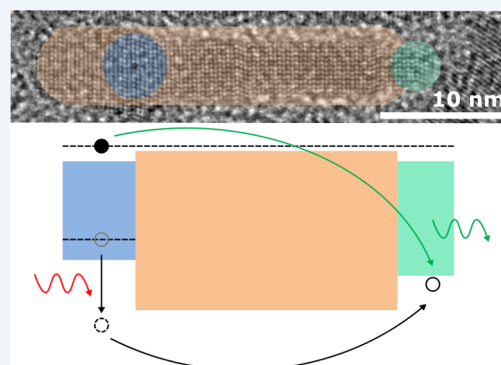


Colloidal Double Quantum Dots

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CONSPECTUS: Pairs of coupled quantum dots with controlled coupling between the two potential wells serve as an extremely rich system, exhibiting a plethora of optical phenomena that do not exist in each of the isolated constituent dots. Over the past decade, coupled quantum systems have been under extensive study in the context of epitaxially grown quantum dots (QDs), but only a handful of examples have been reported with colloidal QDs. This is mostly due to the difficulties in controllably growing nanoparticles that encapsulate within them two dots separated by an energetic barrier via colloidal synthesis methods. Recent advances in colloidal synthesis methods have enabled the first clear demonstrations of colloidal double quantum dots and allowed for the first exploratory studies into their optical properties. Nevertheless, colloidal double QDs can offer an extended level of structural manipulation that allows not only for a broader range of materials to be used as compared with epitaxially grown counterparts but also for more complex control over the coupling mechanisms and coupling strength between two spatially separated quantum dots.



The photophysics of these nanostructures is governed by the balance between two coupling mechanisms. The first is via dipole–dipole interactions between the two constituent components, leading to energy transfer between them. The second is associated with overlap of excited carrier wave functions, leading to charge transfer and multicarrier interactions between the two components. The magnitude of the coupling between the two subcomponents is determined by the detailed potential landscape within the nanocrystals (NCs).

One of the hallmarks of double QDs is the observation of dual-color emission from a single nanoparticle, which allows for detailed spectroscopy of their properties down to the single particle level. Furthermore, rational design of the two coupled subsystems enables one to tune the emission statistics from single photon emission to classical emission. Dual emission also provides these NCs with more advanced functionalities than the isolated components. The ability to better tailor the emission spectrum can be advantageous for color designed LEDs in lighting and display applications. The different response of the two emission colors to external stimuli enables ratiometric sensing. Control over hot carrier dynamics within such structures allows for photoluminescence upconversion.

This Account first provides a description of the main hurdles toward the synthesis of colloidal double QDs and an overview of the growing library of synthetic pathways toward constructing them. The main discoveries regarding their photophysical properties are then described in detail, followed by an overview of potential applications taking advantage of the double-dot structure. Finally, a perspective and outlook for their future development is provided.

■ INTRODUCTION

By virtue of the three-dimensional confinement of excited charge carriers within them, semiconductor quantum dots (QDs) exhibit quantized energy levels and size- and shape-tunable electronic properties. For these properties, QDs are also known as “artificial atoms”. As in atomic systems, coupling between two such “atoms” can lead to a dramatic modification of their individual properties and to the emergence of new functionalities of the dual system. Generally, these coupled systems or double QDs (also known as “QD molecules” by virtue of the analogy with atoms) are realized by coupling of two spatially separated dots or wells through an energetic barrier. The coupling mechanism can be either dipole–dipole interactions or wave function overlap in the excited state and can be reflected in energy transfer, tunneling, and charge transfer between the two systems. Such double QD systems

have been extensively studied in epitaxially grown QDs in the past decade. In contrast, very few realizations have been reported for colloidal synthesized QDs until very recently. This Account details recent progress from both the colloidal chemistry and the photophysics aspects.

The vast majority of studies on colloidal QDs focused on the properties of either isolated QDs or large ensembles of coupled QDs (“QD solids”). Studies of colloidal double QDs have been hindered by the relative complexity of synthesis protocols for their fabrication. Recent advances in heterostructured colloidal QD synthesis open the possibility of manufacturing double QDs, which can be beneficial for various applications and serve as an excellent platform for studying fundamental phenomena.¹

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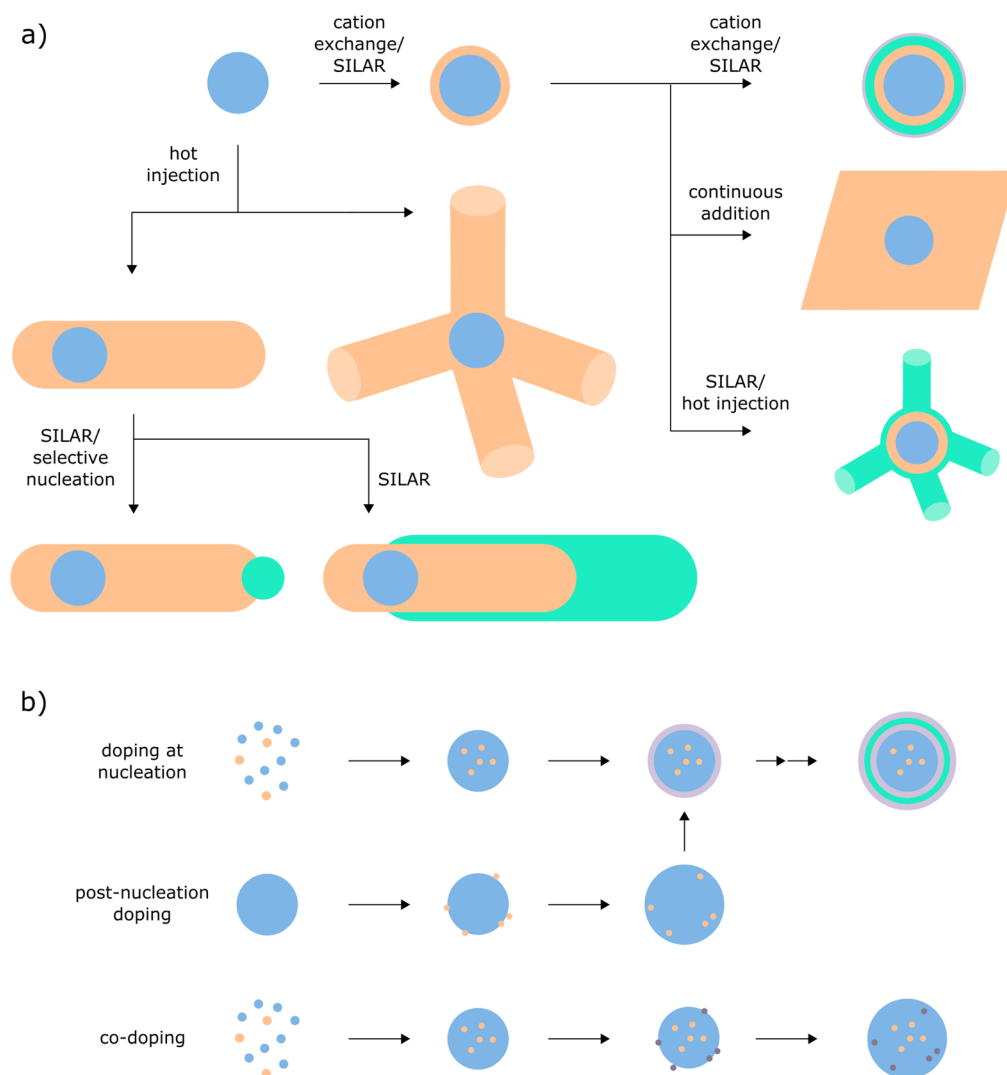


Figure 1. Schematic illustration of the different QD structures described here and the synthetic approaches used to fabricate them for (a) double QDs and (b) doped QDs.

In colloidal QDs, this can be implemented by coupling two semiconductor potential wells either in core/shell/shell formation (QD–QW (quantum well))^{2,3} or by using seeded (or branched) rods tipped by a second semiconductor material (QD–QD).⁴

Double QDs show unique properties such as double emission (two separate luminescence bands), intraparticle charge transfer, and nonlinear effects, such as luminescence upconversion (UC). A related strategy for coupling two quantum moieties in a single QD and realizing dual emission is via doping, where dual emission results from a thermal population of the band edge exciton due to slow recombination from the dopant state. Since dual-emitting doped QDs share some of the properties of double QDs, they are included here as well.

In the following, we briefly describe of the main advances enabling the fabrication of double QDs and present an overview of currently available designs and synthesis protocols. We then turn to describe some of the new photophysical properties of these double QDs, present some of their potential applications, and point at several directions for further development.

■ TOWARD COLLOIDAL DOUBLE QUANTUM DOTS

The main strategy for formation of a double QD relies on introducing barrier layers within the nanoparticle, which separate regions where excited charge carriers are localized. This requires synthesis of heterointerfaces with delicate control both over the conduction and valence band offsets and over the spatial extent of excited carrier wave functions. A few notable landmarks in colloidal synthesis formed the basis for double QD formation. The first is the introduction of quantum wells within QDs in core/shell/shell formation^{5,6} by sandwiching a low bandgap material (HgS) between a spherical core and an external shell composed of a large bandgap material (CdS). The second is fabrication of type-II core–shell heterostructured QD architectures⁷ that allow for spatial separation of excited carriers. The third is the success in dilute doping of QDs as a means for controlling carrier localization by virtue of localized trap states.

Each of these separate advances by itself opened new applications. Quantum wells within a core/shell QD enable one to disentangle the absorption cross section from the degree of quantum confinement. Charge separation within type-II QDs facilitates charge extraction and transport in photovoltaics and photocatalysis.⁸ Further, it modifies the energetics and

dynamics of multiply excited states.⁹ This was exploited to achieve a “single-exciton” optical-gain regime by reducing reabsorption of the band edge stimulated emission.¹⁰ Doping has been utilized to imbue magnetic properties into otherwise nonmagnetic QDs and for controlling emission properties with applications such as superresolution optical microscopy. Yet, none of the above presents a deviation from the notion of a single, spatially isolated quantum system.

The first double QD was presented by the groups of Weller and El-Sayed via the introduction of a double-well onion-like CdS/HgS/CdS/HgS/CdS structure.² The CdS barrier region between the two HgS wells introduces a controlled degree of electronic coupling between them. Nevertheless, the experimental results only indirectly indicate the presence of two coupled systems due to the large spectral overlap between the signatures of the two coupled wells.

A more solid proof of the existence of double QDs requires dual emission, resulting from two spectrally nondegenerate emitters coupled through a sufficiently thick barrier layer. This was introduced in an alternative system, where the coupled emitters are found within the core and within an external shell. The CdSe/ZnS/CdSe³ system clearly exhibited two emission colors whenever the core emission was red-shifted relative to the shell emission. It showed evidence for both tunneling between the core and the outer shell¹¹ and dipole–dipole coupling.³ Effective mass modeling showed that the localization regime of excited carriers can be tuned by varying the core size and the barrier width.^{12,13} Single-dot studies on these rather weakly coupled QD–QW structures showed that the electronic coupling between core and shell due to tunneling increases the core absorption oscillator strength and the optical gain bandwidth.¹⁴ Unfortunately, no correlations in blinking or in spectral diffusion of the two emitted colors were found, limiting the degree of external optical control that can be exercised on their emission.

The introduction of more strongly coupled double QDs, particularly by electrostatic interactions in a quasi-type-I/type-II formation opened the path toward broader applications such as upconversion^{15,16} and intraparticle charge transfer.¹⁷ These QDs exhibited the ultimate proof of dual emission from a single nanoparticle, that is, correlated photon statistics of two emission colors (“two-color antibunching”).⁴ The first demonstrations of these effects used a QD–QD asymmetric heterostructure geometry, based on tip growth on a seeded rod.⁴ In CdSe:Te/CdS/CdZnSe doped-core/rod/dot nanoparticles, the CdS rod served as a thick tunneling barrier between the Te-doped CdSe well and the CdZnSe well only for the holes.⁴ In contrast, since the conduction band is nearly flat, excited electrons can interact with holes excited at either side of the rod. The nonradiative recombination process occurring when more than one electron occupies an excited dot prohibits simultaneous emission from both dots within one excitation cycle. Thus, the emissions of the two dots are antibunched.

■ SYNTHESIS OF COLLOIDAL DOUBLE QUANTUM DOTS

Several architectures have been utilized to fabricate double QDs and closely related dual-emitting QD structures. Figure 1a schematically describes the various types of double QDs that were synthesized and studied in recent years, as well as the different synthetic techniques used to fabricate them. Generally speaking, we can divide double QD structures into two main categories: concentric multishell structures, and elongated

structures including, for example, dot-in-rod and branched QDs. Routes for synthesis of dual emitting doped QDs are shown in Figure 1b.

The first double QDs were based on the core/shell architecture. Starting from a spherical QD, addition of several coating layers resulted in an onion-like structure, composed of narrow band gap semiconducting materials that are separated by a barrier of a wide band gap material. This was usually achieved either by cation exchange or by successive ionic layer adsorption and reaction (SILAR) and SILAR-based methods. In these, precursors were mostly introduced either by alternating injections or in a slow, continuous addition. In both cases, shell growth was gradual and controlled.

Forming onion-like structures by cation exchange was first demonstrated in the CdS/HgS system.^{2,5,6,18} This was achieved by replacing the outer monolayer of CdS QDs with HgS, and then precipitating the Cd²⁺ ions that were released into the solution to form an additional CdS layer. The thickness of the different layers was controlled by further additions and precipitation of Cd²⁺ or Hg²⁺ ions during the growth process. More recently, cation exchange was used to form relatively thick shells (without additional precipitation from solution),^{19–21} forming PbSe/CdSe and PbS/CdS core/shells. These could be further coated via SILAR, both as a “regular” onion-like structure and as elongated branched structures.

The more common method of achieving cocentered double QDs is SILAR. It is a widely used synthetic tool whose advantages include the high degree of control over shell thickness and the ability to achieve spherical coating even in noncubic crystal symmetry.²² One of the more extensively studied systems synthesized using SILAR is the CdSe/ZnS/CdSe^{3,11,14,23–25} core/barrier/shell (or CdSe/ZnS/CdSe/ZnS²⁶). Epitaxial growth was possible despite the relatively large lattice mismatch between ZnS and CdSe. Another example of onion-like double QDs made by similar methods is CdSe/CdS/ZnSe,²⁷ having a type-I/type-II band alignment (see Figure 2b). SILAR-based methods were also used to grow extremely thick CdS shells on zinc-blende (ZB) CdSe cores, resulting in a CdSe/CdS dot-in-bulk (DiB)^{28–30} structure. After the initial CdS shell growth, continuous slow addition of Cd and S precursors enabled formation of a sizable shell. This structure is a double QD due to the abrupt change of the CdS shell’s crystal structure (from ZB to wurtzite (WZ)), resulting in a small energetic barrier in the valence band. ZB/WZ barrier shell formation was indicated to be responsible for double emission in thick cation exchanged shells of CdS or CdSe in PbS/CdS and PbSe/CdSe/CdS QDs. Here too, this is due to the cubic rock salt crystal structure of the PbX core.³¹

As mentioned earlier, double QDs can also be designed as elongated heterostructures, such as rods and tetrapods.^{32–35} Such morphologies were synthesized by seeded growth, using hot injection methods. In this manner, the shape of the secondary material is determined by the crystal structure of the core.^{36,37} Furthermore, due to the lack of spherical symmetry, it is possible to selectively grow yet another crystalline material either on only one or on both tips of an elongated rod. In the context of double QDs, we demonstrated this in several systems, showing either extensive one-sided elongated growth of CdZnSe⁴ or more limited growth of a CdSe dot¹⁵ on Te-doped CdSe/CdS seeded rods. In both cases, selective nucleation was carried out using a SILAR-based technique. An alternative approach for selective nucleation uses thermal decomposition of single-source precursors.³⁸ A more exotic

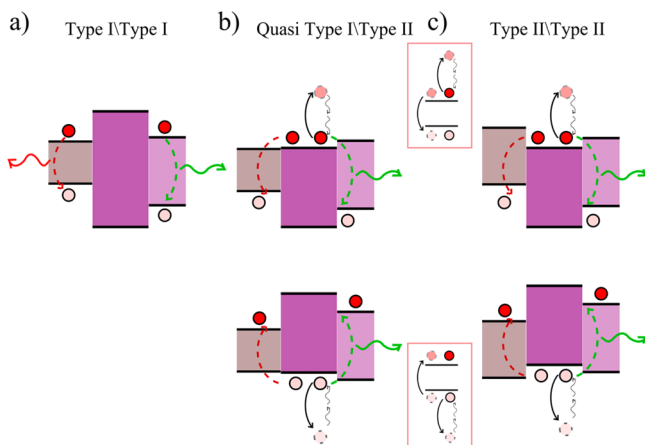


Figure 2. Energy landscapes and electronic interactions in colloidal double QDs. The formation of electrons (red) and holes (pink) is depicted with their locations and possible interactions after excitation. (a) Type-I/type-I band alignment and (b) quasi-type-I/type-II band alignment where a double well is formed either for holes (top) or for electrons (bottom). As a result of Auger interactions, the probability of emission of more than one photon is low, stochastically switching two emission colors. The inset depicts a biexciton Auger interaction, where a nonradiative recombination of one exciton leads to heating up of another electron (top) or hole (bottom), which rapidly cools back to the band edge via a phonon assisted process. Panel c shows a landscape similar to panel b, but with a type-II/type-II band alignment.

design utilized directed attachment of small ZnSe QDs forming thin rods, which later fuse by self-limited self-assembly to form nanorod couples.³⁹

A third strategy for coupling two quantum systems in a single QD and realizing dual emission is doping. As shown in Figure 1b, dopant atoms were incorporated into the crystal lattice either during the initial nucleation of the QD or at a later stage of the synthesis. Dual-emitting doped QDs were synthesized by doping CdSe,⁴⁰ ZnSe, or ZnCdSe with Mn atoms,^{41,42} in all of which dopants were introduced at the first nucleation step. Some of these doped QDs were later coated with one or a few shells using SILAR. Other examples for this doping approach included Cu-doped CdS coated with ZnSe and ZnS.⁴³ We used CdSe doped with only one or a few Te atoms as seeds for the growth of CdS rods by hot injection.^{4,15}

When dopant atoms were introduced after the initial nucleation of the core, the process was usually carried out by controlled addition of the dopant precursor, resulting in deposition of the dopant atoms on the QD surface. This was followed by overgrowth of the host material for better incorporation of the dopants in the crystal lattice. In this approach, doped QDs were usually coated with one or several shell layers using SILAR-based methods. This technique was used to form Cu-doped QDs with both II–VI and III–V hosts, such as Cu:ZnSe/CdSe inverted core/shells,⁴⁴ and Cu:InP/ZnS/InP/ZnS structures.⁴⁵ Finally, these two doping approaches can be combined to create codoped double QDs, by doping ZnSe with both Cu and Mn.⁴⁶

■ THE PHOTOPHYSICS OF DOUBLE QUANTUM DOTS AND POTENTIAL APPLICATIONS

Double QDs enable the investigation of electronic coupling effects between the two subcomponents. This is possible due to the spatial separation of the excited carrier wave functions

within them. The two emitters thus partially maintain their individual characteristics due to the slow cooling between them.

Coupling within double QDs can result in energy transfer (e.g., FRET) or in charge transfer between the two constituents. The dominance of either depends on the details of the band alignment within the structure. Double QDs, which contain two back-to-back heterointerfaces, can be roughly divided according to band alignment at these two interfaces: type-I/type-I, quasi-type-I/type-II, and type-II/type-II. These are depicted in Figure 2a–c. For type-I/type-I structures (Figure 2a) where significant charge transfer between the two dots is inhibited, coupling is reflected in either resonant energy transfer or tunneling.¹¹ In quasi-type-I/type-II and type-II/type-II structures, coupling leads to charge transfer and electrostatic interactions across the type-II heterostructures. In particular, nonradiative recombination via Auger processes (as depicted in the insets of Figure 2) occurs upon double excitation in these systems.

The ability to monitor both emission colors simultaneously from a single particle provides detailed information about the underlying coupled double QD system physics, by observation of correlations in intensity, spectral diffusion, and emission lifetime as well as the photon statistics of the two colors.

Perhaps the simplest measurement that can be performed on dual emitting QDs monitors blinking of the two emitters in a time-correlated manner. Typically, each emitted color exhibits stochastic blinking similar to single dots. The temporal correlation between the two partially reveals the nature of the coupling. In type-I/type-I systems, one can expect little or no correlation due to the absence of long-lived charge-transfer between the two emitters. Carrier interactions in the flat band of quasi type-I/type-II and type-II/type-II should, however, effectively lead to charging of both emitters (one by an electron, the other by a hole), which can reduce both emission intensities in a correlated fashion. Even so, for both CdSe/ZnS/CdSe QDs²⁵ and two-color emitting seeded rods,⁴ no apparent correlation was observed in the blinking traces of the two emitters (depicting millisecond time resolution). In CdSe/CdS/PbS seeded rods, which clearly exhibit longer lived charge transfer, the long wavelength of PbS emission did not enable this measurement.¹⁷

The situation is significantly different when considering short-time correlations, as reflected in photon statistics. Any contribution to nonradiative Auger recombination upon photoexcitation of each of the two systems comprising the QD introduces anticorrelation between the two emission bands on a short time scale, leading to two-color antibunching. This was demonstrated in the CdSe:Te/CdS/CdZnSe⁴ system shown in Figure 3, exhibiting significant negative correlation between the two colors (a deep minimum of $g^{(2)}$ at $\tau = 0$), meaning that simultaneous emission of the two colors is significantly suppressed. In this structure, electrons are nearly delocalized, such that upon double excitation each of the two dots essentially contains a trion. Upon each excitation cycle the emission color is stochastic, but the probability of emission of more than one photon is low. The asymmetric shape of the antibunching curve reflects the different emission lifetimes of the two colors. Realization of two-color antibunching is an important step toward new sources of multicolor nonclassical light.

The high degree of control over photon emission statistics is further exemplified in the recently introduced DiB CdSe/CdS²⁸ core/shell system. The interfacial ZB CdS layer between the ZB

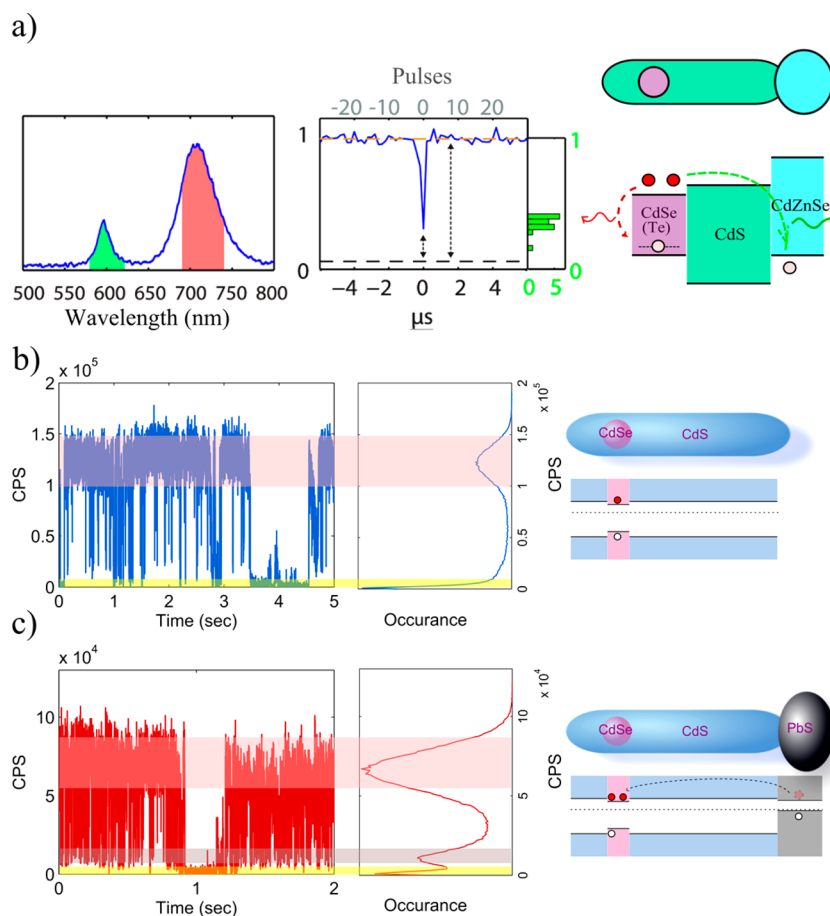


Figure 3. (a) Two-color antibunching from a dual emitting tipped seeded rod: emission spectrum (left), dual color antibunching curve and histogram (middle), and a band alignment illustration (right), adapted with permission from ref 4. Copyright 2012 American Chemical Society. (b, c) Blinking traces, histograms and energy landscape for untipped (b) and PbS tipped (c) CdSe/CdS seeded rods. Whereas the untipped system exhibits two emission levels, corresponding to “on” and “off” states (pink and yellow shading, respectively), the tipped system exhibits a “gray” state (gray shading) associated with hole trapping in the PbS tip. Adapted with permission from ref 17. Copyright 2013 American Chemical Society.

CdSe core and the “bulk-like” WZ CdS shell creates a thin tunneling barrier. The tunneling barrier, combined with the small core size, limits the number of holes in the core, resulting in a dynamic Coulomb hole blockade upon core photoexcitation. Thus, in DiBs, core emission is antibunched even under saturated excitation, while the shell emission is not. The two coupled subsystems thus exhibit completely different photon statistics.

Whereas in all the above systems long-lived charge transfer between the two emitters in a double QD was limited, in quasi-type-I/quasi-type-I heterostructures as depicted in Figure 3c (left), charge transfer can be expected to be long-lived provided that the intermediate layer acts as a sufficiently thick barrier. We realized such a system using PbS tip growth on seeded CdSe/CdS 70 nm long nanorods.¹⁷ In this nanocrystal (NC), photoexcitation of the PbS tip leads to trapping of a hole within the PbS, but the electron can migrate to the CdSe dot, effectively charging it. This is essentially a single-particle analog of charging of QDs in a photoelectrochemical cell. While the entire system is neutral following photoexcitation, the electron donating PbS tip is tens of nanometers away from the CdSe dot and plays no role in the emission dynamics of the CdSe negative trion. The effect of charge transfer is manifested in the blinking traces and histograms of the untipped versus tipped CdSe/CdS (Figure 3 b,c). The PbS hole trap ability to charge the CdSe/CdS with an extra electron results in a higher

probability of trion formation manifested in the blinking trace as a third, intermediate brightness, “gray” state (20% of the “on” intensity). Long lived charging is shown by the switching time scale of 10 ms between the “on” and “gray” states.

Taking advantage of these properties, double QDs and two-color emitting QDs have, to date, been utilized, at least at the level of a proof-of-principle demonstration, for a number of applications:

■ LIGHT-EMITTING DEVICES

The concept of using QDs exhibiting multiple emission colors for white-light-emitting diodes (LEDs) is intriguing, although the benefits, such as enhanced control over energy transfer among QDs emitting at different colors, do not, at this point, clearly outweigh the greater complexity of fabrication and the difficulty to achieve a high quantum yield (QY).²⁶ White light generation with NC-LEDs was demonstrated for CdSe/ZnS/CdSe QD–QWs integrated on a InGaN/GaN LED, and the ability to tune the emission band of the NCs was demonstrated. The hybrid LED uses double QDs as phosphors in conjunction with an electrically driven blue LED.²⁴

Double doped ZnSe QDs (Cu:ZnSe(Mn)) were also shown to emit white light. These NCs exhibit three spatially separated peaks at 415, 495, and 585 nm, corresponding to the ZnSe band edge emission, trap \rightarrow Cu d orbital radiative

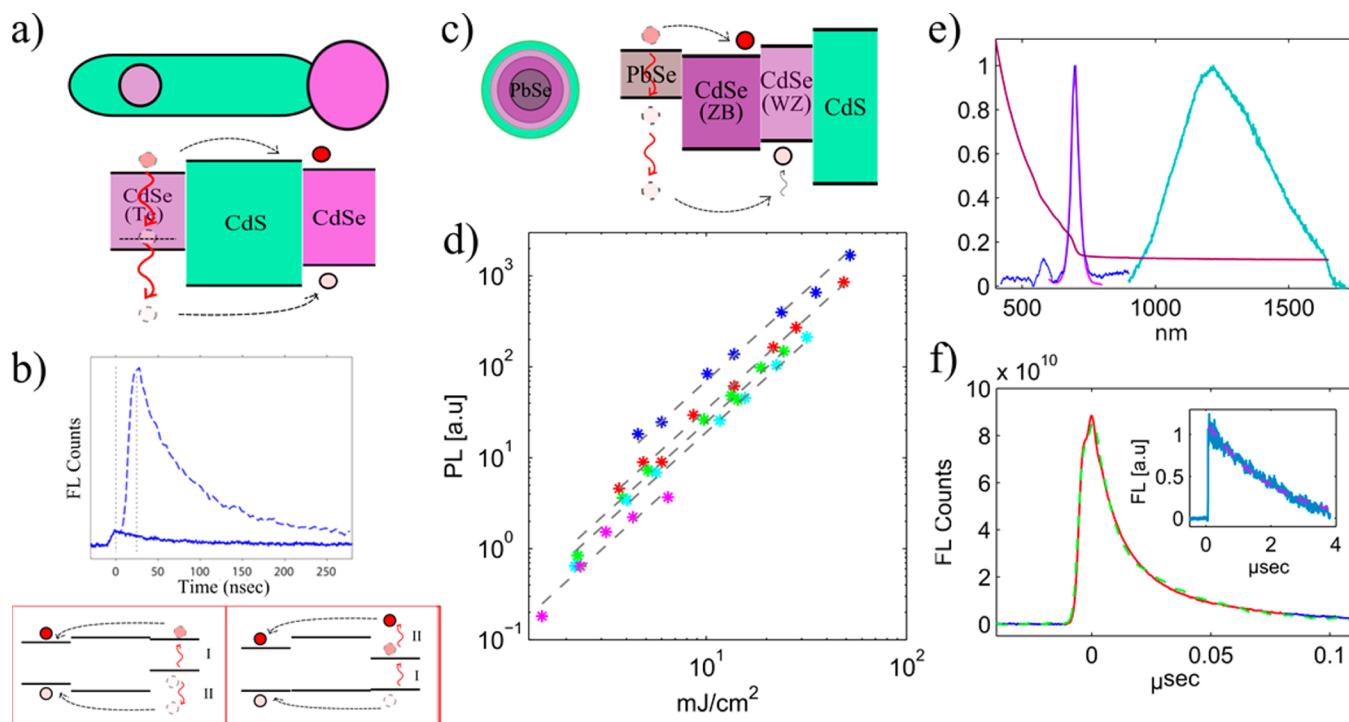


Figure 4. Upconversion in double QDs. (a) CdSe(Te)/CdS/CdSe band alignment and hot hole UC. (b) Upconverted emission transient at 570 nm induced by a weak 680 nm excitation pump (continuous line), followed by a 1064 nm excitation in 22 ns delay probe (dashed line). Insets show UC energy landscape, a double well band alignment for UC by hot carrier trapping (for holes/electrons depicted on left/right, respectively). In contrast, the other type of the charge carriers is delocalized across the particle. (c) PbSe/CdSe/CdS band alignment and hot hole UC. (d) Power dependent UC fluorescence counts for several NIR excitation wavelengths (850, 900, 950, 1050, and 1100 nm, depicted in blue, red, green, cyan, and magenta, correspondingly). Each curve was fitted by a quadratic power law $a(w_{2ph}) \cdot P_{ex}(w_{2ph})^2$ shown as dashed gray lines. (e) Emission spectrum of the UC system, using a 405 nm LED excitation: Visible and NIR emissions are depicted in blue and cyan, correspondingly. The UC spectrum using 850 nm two-photon excitation (pink), corresponding to the integrated transient limits shown in red in panel f, is similar to the above-band gap excited emission spectrum. The vertically shifted absorption spectrum is depicted in maroon. (f) A typical UC transient curve of the visible emission peak at 700 nm is depicted in blue. The transient response is well fitted by a biexponential decay having an average lifetime of 6.3 ± 0.2 ns (dashed green). The PbSe NIR emission lifetime, depicted in blue in the inset, is fitted by a single exponential of 2.1 ± 0.1 μ s (dashed pink). Panels a and b adapted with permission from ref 15, copyright 2013 Macmillan Publishers Limited. Panels c–f adapted with permission from ref 16. Copyright 2016 American Chemical Society.

recombination, and $Mn^{2+}({}^4T_1 \rightarrow {}^6A_1)$ emission.⁴⁶ Recently, copper doping was used to generate double emission in type-I Cu:InP/ZnS/InP/ZnS QD–QWs and in type-II formations using Cu:CdS/ZnSe QDs. The double emission profile of these NCs was shown to be highly tunable, and white LED emission was achieved after incorporation on a blue LED.^{43,45} Their main advantage over conventional QD blends is the large Stokes shift, which reduces self-absorption.

In a different approach, DiBs were implemented for tunable color LEDs. They were shown to operate both under optical excitation and via electrical pumping. The ratio of core vs shell emission in these was controlled by either the optical excitation pump power or by applied bias, enabling continuous tuning of the emission color from red to green.²⁹

■ RATIOMETRIC SENSING

Many QD-based sensors operate based on modulation of the luminescence QY by a desired external stimulus. This type of sensor is often sensitive to changes in light intensity, as well as to interfering factors such as local environment changes (pH, oxygen, aggregation). Dual emitting sensors can provide a more reliable ratiometric measurement of the emission intensity, particularly in the context of local temperature sensing. This was shown in Mn^{2+} -doped CdSe QDs⁴⁰ and in doped core/shell formations of Zn(Mn)Se/CdSe, that are more homoge-

neous and stable.⁴¹ In these QDs, quantum confinement is used to tune the first excitonic excited state close in energy to the $Mn^{2+}({}^4T_1)$ excited state. By doing so, dual emission is achieved, originating either from the $Mn^{2+}({}^4T_1 \rightarrow {}^6A_1)$ spin forbidden transition with a lifetime of ~ 100 ms or from the semiconductor band edge with a lifetime of ~ 10 ns. The proximity of these two excited states and the 10^4 factor difference in decay rates result in thermally assisted repopulation of the excitonic state. Basically, the $Mn^{2+}({}^4T_1)$ acts as a reservoir for excitons, such that small excitonic populations derived from the tail of the Boltzmann distribution result in substantial band edge luminescence. As a function of temperature, the luminescence can be varied from solely Mn^{2+} emission at low temperature to almost exclusive band edge emission at high temperature. Similar ideas were also demonstrated in dual emitting PbS/CdS double QDs.³¹ In a related approach, the thermal equilibrium between band edge and defect emission of CdSe dots could be used for nanothermometry and in LEDs.^{47,48}

■ OPTICAL GAIN

QDs were considered to be promising optical gain media because of their high QY, photostability, color tunability and energy discretization that results from the quantum confinement effect. However, due to the 2-fold spin degeneracy of the

conduction band $1S_e$ state, gain in QDs usually requires some population of biexcitons. The rapid nonradiative decay of the biexciton and the undesired photoinduced absorption (PA), which may overlap stimulated emission (SE), result in poor gain properties for standard QDs. Indeed, type-II heterostructures and doped QDs have been shown to partially or fully remove this degeneracy, thus providing improved gain characteristics.

As an alternative to these, dual emitting CdSe/ZnS/CdSe were proposed for improving gain performance in NCs via the coupling effect of the core and the shell.¹⁴ Compared with standard CdSe QDs, the CdSe/ZnS/CdSe system was shown to have an enhanced SE bandwidth and reduced PA for excitation above the CdSe shell's band edge. This was in addition to an increase in the core band edge SE cross section. The bandwidth increase arises from shell enabled SE, in which additional high energy coupled states support the high energy excitations, and from the coupled shell, which reduces the biexciton binding energy similarly to a type-II heterojunction.

■ PHOTOLUMINESCENCE UPCONVERSION

Upconversion is a nonlinear process in which two, or more, long wavelength (low energy) photons are converted to a shorter wavelength (high energy) photon.^{49,50} It is based on sequential absorption of photons, involving long-lived intermediate energy states. Hence, unlike coherent conversion processes such as second harmonic generation, it is not restricted to upconversion of intense coherent laser radiation. The requirements for UC are long-lived excited states, a ladder-like arrangement of energy levels, and a mechanism inhibiting cooling of hot charge carriers.⁵¹

Colloidal double QDs can aid in materializing UC schemes initially developed in the context of quantum wells. When two wells having different band gaps were placed in proximity to one another, hot carriers ejected from the lower energy one, either by Auger processes or via intraband absorption, could be captured in the higher energy one, leading to UC. The QD analog of this system requires a double well band alignment for one charge carrier (electron or hole) and delocalization across the structure for the other, schematically depicted in the insets of Figure 4b.

We recently presented such UC NC designs with quasi-type-I/type-II band alignment for realizing a double well formation in the VB and a flat CB (see Figure 4). Two such systems are tipped seeded rod formations¹⁵ and core/shell/shell ones.¹⁶ In both, hot holes were sufficiently energetic to be trapped by the high energy well, followed by radiative recombination leading to UC.

The latter PbSe/CdSe/CdS double QDs¹⁶ are of particular interest because they upconvert near-infrared (NIR) light (up to 1.2 μm) to visible light, accessing a spectral region where alternative upconversion nanoparticles (based on either rare-earth doped NCs or triplet-triplet annihilation) do not exist. They require power densities lower by 5 orders of magnitude than nonresonant two-photon absorption and exhibit a relatively small energy loss ($2E_{\text{IR}} - E_{\text{vis}}$). This is shown in Figure 4d depicting the UC power dependent excitation for various excitation wavelengths, each well fitted by a quadratic power law $a(w_{2\text{ph}}) \cdot P_{\text{ex}}(w_{2\text{ph}})^2$, as expected for a nonlinear two photon process. Moreover, their synthesis enables versatility and tunability of both the visible emission color and the NIR absorption/emission edge (see Figure 4e), by tweaking the volume of the intermediate shell and the initial core size. The

intensity at which upconversion saturates depends on the lifetime of the intermediate state, approximately 2 μs in the case of the PbSe core exciton (see inset of Figure 4f). Above saturation, the maximal UC efficiency of this system was 0.7%, comparable to alternative nanocrystalline systems. An additional feature of the UC process in such systems is the ability to induce upconversion with two photons of different energies, as depicted in Figure 4b. In this case, interband absorption is followed by intraband absorption of a lower energy photon, which heats the excited hole and induces upconversion (Figure 4a).

■ CONCLUSIONS AND OUTLOOK

Colloidal synthesis of semiconductor NCs has made giant leaps since the initial studies on hot injection methods. These have made band gap engineering of colloidal NCs a reality in the past decade. Extrapolating from past progress, it is certain that advances in synthesis will enable fabrication of even more complex structures than the ones discussed here. Given these tools, much relies on the ability to cleverly design tailored nanostructures for achieving particular functionalities. Interestingly, most of the research on colloidal double QDs has focused, to date, on room-temperature properties. This is in stark contrast with past work on epitaxially grown systems, which focused on low-temperature properties, both in the context of charge transport and in the context of quantum optics.

The list of potential applications presented above is by far not exhaustive. Double QDs can play a role in numerous other applications where they have not yet been applied. Light harvesting applications can benefit from the long-lived charge separation within the nanoparticle. External control of the emission properties of QDs, such as by charging or dynamic Coulomb blockade, may be beneficial for subdiffraction limited imaging. The use of double QDs may dramatically extend the uses of colloidal QDs as sources of nonclassical light beyond their current application as single-photon emitters and for quantum computation as qubits.⁵²

All of these rely on achieving an improved understanding of carrier dynamics in these more complex nanostructures. At present, our understanding of much of the underlying photophysics of these structures is too crude and not sufficiently quantitative to provide optimal solutions for particular needs. Yet, at the rate of progress made today such complex designed QDs hold a bright future. In less than 30 years, colloidal QDs made their way from a laboratory finding to a component in commercial displays. The availability of structures with potentially enhanced functionality due to the much larger number of degrees of freedom in their design will likely broaden the scope of their use to a broader arena.

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Notes

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