Chapter 6
Conclusions and Future Outlook

Abstract We summarize our report and briefly review the properties of self-assembled NPLs in each orientation that can be useful for optoelectronic applications. We finalize with prospects and possible future directions that can be investigated with the liquid air interface NPL self-assembly.

Keywords LEDs · VCSELs · Charge transport · Energy transfer · Heterostructures

Self-assembly of Cd-based colloidal NPLs at liquid interfaces gained interest toward the end of the 2010s, not very long after the seminal work of Dong et al. that introduced this approach for the deposition of binary nanocrystal superlattice films [1]. Unlike the spherical nanoparticles, the anisotropic shape of the NPLs presents an additional challenge due to the two possible in-film orientations. The reports that have been published thus far met this challenge, creating assemblies with large (up to cm²-scale) domains in the film with a single NPL orientation, with various approaches in terms of experimental parameters and means of orientation control. We have presented a comparative overview of these studies, discussing both the self-assembly aspect and the potential applications of these orientation-controlled thin films.

Figure 6.1 shows differences in face-down and edge-up NPL ensembles and how these properties can be exploited in various optoelectronic applications. It has been shown that out of the two orientations, fluorescence takes place more efficiently in the face-down because stacking leads to the enhancement of FRET-assisted exciton trapping (exciton “sink” into the defected sub-populations of NPLs, if any) in the edge-up ensembles, which results in the reduction of photoluminescence (PL) efficiency (Fig. 1a) [2]. Thus, stacking should be avoided when NPLs that are not near-unity efficient are used as emitters. Face-down orientation is also favorable for NPLs that are to be employed as optically active media for LEDs or vertical-cavity surface-emitting lasers (VCSELs) (Fig. 1b). In the case of LEDs, the in-plane dipole of face-down NPLs can significantly increase the outcoupling efficiency of the electroluminescent light [3]. For VCSELs, both components of the in-plane NPL dipole can contribute to the out-of-plane emission, which propagates in the same direction.
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Fig. 6.1 To stack or not to stack, that is the question: Whether it is wiser to lay nanoplatelets (NPLs) down horizontally, or to make an ensemble of vertically standing NPLs, depends on the application and the feature of the NPLs that is desired to be utilized. 

- **a** Face-down ensembles of NPLs are more emissive than their edge-up counterparts due to the acceleration of energy-transfer assisted exciton trapping in NPL stacks, which reduces photoluminescence efficiency. Adapted with permission from [2]. Copyright 2014 American Chemical Society.
- **b** Out-of-plane emission from face-down NPLs is desirable for devices such as LEDs for enhancement of light outcoupling efficiency and for vertical-cavity surface-emitting lasers (VCSELs), in which in-plane dipole emission can couple into vertical cavity modes more efficiently. Schemes on the left side of the panel are reprinted with permission from [3]. Copyright 2019 American Chemical Society.
- **c** An edge-up NPL monolayer acts as a stronger FRET acceptor than a face-down monolayer. As an exciton sink layer, edge-up orientation can be preferred. Adapted with permission from [4]. Copyright 2019 American Chemical Society.
- **d** The conductivity of edge-up NPL films is superior to face-down films, irregular films with no particular orientation, or in-solution NPLs [5, 6]

As the cavity modes. Therefore, a VCSEL with face-down NPLs as the gain medium can be expected to outperform a VCSEL with edge-up NPLs.

Even though face-down NPLs are typically more emissive than edge-up ensembles, edge-up NPLs can still be valuable and find use in devices. Förster resonance energy transfer (FRET) from QDs to a monolayer of NPLs can take place more efficiently when the NPL monolayer adopts the edge-up configuration (Fig. 1c) [4]. These stacked NPLs have thus potential to be used as an efficient exciton collector layer in exciton harvesting applications. The capability of charge transport was also reported to increase with vertical orientation. Studies of photoconductivity on NPL ensembles carried out via terahertz spectroscopy revealed that the conductivity of
NPLs is much larger for the edge-up orientation than for the face-down [5] (Fig. 1d). These results have been later corroborated with the mobility measurements on edge-up NPL films with stacks as long as 1 µm and on irregular NPL ensembles with no long-range alignment or preferential orientation [6]. The electrical conductivity in the stacked NPL films has been observed to be larger than in the irregular film. Furthermore, charge mobility has been shown to increase with the average length of the stacked NPL chains. These results demonstrate how the NPLs in stacked configuration can be employed in thin film transistors [6].

It is therefore evident that using the proper NPL orientation is essential while employing NPLs in optoelectronics. Liquid air interface self-assembly provides a versatile tool to achieve this control on device scale, not only for exploiting the anisotropy of the NPLs but also to study and understand it.

The capability of constructing multilayered NPL films via sequential deposition of self-assembled NPL monolayers enabled the observation of optical gain and lasing from NPL films with only a few tens of nm thicknesses [7–9]. This paves the way for the realization of electrically pumped NC lasers, for which thicker films would impede pumping because organic ligands act as a barrier against charge transport [10]. In this case, switching to inorganic ligands via a ligand exchange procedure might not be necessary to maintain electrical pumping.

The high precision in film thickness via sequential monolayer deposition means that the self-assembled NPL monolayers can be used as building blocks for creating two- or three-dimensional NPL superstructures. These multilayered films can be combined with other nanofabrication tools such as electron beam lithography to create more sophisticated structures in film [11]. Furthermore, as this technique is readily applicable to other classes of organic-capped NCs, such as quantum dots [1] and nanorods [12], the construction of heterostructures of different classes of NCs is also possible in a layer-by-layer fashion. The prospect of mixing different types of NCs, as well as the different choices of orientation in the case of anisotropic NCs provide additional degrees of freedom for a wide range of possible NC superstructures that can be constructed using liquid interface self-assembly.

References