Switchable opening and closing of a liquid marble *via* ultrasonic levitation

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Abstract

Liquid marbles have promising applications in the field of micro-reactors, where the opening and closing of their surfaces plays a central role. We have levitated liquid water marbles using an acoustic levitator and thereby achieved the manipulation of the particle shell in a controlled manner. Upon increasing the sound intensity, the stable levitated liquid marble changes from a quasi-sphere to a flattened ellipsoid. Interestingly, a cavity on the particle shell can be produced on the polar areas which can be completely healed when decreasing the sound intensity, allowing it to serve as a micro-reactor. The integral of the acoustic radiation pressure on the part of the particle surface protruding into air is responsible for particle migration from the center of the liquid marble to the edge. Our results demonstrate that the opening and closing of the liquid marble particle shell can be conveniently achieved *via* acoustic levitation, opening up a new possibility to manipulate liquid marbles coated with non-ferromagnetic particles.

1. Introduction

Liquid water marbles, formed by the assembly of micro/nanometer sized hydrophobic particles at water droplet-vapor interfaces, have attracted increasing attention in the past decade.[1-5] The formed particle shell prevents direct contact of the liquid with a solid substrate, thus reducing significantly the surface friction of the liquid marble on it.[3] Liquid marbles are therefore excellent micro-reservoirs, which can be easily transported without any leakage of the enwrapped liquid. Owing to this advantage, they have great potential for applications in microfluidics[4,6] and as micro-reactors.[7,8] For example, a liquid marble-based micro-bioreactor has been shown to be an efficient vehicle for culturing living tumor cells[9] and for generating embryoid bodies and facilitating their cardiogenesis.[10] The permeability of the particle shell coating also enables their application for gas sensing and pollution detection.[11,12] The adsorption of particles to the fluid interface leads to an effective surface tension γ_{eff} of the liquid marble, which may be different to that of the bare water surface due to the capillary forces between the interfacial particles.[13-15] As a result, the mechanical and dynamic properties of the liquid marbles depend significantly on the particle type coating the droplet surface.[13]

The manipulation of liquid marbles, either achieving directional motion or controlled opening/closing of the particle shell, plays an important role in their applications. Due to their non-stick property, liquid marbles can be easily moved by gravitational force on a tilted substrate, where the marbles roll not slide. Furthermore, it has been shown that liquid marbles can be actuated with external electric and magnetic fields.[16-18] When exposed to an electric field, the shape of the marble is characterized as a prolate spheroid with eccentricity increasing non-linearly with electric field strength, unlike the case of a bare droplet where a linear dependence of eccentricity has been observed.[19,20] It was also reported that a composite liquid marble, comprised of separate water and diiodomethane compartments, could be actuated with an electric field enabling the climbing of the water compartment on top of the diiodomethane compartment to be accomplished.[16] In cases where the liquid marble was coated by hydrophobic ferromagnetic particles such as Fe_3O_4, the accurate control of the opening and closing of the liquid marble was achieved.[21] However, the ability to open and close liquid marbles coated with non-ferromagnetic particles is yet to be reported. Despite the various manipulation techniques, the levitation of liquid marbles has not been reported.

In this article, we study the manipulation of liquid marbles coated with micron-sized non-ferromagnetic particles. We have accomplished the reversible opening and closing of the liquid marble surface *via* acoustic levitation. We study the dynamic behavior of the levitated liquid marble and focus on how the particle shell on its surface responds to the ultrasound. A mechanism of particle migration is proposed based on the acoustic radiation force analysis on the particle surface in the sound field.

2. Experimental

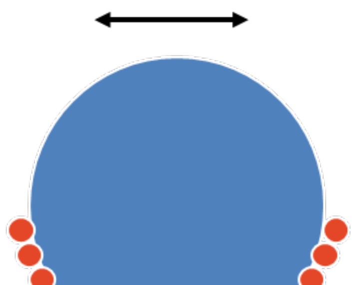
2.1 Materials and liquid marble preparation

The liquid marbles were prepared by rolling water droplets (20 μL) backwards and forwards ten times on a layer of powdered polytetrafluoroethylene (PTFE) particles previously placed on a glass plate,[14] as shown in Figure 1(a). The PTFE particles (Aladdin, China) were hydrophobic and of diameter ~5 μm. The water used in the experiments was purified with an Ultrapure Water System (EPED, China). All the experiments were performed at room temperature (~22 °C) and at a relative humidity of approx. 45%. For each liquid marble, at least 5 levitations were performed and the experiments showed excellent reproducilibity.

2.2 Experimental setup and methods

The acoustic levitator was home-built and composed of an emitter and a reflector arranged coaxially in the gravitational direction and worked at a fixed frequency of 20.5 KHz, as illustrated in Figure 1(b). The cross sectional radii of the emitter and reflector, r_1 and r_2, were 12.5 and 25.0 mm, respectively. The surface of the reflector was concave with a radius of curvature r_3 = 59.4 mm.

In order to adjust the distance d_0 between the emitter and reflector conveniently, the reflector was fixed on a micro-lifting table (LY104SSJ60M, Division of Surplus and Rio Tinto, China). The lift rate of the reflector V_R can be accurately controlled by a servo motor (LK-215B, LIKO China). The photos of the samples were taken by a Nikon D70 camera. The sound field in the levitator was caculated using a commercial finite element software Comsol Multiphystics 4.4.



(a)

(b

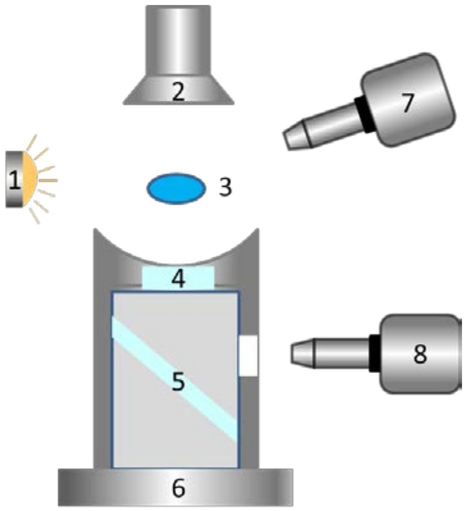


Figure 1. (a) Illustration of the formation of a liquid water marble coated with PTFE particles, (b) schematic view of the experimental setup of the acoustic levitator. 1, light source; 2, emitter; 3, liquid marble; 4, transparent window; 5, mirror; 6, lifting table; 7, camera titled at ~30° for top view; 8, camera for bottom view.

3. Results and discussion

3.1 Static properties of liquid marble

With the protection of the particle layer, the liquid marble exhibits non-wetting behavior on a hydrophilic substrate, Figure 2(a). Moreover, the contact between the inner liquid and a solid chemical material ($KMnO_4$ in the present study) placed outside can be completely prevented. As illustrated in Figure 2(b), a $KMnO_4$ block was deposited on the surface of a liquid marble. It can be supported by the particle shell without dissolving into the liquid inside. This clearly demonstrates that the particle shell of the liquid marble is robust,[22] which favors the liquid marble to serve as a micro-reactor. On the other hand, however, it may also prevent the mixing of chemicals which is a disadvantage for the anticipated chemical reactions.

(a) (b

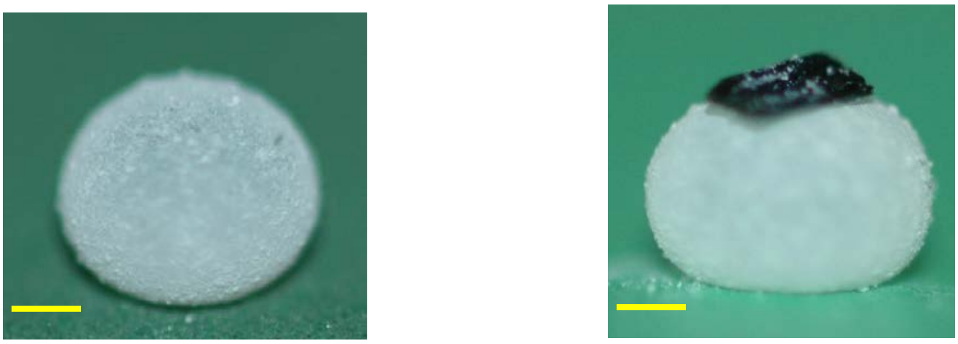


Figure 2. (a) Non-wetting of a liquid water marble on hydrophilic sandpaper, (b) a $KMnO_4$ block deposited on the liquid marble surface. Scale bar = 1 mm.

3.2 Acoustic levitation and open/close switch of liquid marble surface

To accomplish controlled opening and closing of the particle shell of the liquid marble, we levitated the liquid marble *via* ultrasound as shown in Figure 3(a). During the levitation, the gravitational force of the levitated sample is balanced by the acoustic radiation force exerted on the sample surface due to the non-linear effect of ultrasound.[23] Because of the significantly reduced evaporation of water afforded by the particle layer, the liquid marble can be levitated intact for some time until the water eventually evaporates (~1 hr). The numerically calculated sound field in the levitator is shown in Figure 3(b). The samples can be levitated at the nodes of the sound field which possess the potential minima.[24] In the experiments, the samples were levitated at one of the nodes marked A where the best levitation stability was achieved.

In the experiments, the liquid marble is being continuously deformed from a quasi-spherical shape to an oblate spheroid with an increase in the sound intensity induced by decreasing the emitter-reflector distance,[25] since the shape of a liquid droplet is determined by the competition between surface tension and acoustic radiation pressure.[26] More importantly, two cavities appear on the polar areas (center regions of the upper and bottom surfaces) of the liquid marble surface which grow continuously with the increase in sound intensity (Figure 4(a) and (b), snapshots (1)-(3), top and bottom cavities), indicating the particles originally located at the center region migrate to the edge. It should be noted that the cavity may exhibit a star-shape and is not simply circular, similar to the phenomenon of surfactant spreading on a particle raft where a ramified finger morphology of crack fronts was observed.[27] Both phenomena result from the pressure gradient exerted on the particle layer. The difference lies in the origin of the driving force. For the case of surfactant spreading, the pressure gradient is induced by the Marangoni effect arising from concentration gradients. In the present study however, the driving force is the pressure gradient caused by the acoustic field. Interestingly, the cavity completely heals upon decreasing the sound intensity (Figure 4(a) and (b), snapshots (4)-(6)).

(a)

(b)

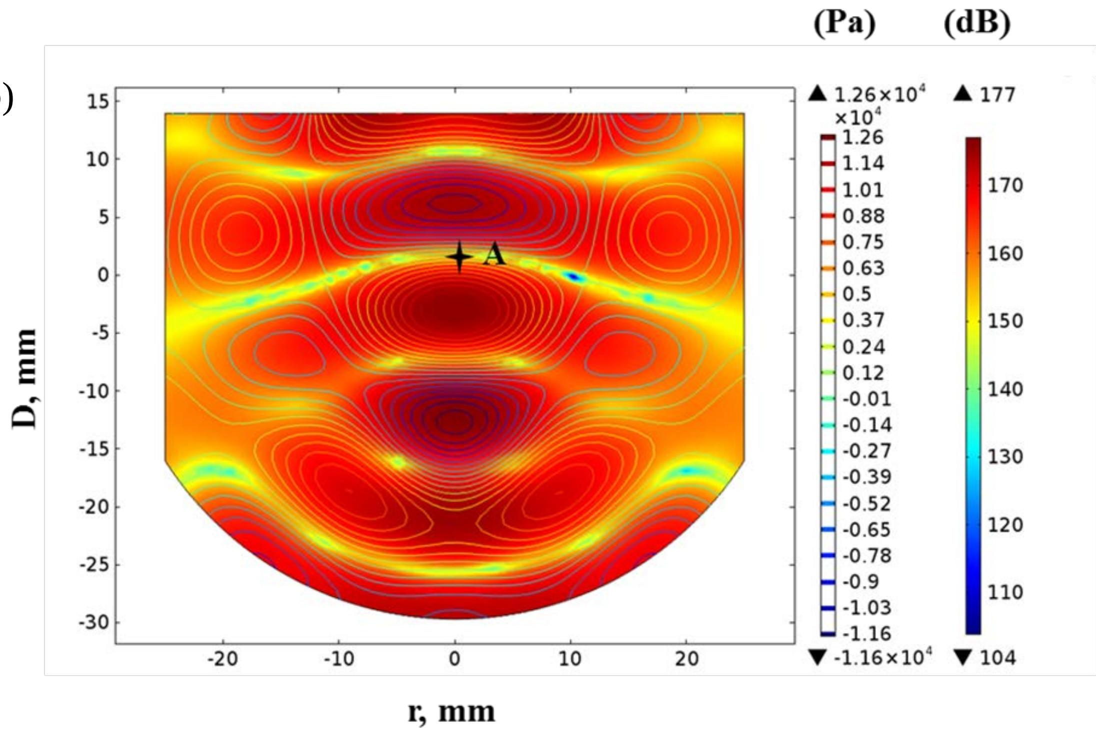
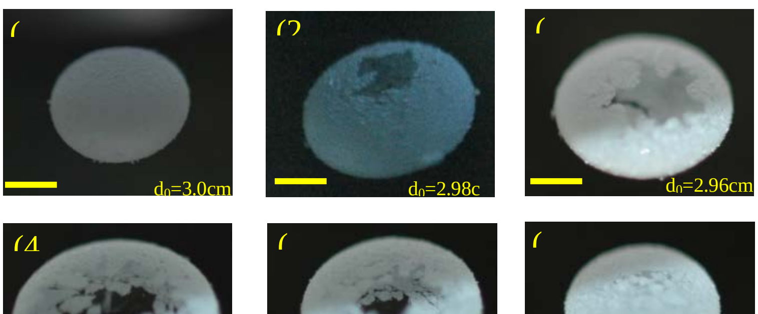


Figure 3. Ultrasonic levitation of a liquid water marble. (a) Image showing a liquid marble being levitated in the levitator (scale bar = 1 cm), (b) the calculated sound field in the levitator. The distance between the reflector and emitter D = 43.5 mm and the cross sectional radius of the reflector r = 25.0 mm. The scales of radiation pressure and sound level are also given. The cross labelled A denotes the levitation position used in the experiments.

(a)



(b)

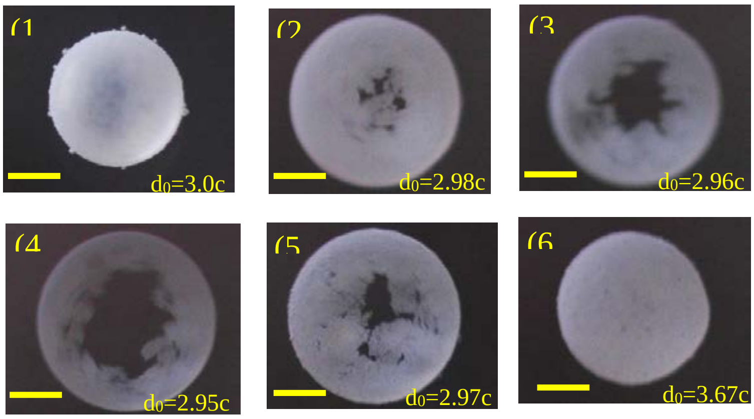


Figure 4. Opening and closing of the particle shell on a liquid water marble under ultrasonic levitation. The liquid marble is photographed with a camera tilted at an angle of ~30° (a) and from the bottom (b) respectively. (1)-(3) A cavity emerges on the surface and grows upon increasing the sound intensity caused by decreasing the emitter-reflector distance d_0, (4)-(6) the cavity heals and closes when d_0 increases. Scale bar = 1 mm.

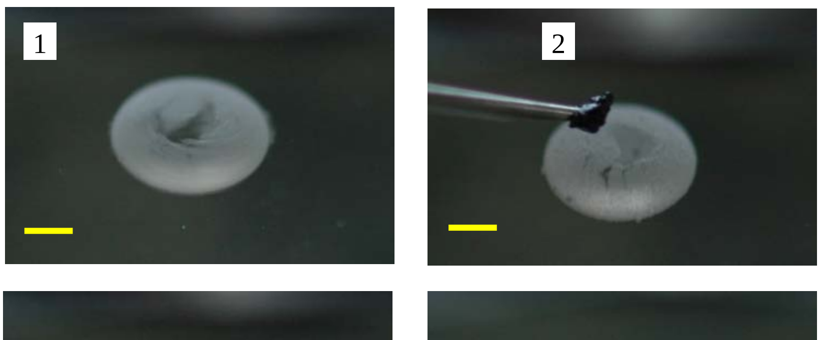
The reversible opening and closing of the liquid marble in the acoustic levitator enables it to act as a smart micro-reactor, as shown in Figure 5(a). A solid block of $KMnO_4$ can be conveniently introduced into the liquid inside when the cavity is produced and its subsequent dissolution can be isolated from the surrounding environment by closing the particle shell. Furthermore, after addition of the chemical material, the recovered liquid marble can be easily taken out from the levitator without damage or leakage of liquid (Figure 5(b)) by inserting a thin solid sheet into the sound field beneath the liquid marble. This varies the sound field and decreases the levitation force dramatically, leading to the liquid marble falling onto the sheet.

Acoustically levitated bare water droplets, as reported by Scheeline and co-workers, can serve as excellent micro-reactors for biophysical measurements or chemical reactions due to their contactless character and the ease of sample handling.[28,29] More recently, it was shown that acoustic levitation can enhance mixing which is promising for micro-reactions.[30] In the present work, we focus on liquid water marbles since they show fascinating performance to act as a micro-bioreactor for culturing living cells[9,10] due partly to the unique properties of the liquid marble shell. In addition, their mechanical robustness and non-adhesive character favor them enduring other treatment or analysis after being removed from the acoustic levitator.

3.3 Particle migration mechanism

It remains to explain why the particles on the liquid marble surface can migrate from the polar area to the equatorial area in the sound field. One possible reason is that acoustic streaming, which is often observed in acoustic levitators with high sound intensity,[31,32] blows the particles along the surface. However, the direction of

(a)



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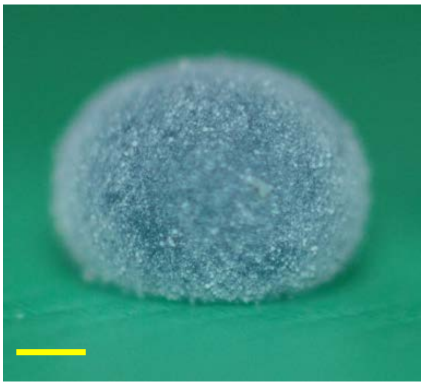

Figure 5. Liquid marble acting as a micro-reactor. (a) Once the cavity emerges (1), a block of $KMnO_4$ is added into the liquid marble and dissolves (2), (3). The particle shell of the liquid marble recovers to the initial state upon decreasing the sound intensity (4), (b) a recovered liquid marble with dissolved $KMnO_4$ inside taken out from the levitator. Scale bar = 1 mm.

the acoustic streaming adjacent to the droplet surface is from the droplet edge to the center,[32] implying that acoustic streaming cannot account for the particle migration which is in the reverse direction.

In order to fully understand the particle migration mechanism, we calculated the acoustic radiation pressure P_A on the liquid marble surface based on King's theory:[33]

$$P_A = \frac{1}{2\rho_0 c_0^2}\langle p^2 \rangle - \frac{1}{2}\rho_0 \langle v^2 \rangle \quad (1)$$

where p is the sound pressure, ρ_0 is the density of air, c_0 is the speed of sound in air and v is the medium particle velocity of air. The angular brackets in Eq. (1) denote the time average over one period of acoustic oscillation. To simplify the analysis, we calculated the acoustic radiation pressure P_A for a bare and smooth liquid droplet but with the same volume as the liquid marble used in the experiments, as illustrated in Figure 6(a). The shape of the droplet is shown in the inset. It is reasonable to suppose that the presence of micron-sized particles on the droplet surface does not change the sound field or the distribution of acoustic radiation pressure since the particle size is much smaller than the sound wavelength. Obviously, on both the upper and the lower surface, P_A decreases from the droplet center to the edge. Therefore, the integral of P_A on the surface area of each particle protruding into air (shown in the inset of Figure 6(b)) may provide the driving force for particle migration and can be written as:

$$f_M = a^2 \int_0^{2\pi} \int_{-\theta^*}^{\theta^*} P_A(\theta, \varphi) \sin(\theta) d\theta d\varphi \quad (2)$$

where a is the radius of the particle and θ^* is the contact angle of the particle at the liquid-air surface measured through the liquid ($\theta^* = 108°$ for PTFE). In eqn. (2), the positive value of f_M represents the force direction from the polar area to the periphery of the drop. Using eqn. (2) the acoustic radiation force exerted on each particle can be calculated. The calculated results for f_M are plotted in Figure 6(b). Clearly, f_M shows a downward trend from the droplet center to the edge and strongly depends on the

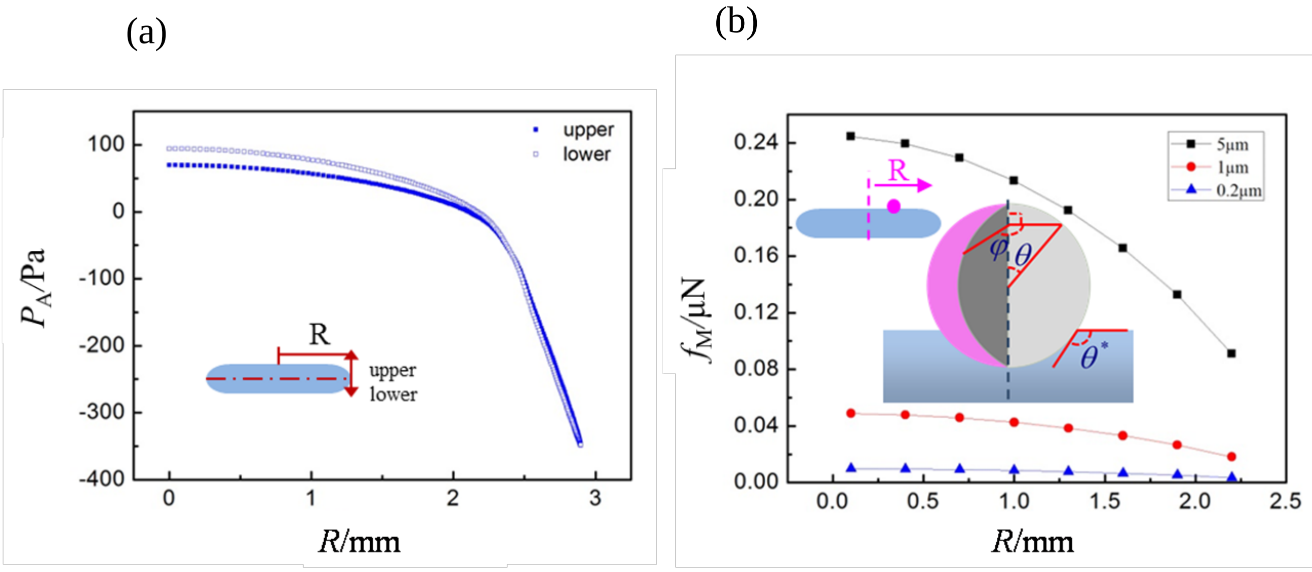

Figure 6. Force analysis for particle migration on the liquid marble surface under acoustic levitation. (a) Simulated acoustic radiation pressure on the levitated droplet, (b) driving force f_M for particle migration exerted on the particle for different particle diameters given. Inset shows the arrangement of a particle on the droplet surface.

particle size and its position. For the 5 μm sized particles used in the experiments, f_M is ~ 0.24 μN at the liquid marble center.

The force resisting the particle migration can be written as:[34]

$$f_r = \frac{1}{8} C_d \pi d_p{}^2 \rho_p V_r{}^2 , \tag{3}$$

with[35]

$$C_d = \frac{24}{\mathrm{Re}_p}(1+0.15\,\mathrm{Re}^{0.687})\,(\mathrm{Re}_p \le 1000) \tag{4}$$

where C_d is the drag coefficient, d_p, V_r and Re_p are the effective length, relative speed and Reynolds number of the particle in water respectively and ρ_p is the particle density. In the present study, Re_p~1.39, d_p~4.85 μm, ρ_p = 2.2 g cm^{-3} and V_r~0.29 mm s^{-1}. Therefore, f_r is~10^{-4} μN, being several orders of magnitude lower than f_M. This suggests the force exerted by the ultrasound on the particle surface is sufficient to drive the particle to migrate from the droplet center to the edge.

It should be noted that the shape change of the liquid marble is also favorable for the opening and closing of the particle shell because it results in a larger surface area which leaves space for particles to migrate. However, shape deformation alone only causes the particle shell to become more dilute. In order to form the cavity on the polar areas of the liquid marble, the acoustic radiation force exerting on the particles plays a vital role.

4. Conclusions

In summary, we have achieved reversible opening and closing of the particle shell coating a liquid water marble through acoustic levitation. Upon increasing the sound intensity, the particles migrate from the polar area of the droplet surface to the equatorial area, leading to the formation of a cavity on the liquid marble surface. In addition, the opened cavity can heal upon decreasing the sound intensity. The driving force for the particle migration originates from the acoustic radiation pressure exerted on the part of the particle surface protruding into air. Our results highlight the promising application of acoustic levitation on the manipulation of non-ferromagnetic solid particles on liquid marble surfaces, which allows it to behave as a micro-reactor.

Acknowledgements

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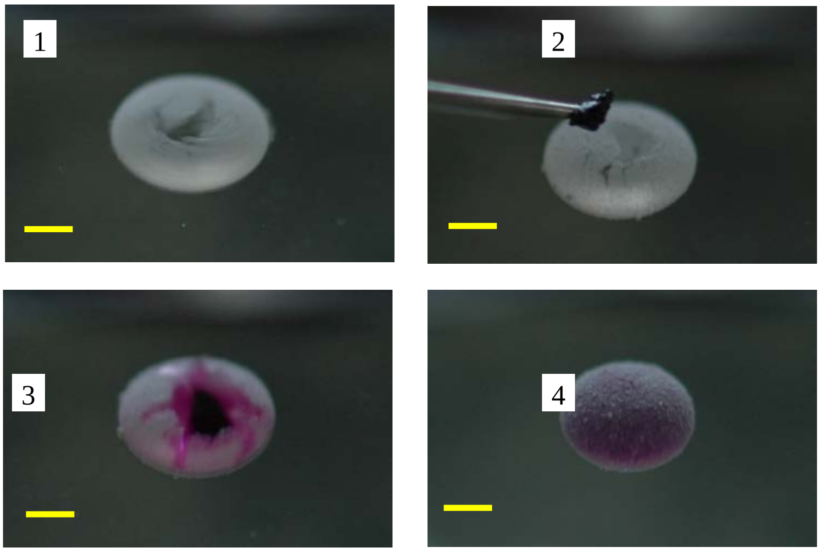
TOC graphic

A cavity on the liquid marble surface can be produced and healed in a controlled manner under acoustic levitation.

(a)



(b)