Interfacial engineering of core/shell heterostructured nanocrystal quantum dots for light-emitting applications

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ABSTRACT
Reviewed in this paper is the recent progress on the interfacial engineering of core/shell heterostructured nanocrystal quantum dots (NQDs) for light-emitting applications, with focus on the composition (energy) gradient interfaces between the core and the shell. The engineered interfaces mitigate the structural stress between the core and the shell and thus reduce the chance to create misfit defects that act as efficient non-radiative recombination centers. In addition, the resultant smoothening of the potential profiles across the interfaces leads to the strong suppression of non-radiative Auger recombination. Efforts to engineer the interfacial structures further promote the optical performances of NQDs and benefit the light-emitting applications utilizing NQDs.

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1. Introduction
Nanocrystal quantum dots (NQDs) \cite{1} exhibit narrow emissions upon a broad range of excitation wavelengths and high luminescence efficiencies, making them promising for use in various light-emitting applications, including displays \cite{2,3,4,5,6,7,8,9,10,11}, solar concentrators \cite{12,13,14}, and lasers \cite{16,17,18}. In the last two decades, the structures of NQDs evolved into sophisticated heterostructures, boosting their optical performances and photophysical stabilities \cite{19,20,21,22,23,24,25}. As a result of the multilateral efforts, core/shell heterostructured NQDs displaying almost 100\% efficiency upon the excitation of both optical \cite{24} or electrical pumping have been successfully realized.

Spectroscopic analysis combined with structural characterization has unveiled that the interfaces of the core/shell heterostructures indeed play important roles in determining the optical properties of NQDs \cite{21,22,23,24,25,26,27}. Specifically, the structural formulation at the core–shell interface affects the formation of misfit defects that are efficient non-radiative recombination centers \cite{21,22,23,24,25,26,27}. In addition, the potential profiles across the interfaces influence the Auger recombination (AR) rates \cite{26,27,28,29,30,31,32}. Beyond gaining photophysical insights into the structure–property relationship, the advances in interfacial engineering have enabled the control of the optical properties of core/shell heterostructured NQDs and have led to substantial advances in their applications \cite{5,24,33}.

In this article, the recent progress in the interfacial engineering of core/shell heterostructured NQDs is reviewed, with focus on the relationship between the structural formulation and the optical properties. The synthetic methods of engineering the interfaces of core/shell heterostructured NQDs are also introduced. Finally, the characteristics of the corresponding NQD-based light-emitting applications in displays and lasers are discussed.

2. Interfacial engineering of core/shell heterostructured NQDs for light-emitting applications

2.1. Enhancement of the single-exciton luminescence efficiency and stability
The use of NQDs in light-emitting applications requires not only high luminescence efficiency for such NQDs but also prolonged stability against electrical, optical, and/or chemical stresses \cite{27}. For NQDs populated with single
excitons (electron–hole pairs), the quantum yield (QY) of NQDs is given by

\[
QY = \frac{k_r}{k_r + k_{nr}},
\]

where \( k_r \) and \( k_{nr} \) denote the rates of radiative and non-radiative recombination of the exciton state, respectively (Figure 1). \( k_r \) is an intrinsic value determined by the structural formulation of NQDs. Therefore, the QYs of NQDs can be promoted by reducing the \( k_{nr} \). By and large, \( k_{nr} \) falls under two categories depending on the trapping sites of the charge carriers (i.e. \( k_{nr} = k_{nr\_surf} + k_{nr\_int} \), where \( k_{nr\_surf} \) and \( k_{nr\_surf} \) are the non-radiative decay rates associated with charge trapping on the surface states and in the internal crystal defects, respectively) (Figure 1(b)). For the type-I heterostructured NQDs, in which both charge carriers stay within the core, the passivation of a core with a thick shell is expected to suppress the surface charge trapping rate (\( k_{nr\_surf} \)) because the surface charge trapping takes place through a tunneling process of charge carriers and leads to the QY enhancement of the NQDs. In addition, NQDs with a thick shell exhibit improved optical stabilities against thermal or photochemical stresses. To take advantage of their efficiency and stability, the core/shell heterostructured NQDs have been made to have thick shells.

Thick shells, however, do not always guarantee the promotion of the QYs of NQDs [34]. Indeed, passivation with thick shells results in an unexpected QY drop in core/shell NQDs. In the conventional core/shell heterostructured NQDs with abrupt interfaces, the misfit defects that are the sources of effective non-radiative recombination centers associated with \( k_{nr\_def} \) emerge near the interfaces due to the intensified structural stress between the core and the shell when the shell thickness reaches a certain value (Figure 1(b)). Beyond the critical thickness at which the misfit defects start to develop, \( k_{nr\_def} \) progressively increases along with the shell thickness, and dictates the QYs for the thick-shell NQDs, leading to the reduction of the QYs (Figure 1(d)). The critical shell thickness and the slope for \( k_{nr\_def} \) over the shell thickness depend on the structural difference, such as the crystal structures and lattice parameters, between the core and the shell. For example, the QYs of CdSe/ZnS...
Figure 2. Schematic illustrations for AR in the cases of (a) the negative trion (two electrons and one hole) and (b) the positive trion (one electron and two holes) [38]. (Reprinted figure with permission from [38], as follows: W. K. Bae et al., MRS Bull. 38 (09), 721, 2013.) Copyright (2013) by the Materials Research Society. (c) AR constant of different types of NQD vs. NQD volume [39]. The AR rate inversely scales with the volumes of NQD regardless of their band types or bandgaps. (Reprinted figure with permission from [39], as follows: István Robe et al., Phys. Rev. Lett. 102 (17), 177404, 2009.) Copyright (2009) by the American Physical Society. (d) Schematic illustration and (e) wavefunction profile of CdSe/CdS giant NQD [45]. (Reprinted (adapted) with permission from [45]. Copyright (2009) American Chemical Society.) (f) Q2X (PL QY × biexciton quantum yield) as a function of the shell thickness [46]. (Reprinted figure with permission from [46], as follows: Y. S. Park et al., Phys. Rev. Lett. 106 (18), 187401, 2011.) Copyright (2011) by the American Physical Society.) Colour images are available online at http://www.tandfonline.com/doi/full/10.1080/15980316.2017.1313179.

NQDs (lattice mismatch = 12%) [19,35] start to drop at a much thinner shell with a much faster rate than the QYs of CdSe/CdS NQDs (lattice mismatch = 3.9%) (Figure 1(d)) [27,28].

To enhance both the QYs and the stabilities, interfacial engineering has been proposed and applied in various types of core/shell heterostructured NQDs (Figure 1(c)). The representative examples include the insertion of intermediate buffer layers (e.g. CdSe/CdS/ZnS or CdSe/ZnS/ZnSe) [36] or alloyed interfacial layers (CdSe/CdSe1−xSx/CdS [28], CdSe/CdZn1−xSeyS1−y/ZnS [21], InP/ZnSe1−xSx/ZnS [23,25]). The interfacial layers whose band edge energy levels and lattice parameters lie in between the core and the shell help mitigate the structural stress and suppress the formation of misfit defects (krt def for thick shells, enabling high PL QYs and prolonged stabilities in core/shell heterostructured NQDs (Figure 1(d,e)).

2.2. Suppression of AR

In addition to single-exciton recombination efficiency, interfacial engineering of the core/shell boundary also benefits the luminescence efficiency of the multicharrier states in NQDs that consist of more than one electron and one hole. It is well known that the multicharrier states in NQDs accompany a fast, non-radiative AR process that substantially reduces the luminescence efficiency of the multicharrier states in NQDs [37]. AR is an inelastic process evolving three charge carriers, in which the recombination energy of the electron–hole pair is given to the third charge carrier rather than emitted as a photon. The simplest cases of multicharrier states in NQDs are a negative trion (two electrons and one hole) and a positive trion (one electron and two holes) [38]. For trions, the recombination of one electron and one hole yields a hot electron (or hole) via AR (Figure 2(a,b)). AR universally takes place in homogeneous (core-only) NQDs regardless of their band structure (direct vs. indirect) or bandgap [39], with a characteristic time scale of 10–100 ps (Figure 2c), far exceeding the radiative recombination rates of charge carriers.

AR plays an important role in determining the performance of the light-emitting applications of NQDs [33]. Continuous illumination with high-energy or high-flux photons can create charged or multi-exciton states within NQDs, which are to undergo non-radiative AR [37,40]. NQDs are also easily charged when they come in contact with semiconductor or metal substrates [41,42]. Bae et al. [33] have shown that the imbalanced injection of charge carriers (electrons and holes) from the neighboring charge transport layers can yield NQD
charging, and as such, the AR process indeed governs the device efficiencies and the efficiency roll-off characteristics [33].

Recent spectroscopic studies evaluated the AR rates for core/shell heterostructured NQDs. In type-I NQDs that accommodate both electrons and holes within the core, the AR rates inversely scale with the effective exciton volume and are similar to that of the core-only NQDs (10–100 ps, Figure 2(c)) [39]. By contrast, quasi-type-II NQDs that hold one charge carrier either in the core or the shell and the other charge carrier to the entire volume, show AR suppression due to the spatial separation of the charge carriers. The representative example is the so-called ‘giant CdSe/CdS NQDs’ with a thick CdS shell (over 16 monolayers) surrounding a CdSe-emitting core (Figure 2(d–f)) [43–45]. The conduction band edge energy levels of CdSe and CdS are similar while the valance band edge energy level of CdS is \( \sim 0.4 \text{ eV higher than that of CdS.} \) This asymmetric band energy offset leads to the strong confinement of the hole wavefunction within the CdSe core but also to the delocalization of the electron wavefunction over the entire CdSe/CdS volume (Figure 2(e)) [45]. In these specific giant NQDs, the non-radiative decay channels of both charge carrier surface trapping and non-radiative AR are highly suppressed (Figure 2(f)), resulting in the complete disappearance of the low-emissivity (OFF) states and the emergence of gray states originating from the negative trions, as observed in the single-QD intensity-time trajectories [40,43–46].

In heterostructured NQDs, the potential shape (smooth vs. sharp) of the interfaces has a significant impact on AR (Figure 3(a,b)) [26,28,29,31,32,47]. Cragg and Efros first predicted that the smooth potential changes from the core to the shell can diminish the AR rates by three orders of magnitude (Figure 3(a)) [31]. Later, Climente et al. [32] further supported the effects of the potential profiles across the interface on the AR rates in heterostructured NQDs. Indeed, spectroscopic studies of individual NQDs demonstrated near-unity biexciton QYs for some giant NQDs due to the strong suppression of AR recombination that far exceeds the expectation based on the universal volume scaling [46]. Park et al. [29] proposed that the interdiffusion of Se and S atoms during the long CdS shelling process via SILAR at an elevated temperature (300°C) yields uncontrolled alloying at the core–shell interfaces, leading to very smooth potential transition and in turn significant AR suppression for some giant NQDs.

To control over-AR, an intentional alloy layer has been incorporated between the core and the shell in heterostructured NQDs [28,48]. Bae et al. [28] developed a fast synthetic method to exclude the unintentional alloying of the interfaces during thick-shelling, and inserted \( \text{CdSe}_{x}\text{S}_{1-x} \) controlled alloy layers. Comparative analysis of CdSe/CdS giant NQDs with and without the intentional alloy layers validated that the smooth potential changes over the alloyed interfaces are indeed responsible for AR suppression (Figure 3(c,d)) [28,29]. The insertion of \( \text{CdSe}_{x}\text{S}_{1-x} \) controlled alloy layers lessens the sharpness of the potential changes over the interfaces between CdSe and CdS, leading to AR suppression particularly for the positive trions [29]. As an ultimate achievement, Nasilowski et al. [48] recently reported gradient CdSe/CdS NQDs that show complete suppression of AR at room temperature (Figure 3(e)).

### 2.3. Synthetic methods

The structural formulation from the cores to the exterior shells can be varied through the stepwise multilayer growth method (Figure 4(a)). The ultimate method for the stepwise multilayer growth is SILAR (a successive ionic layer adsorption and reaction). The first demonstration of SILAR was demonstrated by alternating the ion adsorption on nanocrystals in the aqueous phase [1], and it was later further developed by Peng et al. for adaptation to oil phase chemistry [20]. In principle, SILAR enables the alteration of the chemical compositions of heterostructured NQDs in an atomic scale. Despite its controllability, however, the practical use of SILAR is limited because it requires extensive reaction times to ensure the complete consumption of the injected precursors (e.g. 2 h for each CdS atomic layer shelling). To reduce the reaction time, a single-step synthetic method that utilizes the reactivity difference between the precursors has been proposed to realize composition gradients within heterostructured NQDs, and has been further optimized to control the composition profiles in a variety of heterostructures [5,21].

An alternative approach to designing the interfaces is to utilize the diffusion-assisted alloying process at the core/shell interfaces (Figure 4b). In II–VI heterostructured NQDs, cations (e.g. Cd and Zn) readily diffuse to the other crystalline phase at an elevated temperature [22]. In addition, structural stress is also known to foster the diffusion of cations across the core/shell interfaces. The spontaneous alloying by the external energies creates composition gradient interfacial layers that mitigate the lattice mismatch between the cores and the shells. Interestingly, diffusion-assisted alloying accompanies the spectral shift of absorbance and emission to higher energies as a result of the decrease in the effective core radius along the diffusion process. Owing to this unique feature, diffusion-assisted alloying methods have been intensively
Figure 3. (a) Semilog plot of the AR rate in core/shell heterostructured NQDs as a function of the confinement potential width, 2a, for the case where the hole is ejected into the continuum [31]. (Reprinted (adapted) with permission from [31]. Copyright (2010) American Chemical Society.) (b) AR lifetime for the experiment results (empty circle) and expected values from volume scaling (solid line) (left) and fluorescence line narrowing (FLN) spectra indicating the presence of unintentional CdSe$_{x}$S$_{1-x}$ alloyed interfaces (right) [47]. (Reprinted (adapted) with permission from [47]. Copyright (2011) American Chemical Society.) (c) Schematic illustrations and (d) early-time multi-exciton decay dynamics and corresponding fits for the CdSe/CdS NQDs with sharp interfaces (gray triangles) and the CdSe/CdSe$_{x}$S$_{1-x}$/CdS NQDs with intentional CdSe$_{x}$S$_{1-x}$ alloyed interfaces (red circles) [28]. (Reprinted (adapted) with permission from [28]. Copyright (2013) American Chemical Society.) (e) TEM image of gradient CdSe/CdS NQDs (left) and representative g$^{(2)}$ measurement result ($<N>$ $\sim$ 0.025 μs) showing complete suppression of AR [48]. (Reprinted (adapted) with permission from [48]. Copyright (2015) American Chemical Society.) Colour images are available online at [http://www.tandfonline.com/doi/full/10.1080/15980316.2017.1313179](http://www.tandfonline.com/doi/full/10.1080/15980316.2017.1313179).

Figure 4. (a) TEM images (left, scale bar = 50 nm) and UV-Vis and PL spectra (right) observed during stepwise growth from the CdSe cores (bottom) towards CdSe/CdS/Cd$_{x}$Zn$_{1-x}$S/ZnS NQDs (top) [27]. NQDs for each shelling step are displayed for comparison. (Reprinted (adapted) with permission from [27]. Copyright (2005) American Chemical Society.) (b) TEM images and composition profiles (top) of core/shell NQDs before (left) and after (right) the thermal annealing (scale bar = 10 nm). Schematics illustrate the diffusion of Cd atoms yielding the composition gradient interfaces (bottom, left). PL spectra shifted to higher energies due to the decrease in the effective core radius along the diffusion process (bottom, right) [49]. (Reprinted (adapted) with permission from [49]. Copyright (2015) American Chemical Society.) Colour images are available online at [http://www.tandfonline.com/doi/full/10.1080/15980316.2017.1313179](http://www.tandfonline.com/doi/full/10.1080/15980316.2017.1313179).
utilized for the realization of NQDs with high bandgaps [8,22,24,49].

2.4. Core/shell heterostructured NQDs with engineered interfaces for light-emitting applications

NQDs exhibit narrow emissions but broad absorbance and excellent luminescence efficiencies even in films, making them promising for use in displays, lasers, and solar concentrators. For light-emitting applications, NQDs need to satisfy the criteria for brightness and stability. As demonstrated, interfacial engineering enables heterostructured NQDs to have thick shells that preserve their optical properties from external stresses without harming their luminescence efficiencies. In addition, the core-to-core distances expand for NQDs with thick shells, deterring exciton diffusion in NQD films that cause luminescence efficiency loss [30]. Therefore, thick-shell NQDs with engineered interfaces have been extensively studied as light-emitting materials. One representative achievement is thick-shell NQDs with composition gradient interfaces that outperform those of electroluminescence devices (Figure 5(a,c,d)) [3,5,25]. As a result of the persistent efforts to tailor the formulations at the interfaces, quantum-dot light-emitting diodes with external quantum efficiencies of over 10% with green, blue, and red NQDs have been successfully realized (Figure 5(b)) [5].

In addition, composition (energy) gradients help suppress AR, which limits the realization of NQD lasers [29,48,50]. Recently, Park et al. [18] reported a comprehensive theoretical and experimental study on the relationship between the structural formulation of core/shell NQDs and their optical performance, specifically the biexciton (two electron–hole pairs) quantum yields (Figure 5(a)). The paper’s authors observed that the threshold for the amplified spontaneous emission (ASE) of NQDs with alloyed interfaces is systematically lower than that in the NQDs with sharp interfaces, proving that interfacial engineering indeed benefits the laser performances (Figure 5(b,c)). As an ultimate achievement, the authors were able to reduce the threshold to 6 μJ/cm², the current threshold for an type of NQD.
3. Summary

The interfaces of core/shell heterostructured NQDs have a significant impact on such NQDs’ optical properties. Among a variety of structural formulations, the composition (energy) gradient interfaces enhance the optical properties of the heterostructures of NQDs by suppressing the formation of misfit defects and AR, which are effective non-radiative recombination channels. The efforts to engineer the interfacial structures further promote the optical performances of NQDs and benefit light-emitting applications utilizing NQDs.

Yet the influence of interfacial engineering and the structuring method have been studied mostly in II–VI NQDs, which are limited for practicable usage. As proven with II–VI NQDs, however, interfacial engineering will enhance the optical performances and stabilities of other types of NQD. In particular, the precise control of the interfaces of the Cd-free III–V/II–VI core/shell heterostructured NQDs enhances such NQDs’ optical performances and stabilities and promptly impacts a variety of practicable applications, including display, lasers, solar concentrators, and biomarkers.

Disclosure statement

No potential conflict of interest was reported by the authors.

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