Light-Driven Transport of a Liquid Marble with and against Surface Flows

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Abstract: *Liquid marbles, that is, liquid drops coated by a hydrophobic powder, do not wet any solid or liquid substrate, making their transport and manipulation both highly desirable and challenging. Herein, we describe the light-driven transport of floating liquid marbles and emphasize a surprising motion behavior. Liquid marbles are deposited on a water solution containing photosensitive surfactants. Irradiation of the solution generates photoreversible Marangoni flows that transport the liquid marbles toward UV light and away from blue light when the thickness of the liquid substrate is large enough (Marangoni regime). Below a critical thickness, the liquid marbles move in the opposite direction to that of the surface flow at a speed increasing with decreasing liquid thickness (anti-Marangoni). We demonstrate that the anti-Marangoni motion is driven by the free surface deformation, which propels the non-wetting marble against the surface flow. We call this behavior "slide effect".*

The controlled transport of small amount of liquids is a crucial challenge for the improved performance of miniaturized devices with impact in diagnostics, healthcare, and energy.[1] A robust and versatile strategy involves making fluids flow through microchannels[2] but the confinement and contact of flowing fluids with the channel walls is a source of contamination and clogging. A channel-free possibility involves the manipulation small volumes of fluids in the form of discrete drops deposited on a substrate.[3] In this case, precise control of the wetting properties of the liquid to be transported[4–6] is a challenge that tends to limit the applicability of these strategies. To avoid all of the limitations due to specific liquid/substrate interactions (and especially contamination and wetting issues), Aussillous and Quéré proposed a revolutionary idea. They coated water drops with hydro-

phobic particles and showed that the resulting structures, called liquid marbles, were in a non-wetting situation regardless of their substrate.[7,8] This result led to intense research to manipulate and understand the hydrodynamic behavior of these new entities.[9,10]

However, although a lot of progress has been made in the design and comprehension of liquid marbles, reported studies on their actuation have been limited to only a few cases. A typical strategy involves the use of stimuli-responsive particles, including photosensitive[11,12] and magnetic[13–15] particles suspended in or coating the marble, making remote actuation possible but making each strategy specific to the composition of the liquid marble. Composition-independent approaches were restricted to the use of electric[8,16,17] or ultrasonic[18] stimulation but, in these cases, long-range and precise transport could not be achieved. Photoactuation thus appears as a promising alternative offering contactless, tunable, and highly resolved stimulation.[19,20] However, to our knowledge, only the light-induced collapse of photosensitive particle-coated marbles,[10,11] the locomotion of photothermally coated marbles,[21] and the laser-guided motion of immersed chloroform marbles by local bubble generation[12] have been reported, each of these approaches being specific to the marble composition. Herein, we describe
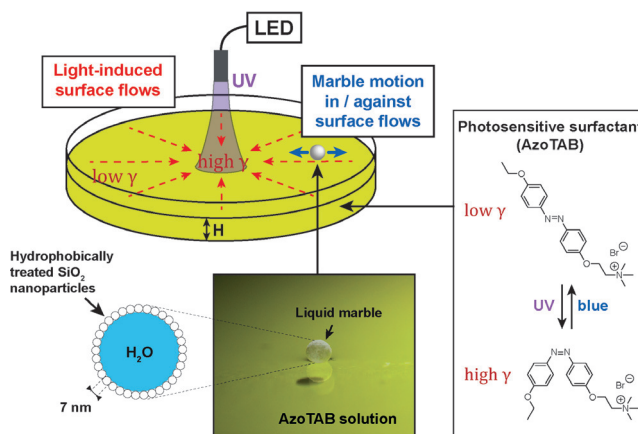
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Figure 1. Optical actuation of a floating liquid marble. A 2 µL liquid marble is deposited on a water solution containing the surfactant AzoTAB (10 mM) contained within a Petri dish (where H is the liquid thickness). A light guide connected to an LED source provides a Gaussian shaped light spot of width w on the liquid surface, at a wavelength of $\lambda = 365$ nm (UV irradiation, 330 W m^{-2}) or $\lambda = 440$ nm (blue light irradiation, 820 W m^{-2}). The resulting gradient of surface tension γ generates light-induced surface flows in the direction of the gradient, which, in turn, trigger the motion of the liquid marble either with or against the surface flows.

for the first time a generic method for remote, long-range, and photoreversible transport of floating liquid marbles. To make it applicable regardless of the marble composition, we deposited marbles on a photosensitive surfactant-laden solution and used the surface flows driven by the light-induced surface tension gradient (Marangoni flows) to actuate the floating marble. We studied the marble motion and discovered a counterintuitive regime where the marble moved in a direction opposite to these surface flows.

We prepared liquid marbles by coating 2 μL water drops with hydrophobically modified fumed silica nanoparticles (see Movie S1 in the Supporting Information). Liquid marbles were deposited carefully in an 8.7 cm diameter Petri dish containing water supplemented by 10 mM of AzoTAB (Figure 1), a photosensitive azobenzene-containing surfactant.[22,23] Liquid marbles floated on this liquid surface, despite the presence of surfactants and a decreased surface tension (γ; around 50 mN m^{-1}) compared to that of water (see Text S1 in the Supporting Information).

A light guide connected to an LED source was used to irradiate the AzoTAB solution. The light guide was maintained at a fixed distance from the liquid surface and generated a light spot of around 15 mm in diameter irradiating at $\lambda = 365$ nm (UV, 330 W m^{-2}) or $\lambda = 440$ nm (blue, 820 W m^{-2}). Under these conditions, UV/blue light irradiation induced a photoreversible increase/decrease of surface tension of 1–2 mN m^{-1} (Figure S1) due to the photoisomerization of AzoTAB accompanied by an increase/decrease of the polarity of its hydrophobic tail.[24,25] UV irradiation of the liquid substrate thus induced converging Marangoni surface flows oriented toward the light spot where surface tension was at its maximum.[26,27] The direction of the surface flows was thus independent of the thickness of the liquid substrate layer H (Figure 2a). However, we found that liquid marbles moved in the direction of the surface flow, that is, towards the UV light, only when the value of H was large enough (Figure 2b, bottom; Movie S3). Surprisingly, liquid marbles moved against the direction of surface flow, that is, away from UV light, when the thickness was smaller than a critical value H^{crit} (Figure 2b top; Movie S2).

When blue light was applied after UV irradiation, the decrease of surface tension in the illuminated area induced diverging Marangoni flows. These diverging flows also gave rise to two motion regimes. For $H > H^{crit}$ the marble moved away from the light spot, that is, along the direction of the light-induced Marangoni flow, whereas for $H <$ H^{crit}, the marble moved toward the blue light, that is, against the direction of the surface flow. Several cycles of photoreversible motion could be achieved upon successive UV/blue light stimulations for both small and large H values (Figure 2c; Movies S4-S5). No marble motion was observed when the same experiment was performed without AzoTAB, showing that light-induced Marangoni flows were instrumental to the marble motion (Movie S6). To our knowledge, this is the first time that photoreversible transport of a floating liquid marble has been reported. Notably, the marble moved
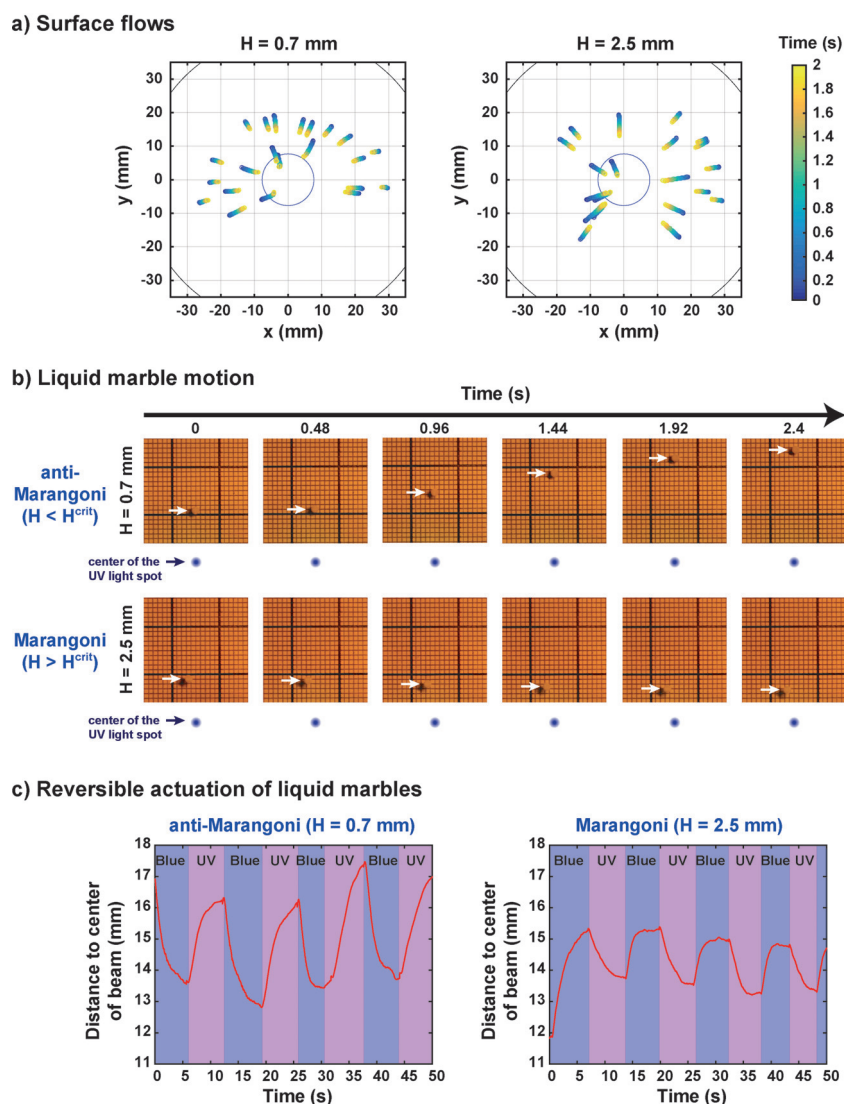

a) Surface flows

b) Liquid marble motion

c) Reversible actuation of liquid marbles

Figure 2. Light-induced marble motion is photoreversible and depends on liquid thickness: Marangoni and anti-Marangoni motion. a) Trajectories of floating tracers upon UV irradiation as a function of time for two different liquid thicknesses (H). The origin of the x–y axes is at the beam center. The purple circle, which has a diameter $2w$, represents the illuminated zone. The black truncated circle shows the edge of the Petri dish. b) Time lapse photographs of a liquid marble (indicated by a white arrow) upon UV irradiation. The center of the light spot is represented by a purple dot. The marble moves against (anti-Marangoni motion, $H = 0.7$ mm) or in the direction (Marangoni motion, $H = 2.5$ mm) of the surface flow, which is oriented toward the light spot in both cases. The irradiation starts at $t = 0$. Corresponding videos are shown in Movie S2 (anti-Marangoni regime) and Movie S3 (Marangoni regime). c) Position of the center of a liquid marble as a function of time upon successive blue and UV light irradiation cycles. Corresponding videos are shown in Movie S4 (anti-Marangoni) and Movie S5 (Marangoni).

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along (Marangoni motion) or against (anti-Marangoni motion) surface flows depending on the thickness of the liquid substrate.

To gain further insight into the origin of this peculiar thickness-dependent motion, we investigated the spatiotemporal evolution of liquid marbles actuated with UV light at different distances from the light spot and for various liquid thicknesses (Figure 3a). Regardless of the H value, each marble reacted to the light stimulation with an accelerated motion for about 1 s followed by a relaxation to a slower and more stable speed. After around 2 s, the fastest moving marbles reached either the edge of the dish or the center of the light spot. For the smallest H values ($H < 1.9$ mm), the marble was moved away from the UV light source with a speed increasing with decreasing H value, indicating a motion against the light-induced Marangoni flows. Note that, in this case, the marble was first attracted to the light spot for a short time (around 0.5 s) before being consistently repelled. For intermediate thicknesses ($1.9 \leq H \leq 2.2$ mm), the motion was very slow with a speed less than 1 mm s^{-1}. For larger liquid layer thicknesses ($H > 2.2$ mm), the marble moved toward the UV spot, in agreement with Marangoni motion. Interestingly, regardless of the distance of the marble from the illumination spot, the average speed (v^*) taken in the time interval (0.5–1 s) decreased with an increase in H value, with an inversion of sign occurring at $H^{crit} \approx 2.0$ mm (Figure 3b). This value appears to be close to the capillary length of the system $l_c = \sqrt{\gamma_0/(\rho g)} = 2.3$ mm, where γ_0 is the liquid/air surface tension (without irradiation), ρ is the density of the AzoTAB solution, and g is gravity. The liquid thickness was thus demonstrated to determine the direction of the marble motion with the transition between anti-Marangoni and Marangoni regimes defined by a value close to the capillary length.

Although the motion of a floating entity in the direction of a Marangoni flow is commonly observed,[26–29] the opposite behavior has been rarely described.[30] When we used a gelled liquid marble, we observed a similar behavior, showing that anti-Marangoni motion was not due to flow inside the marble (see Text S2 in the Supporting Information). Moreover, by closely examining the behavior of the marble upon its displacement, although some slow rotation around the vertical axis was occasionally observed, there was no significant rotation in the direction of motion. We therefore hypothesized that the Marangoni-flow-induced deformation of the AzoTAB solution surface could strongly affect the marble motion behavior and explain, in particular, the anti-Marangoni flow motion.

To explore this hypothesis, we used a custom-built set-up to estimate, using a reflected laser beam, the surface deformation over time upon light actuation (Figure S2). Strikingly, when the UV light was on, although no significant deformation (typically less than 10 µm) could be detected for a large liquid layer thickness ($H = 2.5$ mm), we measured a difference in surface elevation between the edge of the Petri dish and the center of the beam of up to 180 µm at low thickness ($H = 0.7$ mm; Figure 4a). In the latter case, the converging Marangoni flow thus accumulated liquid at the beam center deforming the surface to create a slope, so that
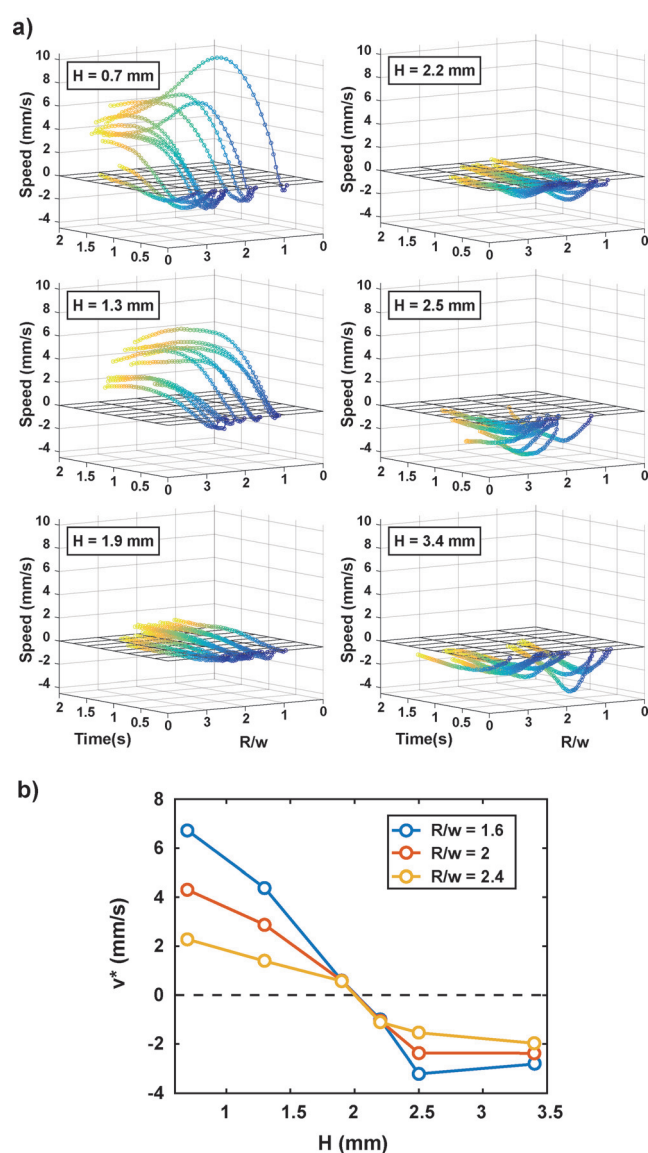

Figure 3. Spatiotemporal analysis of the liquid marble motion shows that the transition between Marangoni and anti-Marangoni regimes occurs at $H = 2$ mm. a) Radial speed of a liquid marble upon UV irradiation as a function of time and initial distance to the beam center (R) normalized by the beam width (w), for various liquid thicknesses (H). UV irradiation starts at $t = 0$. Lines connecting points are drawn as guides to the eye and indicate the trajectory of a given marble. Marangoni flows are oriented toward the beam center, with a positive or negative speed indicating anti-Marangoni or Marangoni behavior, respectively. b) Average speed of the marble (v^*) taken in the interval 0.5–1 s as a function of H value for different values of R/w. The horizontal dashed line indicates $v^* = 0$.

a liquid marble deposited on this system slid against the flow under the effect of gravity. We call this behavior a "slide effect". The slope formation required around 3 s, which was longer than the observation time of marble motion (Figure 3a), showing that although a deformation steady state was not attained in our marble motion experiments, the forming slope was steep enough to propel the marble against the surface flow. It should also be noted that for the larger distances from the beam center, no deformation was observed

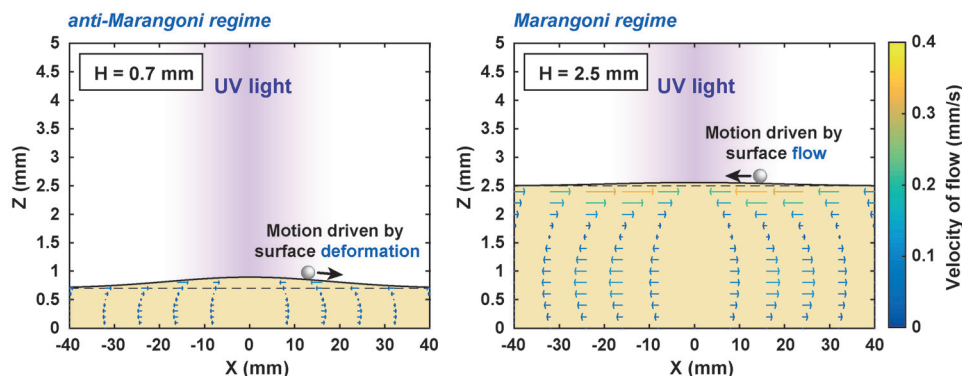## a) Surface deformation
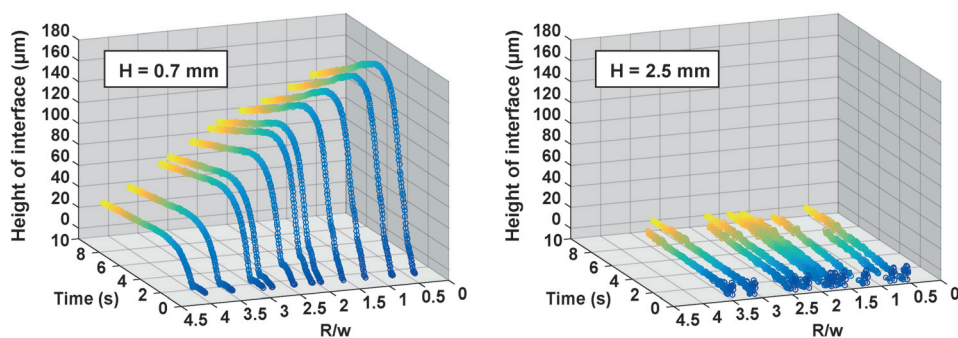
b) Mechanism

Figure 4. Experiments and theory show that light-induced surface deformation depends on liquid thickness and defines the motion regime. a) Measured surface elevation (fixed at zero at the edge of Petri dish) upon UV irradiation as a function of time and distance to the beam center (R) normalized by the beam width (w), for two liquid thicknesses ($H = 0.7$ and 2.5 mm). UV irradiation starts at $t = 0$. Lines connecting points are guides for the eye and indicate the evolution of the surface at a given distance R/w. b) Illustration of the mechanism for both anti-Marangoni (left) and Marangoni (right) regimes. In each graph, the surface shape is a Gaussian fit from the measured deformation averaged in the time interval 3–6 s. The flow profile, indicated by colored arrows, was calculated by our analytical model (see Text S4 in the Supporting Information). For $H = 0.7$ mm, light-induced surface flows induce a significant deformation that propels the marble upstream, whereas for $H = 2.5$ mm, deformation is negligible and the marble moves in the direction of the strong surface flows.

for about 0.5 s, corresponding well with the observation that at $H < H^{crit}$, the marble was moving first, for a short time, in the direction of the Marangoni flows before being propelled in the opposite direction (anti-Marangoni motion; Figure 3a). All of these observations show that the marble moved in the direction of the Marangoni flows when surface deformation was negligible (that is, at $t = 0$–0.5 s for $H < H^{crit}$ and regardless of time for $H > H^{crit}$), and in the opposite direction when surface deformation was strong enough (that is, at $t > 0.5$ s for $H < H^{crit}$).

To evaluate the relevance of this surface-deformation-dependent motion behavior, we built an analytical hydrodynamic model where we derived the velocity profile of the Marangoni flow and the resulting surface deformation (Text S3). To identify the underlying mechanism at the origin of the marble motion, the calculation was carried out in a stationary regime so that analytical solutions could be found to extract essential physical parameters (although dynamic effects, as described previously, are obviously present in this system). When the capillary length (l_c) is smaller than the beam width (w; under our experimental

conditions, $l_c = 2.3$ mm and $w \approx 7.5$ mm), we found a simple expression that describes the local variation of the interface height:

$$\delta h(r) = \frac{3}{2\rho g H}(\gamma(r) - \gamma_0) \qquad (1)$$

where γ_0 is the surface tension in the absence of irradiation, γ is the surface tension upon irradiation, and r is the distance from the beam center. This expression shows that, regardless of H value, the UV-induced increase of surface tension is accompanied by an elevation of the surface, in agreement with the observed surface elevation in the illuminated zone. Moreover, Equation (1) emphasizes the strong effect of the liquid thickness in converting a surface tension gradient into surface deformation: the elevation increases with a decrease in H value, a behavior that was also experimentally observed (Figure 4a). By making a force balance on the floating marble taking into account drag force, weight, buoyancy, and surface tension, we also calculated the speed of the marble V as a function of the distance from the beam center (r) and liquid layer thickness (see Text S3 in the Supporting Information):

$$V(r) = \frac{H}{4\eta}\left[1 - \left(\frac{Al_c}{H}\right)^2\right]\partial_r\gamma \qquad (2)$$

where η is the liquid substrate viscosity and A is a dimensionless parameter related to the geometry of the system expected to be of the order of 1. Recalling that upon UV actuation $\partial_r\gamma$ 0 as surface tension is at a maximum at the center of the beam, this equation thus states that if $H \gtrsim l_c$, the marble is dragged by the surface flow toward the beam center (Marangoni motion) but, as soon as $H \lesssim l_c$, the direction of the motion is reversed and the liquid marble slides upstream (anti-Marangoni motion). This is in remarkable agreement with our experimental results where the observed reversal of motion occurred at $H^{crit} \approx 2.0$ mm (Figure 3b), a value close to the capillary length.

Based on our experimental and theoretical analyses, we can thus propose a mechanism explaining both the Marangoni and anti-Marangoni regimes. Figure 4b shows the behavior of the marble for each regime at $H = 0.7$ mm (anti-Marangoni) and at $H = 2.5$ mm (Marangoni) under stationary conditions.

The plotted surface deformation is a Gaussian fit of the measured deformation averaged over the time interval (3–6 s), which was also used to estimate $\gamma(r)$ using Equation (1). According to this estimate, the γ value was found to increase by 1.0 mN m^{-1} between the edge and the center of the Petri dish, which is in good agreement with the measured increase of γ upon UV irradiation (Figure S1). The flow profile was then calculated using our analytical model and this estimation of $\gamma(r)$ (Text S4). Figure 4b shows that in both anti-Marangoni and Marangoni regimes, the converging surface flow results in a recirculation of the liquid in the bulk, which can occur more easily at a larger thickness. Interestingly, although the speed of the surface flow decreases with a decrease in H value, the resulting surface deformation increases due the confinement of the liquid. This results in i) a strong deformation propelling the marble upstream at low H value (anti-Marangoni regime) and ii) a strong surface flow with negligible surface deformation resulting in downstream marble motion at high H value (Marangoni regime).

In summary, we have shown that liquid marbles can be actuated by light by employing a liquid substrate with a photosensitive liquid/air surface tension. This is achieved by using a photosensitive surfactant dissolved in the liquid substrate, but other ways to trigger a surface tension change could be used, such as local heating upon laser illumination. For a large liquid thickness, the marble is transported by surface Marangoni flows that can be photoreversibly triggered upon UV/blue light irradiation (Marangoni motion). Remarkably, we have discovered that at a liquid thickness smaller than a value close to the capillary length of the liquid substrate, the marble moves in the opposite direction (anti-Marangoni motion). We have shown that, in this case, light-induced surface flows create a slope in the liquid substrate so that gravity propels the marble upstream, a behavior we term the "slide effect". These results emphasize how well-known surface flows[31,32] can be employed as useful operators for the precise actuation of miniature systems.

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