

Magnetic Liquid Marbles: A “Precise” Miniature Reactor

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Miniaturized chemical processes have many advantages, such as reduced use of chemical reagents and solvents, precisely controlled reaction conditions, much shortened reaction time, and the ability to integrate into a digital device.^[1–4] They are very useful for high-throughput analyses and purifications in chemical and biological processes, such as drug discovery,^[5] DNA analysis,^[6,7] protein crystallization,^[8] and the synthesis of molecules or particles.^[9–11] Indeed, considerable efforts have been made to miniaturize chemical processes using various principles. For example, oil/water emulsions have been used to perform chemical reactions in parallel in a large number of emulsified tiny droplets.^[10] Microfluidic “lab-on-a-chip” devices have been designed to manipulate chemical processes within micro-channels either in continuous fluid or disconnected fluid segments separated by an immiscible fluid or gas.^[10,12] Although the channel-based micro-reactors show great potential in high-throughput reaction and integratability to external analysis facilities, the reaction-specific device preparations, the channel-associated cross-contaminations, and the need for external pumps to actuate the fluid motion make them neither universal nor miniature. Also, microfluidics is hard to use to handle a single droplet. Recently, free aqueous droplets in an immiscible fluid (channel-free microfluidics)^[9] has also been proposed as an alternative strategy, but cross-contamination still remains a concern.

In living systems, cells are well-known as the basic structural and functional units^[13] that mediate various biochemical reactions (e.g., catabolism and anabolism) for sustaining the growth and division of cells and hence living systems. Although their structure looks very simple, cells communicate with each other in a highly intelligent way, throughout the whole living system. In this regard, how to mimic living cells, both in structure and function, is the ultimate challenge toward the development of artificial miniature reactors.

Liquid marbles, liquid drops encapsulated with solid powder at the liquid–gas interface, have recently been reported as a new approach to manipulating liquid,^[14] which could be used as miniature reactors. They are non-wetting to any solid surfaces and could be manipulated by external forces, such as gravity,^[14] electrical,^[15] and magnetic,^[16] depending on their components.^[14–19] However, most liquid marbles reported so far have been based on aqueous liquid. Although a few papers^[19] have reported the encapsulation of organic liquids into liquid marbles, the liquids were confined to those having a high surface tension.^[19] The formation of stable liquid marbles from a wide range of organic solvents, especially those that have a low surface tension, is important for chemical reactions, but still remains a challenge.

In this study, we demonstrate the incredible ability of a fluorinated decyl polyhedral oligomeric silsesquioxane (FD-POSS, structure shown in **Figure 1a**) and its combination with hydrophobic magnetic nanoparticles to act as encapsulating agents to prepare stable liquid marbles from both aqueous solution and organic liquids with a surface tension as low as 20.1 dyne cm^{−1}, and the feasibility of using the magnetic liquid marbles as universal “smart” miniature reactors.

FD-POSS was synthesized by the reported method^[20,21] and a fine FD-POSS powder was prepared by a grinding technique. The FD-POSS/Fe₃O₄ nanoparticle composite powders of different ratios (1:10 to 1:1, w/w) were prepared by co-dispersing the fine FD-POSS powder with hydrophobic Fe₃O₄ nanoparticles in ethanol. As shown in the photographs in **Figure 1b**, FD-POSS powders are white and have a certain transparency to visible light but are not responsive to a magnetic field. In ethanol, FD-POSS and Fe₃O₄ nanoparticles had a strong affinity, and they tended to aggregate into powders which showed a superparamagnetic property (Supporting Information). The optical micrographs in **Figure 1c** indicate that FD-POSS and FD-POSS/Fe₃O₄ composite powders are less than 70 μm, and the FD-POSS and Fe₃O₄ nanoparticles formed a randomly blended composite structure. When a thin bed of the powders were coated on a solid surface, the surface became highly repellent to liquids. Water, dimethyl sulfoxide (DMSO), toluene, hexadecane, and ethanol all formed round droplets on the powder coated surface with overall contact angles of 171.1°, 166.2°, 155.7°, 154.4°, and 142.8°, respectively (**Figure 1d**). The powder layer showed strong repellence to other organic solvents (Supporting Information). The composite powders in the studied FD-POSS/Fe₃O₄ ratio range showed a very similar fluid repellency to the pure FD-POSS grains.

Liquid marbles were prepared simply by dropping a small volume of liquid onto the powder surface and subsequently shaking the droplet gently so that the powders covered the entire droplet surface. The as-prepared powders, both FD-POSS

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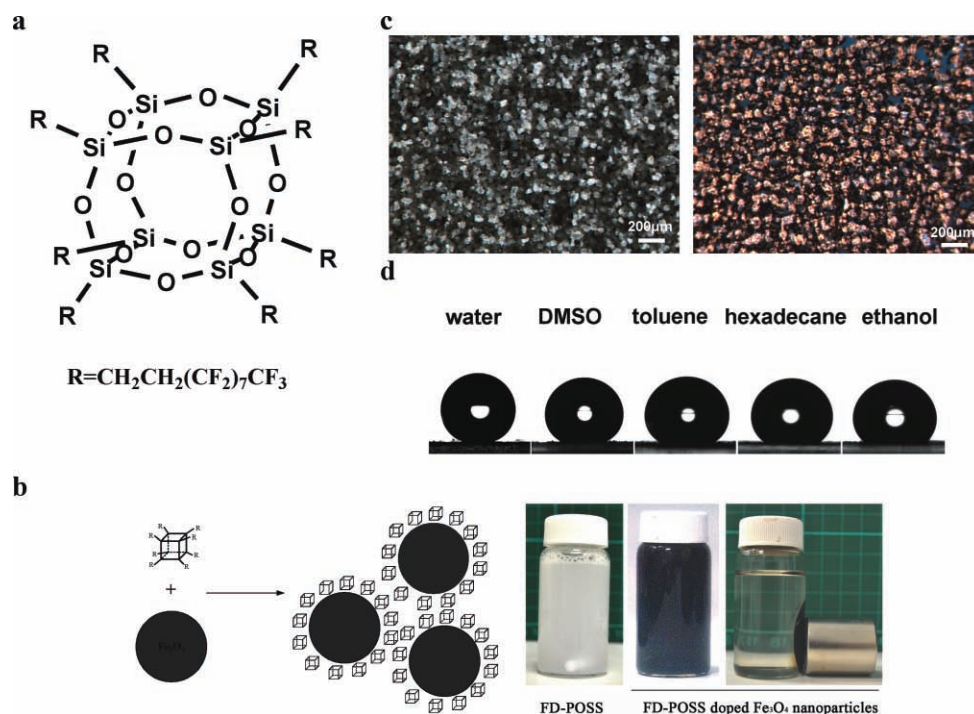


Figure 1. a) Structure of FD-POSS. b) Process to make the FD-POSS/Fe₃O₄ nanoparticle composite. The insert image to the right shows the suspensions of DP-POSS and the FD-POSS/Fe₃O₄ nanoparticle composite powders in solvent and the FD-POSS/Fe₃O₄ under a magnetic field. c) Optical microscopy images of FD-POSS and FD-POSS/Fe₃O₄ powders (FD-POSS:Fe₃O₄ = 1:1, w/w). d) Water, dimethyl sulfoxide (DMSO), toluene, hexadecane, and ethanol droplets on the FD-POSS/Fe₃O₄ powder-coated silicon surface.

and FD-POSS/Fe₃O₄ composite, can encapsulate not only water but also organic solvents to form stable liquid marbles. **Figure 2a** shows photos of liquid marbles prepared from water, DMSO, toluene, ethanol, and octane (3 μ L). Many other organic solvents have also been tested so far and the powders were able to encapsulate a liquid of surface tension as low as 20.1 dynes cm⁻¹ (Supporting Information). The liquid marbles are very stable and they can float not only on water but also on a fluid of low surface tension (Figure 2b).

The superparamagnetic property of the Fe₃O₄ nanoparticles imparts the FD-POSS/Fe₃O₄ powder-encapsulated liquid marbles with a magnet responsive ability. As a result, the liquid marbles can be actuated to move in different directions, or opened and closed reversibly, under a magnetic field. Figure 2c shows magnet opened liquid marbles from different liquids. The opened liquid marble allows it to be covered with another type of hydrophobic material. To demonstrate this, we used pure FD-POSS powder to cover the opened liquid surface of a magnetic liquid marble, and the covered part showed a different color to the magnetic powder covered surface. Consequently, the motion of liquid can be traced easily. Figure 2d illustrates the motion of a white FD-POSS-stained FD-POSS/Fe₃O₄ hexadecane marble under a magnetic field. It can be clearly seen that the marble rotates on a solid surface (top panel), but shifts sideways on a liquid surface (bottom panel).

The magnet opened liquid marble also allows the liquid to be taken from the marble or the marble to be replenished with other liquids. Figure 2e demonstrates the addition of colorful water droplets into a magnet opened hexadecane marble.

Several water droplets were added to the opened marble (10 μ L) to form a water-in-oil bicomponent liquid marble. Oil-in-water bicomponent liquid marbles can also be produced in a similar way. These bicomponent liquid marbles show the ability to prevent the core liquid from rapid evaporation.

To demonstrate the ability to mediate chemical reactions, we used two different ways to undertake a chemiluminescence reaction.^[22,23] One method used two magnetic liquid marbles to carry different reactive agents, one for hydrogen peroxide and the other for bis(2,4,6-trichlorophenyl)oxalate and dye. As shown in Figure 2f (top panel), the two liquid marbles were actuated under a magnetic field to move together and they then coalesced into a larger liquid marble, initiating the chemiluminescence reaction which can be proven by an immediate light emission from the coalesced liquid marble. Another method involved using a bicomponent liquid marble to host two core droplets, one for the oxidant and the other for the fluorescer, in an immiscible fluid. Under gentle movement actuated by a magnet bar, the two core droplets jointed together triggering the chemiluminescence reaction. The image in Figure 2f (bottom panel) clearly indicates the light emitting just from the combined core droplet. Besides the chemiluminescence reaction, other chemical reactions such as photochemical polymerization, nanoparticle synthesis, and an acid–base reaction have also been trialed and proven to be successful (Supporting Information).

One important aspect for miniature chemical reactors is the ability to integrate with purification and analysis facilities. Since the magnetic liquid marbles can be opened and closed reversibly

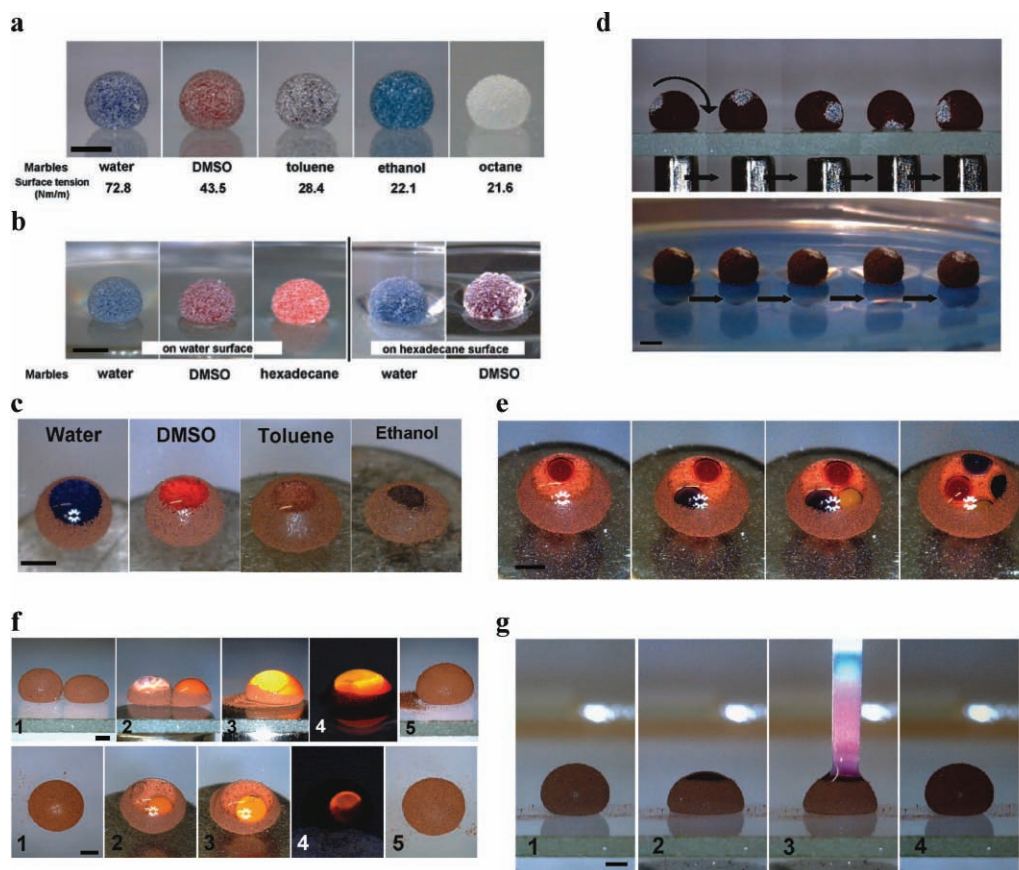


Figure 2. a) Digital graphic images of liquid marbles produced from different liquids and FD-POSS powder (droplet size 3 μL). For easy observation, a small amount of dye was added to the liquid and the existence of the dye has no influence on the stability of the liquid marbles. b) Liquid marbles floating on water and hexadecane surfaces (droplet size 3 μL). c) Magnet opened liquid marbles (droplet size 7 μL). d) Magnet-driven motions of a FD-POSS-stained FD-POSS/ Fe_3O_4 hexadecane marble on a glass slide (top) and water surface (bottom) (droplet size 7 μL). e) Magnet opened hexadecane marbles with different numbers of colored water droplets added (overall droplet size 10 μL). f) A chemiluminescence reaction that occurs as a result of coalescing of two magnetic liquid marbles that contain different reagents (top), and the same chemiluminescence reaction happening within a single liquid marble (bottom) (droplet size 10 μL). g) Chromatographic analysis of liquid in the opened liquid marble (droplet size 10 μL). Scale bar: 1 mm.

by a magnetic field, the reaction liquid can be removed easily by a capillary device for further analyses or directly tested by an optical spectrometer (e.g., UV and fluorescent spectrometers). Figure 2g also shows the direct purification of a reaction product through a narrow chromatographic alumina sheet plugged into the opened liquid marble.

The ability of a hydrophobic powder to repel liquid fluid is mainly determined by the surface chemistry and physical topology of the powder material, the surface tension of a liquid, and the contact mode between the liquid and powder. The FD-POSS molecule comprises eight fluorinated decyl groups which include 136 fluorine atoms surrounding the POSS cage, making the molecule extremely low in surface free energy. The rough surface attributable to the particulate structure facilitates the formation of a non-wetting powdery surface.^[24–26]

In the static state, the encapsulating powders between the droplet and the solid support (Figure 3a) receive the largest liquid pressure. Because of the non-wetting feature, the liquid on a powdery porous layer receives a negative capillary pressure

that pushes the liquid out of the powder layer. Whether a liquid marble can remain stable on a solid surface or not is determined by the ability of the non-wetting powder layer to prevent the liquid breakthrough (i.e., breakthrough pressure, $P_{\text{breakthrough}}$) and the actual liquid pressure generated by the liquid droplet (P_{droplet}). If $P_{\text{breakthrough}} \gg P_{\text{droplet}}$, the actual pressure generated by the liquid droplet is not enough to force through the powder layer hence the liquid marble is stable. When P_{droplet} is close to $P_{\text{breakthrough}}$, it is easy for the liquid to break the powder layer, which leads to breakage of the liquid marble.

Based on the capillary force and the liquid pressure that forces liquid to sag into the powdery pores (Figure 3b,c), the ratio between the breakthrough pressure and the maximum liquid pressure formed by the droplet ($P_{\text{droplet}}^{\text{max}} = \rho g l$, where ρ is the density of the liquid, g is the constant due to gravity, and $l = \sqrt{\gamma_{\text{lv}}/\rho g}$ is capillary length of the liquid), $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}}$, can be estimated as:

$$P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}} = A^* = \frac{H^* \cdot T^*}{H^* + T^*} \quad (1)$$

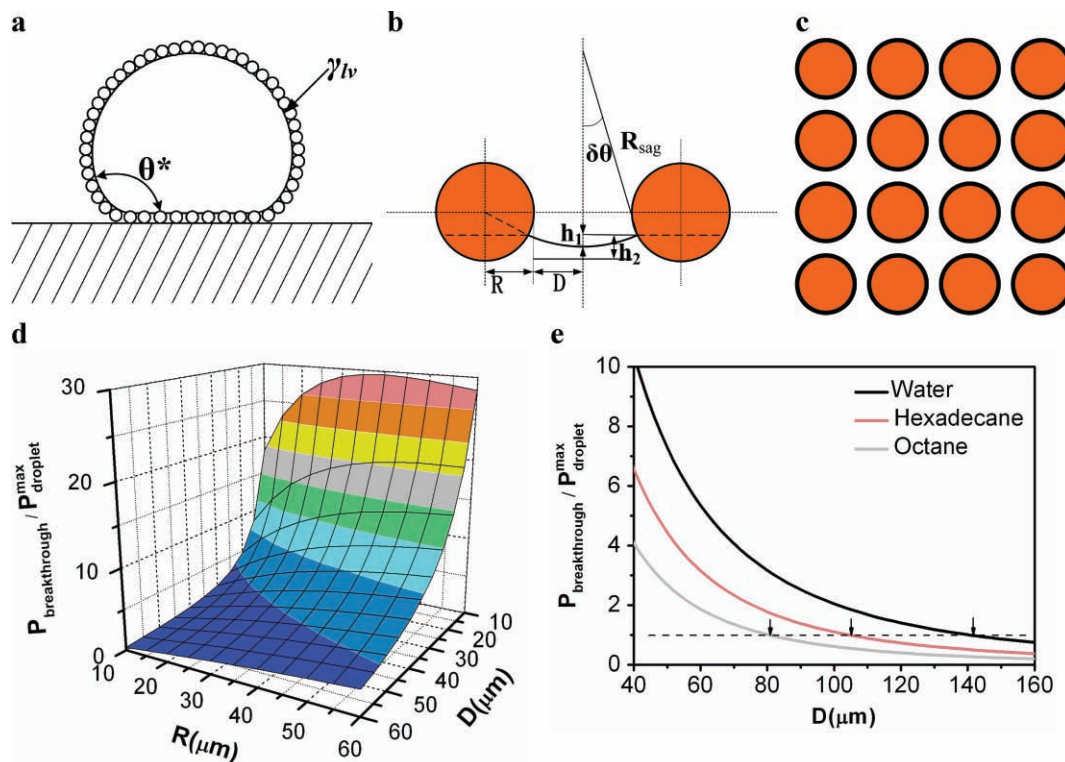


Figure 3. a) Idealized liquid marble with a single layer of powders covering the droplet surface. b) Fluid sagging into two particles and the dimensions for calculation of the breakthrough pressure. c) One powder arrangement used for calculation of breakthrough pressure. d) Dependencies of $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}}$ ratio on R and D for octane ($\theta = 55^\circ$). e) $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}} \sim D$ dependency calculated based on the actual powder dimension for water ($\theta = 120^\circ$), hexadecane ($\theta = 80^\circ$), and octane.

$$H^* = \frac{2\pi(1 - \cos\theta)l_{\text{cap}}}{D(2\sqrt{3}D^* - \pi)} \quad (2)$$

$$T^* = \frac{\pi l_{\text{cap}} \sin(\theta - \psi_{\text{min}})}{R(2\sqrt{3}D^* - \pi)} \quad (3)$$

H^* and T^* are the robustness height and angle determined by the liquid–gas surface tension (γ_{lv}), the particle radius (R), the inter particle distance ($2D$), and the apparent contact angle of liquid on the powder material (θ) (for details see the Supporting Information). The dependency of $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}}$ on the particle radius and the half inter-particle distance for the powder arrangement is given in Figure 3d (the calculation on the other particle arrangement is given in the Supporting Information). It is interesting to note that a maximum $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}}$ ratio occurs when the powder radius is about $35 \mu\text{m}$ and the inter-powder distance is small. Based on the actual powder dimension and surface properties, the $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}} \sim D$ for three studied liquid systems was computed (Figure 3e). When this inter-powder distance is less than $160 \mu\text{m}$ ($D < 80 \mu\text{m}$), the $P_{\text{breakthrough}}/P_{\text{droplet}}^{\text{max}}$ is larger than unity even if the liquid surface tension is very low, suggesting the formation of a very stable liquid marble.

In summary, we have demonstrated the potential of using fluorinated POSS and magnetic nanoparticles as a universal encapsulating agent to prepare liquid marbles from various

liquids. Magnetic manipulation enables the liquid in the marble to communicate with the outside environment on demand, which provides a simple way to integrate with portable purification and analysis facilities. All these features could lead to new universal “lab-on-chip” reactor systems with excellent integration ability to incorporate sample fabrication, actuation, purification, and analysis into a single electronic chip for diverse applications.

Experimental Section

Preparation of FD-POSS/Fe₃O₄ Nanoparticle Composite Powders: (1H,1H,2H,2H-heptafluorodecyl)₈Si₈O₁₂ (FD-POSS), synthesized according to the literature method,^[20] and hydrophobic Fe₃O₄ nanoparticles, prepared by a literature method,^[16] were dispersed in 20 mL of ethanol and continuously stirred for 24 h. The mixture was then isolated from the solution with a bar magnet and dried under vacuum at 60 °C.

Preparation and Magnetic Manipulation of Liquid Marbles: Liquid marbles were prepared by dropping liquid droplets onto a bed of FD-POSS or FD-POSS/Fe₃O₄ nanoparticle grains. Upon gentle shaking of the droplet, the solid powders became stuck to the droplet surface forming a powder-encapsulated liquid droplet (i.e., liquid marble). Magnetic manipulation of the liquid marbles was performed using a neodymium cylinder magnet (diameter 10 mm and length 12 mm). The directed movement of the liquid marbles was recorded using a digital microscope (Dino-Lite AM313).

Supporting Information

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

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