Marangoni Tweezers

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Particle Manipulation Based on Optically Controlled Free Surface Hydrodynamics**

Subramanyan Namboodiri Varanakkottu, Sajan Daniel George, Tobias Baier, Steffen Hardt, Martina Ewald, and Markus Biesalski*

Photoswitchable molecules that undergo reversible structural change upon light irradiation have numerous applications, ranging from life science[1] to interfacial fluid mechanics.[2,3] A few to mention are the creation of a reversible wettability gradient over a solid surface[2] or an interfacial tension gradient at a liquid–liquid interface[3] to transport millimeter-sized droplets. The objective of this article is to demonstrate that photoswitchable molecules also enable the manipulation of micron-sized particles. Commonly employed particle manipulations techniques are, for example optical trapping,[4] dielectrophoresis,[5] optoelectronic tweezers,[6] or plasmonic tweezers.[7] All these schemes rely on the so-called gradient force that scales as the third power of the particle diameter in the Rayleigh regime.[8] For this reason the trapping force rapidly diminishes with decreasing particle diameter. Here we present an optical method for the trapping and manipulation of micron-sized particles adsorbed at a gas–liquid interface based on optically induced Marangoni flow. The hydrodynamic nature of the trapping mechanism implies a force scaling with the particle diameter instead of its third power. The method relies on photoresponsive surfactants adsorbed to the interface that can be reversibly switched between two isomeric states. It is experimentally demonstrated that, using optically induced Marangoni flow, microspheres can be manipulated using lower light intensities compared to conventional optical tweezers.

The principle of creating photoinduced flow patterns is shown in Figure 1 a. Photoresponsive surfactants allow to locally control the surface tension of a liquid using a light beam. The surfactants used in the present study are based on the well-known azobenzene-motif, and exist in two isomeric states, a *trans* and a *cis* state. Light of 325 nm wavelength induces a conformational change from *trans*- to *cis*-azobenzene, light of 442 nm the reverse. To create an air–water interface with photoswitchable surface tension, a molecule abbreviated as $C_4AzoOC_4E_2$ was used which exhibits a higher surface tension if the concentration of the *cis* isomers at the

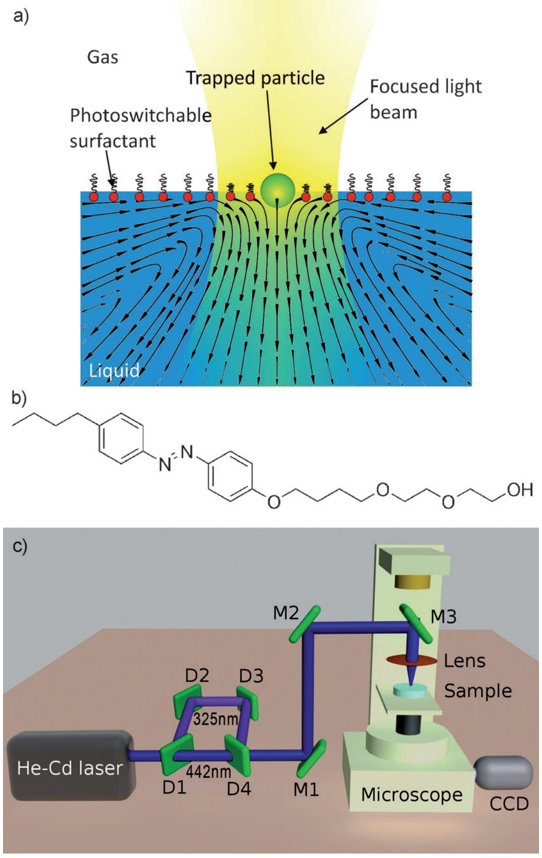

Figure 1. Principle of creating a light-induced flow and experimental setup. a) A laser beam of either 325 or 442 nm wavelength is focused onto a liquid surface covered with photoresponsive surfactants. The local change in surface tension creates an inward (shown in the figure) or outward flow that may be used to trap and manipulate particles. b) Structure formula of the surfactant molecule used in the experiments. c) Experimental setup comprising a dual wavelength (325 and 442 nm) He-Cd laser and a microscope for imaging the flow at the liquid surface.

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[*] S. N. Varanakkottu,[+] Dr. S. D. George,[+] Dr. T. Baier, Prof. S. Hardt
Center of Smart Interfaces, TU Darmstadt
Petersenstrasse 17, 64287 Darmstadt (Germany)
E-mail: hardt@csi.tu-darmstadt.de

M. Ewald, Prof. M. Biesalski
Department of Chemistry, TU Darmstadt
Petersenstrasse 22, 64287 Darmstadt (Germany)

[+] These authors contributed equally to this work.

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interface is increased compared to that of the *trans* isomers.[9] The molecular structure of $\mathrm{C_4AzoOC_4E_2}$ is shown in Figure 1 b. The synthesis of this molecule was carried out according to the literature.[9] When a water surface covered with the corresponding surfactant is locally illuminated with 325 nm light, the surface tension in the illuminated region increases. The gradient in surface tension induces a Marangoni flow directed radially inward in a coordinate frame centered at the focal spot, as depicted in Figure 1 a. The hydrodynamic drag forces due to the inward flow are used for trapping a small particle. It should be emphasized that this flow has a direction opposite to the thermocapillary flow that is generated when a liquid surface is locally heated by a laser beam.[10,11] First indications for the existence of Marangoni flows created by locally illuminating a liquid surface covered with photoresponsive surfactants have been given by experiments in which the surfactant concentration was below the critical micelle concentration (cmc).[12] Here we mainly report experiments with surfactant concentrations above the cmc in which a stronger flow of a different pattern (more suitable for particle trapping) is produced.

First, the flow field resulting from local illumination of the surfactant solution was characterized using particle streak velocimetry (Figure 2 a,b). Figure 2 c shows the flow field obtained at $t = 0.5$ s, corresponding to an exposure starting at $t = 0$ and lasting for 0.5 s. The experiment was performed by focusing 325 nm radiation onto the surface of the liquid layer that was initially in its dark state containing almost exclusively *trans* isomers. Computational fluid dynamics simulations indicate that after about 0.5 s a quasi-stationary flow field has developed. A maximum flow velocity of about 450 $\mu\mathrm{m\,s^{-1}}$ is achieved. When the illumination at 325 nm continues, the flow velocity decreases, bringing the inflow to a halt after about 10 s. Instead, if after 2 s the illumination wavelength is switched to 442 nm, the inward flow is reversed and an outward flow is observed. The profile of this flow is displayed in Figure 2 d.

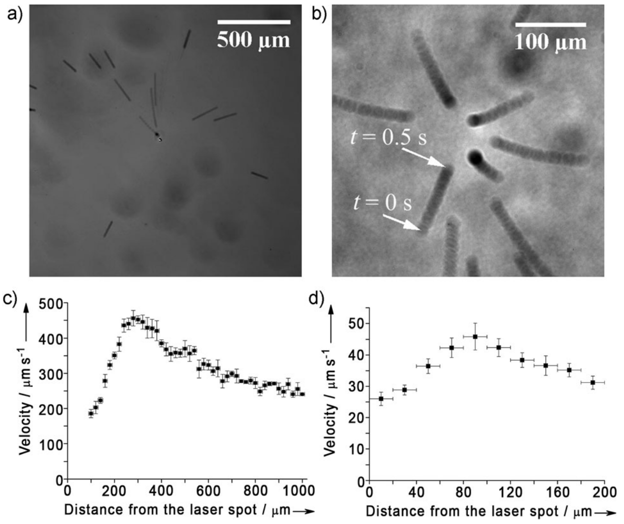

Figure 2. Particle streak velocimetry images and corresponding flow profiles. a) Examples of particle streaks recorded using a 4 × objective when the liquid surface is irradiated with 325 nm light. b) Image of the inward flow recorded using a 20x objective. The arrows indicate the initial and final positions of a selected particle over a time span of 0.5 s. c) Flow profile obtained after 0.5 s exposure with 325 nm light and a laser power of 5 mW. The flow is radially inward. d) Flow profile obtained after 1 s exposure with 442 nm and a laser power of 30 mW following a 2 s exposure with 325 nm light. The flow is radially outward.

The outward flow is substantially slower than the inward flow, and higher light intensities are required to achieve a significant flow velocity of some ten $\mu\mathrm{m\,s^{-1}}$. The experiments demonstrate that because of the reversible nature of the photoisomerization of the surfactant, the resulting flow direction can be reversed by switching from 325 to 442 nm. One of the most striking features of the flow profile of Figure 2 c is the maximum occurring at around 300 µm away from the focal point. The flow at the liquid surface has a dilatational character with $\nabla \cdot \mathbf{u}_s \neq 0$, where $\mathbf{u}_s$ is the velocity at the surface. The radial inflow compresses the surfactant monolayer, and, after some time, leads to the formation of aggregates that are presumably multilayer arrangements of surfactant molecules (see the Supporting Information). The formation of multilayer structures is a process occurring when a Langmuir monolayer is compressed beyond its stability limit.[13–16] In general, the dilatational flow produces a radial surfactant concentration gradient and a surfactant-crowded region close to the focal spot. The crowding is expected to give rise to a region of high (shear and dilatational) surface viscosity, while the surfactant concentration gradient is expected to produce Marangoni stresses.[17,18] It is conjectured that because of the former, an almost immobile liquid surface is formed around the laser focus, which results in a maximum of the velocity occurring at a comparatively large radial distance away from the focal spot. This scenario is supported by the data shown in Figure 3 a, where the averaged flow field after the first 0.5 s is compared to that after the first 0.25 s. It can be seen that for $t = 0.25$ s, the velocity maximum occurs at a smaller value of the radial coordinate. This can be explained by the fact that at this point in time, the surfactant aggregate is less extended than at $t = 0.5$ s, yielding a smaller region with a high surface viscosity.

Figure 3 b shows the flow field generated by 325 nm light after 0.5 s for different values of the laser power. It is observed that the point where the maximum velocity occurs shifts to larger radial coordinates when the laser power is increased, while at the same time the overall velocity magnitude increases. The shift of the velocity maximum can again be explained by the increasing size of the surfactant aggregate, corresponding to a growing region of low surface mobility.

The time scale of the photoisomerization kinetics is inversely proportional to the light intensity.[9] A few instants after the illumination has started, one expects a higher fraction of *cis* isomers in the focal region if the light intensity is increased. Certainly, the photoisomerization time scale will only play a role if it is not much smaller than the time span over which the flow is observed (500 ms in Figure 3 b). The *trans–cis* isomerization time constant determined from transmittance measurements of 50 µM solution at $2.97 \times 10^3\ \mathrm{W\,m^{-2}}$ is 695.26 ± 49 s. From that, assuming the kinetic model of

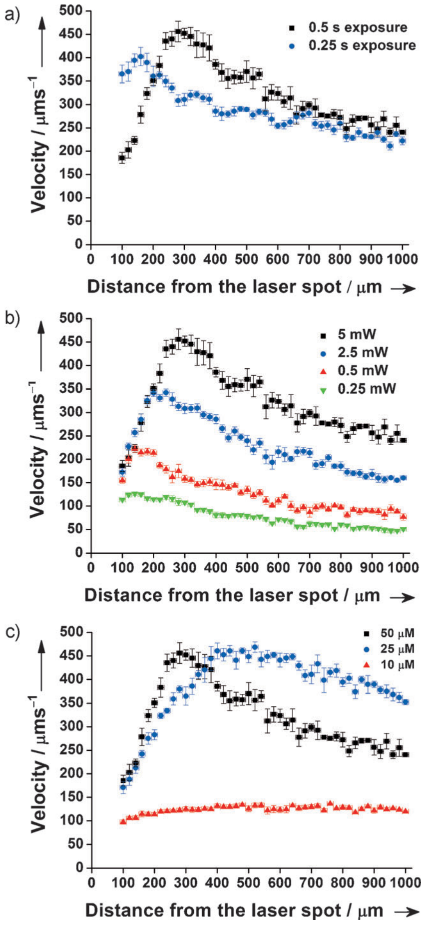

Figure 3. Dependence of the flow field due to laser light of 325 nm wavelength on various parameters. a) Flow profiles at the surface of a 50 μM solution after different exposure times at a laser power of 5 mW. b) Flow profiles at the surface of a 50 μM solution after an exposure time of 0.5 s at different values of the laser power. c) Flow profiles after an exposure time of 0.5 s at a laser power of 5 mW using solutions with different surfactant concentrations.

Ref. [9], a photoisomerization time constant of 41.6 ms is obtained for a light intensity of 0.49×10^8 W m^{-2} (corresponding to a laser power of 0.25 mW at 325 nm), dropping to 2.08 ms when the power is increased to 5 mW. These time scales are roughly of the same order as the flow observation time scale, therefore corroborating the hypothesis that the increase of flow velocity at higher values of the laser power is due to the faster conversion from *trans* to *cis* isomers.

Figure 3 c displays the dependence of the inward flow field on the surfactant concentration. A substantial augmentation of the overall flow velocity is being observed when increasing the surfactant concentration from 10 to 25 μM (Figure 3 c), but no further increase is found (apart from local variations) when elevating the concentration level to 50 μM. It can be speculated that these observations may be explained by the compressibility of the surfactant monolayer. Once a virtually incompressible monolayer is formed, the flow towards the laser spot is impeded. To uncover the dependence of the flow on the surfactant concentration, it is worth noting that the cmc is significantly different for the *trans*- ($\mathrm{cmc}_{\mathrm{trans}} = 1.6$ μM) and the *cis*-enriched ($\mathrm{cmc}_{\mathrm{cis}} = 23.8$ μM) states.[9] Above the cmc the surfactant monolayer is virtually incompressible. On the other hand, when increasing the concentration of the *cis* isomers at the surface by photoswitching, the adsorbed molecules occupy a larger surface area,[12] related to a lower compressibility. Therefore, it seems difficult to estimate the effects of surfactant concentration on the experiments reported here in simple terms.

In general it should be mentioned that the experiments presented here address the dynamic surface-tension behavior of the system under study which is governed by a complex interplay of different processes, most importantly the adsorption/desorption kinetics of surfactants and their diffusion to the surface. However, presumably with the exception of the squeezing out of *cis* surfactants from an overcrowded surface, these processes become relevant on time scales much larger than those considered here.[19]

To the best of our knowledge, there is only one example reported in the literature where a similar radial inflow on a liquid surface was generated using a focused laser beam[20,21] which is, however, based on a different physical mechanism, the thermocapillary effect. Compared to these efforts, an important advantage of the principle presented here is the reduced laser power which is about three orders of magnitude lower.

The photoinduced flow patterns can be used to trap and manipulate microparticles, as will be demonstrated in the following. Light of 325 nm was focused at the air–water interface to drive a single adsorbed 15 μm polystyrene microsphere towards the laser spot, after which one of the mirrors used for guidance of the laser beam was tilted manually. That way the focal spot can be moved over the liquid surface. Figure 4 shows the corresponding particle trajectory as a series of individual frames with a temporal offset of 10 s. From the trajectory the particle velocity as a function of distance along its path was computed, as shown at the bottom of Figure 4. In that case a maximum particle velocity of about 15 μm s^{-1} is obtained. When the mirror is tilted faster and the laser spot moves at about 20 μm s^{-1}, the particle is no longer able to follow the laser spot. To rule out that the particle motion is due to Maxwell stresses originating from the laser radiation, the experiment was repeated with a layer of pure water instead of surfactant solution. In that case the particle is not able to follow the motion of the laser spot, showing that the mechanism underlying particle manipulation is not based on Maxwell stresses. The mechanism also differs from that reported in Ref. [3] where the manipulation of millimeter-sized oil droplets floating on a water surface covered with photoresponsive surfactants was demonstrated.[3] The motion of these oil droplets is due to Marangoni flows induced along the oil–water interface, an effect that cannot be used to manipulate solid objects.

To compare these experiments performed mainly in a regime above the cmc with previously published studies,[12] the surfactant concentration was reduced to 1 μM which is below the cmc. Two classes of additional experiments were conducted, one starting from the dark state (in which the surfactant solution has been equilibrated by keeping it in the dark for 72 h) and one starting from the blue-adapted state (in

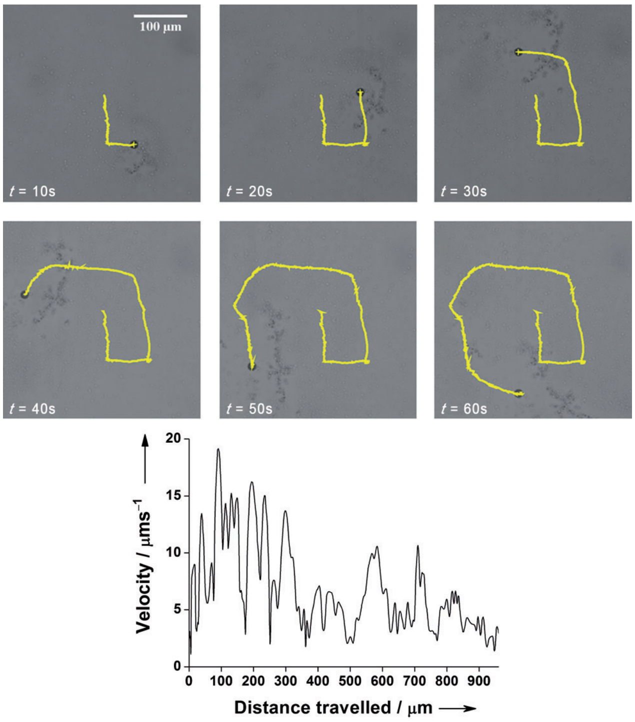

Figure 4. Trapping and manipulation of microsphere using photoinduced flow patterns. Top: Sequence of images showing the particle trajectory after different time spans. The motion was induced by tilting the mirror guiding the laser beam. Bottom: Instantaneous particle velocity as a function of distance travelled obtained from the particle trajectory.

which the surfactant solution has been illuminated with light of 442 nm for 30 minutes). The results presented here are applicable for both blue and dark adapted solutions. In each of these cases, laser spots of 325 nm and of 442 nm wavelength were focused onto the liquid surface. Irradiation with 325 nm resulted in an inward flow towards the laser spot, qualitatively similar to what is described above. The flows created by illumination at 442 nm with solutions below the cmc are qualitatively different from those found with surfactant concentrations above the cmc. In that case we do not observe an inward flow but a quadrupolar flow pattern as shown in Figure 5.

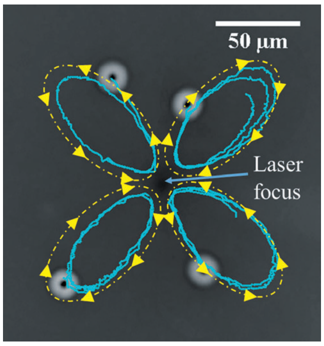

Figure 5. Particle trajectories showing a quadrupolar flow pattern at the surface of a 1 µM surfactant solution upon focused illumination with 442 nm at 30 mW. The dash-dotted lines show the flow direction and the continuous lines the particle trajectories.

The shear stress distribution along the surface of a quadrupolar flow pattern is such that besides regions in which the stress points to the focal spot there are regions in which the stress points away from it. The latter requires a mechanism for the light-induced reduction of surface tension. The photostationary state at 442 nm is composed of 86 % *trans* isomers and 14 % *cis* isomers.[19,22] There are indications that the liquid surface is almost exclusively covered with *trans* isomers,[12] meaning that even with 442 nm light the surface tension can be increased by converting some of the *trans* isomers adsorbed at the liquid surface into the *cis* form. Furthermore, other than in the experiments with concentrations above the *cmc*, below the cmc the surface can be compressed. This means that an inflow into the laser spot locally increases the surfactant concentration. An increase in surfactant concentration corresponds to a reduced surface tension.[9] Therefore, there are two competing effects, one increasing and the other reducing the surface tension. It is speculated that the superposition of these effects may give rise to the quadrupolar flow patterns that may be triggered by a hydrodynamic instability.

These results are at variance with the flow reported in a previous article[12] that gave indications that both the stimulation with blue and UV light results in a radial inflow, visualized by talc particles. The reasons for the discrepancy are currently unclear.

In conclusion, it is shown that photoresponsive surfactants allow creating dilatational flows at a liquid surface, the direction of which can be reversed by switching the laser wavelength. The flow patterns can be used to trap small particles at lower light intensities than with conventional optical tweezers. The favorable force scaling with the particle diameter makes this a promising principle for the manipulation of nanoscale objects. Up to now macromolecules are being handled indirectly in a focused laser beam by attaching them to micrometer-sized particles.[23] Sparing the need to link the molecules to such large objects could greatly enhance the flexibility of optical manipulation techniques.

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