Multiscale Periodic Assembly of Striped Nanocrystal Superlattice Films on a Liquid Surface

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ABSTRACT: Self-assembly of nanocrystals (NCs) into periodically ordered structures on multiple length scales and over large areas is crucial to the manufacture of NC-based devices. Here, we report an unusual yet universal approach to rapidly assembling hierarchically organized NC films that display highly periodic, tunable microscale stripe patterns over square centimeter areas while preserving the local superlattice structure. Our approach is based on a drying-driven dynamic assembly process occurring on a liquid surface with the stripe pattern formed by a new type of contact-line instability. Periodic ordering of NCs is realized on microscopic and nanoscopic scales simultaneously without the need of any specialized equipment or the application of external fields. The striped NC superlattice films obtained can be readily transferred to arbitrary substrates for device fabrication. The periodic structure imparts interesting modulation and anisotropy to the properties of such striped NC assemblies. This assembly approach is applicable to NCs with a variety of compositions, sizes, and shapes, offering a robust, inexpensive route for large-scale periodic patterning of NCs.

KEYWORDS: Self-assembly, stripe pattern, nanocrystal superlattice, contact line instability, periodic patterning

Many structural patterns in nature form spontaneously via self-organization accompanied by energy dissipation in nonequilibrium processes. The formation of patterned surfaces through self-assembly of molecules, polymers, and micro-meter-sized colloids has been intensively pursued in the past decade, both for fundamental scientific interest and for many technological applications. Recent developments in colloidal synthesis allow the growth of metallic, semiconductor, and magnetic nanocrystals (NCs) monodisperse in size, shape, and surface functionalization. These uniform nanoscale building blocks enable the construction of ordered NC arrays (superlattices), which exhibit many properties that differ from their dispersed counterparts. In particular, NC superlattice thin films are emerging as an important class of materials for the fabrication of electronic and optoelectronic devices. Simple methods to rapidly (\(<1\) min) grow large-scale (~cm\(^2\)) NC superlattice films on arbitrary substrates represent significant advances in device fabrication. Another major challenge is developing inexpensive, lithography-free approaches to control the arrangement of NCs on multiple length scales. Prior studies have mainly focused on the pattern formation during the drying of NC dispersions on solid substrates and a wealth of dissipative patterns such as fractal aggregates, rings, and cellular networks have been observed. Such nonequilibrium drying processes have also been reported to yield well-aligned stripes of randomly packed NCs, providing modulation on the microscale without periodicity on the nanoscale. However, far fewer studies have explored the spontaneous microscale pattern formation upon drying NCs on a liquid surface, although liquid—air interfacial assembly such as Langmuir—Blodgett (LB) techniques are widely employed to prepare ordered NC monolayers. Here we present an unusual dynamic assembly process induced by the rapid drying of a NC dispersion in alkanes (hexane or pentane) on the surface of an immiscible polar organic sub-phase (acetonitrile, ethylene glycol, or diethylene glycol) under ambient conditions, enabling centimeter-scale, periodically striped NC superlattice films within 15 s. This facile multiscale assembly process is general for magnetic, metallic, semiconductor, and dielectric NCs and is compatible with heterogeneous integration processes.

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The right column (i–v) illustrates the detailed stripe formation process from the top view. The first- and second-formed stripes are labeled by “1” and “2”, respectively, to show the film sliding motion (indicated by blue arrows) in (iii) and (iv). The dashed oval in (iii) shows the subphase edge where the striped film grows.

Monodisperse NCs used for assembly are synthesized according to literature methods and are dissolved in hexane (or pentane) to form stable colloidal dispersions (see Methods in Supporting Information). The assembly process observed upon drop-casting a NC dispersion on the surface of acetonitrile confined in a Teflon well (∼2 × 2 × 2 cm³) is depicted in Figure 1. An NC monolayer forms immediately upon spreading the NC dispersion, while the remaining dispersion flows rapidly around the perimeter where the subphase surface contacts the Teflon wall (indicated by red arrows in Figure 1ii). The complete wetting of the subphase perimeter by the flowing dispersion initiates NC crystallization as hexane evaporates and a striped film grows from the subphase edge where the two dispersion streams converge (Figure 1iii). Once growth is triggered, the striped film keeps expanding across the subphase as NCs continuously crystallize from the dispersion reservoir pinned at the perimeter. This film growth is macroscopically manifested in the rapid sliding motion of the striped film on the subphase surface as it pushes the initially formed monolayer forward (Figure 1iii,iv). Upon reaching the opposite side of the well, the solid film front is redissolved in the dispersion reservoir. The striped film keeps growing and sliding unidirectionally until the evaporation of hexane is complete (typically <15 s) (Figure 1iv). The resulting striped film can be transferred from the subphase surface to any substrate previously immersed in the subphase (Figure 1).

Striped NC superlattice films are also obtained upon the dynamic assembly of NCs on the surface of acetonitrile confined in rectangular or circular Teflon wells or even on an acetonitrile droplet (∼2 cm in diameter) deposited on a flat Teflon plate. This latter assembly process is captured in Supporting Information Movie S1, where the solid film’s unidirectional sliding motion can be readily observed. These results indicate that the subphase shape and curvature have no significant influence on the dynamic assembly of NCs. The complete wetting of the subphase perimeter by the NC dispersion, regardless of the subphase geometry, is however a prerequisite to induce the striped film formation, with stripes oriented parallel to the contact line in all cases. It is noteworthy that the overall stripe orientations may be varied by controlling the subphase geometry and/or the location at which the drop of the NC dispersion is added (Supporting Information Figure S1), as the striped film typically starts to grow from the point of the Teflon well where the two dispersion streams converge and expands toward the point at which the NC dispersion has been added, as depicted in Figure 1.

Figure 2a shows a photograph of a SiO₂/Si wafer (∼1 × 1.5 cm²) coated with a striped film self-assembled from 10 nm Fe₃O₄ NCs (Figure 2b, inset). Optical microscopy reveals a pattern of parallel stripes with exceptional regularity at micrometer scale (Figure 2b), which accounts for the strong iridescent colors (structural color) as seen in Figure 2a. The diffraction of a laser beam (beam size = ∼1 mm²) by a striped NC film further...

Figure 1. Schematic of self-assembly and transfer of striped NC films.
confirmation of the periodic structure persisting over at least \(100\)\,\(\mu\)m\(^2\) areas (Figure 2c). The stripe periodicity is tunable from a few micrometers to tens of micrometers by changing the concentration of NC dispersions. In general, the interstripe spacing becomes narrower as the NC concentration increases (Supporting Information Figure S2). More significantly, the stripe formation is general in that it is independent of NC compositions, sizes, and shapes. Striped films are obtained upon the dynamic assembly of NCs with a broad range of compositions including metal oxides (10\,nm Fe\(_3\)O\(_4\), Figure 2b), metals (6\,nm FePt, Figure 2d), and semiconductors (7\,nm PbTe, Figure 2e). Self-assembly of non-spherical NCs such as nanorods (20\,nm \(\times\) 45\,nm NaYF\(_{4}\), Figure 2f) and nanocubes (10\,nm PbS, Figure 2g) also leads to striped films.

Atomic force microscopy (AFM) establishes that the stripes are of uniform height and pitch (Figure 3a–c), while scanning electron microscopy (SEM) reveals the detailed ridge structure of the stripes (Figure 3d–f) as well as the ordered nature of the underlying film (valley) (Figure 3g). Each ridge consists of terraced NC superlattices, the thickness of which typically ranges between 2 and 10 NC layers (depending on the concentration and volume of the NC dispersion applied), with the layer width gradually decreasing from bottom (\(\sim 1\)–\(2\)\,\(\mu\)m) to top (\(\sim 100\)\,nm), as seen in Figure 3f and illustrated in Figure 3h. The underlying film can be adjusted from monolayer to multilayer also by varying the NC concentration (Supporting Information Figure S3). Of particular significance is that long-range-ordered NC superlattice structure is preserved despite the dynamic, far-from-equilibrium assembly process, as evidenced by high-resolution SEM (HRSEM) (Figure 3g) and transmission electron microscopy (TEM) (Supporting Information Figure S4).

The striped film formation appears to be governed by a combination of NC self-assembly and other drying-mediated physical events occurring at the three-phase (air–solvent–substrate) contact line. A characteristic feature of the assembly process is the unidirectional motion of the growing film upon the complete wetting of the subphase perimeter by the NC dispersion. A detailed mechanism for this motion is yet to be determined and may be rather complex, as the driving force may result from the interplay of many parameters such as the surface tension and wetting properties of two liquid layers. However, our observations indicate that the film motion is closely related to the solvent evaporation rate as well as the subphase viscosity. When the Teillon well is covered with a glass slide during the solvent evaporation, the film sliding motion is suppressed, yielding an unstriped but well crystallized NC superlattice film (Supporting Information Figure S5). This result indicates that the rapid evaporation of hexane (or pentane) plays a key role in driving the dynamic assembly of NCs, which is further supported by the fact that no film motion or stripe formation are observed if higher boiling solvents such as heptane or octane are used. When a subphase of high viscosity such as ethylene glycol is used, the film sliding rate is reduced, resulting in stripes having uniform height but less uniform interstripe spacing (Supporting Information Figure S6). This result indicates that the lower viscosity of subphases like acetonitrile enables rapid motion of the growing film, which is important for the formation of highly periodic stripes. Although efforts are made to find conditions for stripe formation on an aqueous subphase, only unstriped monolayers or multilayers are obtained, consistent with earlier studies.\(^{24–36}\)

Previous studies of drying-induced pattern formation on solid substrates have demonstrated that stripes can form by two distinct mechanisms of the three-phase (air–solvent–substrate) contact line: (I) the stick–slip motion, where the stripes are parallel to the contact line,\(^2,4,23,32\) and (II) a fingering instability, where the stripes are perpendicular to the contact line.\(^{23,31}\) Monitoring the subphase edge where the stripped film nucleates (indicated by the dashed oval in Figure 3ii) allows us to visualize in situ pattern formation by optical microscopy. Ethylene glycol is chosen as the subphase on which the growing film slides relatively slowly, allowing better observation of the contact-line behavior, although the resulting stripes are less uniform in periodicity.

As revealed by optical microscopy (Supporting Information Movie S2), the striped film continuously grows from the NC dispersion front at the subphase edge, propagating like a wave across the subphase, with stripes parallel to the contact line. A snapshot of Supporting Information Movie S2 is given in Figure 4a. These findings suggest our stripe formation process is analogous to the contact-line stick–slip motion, while further observation reveals that these stripes are formed by a new type of contact-line oscillating instability that has not been observed previously. Figure 4b schematically illustrates the pattern formation mechanism that is proposed based on the observation of the contact-line motion. We surmise that, as the film is sliding on the subphase, the film or the accompanied subphase flow stretches the NC dispersion front (meniscus) until a critical contact angle...

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**Figure 3.** (a) AFM height image of a striped film consisting of 10\,nm Fe\(_3\)O\(_4\) NCs (scan size = 45 \(\times\) 45\,\(\mu\)m\(^2\)). (b) Height analysis of the profile as indicated in (a). (c) Three dimensional AFM image of the film. (de) SEM images of a striped Fe\(_3\)O\(_4\) NC film at low and high magnifications, respectively. (f) HRSEM image of a single ridge as indicated in (e). (g) HRSEM image of the underlying film as indicated in (e). (h) Schematic of the striped NC superlattice film.
is reached. This leads to the pinning of the contact line for a finite period of time (on the order of milliseconds estimated from Supporting Information Movie S2) (Figure 4bii). The greater solvent evaporation rate near the dispersion front drives NCs to pile up at the pinned contact line.4,7,32 The subsequent nucleation of NCs as a ridge relaxes the pinning force, enabling the contact line to recede, depositing a smooth layer of NCs until the next pinning event (Figure 4biii). Because of the continuous film motion as well as the steady NC supply from the dispersion reservoir, the contact line keeps moving back and forth (oscillating) at the subphase edge, resulting in a periodically striated film that is seen to be continuously extruded from the dispersion front. This type of contact-line instability is distinct from the conventional stick–slip process on a solid surface where the slippage occurs in the direction perpendicular to stripes, showing anisotropy in electrical transport.

The facile transfer of the liquid-supported films also allows the creation of complex, higher-order architectures, as those shown in Figure 5 where bilayer films with tunable stripe orientations are produced by sequential transfer of striped NC films (6 nm FePt) films to SiO$_2$/Si wafers. Insets show the corresponding SEM images. (c) TEM image of the 12-fold quasicrystalline-like Moiré pattern that develops upon stacking two layers of 15 nm Fe$_3$O$_4$ NCs. Inset shows the small-angle electron diffraction pattern. (d) TEM image of a bilayer film consisting one layer of 10 nm Fe$_3$O$_4$ NCs and one layer of 6 nm FePt NCs. Inset shows the magnified view.

The periodic structure is found to impart property modulation to NC films, which will expand the NC applicability in solid state devices. To demonstrate this, we incorporate striped PbSe NC films onto quartz substrates prepatterned with Au electrodes and measure the spatially resolved photoc conductivity (see Methods in Supporting Information). The film is treated with hydrazine to enhance the conductivity.4,10 Despite some aggregates arising from hydrazine treatment, the stripe pattern is preserved as revealed by optical microscopy (Figure 4c, top). An oscillatory behavior in photocurrent is observed as the film is scanned under the laser excitation (Figure 4c, bottom), which correlates well with the stripe’s periodic structure. The 2D photocurrent mapping over a large area (20 × 20 μm$^2$) provides a detailed examination of the spatially resolved photoc conductivity (Supporting Information Figure S8), confirming the higher photoc conductivity exhibited by the ridges. We note these ridged thin films are ideal architectures for photovoltaic applications, as corrugated structures have been reported to significantly enhance device performance due to the high interfacial area between the donor and acceptor components.39,40 In addition to the modulated properties, such striped NC films also display interesting in-plane anisotropic properties. The electrical transport measurements show the conductivity along the stripe direction is 20 times larger than that in the direction perpendicular to stripes (Figure 4d). Furthermore, cracks are found to propagate preferentially along the ridges in fractured NC films (Supporting Information Figure S9), suggesting anisotropy in mechanical properties.

Figure 5. (a–b) Optical micrographs of bilayer films with meshlike structures, which are formed by sequential transfer of striped NC (6 nm FePt) films to SiO$_2$/Si wafers. Insets show the corresponding SEM images. (c) TEM image of the 12-fold quasicrystalline-like Moiré pattern that develops upon stacking two layers of 15 nm Fe$_3$O$_4$ NCs. Inset shows the small-angle electron diffraction pattern. (d) TEM image of a bilayer film consisting one layer of 10 nm Fe$_3$O$_4$ NCs and one layer of 6 nm FePt NCs. Inset shows the magnified view.
with different NC compositions are also accessible by sequential film transfer (Figure 5d), providing a simple, efficient way to fabricate multilayer NC superlattice films with arbitrary constituents. Future work can certainly benefit from the ability to form and transfer large-area NC superlattice films.42

In summary, our studies have established a robust approach that harnesses contact-line oscillatory instabilities to direct rapid assembly of NCs into large-area, periodically striped NC films. This far-from-equilibrium assembly process depends largely on the solvent evaporation rate and on the subphase viscosity, rather than on the NC composition, size, and shape. Therefore, it is applicable to a variety of colloidal NCs and may be extendable to other systems such as micrometer-sized colloids and polymers. The ability to transfer the striped NC superlattice films enables the fabrication of devices as well as the rational design of complicated architectures. NC device applications have been growing rapidly in recent years and the push to integrate NC films to solid state devices will be accelerated dramatically by the ability to control the order on both microscopic and nanoscopic scales and the opportunity to harness the intrinsic anisotropies in such periodically modulated NC assemblies.

ASSOCIATED CONTENT

Supporting Information. Experimental details, additional optical, TEM and SEM images, and real-time movies showing the dynamic assembly of striped NC films and the stripe formation process. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(18) Talapin, D. V.; Murray, C. B. Science 2005, 310, 86–89.