Suppression of the Auger Recombination Process in CdSe/CdS Core/Shell Nanocrystals

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ABSTRACT: We investigate the Auger recombination (AR) rate in CdSe/CdS core/shell nanocrystals (NCs) under different interface coninements in terms of the interface bond relaxation mechanism and Fermi’s golden rule. We find that the epitaxial layer of CdS can not only depress the influence of the Coulomb interaction between electrons and holes, but can also change the wave function and quantum confinement, resulting in the reduction of the AR rate. Moreover, the AR lifetime of CdSe/CdS core/shell NCs at a fixed entire dimension is lower than that of bare CdSe because of interface confinement of the wave function. A great drop of the AR rate can be achieved by adding an alloying layer that depresses the interface effect. Our predictions are in agreement with the available evidence, suggesting that the proposed approach could provide a general method to explore the AR process in core/shell NCs.

INTRODUCTION

The Auger recombination (AR) process in nanocrystals (NCs) has become one of the hottest topics in fundamental scientific issues as it takes major responsibility for nonradiative loss, which can decay the dynamics of multie excitons, induce fluorescence intermittency, cause loss of energy in the form of heat, and so on.1–3 To date, various methods have been carried out to explore the geometry, shape, and surface carrier trap assistance effects on the AR process both theoretically4–11 and experimentally.12–19 In particular, compared with bare nanosolids, the core/shell nanostructures show a different AR process.20 The epitaxial layer in the core/shell nanostructures can offer a new pathway to separate the electron and hole because the electron (or hole) may delocalize over the entire core/shell nanostructures.21,22

In general, with the size of a specimen down to the nanoscale, the effect of strong spatial confinement plays an important role in the properties of nanostructures in terms of box thinking, which can relax the translational momentum conservation and increase the magnitude of Coulomb coupling, thereby allowing for an efficient AR rate.22,23 Thus, the increment of core size can reduce the quantum confinement and Coulomb interaction, which is of great benefit to block the AR process.24 Covering an epitaxial layer on the NCs can not only reduce the Coulomb interaction, but also modulate the overlap of electron–hole and control the conduction- and valence-band mixing as well as make the deep band states more delocalized, resulting in the depression of the AR rate9,25–27. Moreover, for the case of core/shell NCs, the local strain induced by the mismatch between the core and the shell can provide an additional driving force, it might expect to

be accompanied by interdiffusion ions at the interface to form the core/alloying/shell NCs, leading to the “smoothing” confinement potential, and thereby suppress the AR process (called “interface engineering”).28,29 Efros et al.6,30 indicated that the interface engineering on an identical one-dimensional potential can reduce the strength of the intraband transition and confinement potential involved in AR or even lead to nonblinking in nanostructures. Klimov et al.31–33 demonstrated a systematic increase in biexciton lifetimes of core/shell NCs with interface engineering compared with that of a sharp interface. Even though a lot of significant efforts have been put forward to illustrate the AR process in NCs, the influences of geometry and shape effects on the AR rate are still underdebated because of the discrepancy between experiment and theory. For example, some studies have shown a linear dependence of the Auger process on the volume and superposition principle22,34 whereas others exhibit an onmonotone curve of biexciton Auger lifetime in core/shell nanostructures.10,20 Therefore, with those discrepancies between experimental measurements and theoretical predictions, it is necessary to understand how the size and interface confinement affect the AR process and establish a systematic study to pursue the mechanism regarding interface engineering.

In order to clarify the influence of the size and interface confinement effects on the AR process, in this contribution, we develop a theoretical model to address the depression
mechanism of the AR process in the core/shell NCs in terms of the bond relaxation method and Fermi’s golden rule. Our results indicate that geometry parameters and interface confinement conditions have a great impact on the energy of surface and interface atoms, electronic structures, and wave function, which determines the AR lifetime in core/shell NCs. Furthermore, the underlying mechanism of the discrepancy among AR lifetimes on NCs with different interface confinements is also discussed.

**PRINCIPLE**

In general, owing to the high ratio of surface-to-volume (SVR) and surface defects in nanostructures, the atomic coherency will be modified, resulting in the physical–chemical properties deviated from the bulk cases.\(^{35,36}\) According to the atomic-bond-relaxation (ABR) mechanism,\(^{37–39}\) lattice strain and strain energy induced by the edge active atoms would take place, leading to the bond of the atoms being shorter and stronger and thereby allowing for modification of the cohesive energy and forcing the system into a self-equilibrium state. Generally, the cohesive energy of a specimen is expressed by

\[
E_{\text{coh}} = zE_0 + \sum_{i \leq n} N_i E_{\text{e}} + \sum_{\xi} N_{\xi} E_{\xi} + \sum_{i \leq n} \left( N_i - N_{\text{int}} \right) \frac{x_m}{z_b}.
\]

and

\[
E_b = S d_b Y(z_b)(\varepsilon(z_b))/2(1 - \nu)
\]

with

\[
\langle \varepsilon \rangle = \begin{cases} \frac{-e_m((D/2 + H)^2 - (D/2)^2)}{|f(1 - 2\nu_p) + G|} & \text{r- and } \theta- \text{ direction} \\ \frac{e_m((D/2 + H)^2 - (D/2)^2)}{v_p} & \text{z- direction} \end{cases}
\]

where \(N\) and \(N_{\text{int}}\) are, respectively, the number of total atoms in the core and atoms in the interface, \(E_b\) is the single bond energy of surface atoms, \(z_b\) and \(N_i\) are the CNs and atomic numbers of surface atoms, respectively, \(n_b\) is the surface shell number, \(E_{\text{e}}\) and \(x_m = 0.5\) are the interfacial bond formation enthalpy and the interface atoms molar ratio, respectively, \(e_i(z_b)\), \(e_i(z_b)\) are the lattice strain (effective CNs) of the core in the radial, tangential, and axial directions, respectively, and \(d_b\) denote the cross section area and bond length of an atom, respectively, \(G = v_p/((D/2 + H)^2 - (D/2)^2) + k(D/2)^2\), \(v_p = (v_r + v_\theta)/2\), the bulk Young’s modulus and Poisson’s ratio in the core (shell) are \(Y_r, Y_s\) and \(v_r, v_s\), respectively.

Furthermore, in terms of band theory,\(^{38}\) the width of the band gap \(E_g\) can be calculated by the first Fourier coefficient of the crystal potential energy, which is proportional to the mean cohesive energy per bond, \(E_b \propto E_{\text{coh}}(\varepsilon)/N\), where \(\varepsilon\) is the mean CNs, \(\gamma_c = \sigma_c d_b/D\) is the SVR ratio, where the shape factor of a spherical NC is \(\sigma = 6\), and \(c_j = 2/(1 + \exp((12 - z)/8z))\) is the bond contraction coefficient. Therefore, the band gap of NCs can be expressed by

\[
E_g = \frac{\sum_{i \leq n} \gamma_i E_i - z_b E_b}{E_b^2} + \sum_{\xi} z_{\xi} E_{\xi} + \gamma_{\text{int}} E_{\text{int}} (E_{\text{e}} - E_b)
\]

with

\[
\gamma_{\text{int}} = 4d_{\text{int}}(1 + \epsilon_i)/D \text{ and } E_b^2 \text{ are the interface-to-volume ratio and band gap of the bulk, respectively.}
\]

With the aim of addressing the relationship between interface confinement and the AR process, we consider that the AR rate from the excited state \(\psi'\) to the final state \(\psi\) can be obtained by using Fermi’s golden rule\(^{23,42}\)

\[
\frac{1}{\tau_\chi} = \frac{2\pi}{\hbar} \sum_{k, l, m} |M_k|^2 \delta(E_k - E_l) dk
\]

with

\[
M_k = \langle \psi' | V(r_i, r_j) | \psi_k \rangle
\]

\(\tau_\chi\) presents the lifetime of the AR, \(V = \varepsilon^2/(k\varphi_{11} - \tau_\varphi)\) is the electron Coulomb potential, \(\hbar = \hbar/2\pi\), \(E(E_i)\) are the energies of the initial (final) states, and \(\hbar\) and \(\kappa\) denote Planck’s constant and dielectric constant, respectively. \(M_k\) is the matrix element of the interparticle Coulomb interaction. We assume that \(M_\chi\) is independent of the projection of the total momentum because of spherical symmetry. Therefore, \(M_\chi\) is determined by the final state with \(k = 1\) and can be calculated by the standard technique of the multipole expansion of the Coulomb potential. Introducing \(x' = r_i/a\) and \(x = r_j/a\), the Auger ionization rate can be deduced as

\[
\frac{1}{\tau_\chi} = \chi^2(k_r, k_g)^2 |C_{k_r}^2 D_{k_g}^2| \left( \frac{1 - \left( \frac{e}{2\pi} \right)^2}{\Delta_r^2(1, k_r) + \Delta_g^2(1, k_g)} \right)^4
\]

where \(\chi(k_r, k_g)^{-1} = 1 - \sin(k_rD)/k_rD + 2\sin^2(k_rD/2) (E_g + 2E)/k_rD(E_g^2 + 2E)\), \(|C_{k_r} D_{k_g}|^2\) is a constant, \(k_g^2 = (E_g^2/2)^2 - E^2/\hbar^2|V|^2\), \(\Delta_r^2(1, k_r) = |E_r - (E_g/2)|^2/\hbar^2|V|^2\), \(E_g, E_f, E_{\text{e}}, E_{\text{int}}\), and \(k_g\) are the energy gap in the matrix material, the Kane matrix element, a free electron energy, the size-quantized electron ground-state energy, the energy of the state measured from the middle of the energy gap, and the ejected electron quasimomentum, respectively, and \(\Delta_r(1, k_r)\) can be obtained by spherical Bessel functions of the second kind. In the case of \(\Delta_r(1, k_r) \rightarrow 1/(k_rD/2)^2\), \(\Delta_r(1, k_r) \approx 0, \hbar^2|V|^2/(DE_{\text{g}}^2) \ll 1, \) and \(\chi \approx 1\). In addition, the matrix element can be expressed as \(M_\chi = J_{k_r, k_g}(k_f, k_rD, k_gD)\), where \(f(k_f, k_rD, k_gD\) and \(J_{k_r, k_g}(k_f)\) are a function of \((k_rD, k_gD)\) and an integral term, respectively.\(^{39}\) Therefore, \(M_\chi\) can be obtained by a product of a rapidly oscillating function and a smooth function \(f(\varphi)\). Thus, \(M_\chi = f(\varphi)\exp(\varphi k_f(k_f\varphi)) \approx f(\varphi)\exp(\varphi k_f(k_f\varphi)) \approx f(\varphi)\exp(\varphi k_f(k_f\varphi)) \approx f(\varphi)\exp(\varphi k_f(k_f\varphi)) \approx 0\) and \(M_\chi \propto f(\varphi)\exp(\varphi k_f(k_f\varphi)) - 1\). Moreover, considering the discrepancy between the core and shell, the electron–hole spatial separation and wave function will be changed in the interface of the core/shell nanostructures. Physically, the AR rate of the NC is
CdS core/shell NCs can be calculated, as shown in Figure 1. Therefore, we suggest the AR lifetime of the NC is modified by the shell thickness with exponential decay, \( \exp(\alpha/(H + \beta L)) \). Thus, the AR lifetime is

\[
\tau_A = A(E_g^m - E_g) \Gamma^{1/2}(1 - \exp(\alpha/(H + \beta L)))
\]

where \( A, \alpha, \) and \( \beta \) are the constants determined by the core, shell, and alloy layer, \( E_g^m \) is the energy gap, \( E_g \) is the quantum size energy of NCs, \( m_e \) is the effective mass of electron, \( D \) is the diameter of NCs (QDs), whereas the diameter of the core/shell and core/alloying layer/shell are, respectively, \( D + 2H \) and \( D + 2H + 2L \), where \( H \) and \( L \) denote the thickness of shell and alloy layer, respectively, as shown in the inset of Figures 1 and 4.

![Figure 1. Predicted band gap of CdSe as a function of diameter in bare CdSe NCs (black line) and total diameter, \( D + 2H \), in CdSe/CdS core/shell NCs and CdS/CdSe/CdS wurtzite core/shell and core/alloying/shell NCs as examples to evaluate the interface effect on the trion AR lifetime. The necessary parameters are listed in Table 1.](image)

**RESULTS AND DISCUSSION**

In order to clarify the AR phenomenon of the semiconductor nanostructures with different interface confinements, we take CdSe/CdS and CdS/CdSe/CdS wurtzite core/shell and core/alloying/shell NCs as examples to evaluate the interface effect on the trion AR lifetime. The necessary parameters are listed in Table 1. Note that in our case, the nanostructure is an idealized structure with identical bands and the carrier traps are ignored.

Using eq 2, the size- and shell-dependent band gap of CdSe/CdS core/shell NCs can be calculated, as shown in Figure 1.

![Figure 2. Predicted AR lifetimes as a function of shell thickness in CdSe/CdS core/shell NCs under various diameters of the core. Clearly, the AR lifetime of CdSe NCs increases as the shell thickness enhances. It can be ascribed to the weak effect of the interface on the AR process. In fact, the shell of CdS can not only reduce the Coulomb interaction and AR process, but can also suppress the quantum confinement and control the overlap between the electron and hole, leading to the slow AR rate. In addition, we also find that with an increase of shell thickness, the difference of AR lifetime under various diameters of CdSe NCs decreases. This can be simply interpreted as the influence of the interface on the band structure, and the electron–phonon interaction drops gradually. Consequently, the AR process is mainly determined by the total volume and Coulomb interaction. Moreover, in order to clarify the impact of the structures on the AR process, the shell-dependent trion AR lifetime of zinc blende CdSe/CdS core/shell NCs under \( D = 3 \) nm is exhibited as well. We find that as the bond parameters of wurtzite CdSe are comparable to those of zinc blende CdSe, the band structures, quantum size energy, and calculation method are very similar for those two structures. As a result, \( r_{\text{bex}}^{\text{wurtzite}} \) is the biexciton lifetime.](image)

**Table 1. Input Parameters for Our Calculations**

| Material | \( a \) [\( \text{nm} \)] | \( d_0 \) [\( \text{nm} \)] | \( \nu \) | \( Y_e \) [\( \text{GPa} \)] | \( E_g \) [\( \text{eV} \)] | \( E_{\text{coh}} \) [\( \text{eV} \)] |
|----------|-------------------|-----------------|-----|-----------------|-----------------|-----------------|
| CdSe     | 0.430 \( ^{54} \) | 0.263 \( ^{54} \) | 0.492 \( ^{56} \) | 42.8 \( ^{26} \) | 1.77 \( ^{57} \) | 1.32 \( ^{58} \) |
| CdS      | 0.414 \( ^{54} \) | 0.251 \( ^{54} \) | 0.483 \( ^{56} \) | 48.3 \( ^{56} \) |

\(^{a}\) \( a, d_0, \nu, Y_e, E_g, \) and \( E_{\text{coh}} \) are the lattice constant, bond length, Poisson’s ratio, Young’s modulus, band gap, and binding energy, respectively, for bulk materials.

Evidently, the band gap of NCs decreases with increasing diameter and shell thickness. These results are expected as the SVR and the influence of quantum confinement, lattice strain, and strain energy decrease with increasing NC diameter and shell thickness. Moreover, it is clear to see that when the total diameter is fixed, the band gap of bare CdSe NCs may be lower than that of core/shell NCs to a large extent. In fact, although increasing the shell thickness can reduce the quantum confinement, lattice strain, and related strain energy, the interface effect may also be induced in core/shell NCs. Smith et al.\(^ {44} \) demonstrated that the interface strain decreases with increasing shell thickness, but the strain cannot decay fully to zero, resulting in a significant amount of elastic strain. Importantly, our results are well consistent with the available results.\(^ {31,45–47} \)

Figure 2A shows the shell-dependent trion AR lifetime in CdSe/CdS core/shell NCs under various diameters of the core. Clearly, the AR lifetime of CdSe NCs increases as the shell thickness enhances. It can be ascribed to the weak effect of the interface on the AR process. In fact, the shell of CdS can not only reduce the Coulomb interaction and AR process, but can also suppress the quantum confinement and control the overlap between the electron and hole, leading to the slow AR rate. In addition, we also find that with an increase of shell thickness, the difference of AR lifetime under various diameters of CdSe NCs decreases. This can be simply interpreted as the influence of the interface on the band structure, and the electron–phonon interaction drops gradually. Consequently, the AR process is mainly determined by the total volume and Coulomb interaction. Moreover, in order to clarify the impact of the structures on the AR process, the shell-dependent trion AR lifetime of zinc blende CdSe/CdS core/shell NCs under \( D = 3 \) nm is exhibited as well. We find that as the bond parameters of wurtzite CdSe are comparable to those of zinc blende CdSe, the band structures, quantum size energy, and calculation method are very similar for those two structures. As a result, \( r_{\text{bex}}^{\text{wurtzite}} \) is the biexciton lifetime.\(^ {a}\)
band $k\cdot p$ method. Note that the nonmonotonic variation of the AR lifetime is not exhibited in our predictions because the coefficients of the matrix element are determined by the special points of the smooth function in our approach. In fact, suppression of Auger rates was also observed in theories, simulations, and experiments. References 10 and 20 show that the AR lifetime changes nonmonotonically with shell thickness and it is longer in the thick-shell core/shell NCs. References 28,31,50-52 show that the AR lifetime increases monotonically with shell thickness.

In terms of eq 5, we calculate the AR lifetimes as a function of total diameter in bare CdSe and CdSe/CdS core/shell NCs under different core diameters, as shown in Figure 3. We can see that both the curves of CdSe/CdS and bare CdSe demonstrate that the AR lifetime increases with increasing total diameter. However, if the total diameter is fixed, the AR lifetime of core/shell NCs is much lower than that of bare NCs. The discrepancy of the AR process between core/shell and bare NCs can be attributed to the interface effect. As the influence of the interface effect, the band structure as well as electron-phonon interaction and wave function in core/shell NCs would differ from that of bare NCs. Generally, the influence of the interface effect on wave function exhibits exponential decay, resulting in the AR rate of CdSe/CdS core/shell NCs being lower than that of bare CdSe when the total diameter is fixed. Importantly, our results are in good agreement with the available results. References 20. and 53 show that the AR lifetimes of bare CdSe NCs with 4-9 and 3-6 nm are, respectively, 100 to $10^4$ ps and 50 to 2 ps$10^3$ ps, which are larger than that of CdSe/CdS NCs with an identical interface. Furthermore, as plotted in Figure 3, we find that if the core diameter of CdSe is fixed, the difference between the AR lifetimes of $D = 3, 4$, and 6 nm becomes weak. In detail, the AR lifetimes of 3, 4, and 6 nm CdSe with 1.5, 1, and 0 nm CdS coating (the total diameter in each of these three samples is 6 nm) are, respectively, 378, 480, and 1792 ps, whereas each of these results is close to $10^3$ ps for that of 4, 3.5, and 2.5 nm CdS coating. This trend is expected as the influence of the interface on the electronic properties decreases with increasing shell thickness, and the electron-phonon interaction and wave function of CdSe NCs become a constant. Similarly, Vaxenburg et al.20 reported that the AR lifetimes of CdSe-CdS with 6 nm (the diameters of the core and shell thickness are, respectively, 3 and 1.5 nm) and 11 nm (the diameter and shell thickness are, respectively, 3 and 4 nm) total diameter are, respectively, about 300 and $10^4$ ps, whereas these results are $10^3$ and $10^4$ ps for the same total diameter (with the core diameter is fixed at 5 nm, but the shell thickness changed from 0.5 to 3 nm).

In order to depress the interface effect on the AR lifetime, an interface alloying layer, CdSeS, is deliberately embedded in CdSe/CdS core/shell NCs, as shown in the inset of Figure 4.

Moreover, the AR lifetime of CdSe/CdSeS/CdS core/alloying/shell NCs compared with that of CdSe/CdS core/shell and bare CdSe NCs is exhibited in Figure 4. Evidently, our results indicate that the AR rate of NCs can be greatly suppressed by the interface alloying layer because of softening of the interface effect. However, we can also find that although the alloying layer is of great benefit to reduce the interface confinement compared with the CdSe/CdS NCs, the AR lifetime of CdSe/CdSeS/CdS is still lower than that of bare CdSe if the total diameter is fixed as the alloying layer cannot completely eliminate the interface effect. For example, the AR lifetime of CdSe/CdSeS/CdS NCs with $D = 3$ nm, $L = 1$ nm, and $H = 1.5$ nm (9 nm total diameter) is 4460 ps, which is about 1.5 and 0.2 times compared to that of CdSe/CdS with $D = 3$ nm and $H = 3$ nm (9 nm total diameter) and bare CdSe with $D = 9$ nm, respectively. Furthermore, the AR process of CdSe/CdSeS/CdS NCs also demonstrates that if the diameter of CdS is fixed, the discrepancy of the AR lifetimes in $L = 0$, 1.5, and 3 nm becomes weak with increasing total diameter. Importantly, our predictions suggest that to further reduce the AR process, one may use the CdSe$_{2-x}$S$_x$ with change in the $x$ from 0 to 1 to replace CdSeS. The gradual change of the alloying layer may provide more “smoothing” confinement potential compared to CdSeS because of its continuous interface. Klimov et al.53,34 observed that the AR of the CdSe/CdS core/shell with a graded alloying interface CdSe$_{2-x}$S$_x$ (x change from 0 to 1) can be greatly suppressed compared with that of CdSe/CdS without the alloying interface. Note that in our calculation, the system is an idealized structure and the influences of the surface trap, valence band, interface softening, and surround effect are ignored so that our predictions may
not fit well to some experimental measurements, such as Bae’s results,20 but are in exceedingly good agreement with those of the simulations and the k-p method.20

## CONCLUSIONS

In summary, we proposed an analytical model to address the depression mechanism of the AR rate of core/shell NCs based on the ABR consideration and Fermi’s golden rule. Our results show that the surface and interface effects can lead to the changes of Coulomb interaction and overlap of electron–hole, thereby allowing for an efficient AR process in NCs. However, increasing the core size and shell thickness in NCs can suppress the AR process effectively because of reduction of the Coulomb interaction and modulation of overlap of the electron–hole. Moreover, our results clarify that the AR lifetime in core/shell NCs can be substantially suppressed in the AR process by covering an alloying layer in the interface that softens the interface confinement on the wave function. However, as the alloying layer cannot completely eliminate the interface effect, the AR lifetime of the core/alloying/shell is still lower than that of bare NCs if the total diameter is fixed. These results indicate that the suppression of the AR process can be achieved by not only increasing the size of the nanostructures that reduces the Coulomb interaction but also softening the interface confinement of nanostructures that modulates the quantum size energy and wave function.

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The authors declare no competing financial interest.

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