Chapter 1
Introduction

Abstract We begin by giving a short overview of colloidal nanoplatelets, and we explain why their orientation-controlled assemblies are of particular interest. We finalize the chapter by giving an outline of our brief.

Keywords Colloidal nanocrystals · Nanoplatelets · Thin films · Self-assembly

About a decade ago, colloidal semiconductor quantum wells (CQWs) have emerged as the latest class of II–VI colloidal nanocrystals (NCs) [1]. Commonly referred to as nanoplatelets (NPLs) today, this class of NCs is distinct from its predecessors in that they have quasi-two-dimensional (2D) shape with atomically precise thickness, to which they owe most of their favorable properties. These properties include one-dimensional quantum confinement, enhanced optical absorption and spectrally narrow absorption, and photoluminescence (PL) emission, which manifested themselves in low-threshold optical gain and lasing [2–4], LEDs with high color purity [5, 6], and efficient solar energy concentration [7].

Due to their quasi-two-dimensional shape, NPLs also possess intrinsic anisotropy. The weak or no confinement of the generated electron–hole pairs, i.e. excitons, across the lateral dimensions and their strong confinement along the vertical dimension, which is typically not more than a few nm, causes the generated excitonic dipoles to be oriented in-plane, and the resulting anisotropy [8]. This is in contrast to spherical QDs, which emit equally in all directions, indicating a random orientation of the emission dipole within. The prospect of directionality in NPL ensembles has been first demonstrated by the observation of polarized light out of needle-like micrometer-long NPL superstructures [9]. Later, it was shown that the far-field emission pattern of the core NPLs is mostly out-of-plane, which is possible only when the dipoles are confined within the NPL plane with no particular preference along either of the two lateral dimensions [8].

Such directionality of light is highly desirable for certain optical and optoelectronic applications. In NC-LEDs, for instance, replacing isotropic emitters (e.g. QDs) with out-of-plane emitting NPLs can result in a significant enhancement in the outcoupling efficiency of the electroluminescence of the emitters and thus the

O. Erdem and H. V. Demir, *Oriented Self-Assembly of Colloidal Semiconductor Nanoplatelets on Liquid Interfaces*, Nanoscience and Nanotechnology,
https://doi.org/10.1007/978-981-19-7052-8_1

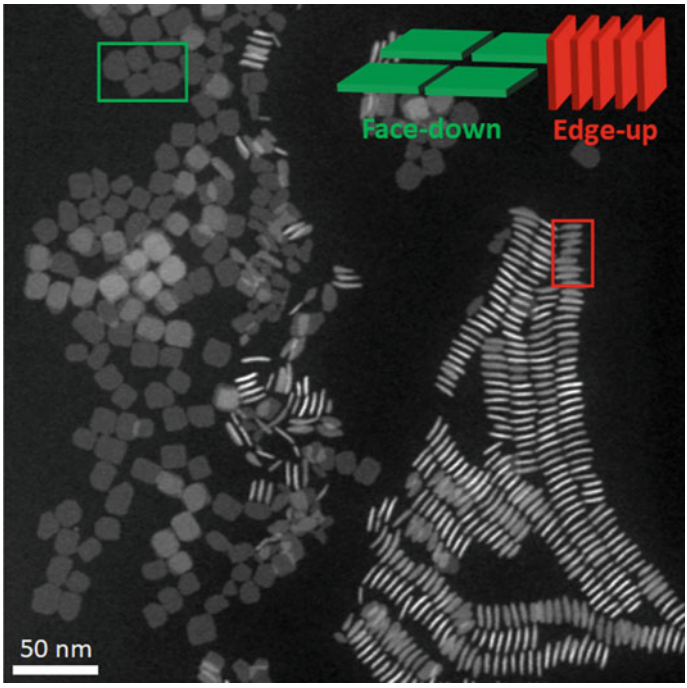

Fig. 1.1 Transmission electron micrograph of CdSe nanoplatelets in face-down (horizontal) or edge-up (vertical) orientations. Inset schematically shows these two orientations co-existing in the ensemble

external quantum efficiency of the device, to the point of exceeding the limit of 20% [10]. Similarly, vertical-cavity surface-emitting lasers can also benefit from such directional emission. However, to make use of their directionality, NPLs must be first directed into the proper orientation when incorporating them into the devices; and given the latest research on the subject, this task proved to be nontrivial.

Being quasi-2D quantum wells with several tens of nm lateral dimensions and a few nm vertical thickness, NPLs can commonly adopt one of two orientations on a solid surface: They can either lie flat on one lateral surface, or they can stand on one of their peripheral edges. The former of these orientations is usually referred to as "horizontal" or "face-down", and the latter as "vertical" or "edge-up". These two orientations are depicted schematically as well as with the transmission electron microscopy (TEM) image in Fig. 1.1. The horizontally oriented NPLs can be seen to be lying flat, with their lateral surface parallel to the TEM grid. On the other hand, vertically oriented NPLs are seen to be standing together on their peripheral edges. Such edge-up NPLs tend to form one-dimensional NPL chains in the ensemble. These structures are called NPL stacks, and the phenomenon of their formation is called *stacking*.

It is quite common for NPL ensembles such as the one in Fig. 1.1 to be in a mixed orientational state, where some NPLs prefer a face-down orientation, while others are stacked. However, this sort of disparity within the ensemble is hardly desirable in terms of utilizing the anisotropic optical properties of the NPLs. For instance, using such films with mixed orientation, it would not be possible to determine the band-edge dipole orientation of the NPLs as done by Gao et al. [8]. It was also demonstrated that NPL stacking can be detrimental to the PL efficiency of the NPL ensembles due to accelerated nonradiative energy transfer within NPL stacks [11, 12]. The findings of these earlier works show that NPLs in an undesired orientation can lead to difficulties in the characterization of the NPLs as well as a decrease in optical performance. It is therefore of utmost interest to control and select the orientation of the NPLs in an ensemble and uniformly dictate it across the ensemble as desired.

In this brief, we overview the self-assembly of NPLs at liquid interfaces, which not only enables control of NPL orientation in film but also makes it possible to construct device scale, highly uniform two- and three-dimensional NPL superstructures with the NPL orientation controlled. Previously, employed to make densely packed superstructures of quasi-0D quantum dots [13, 14] or quasi-1D nanorods [15], liquid interface self-assembly also proves to be useful in controlling both in-film NPL orientation and the film thickness. As the NPLs start to be incorporated into optoelectronic devices and these devices keep shrinking in size, a precise, reproducible method of deposition will be required. Liquid interface self-assembly has the potential to fulfill this requirement as a robust methodology that is adaptable to different NPL compositions.

We begin in Chap. 2 by giving a brief overview of colloidal semiconductor NCs, and specifically nanoplates. In Chap. 3, the background of self-assembly at liquid interface is given, starting all the way from 100-year-old Langmuir–Blodgett films to the state-of-the-art self-assembly of colloidal NCs. We discuss our methodology on NPL self-assembly at liquid interface, as well as other studies and approaches in Chap. 4. In Chap. 5, the utilization of self-assembled NPLs in optoelectronics will be presented. Our concluding remarks and a future perspective are given in Chap. 6.

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