Manipulation of the Optical Properties of Colloidal 2D CdSe Nanoplatelets

Zitong Zhang and Handong Sun*

Driven by the unique optoelectronic features arising from the strong quantum confinement along the thickness direction, rapid development of CdSe-based nanoplatelets (NPL) has accomplished facile bandgap tunability over a broad spectrum via different preparation protocols or various postsynthesis treatments. The anisotropic geometry of NPLs also stimulates the exploitation of self-assembled CdSe NPL superstructures to enhance light extraction efficiency in display technologies and achieves polarized lasing performance or even electrically pumped laser by adjusting the transition dipole orientation. Although several review articles about the general optical properties of CdSe NPLs have been published, none of them focus on the ability of spectral tunability and precise control of orientations in the solid-state phase of CdSe NPLs. Herein, the band structure engineering approaches in the CdSe NPL family are systematically summarized and the optical properties and device performance metrics of these deliberately engineered NPLs are compared. Then, the recent advanced studies of the motivation and assembly methods of geometrically anisotropic CdSe NPL superlattices are discussed. Finally, the current challenges and future outlook on the controlled modification of optical features and the influences of the approaches in the aspect of CdSe NPL–based devices’ performance are highlighted.

1. Introduction

When the physical dimension of materials becomes comparable to the size of the exciton Bohr radius, carriers restricted in these physical dimensions sense strong quantum confinement effects. Meanwhile, the density of states, which plays a decisive role in their optical and electrical properties, evolves from discrete states for 0D quantum dots (QDs) to sprak-like feature for 1D nanorods (NRs) till the step-like feature for 2D nanoplatelets (NPLs). The first successful synthesis of 2D zinc blende CdSe NPLs with controlled atomic-layer thicknesses via the hot-injection method was realized in 2008.[2] Colloidal CdSe NPLs with ultrathin thickness exhibit the strongest quantum confinement effects along the [001] axis direction.[3] Thanks to the precise control of the uniform ultrathin thickness over the whole CdSe NPL ensemble, narrow emission linewidth,[4] large absorption cross-sections,[5] and giant oscillator strengths[6–8] have been reported in these colloidal CdSe NPLs. Moreover, the band-edge wavelength from each population of CdSe NPLs is varied in a discrete manner, which leaves a large spectral gap upon mere alternation of the thickness of NPLs at atomic scale.[8] However, a substantial number of uncoordinated groups exist on the surface of CdSe NPLs due to the large surface-to-volume ratio. These unpassivated surface states act as nonradiative centers that accelerate nonradiative recombination processes and impede the performance of CdSe NPL–based photonic devices.[9,10] For this reason, passivation strategies, such as CdSe-based NPL heterostructures,[11,12] with inorganic semiconductor layers on the surface and optimization of the surface-ligand chemistry,[13] are proposed in the subsequent research. CdSe NPLs with several monolayer (ML) thickness show great sensitivity on the dielectric environment.[14] Thus, changes in the surrounding environment will impart significant effects on the band structures, reflecting on the continuous tuning of the absorption onset and photoluminescence (PL) peak positions. Previous studies on conventional quantum well semiconductors have shown that controlled doping with covalent elements is a powerful strategy to tailor the optoelectronic properties of materials of interest.[15] Inspired by the broad emission tunability by the introduction of dopant centers, controlled doping[16,17] has been used in CdSe NPLs to extend the emission wavelength to a wide range from 393 (purple) to 880 nm (deep red). Figure 1 summarizes the resulting PL quantum yields (PLQY) and linewidths as a function of PL peak positions of the corresponding CdSe-based NPLs prepared by different synthesis methods. As shown in Figure 1, different synthetic strategies will lead to NPL products with dramatic differences in emission properties. For instance, by simply increasing the vertical thickness of CdSe NPLs, the PL peak positions discretely redshift in a broad range while their linewidths still maintain less than 20 nm. However, these pristine NPLs suffer from low emitting efficiencies. By introducing metal dopants

Z. Zhang, Prof. H. Sun
Division of Physics and Applied Physics
School of Physical and Mathematical Sciences
Nanyang Technological University
21 Nanyang Link, Singapore 637371, Singapore
E-mail: HDSun@ntu.edu.sg

* The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adpr.202100045.

© 2021 The Authors. Advanced Photonics Research published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adpr.202100045
Importantly, previous theoretical and experimental work without light extraction structures is greatly hindered by the theoretical upper limit of peak external quantum efficiencies (EQE, determined as the rate of the amounts of radiated photons to the amounts of injected carriers) reaching 20%.\(^{56}\) Importantly, previous theoretical\(^{57}\) and experimental\(^{58}\) works have demonstrated that the EQE can be boosted from 20% to 40% after aligning all random-oriented anisotropic molecules into oriented emitters films. The enhancement of the EQE could be explained by the highest electroluminescence (EL) contribution from the dominant in-plane transition dipole orientations and the reduced light loss caused from total internal reflection at the interface between the transport layer and the NPL emitting layer. For this reason, manipulation of in-plane dipoles in CdSe NPL films becomes a feasible way for the optimization of LED applications containing low-dimensional active nanostructures.

Readers interested in the design principles of assembled anisotropic nanostructure–based LED applications are referred to a published review article.\(^{59}\)

To date, several published review articles have covered the general development of CdSe NPL heterostructures,\(^ {60}\) synthesis protocols of CdSe NPLs,\(^ {61–64}\) and basic optical properties of CdSe NPLs with the roadmap to applications.\(^ {56,65–68}\) However, none of them focus on the systematic comprehension of the powerful tunability of optical properties, especially for the bandgap engineering and precise control of transition dipole alignment in the dSe-based NPL family. Therefore, in this Review, we narrow our scope on the manipulation of emission peak positions as well as self-assembly methods in the class of colloidal...
CdSe-based NPLs. First, several approaches, including thickness tunability, ligand exchange, grading, doping, and heterostructures, to address the issue of bandgap tuning are systematically summarized, along with the discussion on the other key optical features such as linewidth and quantum yield and comparison of the application performance metrics of these corresponding engineered CdSe NPLs. Then the emerging field of CdSe NPL assemblies is reviewed with a focus on the methods and unique optoelectronic attributes of ordered CdSe NPL stacks. In the last part, we discuss the remaining handicaps and the prospects for the progress of tunable optical properties of CdSe NPL systems and their potential use in new optoelectronic devices.

2. Emission Tunability for CdSe-Based NPLs

As a new class of solution-processed quantum wells, colloidal CdSe NPLs possess flat lateral extension up to several hundred nanometers, whereas the atomically precise thickness is less than the physical dimension of the electron–hole pair. As a consequence, the quantum confinement solely along the thickness direction modulates the electronic structures of CdSe NPLs dramatically. The relaxation of quantum confinement effects could be achieved by simply increasing the ML thickness or introducing a semiconductor capping shell layer with bandgap larger than the CdSe core. These methods result in redshift of the emission peak wavelength from the ultraviolet (UV) to near-infrared (NIR) range. In addition, posttreatments of CdSe NPLs such as ligand exchange and partial cation exchange (CE) reactions provide a new direction to adjust the electronic structure thanks to the great sensitivity of CdSe NPLs to the surface chemistry. Taking advantage of the broad emission tunability, proof-of-concept light-emitting and light-harvesting devices have been rapidly developed over the past decade. In this section, we will detail the rapid development of synthesis methods of the CdSe NPL family with focus on the emission tunability and discuss the correlation between application performance and the corresponding preparation routes. This section will be helpful for readers calling for a comprehensive understanding of band structure engineering for 2D colloidal semiconductor materials and serve as a guide for the design of CdSe-based NPLs with desired emission properties.

2.1. The Spectral Tunability Correlated with the Vertical Thickness

A high-vacuum preparation environment and rigorous lattice matching between the deposited layers are required for the preparation of conventional epitaxially grown quantum well semiconductors. Fortunately, these expensive and sophisticated conditions could be avoided in the hot-inject method. Moreover, as a well-known wet-chemistry synthesis approach, the hot-injection method offers degrees of freedom to modulate synthesis parameters such as the types and amounts of precursors and injection temperature and rates. The first hot-injection (HI) preparation of cubic crystalline CdSe NPLs possessing three pure populations with different ML thicknesses governed at the atomic scale was reported in 2008.[3] The thickness of an x-ML NPL is defined as x number of CdSe layers with an additional Cd atomic plane on the outer layers coordinated with organic ligands to maintain charge neutralization. Due to the presence of a strong quantum confinement effect along the vertical dimension, the energy of the lowest excitonic transition varies within the ML thickness. On the basis of the results, the bandgap energy could be discretely tuned from 2.68 eV (462 nm) for 3-MLs to 2.42 eV (512 nm) for 4-MLs and till 2.25 eV (550 nm) for monodispersed 5-ML CdSe NPL pellets. The characteristic step-like excitonic features with narrow linewidth are clearly shown in Figure 2a. In the typical synthesis protocol, cadmium myristate with a long chain and cadmium acetate with a short chain are used as Cd precursors and a selenium mesh acts as a Se precursor.[2,3,6,9] Thicker CdSe NPLs are grown under the condition with larger amounts of cadmium acetate, which are injected at a higher reaction temperature. Unlike thicker-ML CdSe NPLs, which exhibit a moderate PLQY of around 30% and moderate colloidal stability, thinner 3-ML CdSe NPLs grown under a much lower temperature (∼180 °C) demonstrate much lower PLQY (<10%) and a strong tendency of precipitation due to the large lateral surface and poor surface passivation. A recent published work[20] proposed a modified hot-injection method by replacing long-chain cadmium precursors with short-chain cadmium carboxylates to synthesize 3-ML CdSe NPLs with improved PLQY up to 30% and even thinner 2-ML CdSe NPLs with the emission position blueshifted to 393 nm and PLQY up to 11%. Due to the successful realization of colloidal CdSe NPLs with tunable PL peak wavelength spanning from the blue to green spectral region, tremendous efforts have been made in the search for synthetic approaches to produce thicker CdSe NPLs with narrower bandgap. Chu et al.[71] have prepared very thick CdSe NPLs up to 10-MLs via the colloidal atomic layer deposition (c-ALD) method. Thicker NPLs were grown by adding alternative Cd and Se atomic layers onto CdSe cores via phase transfer between polar and nonpolar solvents at room temperature but displayed a faint emission property. Breakthrough was made recently[19] in 2018 to obtain CdSe NPLs with uniform thickness up to 8-MLs by the addition of cadmium chloride under a higher reaction temperature of up to 320 °C. Pure populations of CdSe NPLs with uniform ML thickness are confirmed by negligible inhomogeneous broadening from PL excitation spectroscopy. Figure 2b displays the spectroscopic results of the reported series of thicker NPLs. Almost simultaneously, slightly modified synthesis protocols of 6-ML CdSe NPLs with a higher PLQY of over 45% were reported via slow injection of cadmium chloride aqueous solution[18] or swift addition of cadmium fluoride.[72] The impacts of chlorides and fluoride on the reacting surfaces of NPLs to overcome the high nucleation barrier were the main reason for the construction of thicker CdSe NPLs. In summary, the band-edge energy is tuned stepwise from 3.16 eV (393 nm) to 1.98 eV (625 nm) by simply changing the thickness dimension of the pure population of CdSe NPLs from 2-MLs to 8-MLs.

Pure chroma arising from a narrow linewidth less than 10 nm and a wide gamut stemming from broad bandgap tunability are expected in the NPL-contained light-emitting technology. The first demonstration[73] of an LED application based on CdSe NPLs was conducted in 2015, and the schematic device structure is shown in Figure 2c. With careful design of the transport layers and device structure, EL at 515 nm and a low turn-on voltage of ∼5.5 V of a
4-ML CdSe NPL—based LED device were reported. The optical gain properties and lasing performance with respect to the change of ML thickness were also investigated in the subsequent studies. For example, amplified spontaneous emission (ASE) phenomena under the pump of femtosecond laser pulses were observed in these CdSe NPLs, in which the ASE thresholds and modal gain were calculated as 50 μJ cm⁻² and 600 cm⁻¹, 28 μJ cm⁻² and 160 cm⁻¹ for 3-ML, 4-ML, and 5-ML NPL compact films, respectively. Recently, the ASE performance of 6-ML CdSe NPLs prepared by an optimized synthesis route was also recorded with a threshold of around 21 μJ cm⁻² under femtosecond laser excitation. As shown in Figure 2d, the redshifted ASE peaks of all NPL samples with respect to their corresponding PL positions were ascribed to the biexciton lasing mechanism from the previous literature.

2.2. The Spectral Tunability Correlated with the Ligand Chemistry

The exposed Cd-terminated basal facets of colloidal zinc blende CdSe NPLs are composed of structurally identical polar planes and thus are stabilized by various types of ligands to assure charge neutrality. Although there are several competing formation mechanisms of CdSe NPLs, including oriented attachment with specific precursors, anisotropic Ostwald ripening of small NPLs, and kinetic instability caused by insoluble precursors, the driving force of anisotropic growth for CdSe NPLs with isotropic zinc blende lattice structure is still under debate. However, ligands are believed to play an important role during the anisotropic growth of CdSe NPLs. The effect of ligands also reflects on the self-assembly process when the freestanding NPLs are stacked into columnar structures upon the addition of different surfactant agents. Moreover, ligands help to tune the optical features as well as the charge transport properties of the engineered NPLs. Among all these ligand-related effects, we will focus on the adjustment of electronic band structures of CdSe NPLs via ligand treatment.
Regarding the spectral tunability exerted by the chemisorbed ligands on the surface, redshifts with varied magnitudes are usually observed after the exchange of native carboxylate ligands described as oleic/acetates (OA/CH\(_3\)COO\(^-\)) with various functionalized molecules, including thioclates (1,6-hexanediithiol, HDT), phosphonates (tetradeecylphosphonic acids, TDPA), hexa-decyl-phosphonates (HDPA), hydroxides (OH\(^-\)), hydrogen sulfides (SH\(^-\)), chlorides (Cl\(^-\)), bromides (Br\(^-\)), and iodides (I\(^-\)). The corresponding bandgap energies are listed in Table 1. It is also noted that thinner NPLs with redshift up to 240 meV after ligand treatment are more sensitive to surface modification.

Figure 3 displays the characteristic spectroscopic results of 3-ML and 4-ML CdSe NPLs capped with original OA/CH\(_3\)COO\(^-\) ligands, exchanged HDPA and HDT ligands, respectively.\(^{[82]}\) The origin of these substantial bathochromic shifts was first discussed in the case of CdSe NPLs with HDT and TDPA ligand treatment are more sensitive to surface modification. Positions of the lowest electron-heavy hole excitonic transition (\(E_{1hh1}\)) of original and ligand-exchanged CdSe NPLs with different ML thicknesses from previous reports.\(^{[75,82,83]}\)

Table 1. Bandgap tunability of CdSe NPLs after ligand-exchanged treatments. Positions of the lowest electron-heavy hole excitonic transition (\(E_{1hh1}\)) of original and ligand-exchanged CdSe NPLs with different ML thicknesses from previous reports.\(^{[75,82,83]}\)

| Type of ligands | \(E_{1hh1}\) for 3-ML NPL [eV] | \(E_{1hh1}\) for 4-ML NPL [eV] | \(E_{1hh1}\) for 5-ML NPL [eV] | Shift in \(E_{1hh1}\) compared to OA/CH\(_3\)COO\(^-\) [eV] |
|----------------|-----------------------------|-----------------------------|-----------------------------|----------------------------------|
| OA/CH\(_3\)COO\(^-\)| 2.68                        | 2.42                        | 2.25                        | 0                               |
| HDT            | 2.49                        | 2.32                        | 2.20                        | -0.19                           |
| HDPA           | 2.44                        | 2.27                        | 2.14                        | -0.24                           |
| SH             | 2.46                        | 2.29                        | 2.15                        | -0.22                           |
| OH             | 2.50                        | 2.39                        | 2.21                        | -0.18                           |
| Cl             | 2.44                        | 2.30                        | 2.18                        | -0.24                           |
| Br             | 2.45                        | 2.27                        | 2.16                        | -0.23                           |
| I              | 2.44                        | 2.27                        | 2.16                        | -0.24                           |

Among these surface-modified CdSe NPL systems, PLQYs were found to drop markedly below 10\% accompanied by a broader full width at half maximum (FWHM) due to the poor passivation of trap states along the edges of NPLs.\(^{[14]}\) Moreover, previous studies also discuss that the trigger of closely stacked ribbons upon the addition of organic solutions such as HDPA\(^{[43]}\) and oleic acid\(^{[23]}\) or antisolvents\(^{[85]}\) such as ethanol solutions may reinforce nonradiative recombination through the accelerated FRET processes between the neighboring NPLs, leading to nonemissive features. The only exception is in the class of halogen-exchanged CdSe NPLs with PLQY approaching 70\% and sharp emission linewidth of around 12 nm. Figure 3b shows the evolution of characteristic absorption transitions for CdSe NPLs before and after Br-ligand treatments, along with pictures of NPLs illuminated by UV light before and after the Br-ligand exchange process. The bright emission and narrow linewidth make halogen-treated NPLs potential candidates to be incorporated into display applications in the future. Motivated by the fast

![Figure 3](https://www.adpr-journal.com/articles/2100045/figures/Figure3.jpg)
charge transport, broad spectral tunability, and better dispersion in aqueous solutions of CdSe NPLs with inorganic capping molecules on the surface; ligand exchange treatments will open up access to optimizing the performance of NPL-based field-effect transistors,[86] multifunction solar cell technology,[87] and biomaging applications.[88]

### 2.3. The Spectral Tunability Correlated with Compositional Grading and Doping

Thanks to the matured development of studies on QD semiconductors, compositional grading with isovalent substitutions and doping transition metal ions into host systems have been shown to be facile strategies to alter their optical,[85,89,90] electrical,[91] and magnetic[92] properties. Resembling the case of the 0D QD materials, doping and alloying have been demonstrated as powerful tools to continuously tune the band structure. Successful synthesis of CdSe$_{1-x}$/S$_x$-alloyed NPLs at fixed vertical thickness with varying alloyed concentrations and narrow linewidths was reported by Fan et al. in 2015.[17] The different ratios of anion components in CdSe NPLs was achieved by injecting the Se and S powders as anion precursors with the desired proportion. They found that with the increase of molar fraction of S from 0.25 to 0.5, the PL peak position of graded 4-ML CdSe$_{1-x}$/S$_x$ NPLs gradually blueshifts from 501 to 491 nm in the blue region, as shown in Figure 4a, accompanied by a slightly broadened FWHM up to 15.6 nm as well as a lower PLQY in the range of 10–23%. One year later, Tenne et al. reported the synthesis protocol of CdSeTe NPLs by slowly introducing trioctylphosphine selenide (TOP-Se) and trioctylphosphine telluride (TOP-Te) as anion precursors into the reaction solution.[21] Figure 4b displays the band-edge energy and emission peak position as a function of molar fraction of the Se element. In light of the spectroscopic results, characteristic bowing of the bandgap energy with the increase of Te composition is observed when the molar fraction of Te is larger than 30%, confirming that the system is in the grading regime. In contrast, the redshifted Te-dopant PL appears abruptly due to the presence of the midstate in the band structure when the molar fraction of Te is less than 30%. In this sense, the transformation from the doping regime to the alloyed system could be adjusted depending on the proportion of the introduced Te element.

Doping of CdSe QDs with heavy metal elements such as Mn,[93] Cu,[94] and Ag[95] has been reported since the early 2000s. These dopant ions bring additional midgap states in the bandgap of the host QDs, and thus redshifted dopant-activated PL emission with long lifetime appears while the excitonic features remain intact. By changing the quantum confinement of the host material, the bandgap can be tuned, and the emission wavelength can be shifted accordingly.

---

**Figure 4.** a) Absorption and emission spectra of graded 4-ML-CdSe$_{1-x}$/S$_x$ NPLs. Reproduced with permission.[17] Copyright 2015, American Chemical Society. b) Absorption and emission spectra of graded 4-ML-CdSe$_{1-x}$/Te$_x$ NPLs. Reproduced with permission.[21] Copyright 2016, The Royal Society of Chemistry.
semiconductor or altering the midgap position via choosing different dopant elements, the dopant-related PL wavelength could be tuned in a wide range.\textsuperscript{[96]} Benefiting from the large Stokes shifts in these doped QDs, lots of color conversion and light-harvesting applications\textsuperscript{[97,98]} have been demonstrated. Motivated by the great success made in the doped QD materials, lots of efforts have been made to achieve spectral tunability via doping in the case of CdSe NPLs. However, the uneven distribution of dopant impurities across the flat nanostructures makes the doping process in zinc blende CdSe NPLs remain as a challenge. Although Mn-doped wurtzite CdSe nanoribbons were synthesized on 2009, the position of the dopant-related emission coming from the localized Mn 3d state is nearly fixed regardless of the change of electronic structures of the CdSe host, which hinders the emission tunability in doped CdSe nanostructures.\textsuperscript{[99]} It was not until recently that the controlled doping of heavy metal ions in zinc blende CdSe NPLs was realized. Cu-doped NPLs were first demonstrated by Sharma et al. in 2017.\textsuperscript{[22]} They used a modified-nucleation doping strategy via swiftly introducing dopants into a high-temperature reaction solution, a widely used approach in the case of doped colloidal nanocrystals, to introduce Cu\textsuperscript{+} ions distributed uniformly across the whole NPLs. As shown in Figure 5a, similar to the Cu-doped CdSe QDs, additional broad and redshifted PL appears while the absorption features remain unchanged with the involvement of Cu\textsuperscript{+} cations, suggesting that the bright emission with a PLQY of up to 97% actually comes from the excitonic transition between electrons delocalized in the CdSe core region and holes localized from Cu\textsuperscript{+} dopants.\textsuperscript{[22]} By changing the thickness from 3-ML to 5-ML, Cu\textsuperscript{+} cation–related PL redshifts due to the relaxation of quantum confinement of electrons in CdSe host materials.\textsuperscript{[100]} Regarding the tunability of Cu impurity emission, another way to change the quantum confinement for the host system is to dope Cu ions into CdSe-based heterostructures. Bicolor PL and absorption spectra of Cu-doped CdSe/CdS core/shell NPLs prepared by c-ALD techniques at room temperature are displayed in Figure 5b. Although the PLQY decreases from 97% to 18% after adding a CdS capping layer due to the rigid multiple washing cycles in the c-ALD method, the wavelength of the dopant emission could be extended near 800 nm. Meanwhile, the one-pot HI seeded-growth method has been used to prepare Hg-doped CdSe NPLs by Galle et al.\textsuperscript{[23]} Although the PLQY of the Hg-containing NPLs is lower than 10%, which hinders their performance for various applications of interest, additional PL in the longer wavelength of Hg-related emission is observed when the doping reaction is performed at a slightly lower temperature ($\approx$200 °C). In their research, they attributed the dual emission peaks to the loosely and firmly bound Hg sites in the Hg-doped CdSe NPLs. Unlike the HI-based nucleation doping method, for which it is hard to control the doping level and to investigate the doping reaction kinetics, postsynthesis partial CE, a well-developed doping technique in colloidal CdSe QDs,\textsuperscript{[101,102]} serves as a potential and effective alternative in doped CdSe NPLs. After one year of the report on the one-pot HI method to prepare Cu-doped CdSe NPLs prepared by partial CE method. Reproduced with permission.\textsuperscript{[24]} Copyright 2018, American Chemical Society. d) Absorption and emission spectra of Ag-doped 4-ML-CdSe NPLs synthesized by partial CE method. Reproduced with permission.\textsuperscript{[103]} Copyright 2019, American Chemical Society. e) EL spectra of graded 4-ML-CdSe$_{1-x}$S$_x$ NPLs. Reproduced with permission.\textsuperscript{[17]} Copyright 2015, American Chemical Society. f) Photographs of LSC based on Cu-doped CdSe NPLs before and after illumination. Reproduced with permission.\textsuperscript{[22]} Copyright 2017, Wiley-VCH.
NPLs, Sharma et al. continued the in-depth investigation and proposed a partial CE method to obtain Cu-doped NPLs at a moderate temperature (±60 °C). In the literature, they controlled the Cu doping level across the whole NPLs from surface interstitial sites to deep substitutional states by carefully choosing the type or amount of Cu precursor as well as the reaction time and temperature. The doping kinetics could be resolved by spectroscopy techniques. For instance, as shown in Figure 5c, the PL spectrum involves from biexciton emission with the dominant band-edge recombinations of the host CdSe to the nearly single color dopant-dominate emission as the time of doping reaction increases. Thus, apart from the regulation of quantum confinement for the host material, control of the doping kinetics opens up a new direction of tuning dopant emission positions. In 2019, Ag-doped CdSe NPLs prepared by a partial CE method were reported by two groups. As shown in Figure 5d, Ag-doped CdSe NPLs exhibit spectral tunability in the range of 609–880 nm, with a Stokes shift of up to 1 eV and a PLQY approaching 50%. Identical to the control of the doping level in the Cu-doped CdSe NPLs system mentioned earlier, the Ag doping level, reflected in PL spectroscopy results, could also be adjusted from loose surface doping to substantial substitution with a pristine lattice by monitoring the reaction time and amounts of doping impurities. In the synthesis aspect of doped CdSe NPLs, studies on doping with other metal impurities apart from Mn, Hg, Cu, and Ag are scarce. Although the heterostructure of doped core/shell has been utilized to expand the emission peak wavelength into the NIR region, the PLQYs of the as-prepared NPLs were relatively low because of repeated precipitation with the addition of antisolvent after deposition of every half-layer of the shell. As such, other shell growth methods such as the HI method could be exploited to prepare doped CdSe-based hetero-NPLs emitting in the NIR spectral region without compromising on a high PLQY.

The fields of CdSe NPL-based applications are evolving rapidly with the development of newly synthesized doped NPL materials. Constrained by the size-dependent bandgap, blue-emitting nanostructures with a large surface-volume ratio usually exhibit low efficiency and face a serious photo-stability issue due to the poor surface passivation. Thus, with the rapid development of colloidal nanomaterials, blue-light emitters have become the hot spot in the research field. The successful synthesis of CdSe1-xSx NPLs opens the way to fabrication of the first blue-emitting NPL-based LED device with the EL spectra shown in Figure 5e. Moreover, compared to pristine CdSe NPLs, unique optical properties such as large Stokes shifts, high PLQYs, and broad dopant-activated PL tunability make doped CdSe NPLs promising candidates for light-harvesting applications. An example is a luminescent solar concentrator (LSC), in which the efficient light emission from thin edges could be captured and then converted into electric power in low-cost photovoltaic cells with small area mounted on the thin edge of the LSC in the solar cell industry. Previously, colloidal nanocrystals, including metal-ion-doped QDs, giant CdSe/CdS core/shell QDs, and CdSe/CdS dots-in-rods heterostructures, have attracted the most attention in LSC studies. Among these Stokes-shift-engineered QDs, Cu-doped CdSe QDs with large Stokes shifts and broad solar spectrum coverage become the light-harvesting materials with the most potential. However, in comparison to these Cu-doped CdSe QDs, Cu-doped CdSe NPLs exhibit PLQY higher than 65% and larger Stokes-shifted emission in the NIR regime. As displayed in Figure 5f, Cu-doped CdSe NPLs are sandwiched between two glass substrates. Upon illumination with a high-energy optical source, the light in the NPL region is waveguided through total internal reflection and is eventually emitted at the edges. So far the application of doped CdSe NPLs is limited to LSC devices. However, compared to Ag-doped QDs with a lifetime of up to 220 ns, Cu-doped and Ag-doped CdSe NPLs with higher PLQYs and longer dopant emission lifetimes of up to 512 ns have great potential for use as biosensors. Apart from LSCs and biosensors, doped CdSe NPLs with exceptionally large Stokes shifts also show potential as excellent gain media. Previous study on Te-doped CdSe QDs reported a large blueshifted biexciton center, which is the prerequisite to achieve gain performance in the single exciton regime. Based on their experimental results, the magnitude of the biexciton blueshift is proportional to the Stokes shift of the dopant materials. Therefore, strong Coulomb repulsion will also be expected in doped CdSe NPL systems, which could be exploited to achieve gain performance under lower excitation power.

### 2.4. The Spectral Tunability Correlated with Heterostructure NPLs

In the past decades, epitaxially grown heterostructures have been adopted to discover distinct photophysical phenomena and novel devices in the cases of traditional multiple quantum wells and solution-processed colloidal nanostructures, including QDs and NR semiconductors. The demand of bandgap tunability and improvements of performance in optoelectronics devices have fueled the developments of epitaxial growth of CdSe NPLs. In light of the anisotropic shape of 2D NPLs, epitaxial growth of capping materials is classified into two configurations: the core/shell structure, with the shell grown along both the vertical and horizontal directions of core NPLs, and the core/crown structure, with a crown ring surrounding core NPLs. Based on the choice of epitaxial compounds, the electronic structure with either type-I band alignment in which electron and hole wave functions are overlapped in the same zone or type-II band structure in which electrons and holes are spaced out into different regions is determined. Different epitaxial morphologies and electronic structures of the as-synthesized hetero-NPLs will lead to flexible manipulation of the resulting excitonic properties. Here, we summarize the developments of these advanced CdSe-based hetero-NPLs with a focus on the correlation between different synthesis protocols and the desired bandgap structures as well as the optoelectronic devices’ performance.

#### 2.4.1. The Spectral Tunability Correlated with Core/Shell CdSe-Based NPLs

**Core/Shell CdSe-Based NPLs Synthesized at Moderate Temperature:** The first successful synthesis of epitaxially grown CdSe hetero-NPLs adopted a core/shell configuration and was reported in 2012. CdSe-based core/shell NPLs such as CdSe/CdZnS...
NPLs with PLQY up to 60% were prepared via slowly injecting shell precursors at room temperature by Mahler et al.\textsuperscript{[25]} The improved PLQYs are attributed to better surface passivation provided by the inorganic shell layers, which lower the coupling rates of carriers with surface trap states, thus suppressing the nonradiative recombination processes. Upon the growth of one layer of CdS shell plane on a 4-ML CdSe NPL, the emission wavelength redshifts dramatically from 510 to 586 nm. By injecting zinc precursors along with cadmium precursors into reaction solutions containing 4-ML CdSe NPLs and thioacetamide to grow a CdZnS shell, emission positions as well as excitonic absorption peaks shift toward even longer wavelengths of $\approx$640 nm. Ithurria and Talapin vertically introduced CdS shells layer by layer on 4-ML CdSe NPLs at room temperature via the c-ALD method and systematically studied the optical features of the corresponding core/shell NPLs with CdS shell thickness of up to seven layers at the atomic level.\textsuperscript{[11]} Figure 6a shows the evolution of the characteristic spectroscopic features with the accumulation of inorganic shell layers, in which the center of the PL peak increases 61 nm after the deposition of one CdS layer and redshifts to 665 nm with the deposition of the 7-ML CdS shell. Along with the relaxation of wave functions into the shell region after passivating core NPLs with inorganic CdS layers, slightly broadening linewidths (from 48 meV for core-only NPLs to 54 meV after the deposition of the CdS shell) and moderate PLQYs in the range of 20–40% were also reported.\textsuperscript{[11]} Thanks to the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{a) Absorption and emission spectra of 4-ML-CdSe/CdS core/shell NPLs prepared by c-ALD. Reproduced with permission.\textsuperscript{[11]} Copyright 2012, American Chemical Society. b) Absorption and emission spectra of 4-ML-CdSe/ZnS NPLs prepared by modified c-ALD method under moderate reaction temperature. Reproduced with permission.\textsuperscript{[27]} Copyright 2017, American Chemical Society. c) Absorption and emission spectra of 4-ML-CdSe/Cd$_{x}$Zn$_{1-x}$/S core/shell NPLs with varied sulfur concentrations. Reproduced with permission.\textsuperscript{[24]} Copyright 2019, Wiley-VCH. d) Absorption and PL spectra of Cd$_{x}$Se$_{1-x}$/S$_{y}$/CdS graded core/shell via c-ALD methods. Reproduced with permission.\textsuperscript{[17]} Copyright 2017, American Chemical Society. e) Absorption and emission spectra of CdSe-based core/shell NPLs prepared by HI methods. Reproduced with permission.\textsuperscript{[4]} Copyright 2019, American Chemical Society. f) Absorption and emission spectra of 4-ML-CdSe/Cd$_{x}$Zn$_{1-x}$/S$_{y}$ core/shell NPLs with varying zinc concentrations. Reproduced with permission.\textsuperscript{[10]} Copyright 2019, American Chemical Society. g) Absorption and emission spectra of 4-ML-CdSe$_{1-y}$/S$_{y}$/ZnS core/shell NPLs with varying Se concentrations of the core part. The insets show the TEM images of NPLs. Reproduced with permission.\textsuperscript{[10]} Copyright 2020, American Chemical Society.}
\end{figure}
improved optoelectronic behaviors of CdSe/CdS NPLs,\textsuperscript{[114]} optical gain performance such as pump threshold as low as 6 μJ cm\(^{-2}\) and gain coefficient as high as 600 cm\(^{-1}\) for the onset of ASE under one-photon femosecond laser excitation was demonstrated by Talapin’s group.\textsuperscript{[115]} Another group has also reported similar magnitudes of ASE threshold and gain coefficients for CdSe/CdS NPLs prepared by the c-ALD technique.\textsuperscript{[116]} In the subsequent research on core/shell NPLs synthesized by c-ALD methods, efforts have been made to investigate the broad bandgap tunability with different types of composition-tailored shells. Moreover, pronounced PL redshift of up to 70 nm upon deposition of 1-ML CdS layer creates a large spectral gap between a bare CdSe NPL core and as-prepared hetero-NPLs. Thus, Polovitsyn et al. systematically investigated the photoelectric attributes of hetero-NPLs with a type-I ZnS shell and a CdZnS shell prepared by a modified c-ALD method at moderate reaction temperature of up to 150°C.\textsuperscript{[27]} Large electron-hole overlap in type-I CdSe/ZnS NPLs leads to smaller magnitudes of PL redshift (≤60 nm) upon the growth of a 1-ML ZnS layer and eventually tailors the PL position to 611 nm, with shell thickness up to 14-ML as shown in Figure 6b. Moderate FWHMs are retained and the PLQY slightly increases to 60% and then decreases monotonically with the increase of shell layers due to the pronounced surface roughness resulting from the large lattice mismatch (~12%) between ZnS and CdSe. Although the spectral gap becomes slightly narrower after adopting the type-I electronic structure, the PL peak positions of hetero-NPLs with either ZnS or CdS shells still cannot be continuously tailored due to the discrete layer-by-layer shell deposition styles on atomic scale. Thus, the synthesis of CdSe/Cd\(_{1-x}\)Zn\(_x\)S core/graded-shell NPLs by introducing mixed cation precursors at room temperature was demonstrated by Meerbach et al. This preparation method overcomes the limitation of discrete spectral tunability and fills up the broad spectral gap between bare CdSe NPLs and hetero-NPLs.\textsuperscript{[28]} Figure 6c shows the absorption and emission results of the as-prepared 4-ML-CdSe/Cd\(_{1-x}\)Zn\(_x\)S core/shell NPLs with different portions of sulfur precursors during reaction of the growth of the first shell layer. The PL peak position spans from 520 to 620 nm with increasing amounts of sulfur precursors in the reaction solution. As shown in Figure 6d, synthesis of Cd\(_{1-x}\)Se\(_x\)/CdS graded-core/shell via c-ALD methods was proposed by Kelestemur et al. to tune the PL peak positions from 560 to 650 nm by either modifying the portion of sulfur in the graded core or changing the thickness of the CdS shell.\textsuperscript{[117]} A low gain threshold down to 53 μJ cm\(^{-2}\) was recorded within these Cd\(_{1-x}\)Se\(_x\)/CdS NPLs despite their low PLQYs. At the same time, c-ALD techniques were used to coat doped CdSe core-only NPLs with inorganic semiconductor layers to manipulate the dopant-related PL wavelengths through reducing the quantum confinement of electron wave functions.\textsuperscript{[22,103]} Details of the emission properties of core/shell NPLs are summarized in Table 2.

### Table 2. Summary of emission properties of CdSe-based core/shell NPLs.

| Core/shell materials | Emission peak [nm] | Linewidth [meV] | PLQY [%] | Remarks |
|----------------------|--------------------|-----------------|----------|---------|
| 4-ML-CdSe/CdS        | 571–665            | 54              | <5\textsuperscript{[27]} | c-ALD by Talapin’s group\textsuperscript{[113]} |
| 4-ML-CdSe/Cd\(_{1-x}\)Zn\(_x\)S | 520–620          | 140–160 in green region, 72–87 in yellow-red region | <50 | c-ALD by Eychmüller’s group\textsuperscript{[28]} |
| 4-ML-CdSe/ZnS        | 560–611            | 66–79           | <64      | Shell growth at moderate temperature by Moreels’ group\textsuperscript{[27]} |
| Cu-doped 3-ML- or 4-ML-CdSe/CdS | 750–800          | –               | 12–18    | c-ALD by Demir’s group\textsuperscript{[102]} |
| Ag-doped 4-ML-CdSe/CdS | 737–852           | –               | –        | c-ALD by Moreels’ group\textsuperscript{[103]} |
| 4-ML-CdSe\(_{1-x}\)/CdS | 560–650           | 70–100          | <20      | c-ALD by Demir’s group\textsuperscript{[117]} |
| 4-ML-CdSe/CdS        | 660–670            | 60–70           | 50–60    | HI by Norris’s group\textsuperscript{[120]} |
| 4-ML-CdSe/ZnS        | 612–620            | 76–101          | 52–67    | HI by Norris’s group\textsuperscript{[120]} |
| 4-ML-CdSe/CdS/ZnS    | 660–670            | 67              | <78      | HI by Norris’s group\textsuperscript{[120]} |
| 4-ML-CdSe/ZnSe       | 630–680            | 59              | <47      | HI by Norris’s group\textsuperscript{[120]} |
| 4-ML-CdSe/Cd\(_{1-x}\)Zn\(_x\)S | 607–655          | 56–60           | 88–90    | HI by Norris’s group\textsuperscript{[120]} |
| 6-ML-CdSe/Cd\(_{1-x}\)Zn\(_x\)S | 692              | 57              | 90–95    | HI by Norris’s group\textsuperscript{[120]} |
| 4-ML-CdSe/ZnS        | 602–616            | 77–90           | 85–85    | HI by Demir’s group\textsuperscript{[120]} |
| 4-ML-CdSe/Cd\(_{1-x}\)Zn\(_x\)S | 612–650          | 59–79           | 83–95    | HI by Demir’s group\textsuperscript{[120]} |
| CdSe\(_{1-x}\)/Cd\(_{1-x}\)/Zn\(_x\)S alloyed core/alloyed shell | 554–615          | 82–108          | 34–90    | HI by Demir’s group\textsuperscript{[120]} |
| 4-ML-CdSe/ZnS        | 593                | 74              | <56      | HI by Kovalenko’s group\textsuperscript{[29]} |
| 4-ML-CdSe/CdS        | 632–646            | 66              | 45–60    | HI by Kovalenko’s group\textsuperscript{[29]} |
| 4-ML-CdSe/CdS/Cd\(_{1-x}\)Zn\(_x\)S | 634–648          | 60              | 75–89    | HI by Kovalenko’s group\textsuperscript{[29]} |
monodispersed core/shell QDs obtained via slowly injecting low-reactivity precursors at high temperature ($\approx 300^\circ$C) possess improved optical properties, including better photostability, higher PLQYs, narrower linewidths, and suppressed blinking.$^{[118,119]}$ Unfortunately, CdSe NPLs are not stable at such high temperature and start to dissolve into reaction solutions. It was not until very recently that core/shell hetero-NPLs prepared by the HI method were obtained by three different research groups.$^{[14,29,86,120]}$ Their synthesis protocols are roughly the same despite the minor differences in types, sequences, and amounts of injected precursors, which also leads to final products with slightly different excitonic properties and geometric morphologies. For instance, Norris’s group addressed the NPL etching problem at a high reaction temperature by introducing excess cadmium precursors and adding oleylamine ligands later at elevated temperature to slow down the dissolution of core-only CdSe NPLs.$^{[4,86]}$ Using this HI method, they successfully prepared CdSe-based core/shell NPLs with various types of ZnS, ZnSe, Cd$_{x}$Zn$_{1-x}$S shells in addition to CdSe/ZnS multishells in the type-I regime and CdS shells in a quasi-type II regime. Figure 6e displays the recorded spectroscopic results of the NPL heterostructures with various types of compositional shells. The PL tunability ranges along with the linewidths and PLQYs are also listed in Table 2. Based on their results, CdSe/ZnS core/shell NPLs have broader linewidths and nonuniform shell shapes compared to other HI-grown hetero-NPLs because of the strong interfacial strain between the CdSe core and ZnS shell. However, CdSe/ZnS NPLs exhibit improved PLQY thanks to the strong confinements of carrier wave functions in the type-I regime. Therefore, the addition of CdS inner shells with much smaller lattice contrast (≈4%) between the CdSe core and ZnS outer shells will help to reduce interfacial strains as well as preserve the efficient quasi-type-I electronic structure. Meanwhile, Demir’s group reported modified-HI-prepared CdSe/ZnS NPLs possessing near-unity PLQY and pronounced stability confirmed by the tracking of the PL spectrum after thermal treatments, UV exposure, as well as repetitive purification.$^{[120]}$ Larger bandgap tunability was achieved by using HI routes to synthesize 4-ML CdSe/Cd$_{x}$Zn$_{1-x}$S NPLs. The PL peak positions of these hetero-NPLs with a graded shell layer could be tuned from 612 to 650 nm, as shown in Figure 6f. In comparison to the hetero-QDs with lowest ASE threshold down to 6 μJ cm$^{-2}$ under one-photon femtosecond pulse pumping,$^{[121]}$ the ASE threshold is even lowered to 2.4 μJ cm$^{-2}$ for 4-ML CdSe/Cd$_{x}$Zn$_{1-x}$S NPLs. The superior ASE performance of CdSe-based hetero-NPLs over their 0D counterparts mainly results from the reduced AR rates due to stricter translational momentum conservation in the 2D system.$^{[122]}$ To fill the spectral gap between 510 nm for core-only NPLs to 602 nm for CdSe/ZnS HI-prepared hetero-NPLs, 4-ML graded CdSe$_{1-x}$S$_{x}$ NPLs with higher bandgap energy are used as initial core NPLs to manipulate the optical bandgap upon the growth of the graded Cd$_{y}$Zn$_{1-y}$S shell.$^{[106]}$ The absorption and emission results of CdSe$_{1-x}$S$_{x}$/ZnS alloyed-core/shell NPLs are displayed in Figure 6g. Experimental results of CdSe$_{1-x}$S$_{x}$/Cd$_{y}$Zn$_{1-y}$S alloyed-core/alloyed-shell hetero-NPLs are summarized in Table 2. By introducing an alloyed core in the core/shell synthesis routes, the spectral gap is narrowed to the range of 510–554 nm, which could be potentially covered with graded 5-ML CdSe$_{x}$S$_{1-x}$ NPLs with emission wavelength less than 550 nm. Systematic studies of core/shell NPLs via HI synthesis have also been conducted by Kovalenko’s group.$^{[29]}$ By changing the types of shell compositions and adjusting the thickness of shells, the emission peak could be tailored from 593 nm with ZnS shells to 648 nm with graded Cd$_{y}$Zn$_{1-y}$S shells.$^{[29]}$ Unlike the synthesis routes proposed by previous groups in which all cation precursors were dispersed in reaction solutions before the initial injection of the sulfur precursor, Kovalenko’s group controlled the spatial cation distribution in the shell layers (such as CdS/Cd$_{y}$Zn$_{1-y}$S multishells) through the slow and simultaneously sequential introduction of the cations and sulfur precursors into reaction solutions. The record-low ASE threshold of CdSe/CdS/Cd$_{y}$Zn$_{1-y}$S NPLs with a CdS buffer region and Cd$_{y}$Zn$_{1-y}$S graded shells down to 40 μJ cm$^{-2}$ under one-photon nanosecond laser pulse was also attained.$^{[29]}$ In summary, with the participation of core/shell NPLs into the family of CdSe-based NPLs, the emission color could be tuned continuously from green, yellow, and orange to red without compensating their brightness and sharp linewidths. Based on the recent progress of 4-ML graded-core/graded-shell NPLs synthesized by HI methods, continuous spectral tunability from the blue to green region could be expected with 3-ML CdSe$_{1-x}$S$_{x}$/Cd$_{y}$Zn$_{1-y}$S graded-core/graded-shell hetero-NPLs.

Optoelectronic Applications of Core/Shell CdSe-Based NPLs: Successive reports on the novel preparation routes of core/shell CdSe-based NPLs with pronounced optical properties and gain performance have driven the research down to light-emitting devices and optical amplifiers with continuous tunable emission. The first lasing action from hetero-NPLs with a core/shell configuration was demonstrated with c-ALD-prepared CdSe/CdS NPL concentrated solutions dispersed in cuvette, as shown in Figure 7a.$^{[123]}$ This CdSe/CdS NPL-based liquid laser with a Fabry–Pérot optical resonator exhibits ultralow lasing thresholds down to 4.3 μJ cm$^{-2}$ under three-photon excitation. Two years later, a CW nanolaser was achieved by incorporating c-ALD-grown CdSe/CdS NPLs into a photonic-crystal nanobeam cavity, in which the input pump power down to 0.97 μW was sufficient to initiate CW lasing performance at room temperature.$^{[124]}$ Figure 7b displays the structure of the nanobeam cavity as well as the lasing spectrum. As the most widely studied solution-processable gain media, QDs have also demonstrated CW lasing performance with a much larger lasing threshold of around 7 kW cm$^{-2}$ compared to 0.22 kW cm$^{-2}$ for a CdSe/CdS NPL CW-nanolaser. Moreover, the realization of a QD-based CW laser requires a more sophisticated synthetic protocol to generate uniform biaxial strain to reduce the lasing threshold by lifting the valence band’s degeneracy.$^{[125]}$ The breakthrough of the synthesis of core/shell NPLs by HI methods has provided hetero-NPLs with improved optical properties and thus opened new directions of optimization of applications. Norris’s group fabricated core/shell NPL ring lasers in which the patterned NPL gain medium also acts as an optical whisper gallery mode resonator and the lasing threshold is around 13 μJ cm$^{-2}$ for 4-ML CdSe/Cd$_{y}$Zn$_{1-y}$S NPLs.$^{[4]}$ The architecture of an NPL ring laser and the emission spectrum with several spaced narrow peaks above the onset of lasing performance are shown in Figure 7c. Meanwhile, single-mode lasing performance with a threshold of 0.55 mJ cm$^{-2}$ under two-photon excitation was reported from...
CdSe/Cd$_{x}$Zn$_{1-x}$/C$_0x$ NPLs incorporated into a specially designed surface-emitted optical laser cavity.[108] A photograph of the lasing spot along with the lasing spectrum is shown in Figure 7d. Very recently, lasing operation at room temperature resulting from Mie-resonant bound states in the continuum (BICs) was demonstrated by spin-coating CdSe/Cd$_{x}$Zn$_{1-x}$/C$_0x$ NPLs on arrays of titanium dioxide (TiO$_2$) cylinders.[126] One advantage of the BIC laser is the flexible tunability of the lasing wavelength in the range of the gain bandwidth through simply adjusting the radius of the TiO$_2$ cylinders. In their work, they were able to tailor lasing peak positions from $\approx$633 to $\approx$663 nm by only modulating the cylinder’s diameter from 290 to 310 nm. The typical lasing spectrum and the BIC laser’s structure are displayed in Figure 7e.

Apart from the aforementioned remarkable performance as the gain medium, core/shell NPLs are also regarded as promising alternates for the future light-emitting technology. Upon the report of successful synthesis of CdSe/CdZnS core/shell NPLs in 2014, Chen et al. used these as-synthesized hetero-NPLs as active the emitting layer in a hybrid LED device.[127] With the improvement of charge transport properties via replacing the original long-chain ligands with short ligands and cautious adjustment of the hole-transport layer (HTL), the EL characteristics of ligand-exchanged CdSe/CdZnS NPLs were optimized compared to the published results of bare-CdSe NPL–based LEDs.[128] Details of the parameters of the corresponding EL performance are summarized in Table 3. Then, red-emitting CdSe/CdZnS NPL LEDs were reported with much higher EQE thanks to the better charge balance provided by the deliberately engineered functionalized conjugated polymers as the electron-transport layer (ETL).[129] After the reports of the successful synthesis of core/shell NPLs by HI methods, Kelestemur et al. integrated these high-quality NPLs into an LED device architecture.[29] Based on their results, among all these hetero-NPLs with different shell compositions, display applications with CdSe/CdS/Cd$_{x}$Zn$_{1-x}$/C$_0x$/S as the active emitting layer exhibit the lowest EQE and the highest brightness, which are attributed to the presence of a graded outer shell that acts as a barrier for excess carriers and provides proper surface passivation. Then, Liu et al.
demonstrated the EL operation of HI-prepared CdSe/CdZnS NPLs with a near-unity PLQY in solution and reported the record-high EQE of up to 19.23% in the family of colloidal NPL-based LEDs, which also approaches the limit of EQE (≈20%) without optimized light extraction structures.[120] Motivated by the wide spectral tunability and narrow linewidths of CdSe-based core/shell NPLs, Altintas et al. fabricated efficient emitters based on HI-synthesized CdSe@CdS core/crown NPLs with emission colors continuously tuned in the broad range from green, yellow, and orange to red by adjusting the compositional portions of sulfur in the core region and the zinc element in the shell part.[104] With the reduction of the sulfur concentration for the alloyed core or the decrease of the concentration of zinc components of the graded shell, the EL peaks will continuously shift toward the NIR region. In summary, the previous literature reported that the synthesis of high-quality type-II core/crown CdSe-based NPLs and maintain the same thickness as the cores. With the better passivation of trap states on the edge surface, improved PLQYs are expected. However, unlike the core/shell NPLs with quasi-type-II electronic alignment mentioned in the previous section, CdSe/CdS core/crown NPLs possess type-I electronic structures with the CdS crown serving as an exciton funnel. Optical recombination happens in the CdSe core region in these CdSe/CdS core/crown NPLs, which leads to identical emission peak position to that of the bare CdSe NPLs.[31,90,131,132] Thus, although these type-I CdSe/CdS NPLs exhibit large absorption cross-sections, higher PLQYs, and reduced ASE thresholds,[133] unfortunately they alone are still unable to tune the emission features. Consequently, the synthesis of complex NPL heterostructures with the introduction of outer shell planes surrounding the core/crown hetero-NPLs via c-ALD methods was conducted to expand the spectral coverage in subsequent studies.[134,135] Figure 8a displays the positions of excitonic transition in 4-ML-CdSe/CdS@CdTe core/crown@shell NPLs with type-I band alignment, in which the bandgaps reduce as the number of graded shell layers increases due to the relaxation of quantum confinement effects sensed by the charges in the core region.[36] However, the as-prepared hetero-NPLs exhibit suppressed PLQYs due to the excess precipitation required in the shell-growth c-ALD method. The other strategy to adjust the PL peak wavelength is to synthesize core/crown NPLs within the type-II configuration. The typical candidates include CdSe/CdTe and CdSe/CdSeTe compositional structures. The schematic band structures of these type-II core/crown NPLs are shown in Figure 8b. The first synthesis of CdSe/CdTe core/crown NPLs was reported in 2014 by Dubertret’s group. The PL peak position of as-prepared NPL heterostructures was expanded from 524 to 730 nm as the thickness of the core section increased from 3- to 5-MLs, as shown in Figure 8c.[90] In addition to the strongly redshifted PL resulting from the recombination transitions across the core/crown interface, characteristic optical properties of type-II systems such as broad PL linewidth and longer PL lifetime up to 190 ns were discussed in the previous literature.[33,90] To continuously tune the emission energy,
CdSe/CdSe$_{1-x}$Te$_x$/Cd$_{x}$Se$_{1-y}$/Cd$_{y}$Te$_z$/CdS core/crown NPLs were adopted by Demir’s group.[34,134] Figure 8d shows the evolution of the PL absorption spectra, PLQY, and emission color of flat 4-ML-CdSe/CdS core/crown NPLs with the precise adjustment of compositional portions in the crown region.[34] Although continuous spectral tunability and improved PLQYs up to 95% have been obtained in CdSe/CdSe$_{1-x}$/CdS core/crown NPLs with the precise adjustment of compositional portions in the crown region,[34] poor colloidal stability still hampers further developments in the optoelectronic devices. Therefore, CdSe/CdSe$_{1-x}$/CdS core/multicrown NPL structures were proposed by Dede et al. to address the stacking issue while still maintaining the excitonic features.[132] The detailed excitonic properties of these aforementioned core/crown hetero-NPLs are summarized in Table 4.

Several examples of core/crown NPL–based light-emitting and light-amplified applications have been reported in the literature. With the CdS crown behaving as an exciton funnel, CdSe/CdS core/crown NPLs exhibit remarkable gain performance with gain coefficient up to 650 cm$^{-1}$ and ASE threshold down to 41 and 4.48 mJ cm$^{-2}$ under one- and two-photon absorption excitation, respectively.[133] Proof-of-concept VCSEL was also fabricated by using these novel core/crown NPLs as the gain medium and the measured lasing threshold was as low as 2.49 mJ cm$^{-2}$ under pumped two-photon absorption.[133] Driven by the pure color and high brightness stemming from the narrow linewidth and better surface passivation, CdSe/CdS core/crown NPLs also showed superior LED operation with turn-on voltage down to 2.25 V and peak luminance as well as EQE up to 33 000 cd m$^{-2}$ and 5%, respectively.[32] With the emergence of type-II CdSe/CdS$_{1-x}$/CdS$_x$ core/crown NPLs possessing continuous spectral tunability from 570 to 660 nm,[34] the fabrication of core/crown NPL-containing optoelectronics emitting in the yellow to red region has developed in the recent years. Specifically speaking, Liu et al. reported the remarkably enhanced EL performance of CdSe/CdS$_{1-x}$/CdS$_x$ core/crown NPL–based LEDs with turn-on
Table 4. Summary of emission properties of advanced CdSe-based core/crown NPLs.

| Core/shell materials | Emission peak [nm] | Linewidth [meV] | PLQY [%] | Remarks |
|----------------------|-------------------|----------------|----------|---------|
| 4-ML-CdSe/CdS        | 513               | ~40            | 65–90    | Optimized stability and PLQYs using TOPS-ODE other than S-ODE as sulfur precursor[135] |
| 4-ML-CdSe/CdS @CdS core/crown@shell | 610–650 | 62–90 | 18–40 | Spectral tunability with the addition of CdS shell via c-ALD[35] |
| 4-ML-CdSe/CdS @ZnS core/crown@shell | 575–588 | 81–100 | 35–40 | Spectral tunability with the addition of ZnS shell via c-ALD[36] |
| 4-ML-CdSe/CdS @CdxZny-S core/crown@shell | 575–650 | 66–80 | 35–60 | Spectral tunability with the addition of CdxZny-S shell via c-ALD[36] |
| 3-ML, 4-ML, and 5-ML-CdSe/CdTe | 564, 656, 730 | 190, 156, 160 | 10–50 | Spectral tunability with different NPLs thicknesses[39] |
| 4-ML-CdSe/CdTeSe1-x | 570–660 | 140–190 | 34–95 | Continuous spectral tunability at fixed thickness[34] |
| 4-ML-CdSe/CdTeSe1-x/CdS Core/multicrown | 572–663 | – | 23–70 | Improved colloidal stability and gain performance[42] |

*TOPS-ODE, tri-n-octylphosphine-sulphur dissolved in 1-octadecene; S-ODE, sulphur dissolved in 1-octadecene.

Voltage down to 1.9 V and peak luminescence and EQE as high as 34.520 cd m⁻² and 3.57%.[135] In NPL systems with type-II electronic structures, nonradiative Auger losses and reabsorption effects are strongly suppressed thanks to the spatial segmentation of electrons and holes and remarkably large Stokes shifts. The optical gain performance of CdSe/CdSeₓTe₁₋ₓ core/crown NPLs was investigated by Demir’s group in 2017, in which they measured the ASE threshold down to 26 μJ cm⁻² and gain coefficients approaching 930 cm⁻¹ and they attributed the origin of the gain to the charge-transfer interfacial states.[134] Random lasing operation of drop-cast CdSe/CdSeₓTe₁₋ₓ NPLs on a scratched glass substrate was also achieved with a pumping threshold of 950 μJ cm⁻² under a nanosecond Nd:YAG laser.[136] In addition to CdSe/CdSeₓTe₁₋ₓ NPLs, gain performance was also demonstrated in other core/crown hetero-NPLs consisting of core/multicrown NPLs[128] and complex core/crown@shell NPLs.[35] However, although these core/crown NPLs exhibit much lower ASE thresholds down to 4.15 μJ cm⁻²[112] with respect to the widely studied CdSe/CdS and CdSe/CdSeTe core/crown NPLs, few reports demonstrate lasing operations by integrating these novel core/multicrown NPLs into various optical cavities. Despite the remarkable gain performance, the low PLQY of the current core/crown@shell NPLs with the shell grown by the c-ALD method, which requires several cycles of precipitations, hampers the development of efficient emitters. By introducing shell layers to the core/crown NPL system via an HI method, the low-efficiency issues could be addressed.

3.1. Self-Assembly Approaches and Optoelectronic Properties of CdSe NPL Assemblies

Inspired by the previously reported self-assembly techniques to fabricate colloidal NR assemblies involving solvent evaporation,[138] surface modification,[139] adoption of external fields,[140] addition of antisolvents,[128] and the liquid–liquid interfacial method,[34] similar assembly strategies have also been discovered to assemble CdSe NPLs into hierarchical structures. For instance, the first report on CdSe NPL assemblies triggered by the addition of an antisolvent such as ethanol into CdSe NPL/hexane dispersion was published in 2013.[41] The experimental results of small-angle X-ray scattering (SAXS) with a series of reflection peaks and electron microscopy characterization justified the order of superstructures with face-to-face stacking. The respective SAXS pattern is shown in Figure 9a, which also displays the transmission electron microscopy (TEM) images along with a schematic of these needle-like NPL structures. Colloidal CdSe NPLs, as a new type of 2D material with a large surface-to-volume ratio, exhibit remarkable surface chemistry–dependent optical properties, as discussed in Section 2.2. As a result, ligand-induced self-assembly methods consisting of ligand exchange[44] and addition of excess oleic acid ligands[42,142] have also been investigated to assemble CdSe NPLs into colloidal aggregates. Based on the results, the strong affinity interaction strength, namely, the van der Waals force exerted by rigid brushes of carboxylates ligands on the surface of adjacent NPLs, was regarded as the driving force for the formation of the face-to-face NPL stacking chains.[38] Previously, chiral superlattices with unique electronic and magnetic properties were usually formed by sophisticated pathways such as exchanging with chiral ligands[143] and using specific chiral templates.[144] Surprisingly, chiral ribbons of CdSe NPLs have been
demonstrated with oleic acid treatment in which oleic acid ligand-induced mechanical distortion lowers the overall energy, leading to the formation of the twisted chiral assemblies. Figure 9c displays TEM images of these twisted CdSe NPL ribbons. Motivated by the groundbreaking properties of NPL superstructures, other self-assembly approaches such as the traditional Langmuir technique, solvent-evaporation-mediated inkjet printing technique, stretching-controlled copolymer composites, external electric field-adjusted self-assembly, and liquid-liquid interfacial assembly have also been reported and the fundamental physical properties of these ordered assemblies have been investigated in recent years. Among all these self-assembly methods, liquid-liquid interfacial assembly is the most powerful strategy to achieve both face-down- and edge-up-oriented CdSe NPL stacks by controlling the interaction strength between adjacent NPLs and the NPL-polar subphase at the liquid-liquid interface. Gao et al. adjusted the interfacial energy of NPLs by changing the amounts of oleic acid solution introduced into the subphase; the synthesis schematic as well as TEM images is shown in Figure 9d. However, the addition of excessive insulating oleic acid and the choice of less volatile subphase diethylene glycol (DEG) hamper the synthesized CdSe NPL assemblies in future device fabrication. Consequently, Momper et al. optimized the liquid-liquid interfacial method by replacing DEG with the more volatile acetonitrile and tuning the interaction potential at the liquid-liquid interface by controlling the evaporation rate of the top solvent instead of adding insulating surfactants into the subphase. As the TEM images of the stacked NPLs displayed in Figure 9e show, CdSe NPL assemblies with face-down orientation are kinetically favored under high-evaporation assembly conditions such as assembling at high temperature or in solutions with high vapor pressure; otherwise the edge-up orientation is more thermodynamically favored. Later, Erdem et al. prepared close-packed multilayer CdSe NPL superstructures with all-face-down orientation by modified liquid-liquid interfacial assembly and demonstrated remarkable gain properties, which make NPL superlattices attractive candidates for the next generation of photonics devices. The development of CdSe NPL assemblies with controlled orientation paves the way to investigate orientation-dependent optical properties, including polarized emission and distribution of TDMs. By depositing theses ethanol-treated needle-like NPL stacks on a substrate perpendicular to the NPL large lateral surface, the emission of the superlattice was found to be polarized in the NPL plane, analogous to the experimental and theoretical
Due to the small Stokes shift, the emission peak is up to 20% without further light harvesting. They found that for thick stacks, additional red-shifted absorption dipoles and 2D in-plane distribution of emission dipoles have been observed. The presence of out-of-plane dipole components in NPL aggregates was also confirmed via Fourier-imaging techniques.[157] Previous study of intrinsic TDMs in ML CdSe NPL film via 2D k-space spectra characterization has manifested the 3D isotropic orientation of absorption dipoles and 2D in-plane distribution of emission dipoles.[146] Based on their interpretations of experimental results, the effects of anisotropy of the electronic Bloch states account for the presence of anisotropic 2D emission dipoles.[146] The other report on disentangling the distribution of TDMs for an absorption and emission process in a single CdSe NPL was performed with a higher-order laser scanning microscopy technique and consensus on the TDM distributions was reached.[94] In their analysis, electric field renormalization imposed by the large dielectric mismatch between the inorganic NPL and its organic surrounding medium results in the presence of anisotropic emission dipoles.

Apart from the anisotropic optical properties, efficient energy transfer and pronounced electronic coupling have also been explored in the compact CdSe NPL assemblies. Ultrafast exciton transfer via FRET in the long range over 100 nm and pronounced PL quenching have been observed in cofacial CdSe NPL stacks upon the introduction of ethanol.[44] Efficient FRET outpacing the rate of the AR process due to rapid exciton trapping[49] has also been reported based on these ligand-treated CdSe NPL superstructures. Very recently, theoretical calculation of the influence of molecular coupling on the electronic structure of CdSe NPL stacks via Coulomb interactions to change the polarization of the dielectric between nearby NPLs has been investigated.[158] They found that for thick stacks, additional red-shifted minibands in the electronic structure appeared with tens of melectron volt bandwidth. Therefore, the precise control of the number of assembled layers via the liquid–liquid interfacial assembly method will help to provide experimental information to check the simulation results.

3.2. Potential Applications of CdSe NPL Assemblies

Chiral nanoassemblies with circular dichroism properties are beneficial for applications, including enantiomeric recognition and separation,[159] building block of chiral metasurfaces,[160] and chiral catalysis.[161] Previous studies have demonstrated a versatile and simple strategy to trigger the formation of chiral CdSe NPL assemblies with pitch length up to 400 nm upon the addition of oleic acid.[142,145] Future in-depth research on the twisted CdSe NPL ribbons could be focused on the exploitation of their circular dichroism properties for the development of potential applications.

Enhanced electric and optical coupling strengths between inter-NPLs lead to formation of minibands in the electronic structure[158] and an efficient exciton transfer process over 500 nm migration distance.[49] An ultrafast FRET-mediated exciton tunneling process favors the use of stacked NPLs in the field of light-harvesting photovoltaic cells and biosensors. Moreover, the rate of energy transfer in the NPL stacks is much faster in the face-to-face stacks than in edge-by-edge assemblies,[48] thus, the transfer speed could be controlled by tuning the desired NPL orientation with either face-down or edge-up structure.

In the context of display technologies where nonradiative recombination should be suppressed, face-down superstructures are more favored. The EQE in LEDs is calculated by multiplying the outcoupling efficiency ($\eta_{\text{out}}$) with the internal quantum efficiency (IQE). Assuming that the IQE of the active emitting layer approaches unity, $\eta_{\text{out}}$ becomes the determining factor for the efficiency of LEDs. Although QD-based LEDs are the most widely developed nanostructure-based light-emitting application, their efficiency ($\eta_{\text{out}}$) is up to 20% without further light-extraction approaches due to the transverse magnetic light loss from the isotropic TDMs. Fortunately, the $\eta_{\text{out}}$ of a CdSe NPL assembled layer with face-down structure could approach 40% thanks to the directional emission from the dominant in-plane TDMs. In terms of the potential use of NPL stacks as active gain media in laser devices, gain performance has been reported from face-down-oriented CdSe/Cd$_x$Zn$_{1-x}$S core/shell NPL multilayer superstructures with thickness as thin as 42 nm, corresponding to only six layers of densely packed NPL stacks, which is much smaller compared to the reported thickness of several hundred nanometers for spin-coated or drop-cast NPL film to perform ASE.[52] Recent publications have reported ASE operation with only two layers of CdSe NPL stacks integrated into a TiO$_2$ dielectric waveguide,[153] emphasizing the impressive gain properties of ultrathin CdSe NPL stacks with respect to their traditional spin-coat or drop-cast films. Other than exchanging pristine long-chain organic ligands with short-chain capping ligands, the pronounced gain operation in ultrathin CdSe NPL superstructure also opens up a new direction to boost charge conductivity for the fabrication of NPL-based electrically driven lasers.

4. Conclusion

In the first section of this Review, we discuss several pathways of spectral tunability of CdSe-based NPLs and summarize the emission properties, including peak position, emission linewidth, and PLQY of the resulting CdSe NPLs prepared by the established synthesis protocols and postsynthetic treatments. Thanks to the tremendous efforts made by the scientific community, the rapid developments of various chemistry syntheses of CdSe-based NPLs with quasi-continuous bandgap tunability in the spectral range from the blue to the deep-red region have also
benefited the optimization of solution-processed CdSe NPL optoelectronic and nanophotonic devices. A few selected examples of CdSe-based NPL applications are then presented from the previously published literature, indicating that NPLs are promising candidates for the next generation of smart lighting, display technologies, and the light-harvesting industry. However, several critical issues need to be addressed before the achievement of full coverage of the visible spectrum region by CdSe-based NPLs and the widespread utilization of these bandgap-engineered NPLs in the future light-emitting industry. First, the bandgaps for almost the engineered CdSe NPLs are on the lower-energy side, whereas improvements of the emission properties of blue-emitting CdSe NPLs are very scarce, not to even mention the enhanced performance of blue-emitting CdSe NPL-based optoelectronics devices. Although two strategies, including S doping and the modified synthesis protocol of thinner CdSe NPLs, have been proposed to achieve blue-emitting NPLs, much lower PLQYs and poor stability still impede the development of CdSe NPL-based blue emitters in the lighting and display industry. Thus, efficient and stable blue-emitting CdSe NPLs are strongly demanded as blue is a primary color in the RGB color system. The key to filling the blue gap with efficient thin CdSe NPLs is to passivate the surface trap states either by preparing 4-ML graded CdSe$_{1-x}$/CdS$_x$ NPLs with ligand exchange treatment or synthesizing 3-ML CdSe$_{1-x}$/Zn$_x$Te$_y$Cd$_z$S$_{1-z}$ graded core/graded shell NPLs via an HI method. Second, apart from the blue-emitting NPLs, CdSe-based NPLs with emission in the deep-red region also exhibit stability and efficiency issues, which also block their further integration in sensor or bioimaging applications. Herein, graded-shell growth via the HI method could be performed on Ag- or Cu-doped CdSe NPLs as well as CdSe/CdTe$_{1-x}$ core/crown NPLs to achieve efficient and colloidal-stable NPLs. Third, spectral tunability could also be accomplished by the careful design of an optical cavity in which NPLs are incorporated as mentioned in the discussion of the tuning of CdSe NPL coupling bound states in the continuum from Mie resonance by adjusting the radius of square arrays in the optical resonator.$^{126}$ Meanwhile, the summary of self-assembly methods of CdSe NPL superlattices and the emerging optical properties of these CdSe NPL superstructures have also been reviewed. Assembling CdSe NPL building blocks into hierarchical functional solids induces collective optical and electrical behaviors. As the fundamental studies on the emerging collective behaviors and generation of optical-based devices of CdSe NPL assemblies are still in their infancy, several directions or initiatives of the development of CdSe NPL superstructures are formulated as follows. First, the basic research on the coupling behaviors of NPL assemblies calls for further theoretical and experimental analysis. To date, the research of the collective coupling effects in NPL stacks mainly focuses on the efficient exciton transfer and distribution of TDMs for both absorption and emission processes. Previous studies on the emergent coupling properties of assembled nanostructures demonstrated suppressed PL blinking in close-packed NR clusters,$^{126}$ superfluorescence behavior through the collection of the coherent photon field in perovskite superstructures,$^{163}$ and photon antibunching phenomena with a characteristic sub-Poissonian feature for a CdSe/CdS QD superlattice.$^{164}$ These complex photon-physical phenomena are expected to be observed and characterized in 2D CdSe NPL assemblies, which will motivate the development of nonlinear optical devices based on NPL superstructures. Second, the exploration of self-assembly methods requires further verification of various types of CdSe NPLs as building blocks because the interaction potential of inter-NPLs is sensitive to the size, shape, and ligand chemistry of the individual nanostructures. Third, study of the optical properties of a complex assembled system by mixing different types or TDM orientations of CdSe NPLs will provide fruitful information on the collective inter-NPL coupling interactions. Finally, from the application point of view, the controlled arrangements of CdSe NPL assemblies with either face-down or edge-up configuration inspire the construction of NPL superstructures—based display devices with improved performance. As mentioned previously, the EQE of face-down oriented NPL-based LEDs could be boosted up to 40% with respect to the upper limit of 20% for the isotropic QD-based LEDs. Apart from efficient LEDs, CdSe NPL assemblies also provide new insights into the development of electrically pumped and polarized laser applications.

In conclusion, as a representative candidate of the class of 2D materials, colloidal CdSe NPLs constitute a significant platform for the fundamental research and development of the next generation of optical devices. Knowledge of the spectral tunability and self-assembly methods of CdSe NPLs could facilitate the research of other novel cadmium-free solution-processed 2D materials such as ZnTe,$^{165}$ ZnSe,$^{166}$ HgTe,$^{116}$ and ZnS$^{167}$ NPLs. For example, the emission peak wavelength has been tuned discretely from 345 to 380 nm in the case of CdSe NPLs by modulating the vertical thickness over the NPL ensemble.$^{116}$ Moreover, successful synthesis of Mn-doped ZnS NPLs with improved PLQY has been reported.$^{168}$ From the industrial perspective, efficient heavy-metal-free NPL emitters with green, blue, and red color should be highly pursued for display technology to achieve scalable and low-cost products without the consideration of integrating complex illuminators with distinct shapes, compositions, or ligand chemistries into the display.

Acknowledgements
This work was supported by A*STAR under project AME-IRG-A20E5c0083 and Ministry of Education Singapore through the Academic Research Fund under Projects MOE Tier 1 RG95/19 (S).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
bandgap tunability, CdSe nanoplatelets, coupling, optoelectronics, self-assembly, 2D materials
Zitong Zhang is a Ph.D. candidate in the School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore. She received her B.Sc. degree in materials science and engineering from Sichuan University, Chengdu, China. Her main research interests include materials synthesis, fundamental photophysical research, and applications based on colloidal CdSe NPLs.
Handong Sun has been with the School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, since 2007. His research works focus on optical spectroscopy, optoelectronic materials and devices, semiconductor optics, etc. He was elected to be a Fellow of the American Physical Society with citation “For outstanding contributions to optoelectronics with novel characterization and deep understanding of photonic materials and structures, leading to practical high-performance devices” in 2016.