Inkjet-Printed Colloidal Quantum Dot Superlattices

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Primary CNF Tools Used: Dimatix printer

Abstract:

In this work, we investigated whether inkjet printing is a suitable method to form nanocrystal superlattices on top of (sub-)mm sized droplets or not. We identified the choice of solvent as a bottleneck in the process. We reviewed and adapted the common and system-specific constraints and found a suitable candidate. We successfully prepared highly ordered superlattices using dodecane, and explored the limitations of the approach.

Summary of Research:

Colloidal quantum dot (CQD) superlattices with epitaxial connections between the constituents are exciting bottom-up fabricated metamaterials with properties adjustable between zero and three dimensions. Assemblies can be achieved on solid substrates, but the shrinkage and consequent mechanical strain following the fabrication leads to cracks and low domain sizes. Liquid "substrates" offer the necessary translational and rotational freedom for highly ordered systems.

In this approach, a thin film of a liquid is layered onto an immiscible second liquid, with CQDs dissolved in the top phase and not soluble in the bottom phase [1]. The method works well on the centimeter scale when a microliter scale volume of the top liquid is manually injected using a pipette. Automation and scaling down to the sub-mm level require a different approach to liquid handling.

In this work, the CNF Dimatix Materials printer was used to jet picoliter sized droplets of a CQD solution onto an immiscible glycol droplet (see Figure 1a). The glycol droplets were created using patterned Si substrates; the two approaches used to contain the glycol are geometric contrast (created by etching wells of the desired shape into the wafer) and wetting contrast (created by lithographic definition of wetting and nonwetting regions, as shown in Figure 1b). While the former approach provided better glycol droplet stability, the latter allows the samples to be picked up by stamping for TEM characterization, and is more suitable for prospective integration into device fabrication processes.

The approach is a modified, more complex version of that developed for the creation of ordered polymer thin films [2]. The key problem we had to solve was the choice of solvent, as any common printing additives affect the superlattice assembly. Multiple thermodynamic and kinetic constraints need to be fulfilled for the formation of high-quality films. The constrains related to the inkjet printing stem from fluid dynamics: (a) the kinetic energy has to be higher than the surface free energy so that a droplet forms, (b) the droplet acceleration, the viscous and surface forces have to be in balance so that a droplet forms and does not fall apart and (c) the same forces need to allow the droplet to break off from the jetter [3].

These constraints are expressed in terms of the dimensionless Reynolds number ($Re = \rho v d/\gamma$) and Weber-number ($We = \rho v^2 d/\mu$) as $We < 1/16\ Re^2$, $We > 1/200\ Re^2$ and $We > 4$. The numerical relations are only approximate and strongly depend on the details of the instrument. However, the general idea applies: low enough surface tension and viscosity are required for droplets to form, but the droplets have to be stabilized by high enough viscosity and surface tension.

A fourth constraint is set by the aim that the jetted droplet does not splatter the subphase droplet [4]. This is described by $We' = \rho v^2 d^3/\gamma_s h_s^2 < 1$, where the subscript "s" indicates subphase property. Using EG, this can be converted into $We < 40$, suggesting that high viscosity and low jetting velocity are required. The constraint for spreading of the CQD solution on glycol is expressed as coefficient $S = \gamma_{02} - (\gamma_{01} + \gamma_{12})$, where 0 is air, 1 is top and 2 is bottom liquid; only a system with

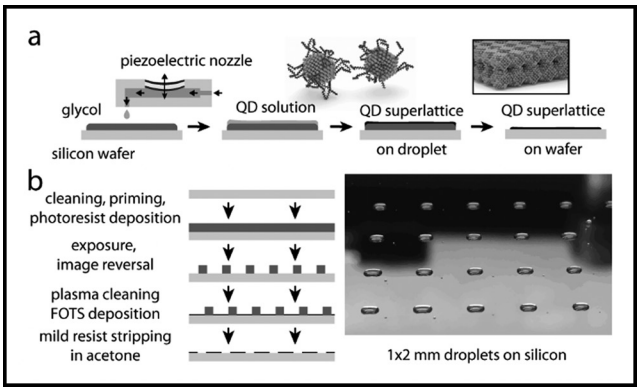

Figure 1: a) Scheme for the interfacial assembly of CQD superlattices using inkjet printing; b) scheme for creating droplets on substrates using wetting contrast and example droplets.

S > 0 fully spreads into a flat film. This constraint requires a solvent with low surface tension, in contrast with the high surface tension requirement of the jetting process. The final, and most important set of constraints is the immiscibility with glycol and high solubility of the CQDs. From all common solvents, alkanes with more than 10 carbon are the only suitable ones.

We performed a set of experiments with pure alkanes and their mixtures with polar solvents, and we found that dodecane is the only suitable candidate. Shorter alkanes, such as decane are not viscous enough for the jetting process (even dodecane requires a low velocity to form stable droplets), and longer alkanes do not spread well on glycol due to a high surface tension. However, we managed to optimize the jetting parameters for dodecane and the derived CQD solution without the use of additives. Example superlattices are shown in Figure 2. Good homogeneity and local order are observed in line with previous reports on large-scale samples [5].

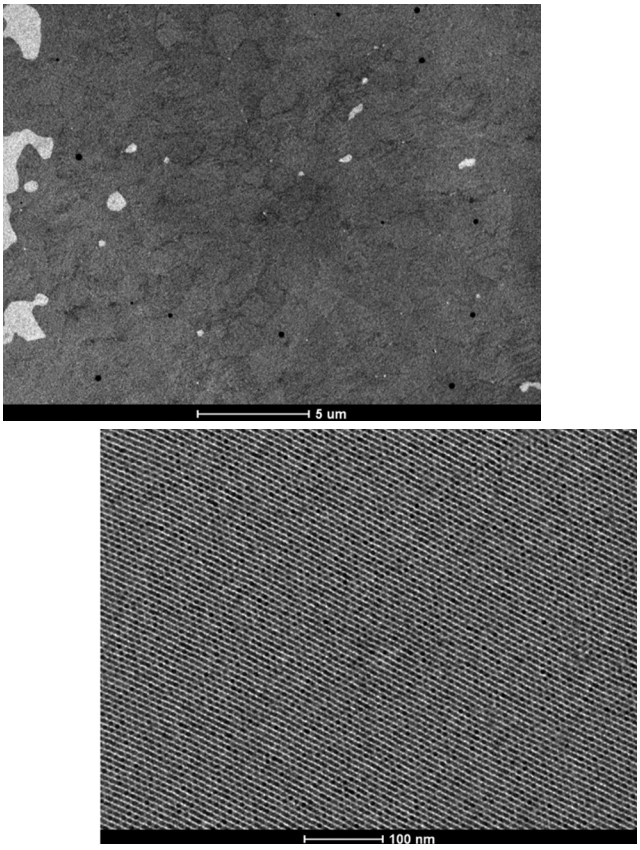

Figure 2: Two TEM images of CQD superlattices formed on glycol droplets via inkjet printing.

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