Effect of Zero- to One-Dimensional Transformation on Multiparticle Auger Recombination in Semiconductor Quantum Rods

H. Htoon, J. A. Hollingsworth, R. Dickerson, and V. I. Klimov
Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
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We study the effect of the zero- to one-dimensional (1D) transformation on multiparticle Auger recombination using a series of elongated semiconductor nanocrystals (quantum rods). We observe a transition from the three- to two-particle recombination process as the nanocrystal aspect ratio is increased. This transition indicates that in the 1D confinement limit, Auger decay is dominated by Coulomb interactions between 1D excitons that recombine in a bimolecular fashion. One consequence of this effect is strongly reduced decay rates of higher multiparticle states that lead to increased optical-gain lifetimes and efficient light amplification due to involvement of excited electronic states.

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Auger processes play an important role in many types of materials systems from atoms and molecules to organic and inorganic semiconductors [1]. These processes are based on long-range Coulomb interactions, and in semiconductor materials, they can open a new nonradiative recombination channel (Auger recombination) in which the electron-hole (*e-h*) recombination energy is transferred to a third particle (an electron or a hole) that is reexcited to a higher-energy state [2]. Because of the restrictions imposed by energy and momentum conservation, such multiparticle Auger recombination is relatively inefficient in bulk semiconductors. However, Auger decay is greatly enhanced in zero-dimensional (0D) quantum dots (QDs), for which the breakdown in translation symmetry leads to the relaxation in momentum conservation [3].

In addition to being of fundamental interest, studies of multiparticle Auger effects are of great practical importance because these effects strongly impact both optical-gain and resonant optical nonlinearities [4]. In particular, in the case of "ultrasmall" (sub-10 nm) semiconductor nanocrystals (NCs) ultrafast Auger recombination of multi-*e-h* pair states severely limits optical-gain lifetimes [5], which represents a major complication for achieving the lasing regime. Therefore, the development of methods for suppressing the Auger decay is an important step towards practical lasing applications of NCs.

In this Letter, we explore NC shape control as a means for suppressing Auger recombination rates while preserving the ability to independently tune the confinement energies and, hence, the emission wavelengths. Specifically, we study the effect of a gradual change in the degree of carrier confinement on Auger recombination as the confinement regime is tuned (by elongating a NC) from 0D (QDs) to 1D (quantum wires). The 0D to 1D transition is expected to affect Auger processes via several competing trends. On the one hand, the kinematic restrictions due to restoration of momentum conservation along one direction should reduce the efficiency of Auger effects. On the other hand, the opposite trend is anticipated due to the concurrent transition from a discrete to a quasicontinuous density of energy states, which simplifies meeting energy-conservation requirements.

A change in the relative strength of the *e-h* coupling should also strongly influence Auger recombination. In sub-10 nm QDs, the confinement energies are significantly greater than the *e-h* "excitonic" interactions and, therefore, electrons and holes can be treated as independent, *uncorrelated* particles [6]. In this case, Auger recombination can be described in terms of a *cubic,* three-particle process, as was recently observed experimentally for CdSe NCs [7]. Conversely, as the NC aspect ratio is increased, the confinement energy in the direction of the long axis can become comparable with or smaller than the *e-h* interaction energy, leading to the formation of 1D excitons. In this case, the Auger recombination can occur as a two-particle, *bimolecular* process in which the recombination energy of one exciton is transferred to the other exciton.

To study the effect of the 0D to 1D transformation on Auger recombination, we use a series of elongated CdSe NCs (quantum rods) with controlled aspect ratios. We observe that the Auger recombination changes from a three- to a two-particle process as the rod aspect ratio is increased, approaching the 1D confinement limit. Comparison of rods and dots of the same volume indicates that rods show a faster Auger decay, which likely results from a larger surface area that dominates the matrix element of the Auger transitions. On the other hand, because of the weak dependence of the rod emission energy on its length, it is possible to tailor the rod dimensions (width and length) in a way to achieve effective suppression of Auger recombination for a specific emission wavelength. Such "engineering" of Auger rates allows us to significantly increase optical-gain lifetimes and to extend the gain region into the range of

high-energy transitions involving excited electronic states.

We fabricated highly monodisperse spherical and elongated NCs [see transmission electron microscopy (TEM) images in Figs. 1(a) and 1(b)] using organometallic synthetic procedures adapted from Refs. [8,9]. Here, we concentrate on five rod samples that have approximately the same radius (r) of 2.3 nm and different lengths (l) of 22 (sample No. 1), 29 (No. 2), 36 (No. 3), 40 (No. 4), and 44 nm (No. 5). These samples have ~5%–7% and ~10% standard deviations for radii and lengths, respectively. The data collected for rod samples are compared with that of a quantum-wire-like structure ($r = 0.7$ nm, $l =$ 70 nm) and several samples of spherical NCs (QDs) with radii from 2 to 4 nm.

To study ultrafast dynamics of multiparticle states, we apply a femtosecond (fs), transient absorption (TA) experiment in which the transmission of the sample excited with 100 fs, 3.1 eV pump pulses is monitored in both spectral and time domains using variably delayed, broadband pulses of a fs, white-light continuum. As a measure of the average number of e-h pairs per NC, $\langle N \rangle$, we use a pump induced absorption change, $\Delta\alpha$, at the position of the lowest 1S absorption resonance. To calibrate this change in terms of the average population of NCs, we perform pump-dependent absorption saturation measurements [inset of Fig. 1(c)] [7]. Since for fs excitation initial NC population, $\langle N_0 \rangle$, is proportional to a pump fluence, we can use the saturation curves for translating $\Delta\alpha$ dynamics into the dynamics of NC average populations.

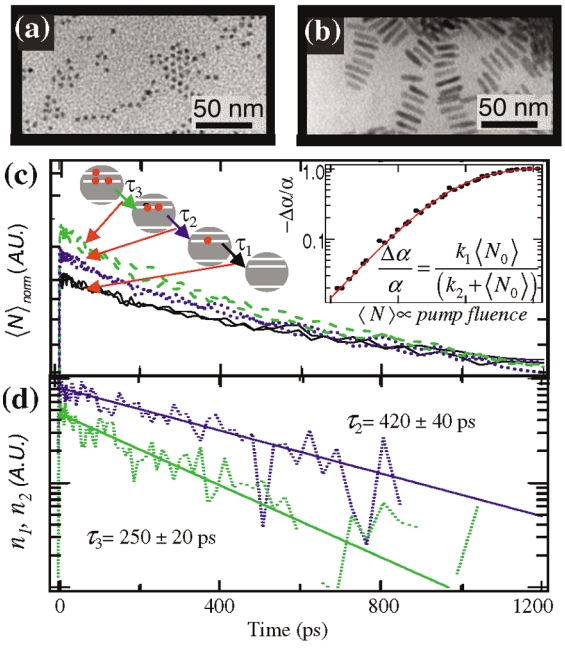

FIG. 1 (color). TEM images of typical QD (a) and quantum rod (b) samples. (c) Population dynamics for rod sample No. 5 measured at progressively higher excitation densities (from 3 to 50 μJ cm^{-2} per pulse). Inset: Pump-dependent absorption saturation at the position of the lowest 1S transition (symbols) fit to the formula shown in the figure. (d) The exponential dynamics of two (blue) and three (green) e-h pair states extracted from traces in (c).

Figure 1(c) shows an example of population decay curves measured for rod sample No. 5 (hexane solution) at different pump fluences. The traces are normalized to match their tails at long times after excitation when the decay is dominated by dynamics of singly excited NCs, independent of the initial carrier densities. The fast initial TA relaxation is strongly pump dependent and is characterized by time constants that are significantly shorter than those observed for the radiative decay in both dot [10] and rod samples, suggesting that it is not due to radiative recombination. Further, since the decay becomes more rapid with increasing pump level, it cannot be attributed to fast carrier surface trapping. The latter mechanism would lead to the opposite trend due to saturation of surface traps. Based on these considerations, we conclude that the initial, pump-dependent relaxation results from multiparticle Auger recombination.

Interestingly, although the pump fluence is varied in regular increments, normalized decay curves clearly cluster into three isolated groups. This effect ("quantization" of multiparticle decay rates) was observed previously by us for spherical NCs [7] and is due to the fact that the populations of individual NCs change in discrete steps from 0 to 1, 2, etc., e-h pairs, and each of these N e-h pair states is characterized by a specific (*discrete*) decay constant.

According to estimated carrier densities [11], the lowest group of curves in Fig. 1(c) can be assigned to the decay of singly excited rods ($\langle N_0 \rangle < 1$). The next two groups of traces correspond to the situation for which a significant number of rods in the sample become excited first with two (blue curves) and then with three (green curves) e-h pairs. Auger decay of two and three e-h pair states leads to fast initial decay components observed in the blue and green traces, respectively. Single exponential dynamics of these states [Fig. 1(d)] can be extracted from $\langle N(t) \rangle$ dynamics by using a simple subtraction procedure described in Ref. [7].

To experimentally detect the effect of the 0D to 1D transition on Auger rates, we compare the decay times of two (τ_2) and three (τ_3) e-h pair states for NCs with different aspect ratios. As discussed earlier, in strongly confined QDs, Auger recombination occurs due to the interactions of *three* uncorrelated charge carriers and can be described by a cubic rate equation: $dn/dt = -C_3 n^3$, where n is the carrier density (for NCs, $n = N/V_0$, V_0 is the NC volume) and C_3 is the Auger constant. Introducing a lifetime of the N e-h pair state as $\tau_N = -N(dN/dt)^{-1}$, we can obtain $\tau_N = (C_3 N^2/V_0^2)^{-1}$. The latter expression indicates that for cubic decay, the ratio of τ_2 to τ_3 is 2.25. Similar reasoning suggests that for quadratic, bimolecular recombination of excitons

(expected in the 1D regime) $\tau_N = (C_2 N/V_0)^{-1}$ and hence $\tau_2/\tau_3 = 1.5$ (C_2 is the bimolecular decay constant).

In Fig. 2(a), we plot the ratio of the measured τ_2 and τ_3 time constants as a function of the NC aspect ratio (ε). For quantum dots ($\varepsilon = 1$), this ratio is 2.18; i.e., it is very close to the one expected for a cubic decay process. As ε is increased, the ratio τ_2/τ_3 gradually approaches 1.5, which is the limit expected for the quadratic recombination regime. This result provides a strong indication that in sufficiently long rods ($\varepsilon > 8$) e-h pairs are bound into 1D excitons and these excitons recombine in a bimolecular fashion.

The transition from cubic to bimolecular recombination is also clearly manifested in the case of high excitation densities ($\langle N \rangle \gg 1$) for which "discrete" lifetimes of individual multiparticle states cannot be extracted from the experimental data. To analyze this "continuous" regime, we compare the population dynamics measured at high pump intensities with solutions of the rate equations for cubic and quadratic decays, treating N as a continuous variable. In the regime of high excitation densities, the initial carrier dynamics are dominated by the nonlinear Auger process, which allows us to obtain the following solution of the rate equations: $[N_0/N(t)]^{\beta-1} - 1 = [C_\beta N_0^{\beta-1}/(\beta - 1)]t$, where $\beta = 2$ or 3 for bimolecular or cubic Auger processes, respectively. We calculate the left hand side of the above expression for both values of β using high-excitation-intensity population dynamics, $\langle N(t) \rangle$ (measured at $\langle N_0 \rangle > 10$), and compare the obtained traces with the linear time dependence. Figure 2 shows the results of this comparison for $\beta = 3$ (b) and 2 (c) for samples of spherical NCs (QDs), short quantum rods (sample No. 1), and long quantum-wire-like NCs. For both QDs and short rods, the traces obtained for $\beta = 3$ show a linear time dependence, while the $\beta = 2$ data clearly deviate from it. This result indicates that the carrier decay occurs via a cubic recombination process in both of these samples, which is consistent with conclusions based on the analysis of the "quantized" recombination regime. On the other hand, the data points for the quantum-wire sample show a linear time dependence for $\beta = 2$ and nonlinear dependence for $\beta = 3$, indicating the quadratic, bimolecular decay channel.

Our previous study of QDs [7] shows that Auger decay times scale linearly with NC volume. If we compare the Auger decay times in rods of the same width but with different lengths, we observe the same type of linear dependence [Fig. 3(a)]. However, the two-e-h pair lifetime is shorter in rods than in dots of the same volume. This result can be rationalized by analyzing the matrix element of the Auger transition. Since the Auger electron/hole in the final state has a very large momentum, its wave function oscillates very rapidly which strongly decreases the matrix element for the interior of a NC. On the other

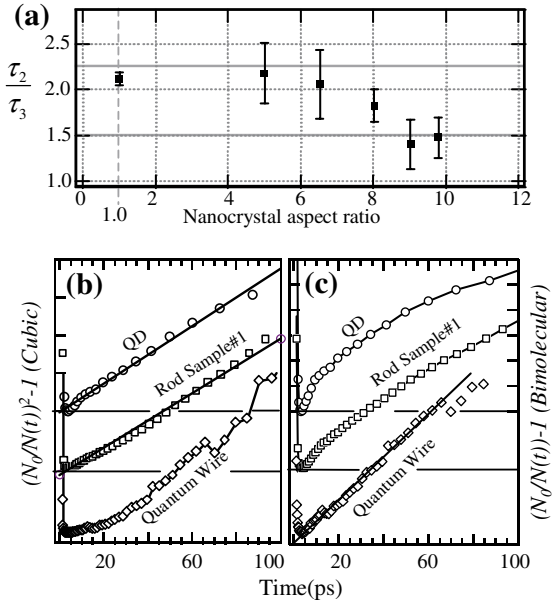

FIG. 2 (color online). (a) The ratio of the measured τ_2 and τ_3 decay constants as a function of the NC aspect ratio. The plot of $([N_0/N(t)]^2 - 1)$ (b) and $([N_0/N(t)] - 1)$ (c) vs time for QDs ($r = 2.3$ nm), short quantum rods (sample No. 1), and a quantum-wire-like sample.

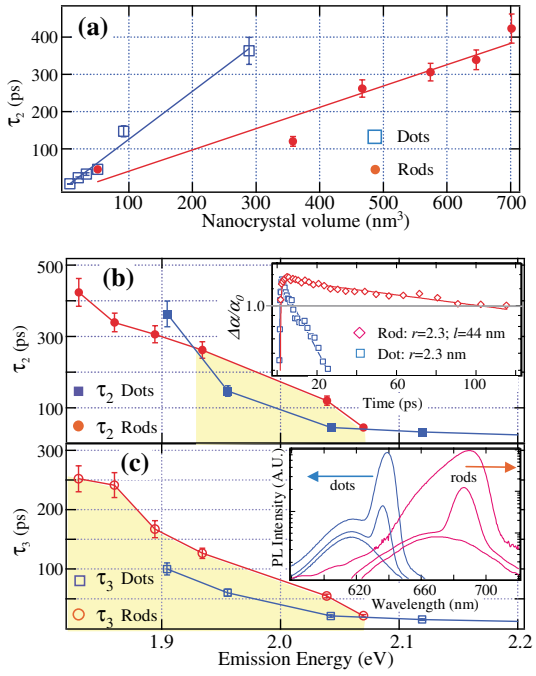

FIG. 3 (color). (a) The two-e-h pair decay time as a function of the NC volume for dot and rod samples. The time constants τ_2 (b) and τ_3 (c) for rods and dots plotted as a function of the emission energy. Insets: comparison of optical gain dynamics (b) and ASE spectra (c) for dot and rod samples. The ASE spectra are taken at progressively higher pump fluences from 0.4 to 4.0 mJ cm^{-2} and from 0.05 to 2.0 mJ cm^{-2} for dot and rod samples, respectively.

hand, because of the abrupt change in the confinement potential at the NC surface, the ground state wave function has high-momentum Fourier components in the near surface area, which provides a dominant contribution to the Auger transition matrix element [12]. The elongated rods, which have a larger surface area than the dots of the same volume, could therefore have shorter Auger times.

Although Auger decay is more efficient in rods than in dots of the same volume, the weak dependence of the confinement energy on the rod length [13], combined with the linear scaling of the decay time with the rod volume, can be used to suppress Auger recombination for a specific emission wavelength. In Fig. 3, we plot the two (b) and three (c) *e-h* pair Auger decay times as a function of the emission energy for dot and rod samples. These plots indicate that for this particular set of rods ($R = 2.3$ nm), there is a spectral window (1.93–2.14 eV) in which rods show a slower two-*e-h* pair Auger decay than dots. On the other hand, the three-pair decay is slower for rods over the entire spectral range studied, which is partially because of a slower scaling of the recombination time with N ($1/N$ in rods vs $1/N^2$ in dots). The reduced Auger decay rates lead to the increased optical-gain lifetime (τ_g) [14,15]. The direct measurements of gain dynamics [inset of Fig. 3(b)] indicate that for rod sample No. 5, τ_g is $\sim$100 ps, while it is less than 10 ps for dots emitting in the same wavelength range [16]. The reduced rates of Auger recombination also imply that elongated particles can produce lasing at lower loading factors [5] than dots, which was recently proven by observations of quantum rod lasing in solutions with relatively low NC concentrations [17].

The extended lifetimes of states with $N > 2$ in long rods allow realization of optical amplification using the transitions that involve high-energy, excited electronic states. Such an amplification regime is difficult to achieve in dots because of a rapid shortening of Auger times for states with $N > 2$ ($\tau_N \propto N^2$). In the inset of Fig. 3(c), we compare the spectra of amplified spontaneous emission (ASE) for dot and rod samples. In QDs, an ASE band (a sharp feature at $\sim$640 nm) does not show significant spectral changes as the pump fluence is increased. However, the ASE band for rods shows a pronounced broadening towards shorter wavelengths at higher pump fluences, indicating a contribution from transitions involving excited electronic states. The participation of higher-energy transitions in optical amplification leads to the extension of the usable gain spectral range that can potentially allow a wide-range tunability of the lasing color using the same sample.

In conclusion, we have used a series of CdSe elongated NCs (quantum rods) to study the effect of the 0D to 1D transition on nonradiative Auger recombination. We observe a transition from cubic to quadratic decay as the rod aspect ratio is increased above $\sim$8. This observation indicates that in long quasi-1D rods, Auger decay occurs as a result of bimolecular, exciton-exciton interactions. We also study the effect of the sample dimensionality on its optical-gain performance. We observe that the use of elongated NCs allows one to reduce nonradiative carrier losses arising from Auger recombination compared to spherical NC emitting at the same wavelength. This reduction leads to an increased optical-gain lifetime and an extended gain spectral range.

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