

Synthetic Control of Exciton Behavior in Colloidal Quantum Dots

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ABSTRACT: Colloidal quantum dots are promising optical and optoelectronic materials for various applications, whose performance is dominated by their excited-state properties. This article illustrates synthetic control of their excited states. Description of the excited states of quantum-dot emitters can be centered around exciton. We shall discuss that, different from conventional molecular emitters, ground-state structures of quantum dots are not necessarily correlated with their excited states. Synthetic control of exciton behavior heavily relies on convenient and affordable monitoring tools. For synthetic development of ideal optical and optoelectronic emitters, the key process is decay of band-edge excitons, which renders transient photoluminescence as important monitoring tool. On the basis of extensive synthetic developments in the past 20–30 years, synthetic control of exciton behavior implies surface engineering of quantum dots, including surface cation/anion stoichiometry, organic ligands, inorganic epitaxial shells, etc. For phosphors based on quantum dots doped with transition metal ions, concentration and location of the dopant ions within a nanocrystal lattice are found to be as important as control of the surface states in order to obtain bright dopant emission with monoexponential yet tunable photoluminescence decay dynamics.

INTRODUCTION

Colloidal quantum dots are single-crystalline semiconductor nanocrystals with their sizes in quantum confinement regime, which renders them as size-dependent and solution-processable materials for optical and optoelectronic applications.^{1–4} For example, quantum dots as emissive materials can readily offer continuously color-tunable and narrow emission with versatile excitation.⁵ They are capable to act as either fluorophores or phosphors.⁶ Generally, excited states dominate performance of any optical and optoelectronic materials, especially emissive materials. For colloidal quantum dots, their excited states are usually described as exciton—a pair of photo- or electro-generated electron and hole bonded together through Coulomb interaction. In principle, synthetic chemistry should yield quantum dots with well-controlled excitons.

Exciton in a quantum dot is unique in many ways in comparison with the excited states of either molecular species or bulk semiconductors. In a quantum dot, exciton delocalizes within the entire nanocrystal, which effectively dissipates the excited-state energy to a huge amount of chemical bonds in a nanocrystal, such as ~40 000 Cd–Se bonds in a 10 nm CdSe quantum dot. As a result, crystal structure—including bond

length and bonding configuration—of a quantum dot in its excited states barely deviates from the thermodynamically stable crystalline structure at the ground state. This is in stark contrast to the excited states of a typical organic molecule. In comparison to an exciton in bulk semiconductor, exciton in a quantum dot is largely exposed to the physical boundary between the nanocrystal and its ligands/solvent due to the limited physical size. Furthermore, it is a constructive idea to view colloidal quantum dots as inorganic–organic complexes because of the crucial role of organic ligands.^{7,8} During their synthesis, ligands are necessary not only to stabilize the inorganic nanocrystals but also act as convenient means to control their nucleation and growth.⁹ Ligands bonded on the surface of quantum dots could modify surface electronic states, which would thus significantly influence behavior of the excitons.

The structural features discussed above imply that optimal characteristics of exciton in a quantum dot can only be achieved by precise control of both interior crystal and surface structure. Synthetic efforts on controlling interior crystal structure of quantum dots have been widely explored in the past. Synthesis of CdSe quantum dots in organic coordinating solvents under high temperatures with organometallic precursors earmarked possibility to control the interior crystallinity of the nanocrystals.^{10,11} Since then, synthetic chemists have been focused on control of the size and shape of single-crystalline quantum dots,^{11–15} “greener synthetic schemes” for better control and reproducibility,^{16–20} mechanisms on nucleation and growth,⁹ and expansion of available compositions.^{21–23}

Studies on exciton behavior in quantum dots have been mostly carried out by a separate group of scientists in the recent years, i.e., experimental and theoretical spectroscopists. However, it is interesting to notice that, though specialists enjoy playing in their own choice of subjects, advancement of synthetic chemistry has always promoted spectroscopic studies of excitons.

With great achievements on both spectroscopic studies of excitons and synthetic chemistry in the past ~30 years, there might be new opportunities to reunite two subjects. This would add a new emphasis into the synthetic chemistry of quantum dots, which is control of their exciton behavior. In this sense, synthetic chemistry of colloidal quantum dots would depart from organic synthetic chemistry. Synthetic chemistry of organic compounds usually aims to ground-state structures. This would be true even for organic molecules as optical and optoelectronic materials because the ground state and excited states for a given organic molecule are usually on precise

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correlation with each other. This is not the case for colloidal quantum dots because of their extremely large molecular mass and difficulty to fully characterize the surface structure—including both inorganic surface and its organic ligands. As a result, colloidal quantum dots with indistinguishable ground-state properties under current characterization tools might possess vastly different exciton behavior.

MONITORING EXCITON PROPERTIES IN A QUANTUM DOT WITH PROPER TOOLS DURING SYNTHESIS

Figure 1 summarizes most common processes associated with the excited states of a quantum dot. Excitation of an electron

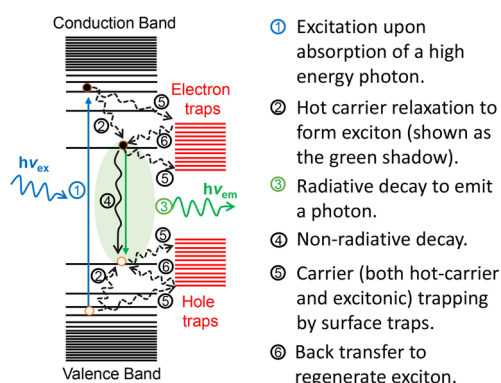


Figure 1. Scheme of basic processes involving various excited states in a quantum dot upon photoexcitation.

from the occupied orbitals (valence band) of a quantum dot to its unoccupied orbitals (conduction band) usually generates a hot electron in the conduction band and a hot hole in valence band (Step 1 in Figure 1). Hot electron (hole) relaxes to the lowest unoccupied orbital (highest occupied orbital) of the nanocrystal and form a band-edge exciton bounded by Coulomb interaction (Step 2 in Figure 1). A pair of hot electron/hole is often called “hot exciton”. For simplicity, we would label them as hot carriers. If no confusion, “exciton” refers to a pair of electron/hole at the band edge, which is more precisely called band-edge exciton (Shown as a green oval in Figure 1). Hot carriers and band-edge excitons may be captured by the corresponding traps (Step 5 in Figure 1). If the trap states are at proper energy position and can trap carriers for a sufficiently long period of time, the trapped carriers might back-transfer to regenerate an exciton (Step 6 in Figure 1) and lead to nonintrinsic decay channel(s) for the quantum dot to come back to the ground state.

Though more stable than hot carriers, the exciton is still metastable, which has several ways to come back to the ground state, i.e., radiative decay (Step 3 in Figure 1), nonradiative decay (Step 4 in Figure 1), and trapping discussed above (Step 5 in Figure 1).

Evidently, the ground state is the only steady state and all other states including hot carriers, band-edge exciton, and trap states are transient states. Usually, typical ground-state properties of colloidal quantum dots applied for monitoring synthesis and characterizing synthetic products include size, shape, size/shape distribution, interior crystal structure, and sometimes number/type of organic ligands. As discussed in the previous section, these do not directly dictate the excitonic

properties though they offer a necessary basis for controlling the exciton behavior.

From a technical point of view, synthetic control of exciton behavior in a colloidal quantum dot calls for closely monitoring the responses of excitons against variations of synthetic conditions. When discussing monitoring exciton behavior in synthesis, we are considering means that are compatible with synthetic development in economic cost, time consumption, and convenience.

Coupled with electron microscope and diffraction techniques, spectroscopic techniques commonly used for monitoring synthesis of quantum dots include absorption, photoluminescence, and photoluminescence excitation. Absorption spectra are related to generation of excitons. Photoluminescence spectra coupled with photoluminescence quantum yield—defined as the ratio between emitted and absorbed photons—reveal certain aspects of the radiative decay of excitons. Photoluminescence excitation spectrum records photoluminescence intensity versus excitation wavelength, which can be readily obtained using a typical fluorimeter and well suited for monitoring synthesis. If photoluminescence excitation spectrum of a sample closely resembles its absorption spectrum, one would conclude that the hot-carrier decay—including hot-carrier relaxation and hot-carrier trapping in Figure 1—is independent of excitation wavelength. If photoluminescence excitation spectra at various wavelengths on the photoluminescence spectra coincide with each other, it indicates that the sample is composed of a batch of nanocrystals with the same photoluminescence. Monodispersity of photoluminescence of a sample of colloidal quantum dots can further be measured by photoluminescence peak width (usually full-width-at-half-maximum, fwhm), which should ideally be independent to that of single-dot photoluminescence (see below).

The spectroscopic techniques mentioned above are all steady-state optical measurements. Thus, they are far from being sufficient to define those transient states within a quantum dot.

The most important signature of a transient state is its decay dynamics, which are usually probed by transient absorption and transient photoluminescence. The hot hole/electron states for common quantum dots are nearly nonemissive transient states with extremely fast decay dynamics. Their decay can thus only be followed by femtosecond/picosecond transient absorption, which is very costly and inaccessible for monitoring synthesis. Exciton—more precisely band-edge exciton—is usually an emissive transient state with an intrinsic lifetime being around several tens of nanoseconds. Due to rapid development of spectroscopic techniques, commercial instruments of transient photoluminescence with ~ 1 ns time resolution are becoming as affordable as a high-end steady-state fluorimeter. The time scale for transient photoluminescence measurements is around 1 min. Importantly, transient photoluminescence is *background-free* and *calibration-free* measurements. In addition, transient photoluminescence can indirectly provide information on other pathways shown in Figure 1 (see below). These features make transient photoluminescence as the most powerful tool to monitoring exciton behavior during growth of quantum dots.

If the photoluminescence quantum yield of a sample is 100% and the photoluminescence decay is single-exponential, one could exclude trapping of excitons (see Figure 1). Furthermore, though it is impossible to extract information on hot-carrier relaxation from transient photoluminescence measurements, it

is safe to conclude that the hot carriers all go through the relaxation process without hot-carrier trapping.

If synthetic target is to develop quantum-dot emitters for applications, attentions should be paid to durability of the photoluminescence, including both photochemical and photophysical stability. Photochemical stability is mainly photobleaching of quantum dots. Photobleaching here refers to irreversible decay of luminescence properties of quantum dots under photoirradiation. Photophysical stability mainly concerns photoluminescence blinking of single quantum dot. Discovered in 1996,²⁴ photoluminescence blinking of single quantum dot refers to randomly switching between distinguishable brightness states of single quantum dot under constant excitation. At present, the sole solution to photochemical and photophysical stability is epitaxial growth of core/shell quantum dots with high quality, which has already shown significant advancement for battling photoluminescence blinking.^{25–29} Photochemical stability can be easily monitored by photoluminescence and absorption. Photoluminescence blinking is undetectable at ensemble level, and single molecular spectroscopy is needed for monitoring it. In addition to monitoring photoluminescence blinking, single molecular spectroscopy can provide further insight on the exciton behavior of quantum dots that are smoothed away by typical ensemble measurements.

It is interesting to note that approximately one impurity molecule per quantum dot could convert a quantum dot sample from highly emissive to barely luminescent.³⁰ Currently available tools for structure characterization are difficult to identify the corresponding structural defects at such a low level. Spectroscopic tools discussed above are more or less the only means to assist synthetic development for such a level of precise control.

■ SYNTHETIC CONTROL ON GENERATION OF EXCITONS

Photo- or electro-excitation of a quantum dot generates hot carriers (Step 1 in Figure 1), which eventually form an exciton. Excitation process is relatively simple, which is characterized by absorption spectroscopy, hole-burning, and photoluminescence-excitation spectroscopy (Figure 2). Among them absorption spectroscopy is the most common means for monitoring synthesis.¹⁰

Steigerwald and Brus reported the first set of absorption and hole-burning spectra with multiple sharp absorption features for CdSe quantum dots (Figure 1a).¹⁰ They correctly pointed out that sharp absorption features are not only a result of narrow size distribution but also related to high crystallinity of the quantum dots formed at elevated temperatures. Theory taught us that symmetry, size, shape, and other lattice factors might greatly alter the electronic structures of quantum dots with a given composition.³¹ Synthesis of quantum dots before 1990 was performed under relatively low temperatures and mostly in aqueous media. The resulting quantum dots in that time period were of poor crystallinity.¹⁰

In the systematic studies of this powerful synthetic scheme, i.e., organometallic approach in coordinating solvent under high temperatures, Murray et al. quantitatively analyzed the crystal structure of the ensemble samples.¹¹ They concluded that the CdSe quantum dots were single crystalline with ~ 3 stacking faults along their (002) direction of the wurtzite lattice. Late studies confirmed that such stacking faults did not show detrimental effects on emissive properties of CdSe quantum dots (see below).^{32,33}

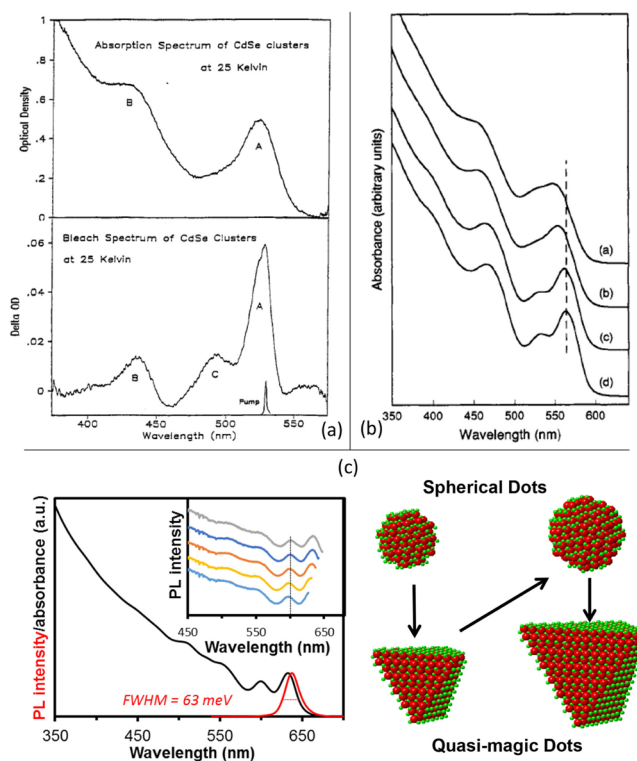


Figure 2. (a) Absorption and hole-burning spectra of CdSe quantum dots. Reproduced from ref 10 with permission from 1990 American Chemical Society. (b) Evolution of absorption spectra of CdSe quantum dots during sequential size-selective precipitation. Reproduced from ref 11 with permission from 1993 American Chemical Society. (c) Left: absorption and photoluminescence spectra of CdSe quantum dots with corresponding excitation spectra at different photoluminescence wavelengths (inset). Right: shape evolution of the CdSe quantum dots synthesized with layer-by-layer growth followed by intraparticle ripening. Reproduced from ref 34 with permission from 2016 American Chemical Society.

Murray et al. further improved size distribution of the CdSe quantum dots by size-selective precipitation.¹¹ They applied absorption spectroscopy to monitor the progress (Figure 1b). Similarly, temporal evolution of absorption spectra has been widely employed for following formation process of quantum dots.⁹

With well controlled size/shape distribution and interior crystal structure, excitation properties might depend on surface perfection of the nanocrystals. Recently, a new synthetic technique³⁴ was developed for obtaining quantum dots with extremely sharp absorption features, whose corresponding excitonic emission spectrum was as narrow as single-dot photoluminescence reported in literature³⁵ (Figure 2c, left panel). This new scheme includes two steps, i.e., layer-by-layer growth followed by intraparticle ripening (Figure 2c, right panel). In the first step, the conventional layer-by-layer growth known in the field of crystallization³⁶ resulted in CdSe nanocrystals with hexahedral shape terminated with six low-index and nearly atomically flat facets.³⁶ Such facets have only been achieved with those tiny “magic size clusters” (~ 1 nm in size).^{37–41} In the typical size range of quantum dots, hexahedrons are significantly larger in surface area than spheres, which are thus unstable under typical growth conditions. This problem was overcome by high concentration of relatively strong carboxylate ligands in solution to compensate the surface

dangling bonds. Consistent with this, by reducing the surface coordination, the hexahedrons were converted into monodisperse spheres in the second step.³⁴ Absorption and photoluminescence spectra confirmed monodispersity of both shapes, indicating the second step as intraparticle ripening.¹⁶

■ SYNTHETIC CONTROL OF HOT-CARRIER BEHAVIOR

Results in Figure 2c (left panel, inset) illustrate that, at different emission wavelengths, several photoluminescence excitation spectra almost overlap with each other and resemble the corresponding absorption spectrum. While the first feature supports homogeneity of the nanocrystals, the second feature illustrates that the hot-carrier decay pathways—including both relaxation and trapping of the hot carriers in Figure 1—are independent of the excitation energy. In literature, similarity of photoluminescence excitation and absorption spectra has also been applied for monitoring the hot-carrier decay dynamics during synthesis of core/shell quantum dots.^{42,43}

Hot-carrier behavior is important, because of multiexciton generation,^{44,45} photocatalysis,^{46–49} and photovoltaic devices.^{50,51} Unfortunately, control of hot-carrier behavior in quantum dots is much less developed in comparison to other processes associated with excitons. As pointed out above, the main reason is the difficulty to identify monitoring tools for the extremely fast dynamic processes with affordable cost for typical synthetic laboratories.

With strong expertise in ultrafast spectroscopy, the Guyot-Sionnest's group designed a CdSe/ZnS/ZnSe/CdSe core/multishell quantum dot with alkylthiols as ligands for controlling hot-carrier decay.⁵² In these quantum dots, the thick ZnS and ZnSe shells were designed to isolate the hot electron and hole. Outer CdSe shell was employed to reduce the electron trapping probability. Alkylthiol ligands played two roles: trapping hole from quantum dots to suppress the electron–hole Auger process and reduce vibration modes in the window of intrabandgap to suppress possible surface relaxation of the hot electron. Their results revealed that the hot-electron relaxation time from a hot state (1Pe) to its ground state (1Se) in these quantum dots were found to be slowed down to ~1 ns, which was thousand times longer than that in plain CdSe quantum dots.

■ SYNTHETIC CONTROL OF BAND-EDGE EXCITONS IN PLAIN CORE QUANTUM DOTS

As mentioned above, suitable tools for monitoring band-edge exciton behavior during synthesis are widely available. As a result, scientists are quite often following responses of exciton decay upon changing synthetic/solution conditions.^{53–56} For example, Omogo et al. followed how ligands, solvents, and surface composition impacted exciton decay of CdTe quantum dots using photoluminescence decay dynamics (Figure 3a) and quantum yield measurements (Figure 3b).⁵⁷ As expected, these chemical parameters affected behavior of excitons drastically.

An ideal emitter should possess monoexponential decay dynamics and 100% quantum yield for its emission. However, photoluminescence decay dynamics of quantum dots was usually multiexponential, which was true even for the mostly studied CdSe quantum dots until recently. Complex photoluminescence decay dynamics can be either homogeneous or heterogeneous, which is distinguishable through single-dot spectroscopy. Until recently, results in literature indicated that,

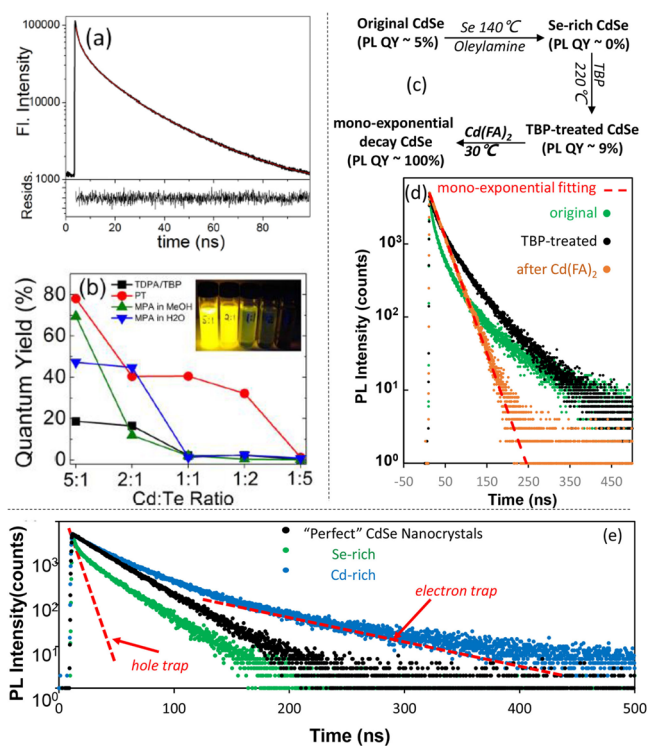


Figure 3. (a) Typical transient photoluminescence of CdTe quantum dots with fitting residual. (b) Evolution of photoluminescence quantum yield of CdTe quantum dots with different surface Cd and Te atom ratio. Reproduced from ref 57 with permission from 2013 American Chemical Society. (c) Surface modification scheme for the CdSe quantum dots. (d) Evolution of photoluminescence decay curves of CdSe quantum dots during the surface modification. (e) Photoluminescence decay curves of CdSe quantum dots with different surface states. Reproduced from ref 33 with permission from 2015 American Chemical Society.

at single-dot level, photoluminescence decay dynamics of single quantum dot was multiexponential.^{58,59} For typical plain core quantum dots, possible reasons for being nonideal in emission should include interior crystallinity,^{11,60} surface anion/cation stoichiometry,^{61,62} surface ligands,^{53,57,63,64} and solvent environment.^{57,64,65} With typical inert organic solvents applied in synthetic developments, the last factor could often be ruled out. Recently, experiments were carried out to synthetically address the other issues for CdSe quantum dots.^{33,32} CdSe quantum dots could exist in either zinc-blende (cubic) or wurtzite (hexagonal) phases. Given the identical coordination environment and bond length in these two phases, formation of the third type of CdSe quantum dots—single crystal with multiple stacking faults¹¹—was common. A chemical procedure was designed to address all surface-related issues (Figure 3c)³³ after synthesis of three types of CdSe quantum dots.³² Results were qualitatively the same for three types of CdSe quantum dots, we take the ones with zinc-blende structure as the model system to discuss below.

The original CdSe quantum dots in zinc-blende structure were synthesized following standard protocols,²⁰ which resulted in quantum dots with cadmium fatty acid salts ($\text{Cd}(\text{Fa})_2$) as the ligands. After purification, the absolute photoluminescence quantum yield was determined to be ~5% measured using an integration sphere, and photoluminescence decay dynamics was multiexponential (Figure 3c). Treatments of original CdSe quantum dots with Se fine powder suspended in octadecene

with amines in solution should convert the quantum dots to be Se-rich on the surface. This Se treatment step was carried out until it completely quenched photoluminescence of the quantum dots. It should be pointed out that Se treatment step was reported previously in literature for the same purpose.⁶¹ The variation in the recent report³³ was to completely quench photoluminescence in this step, which presumably removed all original carboxylate ligands on the surface of the nanocrystals.

Addition of tributylphosphine (TBP) into the solution with the Se-rich CdSe quantum dots recovered the photoluminescence with quantum yield being ~9%. The photoluminescence decay dynamics was multiexponential and the average decay lifetime was apparently longer than that of the original CdSe quantum dots (Figure 3d). These results were found to be consistent with literature reports, where organophosphines are ligands to help recovery of photoluminescence for II–VI quantum dots with anionic surface.^{55,61}

The most important step for the scheme in Figure 3c was titration of the TBP-treated quantum dots with cadmium fatty acid salts. Our hypothesis was that a balanced Cd/Se ratio must be in place for ideal quantum-dot emitters.⁶⁶ In principle, any deviation from a balanced Cd/Se surface stoichiometry should create either hole traps with excess Se or electron traps with excess Cd. At a certain concentration of Cd fatty acid salts at ambient temperatures, the photoluminescence decay dynamics became nearly perfect monoexponential (Figure 3d) and the quantum yield reached 100%.

It should be mentioned that the peak photon counts recorded for a decay dynamics curve should be sufficiently high, ~5000 photons being used in the experiments in Figure 3d. The goodness of fitting should be <1.300 (0.986 for the linear fitting in Figure 3d).⁶⁷ These settings imply that the decay dynamics for the final quantum dots in Figure 3d was monoexponential within 3–4 orders of magnitude, which was ~2 orders of magnitude more accurate than measurements of photoluminescence quantum yields could offer.

Using the scheme in Figure 3c, we obtained CdSe quantum dots with monoexponential photoluminescence decay dynamics and 100% quantum yield for all three different crystal structures, namely zinc-blende, wurtzite, and mixed phases.³³ Experimental results further confirmed that such a monoexponential lifetime was reproducible for a given size and crystal structure. Thus, it is reasonably safe to regard such a lifetime as the photoluminescence decay lifetime for the intrinsic radiative channel for CdSe quantum dots with the given size and crystal structure. With standard lifetime values available, photoluminescence quantum yield measurements become secondary.

With standard samples available, Figure 3e shows that excess Se on the surface would bring in short-lifetime channel(s), consistent with the literature assignments for surface Se sites, i.e., deep surface hole traps.⁶¹ CdSe quantum dots with excess Cd ions on the surface were prepared by treating the “perfect CdSe quantum dots” with excess cadmium fatty acid salts under elevated temperatures. Results in Figure 3e indicate that a long-lifetime component appeared for the excess surface Cd sites, which is consistent with delayed photoluminescence caused by shallow surface traps.^{68,69} Delayed photoluminescence is a special type of radiative decay of band-edge exciton that is formed by the back-transferred carriers from shallow traps (Figure 1, process 6). The “perfect CdSe quantum dots” and photoluminescence decay dynamics were also applied to

identify the effects of surface ligands. Not surprisingly, some of the ligand effects were found to be inconsistent with qualitative assessment in literature.³³

It is worth to discuss a key issue on application of photoluminescence decay dynamics for analysis of the excitonic emission. In literature, the average lifetime of photoluminescence decay is commonly applied to compare photoluminescence quantum yields upon a certain treatment of an ensemble of quantum dots based on the equation as follows.

$$\text{quantum yield} = \frac{1/\tau_r}{1/\tau_r + 1/\tau_{nr}} = \frac{1/\tau_r}{1/\tau_{exp}} = \frac{\tau_{exp}}{\tau_r}$$

Here τ_r , τ_{nr} , and τ_{exp} are lifetime values of radiative decay, nonradiative decay, and experimentally detected photoluminescence decay, respectively. If we assume τ_r is the intrinsic radiative decay lifetime, it should be a constant. Therefore, photoluminescence quantum yield is proportional to the experimentally detected lifetime, τ_{exp} . However, when the average lifetime becomes longer, the photoluminescence quantum yield might be significantly lower (compare the photoluminescence quantum yield data in Figure 3c and decay curves in Figure 3d for three emissive samples). In our experience, such inconsistency is quite common (also see Figure 3e). Careful inspection shows that the above equation can only be applicable under some restrict conditions. First of all, samples should be homogeneous. For example, existence of nonemissive quantum dots would make the photoluminescence quantum yield be overestimated using this equation. For samples without heterogeneous issue, both radiative and nonradiative processes should share the same excited state. When either hot-carrier trapping (see Figure 1) or delayed photoluminescence—emission from excitons reformed by back transfer of the carriers from trap states—is in place, the above equation may most likely become incorrect. For these complex conditions, photoluminescence decay dynamics and quantum yield need to be analyzed using a mathematic model specifically developed for the given system.

■ SYNTHETIC CONTROL OF BAND-EDGE EXCITON BEHAVIOR IN CORE/SHELL QUANTUM DOTS

Stability and durability of plain core quantum dots are known to be problematic.^{63,70,71} For instance, purification by extraction and precipitation would greatly impact the emission properties of those “perfect CdSe quantum dots” in Figure 3d.³³ Epitaxial growth of a shell with relatively wide bandgap to prevent the exciton from delocalization to the surface has been explored as a practical strategy to battle this issue.^{42,70,72–75}

Results on plain core quantum dots discussed in the above section tell us that, with nearly 30 years efforts, control of interior crystal structure is relatively easy. The key for controlling exciton behavior is synthetically engineering the surface. This conclusion is further supported by our recent results on synthesis of core/shell quantum dots.

CdSe/CdS core/shell nanocrystals are the most developed system in the field.^{14,26,27,42,70,76,77} Despite of their single-crystalline nature, their emission properties were usually far from being ideal. These facts promoted us to develop new synthetic strategies with extensive emphasis on surface treatments. Shown in Figure 4a, CdSe/CdS core/shell nanocrystals was synthesized by coupling epitaxial growth through either single-precursor approach or successive-ion-layer-adsorption-and-reaction (SILAR) approach and surface

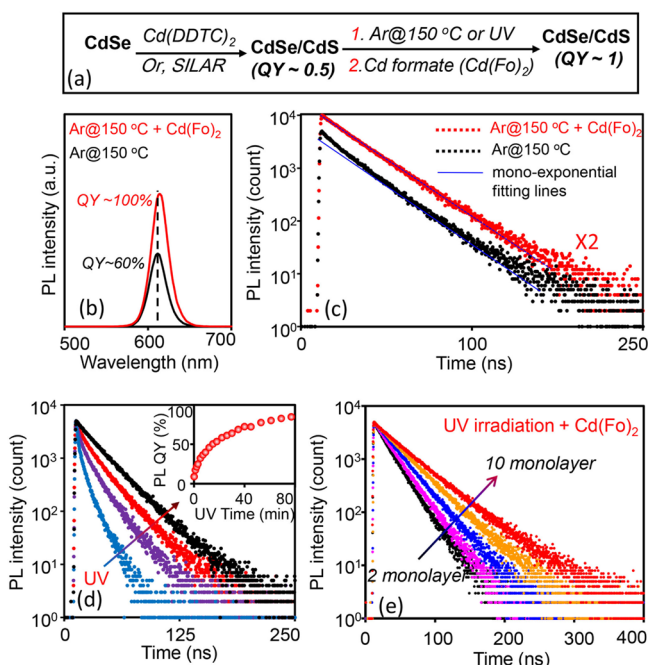


Figure 4. Synthetic scheme and optical properties of CdSe/CdS core/shell quantum dots. (a) The scheme. (b and c) Change of photoluminescence spectrum and photoluminescence decay curves of CdSe/CdS core/shell quantum dots after Ar bubbling (black) and addition of Cd(Fo)₂ (red). (d) Evolution of photoluminescence decay curves and photoluminescence quantum yields (inset) of CdSe/CdS core/shell quantum dots under UV irradiation. (e) Photoluminescence decay curves of CdSe/CdS core/shell quantum dots with 2- 10 monolayers of CdS shell. Reproduced from ref 78 with permission from 2016 American Chemical Society.

engineering after the epitaxial growth.⁷⁸ Concentrating on exciton behavior, we identified all major surface traps for these core/shell quantum dots, namely H₂S and related species adsorbed on the surface, surface S sites, and surface Cd sites, all of which were found to be removable by the strategy in Figure 4a.⁷⁸

Photoluminescence quantum yield of the CdSe/CdS core/shell quantum dots after epitaxy without surface engineering was significantly below 100% and varied significantly from sample to sample, with ~50% as a typical number for those with 5 monolayers of epitaxial CdS shells. It should be pointed out that such irreproducibility has been quite common for synthesis of core/shell quantum dots.^{79,80} The first surface-treatment step in Figure 4a was removal of H₂S through either photochemical decomposition by UV irradiation or Ar bubbling. The second surface-treatment step was addition of cadmium formate (or other cadmium fatty acid salts) to passivate the surface S sites. It was interesting to find that, unlike the plain-core CdSe quantum dots, excess Cd salts on the surface of CdSe/CdS core/shell quantum dots did not show noticeable negative impact to the emission properties as long as the epitaxial CdS shells were two or more monolayers in thickness.⁷⁸

For the CdSe/CdS core/shell quantum dots grown by the SILAR approach, it was crucial to treat the nanocrystals after epitaxy with the S-octadecene solution. This process should convert the quantum dots to be S-rich on their surface and nearly nonemissive, indicating complete removal of cadmium carboxylates on surface of the nanocrystals. Without this

additional reaction step in epitaxy, the surface treatment procedure in Figure 4a showed little impact on the emission properties of the CdSe/CdS core/shell quantum dots.⁷⁸

Figures 4b and 4c show photoluminescence spectra, quantum yields, and decay curves for a typical sample (with 5 monolayers of the epitaxial CdS shells) after each step of the surface treatments. Evidently, the Ar-bubbling treatment could somewhat boost the photoluminescence quantum yield and convert the photoluminescence decay dynamics to be nearly monoexponential (Figures 4b and 4c). The second step, namely addition of cadmium formate, completely filled the traps, which resulted in a final product with unity quantum yield and monoexponential photoluminescence decay (Figures 4b and 4c). Studies further revealed another function of the Ar-bubbling step, which was to remove excess H₂S to avoid formation of small CdS particles in the second surface-treatment step.⁷⁸

Ar bubbling was found to be applicable for the original reaction mixtures in the reaction flask. Alternatively, UV irradiation was identified as an efficient mean for the first surface-treatment step if the quantum dots were in a dilute solution. For instance, if one intended to obtain a series of core/shell quantum dots with different CdS shell thicknesses in one run of synthesis, UV irradiation of the aliquots taken at different reaction time intervals became a better choice than the Ar bubbling. Figure 4d shows temporal evolution of the photoluminescence decay dynamics upon UV irradiation for a typical CdSe/CdS sample (with 5 monolayers of the epitaxial CdS shells). The short-lifetime channels related to deep traps were found to be gradually removed upon UV irradiation for this and other samples. Consistent with these results, the photoluminescence quantum yield of the solution increased steadily upon the UV irradiation (Figure 4d, inset). Both photoluminescence decay dynamics and quantum yield would reach constant when the UV radiation was completed. Addition of cadmium fatty acid salts would reproducibly generate a series of CdSe/CdS core/shell quantum dots with near unity quantum yield and monoexponential decay dynamics (Figures 4a and 4e).

Near unity quantum yield and monoexponential decay dynamics shown implied that there should be no detectable interfacial traps between CdSe cores and their CdS shells for the final products in Figure 4.

Comparison between CdSe plain-core³³ and CdSe/CdS core/shell quantum dots⁷⁸ would help us to draw a few useful conclusions about synthetic control of exciton behavior by the epitaxial shells.

First, traps from the inorganic surface of CdSe plain core and CdSe/CdS core/shell quantum dots are quite similar, i.e., cationic sites as shallow electron traps and anionic sites as deep hole traps. Furthermore, these traps are sensitive to surface ligands to a certain extent.

Second, epitaxial shells with wide bandgap can help to isolate the surface traps from the excitons. For the CdSe/CdS core/shell quantum dots, the cationic and anionic sites can be isolated by ~2 and ~10 monolayers of the CdS shells, respectively.⁷⁸ Given most ligands being for surface cations, removal/exchange of surface ligands by purification/ligand exchange do not affect the optical properties of most CdSe/CdS core/shell quantum dots as long as the new ligands do not bring in new traps.

Third, results on the adsorbed H₂S species reveal that the excitons in CdSe/CdS core/shell quantum dots can still

respond to outside environment if there are appropriate energy states. This explains the ideal performance of light-emitting diodes⁸¹ based on the CdSe/CdS core/shell quantum dots described above. It further supports exploration of photocatalytic and photovoltaic applications of core/shell quantum dots with similar band alignment between the core and shells.^{54,82–84}

Fourth, one main goal for synthesis of core/shell quantum dots is to greatly improve photophysical and photochemical stability of quantum dots. Photoluminescence blinking of single quantum dot is an apparent roadblock for most of their applications, given continuous excitation and constant emission being prerequisite for many applications.⁸⁵ Suppression of photoluminescence blinking requires a high level of synthetic control on excited states, which at present can only be achieved with core/shell quantum dots.

Finally, photobleaching should be associated with photochemical reactions on surface of quantum dots. Our recent results demonstrated that it is possible to almost completely suppress photobleaching by confining the wavefunctions of excitons into the core and inner part of the shells of a core/shell quantum dot.⁸⁶ Without exposure of either electron or hole wave function to the inorganic–organic interface of the core/shell quantum dot, photochemical reactions cannot occur.

■ SYNTHETIC CONTROL OF EXCITON BEHAVIOR FOR DOPED QUANTUM DOTS (D-DOTS)

Quantum dots can be synthesized as nanophosphors by controlled doping of transition metal ions into their lattices. The optically forbidden d-d transitions of the dopant ions possess photoluminescence decay lifetime in the range between microseconds to milliseconds, instead of tens of nanoseconds for the band-edge excitonic emission (see Figure 4 for examples). Mn doped ZnSe quantum dots (Mn:ZnSe d-dots) are such examples.^{87,88} It should be pointed out that the emissive state of d-dots is not truly a conventional excitonic state. It is better described as a trapped exciton on a dopant ion.

D-dots, such as Mn:ZnSe, Cu:ZnSe, Cu:InP, and others, have been developed as alternatives of cadmium-based quantum dots as emitters.^{89–92} However, existing synthetic schemes do not provide means to control the decay lifetime of the dopant emission needed for phosphors. It is known that the slow decay dynamics of the dopant emission is due to the forbidden d-d transitions of transition metal ions, which also explains their very low extinction coefficients in comparison to the host quantum dots.^{88,93} Though they did not obtain Mn:ZnSe d-dots with monoexponential decay lifetime of the dopant emission, by increasing dopant concentration, the Gamelin's group indeed observed a short-lifetime component in addition to the typical decay lifetime of the dopant emission.⁹⁴ More importantly, the decay lifetime of the short-lifetime component was found to decrease with increase of the dopant concentration in the host nanocrystals. They suggested that the long decay lifetime at extremely low concentration of dopant ions should be the intrinsic lifetime associated with the emission from isolated Mn ions in ZnSe quantum dots, and the short-lifetime component should be a result of Mn–Mn coupling. This is so because the Mn–Mn interaction should partially remove the spin forbidden rule for the d-d transition.⁸⁷

Analysis above suggests that, if one could uniformly distribute the Mn ions within one quantum dot and control the concentration precisely among all dots in one sample, it should be possible to synthesize d-dots with tunable and

monoexponential decay lifetime for the dopant emission. Synthetic schemes were developed for such d-dots.⁶ Compared to intrinsic quantum dots, control of the decay dynamics of dopant emission was found to be significantly more complex. Position, concentration, and interior distance of dopant ions within a d-dot were three additional challenges for the synthetic development.^{95–98} Figure 5a shows that we were able to obtain

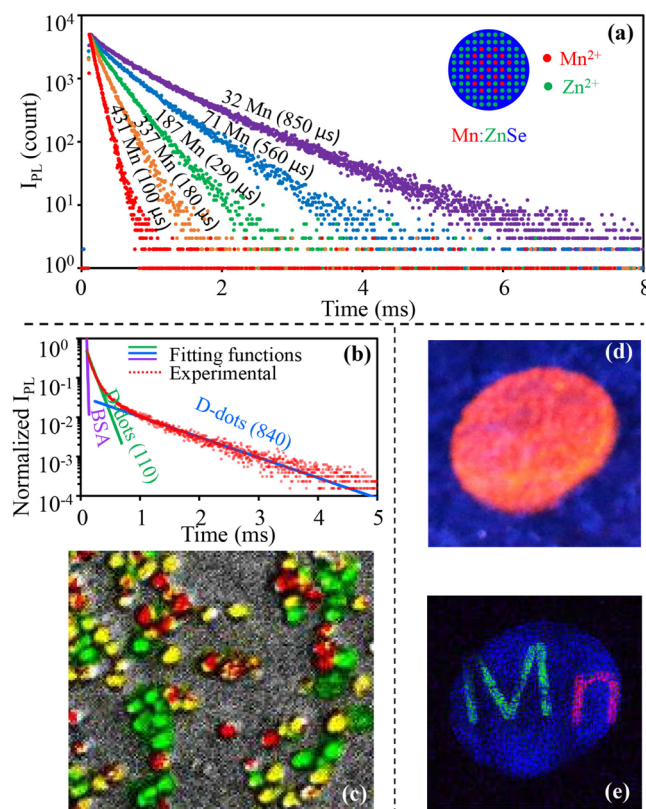


Figure 5. Emission properties and applications of the d-dots with controlled photoluminescence decay dynamics. (a) Photoluminescence decay curves of Mn:ZnSe d-dots with different Mn²⁺ concentration. (b) Typical fitting results of a photoluminescence decay curve recorded from the mixture of BSA and two batches of d-dots with different photoluminescence decay lifetime. (c) Cell image obtained with photoluminescence lifetime multiplexing measurements. (d and e) Antifake pattern under UV irradiation and corresponding pattern obtained with photoluminescence lifetime multiplexing measurements. Reproduced from ref 6 with permission from 2016 American Chemical Society.

a series of Mn:ZnSe d-dots with a diverse range of number of dopant ions per dot, and the decay dynamics of the dopant emission was indeed tunable in a large time window and sufficiently monoexponential.⁶ Again, the key for this synthetic development was following the decay dynamics of the dopant emission during synthesis. Furthermore, by closely following the photoluminescence decay dynamics and other structural parameters, we successfully synthesized bright and stable Mn:ZnSe/ZnS core/shell d-dots with similar decay dynamics shown in Figure 5a.⁶

With the microsecond to millisecond yet tunable decay lifetime, Mn:ZnSe/ZnS core/shell d-dots were explored as ideal emitting materials for photoluminescence lifetime multiplexing.^{99,100} Photoluminescence lifetime multiplexing could be carried out with an inexpensive homemade system with a microsecond pulsed lamp and a commercial high-speed

camera.⁶ Due to the largely tunable range of photoluminescence lifetime, decoupling of the signals was quite straightforward and interference of autoluminescence of the detection targets could be readily avoided (Figure 5b). To our knowledge, photoluminescence lifetime multiplexing was introduced ~20 years ago.^{101,102} Due to lacking of bright emitters with tunable and monoexponential decay lifetime in microsecond to millisecond window, this promising technique has been under-developed in comparison with photoluminescence color multiplexing.¹⁰⁰

Two examples of applications of the Mn:ZnSe/ZnS core/shell d-dots for photoluminescence lifetime multiplexing are shown in Figure 5.⁶ In Figure 5c, living cells labeled with three types of d-dots with distinguishable photoluminescence lifetimes were resolved readily by photoluminescence lifetime multiplexing. Figure 5d is the photoluminescence image under a UV lamp of a spatially overlapped pattern of an oval, a letter M, and a letter n. Each component was labeled with a type of d-dots with unique photoluminescence decay lifetime, which allowed resolution of three components in Figure 5e.

CONCLUSION AND PERSPECTIVE REMARKS

Synthetic control of exciton behavior of colloidal quantum dots yielded nanocrystals with near-unity photoluminescence quantum yield, monoexponential photoluminescence decay dynamics, and comparable to single-dot photoluminescence peak width. The main tasks in such synthetic developments are identified as engineering the nanocrystal surface, including the anion–cation stoichiometry, organic ligands, and inorganic epitaxial shells. A group of characterization tools, especially transient photoluminescence spectroscopy, are found to be convenient, affordable, and powerful for monitoring the synthetic efforts for controlling the exciton behavior. Affordable methods for following the extremely fast processes of hot-carrier relaxation and trapping are needed to provide a full picture of generation and decay of excitons. In addition, structural tools are highly desirable to correlate outstanding optical properties and surface structures for further development of this field.

Synthesis of colloidal quantum dots has long been focused on monodispersity of size and shape. As optical and optoelectronic emitters, it makes sense to pursue “optically monodisperse” quantum dots. By inspection of key parameters as emitters, optically monodisperse quantum dots should include a group of parameters, namely, intrinsic peak width of ensemble photoluminescence and absorption, monoexponential photoluminescence decay dynamics, unity photoluminescence quantum yield, nonblinking at single-dot level, and high durability against photobleaching. Tuning synthetic focus to the control of exciton behavior of quantum dots sheds light on synthesis of such ideal quantum-dot emitters.

Colloidal quantum dots are unique in many ways in comparison to other types of emissive materials. Because of their extremely high extinction coefficients and nearly identical crystal structure of excited and ground states, quantum dots can readily generate biexcitons and multiexcitons. The synthetic schemes and monitoring techniques developed for controlling exciton behavior should help to explore these interesting nonlinear emitters, which is barely explored at present. Bi- and multiexciton emitters are not only interesting for fundamental understanding of quantum dots but also of importance for a variety of applications, such as high-power light-emitting-

diodes,^{27,81,103} lasers,^{104,105} entangled quantum light sources,^{106,107} etc.

Though this perspective is centered on quantum-dot emitters, applications of quantum dots as photocatalysts and photovoltaic materials are of great interest in the field.^{54,83,108–110} These applications have been mostly applying generic quantum dots at present. Synthetic development specifically for these applications is an interesting avenue to explore. Such synthetic efforts are undoubtedly related to control of the excited states of quantum dots but should be in a different way from that for quantum-dot emitters.

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Notes

The authors declare no competing financial interest.

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