How to Make a Surface Act as a Micropump

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In this paper, the phenomenon of light-driven diffusioosmotic (DO) long-range attractive and repulsive interactions between micro-sized objects trapped near a solid wall is investigated. The range of the DO flow extends several times the size of microparticles and can be adjusted to point towards or away from the particle by varying irradiation parameters such as intensity or wavelength of light. The “fuel” of the light-driven DO flow is a photosensitive surfactant which can be photo-isomerized between trans and cis-states. The trans-isomer tends to accumulate at the interface, while the cis-isomer prefers to stay in solution. In combination with a dissimilar photo-isomerization rate at the interface and in bulk, this yields a concentration gradient of the isomers around single particles resulting in local light-driven diffusioosmotic (I-LDDO) flow. Here, the extended analysis of the I-LDDO flow as a function of irradiation parameters by introducing time-dependent development of the concentration excess of isomers near the particle surface is presented. It is also demonstrated that the I-LDDO can be generated at any solid/liquid interface being more pronounced in the case of strongly absorbing material. This phenomenon has plenty of potential applications since it makes any type of surface act as a micropump.

1. Introduction

Generation of liquid transport with spatio-temporal control has drawn tremendous attention over the past few decades due to a large number of microfluidic based applications such as improvement of biochemical assays, generation of highly portable diagnostic devices, microfluidic synthesis, sorting and focusing mechanism for cells and colloids, and many others.[1–13] To force liquid flow one can either pump it externally or utilize different types of surface bound phenomena such as electro- or diffusioosmosis.[14–17] In the former case a design of hydrodynamic flow patterns in microfluidic assay is fixed to a chamber geometry and cannot be easily changed. In the case of osmotic-based flows, one generates gradients in solute concentration at the solid/liquid interface which allows for local manipulation of fluid pattern retaining the possibility to simultaneously employ large scale flows as described theoretically,[18–24] In an experiment, the challenging task of using DO flows for various applications is to find a way for the generation of solute concentration gradients with precise local control; in a reversible manner and at an arbitrary surface. There is a body of research where the gradient of a solute concentration is generated by utilizing smart constructed line of microfluidic channels connected to pressurizing reservoirs containing solute, solvent, and tracer particles.[25–29] In emerging approaches for the generation of local DO flows one utilizes micropumps such as ion exchange resin (IEX),[30,31] titanium dioxide colloids,[32] or natural enzymes.[33,13] Here, the flow is induced by a gradient of ions generated by and at the particle/micropump and cannot be easily relocated and adjusted in terms of flow direction and strength.

Recently, we have introduced a light-driven diffusioosmotic (LDDO) phenomenon which allows us to fulfill all of the above mentioned requirements, i.e., we are able to generate DO flows with adjustable direction and strength. Moreover, it is possible to do it locally, reversibly and at any place on a surface in one closed system.[34] At the heart of the mechanism is a photosensitive azobenzene containing surfactant which can be switched by light between two isomers: more hydrophobic trans- and hydrophilic cis-one.[35,36] As a consequence, the properties of the surfactant solution differ significantly depending on the isomer type of the surfactant, e.g. critical micellar concentration (CMC) varies by several times between trans- and cis-isomers, where for trans is larger than the latter.[35,37] During exposure of the surfactant solution to illumination with modulated light, one generates solute gradients represented by the different concentrations of trans- and cis-isomers. Owing to the different polarities of the trans and cis molecules, the strength of the interaction potential of the surfactant can be switched by light such that, depending on the irradiation wavelength, one can generate the DO flow pointing either into or out of the illuminated area. The colloids trapped near the surface are passively dragged along the DO flow and form either a densely packed crystal or a cleaned surface.[38]
The same mechanism is responsible for the so-called local-light driven diffusioosmotic (l-LDDO) flow generated by a single colloid possessing a large solid/liquid interface. When porous silica particles are immersed in a water solution containing surfactants in the trans-state, the surfactant molecules are absorbed by the particles. Under irradiation with UV light that promotes trans-cis isomerization, the more hydrophilic cis-isomers diffuse out the particles. The emergence of a laterally inhomogeneous excess of cis-molecules around the particle close to the solid-liquid interface leads to a local generation of DO flow (l-LDDO flow). The l-LDDO flow strength (defined as flow velocity and extent) and direction depend on the intensity and irradiation wavelength. For instance, if blue light is used at the photo-stationary state, the ratio of trans to cis isomers is 67% to 33% in solution. This results in a continuous flow of cis isomers out of the particle and trans isomers into the particle; leading to the continuous, local, and radially directed flow around a single colloid making it act as a “micropump” (see scheme in Figure 1).

The duration of this flow is defined only by irradiation time and can proceed over hours till the light is simply switched off. Under exposure to UV light, at some point most of the isomers will be in the cis-state, the continuous exchange of isomers is very low and the flow stops. Moreover, at the beginning of irradiation with UV light of low intensity, the colloid may experience long-range diffusioosmotic attraction. This process is transient and is reversed with increasing irradiation time.

Here we discuss a mechanism of the transient diffusioosmotic (DO) attraction and permanent DO repulsion by expanding the analysis of the l-LDDO flow proposed elsewhere. For this, we introduce the time dependence of the concentration excess of isomers during the irradiation process. Assuming that the trans-cis photo-isomerization kinetics is slower in the particle in comparison to the bulk, we have calculated the inversion of the concentration excess during irradiation with UV light, while exposure to blue light builds concentration excess of the same sign. We confirm this experimentally using tracer particles to probe the l-LDDO flow generated at different surfaces such as hair, sand corn, wood stick, and so on. In this way, we demonstrate that surfaces capable of absorbing large amounts of photosensitive surfactant can act as a micropump.

2. Experimental Section

2.1. Materials

Light responsive surfactant. The azobenzene containing trimethyl-ammonium bromide surfactant (C4-Azo-OC6TMAB) was synthesized as described elsewhere. The surfactant (Figure 2a)
consists of a spacer of 6 methylene groups between the positively charged trimethyl-ammonium bromide head group and the azobenzene unit with butyl tail attached. A stock solution of surfactant of 10 mM concentration was diluted to the required concentrations ranging from 0.1 to 2 mM. Water (Milli-Q system) with a specific resistance larger than 18 MΩ·cm was used to prepare aqueous solutions. Figure 2b shows characteristic UV-vis absorption spectra of the surfactant recorded at photo-stationary state under exposure to light of different wavelengths. The trans-isomer (denoted as dark) had a characteristic absorption band (π−π* transition) with a maximum at 351 nm. The spectrum of the cis-isomer was characterized by two absorption bands with maxima at 365 nm and 400 nm, respectively.

Figure 2. a) Chemical structure of the photo-sensitive surfactant (C4-Azo-OC6TMAB) and the two isomers of the azobenzene group. b) UV-vis absorption spectra of azobenzene containing surfactant at photo-stationary state recorded during irradiation with light of different wavelength as indicated in the legend. c) Cartoon of dynamic exchange of both isomers under illumination. d) Scheme of the l-LDDO flow of velocity v (green horizontal arrows) generated around single particle; concentration of the cis-isomers near the particle interface, \( c_{C,P} \), and in bulk, \( c_{C,B} \); green arrow indicates the isomer concentration gradient; red circular arrows demonstrate dynamic exchange, i.e., adsorption/desorption of the surfactant molecules; blue arrows depict osmotic pressure, P. e) Scheme of the plain and porous particles with effective area contributing to net isomer exchange.
maxima at 313 nm (π-π* transition) and 437 nm (n-π* transition). The lifetime of the metastable cis-isomer in the dark or in red light (λ = 625 nm) is ≈48 h at 23°C. 

Non-porous silica colloids of d = (1.5 ± 0.2) µm in diameter and mesoporous silica colloids of (5.0 ± 1.0) µm in diameter were purchased from micro-Particles GmbH (Germany).

The aqueous dispersion of all particles was mixed with surfactant solution at different concentrations and kept at least 1 h for equilibration. A chamber with a volume of 40 µl was used in order to provide a closed environment. When an aqueous dispersion of azobenzene containing surfactant and porous or non-porous silica colloids was placed on a chamber, the colloids sediment down to a glass surface. All samples were kept in the dark or in red light to prevent unwanted photo-isomerization. The measurements were conducted at room temperature of T = 23°C.

2.2. Methods

An inverted microscope Olympus IX73 equipped with a light source of various wavelengths was used for the measurements. The global irradiation was performed with LED lamps from Thorlabs of different wavelengths: UV (λ = 365 nm, M365LP1), blue (λ = 455 nm, M455D2 and λ = 491 nm, M490L3), green (λ = 532 nm, M530L4), red LED (λ = 625 nm, M625L1-Cl, Thorlabs GmbH) was used for imaging as it does not affect the photo-isomerization rate of the azobenzene molecule. The illumination power was directly measured at the sample position prior to each measurement using an optical power meter PM100D with a sensor S170C (Thorlabs GmbH, Germany). The intensities between 0.2 mW cm⁻² and 20 mW cm⁻² were applied in the experiments. The optical path length was 0.5 mm. Time-resolved micrographs were recorded with a CCD camera (Hamamatsu ORCA-Flash4.0 LT (C11440)) at 1 or 2 frames per second and were analyzed using the software Fiji ImageJ with an implemented tracking algorithm (Mosaic Plugin) by Kourmoutsakos.[46]

2.3. Theoretical Background

An estimate of the velocity of l-LDDO flow has been derived in our previous publication:[49]

\[ \nu_{LDDO} = \frac{k_0 \cdot T \cdot \phi_0}{4\pi \cdot \eta \cdot l_0 \cdot D \cdot T} \Delta C_C \]

(1)

where \( \Delta C_C \) is the local excess of cis-isomer concentrations near the particle, \( \eta \) is the viscosity, \( k_0 \) is the Boltzmann constant, \( T \) is the temperature, \( l_0 \) is the Bjerrum length, \( \phi_0 = eD/k_B T \) is the dimensionless wall electrostatic potential, \( D \) is the diameter of the particles, \( I \) is the ionic strength in the bulk. \( \Delta C_C \) can be understood as the cis-isomer concentration difference between the area near the particle and the bulk:

\[ \Delta C_C = C_{C,P} - C_{C,B} \]

(2)

where \( C_{C,P} \) and \( C_{C,B} \) are the cis isomer concentration near the particle interface and in the bulk, respectively (Figure 2d). In Equation 1 \( \Delta C_C \) is assumed to be constant over time, which was true only for the case of the photo-stationary state. The latter was not achieved instantaneously and requires some time of irradiation ranging between seconds and minutes (intensity and wavelength dependent). It has recently been shown that the photo-isomerization rate of the surfactant in bulk and at the interface (such as surfaces, polymers, aggregates) differs.[47,48] Here we expand the analysis of \( \Delta C_C \) to give an estimation of the fluid flow direction and strength for the l-LDDO velocity considering the change in the excess of concentration with the irradiation time as a consequence of isomerization rate, which was especially important for the first few seconds of irradiation till the photo-stationary state was achieved:

\[ \frac{d\Delta C_C}{dt} = \frac{dC_{C,P}}{dt} - \frac{dC_{C,B}}{dt} \]

(3)

where \( dC_{C,P}/dt \) and \( dC_{C,B}/dt \) are time-dependent changes in the cis-isomer concentrations at the particle interface and in bulk solution. Inserting rate equations of isomerization at interface, \( dC_{C,P}/dt \), and bulk, \( dC_{C,B}/dt \), one gets:

\[ \frac{dC_{C,P}}{dt} = k_{TC1} \cdot I \cdot C_{T,P} = k_{TC1} \cdot I \cdot A_{eff} \cdot \theta_I (C_{T,B}) \]

(4)

and \( dC_{C,B}/dt \):

\[ \frac{dC_{C,B}}{dt} = k_{TC} \cdot I \cdot C_{T,B} - k_{CT} \cdot I \cdot C_{C,B} \]

(5)

and finally:

\[ \frac{d\Delta C_C}{dt} = I \left[ k_{TC1} \cdot A_{eff} \cdot \theta_I (C_{T,B}) - (k_{TC} \cdot C_{T,B} - k_{CT} \cdot C_{C,B}) \right] \]

(6)

where \( k_{TC}, k_{CT} \) are the isomerization rate constants of trans-cis and cis-trans in bulk, \( I \) is the light intensity, \( A_{eff} \) is the effective area for surfactant adsorption, \( \theta_I (C_{T,B}) \) is the trans isomer surface coverage, \( C_{T,B} \) and \( C_{C,B} \) are the trans and cis isomers concentration in bulk, \( k_{TC1} \) is the isomerization rate constant of trans-cis process at the interface. Here we include the fact that the interface was effectively covered only by the trans isomers (surface coverage \( \theta_I \gg \theta_\lambda \)), since the desorption rate of cis-isomers was much faster compared to trans-isomers, \( k_{C,C} >> k_{A,\lambda} \).[47] It means that, at the interface, the isomerization rate was one-directional, i.e., from trans to cis, and was not compensated by the reverse isomerization as observed in bulk solution (equilibrium between trans and cis isomers). Details concerning the derivation of Equation 6 were presented in the Supporting Information (Sections 1–3). By integrating the Equations 4 and 5, the time-dependent concentration of cis isomers near the particle was calculated, \( C_{C,P} \):

\[ C_{C,P} = C_{T,0} - C_{T,0} \cdot \exp(-k_{TC1} \cdot I \cdot t) \]

(7)

and in bulk, \( C_{C,B} \):

\[ C_{C,B} = C_{T,0} - C_{T,0} \cdot \exp\left[-\left(k_{CT} + k_{TC}\right) \cdot \frac{k_{PC} + k_{TC} \cdot \exp\left(-[k_{PC} + k_{TC}] \cdot I \cdot t\right)}{k_{PC} + k_{TC}}\right] \]

(8)

Inserting Equations 7 and 8 into Equation 2, one gets the \( \Delta C_C \) as a function of irradiation time, intensity, and effective concentration.
area for isomer adsorption, \( A_{\text{eff}} \) (size and porosity of the particles). A positive value of \( \Delta c_C \), i.e., when \( c_{C,P} > c_{C,B} \) corresponds to an outgoing flow near planar substrate (pointing out of the particle) and was inverted by the negative sign. The time-dependent \( \Delta c_C \) correlates well with the experimentally measured change in sign of velocity as will be shown in Figure 3. So it can now be stated that, in a first approximation the velocity at a point fixed in space scales with the current value of \( \Delta c_C \).

It should be mentioned that the time-dependent change in the concentration gradient should also be altered by the kinetic of surfactant adsorption and desorption on a surface. However, since both the processes have different time scales, i.e., net concentration change of isomers from photo-isomerization (tens of seconds to get a photo-stationary state) and adsorption/desorption (few seconds), the influence of the adsorption kinetic was neglected. Considering the porous particle, one should additionally take into account that the diffusion coefficient of azobenzene inside porous glass (\( D = 4.2 \, \mu \text{m}^2 \, \text{s}^{-1} \)) was much lower than that in bulk (\( D \approx 2.4 \times 10^3 \, \mu \text{m}^2 \, \text{s}^{-1} \)). Here, the calculated values of \( k_{TC,I} \) indicate that the average isomerization rate constant was smaller for the entire particle, basically resulting from the reduced diffusion ability of the surfactant molecules inside the pores as well as due to steric hindrance within the pores; similar to molecules located in micelles. This effect was much more pronounced for big porous particles \((d = 20 \, \mu \text{m}, t_D = 11.9 \, \text{s} \rightarrow k_{TC,I}/k_{TC} = 0.15)\) than for the small porous particle \((d = 5 \, \mu \text{m}, t_D = 0.7 \, \text{s} \rightarrow k_{TC,I}/k_{TC} = 0.95)\).

![Figure 3](https://www.advancedsciencenews.com/)

3. Results and Discussion

Figure 3a,b shows the values of time resolved concentration difference of cis-isomers, \( \Delta c_C \), during irradiation with light of different wavelength blue (\( \lambda = 455 \) nm) and UV (\( \lambda = 365 \) nm) as calculated using Equations 2, 7, and 8. For calculations we use \( c_{T,0} = 1 \, \text{mM} \), \( k_{TC,I} = 0.0045 \, \text{cm}^2 \, (\text{mW} \cdot \text{s})^{-1} \) for 20 \( \mu \text{m} \) particle diameter or \( k_{TC,I} = 0.030 \, \text{cm}^2 \, (\text{mWs})^{-1} \) for 5 \( \mu \text{m} \) particle diameter. As can be seen, under irradiation with blue light the \( \Delta c_C \) is always positive implying outgoing DO flow, while in the case of UV light temporal attractive and repulsive DO flow can be generated. This is possible because the isomerization rate constant at the interface of the particles, \( k_{TC,I} \), is smaller than...
in bulk, \(k_{TC}^{[49]}\). Indeed, during exposure to UV light, since the value of \(k_{CT}^{[49]} \ll k_{TC}^{[49]}\) the Equation 5 can be approximated by:

\[
\frac{dc_{CT}}{dt} \sim -k_{TC} \cdot c_T
\]

therefore, the cis-trans photo-isomerization at the beginning of irradiation is neglected. Under consideration that \(k_{TC,I} < k_{TC}\), temporally negative gradient of \(\Delta c_C\) appears followed by positive one developed over isomerization time (see Equations 2, 7, and 8) as a function of irradiation time. Values for calculation of theoretical \(\Delta c_C\) from parameter \(k_{TC,I} = 0.0045 \text{ cm}^2 (\text{mWs})^{-1}, k_{TC,I}/k_{TC} = 0.15, c_{T_0} = 1 \text{ mM}, I = 3 \text{ mW cm}^{-2}\) Green dashed line marks the time at which the attractive turns to repulsive DO flow followed by Brownian motion.

Figure 4. a–e) Optical micrographs taken at a different times under exposure to UV light of the tracer particles \((d = 1.5 \mu m, \text{small black spheres})\) which are (a, b) first attracted to the large porous particle \((d = 26 \mu m, \text{in the center})\) followed by repulsion (c, d) and finally thermal motion (e). Red arrows indicate the flow direction. The corresponding video is provided in Supporting Information, Video S1, Supporting Information. f) Nearest particle distance ratio \(NPD/NPD_0\) (black data points) and the change in \(\Delta c_C\) (red curve, calculated using Equations 2, 7, and 8) as a function of irradiation time. Values for calculation of theoretical \(\Delta c_C\) from parameter \(k_{TC,I} = 0.0045 \text{ cm}^2 (\text{mWs})^{-1}, k_{TC,I}/k_{TC} = 0.15, c_{T_0} = 1 \text{ mM}, I = 3 \text{ mW cm}^{-2}\) Green dashed line marks the time at which the attractive turns to repulsive DO flow followed by Brownian motion.

Under irradiation with blue light (455 nm) according to Equation 8 the forward isomerization, i.e., trans-cis, is compensated by a reverse isomerization, cis-trans, resulting in a constant amount of the trans- and cis-isomers (photo-stationary state). As can be seen from the plot, small negative values of \(\Delta c_C\) can be observed also for irradiation with blue light at the very beginning of light exposure, which is in comparison to irradiation with UV light is, however, small (≈0.004 mM), and most probably is not enough to generate inwards flow, since experimentally, we observe the l-LDDO flow to point only out of the particle generating repulsive DO flow.

To visualize the temporal attractive and repulsive DO flow under UV exposure, we analyze the process by acquiring the motion of small tracer particles around one large porous colloid. At the small intensity of the UV light (I = 3 mW cm\(^{-2}\)), the tracer particles are first attracted to the porous colloid during the initial 230 seconds of irradiation (Figures 4a and 3b), afterwards, the repulsive DO flow sets on and the tracer particles are removed in a radial direction out of the porous one (Figures 4c,d). The repulsive DO flow decays within the next 4 min of irradiation followed by the l-LDDO flow and thermal motion of the tracer particles (Figure 4e). The decay of the l-LDDO flow under UV exposure is explained by the conversion of a majority of isomers into cis-state, i.e., consumption of fuel stored in the particles.\(^{[44]}\) The change in time dependent normalized nearest particle distance of tracer colloids, \(NPD/NPD_0\) (\(NPD_0\) is calculated for Brownian motion of the particles, i.e., without irradiation) (see black squares in Figure 4f) correlates with the sign of the cis-isomers excess concentration, \(\Delta c_C\), near the porous particle (red curve in Figure 4f): \(\Delta c_C < 0\) corresponds
to inwards directed flow, $\Delta c > 0$ indicates the outwards flow. The minimum of the $\Delta c$ value at $t \approx 25$ s marks the maximal attractive flow, followed by deceleration and inversion.

In our previous publication, we have described similar behavior of an ensemble of porous particles of 5 µm in diameter (Figure S4 in Supporting Information), where at high intensity of UV light only DO repulsion between the particles have been observed, while low intensities generate transient DO attraction and repulsion.\cite{44} Applying the introduced analysis here, we have reconstructed the time-dependent development of the concentration excess, $\Delta c$, and have found an excellent agreement with the experimental results (see red curves in Figures S4f-j, Supporting Information).

To demonstrate experimentally the persistence of the repulsive DO flow under blue light exposure, we analyze the motion of the tracer particles (non-porous colloids of $d = 1.5$ µm) around large porous particles of different diameters (Figure 5a).

Under illumination with blue light ($\lambda = 455$ nm) the $l$-LDDO flow generated around each porous particle pushes the tracer colloids out in radial direction over distances up to several tens of micrometers and the flow maintains during the whole illumination time (see Figure 5 and corresponding Video S2, Supporting Information). The extent of the DO flow depends on the diameter of the porous particle, i.e., the amount of stored surfactant, as illustrated for four porous particles of 5, 18.3, 21.7, and 26.9 µm in diameter (Figure 5b). The radius of the cleaned area at saturation, $R_{C,max}$ (Figure 5c), as well as the DO velocity (slope of the curves at the beginning in Figure 5a) increases linearly with particle diameter, i.e., with the effective area available for adsorption of trans-surfactant depicted according to Equation 6 (Figure 5c, details of calculations are reported in Supporting Information, Section 4).

The dependence of the extent of the $l$-LDDO flow on irradiation intensity is shown for one selected porous particle of 20 µm in diameter (Figure 6, see also Videos S3 and S4 in Supporting Information). The average velocity of the tracer

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**Figure 5.** a) Dependence of the radius of the cleaned area on irradiation time for four porous particles. b) Optical micrographs of the four porous particles of diameter $d = 5, 18, 22$ and 27 µm surrounded by tracer non-porous particles ($d = 1.5$ µm) of irradiation with blue light ($\lambda = 455$ nm, $I = 5$ mW·cm$^{-2}$). The scale bar is 20 µm. c) Dependence of the maximal radius of the cleaned area on the effective area of porous particles. The inset shows $R_{C,max}$ as a function of the particle radius $R_p$. The red dashed line visualizes a linear trend of the data.
Figure 6. a–d) Optical micrographs of the cleaned area around 20 µm porous particle under irradiation with blue light (λ = 455 nm, I = 5 mW cm⁻²) as a function of irradiation intensity indicated on the micrographs. The corresponding video is provided in Supporting Information, Videos S3 and S4. e) Time dependence of the cleaned area on intensity as indicated in the legend. f) Maximal cleaned radius $R_{\text{max}}$ and initial particle velocity (for the first 20 s of irradiation) as a function of light intensity. The results show strong intensity dependence of the flow strength, i.e., the flow velocity and extent (value of $R_{\text{max}}$).

Figure 7. a) Optical micrographs of the non-porous particles (left) and b) porous colloids (right) after 65 seconds of irradiation. Dependence of the separation rate on the light intensity for porous and non-porous particles in linear scale (b), and as log-log plot c). The wavelength of incident light is 455 nm, the particle diameter is 5 µm. Corresponding raw data are provided in Figure S3 (see Supporting Information, Section 5). Corresponding videos are provided for porous (Videos S5, S6, and S7, Supporting Information) and none-porous (Videos S8, S9 and S10, Supporting Information) silica particles.
particles increases from 0.1 µm s⁻¹ to 1.5 µm s⁻¹ with increasing the intensity from 0.16 to 10 mW cm⁻² (see red circles in Figure 6f).

We should mention that since the surfactant molecules adsorb also on a surface of plain particles, the l-LDDO flow is generated at the non-porous colloids as well, however, the extent of flow is significantly less. Figure 7 depicts the difference between the DO repulsion of porous and non-porous particles at other parameters fixed (c_{azo} = 2 mM, λ = 455 nm). We have found that the separation rate increases with intensity for

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**Figure 8.** a) Nearest particle distance as a function of time for porous silica colloids (d = 5 µm) calculated from Videos S11 - S14 (Supporting Information). b) Separation rate κ and photo-isomerization rate, k_{TC}, taken from published in our recent work⁴⁹ as a function of the wavelength obtained from fitting the data with Equation 10. Note, that the data for 365 nm are fitted with delayed time due to the existence of the attractive flow at the beginning of irradiation. Dashed lines in red and dark illustrate the data trend.

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**Figure 9.** Optical micrographs of the different objects and tracer particles (d = 1.5 µm) under irradiation with blue light (I = 10 mW cm⁻²): (a) nail, (b) hair, (c) dust, (d) soil, (e) sand corn, (f) wood sting. Corresponding videos are provided in Supporting Information, Videos S15-S20, Supporting Information. SEM micrographs of the corresponding surfaces are inserted. The black scale bar is 100 µm, white scale bar is 2 µm.
both types of particles and shows more than 30 times smaller values for non-porous colloids (Figure 7b,c). The analysis is based on the calculation of using $NPD$ values as a function of irradiation time:

$$NPD = NPD_0 + (NPD_e - NPD_0) \exp(-\kappa \cdot t) \quad (10)$$

where $NPD_0$ and $NPD_e$ are the nearest particle distance at the initial state and equilibrated during irradiation, respectively. $\kappa$ is the separation rate of two adjacent particles and $t$ is the time.

Expanding the analysis of the $l$-LDDO flow over more wavelength, i.e., 365, 490, and 532 nm ($I = 1 \text{ mW cm}^{-2}$ is kept constant for all wavelength) (Figure 8a) we have found that with increasing irradiation wavelength, the separation rate, $\kappa$ (see Equation 10), decreases (Figure 8b). In the case of blue and green light, the continuous generation of cis-isomers in steady state is low (20% and 10%, respectively) resulting in a weak DO flow (Figure 8a,b). Its effective dynamic isomerization rate is illustrated in Figure S5a, Supporting Information). For UV (365 nm) light, although, the initial separation rate is fast (the rate of isomerization is fast), during further continuous irradiation, the amount of trans isomers drops down to 10% in the steady state (effective surfactant exchange displayed in Figure S5b, Supporting Information) and thus the cis isomer gradient decays with Brownian motion of the particles overtaking the DO repulsion (see details in Supporting Information, Section 6).

With the knowledge gained, we would like to show that as long as the dynamic exchange of trans- and cis-isomers at a surface of an object exists, any kind of interface can generate $l$-LDDO flow. Here we demonstrate it by using different micro-sized objects (see Figure 9) such as human nail (a) and hair (b), dust (c) earth soil (d), sand corn (e) and a small part of a wood sting (f). During illumination with blue light ($\lambda = 455\text{nm}, I = 10 \text{ mW cm}^{-2}$) all micro-sized objects show an outgoing $l$-LDDO flow of different strength, i.e., different cleaned areas of tracer particles. This can be explained by the roughness of the objects as well as the different affinity of both isomer to the surface of these objects (see details in Supporting Information Section 7).

For instance, one can see from the SEM micrograph (inserted in the optical micrographs), that the sand corn has quite a rough surface, i.e., larger $A_{eff}$, in addition to the negative charge of the surface due to the presence of the silica oxide and thus exhibit stronger $l$-LDDO flow.

4. Conclusion

Here we demonstrate that objects dispersed in an aqueous solution of photosensitive surfactant can generate local-light driven diffusioosmotic ($l$-LDDO) flow and thus act as a micropump. The driving mechanism of the DO flow is based on the photo-isomerization of the surfactant molecules during exposure to light of an appropriate wavelength. Two states of the surfactant, trans- and cis-, have dissimilar photo-isomerization rates and different affinity to a solid/liquid interface providing a continuous exchange of both isomers between the interface and the bulk. This yields a concentration gradient of cis isomers and a consequent gradient in the osmotic pressure around the particles generating local DO flow along the solid surface. The radially directed flow can be adjusted to point towards or away from the particle by variation of the irradiation wavelength making the particle active with respect to interaction potential. It means that by generation of the DO flow at single colloids we introduce diffusioosmotic repulsive (outwards directed flow) or attractive (inwards direction) interactions, the range of which is determined by the extent of DO flow. We have shown that the strength of $l$-LDDO flow depends on the amount of the surfactant molecules absorbed by the particle as well as irradiation parameters. We extend the analysis of the mechanism of LDDO flow formation by introducing the time dependency of the concentration excess near the particle utilizing recently reported kinetics of surfactant photo-isomerization. The increase in intensity results in stronger DO flow, while variation of the wavelength has a more complex influence on the $l$-LDDO flow. Indeed, we have demonstrated that under UV light at low intensity, the DO flow can change its direction during light exposure from temporal attractive to repulsive, while irradiation with blue light results in continuously repelling flow. The fact, that any object capable to absorb selectively one of the isomers and thus generate $l$-LDDO flow can be used in many practical applications such as removal of contaminating particles out of an active surface, local pumping of a solute, or local mixing near the active object, as well as adjustment of the interaction strength and sign between active particles by generating DO repulsion or attraction flows.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

N.L. synthesized surfactant. M.B., M.U., and A.S. performed measurements. A.S. performed data analysis. M.B. and S.S. supervised experiments, data treatment as well as wrote the manuscript, S.S. conceived and organized the project.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.
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