The Influence of Light Exposure on Electrohydrodynamic (EHD) Printing of CdS/CdSe Quantum Dots

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Abstract

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This study investigates whether 395 nm light enhances the EHD printability of CdSe/CdS quantum dots (QDs) by affecting the material's response under a fixed voltage. Experimental results show that, under identical voltage conditions, printing is significantly enhanced with 395 nm illumination, whereas minimal deposition occurs in the absence of light. This finding suggests that optical excitation may influence charge dynamics or dipole formation within the ink, potentially altering its response to the applied electric field.

By demonstrating a clear correlation between light exposure and enhanced EHD printing, this work provides a foundation for further exploration of optically controlled material deposition.

Understanding this effect could lead to new strategies for precision printing of optoelectronic materials, enabling tunable and high-resolution patterning techniques.

Keywords:

Electrohydrodynamic printing, quantum dots, CdSe/CdS, light-assisted printing, charge dynamics, nanomaterial deposition, optoelectronics

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1. Introduction, Background and Motivation

1.1 Introduction

Electrohydrodynamic (EHD) printing is an advanced additive manufacturing technique that enables high-resolution deposition of functional materials by utilizing electric fields to control ink ejection. Unlike traditional inkjet printing, which relies on nozzle pressure to dispense ink, EHD printing exploits electrostatic forces acting on a liquid meniscus, forming a stable Taylor cone that emits ultrafine droplets or continuous jets. This technique achieves sub-micrometer and even nanoscale patterning, making it particularly attractive for applications in nanomaterials, optoelectronics, and high-resolution printing [1].

Among the various materials utilized in EHD printing, quantum dots (QDs) have emerged as promising candidates due to their tunable optical properties, high photoluminescence quantum yields, and potential applications in next-generation display technologies, light-emitting devices, and photodetectors [2]. Specifically, CdS/CdSe core-shell quantum dots have been widely studied for their enhanced stability, charge transport properties, and spectral tunability [3]. However, achieving precise and reproducible deposition of QD inks via EHD printing remains a challenge due to their complex interactions with electric fields, surface charge distribution, and ink formulation parameters.

One of the critical challenges in EHD printing is controlling the printability of materials with varying dielectric properties and polarizability. The ink's response to the applied electric field depends on factors such as solvent composition, quantum dot surface charge, and environmental conditions [4]. Any external stimulus that modifies the charge dynamics or polarizability of the ink could potentially alter the printing behavior. In this context, light exposure presents an intriguing, yet largely unexplored, factor that could influence the electrohydrodynamic printing process.

It is hypothesized that light exposure may affect the EHD printing of CdS/CdSe QDs by modifying their polarizability and charge distribution. When quantum dots are illuminated with light of appropriate wavelengths, photoexcitation can generate charge carriers, altering their interaction with the external electric field and potentially modifying the ink's printability [5]. Additionally, transient charge redistribution after illumination could impact the stability of droplet formation and deposition, as previously observed in optically stimulated charge dynamics in nanomaterials [6].

Understanding the influence of light exposure on EHD printing could lead to new strategies for enhancing print precision, stability, and controllability. If validated, this mechanism could enable light-assisted printing techniques, where optical control is integrated into printing systems for real-time modulation of droplet ejection and material patterning. Such advances could benefit applications in optoelectronic device fabrication, flexible displays, photonic circuits, and high-resolution printed electronics [7].

This study aims to investigate whether and how light exposure influences EHD printing of quantum dots, providing experimental insights into the interplay between optical excitation, charge dynamics, and electrohydrodynamic behavior. The findings could pave the way for novel optically controlled printing methodologies, contributing to the broader field of high precision nanomanufacturing.

2. Background and Motivation

2.1 Electrohydrodynamic (EHD) Printing

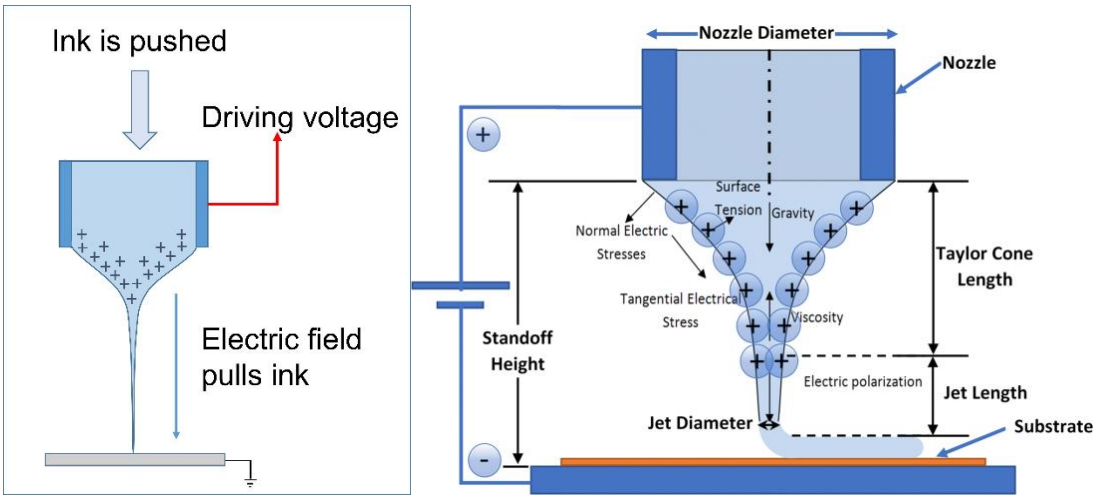


Fig. 1). EHD printing principle and relative concepts [8][9]

Electrohydrodynamic (EHD) printing is an advanced additive manufacturing technique that utilizes electrostatic forces to achieve high-resolution deposition of functional materials. EHD printing operates by applying a high electric field between a conductive nozzle and a substrate, inducing the ejection of ink droplets onto the substrate. The process begins with the formation of a Taylor cone, a conical shape assumed by the liquid meniscus under the influence of the electric field. When the electrostatic forces overcome the surface tension of the liquid, a fine jet is emitted from the apex of the Taylor cone, leading to droplet deposition on the substrate [10].

Taylor Cone Formation: The concept of the Taylor cone was first introduced by Sir Geoffrey Ingram Taylor in 1964, describing the deformation of a liquid droplet under an electric field into a cone with a semi-vertical angle of approximately 49.3 degrees. This shape results from the balance between electrostatic forces pulling the liquid outward and surface tension pulling it inward. The precise formation of the Taylor cone is critical for stable jetting and consistent droplet ejection in EHD printing [11].

Electrostatic Forces and Droplet Ejection Mechanisms: In EHD printing, the electrostatic forces acting on the liquid are governed by the applied voltage, the properties of the ink (such as conductivity and viscosity), and the geometry of the nozzle. Once the electric field strength reaches a critical threshold, it overcomes the liquid's surface tension, resulting in the emission of a jet from the Taylor cone. This jet subsequently breaks up into fine droplets due to Rayleigh instability or is directly deposited onto the substrate as a continuous line, depending on the printing parameters.

Current Challenges in Controlling Droplet Size, Stability, and Uniformity: Despite its potential for high-resolution patterning, EHD printing faces several challenges that hinder its broader application, particularly concerning the control of droplet size, stability, and uniformity.

Droplet Size Control: Achieving consistent droplet sizes is essential for uniform material deposition. Factors influencing droplet size include the ink's viscosity, surface tension, flow rate, and the applied voltage. Variations in these parameters can lead to inconsistent droplet formation, affecting the resolution and quality of the printed patterns.

Jet Stability: Stable jet formation is crucial for continuous and precise material deposition. Instabilities such as whipping or pulsation can disrupt the jet, leading to defects in the printed structures. These instabilities are influenced by factors like electric field strength, ink properties, and environmental conditions. Maintaining a stable Taylor cone-jet requires careful optimization of these parameters [12].

Uniformity of Deposited Patterns: Uniform deposition is vital for the functionality of printed devices. Non-uniformities can arise from fluctuations in droplet size, jet instability, or inconsistencies in the substrate surface. Achieving high uniformity necessitates precise control over the printing parameters and a thorough understanding of the interactions between the ink, electric field, and substrate.

Addressing these challenges is critical for advancing EHD printing technology and expanding its applications in areas such as flexible electronics, biomedical devices, and nanofabrication.

2.2 Quantum Dots for Optoelectronic Applications

Quantum dots (QDs) are semiconductor nanocrystals that exhibit unique optical and electronic properties due to quantum confinement effects, making them highly suitable for optoelectronic applications. Among various QD structures, CdS/CdSe core-shell quantum dots have garnered significant attention. This section delves into their structure, properties, and relevance in printing applications.

Structure and Properties of CdS/CdSe Core-Shell Quantum Dots

CdS/CdSe core-shell quantum dots consist of a cadmium selenide (CdSe) core encapsulated by a cadmium sulfide (CdS) shell. This configuration offers several advantages:

- Enhanced Photoluminescence: The CdS shell passivates surface trap states of the CdSe core, leading to increased photoluminescence efficiency.
- Improved Stability: The core-shell structure provides better chemical and photostability, essential for optoelectronic device longevity.
- Tailored Optical Properties: By adjusting the core size and shell thickness, emission wavelengths can be precisely controlled, enabling customization for specific applications.

Dielectric Properties and Optical Characteristics

The dielectric properties and optical characteristics of CdS/CdSe core-shell QDs are pivotal for their integration into optoelectronic devices:

- Dielectric Properties: The core-shell architecture influences the dielectric constant, affecting charge separation and recombination rates. This modulation is crucial for optimizing device performance.
- Optical Characteristics: These QDs exhibit size-dependent absorption and emission spectra, allowing for tunable photoluminescence. The suppression of Auger recombination in core-shell structures further enhances emission efficiency [13].

Relevance in Printing Applications

The unique properties of CdS/CdSe core-shell QDs make them highly relevant for printing applications in optoelectronics:

- Ink Formulation: Their colloidal stability facilitates the formulation of inks suitable for various printing techniques, including inkjet and electrohydrodynamic (EHD) printing.
- Device Fabrication: Printed QD layers can be employed in light-emitting diodes (LEDs), photodetectors, and solar cells, leveraging their tuneable optical properties [14].
- Scalability: Printing technologies enable large-area and cost-effective fabrication of QD-based devices, essential for commercial applications.

In summary, CdS/CdSe core-shell quantum dots, with their tailored structure and properties, play a pivotal role in advancing printed optoelectronic devices.

2.3 Light-Material Interactions in Nanomaterials

Understanding the interactions between light and nanomaterials is crucial for advancing optoelectronic applications. Light exposure can significantly influence the charge carrier dynamics in semiconductors, leading to changes in material properties and device performance. This section explores the effects of light exposure on charge carrier dynamics in semiconductors and discusses potential mechanisms, including photon-induced carrier

excitation, polarizability changes, surface charge redistribution, and dipole alignment under an electric field.

2.3.1 Effect of Light Exposure on Charge Carrier Dynamics in Semiconductors

When semiconductors absorb photons with energies exceeding their bandgap, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. This process, known as photoexcitation, increases the number of free charge carriers, thereby enhancing the material's conductivity. The dynamics of these photoinduced charge carriers—such as their generation, recombination, and transport—are pivotal in determining the performance of optoelectronic devices. Techniques like time-resolved spectroscopy have been employed to study these ultrafast processes, providing insights into carrier lifetimes and mobility [15].

2.3.2 Potential Mechanisms

Photon-Induced Carrier Excitation and Polarizability Changes: Upon light absorption, the excitation of electrons to higher energy states not only increases the carrier density but also affects the material's polarizability—the measure of how the electron cloud within a material responds to external electric fields. The induced dipole moments from photoexcitation can alter the dielectric properties of the material, influencing interactions with electromagnetic fields and affecting processes like electrohydrodynamic printing. For instance, changes in polarizability can modify the electrostatic forces during droplet formation, impacting printing resolution and accuracy.

Surface Charge Redistribution and Dipole Alignment Under an Electric Field: Light exposure can lead to the redistribution of surface charges in nanomaterials. Studies have shown that photoexcitation can cause non-uniform charge distribution, resulting in localized electric fields that influence molecular bonding and surface interactions. For example, research on single

nanoparticles has demonstrated that surface charges play a fundamental role in shaping catalytic properties, with light-induced charge dynamics affecting surface molecular bonding.

Additionally, when an external electric field is applied, the photoinduced dipoles within the material tend to align with the field direction, leading to anisotropic properties. This alignment can influence various processes, such as directed growth of nanostructures and modulation of electronic properties. For instance, optical dipole forces have been utilized to direct the growth of semiconductor nanostructures along the polarization direction of incident light, demonstrating the interplay between light-induced dipoles and external fields.

In summary, light-material interactions in nanomaterials involve complex mechanisms that significantly impact charge carrier dynamics and material properties. A comprehensive understanding of these processes is essential for optimizing the performance of optoelectronic devices and developing advanced fabrication techniques.

2.4 Prior Studies on Light-Assisted Printing and Deposition

Advancements in additive manufacturing have led to the development of various light-assisted printing and deposition techniques. This section reviews research on optically controlled inkjet printing, photopolymerization, and photonic sintering, and discusses how the current study extends the field by examining light-assisted electrohydrodynamic (EHD) printing of quantum dots (QDs).

2.4.1 Research on Optically Controlled Inkjet Printing, Photopolymerization, and Photonic Sintering

Optically Controlled Inkjet Printing: Inkjet printing, a non-contact digital printing technology, has been extensively utilized for fabricating optical and photonic devices. Its capability to deposit microstructures as small as 30 microns with precise control over droplet properties enables high-resolution patterning. This technique has been applied in manufacturing optical

components such as microlenses, waveguides, and integrated lasers, as well as large-area light-emitting diode displays and solar cells.

Photopolymerization: Photopolymerization-based 3D printing processes, such as stereolithography (SLA), utilize light to selectively cure liquid photopolymers, enabling the fabrication of complex optical elements with high precision. These methods have been employed to produce components like microlenses and waveguides, essential for integrated photonic systems.

Photonic Sintering: Photonic sintering involves using intense pulsed light to rapidly fuse nanoparticles, forming conductive patterns without significant thermal impact on underlying substrates. This technique has been applied to sinter inkjet-printed copper traces, optimizing electrical resistivity and mechanical properties for flexible electronics applications.

2.4.2 Extension to Light-Assisted EHD Printing of Quantum Dots

While significant progress has been made in light-assisted printing techniques, the integration of optical control in EHD printing, particularly for QD materials, remains underexplored. Recent studies have demonstrated the potential of EHD printing for high-resolution patterning of QDs, achieving pixel resolutions up to 2540 pixels per inch (PPI) in QD light-emitting diodes (QLEDs) [16].

The current study aims to extend this field by investigating the effects of light exposure on the EHD printing process of CdS/CdSe core-shell QDs. Specifically, it explores how optical excitation influences the polarizability and charge distribution of QDs during printing, potentially leading to enhanced control over droplet formation and deposition accuracy. This research could pave the way for novel light-assisted EHD printing methodologies, offering precise control over nanomaterial deposition for advanced optoelectronic applications.

3. Methods, Results and Discussion

3.1 Methods

3.1.1 Materials and Sample Preparation

Quantum Dot Preparation:

CdSe quantum dots were synthesized using an improved hot-injection method, involving precursor preparation, nucleation, and controlled growth. First, Cd-oleate precursor was prepared by heating 130 mg (1 mmol) CdO, 16 g ODE (1-octadecene), and 0.6 g OLAC (oleic acid) in a 100 mL three-neck flask at 110 °C under vacuum for 45 minutes to remove moisture and impurities. After introducing nitrogen, the temperature increased to 290 °C for 5 minutes, forming cadmium-oleate, indicated by a color change from red to transparent. The reaction mixture was then cooled to 100 °C, and 2.0 g TOPO (tri-n-octylphosphine oxide) and 1.8 g HDA (hexadecylamine) were added as surfactants. Following vacuum treatment at 110 °C for 15 minutes, the temperature was raised to 290 °C under nitrogen. At this stage, a selenium precursor solution (100 mg Se dissolved in 2 mL TOP) was rapidly injected, and the reaction was allowed to proceed for 2 minutes before being quenched by rapid cooling with a water bath. The resulting CdSe quantum dots were purified by washing with ethyl acetate and toluene (3×).

To grow the CdS shell, Cd-oleate precursor was synthesized separately by heating 1.28 g CdO, 31.5 mL OLAC, and 18.3 mL ODE at 110 °C under vacuum for 1 hour, followed by heating to 160 °C under nitrogen for 30 minutes. The solution was stored in an N_2 glovebox to prevent oxidation. For shell growth, 100 nmol CdSe QDs dispersed in 6 mL ODE were degassed at 110 °C under vacuum for 1 hour, and the temperature was then increased to 310 °C. At 240 °C, 0.2 M Cd-oleate and 0.2 M 1-octanethiol were co-injected at 0.05 mL/min for 45 minutes,

resulting in a controlled CdS shell thickness. The final CdSe/CdS QDs were purified by washing with ethanol and toluene (3×).

For EHD printing, the purified CdSe/CdS QDs were precipitated and redispersed in a 1:1 mixture of octane and hexadecane to ensure compatibility with the electrohydrodynamic printing process. The ink concentration was adjusted to achieve an optical density (OD) of 0.8 in a 1 cm path length cuvette at the first exciton absorption peak, ensuring optimal nanoparticle dispersion and ink stability [17].

Substrate Preparation:

Silicone films were cut into 15 mm × 15 mm wafers and underwent a sequential cleaning process. The wafers were first washed with a 2% DET (diethylenetriamine) + deionized (DI) water solution, followed by rinsing with DI water, acetone, and isopropanol (IPA) to remove surface contaminants. After drying, a thin layer of trichlorosilane was deposited onto the wafer surface at 160 °C for one hour to enhance hydrophobicity.

3.1.2 Electrohydrodynamic Inkjet Printing

Electrohydrodynamic (EHD) inkjet printing was performed using pulled borosilicate glass capillary pipettes with an internal nozzle diameter ranging from 1 to 3 μm. These custom-fabricated printheads featured an inlaid gold electrode along the interior wall, enabling precise control of the electric field near the printing medium.

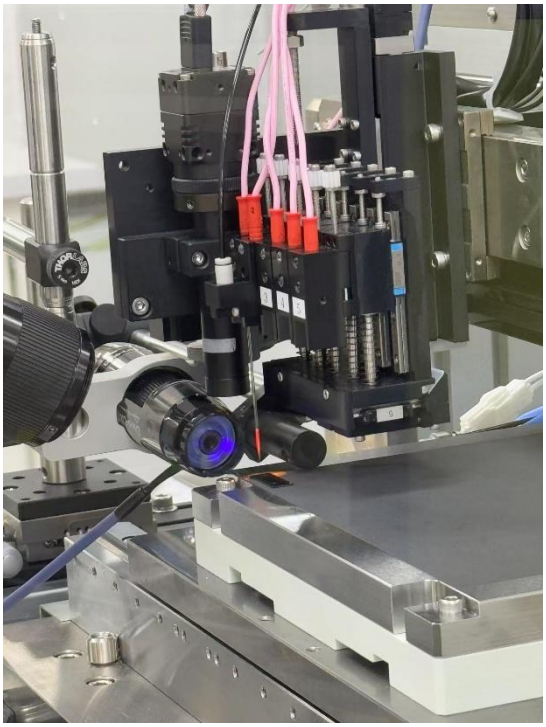


Fig. 2). Electrohydrodynamic Inkjet Printer setup

The printhead was mounted onto the printer, and the substrate was secured on a grounded vacuum chuck stage. An alignment procedure was conducted to ensure the designed printing patterns were accurately mapped onto the substrate. A 395 nm LED light source was mounted on the printer, positioned to illuminate the nozzle area, allowing for controlled optical excitation during the printing process. Printing was carried out under controlled conditions with a bias of 0 V, an amplitude ranging from 300 to 1000 V, and a frequency of 1000 Hz.

3.1.3 Experimental Design

To investigate the effect of optical excitation on EHD printing, a series of controlled experiments were conducted by systematically varying the applied voltage. The initial printing voltage was set at 1000 V with a holding time of 0.05 s, and gradually decreased in steps down to 300 V. At each selected voltage, a 40 × 40 array of quantum dots was printed under two conditions: with and without 395 nm LED illumination.

The printed arrays were subsequently characterized using fluorescence microscopy (FM), dark-field (DF) microscopy, and bright-field (BF) microscopy to analyze differences in dot size, uniformity, and optical response. By comparing the printed patterns obtained under light and dark conditions, this study aims to determine whether light exposure enhances deposition efficiency, influences dot morphology, or alters the stability of the EHD printing process, providing insights into the potential role of light-assisted control in precision nanomaterial printing.

4. Results and Discussion

4.1 Voltage-Dependent Effect of Light Exposure on EHD Printing

To investigate the impact of 395 nm LED illumination on electrohydrodynamic (EHD) printing, a systematic study was conducted across a voltage range of 200 V to 1000 V. At each voltage, a 40 × 40 quantum dot array was printed under two conditions: with and without LED illumination. The printed patterns were characterized using fluorescence microscopy (FL), dark-field (DF) microscopy, and bright-field (BF) microscopy to evaluate the effect of optical excitation on printability.

Table 1. Summary of Key Findings

Voltage Range	Printing Without LED	Printing With LED	Effect of Light Exposure
200–500 V	No printing observed	No printing observed	Electric field insufficient; low-polarity ink does not respond strongly.
500–540 V	Minimal or no printing	Clear, well-defined printing	Light enhances polarizability, enabling ink ejection.
550-600 V	Partial printing	More uniform and complete printing	Light improves deposition consistency and array completeness.
600–1000 V	Consistent printing	Consistent printing	Electric field dominates; light has no observable impact.

The results revealed a distinct voltage-dependent behavior:

Low Voltage Range (200–500 V) – Insufficient Driving Force for Printing

In this range, printing did not occur, regardless of whether the 395 nm LED was on or off.

This suggests that at voltages below 500 V, the applied electric field was too weak to induce stable Taylor cone formation and ink ejection, even in the presence of light.

The use of a 1:1 octane/hexadecane solvent system, which has relatively low polarity, may further contribute to this threshold behavior, as the ink system does not respond strongly to weaker electric fields.

Moderate Voltage Range (500–600 V) – Light-Enhanced Printing Effect

In this voltage range, a clear difference was observed between the illuminated and non-illuminated conditions.

With LED illumination, well-defined quantum dot arrays were successfully printed.

Without LED illumination, little to no printing occurred, indicating that the applied voltage alone was insufficient to drive ink ejection.

The observed light-assisted printing effect suggests that photoinduced charge carriers play a role in enhancing ink polarization, effectively lowering the threshold voltage required for stable Taylor cone formation.

The presence of the CdS shell in the quantum dots, which has a relatively high dielectric constant, may contribute to the enhanced response under optical excitation. The excited charge carriers could further increase the local polarizability of the ink, making it more responsive to the applied electric field.

High Voltage Range (600–1000 V) – Electric Field Dominated Printing

In this range, printing occurred consistently, whether the LED was on or off.

No noticeable difference was observed in the printed arrays when comparing illuminated and non-illuminated conditions under optical microscopy.

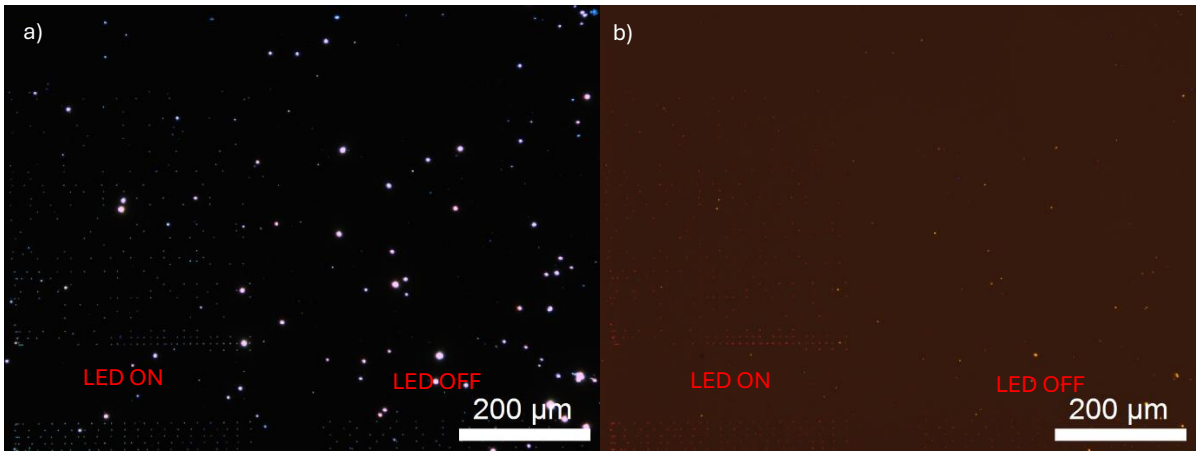
This suggests that at high voltages, the applied electric field is sufficient to induce stable ink ejection, and any additional effect from photoinduced charge carriers becomes negligible.

The low polarity of the octane/hexadecane solvent system does not appear to hinder printing at these voltages, as the electric field alone is strong enough to drive the ejection process.

4.2 Detailed Analysis of 530V, 540V, and 550V Printing Results

To further analyze the voltage-dependent impact of 395 nm LED illumination, a focused comparison was conducted at 530 V, 540 V, and 550 V. The printed arrays were examined under dark-field (DF) and fluorescence (FL) microscopy to assess deposition uniformity, dot completeness, and emission intensity.

530 V & 540 V: Strong Light-Enhanced Printing Effect



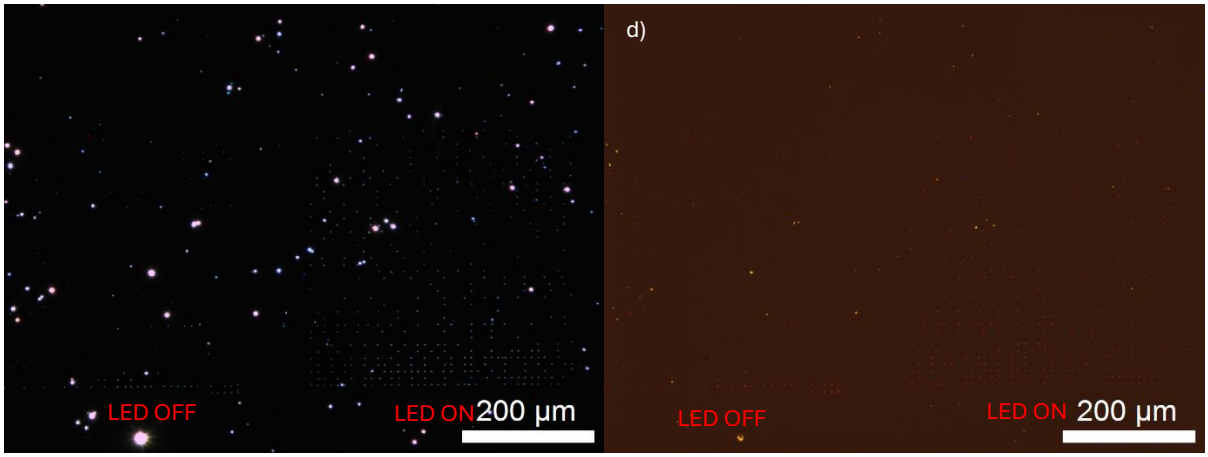


Fig. 3). (a) Dark-field (DF) images of 40 × 40 quantum dot arrays printed at 530 V, comparing conditions with and without 395 nm LED illumination. (b) Fluorescence (FL) microscopy images of the same printed arrays at 530 V. (c) Dark-field (DF) images of printed arrays at 540 V under LED on and off conditions. (d) Fluorescence (FL) microscopy images of the corresponding printed arrays at 540 V.

As shown in Figures 3, at 530 V and 540 V, the no-LED condition resulted in minimal or nearly absent printing. DF and FL microscopy revealed that only a few isolated dots were formed, and their distribution was highly inconsistent. This suggests that, under these conditions, the applied electric field was near but not sufficient to fully induce ink ejection.

However, when the LED was turned on, a well-defined and uniform 40 × 40 quantum dot array was observed. Under FL microscopy, the printed dots exhibited strong photoluminescence, confirming the presence of deposited quantum dots. This stark difference indicates that 395 nm illumination significantly enhances the ink's response to the applied field, likely by generating photoinduced charge carriers that increase the ink's polarizability, thus enabling stable Taylor cone formation and droplet ejection.

550 V: Partial Printing Without Light, Enhanced Array with Light

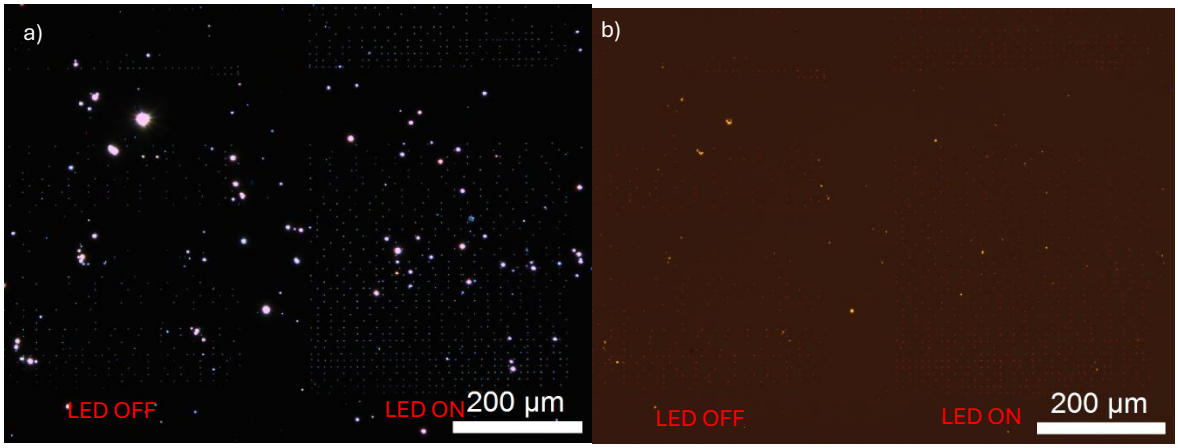


Fig. 4). a) Dark-field (DF) images of printed arrays at 540 V under LED on and off conditions. b) Fluorescence (FL) microscopy images of the corresponding printed arrays at 540 V.

At 550 V, a noticeable transition was observed. In the absence of LED illumination, some degree of printing was detected, but the pattern was incomplete, with gaps and inconsistent dot formation (Figure 4). This suggests that at this voltage, the electric field was just above the threshold for inducing ink ejection, allowing for partial deposition without the need for optical excitation.

With LED illumination, the printed array was more complete and uniform, with better-defined individual dots and more consistent spacing. The FL images further confirmed a higher density of deposited quantum dots under illuminated conditions. These results imply that while 550 V is approaching the regime where the electric field alone is sufficient for printing, optical excitation still provides a stabilizing effect, enhancing uniformity and deposition efficiency.

4.3 Dependence of Threshold Voltages on Printing Conditions

While the results clearly demonstrate the voltage-dependent effect of light exposure on EHD printing, it is important to note that the specific voltage thresholds identified in this study are not absolute. The required voltage for stable printing is influenced by multiple factors,

including printing height, holding time, ink composition, nozzle geometry, and environmental conditions.

In this study, all voltage values were determined under a fixed printing height of 5 μm and a holding time of 0.05 s. Under different printing conditions, such as a greater printing height, a shorter or longer holding time, or variations in ink viscosity, the voltage range at which light exposure enhances printing may shift.

For example, an increase in printing height would require a higher voltage to maintain the necessary electric field strength for Taylor cone formation, potentially shifting the light-enhanced printing window (500–600 V) to a higher range. Similarly, changes in holding time could affect ink accumulation at the nozzle tip, altering the threshold at which printing occurs.

Thus, while the observed trend—that light exposure significantly enhances printing at intermediate voltages but has little effect at very high or very low voltages—remains valid, the exact voltage values should be interpreted within the context of the specific experimental conditions. Future studies could further explore how variations in height, holding time, and ink formulation affect the critical voltage range for light-assisted printing, potentially enabling a broader understanding of optically controlled EHD printing across different parameter regimes.

4.4 Influence of Ink Composition on Light-Assisted Printing

The solvent system used in this study (1:1 octane/hexadecane) is relatively nonpolar, meaning it does not inherently respond strongly to applied electric fields. Previous studies have shown that highly polar solvents can enhance the stability of EHD printing by promoting charge redistribution within the ink, improving ink ejection and droplet formation.

However, the CdSe/CdS quantum dots used in this study contain a CdS shell with a relatively high dielectric constant, which may compensate for the low polarity of the solvent system. Under 395 nm illumination, charge carriers can be photoexcited within the quantum dots,

further increasing their effective polarizability. This effect appears to be most significant in the 500–600 V range, where the electric field is near the threshold for stable printing, making the ink more responsive to optical excitation.

At higher voltages (600–1000 V), the electric field alone dominates the printing process, overcoming any differences in solvent polarity or optical excitation. This explains why no significant difference was observed in printed patterns with or without light in this voltage range.

At lower voltages (<500 V), neither the applied electric field nor optical excitation was sufficient to initiate printing. This suggests that the low intrinsic polarity of the ink, combined with an insufficient electric driving force, prevented stable Taylor cone formation and ink ejection.

4.5 Light-Enhanced EHD Printing and Ink Polarization

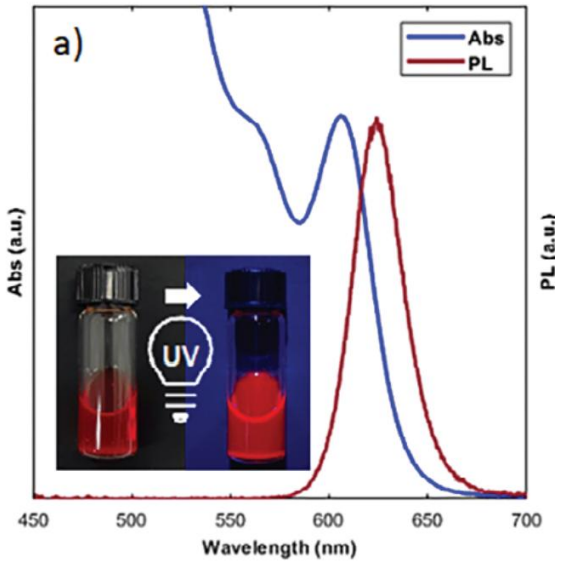


Fig. 5). a) Normalized absorption and PL spectra of CdSe/CdS quantum dots. Inset: Image comparison of the colloidal QD ink under ambient and ultra-violet (UV) lighting conditions.[17]

The optical properties of the CdSe/CdS quantum dots used in this study are shown in Figure X. The absorption spectrum exhibits strong absorption near 395 nm, indicating that the LED illumination used in the printing process interacts effectively with the quantum dot ink. The photoluminescence (PL) spectrum, centered at 630 nm, confirms the optical activity of the synthesized quantum dots.

While photoluminescence demonstrates the quantum dots' ability to emit light upon excitation, it is unlikely that direct photoexcitation alone is responsible for the enhanced printability. Instead, we hypothesize that 395 nm illumination may influence the ink's polarizability, thereby altering its response under an applied electric field. Previous studies suggest that materials with a high dielectric constant or strong dipole moments are more easily manipulated in EHD printing. Since CdS has a relatively high dielectric constant, optical excitation may induce transient charge redistribution within the quantum dot shell or modify the surrounding solvent environment, leading to increased ink polarizability.

This increased polarizability could, in turn, lower the threshold voltage required for stable Taylor cone formation, explaining why printing is significantly enhanced in the 500–600 V range under LED illumination. The spectral overlap between the LED wavelength and the quantum dot absorption range suggests that light may be modulating the dielectric response of the ink, making it more susceptible to electric field-driven droplet formation and ejection.

4.6 Implications for Light-Assisted EHD Printing and Ink Design

The results indicate that light exposure can effectively lower the threshold voltage required for EHD printing, but only within a specific voltage window (500–600 V). This suggests that light-assisted printing could be particularly useful for:

Optimizing printability of low-polarity inks

Tunable deposition via optical control

Reducing voltage requirements for sensitive substrates

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5. Conclusions and Future Work

5.1 Conclusion

This study demonstrates that 395 nm LED illumination enhances EHD printing within a specific voltage range (500–600 V), but has no observable effect at lower (<500 V) or higher (>600 V) voltages. The results suggest that optical excitation can influence ink polarization and charge dynamics, effectively lowering the threshold voltage required for stable printing. The use of a low-polarity octane/hexadecane solvent system likely contributes to the observed threshold behavior, while the CdS shell's high dielectric constant may facilitate the light-induced enhancement effect.

These findings highlight the potential of optically assisted EHD printing as a means of improving printability for low-polarity inks, enabling spatially controlled deposition, and reducing operational voltage requirements for delicate substrates.

5.2 Future Work

While this study demonstrates that 395 nm LED illumination enhances EHD printing within a specific voltage range (500–600 V), the underlying mechanism remains to be fully understood. Future research should focus on confirming whether light exposure influences the ink's polarizability and further explore the generalizability and applications of optically controlled EHD printing.

A critical next step is to directly measure whether 395 nm illumination affects the ink's dielectric properties, which could provide conclusive evidence that light enhances printability by increasing the ink's polarizability. This can be achieved through dielectric spectroscopy to

compare the dielectric constant of the ink under light and dark conditions, as well as zeta potential measurements to examine whether photoinduced charge redistribution occurs at the ink-solvent interface. Additionally, electrochemical techniques could be employed to assess changes in ink conductivity and capacitance under illumination, further clarifying how optical excitation alters the charge dynamics within the ink. If light exposure significantly modifies the ink's response to an applied electric field, this would validate the hypothesis that photoinduced polarizability enhancement is responsible for the observed printing behaviour.

Another important aspect to investigate is whether the enhancement effect is specific to 395 nm illumination or if it extends to other wavelengths. Future experiments should test printing performance under UV (365 nm), blue (450 nm), and green (520 nm) LEDs to determine whether the effect correlates with the quantum dot absorption spectrum or if it arises from a more general optical modification of the ink. If only wavelengths that overlap with the CdSe/CdS absorption spectrum induce significant changes, this would suggest that direct photoexcitation of the quantum dots plays a role in altering their dielectric response. However, if wavelengths beyond the absorption range also influence printing, it may indicate that optical excitation alters the ink-solvent interactions or modifies the surface energy of the ink droplets, indirectly affecting EHD printability.

Since this study focused on CdSe/CdS quantum dot inks in a 1:1 octane/hexadecane solvent system, it is also necessary to determine whether the observed light-enhanced printing effect is specific to this material system or if it can be generalized to other inks. Future research should examine whether similar enhancements occur with different quantum dot compositions (e.g., PbS, InP) or alternative colloidal systems. Additionally, testing printing performance with higher-polarity solvents could help assess whether solvent dielectric properties contribute to the observed effect. If light exposure improves printability across multiple ink formulations,

this suggests that optically controlled EHD printing could be broadly applicable to different nanomaterial deposition processes.

Finally, it is essential to investigate the long-term stability and reproducibility of light-assisted EHD printing to determine whether the observed enhancement remains consistent over multiple trials. Future studies should perform repeated printing experiments under controlled conditions, tracking changes in threshold voltage, dot uniformity, and printing efficiency over time. Additionally, the potential impact of prolonged optical excitation on ink stability should be evaluated, as photooxidation or prolonged charge accumulation could degrade ink performance over extended periods. If light-enhanced printing proves to be stable and reproducible, this approach could enable new strategies for high-precision patterning, spatially selective deposition, and tuneable material processing in advanced nanofabrication techniques.

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