Multi-Responsive Janus Liquid Marbles: The Effect of Temperature and Acidic/Basic Vapors

Zhiguang Xu, Yan Zhao,* Liming Dai, and Tong Lin*

Increasing demand for manipulation of small-volume liquids in miniature systems has greatly promoted the development of new droplet microfluidics based on liquid marbles. Liquid marbles are liquid droplets encapsulated with a shell of loosely packed non-wetting particles. Those particles sitting at the liquid–air interface on liquid marbles prevent the liquid from directly contacting with the substrate, allowing liquid marbles to move freely on various solid surfaces without wetting the surface. We, along with other researchers, have previously demonstrated that liquid marbles are promising for various applications, including microreactors, gas sensors, micropumps, and accelerometers.

The ability to move and release liquid from a liquid marble in response to an external stimulus enables liquid marbles to act as universal cargo carriers for microfluidic assays. Stimuli-responsive liquid marbles have been devised by endowing either the shell or the liquid with responsive ability. As far as we are aware, however, all the reported liquid marbles can respond to only single stimulus, such as pH, electric field, or magnetic field. Liquid marbles that are able to respond to multiple external stimuli are highly desirable for multifunctional applications in various environments, but have not realized yet.

Here, we report the first development of a multi-responsive liquid marble that can be repositioned by an external magnetic field and ruptured upon exposure to either infrared (IR) radiation or acidic/basic vapors. The newly developed multi-responsive liquid marbles could be used as sensors to visually detect acid/base gases, handle small volumes of toxic chemicals in harsh environments, deliver reagents for exothermic reactions on site, or control cargo releases in microfluidics.

To demonstrate the multi-responsive feature, we prepared a Janus liquid marble composed of a water drop, a magnetic semi-shell (brown) and a nonmagnetic semi-shell (white) based on the unique opening feature of magnetic liquid marbles that we reported in our previous work (Figure 1a,b). The brown powder was hydrophobic Fe₃O₄ nanoparticles or a mixture of wax and hydrophobic Fe₃O₄ nanoparticles (wax/Fe₃O₄ powder), while the white powder was a mixture of decanoic acid (DA) and heptylamine (HA)-modified titanium oxide nanoparticles (DA–TiO₂/HA–TiO₂, see Figure S1, Supporting Information). To prepare such a Janus liquid marble, a magnetic liquid marble was positioned at the lower surface of a glass plate using a magnet bar. By moving the magnet bar toward the liquid marble, the bottom surface of the magnetic liquid marble was opened (Figure 1b, left). The liquid marble was held at the open state and nonmagnetic DA–TiO₂/HA–TiO₂ powder was then brought into contact with the exposed liquid hemisphere. As a result, the DA–TiO₂ and HA–TiO₂ particles attached to the water surface, leading to the formation of a Janus liquid marble (Figure 1b, right). It is noted that Janus liquid marbles have been prepared by collision and coalesce of two liquid marbles, which are prepared from different powders. Here, our method is completely different from the previous art, and it is more controllable in droplet size and shell profile. Stimulus-induced wettability change of the powders will allow the Janus liquid marble to rupture under a stimulus particular to each type of powder. The Janus liquid marble ruptured upon IR irradiation when the temperature-responsive wax/Fe₃O₄ semi-shell contacted with the glass substrate (Figure 1c and movie S1, Supporting Information), and ruptured upon exposure to either ammonium hydroxide or acetic acid vapor when the pH-responsive DA–TiO₂/HA–TiO₂ semi-shell contacted with the glass substrate (Figure 1d and movies S2, S3, Supporting Information).

Hydrophobic Fe₃O₄ nanoparticles used in this study were synthesized by coprecipitation of Fe(II) and Fe(III) salts in an ethanol–water solution with ammonia in the presence of a fluorinated alkyl silane. The as-obtained Fe₃O₄ particles had a diameter of ~10 nm and exhibited a superparamagnetic behavior (see Figure S2, Supporting Information). The temperature-responsive wax/Fe₃O₄ powder was prepared by mixing wax (melting point, 53–57 °C) with the Fe₃O₄ particles at 70 °C, which was then grinded into a fine powder in liquid nitrogen. Because of the hydrophobicity of both wax and Fe₃O₄ nanoparticles, the apparent contact angle of a water drop placed on a bed of the wax/Fe₃O₄ powder was as high as 154 ± 2° (see Figure S3, Supporting Information).

Like magnetic liquid marbles reported in our previous work, liquid marbles prepared with the wax/Fe₃O₄ powder (Figure 2a) had magnetic-field-responsive features. Unlike the previously reported magnetic liquid marbles, the wax-containing liquid marble ruptured when it was irradiated by IR light due to the melting of the wax in the magnetic shell (Figure 2b and Movie S4, Supporting Information). IR thermography imaging was employed to measure the temperature of the marble surface. Immediately before the liquid marble
being ruptured, temperature at the contact point between the liquid marble and glass substrate was found to reach ca. 60 °C (Figure 2c and Movie S5, Supporting Information), which was slightly higher than the wax melting point, indicating that the liquid marble rupture was caused by the melting of wax. The observed thermo-responsive rupture could be used for triggering release of encapsulated cargo on water surface (see Figure S4, Supporting Information).

Thermo-responsive wettability is often achieved using temperature-responsive polymers having a lower critical solution temperature (LCST), such as poly-N-isopropylacrylamide.[8] In this case, the surface switches from hydrophilic to hydrophobic above LCST. Temperature-induced wetting transition with polymers having an upper critical solution temperature (UCST) (i.e., hydrophobic-to-hydrophilic switch above UCST) is still challenging. To achieve thermo-responsive liquid marbles, we developed in this study an alternative way to address this difficulty by melting the shell of wax/Fe₃O₄ liquid marbles with increasing temperature. Figure 2d illustrates the change in the liquid–air

Figure 1. a) Photo of a Janus liquid marble (7 µL) having a magnetic semi-shell (brown) and a nonmagnetic semi-shell (white). b) Preparation of a Janus liquid marble by opening a magnetic liquid marble from its bottom, followed by covering the exposed water surface with different (e.g., gas-responsive) powder. c) Thermo-triggered rupture of a Janus liquid marble (the brown-colored temperature-responsive shell contacted with the glass substrate). d) Gas-triggered rupture of a Janus liquid marble (the white-colored gas-responsive shell contacted with the glass substrate). The wet pH test strip showed pH in the range 9 to 10 and 3 to 4 for the ammonium hydroxide and acetic acid exposure, respectively. Left: Fe₃O₄ liquid marble; right: responsive Janus liquid marble; middle: a small aluminum container for ammonium hydroxide or acetic acid as the vapor source.

Figure 2. a) A liquid marble (7 µL) prepared with wax/Fe₃O₄ powder. b) Thermo-triggered rupture of the wax/Fe₃O₄ liquid marble on the glass substrate. c) IR thermographic images to show the collapse of the liquid marble when the surface temperature at the marble/substrate contact point reached ca. 60 °C (I: Fe₃O₄ liquid marble; II: wax/Fe₃O₄ liquid marble). d) Schematic illustration of the liquid–air interface profile of a liquid marble at a stable state (left) and just starting to rupture (right), highlighting the change of D, h₁, and h₂ induced by the wax melting.
interface profile of the wax$/$Fe$_3$O$_4$ liquid marble induced by wax melting. At a stable state, the hydrophobic particles prevented the liquid–air interface from contacting the substrate. Between two adjacent particles, the sagging height of the liquid–air interface caused by gravity, \( h_1 \), scales as \( h_1 \sim D^2/l_{\text{cap}} \), where \( D \) is the distance between the adjacent particles, \( l_{\text{cap}} = \sqrt{\gamma \nu / \rho g} \) is the capillary length of the liquid, \( \gamma \) is the surface tension, \( \rho \) is the liquid density, and \( g \) is the acceleration due to gravity.\(^9\) When wax melted, the radius of particle \( R \) decreased, resulting in the decrease in \( h_2 \), which is the height of the three-phase (solid–liquid–air) contact point above the substrate, but increase in \( D \), and hence the increase in \( h_1 \). When \( h_1 \) was equal to \( h_2 \), the liquid–air interface touched the substrate, disintegrating the liquid marble.

In addition to the temperature-triggered hydrophobic-to-hydrophilic switch, multi-responsive liquid marbles can also be used to promote a gas-triggered hydrophobic-to-hydrophilic wettability transition. For this purpose, titanium oxide nanoparticles modified with long-chain carboxylic acid or amine were synthesized simply by mixing titanium (IV) butoxide with DA or HA in ethanol, followed by addition of a small amount of water to the mixture. The samples thus obtained were characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) (see Figure S5, Supporting Information). DA–TiO$_2$ particles had a diameter of \( \approx 300 \) nm and changed from hydrophobic to hydrophilic upon exposure to ammonium hydroxide vapor (Figure 3a), while the HA–TiO$_2$ particles had a diameter ranging from 80 to 400 nm and exhibited hydrophobic-to-hydrophilic change upon exposure to acetic acid vapor (Figure 3b). The observed basic and acidic gas responsive features were attributed to the ionization of carboxyl and amine groups, respectively.\(^{10}\)

As expected, the liquid marbles prepared from DA–TiO$_2$ and HA–TiO$_2$ particles ruptured upon exposure to ammonium hydroxide and acetic acid vapors, respectively (Figure 3 and Movies S6, S7, Supporting Information). The response time was dependent on the concentration of acid or ammonia vapor in the air (see Figure S6, Supporting Information). In this study, the lowest vapor concentration used to rupture the liquid marble was estimated to be \( \approx 2.41 \times 10^{-5} \) and \( 2.65 \times 10^{-5} \) mol L$^{-1}$ for ammonia and acetic acid, respectively. As a control, the liquid marble prepared from Fe$_3$O$_4$ particles remained stable even after a prolonged gas exposure. Figure 3c illustrates the liquid–air interface change of a liquid marble induced by the decrease in the contact angle of the particle, \( \theta \). When \( \theta \) decreased, the particles moved from the

\[ \text{Figure 3. a) DA–TiO}_2 \text{ and b) HA–TiO}_2 \text{ particles used to prepare liquid marbles (7 \( \mu \)L), their scanning electron microscopy (SEM) images and chemical compositions, and the water contact angle of a bed of the particles as a function of exposure time to ammonium hydroxide and acetic acid vapor, respectively (top panels). The rupture of the liquid marbles, left: Fe$_3$O$_4$ liquid marble; right: responsive liquid marble; middle: a small aluminum container for ammonium hydroxide or acetic acid as the vapor source (bottom panels). c) Schematic illustration depicting the rupture induced by the decrease in \( \theta \).} \]
air phase to the inner liquid phase, with the liquid–air interface being exposed towards the substrate. Once the liquid–air interface touched the substrate, the liquid marble started to collapse.

More interestingly, liquid marbles prepared with a mixture of DA–TiO₂ and HA–TiO₂ particles (1:1, wt/wt) can rupture (see Figure S7, Supporting Information). The Janus liquid marble was also responsive to external magnetic field because of the magnetic part of the shell. It rolls on a glass substrate, while slides on water surface under the actuation of a magnet bar positioned below the glass slide or water container (see Figure S8, Supporting Information).

In conclusion, a Janus liquid marble with multi-responsive ability to magnetic forces, IR radiation, and acidic/basic vapors has been successfully prepared. Such multi-responsive liquid marbles could find various applications in many areas, including sensors, miniaturized smart containers for handling small volumes of toxic chemicals, and delivering reagents for exothermic reactions on site and on demand, and targeted cargo release in microfluidics.

Experimental Section

Synthesis of the Highly Hydrophobic Fe₃O₄ Nanoparticles: Typically, 1.5 mL aqueous NH₄OH solution was added dropwise to 200 mL water/ethanol (4:1, v/v) containing FeCl₃·6H₂O (0.85 g, 3.14 mmol), FeCl₂·4H₂O (0.30 g, 1.51 mmol), and tridecafluorooctyltriethoxysilane (0.20 mL, 5.23 mmol) under nitrogen protection and vigorous stirring. After stirring for 24 h, the resulting precipitate was isolated from solution with a bar magnet, washed with water/ethanol mixture for three times, and dried at 60 °C.

Preparation of the Wax/Fe₃O₄ Powder: The wax/Fe₃O₄ powder (1.8:1, w/w) was prepared by melting the wax (paraffin wax, T_m = 53–57 °C), mixing with highly hydrophobic Fe₃O₄ nanoparticles, and then grinding in liquid nitrogen.

Synthesis of the DA–TiO₂ Nanoparticles: First, 1 g titanium (IV) butoxide (TBT) was dissolved in 12.7 mL ethanol and 0.4 g DA was dissolved in 127 mL ethanol. The TBT solution was then slowly added dropwise into the DA solution with stirring at room temperature. 17 g MilliQ water was slowly dropped into the mixture solution with vigorous stirring. The mixture solution reacted for 3 h at room temperature. The product was obtained via centrifugal separation and dried at 45 °C for 10 h under vacuum.

Synthesis of the HA–TiO₂ Nanoparticles: Typically, a solution of 1 g TBT in 12.7 mL ethanol was slowly added dropwise into a solution of 0.37 g HA in 82 mL ethanol under stirring at room temperature. Then 3.2 g MilliQ water was slowly dropped into the mixture solution under vigorous stirring. The mixture solution reacted overnight at room temperature. The product was obtained via centrifugal separation and dried at 45 °C for 10 h under vacuum.

Characterization: Contact angle was measured using a contact angle measurement system (CAM101, KSV Instruments Ltd). Transmission electron microscopy (TEM) observation was undertaken on JEOL JEM-2100 microscope at an acceleration voltage of 200 kV. Magnetic properties were measured using a Quantum Design MPMS-5 DC-SQUID (superconducting quantum interference device) susceptrometer. An IEC thermo tracker IR camera was used to record the temperature change of the liquid marble surface. The recorded thermal images were processed with Image Pro II 4.0.6 micron infrared software.

Preparation of the Liquid Marbles: Liquid marbles were formed by rolling a water drop on appropriate fine powder. Due to the tendency to minimize the surface free energy, the powder spontaneously self-organized on the water/air interface and formed a uniform cover layer on the water drop. Liquid marbles were placed on a glass surface or water surface. Their magnetic actuation was realized by moving the magnet (a permanent neodymium cylinder magnet, 4 mm diameter × 20 mm length) positioned beneath the glass slide or water surface.

Supporting Information

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

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