle and that the particle remain adsorbed at the oil/water interface.⁶⁴ The particle attachment energy is the energy to detach the particle from the water/oil interface; when the particle attachment energy is greater than the thermal energy of Brownian motion ($k_B T$), the particle is irreversibly adsorbed at the water/oil interface.

$$S(w/o) = \gamma_{os} - \gamma_{ow} - \gamma_{ws} \quad (1)$$

$$E_{att} = -\pi R^2 \gamma_{ow} (1 - |\cos(\theta_{ow})|)^2 \quad (2)$$

To calculate $S(w/o)$ and E_{att} , we first determined the interfacial energies (γ_{os} , γ_{ow} , and γ_{ws}) and the equilibrium three-phase contact angle (θ_{ow}). Sessile drop measurements (**Table S1**) were

used to estimate the surface energies of HSAM and FSAM surfaces using **Equation 3**^{65, 66}; the polar and dispersive components of water (polar component : $\gamma_w^p = 51.0$ mN/m, dispersive component : $\gamma_w^d = 21.8$ mN/m) and ethylene glycol (polar component : $\gamma_{EG}^p = 19.0$ mN/m, dispersive component : $\gamma_{EG}^d = 29.0$ mN/m) (**Table S2**).⁶⁷

$$\gamma_{lv}(1+\cos\theta) = 2(\gamma_{sv}^d\gamma_{lv}^d)^{1/2} + 2(\gamma_{sv}^p\gamma_{lv}^p)^{1/2} \quad (3)$$

Then, we calculated the interfacial energies of water/solid (γ_{ws}) and oil/solid (γ_{os}) on the HSAM and FSAM surfaces using **Equation 4**⁶⁸ with the sessile (**Table S1**) and pendant (**Table S3**) drop measurements of various oils. In **Table S1**, the interfacial energies of oil / HSAM ($\gamma_{os, HSAM}$) are substantially lower than those of FSAM ($\gamma_{os, FSAM}$), with silicone oil as an exception; this exception reflects the similarly low surface energies of silicone oil and FSAM.^{69, 70}

$$\gamma_{ws} = \gamma_{sv} - \gamma_{wv}\cos(\theta_w), \quad \gamma_{os} = \gamma_{sv} - \gamma_{ov}\cos(\theta_o) \quad (4)$$

Using **Equations 1–4** and the measurements (**Tables S1–S3**), we obtained negative values of spreading coefficients, indicating favorable oil spreading on both HSAM and FSAM particle surfaces and enabling the formation of stable oil layer. In addition, the particle attachment energies were several orders of magnitude greater than $k_B T$ (**Table S2**), indicating irreversible particle adsorption and excellent interfacial stability. Nevertheless, HSAM is more effective than FSAM at promoting oil spreading on hydrogel surfaces because HSAM exhibits better oil wettability for most oils (consistent with **Figure 2d**). This is attributed to inherently oleophobic nature of FSAM surface, due to its lowest surface energy.^{57, 58}

Furthermore, to evaluate the driving force responsible for oil spreading, we systematically calculated the capillary force (F_c), which originates from the combined imbibition and meniscus

pumping. The packing density of primary particle layer was quantified to be $88 \pm 2\%$, corresponding to porosity ($100\% - \text{packing density}$) of $12 \pm 2\%$. The total energy difference (ΔE) between hydrogel marble ($E(i)$) and oil covered hydrogel marble ($E(f)$) was calculated using **Equations 5 and 6**.

$$E(i) = S_s\gamma_{sv} + S_w\gamma_{wv} + S_{ws}\gamma_{ws}, \quad E(f) = S_s\gamma_{so} + S_w\gamma_{ow} + S_o\gamma_{ov} + S_{ws}\gamma_{ws} \quad (5)$$

$$\Delta E = E(i) - E(f) = S_s(\gamma_{sv} - \gamma_{so}) + S_w(\gamma_{wv} - \gamma_{ow}) - S_o\gamma_{ov} = F_c d \quad (6)$$

where S_s , S_w , S_{ws} , and S_o are surface areas of particles assumed as hemisphere, thin water layer on hydrogel, particles contact with hydrogel assumed as hemisphere, and oil layer, respectively. γ_{sv} , γ_{wv} , γ_{ws} , γ_{so} , γ_{ow} , and γ_{ov} are interfacial energies at particle/air, water/air, water/particle, particle/oil, oil/water, and oil/air, respectively. d denotes distance of oil wetting. By substituting the experimentally determined interfacial energies obtained from **Table S1, S2, and S3** into the **Equations 5 and 6**, the ΔE and F_c were theoretically estimated to be $0.17 \mu\text{J}$ and 0.14 mN , respectively.

Accordingly, we implemented the MLM-encapsulation on hydrogels by combining two particle layers with sandwiched oil layer: HSAM particles as the primary interfacial stabilizers (enhancing oil wettability and stabilizing the water/oil interfacial energy) and FSAM particles as the secondary stabilizers (stabilizing the oil/air interfacial energy and producing a solid outer surface). Additionally, to verify the reproducibility and reliability of the MLM shell, we systematically monitored the weight of the castor oil layer in 20 independently prepared samples fabricated on spherical hydrogels (diameter: 8 mm). Under these identical fabrication conditions, the oil layer weight was consistently measured as $76.6 \pm 0.1 \text{ mg}$, indicating excellent

reproducibility of the coating process. Assuming ideal spherical geometries for both the hydrogel core and the MLM, the theoretical oil layer thickness was calculated to be $529 \pm 1 \text{ }\mu\text{m}$.

MLM shell for anti-dehydration

Hydrogels exposed to ambient air readily lose water through evaporation within a few hours, leading to the deterioration of their intrinsic properties. The MLM-encapsulation effectively suppresses dehydration by forming a protective, non-volatile oil layer around the hydrogel (**Figure 3a**). To evaluate this anti-dehydration performance, we monitored the weight changes of poly(acrylic acid) (PAA) hydrogels under four conditions: bare hydrogel, hydrogel marble, oil-coated hydrogel marble, and MLM-encapsulated hydrogel (**Figure 3b** and **3c**). Castor oil was used as the encapsulating medium of the MLM, and the hydrogels were stored in air (temperature = $20.1 \pm 0.1 \text{ }^{\circ}\text{C}$, relative humidity < 20%) for 7 days. The bare hydrogel and hydrogel marble were almost completely dehydrated and shrank within 1 day, as their water-rich surfaces were directly exposed to the atmosphere. In contrast, the MLM-encapsulated hydrogel retained more than 90% of its initial weight. Notably, the oil-coated hydrogel marble without secondary stabilizing particle layer gradually dehydrated due to oil leakage (see **Figure 1**), further highlighting the importance of the secondary particle layer in maintaining stability.

Consistent with our theoretical analysis of spreading coefficients and particle attachment energies with a range of oils, including castor oil, paraffin oil, silicone oil, and soybean oil, (**Table S2**) the HSAM particles effectively promoted the formation of thin oil layer on the hydrogel surface while preserving high interfacial stability. Stable MLM-encapsulations were achieved as

varying the hydrophobic oils. In all cases, MLM-encapsulated hydrogels preserved more than 70% of their water content after 7 days (**Figure 3d** and **S4**). In addition, the effect of oil viscosity on MLM structure was investigated utilizing silicone oils with different viscosities (10, 100, and 1000 cSt), whose surface tensions are nearly identical (20.1, 20.9, and 21.2 mN/m, respectively). Depending on viscosity, the wetting speeds of oils were changed, as lower viscosity oil exhibited higher mobility. Nevertheless, the resulting MLM was stably formed on the hydrogels, regardless of oil viscosity. Consistent with these observations, the spreading coefficients of water in oil ($S(w/o)$) and particle attachment energies (E_{att}) for the different silicone oils were theoretically predicted to be nearly identical. The versatility of this approach was further confirmed with different hydrogel types, including polyacrylamide (PAAm), poly(N-isopropylacrylamide) (PNIPAm), polyethylene glycol diacrylate (PEGDA), and poly(vinyl alcohol) (PVA). All hydrogels retained more than 80% of their initial water content after 7 days of MLM-encapsulation (**Figure 3e** and **S5**). Moreover, the anti-dehydration performance of the MLM-encapsulation was evaluated under various conditions, including high relative humidity (RH > 80%), mechanical fatigue (bending), UV exposure (UVA, 10 mW/cm²), and temperature cycling by alternately storing the samples in an oven (80 °C) and a refrigerator (5 °C) for 30 min each (**Figure S6**). Under high-RH conditions, water retention increased to $105.2 \pm 0.2\%$ after 7 days, which was attributed to water vapor penetration through the MLM layer. Under mechanical fatigue and UV exposure, water retention decreased to $85.2 \pm 0.1\%$ and $90.9 \pm 0.2\%$ after 7 days, respectively. During temperature cycling for 5 cycles, water retention decreased by approximately 3% after each high temperature (80 °C) treatment, while no significant change was observed at low temperature (5 °C). Notably, even for hydrogels with complex geometries, such as alphabet-shaped structures, MLM-encapsulated samples exhibited clearly suppressed water evaporation, demonstrating the

robustness and versatility of the coating (**Figure 3f**).

The effective anti-dehydration capability of the MLM shell also enables free-standing, hydrogel-based cell storage systems. As a demonstration, human dermal fibroblast (HDF) cells were cultured for 3 days in gelatin methacryloyl (GelMA) hydrogels as the representative cell type which are widely used in tissue engineering e.g. extracellular matrix (ECM) production, tissue remodeling, and wound healing.^{13, 14, 15, 49, 71} Bare and MLM-encapsulated cell-laden hydrogels were stored in air for 1 day. Subsequently, the MLM coating was gently removed from the hydrogel by dipping in *n*-hexane for 1 min. Notably, because the MLM is physically established without chemical reactions, the encapsulation layer can be easily removed by washing with oil soluble solvent (**Figure S7**). The *n*-hexane washing process selectively removed the MLM shell without cytotoxicity, as the high-water content of the hydrogel effectively prevented solvent penetration. Owing to highly hydrated and strongly hydrophilic polymer network, non-polar solvents such as *n*-hexane exhibit low solubility and unfavorable partitioning within the hydrogel, resulting in minimal solvent penetration during short exposure periods.⁷² Cell viability ($99.9 \pm 0.1\%$ in GelMA before dehydration) was assessed using confocal fluorescence microscopy (**Figure 3g**). After storing 1 day in air, cells in the bare hydrogel were all dead (red color) because of dehydration of hydrogel (cell viability: 0%), while most cells in the MLM-encapsulated hydrogel were alive (green color) in water containing hydrogel (cell viability: $99.1 \pm 0.2\%$). Above results demonstrate the potential of MLM-encapsulation for creating free-standing hydrogel-based systems for cell storage.

Mechanical properties of MLM-encapsulated hydrogels

Previously reported encapsulation approaches mostly depended on solidified polymeric coatings. As summarized in **Table 1**, these coatings typically require thick and/or stiff layers, which substantially alter the intrinsic mechanical properties of hydrogels, most notably by increasing Young's modulus. In contrast, the MLM shell, composed of mobile particle layers and a fluidic oil layer, exerts negligible influence on the mechanical behavior of the underlying hydrogel. To evaluate this effect, we measured the tensile and compressive moduli of bare and MLM-encapsulated PAA hydrogels (**Figure 4a** and **4b**). The tensile and compressive moduli of MLM-encapsulated hydrogels (179.5 and 181.0 kPa) were nearly identical to those of bare hydrogels (188.3 and 187.6 kPa). After 7 days in ambient air, bare hydrogels dehydrated and stiffened dramatically (33.0 and 59.6 MPa), whereas MLM-encapsulated hydrogels retained mechanical properties similar to their initial state (195.8 and 204.8 kPa). These results demonstrate that MLM-encapsulation preserves hydrogel softness and enables their use in air, for instance in soft actuators, without compromising mechanical integrity.

Encouraged by this combination of softness and stability, we fabricated magnetically responsive hydrogel actuators by incorporating magnetic iron oxide nanoparticles into PVA hydrogels (**Figure 4c**). Both bare (**Figure 4d**) and MLM-encapsulated (**Figure 4e**) actuators initially exhibited reversible bending in response to a magnetic field, with comparable maximum bending angles of $\sim 45^\circ$, reflecting the negligible mechanical impact of the MLM coating. However, bare actuators ceased bending within 2 h in air due to dehydration, a longstanding limitation of hydrogel based soft actuators. In contrast, MLM-encapsulated actuators maintained full functionality under repeated mechanical stress for more than 7 days, highlighting the potential of MLM-encapsulation for long-term stability in air.

Beyond mechanical protection, the MLM shell also offers reversible permeability. The MLM can be temporarily opened and resealed: for example, a needle can puncture the shell to inject a solution into the hydrogel, after which the opening self-restores. Successful recovery of the punctured MLM shell was observed by optical microscopy (**Figure S8**). The MLM shell was easily pierced with a needle, allowing additional materials to be injected or removed from the hydrogel. Then, after removing needle, the MLM was immediately restored in few seconds due to its fluidic characteristic. To confirm complete restoration MLM, we measured the water retention of hydrogels with MLM coating for 7 days after 5, 10, and 20 needle puncture-recovery cycles (**Figure S9**). After 7 days, the MLM coating suppressed the dehydration of hydrogels even after needle punctures. The hydrogels preserved their weights with $88.5\% \pm 0.5\%$, $87.1\% \pm 0.2\%$, and $85.0\% \pm 0.2\%$ after 5, 10, and 20 puncture-recovery cycles, respectively. As the number of puncture-recovery increases, the anti-dehydration performance tends to decrease slightly because of oil loss on the needle, nevertheless, the MLM exhibited good anti-dehydration performance for 7 days after 20 puncture-recovery cycles. Using this property, we developed an injectable hydrogel microreactor. As a proof of concept, we carried out a glucose based enzymatic-cascade reaction involving glucose oxidase (GOX) and horseradish peroxidase (HRP).⁷³ PVA hydrogels containing GOX and HRP were encapsulated with the MLM shell (**Figure 4f**). A glucose aqueous solution containing potassium iodide (KI) was injected through the MLM into the hydrogel. GOX converted glucose and oxygen (O_2) into gluconic acid and hydrogen peroxide (H_2O_2), which was subsequently consumed by HRP to oxidize KI into iodine (I_2). The hydrogel turned dark brown, confirming successful reactant injection and cascade reaction. After needle withdrawal, the MLM coating spontaneously recovered its integrity, fully resealing the hydrogel. Thus, the MLM not only prevents dehydration but also isolates hydrogels and their reactants from external stress while

allowing on-demand reagent injection. These features establish MLM-encapsulated hydrogels as promising platforms for long-term, self-contained microreactors.

Solidification of MLM for rigid shell

In cases where rigidity is required, the MLM can be easily solidified by crosslinking or crystallizing the intermediate oil layer. We investigated two strategies for achieving this solidification (**Figure 5a**): (i) incorporating cross-linkable oils and (ii) using oils with melting points above room temperature. In the first approach, UV-curable urethane acrylate prepolymer (pre-PUA) and UV-curable polysilicone were introduced into the oil layer. Upon exposure to UV-A light (10 mW cm^{-2} , 365 nm) for 30 min, the pre-PUA and polysilicone crosslinked, forming a solid layer. In the second approach, melted paraffin wax (melting point: 53–58 °C) was applied to the MLM at ~60 °C and subsequently solidified upon cooling to room temperature. The resulting solidified MLM (S-MLM)-encapsulated hydrogels exhibited markedly enhanced mechanical robustness, in sharp contrast to both bare hydrogels and fluidic MLM-encapsulated hydrogels containing pre-PUA (**Figure 5b** and **S10**).

The S-MLM generated a hydrophilic core–hydrophobic shell structure analogous to natural fruits such as grapes, in which hydrophilic flesh is protected by a hydrophobic skin against environmental stress and dehydration (**Figure 5c**). The hydrogel/S-MLM interface, formed by crosslinked PUA, was visualized using OM (**Figure 5d** and **S11**). To differentiate between the primary and secondary stabilizing particles, two sizes of glass beads were used: larger beads for the HSAM-treated primary layer and smaller beads for the FSAM-treated secondary layer. The

OM images confirmed a well-defined layer-by-layer structure across the entire hydrogel surface, including the edge. A thin void was observed between the hydrogel surface and the primary particle layer, attributed to residual water from the native hydration layer on the hydrogel. This feature is consistent with top view image of oil-coated hydrogel marbles (**Figure S12**). The FSAM-treated secondary particle layer was positioned at the outermost surface, with the crosslinked PUA layer occupying the space between the two particle layers. Notably, the observed thickness of oil layer was $531 \pm 2 \text{ }\mu\text{m}$, which is closely consistent with the theoretical oil thickness estimated from weight measurement. The good agreement between theoretical and experimental values demonstrates that the MLM fabrication process yields uniform and well-controlled shells with high reproducibility.

Because both the FSAM particles and the solidified oil have low surface energies, the overall S-MLM surface is hydrophobic, allowing S-MLM-encapsulated hydrogels to float on water. For example, PAA hydrogels encapsulated with crosslinked PUA and FSAM-treated magnetic iron oxide nanoparticles as the secondary particle layer demonstrated a hydrogel-based boat that floated stably in water and responded to magnetic fields (**Figure 5e**). Such constructs illustrate the potential of S-MLM-encapsulated hydrogels for water floating microrobots or transport systems.

In addition, the S-MLM enables effective hydrogel passivation in various solvents. This capability was demonstrated by incubating hydrogels in dye solutions. As shown in **Figure 5f**, both bare and S-MLM-encapsulated PAA hydrogels with paraffin wax were immersed in an aqueous Rhodamine B solution. After 3 days, the bare hydrogel turned red, indicating dye penetration, whereas the S-MLM-encapsulated hydrogel remained unchanged. Dye obstruction was further confirmed more clearly after removing the S-MLM, which revealed a transparent

hydrogel with no detectable dye infiltration. Furthermore, the durability of the S-MLM shell was systematically evaluated in a wide range of solvents including polar solvents (water, ethanol, and acetone) and nonpolar solvents (*n*-hexane, cyclohexane, and toluene). S-MLM-encapsulated hydrogels using PUA and polysilicone as oil layer were immersed in each solvent for 3 days, and their weight changes were monitored before and after immersion (**Table S4**). In all cases, the samples exhibited no significant change in their weights ($< 2\%$), indicating that solvent penetration was effectively suppressed. These results confirm the robust resistance and long-term durability of the S-MLM-encapsulation in diverse solvents. Based on this surface passivation capability against various solvents, the viability of HDF cells contained in GelMA hydrogels was further assessed using UV-cured polysilicone due to excellent biocompatibility and effective anti-dehydration performance of silicone-based materials.^{74, 75, 76} After 3 days of incubation, both bare and S-MLM-encapsulated cell-laden hydrogels were immersed in ethanol (**Figure 5g**). In bare hydrogels, cells were rapidly damaged, with viability dropping to 0% within 10 min. In contrast, S-MLM-encapsulated hydrogels maintained over $99.2 \pm 0.1\%$ viability, confirming complete ethanol blocking. The swelling ratio of poly(dimethylsiloxane) (PDMS) in ethanol has been reported to be 1.04, indicating that ethanol molecules have limited ability to penetrate PDMS.⁷⁷ Because UV-cured polysilicone is chemically identical with PDMS, S-MLM shell was highly resistant to swelling in ethanol. Additionally, owing to effective passivation, the S-MLM-encapsulation successfully suppressed dehydration even under harsh conditions, including high vacuum and high temperature (**Figure S13**). The S-MLM-encapsulated hydrogels preserved $92.8 \pm 0.3\%$ after 3 hours under high vacuum ($\sim 10^{-4}$ Pa), enabling scanning electron microscopy observation without significant damage to the hydrogel. Under high temperature (80 °C), the water retention decreased to $85.3 \pm 0.1\%$ after 7 days. Notably, despite providing an isolated environment, the MLM

(including S-MLM) can be easily removed without damaging the underlying hydrogel, as it is physically rather than chemically bonded. This reversibility greatly broadens the potential of MLM-based hydrogels as incubators for biomaterials.

Discussion

In this study, we introduce an “Multi-layered marble” (MLM) structure that enables uniform coating of hydrogel surfaces with hydrophobic oils. Our MLM-encapsulation is an expanded concept of liquid marbles, and it represents stable hydrophobic shells around hydrogels by stabilizing the hydrogel/oil interface. The MLM consists of three layers: i) a primary particle layer, ii) an oil layer, and iii) a secondary particle layer. The primary particle layer, consisting of HSAM treated particles, stabilizes an unstable water/oil interface, thereby allowing a stable and uniform thin oil layer on hydrated hydrogel surfaces. The secondary particle layer, composed of FSAM treated particles, covers the oil layer that makes top surface solid again. Importantly, the oleophobicity of the FSAM-treated particles prevents oil leakage, ensuring long-term stability. The MLM provides highly effective dehydration suppression, enabling prolonged hydrogel stability in air. It also creates an isolated environment around hydrogels, which is advantageous for applications such as microreactors and cell incubators. A notable feature of MLM-encapsulation is its reversibility: the layered structure can be temporarily opened by needle insertion for solution injection or removal. Once the needle is withdrawn, the puncture is rapidly restored due to the mobility of the layers, enabling complex, repeated reactions within MLM covered hydrogels. Furthermore, depending on mechanical requirements, the oil layer can be used in either fluidic or solidified form, broadening the versatility of this platform.

The MLM approach is simple, adaptable, and compatible with hydrogels of diverse shapes and compositions. Overall, this work establishes a universal strategy to achieve homogeneous oil encapsulation of hydrophilic hydrogel surfaces. By integrating stability, reversibility, and adaptability, the MLM platform offers a promising route toward future advancements and applications in hydrogel technologies.

Methods

Materials. Triethoxy(octyl)silane (97%), triethoxy(1H,1H,2H,2H-perfluoro-1-octyl)silane (98%), glass beads (200–300 μm and 0–50 μm), ethylene glycol dimethacrylate (98%), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (98%), acrylamide (99%), N,N'-methylenebis(acrylamide) (99%), paraffin wax (melting point: 53–58 $^{\circ}\text{C}$), iron(II,III) oxide (nanopowder, 50–100 nm), gelatin (from cold-water fish skin), methacrylic anhydride, and lithium phenyl-2,4,6-trimethyl-benzoylphosphinate (LAP) were purchased from Sigma-Aldrich. Hydrochloric acid (35–37 wt%), *n*-hexane (95%), toluene (99.8%), ethanol (94.5%), dimethyl sulfoxide (99%), and poly(vinyl alcohol) #500 were obtained from Samchun Chemical. Acrylic acid (99%), N-isopropylacrylamide (98%), glutaraldehyde (50% in water), and polyethylene glycol diacrylate (n =approx. 9, stabilized with MEHQ) were supplied by Tokyo Chemical Industry. Dulbecco's Modified Eagle Medium (DMEM), fetal bovine serum (FBS), penicillin/streptomycin (P/S), Dulbecco's phosphate-buffered saline (DPBS, 1X), and 0.25% trypsin-EDTA were purchased from Gibco BRL. Glucose oxidase from *Aspergillus niger* Type X-S (GOX; EC 1.1.3.4), D-(+)-glucose (mixture), potassium iodide (KI), and horseradish peroxidase (HRP; EC 1.11.1.7) were provided by Thermo Fisher Scientific. Acetone (99%), cyclohexane (99.7%), and Rhodamine

B were purchased from FUJIFILM Wako Pure Chemical Corporation. Urethane acrylate prepolymer (PUA MINS 301 RM) was obtained from Minuta Technology. UV-curable polysilicone (KER-4000UV) was produced from Shin-Etsu Silicones of America, Inc.

Preparation of hydrophobic particles. Hydrophobic particles, including hydrocarbon (HSAM) and fluorocarbon (FSAM) self-assembled monolayer-treated particles, were prepared by solution-based method. First, the surfaces of inorganic particles were activated by stirring in 1 M hydrochloric acid solution for 1 h. The particles were then washed three times with deionized water, followed by sequential solvent exchange to ethanol and then toluene. Surface-modifying agents (triethoxy(octyl)silane or triethoxy(1H,1H,2H,2H-perfluoro-1-octyl)silane) were dissolved in toluene at 3 mM, and the surface activated particles were dispersed in this solution and stirred for 24 h. After surface modification, the particles were centrifuged multiple times with toluene and finally dried in air overnight. To verify successful surface modification, Fourier-transform infrared (FT-IR) spectroscopy (Nicolet 6700, ThermoFisher Scientific) was performed on bare, HSAM-treated, and FSAM-treated glass particles (**Figure S14**). In addition, the infrared spectra of the surface-modifying agents were measured as references. The bare glass beads exhibited only characteristic Si–O–Si peaks at 500 and 1080 cm^{-1} . In contrast, HSAM-treated particles displayed distinct C–H (2920 and 2867 cm^{-1}), Si–O–C (958 cm^{-1}), and Si–C (789 cm^{-1}) peaks. FSAM-treated particles showed characteristic C–H (2984 and 2853 cm^{-1}), C–F (1202 and 1090 cm^{-1}), Si–O–C (903 cm^{-1}), and Si–C (798 cm^{-1}) peaks associated with fluorinated silane groups.

Preparation of poly(acrylic acid) (PAA) hydrogel. Acrylic acid (6.85 mL) and ethylene glycol dimethacrylate (190 μL) were dissolved in deionized (DI) water (6.5 mL). Next, 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (45 mg), dissolved in dimethyl sulfoxide (300 μL) as a

photo-initiator, was added to the aqueous solution. The pre-gel solution was injected into PTFE mold frames (thickness: 100–1000 μm) sandwiched between glass slides and polymerized under UV-A irradiation (10 mW cm^{-2} , 365 nm) for 20 min. Hydrogel films were immersed in DI water for 3 days to remove residual monomers, with daily water changes.

Preparation of polyacrylamide (PAAm) hydrogel. Acrylamide (462 mg) and N,N'-methylenebis(acrylamide) (3 mg) were dissolved in DI water (6.5 mL). Subsequent steps were identical to those used for PAA hydrogel preparation.

Preparation of poly(N-isopropylacrylamide) (PNIPAm) hydrogel. N-Isopropylacrylamide (736 mg) and N,N'-methylenebis(acrylamide) (3 mg) were dissolved in DI water (6.5 mL), followed by the same procedure as PAA hydrogel preparation.

Preparation of polyethylene glycol diacrylate (PEGDA) hydrogel. Polyethylene glycol diacrylate (4.33 g) and ethylene glycol dimethacrylate (190 μL) were dissolved in DI water (6.5 mL), followed by the same procedure as PAA hydrogel preparation.

Preparation of poly(vinyl alcohol) (PVA) hydrogel. Poly(vinyl alcohol) (0.1 g) was dissolved in DI water (1 mL) at 70 $^{\circ}\text{C}$ overnight with stirring. Glutaraldehyde (125 μL) and 1.2 M hydrochloric acid (50 μL) were then added. The pre-gel solution was injected into PTFE mold frames (thickness: 100–1000 μm) sandwiched between glass slides and allowed to polymerize for 2 h. Hydrogel films were immersed in DI water for 3 days to remove residuals, with daily water changes.

Fabrication of multi-layered marble (MLM) shell on hydrogel. MLM shells were fabricated sequentially in three steps: primary particle layer, oil layer, and secondary particle layer. The primary particle layer was formed by gently rolling the hydrogel over a bed of HSAM particles.

Next, sufficient oil was dropped onto the hydrogel marble and allowed to spread for several minutes until the hydrogel was fully cloaked; cloaking time depended on hydrogel size and oil viscosity. Finally, the oil-coated hydrogel marble was rolled over a bed of FSAM particles to form the secondary particle layer using the same procedure as for the primary particle layer.

Preparation of spherical hydrogel. PDMS grafted glass Petri dishes were prepared for the oil bath following a previously reported method.⁷⁸ Pre-gel solutions of the desired hydrogel were dropped into a silicone oil bath using a micropipette. The droplets were polymerized under UV-A irradiation (10 mW cm^{-2} , 365 nm) for 20 min. The resulting spherical hydrogels were washed three times with *n*-hexane to remove residual oil. After rinsing, the hydrogels were immersed in DI water for 3 days to remove residual monomers, with daily water changes.

Preparation of magnetic PVA hydrogel actuator. Magnetic PVA pre-gel solution containing 10 wt% iron oxide nanoparticles was injected into PTFE mold frames (thickness: 200 μm) sandwiched between glass slides and polymerized for 2 h. The resulting hydrogel was cut into small pieces, which were placed into the mold, and the remaining space was filled with bare PVA pre-gel solution. After polymerization, the hydrogel film was immersed in DI water for 3 days to remove residuals, with daily water changes.

Preparation of gelatin methacrylate (GelMA) hydrogel. Gelatin was dissolved in Dulbecco's phosphate-buffered saline (DPBS) at 50 °C to a 10% w/v solution, followed by the addition of methacrylic anhydride to 8% v/v. The mixture was stirred for 3 hours and then dialyzed in DI water at 50 °C for 3 days using a 12–14 kDa MWCO dialysis membrane (Cellu Sep, Dongil Biotech, Seoul, Republic of Korea). Post-dialysis, the solution was lyophilized for 4 days and stored at –20 °C.

Cell culturing and cell encapsulation in GelMA hydrogel. Human dermal fibroblasts (HDFs), sourced from the American Type Culture Collection (ATCC, Manassas, VA, USA), were cultured in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin (P/S) in a 5% CO₂ incubator at 37 °C. The culture medium was replaced every three days, and cells were subcultured at 70–80% confluence. For cell encapsulation, freeze-dried GelMA was reconstituted to 5% w/v in DMEM, warmed to 37 °C, and 0.3% w/v lithium phenyl-2,4,6-trimethyl-benzoylphosphinate (LAP) was added as a photo-initiator. The solution was sterile-filtered (0.22 µm). Cultured HDFs were trypsinized, centrifuged to obtain pellets, and resuspended in the GelMA pre-gel solution at 1×10^6 cells/mL. Aliquots (20 µL) were crosslinked using a UVP Crosslinker CL-1000L (100 µJ cm⁻², 365 nm, Analytik Jena US) for 3 min. The hydrogels were washed with DPBS, transferred to culture plates, and incubated under the same conditions, with daily medium changes for 3 days.

Evaluation of viability of cells encapsulated in GelMA hydrogel. To assess cell viability, MLM coatings were removed by rinsing hydrogels with *n*-hexane, followed by three washes with DPBS. Hydrogels were then stained using the Live/Dead Viability/Cytotoxicity Assay Kit (Thermo Fisher Scientific) and protected from light until confocal imaging was performed using an LSM 700 microscope (Carl Zeiss).

Preparation of enzymatic-cascade microreactor. Aqueous enzyme dispersion containing 0.4 wt% glucose oxidase (GOX) and 0.1 wt% horseradish peroxidase (HRP) was prepared. Preformed PVA hydrogels (~0.8 mL) were immersed in enzyme dispersion (50 mL) for 1 day and the enzyme laden hydrogel (0.39 wt% of GOX and 0.1 wt% of HRP in hydrogel) washed by DI water to clean surface. Subsequently, the prepared hydrogel coated with MLM. For the glucose assay, KI (150 mM) and

glucose (12.5 mM) aqueous solutions were mixed in a 1:4 volume ratio to form the reaction cocktail. The cocktail (50 μL) was added to the MLM-encapsulated hydrogel, and color changes resulting from the enzymatic-cascade were monitored.

Sessile and pendant drop measurement. A sessile and pendant drop measurement instrument (DSA100, KRÜSS) was used to determine contact angles and tensions. The static contact angles were measured by dropping 10 μL of liquid on the substrate. Equilibrium three-phase contact angles (θ_{ow}) were measured by dropping 10 μL water droplet on the substrate in an oil bath. Oils (castor oil, paraffin oil, silicone oil, soybean oil) were slowly added to the bath. Surface tensions of oils were measured by dosing (rate: 0.6 $\mu\text{L s}^{-1}$) the oils until the pendant droplet detached from the needle. Interfacial tensions between water and oils were measured similarly by dosing (rate: 0.6 $\mu\text{L s}^{-1}$) the water into the oil bath until detachment.

Tensile and compressive moduli measurement. The mechanical properties of the hydrogels were measured by universal testing machine (UTM, Model 2530-1 kN, Instron). The setup for tensile and compression tests is simply illustrated in **Figure S15**. The tensile test was conducted with $100 \times 20 \times 2 \text{ mm}^3$ specimens and the compression test was conducted with $20 \times 20 \times 2 \text{ mm}^3$ specimens. The same test machine was employed in both cases, the two holders used in the tensile test were replaced by load cell with compression platen in the case of the compressive tests. Both test types were conducted at constant speed (rate: 0.01 mm s^{-1}) for the movement of the upper holder or load cell. This holder moved upward in the case of the tensile test and load cell moved downward in the case of the compression test.

Image analysis. Quantitative analysis of optical and confocal fluorescence microscope images were performed using ImageJ (version 1.52a).

Data Availability

All data supporting the findings of this study are included in the Article, Supplementary Information, and Source data file. Source data are provided with this paper. All data are available from the corresponding author on request.

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Author Contributions Statement

The manuscript was written through the contributions of all authors. H. Kim carried out experiments and measurements and performed the analytic calculations. J. Ko guided fabrication of hydrogels and hydrogel actuator. S. Wooh is the supervisor of this work. S. Y. Jang carried out cell viability experiments. J. E. Lee supported enzymatic-cascade reaction experiments. J. Yoo and S. Fujii contributed as the advisors of this work.

Competing Interests Statement

The authors declare no competing interest.

Table 1: Summary of previously reported methods for hydrogel encapsulation.

Method	Materials	Process	Performance	Applications	Ref
Elastomer coating	Sylgard 184, Ecoflex, polyurethane, latex, VHB	Benzophenone treatment on elastomer, hydrogel synthesis by UV irradiation	<Deswelling> - No change after 2 d drying < Mechanical property> - No change with Ecoflex (lower thickness than hydrogel)	Microfluidics, Channel, circuit	22
Elastomer coating	Sylgard 184, Ecoflex	Benzophenone treatment on elastomer, hydrogel synthesis by UV irradiation	<Deswelling> - 21.4 wt% change after 3 d drying < Mechanical property> - None	Triboelectric generator	30
Double hydrophobic coating	Octyl acrylate, dodecyl acrylate, stearyl acrylate, silicone oil	Polymerization, immersing in hot silicone oil bath (120 °C)	<Deswelling> - 4.1 wt% change after 7 d drying <Swelling> - 22.6 wt% change after 7 d immersing in water < Mechanical property> - Tensile strength 108% increase - Compressive strength 110% increase	None	24
Double hydrophobic coating	(3-aminopropyl) triethoxysilane, stearic acid, silicone oil	Chemical bonding, immersing in silicone oil bath (room temperature)	<Deswelling> - 22.4 wt% change after 5 d drying < Mechanical property> - Tensile strength 125% increase - Compressive strength 127% increase	None	23
Organogel coating	Butyl acrylate, lauryl acrylate	Polymerization	<Swelling> - 3% change after 200 h immersing in water < Mechanical property> - Tensile stress 10% decrease	Sensor	31
Organogel coating	Butyl acrylate, ethylene glycol dimethacrylate	Polymerization	<Deswelling> - 5 wt% change after 2 d drying < Mechanical property> - Tensile stress 400% decrease	Sensor	32
Out work (MLM)	HSAM particle/oil/FSAM particle	Hydrogel rolling, oil dropping	<Deswelling> - 5 wt% change after 7 d drying < Mechanical property> - 5% change	Actuator, microreactor, cell incubator	

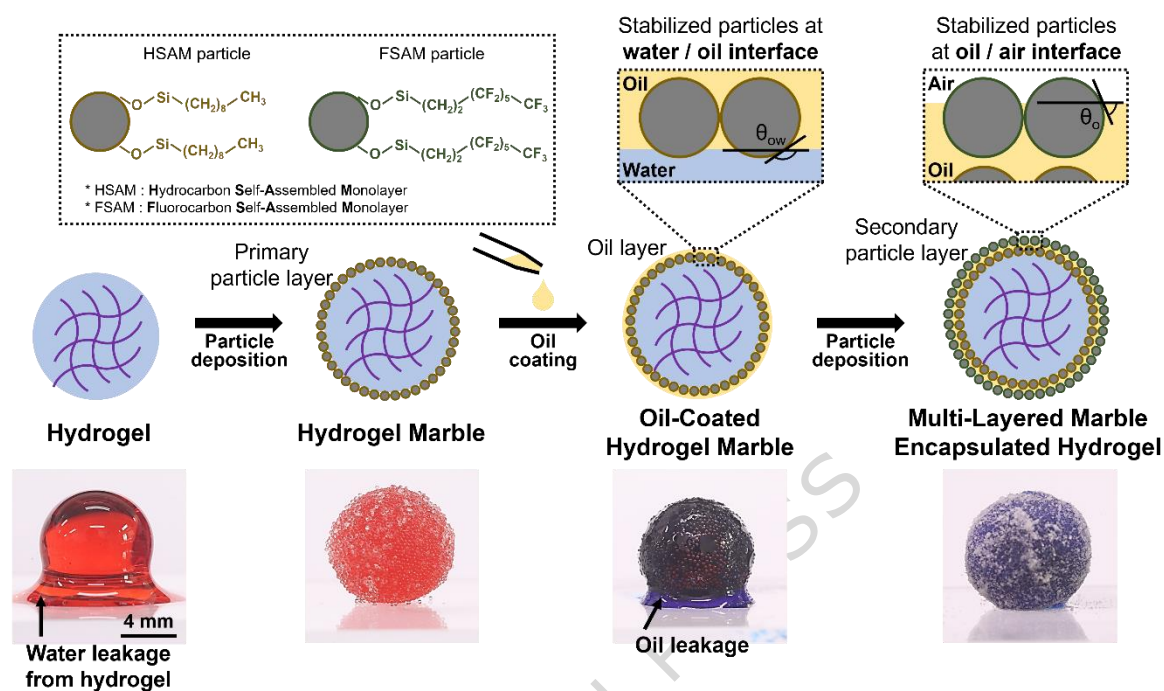


Figure 1: Hydrogel encapsulation using the multi-layered marble (MLM) structure. Stepwise schematic illustration (top and middle) and photographic images (bottom) showing the hydrogel encapsulation process using MLM structure.

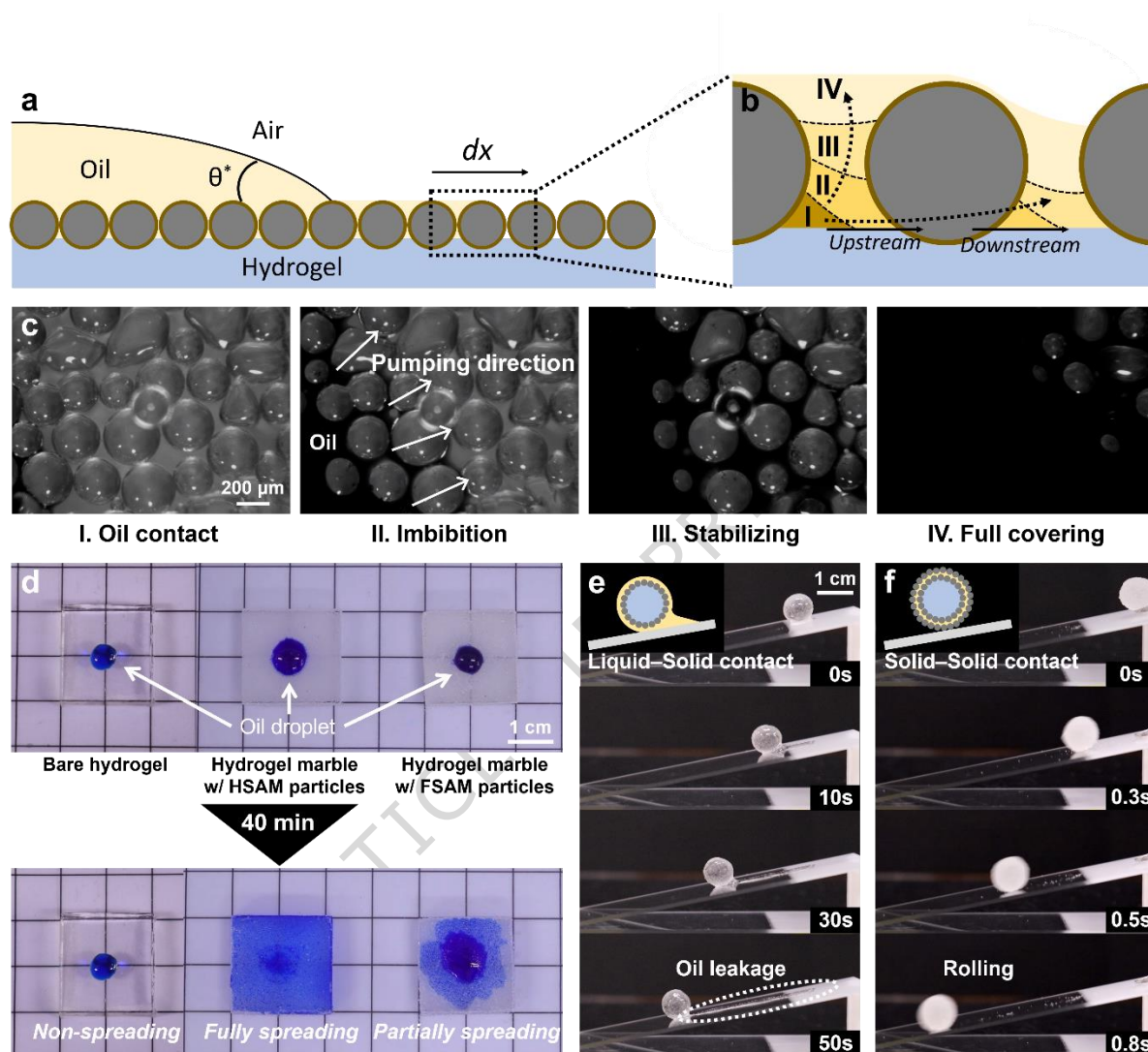


Figure 2: Role of primary and secondary particle layers. Schematic illustrations of oil spreading mechanisms on particle-coated hydrogel surfaces: a) Imbibition-induced wetting; b) Meniscus pumping effect. c) Optical microscope snapshots from a video showing oil spreading over a PAA (poly(acrylic acid)) hydrogel marble. d) Comparison of oil spreading over time on bare PAA hydrogel versus HSAM (hydrocarbon self-assembled monolayer)- or FSAM (fluorocarbon self-assembled monolayer)-coated hydrogel marbles. Video snapshots showing slide behavior of e) oil-coated PAAm (polyacrylamide) hydrogel marble and f) MLM (multi-layered marble)-encapsulated hydrogel, respectively.

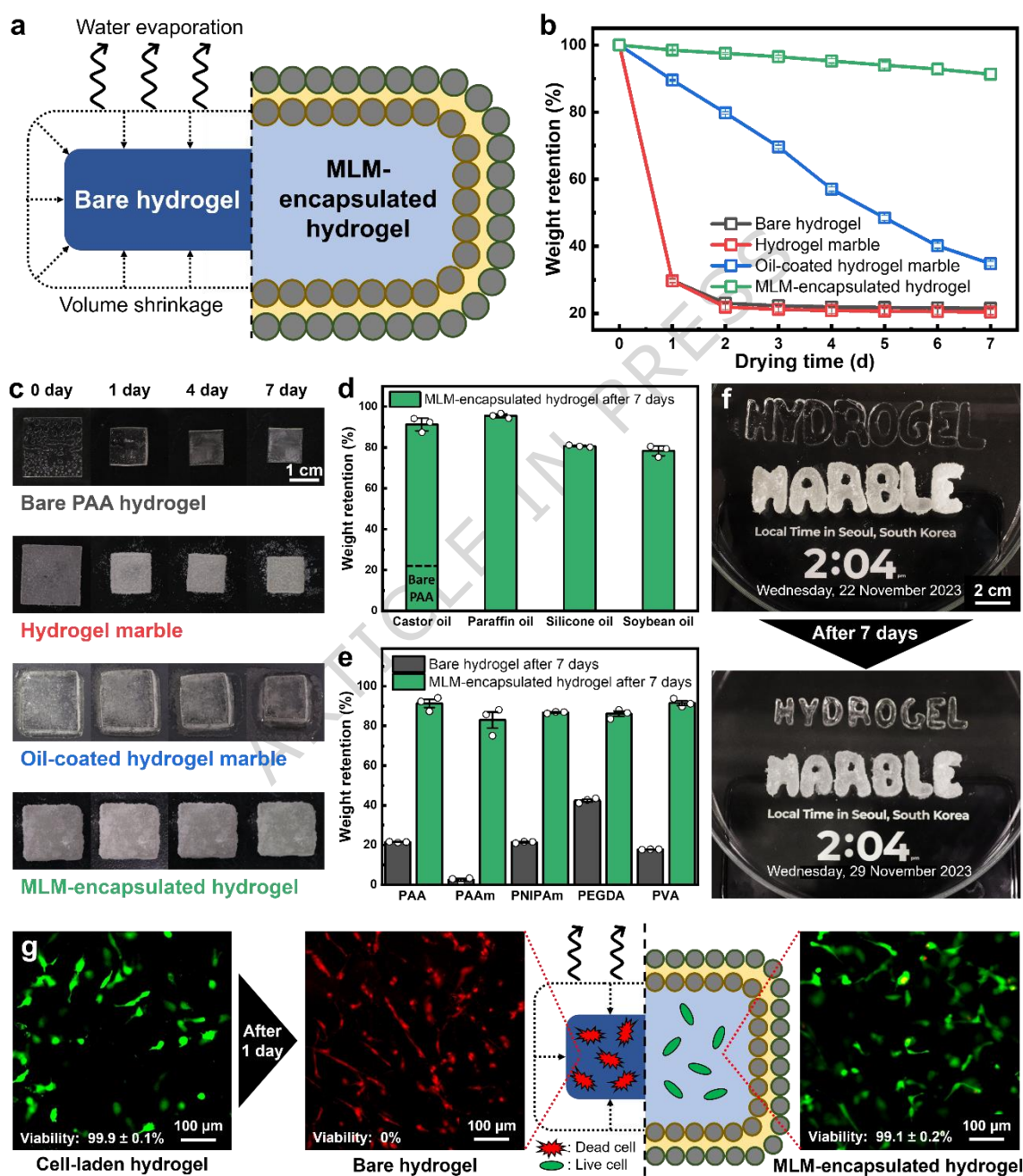


Figure 3: Anti-dehydration properties of MLM (multi-layered marble)-encapsulation. a) Schematic illustration comparing dehydration in bare hydrogel with water retention in MLM-encapsulated hydrogel.

b) Weight retention and c) photographic images of bare PAA (poly(acrylic acid)) hydrogel (black), hydrogel marble (red), oil-coated hydrogel marble (blue), and MLM-encapsulated hydrogel (green) for 7 days (oil: castor oil). d) Weight retention of MLM-encapsulated PAA hydrogels with various oils. e) Weight retention of bare (black) and MLM-encapsulated (green) PAA, PAAm (polyacrylamide), PNIPAm (poly(N-isopropylacrylamide)), PEGDA (polyethylene glycol diacrylate), and PVA (poly(vinyl alcohol)) hydrogels with castor oil. Data in b), d), and e) are presented as mean values $\pm$ SEM (standard error of the mean) with individual data points shown (n=3). f) Photographic images comparing alphabet-shaped bare and MLM-encapsulated (oil: castor oil) hydrogels initially and after 7 days in air. g) Laser scanning confocal fluorescence microscope images of live / dead assay of human dermal fibroblast cell-laden bare and MLM-encapsulated gelatin methacryloyl hydrogels after 1 day in air (Live: green, Dead: red). Representative images from one of three independent experiments with similar results are shown. Quantitative data are presented as mean $\pm$ SEM (n = 3).

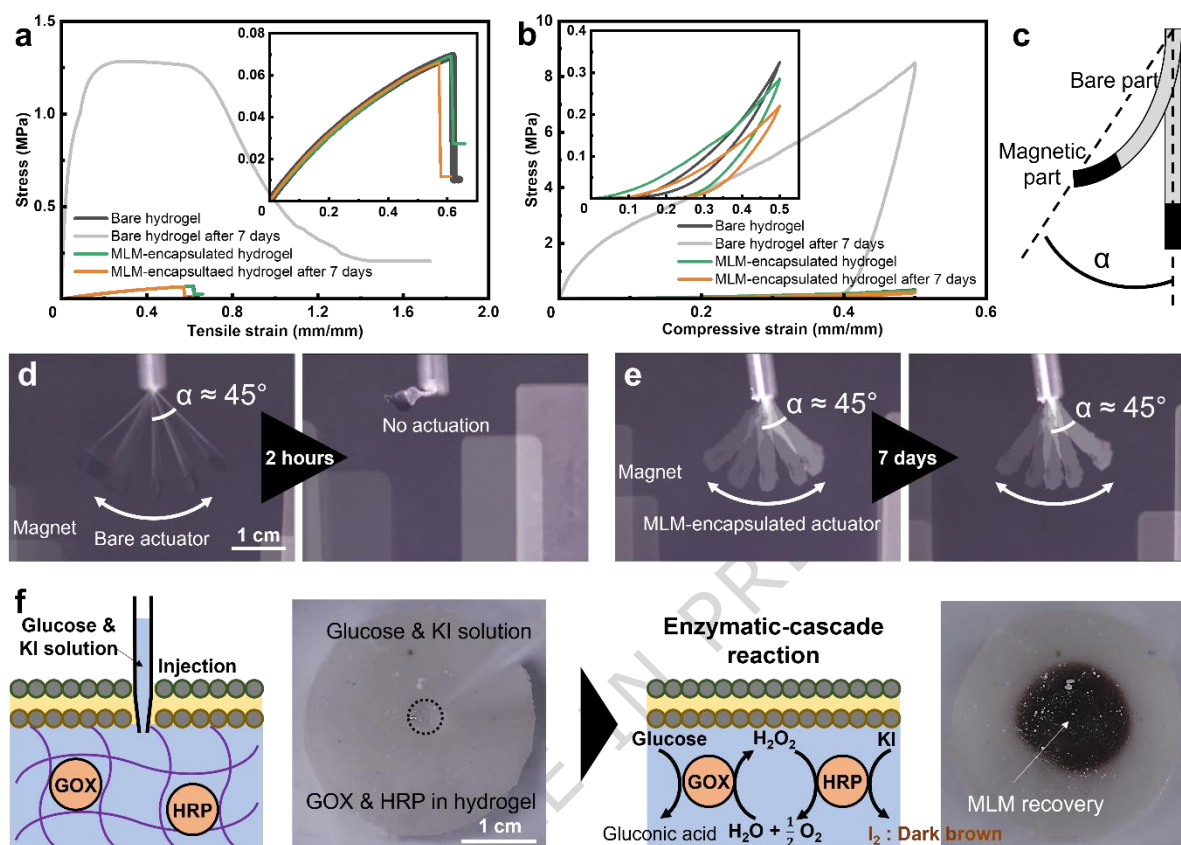


Figure 4: Mechanical properties of MLM (multi-layered marble)-encapsulated hydrogel. a) Tensile and b) compressive stress–strain curves of bare and MLM-encapsulated PAA hydrogels before and after 7 days (Bare hydrogel: black, Bare hydrogel after 7 days: light gray, MLM-encapsulated hydrogel: green, MLM-encapsulated hydrogel after 7 days: orange). Inset shows the enlarged low-strain region. c) Schematic illustration of magnetically responsive hydrogel actuator showing bending angle (α). Hydrogel actuating trajectory of d) bare and e) MLM-encapsulated magnetic PVA (poly(vinyl alcohol)) hydrogels initially, after 2 h, and after 7 days in air. f) Schematic illustration and photographic images showing MLM-encapsulated PVA hydrogel functioning as an injectable microreactor during an enzymatic-cascade reaction.

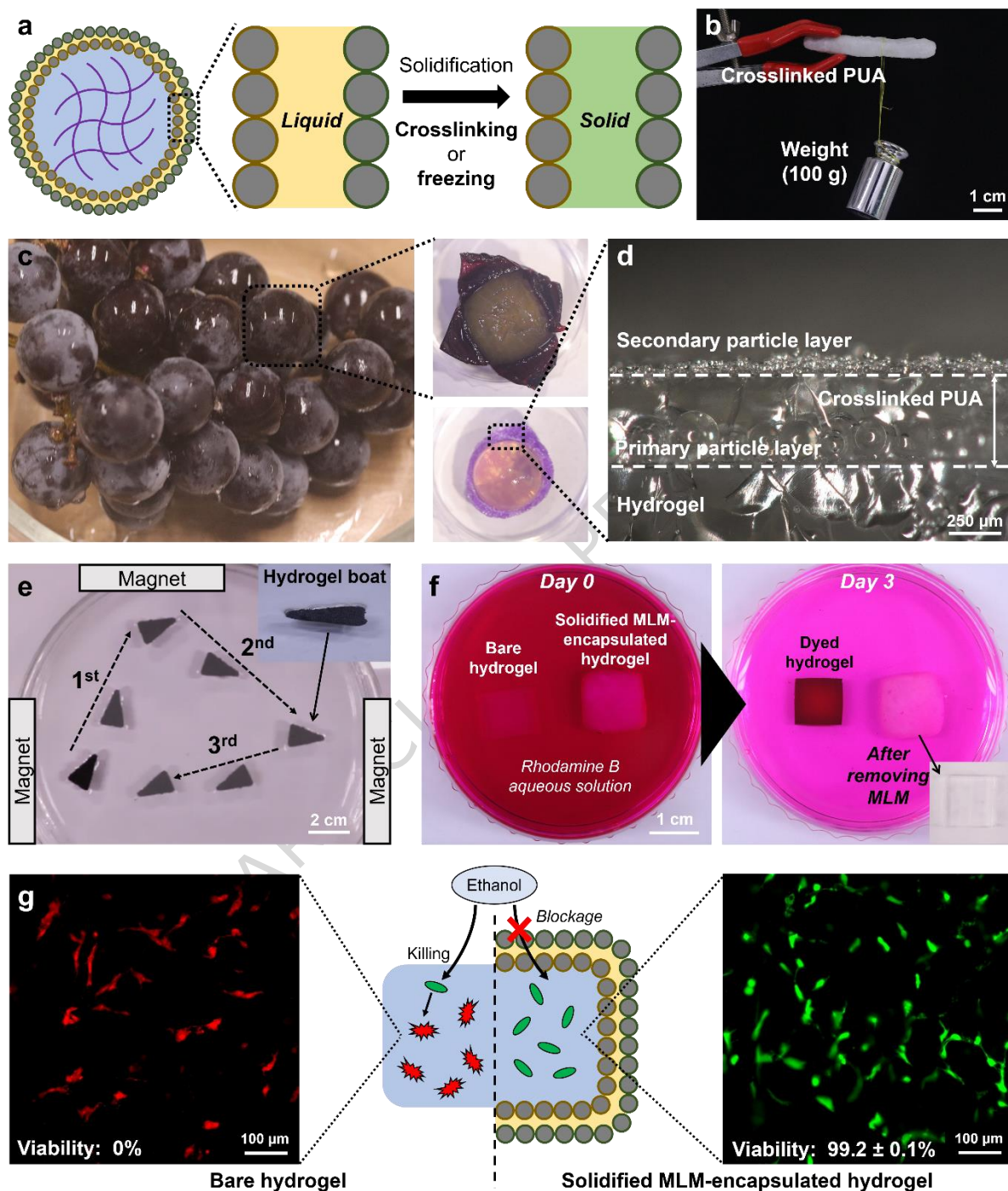


Figure 5: Solidification of MLM (multi-layered marble)-encapsulation. a) Schematic illustration of solidification methods of MLM. b) Photographic image of solidified MLM (S-MLM)-encapsulated PAA (poly(acrylic acid)) hydrogel with crosslinked PUA (polyurethane acrylate). c) Photographic images of grapes, peeled grape, and grape-like S-MLM-encapsulated PAA hydrogel. d) Cross-sectional optical

microscope image of S-MLM-encapsulated PAA hydrogel showing layer-by-layer structure. Representative image from one of three independent experiments with similar results are shown. Quantitative data are presented as mean $\pm$ SEM (standard error of the mean) ($n = 3$). e) Trajectory of magnetically driven S-MLM-encapsulated hydrogel boat on water. f) Photographic images of bare and S-MLM-encapsulated PAA hydrogels with paraffin wax dipping in rhodamine B aqueous solution for 3 days. g) Schematic illustration and laser scanning confocal fluorescence microscope images of human dermal fibroblast cell-laden bare and S-MLM-encapsulated gelatin methacryloyl hydrogels (3 days incubated) after ethanol exposure for 10 min (Live: green, Dead: red). Representative images from one of three independent experiments with similar results are shown. Quantitative data are presented as mean $\pm$ SEM ($n = 3$).

Editorial Summary

Hydrogel encapsulation prevents dehydration, but maintaining interfacial stability with hydrophobic shells remains challenging. Here, the authors use a multi-layered marble strategy composed of two hydrophobic particle layers with sandwiched oil layer that stabilizes the interface.

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