Electrohydrodynamic NanoDrip Printing and Applications in Light-Matter Interactions

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“Uhrrr Ahhhhhrrrr Aaaarhhg...”

- Chewbacca
Abstract

Electrohydrodynamic printing in the microdripping regime can eject droplets much smaller than the printing nozzle opening. By employing nozzles in the range of 1 μm and circumventing related challenges, the process has been downsized to the nanoscale. As the ejected droplets are in fact not in the micro- but in the nanometer regime, the process is called NanoDrip printing. By and accounting for the time scales of solvent vaporization on the deposition substrates, including related wetting and particle-substrate interaction phenomena, not only two-dimensional, but also high resolution, three-dimensional nanostructures can be realized for various nanoparticle dispersions.

The aim of this work is to gain a deeper understanding of the physics behind this nascent technology, showcasing applications for the 3D printing capability of the NanoDrip printing and expanding the range of applications to plasmonics and RGB color printing at the diffraction limit by combining precisely placed various quantum dot dispersions with other nanostructures to extract related functionalities in a rather facile manner.

Despite demonstrated capabilities in earlier works, the fundamental understanding of important aspects of the physics of NanoDrip printing needs further improvement. The first part of this thesis addresses the topics of charge content and transport in NanoDrip printing. Quantum dot and gold nanoparticle dispersions are employed in combination with a specially designed, auxiliary, asymmetric electric field, targeting the understanding of charge locality (particles vs. solvent) and particle distribution in the deposits as indicated by the dried nanoparticle patterns (footprints) on the substrate. Experiments and simulations show that droplets of alternating charge can be spatially separated when applying an ac field to the nozzle. The nanoparticles within a droplet are distributed asymmetrically under the influence of the auxiliary lateral electric field, indicating that they are the main carriers. Furthermore experiments are conducted showing the ligand length of the nanoparticles in the colloid affects their mobility after deposition (in the sessile droplet state).

The controlled fabrication of functional nanostructures with extreme resolution finds a host of applications exemplified by the broad area of surface/light interaction. Nonplanar features of such structures can significantly enhance their performance and tunability, but their facile generation remains a challenge. In the subsequent part of the dissertation we show that EHD NanoDrip printing is able to generate precise out-of-plane forests of plasmonic nanopillars with resolutions at the diffraction limit, directly integrated in metal-insulator-nanocomposite configurations. Furthermore, the
capability of the method to generate such features on non-flat substrates is demonstrated experimentally. The nanocomposite nature of the printed material allows the fine-tuning of the overall visible light absorption from complete absorption to complete reflection by simply tuning the pillar height. Almost perfect absorption (95% on average) over the entire visible spectrum is achieved by a nanopillar forest covering only 6% of the printed area. Adjusting the height of individual pillar groups by design, on-demand control of the gray scale of a micrograph with a spatial resolution at the diffraction limit is demonstrated.

In Chapter 4 the focus is shifted to generating color images with resolution at the diffraction limit, expanding the capability to print gray-scale images. For this we use inks of red, green and blue quantum dot dispersions. Placing controllable amounts of quantum dots at well-defined locations allows to print full-color RGB images with a pixel-to-pixel spacing of 250 nm, thus reaching the diffraction limit. As the emission spectrum of the quantum dots is narrower than the emitters used in standard display technology, the color gamut that can be displayed far exceeds the sRGB mode. In order to control the intensity of the color emission per pixel, the sample is moved with varying speed under the continuously ejecting nozzle, in contrast to the point-to-point discretely printed pillars in the previous section. A photorealistic 94x125 μm picture of a parrot is shown.

The last chapter shows the results of a collaboration with the Optical Materials Engineering Laboratory, where the ability to print few or single nanoparticles in well-defined locations is used for plasmonic applications. Quantum dots are printed either on top of several micron high gold or silver wedges or in plasmonically interesting spots in reflectors on a flat substrate. The printing system allows to launch surface plasmon polaritons at arbitrary positions, which is shown in a number of experiments.
Zusammenfassung


des Nanokomposites übernehmen. Des Weiteren wird experimentell gezeigt,
dass mit dieser Methode sogar Säulen auf nicht flachen Substraten gedruckt
werden können. Die speziellen Eigenschaften des Nanokomposites erlauben es,
die gesamte Absorption von sichtbarem Licht von vollständiger Absorption zu
vollständiger Reflexion zu variieren, indem die Höhe der Säule variiert wird.
Nahezu perfekte Absorption (durchschnittlich 95%) über das gesamte sichtbare
Spektrum wird mit einem Nanosäulen-Wald erreicht, der bloss 6% der Fläche
bedeckt. Indem die Säulenhöhe kontrolliert variiert wird, kann die
Grauschattierung eines Bildes mit einer Auflösung nahe am Diffракtionslimit
verändert werden, in anderen Worten, es können Schwarzweissbilder gedruckt
werden, die auf einem menschlichen Haar Platz fänden.

Denkt man von eben diesen Schwarzweissbildern einen Schritt weiter, kommt
man zu Farbbildern: Die Goldnanopartikel werden hier durch rote, blaue und
grüne Quantendots ersetzt. Indem die Menge der gedruckten Quantendots
genau kontrolliert wird, lassen sich farbechte RGB-Bilder mit einem Pixel-
Abstand von 250 nm – folglich am Diffракtionslimit – drucken. Da das
Emissionsspektrum der Quantendots schmaler ist als das der Emitter, die in
normaler Displaytechnologie verwendet werden, kann mit den Quantendots
ein weit grösserer Farbbereich abgedeckt werden als im sRGB-Standard. Die
Intensität der Farbemission pro Pixel wird kontrolliert, indem das Substrat mit
variable Geschwindigkeit unter der kontinuierlich druckenden Druckdüse
bewegt wird. Dies steht im Gegensatz zu den Säulen-Wäldern im vorherigen
Teil, wo jeder Pixel separat gedruckt wird. Die Vielfalt der Schattierungen und
die Genauigkeit der Auflösung wird anhand eines 94x125 μm grossen
fotorealistischen Bildes eines Papageis gezeigt.

Das letzte Kapitel zeigt die Resultate einer Zusammenarbeit mit dem Optical
Materials Engineering Laboratory, wobei mehrere oder einzelne Quantendots
mit Submikrometer-Genauigkeit für plasmonische Anwendungen platziert
wurden. Die Quantendots werden auf die Oberkante von Gold- und Silberkeilen
gedruckt, oder auch in die plasmonischen Hotspots von Reflektoren auf flachen
Substraten. Durch die gedruckten Quantendots können sogenannte
Oberflächen-Plasmon-Polaritonen von frei wählbaren Positionen aus gestartet
werden, was in mehreren Experimenten mit verschiedenen Geometrien gezeigt
wird.
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While my name alone stands as the author of this thesis, the work described here would not have been possible without the unwavering support, great help and useful advice of many people.

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1 Introduction

1.1 Motivation

When the printing press was invented by Johannes Gutenberg in the 15th century, the printing technology revolutionized the way information was spread and made it accessible to a wider public. In the last 500 years printing on paper, parchment and other surfaces has come a long way from the moveable letters set in the frame of the printing press. One of the greatest advantages of the original printing press is at the same time also a downside: It can reproduce thousands of copies from one single frame, however, setting the letters in the frame is time-consuming and therefore expensive. It is only profitable if many copies of the same page are made. The modern-day, ubiquitous printers do not need any template or mask and printing a single page is as economical (per piece) as one thousand pages. In fact, the 3D-printers developed in the last few years are even capable of building customized three-dimensional objects without the need for a mold.

In recent years the digitalization has once again revolutionized the way we access information. This has been enabled by the continuous development of nanofabrication technology. One of the core techniques to fabricate integrated circuits – the heart of modern-day electronics – is photolithography. While the demand for high throughput, high reliability and ever-smaller feature size has led to a host of subfields and specialized techniques within lithography, the working principle remains the same and is shown schematically in Figure 1.1.

A wafer is cleaned of all contaminants and spin-coated with a photosensitive polymer, called photoresist. A mask is brought close to or in contact with the photoresist, the photoresist below the transparent parts of the mask is exposed to UV radiation for a predefined amount of time, rendering either a soluble photoresist insoluble in the developer (negative resist) or vice versa (positive resist, as shown here). The soluble part of the resist is then washed away in the developer, exposing parts of the wafer. On this patterned wafer one can now either perform a deposition or an etching step, either adding a layer of another material or removing material from the wafer in the exposed areas. Finally, the remaining photoresist is removed.
Figure 1.1: Working principle of photolithography; a) the resist is spin-coated on the wafer, the mask placed on top of it and is exposed; b) the resist is developed; c) a layer of an additional material is deposited on top of the resist, the resist is then removed, leaving only the material deposited directly on the wafer; d) the wafer is etched where exposed, the resist is subsequently removed.

Hence, photolithography is an inherently mask-bound technology, in many ways analogous to Gutenberg’s printing press, where fabricating the mask is expensive and time-consuming, and the process becomes economical only for very large quantities. Furthermore, conventional photolithography has limitations when it comes to nonplanar substrates as well as three-dimensional fabrication and is generally applicable only to materials used in the chip fabrication industry, thus not suited for soft substrates. This has led to the development of a host of alternative technologies, addressing the above-mentioned issues.\(^3\) As the technology used in this work enables three-dimensional printing on soft and nonplanar substrates, this introduction focuses on such methods.

So-called nanoimprint lithography\(^4-6\) or hot embossing is specifically used to structure polymeric materials, down to a resolution of 5 nm.\(^7\) A rigid, structured mold is pressed into a polymer which is heated above its glass transition temperature. The assembly of mold and polymer is then cooled to harden the polymer and the mold is removed. A variety of polymers (PMMA, biomolecules, block polymers, etc.) have been successfully imprinted with nanoimprint lithography.\(^3\) One of its greatest advantages is the capability to imprint entire wafers in one step at a very high resolution. However, nanoimprint lithography is not applicable to non-planar substrates.

Microcontact printing\(^8\) also employs a structured master, however in this case master is a soft PDMS stamp. The stamp is covered with a solution of molecules
(“ink”) and placed on the desired surface. If the adhesion of the ink to the surface is greater than to the stamp, the ink is transferred onto the substrate where in contact. The working principle is thus analogous to a large-scale stamp. The softness of the PDMS stamp allows to transfer patterns onto non-planar surfaces. A variety of materials (biomolecules, polymers, colloidal quantum dots) have been transferred with microcontact printing. The number of materials is however limited due to the material properties of the PDMS stamp. Organic solvents for example cause the PDMS to swell, altering the shape of the structured surface.

The above-mentioned techniques all depend on a master pattern, be it on a mask, a mold or a stamp. This master pattern is then transferred onto multiple substrates, yielding identical results. This massively serial production of the same pattern is extremely useful and desired for many applications in modern-day industry. However, in particular in research, only very few or even one single sample with the same pattern is required or a number of variations of a pattern to cover several parameters are desired. In that case the fabrication of the mask is disproportionately expensive and time-consuming. A mask-free flexible deposition technique is therefore advantageous.

Such direct deposition techniques include dip-pen nanolithography, two-photon polymerization and direct writing. Dip-pen nanolithography utilizes an atomic force microscopy tip to transfer molecules to a surface by means of capillary forces, yielding sub-micrometer feature resolution. While two-photon polymerization and direct writing both feature three-dimensional capabilities, their resolution is in the micrometer regime.

The electrohydrodynamic printing method introduced in the next section offers maskless, three-dimensional printing capabilities in the nanometer regime, applicable without expensive clean-room facilities. Potential applications have been envisioned and demonstrated.

1.2 Electrohydrodynamic Printing

The effect of electrohydrodynamic (EHD) ejection has been known for almost 100 years. Several ejection modes have been identified and experiments have been conducted for a vast range of liquids. The most prominent mode is the Taylor cone-jet mode, it has been used for example for nanoparticle synthesis, thin film deposition or mass spectrometry.

In contrast to conventional inkjet printing, where the ink is ejected by applying pressure to the back of the printing nozzle, in the case of electrohydrodynamic ejection a voltage is applied to the liquid. The electric shear stress at the surface of the liquid counteracts the surface tension and pulls the liquid into a meniscus
out of the nozzle, where the liquid is – depending on the ejection mode – pulled into one or several jets, or droplets of varying size.

Figure 1.2: The modes of electrospraying, adapted from Jaworek et al. 17

More recently, EHD ejection has been employed to print two-dimensional patterns23 consisting of metallic nanoparticles,24 DNA,25 silica nanoparticles26 and polymers.27 While the resolution of these patterns mostly remains in the range of several micrometers, Rogers and his collaborators achieved a critical dimension of 1 μm.27

Patrick Galliker28 and Julian Schneider,29 former PhD students of LTNT, developed an electrohydrodynamic printing mechanism termed NanoDrip printing, where nanoparticle dispersions are employed as inks. While the ejection mode is in the microdripping regime according to the categories used by Jaworek, the term nanodripping is more accurate, as the ejected droplets have a diameter of less than 100 nm. They showed printed structures with a critical dimension as small as 50 nm.30 In addition to the small scale the technology also allows to print three-dimensional, out-of-plane structures, rendered possible by the so-called auto-focusing effect.

The ejection mechanism and the auto-focusing effect are illustrated in Figure 1.3. As a voltage is applied to the electrically conductive nozzle, the ink is pulled into a meniscus. From this meniscus single droplets of a much smaller size than
the nozzle opening are ejected at regular time intervals. If the sample is not moved relative to the nozzle, the droplets will all land in one spot, evaporate before the arrival of the next droplet and leave behind only the dried nanoparticles. With every droplet the pile of nanoparticles will increase in size. While there is a slight deviation in the droplet flight paths in the beginning, as the pile of nanoparticle grows, following droplets are inevitably pulled toward that pile, eventually growing into a well-defined pillar. Since the droplets are printed by means of an electric field, the dried nanoparticles act as a lightning rod, effectively concentrating the electric field and thus attracting the charged droplets. Since the first few droplets do not profit from this enhancement effect, they land in an area with about twice the diameter of subsequently built pillar.

Figure 1.3: Illustration of the auto-focusing effect.30

The elastic modulus of such pillars printed with a gold nanoparticle dispersion was characterized in a separate work.31 The estimated value was found to be close to the one of PDMS. However, when the structures are exposed to a thermal annealing,32 the elasticity significantly decreased.

By adapting the printing mode, several special features of the technology could be shown: When no voltage is applied to the nozzle, the solvent at the nozzle keeps evaporating, which effectively leads to an increase of the nanoparticle concentration. Eventually the nozzle will be clogged in this fashion, but if the time between voltage pulses is chosen to be short enough, the first few ejected droplets are larger with a higher nanoparticle concentration. This effect can be controllably utilized to print bigger (diameter ~1 μm), more stable structures. In this manner a three-dimensional platform with printed gold micropores was produced to study cell migration.32

In order to print well-defined structures it is crucial that the solvent of a landed droplet evaporates before the arrival of the subsequent droplet, as this would otherwise lead to liquid accumulation. The fast evaporation is generally ensured by using hydrophilic substrates which enhance the droplet spreading and hence increase the solvent evaporation rate. Galliker et al.33 showed that
on a substrate coated with a hydrophobic layer a liquid droplet could be sustained in an equilibrium state, when the evaporation rate equals the feeding rate by printed droplets. The authors envision such a sustained droplet could be used for microfluidic applications, such as crystallization or concentration-dependent chemical reactions.

While in general nanoparticle dispersions were used as printing inks, Schneider et al.\textsuperscript{34} employed a metal salt solution. Using the sessile droplet approach described above, they showed that it could effectively serve as an attoliter droplet reactor where single gold nanoparticles were formed. In combination with the high deposition precision inherent to the NanoDrip printing technology, they could therefore position single gold nanoparticles in a well-defined array.

The experiments described in this thesis are all carried out on an in-house built printing setup, based on the back-bone of an inverted microscope (details see Figure 1.4). The sample is placed on a glass plate which is coated with indium tin oxide such that it can be used as a ground electrode in case the sample is non-conductive. Nanometer-precision positioning is enabled by an xyz piezostage (MadCityLabs Inc.\textsuperscript{35}) which is mounted on a long-range mechanical microstage by the same supplier.
The nozzles are single-use only and are fabricated in-house: Glass capillaries with an outer diameter of 1 mm are pulled into nozzles with an opening diameter of 1000-2000 nm with a Sutter P-97 pipette puller. The nozzles are cleaned with an oxygen plasma for 60 sec before coating the outsides of the nozzle with 10 nm titanium and 100 nm gold with an e-beam deposition process (MEB550S Plassys) to render them conductive. The electrical contact between the gold layer and the liquid in the nozzle is facilitated by evaporating at a 70° tilt angle to deposit gold on the inner rim of the nozzle. In order to guarantee a reproducible printing process, the quality of every nozzle opening is checked in a scanning electron microscope (SEM) to determine its outer opening diameter and detect any irregularities along the opening, such as chipped edges or uneven cross sections (Figure 1.5). The nozzles can then be chosen according to the needs for size and quality depending on the experiment.
The nozzle is mounted on a manual xyz microstage with which it is approached to the substrate. Printing is generally conducted at a nozzle-substrate distance of 4-5 μm, albeit specialized applications might demand a longer working distance.

The ink is filled into the nozzle from the back opening, from where capillary forces draw it to the front; if necessary pressure can be applied to the back of the nozzle to force the ink to the tip. The back pressure is removed for the actual printing process.

Two separate optical paths allow the observation of the printing process: On the one hand transparent samples can be viewed from the bottom, through the ground electrode. In order to achieve maximum resolution, a confocal laser scanning microscope with interferometric scattering (iSCAT\textsuperscript{30,38}) is employed. The laser beam is scanned across a plane with two acousto-optic deflectors (AOD, see also Figure 1.4), thus illuminating the sample. Optimal resolution can be achieved by projecting the scanned area of the sample on the full sensor of the camera. On the other hand a side objective is mounted next to the nozzle holder, yielding a bird’s eye view of the nozzle, the substrate and the printed structures. While its resolution is limited, it is particularly useful for non-transparent substrates, where the optical access from the bottom is not available.
The printing process is initiated by applying a voltage to the capillary. In order to print intricate patterns with varying voltages and simultaneous stage movements a combined user interface for both the piezostage and the microstage of the sample as well as the high voltage source was programmed by Martin Schmid. By inputting a text file with pre-defined commands for the stage movement and the voltage signal arbitrarily long programs can be run automatically.

Long-term experiments can only yield good results with a nanometer resolution if the environmental conditions can be held as stable as possible to avoid thermal drifts. The setup is therefore placed in a temperature-controlled laminar flow box. Furthermore vibrations of the nozzle relative to the substrate need to be avoided. The entire setup is hence mounted on a passively and actively damped optical table from Newport.39

1.3 Nanoparticle Dispersions
The nanoprinting technology described in the previous section heavily depends on the quality of the inks used for the printing. An ink needs to be stable at least for the duration of the printing session, ideally for the duration of months, thus guaranteeing reproducible printing results. All of the inks used in this work are nanoparticle dispersions, either gold nanoparticles with a diameter of 5 nm or quantum dots of various size and materials. In both cases a narrow size distribution is of great importance, for reproducible 3D structures on the one hand and for a narrow emission spectrum on the other.

One of the most critical parameters of the solvent is its evaporation rate: It needs to be low enough to avoid clogging at the nozzle yet high enough to ensure fast evaporation once a droplet has landed on the substrate. We found that tetradecane fulfills this condition quite well and is also a suitable liquid for stable dispersions.

It is of paramount importance to know the detailed specifications of the dispersions used for printing: The ligands which stabilize the nanoparticles not only determine the mobility of the nanoparticles on the substrate (due to reduced van-der-Waals forces, see Chapter 2), even minute amounts of free ligands in the solvent influence the printing behavior. Knowing the ligand is also crucial in case it needs to be removed after printing or in order to model the optical response of printed structures accurately (see Chapter 3). As commercial suppliers are generally not willing to release the above-mentioned details, all the inks used in this work are supplied by the Optical Materials Engineering Laboratory (OMEL, ETH).
Gold nanoparticles are interesting for a number of reasons: They are excellent absorbers, as shown in Chapter 3 of this work. Their small size also leads to melting point depression\(^{40}\) which makes them a preferred material for conductive lines, such as shown by Schneider, et.al.\(^{41}\) Furthermore, for reasons we do not yet fully understand, gold nanoparticle inks are not only interesting from a scientific point of view, they also build 3D structures more readily than for example silver nanoparticles. The synthesis of the gold nanoparticle dispersions and the subsequent ligand exchange follows published recipes.\(^{42-44}\)

Quantum dots are semiconductor nanocrystals.\(^{45,46}\) Their small size of only a few nanometers leads to an interesting quantum mechanical effect, placing its electronic energy structure between the one of a single molecule and that of a bulk semiconductor (Figure 1.6). A bulk semiconductor has a valence and a conduction band separated by a band gap of energy \(E_G\), which is the minimal energy needed to excite an electron from the valence band to the conduction band. This creates an electron-hole pair, called exciton. This exciton has a finite size, defined by twice the Bohr exciton radius, which is the typical distance between an electron and its hole. If a semiconductor nanocrystal is smaller than its material-dependent Bohr exciton radius, the exciton becomes spatially confined, leading to discrete electronic transitions and size-dependent fluorescence spectra. The details of the absorption and emission behavior of quantum dots are the objective of ongoing research and out of the scope of this thesis.

![Figure 1.6: Schematic of the electronic energy states for a single molecule, a bulk semiconductor and a quantum dot as an intermediate between a single molecule and a bulk semiconductor.](image)

The quantum dots used in this work are produced with colloidal synthesis methods, yielding quantum dots with emission spectra across the visible range, including blue, green, yellow and red. In addition to the optically active core one or two protective shell layers are added in order to protect them from oxidizing influences during printing, see also Chapter 5. They are stored in hexane for long-term stability and transferred to tetradecane for printing, the
dilution normalized to an optical density of 5.0. Depending on the printing application, this standardized dispersion can be further diluted.

Figure 1.7 shows a photograph of three fluorescing quantum dot dispersions used for printing in Chapter 5.

![Figure 1.7: Photograph of three vials filled with fluorescing colloidal quantum dots. The different size of the quantum dots (increasing from left to right) leads to different emission spectra.](image)

### 1.4 Plasmonics

The following section gives a short introduction into the field of plasmonics, focusing on the so-called surface plasmon polaritons (SPPs). It studies the interaction of light with the free electrons of a metal, or more specifically, surface plasmon polaritons or localized surface plasmons, their behavior, properties and applications.

Under the influence of electric fields the free electrons in a metal can oscillate coherently. Plasmons are quanta of these oscillations. In order to differentiate the oscillations in a bulk material from surface phenomena, they are called bulk plasmons.

Two other subcategories of plasmons exist: On the one hand there are surface plasmons, where the oscillations occur as a surface wave at the interface of a metal and a dielectric (often, the dielectric is simply air). On the other hand, in the case of small nanostructures, the oscillations are localized due to the small geometry and are termed localized surface plasmons.
Surface plasmon polaritons are a combination of photons and surface plasmons: They are basically a light wave travelling along the metal-dielectric interface, pulling along the free charges in the metal. This mix of optical and electronic properties leads to the interesting effect that SPPs interact on the one hand with light, but on the other hand they are localized on a length scale much smaller than optical wavelengths. In other words, with the help of SPPs one can concentrate light far beyond the diffraction limit in true nanometer-sized spots. Among the potential applications are sensors for gases or biomolecules, high resolution optical imaging or hybrid circuits with electronic and plasmonic elements.

In order to understand the effects involved for SPPs it is necessary to look at the electromagnetic equations describing them. For any propagating electromagnetic wave, the frequency $\omega$ is connected to the wave vector $k$ by the so-called dispersion relation. For light traveling in a planar wave through a homogeneous medium, this relation is simply:

$$k = \frac{n}{c} \omega$$  \hspace{1cm} (1)$$

Where $n$ is the refractive index of the medium and $c$ the speed of light in vacuum. For SPPs the dispersion relation is more complex and can be derived to:

$$\beta = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$  \hspace{1cm} (2)$$

Where $\beta$ is the component of the wavevector in the propagation direction, $\varepsilon_m$ and $\varepsilon_d$ are the dielectric function of the metal and the dielectric, respectively. A typical dispersion diagram is shown in Figure 1.9. The straight lines are the dispersion relations for planar waves in a dielectric, called light lines. To the left of the light lines is the behavior of the metal above the material-dependent plasmon frequency, the metal supports propagating modes and behaves dielectric-like. For very low wave vectors, the behavior is similar to a “normal” light wave along the interface, for $\beta \rightarrow \infty$ the group velocity $v_g = \frac{d\omega}{dk}$ becomes...
zero, the surface plasmons approach an electrostatic solution (the model considered here assumes a purely real and lossless $\varepsilon_m$, real metals have a complex $\varepsilon_m$ where $\beta$ does not reach infinity). In the intermediate regime SPPs can propagate.

![Figure 1.9: Dispersion relation plot](image)

The dispersion relations of SPPs at an air-metal and a silica-metal interface are plotted. The axes are normalized with the material-dependent bulk plasmon frequency $\omega_p$. The dispersion relations of light in the respective dielectric is also indicated. Adapted from \(^{47}\)

Keeping in mind that the wave vector $k$ is proportional to the momentum of the wave, a momentum mismatch between the light line and the SPP dispersion relation becomes apparent: At a given frequency, the momentum of the planar wave is always smaller than the momentum of the corresponding SPP. It is hence not possible to excite SPPs with far-field radiation without the use of special techniques. Such momentum matching techniques include prisms, gratings, near-field excitation or – as is employed in Chapter 5 of this work – quantum dots.

By shaping the geometry of the metal, the dielectric or both, waveguides, lenses and mirrors can be designed to direct SPPs in a fashion similar to traditional optics.\(^{54, \, 55}\) Wedge waveguides in combination with plasmonic mirrors and scattering centers are used in this thesis.
1.5 Thesis Outline

This thesis is structured in 6 chapters, including this introduction. In the introduction, the work is motivated, the general mechanism of electrohydrodynamic printing explained and previous work on the topic is discussed.

Chapter 2 gives a deeper insight into the charge transport in the NanoDrip printing mode. By exposing the ejected droplet to an asymmetric electric field, I show that on the one hand the droplets as a whole are deflected and on the other hand the dried nanoparticles on the substrate form an asymmetric shape.

Chapter 3 focuses on the capabilities of the nanoprinting technology to build out-of-plane structures, more specifically, vertical pillars. As the printed pillars consist of a mix of gold nanoparticles, surfactants and trapped air, they form a metamaterial with a very large absorption cross section across the visible range. Tuning the material properties of the metamaterial by rational design, the absorption spectrum can further be altered. When printing these pillars in an array, each pillar appears as a pixel with a darkness depending on the pillar height. In this fashion grey-scale images can be reproduced close to the diffraction limit.

Taking the concept of printing images one step further, in Chapter 4 color images with an overall size of less than 300 μm are realized by printing quantum dots of varying colors. As the quantum dots have a very narrow emission spectrum, RGB images could be realized not only at a diffraction-limited resolution but also with a color range far exceeding the sRGB mode employed by conventional screens and displays.
In parallel to simply printing color images of increasing quality, the precise placement of quantum dots for plasmonic applications was pursued in several projects in close collaboration with Stephan Kress from OMEL, ETH. The developments and findings of these projects are summarized in Chapter 5.

Finally, a few applications are discussed, which could be pursued in future projects, some of which have already been started, yielding promising results.
2 Charge Effects and Nanoparticle Pattern Formation in Electrohydrodynamic NanoDrip Printing of Colloids

The following chapter is partly based on the following publication:


2.1 Abstract

Advancing open atmosphere printing technologies to produce features in the nanoscale range has important and broad applications ranging from electronics, to photonics, plasmonics and biology. Recently an electrohydrodynamic printing regime has been demonstrated in a rapid dripping mode (termed NanoDrip), where the ejected colloidal droplets from nozzles of diameters of $O(1 \mu m)$ can controllably reach sizes an order of magnitude smaller than the nozzle and can generate planar and out-of-plane structures of similar sizes. Despite demonstrated capabilities, our fundamental understanding of important aspects of the physics of NanoDrip printing needs further improvement. Here we address the topics of charge content and transport in NanoDrip printing. We employ quantum dot and gold nanoparticle dispersions in combination with a specially designed, auxiliary, asymmetric electric field, targeting the understanding of charge locality (particles vs. solvent) and particle distribution in the deposits as indicated by the dried nanoparticle patterns (footprints) on the substrate. We show that droplets of alternating charge can be spatially separated when applying an ac field to the nozzle. The nanoparticles within a droplet are distributed asymmetrically under the influence of the auxiliary lateral electric field, indicating that they are the main carriers. We also show that the ligand length of the nanoparticles in the colloid affects their mobility after deposition (in the sessile droplet state).

2.2 Introduction

Electrohydrodynamically driven liquid ejection from nozzles (EHD) has been known for several decades. Different regimes of EHD ejection have been investigated and categorized, the most well-known of which being the Taylor cone and jet regime, where a continuous jet emanates from the apex of a sharply focused meniscus at the opening of a nozzle. Due to instabilities, this jet may break up into droplets containing like charges, which are then sprayed onto a surface. In the so-called microdripping regime, the applied electric field is smaller, the meniscus less focused and instead of a jet, a small portion of the meniscus at its apex breaks off continuously, generating a continuous stream of droplets markedly smaller than the size of the meniscus itself and the
nozzle opening. Recent studies have realized a dripping regime at the nanoscale (NanoDrip), able to generate structures from colloidal inks not only with ultra-high planar resolution, but also out-of-plane and on non-flat, prestructured substrates.

In the NanoDrip process, typically, a gold-coated nozzle with an opening diameter of 1-2 μm filled with a nanoparticle dispersion is brought within a few (3-10) μm of the substrate. When applying an electric field between the nozzle and the substrate, droplets with diameters down to a good order of magnitude smaller than the nozzle opening are ejected. Each droplet lands on the substrate and the solvent evaporates before the arrival of the subsequent droplet, leaving behind only the pattern formed by the dried nanoparticle content of the ink.

This versatile technology can be used in a broad range of applications, such as for cancer cell studies, printed electronics, plasmonic applications or single crystal deposition. The versatility is accompanied by a host of related challenges when it comes to substrates (soft and hard, conductive and nonconductive, flat and prestructured) and the materials to be deposited in terms of ink content (metal or semiconductor nanoparticles and metal salts). In order to define the optimal working conditions for each application, a thorough understanding of the physical processes involved in the ejection and deposition of the nanoparticle dispersions is needed. Based on these findings the printing process parameters and the nanoparticle dispersions could then be tailored according to the needs of a specific application.

Several studies have investigated the properties of the EHD spraying in the Taylor cone regime for a range of liquids, such as glycerin or distilled water. However, despite progress and their obvious importance, our knowledge of charge transport mechanisms in the nanodripping regime is still incomplete. Here we show how the charge transport for EHD NanoDrip printed nanoparticle dispersions differs fundamentally from conventional EHD spraying. In the Taylor regime and for more conductive liquids, naturally existing ions in the liquid ink (e.g. by dissociative processes, H3O+ and OH− in the case of water) or molecules easily ionized (for example because they have double bond structures) will act as charge carriers. Depending on the polarity of the applied voltage, electrons or holes are transferred to the liquid. On the other hand, if the goal is to precisely print nanoparticle structures with a submicron spatial resolution, as often the case in the NanoDrip process, the choice of solvent is constrained by other factors necessary for the process. For example, the solvent needs to combine with the various nanoparticles to form stable dispersions for different applications while not containing any significant amount of free ligands or other byproducts as these may adversely influence
the properties of the printed material. In addition, the vapor pressure employed has an upper bound, because fast evaporation may clog the small nozzle (order of a micron nozzle opening) as well as a lower bound, since the evaporation of a droplet on the substrate must be complete before the arrival of the next droplet, to avoid puddle formation, which would be detrimental to the generation of nanostructures and to out-of-plane nanoprinting.\textsuperscript{30-32}

In this work we investigate charge transport in the nanodripping regime by printing nanoparticles dispersed in tetradecane, a solvent fulfilling all of the above-mentioned requirements. The electrical conductivity of tetradecane in its pure form was measured to be as low as $3 \cdot 10^{-12} \text{S/cm}$, which is 4 orders of magnitude lower than ultra-pure water. Ions by dissociation, or molecules with double bonds do not exist in tetradecane and can hence not act as charge carriers. Electrohydrodynamic ejection of pure tetradecane in a dripping mode is consequently not possible (this has been shown experimentally in earlier works\textsuperscript{28, 63}). Hence, unlike in the Taylor cone process, it is highly improbable that the electric charge transport stems from the solvent itself. The aim is to gain an in-depth understanding of the charge content in droplets ejected by NanoDrip printing and its effect on the forces acting on the droplets and the nanoparticles in the droplets. To this end, we show experimentally that the charges in ejected droplets in the nanodripping regime are carried by the nanoparticles themselves rather than the solvent. Whether the charges are distributed throughout a liquid solvent, under the prerequisite that the liquid is conductive enough to carry the appropriate amount of charges, or whether they are localized on nanoparticles, does not fundamentally change the ejection mechanism. When the nanoparticles carry the charges, they will move to the surface of the meniscus and then induce electrohydrodynamic dripping, just like ions do in the case of more conductive liquids. Since we cannot observe the droplet flight directly due to the extremely small length and time scales involved, we modulate the droplet orbit while in flight with a specially designed asymmetric electric field and draw conclusions from the study of the patterns of the dried nanoparticle content on the substrate (termed footprints) after solvent vaporization, a posteriori.
2.3 Materials and Methods

Figure 2.1 Schematic of the printing setup (a) and top view scanning electron micrograph of the lateral electrodes on the glass substrates (b). The gold-coated nozzle in the z direction is kept at 200V at 10 μm from the glass substrate, while the substrate is moved in the x direction, parallel to the electrodes. Single droplets are deposited on the substrate, well separated from each other; droplets are printed in the gap between a ground and a positive electrode, leading to well-separated dried nanoparticle footprints.

All experiments are carried out on an in-house-built printing setup (Figure 2.1a). A glass capillary is pulled into a nozzle with a Sutter P-97 pipette puller. The nozzle, with an opening diameter of approximately 2 μm, is then coated with 10 nm Ti and 100 nm Au and rendered conductive. The substrate is mounted on a 3D piezo-stage from MadCityLabs, the nozzle is filled with the nanoparticle dispersion (self-driven by capillarity) and is brought within 10 μm of the substrate. In the standard printing mode, the sample is positioned on a grounded plate, and ejection is induced by applying a voltage of 125-250 V to the nozzle.

In order to study the charge transport of electrohydrodynamic ejection in the nanodripping mode, we added a lateral component to the electric field, realized with the help of gold electrodes designed for this purpose, with a separation of 2 μm deposited on a glass wafer with conventional photolithography. This allowed us to apply an electric field between these lateral electrodes. A scanning electron micrograph (SEM) image of the lateral electrodes before nanoparticle deposition is shown in Figure 2.1b, where the ground and the positive electrode are marked. When printing in a straight line along the x-axis between the lateral electrodes, the ejected, charge carrying droplets are deflected in the y direction, normal to the direction of motion of the stage. The
deflection of the droplets is a function of the voltage applied to the lateral electrode. The lateral voltage has to be low enough such as not to interfere with the electric field at the nozzle, as this would disturb the ejection process and yet high enough to yield a measurable deflection on the substrate. We employ a constant lateral voltage of 30 V throughout this study which fulfills both conditions. In order to study the properties of a single droplet footprint, the stage is moved rapidly to ensure sufficient separation of the footprints of individual droplets.

Three useful nanoparticle dispersions covering a range of applications\textsuperscript{56, 57, 64} are used in this work. These are CdSe-CdS-ZnS core-shell-shell quantum dots with a diameter of 10 nm coated with oleic acid and 5 nm gold nanoparticles stabilized with either octanethiol or dodecanethiol. The synthesis of all three inks have been described in detail elsewhere and are out of the scope of this thesis.\textsuperscript{9, 57, 64} In order to study the polarity of the droplets as well as the charged nanoparticles we used the quantum dot ink, because of its better visibility in the SEM due to the larger size of the quantum dots compared to the gold nanoparticles.

![TEM images of the CdSe-CdS-ZnS quantum dots used for printing in this chapter.](image)

Figure 2.2: TEM images of the CdSe-CdS-ZnS quantum dots used for printing in this chapter.
Figure 2.3: AFM (a,c) and SEM (b,d) images of printed quantum dot footprints. The height of the footprints corresponds to one monolayer of quantum dots with a diameter of around 10 nm, as measured in the TEM scans. The AFM tip radius is nominally 8 nm, which means that the crevices between the single dots cannot be resolved. They can however very well be distinguished in the SEM graphs of the identical footprints on the right.

2.4 Results and Discussion

In Figure 2.4 three SEM images show footprints transitioning, going from left to right, from absence to presence of a lateral electric field. The ground and positive lateral electrodes are labeled and the footprints are artificially colored according to their charge (red: positive, blue: negative) for better visibility. The dashed line is a guide to the eye to mark where the droplets would land in the absence of a lateral field. If a positive or negative dc pulse is applied to the nozzle in the NanoDrip mode, charged droplets are ejected towards the substrate as can be seen in Figure 2.4a and b, respectively. The droplets are deflected towards the lateral ground or positive electrode when printing between the electrodes (right-hand side of the picture). No deflection is seen on the left hand side, where there is no influence of the lateral electric field and the footprints show the typical impact pattern of submicron quantum dot dispersion droplets. In Figure 2.4c an ac voltage is applied between the nozzle and the ground plate. Since the colloidal ink is expected to contain both positive and negative charges with no apparent preference, this leads to the ejection of positively charged drops during the positive phase of the signal and, vice
versa, negatively charged drops during the negative phase of the signal. Accordingly, a separation of positively and negatively charged droplets between the lateral electrodes can be observed when the lateral electric field is present, while all droplets land on a straight line without the influence of this field (colored in green).

Figure 2.4 Scanning electron micrograph showing footprints transitioning from absence of a lateral electric field on the left to presence of a lateral field on the right; the positive and ground electrodes are labeled. The footprints are artificially colored according to their charge (red: positive, blue: negative, green: alternating) for better visibility. The dashed line is a guide to the eye showing where the footprints would be located in an undisturbed field (left side of the images). Results are shown for a positive nozzle voltage (a), a negative nozzle voltage (b) and an ac voltage at the nozzle (c). The droplets are deflected in flight, positively charged droplets towards the ground electrode and negatively charged droplets towards the positive electrode. In the case of an ac field at the nozzle ejection alternates between positively and negatively charged droplets.

In Figure 2.5 close-up SEM micrographs of quantum dot footprints are shown to demonstrate the effect of the lateral electric field. Figure 2.5a shows a footprint outside the region of the lateral electrodes for comparison purposes. There is a clear rotational symmetry in the deposition of the quantum dots. Due to the relatively large size of the droplet there is an outward flux of the nanoparticles, leading to a partial coffee-stain effect. Figure 2.5b-d show footprints placed between the lateral electrodes. To this end, Figure 2.5b and c show footprints from a positively and a negatively charged droplet, respectively, and Figure 2.5d the footprints of droplets ejected by an ac signal.
Figure 2.5 High magnification micrographs of footprints without lateral electric field (a) and in the presence of a lateral electric field (b-d) for positive, negative and ac voltages at the nozzle, respectively, the dashed line indicates where the droplet would land in an undisturbed field (absence of a lateral field). Comparing (a) and (b), a considerable population of quantum dots has moved downwards in the electric field (arrow) direction. The number of displaced quantum dots is around 280, which is of the same order of magnitude as the number of elementary charges per droplet as calculated in Figure 2.7.

The shape of the footprints is now oval with the nanoparticles showing a clear tendency to concentrate towards the direction of the electric field, indicated by the arrow and violet shading in Figure 2.5b. The electric field on the substrate between the lateral electrodes is uniform, such that a dielectrophoretic force (proportional to field gradients) can be excluded. The evaporation of the solvent is rotationally symmetric and hence evaporative fluxes cannot be responsible for such an asymmetric placement of the nanoparticles. The following simple model assesses the deformation of a charged, hemispherical droplet in the electric field between the lateral electrodes:
Following Gent’s model\(^{67}\) of a volumetric force acting on a droplet we obtain:

\[
F_{el} = F_{hysteresis} \tag{3}
\]

\[
QE = \frac{4}{\pi} R \gamma_{C14} (\cos(\theta_R) - \cos(\theta_A)) \tag{4}
\]

Where \(Q\) is the total charge of the droplet, \(E\) the electric field between the lateral electrodes, \(R\) the sessile droplet radius and \(\gamma_{C14}\) the surface tension of tetradecane. Further assuming a hemispherical droplet with a contact angle of 90° as a first approximation,\(^{68}\) we take \(\theta_R=90°+\delta\) and \(\theta_A=90°-\delta\) for the receding and the advancing angle in the deformed droplet, respectively. For small \(\delta\) the cosine function can be simplified and the equation can easily be solved for the deformation angle \(\delta\):

\[
\delta = \frac{QE}{2R\gamma_{C14}} = 1.8° \tag{5}
\]

With \(Q=225q_0\), \(E=1.5 \times 10^7 \text{ V/m}\) (homogenous field between electrodes at 30V, separated by 2 \(\mu\)m), \(R=250\) nm (droplet contact radius, taken from Figure 2.5b), \(\gamma_{C14}=26.56\) mN/m\(^{69}\). This would lead to advancing and receding contact angles of 91.8° and 88.2°, respectively. This small deflection hardly justifies the massively asymmetric nanoparticle deposition we observe.

The explanation is that nanoparticles, themselves electrically charged, move in the electric field until they reach the drop boundary (contact line region). The interplay of the coffee-stain effect and the lateral electric field then leads to the particular oval footprint shape shown in Figure 2.5b-d. The total number of quantum dots in the footprint in Figure 2.5b is 1360. If they were distributed symmetrically, the violet area would contain about 470 particles, while in reality there are 750 particles. The difference of roughly 280 particles carry charge and are therefore pulled to one side by the electric field.

The claim that the charges are located on the nanoparticles rather than in the solvent can be further underpinned by examining the Born energy of an ion:\(^{70}\)

\[
\mu = \frac{Q^2}{8\pi\varepsilon_0\varepsilon a} \tag{6}
\]
Where \( \mu \) is the Born energy, \( Q \) the charge of the ion, \( a \) is the radius of the ion, \( \varepsilon_0 \) and \( \varepsilon \) are the vacuum permittivity and the dielectric constant of the medium, respectively. The energy can be minimized by moving the charge from a medium of low dielectric constant to a medium of higher dielectric constant. In the case of the quantum dot dispersion, CdSe has a higher dielectric constant than tetradecane and is therefore a favorable location for the charges. The energy minimization holds even more for metallic nanoparticles, where a charge can be delocalized over the volume of the nanoparticles. The ejection frequencies observed in the experiments here indicate that it takes about 10 ms to eject a single droplet. The thermodynamic energy minimization process is of a much shorter time scale, hence the charges are located on the nanoparticles already at the onset of the droplet ejection.

Knowing the weight of the droplet, the nozzle-substrate distance and the magnitude of the involved electric fields it is possible to estimate the charge carried by one single droplet by measuring the deflection of the footprints between the electrodes. It has been shown earlier\(^{30} \) that in NanoDrip printing the diameter of the footprint is of the same order of magnitude as the diameter of the corresponding airborne droplet. We can hence estimate the weight of one droplet generating any given footprint. The nozzle-substrate distance is controlled with the piezo-stage and the electric field in the space between the nozzle and the substrate can be determined with numerical simulations.

The forces acting on the flying droplet are threefold: The force due to the electric field in the downward z-direction, the force due to the electric field in the lateral direction induced by the side electrodes and the Stokes drag for laminar flow around each droplet in flight, directed against the flight direction.

We carried out 3D electrostatic simulations with the commercial software COMSOL. A color plot of the cross-section of the electric field in the region between the nozzle and the substrate with the lateral electrodes is depicted in Figure 2.7a. The hemisphere at the tip of the nozzle represents the liquid meniscus, which is generated when a voltage is applied to the nozzle (the apex of this meniscus is what is printed in the NanoDrip mode, as depicted in Figure 2.1a). COMSOL offers a feature where the flight path of a charged particle (here droplet) with predefined mass and charge is calculated. It also allows accounting for additional forces such as the Stokes drag, which for spheres of size comparable to the mean free path in air is given by:

\[
F_D = \frac{-6\pi\eta R \nu}{1 + Kn (a + b e^{\frac{\varepsilon}{k\eta}})}
\]  

(7)
where $\eta = 1.983 \cdot 10^{-5} \text{Pas}$ is the viscosity of air, $R$ the droplet radius, $v$ the droplet velocity, $Kn = \frac{\lambda}{R}$ the Knudsen number with $\lambda$ the mean free path of air, and $a=1.252$, $b=0.399$ and $c=1.1$ are empirical coefficients to account for the Cunningham slip correction factor for droplet sizes comparable to the mean free path of air.\textsuperscript{71}

In Figure 2.7b the flight paths from the nozzle to the substrate for droplets of equal size but varying charges are shown. The deflection decreases with increasing charge. The greater the charge of a droplet is, the stronger its acceleration after leaving the nozzle and the higher its velocity when entering the space where the lateral electric field is appreciable. This has a negative effect on the droplet lateral deflection before landing on the substrate. The deflection of a positively charged droplet ejected from a nozzle with a potential of 200 V is shown in Figure 2.4a and measured to be 450 nm. For an order of magnitude estimate we assume the droplet diameter in-flight to be about 200 nm.

The Rayleigh limit poses a natural upper bound to the charge $Q_0$ a liquid drop can carry:
\[ Q_0 = 8\pi \sqrt{\varepsilon_0 \gamma R^3} \] 

where \( \varepsilon_0 \) is the vacuum permittivity, \( \gamma \) the surface tension of the droplet (for tetradecane \( \gamma = 26.56 \text{ mN/m} \)) and \( R \) is the droplet radius. The maximum charge a droplet with a diameter of 200 nm could carry before breaking up is hence estimated to be \( 3.9 \cdot 10^{-16} \text{ C} \), which corresponds to about 2400 elementary charges. The deflection of the droplets in the experiment is indicated with a dashed line in Figure 2.7b, and corresponds to a charge of \( 3.6 \cdot 10^{-17} \text{ C} \) or about 225 elementary charges, which is close to 10\% of the Rayleigh limit. Other groups have measured the charge of EHD ejected droplets in a larger scale dripping mode (generated droplet diameter in the range of a few \( \mu \text{m} \) to a few hundred \( \mu \text{m} \), and found charges ranging from around 10\% of the Rayleigh limit \( 22 \) up to about half the Rayleigh limit \( 16 \). While the large charges were measured for droplet diameters of 200-300 \( \mu \text{m} \), the small charges were measured for droplets in the range of a few \( \mu \text{m} \). Since the droplet diameters in this work are even smaller, we believe our results are in acceptable agreement with the existing literature. Since we estimate the inflight droplet diameter based on the footprint diameter, to quantify the effect of this estimate, the simulated flight paths for droplets with a range of diameters (150-300 nm) and a charge corresponding to the same percentage of the Rayleigh limit (eq. 3) as the 200 nm droplet in Figure 2.7b is plotted in Figure 2.7c. The larger a droplet is, the smaller its deflection due to its greater inertia and the higher its speed close to the lateral electrodes. Hence the 150 nm droplet sets the upper bound for the depicted range and the 300 nm droplet the lower bound.

When comparing Figure 2.5a and b we see that a considerable population of nanoparticles is displaced in the presence of the lateral field. While it is not possible to directly measure the individual quantum dot charges, the roughly 280 asymmetrically displaced quantum dots in Figure 2.7b are of the same order of magnitude as the number of elementary charges per droplet predicted by the simulations. The same effect can be observed in Figure 2.5c, where negatively charged quantum dots moved upwards toward the 30 V electrode and in Figure 2.5d, (ac-field at the nozzle) where droplets of alternating charge are ejected and are deflected alternatingly upwards and downwards according to their respective charge.

The above evidence shows that the droplets as whole carry either positive or negative charges and that the nanoparticles themselves are the carriers of these charges. The assessment of the forces acting on the nanoparticles requires a more detailed discussion. The main forces acting between the substrate and the nanoparticles in a sessile droplet are van der Waals-forces and – if the nanoparticle carries a charge – Coulomb forces. Given the electric

\[ \text{Comparison of experiment and simulation} \]

\[ \text{Van der Waals-forces} \]
field, the Coulomb force can be calculated by multiplying this field with the charge. The van der Waals-forces are caused by electromagnetic interactions between the nanoparticle and its surrounding, comprising not only the glass substrate and tetradecane but also other nanoparticles and the surfactant on the nanoparticle. We circumvent the obvious complexity in estimating the magnitude of the force acting on a nanoparticles in solution close to the substrate, by drawing conclusions from the simple case of the dependence of such a force on the distance from the substrate considering the arrangement of a sphere and an infinite plane separated by a small distance in vacuum. The force is then given by:\textsuperscript{70}

\[ F(d) = -\frac{AR}{6d^2} \]  

\text{Where F is the force acting on a single nanoparticle, A is the Hamaker constant accounting for the two interacting materials, here gold and glass, R is the nanoparticle radius and d the distance between the particle surface and the substrate. In order to exclude all other influences, we compare two gold nanoparticle dispersions, which differ from each other only by the length of the octanethiol and dodecanethiol ligand. The length of a thiol-capped surfactant on gold nanoparticles with a diameter of 5 nm has been measured to be 0.73 nm for octanethiol and 0.93 nm for dodecanethiol by Wan et al.\textsuperscript{72}. These lengths define the smallest distance between the nanoparticle and the substrate. Considering that the van der Waals-force is inversely proportional to the square of the separation (eq. 4), the force magnitude for dodecanethiol-capped nanoparticles is 60% of the force magnitude for octanethiol-capped nanoparticles. The effect of this difference on the strength of the van der Waals-force is illustrated in Figure 2.8, where two footprints located between the lateral electric field electrodes are shown, printed at a nozzle voltage of -150 V. The footprint in Figure 2.8a consists of octanethiol-capped gold nanoparticles and the one in Figure 2.8b of dodecanethiol-capped particles. While in the case of octanethiol there is no visible influence of the lateral field breaking the circular symmetry of the footprint pattern (Figure 2.8a), a clear movement of the negatively charged particles towards the 30 V electrode can be seen for dodecanethiol-capped particles (Figure 2.8b). While the Coulomb force is the same in both cases, the van der Waals-force is much stronger for the shorter surfactants, effectively inhibiting any particle movement.
2.5 Conclusion

In conclusion, we studied the physics of charge content of submicron-sized droplet colloids in tetradecane (effectively a dielectric liquid), electrohydrodynamically ejected in the nanodripping mode, by examining the deposited dry nanoparticle patterns (footprints). In addition to the vertical electric field for ejecting the droplets from the nozzle, we employed an auxiliary lateral electric field directly on the substrate, deflecting on the one hand the droplets in flight and on the other hand acting on the charges within the droplet after landing during drying. By combining experiment and simulations we estimated that the ejected droplets carry electrical charges of the order of 10% of the Rayleigh charge limit, in accordance with publications from other groups. The results strongly support the argument that such charges are carried by the nanoparticles, for both materials employed, quantum dots and gold nanoparticles. By comparing estimates of van der Waals-forces acting on a nanoparticle on the substrate, we further showed that depending on the length of the surfactant, the charged nanoparticles can be either immobilized or move in the applied lateral electric field.
3 Direct Printing of Out-of-Plane Nanostructures: Tunable Metamaterial Absorber Arrays at the Diffraction Limit

The following chapter is partly based on the following publication:


### 3.1 Abstract

The controlled fabrication of functional nanostructures with extreme resolution finds a host of applications exemplified by the broad area of surface/light interaction. Nonplanar features of such structures can significantly enhance their performance and tunability, but their facile generation remains a challenge. Here we show that electrohydrodynamic printing in a rapid nanodripping mode, is able to generate precise out-of-plane forests of plasmonic nanopillars with resolutions at the diffraction limit, directly integrated in metal-insulator-nanocomposite configurations. Furthermore, we demonstrate the capability of the method to generate such features on non-flat substrates. The nanocomposite nature of the printed material allows the fine-tuning of the overall visible light absorption from complete absorption to complete reflection by simply tuning the pillar height. Almost perfect absorption (95% on average) over the entire visible spectrum is achieved by a nanopillar forest covering only 6% of the printed area. Adjusting the height of individual pillar groups by design, we demonstrate on-demand control of the gray scale of a micrograph with a spatial resolution at the diffraction limit. These results constitute a significant step forward in ultra-high resolution, facile fabrication of out-of-plane nanostructures, important to a broad palette of light design applications.

### 3.2 Introduction

The explosive growth of micro- and nanofabrication in recent years is presenting printing technology with a broad palette of new opportunities and related challenges. Complementing the capabilities of large scale and high throughput printing processes, three-dimensional microprinting enables the fabrication of devices of sizes down to a few tens of microns. With respect to the resolution of planar printed pictures, the diffraction-limit (accessible with comparatively facile far-field optics) is being reached. It has been shown that intelligent structuring of the top metal layer of a metal-insulator-metal (MIM) configuration enables the fine-tuning of the absorption spectrum, paving the way toward reproduction of color images at the diffraction limit. However, previous fabrication approaches of such structures...
have always included expensive and difficult to upscale steps, such as electron-beam lithography or focused ion beam.

We have demonstrated an electrohydrodynamic printing method termed NanoDrip printing\cite{30} able to print colloids of various materials ranging from quantum dots\cite{56,57} to metallic nanocrystal particles\cite{32} in plane with feature sizes down to a few tens of nanometers. In this chapter we advance the unique capabilities of this methodology to print out-of-plane nanostructures, we demonstrate the controllability of this process through the printing of arrays of nanopillars with height and spacing specificity, and show how with this technique gray scale images at resolutions close to the diffraction limit can be readily fabricated in an open atmosphere. This technology embodies a facile, inexpensive and on-demand approach, capable of tailoring light absorption at a sub-micron length scale. We also show that NanoDrip printing can generate in- and out-of-plane patterns of nanostructures on non-planar, rigid or soft substrates and therefore brings with it compatibility as well as additional capabilities to those of other micro- or nanofabrication methods. Finally, we demonstrate that the material composition and nanofabrication precision of the printed out-of-plane nanopillar patterns enable the tuning of their overall absorption, a necessary requirement to achieve true submicron gray-scale resolution.

### 3.3 Experimental Section

The synthesis of the gold nanoparticles follows a published recipe.\cite{42} It results in nanocrystals of approximately 5 nm in size (see transmission electron microscope images in Figure 3.1). The ligand exchange of the originally dodecanethiol-capped nanoparticles to the desired alkylthiolate capping ligand (octanethiol, decanethiol, dodecanethiol) follows an earlier published recipe.\cite{43} In order to guarantee the comparability of the three inks the steps for the ligand exchange are even performed for dodecanethiol. The concentration of the final ink is approximately 13 mg Au per ml tetradecane. As the particles are synthesized by Stephan Kress of the Optical Materials Engineering Laboratory, details of the preparation process are out of the scope of this work and are not given here. The interested reader can find more information in S. Kress’ dissertation.\cite{86}

A clean silicon wafer is Ar-sputtered for 60 s; first 100 nm Au (Plassys E-beam) and then 60 nm SiO$_2$ (Oxford Instruments PECVD 80Plus) is deposited. Details of the printing mechanism can be found in the introduction of this thesis; the piezo stage (Mad City Labs XYZ Nano-Drive) motion was controlled by an in-house built control unit. The pulse lengths for the pillar generation were varied from 500 ms to 2500 ms to print pillars of increasing height. The pillars for the
Absorption measurements were printed in a hexagonal array with a 500 nm pitch.

![Figure 3.1 Transmission electron microscopy (TEM) image before ligand exchange (a) and after ligand exchange (decanethiol) (b)](image)

Absorption measurements are performed using an in-house-built inverted microscope equipped with an air objective (numerical aperture 0.75) for exciting the sample and collecting the reflected and scattered light. The absorption spectra are obtained in the range from 400 to 800 nm with an Acton SP2500 spectrograph equipped with an eXcelon detector from Princeton Instruments. A xenon lamp was used as a light source, a neutral density filter was employed to dampen the characteristic high intensity peaks for longer wavelengths in the spectrum of the xenon lamp. The absorption was calculated according to the following equation:

\[
A = \frac{L - R}{L - DC}
\]

where \(A\) is the absorption, \(L\) is the spectrum of the lamp measured with a silver mirror, \(R\) is the spectrum of light reflected and scattered by the pillar arrays, and \(DC\) is the intrinsic spectral dark count of the spectrometer.

SEM micrographs were taken with a Zeiss ULTRA plus scanning electron microscope after sputter-coating a thin Au/Pd layer onto the samples to reduce charging of the non-conductive sample.
The details of the printing process can be seen in Figure 3.2a. A gold-coated thermally drawn and tapered glass pipette with an opening of 1000-1500 nm is filled with a nanoparticle-laden dispersion (ink) and connected to a high voltage source. The substrate is placed on an electrically grounded piezo-stage and brought within 5 \( \mu \)m of the pipette tip. By applying a DC voltage of 125-175 V during the time period required for printing each nanostructure, attoliter-sized ink droplets (50-100 nm diameter) of precisely controllable volume are electrohydrodynamically pulled out of the apex of the stable meniscus at the end of the pipette. The droplets land on the substrate and their solvent evaporates before the arrival of the next droplet, leaving behind only its nanoparticle content confined in a substrate region within the initial diameter of the droplet. While the first few droplets printed on one spot land on an area of about twice the droplet diameter, they rapidly build an out-of-plane structure which acts as a lightning rod within the applied electric field and the following droplets land precisely on top of the so grown structure. In this fashion an out-of-plane pillar with the diameter equal to the droplet diameter is created. The diameter of a pillar can be flexibly varied from 50 to 150 nm by...
changing the pipette opening diameter or the applied voltage (Figure 3.2b-d). The height of each printed pillar is proportional to the number of ejected droplets and is hence defined by the duration of the applied electrical pulse (Figure 3.2e-g). Therefore, the height, position and diameter of each pillar can be controlled on demand using our in-house built electrical and positioning control units.

In this work we were able to print reproducibly out-of-plane pillars with a diameter of 120 nm and heights in the range of 200-1000 nm in a hexagonal arrangement with a pillar-to-pillar spacing of 500 nm. This corresponds to a maximum aspect ratio of the pillars of more than 8. While for single pillars aspect ratios of up to 17 have been shown in an earlier publication, when printed in a dense array, neighboring pillars bend towards the applied electric field due to their soft nature and it is not possible to obtain a well-defined array of such vertical pillars. With shorter pillars however, it is possible to print arrays with a smaller pillar-to-pillar spacing (see also Figure 3.10). In Figure 3.2h an SEM of pillar arrays is displayed at a 30° viewing angle.

Our bottom-up approach allows the precise deposition of such pillar arrays also on non-planar substrates. We demonstrate this by printing pillars near and exactly on top of a template-stripped silver wedge with a wedge angle of 70 degrees (Figure 3.2 i,j). This capability enables NanoDrip printing to overcome a major drawback of mask-dependent technologies such as nano-imprint lithography, which require a flat substrate.

Furthermore, our approach can be used to print on soft substrates: In Figure 3.3 we show the letters ETH ZURICH printed with gold nanoparticles on a human hair, more specifically, one of mine. This experiment required no pre-treatment such as chemical cleaning steps, reliable printing could be achieved directly.
In this chapter we employ three different inks, which are composed of 5 nm spherical gold nanoparticles dispersed in tetradecane and coated with either octanethiol, decanethiol or dodecanethiol monolayers. While the printing behavior itself is not influenced by the different length of the ligands, the nanoparticle-to-nanoparticle distance in the printed gold-air nanocomposite scaffold is a linear function of the alkyl chain length. This distance in turn influences the gold-to-air ratio in the printed structures.

### 3.4 Numerical Modeling

To model the electrical properties of printed structures, needed for the quantification of their interaction with light, we use the Bruggeman’s effective medium theory which considers the printed gold-air nanocomposite as a homogeneous medium with an effective dielectric function given by

\[
\varepsilon = \frac{1}{\varepsilon_{\text{eff}}} = \left( \frac{3\varepsilon_\text{gold} - 1}{3\varepsilon_\text{air} - 1} \right) + \frac{2\varepsilon_\text{air}}{3\varepsilon_\text{gold} + 2\varepsilon_\text{air}}
\]

where FF is the volumetric filling fraction of gold and \(\varepsilon_{\text{air}}\) and \(\varepsilon_{\text{gold}}\) are the permittivities of air and gold, respectively. The sign is chosen such that the imaginary part of the dielectric function is positive. Both the gold nanoparticles and the surrounding dielectric are treated equally in the mixture, which is in contrast to the Maxwell-Garnett effective medium theory, where a relatively low concentration of metallic inclusions is set in a dielectric host medium. The commercial simulation software LUMERICAL which is based on a finite-difference time-domain (FDTD) method is used to numerically model the
fabricated structures. Both in experiment and simulations, the pillars are placed on a 60 nm thick layer of SiO₂ deposited on an optically thick gold layer (inset Figure 3.6b). It was previously shown that thin layers of gold-dielectric nanocomposites are very good absorbers of visible light.\(^{90}\) Having the nanopillars on top of a reflector enables absorption of the impinging light at the nanocomposite material both at direct incidence and also after reflection by the gold layer. This increases the total absorption with the same surface coverage of the pillars, and therefore provides a larger range of absorption tunability.

The dielectric function of a bulk metal can be decomposed into a bound- and a free-electron term:

\[
\varepsilon_{\text{bulk}} = \varepsilon_{\text{bound-electron}} + 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{\text{bulk}}}
\]  

(12)

where \(\omega_p\) is the bulk plasma frequency \((1.3 \cdot 10^{16} \text{ s}^{-1})\) and \(\gamma_{\text{bulk}}\) \((1.64 \cdot 10^{14} \text{s}^{-1})\) is the damping constant in the Drude model. \(\varepsilon_{\text{bound-electron}}\) is obtained by subtracting the free electron part from \(\varepsilon_{\text{bulk}}\).\(^{91}\)

For particles which are small compared to the mean free path of the conduction electrons, the dielectric function differs from the bulk values. In that case collisions of the electrons with the particle surface gain importance as an additional damping factor. Kreibig and Fragstein\(^{92}\) show that for small particles the effective mean free path becomes a function of the particle radius and the damping constant can be extended as follows:

\[
\gamma(R) = \gamma_{\text{bulk}} + C \frac{v_F}{R}
\]

(13)

where \(v_F\) is the Fermi velocity \((14.1 \cdot 10^{14} \text{ nms}^{-1})\), R the nanoparticle radius (here: 2.5 nm) and C a constant accounting for details of the scattering process. C=1 for isotropic scattering\(^{91}\) was chosen for this work. With the above formulas the dielectric function for the gold nanoparticles could be obtained, yielding the dielectric function plotted in Figure 3.4.
While for the dielectric function of the gold back-reflecter the data from Johnson and Christy\textsuperscript{93} for bulk gold is used, the permittivity of the pillars is calculated from equation (11). The gold nanoparticles in a printed pillar are loosely and randomly packed (Figure 3.5). The packing density of such particles has been shown theoretically to be 55\% for touching spheres\textsuperscript{94}.

In order to account for the volume taken up by the surfactant one needs to subtract the volume fraction filled by the spherical shell of the alkyl derivatives, the thickness of which is known from the interparticle distance measurements by Wan et.al\textsuperscript{72}. The volume fraction and hence the fill factor of gold then reduces to less than half of the value for touching solid spheres. The FF values used for the simulations for all three cases studied in this work can be found in Table 1.
Table 1 Interparticle distance and volume filling fraction of different thiol-coated nanocrystals.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Interparticle distance$^{72}$ [nm]</th>
<th>Volume filling fraction (FF) of random loose packed ligand-coated gold nanospheres</th>
<th>Schematic Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octanethiol</td>
<td>1.45 $^{a)}$</td>
<td>25.6%</td>
<td><img src="image" alt="Schematic" /></td>
</tr>
<tr>
<td>Decanethiol</td>
<td>1.65</td>
<td>23.4%</td>
<td><img src="image" alt="Schematic" /></td>
</tr>
<tr>
<td>Dodecanethiol</td>
<td>1.85</td>
<td>21.4%</td>
<td><img src="image" alt="Schematic" /></td>
</tr>
</tbody>
</table>

$a)$ value interpolated from$^{95}$

### 3.5 Results and Discussion

Figure 3.6a shows the measured absorption spectra of pillar arrays printed with the decanethiol-capped ink. Increasing the pillar height increases the total absorption. 95% absorption over the entire visible spectrum and even into the near infrared is achieved with a pillar height of 560 nm. An extraordinary point here is that this nearly perfect absorption over the entire surface is achieved with a pillar array that covers only 6% of the surface (top view). As indicated by the dashed line, the gold back reflector has an intrinsically high absorption between 450 and 500 nm, yielding the familiar yellow color of the noble metal. Simulations of arrays with the same height as in Figure 3.6a are depicted in Figure 3.6b.

Figure 3.6c shows the measured absorption spectra for absorbers printed with inks with three different ligands, i.e. octanethiol, decanethiol and dodecanethiol. The calculated FF values for each case are reported in Table 1. While the absorption over the visible range is comparable in all three cases, the drop-off wavelength is a function of the filling fraction. The gold-air nanocomposite filling fraction influences the wavelength range where the effective electrical conductivity is substantial. The electrical conductivity is responsible for ohmic losses, hence the overall absorption band can be tuned using the FF value. The broad absorption spectrum is due to the fact that in all the three cases we have an FF close to the percolation limit (33%).$^{88}$

38
Figure 3.6 Measurements (a) and simulations (b) of absorber arrays with different pillar heights. Dashed line in (a) is the absorption spectrum of the gold-glass substrate before printing. Measurements (c) and simulations (d) of absorber arrays with different inks. The pillar height in all three cases is approximately 600 nm; e) color plot of absorption spectrum with various pillar heights; f) Total reflection of the solar spectrum (AM1.5) as a function of pillar height, based on the simulations displayed in (e). The inset shows optical images of three absorber arrays with pillar heights of 200, 420 and 560 nm. The three points on the plot correspond to the printed arrays.

The simulated spectra in Figure 3.6d also show a similar trend as the measurements in terms of the absorption levels and drop-off wavelengths. However, some of the spectral feature details in the simulations are not observed in the measurements. The reason can be attributed to deviations from the ideal structures simulated, such as to the surface roughness and non-homogeneities of the printed structures, which are not accounted for in the simulations and also to the non-ideality of the Bruggeman’s theory in approximating the effective permittivity of the printed structures (equation 11).
Figure 3.6e shows the simulated absorption as a function of wavelength $\lambda$ and pillar height. Here, the excellent tunability of the absorption spectrum achieved by only changing the pillar height is demonstrated. The gray scale range can be covered practically in its entirety by printing pillars with heights ranging from zero (perfect reflection, white) to 650 nm and above (nearly perfect absorption, black). In the current study, the absorption at lower wavelengths (below 550 nm) is maintained even for pillar height equal to zero. This is a result of intrinsic losses of bulk gold and when the pillar height is zero, absorption takes place entirely in the gold back reflector. To isolate the pure effect of pillar absorption if so desired, one can use silver instead of gold as the back reflector (see Figure 3.10). A thin silver layer has negligible absorption and is often used as a perfect mirror in the visible range, yielding white color (perfect reflection) in the absence of pillars.

We calculate the total absorption of sunlight (standard light source) as a function of pillar height with the following equation:

$$A_{tot} = \frac{\int A(\lambda)I(\lambda)d\lambda}{\int I(\lambda)d\lambda}$$  \hspace{1cm} (14)

where $A(\lambda)$ and $I(\lambda)$ are the absorption reported in Figure 3.6e and the solar irradiance for the standard AM1.5 (air mass) spectrum, respectively, the integration is performed over the visible spectrum, 400-700 nm. The perception of light intensity coming from a reflecting surface to the human eye, is proportional to the logarithm of the light reflected from the surface.\(^96\)

Therefore, the semilog plot of reflection (= 1 – absorption, where absorption is calculated from equation (2)) reported in Figure 3.6f represents the eye’s perception of the brightness of the printed absorbers with different pillar heights. Changing the pillar height, we can tune this brightness practically across the entire gray scale range. The optical images of three arrays of printed pillars with various heights are displayed in the micrographs in the inset to Figure 3.6f. Three points corresponding to these three arrays are indicated on the curve in Figure 3.6f.

In order to expand the parameter study displayed in Figure 3.6, starting with a standard array of decanethiol-coated gold nanoparticle pillars, we varied the pillar diameter on the one hand and the pillar-to-pillar spacing on the other hand.
Figure 3.7 The effects of pillar diameter (a),(b) and pillar-to-pillar spacing (c),(d) on absorption. (a) and (c) are experimental and (b) and (d) are simulation results. The parameters for the different plots are given in the table below.

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pillar-to-pillar spacing</td>
<td>500 nm</td>
<td>500 nm</td>
<td>Variable</td>
<td>Variable</td>
</tr>
<tr>
<td>Pillar height</td>
<td>470 nm</td>
<td>470 nm</td>
<td>700 nm</td>
<td>700 nm</td>
</tr>
<tr>
<td>Pillar diameter</td>
<td>Variable</td>
<td>Variable</td>
<td>100 nm</td>
<td>100 nm</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Decanethiol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data source</td>
<td>Measurement</td>
<td>Simulation</td>
<td>Measurement</td>
<td>Simulation</td>
</tr>
</tbody>
</table>

In Figure 3.6 we analyzed arrays with a pillar diameter of approximately 120 nm. In Figure 3.7 (a: experiments, b: FDTD simulations) we show the absorption spectra of three different pillar diameters, all with a pillar height of about 470 nm. The absorption increases with increasing pillar diameter. However, there is an upper limit to the pillar diameter, which can be printed reproducibly in an array with 500 nm pillar-to-pillar spacing: For diameters larger than 120 nm it is difficult to print regular arrays with a pillar height of 470 nm. The greater proximity of pillars to each other leads to a negative influence on the printing process, in that the droplets are diverted towards the already printed pillars, rendering the realization of a regular array prohibitively difficult.

In Figure 3.7c and d we studied the influence of the pillar-to-pillar spacing on the absorption spectrum, in experiments and simulations, respectively. The pillar height in this case is 700 nm, and the diameter 100 nm. The absorption decreases with increasing pillar-to-pillar spacing, which can be understood by
considering that by increasing the spacing we deposit less of the nanocomposite material, which is responsible for the absorption.

Figure 3.8 shows in experiment and simulation the absorbtivity of an unstructured gold metamaterial layer. The printed metamaterial patch in Figure 3.8a and b contains approximately the same amount of material as a pillar array with pillar heights of 600 nm, which have been shown to be highly absorptive over a broad bandwidth. Both measurement and simulation (Figure 3.8c) however show that unstructured metamaterial patches do not show a comparable absorption spectrum. This illustrates the importance of printing the metamaterial in a structured, out-of-plane fashion.

In addition to being able to largely tune the absorption of each pillar by simply varying its height, another important advantage of the NanoDrip printing method lies in its ability to place pillars at small distances (tight pitch control). These properties enable printing gray scale images with sub-micron pixel size (spatial resolution) determined by the pillar-to-pillar distance, which in this work is 500 nm. The latter can be even further reduced for pillars smaller than 1000 nm in height (see also Figure 3.10 with 400 nm pillar-to-pillar pitch).
Figure 3.9 Printing grey scale images. a) black-and-white photograph of Charlie Chaplin, adapted with permission from Charlie Chaplin™, copyright Bubbles Incorporated SA. b) bright field optical micrograph of a printed reproduction with a 500 nm pixel size, the rectangles represent the regions from which images in c) and d) are acquired; c) scanning electron micrograph of the area around the eye. The perimeter of the eye is indicated with the dashed line. While the pillar diameter remains the same for darker and brighter pixels, the increased height of the pillar leads to decreased brightness of the pixel; d) a 30° tilted view scanning electron micrograph of the collar area. The height difference of bright and dark areas is clearly discernible. Scale bars correspond to 40 μm (b), and 2 μm (c,d).

Figure 3.10 Printed picture of the Golden Gate Bridge with a pillar-to-pillar pitch of 400nm. The substrate is optically thick silver with 60nm Al₂O₃ as a spacer layer.

Figure 3.9 shows an exemplary picture printed with the method reported in this chapter. The 395x353 pixel sized picture of Charlie Chaplin (adapted with permission from Charlie Chaplin™, copyright Bubbles Incorporated SA) is
printed in 8 shades of gray ranging from dark to bright. Seven different pillar heights (250-1750 ms pulse length per pillar) are used to produce the darker shades and white corresponds to no pillar printed. In order to adequately represent the pixels, the pillars are printed in a Cartesian grid with a pixel-to-pixel spacing of 500 nm, resulting in an image size of ca. 200x175 µm, corresponding to 50’000 pillars per inch and a resolution of out-of-plane printed pillars close to the diffraction limit. This makes the method presented here comparable to electron beam lithography (EBL) based methods,\textsuperscript{83} featuring more than 2 orders of magnitude higher resolution in printing out-of-plane structures than a standard commercial inkjet printer for planar structures. The scanning electron micrographs in Figure 3.9c,d show that while the pillars look almost identical from the top (Figure 3.9c), they are designed to vary in height as desired (30° tilted view, Figure 3.9d) and therefore yield different shades of gray in an optical image.

Figure 3.10 shows a reproduction of the Golden Gate Bridge with the same principle as for Charlie Chaplin. In order to showcase the influence of the gold back reflector, an optically thick silver layer covered with a 60 nm Al₃O₅ spacer layer is used. In addition the pillar-to-pillar spacing is reduced to 400 nm and thus approaching the diffraction limit even more closely.

3.6 Conclusion

In closing, we were able to directly print in an open atmosphere arrays of closely-spaced, out-of-plane nanopillars made of a gold-air composite. Adjusting the pillar heights in a metal-insulator-nanocomposite plasmonic configuration, we demonstrated tuning of the absorption performance of the printed arrays from total absorption (dark) to total reflection (white). We showed that the bandwidth and absorption level of the printed absorbers can be controlled independently by varying the metal filling fraction and pillar height, respectively. Furthermore, we demonstrated the printing of gray-scale micrographs with ultra-small pixel sizes (500 nm) by adjusting the height of each pillar in an array. Other main advantages of our method include the flexibility to print on non-flat substrates and its independence of any mask and of expensive clean-room steps. The capability to realize the features presented here is relevant to a host of applications, such as the generation of individualized security or proof of authenticity features invisible to the naked eye, and optical data storage.
4 Full-Spectrum RGB Color Printing

The following chapter is partly based on the following publication:


4.1 Abstract

Color printing at the diffraction limit has been recently explored by fabricating nanoscale plasmonic structures with electron beam lithography, albeit only a limited color range and constant intensity throughout the structure have been demonstrated. Here we show an alternative, facile approach relying on the direct nanoprinting of controlled amounts of red, green and blue (RGB) quantum dots at a 250 nm resolution. The narrow emission spectrum of the dots allows the coverage of a very broad color space, exceeding standard RGB (sRGB) of modern display devices. We print color gradients of variable intensity, which to date could not be achieved with diffraction-limited resolution. Showcasing the capabilities of the technology, we present a photo-realistic printed image of a colorful parrot with a pixel size of 250 nm.

4.2 Introduction

Chronologically we started working with quantum dots for plasmonic applications before employing them for color printing. However, when printing with quantum dots with various emission wavelengths, printing color pictures comes as quite a natural extension. The development of the quantum dot ink quality and the control capabilities of the printing setup ran in parallel, enabling the evolution from simple, 3-color stick-figure-like drawings of Christmas trees (Figure 4.1) to photo-realistic RGB printed images (Figure 4.2), currently certified as a Guinness world record.97
Figure 4.1: Two color pictures printed in December 2013 (a) and December 2014 (b). In the course of one year the stage control was upgraded from the interface provided by the company to an in-house built control environment, allowing more complex shapes to be printed. In addition, the quantum dot inks were further improved, leading to the more homogeneous deposition.

Figure 4.2: Full scale color RGB color image of clown fishes, printed fall 2015. This image was printed by Patrick Galliker, using the quantum dot inks developed for this work, it is currently certified as a Guinness world record for the smallest inkjet-printed color image.
While the images in Figure 4.1 and Figure 4.2 were used internally or for publicity reasons, the following pages will elaborate on the technique used to print photorealistic images, even at the diffraction limit resolution of 250 nm.

Colloidal quantum dots have size-dependent emission spectra. Since they can be stably dispersed in solution, they are ideal candidates for ink-jet and microcontact printing, as has been shown for a palette of applications ranging from light-emitting devices, to displays and photodetectors. However, the resolution of these technologies is limited to a few microns. The diffraction limit of approximately 250 nm represents the smallest resolution at which color printing is resolvable with optical microscopes and therefore constitutes the lowest resolution limit for all related applications. Several groups have shown diffraction-limited color printing not based on dyes or quantum dots but by means of plasmonic structures. They employed metal-insulator-metal structures, which selectively reflect a portion of the incident light, depending on the structure size and shape. The drawbacks of this approach are on the one hand the limited color range compared to modern computer displays and on the other hand the electron beam lithography steps necessary for the fabrication of the nanometer-sized structures, rendering the process highly expensive and difficult to upscale. Furthermore, for photorealistic color printing, it is necessary not only to generate a large range of hues but also to deliver a variation of intensity of those hues from dark to bright.

We have introduced an electrohydrodynamic printing technology termed NanoDrip printing, capable of printing three-dimensional structures with a critical dimension of less than 100 nm, and placement precision down to a few nanometers. The deposited materials range from metal nanoparticles and metal salts to a variety of quantum dots.

In this chapter we present a facile method to generate full-color printed images with a diffraction-limited resolution based on red, green and blue colloidal quantum dots, representing an RGB color space analogous to the one applied in modern computer displays, with a color gamut far exceeding the sRGB norm. By employing a recently developed open-atmosphere, ink-based printing technique, we overcome limitations set by previous mask-based, plasmonic techniques by massively increasing the range of colors while maintaining high flexibility and low cost.
4.3 Materials and Methods

Figure 4.3 Schematic of the printing setup used in this work. The colloidal quantum dot dispersion is printed with rapidly generated nanodrops from the apex of a larger stable meniscus at the nozzle, at 225V. A controllable amount of quantum dots is deposited with high precision, this amount being a function of the substrate speed under the stationary nozzle.

Figure 4.3 shows a schematic of the printing setup used here. Briefly, a glass capillary is pulled into a nozzle with an opening diameter of 1000-1100 nm, which is coated with 10 nm Ti and 100 nm Au to render it conductive. The capillary is filled with the quantum dot dispersion and brought within 5 μm of the glass substrate, which lies on a grounded holder, mounted on a piezo stage (not shown in the schematic). By applying a dc voltage of 225 V, droplets with a diameter of down to ten times smaller than the nozzle opening are ejected regularly and rapidly from the apex of a larger stable meniscus hanging at the opening of the nozzle at a frequency of about 100 Hz. The substrate is then moved by the piezo-stage under the nozzle at a speed controllable by an in-house built control unit. As the ejection frequency remains constant, the amount of deposited material is solely defined by the speed at which the substrate is moved. In this manner, the amount of material deposited at a certain location can be precisely controlled, since more droplets are deposited per area at a lower stage speed and less at higher stage speeds. The intensity of the emitted light by colloidal quantum dots covering a certain area is a function of the number of quantum dots deposited in that area. By varying the speed of the stage the emitted light intensity can hence be controlled.
The emission intensity of a sub-diffraction spot of printed quantum dots is a nonlinear function of the number of quantum dots, since the bottom layers may experience some quenching. Furthermore, the conversion between the 8 bit RGB value (0-255 for each color) and the spectrally measured intensity is non-linear as well. This accounts for the fact that the light sensitivity of the human eye spans several orders of magnitude and the perception of intensity is hence logarithmic. The RGB value to printing speed conversion was therefore fitted with the following function:

$$v = \frac{1560 - 4.791x}{x + 11.04}$$

(15)

Where $x$ is the RGB value (0-255) and $v$ is the resulting velocity in $\mu$m/s, ranging from 141 $\mu$m/s to 1.3 $\mu$m/s. This ensures a maximal contrast between dark and bright areas while at the same time accounting for the limited acceleration capabilities of the piezo-stage. If the maximal speed were selected to be too high, sharp changes from bright to dark pixels would be blurred due to the finite acceleration.

The emission from the green and more so from the blue quantum dots can be absorbed by the red dots and increase their emission while decreasing the far-field signal of the green and blue dots. In order to compensate for this effect, $x$ was increased by 40% of the red RGB value per green pixel and 50% of the red RGB per blue pixel. This combination was found to lead to a balanced white while maintaining an even brightness for the separate colors.

All photographs in this chapter are taken with a Nikon 600 commercial camera mounted on a Nikon Eclipse LV100 microscope. The emission spectra were taken with an Andor Shamrock 303i spectrometer through a 200 $\mu$m slit at a sensor temperature of -75°C.

### 4.4 Results and Discussion

![Figure 4.4 a) Absorption and b) emission spectra of the printed quantum dots; c)-e) Photographs of monochromatic gradients with varying intensity. The intensity is a function of the amount of deposited](image)
The three different quantum dot dispersions used here are all synthesized in-house, the synthesis procedures for the red, green and blue dots are described elsewhere.\textsuperscript{57, 105} We use CdSe-CdS-ZnS core-shell-shell semiconductor nanocrystals for the red and green quantum dots, the blue quantum dots are CdS-ZnS core shell nanocrystals with a composition gradient. The quantum dots feature emission peaks at 461 nm, 538 nm and 625 nm for a blue, green and red color, respectively. Detailed absorption and emission spectra can be found in Figure 4.4 a, b. The dilution of the dispersions in tetradecane is adjusted to ensure that very few quantum dots are contained in one ejected droplet, enabling fine tuning of the amount of deposited quantum dots and, consequently, of the emission intensity.

The inks are synthesized in-house, following published protocols.\textsuperscript{57, 105} All colors are dispersed in n-tetradecane and are concentration-adjusted for an optical density of 5.0 at the first exciton. They are further diluted to a ratio of 1:10 (red), 1:7 (green) and 1:6 (blue) for printing. This accounts for the fact that the brightness of the red dots is higher than the green and blue ones. For an RGB image, the brightness of all colors has to be homogeneous.

Figure 4.4c-e shows photographs of printed, monochrome gradients for red, green and blue. Continuous lines are printed, varying the speed from slow on the left to very fast on the right, with a line-to-line spacing of 250 nm. The printing speed is defined for every individual 250 nm long section of a printed line, thus creating a pixel size of 250 nm. Arbitrary monochrome patterns with a diffraction-limited resolution can easily be printed. Since the speed of the stage could in theory be varied in incrementally small steps (~10 nm), we chose to employ 256 speed levels in analogy to the available brightness levels of an 8-bit image, where the brightness can be incremented from 0 to 255.
Figure 4.5: Color gamut. a) CIE Chromaticity diagram: the white dashed line shows the sRGB colors that can be generated by conventional display devices. The black lines are calculated from the spectroscopy measurements of the two-color gradients shown in b)-d). A photograph of the printed gradients (7.5x130 μm) is shown next to the spectral graphs. The horizontal dashed line in b) is a guide showing the correspondence of printed color and spectral intensity.

Figure 4.5a shows the CIE 1931 chromaticity diagram\textsuperscript{107}. The colored area encompasses the color range perceivable by the human eye. The curved edge represents single-wavelength spectral colors, moving inwards, the colors are generated by a more broadband spectrum. The white, dashed triangle marks the amount of colors that can be displayed within the sRGB gamut of standard display technology. It is limited by the broad emission spectrum of the RGB pixels in a display device. The quantum dots have a much narrower emission spectrum, hence their pure emission is located closer to the edge of the CIE 1931 gamut and spans a considerably larger color gamut than sRGB. This enables the generation of more hues.

The edge of the color gamut is represented by mixing the two colors of the adjacent corners. For each color combination (green-blue, red-blue and red-green) a gradient was printed on a glass substrate by depositing the two different needed inks sequentially. The spectra of the three corresponding color gradients are displayed in Figure 4.5b-d. The spectral intensity over the wavelength is plotted along with the printed gradient in the y direction. A photograph of the printed gradient is shown to the left of each spectral graph. While, for example, the apparent color in the middle of the red-green gradient is yellow, the spectrum shows that it is actually a mix of red and green with varying intensity (Figure 4.5d). Since the photographs are displayed in the
conventional sRGB color space, not all the colors of the gradients shown here can be represented in their true hue, because they lie outside of the sRGB gamut. The effect becomes more pronounced if such a photographed image is printed on paper and in the process converted to the CMYK color space.

The full capability of the color printing simultaneously at the diffraction limit and with a wide color gamut is best exemplified with a colorful microscale picture. The parrot shown in Figure 4.6a has a good representation of different colors, ranging from the pure red, blue and green to mixes such as yellow and teal as well as bright white, represented by an even mix of all three base colors. The printed image has a line-to-line spacing of 250 nm, the speed at which the stage is moved under the printing nozzle is defined in 250 nm steps, leading to a pixel-to-pixel distance of 250 nm. The overall height of the image is 94 x 125 μm, close to the size of the cross section of a human hair. Figure 4.6b shows the image after the first printing step, displaying how the intensity of the red color is tuned. The green and blue quantum dots are printed sequentially on top of the red dots, following an alignment procedure. The photograph in Figure 4.6c shows the final full-color printed parrot. However, these photographs can be merely viewed as a representation of the true richness of the real colors since the gamut of the printed image exceeds the gamut of the camera, in particular for green hues.
Figure 4.6: Full-Color RGB image. a) photograph of a colorful parrot; b) deposition of one color for an RGB image; c) full-color RGB image of a printed parrot, the total image size is 94x125 μm, roughly the size of the cross section of a human hair; SEM Micrographs of a parrot’s head printed with red, green and blue quantum dots. (d) the eye as well as the structure of the feathers on the head can be distinguished, the orientation of the printed lines which form the picture are visible; (e) close-up image of the transition of the dark background at the top (the lines are printed in the top-down direction) to the bright feathers is clearly distinguishable. The fast deceleration of the piezo-stage allows to form a sharp contrast within a few hundred nanometers.

A full-color, photorealistic, printed image has to be printed with three different inks and consequently with three different nozzle-printheads. The second and the third nozzle need to be aligned carefully to the first image to avoid chromatic off-sets. Since the mounted sample is left untouched on the stage, there is no rotational misalignment. Before printing the desired image, four lines (here: red) are printed at a well-defined location from the starting point, two lines for each axis (Figure 4.7). When switching to the next color, the nozzle is aligned manually to a precision of less than 2 μm. 20 points are then printed across the red line, each dot with an offset of 100 nm from its predecessor. With the help of the high-resolution iSCAT-microscopy mode\textsuperscript{30} it is possible to determine which dot has no off-set with respect to the line. After providing this information for each axis to the printing software program, it is straightforward to achieve an alignment error of less than 100 nm.
4.5 Conclusion

In summary, we report a relatively simple, direct method based on EHD NanoDrip printing, to generate full color images with a diffraction limited resolution based on red, green and blue colloidal quantum dots and a color gamut far exceeding the range of the sRGB norm used for displays. The capability to control the amount of deposited material allows the arbitrary mixing of colors to render different hues and simultaneously enables precise, pixel-wise brightness control.
5 Quantum Dots for Plasmonic Applications

The following chapter is partly based on the following publications:


5.1 Preface

The colorful printed images presented in the previous chapter are enabled by two main factors: One the one hand the submicron placement precision of nanoparticles on a substrate and on the other hand the availability of stable quantum dot dispersions with a narrow-band emission spectrum. The latter was achieved in close collaboration with Stephan Kress from the Optical Materials Engineering Laboratory led by Prof. Norris. The collaboration has been very fruitful so far, leading to three published papers and more to follow. It is in the nature of the collaboration that the combined, substantial contributions from two separate doctoral theses have led to new proofs of concept and applications. In order to account for that, the focus in this chapter is set on the printing aspects of the collaboration while only giving a summary of the achievements in the field of plasmonics. For more details about the plasmonic aspects of printed quantum dots the interested reader is referred to the above-mentioned publications or the doctoral thesis of Stephan J.P. Kress.86

5.2 Near-Field Light Design with Colloidal Quantum Dots for Photonics and Plasmonics

5.2.1 Abstract

Colloidal quantum-dots are bright, tunable emitters that are ideal for studying near-field quantum-optical interactions. However, their colloidal nature has hindered their facile and precise placement at desired near-field positions, particularly on the structured substrates prevalent in plasmonics. Here, we use high resolution electro-hydrodynamic printing (<100 nm feature size) to deposit countable numbers of quantum dots on both flat and structured substrates with a few nanometer precision. We also demonstrate that the autofocusing capability of the printing method enables placement of quantum dots preferentially at plasmonic hot spots. We exploit this control and design diffraction-limited photonic and plasmonic sources with arbitrary wavelength, shape, and intensity. We show that simple far-field illumination can excite
these near-field sources and generate fundamental plasmonic wave-patterns (plane and spherical waves). The ability to tailor subdiffraction sources of plasmons with quantum dots provides a complementary technique to traditional scattering approaches, offering new capabilities for nanophotonics.

5.2.2 Introduction

Colloidal quantum dots are semiconductor nanocrystals with emission spectra tunable with their size.\textsuperscript{45} The CdSe cores employed in this work for example can be tuned over the entire visible range,\textsuperscript{108} making them interesting candidates for the field of nanophotonics.\textsuperscript{48, 55, 109}

Nanophotonics investigates light-matter interactions at length scales below the diffraction limit.\textsuperscript{48, 51, 55, 109} One of the main challenges is to couple the external light source (typically a laser) to the local electromagnetic modes of interest. Often, this modes include surface plasmon polaritons (SPP). As has been explained in the introduction of this thesis, however, due to a momentum mismatch far-field photons cannot directly excite SPPs. A number of near-field light sources, such as bumps, grooves, apertures and nanoparticles have been used to either directly excite SPPs or emit near-field photons that can do so.

Quantum dots would be a very well-suited near-field light source. They do not act as a scatterer but rather are broadband absorbers (Figure 5.1a), which emit photons or SPPs in a narrow, lower energy band (Figure 5.1b). This brings the advantage that different quantum dots with different emissive properties can be excited simultaneously with one UV light source. This property has been exploited extensively in the previous chapter to create multicolor pictures. If the quantum dots are precisely placed in the plasmonic structure, the excited nanocrystals would then be sitting in the local plasmonic resonance mode of interest, such that their nanophotonic interactions can be studied.

Figure 5.1: Absorption and emission spectra. (a) Absorbance spectra of the CdSe/ZnS core/shell quantum dots in tetradecane; (b) fluorescence spectra of the printed CdSe/ZnS quantum dots.
However, the nanometer-sized nanocrystals are very hard to place precisely with classical nanotechnological tools. To date different studies have used random placement,\textsuperscript{10} stamping,\textsuperscript{99, 111} self-assembly\textsuperscript{112} or electron-beam-lithography techniques.\textsuperscript{113, 114} These techniques are all limited to flat substrates, posing a severe restriction to nanophotonics, where structured substrates are employed to concentrate light into sub-diffraction volumes.

5.2.3 Results and Discussion
The electrohydrodynamic NanoDrip technology is ideally suited the fulfill the needs for precise placement of a controllable number of quantum dots at well-defined locations, even on highly structured substrates, such as for example wedges with a height of tens of micrometers. In fact, as the electrohydrodynamically ejected droplets are accelerated towards the substrate by an electrostatic field, the heightened structures act like lightning rods as an electric field concentrator and effectively attract the flying droplets to the tip of structure.

For the following experiments, two different quantum dots are used: CdSe/ZnS and CdSe/CdS core/shell nanocrystals. They were synthesized adapting known protocols for the appropriate size and therefore emission.\textsuperscript{115-117} For printing the quantum dots are transferred to tetradecane, where they could be stored in a stable dispersion for long periods of time.

![Figure 5.2: Blueshift of core-only quantum dots, (a)-(c) dried remnants of drop-cast quantum dots. The dots blue-shift under UV light exposure; (d) the same blue-shift can be seen for printed structures, induced by the high electric fields involved during printing.](image)

The core/shell architecture of the quantum dots is necessary to protect the active core from environmental influences. Experiments show that dropcast quantum dots which are exposed to intense UV radiation over more than a few
minutes show a blue-shift in their emission. In Figure 5.2a-c a small circle within the fluorescent area was exposed to UV radiation leading to a color change, very pronounced for green and yellow, less so for the red quantum dots. This effect is thought to be induced by oxidation of the quantum dot surface and hence leads to a decrease of the active core size. As the red dots are the largest ones, deterioration of the surface leads to a smaller relative volume change of the active core than for the smaller dots.

In Figure 5.2d printed test structures with all three core-only inks are shown, the ink source is indicated in the inset. The high electric field (close to the breakdown limit of air), to which the dots are inevitably exposed during the printing process, leads to the same blue-shift as by UV exposure. In order to avoid this effect, the active core of all quantum dots used in this thesis are protected by 1-2 shell layers.

The printing setup employed for the experiments in this chapter has been described in detail earlier in this thesis. As the substrates in this chapter are all metallic, they have been electrically grounded directly instead of positioning them on a separately grounded electrode.

Figure 5.3: Illustration of printed quantum dots, lines and dots of different dimensions for each color (red, yellow and green) (a-c, g-i); (d,f) SEM micrographs of printed lines and dots; e) photograph of the ready-to-print quantum dot dispersions.

Figure 5.3 shows fluorescence images and electron micrographs of printed lines (Figure 5.3a – d) and spots (Figure 5.3f – i) using inks prepared from three different colors of CdSe/ZnS core/shell quantum dots (Figure 5.1). In these experiments, the nozzle was brought within 5 μm of a flat template-stripped. 50
gold surface (root-mean-squared roughness <1 nm). For the lines, the nozzle was translated at speeds of 10 μm per second. For the spots, the nozzle remained steady for 25–500 ms while attoliter-sized droplets (∼100 nm in diameter) were ejected. The lines were printed with a 3 μm spacing and 1 to 19 overprints to obtain fluorescence with various intensities. We printed the spots with a 3 μm spacing between neighboring rows and a 1 μm spacing between nearest neighbors within the row.

Figure 5.4: Reproducibility of printed points. (a) fluorescence image of green printed spots, the cross section of the emission spectra displayed in (b) and (c) are indicated; (d) 3D false color representation of the emission intensity.

According to the concentration of the quantum dots in the ink, each droplet should contain only a few quantum dots. However, evaporation at the nozzle preconcentrates the quantum dots prior to droplet ejection, meaning that the first few ejected droplets in each pulse contain considerably more quantum dots than the subsequent ones. The size and fluorescence intensity of the printed lines and spots can be controlled by varying the printing parameters, such as the magnitude of the voltage pulse, the translation speed of the nozzle, the number of overprints, and so forth. An important feature of the method is that if these parameters are fixed, the printing process is extremely reproducible, both for a given ink (Figure 5.4) as well as different inks (i.e., different-sized quantum dots). For example, quantum-dot lines with widths of
220, 150, and 100 nm are demonstrated for all three inks in Figure 5.3. The data confirm that irrespective of the quantum-dot color (and thus size), this technique can consistently print the same lines and spots down to sub-diffraction resolutions. This offers great flexibility for the generation of light patterns on plasmonic and photonic surfaces.

Figure 5.5 shows a more detailed analysis of the printed quantum dots. High magnification scanning electron micrographs show the arrangement of quantum dots in a 120 nm wide printed line and a printed spot with a 180 nm diameter. The CdSe/CdS core/shell quantum-dot ink (0.5 optical density in a 1-mm cuvette) was first diluted with an equivalent amount of tetradecane. The line shown was printed with no overprints and the spot was deposited with a voltage-pulse duration of 25 ms. The line width corresponds to about 15-20 quantum dots, as can easily be verified by counting the clearly discernible nanocrystals in Figure 5.5a. The quality of the arrangement of the quantum dots is exceptionally well, comparable to spin-coated or dip-coated samples. This is advantageous for nanophotonics where the concentration of the emitters can be important for exploring light-matter interactions. Figure 5.5c and f show the emission cross section of the printed line and spot, respectively. The red dots are the measured data (image taken with a cooled cMOS camera through a Nikon 100x, 0.9 NA air immersion objective), they remain within 10% of an ideal point source (solid black curve). In theory, this means that any light pattern can be printed with such near ideal point sources. In practice, this is of course
limited by factors also introduced in earlier chapters, such as the stage positioning precision, droplet deflection by already existing printed structures, long-term stability of the setup etc.

All the above experiments were on flat substrates. Figure 5.6 shows a line printed with several overprints on a long wedge. With the help of the side objective the sample can be manually rotated to align the wedge with the axes of the stage. This enables printing lines parallel to a wedge. Printing perfectly on top of the wedge in the location of interest for nanophotonics is however highly improbable with mere optical alignment, as the needed precision is far greater than the resolution of the side objective of the printing setup.

![Figure 5.6: Quantum dots printed along wedge. A long line (a) is printed precisely on top of a wedge with several overprints (b-d).](image)

However, we can take advantage of the similarity of the electrostatic field responsible for printing and the electromagnetic fields defining where the plasmonically interesting spots are located. As the field maxima are in the same location (here, at the tip of the wedge), the ejected droplets are preferentially guided towards the tip of the wedge, enabling printing quantum dots at a sub-diffraction placement precision.
Figure 5.7: Illustration of the electric field-guided deposition. (a) low voltage print perpendicular to wedge axis, enhancement from no ejection, slow ejection of large droplets, fast ejection of small droplets and back to no ejection; (b) nozzle is moved in straight lines across pyramid, the droplets are deflected by the enhanced field around the tip of the pyramid; (c)-(d) 5 μm long lines printed on top of wedges with high placement precision; (e) fluorescence image of the line displayed in (d).

Figure 5.7 exemplifies the field enhancement. In Figure 5.6a the printing nozzle is moved perpendicular to the wedge orientation, at a height of 5 μm from the wedge tip. The voltage is close to the lower ejection limit. At a higher nozzle-substrate distance (e.g. at the bottom of the wedge) no droplets are ejected, reducing the distance (at the wedge slope) initiates printing of large droplets, as could always be seen at very low field strengths\(^3\). Close to the tip the field strength is disproportionally increased, leading to the fast ejection of small droplets. Figure 5.7b shows that the field strength across out-of-plane structures is in fact not only strong enough to change the printing mode from no ejection to fast ejection of small droplets but it can also deflect ejected droplets. The nozzle was moved across the pyramid in straight lines, but the footprints of the droplets are clearly deflected towards the tip of the pyramid, where the field enhancement is the strongest.
In consequence, it is possible to print on top of a wedge in perfect alignment with high reproducibility (Figure 5.7c). This can be used to excite the strongly confined waveguide mode that exists for surface plasmon polaritons along the apex of the metallic wedge. This waveguide can be excited by quantum dots placed in the near field of the wedge tip.

Figure 5.8 shows two examples of plasmonic circuits, where active elements – here the sources represented by the quantum dots – and passive elements such as waveguides. In the first case (Figure 5.8a,c,e) a bump (bright line in Figure 5.8a) was created on a smooth gold surface by means of template-stripping from a silicon mask in which a groove had been cut with a focused ion beam tool. The CdSe/CdS core/shell quantum dot line (dark line in Figure 5.8a) was then printed with 3 overprints at an angle of 12.5° to the Au bump line. When the quantum dots are excited with UV light, they appear as a bright line in the fluorescence image (Figure 5.8c). At the same time photons are emitted at the bump on the gold surface, with an intensity dependent of the distance from the quantum dot line. By plotting the signal intensity along the bump line as a function of the distance from the quantum dot line, it is possible to fit an exponential decay with a decay constant of 7.8 μm. Comparing this value with the decay constant of 7-8 μm measured on the same gold film with a slit-groove technique, we can deduce that indeed surface plasmon polaritons are coupled into the gold film via the quantum dots and are coupled out into photons at the bump.

The second example (Figure 5.8b,d,f) shows a circular bump with a quantum dot spot in the center, printed with a 100 ms voltage pulse. As the surface plasmon polaritons spread in a circular wave pattern from the point source, the outcoupled intensity should be equal around the circumference of the circular bump. This is indeed the case, as can be seen in Figure 5.8d and f. This showcases not only the propagation of the surface plasmon polaritons wave but also the precise placement even on a flat substrate.
5.2.4 Conclusion

In conclusion, we have demonstrated a simple method for near-field light design for nanophotonics. We used electrohydrodynamic NanoDrip printing to place highly fluorescent quantum-dot patterns with arbitrary color, shape, and intensity with subdiffraction resolution and nanometer precision on planar and structured substrates. The deposits involve a countable number of quantum dots, which can be electrostatically guided toward electromagnetic hotspots on structured plasmonic substrates. Hybrid quantum-dot-plasmonic circuits can be easily created that generate, guide, and out-couple surface plasmon polaritons. In such circuits, the quantum dots act as local plasmonic sources when illuminated with ultraviolet light from the far field. Thus, a method for
nearfield light design is provided without the constraints of earlier techniques for integrating quantum dots into nanophotonics devices.

5.3 Wedge Waveguides and Resonators for Quantum Plasmonics

In a follow-up paper the wedge waveguiding of plasmon polaritons was investigated in more detail. In order to study the wave propagation along the apex of the wedge, bumps across the apex were introduced, fabricated with the same template-stripping procedure as for the bumps in Figure 5.8, this time using silver instead of gold surfaces to optimize the plasmonic performance.

The quantum dots used here are CdSe-CdS-ZnS core-shell-shell nanocrystals with a very high quantum yield (90% in liquid) and a narrow emission spectrum. They provide the same resilience to the high electric field during printing as the nanocrystals used in the previous paper.

For the novel findings related to plasmonics the interested reader is referred to either the published paper or the doctoral thesis of Stephan Kress, they are not topic of this work. Two novel developments of the electrohydrodynamic printing technology were made for this publication and are discussed here shortly:

As has been mentioned earlier, the first few droplets ejected at the beginning of a voltage pulse contain a higher concentration of quantum dots, since the solvent evaporates at the tip of the nozzle during stand-by time, leaving behind the nanoparticles and thus gradually increases the particle concentration. For many applications this is not relevant or can even be exploited, but for plasmonic applications, this asymmetric deposition can have a negative influence on the performance. The effect can be seen well in Figure 5.6b, where at the beginning of the line, the number of deposited quantum dots is clearly increased.

This problem was circumvented here by introducing a so-called pre-flush. Before printing a line or a spot on a wedge, the nozzle is moved several tens of microns away from the plasmonically interesting structure. A 500 ms voltage pulse is applied to drain the nozzle tip of all accumulated nanocrystals. The nozzle is then moved back to the starting position of the quantum dot deposition at the maximum stage speed and printing is initiated. By keeping the time between the draining and the actual printing as short as possible, the first ejected droplets were not discernible from the rest of the voltage pulse any more.
In order to study the wedge waveguides it was necessary to deposit a small number of quantum dots or even a single emitter precisely on top of the wedge apex. Figure 5.9 shows both cases. To deposit a few quantum dots, the quantum dot dispersion (normalized to an optical density of 0.5 for 1mm path length) was diluted 1:10 in tetradecane. The pre-flushing and a subsequent voltage pulse of only 20 ms then led to the small deposit in Figure 5.9a.

![Image](image)

**Figure 5.9: Alignment precision. Several (a) as well as one single (b) quantum dot can be placed with a precision approaching the singe-digit nanometer precision.**

Printing single quantum dots required a more sophisticated approach: The ink was diluted 1:30 in tetradecane. In order to place one single quantum dot right on the apex of wedge we once again took advantage of the electrostatic field enhancement at the apex: The nozzle was moved perpendicular to the wedge array, at a very low height (2 μm from the wedge apex) with a constant low voltage pulse. Normally, this low voltage would not be high enough to initiate droplet detachment, however, in the vicinity of a wedge apex the field enhancement leads to the ejection of a droplet. Statistically, one of every few droplets will contain a single quantum emitter. One such case is shown in Figure 5.9.

By moving the nozzle back and forth across the wedges several times with a small offset, it was possible to print several well-separated single quantum dots on top of the wedge. This allowed to measure fluorescence time series, showing the typical blinking behavior of single quantum dots. At the end of the wedge, the launched wedge plasmon polaritons are coupled out as a weak photon signal (Figure 5.10), which is strongly correlated to the blinking signal of the single quantum emitter.

The detrimental importance of perfect alignment is illustrated in Figure 5.10f and g: The scattered signal at the end of the wedge is only synchronized to the blinking of the second quantum dot of the three located on the wedge. The other two do not induce a scattering signal as strong as the former one, which is due to a minute offset of the emitters to the apex of the wedge.
Figure 5.10: Blinking of single quantum dots on a wedge. (a) fluorescence image of three separated, single quantum dots on a wedge; b,c time traces of the fluorescence signal of QD 2 and the wedge end, the signals are clearly correlated; f,g synchronized on/off states of QD2 and the wedge end (QD1 and QD3 do not have a strong coupling signal, indicating non-ideal alignment to the wedge apex); h single quantum dot on wedge.
6 Outlook

This work showed a few of the most promising applications for electrohydrodynamic printing in the nanodripping mode. The technique of depositing nanoparticle-laden droplets of a diameter down to 50 nm is however still at its beginning and many improvements can be made to the printing system itself, some aspects of the printing mechanism are to this day not fully understood and while some applications have been hinted at in this work and others, more will certainly follow.

The capability to print on soft substrates as well as sub-diffraction-sized spots has spurred the idea to use quantum dots for reference-free traction force microscopy of biological cell movements. Small points of quantum dots are printed in a regular array on a soft PDMS-like substrate. Cells are then seeded onto the substrate. During their movement they exert forces on the soft substrate, thereby deforming it. The deformation of the substrate can then simply be mapped by fluorescence microscopy. Knowing the mechanical properties of the substrate as well as the initial locations of the points in the array, the forces exerted by the cells can be calculated. For biological applications the traction and other deforming force measurements can be expanded to non-flat substrates with gratings or areas with different adhesive properties for the cells. In combination with the nanoprinted arcs one could envision adding quantum dots to the gold inks used for fabricating the arcs and subsequently tracking the deformation of the arcs caused by cells passing through the arcs.

The newest results of printed CdSe/CdS/ZnS core-shell-shell quantum dots in cavities on a silver substrate indicate that by pumping the quantum dots with an external laser, surface plasmon amplification by stimulated emission of radiation – the surface plasmon equivalent of a laser – can be achieved. This highly interesting effect will certainly be investigated in much more detail and is a great candidate for many interesting applications in the field of nanophotonics.

Currently the printing system is completely at a research grade and laboratory scale. If the long-term goal is to bridge the gap to industrial applications, be it for electronic applications, display technology, anti-counterfeiting tools or others, there is a need for massive upscaling. A print head with multiple nozzles would have to be developed along with the necessary control mechanisms for parallel printing. In order to automatically print on a full wafer or several samples, a feedback mechanism to control the nozzle positions and potentially the alignment to already existing structures on the substrate are needed.
Hand-in-hand with feedback technology goes a more in-depth understanding of the ejection mechanism in general to render it more stable over long periods of time. While we have shown the charging of droplets and the particles therein, no direct observations of the ejection event at the nozzle has been made to this day as the time and length scales are extremely small. In order to avoid clogging of the nozzle and long-time drifts of the printing behavior by design rather than by rule-of-thumbs, a dedicated study of the ejection events over longer periods of time are necessary. Both the environmental conditions such as temperature and humidity as well as the properties of the ink (nanoparticles size and concentration, surface tension, vapor pressure, viscosity, etc.) influence the printing.

In parallel to bringing the printing setup to a more sophisticated level, the range of applications can be widened and existing applications studied more in-depth. The absorbing out-of-plane antenna arrays introduced in this work are in principal rather simple out-of-plane pillars. The versatility of the nanoprinting technology allows to print tilted pillars. Tilting pillars in an array, possibly even varying their tilt direction might yield new and interesting insights into the light-metamaterial interaction. No post-processing of any kind was done with the pillar arrays in this work. Introducing such steps as for example annealing or plasma treatments will change the composition of the metamaterial and lead to new spectral responses.

Last but not least NanoDrip printing has been shown to be a very valuable tool in the field of plasmonics. The capability to controllably place a few or even single quantum dots of any material and emitting color at well-defined spots with a precision down to a few nanometers will certainly lead to more interesting findings in the field.
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