Photocontrolled Motion

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Photomanipulation of a Droplet by the Chromocapillary Effect**

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Operations (driving, mixing, and handling) with small amounts of liquid usually rely on complex architectures that involve active (pumps and valves) and passive (channels) elements.[1] Manipulation of liquid droplets by light is thus a promising yet challenging alternative. The most common strategy toward this goal uses solid surfaces with specific photosensitive surface properties.[2] When a liquid droplet is deposited on such substrates, illumination by light induces a gradient of wettability to result in simple and low-speed motion (ca. 30 μm s^{-1}) of the droplet. Herein we show that light can be used to create a wavelength-dependent interfacial tension gradient at a liquid/liquid interface, thus inducing an interfacial flow that is able to generate droplet motion in the opposite direction to the gradient. This phenomenon, the chromocapillary effect, is obtained by illuminating an oil droplet that floats on a water bath containing a surfactant whose polarity depends on the illumination wavelength. Firstly, the partial illumination of the droplet results in a reversible, wavelength-dependent motion of the droplet that can be repeated over several cycles. Then, a two-color concentric illumination allows one to build a "chromocapillary trap", which is used to manipulate the droplet along trajectories of any desired shapes, with a speed of 300 μm s^{-1} and good precision.

Fluid motion induced by an interfacial tension gradient can be obtained by thermal,[3] electrical,[4] electrochemical,[5] chemical,[6] or physicochemical methods.[7] The use of light as an external stimulus offers unique advantages, especially for the fine control of the position, area, and intensity of the excitation. Several research groups have reported photo-induced motion of a liquid droplet located on a substrate with photoswitchable wettability,[2,8] or microscale solid objects on photosensitive liquid crystals.[9] In the case of solid/liquid interfaces, specific chemical protocols have to be applied to generate a substrate with adequate photodependent wetting properties. Upon asymmetrical illumination of the substrate, the surface energy gradient can induce a translational motion of the droplets, which can be moved at speeds up to about 30 μm s^{-1} along simple trajectories. Another strategy is to use a laser beam to asymmetrically heat a droplet, thus generating a straight motion of the droplet by the thermocapillary effect.[10] Herein, we describe a new phenomenon, the chromocapillary effect, which can be used for the controlled manipulation of liquid droplets using light, without any surface chemical modification, and is applicable to various types of liquids.

Our experimental system consists of a 3 μL oleic acid droplet floating on an aqueous solution placed in a Petri dish (5.1 cm in diameter; Figure 1). To obtain a light-sensitive liquid/liquid interface, a cationic photosensitive azobenzene trimethylammonium bromide surfactant (AzoTAB) was dissolved in the aqueous phase. The apolar tail of AzoTAB contains a photosensitive azobenzene group,[11] which photoisomerizes into *trans* (less polar) and *cis* (more polar) configurations upon visible and UV illumination, respectively (Figure 1 a). This photodependent polarity has been used to reversibly control the folding transition of DNA,[12] as well as transcription and translation reactions.[13] We used AzoTAB to modulate the interfacial tension γ between the floating oil droplet and the aqueous solution by changing the illumination wavelength (Figure 1 b). We used an AzoTAB concentration of 2 mM, which is below the critical micelle concentration of AzoTAB in water (ca. 10 mM). Surface tension measurements by the pending droplet method indicated that the value of γ increased from around 7 mN m^{-1} to around 8 mN m^{-1} upon UV illumination. This increase of around 1 mN m^{-1} is weak, but could be measured reproducibly. The principle of the chromocapillary effect is shown in Figure 1 c. It is possible to create an oil/water interfacial tension gradient by partial illumination of the droplet with 365 nm light or a combination of 365 nm and 475 nm light. This gradient results in a flow at the droplet interface from low γ to high γ values with respect to the droplet center, and droplet motion in the opposite direction with respect to the liquid bulk.

First, we used a 10 × microscope objective to partially illuminate the droplet at 365 nm (Figure 2 a, left). We observed that the droplet spontaneously moved away from the illuminated area, that is, from high γ (UV illuminated

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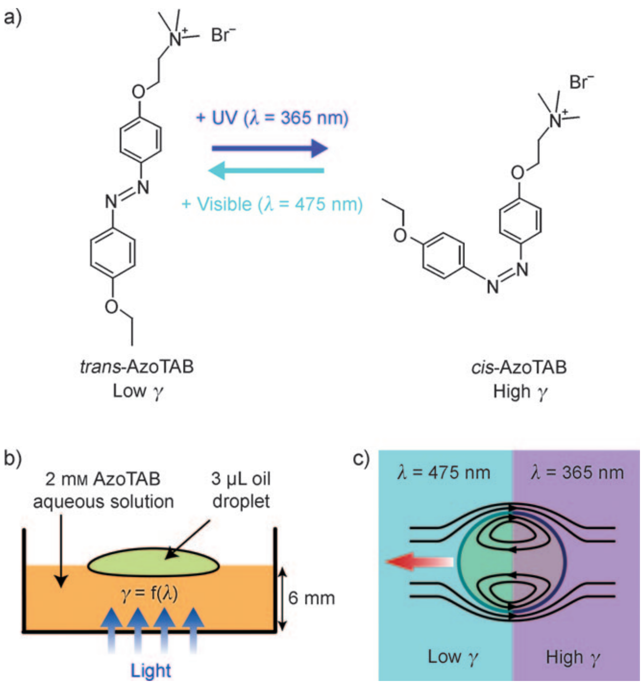

Figure 1. Wavelength-dependent interfacial tension gradient generated by light induces droplet motion by the chromocapillary effect. a) Molecular structure of the photosensitive surfactant AzoTAB. b) Representation of our experimental system (side view). The oil/water interfacial tension γ is dependent on the illumination wavelength. c) Principle of the chromocapillary effect (top view). Arrows qualitatively indicate the flow field profile inside and outside the droplet oil/water interface.

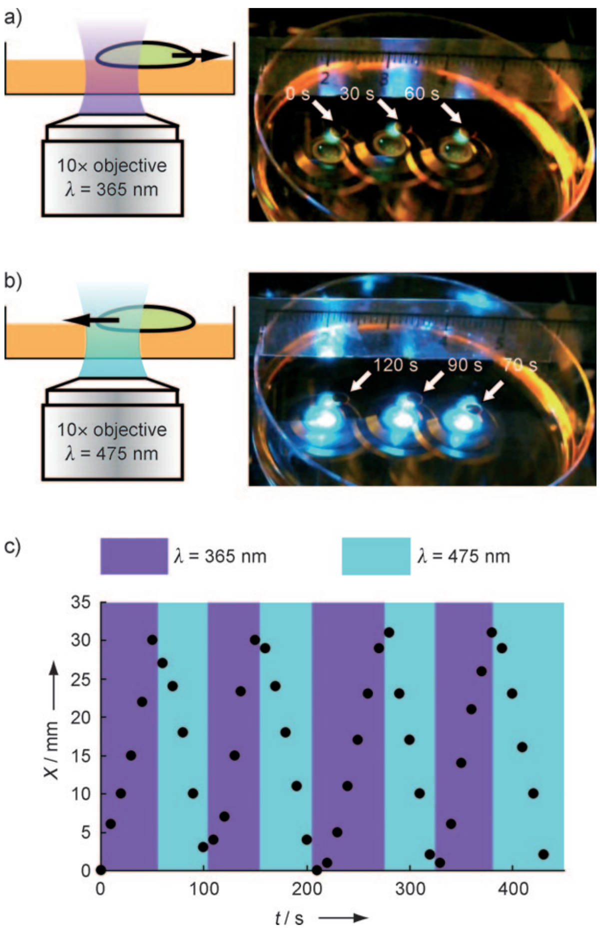

Figure 2. Reversible, wavelength-dependent motion of a droplet under partial illumination. Representation (left) and photomontage (right) of the droplet motion under partial illumination at a) $\lambda = 365$ nm, followed by partial illumination at b) $\lambda = 475$ nm. The objective follows the droplet to maintain the partial illumination. Photomontages were obtained by superposition of frames taken from Movie S1 in the Supporting Information. The white arrows indicate the time and position of the droplet. The ruler on the Petri dish is graduated in centimeters. c) Position X of a droplet along the diameter of the Petri dish, as a function of time t and λ, for four cycles of 365 nm/475 nm illumination.

area, mainly *cis*-AzoTAB) to low γ values (nonilluminated area, mainly *trans*-AzoTAB). By following the droplet to maintain the partial illumination, the droplet motion was maintained along a distance of a few centimeters at a speed of about 300 $\mu m\,s^{-1}$ (Figure 2a, right). After UV illumination, when the same droplet was illuminated in the same manner at 475 nm, we observed motion in the opposite direction (Figure 2b, left), that is, the droplet moved toward the illuminated area. Since the nonilluminated area was enriched in *cis*-AzoTAB during the first photoinduced motion, the droplet moved again from high γ (nonilluminated area, enriched in *cis*-AzoTAB) to low γ values (area illuminated at 475 nm, mainly *trans*-AzoTAB). The droplet motion was maintained over a similar distance (a few centimeters) and with a similar speed (ca. 300 $\mu m\,s^{-1}$; Figure 2b, right). If only visible light illumination was initially applied, no significant motion was observed, thus showing that the solution has to be previously enriched in *cis*-AzoTAB to obtain a significant effect with visible light illumination. Movie S1 in the Supporting Information shows one cycle of this forward ($\lambda = 365$ nm) and backward ($\lambda = 475$ nm) motion. Interestingly, this wavelength-dependent motion can be repeated with the same droplet for several cycles over distances of centimeters (Figure 2c). To the best of our knowledge, this is the first report of the reversible, wavelength-dependent motion of a liquid droplet.

We interpret this motion to be a consequence of a chromocapillary effect, which is analogous to the thermocapillary effect, but the origin of the interfacial tension gradient lies in the wavelength-dependent interfacial properties. As explained by Young et al., an interfacial tension gradient induced by a thermal inhomogeneity can generate a Marangoni flow at a liquid/gas interface from lower to higher interfacial tension.[14] In the case of a bubble immersed in water, this flow induces the motion of the bubble toward the area of lower interfacial tension.[14] The flow profile for a droplet is qualitatively depicted in Figure 1c: the flow is unidirectional from low γ to high γ values outside the droplet and is recirculating inside the droplet. The existence of the recirculating flow was confirmed by observing the motion of micrometer-sized polystyrene particles added to the oil droplet under partial illumination at 365 nm (see Movie S2 in the Supporting Information). Moreover, in the absence of AzoTAB in the aqueous medium, no significant motion was observed regardless of the illumination wavelength. This result indicates that the wavelength-dependent motion arises from an interfacial tension modification of the oil/water interface generated by light and not by a thermal effect, which can be considered here as negligible. Finally, when a droplet of AzoTAB solution was immersed in silicone oil, which has a lower density, a similar motion was observed that occurred over only a few millimeters (see Figure S1 in the Supporting Information). This observation indicates that a reservoir of photosensitive tension-active molecules outside the droplet is necessary for motion to be maintained. If the photosensitive molecule is inside the droplet, the recirculation flow rapidly homogenizes the concentration inside the droplet and it is impossible to maintain a stationary interfacial tension gradient. In contrast, when the photosensitive molecule is outside the droplet, the partial illumination allows the *cis*/*trans* concentration profile to be kept constant and the interfacial tension gradient and droplet motion to be maintained over a long distance.

We have shown that the oil droplet spontaneously moved toward areas illuminated with visible light (475 nm, low γ) and was repelled from zones illuminated with UV light (365 nm, high γ) because of the interfacial tension gradient induced by a partial illumination of the droplet. We therefore built a "chromocapillary trap", which consists of a concentric two-color illumination of the droplet (Figure 3 a). A 2.5 × objective lens was used to provide UV illumination (365 nm) on a large area around the droplet while a visible light beam filtered at 475 nm was focused using a microscope condenser to illuminate the droplet on an area larger than the droplet diameter but smaller than the UV illumination zone. Movie S3 in the Supporting Information shows that a droplet "thrown" by a pipette tip is efficiently stopped by the trap and tends to localize at the center of the visible light zone. Then, by moving the Petri dish at a constant speed v, we observed that the droplet remained in the fixed trap, and thus moved relative to the Petri dish. Figure 3 b shows the relative position of the droplet as a function of v. For speeds up to 200 μm s^{-1}, the droplet remains in the trap center and closely follows the imposed motion. For $200 < v < 400$ μm s^{-1}, the droplet progressively moves out of the trap center but still follows the trap. At $v = 420$ μm s^{-1}, the droplet moves significantly slower than the trap and eventually leaves it. At higher speeds, the droplet cannot follow the trap anymore. These results show that the droplet can be efficiently trapped by a two-color illumination and precisely guided at speeds up to the order of 300 μm s^{-1}. We then moved the trap relative to the Petri dish at $v \approx 200$–300 μm s^{-1} along complex and precise pathways to form the shapes of letters and symbols. Figure 3 c shows the superposition of images taken at different times during the droplet motion and Figure 3 d shows the position of the droplet center as a function of time. All these results show that the droplet follows the pathways imposed by the trap motion remarkably well, even along paths with relatively complex geometries.

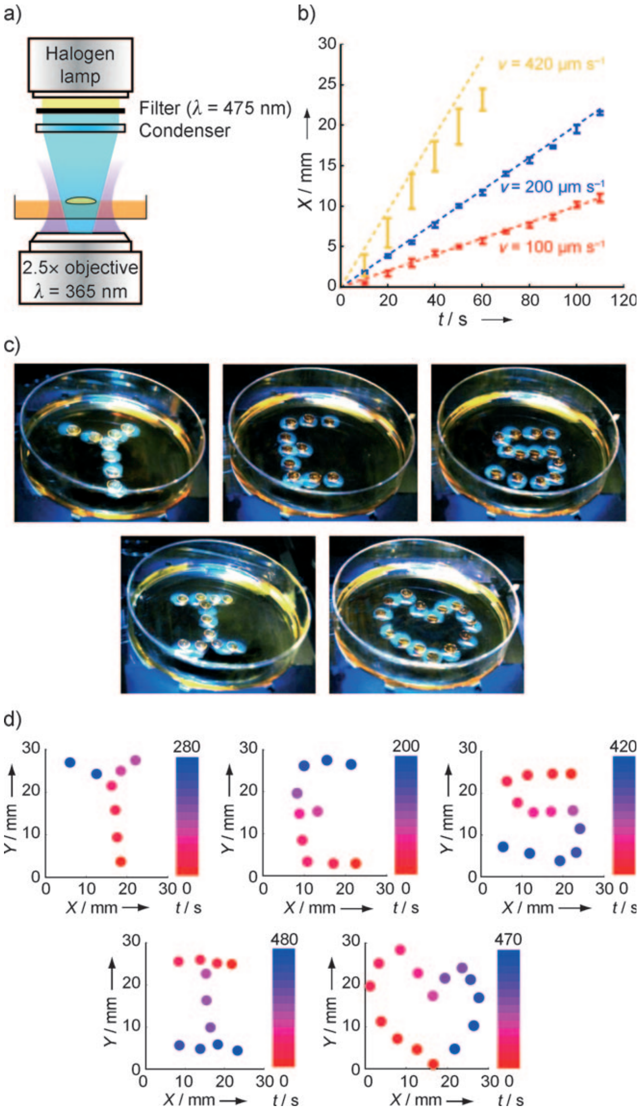

Figure 3. A "chromocapillary trap" created by a concentric two-color illumination allows the controlled and fast manipulation of the droplet along complex trajectories. a) Experimental setup for the two-color illumination and trapping of the droplet. The droplet motion is obtained by moving the Petri dish using a microscope stage at a speed v. b) Position of the droplet center along the Petri dish diameter as a function of time t for a linear motion at $v = 100$, 200, and 420 μm s^{-1}. Bars represent the average droplet center ± standard deviation for three replicates. Dashed lines represent the linear motion of the Petri dish. c) Photomontages of the motion of a droplet along complex trajectories reproducing the letters "Y", "E", "S", "I", and a heart shape, and d) corresponding spatiotemporal positions. Photomontages were obtained by the superposition of frames taken from movies (one movie per trajectory); the 2.5 × microscope objective has been erased for all images for better visibility. Movie S4 in the Supporting Information shows the motion along an "N" trajectory, and Figure S2 shows the resulting photomontage. In the spatiotemporal diagrams, symbols give the *X*–*Y* position of the droplet center and the symbol color indicates the time *t*.

We have demonstrated the light-induced generation of droplet motion by a wavelength-dependent liquid/liquid interfacial gradient (the chromocapillary effect). This phenomenon was exploited for easy, fast, and precise manipulation of a floating oil droplet. The chromocapillary effect offers new possibilities for the use of light as an external stimulus for the motion of liquids and the conversion of light. This new strategy, which is applicable to various organic/aqueous systems, makes the controlled manipulation of millimeter-sized liquid solutions by light possible (macroscopic optical tweezers). Our method can be integrated into micro- or millifluidic systems and will open new perspectives for light-driven fluidics, safe handling of dangerous liquid samples, and smart photoactive materials.

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