Influence of the Core Size on Biexciton Quantum Yield of Giant CdSe/CdS Nanocrystals

UTD AUTHOR(S): Siddharth Sampat and Anton V. Malko

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Semiconductor nanocrystals (NCs) have long been known to possess attractive physicochemical properties, such as facile chemical preparation methods, tunability of emission wavelength, and high photoluminescence (PL) quantum yields (QYs) of the excitonic (X) emission. Such useful properties make NCs attractive for a large range of applications from biological imaging to light emitting diodes (LEDs) to lasers and photon sources for quantum optics experiments. In particular, engineering of NC photon emission statistics presents an opportunity to address specific applications. Regulated emission of individual photons is desired for single photon sources in quantum cryptography, while multiexcitonic (MX) emission may be essential for generation of entangled photon pairs in quantum computing, as well as for lasing applications.

To this end, the majority of research has been conducted with core/shell NC structures in which the emitting core is overcoated with a thin layer of a semiconductor material with much higher bandgap. This results in enhanced carrier localization and better surface passivation, with group II–IV materials such as CdSe/ZnS being prime examples of this strategy. This strategy has been quite successful to obtain NCs with high excitonic quantum yields. However, while large core standard NCs could possess moderately high biexcitonic (BX) quantum yields measured at cryogenic temperatures, room temperature emission does not show much of the MX emission and still possess the phenomenon of fluorescence intermittency or PL “blinking”. Blinking behavior is commonly pictured as the NC cycling between states of high-(ON) and low-(OFF) PL intensity levels. Such blinking behavior was initially attributed to an NC switching between neutral (X) and various charged (X*) states. However, later studies uncovered evidence that pointed towards a more complex nature of the blinking process, and several blinking mechanisms have now been proposed.

In parallel with the efforts to understand PL blinking behavior, concentrated effort has been undertaken to suppress PL blinking and to realize continuous photon emission from a single NC. Early attempts focused on reduction of the density of the trapping sites on the NC outer surface via manipulation of ligand and/or solution environment of the NCs. While moderately successful, these methods have proven to be highly environmentally specific, thus limiting their practical utility. More recently, an all-inorganic approach realized by modification of the NC core/shell hetero-structure has proven to be highly successful. Here, suppressed and even non-blinking behavior and suppressed Auger recombination is realized by overcoating an NC core with a thick (generally 3–5 nm) wider bandgap shell, where the core/shell interface is either quasi type I or type II in nature. The approach was initially demonstrated for CdSe and has now been extended to InP cores. These multi-shell NCs have been called “giant” (g-NCs) due to their thick shells. Recently, fully non-blinking behavior was obtained by this method for the CdSe/CdS g-NC system.

In addition to blinking suppression, g-NCs have shown many other interesting photophysical properties that considerably

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Benjamin D. Mangum, Siddharth Sampat, Yagnaseni Ghosh, Jennifer A. Hollingsworth, Han Htoon and Anton V. Malko

We present a systematic study of photoluminescence (PL) emission intensity and biexciton (BX) quantum yields (QYBX) in individual “giant” CdSe/CdS nanocrystals (g-NCs) as a function of g-NC core size and shell thickness. We show that g-NC core size significantly affects QYBX and can be utilized as an effective tuning parameter towards higher QYBX while keeping the total volume of the g-NC constant. Specifically, we observe that small-core (2.2 nm diameter) CdSe/CdS NCs with a volume of ~200 nm^3 (shell comprises 4 CdS monolayers) show very low average and maximum QYBX's of ~3 and 7%, respectively. In contrast, same-volume medium-core (3 nm diameter) NCs afford higher average values of ~10%, while QYBX's of ~30% are achieved for same-volume large-core (5.5 nm diameter) CdSe/CdS NCs, with some approaching ~80%. These observations underline the influence of the g-NC core size on the evolution of PL emissive states in multi-shell NCs. Moreover, our study also reveals that the use of long anneal times in the growth of CdS shells plays a critical role in achieving high QYBX.
differ from those of “regular”, thin shell CdSe/ZnS NCs. It was recently shown that thick-shell g-NCs have considerably reduced Auger recombination rates, far beyond of what is expected from simple volume scaling model.\textsuperscript{27} As a result of the suppressed Auger recombination, thick-shell CdSe/CdS g-NCs have been shown to possess high biexcitonic (BX) and higher-order multiexcitonic (MX) quantum yields (QY) to a level allowing spectroscopic visualization of MX PL signatures. In particular, PL emission corresponding to the biexcitonic state and up to the 5th excitonic state were observed in the low-temperature PL spectra of single CdSe/CdS g-NCs.\textsuperscript{28–29} However, a wide variation of BX emission strengths have been shown to exist among g-NCs of the same nominal size – values of QY\textsubscript{BX} ranged from 0.1 to near unity.\textsuperscript{27} It was also shown that Auger rate and, correspondingly, emission of charge excitons and biexcitons are dependent on the CdS shell thickness, with thicker shells rendering better Auger suppression.\textsuperscript{27,28–33} Meanwhile, modification to the PL emission behavior has been observed in intermediately thick g-NCs (CdS thickness of \textasciitilde 8–12 ML). In such samples, excitonic emission is switching between a fully “ON” state and moderately emissive, “GRAY” state with emission quantum yield typically on the order of 10–30\%,\textsuperscript{33,34}

Thus far, the majority of the studies have been focused mainly on the influence of shell thickness on suppression of Auger recombination and blinking. On the other hand, it was recently observed that g-NC volume can also have a strong influence on blinking behavior.\textsuperscript{35} Utilizing an optimized shell-growth procedure for more consistently shaped, sized and properties-uniform g-NCs, we synthesized a g-NC series comprising different core sizes and shell thicknesses. We observed that there existed a common volume threshold (\textasciitilde 750 nm\textsuperscript{3}) for realizing non-blinking behavior over long observation times of \textasciitilde 1 hour.\textsuperscript{36} An open question remains as to whether any additional impact of g-NC volume and/or core-size should be expected in the context of both blinking behavior and Auger recombination. Specifically, due to strong asymmetry in the alignments of the conduction and valence bands, an increase of the core size might give rise to a reduction in hole confinement, while barely impacting the electron wavefunction, which is significantly more delocalized into the g-NC shell layer. Such an impact on the hole is important in the context of Auger recombination suppression because reduction of hole confinement is expected to lead to the suppression of X\textsuperscript{+} trion Auger recombination. Significantly, Auger rates for X\textsuperscript{+} are higher than those for X\textsuperscript{−}.\textsuperscript{32} Thus, limiting the X\textsuperscript{+} Auger rates is expected to have a disproportionately stronger impact on overall Auger recombination efficiencies and, thereby, on QY\textsubscript{BX}. Additionally, it may also be significant that by using a larger core, one would be able to better separate the NC center from the core–shell interface, where trap sites that can influence blinking and Auger recombination processes may exist.

Clearly, there is a need to further expand understanding of core-size- and particle volume effects by exploring PL blinking behavior in more detail and, importantly, by quantifying their impact on QY\textsubscript{BX}’s. In particular, in this work we focus on three series of g-NCs with different core sizes (diameter, d = 2.2, 3 and 5.5 nm) and shell thickness ranging from 2–18 ML.

Time-tagged, time-correlated single photon counting (TCSPC) technique under pulsed excitation has been applied in order to simultaneously record PL intensity and lifetime fluctuations on over 200 different individual g-NCs. Values of g-NCs’ QY\textsubscript{BX} are determined from the area ratio of center and side peaks of the 2nd order photon correlation function (g\textsuperscript{(2)}) as previously described.\textsuperscript{27} For g-NCs with QY\textsubscript{BX} > 0.5 values, we employ the time gated 2nd order photon correlation spectroscopy technique demonstrated recently by Mangum et al.\textsuperscript{36} to determine that the high peak area ratio is indeed a result of efficient BX recombination and has not resulted from emissions of multiple g-NCs forming a cluster. It is determined that core size has a conclusive effect on the blinking behavior and photon statistics of the BX emission. Transitioning through g-NC core sizes, blinking behavior and QY\textsubscript{BX} evolve from a variety of blinking behaviors (ON–OFF and ON–GRAY states) coupled with nearly zero QY\textsubscript{BX} for small cores (d = 2.2 nm) to essentially non-blinking g-NCs with average QY\textsubscript{BX} \textasciitilde 40\% for large cores (d = 5.5 nm). Several Auger-related mechanisms are invoked to explain the observed progression of blinking behaviors and evolution of biexcitonic QYs.

Results and discussion

In Fig. 1–3, PL emission characteristics of 9 representative g-NCs from three sample series with different CdSe core sizes of 2.2 nm (small), 3 nm (medium), and 5.5 nm (large) diameters are shown. Columns A–D of the figures represent PL time trajectories (blinking traces), histograms of the PL intensity distributions, fluorescence lifetime intensity distributions (FLID) and the 2nd order photon correlation function (g\textsuperscript{(2)})

Fig. 1 shows representative data for small core samples with 4, 8, and 15 CdS ML shells. As seen, small core/4CdS and small core/8CdS ML samples show “regular” blinking behavior, characterized by clear ON–OFF statistics. However, an intensity distribution histogram for the sample with 15 ML thick shell shows two peaks that correspond to the moderately emitting “GRAY” level of approximately 30\% PL efficiency and bright “ON” level. The FLID distribution also points to the existence of two emissive states, with PL lifetimes of ca. 20 ns (GRAY state) and ca. 60 ns (ON state). As the PL emission never goes down to a completely OFF level, we classified such g-NC as non-blinking g-NC. While more than 50\% of 15 shell g-NCs exhibit this ON/GRAY fluctuation behavior, it was observed in only one out of 15 g-NCs with 8 ML shell. A similar transition from ON/OFF to non-blinking ON/GRAY PL intensity fluctuations can also be observed for medium core size g-NCs as their shell thickness is increased from 2 to 18 MLs, albeit transition to ON/GRAY state occurs at thinner shell thickness (data for 2 ML sample with ON/OFF statistics is not shown). However, non-blinking g-NCs exhibiting ON/GRAY fluctuations reach 50\% of the total population at much thinner shell thicknesses of 7 ML as compared to 15 ML for the small core sample. Fig. 2 row 1, column A and B display exemplary traces and histogram of a 7 ML shell, medium core g-NC showing ON/GRAY PL fluctuations. An even thinner shell of 5 ML is required for the large core (5.5 nm diameter) g-NCs to achieve non-blinking ON/GRAY fluctuation.
in 50% of the population. Fig. 3, row 1 shows one such g-NC as an example. Despite the fact that large core g-NCs require thinner shell to achieve suppression of ON/OFF blinking, due to larger core diameter, volumes of both medium core 7 ML and large core 5 ML samples are approximately equal at 400–500 nm³. These findings reaffirm our earlier report that a larger core affords suppressed blinking behavior at thinner shells and there is a core-size independent, threshold volume of 750 nm³ for emergence of non-blinking g-NC population. The volume threshold for the observation of ON/GRAY fluctuations in this experiment (400–500 nm³) is much lower than 750 nm³ volume we reported previously because more sensitive TCSPC measurements of this experiment allow us to detect GRAY levels that were not possible to detect in our previous CCD based blinking experiment. However due to the parallel nature of the CCD experiment, we were able to collect blinking statistics from a larger number of g-NCs (over a hundred for each core/shell g-NC ensemble) for much longer times (~1 hour) in this previous study. It is also important to note that observation time plays an important role in assessing blinking statistics, where shorter observation times (e.g., 180–300 s) afford an apparently enhanced suppressed/non-blinking population compared to a more rigorous long observation time (e.g., 1 h). In accord with our previous shell thickness-dependent study, the narrowing of the distribution of PL intensity fluctuations with the increase of the shell thickness, and convergence of PL fluctuations towards a shot-noise limited regime (single emissive level) at the thickest shell were observed for all three different core sample series. We, however, could not observe any systematic influence of the core size on emergence of g-NCs with fluctuation free single level emissions.

Detailed analysis of biexcitonic quantum yields (QYBX) extracted from the g(2) traces of columns D of Fig. 1–3 reveals a clear systematic influence of the core size on QYBX. To demonstrate this point, we compiled the QYBX values of more than 200 individual g-NCs as the function of their volume as well as core size and shell thickness as shown in Fig. 4. In the case of small (2.2 nm) core g-NCs (green data points), vanishingly small QYBX values at thin, 4 and 8 ML shell thicknesses and gradual rise of the QYBX values with the increase of the shell thickness are observed. However, even for the thickest (18 ML) shell samples we only observe maximum QYBX ~ 0.35 with the average QYBX ~ 0.18. QYBX values increase and their distributions become wider as g-NCs core sizes increase to 3.0 nm (medium: blue data points) and 5.5 nm (large: red data points). QYBX of medium and large core g-NCs also show very weak shell thickness dependence and overall average values of QYBX ~0.2

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**Fig. 1** Small core dots. Columns A – blinking traces, columns B – probability distributions, columns C – FLIDs, columns D – antibunching traces. Color scale on panels C indicates number of occurrences of a lifetime value recorded per each 100 ms time bin in a blinking trace at a corresponding panel A.
and \(~ 0.4\) respectively. Largely, this data show a significant influence of the g-NC core size on biexcitonic quantum yields.

To demonstrate the influence of the core size on QY\textsubscript{BX} more clearly, minimum, average and maximum values of the QY\textsubscript{BX} observed in narrow volume ranges of 200–250 nm\textsuperscript{3}, 950–1050 nm\textsuperscript{3} and 1450–1550 nm\textsuperscript{3} as the function of their core size are plotted in Fig. 5(a)–(c), respectively. The data points for the smallest volume range (Fig. 5(a)) display the strongest effect, as the values of QY\textsubscript{BX} increase by factor of 4–8 from negligible values of less than 0.05 to a maximum of 0.72 (average of 0.35). Despite that the maximum and average QY\textsubscript{BX} of small core sample increase with the shell thickness, significant increase of QY\textsubscript{BX} values was observed for the two larger volume ranges displayed in Fig. 5(b) and (c). Further, we plotted a population fraction of the dots in high, medium and low QY\textsubscript{BX} ranges of QY\textsubscript{BX} > 0.4 (Fig. 5(d)), 0.2 < QY\textsubscript{BX} < 0.4 (Fig. 5(e)) and QY\textsubscript{BX} < 0.2 (Fig. 5(f)) for dots with different core sizes as the function of their shell thicknesses and volume. Fig. 5(d) (red circles) show that more than 20\% of large core g-NCs exhibit high QY\textsubscript{BX} even at 2 ML shell-thickness (volume \(< 200\text{ nm}^3\)) and this population fraction can grow up to 50\% at the shell thickness of 9 ML (volume \(\sim 1000\text{ nm}^3\)). For the g-NCs with medium core, significant high QY\textsubscript{BX} g-NCs population only emerges at shell thickness/volume \(\gtrsim 9\text{ ML}/700\text{ nm}^3\) (Fig. 5(d), blue squares).

None of the small core g-NCs were observed to exhibit high QY\textsubscript{BX} and only a small fraction is observed to show medium QY\textsubscript{BX} at the thickest shell of 18 ML and volume of 1500 nm\textsuperscript{3} (Fig. 5(f), green diamonds). Fig. 5(f) shows that while low QY\textsubscript{BX} g-NCs constitute a majority of population (\(\sim 60\%\)) in case of small and medium core samples for all the shell thickness, they become minority in case of large core sample (\(< 20\%\)). These plots clearly indicate that the size of g-NC core can be utilized as an effective tuning parameter toward achieving higher BX quantum yields at the smaller NC volume.

Due to the large differences in the degree of spatial confinement stemming from very different magnitudes of conduction and valence band offsets between CdSe and CdS, holes are largely confined to the core, while electrons are delocalized over the entire volume of a g-NC. Combined with the higher density of the valence band states, it results in positive trions having much larger non-radiative Auger rates as compared to negative ones. As the result of such imbalance, the biexciton decay is mostly defined by the positive trion’s Auger recombination.\textsuperscript{35} The weakening of the hole’s confinement resulting from the increase of the g-NC core size can therefore lead to the reduction of the Auger recombination rates for positive trions and increase of the QY\textsubscript{BX} that we observed.
However, we argue that the increase of the core volume alone cannot explain the observed large QYBX values. As previously discussed for purely radiative processes, one can apply free-carrier scaling of radiative decay rates. Under such conditions, it is expected that the biexciton radiative lifetime $\tau_{\text{BX}} = \tau_X/4$, where $\tau_X$ is exciton radiative lifetime. Prior studies of regular CdSe dots in the same size range have shown characteristic excitonic lifetimes on the order of 10–20 ns and weakly dependent of the NC size, while measured biexcitonic times span the range from $\tau_{\text{BX}} \sim 10$ ps for small, $d = 2.4$ nm NCs to the maximum of $\tau_{\text{BX}} \sim 150–200$ ps for larger, $d = 5.5$ nm NCs. Given that Auger scaling in standard CdSe NCs is purely volumetric and considering that excitonic QYX in high-quality CdSe (and CdSe/CdS) dots is close to unity, maximum assumed QYBX values should not be more than a few percent only as $QY_{\text{BX}} < 4\tau_{\text{XX}}/\tau_X$ where $\tau_{\text{XX}}$ is the measured biexciton lifetime. On the other hand, measured QYBX values for largest shell CdSe/CdS samples reach to $QY_{\text{BX}} \sim 80\%$ and measured biexcitonic decay times are on the order of $\tau_{\text{BX}} \sim 5–10$ ns. Clearly, some other mechanism should be contributing to the relaxation of the Auger recombination constrains.

In a theoretical study, Cragg and Efros modeled that Auger rates of an NC with a smooth confinement potential can exhibit a much more dramatic (several orders of magnitude) change with the core size as compared to a NC with abrupt confinement potential. Based upon this theory, some prior studies have attributed the suppression of Auger recombination and hence the observation of larger QYBX to smooth confinement potential of holes resulting from unintentional interfacial alloying during the growth of the CdS shell. However, a recent study comparing intentionally alloyed CdSe/CdS g-NCs, in which a CdSe$_{1-x}$S$_x$ transition region of $\sim 1.5$ nm width (3–4 MLs) was created at the

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Fig. 3 Large core dots. Columns A – blinking traces, columns B – probability distributions, columns C – FLIDs, columns D – antibunching traces. Bottom part of panel C2 – $100 \times$ magnification of FLID showing very weak ‘GRAY’ state. Color scale on panels C indicates number of occurrences of a lifetime value recorded per each 100 ms time bin in a blinking trace at a corresponding panel A.

Fig. 4 Biexciton quantum yields extracted from $g^2(t)$ measurements for three different core sizes.

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core/shell interface, with nominally non-alloyed CdSe/CdS counterparts reported only modest ensemble $Q_{\text{YBX}}$ values for either type of sample. Furthermore, although an improvement from 3% to 11% was indeed observed upon intentional alloying, this apparent enhancement is relatively small compared to our observations for different core sizes. Specifically, we show a factor of ~8 increase in $Q_{\text{YBX}}$ at the volume of ~200 nm$^3$ and a factor of ~5 at the volume of ~1000 nm$^3$ with large absolute average $Q_{\text{YBX}}$ values of ~30% and ~40% respectively that can be achieved via a simple increase of g-NC core size. Since any synthesis-induced interfacial properties should be constant for all of our samples, irrespective of the core size, we conclude that alloying has little effect on the enhancement of $Q_{\text{YBX}}$ that we obtain as a function of increasing core size, and change in the core size alone should have the more prominent effect on $Q_{\text{YBX}}$ in these dots. Furthermore, the alloying mechanism does not well explain the high $Q_{\text{YBX}}$ values (0.35) obtained in large core CdSe/CdS NCs that are overcoated with only 2 ML of CdS shell. Overall, these data raise intriguing and important questions about the completeness of volumetric scaling and interfacial alloying models commonly been used to explain modifications of the Auger rate.

As an alternative to these models we consider recently proposed model of trap-assisted Auger recombination. As discussed by Cohn et al., Auger process can occur via a carrier (electron) trapped at the surface of the shell or at the core/shell interface and could also be size dependent. It is possible that smaller core g-NCs with thin shells may have higher density of the trap sites at the core/shell interface due to larger strain and therefore exhibit stronger Auger recombination and lower $Q_{\text{YBX}}$. The variation in density of traps in this picture could also explain the wide variation of the observed $Q_{\text{YBX}}$ values for thin shell g-NCs. This model is further supported by recent publications that point out to a rather substantial dependence of the electron wavefunction’s penetration outside of the CdSe core as function of the core size. It was shown that the probability to find an electron outside of the core decreases 4-fold when the NC diameter only changes from $d = 2.3$ nm to $d = 2.8$ nm. Such strong core size dependence can certainly contribute to the trap-assisted Auger mechanism affecting biexcitonic quantum yield, especially for small core/thin shell nanocrystals. However, a more detailed experimental approach involving controlled alloying under the Successive Ionic Layer Adsorption and Reaction (SILAR) growth conditions and corresponding measurements of the biexcitonic QY is needed to fully uncover the mechanisms.

**Conclusions**

In summary, we have demonstrated clearly that the size of the g-NC core can be utilized as an effective tuning parameter to achieve core/shell dots with high $Q_{\text{YBX}}$ at the smallest possible volume. Specifically, our study has revealed that for an ensemble of g-NCs with 5.5 nm cores and 5 ML thick shells, we could achieve an average $Q_{\text{YBX}}$ approaching 40% and complete suppression of ON/OFF blinking in more than 50% of the g-NCs. These g-NCs have nominal diameter of only 9.5 nm. Such relatively small non-blinking g-NCs with high $Q_{\text{YBX}}$ could be highly beneficial for technological applications such as lasing, light amplification and entangled photon-pair generations. Additionally we would like to note that a recent attempt to suppress Auger recombination via the use of intentional alloying achieved only a factor of 3 enhancement of the $Q_{\text{YBX}}$ from 3% to 11% at the NC size of ~16 nm diameter. In contrast, we show here that it is possible to realize a factor of 4 to 8 enhancement with average $Q_{\text{YBX}}$ approaching 40% at a much smaller diameter of ~10–11 nm by simply increasing the size of the g-NC core. This observation suggests that the size of the g-NC core has an equal or stronger influence on Auger suppression compared to interfacial alloying. Furthermore, we achieved significantly higher average $Q_{\text{YBX}}$ for our g-NCs grown using long SILAR anneal times compared to much lower $Q_{\text{YBX}}$ reported for g-NCs grown via rapid shell growth (40% vs. 3%). Thus, in addition to our earlier observation that long anneal times enhanced ensemble PL and blinking statistics, this new result clearly suggests that slow shell growth also leads to stronger suppression of Auger recombination, even compared to intentionally alloyed systems. This may be a result of the slower shell growth allowing more complete healing of defects at the CdSe/CdS core/shell interface and enhanced suppression of defect-assisted Auger recombination. The ability to obtain...
high biexcitonic quantum yields by simply tuning g-NC core size is important for achieving improved performance of the light-emitting devices where Auger recombination greatly impacts LED efficiency and the onset of the current roll-off.46

Methods

In our experiments we use CdSe/CdS core shell g-NCs synthesized via a modified successive ion layer deposition procedure described in ref. 22. For single-dot spectroscopy, g-NCs prepared in hexane are dispersed onto a quartz substrate with the density on the order of 0.01 per μm². The sample is mounted on a translation stage of an optical microscope and NCs are excited at 405 nm with 50 ps pulses through a 0.7 NA objective lens that is also used to collect PL. The pulse-to-pulse separation (variable from 400 ns to 2000 ns) is set to be much longer than the PL decay times in order to ensure complete relaxation of excitons between sequential laser pulses. Collected PL is sent to a pair of Perkin-Elmer avalanche photodiodes (SPCM AQR-14) positioned at two arms of the standard Hanbury-Brown–Twiss (HBT) arrangement with 50/50 emission signal split. For PL blinking traces and corresponding FLIDs only one of the detectors is used, while for BX quantum yield signal split. For PL blinking traces and corresponding FLIDs we kept average number of excitations per pulse low, in the range of 0.5 < 〈N〉 < 0.7 in order to avoid higher order exciton effects. Before going into the HBT system, the PL emission is passed through long-pass excitation/emission filters that reject scattered laser light. Additionally, each of the detectors has 680 nm short-pass filter to avoid APD after pulsing light. Time-correlated single photon counting (TCSPC) is performed using PicoQuant TimeHarp or HydraHarp electronics. The resulting photon distributions are processed using either Symphotime software (data for small core dots) or via the home-made IGOR-based software (medium and large cores).

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References


39 This relation follows from the fact that in CdSe nanocrystals, the lowest state is two-fold degenerate and, at room temperature, any spin memory for the holes is lost (dark-bright exciton mixing). Thus, biexciton radiative decay can be represented via all possible combinations of any of the two electrons recombining with any two of the holes (hence free-carrier model), thus leading to the relation $\tau_{\text{BX}} = \tau_{\text{Y}}^{1/4}$.


43 A. W. Cohh, A. M. Schimpf, C. E. Gunthard and D. R. Gamelin, Size dependent trap-assisted Auger