Inkjet Printing of Epitaxially Connected Nanocrystal Superlattices

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Principal Investigator(s): Tobias Hanrath

User(s): Daniel M. Balazs, N. Deniz Erkan, Michelle Quien

Affiliation(s): School of Chemical and Biomolecular Engineering, Cornell University

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Contact: tobias.hanrath@cornell.edu, daniel.balazs@cornell.edu, nde26@cornell.edu, mq65@cornell.edu

Primary CNF Tools Used: Dimatix Printer

Abstract:

Access to a growing library of colloidal nanomaterials provides building blocks for complex assembled materials. The journey to bring these prospects to fruition stand to benefit from the application of advanced processing methods. Epitaxially connected nanocrystal (or quantum dot) superlattices present a captivating model system for mesocrystals with intriguing emergent properties. The conventional processing approach to create these materials involves assembling and attaching the constituent colloidal nanocrystals at the interface between two immiscible fluids. Processing small liquid volumes of the colloidal nanocrystal solution involves several complexities arising from the concurrent spreading, evaporation, assembly and attachment. The ability of inkjet printers to deliver small (typically picoliter) liquid volumes with precise positioning is attractive to advance fundamental insights into the processing science, and thereby potentially enable new routes to incorporate the epitaxially connected superlattices into technology platforms. This project identified the processing window of opportunity, including nanocrystal ink formulation and printing approach to enable delivery of colloidal nanocrystals from an inkjet nozzle onto the surface of a sessile droplet of the immiscible subphase. We demonstrate how inkjet printing can be scaled-down to enable the fabrication of epitaxially connected superlattices on patterned sub-millimeter droplets. We anticipate that insights from this work will spur on future advances to enable more mechanistic insights into the assembly processes and new avenues to create high-fidelity superlattices.

Summary of Research:

Bringing the heralded prospects of nanocrystal (NC) assemblies to fruition is contingent on better understanding of and control over the formation mechanism and the emerging structure-property relationships; both of these tasks rely critically on access to high-fidelity superlattices. Recent interfacial assembly and attachment studies point towards the need for more advanced processing methods to provide refined control over the delivery of the NC solution to the fluid interface. The volume of the deposited solution is a key consideration in the process of creating a liquid thin film from which NCs assemble on the surface of the sessile liquid subphase and attach to form epitaxially connected superlattices. Considering a typical NC colloidal concentration in the range of ~ 2-300 mg/ml, the formation of a monolayer NC film requires deposition of an ink film thickness of a least 100 nm. In the case of microliter droplets deposited from a conventional micropipettor, this film thickness requires spreading across an interface area of ~ 10^2 cm^2 [1]. Translating processing insights from earlier studies with cm2 scale surfaces to smaller interfaces in which dynamic processes can be better controlled therefore requires the ability to deposit smaller solution volumes. In this context, the ability of inkjet printers to deliver small (typically picoliter) liquid volumes with precise positioning is very attractive for both scientific and technological reasons. For example, Minemawari, et al. [2], successfully demonstrated inkjet printing of single crystals of organic semiconductors on the surface of micrometer-sized antisolvent droplet. Beyond providing an experimental testbed to refine our mechanistic understanding of the assembly and

PROCESS & CHARACTERIZATION

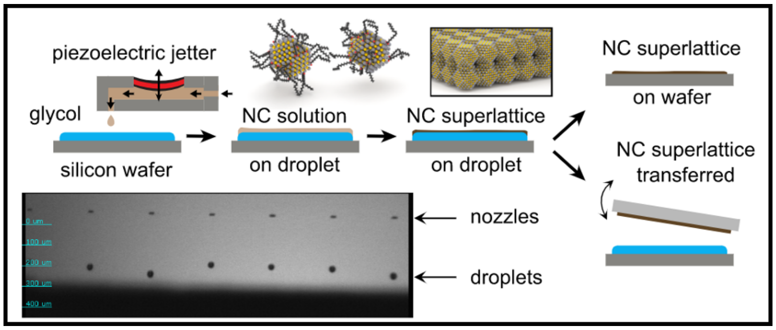

Figure 1: Sketch of the experimental setup. A colloidal NC ink is jetted on to of a sessile droplet of an immiscible subphase. NCs in the thin liquid film then assemble and attach to form an epitaxially connected superlattice (epi-SL) which can subsequently be transferred to a solid substrate.

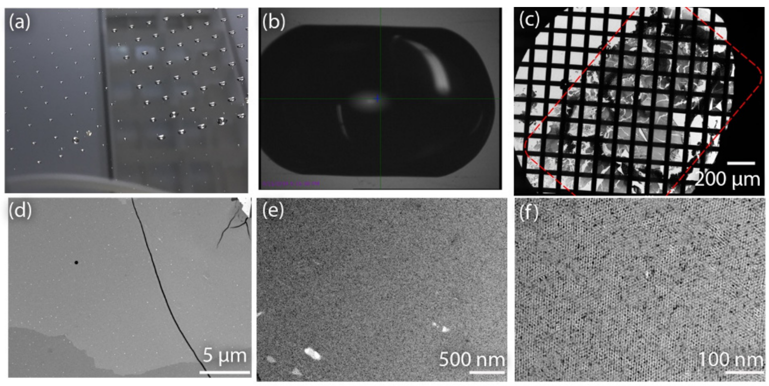

Figure 2: Multi-scale analysis of NC printed on patterned droplet. a) Optical image of droplets formed by spreading ethylene glycol on a patterned-fluorinated substrate; b) optical micrograph image of such a droplet; c) TEM image of a ~ 3 monolayer thick NC film prepared on a 1-by-1.5 mm droplet by inkjet printing; the shape of the droplet is marked showing complete spreading and coverage; d-f) the local homogeneity and superlattice structure are similar to those of samples prepared on larger scale.

attachment, inkjet printing of NC assemblies at fluid interfaces also has notable technological implications as this fabrication strategy could enable creation of epi-SLs in more complex geometries required for device integration. Inspired by these prospects, we set out to translate this approach to enable the delivery of colloidal NCs on top of an immiscible fluid interface.

In this project, we sought to build on these insights to identify a window of opportunities (including ink formulation and printing approach) to enable delivery of colloidal NCs onto the surface of a sessile droplet. Basic aspects of the processing workflow are summarized in Figure 1. We identified critical considerations for the NC ink formulation including NC solute concentration and NC surface ligand coverage, choice of solvent (with regards to NC solubility, vapor pressure and viscosity). The processing window of opportunity for stable inkjet printing is constrained by several factors. We examined inkjet printing of NC inks in the parameter space defined by the Reynold and Weber numbers. We established the basic relationship between fluid dynamic conditions during inkjet printing and the structural fidelity of the NC superlattice. We analyzed the structure of NC films formed on a geometrically contained droplet. The results of this project were recently published in Nano Research [3]. We anticipate that insights from this work will spur on future advances to enable more mechanistic insights into the assembly processes and new avenues to create high-fidelity superlattices.

References:

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