Assembling nanocrystal superstructures

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Morphological Control over Nanoplatelet Thin Films and Nanowires

The day we stop exploring is the day we commit ourselves to live in a stagnant world, devoid of curiosity, empty of dreams.

— Neil deGrasse Tyson

The planar design of optoelectronic devices favors the use of 2D materials. However, the high fabrication costs of these materials discourage their use on the market. The recent advances in colloidal synthesis have allowed the production of colloidal quantum wells, semiconductor nanoplatelets (NPs), with the potential of cutting fabrication costs while keeping a high sample quality standard. To be used as active layer in macroscopic devices, NPs must be assembled in a close-packed thin film, displaying morphological uniformity over several micrometers. Here, we assemble NPs at the air/liquid interface in 2D patches several micrometers-large, distinctly displaying nematic order. We show that this configuration is the most energetically favored, and that the edge-to-edge distance between neighboring NPs can be tuned by ligand exchange. This closer packing allows a more efficient electronic coupling between NPs,
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as directly observed through the red-shift of optical resonances. Finally, we direct the assembly of NPs into stacked superstructures by exploiting depletion interactions, to form nanowires several micrometers-long. The degree of control over the colloidal assembly of NPs reported here opens up new possibilities for the development of optoelectronic devices based on NPs.
6.1 Introduction

Optoelectronic devices typically feature a planar design. This device architecture is ideally suited for 2D optoelectronic materials: In these materials, charges are confined to the plane of conduction, where they can travel freely. Unfortunately, traditional fabrication methods for these materials employ slow and expensive techniques such as molecular beam epitaxy, atomic layer or chemical vapor depositions, discouraging large-scale use. [140] [141] Recently, this scenario has dramatically shifted with the development of efficient and inexpensive synthetic routes for semiconductor nanocrystals, with nanoplatelets (NPs) representing particularly promising candidates. [125] [142]

Semiconductor NPs are 2D colloidal nanocrystals characterized by a well-defined thickness of a few atomic monolayers, while their lateral dimensions lie in the range of several nanometers. [125] To form the active layer of a macroscopic device, NPs must be assembled into a thin film. While a variety of nanocrystal assembly methods exists. [143] the evaporation-driven assembly at the air/liquid interface is probably the most promising, having been used to grow 2D crystalline films of spherical and rod-like nanocrystals. [144] [147] In fact, this method has also recently been used to drive the assembly of semiconductor NPs into face-down or edge-up superstructures. [148] However, because of their large surface area per unit volume, NP assembly is strongly biased by surface effects when compared to 3D nanocrystals; as an example, the addition of antisolvent can result in stacks of NPs, rather than in a 2D film. [149]

While the assembly of NPs remains an active area of research, the pressing issue of ligand exchange of the assembled superstructures has also risen. NPs are typically passivated by organic ligands consisting of aliphatic chains connected to a functional group bound to the surface, e.g. oleates (OA). These ligands are electronically insulating, and a ligand exchange with shorter ligands is necessary to boost film conductivity. [56] [123] Therefore, next to the assembly of NPs into 2D films, a ligand exchange method that does not disrupt film morphology is also needed.

In this chapter, we investigate the assembly of CdSe NPs at the air/liquid interface. We show that this procedure leads to the assembly of NPs into 2D thin films several micrometers wide. Subsequently, we assess the influence of ligand exchange on the morphology of NPs films. We conclude that while ligand exchange with short ligands stabilized by thiolate or carboxylate groups does not disrupt film morphology, the use of sulfonate groups results in a disordered film. Finally, we direct the assembly of NPs into nanowires several micrometers-long by exploiting depletion interactions with an excess of free ligands in solution of $\geq 10^2$ per NP.
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6.2 Experimental details

![Figure 6.1: Schematics of NP deposition and assembly process. (a) A dispersion of NPs in toluene is layered on ethylene glycol. (b) The toluene phase evaporates in time. (c) After complete evaporation, NPs form a dense film at the interface. (d) Schematic of NP dispersion before assembly. (e) Schematic of NPs assembled in a 2D thin film.](image)

We synthesize $l = 21.3 \pm 1.6 \text{nm}$ long, $w = 5.6 \pm 0.8 \text{nm}$ wide and $t = 1.2 \text{nm}$ thick CdSe NPs passivated with OA ligands according to a procedure reported in the literature. $[129]$ The low aspect ratio of 3.8 was purposely chosen to minimize NP twisting that can make the assembly in 2D films challenging. $[56][150]$ A 1mL volume of $\approx 1.2 \times 10^{-8} M$ NP dispersion in toluene was gently layered on top of 3.5 mL of ethylene glycol placed in a glass petri dish in the fume hood (Figure 6.1a). The petri dish was immediately covered with a watch glass to slow down evaporation, and left untouched for overnight (Figure 6.1b). Upon toluene evaporation, the NPs assembled in a thin film (Figure 6.1c-e). The NP superstructures were collected by placing a substrate in the subphase held by a tweezer and gently raising it through the air/liquid interface. The choice of substrate ranged from carbon-coated TEM grids to quartz substrates made hydrophobic after being treated with 3-mercaptopropyl trimethoxysilane. $[151]$
6.3 Results and discussion

6.3.1 Nanoplatelet assembly in 2D thin films

The microscopic investigation of the assembled film shows patches several micrometers wide, consisting of lighter and darker regions (Figure 6.2a). While the darker regions consist of disordered multilayers, a closer inspection reveals that the lighter regions consist of NPs lying face-down, that is, with the [001] crystallographic direction parallel to the normal to the substrate and assembled in a one NP-thick 2D film (Figure 6.2b). The assembled NPs show a degree of orientational and translational order, qualifying the structure as smectic with a grain size of a few hundred nanometers. The figure’s inset shows the assembled superstructure magnified. The translational order is further confirmed by the Fourier transform of the image, identifying two dominant frequencies indicated by colored circles. The lower frequency, \( q_1 = 0.27 \text{nm}^{-1} \), corresponds to the center-to-center distance of NPs measured along the long-axis, resulting in an average edge-to-edge distance of \( d_1 = 2\pi/q_1 - l \approx 2.0 \text{nm} \). Instead, the higher frequency, \( q_2 = 0.77 \text{nm}^{-1} \), corresponds to the center-to-center distance of NPs measured along the short-axis, resulting in an average edge-to-edge distance of \( d_2 = 2\pi/q_2 - w \approx 2.6 \text{nm} \). Using standard bond lengths and angles, an OA ligand can be approximated as a cylinder of length \( \ell = 1.9 \text{nm} \): Since both \( d_{1,2} < 2\ell \), we conclude that either OA ligands on neighbouring NPs are interdigitating, or a low ligand surface coverage characterizes the edges of NPs, allowing OAs to bend away from the normal to the edge. Recent work supports the latter scenario, since ligands bound on facet edges appear to be the most labile. In either case, this observation suggests that ligands play an active role in the assembly of NPs.

NPs can also assemble in a disordered fashion, although less frequently observed (Figure 6.2c). This is typically the case for sub-micrometer patches such as the one visible at the bottom-right edge of Figure 6.2a (arrow). If the rate of evaporation is too high, nanoplatelets may not have enough time to pack in an ordered fashion and aggregate in a disordered, kinetically trapped superstructure. Interestingly though, NPs still assemble with the same crystallographic orientation with respect to the substrate as in the case of ordered superstructures. Irrespective of kinetics, the energetically most favourable configuration seems to be the one that maximizes the NP surface area in contact with ethylene glycol. This result may seem unexpected: The hydrophobic nature of OA ligands should minimize the contact with hydrophilic ethylene glycol. We can justify this apparent discrepancy by surface tension arguments. By laying flat, each NP replaces an area \( A_{\text{flat}} \) of interface between air and ethylene glycol with an interface between oleic acid and ethylene glycol, therefore saving \( \Delta E_{\text{flat}} = (\gamma_{\text{air/EG}} - \gamma_{\text{OA/EG}}) A_{\text{flat}} = (\gamma_{\text{air/EG}} - \gamma_{\text{OA/EG}})(l + d_1)(w + d_2) \approx 7 \times 10^{-18} \text{J} \approx 1800 k_B T \) in interfacial energy, where \( \gamma_{\text{air/EG}} \approx 47.7 \times 10^{-3} \text{J/m}^2 \) is the surface tension of
Figure 6.2: Nanoplatelets assembled at the air/liquid interface. (a) Low-magnification STEM micrograph of assembled nanoplatelets. Lighter areas correspond to a monolayer of NPs, while darker areas correspond to 3D aggregates. The arrow indicates a smaller patch consisting of NPs assembled in a disordered fashion. (b) Intermediate-magnification micrograph of nanoplatelets assembled in a monolayer. Top inset: Ten-fold magnified detail of the monolayer. Bottom inset: Fast Fourier transform of the original image. (c) Intermediate-magnification micrograph of nanoplatelets assembled in a disordered fashion. Inset: Ten-fold magnified detail of the superstructure.
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Figure 6.3: Effect of ligand exchange on ordered NP superstructures. Representative micrographs of assembled NPs ligand exchanged with TG (a), EDT (b), and DMPS (c) ligands. (d) Influence of ligand exchange on the edge-to-edge distance of NPs in superstructures. Insets are ten-fold magnified. (e) Light-absorption spectra of NP superstructures before and after ligand exchange (full lines). Dashed lines indicate the absorption spectra after subtraction of the spectrum of NPs passivated with OA. (d) and (e) do not report the data relative to ligand exchange with DMPS because this resulted in low-density, disordered films with measured light-absorption below the experimental detection limit.

\[
\begin{align*}
\gamma_{OA/EG} &= \sqrt{\gamma_{air/OA}} - \sqrt{\gamma_{air/EG}}^2 \approx 8.7 \times 10^{-3} \text{J/m}^2 \\
k_B &\text{ is Boltzmann’s constant, and } T \text{ is the temperature.}
\end{align*}
\]

The same NP laying on the edge would save

\[
E_{\text{edge}} = (\gamma_{air/EG} - \gamma_{OA/EG})A_{\text{edge}} = (\gamma_{air/EG} - \gamma_{OA/EG})(l + d_1)(t + d_3) \approx 5 \times 10^{-18} \text{J} \approx 1200k_B T,
\]

to a higher energy configuration. It should be noted that these estimates are rather conservative since considering the area spanned by the ligands effectively decreases the ratio \(A_{\text{flat}}/A_{\text{edge}}\) from \(\sim 4.7\) (no ligands) to \(\sim 1.5\) (ligands). Taking this into account, we propose the intervals of confidence: \(E_{\text{flat}} = 1100 - 1800k_B T\) and \(E_{\text{edge}} = 200 - 1200k_B T\) which better illustrate that NPs laying face-down minimize the surface energy of the system.
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6.3.2 Ligand exchange and film morphology

To be used as active film in optoelectronic devices, the film of NPs must be conductive. Therefore, the native insulating OA ligands must be replaced with shorter molecules allowing for charge transport. We tested the influence of ligand exchange on the superstructures by using three different thiolated ligands: 1,2-ethanedithiol (EDT), thioglycolate (TG), and 2,3-dimercapto-1-propanesulfonate (DMPS). The ligand exchange was performed after superstructure formation, by adding a sufficient volume of 0.2M solution of ligand to the subphase to obtain a final concentration of $3 \times 10^{-3} M$ in ethylene glycol. The ligand exchange has a considerable effect on the NP superstructures, as shown in Figure 6.3. Ligand exchange with TG or EDT ligands did not disrupt significantly the smectic order. Surprisingly instead, exchange with DMPS resulted in a disordered film (Figure 6.3a-c); we tentatively attribute this effect to the larger electron cloud of the sulfonate group providing a stronger electrostatic inter-NP repulsion. By analyzing the Fourier transforms of the images, we extract the distance between neighboring NPs for the different ligands (Figure 6.3d). Ligand exchange with TG and EDT decreases the inter-NP distance dramatically, reaching a shortest edge-to-edge distance along the short-axis of $d_1 \sim 0.2 \text{nm}$ after the ligand exchange with EDT. This value is likely limited by the resolution of the instrument.

When nanocrystals are in such close proximity, coupling effects are expected to arise. Optical spectroscopy can be useful to probe the strength and nature of these effects. Thus, we measure the optical absorption spectrum of NP films before and after ligand exchange, full lines in Figure 6.3. The spectrum of NPs passivated with OA is characterized by a band-edge at 509 nm and sharp excitonic features. After ligand exchange, these features are substantially modified, the most remarkable effect consisting in the appearance of an additional electronic transition below the band-edge at 529 nm. This transition is present for both TG- and EDT-exchanged samples. To harness valuable information relative to this new transition, we take the difference between the absorption spectra after and before ligand exchange, dashed lines in Figure 6.3. The result consists in an absorption spectrum remarkably similar to the film of NPs before ligand exchange, but with all transitions red-shifted by 20 nm. By taking the intensity ratio of shifted and unshifted transitions, we quantify that a subset of 46% TG-exchanged and 44% EDT-exchanged NPs shows the observed redshift. We associate the nature of the redshift to the decrease in inter-NP distance induced by ligand exchange: as the long OA ligands are replaced by shorter TG or EDT molecules, the electronic states of individual neighboring NPs can couple more efficiently, leading to coupled states at lower energy by $\Delta E \approx 92 \text{meV}$. We can imagine these coupled states as the nanocrystal analogue of molecular orbitals, where electrons occupy the bonding orbital positioned at a lower energy respect to the uncoupled atomic levels. For the sake of clarity, we consider other effects that may result
in a shift of electronic states. Ligand dipole-related effects can be easily refuted, as they would identically affect states in the valence and conduction band, but not the absorption spectrum. Another possibility could be nanocrystal-ligand state-mixing, but this effect is not expected with the ligands under consideration here but rather with thiostannate complexes or conjugated molecules. We thus conclude that the coupling between NPs is indeed the cause of the redshift of excitonic features in the absorption spectrum.

### 6.3.3 Nanoplatelet assembly in stacked superstructures

The route to improving crystalline domain size goes through a deeper understanding of colloidal interactions. Improving the colloidal stability of NPs should allow the superstructure more time to reach its minimum energy configuration, therefore yielding larger crystallites. At the beginning of the assembly NPs are stabilized by OA ligands; therefore, we try to increase the colloidal stability of NPs by improving surface passivation. To do so, we add an excess of $10^3$ OA ligands per NP to the NP dispersion in toluene prior to the layering on the ethylene glycol phase. To our great surprise, the microscopic investigation of the superstructures collected after complete evaporation of the hydrophobic phase revealed a markedly different morphology: Nanowires several micrometers long, and consisting of NPs stacked along the [001] crystallographic direction (Figure 6.4a-c). This morphology is further confirmed by small-angle X-ray scattering, revealing diffraction peaks at $q^* = 1.187 \text{nm}^{-1}$ and $2q^*$, Figure 6.4d. The positions of these diffraction peaks agree well with a real-space interparticle distance of $t + d_3 = 2\pi/q^* = 5.3\text{nm}$, as indicated in Figure 6.4c.

To obtain insight into the kinetic detail of the assembly of NPs, we measure the decay of the correlation function of the light scattered at the interface between the hydrophobic and hydrophilic phases, as toluene evaporates (Figure 6.5a). The decay of the correlation function, $g_2(\tau)$, is due to the Brownian motion of the scattering objects. Specifically, the hydrodynamic radius, $R_H$, of scattering objects is directly proportional to the correlation function decay time $\tau_c$ via $R_H = (k_BT/6\pi\eta)q^2\tau_c$, where $\eta$ is the solvent’s viscosity, $q = (4\pi n/\lambda) \sin(\theta/2)$ the scattering vector, $n$ is the solvent’s refractive index, $\theta = 90^\circ$ the scattering angle, and $\lambda$ the wavelength of the laser used to probe the dynamics. In time, $\tau_c$ shifts to longer delay times as a result of the increase in effective size as the NPs assembly, Figure 6.5b. By fitting each correlation function to an exponential decay with decay time $\tau_c(t)$, we can extract the dynamic change of $R_H(t)$ during NP assembly (Figure 6.5c). The initial hydrodynamic radius $R_H(0) = 22\text{nm}$ is consistent with the size of NPs used here, indicating that NPs are well dispersed at the beginning of the experiment. The hydrodynamic radius progressively increases as a function of time over the duration of the experiment, to reach values of $\sim 500\text{nm}$. We thus directly observe the assembly process as it unfolds. We use this technique to understand more about the role of the excess...
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Figure 6.4: NP nanowires. (a) Low-, (b) intermediate-, and (c) high-magnification STEM micrographs of micrometer-long nanowires consisting of stacked NPs obtained with an excess of $10^3$ OA per NP. (d) Azimuthally-averaged small-angle X-ray scattering pattern of stacked NPs in toluene in the presence of excess OA ligands. Inset illustrates the morphology of the stacked superstructures.

ligand in the assembly process. To do so, we vary the amount of excess OA added to the toluene phase at the beginning of the experiment, in a range from $1$ to $10^4$ ligands per NP. Changing the excess amount of ligands influences the assembly kinetics, as
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Figure 6.5: NP assembly kinetics in the presence of excess OA ligand. (a) Schematic of the geometry of the measurement. (b) Scattered light intensity correlation function measured during the assembly for an excess of $10^2$ OA ligands per NP. (c) Hydrodynamic radius as a function of assembly time for samples featuring a wide range of excess OA ligands per NP. Inset: Late time kinetics and single-exponential fits. (d) Characteristic $t^*$ assembly times for a wide range of excess OA ligands per NP.

demonstrated by plotting the characteristic time $t^*$ defined as $R_H(t^*)/R_H(0) = e$ as a function of the number of excess ligands per NP (Figure 6.5d). For relatively low ligand concentrations, $1 - 10$ OA/NP, the characteristic growth time, $t^*$, is unaffected; however, when adding more ligands the growth kinetics first slow down and then speed up, ending up with overall faster assembly kinetics.

Nanoparticle assembly can be characterized by diffusion- or reaction-limited kinetics. [156] In the latter case, the average cluster size, $R$, increases exponentially in time: $R(t) = R_0 \exp(t/t^*)$. The aggregation process measured here is consistent with
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Figure 6.6: Influence of depletant branching. NP assembled in the presence of the indicated excess of OA (top) and HDA (bottom) ligands per NP. Both ligands result in similar stacked superstructures. Insets are ten-fold magnified.

reaction-limited kinetics, as shown by the exponential fits in the inset of Figure 6.5c. Energetically, reaction-limited aggregation is described by a pair-potential consisting of a repulsive barrier $E_b$ that can be overcome with probability $p \sim \exp(-E_b/k_BT)$, resulting in irreversible aggregation. This barrier is typically the result of superposition of repulsive with attractive components. Here, the repulsive interaction can be identified in the steric repulsion by long OA ligands grafted onto the surface of NPs. Instead, the short-ranged van der Waals attraction eventually results in irreversibly bound NPs. However, the observation of aggregation kinetics that depend on the molar excess of ligands suggests the presence of a second attractive interaction, that must depend on ligand concentration: We identify this interaction as depletion. [33][157] with OA micelles acting as the depletant. When two NPs collide and their interparticle distance decreases below $d < 2\ell$, the volume $\Delta V$ between the surfaces of NPs becomes depleted of micelles and results in an increase in the total volume that can be occupied by the depletant $V_0 \rightarrow V_0 + \Delta V$, and therefore in a decrease in free energy by an amount proportional to $c\Delta V$, where $c$ is the concentration of micelles. Hence it follows that stacked NPs represent the lowest energy configuration in presence of a depletant, since stacking results in the largest increase in depleted volume.
for this nanocrystal geometry: $\Delta V = 2\ell(l + d_1)(w + d_2)$, where $2\ell$ is the diameter of an OA micelle. Increasing the concentration of depletant should result in monotonically faster assembly, contrary to our observations for low concentrations, Figure 6.5d. We suggest that assembly kinetics initially slow down because of the improved NP passivation by the excess added ligands, therefore increasing the steric contribution. Once depletion becomes the dominant interaction, the assembly kinetics do become monotonically faster in time as expected. To exclude secondary effects, such as the energetically favored ligand-ligand interdigitating contribution promoted by the improved surface passivation, we use a different depletant, 2-hexyldecanoic acid (HDA). Due to the branched nature of HDA, we expect ligand interdigitation to play a minor role in this case. Yet, microscopic investigation of NPs assembled in the presence of $10^3 - 10^5$ molar excess HDA reveals nanowires consisting of stacked NPs, very similar to what we observed with excess OA (Figure 6.6). We therefore conclude that depletion interaction indeed plays a key role in the assembly of NPs into nanowires in presence of an excess amount of ligands.

6.4 Conclusions

We have shown that the assembly of NPs spans a rich phase-space of superstructure morphology. By exploiting assembly at the air/liquid interface, NPs can assemble face-down into patches several micrometers-large featuring smectic order with ordered grains of hundreds of nanometers. Ligand exchanging these ordered superstructures results in a marked decrease in the edge-to-edge distance down to sub-nanometer spacings; we deemed these low spacings favorable to electronic coupling, allowing the individual NP wavefunction to leak to the nearest neighbors. Finally, by modulating the pair potential through depletion interaction we directed NP assembly to obtain nanowires several micrometers long consisting of stacked NPs. We anticipate that by improving further our understanding of interparticle interactions and nanocrystal energetics we should be able to produce optical devices that actively respond to external stimuli, simultaneously modifying superstructure and function.