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Full Paper

Light Scattering Enhancement at the Absorption Edge in Dewetting Droplets of Cyanine Dyes

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Diffraction properties of thin films of dewetted cyanine dye droplets are investigated and related to the complex refractive index. Strong changes in the index of refraction are often found near the absorption edge of organic dyes. Within a small window of droplet morphologies, scattering efficiency is maximized and becomes wavelength-selective. The origin of the high scattering efficiency is found to be in the enhancement of scattering at the absorption edge of the dye, where anomalous refractive index dispersion occurs. For a comprehensive understanding of the scattering effect, an analytical solution for the diffraction of an array of scatterers is presented. Finite-difference time-domain (FDTD) simulations of the extinction properties are performed and good agreements to the experiments are found.

These results pave the way to an easy fabrication of new organic-based optical devices such as refractive index-based sensors or color selective diffraction gratings.

1. Introduction

Electromagnetic scattering by particles is a universal phenomenon that manifests itself in a large number of everyday-life visual effects such as rainbows or clouds. From a technological standpoint, light scattering has attracted much attention in the last decades in the fields of nano-optics and nano-photonics because light-matter interactions with structures of sub-wavelength dimensions allows overcoming limitations of conventional optical elements at these scales.^[1] Numbers of devices allowing to control light at the nanoscale such as nano-antennas^[2,3] or light trapping structures in photovoltaic devices make use of plasmonic effects in metallic nano-structures.^[4–6] Large efforts have also been put in the study of high refractive index dielectric cavities^[7,8] for they allow overcoming intrinsic optical losses associated with plasmonic structures in the visible range^[9] and are compatible with conventional semiconductor processing techniques.^[10–12]

Mie theory, in its original form, gives an analytical solution to Maxwell's equations in the case of a plane electromagnetic wave interacting with a spherical particle of arbitrary size.^[13,14] The theory is particularly useful for particles which dimensions are similar to that of the wavelength of the incident light, where neither ray optics nor Rayleigh's approximation apply. In this case, light scattering (often called "Mie scattering") results from the confinement of strong electromagnetic modes (Mie modes) in the volume of the particle. However, in low refractive-index structures, light scattering can be considerably different from classical resonant mechanisms and has been described as weak (lossy) Mie resonances

or as non-resonant Mie scattering.^[15] Although Mie theory was originally derived for homogenous spherical particles, a number of extensions to the theory have been analytically or experimentally demonstrated, highlighting the effect of changes on the particle geometry^[16] and composition on the optical properties of the structure. Various photonic devices with selective spectral properties can thus be obtained by tuning the morphology (and in turn the optical properties) of such scattering nano-structures.^[17]

While most photonic nano-structures, such as optical microcavities, plasmonic metal nanostructures and photonic crystals, make use of either metallic or inorganic materials with high dielectric constants, only little effort has been devoted to study sub-wavelength scattering effects from organic material systems.^[15,18] Yet organic materials are attractive in terms of the versatility of their fabrication processes and low cost compared to metallic and inorganic dielectric materials, allowing fabrication of large area devices.

Organic chromophores, such as cyanine dyes, show interesting intrinsic electro-optical properties. Mostly known for their role as sensitizers in photographic films,^[19] this class of organic semi-conductors has recently been investigated as amorphous active layers in organic solar cells^[20–22] and light-emitting electro-chemical cells.^[23] The high oscillator strength of cyanine dyes accounts for their pronounced light absorption in the visible wavelength range. Together with strong absorption bands, cyanine dyes also exhibit significant variations in their refractive index that can be described by the Lorentz oscillator model.^[24] Few studies have reported on the effect of variations in refractive index in absorbing materials on the scattering from particles.^[25,26]

In this work, we fabricated droplets of 1-Ethyl-2-[3-(1-ethyl-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)-1-propen-1-yl]-3,3-dimethyl-3*H*-indolium perchlorate (CyC) of different shape on glass substrates by dewetting during spin-coating.^[27,28] The droplet ensemble gives rise to diffraction. Diffraction depends on the scattering properties of the individual scatterers,

as well as on the nearest neighbor arrangement of the scattering elements. Only first order diffraction is notable and shows an unusual wavelength dependence with high intensity near the absorbance edge of the dye. In a first part of the paper we describe the dye droplet ensemble (2.1.). In a second part, we show the results of experimentally recorded diffraction efficiencies for different samples. Depending on droplet size, a very different behavior is found (2.2). In the third part we demonstrate that the diffraction is complementary to transmission measured by UV-Vis. These measurements allow defining three distinguishable scattering regimes (2.3.). In section 2.4. we introduce an analytical solution that connects the arrangement of the scattering elements with the scattering properties of the individual scatterers (dye droplets). While we find an amazing consistency between theory and experimental data, reproducing three different scattering regimes, the analytical solution hardly illustrates the reason for the scattering behavior. For this purpose we present FDTD simulations of the system (2.5.-2.7.). Again, the simulations reproduce the experiment, and also bring an intuitive understanding of how anomalous dispersion of the refractive index at the absorption edge of the dye causes the narrowing down of the extinction peak compared to Mie scattering. From the simulations, electrical field distributions can be extracted that reveal the origin of the scattering contrast: the interaction between the dye droplets and light can be best described as a non-resonant form of Mie-scattering whereby the droplets act as micro-lenses defocusing the light.

While in earlier publications we attributed the apparition of the new spectral feature solely to the formation of aggregates and resonantly enhanced scattering,^[29–31] we here decipher to what extent the unusual scattering phenomena can be attributed to the droplet morphology alone.

2. Results and Discussion

2.1. Droplets Formation

Films consisting of micro-droplets of CyC dye were fabricated by spin-casting the dye from saturated ethanol solutions. The liquid dewets from the glass substrate and self-assembles into droplets upon solvent evaporation. The processes leading to droplet formation are complex and involve the formation of film instabilities due to temperature and concentration gradients (Marangoni instability), Van der Waals interactions and solvent evaporation.^[32, 33]

Figure 1. (a) Scanning probe microscopy images of CyC droplets samples cast at different velocities. (b) Representative SPM profiles and (c) mean droplet height and radius as a function of casting velocity. Error bars on the droplets radius and height represent the standard deviation within the sample measured for each velocity. (d) 3D view of the effect of water added to the precursor CyC solution on the morphology of the drops (0%vol, 4%vol, 10%vol from top to bottom). (e) 2D-FFT of the SPM image of CyC droplets cast at 2500 rpm.

Droplets of different size were obtained by varying the rotational speed from 300 rpm to 2500 rpm during spin-casting (SPM images **Figure 1(a)**). Figure 1(b) shows profiles of droplets cast at different rotational speeds. While the smaller droplets take the form of almost spherical caps (some are almost hemispherical), larger droplets take the shape of an oblate spherical cap. Figure 1(c) shows mean droplet radius and height as function of casting velocity for the images shown in Figure 1(a). As already obvious from the profiles shown in Figure 1(b), the droplet form varies with different spin speeds, coming closest to hemispherical for a casting velocity between 1000 and 1500 rpm. Nevertheless, in a first approximation, we describe the droplet morphology by two parameters: the droplet radius and their aspect ratio s , defined as the height/radius ratio. For a hemispherical droplet s would be 1. The droplet height and radius should be understood as mean value measured on a reasonable number of droplets by scanning probe microscopy. Parameters controlling the droplet shape are contact angle, surface tension and droplet volume. Surface tension limits the minimum droplet size.^[34] More details on the control of droplet formation in the CyC system can be found in earlier work.^[35] Analysis of the height and size distribution of the droplet samples show the unimodal nature of the distribution for spin-coating speeds above 300 rpm (Supporting Information Figure S1). A strategy to control the droplet aspect ratio is to add water to the CyC initial ethanol solution in a controlled manner. Figure 1(d) shows the 3-dimensional views of droplets cast at the same rotational speed but from initial solutions containing an increasing amount of water (0 vol%, 4 vol% and 10 vol%). Addition of water to the initial dye solution results in an increase in the surface tension of the solution, leading to a change in the droplets' morphology from spherical cap (dry ethanol solution) to almost hemispherical (10 vol% water).

2.2. Diffraction

The characteristic droplet size and spacing resulting from the spinodal dewetting process

gives rise to a characteristic ring pattern in the Fourier transform of the droplet arrangement (see Figure 1(e)).^[31] We compare this to the Fraunhofer diffraction pattern of the sample. Also here we observe a ring pattern typical for a spinodal diffraction structure. To quantify the data, we record the intensity of the scattered light with a detector mounted to a goniometer that probes the polar angle. Diffraction intensities are then integrated over the azimuthal angle and are shown as a function of scattering (polar) angle and wavelength in **Figure 2** for three different morphology regimes, characteristic for three different diffracting behaviors.

Figure 2. Diffraction angles and wavelength dependence of diffraction intensity from samples of three different morphology types: (a) $r = 449$ nm, $h = 165$ nm; (b) $r = 647$ nm, $h = 279$ nm; (c) $r = 483$ nm, $h = 543$ nm.

The diffraction intensity depends strongly on wavelength and droplet dimensions. In a morphology Regime 1 (height below 225 nm), diffraction is restricted to wavelengths below $\lambda = 600$ nm, in a morphology Regime 3 (height above 350 nm) the main contribution to diffraction stems from wavelengths above $\lambda = 650$ nm, and in a morphology Regime 2 (height between 225 nm and 350 nm) the main diffraction contribution is observed for wavelengths around $\lambda = 610$ nm. Here the diffraction intensity is higher than in the other Regimes. The course of the diffraction angle with wavelength can be roughly estimated from Figure 2, it shows a rather linear dependence, which proves that light is indeed diffracted from the droplet ensemble and the individual droplets represent the scattering objects. Higher diffraction

orders only become visible at very long integration times.

What exactly provides the scattering contrast is the subject of the following sections, diffraction here obviously does not only depend on absorption and index of refraction of the droplets, but also on droplet dimensions.

2.3. Extinction and Contribution of Scattering

We continue our analysis by looking at the extinction properties of the films. Our diffraction and UV-Vis measurements fully complement each other. UV-Vis detects transmission of light that is scattered up to 5° and finally converted into extinction. All of our samples, on the other hand, scatter light into an angle larger than 5° (Figure 2). Absorbance can be measured with an integrating sphere. The diffraction component to extinction can thus be extracted from the UV-Vis measurement. The data have to be analyzed carefully though because most of the droplets are thicker than 100 nm from whereon all incoming light is absorbed and coverage of the substrate with droplets greatly determines the absolute values. For a continuous CyC film and samples corresponding to the diffraction pattern shown in Figure 2, we show UV-Vis extinction spectra as obtained from a transmission measurement and absorbance data as obtained from the integrating sphere (**Figure 3(a)**) The thin film sample shows a spectrum that closely follows the imaginary part of the index of refraction (absorption coefficient k) as measured by ellipsometry (Figure 3(b)). The two peaks at 575 nm and 525 nm correspond to the absorption of the monomer and dimer form of the dye, respectively.^[31]

The UV-Vis extinction spectra of the droplet samples exhibit very different profiles. In particular, the three scattering Regimes identified above also lead to three distinguishable extinction profiles (Figure 3(a) and (c)). The diffraction contribution in extinction is more or less represented by the difference between the extinction and absorbance profiles. As the

samples also diffract light in the absorbance region (Figure 2), absorbance never reaches the values of extinction. In Regime 2 the contribution to scattering in the absorption region is largest. The absorbance spectra from the integrating sphere exhibit flat profiles attributed to the strong absorption from the droplet samples.

The accuracy of UV-Vis spectroscopy allows for a detailed analysis of all droplet samples. When plotting the extinction peak position as a function of the droplet height, we find that all data fall onto one mastercurve (Figure 3(d)). Within the range in radii we find for a certain height we can thus use the average droplet height to also quantify the scattering behavior. Height and radius of all droplets investigated in Figure 3 are shown in the Supporting Information. To further justify this choice we performed FDTD simulations on the droplets (described in detail in section 2.6.) that confirm that height is a most sensitive parameter to describe optical behavior. In smaller droplets (droplet height $h < 225$ nm, Regime 1) the extinction spectrum shows a profile close to that of a continuous film. However, an additional feature appears, red-shifted compared to the monomer peak, significantly broadening the extinction between $\lambda = 550$ nm and 600 nm.

Moreover, a small extinction tail characteristic of light scattering from the sample is visible in the non-absorbing region of the dye, above 600 nm. For larger droplets (droplet height $h > 375$ nm, Regime 3) the extinction deviates quite substantially from the thin film absorption profile. It is characterized by a flat extinction profile in the absorbing region of the dye and a broad prominent feature at long wavelengths (Regime 3). This long wavelength feature is reminiscent of Mie scattering observed in non-absorbing particles of constant refractive index. Extinction in the absorption region of the dye remains featureless because the incoming light is fully absorbed within a droplet.

For samples in the intermediate Regime 2 ($225 \text{ nm} < h < 350 \text{ nm}$), the extinction peak resembles an optical resonance. The peak narrows down and gains intensity. The peak lies

between $\lambda = 600$ nm and $\lambda = 610$ nm. The spectra also show an extended scattering tail into the long wavelength region. The peak maximum now is fully outside of the absorption band of the dye, but coincides with the region where the dye shows a strong variation in the refractive index (Figure 3(b)). The strong variations of the refractive index near the absorption edges are a natural consequence of the oscillatory nature of the electronic absorption and are consistent with Kramers-Kronig relations.^[24,36] This observation suggests that the sharp scattering features are also related to the index of refraction n . This effect will be discussed in more details later.

Figure 3(c) shows normalized extinction spectra of a set of samples with increasing droplet height (but varying aspect ratios). In this presentation the similarity of the spectra of the different Regimes becomes clear. Each Regime can thus be assigned to a certain range of droplet height or to a range of extinction peak wavelengths. Droplets with a height below $h = 225$ nm can be assigned to Regime 1 (peak wavelength between $\lambda = 595$ nm and $\lambda = 598$ nm), droplets with a height between 225 nm and 350 nm can be assigned to Regime 2 (peak wavelength between $\lambda = 600$ nm and $\lambda = 610$ nm), while droplets higher than 350 nm are assigned to Regime 3. Interestingly enough, the peak extinctions of Regime 1 and 2 are all in a wavelength region where n is sharply increasing and decreasing, respectively.

Figure 3. (a) Extinction (lines) and absorbance (circles) spectra of droplet samples characteristic from regimes 1, 2 and 3 (pink dashed, blue full and red dot-dashed respectively) compared to a thin film (black dotted line). Depending on the droplet morphology, extinction spectra exhibit different profiles attributed to different scattering regimes. Regime 1, 2 and 3 correspond to pink dotted, blue full and red dotted-dashed lines, respectively. (b) Optical constants of CyC in a continuous film measured by ellipsometry. n and k are the real and imaginary part of the refractive index, respectively. (c) Normalized extinction spectra of droplet samples in the height range from $h = 160$ nm to $h = 550$ nm, indicated by different color tones and line types specified in (d). The characteristic shape of the profiles allows assigning each spectrum indisputably to one of the three “regimes” indicated by different

colors. (d) Wavelength of extinction maximum versus droplet height from the spectra shown in (c). Bordered symbols correspond to the samples presented in (a).

2.4. Arrays of scatterers in a diffraction plane

To fully understand the optical behavior of the thin film we have to understand how the optical properties of the individual droplets generate an optical contrast leading to the observed diffraction pattern. In the following we perform an analytical study of the diffraction of an array of scatterers taking strong variations in n and k into account (Figure 3(b)). The full derivation of the formulas can be found in the Supporting Information. The total diffracted field of an array of identical scatterers in the far field is given by the product of two terms: (i) the Fourier transform of the individual scatterer which gives rise to the envelope of the diffraction field; and (ii) the sum of phase terms which incorporates the distribution of the scattering elements. While a completely random arrangement of scattering elements does not give rise to any preferred diffraction angles, the diffraction cone observed in our experiments can be explained by a distribution of scattering elements with a (quasi-)constant nearest neighbor distance $p = \lambda / \sin \theta_{cone}$, as suggested by the Fourier transform of the SPM images (Figure 1(e)). Higher diffraction orders are very weak in this example.

We define the efficiency of scattering M as the ratio of the first and zeroth order (forward scattering) signal. M is given by the Fourier transform of a single scatterer alone, as the sum of phase terms is equal for all orders of the diffraction signal.

$$M = \frac{I(m=1)}{I(m=0)} = \frac{|\psi_P(\mathbf{k} = \mathbf{k}_1)|^2}{|\psi_P(\mathbf{k} = \mathbf{0})|^2} = \left| \frac{N \times FT[\tilde{d}(\mathbf{x})](\mathbf{k} = \mathbf{k}_1)}{A + N \times FT[\tilde{d}(\mathbf{x})](\mathbf{k} = \mathbf{0})} \right|^2 \quad (1)$$

where N is the number of scatterers on an area A , $\mathbf{k}_1$ the direction of first order scattering, while $\tilde{d}(\mathbf{x}, \mathbf{x}_0)$ describes the transmission behavior of the individual element, which

represents a material with a complex refractive index $\tilde{n} = n + ik$. The real part n leads to a phase shift of the transmitted light, while k describes absorption. For simplicity, we describe the scatterers as cylinders with radius r and height h . We then arrive at the following expression:

$$M = \frac{\left| N \times [\exp(i\Phi) \times t - 1] \pi r^2 \frac{2J_1\left(2\pi \frac{r}{p}\right)}{2\pi \frac{r}{p}} \right|^2}{\left| A + N \times [\exp(i\Phi) \times t - 1] \pi r^2 \right|^2}, \quad (2)$$

where t is the amplitude transmission coefficient of the diffraction element, while ϕ is the phase change. As the distance p between neighboring scatterers is larger than their diameter, $p > 2r$, the argument of the Bessel function J_1 is smaller than π . Introducing the fill factor

$$F = \frac{N \times \pi r^2}{A} \quad (3)$$

i.e. the ratio of the area occupied by the scatterers divided by the total area, we find

$$M = F^2 \left| \frac{2J_1\left(2\pi \frac{r}{p}\right)}{2\pi \frac{r}{p}} \right|^2 \frac{|\exp(i\Phi) \times t - 1|^2}{|1 + F \times [\exp(i\Phi) \times t - 1]|^2} \quad (4)$$

In the general case, the phase shift and transmission through a thin film are related to the complex refractive indices according to ^[37]

$$t \times \exp(i\Phi) = \frac{t_{01}t_{12} \exp(-i\beta_1)}{1 + r_{01}r_{12} \exp(-2i\beta_1)} \times \exp(i\beta_0) \quad (5)$$

where

$$\beta_i = \frac{2\pi}{\lambda} h \tilde{n}_i, \quad t_{ij} = \frac{2\tilde{n}_i}{\tilde{n}_i + \tilde{n}_j}, \quad r_{ij} = \frac{\tilde{n}_i - \tilde{n}_j}{\tilde{n}_i + \tilde{n}_j} \quad (6)$$

$\tilde{n}_j$ is the complex refractive index of air ($j = 0$), of the scatterer ($j = 1$) and the substrate ($j = 2$), respectively.

Figure 4 shows the first order diffraction efficiency, Equation (4) with the optical parameters of CyC on a BK7 glass substrate, a fill factor of $F = 0.25$, and different radii r and height h of

the individual scattering element according to the three Regimes. The average nearest neighbor distance p was estimated from $F = \pi r^2 / p^2$.

Figure 4. Simulated diffraction efficiencies for the three Regimes.

The analysis shows that close to the absorption band diffraction can be enhanced. The

analysis also qualitatively reproduces the different scattering plots given in Figure 2.

For larger droplets a strong dependence of the scattering spectra on droplet size is observed.

The broad scattering feature indicates a non-resonant Mie type phenomenon at the individual droplets and is addressed in the next section.

2.5. Anomalous Dispersion Effect

For a further understanding we performed FDTD simulations for assemblies of droplets of different diameters. The intermediate droplet size regime is of prime interest because in this case the scattering contribution is close to the absorption edge of the dye. The scattered electric field distribution around the individual droplets was simulated. The transmitted power through a randomly distributed grating of dye droplets was calculated for the (0,0) grating order. The near-field solution was propagated into the far-field and extinction spectra were calculated. For a meaningful analysis, the experimental values for the optical constants of the dye were used in the simulations. For the sake of clarity, in a first set of simulations droplets were taken to be hemispherical (height = radius).

Figure 5(a) shows the simulated extinction spectra of samples with heights ranging from 50 nm to 470 nm. Along general lines, the simulations follow the experimentally observed trends, but show differences in some details. In the experiment, sharp transitions can be identified between three different extinction profiles with characteristic features when increasing the droplet height (Figure 5(b)). In the simulations, the spectral changes can be best described by a smooth transition of the main extinction peak from an absorption peak with maximum at $\lambda = 585$ nm into a broad scattering feature reminiscent of Mie scattering at longer wavelengths. In between, for a droplet height of $h = 230$ nm extinction reaches a maximum while the FWHM is smallest. Intuitively, it can be understood that the Mie-peak is never observed in wavelength regions where the dye absorbs since only little light is transmitted through the droplets.

Figure 5. (a) Simulated extinction spectra of hemispherical droplets of varying radius. (b) Simulated extinction maxima as a function of droplet height (here height = radius). The values are comparable to the experimental data (Figure 3(d)).

Now that we validated the FDTD simulations, through the comparison of simulated and experimental extinction spectra, we can rationalize the resonance peak character of scattering from samples of Regime 2. For that we look at the dependence of the scattering efficiency on the optical constants n and k of a particle of given size.^[38] If n is rapidly changing across the spectrum (as it is the case at an absorption edge) the scattering efficiency will also vary rapidly. In **Figure 6** the extinction efficiencies of a hemispherical droplet of $h = 375$ nm with different constant values of n and k (taken from the dispersion relation of the dye) are shown. The extinction features of these artificial droplets are rather broad but show large variations when varying the n and corresponding k values. The extinction spectrum of a dye droplet is then constructed by picking for each λ the extinction value of the corresponding pair of n and k (Figure 6, solid red line). More details on that procedure are found in [25]. Even though this approach does not represent a real physical situation, it is useful to understand the effect of a strongly varying n index, sometimes called anomalous dispersion artefact,^[25] on extinction spectra.

Figure 6. Extinction spectra simulated for an ensemble of hemispheres with radius $r = 375$ nm and fixed optical constants taken from the dispersion relation of the dye (thin blue, green and yellow lines). From these curves the effective extinction of the droplet ensemble with varying k and n is constructed (thick red solid line).

2.6. Effect of Droplet Height and Size Distribution on Extinction Spectra

In section 1 describing droplet formation we had pointed out that in the standard dye solution the aspect ratio decreased with increasing droplet radius. We also pointed to the possibility to adjust the aspect ratio by adding water to the solution. In the experiments we were analyzing samples with different aspect ratios and came to conclude that only the droplet height h determines the optical response. We here consolidate this observation with a FDTD simulation. In a first step, we keep the radius constant and vary the height (**Supplementary Figure S4 (a)**). Varying the height alone can cause transitions from one regime to another. In the second case, we keep the height constant and vary the radius (**Supplementary Figure S4(b)**). As expected in this case, only small spectral changes are observed, while the

scattering efficiency increases with increasing radius. Along the same lines, the effect of a more realistic droplet size distribution versus monodisperse droplets was also evaluated. As visible from Supplementary Figure S4(c) and (d), the presence of droplets of smaller size significantly broadens the main extinction peak, while the effect of a radius size distribution at constant height on the spectral features is limited. The thickness dependency of the extinction behavior as well as the scattering peaks can be compared to thin-film interferences in low-index layers. In this case, scattering results from reflection or refraction effects at the boundaries between the different media that are involved. Thin film interference phenomena typically show a thickness dependency and high damping due to the fact that light is not resonantly oscillating within the film. The dye droplet indeed cannot confine light and the scattering behavior results from an interference-like phenomenon, as described in the next section. This again speaks for droplet height as the most relevant parameter to describe the optical phenomena.

2.7. Non-Resonant Form of Mie Scattering

So far we attributed the long wavelength extinction feature to Mie-scattering, whereby Mie scattering refers to a situation where the size of the scattering particles is comparable to the wavelength of the incoming light. We already suspected that the low index nature of our material is not able to confine electrical modes within the droplet. In order to better understand the exact nature of the scattering process, we simulate the electrical near-field intensities by the FDTD method.

Figure 7. Cross-sections (top row) and top view (bottom row) of the simulated near-field intensity within CyC droplets of height 500 nm ((a) and (e)), 350 nm ((b) and (f)), 250 nm ((c) and (g)) and 70 nm ((d) and (h)) on a glass substrate. For each droplet radius, simulation is performed at the wavelength of maximum extinction.

Figure 7 shows the intensity of the electromagnetic wave for cross-sections along the propagation direction and top views at the interface between the droplet and the glass substrate at the extinction maximum for CyC spherical caps on a glass substrate for heights $h = 500$ nm, 350 nm, 250 nm and 70 nm, representing Regimes 3, 2, 2 and 1, respectively. While the height/radius ratios in these samples are 1, the shape is not strictly hemispherical to better represent the experimental situation. Droplets are illuminated from top by a linearly polarized plane wave light source. Each droplet is illuminated at the maximum extinction wavelength ((a) and (e) $\lambda = 700$ nm, (b) and (f) $\lambda = 629$ nm, (c) and (g) $\lambda = 611$ nm, (d) and (h) $\lambda = 595$ nm), where the contribution from scattering is maximum.

The non-resonant nature of the scattering can also be seen from the time sequence of a wave packet travelling through the droplet (see Supporting Information). Generally speaking, the spherical caps act as a micro-lens due to the phase difference the light wave experiences when

travelling through the droplet with respect to vacuum. Assuming a thin structure this phase difference can be expressed as $\Delta\phi = z(n - 1)$, where z is the distance traveled through the drop and n the real part of the refractive index. It is clear from the previous expression that the accumulated phase difference depends on the point of entry and the total distance traveled through the droplet and that it is maximum for light travelling through the center of the droplet.^[39] The accumulated phase difference results in the formation of constructive / destructive interferences in the near field around and beyond the droplet and leads to a complex E-field pattern. Depending on height, radius and wavelength, the incoming plane wave travelling through a droplet will eventually bend. For droplets of 500 nm (corresponding to Regime 3), 350 nm and 250 nm (corresponding to Regime 2) height, at the wavelength of maximum extinction, the incoming wave is focused behind the droplet forming a source of scattered light.

We now describe the optical characteristic when decreasing the droplet size, focusing especially on the resonant type Regime 2. We note that the field intensity inside a droplet is generally lower than in the surrounding vacuum, and is lowest for the peak wavelength in Regime 2. Secondly, a stationary interference pattern is observed in front of the droplet, which can be a rough indication of the scattering cross-section of the individual droplet. This modulation of field intensity is also largest for the peak wavelength in Regime 2. For larger droplets, light is focused onto one point well below the substrate plane. As one decreases the droplet size, the focal point moves closer to the interface between droplet and substrate, where it splits into two points (for non-polarized light a ring would be observed). For 70 nm droplets (Regime 1) in the absorption range, most of the light is absorbed by the droplets and the focal points are guided to the contact line of the droplet above the substrate.

Similar to Regime 1, the far-field optical response is dominated by diffraction of the droplet array. The diffraction contrast in Regime 2 and 3 is a result of defocusing the incoming wave behind the focal points.

2.8. Towards Sensor Applications

Generally speaking, dielectric materials find a wide range of applications in optical sensing based on resonant structures such as nanofibers, photonic crystals and diffraction gratings. In this section we demonstrate the potential of our cyanine droplet system for refractive index-based sensor applications. Changes in the refractive index surrounding a classical resonant Mie scattering structure induces only limited spectral changes. However, in the case of non-resonant structures like ours, the extinction response shows high sensitivity to variations in the refractive index of the medium surrounding the droplets.

Figure 8(a) shows the variation in the spectral response when droplets showing a Regime 3 type extinction are immersed in cyclohexane ($n_{\text{cyclohexane}} = 1.426$). In this case a large spectral shift is observed from 710 nm for the pristine structure to 610 nm for the structure immersed in cyclohexane. After removal and drying from cyclohexane, the original extinction profile is recovered.

Figure 8(b) shows the simulated spectral changes obtained for incremental variations of the refractive index surrounding the structure from 1.0 to 1.5. The broad extinction peak observed for the droplets in air narrows down and blue-shifts proportionally to the changes in refractive index. Such sensitivity to small incremental changes is extremely promising for the design of refractive index-based sensors.

Figure 8. (a) Significant changes in the extinction profile of an array of CyC droplets is measured when the surrounding index of refraction is changed from 1.0 (air) to 1.43 (cyclohexane). (b) Simulated changes in the extinction profiles of 500 nm droplets sample for incremental variations in the refractive index surrounding the structure.

3. Conclusion

We have demonstrated an easy fabrication method for diffracting arrays of cyanine dye droplets with very specific optical properties. The arrays diffract light in different wavelength ranges depending on the thickness of the individual droplets. In particular, for droplets with thicknesses in the range of 225 nm to 350 nm, diffraction occurs mainly within a narrow wavelength window. Strong wavelength selectivity occurs when a non-resonant form of Mie scattering interferes with a strong variation of the index of refraction at the absorption edge of the dye. In that scattering regime, the droplet acts as a wavelength selective diffracting micro lens. Strong, resonance type features in extinction are here a pure effect of the droplet geometry and the index of refraction variation. We are confident that the droplet fabrication process can be applied to dyes with absorption bands at different wavelengths hence allowing tuning the diffraction selectivity to different colors.

A proof-of-concept for the application of these arrays as refractive index-based sensor has been presented. The sensing mechanism is based on the variation of the scattering efficiency when the array is exposed to environmental media of different refractive indices.

The strong wavelength dependence of scattering in Regime 2 is particularly interesting as it can find applications in wavelength selective diffraction and in wavelength selective switches. Finally, micro-lens arrays as such find numerous applications,^[40] miniaturization of lenses with small focal spot size and depth of focus are a key factor for sub-diffraction optics.^[41]

4. Experimental Section

Dye Preparation:

1-Ethyl-2-[3-(1-ethyl-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)-1-propen-1-yl]-3,3-dimethyl-3*H*-indolium perchlorate (CyC) was synthesized in our laboratory.^[42] A saturated solution of CyC was prepared by dissolving 10.2 mg mL⁻¹ ^[31] of the dye in ethanol (puriss., over molecular sieve (H₂O ≤ 0.01%), Sigma-Aldrich). In order to obtain larger hemi-spherical droplets, de-ionized water was intentionally added to the saturated ethanolic solution (up to 10 vol%). Solutions were stirred for at least 24 hours before use.

Droplet Formation:

2.5 × 2.5 cm² microscopy glass slides were used as substrates. The slides were cleaned by ultra-sonication in an acetone bath for 5 minutes followed by an ethanol bath for another 5 minutes. Substrates were then blow-dried with nitrogen. CyC droplets were obtained by spin-casting the dye saturated solution on glass substrates. 0.3 mL of dye solution was first filtered and distributed on the substrates, followed by a slow rotation at 200 rpm for 3 seconds. The rotational speed was then increased to the desired value (ranging from 300 rpm to 2500 rpm) at a rate of 3000 rpm s⁻¹ and the samples were spun for 60 seconds.

Scanning Probe Microscopy:

The samples' morphology was evaluated by scanning probe microscopy (SPM) using a NanoSurfMobile S (Nanosurf AG, Switzerland) in tapping mode at 170 kHz with rectangular silicon cantilevers (Nanosensors: MikroMasch, Lady's Island, SC) with a force constant of ~ 40 N/m and a tip radius of 10 nm. The droplet thickness was measured with WsXM software.^[43] Droplet radii were measured using ImageJ software, by fitting a circle.

Extinction Measurements:

Extinction spectra of the sample were measured using a Varian Cary 50 UV-Vis spectrophotometer. Absorbance was measured with the Horiba Jobin Yvon Fluorolog FL-3 equipped with an integrating sphere (Horiba Jobin Yvon F-3018).

Angle Resolved Scattering:

Light diffraction was measured with a photodiode mounted to a motorized goniometer. The light source was a xenon lamp (LOT-Oriel, U.K.) coupled to a monochromator (Omni- λ 300, Zolix, China). The beam was optically focused on the sample surface, with a focal length of 175 mm and a spot size of 1 mm². The angle of incidence was 90°. The increment in wavelength was 4 nm, the goniometer angle steps were 2°. The mechanical scanning range of the monochromator is 0 -1200 nm.

FDTD Simulations:

Finite-difference time-domain (FDTD) simulations were performed using Lumerical FDTD Solution software (Lumerical Inc., Canada). Perfectly matched boundary conditions on all the sides of the simulation box were used for single droplet simulations, whereas periodic conditions were used for the simulation of a droplet ensemble. The wavelength range of the simulation was 400-800 nm or 400-1000 nm. The arrangement of droplets for the simulations

was adapted from experimental data and is shown in the Supporting Information. Optical constant values (n,k) of CyC were obtained by ellipsometry on a continuous dye film.

Ellipsometry:

Values of the optical constants (n,k) of CyC were obtained on a continuous dye film, using a spectroscopic ellipsometer M2000VI (J.A. Woollam, USA).

Supporting Information

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

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SYNOPSIS TOC

Arrays of sub-micrometer sized cyanine dye droplets are formed on substrates by a dewetting process. Depending on the droplets' dimensions, scattering follows the behavior of one of three different extinction regimes. The new extinction features originate from the enhancement of light scattering at the absorption edge of the dye, where strong variations of the refractive index occur.

Cyanine dye, dewetting droplets, scattering

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Light Scattering Enhancement at the Absorption Edge in Dewetting Droplets of Cyanine Dyes

TOC Figure