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Heterostructuring Nanocrystal Quantum Dots Toward Intentional Suppression of Blinking and Auger Recombination

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Abstract

At the level of a single particle, nanocrystal quantum dots (NQDs) are observed to fluoresce intermittently or “blink.” They are also characterized by an efficient non-radiative recombination process known as Auger Recombination (AR). Recently, new approaches to NQD heterostructuring have been developed that directly impact both blinking and AR, resulting in dramatic suppression of these unwanted processes. The three successful hetero-NQD motifs are reviewed here: (1) interfacial alloying, (2) thick or “giant” shells, and (3) specific type-II electronic structures. These approaches, which rely on modifying or tuning internal NQD core/shell structures, are compared with alternative strategies for blinking suppression that rely, instead, on surface modifications or surface-mediated interactions. Finally, in each case, the unique synthetic approaches or challenges addressed that have driven the realization of novel and important functionality are discussed, along with the implications for development of a comprehensive ‘materials design’ strategy for blinking and AR-suppressed heterostructured NQDs.

Keywords

nanocrystal quantum dots; blinking; Auger recombination; core/shell; giant; alloyed; type II

Semiconductor nanocrystal quantum dots (NQDs) are nearly ideal fluorophores for a range of applications from single-particle tracking in a biological setting to large-scale lighting. As a result of quantum confinement effects, the characteristic semiconductor bandgap (or energy separation between the bottom of the conduction band and the top of the valence band) can be precisely tuned by controlling the size of the NQD. The resulting “color-tuned” emission is narrowband (color pure) and efficient, with quantum yields (QYs) approaching 100% for optimized examples. NQDs are easy to excite optically, as the absorption profile is quasi-broadband and insensitive to the refractive index of a surrounding medium, while absorption cross sections are high (>1–2 orders-magnitude larger than molecular dyes).¹ Furthermore, compared to alternative fluorophores, such as organic dyes, NQDs are relatively photostable.²

NQDs are synthesized in the solution phase, and coordinating ligands, which are used during growth to stabilize particles against rapid and uncontrolled growth, render as-prepared NQDs soluble in nonpolar or polar solvents, depending upon the initial choice of growth ligand(s). Significantly, NQD surface chemistry is easy to control post-synthesis by way of various well-developed ligand exchange or encapsulation protocol, allowing initially non-polar-soluble NQDs to be made water-soluble. In addition, these functional optical

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nanomaterials are processible from the solution phase into a variety of solid-state conditions from simple NQD monolayers to NQD-polymer or sol-gel composites. This flexibility adds to the overall utility of NQD emitters for disparate purposes.

Despite these enabling characteristics, however, NQD-based applications are challenged by several factors. First, NQD optical properties are frustratingly sensitive to their surface chemistry and chemical environment. The coordinating organic ligands that are used to passivate the NQD surface not only dictate NQD solubility and chemical compatibility, but comprise important contributors to single-NQD and ensemble-level optical performance. By saturating so-called ‘dangling bonds,’ ligands reduce the number of defect or trap states available as nonradiative recombination centers. Unfortunately, ligands are labile and can become detached from the NQD surface. Further, as organic molecules, they can be damaged by exposure to the light sources used for NQD photoexcitation. Ligand loss either through physical separation or photodegradation results in uncontrolled changes in QYs and even permanent photoinduced quenching of emission, known as *photobleaching*. The under- or unpassivated NQD attempts to saturate dangling bonds through surface reconstruction (atomic rearrangements), but inadequately coordinated surface atoms remain that are the source of surface trap-states.³ Buildup of nonradiative recombination channels likely ultimately leads to complete photobleaching. NQD quenching can also be understood as resulting from direct oxidation of NQD surface atoms, with photobleaching occurring more rapidly in air compared to an oxygen-free environment.⁴

Ligand dependencies can be lessened by overcoating the NQD with an inorganic shell of a wider bandgap semiconductor material. Indeed, core/shell NQDs are generally “brighter” and more photostable over time compared to their core-only counterparts. They are also more likely to emit exclusively excitonic band-edge emission that is unadulterated by so-called “trap” emission, characterized by a broad, red-shifted peak intensity. The addition of a wide-gap shell also reduces losses in photoluminescence (PL) efficiencies that occur when NQDs are subjected to ligand-exchange reactions or processed into solid-state films or composites.

Nevertheless, conventional core/shell NQDs (Figure 1a,e) are still characterized by a second set of factors impacting their potential utility for the range of envisioned applications – fluorescence intermittency (blinking) and non-radiative Auger recombination (AR). These attributes of NQD emitters can be considered “intrinsic” properties, as they derive (at least in part) from fundamental NQD photophysics. From this perspective, they are perhaps more challenging to address through new synthesis strategies compared to exclusively surface and environmental factors. The limited, recent successes are described in this review.

“Intrinsic” non-radiative processes that limit NQD utility as light emitters: Blinking and Auger recombination (AR)

At the level of a single dot, NQDs fluoresce intermittently, or blink.^{5–7} Blinking is not limited to NQDs, but is exhibited by a number of fluorophores, including molecular dyes,⁸ and fluorescent proteins.⁹ In NQDs, this process has most commonly been attributed to an ‘Auger model.’^{5,10} In that model, the bright or ‘on’ state corresponds to a charge-neutral NQD, while the dark or ‘off’ condition occurs when the NQD carries an extra charge. The charged NQD is susceptible to non-radiative AR, whereby the energy of a photogenerated electron-hole pair (exciton) is transferred to the extra carrier (electron in the case of a negatively charged NQD, hole in the case of a positively charged NQD), rather than recombining radiatively to emit a photon. NQD blinking, then, arises from the cycling of NQDs between bright uncharged and dark charged states. NQD charging may result from Auger-assisted photoionization (direct or ‘two-step’ trap-mediated⁵) or various tunneling

processes (e.g., Auger-assisted tunneling, conduction-band carrier tunneling⁶) to a range of potential traps on the QD surface or in the surrounding environment (e.g., ligands, liquid or solid matrix, solid substrate).

Importantly, AR in conventional NQDs is very efficient and has implications beyond NQD blinking. AR is efficient as a result of properties that have traditionally been considered “inherent” to NQD physics. Namely, NQDs possess: (1) a strong confinement potential that enhances exciton-exciton coulomb interactions,¹¹ (2) good spatial overlap between electron-hole (eh) wavefunctions,^{12–14} and (3) an abrupt change in quantum-confinement potential at the NQD:surface interface.¹⁵ For this reason, non-radiative AR outcompetes radiative e-h recombination when the NQD is charged.¹¹ The combination of an excess carrier (charge) and a photo-generated exciton is known as a ‘trion.’ Other possible excited-state conditions can exist as well. An NQD can be populated with multiple excitons at the same time, e.g., two (biexciton), three (triexciton), etc. (multiexciton), along with charged versions of these states. Unfortunately, AR not only quenches trion emission, but also emission from multiply excited NQDs. Thus, besides its key role in blinking—a phenomenon central to applications that demand stable emission at the single-NQD level (e.g., long-duration single-particle tracking, single-photon sources, etc.)—AR has important implications for ensemble-level NQD performance. For example, the ability of AR to quench multiexcitons limits the utility of NQDs as emitting layers in light-emitting diodes (LEDs),¹¹ as LED design and operating conditions tend to promote injection of multiple e-h pairs or establishment of an e-h imbalance in the NQD layer, which effectively “activates” non-radiative AR and constrains device efficiencies.^{16,17} Furthermore, AR can cause permanent photobleaching in the event that NQDs become permanently charged. In the context of NQD lasing applications, AR severely limits the lifetime and bandwidth of optical gain,¹⁸ while in the case of NQD photovoltaics, AR restricts the available time to extract multiple excitons generated via carrier multiplication.¹⁹ *For these reasons, in addition to its role in blinking, remedies for efficient AR are technologically significant.*

Recently, the ‘Auger model’ for NQD blinking was challenged.^{20,21} New time-resolved emission data were reported that were proposed to be inconsistent with a model that ascribes ‘off’ periods to a charged state.^{20,21} However, the apparent controversy was then resolved by the discovery that two distinct blinking mechanisms could be responsible for NQD blinking and that within a single population of NQDs, both processes could be observed.²² In this way, the traditional “charging model” for blinking remains as a viable pathway to blinking behavior. In addition, however, an alternative pathway has now been described that accounts for the random cycling between bright and dark states by way of “hot” (energetic) electron capture to surface trap-states. Trapping of a hot electron to an interband trap state effectively short circuits radiative electron-hole recombination, but it does not (necessarily) entail NQD-charging nor require AR processes to reduce NQD emission intensity to a “dark” state.²² In the case of the conventional (charging/AR) blinking model, low PL intensities are characterized by shorter emission lifetimes compared to bright-state emission, for which radiative lifetimes are longer. In contrast, blinking behavior resulting from the newly identified “hot-electron capture” model is not characterized by fluctuating emission lifetimes, as only the intensity fluctuates, an observation consistent with the NQD remaining uncharged. Fluctuations in the occupancy of electron-accepting surface trap states result in the fluctuating intensity, or blinking behavior.

The above considerations suggest that “synthetic solutions” to the blinking problem will vary depending on the nature of the blinking process that prevails in any given system or NQD/environment combination. For some NQDs, or, perhaps, even entire NQD systems, it may only be necessary to suppress hot-carrier-trapping processes and not necessary to address the fundamental NQD property of AR. Alternatively, in situations where charging is

prevalent, AR will need to be suppressed to avoid trion quenching. Significantly, the ability to suppress AR has implications beyond blinking.

Surface modification to suppress NQD blinking: Approaches and pitfalls

Initial efforts to eliminate NQD blinking addressed the charging portion of the blinking problem, which may now also be viewed as surface trapping without charging (as discussed above). This aim has commonly been achieved through supplementation with surface-bound or surface-associated reducing or electron-donating species (e.g., -mercaptoethanol, propyl gallate, oligo(phenylene vinylene)) that electronically passivate (“fill”) surface trap states and suppress pathways for photoinduced charge formation^{23–26} or electron capture. Additionally, charge-accepting species (e.g., TiO₂ nanoparticles) have been used to provide enhanced routes for “de-trapping” and reneutralization.²⁷ Regarding the “ligand” approach, the extent of blinking suppression and modification to blinking statistics depends strongly on the degree of ligand coverage.²⁵ In fact, we showed previously that thiolate ligands can be responsible for both emission enhancement and emission quenching in the case of CdSe/ZnS core/shell NQDs.²⁶

For that core/shell NQD system, we probed changes in e-h dynamics to directly monitor ligand-induced effects on surface-trap states.²⁶ Using transient absorption (TA) techniques, which entailed measuring time-dependent changes in 1S absorption after excitation of an NQD solution (100 fs time resolution), we were able to isolate electron dynamics. Addition of -mercaptoethanol (BME) – the ligand previously reported to suppress NQD blinking²³ – to a solution of polymer-coated CdSe/ZnS NQDs (pH 7.2) was found to permanently eliminate a fast component (decay time ~2 ps). This indicated the stable passivation of electron traps upon BME addition. However, we also studied time-resolved PL (t-PL), which is sensitive to both electron and hole dynamics (70 ps time resolution). We observed an increase in PL amplitude immediately following BME addition without a change in nanosecond dynamics, which was consistent with the passivation of electron traps observed in the TA experiment. Significantly, within a few hours, an additional decay channel (decay time ~1.6 ns) appeared. As the TA data did not indicate any change in the electron dynamics on the nanosecond scale, the new decay channel was attributed to hole dynamics and the formation of hole traps. Notably, the new traps had a deleterious effect on NQD photophysical properties, causing sharp declines in emission efficiencies. We also determined that the anionic form of the thiol ligand (thiolate) was responsible for both of these processes: i.e., thiolate deactivates existing electron trap states at low concentrations (enhancing PL) and introduces new hole trap states at higher concentrations (decreasing PL). Further, the actual concentration of the thiolate anion depends on absolute initial thiol concentration, but also pH conditions and exposure times.

Thus, it seems apparent that ligand approaches to blinking suppression suffer from inadequate reproducibility and robustness due to significant dependencies on local concentration,^{25,26} chemical environment and time.²⁶ For these reasons, we and others have explored NQD core/shell heterostructuring (Figure 1) as an alternative approach to blinking suppression. Furthermore, by structurally modifying an NQD through heterostructuring, it is also possible to alter intrinsic AR in addition to blinking. For example, AR is suppressed in elongated (larger volume) nanorods, where exciton-exciton coupling is reduced,²⁸ and in type-II heterostructures (Figure 1i), where electron-hole overlap is reduced and even repulsive Coulombic interactions can develop.²⁹ That said, simply making semiconductor nanostructures larger (e.g., as a rod or nanowire) does not result in suppressed blinking,^{30,31} while until very recently (see below) it has not been possible to even observe single-dot emission from type-II NQDs due to insufficient stability and rapid photobleaching. Alternatively, alloying of the core/shell interface (Figure 1c,g) has theoretical support for its

ability to dramatically suppress AR by inducing a smoothing of the confinement potential.³² Taken together, several NQD heterostructures are implicated as possible candidates for realizing both blinking and AR suppression. These are reviewed here: (1) interfacial alloying, (2) thick or “giant” shells, and (3) specific type-II electronic structures, with particular emphasis given to synthetic challenges or peculiarities in each case that have driven the realization of unique and important functionality.

NQD heterostructuring to suppress blinking and AR

1. Interfacial alloying

Non-blinking NQDs were prepared from alloyed CdZnSe cores (presumed to be ‘graded’ alloys) capped with a ZnSe shell (Figure 2).³³ These heteronanostructures were thought to be characterized by a gradually changing potential energy function progressing smoothly from the NQD center to its outer surface, resulting from smooth compositional changes. This is in contrast with more standard core/shell constructs whose energy level diagrams are characterized by stepped energy progressions from core to surface, or even with core/shell/shell systems that constitute an intermediate case where a stepwise progression in energy remains but the magnitude of each progressive step in energy (and lattice spacing) is reduced (Figure 1a,b,e,f). Core/shell/shell structures have been demonstrated to improve emission efficiency and NQD stability compared to core/shell structures,³⁴ but this approach did not result in significantly altered blinking or AR suppression.

In contrast, the alloyed CdZnSe/ZnSe core/shell NQDs exhibited highly unusual photophysical properties. First, blinking behavior was absent, resulting in stable, non-fluctuating single-dot PL-versus-time traces for >98% of the 120 studied CdZnSe/ZnSe NQDs (Figure 2). Further, these continuously emitting NQDs had a short PL decay lifetime compared to conventional CdSe NQDs (~5 ns versus ~20 ns, respectively). In addition, the single-NQD PL spectra comprised three distinct peaks rather than the usual one, and the magnitude of separation between the peaks was the same from dot-to-dot (Figure 3).³³

To account for these unique photophysical properties, the authors proposed a model that was consistent with each of the observations (Figure 3). They described the emission as resulting from the radiative recombination of a trion (charged exciton) in NQDs in which AR processes were significantly suppressed. AR suppression was thought to be a feature of the compositionally graded structure. Specifically, in conventional core and core/shell NQDs, the transition from core-to-surface or core-to-shell-to-surface is compositionally and energetically abrupt (Figure 1a,e). This results in the breaking of strict momentum conservation and allows AR to be efficient.¹⁰ In contrast, ‘soft confinement’ of electrons and holes, should significantly reduce AR efficiency. When the nanocrystal is heterostructured as in Ref. 33, non-blinking behavior and emission from charged or multiexciton states can result. Similar observations have been made in the case of some epitaxially grown (‘self-assembled’) QDs that share a similar internal structure.³⁵

Furthermore, the mechanism for blinking suppression in interfacially alloyed NQDs appears quite distinct from that operating in the case of ligand-induced blinking suppression. The multiple peaks and *shorter* lifetimes obtained for the alloyed core/shell structure are in contrast with the single-peak PL spectra and *longer* radiative lifetimes obtained by ligand approaches.²⁶ Therefore, unlike ligand-induced blinking suppression, elimination of surface-state traps is likely not the enabling feature of the CdZnSe/ZnSe system. Rather, AR suppression must be involved, and, in fact, traps are clearly still present, as emission derives from trion (‘charged’) states.

The precise internal structure of the non-blinking CdZnSe/ZnSe NQDs, therefore, plays the key role in realizing the observed unusual properties. For this reason, it is valuable to consider the synthetic methods employed to fabricate this core/shell heterostructure. Synthesis of the alloyed CdZnSe core was guided by prior literature³⁶ that described a step-wise procedure by which binary CdSe cores are first synthesized, then an aliquot of the cooled, crude reaction mixture is reheated to an “alloying point.” To the CdSe cores held at an alloying temperature, diethylzinc (Et_2Zn) and tri-n-octylphosphine-selenide (TOP-Se) precursors are added. The alloying-temperature regime was determined by observing the evolution of the emission wavelength maximum of the resulting product of CdSe NQDs and Zn/Se precursors as a function of temperature. Specifically, Ref. 36 identified 270 °C as the point at which alloying occurs. In the case of non-blinking CdZnSe/ZnSe NQDs, the CdZnSe cores were synthesized at 300 °C. In both references^{33,36} the starting CdSe binary cores were synthesized using excess Se to form a Se-rich surface,³⁶ and the core reaction was cooled to room temperature before an aliquot of the crude reaction mixture was reheated to an alloying temperature (>270 °C). Also, alloying appeared to be preceded by initial formation of a ZnSe shell that rapidly succumbs to compositional mixing with the CdSe core. This temperature-controlled, outside-in diffusion-mediated process likely resulted in graded alloy cores,³⁷ as opposed to homogeneous cores characterized by uniform composition across the entire core. Presumably, this is an essential feature of the core material used in Ref. 33 to achieve non-blinking/suppressed AR behavior. Interestingly, Ref. 36 reported exceptionally high QYs for their alloyed NQDs (up to 85%) combined with unusual stability in QY, PL peak shape and emission wavelength position following heating in air-saturated aqueous solutions (compared to non-alloyed CdSe/ZnS core/shell NQDs). They attributed this robustness to larger particle sizes (lesser surface:volume ratio) and a “hardened” lattice structure (increased covalency) characteristic of the alloy, among other features.³⁶ With this apparently uniquely stable and bright core as a starting point, Ref. 33 further added a binary ZnSe shell.

To date, the interfacial alloying approach to blinking and AR suppression appears to be limited to the CdZnSe/ZnSe system. A possible exception is the CdTe/CdSe core/shell NQD that has been described as exhibiting suppressed blinking.^{38,39} The original reports on this system suggested that the core/shell interface might be unintentionally alloyed,³⁹ while a more recent report (pertaining to a different NQD system) referred more specifically to a “CdTe/CdTe_xSe_y” alloy structure.⁴⁰ These nanocrystals exhibited multiexcitonic emission under continuous wave excitation at 4 K, providing evidence for suppressed AR. A single contour plot of single-dot μ -PL intensity versus the emission energy over time (150 s) was provided as evidence for blinking suppression (emission intensity varies by only ~10% in contrast with more highly fluctuating conventional NQDs). This system would benefit from further study to reveal the actual compositional variations and to validate the blinking behavior.

2. Thick-shell or “giant” non-blinking NQDs

Thick-shell and “giant” CdSe/CdS NQDs are a novel type of heterostructured NQD characterized by suppressed or nonblinking emission that has been rigorously studied, along with strongly suppressed AR. Before the initial reports describing blinking suppression for this system,^{41,42} it was perhaps not obvious that application of a thick shell would lead to suppressed blinking. Though it is now long well known that application of a higher bandgap inorganic semiconductor shell to an emitting core will result in significant improvements in ensemble QYs and NQD “shelf-life,”^{43,44} blinking in such “conventional” core/shell systems has never been significantly impacted.^{45–47} In fact, an initial attempt to assess the effect of shell thickness on NQD blinking reported no dependence.⁴⁹ This result was used as an argument against the relationship between surface effects (charging processes) and

blinking. However, the fact that this report⁴⁹ studied CdSe/ZnS, rather than CdSe/CdS NQDs, is likely significant. Compared to the CdSe/CdS system, the CdSe/ZnS is characterized by a larger lattice mismatch (~11% compared to ~4%). Due to this lattice mismatch, pressure is induced in the structure that can be high even for lesser mismatch values,⁵⁰ which can induce formation of defects in the shell that act as carrier trapping sites not accounted for when simply considering shell-thickness effects on blinking for CdSe/ZnS NQDs.⁴² Additionally, the various reports describing at least temporary suppression of blinking using ‘charge-mediating’ molecules (see above) seem to affirm the significance of NQD charging and/or involvement of surface-trap states.^{23–25}

Thus, a *properly constructed* thick shell may indeed be considered as a probable route to blinking-suppressed behavior through a direct impact on NQD-charging and/or surface-trapping processes. The thick shell may serve as an effective barrier to surface-related carrier trapping or even reduced direct-photoionization processes. Indeed, the reports of suppressed blinking in thick and “giant” shell CdSe/CdS described significant blinking suppression and a strong dependence on shell thickness.^{41,42}

Dubertret’s group reported the synthesis of thick-shell CdSe/CdS NQDs comprising up to ~8 CdS monolayers for which 68% of 165 dots did not blink when observed individually at 33 Hz (30 ms frame exposure or integration time) for 5 min (Figure 4a).⁴² In this report, the percentage of non-blinking NQDs was shown to increase dramatically with shell thickness (from ~1 monolayer to ~8 monolayers CdS) when observed for a period of 1 minute (30 ms integration time), with the thickest shell sample realizing 95% of NQDs possessing on-times >99% (Figure 4c,d). Here, experimental integration time was shown to have a significant impact on the apparent fraction of nonblinking NQDs. For example, longer integration times masked periods when an NQD was ‘off’ if the ‘off period’ was short compared to the integration time. For this reason, the reported fraction of non-blinking NQDs was lower in the case of a 30 ms integration time compared to longer 100 ms or 1 s integration times (non-blinking percentages: 68% versus 83% or 96%, respectively; Figure 4a).

Our report on suppressed-blinking in CdSe/CdS NQDs described the synthesis of ultra-thickshell or “giant” CdSe/CdS NQDs (g-NQDs).⁴¹ In this case, the shell was prepared by successive addition of almost 20 monolayers of shell material (Figure 5). Besides modified blinking behavior, these constructs were characterized by robust ensemble PL that was uniquely insensitive to changes in ligand concentration and identity, as compared to optimized multishell and core-only NQDs. Specifically, following multiple washing steps (cycles of precipitation and re-dissolution), the g-NQD QYs did not change ($\pm 5\%$; Figure 5f), while ensemble QYs for standard multishell NQDs, such as CdSe/2CdS-2ZnS and CdSe/2CdS-3Cd_xZn_yS-2ZnS (where x is varied successively from 0.13 to 0.80), dropped by approximately 30% (Figure 5f) and those for core-only samples dropped by more than 80% (Figure 5f) after 7 washing cycles. g-NQD ensemble PL was similarly unaffected by transfer into the aqueous phase initiated by standard thiol ligand-exchange procedures. It was also evident in this early work that g-NQDs are characterized by a large effective Stokes shift, owing to the condition that absorption is dominated by the very thick CdS shell (absorption onset: ~515 nm), while emission (in the case of properly synthesized NQDs) derives exclusively from the CdSe core (Figure 5e). Significantly, this core emission from the thick-shell core/shell NQD is red-shifted compared to the starting CdSe core PL due to extension of the core electronic wavefunction into the CdS shell (see further discussion below). We recently used this feature of CdSe/CdS g-NQDs to demonstrate improved performance as down-conversion materials for lighting applications resulting from reduced self-reabsorption enabled by the large separation in energy between absorption and emission.⁵¹

Improved ensemble-level performance was complemented by enhanced photostability at the single-dot level. Under continuous excitation conditions (205 mW laser focused on a 50 μm spot), we obtained long, ~ 1 -hour blinking statistics for a large population of >500 dots and observed that $>20\%$ of the g-NQDs were non-blinking (on-time fraction >0.99) and $>40\%$ showed significantly suppressed blinking (on-time fraction >0.8) (Figure 6). In contrast, for classically blinking NQDs, represented here by commercial core/shell NQDs (Qdot655ITK), the majority of dots ($>70\%$) had on-time fractions of <0.2 . Furthermore, conventional core/shell NQDs photobleach under these excitation conditions with a $t_{1/2}$ of ~ 15 min, while g-NQDs do not photobleach during the long observation time.⁵¹

Subsequently, the explicit correlation of shell thickness with extended blinking-suppressed or non-blinking behavior, as well as photobleaching trends, were determined (Figure 7).⁵² For long-observation times (~ 1 h), shells comprising >10 CdS monolayers afforded enhanced blinking suppression compared to only moderately thick shells. Though this trend was clear, batch-to-batch variability afforded some scatter in percent non-blinking population for any given shell thickness, *e.g.*, non-blinking populations for 16-monolayer CdSe/CdS NQDs ranged from ~ 35 – 45% (Figure 7b). Non-blinking fraction was also observed to be a strong function of observation time. For example, a CdSe/16CdS sample was characterized by approximately 80%, 65%, and 40% non-blinking populations when observed for 0.5, 5, and 54 min, respectively.⁵² It is important to note that for all of these many-dot/long-time observations of blinking behavior, single-dot PL was collected through a 40x, 0.6NA microscope objective and imaged onto a liquid-nitrogen-cooled charge-coupled device (CCD) detector. Using a more sensitive time-correlated single-photon counting (TCSPC) system to observe single-dot behavior, however, it becomes evident that a larger percentage ($>80\%$) of g-NQDs never turn into a completely ‘off’ state, but, instead, their intensity fluctuates to such an extent that using a CCD approach the lower intensity state is interpreted as an ‘off’ state. Also using TCSPC methods, it is further possible to reduce integration times to 1–100 ms and confirm that blinking suppression for g-NQDs is not a function of integration time.⁵²

Impact of the thick-shell approach on AR—Initially understood as a shelling effect on the carrier trapping or NQD charging part of the blinking “equation,” the thick-shell or g-NQD approach was soon recognized to also influence the intrinsic NQD property of AR,^{53–55} similarly to the interfacial-alloying approach to non-blinking NQDs. A dramatic increase in CdSe/CdS NQD biexciton lifetimes (τ_2) of more than two orders-of-magnitude (from 60 ps to 23 ns) with increasing shell thickness from 0 to 14 CdS monolayers was reported,⁵⁵ where strongly enhanced biexciton lifetimes indicate a significant suppression of AR. In fact, extracted g-NQD AR lifetimes were estimated to be ~ 15 – 210 ns,⁵⁴ compared to 60 ps AR lifetimes for a reference core-only CdSe NQD. Such extreme AR suppression affords enhanced ensemble properties useful for a range of NQD light-emission applications, such as low-threshold optical amplification over a large bandwidth⁵⁴ and new exciton-to-photon conversion pathways through efficient biexciton and higher-order multiexcitonic emission.^{56,57}

Both larger overall particle size and partial electron-hole spatial separation (due to a ‘quasi-type II’ electronic structure; see below discussion), can effect reductions in AR; however, these contributions to AR suppression have been considered insufficient to realize the extreme reductions in AR efficiency observed for thick-shell and g-NQD CdSe/CdS NQDs.^{54,55} Instead, unintentional interfacial alloying can be invoked as a possible explanation for the remarkable reductions in AR for this system, and interpretations of some spectroscopic evidence from fluorescence-line-narrowing (FLN)⁵⁵ and Raman spectroscopy⁵⁸ studies also suggest this as a possibility. However, replication of the FLN measurement, for example, with an intentionally alloyed control sample or improved use of

alloyed controls in other instances, coupled with direct structural validation of the existence of an interfacial alloy, is needed to further clarify the important question: can extreme AR suppression be achieved in heterostructured NQDs without invoking interfacial alloying?

Peculiarities of thick-shell synthesis—To date, fabrication of thick and “giant” shells in the CdSe/CdS system has relied on a synthesis technique known as successive ionic layer adsorption and reaction (SILAR) core/shell growth to realize epitaxial, largely defect-free CdS shells. SILAR was originally developed for the deposition of thin films onto solid substrates and subsequently adapted to NQD shell growth.^{59,60} The approach entails monolayer-by-monolayer shell addition that is enabled by sequential addition of cationic and anionic precursors sufficient to afford a complete monolayer of shell at each shell-addition step. NQD SILAR methods have been sufficiently refined to allow for precise control over shell thickness and shell monolayer additions. Homogenous nucleation of the shell material is largely avoided and higher shell-growth temperatures are tolerated because the cationic and anionic species do not coexist in the growth solution. SILAR is perhaps not required for growth of thin shells nor for perfectly lattice-matched systems; however, this approach has been clearly shown, for example, to improve the size distribution of moderately thick-shell CdSe/ZnS core/shell NQDs (large lattice match: 12%) compared to their single-injection counterparts.⁶¹ Originally demonstrated for a single-composition shell (CdS over CdSe) up to five monolayers thick,^{60,61} the approach has since been extended to multi-shell architectures,⁶² and now to thick (~7–9 shell monolayers)^{42,63} and ‘ultra-thick’ shell systems (>10 monolayers)^{41,52} as discussed above. The resulting nanocrystals are highly crystalline, uniform in shape, and electronically well passivated.

Synthesis of thick-shell core/shell NQDs has benefitted from the controlled, SILAR approach to growth. This method has generally relied on a traditional combination of precursors, ligands and solvent. Specifically, “bare” CdSe cores (washed of excess core-growth ligands) are dispersed in the high-boiling solvent, octadecene (ODE), to which the primary fatty amine, oleylamine, is also added. Cadmium oleate and elemental sulfur dissolved in ODE comprise the cadmium and sulfur precursors that are added sequentially during SILAR growth. Significantly, SILAR shell addition proceeds roughly as expected, with the predicted number of shell monolayers (calculated based on the amount of precursor added) generally matching the number of shell monolayers obtained (determined from transmission electron microscopy, TEM, sizing), even in the case of the ultra-thick-shell g-NQDs (>10 shell monolayers).⁴¹ However, given that SILAR is a relatively complex step-wise process (compared to rapid single-injection or even continuous injection methods) whose application here ultimately leads to nanostructures that are dominated (on a per-particle volume basis) by the shell material, a systematic exploration of the shell-addition process should aid in the optimization and further extension of this approach to other thick-shell systems. It is notable that despite extensive exploration of thick-shell/g-NQD photophysical properties,^{53–57} and even practical demonstrations of their utility in light-emitting devices,^{51,64} relatively less is known about the details of the shell-growth process that leads to these remarkable characteristics. Thus, to better understand correlations between CdSe/CdS structure and the unusual photophysical properties afforded by this system, as well as any batch-to-batch or even within-batch variability in ensemble-level and single-dot photophysical properties, assessments of a range of key shell-growth parameters have been initiated. It is now known that modifications to these SILAR growth parameters can impact particle shape, crystal structure, and performance.

First, the effect of the primary amine was explored.⁶³ The results of this study led to the conclusion that fatty primary amines favor the wurtzite (hexagonal) crystal structure; whereas, in the absence of these ligands, fatty carboxylic acids seem to stabilize the zinc blende (cubic) structure. Furthermore, it was observed that the presence of primary amines

during shell growth can lead to partial or even complete conversion of starting zinc blende CdSe cores into wurtzite structures, with the ligand having a stronger effect than temperature on determining which crystal structure prevails. Smaller zinc blende cores were observed to succumb to a complete phase transition, while larger cores (smaller surface:volume ratio) experienced only a partial crystalline transition by way of the surface-driven and ligand-mediated process. Subsequent CdS shell growth by SILAR onto initially zinc blende CdSe cores was found to result in highly polytypic core/shell structures, where each particle contained both wurtzite and zinc blende domains as visualized in high-resolution TEM.⁶³ These mixed-phase structures tended to be slightly rod-shaped, exhibiting visible stacking faults that did not appear to significantly affect ensemble QYs, which remained high.

To determine whether purely zinc blende core/shell structures could be obtained starting with zinc blende cores but in the absence of primary amine during shell growth, the SILAR approach was abandoned and a continuous injection protocol was used instead.⁶³ Additional changes included the use of both a tertiary amine [trioctylamine (TOA)] and the common phosphine ligand, trioctylphosphine (TOP). It is not clear whether a SILAR approach employing TOA instead of oleylamine would have produced the same outcome, as this experiment was not reported. As conducted, the resulting core/shell NQDs were purely zinc blende and tetrahedral in shape (characteristic of 'cubic' structures) if grown at 240 °C (Figure 8) and ~spherical if synthesized at 300 °C. It was further concluded that blinking properties for polytypic NQDs were unaffected by the presence of stacking faults and afforded similar blinking suppression compared to pure zinc-blende or pure wurtzite NQDs. However, the blinking data (non-blinking fraction versus time) is only reported for 70 s and does not include a pure wurtzite example. That said, if this data can be directly compared with this group's previous accounts of wurtzite CdSe/CdS NQDs, it would appear that the zinc blende/polytypic results (~30% non-blinking; 33 Hz; 70 seconds) is not competitive with the earlier wurtzite results (~68%, 33 Hz; 5 minutes). Thus, the precise impact of crystal structure and even internal "defect" structure on blinking properties remains to be definitely determined.

A notable difference between conventional SILAR or even thick-shell CdSe/CdS synthesis⁴² compared to "g-NQD" synthesis⁴¹ is the use of longer reaction times in the latter case. While standard SILAR employs ~10-minute cycling times, g-NQD synthesis has been characterized by much longer and "asymmetric" reaction times, e.g., 1 hour anneals following each sulfur addition and 3 hour anneals following each cadmium addition.⁴¹ This distinguishing feature of the g-NQD synthesis was recently revisited.⁶⁵ Quantum yields at three different shell thicknesses (5, 11, and 15 monolayers CdS) were compared for different combinations of anneal times. All other reaction parameters (including the CdSe cores) were identical, and reported QYs comprised an average over 2–3 reactions. As expected, in all cases QYs dropped with increasing shell thickness. More significantly, the standard 10-minute anneals, when applied to both Cd and S, afforded the lowest QYs recorded for each shell thickness. Long S anneal times of 3 hours combined with either long (1 hour) or short (10 minute) Cd anneals also resulted in relatively poor QYs. All three of these anneal protocol produced 15-monolayer g-NQDs with unacceptable QYs of ~5%. In contrast, long Cd anneal times (3 hours) combined with either short or moderate S anneal times (10 minutes or 1 hour) resulted in "usable" QYs at both 11 and 15-shell monolayers that varied from ~25–40% to 20–25%, respectively, with the 3-hour Cd/1-hour S combination affording the higher QY at the thickest shell. Batch-to-batch variability in QY (with significantly higher g-NQD QYs occasionally observed) to some extent tempers our confidence in these results; nevertheless, the trend is clear that long Cd and shorter S anneal times favor higher QYs at thick shells, while very long S anneal times are detrimental.

In addition to anneal times, other growth parameters have been systematically explored for their impact on structural and photophysical properties of CdSe/CdS NQDs.⁶⁵ These are shown schematically in Figure 9. A complicating factor of thick CdS-shell growth is that at some point during the shell-addition process the reaction mixture becomes turbid. This transition from clear to turbid always follows a Cd addition cycle, and the onset has now been determined to be a strong function of the particular choice of SILAR reaction parameters. Initially, the apparent “precipitation” is fully reversible upon addition of even a few drops of S precursor solution. For later shell cycles, however, an entire S aliquot is required to clear the solution, and, finally, the solution remains turbid even after addition of the anion. We have attributed within-batch and batch-to-batch structural or optical-property inconsistencies, at least in part, to the observation of “turbidity/solubility cycling.” For this reason, reaction-parameter modifications were targeted at suppressing this process.⁶⁵

First, replacing octadecene with octadecane as the non-coordinating solvent afforded a dramatic shift of the onset of turbidity cycling from ~7 to 11 shelling cycles. Combined with limited dilution at later stages of growth (sufficient octadecane added to reduce reactant concentrations by ~20%), the new solvent also yielded enhanced regularity and uniformity in particle shape. In contrast, however, more extreme dilution (~80% reduction in reactant concentrations) had a deleterious effect on NQD structure and properties. Although turbidity cycling was suppressed, the resulting particle structures and optical properties were non-ideal – particles were shaped like ‘half-moons’, clearly polytypic (mixed wurtzite/zinc-blende) and afforded low ensemble QYs.

Second, the effects of different coordinating ligands were investigated. As described earlier, the traditionally used ligands are the primary fatty amine, oleylamine, and the fatty acid, oleic acid (OA). The amine is added in its entirety at the start of the shell-addition process, while oleic acid is added with each aliquot of cadmium precursor in a ratio of 1:4 or 1:10 Cd/OA. The primary amine can serve both as a coordinating ligand and as a base to deprotonate the fatty acid to form oleate. Oleate then covalently binds to surface Cd ions (preferentially compared to oleic acid⁶⁵), while oleylamine datively couples to Cd. Analysis of FTIR spectra obtained for CdSe/CdS NQDs synthesized using different ligand/precursor ratios and/or ligands suggested that the extent to which the amine serves as a coordinating ligand is determined by the amount of oleic acid (oleate) present in the reaction. When less oleic acid is added to the reaction with each addition of cadmium precursor (1:4 Cd/OA), amines are found coordinated to the NQDs. In contrast, higher oleic acid amounts (1:10 Cd/OA) result in oleate dominating ligand coverage at thicker shells. Both Cd/OA ratios can result in high-quality, wurtzite NQDs with good QYs, though dominance of oleate ligands affords noticeably more highly faceted particles.⁶⁵

We now also know that it is possible to completely eliminate ‘turbidity cycling’ by replacing oleylamine with the secondary amine, dioctylamine.⁶⁵ Importantly, however, the resulting core/shell NQDs are non-emissive. Furthermore, they exhibit an unusual octahedral shape combined with a wurtzite crystal structure, with FTIR studies revealing the dominance of oleate ligands at thick shells (for both 1:4 and 1:10 Cd/OA ratios). In this case, the secondary amine was considered to serve as an effective base (producing oleate), but its role as a ligand was thought to be compromised by its relatively greater steric bulk (compared to oleylamine), limiting its ability to compete with oleate for NQD surface sites. In addition, the ability of oleate to form strong covalent bonds with Cd likely favored the unique octahedral morphology, as this crystal shape exposes multiple (four) purely Cd-terminated faces for oleate binding. Thus, when oleate is favored as the coordinating ligand (e.g., dioctylamine/oleic acid combination or oleylamine/oleic acid combination with 1:10 Cd/OA ratios), thick-shelling favors crystal shapes that terminate with ‘all-Cd’ faces (four Cd faces in the case of octahedral structures and one in the case of hexagonally faceted particles).⁶⁵

The effect of reaction stoichiometry on turbidity cycling and the resulting NQD structures and properties has also been investigated. In general, SILAR shelling protocols employ addition of stoichiometric amounts of precursor. The number of core NQDs present in a reaction is determined, and the amount of anion and cation required to grow exactly one monolayer of shell material is calculated based on this NQD-core concentration, as well as the size of the cores. The effective “core” size increases with each addition of a shell layer, requiring increasing amounts of per-monolayer shell precursors as the reaction proceeds. A 100% conversion of the shell precursors is assumed and largely borne out by the observation that core/shell particle sizes determined by TEM are close to that calculated based on the known starting CdSe core size and the thickness of a monolayer of CdS (1/2 wurtzite c lattice parameter: 0.3375 nm). However, an excess of feedstock might actually better support the dynamic equilibrium of shell adatom addition, re-dissolution, and rearrangement that occurs at the solvent/NQD interface during shell-monolayer formation. To this end, precursor:NQD ratios were enhanced by 1% and 10%. Although turbidity cycling was significantly suppressed or eliminated, respectively, by enhancing precursor concentrations, these conditions resulted in non-ideal moderately emissive rod-shaped (1%) or poorly emitting irregularly shaped/sized particles (10%). Nevertheless, by combining a moderate (1%) increase in precursor concentrations with an increase in oleic acid (2.5x more OA added per cycle midway through shell growth), it is possible to fine-tune shell addition to achieve high QYs and well-shaped hexagonally faceted particles. Interestingly, turbidity cycling returns as a characteristic feature of the reaction but can be postponed until >10 shell monolayers, and does not seem to have a deleterious impact on structural or optical properties.

A dipole-dipole coupling mechanism was proposed to account for the different observations of enhanced, reduced or eliminated turbidity cycling as a function of reaction conditions and resulting particle shape and crystal structure.⁶⁵ The fact that wurtzite CdSe NQDs are characterized by a particle-size-dependent permanent dipole moment was considered the underlying cause of particle-particle associations that resulted in enhanced solution turbidity. Further, ligand effects on dipole screening, as well as the influence of surface reconstruction/relaxation processes on reducing dipole moments (potentially by nearly an order-of-magnitude)⁶⁶ were thought likely sources of the cyclic nature of the process, influenced by whether the cation or the anion had been most recently added to the reaction mixture.⁶⁵ Significantly, the reaction conditions that afforded zinc-blende or primarily zinc-blende thick-shell CdSe/CdS NQDs, or even hexagonal CdSe/CdS NQDs that adopted a more conventionally cubic shape (i.e., octahedral), did not exhibit turbidity cycling, consistent with a dipole-dipole-mediated process dependent on an underlying wurtzite crystal structure and hexagonal faceting.

Despite our initial hypothesis that elimination of turbidity cycling would improve shell growth and enhance thick-shell properties, to date, the conditions leading to complete solution clarity also produce non-optimal core/shell structural and optical properties. In contrast, the highest quality g-NQDs (structurally and optically) seem to benefit from conditions that entail at least some degree of turbidity cycling (ideally controlled to manifest late in the shell-addition process and tempered by moderate dilution). The more optimized procedures now consistently produce g-NQDs (>15 CdS monolayers) with QYs >50% from batch-to-batch.⁶⁵

In summary, the thick-shell approach to suppressed blinking behavior is highly effective and can result in essentially completely suppressed blinking and dramatic reductions in AR efficiency. It is also evident that this approach is highly dependent on the precise method used for shell growth. New understanding of the constraining synthetic parameters for optimal monolayer-by-monolayer shell growth out to ~20 shell monolayers suggest the

following as effective: long Cd (3 h) and moderate S (1 h) anneal times combined with octadecane solvent (“excess” added late in shell growth to reduce reaction concentration by ~20% and effect a partial reduction in solution turbidity), oleylamine and oleic acid (in excess) coordinating ligands, and a somewhat non-stoichiometric precursor:NQD ratio (1% enhanced in precursors).

The influence of core size on non-blinking fraction—Although much attention has been given to the effect of shell thickness on thick-shell CdSe/CdS NQD photophysical properties, the effect of tuning core size from very small (~2 nm) to very large (>5 nm) has been relatively less explored. Recently, it was shown that for all core sizes the “nonblinking” NQD fraction increases as a function of shell thickness (Figure 10a).⁶⁵ Interestingly, however, the onset of blinking-suppression begins at different shell thicknesses for different core sizes: the largest cores exhibit the earliest onset of nonblinking behavior, while the smallest cores reach this transition at significantly thicker shells. This trend results in the largest cores (5.5 nm) achieving essentially fully suppressed blinking at thick shells (>85% of the NQDs are nonblinking for the ~1 hour observation time), while the smallest cores (2.2 nm) exhibit relatively little nonblinking behavior even after addition of ultra-thick CdS shells (Figure 10b). This result is clearly a particle-volume effect, as is evident when nonblinking NQD fraction is instead plotted as a function of NQD volume (Figure 10c). Below a “threshold” volume blinking is not suppressed and above this volume nonblinking fractions increase roughly linearly with further increases in particle volume. Whether achieved by a combination of a small core and a thick shell or a large core and a relatively thinner shell, the core/shell NQD volume of ~750 nm³ appears to be the minimum volume required for transitioning to non-blinking behavior in the CdSe/CdS system (a similar threshold was observed for emission lifetimes).⁶⁵

It is important to note that this reported “volume threshold” for non-blinking behavior is specific to our unusually long ~1-hour observation times. *Using less rigorous, shorter test times (e.g., the more typical 300 s) will shift the threshold volume to significantly smaller sizes*, suggesting that the desired CdSe/CdS size will depend on the intended application and its necessity for a short or a long observation time.⁵²

3. Thick-shell Type II NQDs

Recently, the thick-shell approach to blinking suppression was applied to an InP core to realize a novel InP/CdS core/shell NQD (Figure 11).⁶⁷ The combination of an InP core and a CdS shell results in a fully type-II electronic structure that is characterized by complete spatial separation of the excited state electron-hole pair (Figure 1i and Figure 11a). The hole is energetically confined to the InP, while the electron resides in the CdS shell. Here, the bandgap energy derives from a spatially indirect transition,^{68,69} or charge-transfer state,⁷⁰ that involves electron-hole recombination across the core-shell interface. Thus, the bandgap can be smaller than that achievable by either the emitting core or the shell material alone, and exciton lifetimes are typically long.^{71,72}

In the case of InP/CdS, it was indeed observed for all shell thicknesses (1–10 CdS monolayers) that core/shell bandgap energies were smaller (“redder”) than the bandgap energies for equivalently sized InP NQDs, consistent with the formation of a type-II electronic structure at very early stages of shell growth. Furthermore, the well-defined 1S absorption peak of the starting InP cores broadened and red-shifted upon initial shell addition, similar to previous accounts of type-II NQD absorption trends.⁷¹ Here, however, InP/CdS NQD absorption was subsequently dominated by the thick CdS shell (wavelengths <520 nm), resulting in a large “effective” Stokes shift (separation between emission and absorption) like CdSe/CdS g-NQDs, but unlike previously reported type-II NQDs.

Significantly, it was further observed that photoluminescence excitation (PLE) spectra followed similar trends as the absorption spectra. The coincidence of absorption and PLE spectra showed that electron-hole pairs created in the absorption-dominating thick shell can efficiently relax into the emitting indirect or charge-transfer state. Finally, radiative lifetimes for the type-II InP/CdS increased approximately linearly as a function of shell thickness, exhibiting a more dramatic enhancement compared to their quasi type-II counterparts for which PL lifetimes tended to plateau after a certain number of shell monolayers had been added (or a total particle volume had been reached).⁶⁵

The fully type-II nature of the InP/CdS core/shell system also distinguishes this class of NQD with respect to blinking behavior. Like CdSe/CdS NQDs, InP/CdS NQDs were observed to exhibit suppressed blinking, but the correlation with shell thickness was less clear. Even thin-shell InP/CdS NQDs (InP/1CdS and InP/4CdS) exhibited significant blinking suppression (Figure 12a), with ~15–25% of the dots demonstrating on-time fractions of >0.80 of the observation time (5 min). In contrast, for both quasi type-II CdSe/CdS and type-I CdSe/ZnS NQDs, 0% of an NQD population possesses on-time fractions >0.80 at these shell thicknesses (1 h observation times; although ~20% of thin-shell CdSe/CdS NQDs exhibited on-time fractions >0.20 compared to 0% in the case of CdSe/ZnS).⁵² Blinking suppression further improves as shell thickness is increased to 3.84 nm (InP/10CdS), with >60% of the InP/10CdS NQDs characterized by on-time fractions >0.80 and several dots exhibiting fully non-blinking behavior (Figure 12a, InP/10CdS “dot indices” 2, 9, 10, and 11).

Taken together, it is tempting to conclude that partial to complete electron-hole spatial separation manifests as some degree of blinking-suppressed behavior even in the case of thin-shells, as observed previously in the comparison of CdSe/CdS and CdSe/ZnS NQDs⁵² and now more strongly in the early-onset blinking suppression of InP/CdS NQDs.⁶⁷ That said, more examples of different combinations of shell thickness and electronic structure, also taking into account the possible effects of core/shell interface (lattice mismatch, alloying), are required to quantitatively define the ideal “architectural parameters” for designing non-blinking behavior into the NQD heterostructure.

Unlike blinking behavior, InP/CdS photobleaching and biexciton lifetimes trended definitively with shell thickness. The thinnest shell NQDs photobleached with a half-life of ~15 minutes, consistent with conventional NQD behavior,⁴¹ while ~60% of thick-shell InP/10CdS NQDs did not photobleach over long times (>3 h) (Figure 12c). In addition, the ratio between single and biexciton lifetimes (a measure of the relative strength of AR) decreased from 3276 to 97.5 from InP/1CdS to InP/10CdS, indicating a significant reduction in AR with increasing shell thickness, though, significantly, not a “zero” contribution.⁶⁷ Here, the suppressed AR may play a role in blinking suppression, but is not sufficient to conclusively describe InP/CdS blinking as AR-mediated.

It is important to point out that the InP/CdS system is an unusually “stable” type-II NQD. It is the first type-II system for which of room-temperature single-dot PL was obtained. In other cases, photobleaching under single-dot excitation conditions has prevented such analyses.³⁷ The enhanced stability also enabled for the first time detection of single infrared emitters without the aid of specialized detectors. Even nominally brighter type-I infrared-emitting NQDs have proven difficult to assess by standard methods, requiring use of highly specialized single-photon detectors to surmount materials issues of instability and relatively long emission lifetimes.⁷³

Addressing challenges to synthesis of high-quality core/shell NQDs comprising InP cores—To achieve this unusual degree of stability in optical

performance, peculiarities of InP nanoparticles had to be surmounted in the synthesis of InP/CdS NQDs. Specifically, InP cores are far more susceptible to surface oxidation and particle etching compared to CdSe NQDs.⁷⁴ The tendency to oxidize requires unusual care in applying air-free procedures prior to shell growth, while susceptibility to surface etching prevents use of high growth temperatures combined with acidic or basic ligands.⁷⁵ It is likely for these reasons that relatively fewer successful high-temperature, SILAR-based preparations of core/shell NQDs with InP cores have been reported.⁷⁶ To render InP NQDs amenable to thick CdS shell growth, a first shell monolayer was applied using lower, nonideal shell-growth temperatures to serve as a “protective” layer for subsequent shell additions that employed conditions optimized for higher quality shell growth.⁶⁷ The approach worked and resulted in high-quality thick shells that retained the thermodynamic crystal structure for CdS – the hexagonal or wurtzite phase. The underlying cubic or zinc-blende InP core did not alter the tendency of the chosen shell-growth parameters (similar to that used for optimal CdSe/CdS g-NQD shell growth) to produce hexagonal shells. Presumably benefiting from the combination of a controlled-growth approach and a small lattice mismatch (<1%), the resulting core/shell particles were regularly shaped and exhibited hexagonal faceting at thick shells, in contrast with some previously reported type-II systems.^{68,71}

CONCLUSION

Three approaches to NQD heterostructuring that enable suppression of blinking and AR have been reviewed here: (1) interfacial alloying, (2) thick or “giant” shells, and (3) specific type-II electronic structures. Each has been applied with the intention to control or eliminate non-radiative processes that otherwise hinder application of NQDs for a range of uses from single-particle tracking and advanced bioimaging to lasing, single-photon light sources and solid-state lighting. As a result of these recent studies, structural motifs are beginning to emerge as design criteria for realizing non-blinking and dramatically suppressed AR functionality. These include—either individually or in concert—the inclusion of compositional gradients at a core/shell interface, the extension of a shell layer out to many monolayers, and the introduction of some degree of ‘type-II’ character into the core/shell electronic structure. However, more and systematic studies of these parameters, along with improved theoretical understanding, are required to afford a truly predictive capability for rational design of the next non-blinking/suppressed AR heterostructured NQD.

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Figure 1.

Heterostructured nanocrystal quantum dots: variations on a theme. Core/shell heterostructures comprising (a) a conventional thin shell, (b) multiple shells of different compositions, (c) a compositionally graded core-shell interface, and (d) a thick or “giant” shell. Potential energy diagrams depicting (e) a type I band alignment, where both carriers (electron: closed circle; hole: open circle) are localized in the core, (f) a stepped type I band alignment resulting from multishell growth, (g) a gradually changing potential energy function resulting from interfacial alloying, (h) quasi type II band alignment, where one carrier (here, the electron) is partially delocalized into the shell, and (i) type II band alignment characterized by complete spatial separation of the carriers. (h) and (i) are both drawn for the particular case of a thick shell, as shown in (d).

Figure 2.

Single-nanocrystal images and photoluminescence intensity time traces. (a) Electron micrograph of a CdZnSe/ZnSe nano-crystal with diameter ~ 5 nm and length ~ 6.7 nm. Chemical information with atomic resolution was not achieved owing to difficulties obtaining energy-loss signals from Zn, and the weak contrast between Cd and Zn. (b) Photoluminescence image ($\sim 3 \mu\text{m} \times 3 \mu\text{m}$) from a single CdZnSe/ZnSe nanocrystal (different nanocrystal from a). (c), (d) Time dependent photoluminescence intensity traces from a single CdZnSe/ZnSe nanocrystal (c) and a CdSe/ZnS nano-crystal (d). Similar time traces were obtained from 118 ($>98\%$) of 120 CdZnSe/ZnSe nanocrystals studied. Reprinted by permission from Macmillan Publishers Ltd: Nature (Ref. 33), copyright 2009.

Figure 3. Single-nanocrystal photoluminescence spectra and the “shakeup process.” (a) Photoluminescence spectra of five selected single CdZnSe/ZnSe nanocrystals. (b) Photoluminescence spectrum of a single CdSe/ZnS nanocrystal. (c) Diagram of a shake-up process used to explain the multi-peaked photoluminescence spectrum from a single CdZnSe/ZnSe nanocrystal. The annihilation energy of the trion (spacing between two dashed lines) is distributed between the emitted photon energy (shown by blue, green and red arrows) and the energy of the extra hole, which could occupy one of many allowed levels after recombination. Reprinted by permission from Macmillan Publishers Ltd: Nature (Ref. 33), copyright 2009.

Figure 4.

Intensity fluctuations and blinking behaviour of single CdSe–CdS QDs visualized with a CCD camera. (a) Fraction of nonblinking quantum dots as a function of integration time. Images are acquired continuously for 5 min. Statistics on 165 QDs. Measurements were made on a dried QD film. (b) The same sample and recording conditions as in a. Number of dark states versus maximum emission intensity for each QD. Inset: Proportion of QDs emitting at a given maximum intensity. (c) Percentage of QDs that have not blinked versus time for different CdS layer thicknesses. Different layers are obtained by successive injections of shell precursors. All films were acquired in the same conditions and the statistics for each layer were on at least 120 QDs using automatic home-made software. Images were acquired continuously for 1 min at 33 Hz. Inset: fluorescence lifetime for the various shell thicknesses. (d) Percentage of time a QD spends in a dark state during 1 min measurement at 33 Hz. Red, CdSe with eight CdS shells; blue, CdSe–ZnS QDs. Statistics on more than 150 QDs for each QD type. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials (Ref. 42), copyright 2008.

Figure 5.

Transmission electron microscopy (TEM) images for (a) CdSe NQD cores, (b) CdSe/19CdS g-NQDs, and (c) CdSe/11CdS-6Cd_xZn_yS-2ZnS g-NQDs. (d) Absorption (dark blue) and PL (light blue) spectra for CdSe NQD cores. (e) Absorption (dark red) and PL (light red) spectra for CdSe/19CdS g-NQDs (inset: absorption spectrum expanded to show contribution from core). (f) Normalized PL compared for growth solution and first precipitation/redissolution for CdSe/11CdS-6Cd_xZn_yS-2ZnS and CdSe/19CdS g-NQDs (red), CdSe/2CdS-2ZnS and CdSe/2CdS-3Cd_xZn_yS-2ZnS NQDs (green), and CdSe core NQDs (blue). Dashed line indicates no change. Reprinted from Ref. 41.

Figure 6. Single NQD studies. (a) Emitting NQD fraction over time: Qdot655ITK (black); g-NQD CdSe/19CdS (red). (b) Fluorescence image and (c) on-time histograms of Qdot655ITK (left) and CdSe/19CdS g-NQD (right). Insets in (c) show fluorescence time traces of the circled NQDs in (b). Temporal resolution is 200 ms. Reprinted from Ref. 41.

Figure 7. Single-NQD photoluminescence studies. (a) On-time histogram of a CdSe/19 CdS g-NQD population constructed from analysis of typically >100 individual g-NQDs. An example fluorescence time trace (used to prepare a histogram) for an individual CdSe/19 CdS g-NQD is shown in the inset to (a). Plot of 'percent NQD population' versus the number of CdS shell monolayers for different on-times (b). Two preparations/analyses are plotted for the 10-, 16-, and 19-shell systems, providing an indication of experimental variability in (b). Photobleaching behavior: plots of emitting NQD fractions over time are presented for CdSe/5 CdS (top left), CdSe/10 CdS (top right), CdSe/15 CdS (bottom left), and CdSe/19 CdS (bottom right) core/shell NQDs (c). Reprinted from Ref. 52.

Figure 8. TEM picture of perfect zinc blende CdSe/CdS tetrahedral nanocrystals (edge length: 9 nm). FFT of HRTEM image reveals a characteristic [110] zone axis. Reprinted from Ref. 63.

Figure 9.

SILAR Reaction Scheme for Growth of Thick-Shell Core/Shell NQDs. Blue text denotes general reaction parameters and reaction flow, while green text shows options for modifying specific reaction conditions to influence g-NQD physicochemical and optical properties. Reprinted from Ref. 65.

Figure 10.

(a) Non-blinking NQD fraction (defined as the population of NQDs “on” for 99% of the observation time) as a function of shell thickness for different core sizes. Core size is indicated within the figure, where d refers to diameter. (b) Histogram of blinking statistics for thick-shell NQDs fabricated using an extra-large (top) or a small (bottom) CdSe core. For approximately the same shell thickness, the large core achieves essentially complete suppression of blinking. (c) Non-blinking NQD fraction as a function of total particle volume for different starting core sizes [see (a) for legend]; shaded region highlights the particle volumes that fall below the “threshold volume” of $\sim 750 \text{ nm}^3$, above which non-

blinking fraction increases approximately linearly with NQD volume. For (a)–(c), observation time used to obtain blinking statistics is ~1 hour. Modified from Ref. 65.

Figure 11.

InP/CdS core/shell NQDs. (a) Schematic of the InP/CdS core/shell structure and the relative bulk bandgap alignment of the core and shell materials. Localization of the excited electron in the CdS shell and the resulting hole in the InP core is indicative of type-II bandgap structure. (b-e) TEM images of InP/CdS core/shell nanocrystals after 1, 4, 7, and 10 successive shell depositions, respectively. The scale bar for all four images is 5 nm. Reprinted from Ref. 67.

Figure 12.

Blinking and photobleaching. (a) Summary of blinking behavior for multiple individual NQDs for several shell thicknesses. Each dot index represents the blinking behavior of one dot. Black regions in each image represent times when the dot is in the “off” state. Colored regions correspond to “on” states. Green, orange, and red traces represent single dot data from InP/1CdS, InP/4CdS, and InP/10CdS, respectively. (b) Representative intensity trajectories of single NQDs (both InP/10CdS). The top and bottom traces correspond to dot indices 4 and 10 in the top panel, respectively. (c) Relative photobleaching from each sample over time. NQDs drop-cast and imaged under wide-field laser excitation (405 nm) using a CCD with 1 s integration time for three hours. The number of dots having a PL

intensity above a threshold value was tabulated for each frame. The fraction of dots meeting this criterion (relative to the number of dots present at $t = 0$) is plotted as a function of time. Reprinted from Ref. 67.