

Multiexciton Annihilation and Dissociation in Quantum Confined Semiconductor Nanocrystals

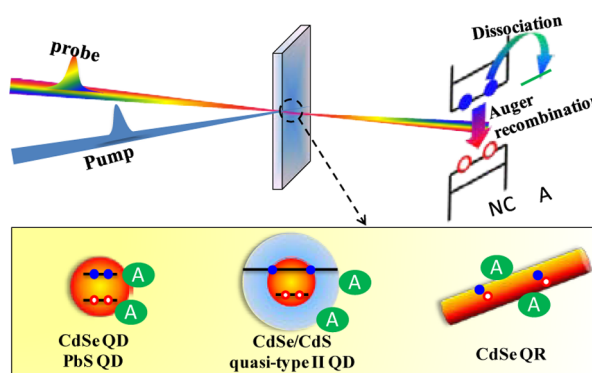
HAIMING ZHU, YE YANG, AND TIANQUAN LIAN*
*Department of Chemistry, Emory University, Atlanta, Georgia 30322,
United States*

RECEIVED ON JULY 10, 2012

CONSPECTUS

Recent reports of multiexciton generation (MEG), a process by which one absorbed photon generates multiple excitons, in lead chalcogenide nanocrystals (NCs) have intensified research interest in using this phenomenon to improve the efficiency of solar energy conversion. Practical implementation of MEG processes in solar cells and solar-to-fuel conversion devices requires the development of materials with higher MEG efficiencies and lower excitation thresholds than are currently available, as well as schemes for efficient multiexciton extraction before the ultrafast exciton-exciton annihilation occurs.

This Account focuses on the extraction of multiexcitons by interfacial electron transfer in model NC-molecular acceptor complexes. We provide an overview of multiexciton annihilation and multiexciton dissociation (MED) processes in NC-acceptor complexes of (i) CdSe quantum dots (QDs), (ii) CdSe/CdS quasi-type II core/shell QDs, (iii) CdSe quantum confined nanorods (QRs), and (iv) PbS QDs. We show that ultrafast electron transfer to adsorbed molecular acceptors can efficiently dissociate multiexcitons generated by absorption of multiple photons in (i), (ii), and (iii). Compared to core-only CdSe QDs, the electron hole distributions in CdSe/CdS quasi-type II QDs and CdSe QRs significantly improve their MED efficiencies by simultaneously retarding Auger recombination and facilitating interfacial electron transfer. Finally, in PbS-methylene blue (MB⁺) complexes, we show that the presence of electron acceptors does not affect the MEG efficiency and electron transfer to MB⁺ efficiently dissociates the multiple excitons generated in PbS QDs. Our findings demonstrate that ultrafast interfacial charge transfer can be an efficient approach for extracting multiexcitons, and wavefunction engineering in quantum confined NCs can further improve MED efficiency.



I. Introduction

The size dependent electronic and optical properties of quantum confined spherical semiconductor nanocrystals (NCs), that is, quantum dots (QDs), have been extensively studied in the past decades.^{1–3} In recent years, nonspherical semiconductor NCs and nanoheterostructures consisting of two or more component materials in desired morphology have also been developed.^{4–6} Through the choice of constituent materials and by varying the degree of quantum confinement (via size and shape), their photophysical properties, including energy levels, emission quantum yield, and carrier dynamics, can be controlled, offering exciting opportunities for advanced applications.^{4–8}

A unique property of semiconductor NCs is the generation and accommodation of multiple excitons (electron and

hole, e–h, pairs bound by Coulomb interaction) per particle by either optical excitation or electric pumping. These multiple excitons can be converted to multiple emitted photons or separated external charges, with potential applications in advanced nanoscale optoelectronic devices ranging from high power light emitting diodes,^{9,10} low-threshold lasing media,^{11–13} and multiphoton sources¹⁴ to highly sensitive photodetectors and efficient photovoltaic/catalytic cells.^{15–17} Recent reports of multiexciton generation (MEG) by one absorbed photon have intensified the interest of using semiconductor NCs as light harvesting and charge separating components for delivering multiple carriers in photocatalytic and photovoltaic devices, despite its modest efficiency.^{18–22} However, Auger recombination, wherein an electron–hole pair recombines by transferring

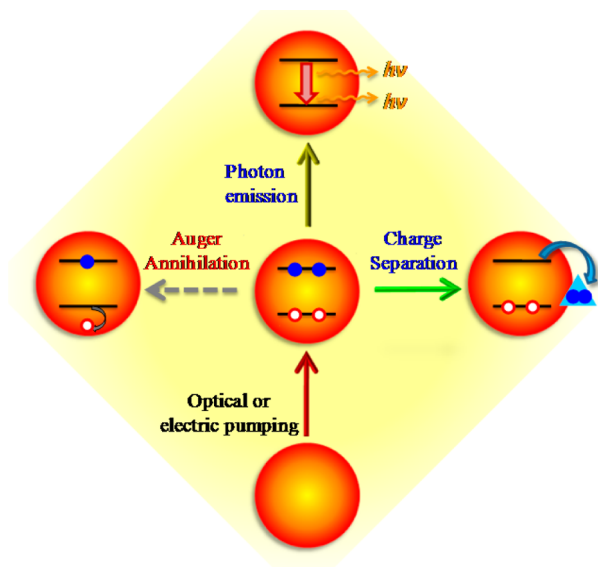


FIGURE 1. Schematic depiction of multiexciton generation, annihilation, and conversion to emitted photons or separated charges. The competition between Auger annihilation and photoemission or charge separation determines the multiexciton conversion efficiencies.

its energy to another particle (carrier or exciton), significantly shortens the multiexciton lifetime.^{23,24} Therefore, the development and improvement of advanced NC based optoelectronic devices requires the understanding of multiexciton annihilation (MEA) dynamics in NCs and schemes for their efficient conversion to emitted photons (for emission applications) or separated external charges (for photovoltaic/catalytic applications) in competition with their fast Auger recombination (as shown in Figure 1). One possible scheme for the utilization of short-lived multiexcitons in solar energy conversion is the ultrafast exciton dissociation by interfacial charge transfer from NCs to acceptors.^{21,25–28}

In this Account, we summarize our recent studies of MEA and multiexciton dissociation (MED) dynamics in quantum confined semiconductor NCs by transient absorption (TA) spectroscopy. We start with a general description of Auger recombination processes in NCs. This is followed by the MEA and MED studies in CdSe QDs, CdSe/CdS quasi-type II core/shell QDs, and CdSe quantum rods (QRs), in which multiexcitons are generated by the absorption of multiple photons. By comparing to the well-studied CdSe QDs, we discuss how the band alignment in CdSe/CdS quasi-type II QDs and one-dimensional excitonic structure in CdSe QRs slow down MEA rate and maintain ultrafast electron transfer (ET) to the electron acceptor (methylviologen, MV^{2+}), leading to more efficient MED. Finally, using PbS QD–methylene blue (MB^+) as a model QD–acceptor system, we examine whether the presence of electron acceptor affects the MEG

efficiency and whether multiexcitons generated through MEG can be efficiently dissociated.

II. Quantifying MEA and MED Dynamics in Semiconductor NCs

In bulk semiconductors, assuming equivalent electron and hole density n , Auger recombination is a three-particle collision process and can be generally described by $dn/dt = -C_A n^3$, where C_A is the bulk Auger coefficient.²⁹ However, for semiconductor NCs, because of the quantized number of excitons, N , in a given NC, Auger recombination occurs sequentially ($N \rightarrow N - 1 \dots \rightarrow 2 \rightarrow 1$) with a quantized Auger rate constant, k_N , for the decay from N to $N - 1$ exciton states (Figure 2A).^{23,30} The average multiexciton decay kinetics in a NC ensemble is given by the distribution of exciton numbers, $P(N,t)$, whose temporal evolution is governed by a set of coupled rate equations, $dP(N,t)/dt = k_{N+1}P(N+1,t) - k_N P(N,t)$.^{14,27,28,30,31} These equations can be solved to reveal the multiexciton decay kinetics if the initial exciton distribution $P(N,0)$ and the Auger decay rate constants k_N are known.

The initial exciton distribution can be assumed to obey the Poisson distribution $P(N,0) = w^N e^{-w}/N!$, where w is the average number of excitons per NC. This assumption, which implies that the photon absorption process of a NC is random and unaffected by its exciton population, is valid as long as the excitation transition is not saturated.²⁸ Although in principle w can be determined using the relationship, $w = j\sigma$, this method is not reliable because j , the photon flux in the probe region, and σ , the NC absorption cross section at the excitation wavelength, are often not accurately determined. Instead, it can be more reliably obtained by fitting the excitation power dependence of NC transient signals.^{24,26–28}

As shown in Figure 2B, statistically, the Auger decay rate constant k_N scales with the number of excitons according to (i) $k_N \approx C_3/2N^2(N-1)$, in the independent carrier model, or (ii) $k_N \approx C_2/2N(N-1)$, in the excitonic model.^{23,30–33} In model (i), the electrons and holes are independent carriers and Auger recombination involves three-carrier collisions. C_3 , the three particle Auger recombination rate constant, is related to the biexciton state lifetime ($C_3 = 1/2\tau_2$). In model (ii), the electrons and holes are bound as excitons and Auger recombination occurs through exciton–exciton two-particle collision with an Auger recombination rate constant $C_2 = 1/\tau_2$. By fitting the excitation intensity dependent exciton decay kinetics to these models, one can quantitatively determine the exciton distribution under any excitation power and reveal the Auger recombination mechanisms.^{27,28,30,31,34}

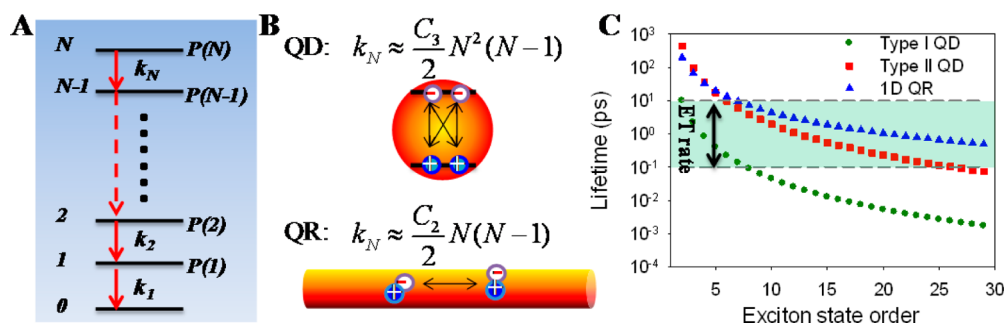


FIGURE 2. (A) Sequential multiexciton Auger recombination process from $N \rightarrow N-1 \rightarrow \dots \rightarrow 2 \rightarrow 1$. k_N is the Auger decay rate constant from an N -exciton state to $N-1$ state and $P(N)$ is the probability of having NCs with N excitons. (B) Schemes showing independent carrier (upper) and excitonic (lower) Auger recombination models and their rate scaling law. (C) The lifetime of N -exciton states ($N = 1-30$) of CdSe QDs,²⁵ quasi-type II CdSe/CdS QDs,²⁸ and CdSe QRs.²⁷ Typical ET times from NCs to molecular adsorbates (100 fs to 10 ps) are indicated in the shaded area, suggesting that more efficient multiple exciton dissociation can be achieved in CdSe QRs and CdSe/CdS core/shell QDs than in CdSe QDs. Adapted with permission from ref 27. Copyright 2012 American Chemical Society.

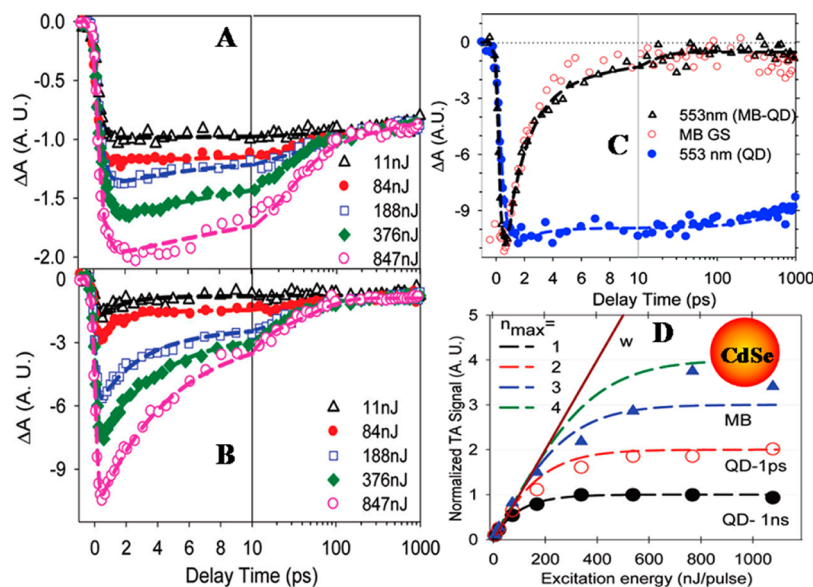


FIGURE 3. Normalized 1S (A) and 1P (B) bleach recovery kinetics of CdSe QDs under indicated excitation intensities (dashed lines are multiexponential fitted curves). (C) Comparison of 1S exciton bleach recovery kinetics in QDs (blue) and 1S exciton bleach recovery kinetics (black) and MB^+ ground state bleach formation kinetics (red) in QD- MB^+ complexes. (D) Normalized QD 1S exciton bleach amplitudes at 1 ps (red open circles) and 1 ns (black filled circles) and peak MB^+ ground state bleach amplitude (blue triangles) in CdSe- MB^+ complexes as a function of excitation pulse energy. Also shown are the average number of excitons per QD (brown solid line) and fit of normalized TA signal with different maximum number of dissociated excitons. Adapted with permission from ref 26. Copyright 2010 American Chemical Society.

Along with the transient signal of reduced molecular adsorbate, the number of dissociated excitons can also be quantitatively determined, enabling the study of MED in various NC-adsorbate complexes.²⁵⁻²⁸

III. MEA and MED in CdSe QDs

We first examine MED from CdSe QDs (generated by the absorption of multiple photons) because of previous report of MEA^{23,33,34} and ultrafast ET to adsorbed acceptors.^{35,36} Figure 3A shows the 1S exciton bleach recovery kinetics of CdSe QDs (first exciton peak at ~ 553 nm) under different

excitation intensities. These TA kinetics, which have been normalized at 1 ns, are independent of the intensities after ~ 200 ps, reflecting the completion of MEA and the presence of only the long-lived single exciton state. Before ~ 200 ps, the kinetics show a fast decay component whose amplitude increases at higher excitation intensities. The 1S exciton bleach in CdSe QDs have been shown to result from the state filling of the 2-fold degenerate 1S electron level,²⁴ and QDs with two or more excitons contribute to the same 1S exciton bleach amplitude. Therefore, the fast bleach recovery component (~ 50 ps) reflects the decay from biexciton to

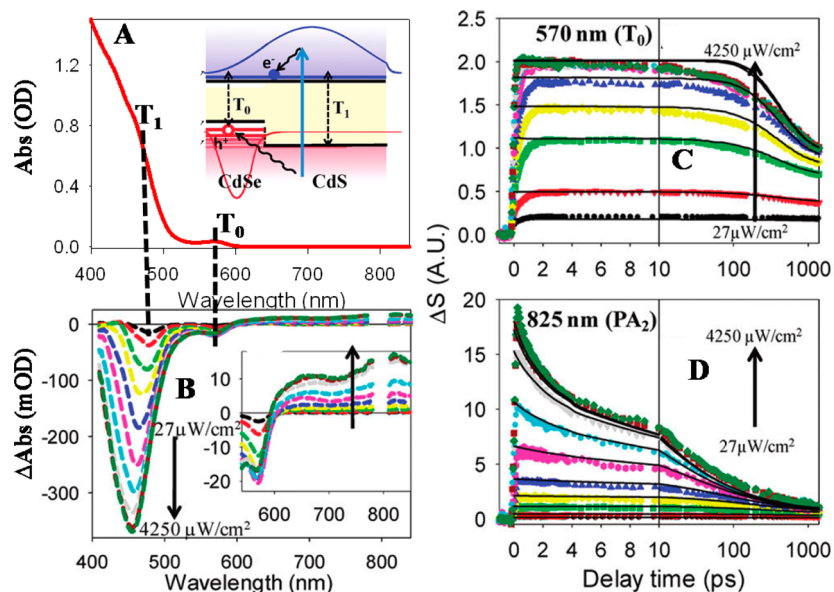


FIGURE 4. MEA in quasi-type II CdSe/CdS core/shell QDs. (A) UV-vis absorption spectrum. Inset: schematic energy level diagram, lowest energy electron and hole wave functions and T_0 and T_1 optical transitions. (B) TA spectra at 0.3 ps after 400 nm excitation at different intensities. Inset: expanded view of the TA spectra between 500 and 840 nm. (C and D) Normalized transient kinetics (symbols) at T_0 (C) and PA (D) bands and fits (solid line) to independent carrier Auger recombination model. Definition of the ΔS and description of the fitting model can be found in ref 28. Adapted with permission from ref 28. Copyright 2012 American Chemical Society.

single exciton states.²⁶ This biexciton state lifetime is consistent with reported values for CdSe QDs, which has been shown to be size dependent and increases nearly linearly with the QD volume.^{23,33}

Although the 2-fold degenerate 1S exciton bleach signal is not sensitive to the presence of higher ($N > 2$) exciton states (as shown in Figure 3A and D), Klimov and co-workers have reported the multiexciton state ($N = 2-4$) lifetimes by successive subtraction of 1S exciton kinetics under different excitation intensities.^{22,23,30} In principle, in higher order exciton states, the 1P electron level should be filled, leading to the bleach of the 1P exciton transition. Indeed, additional fast decay components were observed in the 1P bleach recovery kinetics, as shown in Figure 3B, from which an averaged lifetime of $N (>2)$ exciton states was estimated to be 2.6–4.5 ps.²⁶ A more detailed analysis was hindered by the presence of other TA signals, such as the exciton–exciton interaction induced peak shift. Kanemitsu and co-workers reported a photoinduced absorption (PA) signal in the near IR region that is proportional to excitation intensity. The analysis of the excitation intensities dependence of the PA kinetics shows that the Auger recombination process in CdSe QDs can be well described by the independent carrier model (Figure 2B).³⁴

In CdSe QD–methylene blue (MB^+) complexes, an ultrafast ET (with a time constant of ~ 2 ps) from singly excited

QDs to adsorbed MB^+ molecules was observed (Figure 3C).²⁶ This ET rate is much faster than the single (~ 15 ns) and biexciton (~ 50 ps) state lifetimes and comparable with the averaged higher order ($N > 2$) exciton state lifetime (~ 3 ps) of the QD, suggesting the possibility of dissociating multiexcitons by interfacial ET. To monitor the MED efficiency, the intensity dependence of the QD 1S exciton bleach signal in QDs and the MB^+ bleach amplitude in QD– MB^+ complexes were compared. The initial exciton distributions are the same in free QDs and QD– MB^+ complexes under the same excitation intensity and can be determined by analyzing the 1S exciton bleach amplitude in free QDs (Figure 3D).²⁶ Fitting of the intensity dependent MB^+ ground state bleach amplitudes to a model that assumes a maximum number of dissociated excitons per QD– MB^+ complex reveals that up to three excitons can be dissociated per complex (Figure 3D).²⁶ A similar study of CdSe–methylviologen (MV^{2+}) complexes reported the dissociation of as many as four excitons per QD.²⁵

These proof-of-principle studies demonstrate that ultrafast ET from QDs can compete with MEA. However, the MED efficiency is determined by the competition of ET and Auger recombination. The ultrafast ET rates to the model electron acceptors used in these studies may not be generally attainable in QD–catalyst complexes. Therefore, it is essential to explore approaches to optimize the NC structures and

compositions to simultaneously slow down Auger recombination and facilitate charge transfer. Next, we discuss two ways of optimizing MED efficiency using quasi-type II CdSe/CdS core/shell QDs and CdSe QRs.

IV. MEA and MED in CdSe/CdS Quasi-Type II Core/Shell QDs: The Effect of Band Alignment

Auger recombination rate, which depends on electron–hole overlap, can be reduced in (quasi-) type II core/shell QDs, such as CdTe/CdSe, CdSe/CdS, due to the spatial separation of the electron and hole wave functions,^{37,38} and interfacial alloy formation.^{38,39} The e–h spatial separation also has important effect on their charge separation properties. Compared to core-only QDs, the localization of electrons in the shell in type II CdTe/CdSe core/shell QDs and the extension of electron wave function into the shell in quasi-type II CdSe/CdS core/shell QDs can facilitate ultrafast ET to adsorbed acceptors and slow down the subsequent charge recombination.^{28,40} The combination of prolonged multiexciton lifetime and fast ET rate suggests that MED efficiency can be enhanced in (quasi-) type II NCs.²⁸

As shown in 4A and B, both steady state and transient absorption spectra of CdSe/CdS quasi-type II QDs (1.2 nm core radius and 2.2 nm shell thickness) show two distinct bands, corresponding to CdSe core based lowest energy transition (T_0) and CdS shell based transition (T_1), respectively. The TA spectra of CdSe/CdS QDs (Figure 4B) show three spectral signatures: bleaches at T_0 and T_1 transitions and a broad PA signature at >650 nm. With increasing exciton numbers, the T_0 bleach band gradually increases and saturates at two excitons per QD, which can be attributed to the state filling of the 2-fold degenerate 1S electron level, similar to those in CdSe QDs. The T_1 bleach shows blue shifting of peak position to higher energy and broadening of bandwidth, which can be qualitatively understood by dynamic Burstein–Moss shift and suggests a quasi-continuum nature of the T_1 transition.²⁸ The broad PA signal can be assigned to hole-induced absorption through selective charge removal experiments.²⁸ The PA signal, whose amplitude is shown to be proportional to exciton numbers in QDs, provides a convenient probe to follow the MEA process. By simultaneous fitting of T_0 and PA kinetics (Figure 4C and D), a biexciton lifetime of ~ 440 ps was obtained, which is much longer than that of CdSe QDs of similar confinement energy. This fitting also shows that MEA in CdSe/CdS quasi-type II core/shell QDs can be well described by an independent carrier model (Figure 2B upper).²⁸ Compared with CdSe QDs, CdSe/CdS quasi-type II QDs maintain the same Auger rate

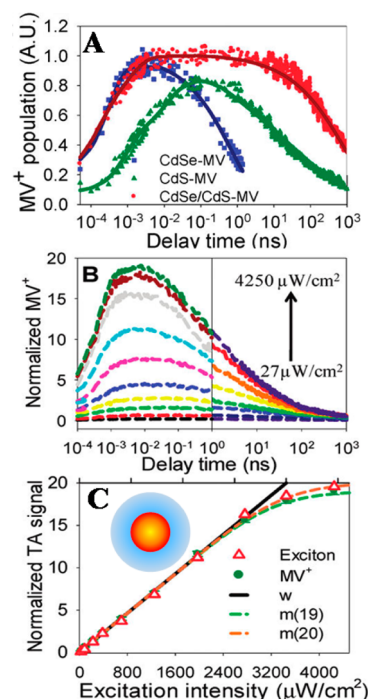


FIGURE 5. Single and multiple exciton dissociation in CdSe/CdS-MV²⁺ complexes. (A) Comparison of normalized MV^{+•} radical formation and decay kinetics in QD–MV²⁺ complexes of CdSe, CdS, and CdSe/CdS after 400 nm excitation in single exciton conditions. (B) Kinetics of normalized MV^{+•} radical TA signal in QD–MV²⁺ complexes at different excitation intensities. (C) Normalized MV^{+•} radical signals in QD–MV²⁺ complexes (green filled circles), normalized initial PA amplitudes (red open triangles), and fits of average number of excitons (black lines) as a function of excitation intensities. Adapted with permission from ref 28. Copyright 2012 American Chemical Society.

scaling law but slow down the MEA rates by reducing the Auger rate constant C_3 .

As shown in Figure 5A, the charge separation process in CdSe/CdS–MV²⁺ complexes is still as fast (~ 180 fs) as that in CdSe QDs but the charge recombination (back electron transfer from MV^{+•} to hole left in QDs) is more than 3 orders of magnitude slower (~ 0.4 μ s).²⁸ This can be attributed to the delocalized electron over the core and shell and core-confined hole in the quasi-type II structure, which maintains strong electronic coupling for ET to MV²⁺ and reduces the coupling for the subsequent charge recombination. With increasing excitation intensity, the normalized MV^{+•} radical signal, which represents the average number of MV^{+•} radicals per QD, closely follows the initially generated exciton numbers in QDs, indicating all excitons are dissociated by ET to MV²⁺ with unity quantum yield (Figure 5B and C). At the highest excitation intensity under 400 nm, as many as 19 excitons were generated and dissociated from each CdSe/CdS quasi-type II core/shell QD to produce 19.1 ± 0.5 MV^{+•} radicals. This MED efficiency greatly exceeds that

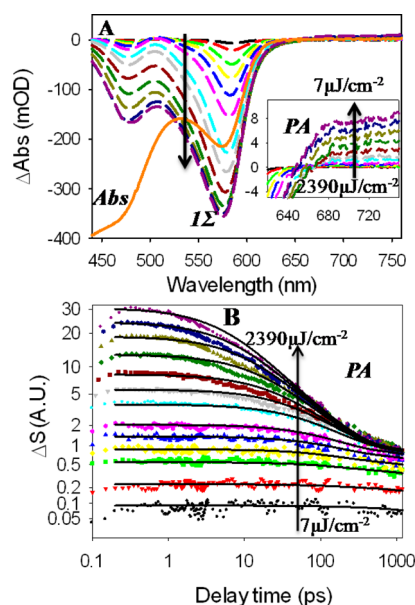


FIGURE 6. Excitation intensity dependent TA spectra and kinetics in CdSe QRs. (A) TA spectra at 1.5 ps after 400 nm excitation of different intensities and the steady state absorption spectrum of CdSe QRs (orange circles, inverted). (Inset) Expanded view of the PA feature at 600–770 nm. (B) Normalized PA kinetics (symbols) at different excitation intensities and their fit (solid lines) by the excitonic Auger recombination model. Adapted with permission from ref 27. Copyright 2012 American Chemical Society.

in CdSe QD and can be attributed to the ultrafast charge separation and slow Auger recombination in the quasi-type II nanoheterostructures.²⁸

V. MEA and MED in CdSe QRs: The Effect of Nanocrystal Shape

As a second approach to enhance MED efficiency, we seek to modify the scaling law for Auger recombination rate. As shown in Figure 2B, compared to the N^3 scaling law of the independent carrier model, the Auger recombination rate for exciton–exciton bimolecular collision (thus dependent on N^2) increases much slower with N , prolonging the lifetimes of higher exciton states.²⁷ In QRs, in which the carriers are quantum confined in the radial direction, the electron–hole Coulomb interaction can be described by an effective one-dimensional potential that depends on their separation along the nanorod axis.^{41–43} Because of the dielectric contrast between the rod and surrounding medium, the electron–hole binding energy is significantly enhanced compared to spherical QDs.^{41–43} As a result, the Auger recombination process in QRs is expected to proceed via exciton–exciton collision, following the excitonic model.^{32,44}

As a model for 1D excitonic materials, we examined MEA and MED dynamics in CdSe QRs (3.2 nm in diameter and

28.9 nm in length).²⁸ The quantum confinement in the radial direction gives rise to the 1Σ and 1Π exciton manifolds in their spectrum (Figure 6A). The TA spectra of CdSe QRs at 1.5 ps (Figure 6A) show that with increasing excitation intensities, in addition to increased amplitudes, the 1Σ band bleach shifts to higher frequencies, broadens in bandwidth, and gradually approaches the steady state absorption spectrum of the 1Σ band, consistent with the presence of a manifold of 1D excitonic states in QRs.^{41,42} Selective charge removal studies indicate that the 1Σ TA bleach of CdSe QRs can also be attributed to conduction band (CB) electron state filling, similar to that in CdSe QDs.

Subtraction of $1\Sigma_0$ kinetics at two lowest excitation intensities yields a biexciton lifetime of ~ 201 ps. It is about four times longer than that in CdSe QDs (~ 50 ps) with similar confinement energy, which can be attributed to the much bigger volume along the axial direction in CdSe QRs. A similar subtraction procedure was used previously to determine the lifetimes of bi- and triexciton states in CdSe QRs.³² However, because of the excitation intensity dependent shifting and broadening of 1Σ bleach in QRs, its amplitude does not scale linearly with the number of excitons. Therefore, a quantitative analysis of the higher exciton states dynamics would require a detailed modeling of the structure and transition strength of the 1D exciton states within the 1Σ manifold. Instead, we monitor the MEA dynamics in CdSe QRs by a broad PA signal in the near IR region (as shown in Figure 6A inset), which has been shown to result from the presence of holes and to scale linearly with the average exciton numbers.²⁷ These kinetics can be much better described by the excitonic model than the independent carrier model (Figure 6B), indicating that Auger recombination in CdSe QRs occurs mainly through exciton–exciton bimolecular collision.²⁷ Such excitonic behavior is consistent with the strongly bound 1D excitons formed in CdSe QRs. Therefore, compared with CdSe QDs, the elongation along the axial direction of CdSe QR increases the volume, greatly reducing the Auger rate constant. In addition, the formation of 1D exciton modifies the Auger rate scaling law, which further lengthens the N -exciton state lifetime in QRs (as shown in Figure 2C).

Although the CdSe QR has a much bigger volume than a typical QD, it is still quantum confined in the radial direction, maintaining a large amplitude of electron wave function at the surface to enable ET to acceptors.²⁷ As shown in Figure 7A, a single exponential fit of MV^{+*} radical formation kinetics yields a ~ 59 fs ET time in CdSe QR- MV^{2+} complexes, which is comparable to that in CdSe and CdSe/CdS QD- MV^{2+} complexes. At the highest 400 nm excitation intensity, as

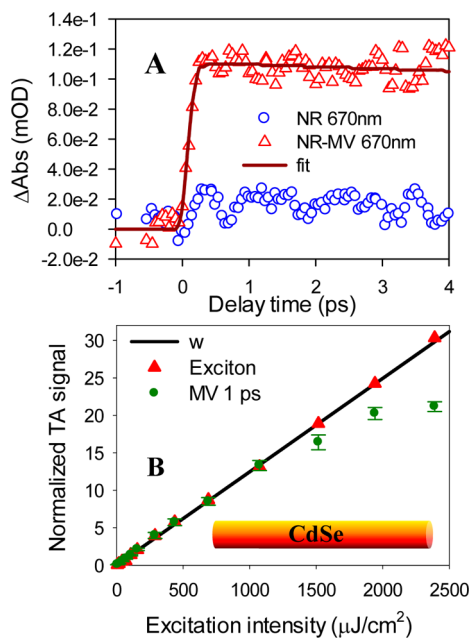


FIGURE 7. Single and multiple excitons dissociation in CdSe QR–MV²⁺ complexes. (A) Comparison of TA kinetics at 670 nm of CdSe QRs and CdSe QR–MV²⁺ complexes after band edge (590 nm) excitation. Best fit to the kinetics yields a rise time of ~ 59 fs. (B) Normalized MV²⁺ radical signal at 1 ps in QR–MV²⁺ complexes (green filled circles), normalized PA signal of free QDs (red triangles), and the average initial number of excitons per QD (black line) at different excitation intensities. Adapted with permission from ref 27. Copyright 2012 American Chemical Society.

many as 21 excitons can be dissociated from each CdSe QR to adsorbed MV²⁺, greatly exceeding the MED efficiency of CdSe QDs (Figure 7B).²⁷ The enhanced MED from CdSe QRs can be attributed to ultrafast ET rate and reduced rate of multiexciton Auger annihilation. It should be noted that at the highest excitation power, not all excitons are dissociated, which is likely limited by the competition between Auger annihilation and electron transfer.

It is interesting to note that in CdSe QDs, quasi-type II CdSe/CdS QDs, and CdSe QRs, the average ET rates shows negligible decrease with increasing numbers of dissociated excitons, despite the expected increase of electron–hole attraction. The origin of this independence is still under investigation. With increasing numbers of dissociated excitons, the charge recombination of MB[•] or MV^{•+} radicals with the holes left in NCs becomes faster (Figure 5B), consistent with the bimolecular nature of this process.

VI. MEG and MED in PbS QD–Acceptor Complexes

In previous sections, it is demonstrated that multiexcitons generated by the absorption of multiple photons can be efficiently dissociated by ET to adsorbed acceptors in competition

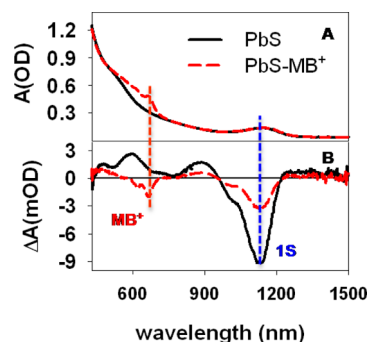


FIGURE 8. Vis-NIR steady state (A) and transient (B) absorption spectra of PbS QDs (black solid lines) and PbS–MB⁺ complexes (red dashed lines). Adapted with permission from ref 48. Copyright 2012 American Chemical Society.

with MEA in NCs. In this section, we extend this multiexciton extraction approach to PbS QD–MB⁺ complexes because of the reports of MEG in lead chalcogenide QDs and NRs,^{18,20,45} and ultrafast interfacial ET from PbS QDs to electron acceptors.^{46,47}

The absorption spectrum of PbS–MB⁺ complexes in heptane (Figure 8A) shows the 1S exciton band at 1140 nm (a bandgap, E_g , of 1.08 eV) and broad higher energy absorption features in the visible region of PbS QDs as well as the ground state absorption band (centered at 667 nm) of MB⁺ molecules. The TA spectrum of free QDs shows the 1S exciton bleach signal due to the state filling of both the 1S electron and hole levels and an exciton induced absorption (EIA) feature in the visible.⁴⁷ The TA spectrum of the PbS–MB⁺ complex shows reduced amplitudes of QD 1S exciton bleach and EIA signals as well as a MB⁺ ground state bleach (GSB) at 667 nm, indicating ET from excited QDs to MB⁺ molecules. From these overlapping signals, the kinetics of MB⁺ ground state formation can be obtained, revealing a ~ 2.3 ps ET time from the QD single exciton state to MB⁺.⁴⁷

Excitation intensity and wavelength dependent measurements are carried out to quantify MEG and MED efficiency in the QD–MB⁺ complex. We compare the kinetics measured at 800 nm ($\sim 1.45 E_g$) and 400 nm ($\sim 2.9 E_g$) excitation, below and above the MEG threshold, respectively. Furthermore, because of the statistical nature of the photon absorption process, it is difficult to avoid the absorption of multiple photons under transient absorption conditions. To accurately determine the MEG efficiency, a pump power dependence study is needed to remove the contributions of multiple photon absorptions. The kinetics of 1S exciton bleach in free PbS QDs excited at 800 nm (Figure 9A) and 400 nm (Figure 9D) show increasing amplitudes of the fast decay component at higher excitation powers due to the presence of multiple excitons and can be well described by the

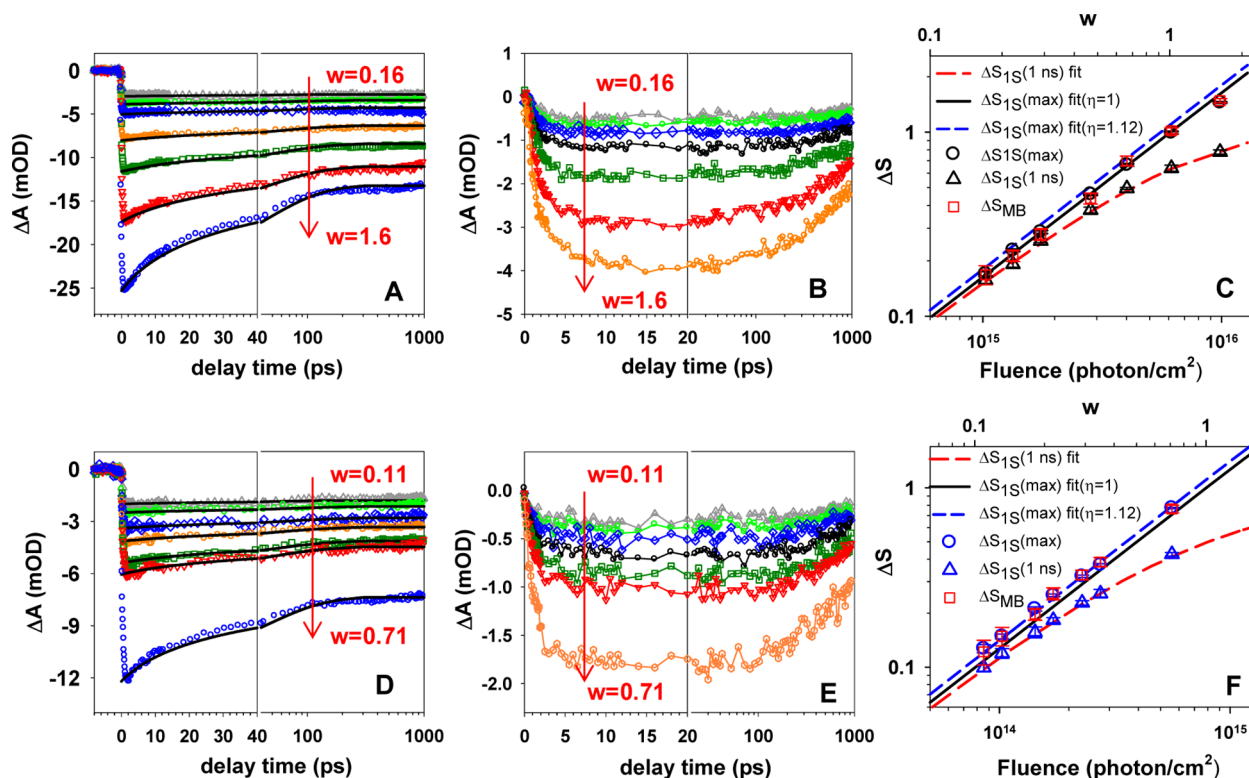


FIGURE 9. MEG and MED in PbS–MB⁺ complexes. Pump intensity dependent 1S exciton bleach kinetics of PbS QDs (A and D) and MB⁺ ground state bleach kinetics of PbS–MB⁺ complexes (B and E) after 800 nm (A, B) and 400 nm (D, E) excitation. The solid lines are fits according to the independent carrier Auger recombination model. Normalized MB⁺ GSB signal (ΔS_{MB}) and 1S exciton bleach signals at early ($\Delta S_{1S}(\max)$) and long ($\Delta S_{1S}(1 \text{ ns})$) delay times as a function of excitation fluence after (C) 800 nm and (F) 400 nm excitation. Fits to $\Delta S_{1S}(\max)$ ($\eta = 1$, $\eta = 1.12$) and $\Delta S_{1S}(1 \text{ ns})$ according to a model described in ref 48 are also shown. Adapted with permission from ref 48. Copyright 2012 American Chemical Society.

independent carrier Auger recombination model. We define normalized amplitudes of the initial ($\Delta S_{1S}(\max)$) and long time ($\Delta S_{1S}(1 \text{ ns})$) 1S exciton bleach to reflect the number of excitons per QD at those delay times. Best fits to these amplitudes as a function of excitation power according to a model that accounts for the contributions of both the MEG and multiphoton absorption yield a MEG efficiency of $112 \pm 2\%$ at 400 nm,⁴⁸ consistent with the latest reported values for PbS QDs.¹⁹ The kinetics of MB⁺ bleach formation in PbS–MB⁺ complexes are also measured under the same 800 nm (Figure 9B) and 400 nm (Figure 9E) excitation conditions. The normalized amplitudes of the maximum MB⁺ GSB signal, ΔS_{MB} , which represent the average number of reduced MB⁺ molecules (or dissociated excitons) per QD, follows the initial number of excitons in free QDs (Figure 9C and F). These findings suggest that all excitons are dissociated in PbS–MB⁺ complexes and the presence of strong electron acceptors does not influence the MEG efficiency of PbS QDs. This study demonstrates that ultrafast interfacial ET can be an efficient way for extracting multiple excitons generated via the MEG process.

VII. Summary and Outlook

In this Account, we provide an overview of MEA and MED processes in CdSe QDs, CdSe/CdS quasi-type II core/shell QDs, CdSe QRs, and PbS QDs. Multiexciton states in these NCs are generated by both the multiple photons absorption (for the first three classes of NCs) and MEG (for PbS) processes. In CdSe and PbS QDs, the strong quantum confinement in NCs enhances the rates of interfacial ET to acceptors, enabling efficient dissociation of multiple excitons by ultrafast electron transfer in QD–acceptor complexes. In addition, the electron and hole spatial distributions and energetic properties in quantum confined NCs can be readily controlled to optimize the MED efficiency by simultaneously facilitating exciton dissociation and retarding Auger annihilation. This wavefunction engineering approach to MED optimization was demonstrated in CdSe/CdS quasi-type II QDs and CdSe QRs through the control of material compositions and dimensions.

The understanding and controlling of multiexciton Auger recombination and the efficient conversion of multiexcitons to emitted photons or separated external charges are of

considerable interest for advanced NC based optoelectronic devices. In addition to interfacial charge transfer, multiexciton extraction by energy transfer to other NCs or molecules should also be explored. In practical solar energy conversion systems, efficient multiexciton extraction would need to be coupled with schemes for efficient multiexciton generation under the solar flux. Direct MEG by one higher energy photon, as demonstrated in PbS–MB⁺ complexes, is a potentially promising way if nanomaterials with lower MEG energy threshold and higher MEG efficiency can be developed. MEG processes with a lower threshold have been reported in type II nano-heterostructures⁴⁹ and QRs,⁴⁵ which coupled with the expected enhanced MED efficiency suggests a promising direction for material exploration. Alternatively, methods to enhance light harvesting rates in advanced nanostructures, such as plasmonic enhancement or NC–antenna complexes, should also be investigated.

The authors gratefully acknowledge the support from the National Science Foundation (CHE-0848556).

BIOGRAPHICAL INFORMATION

Haiming Zhu received his B.S. degree in Chemistry from the University of Science and Technology of China in 2008 and is now a Ph.D. student in the laboratory of Tianquan Lian. His research focuses on the carrier dynamics and charge transfer properties of quantum confined semiconductor nanomaterials and their applications in solar energy conversion.

Ye Yang obtained his B.S. degree in chemistry from the University of Science and Technology of China in 2008 and is now a Ph.D. student at Emory University supervised by Tianquan Lian. His research interests include ultrafast charge carrier extraction from quantum dots and other photovoltaic nanomaterials.

Tianquan (Tim) Lian received his B.S. degree from Xiamen University in 1985, M.S. degree from the Chinese Academy of Sciences in 1988, and Ph.D. from the University of Pennsylvania in 1993. He is currently the William Henry Emerson Professor in the Department of Chemistry, Emory University. Tim Lian's research interest is focused on ultrafast dynamics in photovoltaic and photocatalytic nanomaterials.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: tlian@emory.edu. The authors declare no competing financial interest.

REFERENCES

- Brus, L. E. Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. *J. Chem. Phys.* **1984**, *80*, 4403–4409.
- Norris, D. J.; Sacra, A.; Murray, C. B.; Bawendi, M. G. Measurement of the size dependent hole spectrum in CdSe quantum dots. *Phys. Rev. Lett.* **1994**, *72*, 2612–2615.
- Alivisatos, A. P. Semiconductor clusters, nanocrystals, and quantum dots. *Science* **1996**, *271*, 933–937.

- Donega, C. d. M. Synthesis and properties of colloidal heteronanostructures. *Chem. Soc. Rev.* **2011**, *40*, 1512–1546.
- Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev.* **2005**, *105*, 1025–1102.
- Smith, A. M.; Nie, S. Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering. *Acc. Chem. Res.* **2010**, *43*, 190–200.
- Zhu, H.; Lian, T. Wavefunction engineering in quantum confined semiconductor nano-heterostructures for efficient charge separation and solar energy conversion. *Energy Environ. Sci.* **2012**, *5*, 9406–9418.
- Zhu, H.; Song, N.; Lv, H.; Hill, C. L.; Lian, T. Near unity quantum yield of light-driven redox mediator reduction and efficient H₂ generation using colloidal nanorod heterostructures. *J. Am. Chem. Soc.* **2012**, *134*, 11701–11708.
- Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer. *Nature* **1994**, *370*, 354–357.
- Shen, Y. C.; Mueller, G. O.; Watanabe, S.; Gardner, N. F.; Munkholm, A.; Krames, M. R. Auger recombination in InGaN measured by photoluminescence. *Appl. Phys. Lett.* **2007**, *91*, 141101–141103.
- Klimov, V. I.; Ivanov, S. A.; Nanda, J.; Achermann, M.; Bezel, I.; McGuire, J. A.; Piryatinski, A. Single-exciton optical gain in semiconductor nanocrystals. *Nature* **2007**, *447*, 441–446.
- Kambhampati, P. Unraveling the Structure and Dynamics of Excitons in Semiconductor Quantum Dots. *Acc. Chem. Res.* **2010**, *44*, 1–13.
- Kambhampati, P. Multiexcitons in Semiconductor Nanocrystals: A Platform for Optoelectronics at High Carrier Concentration. *J. Phys. Chem. Lett.* **2012**, 1182–1190.
- Fisher, B.; Caruge, J. M.; Zehnder, D.; Bawendi, M. Room-Temperature Ordered Photon Emission from Multiexciton States in Single CdSe Core-Shell Nanocrystals. *Phys. Rev. Lett.* **2005**, *94*, 087403.
- Sukhovatkin, V.; Hinds, S.; Brzozowski, L.; Sargent, E. H. Colloidal Quantum-Dot Photodetectors Exploiting Multiexciton Generation. *Science* **2009**, *324*, 1542–1544.
- Sambur, J. B.; Novet, T.; Parkinson, B. A. Multiple Exciton Collection in a Sensitized Photovoltaic System. *Science* **2010**, *330*, 63–66.
- Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H.-Y.; Gao, J.; Nozik, A. J.; Beard, M. C. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011**, *334*, 1530–1533.
- Nair, G.; Geyer, S. M.; Chang, L.-Y.; Bawendi, M. G. Carrier multiplication yields in PbS and PbSe nanocrystals measured by transient photoluminescence. *Phys. Rev. B* **2008**, *78*, 125325.
- Stewart, J. T.; Padilha, L. A.; Qazilbash, M. M.; Pietryga, J. M.; Midgett, A. G.; Luther, J. M.; Beard, M. C.; Nozik, A. J.; Klimov, V. I. Comparison of Carrier Multiplication Yields in PbS and PbSe Nanocrystals: The Role of Competing Energy-Loss Processes. *Nano Lett.* **2011**, *12*, 622–628.
- Miaja-Avila, L.; Tritsch, J. R.; Wolcott, A.; Chan, W. L.; Nelson, C. A.; Zhu, X. Y. Direct Mapping of Hot-Electron Relaxation and Multiplication Dynamics in PbSe Quantum Dots. *Nano Lett.* **2012**, *12*, 1588–1591.
- Chan, W.-L.; Ligges, M.; Jaiilaubekov, A.; Kaake, L.; Miaja-Avila, L.; Zhu, X.-Y. Observing the Multiexciton State in Singlet Fission and Ensuing Ultrafast Multielectron Transfer. *Science* **2011**, *334*, 1541–1545.
- Tyagi, P.; Kambhampati, P. False multiple exciton recombination and multiple exciton generation signals in semiconductor quantum dots arise from surface charge trapping. *J. Chem. Phys.* **2011**, *134*, 094706.
- Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. Quantization of multiparticle Auger rates in semiconductor quantum dots. *Science* **2000**, *287*, 1011–1013.
- Klimov, V. I. Spectral and Dynamical Properties of Multiexcitons in Semiconductor Nanocrystals. *Annu. Rev. Phys. Chem.* **2007**, *58*, 635–673.
- Matylytsky, V. V.; Dworak, L.; Breus, V. V.; Basche, T.; Wachtveitl, J. Ultrafast Charge Separation in Multiexcited CdSe Quantum Dots Mediated by Adsorbed Electron Acceptors. *J. Am. Chem. Soc.* **2009**, *131*, 2424–2425.
- Huang, J.; Huang, Z.; Yang, Y.; Zhu, H.; Lian, T. Multiple Exciton Dissociation in CdSe Quantum Dots by Ultrafast Electron Transfer to Adsorbed Methylene Blue. *J. Am. Chem. Soc.* **2010**, *132*, 4858–4864.
- Zhu, H.; Lian, T. Enhanced Multiple Exciton Dissociation from CdSe Quantum Rods: the Effect of Nanocrystal Shape. *J. Am. Chem. Soc.* **2012**, *134*, 11289–11297.
- Zhu, H.; Song, N.; Rodríguez-Córdoba, W.; Lian, T. Wave Function Engineering for Efficient Extraction of up to Nineteen Electrons from One CdSe/CdS Quasi-Type II Quantum Dot. *J. Am. Chem. Soc.* **2012**, *134*, 4250–4257.
- Landsberg, P. T. *Recombination in semiconductors*; Cambridge University Press: Cambridge, 2003.
- Barzykin, A. V.; Tachiya, M. Stochastic models of charge carrier dynamics in semiconducting nanosystems. *J. Phys.: Condens. Matter* **2007**, *19*, 065105.
- Wang, F.; Dukovic, G.; Knoesel, E.; Brus, L. E.; Heinz, T. F. Observation of rapid Auger recombination in optically excited semiconducting carbon nanotubes. *Phys. Rev. B* **2004**, *70*, 241403.

- 32 Htoon, H.; Hollingsworth, J. A.; Dickerson, R.; Klimov, V. I. Effect of Zero- to One-Dimensional Transformation on Multiparticle Auger Recombination in Semiconductor Quantum Rods. *Phys. Rev. Lett.* **2003**, *91*, 227401–227404.
- 33 Klimov, V. I.; McGuire, J. A.; Schaller, R. D.; Rupasov, V. I. Scaling of multiexciton lifetimes in semiconductor nanocrystals. *Phys. Rev. B* **2008**, *77*, 195324.
- 34 Ueda, A.; Tayagaki, T.; Kanemitsu, Y. Dynamics of Quantized Auger Recombination in CdSe Nanocrystals Studied by Femtosecond Intraband Pump–Probe Spectroscopy. *J. Phys. Soc. Jpn.* **2009**, *78*, 083706.
- 35 Huang, J.; Stockwell, D.; Huang, Z.; Mohler, D. L.; Lian, T. Photoinduced Ultrafast Electron Transfer from CdSe Quantum Dots to Re-bipyridyl Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 5632–5633.
- 36 Zhu, H.; Song, N.; Lian, T. Controlling Charge Separation and Recombination Rates in CdSe/ZnS Type I Core–Shell Quantum Dots by Shell Thicknesses. *J. Am. Chem. Soc.* **2010**, *132*, 15038–15045.
- 37 Oron, D.; Kazes, M.; Banin, U. Multiexcitons in type-II colloidal semiconductor quantum dots. *Phys. Rev. B* **2007**, *75*, 035330.
- 38 García-Santamaría, F.; Brovelli, S.; Viswanatha, R.; Hollingsworth, J. A.; Htoon, H.; Crooker, S. A.; Klimov, V. I. Breakdown of Volume Scaling in Auger Recombination in CdSe/CdS Heteronanocrystals: The Role of the Core–Shell Interface. *Nano Lett.* **2011**, *11*, 687–693.
- 39 Cragg, G. E.; Efros, A. L. Suppression of Auger Processes in Confined Structures. *Nano Lett.* **2010**, *10*, 313–317.
- 40 Zhu, H.; Song, N.; Lian, T. Wave Function Engineering for Ultrafast Charge Separation and Slow Charge Recombination in Type II Core/Shell Quantum Dots. *J. Am. Chem. Soc.* **2011**, *133*, 8762–8771.
- 41 Shabaev, A.; Efros, A. L. 1D exciton spectroscopy of semiconductor nanorods. *Nano Lett.* **2004**, *4*, 1821–1825.
- 42 Bartnik, A. C.; Efros, A. L.; Koh, W. K.; Murray, C. B.; Wise, F. W. Electronic states and optical properties of PbSe nanorods and nanowires. *Phys. Rev. B* **2010**, *82*, 195313.
- 43 Vietmeyer, F.; McDonald, M. P.; Kuno, M. K. Single nanowire microscopy and spectroscopy. *J. Phys. Chem. C* **2012**, *116*, 12379–12396.
- 44 Vietmeyer, F.; Frantsuzov, P. A.; Janko, B.; Kuno, M. Carrier recombination dynamics in individual CdSe nanowires. *Phys. Rev. B* **2011**, *83*, 115319.
- 45 Cunningham, P. D.; Boercker, J. E.; Foos, E. E.; Lumb, M. P.; Smith, A. R.; Tischler, J. G.; Melinger, J. S. Enhanced Multiple Exciton Generation in Quasi-One-Dimensional Semiconductors. *Nano Lett.* **2011**, *11*, 3476–3481.
- 46 Yang, Y.; Rodríguez-Córdoba, W.; Xiang, X.; Lian, T. Strong Electronic Coupling and Ultrafast Electron Transfer between PbS Quantum Dots and TiO₂ Nanocrystalline Films. *Nano Lett.* **2012**, *12*, 303–309.
- 47 Yang, Y.; Rodríguez-Córdoba, W.; Lian, T. Ultrafast Charge Separation and Recombination Dynamics in Lead Sulfide Quantum Dot–Methylene Blue Complexes Probed by Electron and Hole Intraband Transitions. *J. Am. Chem. Soc.* **2011**, *133*, 9246–9249.
- 48 Yang, Y.; Rodríguez-Córdoba, W.; Lian, T. Multiple Exciton Generation and Dissociation in PbS Quantum Dot–Electron Acceptor Complexes. *Nano Lett.* **2012**, *12*, 4235–4241.
- 49 Gachet, D.; Avidan, A.; Pinkas, I.; Oron, D. An Upper Bound to Carrier Multiplication Efficiency in Type II Colloidal Quantum Dots. *Nano Lett.* **2009**, *10*, 164–170.