Auger Recombination Lifetime Scaling for Type I and Quasi-Type II Core/Shell Quantum Dots

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ABSTRACT: Having already achieved near-unity quantum yields, with promising properties for light-emitting diode, lasing, and charge separation applications, colloidal core/shell quantum dots have great technological potential. The shell thickness and band alignment of the shell and core materials are known to influence the efficiency of these devices. In many such applications, improving the efficiency requires a deep understanding of multie excitonic states. Herein, we elucidate the shell thickness and band alignment dependencies of the biexciton Auger recombination lifetime for quasi-type II CdSe/CdS and type I CdSe/ZnS core/shell quantum dots. We find that the biexciton Auger recombination lifetime increases with the total nanocrystal volume for quasi-type II CdSe/CdS core/shell quantum dots and is independent of the shell thickness for type I CdSe/ZnS core/shell quantum dots. To perform these calculations and compute Auger recombination lifetimes, we developed a low-scaling approach based on the stochastic resolution of identity. The numerical approach provided a framework for studying the scaling of the biexciton Auger recombination lifetimes in terms of the shell thickness dependencies of the exciton radii, Coulomb couplings, and density of final states in quasi-type II CdSe/CdS and type I CdSe/ZnS core/shell quantum dots.

The viability of many semiconductor nanomaterial-based applications relies upon the ability to control multie excitonic states. For example, in typical nanomaterial-based lasers, generating population inversion requires two excitons in the nanosystem and, thus, the properties of the biexcitonic state determine, among other factors, the efficiency of the device. In fact, this is arguably the case for other applications such as light-emitting diodes and photocatalysts. Therefore, understanding the properties of the biexcitonic state and its decay channels is central to improving and further developing many light-induced applications.

One of the major decay channels of the biexcitonic state is Auger recombination (similar to exciton–exciton annihilation), which is a nonradiative process in which an electron and hole recombine and transfer their energy to a nearby electron or hole in a Coulomb-mediated process (Figure 1). Auger recombination typically is the dominant decay channel of biexcitons in semiconductor nanocrystals as it usually occurs on a subnanosecond time scale.

An aspect of biexciton Auger recombination that has attracted a great deal of attention over the years is how the rate of biexciton Auger recombination decay depends on the size of the nanocrystal. For single-material colloidal quantum dot (QDs), the linear dependence of the biexciton lifetime with the QD volume has become known as the “universal volume scaling law”. Although the size of a single-material colloidal QD is a knob that can be tuned to change the biexciton lifetime and, thus, the efficiency of nanodevices that rely on biexcitonic states, changing the size also drastically impacts single-exciton properties. On the other hand, heterostructure nanomaterials have many experimentally tunable parameters, including the relative size and band alignments between the individual component materials, that can be chosen to optimize the performance of nanodevices. For example, independently tuning the shell thickness and band alignment has resulted in heterostructure nanocrystals with near-unity quantum yields along with promising light-emitting diode and lasing properties.}

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heterostructure nanosystems and apply it to elucidate the shell thickness dependence of AR in quasi-type II CdSe/CdS and type I CdSe/ZnS core/shell QDs (Figure 1). The stochastic approach, which also accounts for electron–hole correlations, reduces the scaling with the system size \(N\) of calculating AR lifetimes from \(O(N^6)\) to \(O(N^2)\) and predicts quantitatively accurate AR lifetimes in comparison to experiments. Additionally, the AR formalism predicts that adding a shell with a quasi-type II band alignment (CdSe/CdS QDs) results in an increase in the AR lifetime, in agreement with previous experimental and theoretical results,\(^1\) whereas the addition of a shell with a strictly type I band alignment (CdSe/ZnS QDs) has little impact on the AR lifetime. Lastly, we explain the shell thickness dependences of the AR lifetimes in terms of the size dependencies of the root-mean-square exciton radius, Coulomb coupling, and density of final states in quasi-type II CdSe/CdS and type I CdSe/ZnS core/shell QDs.

AR is a Coulomb-mediated process for which an initial biexcitonic state \((\text{IB})\) of energy \(E_\text{S}\) via Coulomb scattering \((V)\). An AR lifetime \((\tau_{\text{AR}})\) for a nanomaterial can be calculated using Fermi’s golden rule where we average over thermally distributed initial biexcitonic states and sum over all final decay channels into single excitonic states:

\[
\tau_{\text{AR}}^{-1} = \sum_B \frac{2\pi}{\hbar} \sum_S |B(V|S)\delta(E_B - E_S) |
\]

(1)

where the delta function \([\delta(E_B - E_S)]\) enforces energy conservation between the initial and final states and the partition function \((Z_B = \sum_S \exp(-\beta E_S))\) is for the initial biexcitonic states (we assume Boltzmann statistics for biexcitons). Utilizing the interacting framework, previously developed by Philbin and Rabani,\(^1\) a deterministic calculation of an AR lifetime can be performed using

\[
\tau_{\text{AR}}^{-1} = \frac{2\pi}{\hbar Z_B} \sum_B e^{-\beta E_B} \sum_{a,i} \sum_{b,j,k} c_{a,i}^B c_{b,j,k}^B V_{abck} \delta(E_B - \varepsilon_a + \varepsilon_b) \\
+ \frac{2\pi}{\hbar Z_B} \sum_B e^{-\beta E_B} \sum_{a,i} \sum_{b,j,k} c_{a,i}^B c_{b,j,k}^B V_{abck} \delta(E_B - \varepsilon_a + \varepsilon_b) \\
\]

(2)

where indices \(a, b, \) and \(c\) refer to the electron (unoccupied) states, \(i, j, \) and \(k\) refer to the hole (occupied) states with corresponding energies \(\varepsilon_a\) and \(\varepsilon_b, r, s, \) and \(u\) are general indices, and \(V_{abck}\) is the Coulomb coupling given by

\[
V_{abck} = \iint \frac{\phi_i^*(r)\phi_k^*(r')\phi_j(r)\phi_l(r')}{|r - r'|} \ d^3r \ d^3r'
\]

(3)

The coefficients \((c^{\text{IB}}_{a,i})\) in eq 2 are determined by solving the Bethe–Salpeter equation for the singlet excitonic states,\(^3\) as we assume in this Letter that the AR process involves an initial singlet biexciton decaying into a final singlet exciton. For more details, see ref 14. The formalism presented above includes spatial correlations within the electron–hole pairs but ignores them between the two excitons\(^3\) and in the final electron–hole pair (Figure 1). This approximation for the final state is valid in a majority of nanomaterials as the energy of the final electron–hole pair is approximately twice the optical gap, which is well above the typical exciton binding energy in all semiconductor nanomaterials.\(^3\) In other words, the criterion for being able to approximate the final high-energy excitonic state as an uncorrelated electron–hole pair instead of a Wannier or Frenkel exciton is that \(E_{\text{opt}} > E_{\text{B}}\) where \(E_{\text{opt}}\) is the optical gap and \(E_{\text{B}}\) is the exciton binding energy. It was previously shown that this interacting (i.e., exciton-based) AR formalism (eq 2) predicts quantitatively accurate AR lifetimes for both single-material QDs and nanorods.\(^1\) On the other hand, noninteracting formalisms that ignore all electron–hole correlations in the initial biexcitonic state predict neither accurate AR lifetimes nor the scaling of the lifetimes with respect to QD volume except for QDs in the very strong confinement regime\(^3\), highlighting the importance of electron–hole correlations and the resulting Wannier exciton formation in semiconductor nanomaterials.\(^1\)

The main drawback of the exciton-based (interacting) AR formalism for calculating AR lifetimes (eq 2) is the computational cost. Formally, the steepest scaling involved in eq 2 is diagonalization of the Bethe–Salpeter Hamiltonian to obtain the coefficients \((c_{a,i}^B)\), which formally scales as \(O(N^6)\). However, in practice this takes <1% of the computational time for nanomaterials with \(\leq 10000\) atoms because only a few low-lying energy states are required to calculate the AR lifetime due to the Boltzmann factors in eq 2. The majority of the computational time is spent on calculating all of the Coulomb matrix elements, \(V_{abck}\) and \(V_{b,j,k}\), that couple the initial
biexcitonic states with the final electron–hole pairs. The number of Coulomb matrix elements that must be calculated scales as $O(N_{\text{final}}^2 N_{\text{h}} + N_{\text{final}}^2 N_{\text{e}}^2) \sim O(N_{\text{h}}^4)$, where $N_{\text{final}}$ is the number of high-energy final electron (hole) states and $N_{\text{e}}$ is the number of band-edge electron (hole) states [Figure S1 contains a representative density of states in the regions of $N_{\text{e}}$ and $N_{\text{h}}$, final], and the cost of calculating each Coulomb matrix element scales with the number of real-space grid points $(N_{\text{grid}})$ as $O(N_{\text{grid}}^2 N_{\text{grid}})$ to give the overall scaling of $O(N_{\text{grid}}^4)$. This limits the application of eq 2 to relatively small systems ($<1000$ atoms).

To reduce the computational effort and scaling of the rate-limiting step, we employ a plane-wave stochastic representation of the Coulomb operator:35

$$V_{\text{out}} \approx \langle R_{\text{ee}}^\dagger R_{\text{ee}}^\dagger \rangle \zeta$$

(4)

where the notation $\langle \cdot \cdot \cdot \rangle_{\zeta}$ denotes an average over $N_{\text{u}}$ stochastic orbitals (defined below)

$$R_{\text{ee}}^\dagger = \int \psi^*_{\text{u}}(\mathbf{r}) \psi_{\text{v}}^* (\mathbf{r}) \theta^\dagger_{\text{v}}(\mathbf{r}) \ d^3 \mathbf{r}$$

(5)

and $\theta^\dagger_{\text{v}}(\mathbf{r})$ is a stochastic representation of the Coulomb integral given by

$$\theta^\dagger_{\text{v}}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{k} \sqrt{\tilde{u}_{\text{v}}(\mathbf{k})} e^{i \mathbf{k} \cdot \mathbf{r}}$$

(6)

In these equations, $\psi_{\text{v}}(\mathbf{r})$ is a random phase between 0 and $2\pi$ at each $k$-space grid point, $\tilde{u}_{\text{v}}(\mathbf{k}) = \frac{4\pi}{\sqrt{\mathbf{k}^2 + \mathbf{k}^2}}$ is the Fourier transform of the Coulomb potential, and the stochastic orbitals $[\theta^\dagger_{\text{v}}(\mathbf{r})]$ are indexed by $\zeta$. By inserting eq 4 into eq 2, we obtain

$$\tau_{\text{AR}}^{-1} = \tau_{\text{AR,e}}^{-1} + \tau_{\text{AR,h}}^{-1}$$

$$\tau_{\text{AR,e}}^{-1} = \frac{2\pi}{h z_{\text{B}}} \sum_{a, i} e^{-i \phi_{a,i}^*} \sum_{b, j} \langle \sum_{k, \zeta} \gamma_{a, i, \zeta} R_{a, i, \zeta} R_{b, j, \zeta}^* \rangle_{\zeta} \delta (E_B - E_a + E_i)$$

$$\tau_{\text{AR,h}}^{-1} = \frac{2\pi}{h z_{\text{B}}} \sum_{i} e^{-i \phi_{a,i}^*} \sum_{j} \langle \sum_{k, \zeta} \gamma_{j, i, \zeta} R_{a, i, \zeta} R_{b, j, \zeta}^* \rangle_{\zeta} \delta (E_B - E_a + E_i)$$

(7)

where $\tau_{\text{AR,e}}$ and $\tau_{\text{AR,h}}$ are the lifetimes for the electron and hole channels, respectively (Figure 1). The calculation of an AR lifetime using eq 7 scales as $O(N_{\text{h}}^4)$.

To further reduce the computational scaling and complexity, we utilize the stochastic resolution of the identity36,37 within the subspace of the final high-energy electron and hole parts of the Hamiltonian. In simpler terms, we sample the final high-energy electron and hole states to reduce the scaling with the number of final excitonic states. Thus, we arrive at a general expression for calculating AR lifetimes of semiconductor nanomaterials using an efficient, doubly stochastic formulation of the interacting (exciton-based) AR formalism

$$\tau_{\text{AR}}^{-1} = \tau_{\text{AR,e}}^{-1} + \tau_{\text{AR,h}}^{-1}$$

$$\tau_{\text{AR,e}}^{-1} = \frac{2\pi}{h z_{\text{B}}} \sum_{a, i} e^{-i \phi_{a,i}^*} \sum_{b, j} \langle \sum_{k, \zeta} \gamma_{a, i, \zeta} R_{a, i, \zeta} R_{b, j, \zeta}^* \rangle_{\zeta} \delta (E_B - E_a + E_i)$$

$$\tau_{\text{AR,h}}^{-1} = \frac{2\pi}{h z_{\text{B}}} \sum_{i} e^{-i \phi_{a,i}^*} \sum_{j} \langle \sum_{k, \zeta} \gamma_{j, i, \zeta} R_{a, i, \zeta} R_{b, j, \zeta}^* \rangle_{\zeta} \delta (E_B - E_a + E_i)$$

(8)

where the indices $\theta_{a,i}, i^* a, \theta^i$ in eq 8 are sampled final states from the complete set of single excitonic states $(a, i$ pairs) in eq 7. Energy conservation in eq 8 has been taken into account when forming the stochastic orbitals that sample the final excitonic states; namely, we sample only states that preserve energy. The computational cost of eq 8 is $O(N_{\text{h}}^4)$. This scaling does assume that the number of stochastic orbitals required to properly converge the calculations does not increase with system size, which has shown to be true for a variety of electronic structure methods.36–40 Another beneficial feature of eq 8 is that it is embarrassingly parallel over all sets of stochastic orbitals. The acceleration that arises from using eq 8 instead of eq 2 ranges from $\sim 5$ for QDs with 1000 atoms to $>1000$ for QDs with 10000 atoms. This acceleration made the study of the large core/shell QDs presented in the remainder of this Letter possible. The Supporting Information contains more information about the derivation, implementation, and computational cost of the equations presented above.

We have implemented the equations presented above using the semiempirical pseudopotential method to model the electron and hole states.36,41–43 We utilized the filter–diagonalization technique44,45 to selectively calculate the low-energy electron and hole states required to accurately describe the excitonic states that compose the initial biexcitonic state and the high-energy electron and hole states that satisfy energy conservation. The Bethe–Salpeter equation31 was solved within the static screening approximation, and all electronic structure calculations were performed using the minimum energy atomic configuration obtained via molecular dynamics minimization36 of the heterostructure QDs. This computational scheme has been shown to predict quantitatively accurate single excitonic properties (e.g., optical gap and emission polarizations) and accurately takes into account the important effects of strain in heterostructure nanomaterials that arise from the lattice mismatch between core and shell materials.18,19

Figure 2 displays the calculated AR lifetimes using eq 8 for the $d_{\text{core}} = 3.8$ nm CdSe/CdS QDs along with the experimentally measured AR lifetimes26 and AR lifetimes calculated using a non-interacting, free-carrier-based formalism.34 Quantitative agreement with the experimental measurements on similarly sized CdSe/CdS QDs is observed when eq 8 is used. It is important to note that all of the core/shell QDs studied in this work have sharp core/shell interfaces.25
words, there is no alloying region between the core and shell materials that is known to have important consequences for AR lifetimes.21,27,29 The quantitative agreement shows the generality of the interacting (exciton-based) AR formalism for predicting quantitatively accurate AR lifetimes in nanomaterials. It is worth noting that a non-interacting (free carrier-based) AR formalism predicts incorrect AR lifetimes in core/shell QDs, similar to the single-material case.14

Figure 3 summarizes the main result of this work. The top panel of Figure 3 compares calculated AR lifetimes for CdSe cores with a diameter of 2.2 nm (d_{core} = 2.2 nm) as a function of the number of shell monolayers (MLs) for both CdS and ZnS from 0 to 8 MLs. This constitutes a range of nanocrystal sizes from approximately 200 atoms (V_{QD} \sim 5 \text{ nm}^3) to nearly 10000 atoms (V_{QD} \sim 350 \text{ nm}^3). Figure 3 highlights the dramatically different impact that growing a quasi-type II shell (CdS) has on the AR lifetime compared to growing a type I (ZnS) shell on a QD core (CdSe). Specifically, the addition of more and more CdS MLs leads to the AR lifetime increasing from \sim 5 \text{ ps for the 0 ML QD to } \sim 150 \text{ ps upon addition of 4 and 8 MLs of CdS, respectively, for the d_{core} = 2.2 \text{ nm CdSe QD core. On the other hand, for the same CdSe core, the addition of 4 and 8 MLs of ZnS does not lead to an increase in the AR lifetime.}

To understand the vastly different shell thickness dependencies of the AR lifetimes between CdSe/CdS and CdSe/ZnS QDs, we plot the root-mean-square exciton radius \left( \sqrt{\langle r_{e-h}^2 \rangle} \right) where r_{e-h} is the electron–hole radial coordinate)47 as a function of the number of shell MLs for both series of core/shell QDs in the bottom panel of Figure 3. For CdSe/CdS QDs, the root-mean-square exciton radius systematically increases with the number of shell MLs. On the other hand, for CdSe/ZnS QDs there is an increase upon adding the first ZnS layer, but then the addition of more and more ZnS MLs barely changes the root-mean-square exciton radius. Specifically, the root-mean-square exciton radius increases from 1.11 to 1.46 nm upon going from 4 to 8 MLs of CdS but increases only from 1.08 to 1.14 nm upon going from 4 to 8 MLs of ZnS for the same d_{core} = 2.2 \text{ nm CdSe core (bottom panel of Figure 3).}

These different dependencies of the AR lifetime and root-mean-square exciton radius with shell thickness are a direct consequence of the quasi-type II26,48 and type I nature of the CdS and ZnS shells, respectively. Figure 4 shows the hole and electron carrier densities of the lowest-energy excitonic state (i.e., electron–hole interactions have been included) projected onto the x-axis of the core/shell QDs for the d_{core} = 2.2 \text{ nm CdSe QD cores with 0, 4, and 8 MLs of CdS and CdSe/ZnS (blue) core/shell QDs with a CdSe core diameter of 2.2 nm.}
and, thus, increasing the root-mean-square exciton radius in larger CdS shell nanocrystals leads to a decrease in the level of Coulomb coupling involved in AR calculations. This result can be understood by noting that the more the electron and hole wave functions overlap, the larger the Coulomb matrix elements, as the product $\phi_e^r(\mathbf{r}')\phi_h^r(\mathbf{r})$, where $\phi_e^r(\mathbf{r}')$ and $\phi_h^r(\mathbf{r})$ are wave functions for an initial electron and hole, respectively, arises in the Coulomb coupling (eq 3).

The type I band alignment of CdSe/ZnS core/shell QDs results in the addition of ZnS MLs barely changing the root-mean-square exciton radius and not increasing the AR lifetime. Surprisingly, the AR lifetimes for all CdSe/ZnS core/shell QDs are slightly shorter, with lifetimes of $\sim 2$ ps, compared to the AR lifetime of $\sim 5$ ps for the bare CdSe core (Figure 3). To elucidate whether the compressive strain of the ZnS shell causes the decrease in the AR lifetime, we performed AR lifetime calculations on strained CdSe cores. Specifically, we performed molecular dynamics-based structural minimizations with ZnS shells and then removed the ZnS shells before performing the electronic structure calculations. This procedure resulted in compressively strained CdSe QDs, where the degree of compressive strain was related to the number of ZnS MLs that were present during molecular dynamics minimization (Table S4). Our calculations on this series of CdSe QDs show that the AR lifetime decreases from $\sim 5$ to $\sim 2$ ps with an increase in the strain on the CdSe QD (Table S5). Interestingly, the AR lifetime decreasing by $\sim 250\%$ upon adding strain to the CdSe QD is much greater than would be expected due to just a volumetric change as the compressive strain changes the CdSe QD volume by only $\sim 10\%$. We were able to trace the decrease in the AR lifetime to a decrease in the hole channel AR lifetime. Furthermore, the decrease in the hole channel AR lifetime was caused by an increase in the average Coulomb coupling matrix elements ($V_{\text{int}}$) of the hole channel and not by any substantial changes in the density of the final states (Table S6). Thus, it appears that the hole channel is more sensitive to stress-induced structural changes, and this suggests performing more comprehensive studies on the impact of strain on AR lifetimes is worthwhile, as strain may be playing a role in other nonmonotonic dependencies of AR in core/shell nanomaterials.

The goals of this study were to elucidate how biexciton Auger recombination in colloidal core/shell QDs can be accurately modeled and efficiently computed and to uncover some of the underlying physics of excitons and biexcitons in core/shell QDs by testing different approximations. To achieve these goals, we developed a stochastic computational scheme for calculating the nonradiative decay rate of biexcitonic states. This efficient, stochastic method for calculating Auger recombination lifetimes presented in this Letter is general and can be used for any confined nanomaterial. We also utilized this efficient method for calculating quantitatively accurate biexciton Auger recombination lifetimes within an interacting (exciton-based) formalism to elucidate the different impact of growing quasi-type II (CdS) and type I (ZnS) shells on QD cores (CdSe). Specifically, we showed that the Auger recombination lifetime monotonically increases as the number of quasi-type II shell monolayers increases whereas the Auger recombination lifetime is mainly unchanged upon the addition of type I shells.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01460](https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01460).

A detailed derivation of the equations along with additional information and discussion of the implementation and computational cost of the theory using the semiempirical pseudopotential method, filter—diagonalization technique, Bethe—Salpeter equation, and Fermi’s golden rule in the Auger recombination lifetime calculations presented in this Letter as well as the procedure used to construct the configurations of the nanosystems.

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**Author Contributions**

J.P.P. developed the theoretical framework and computer code, performed the calculations, and wrote the paper, and E.R. developed the theoretical framework and wrote the paper.

**Notes**

The authors declare no competing financial interest.

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