Chapter 3
Self-Assembly of Colloidal Nanocrystals

Abstract We describe different approaches to colloidal nanocrystal self-assembly and review the reports where different NC superstructures were constructed using these techniques.

Keywords Self-assembly · Solvent destabilization · Evaporation · Langmuir–Blodgett · Binary nanocrystal superlattices

Quantum dots (QDs) are sometimes referred to as “artificial atoms”, partly due to the spherical volume they occupy, but mostly because of their atom-like, discrete electronic structure near the band edge [1]. Similar to atoms binding to one another through covalent, metallic, or ionic bonding, colloidal nanocrystals (NCs) can also attach themselves to each other, in most cases through van der Waals interactions between their ligands [2]. Therefore, it is in principle possible to use NCs as building blocks of NC superstructures, similar to the way atoms make up matter. Intensive effort has thus been put into making ordered NC superlattices from monodisperse NC colloids. Highly emissive, perfectly color tunable nanoemitters as they are, for an important part of the applications they are employed in, colloidal NCs need to be deposited onto substrates in the form of thin NC films. Self-assembly techniques can help forming such films of ordered, close-packed NC superlattices in the desired dimensions at the macro scale.

In general, self-assembly refers to the spontaneous arrangement of individual entities into an ordered structure [3]. Before the particles assemble themselves, they are collectively in a mobile state where they can move freely or with a certain degree of freedom. During the self-assembly process, the system “cools off” to a thermodynamically favorable state wherein the particles come together in an ordered structure. Self-assembly is initiated by destabilizing the system so that the particles are enforced to exist in another stable state. The properties of the self-assembled structure are determined by the particle–particle interactions as they come into proximity, or the interactions between particles and the surroundings, as well as the ambient conditions under which self-assembly takes place.
The tendency of nanoscale particles into forming ordered structures under appropriate conditions has been known long before the colloidal NCs. Proteins and peptides [4, 5], DNA [6–8], fatty acid molecules [9, 10], and organic dyes [11, 12] are among the particle systems with which self-assembly is extensively studied. These organic superstructures find applications in biosynthesis, electron transport, and nanosensing [13].

In the case of colloidal NCs, the most common approaches for self-assembly are based on solvent destabilization or solvent evaporation. Solvent destabilization can be initiated by adding an anti-solvent to the NC solution in order to create ordered NC aggregates. Evaporation-based self-assembly can be carried out directly on the substrate, or on a liquid surface, to be subsequently transferred to the substrate. Below we briefly review these different approaches.

3.1 Common Approaches to Colloidal NC Self-Assembly

The first studies on colloidal NC self-assembly are almost as old as the colloidal NCs themselves and since then a vast collection of literature has been generated on this topic. Herein, we will merely present a description of some of the most common methods with a few examples for each. Readers interested in a deeper perspective on NC self-assembly can refer to the seminal review of Boles et al. [3].

3.1.1 Solvent Destabilization

Colloidal solutions remain stable as long as there is a counteracting force to van der Waals attraction between the particles. For the colloidal NCs, this counteracting force stems from the ligands attached to the NC surface. The addition of a non-solvent to the NC solution can reduce this steric barrier against particle flocculation and give rise to NC aggregation [14]. This aggregation of NCs can be exploited to create NC superlattices. With this approach, micron-sized NC superlattices that are visible under optical microscope were previously created [15, 16]. These superlattices can adopt different shapes in solid state including a disk, a polyhedron, and a sphere [3].

The schematic depiction of PbSe QDs assembly with solvent destabilization is depicted in Fig. 3.1a. Herein, controlled addition of isopropanol into the PbSe NC ensemble dissolved in toluene results eventually in a clear isopropanol-toluene interface. When the vial with the separate phases is sealed, the two phases slowly diffuse into each other, which leads to the formation of PbSe NC superclusters on the inner walls and at the bottom of the vial. The TEM imaging (Fig. 3.1b) and the X-ray scattering measurements (Fig. 3.1c, d) on the superclusters reveal that they have a body-centered cubic crystal structure with long-range ordering [16].
3.1 Common Approaches to Colloidal NC Self-assembly

Fig. 3.1  
(a) Controlled addition of isopropanol (IPA) into a colloidal dispersion of PbSe NCs in toluene, leading to “slow diffusion” and in turn aggregation of NCs into micron-sized clusters. 
(b) Scanning electron micrograph (SEM) of the ordered PbS NC superclusters. Scale bar: 20 nm. Inset: FFT of the SEM image. 
(c) Small- and (d) wide-angle X-ray scattering patterns of the NC superclusters in [111] projection. 
(e) Doctor blade-assisted evaporation-based self-assembly of Fe₃O/CoFe₂O₄ colloidal NCs on a silicon substrate. 
(f) Transmission electron micrograph (TEM) showing face-centered cubic (fcc) and hexagonal close-packed (hcp) arrangements in the self-assembled QD ensemble. 

a–d adapted with permission from [16]. Copyright 2018 American Chemical Society. 
e, f Adapted with permission from [17]. Copyright 2010 American Chemical Society

3.1.2 Solvent Evaporation on Substrate

NC self-assembly with solvent evaporation on solid surfaces has first been demonstrated with CdSe QDs [18] shortly after the emergence of the colloidal QDs. In this work, a mere 10% of octanol was added as a destabilizing agent to a QD dispersion of octane and the solvent was slowly evaporated at 80 °C. The resulting macrocrystals had sizes ranging from 5 to 50 µm [18]. Similar long-range ordering has been obtained with PbSe NCs dissolved in hexane:octane (9:1) mixture, directly drop-casted onto a substrate [19]. The presence of octane here slows down the evaporation and allows controlled deposition of the NCs. The evaporation-based self-assembly has also been used in combination with a doctor blade, which was used for facilitation of the spreading of the NC solution across the solid substrate after the drop-casting,
during the solvent evaporation (Fig. 3.1e). The oleic acid-capped Fe$_x$O/CoFe$_2$O$_4$ core/shell spherical NCs self-assembled in this work have film thickness ranging from 1 to 3 monolayer and display local formation of face-centered cubic and hexagonal close-packed superlattices (Fig. 3.1f) [17].

Construction of NC superlattices can be extended to ensembles composed of multiple species of NCs. Using evaporation-based approaches, binary nanoparticle superlattices (BNSLs) of semiconductor–semiconductor [20], metal–semiconductor [21, 22], and metal–metal nanoparticles [23] have been created (Fig. 3.2a–h). The crystalline structure of the BNSL is determined by the choice of different size ratios of the nanoparticle moieties as well as the stoichiometry (i.e. concentration ratio) of the two different species in solution. Using PbSe QDs of two different sizes and CdSe QDs, formation of a ternary superlattice on TEM a grid has also been demonstrated (Fig. 3.2i) [24].

![Fig. 3.2 a–h Binary nanocrystal superlattices (BNSLs) of colloidal CdSe and CdTe QDs self-assembled using slow evaporation on TEM grid. Formation of cuboctahedral-AB$_{13}$, icosahedral-AB$_{13}$ and AB$_2$ crystal structures are observed with different ratios $\gamma_{\text{eff}}$ of radii of CdSe and CdTe QDs and different stoichiometries of theirs in solution. Adapted with permission from [20]. Copyright 2008 American Chemical Society. (i) Coexistence of icosahedral AB$_{13}$ (ico-AB$_{13}$) and cuboctahedral AB$_{13}$ (cub-AB$_{13}$) lattice structures in a BNSL of PbSe and Pd nanoparticles. Adapted with permission from [22]. Copyright 2005 American Chemical Society](image-url)
3.1.3 **Langmuir–Blodgett Deposition**

Evaporation of an NC solution can be carried out not only on solid substrates but also on liquid surfaces, to be subsequently transferred to a substrate. The assistance of a liquid medium for controlled thin film deposition has a history of more than 100 years in the Langmuir–Blodgett (LB) technique, commonly for deposition of fatty acid molecules with a functional group that is soluble in water attached to an alkyl chain that is not (e.g. oleic acid and stearic acid). As the NCs are commonly encapsulated by such long organic chains, they can also be deposited as thin films using the LB technique. This process is illustrated in Fig. 3.3a for organic-capped QDs. The QD solution is dropped on water and spread across the water interface. After the evaporation, the QDs floating on the water surface are compressed by the movable barriers of the Langmuir trough until they become a tightly packed monolayer. The previously submerged substrate is then lifted off vertically at a constant, slow speed while the barriers keep compressing the QD monolayer to maintain the surface pressure. At each step of lift-off or immersion, an additional QD monolayer is deposited onto the substrate.

![Fig. 3.3](image)

**Fig. 3.3** a Schematic description of layer-by-layer deposition of self-assembled QD monolayers using Langmuir–Blodgett (LB) method. [i] Dropping the QD solution onto water surface, [ii] Evaporation of the QD solvent, [iii] Compression of the QDs by the barriers, [iv] substrate lift-off, and [v] immersion. b Fluorescence image of a four-monolayer thick ZnS/CdSe core/shell QD film prepared using LB deposition on a glass slide. Adapted with permission from [25]. Copyright 2008 American Chemical Society. c TEM imaging of one LB-deposited CdSe QDs monolayer. Adapted with permission from [26]. d Absorbance of multilayered CdS QD films on glass slide. Reprinted with permission from [27]. Copyright 1994 American Chemical Society.
Deposition of highly uniform NC films with LB technique has been demonstrated for core and core/shell QDs [25–27]. Such films display homogeneous brightness across the substrate, as seen in Fig. 3.3b. The TEM image in Fig. 3.3c shows the tight packing of an LB-deposited monolayer of CdSe QDs on a TEM grid [26]. The precision in thickness control can be observed via absorbance measurements of LB films having a different number of QD monolayers (Fig. 3.3d). Herein, the absorbance at the peak of the band-edge is seen to be proportional to the number of QD monolayers on film, which demonstrates high throughput of the LB deposition [27].

For a historical background on LB technique, the readers are referred to [28–32]. Reviews that focus on LB deposition of inorganic NCs are also available [33, 34].

3.1.4 Self-Assembly at Liquid Interfaces

A more recent approach on NC self-assembly is known as liquid–air (or liquid–liquid) interface self-assembly. Similar to the LB deposition, a liquid surface is also employed here prior to the transfer of NC membrane onto the film. However, with the liquid interface self-assembly, the barrier for the membrane compression is not a requirement as much smaller beakers than a regular Langmuir trough are used to contain the subphase. The resulting NC membranes after evaporation can have a thickness of more than one monolayer, in contrast to the sub-monolayer thickness of the initial membrane in the LB method. In addition, while LB films are deposited one monolayer at a time at successive immersion and lift-off steps, the transfer of self-assembled membrane in liquid interface self-assembly is usually composed of a single step [35, 36].

The procedure of liquid interface self-assembly is schematically described in Fig. 3.4a. The NCs dissolved in an organic, nonpolar solvent are dropped onto a polar subphase (e.g. water, acetonitrile and ethylene glycol). As this subphase is immiscible with and denser than the NC solvent, the NC solution stays on top without mixing with the subphase and spreads across the interface. A thin membrane of NCs is formed after solvent evaporation. As the substrate is removed, part of the NC film is transferred to it.

An interesting display of the capabilities of liquid interface self-assembly is demonstrated with Fe$_3$O$_4$ NCs dispersed in hexane [37]. Using acetonitrile or ethylene glycol as the polar subphase, the formation of stripe-shaped macro-scale patterns has been observed during the self-assembly via fast evaporation of the NC solvent (Fig. 3.4b–f). Formation of the stripe patterns has been attributed to the two different streams of NC solvent interfering with each other, one traveling through the subphase perimeter and the other flowing across the liquid interface. The pattern formation has been observed only when complete wetting of the subphase perimeter by the NC dispersion is achieved. To ensure the complete wetting of the subphase perimeter, the NC solution is dropped from one of the edges of the square-shaped Teflon well [37].
Liquid interface self-assembly also enables large-area deposition of BNSLs, as demonstrated with Fe₃O₄ and FePt nanoparticles [35]. Using diethylene glycol as the subphase, long-range ordering in the AlB₂-type crystalline structure has been observed. The thickness of the superlattice is changing between one to three unit cells, pointing to multilayered deposition, albeit partially. Similar BNSLs have been achieved with Fe₃O₄ and Au nanoparticles (Fig. 3.4g–i) [38]. Using two differently sized Fe₃O₄ NCs and FePt metal nanoparticles, a ternary NC superlattice has also been observed in the same work (Fig. 3.4j). BNSLs of non-spherical nanoparticles have been demonstrated with GdF₃ rhombic platelets and Gd₂O₃ tripodal platelets assembled on the diethylene glycol interface [39]. Both species are seen to form one-dimensional stacks of their own kind, while stacks of rhombic platelets are enclosed by stacks of tripodal platelets on both sides (Fig. 3.4k). TEM imaging in Fig. 3.4l reveals the alternating stacks of rhombic and tripodal platelets in one direction, with ordering on micrometer scale lengths [39].

The liquid–air interface can also be used as a medium for surface functionalization of the NC membranes before the transfer of the membrane onto the substrate. This approach has been employed with the ligand exchange of indium tin oxide (ITO) NCs.
on the dimethylsulfoxide interface [40]. The exchange of native organic ligands of ITO NCs with a shorter, more conductive phthalocyanine derivative, which acts as a cross-linker between neighboring NCs, has been carried out, while the membrane of ITO NCs resides on the interface. The NC film has been transferred to the substrate after the completion of the ligand exchange. The resulting ITO thin films show conductivity that can be as much as nine orders of magnitude higher than films of ITO NCs capped with native organic ligands [40]. Another related report demonstrated the annealing of PbSe NCs on the ethylene glycol interface [41]. Herein, aniline is used as the oleate stripping agent, which results in the fusion of neighboring PbSe NCs into each other on their (001) facets, creating a 2D NC array with enhanced charge mobility [41].

3.2 Self-Assembly of Anisotropic Nanocrystals

In solid ensembles of anisotropic NCs such as quasi-one-dimensional nanorods (NRs) or quasi-two-dimensional nanoplatelets (NPLs), there is one additional degree of freedom in comparison with the spherical NCs, namely the particle orientation. In such quantum confined nanostructures, the orientation can dictate the direction-dependent electronic and optical properties, interparticle interactions, and as a result, the ensemble properties. Therefore, being able to control the in-film orientation of anisotropic NCs are of great interest.

The aforementioned methods of NC self-assembly can also be used for orientation-controlled deposition of anisotropic NCs. In the case of NRs, vertically oriented ensembles have been obtained with evaporation-induced self-assembly (Fig. 3.5a) [42, 45]. Horizontal alignment of NRs has been achieved using LB technique (Fig. 3.5b) [43]. With liquid–air interface self-assembly, it has been possible to deposit NR multilayers in either fully horizontal or fully hexagonal packing [44]. Control of NR orientation is achieved by using different subphases in the self-assembly deposition (Fig. 3.5c–e). The changes in the preferential NR orientation have been attributed to the differences in viscosities, surface tensions, and dielectric constants of the polar subphases used in the study [44]. With the vertically oriented NR ensembles, polarization-dependent response to excitation has been observed with excitation anisotropy as high as 0.45, while virtually no excitation anisotropy was recorded for randomly oriented or horizontally aligned NRs (Fig. 3.5 f–h). These results indicate that liquid interface self-assembly can be an alternative to using the external electric field for alignment of nanowires [44].

The initial studies on self-assembly of colloidal NPLs have been conducted utilizing destabilization-based self-assembly. In a destabilized NPL solution, NPLs tend to aggregate by attaching to each other on their lateral faces, which results in the formation of one-dimensional NPL chains. This phenomenon is known as NPL stacking.

Early studies on stacked NPLs revealed that the optical properties of stacked NPL ensembles differ from nonstacked ones. For example, giant (>10 µm-sized)
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Fig. 3.5  TEM image of vertically oriented NRs deposited via evaporation-induced self-assembly. Adapted with permission from [42]. Copyright 2010 American Chemical Society. **b** Horizontally aligned NRs via Langmuir-Blodgett deposition. Inset is the Fourier transform of the TEM image. Adapted with permission from [43]. Copyright 2001 American Chemical Society. TEM image of NR ensembles self-assembled using **c** dimethylacetamide, **d** diethylene glycol, and **e** water as the subphase. **f**–**h** Photoluminescence intensity versus polarization angle of excitation for ensembles in **c**–**e**, respectively. Adapted with permission from [44]. Copyright 2015 American Chemical Society

clusters of unidirectional NPL chains created by ethanol-induced stacking displayed polarized photoluminescence (PL) emission (Fig. 3.6a, b), with the polarization of a single micron-sized “needle” as high as 71% [46]. The strong axis of polarization is perpendicular to the axis of the needle (Fig. 3.6b), hinting that the emission dipoles of NPLs are confined in-plane. In-plane emission dipoles in core NPLs have been later verified using liquid-interface assisted self-assemblies of NPLs [47].

Our work on stacking of colloidal NPLs revealed that the degree of stacking in an ensemble affects the optical performance of the NPLs drastically. In this work, we have used varying amounts of ethanol to control the degree of stacking. Gradually adding ethanol to an NPL ensemble and taking steady-state and transient PL measurements at each step, we have confirmed that the increasing degree of stacking causes a reduction in the PL lifetime (Fig. 3.6e) as well as quantum yield (Fig. 3.6f). These modifications could be well explained by energy transfer-assisted charge trapping inside NPL stacks, of which the effect is increasingly more significant as the number and length of NPL stacks grow [48]. Diffusion of excitonic energy by ultra-fast nonradiative energy transfer within a stack has been further verified by monitoring the diffusion of the PL emission on locally excited NPL stacks (Fig. 3.6c, d) [49]. Herein, the authors added excess oleic acid into the NPL solution and initiate slow evaporation to create NPL stacking. A similar approach had been previously used to create NPL stacking as well as twisting in the individual NPLs in a stack [50]. It is also possible to change the length of stacked NPL chains by varying the concentration of excess oleic acid [51].
Fig. 3.6  a Needle-like assemblies of colloidal CdSe nanoplatelets (NPLs), together with the schematic of NPL stacks within the needles. b Polarization dependence of the photoluminescence emission of NPL microneedles. c Migration of excitonic energy within an NPL stack via ultrafast intra-stack nonradiative energy transfer. d Recorded photoluminescence (PL) along a one-dimensional NPL chain that is locally excited. e Change in the PL decay of an NPL ensemble controlled by the degree of stacking (i.e. amount of ethanol added to the solution). f Decrease in PL quantum yield of an NPL ensemble with the increasing degree of stacking. a, b Adapted with permission from [46]. c, d Adapted with permission from [49] e, f Reprinted with permission from [48]. Copyright 2014, 2020 American Chemical Society

The aforementioned studies are a clear indication that controlling NPL orientation is essential not only to understand the anisotropy in the NPLs but also to utilize it. The work of Gao et al. [47] paved the way for using liquid interface self-assembly to control NPL orientation on solid films. In Chap. 4, we will delve into the follow-up work and more recent progress on self-assembly of NPLs on liquid interface.
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