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Communication:**Liquid Marbles in Liquid**

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Abstract

Traditional liquid marbles (LMs), liquid droplets encapsulated by hydrophobic particles at the liquid-gas interface, are restricted by their short lifetime and low heat transfer efficiency. For the first time, we designed a new paradigm for LMs immersed in various liquid mediums with massive enhanced heat transfer and spatial recognition, while without compromising the structural integrity; the lifetime of the liquid marbles in liquid (LMIL) was extended by *~1000 times* compared to classical LMs in air or naked droplets in organic reagents. The LMIL showed promising reverse structural reconfigurability while under external stimuli and maintaining their functionality for a very long period of time (*~ weeks*). These superior behaviors were further exploited as a miniature reactor with prolonged lifetimes and excellent temperature control, combined with its feasible operation, will open up new opportunities in the advanced chemical and biomedical engineering fields. Here, we also showed that LMIL can be applied in methylene blue degradation and three dimensional (3D) in-vitro yeast cell cultures. Our findings have important implications for real-world use of liquid marbles, with a number of applications in cell culture technology, lab-in-a-drop, polymerization, encapsulation, formulation and drug delivery.

Introduction

Liquid marbles (LMs) are liquid droplets encapsulated by hydrophobic particles at the liquid-gas interface; this phenomena has recently drawn increasing interest due to their superior mobility,^[1-4] elasticity^[5] and stability.^[6,7] These beneficial characteristics have allowed LMs to be successfully applied as microreactors,^[8-11] in microfluidic control,^[12-15] gas sensing and many other engineering areas.^[16-19] Compared with the uncoated ‘naked’ droplets, LMs can be manipulated as non-sticky fluidic cells with significantly reduced surface friction and increased drop operability.^[20-22] Based on the nature of the internal fluid and variations of physical properties of coated particles, external stimuli such as electric field,^[23-26] photon, visible light,^[27] magnetic field^[28, 29] and mechanical force^[30-32] can be used to manipulate the LMs’ properties. In addition, LMs with shells composed of multi-layers of particles can be engineered for precise control of chemical dosing by allowing them to coalesce and disintegrate at specific interval.^[33, 7] The combination of simple manipulation, accurate control and overarching benefits of microreactors give LMs promising advantages in both chemical analysis and biomedical applications.

The hydrophobic shell is the essential building block of LMs that generate many of their benefits, for example, it prevents the direct contact between the internal liquid and the wetting surface.^[34-36,58] The porous shell also allows for the mass transfer of gas/vapor in and out of the LM, making it possible for use as gas sensors^[37, 38] and gas-liquid microreactors.^[39] Although LM is proved to possess an enhanced stability than

one in naked droplet,^[40, 41] the porous nature of the particle shell, that leads to undesirable rapid evaporate rate, inevitably limits its potential in applications which require longer lifetime. A precise control of evaporation rate is required for genetic analysis, biochemical reactions, and solid particle and liquid droplet transport.^[57] Moreover, for reactions requiring constant thermal energy supply or precise temperature control, LM-based microreactors are not fully developed yet. Even though in previous study a laser was successfully applied to the LM, allowing it to act as a photothermal microreactor,^[42] it still does not satisfy the requirement for uniform and rapid control of temperature and heating rate.

Herein, we propose to immerse LMs in liquid environments, sealing the encapsulated liquid droplet with an organic reagent. Hence, keeping the LMs advantageous in terms of their mechanical and physical properties but boosting their lifetime, this in turn will allow for use in long-term and temperature-controlled applications, such as a miniature lab-in-a-drop. We investigated suitable coating powders and organic reagents to ensure a stable miniature reacting platform. It was found that hydrophobic powders and organic reagents with high polarity best meet the requirements. We also demonstrated the manipulation of LMs in liquid for diverse functionalities by employing magnetic and photothermal stimuli. Furthermore, the sealing reagent ensured precise temperature adjustment and generated uniform temperature profile distribution of the LM microreactor. The reaction kinetics of methylene blue (MB) degradation and 3D culture of yeast cells were investigated to understand their durability and build a temperature

controlled microreactor. We anticipate that the new class of liquid marbles we developed will be applicable in the food, biotechnological and pharmaceutical processes.

Results and Discussion

The loose texture of the coating particles on the LM surface is a double-edged sword as mentioned above. When water LMs are in ambient conditions, which are considered a moderately volatile environment, they will evaporate over time leaving only a folded particle shell within an hour (Figure 1a). To overcome this issue, that is, to extend the LMs' lifespan, an enclosed external environment needs to be introduced to suppress the evaporation process (Figure 1b). Here we established a simple and effective strategy of sealing LMs with organic reagents, Figure 1c, which suggested a much higher stability than LMs in air as seen by the negligible changes in droplet diameter and height. More surprisingly, these undeformed particles could be maintained for months at room temperature, that is to say, the lifetime of LMs in liquid extended by more than 1000 times than LMs in air, which completely evaporated within only 50 minutes. Furthermore, comparing with research by Chandan et. al^[46] that heating water marble coated by perfluorinated silica nanoparticle (PFSN) floated in water pools, of which the LM lifetime decreased from 480 mins to 2 mins when the pool temperature was raised from 20 °C to 40 °C; the distinct evaporation phenomenon and deformation of LMs in this research could be noticed when the bath was heated to 60 °C, and the lifetime at this temperature was approximately 5 mins. It suggests that the stabilities of our LMs

in this work have been greatly improved at both room and elevated temperatures. This stability is exemplified in our organic pollutant degradation investigation at various temperatures, elaborated in the following section. In contrast, naked liquid droplets without protective hydrophobic surface particles deformed readily in octadecene and settled to the bottom surface under the effect of gravity after two weeks (Figure 1d), thus demonstrating the necessity of fabricating LMs, instead of simply a bare droplet, for use as microreactors.

Conventional LMs are fabricated by rolling the aqueous drop on the surface of hydrophobic particles, allowing the particles to fully cover the droplets surface,^[47-49] followed by transferring them into organic solvent, known as a “LM-in-liquid” concept (Figure 1e). The immersed LMs can be easily extracted from the solution without any changes in morphology or shell destruction, which is importantly useful for further treatment and testing (Figure S1a, Supporting Information). In virtue of liquid density differences, the LM was demonstrated to suspend itself firmly at the liquid-liquid interface; this reduces the friction^[50-53] when being manipulated by external stimuli compared to when placed on a solid surface (Figure S1b, Supporting Information).

To optimize the performance of LMIL, an appropriate coating material and liquid environment needs to be sought that will be beneficial for each specific system. Lin et al.^[33] reported that the hydrophobicity of materials is the utmost parameter to provide balance at the liquid-liquid interface, with almost all hydrophobic materials believed to

function. In this work, various hydrophobic materials (physical properties shown in Table S2 and Figure S5, Supporting Information): carbon dots functionalized with polyhedral oligomeric silsesquioxane (CDs@POSS), polyhedral oligomeric silsesquioxane (POSS), polystyrene and graphite powder were used to coat the LMs in multi-layers; all of which showed stable performance (Figure 1f). Particle distribution on LMs and LMIL were investigated by an optical microscope, showing a much thinner coating layer of LMIL with less particle agglomeration (Figure S4, Supporting Information). The impact of different organic reagents used as the external liquid environment towards the stability of LMIL was further investigated. Some physical properties of organic liquid are considered, while density, surface tension measured experimentally^[54,55] and the effective surface tension roughly estimated by the simple puddle height method^[56] showed no correlations with the stability of the LMIL (Table S1, Supporting Information). It was found that only reagents with larger polarities (> 0.1, tested in this work) maintained the spherical morphology, while the LM shell collapsed when submerged in reagents with lower polarity, causing the droplet to flatten out (Figure 1g). In addition, LMIL can be kept and remain stable in edible oil such as corn oil, soybean oil and olive oil (Figure S1c, Supporting Information), suggesting their potential for use in biomedical and life science.

Compared with common bulky reactor, LMs as miniature reactors surrounded by air were confirmed to intensify the chemical reaction when initiated by multiple stimuli, while such external stimuli (light/electric field/magnetic field) were also reported to

have inferior stability and homogeneity compromising the precise control of the process.^[45] Rapid heat transfer and uniform temperature distribution are important characteristics for a high-performance reactor. Inspired by water-bath heating, we hypothesized that LMs heated in organic liquid baths could achieve precise temperature control rapidly. The bath heating response behavior of LMIL was investigated by heating the organic solvent to a specific temperature, then transferring the LMs (10 μ L) into the bath whilst continually monitoring their spatially distributed temperature by an infrared camera. The temperature of the liquid droplets surface instantaneously increase to 48 $^{\circ}$ C (identical to the external bath temperature) as the LMs were placed into the bath. Heat was then promptly transported radially to the center of the LM, finally manifesting a uniform spatial temperature distribution within 1 minute (Figures 2b, c). In addition, the effect of various bath temperatures and LM sizes have on the LM spatial temperatures was also explored. A higher bath temperature caused the central temperature of the LMs to rise much more quickly, because the heat transfer efficiency is enhanced by the temperature gradient between the internal and external liquids (Figure S2a, Supporting Information). Smaller LMs have a slightly higher heat transfer rate due to their larger specific surface area (Figure S2b, Supporting Information), leading to a more rapid temperature control.

Here LMIL are used to apply precise levels of heating for microreactors, evidence of which is shown via MB degradation at different bath temperature. As illustrated in Figure 2a, LMs containing MB and NaBH₄ were taken out of the liquid bath every

minute to measure the concentration of MB by UV–Vis spectrometry. A decreasing absorption peak at 665 nm indicates the degradation of MB (Figure 2d). The degradation process of MB by NaBH₄ is a pseudo-first-order reaction:^[44]

$$\ln(C / C_0) = -k_{app}t \quad (1)$$

in which k_{app} and t refer to reaction rate constant and time, respectively. The reaction rate doubles for every 10 °C increase of bath temperature (Figure 2e), demonstrating an increasingly enhanced degradation performance of bath heated LMs. Owing to the precise and reproducible control of the liquid bath heater, LMs in liquid offer promising prospect for confirmation of reaction kinetics.

LM-based cell culturing in an ambient environment has been reported previously;^[7] this study further showed that the microenvironment of the cells within the LM could be sustained at optimal conditions. The improvement of 3D cell culture technology can be demonstrated through the long-term incubation of yeast cells in LMIL (Figure 3a). As shown in Figure 3b, the yeast cells are bound together tightly and assemble themselves into a large 3D amalgamation. Such cell-stacking is identified by visualizing the different planes of the bulk cell. LM-based confined spatial stereoscopic environments ensured the growth in three dimensions, with the liquid bath providing an optimum and stable temperature for cell cultures (27 °C in this work). We compared the traditional 2D cell culture in plate with our method (Figure 3c). The yeast cells tend to grow along

the wall and scatter on the bottom of plate (Figure 3d), limiting the amount and quality of cell products.

Typical LMs can be manipulated by multiple stimuli, such as photothermal or magnetic field, which enable the LMs to interact with the outside environment;^[43] such manipulation profile in liquid environment was also demonstrated in this research. As shown in Figures 3e and S3, Supporting Information, the magnetic particles got attracted to the applied magnetic field, whilst still maintaining the shape. When the field was removed, the magnetic particles reassembled themselves to cover the surface of the LMs. The successful extraction of liquid products from LMIL without collapse, making it realizable and feasible to harvest products after chemical reactions. Moreover, the LMIL stimulated by a laser was able to move at 1 mm/s; and bubbles were observed to emerge from the LMs surface when exposed to high flux laser irradiation, demonstrating that high heat flux destroys the stability of LMs in a liquid environment (Figure 3f). The profile of how the external stimuli controls the LMs movement and directionality is similar to that of LMs in air, comparing with our previous research.^[45]

Conclusion

In summary, we present a new concept for “LM-in-liquid” as a long-term and temperature-controlled miniature reactor. It is demonstrated that the multiple hydrophobic powders and organic reagents with large polarities enables the fabrication of a stable miniature platform, which greatly improves the lifetime of LMs to 1000

times higher than in traditional air conditions. The performance of the LMs submerged in the heated liquid bath demonstrated the process of rapid heat transfer in all spatial directions, ensuring precise and uniform temperature control. This combination of benefits creates an attractive opportunity for long-term organic pollutant decomposition and cell cultures. We examined the degradation rate of MB under different temperatures and investigated the formation of 3D yeast cell cultures, with the yeast cultures forming tightly stacked three-dimensional structures, in contrast with the 2D spreading growth in a plate culturing. Similarly observed in air, the opening and closing of the in liquid LM shell can be controlled under the effect of magnetic field, whilst maintaining the internal droplet stability. Additionally, an external laser can be utilized to induce movement of the LM at a small velocity. The LM-in-liquid system is a simple and versatile platform to be applied for ultrafast, flexible and miniature chemical reactors; and can certainly benefit in the environmental science field in regard to pollutant degradation, gas analysis and sensing, bioengineering for regenerative medicine, health care products and clinical diagnostics.

Experimental Section

Materials and preparation of liquid marbles in liquid: LMs were obtained by rolling a certain volume of aqueous solution or deionized water on a surface of hydrophobic powders, of which the CD@POSS particles were prepared according to our previous research,^[45] whilst all other powders were purchased from Sigma-Aldrich. Then, the obtained LMs were transferred and submerged into organic reagents, thus, forming the

LM in liquid system. The colored water contained within the LM is dyed by MB, rhodamine B and other soluble metal ions. All the chemicals were used without further purification or modification.

Degradation of methylene blue: The degradation of MB was achieved by the reduction of NaBH₄. Typically, one 10 μ L drop containing 20 mM MB and another 10 μ L drop containing 1 M NaBH₄ (all were dissolved in deionized water) were mixed on the surface of hydrophobic powders. This mixture was then immediately rolled to form the LM. After that, the LMs were transferred into the heated bath and noted as $t = 0$ s. For every minute, the LMs were removed and tested by UV–Vis spectrometry (A Shimadzu UV-2600).

Culturing of Yeast Cell: Instant dry yeast was purchased from Angel Yeast Company. Firstly, 200 mg yeast and 1g glucose were dispersed in 20 mL deionized water, then, a single drop of this solution was coated by CD@POSS to form the LM and then placed into the octadecene at 27 °C. The obtained cells were observed by microscope after an incubation period of two days.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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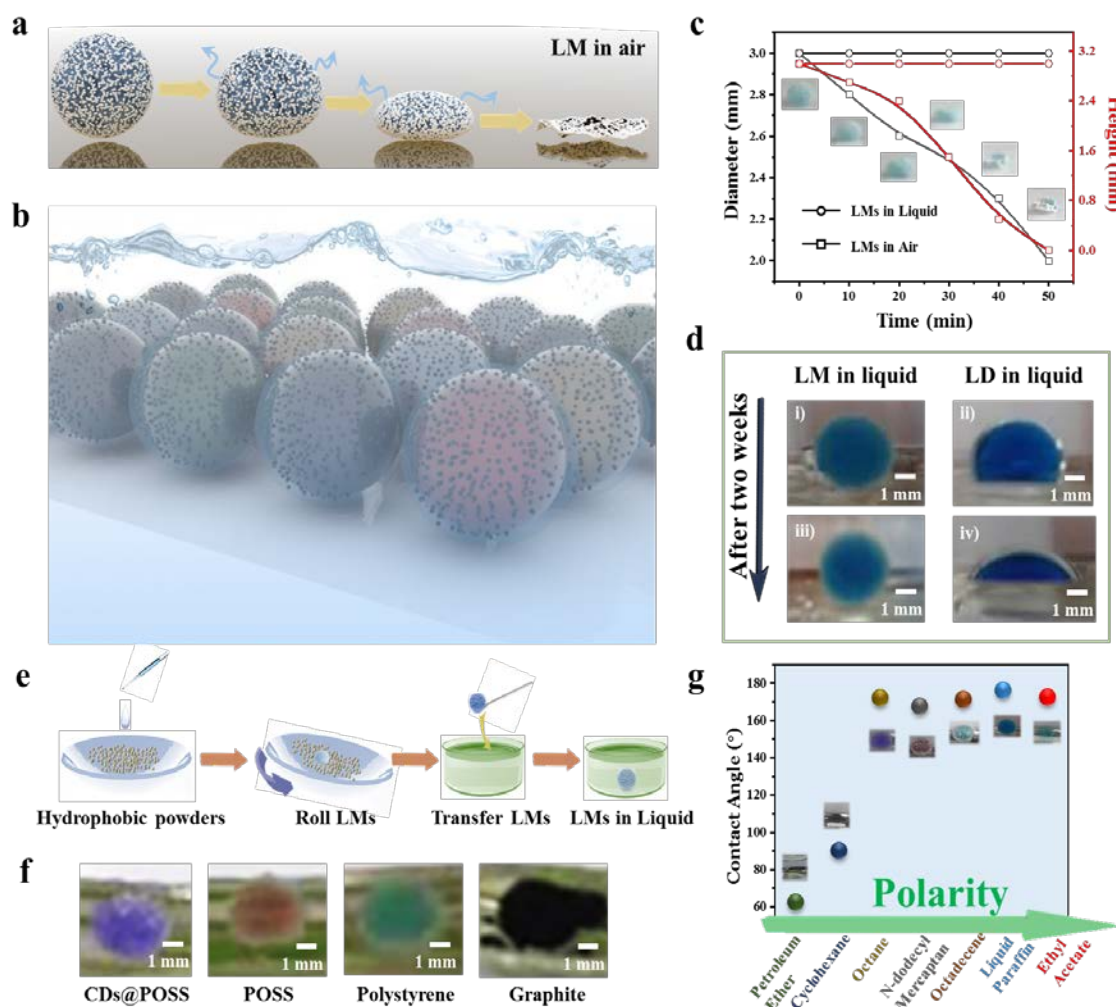


Figure 1. a) Schematic illustration of time-dependent morphology transformation of LMs in air. b) Schematic for the prevention of evaporation by placing water LMs in organic reagents. c) Change in diameter and height of LMs in air and octadecene along with time. d) Optical images showing comparison of morphological changes between water LM-in-octadecene (LM in liquid) and water droplet-in-octadecene (LD in liquid) after two weeks. e) Schematic illustration of preparation process of LMs in liquid. f) Images of four LMs coated in different powders submerged in octadecene: CD@POSS, POSS, polystyrene and graphite powder, respectively. g) Contact angle of LMs in organic reagents of different polarities.

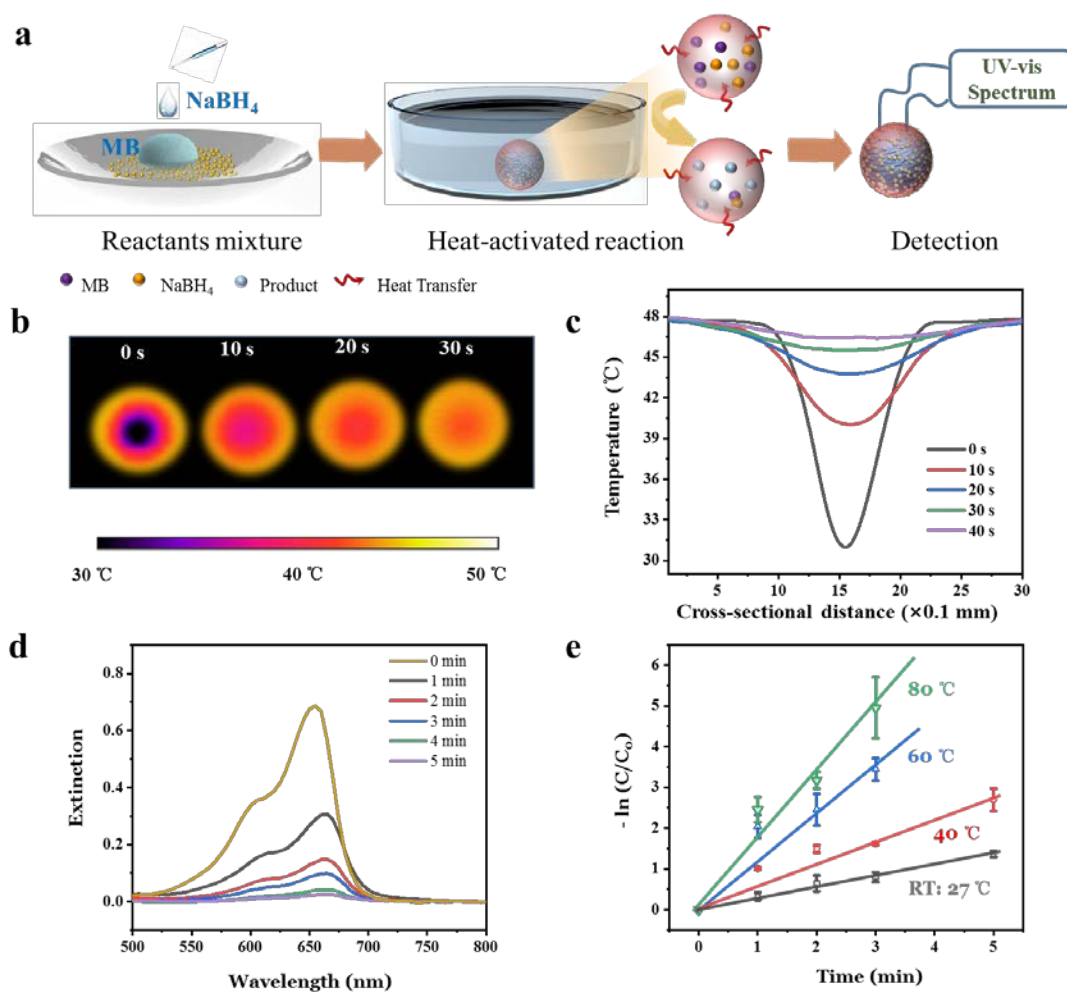


Figure 2. a) Schematic illustration of MB degradation process. b) Snapshots of LM temperature profiles, and c) plots of spatial temperature profiles of bath-heated LMs. d) UV-vis spectra of MB solutions extracted from heated LMs at different times. e) Plots of normalized MB concentrations against time for different bath temperatures.

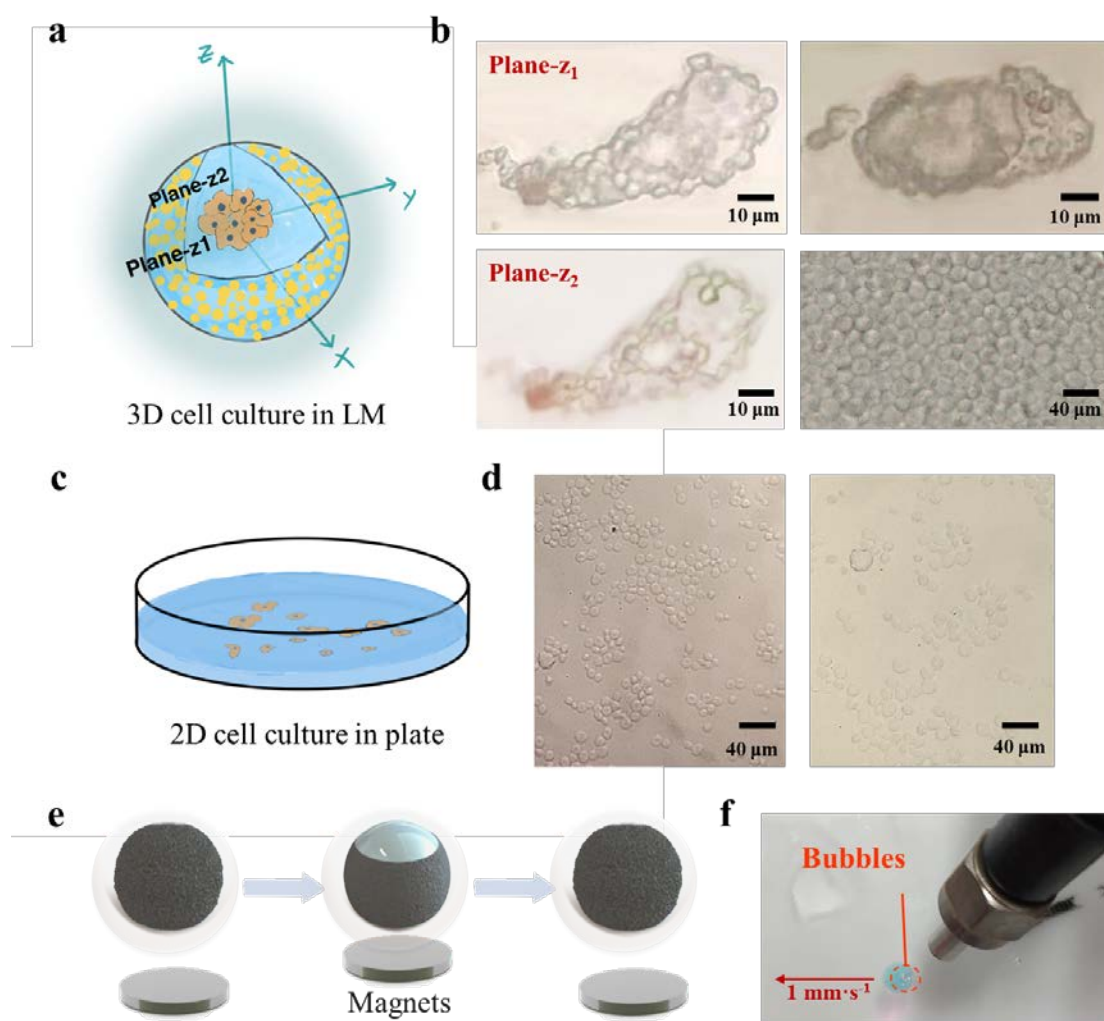


Figure 3. a) Schematic diagram and b) optical micrographs comparing the 3D culturing of yeast cells in 10 μL LM and corresponding c) 2D schematic and d) micrographs of the yeast cell cultures in a petri dish. e) Schematic diagram showing LM being manipulated by magnets in liquid. f) Optical image showing light-responsive LM in liquid.