

Surface Chemistry of Semiconducting Quantum Dots: Theoretical Perspectives

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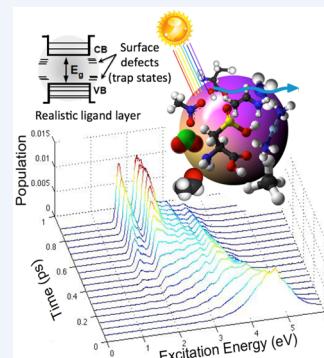
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CONSPECTUS: Colloidal quantum dots (QDs) are near-ideal nanomaterials for energy conversion and lighting technologies. However, their photophysics exhibits supreme sensitivity to surface passivation and defects, of which control is problematic. The role of passivating ligands in photodynamics remains questionable and is a focus of ongoing research. The optically forbidden nature of surface-associated states makes direct measurements on them challenging. Therefore, computational modeling is imperative for insights into surface passivation and its impact on light-driven processes in QDs.

This Account discusses challenges and recent progress in understanding surface effects on the photophysics of QDs addressed via quantum-chemical calculations. We overview different methods, including the effective mass approximation (EMA), time-dependent density functional theory (TDDFT), and multiconfiguration approaches, considering their strengths and weaknesses relevant to modeling of QDs with a complicated surface. We focus on CdSe, PbSe, and Si QDs, where calculations successfully explain experimental trends sensitive to surface defects, doping, and ligands.

We show that the EMA accurately describes both linear and nonlinear optical properties of large-sized CdSe QDs (>2.5 nm), while TDDFT is required for smaller QDs where surface effects dominate. Both approaches confirm efficient two-photon absorption enabling applications of QDs as nonlinear optical materials. TDDFT also describes the effects of morphology on the optical response of QDs: the photophysics of stoichiometric, magic-sized X_nY_n ($X = \text{Cd}, \text{Pb}; Y = \text{S}, \text{Se}$) QDs is less sensitive to their passivation compared with nonstoichiometric $X_{n\neq m}Y_m$ QDs. In the latter, surface-driven optically inactive midgap states can be eliminated by anionic ligands, explaining the better emission of metal-enriched QDs compared with nonmetal-enriched QDs. Ideal passivation of magic-sized QDs by amines and phosphine oxides leaves lower-energy transitions intact, while thiol derivatives add ligand-localized trap states to the band gap. Depending on its position, any loss of ligand from the QD's surface also introduces electron or hole traps, decreasing the QD's luminescence. TDDFT investigations of QD–ligand and QD–QD interactions provide an explanation of experimentally detected enhancement of blinking on-times in closely packed Si QDs and establish favorable conditions for hole transfer from the photoexcited CdSe QD to metal–organic dyes. While TDDFT well describes qualitative trends in optical response to stoichiometry and ligand modifications of QDs, it is unable to calculate highly correlated electronic states like biexcitons and magnetic-dopant-derived states. In these cases, multiconfiguration methods are applied to small nanoclusters and the results are extrapolated to larger-sized QDs, providing reasonable explanations of experimental observables.

For light-driven dynamics, the electron–phonon couplings are important, and nonadiabatic dynamics (NAD) is applied. NAD based on first-principles calculations is a current grand challenge for the theory. However, it can be accomplished through sets of semiclassical approximations such as surface hopping (SH). We discuss validations of approximations used in photodynamics of ligated and doped QDs. Time-domain DFT-based SH-NAD reveals the ligand's role in ultrafast energy relaxation and the connection between the phonon bottleneck and the Zeno effect in CdSe QDs. The calculated results are helpful in controlling both dissipation and radiative processes in QDs via surface engineering and in explanations of experimental data.



1. INTRODUCTION

In many respects, colloidal semiconductor quantum dots (QDs), also called nanocrystals, possess a unique combination of electronic and optical properties that opens new ways to utilize them in next generation of energy conversion and solid-state lighting technologies.¹ Their appealing properties include unmatched photostability and size-tunability of absorption and photoluminescence (PL) as well as the ability to generate multiple excited electron–hole pairs from a single photon via the carrier multiplication process, which enhances the efficiency of photovoltaics.² Additionally, QDs can be produced cheaply

by colloidal synthesis,³ which makes them ideal materials for photovoltaics and lighting applications.

However, the main roadblock for practical applications of QDs is their sensitivity to surface chemistry. Despite promising properties, the efficiency of QD-based photovoltaics and light-emitting devices is lower than in traditional technologies.⁴ These losses are caused by inefficient interfacial charge transport governed by QD surface defects. However, the question of exactly how surface defects influence the photo-

Received: April 27, 2016

Published: September 26, 2016

physics of QDs is still unanswered. Experimentally, this task is difficult since electronic transitions associated with surfaces and interfaces are optically inactive. Recently, some progress in experimental studies of QD surface states has been achieved by means of scanning tunneling spectroscopy.⁵ Nonetheless, manipulations of carrier multiplication, charge transfer, and PL via QD surface passivation remain elusive and are the effort of most current research.^{6,7} Atomistic computations could provide valuable insights into these issues. This Account outlines existing challenges and recent progress in modeling of surface effects on the photophysics of QDs, focusing mainly on CdSe, PbSe, and Si QDs, which are the most studied materials both experimentally and computationally.

2. MODELING OF GEOMETRIES AND ELECTRONIC STRUCTURES

As experimentally established, colloidal QDs consist of an inorganic core (inner atoms) retaining the geometry of the bulk crystal lattice, an inorganic surface (outer atoms) with a morphology distinct from that of the core, and a layer of ligands bonded to the surface.⁸ The core determines the QD's photophysical properties according to its bulk materials, the shape, and confinement effects, while the surface perturbs these properties. Figure 1 schematically shows the classification of nanostructures between two limiting cases of clusters and bulk crystals and possible effects of surface and ligand layers on their electronic structure.

The dividing line between the bulk and QDs is well-defined: QDs are nanostructures within the limits of quantum

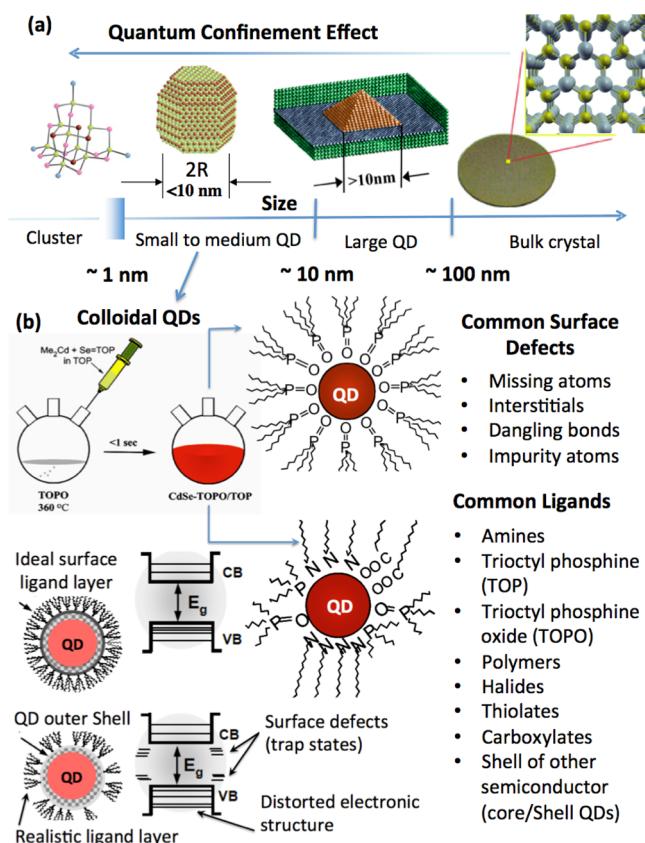


Figure 1. (a) Schematic classification from clusters to QDs to bulk and (b) effects of ligand passivation on the band gap of QD. Adapted from ref 7. Copyright 2015 American Chemical Society.

confinement effects, where the exciton Bohr radius is greater than or equal to the QD radius.⁹ However, the lower limit between a QD and a cluster is unclear. Therefore, the terms "cluster" and "ultrasmall QD" are often used interchangeably. In either case, the electronic structure of the nanosystem is dictated by its geometry, including the system size (confinement effects), the stoichiometry, and the interface between passivating ligands and the QD surface (surface effects). Below we consider each of these factors in detail.

2.1. Large-Sized Nanocrystals and Confinement Effects

Experimental studies involve relatively large colloidal QDs with sizes of 3–12 nm.¹⁰ However, the lack of information on precise structures coupled with the large sizes (thousands of atoms) make atomistic simulations of QDs challenging. The simplest model approaches to the electronic structure of QDs include the effective mass approximation (EMA) and $\mathbf{k}\mathbf{p}$ theory, where single-particle wave functions are treated as products of Bloch and envelope functions, with the former describing electron motion within the periodic crystal lattice and the latter within the spherical confinement potential.¹¹ These methods well predict the size dependence of optical gaps¹² and Auger⁹ and reverse Auger¹³ processes in large QDs but fail for small QDs with sizes of a few crystal units¹⁴ (Figure 2a,b; the exact size regime depends on the material type). For small QDs, the EMA fails because surface structural features override the spherical shape, while Bloch functions become invalid within the limits of several crystal units.

Our joined experimental and computational studies examined the applicability of the EMA to describe not only linear absorption but also nonlinear optical (NLO) properties such as two-photon absorption (2PA) in CdSe QDs.¹⁵ For small QDs, 2PA cross sections were found to be higher than those of the best-known NLO materials, enabling QDs to be potential competitors in the endeavor for NLO applications. The EMA well describes both linear and nonlinear absorption in large QDs (>3.5 nm). For intermediate sizes (2–3.5 nm), where surface structural features dominate the shape, the EMA becomes inaccurate (Figure 2c,d). For <2.5 nm QDs, with large surface-to-volume ratios, the significant deviations between the EMA and measurements require an explicit description of the surface chemistry for proper simulations of their optical properties.¹⁵

An additional limitation of the EMA includes its treatment of the QD surface as an infinite potential barrier around the core, while neglecting any surface effects. More recent semiempirical models represent the QD core using tight-binding or pseudopotential approaches, while the ligand shell is modeled through parametrized potentials.^{11,16} However, realistic descriptions of the surface layer and QD–ligand bonding are incomplete in these approaches because of the nonperiodic and highly complicated forms of potentials at interfaces. Some efforts have been made to model ligated QDs using force fields¹⁷ and Monte Carlo calculations.¹⁸ However, the parametrization present in such methods needs to be verified for each material, making the accuracy of these approaches questionable. First-principles quantum-chemical methods, e.g., density functional theory (DFT), are able to provide this information to a reasonable degree of accuracy. Therefore, DFT and linear-response time-dependent DFT (TDDFT) have become the common methods of choice for simulating structural and optical properties in both molecular systems and solids consisting of hundreds of atoms.⁷ Unfortunately,

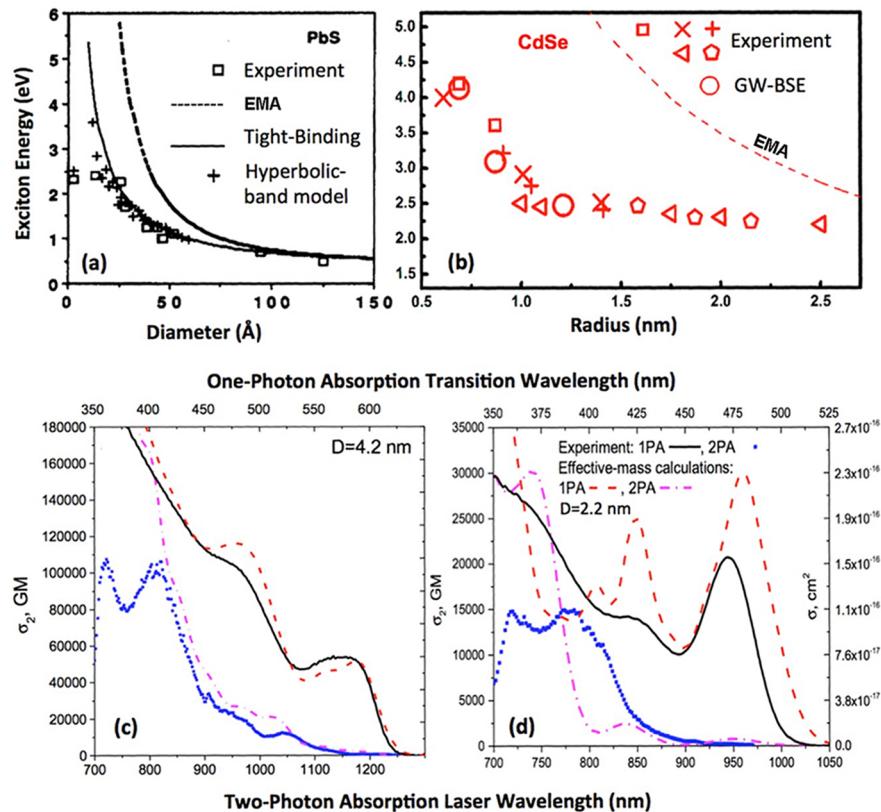


Figure 2. Performance of the effective mass approximation (EMA) in determining (a, b) the lowest exciton energies in (a) PbS and (b) CdSe and (c, d) linear vs nonlinear absorption in CdSe QDs. Reprinted from (a) ref 12, (b) ref 14, and (c, d) ref 15. Copyright 1991, 2015, and 2014 American Chemical Society, respectively.

utilization of DFT-based methods is limited by nonlinear scaling with system size and uncertainty related to the chemical composition and morphology of QD surfaces. The latter has been partially overcome by recent optical and mass spectroscopy measurements of small “magic-sized” QDs.¹⁹

2.2. Magic-Sized versus Nonstoichiometric Nanostructures

Magic-sized QDs (msQDs) are believed to be ultrastable, while preserving their crystal structure motif and electronic features similar to larger-sized QDs. The smallest magic-sized Cd_nSe_n QDs, with $n = 33$ or 34 , have been observed in mass spectrometric studies²⁰ and detected as 1–2 nm structures.¹⁹ Ultrasmall PbSe/PbS msQDs also have been observed experimentally.²¹ All msQDs demonstrate good photostability, narrow emission line widths, and high quantum yields, while the quantum confinement systematically blue-shifts optical gaps.

The stability of msQDs has been confirmed through the Monte Carlo basin hopping method and DFT-based optimization^{18,22} of various Cd_nSe_m species ($n, m = 6–54$) and their different stereoisomers,²³ including those generated from bulklike and nonbulk geometries.²⁴ The lowest-energy structures have $n = m$ and well-opened energy gaps, while less stable systems exhibit drastically smaller energy gaps.²³ Non-msQDs have surface atoms with unsaturated dangling bonds, introducing optically inactive states inside the QD band gap.²⁵ In contrast, optimization of stoichiometric msQDs constructed from bulk crystal structures results in rearrangements of surface atoms that mostly saturate dangling bonds and widen band gaps.²⁶ Such surface reconstruction or self-healing²⁷ leads to nanostructures with high-stability, maximum energy gaps²⁵ and

optically allowed (bright) lowest-energy transitions.²⁸ Therefore, 1–2 nm Cd_nX_n and Pb_nX_n ($\text{X} = \text{S}, \text{Se}, \text{Te}$) msQDs constructed from bulk crystal structures with approximately spherical shapes and optimized to geometries with the lowest number of dangling bonds are often taken as common models of QDs in quantum-chemical simulations.⁷ First, such geometries have been experimentally proven to represent chemically and optically stable nanostructures. Second, the small size of these systems allows for calculations of both ground- and excited-state properties at relatively higher levels of theory, such as TDDFT, providing data comparable with experimental absorption spectra.²⁴ As is common for DFT, the calculated energy gaps and optical spectra of QDs are sensitive to the functionals and basis sets used. Benchmark DFT-based studies of CdX ($\text{X} = \text{S}, \text{Se}, \text{Te}$) msQDs performed by our group²⁹ and others³⁰ have demonstrated that semilocal generalized gradient approximation functionals, such as PBE, provide satisfactory results for geometries and vibrational frequencies, while the hybrid functional PBE0 is optimal for both ground- and excited-state calculations, as overviewed in our recent review.⁷

Recently, modeling of nonstoichiometric QDs is attracting significant attention, since it has been experimentally detected that anionic surfactants used in QD growth drive metal enrichment of QD surfaces.¹⁰ With diminishing QD size, the metal to nonmetal ratio increases. Nonstoichiometric surface composition also influences QD emission. Thus, the PL of CdS QDs is quenched in S-enriched systems but recovered in Cd-enriched QDs.³¹ DFT calculations explain this difference in terms of midgap states originating from surface sulfurs that mediate hole trapping and nonradiative recombination in S-

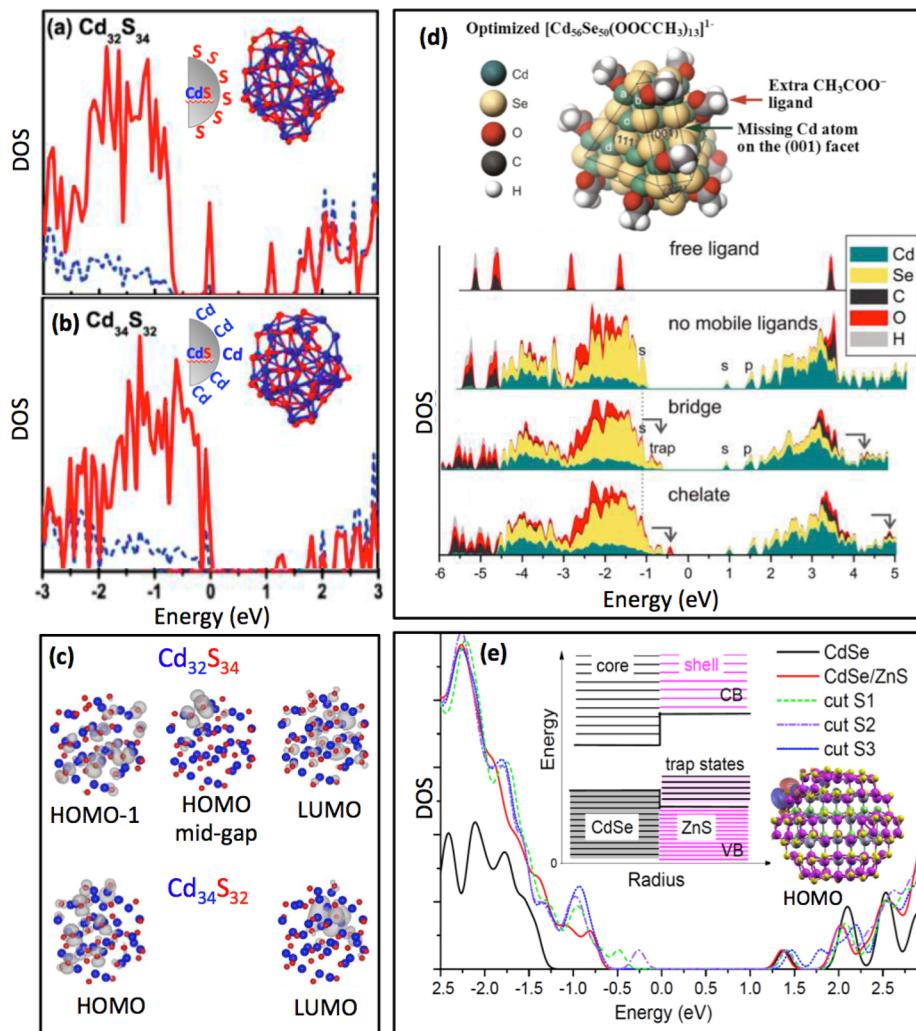


Figure 3. Effects of stoichiometry on the electronic structures of QDs. (a, b) In CdS QDs, S-enriched surfaces result in hole-trap midgap states (a), while Cd-enriched QDs show electron midgap states (b). (c) Frontier molecular orbitals in S-enriched QDs have stronger localized trap character than those in Cd-enriched QDs. (d) The number and position of carboxylate ligands mediate trap states in Cd-enriched CdSe QDs. (e) Shell defects due to lost sulfur at different positions (cut-S1, -S2, -S3) in Cd₃₃Se₃₃/Zn₇₈S₇₈ QDs introduce surface-localized hole traps. (a–c) Adapted from ref 31. Copyright 2012 American Chemical Society. (d) Adapted from ref 33. Copyright 2011 American Chemical Society. (e) Adapted with permission from ref 36. Copyright 2013 American Physical Society, respectively.

enriched QDs (Figure 3a). Improved emission of Cd-enriched structures results from more delocalized surface-associated orbitals than in S-enriched QDs (Figure 3c). Consequently, not all surface states have a traplike nature corresponding to strong orbital localization and optically inactive (dark) character.

DFT calculations of nonstoichiometric PbSe QDs with disproportionate numbers of metal and nonmetal ions indicate the appearance of trap midgap states, although they can be eliminated by adsorbed anionic ligands.³² DFT calculations³³ of Cd-enriched zinc blende CdSe QDs show that the presence of trap midgap states depends on the number of carboxylate ligands and their mode of attachment to cadmium (Figure 3d). On the contrary, irrespective of the attachment, we found no midgap states associated with the anchoring carboxylate groups at the band gap of the stoichiometric wurtzite Cd₃₃Se₃₃ msQD.^{34,35} These calculations indicate that the photophysics of msQDs is less sensitive to their surface chemistry compared with nonstoichiometric QDs.

2.3. Core/Shell Nanostructures

The optical and structural stabilities of QDs are also enhanced in structures where a shell of a different semiconductor covers the QD core, i.e., core/shell QDs, since the inorganic shell protects the QD core from environmental effects. However, defects in the core–shell interface have a strong impact on the QD’s optical response.¹ Our DFT calculations³⁶ on a CdSe/ZnS QD constructed from a Cd₃₃Se₃₃ core and a single-layer Zn₇₈S₇₈ shell demonstrate that the ZnS shell brings occupied states near the valence band (VB) edge localized at a single sulfur atom (hole-trap states) but does not affect the conduction band (CB) (Figure 3e). Upon phonon-induced relaxation, this suggests hole leakage into the shell while an electron remains inside the core, resulting in charge-separated states.

Removal of S atoms from the shell, representing shell defects, creates additional trap states close to the edge of the VB, with a minor effect on the CB. Analysis of molecular orbitals reveals less isolation between an electron and a hole in the presence of shell defects, opening up the Auger relaxation pathway and

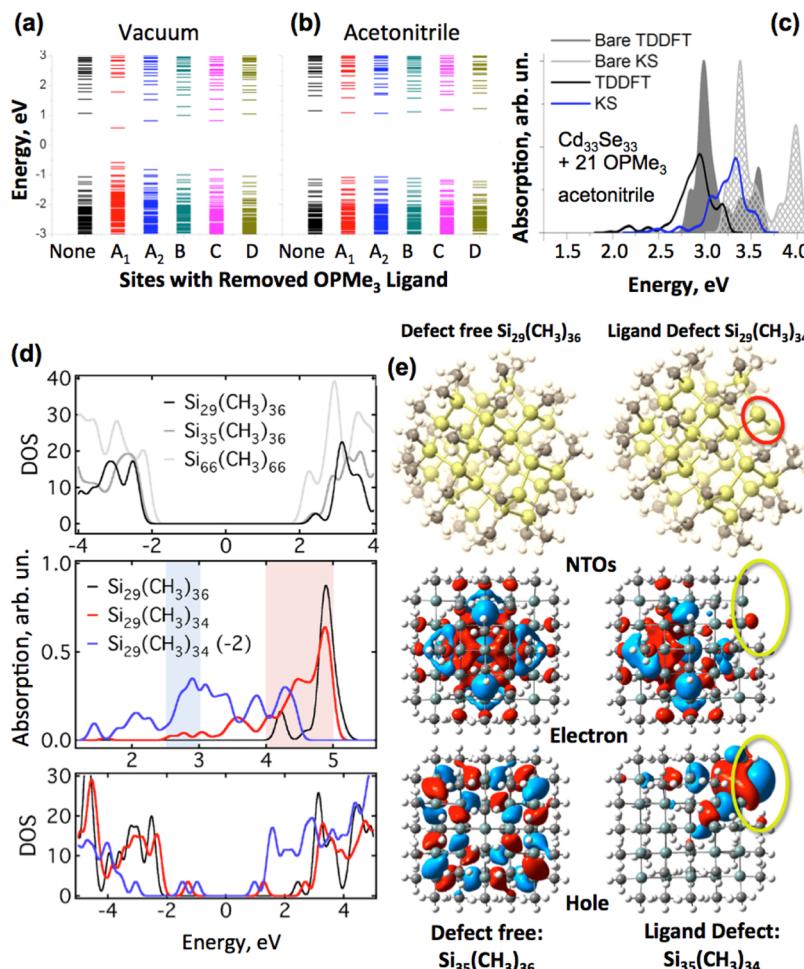


Figure 4. Effect of ligand-derived surface defects on the electronic and optical properties of QDs. (a, b) Depending on its position, removal of one OPMe₃ ligand from Cd₃₃Se₃₃ introduces midgap states (a), while polar solvents eliminate midgap states (b). (c) Absorption spectra of Cd₃₃Se₃₃ passivated by OPMe₃ (lines) and the bare QD (shaded areas) computed by TDDFT (black line and solid gray) and single-particle KS approaches (blue line and gray pattern). (d) DOS and absorption spectra of Si QDs affected by the QD's size (top) and ligand-associated defects and charges (middle and bottom). (e) Structure and excited-state orbitals (NTOs) contributing to the lowest optical transitions in defect-free and ligand-defected Si QDs. (a–c) Adapted with permission from ref 41. Copyright 2012 Royal Society of Chemistry. (d, e) Reprinted from ref 45. Copyright 2015 American Chemical Society.

rationalizing why imperfect shells lead to fast electron relaxation as observed experimentally.³⁷ Unfortunately, only a few DFT investigations of core/shell QDs have been reported^{38,39} to date.

3. THE ROLE OF LIGANDS IN PHOTODYNAMICS

Spectroscopic experiments indicate that different surface ligands differently affect both radiative and nonradiative processes in QDs.^{6,40} First-principles simulations of excited processes in QDs are capable of answering how to control the photodynamics of QDs via ligands.

3.1. Excitations by TDDFT: Ligand and Defect Impacts

Among practical methods that can reasonably describe excitations in molecules is linear-response TDDFT. It includes only the one-electron density matrix, which allows for inclusion of electron–hole interactions at moderate computational time. This robustness has made TDDFT a workhorse for the computation of photoexcitations in nanomaterials and solids, including ligated QDs.^{28,29,41} Using TDDFT with the B3LYP functional and mixed LANL2DZ (QD atoms)/6-31G* (ligand atoms) basis set, we found that neutral ligands (amines,

phosphines, and phosphine oxides) do not contribute to states near the energy gap of CdSe msQDs.^{28,41} Therefore, the lower-energy optical transitions have predominantly QD character. However, inside the valence and conduction bands, ligands introduce many hybridized states with wave functions delocalized over both the QD and the ligands. These hybridized states are optically inactive and negligibly affect the QD's absorption, but they contribute to nonradiative processes.⁴²

Conversely, thiols and thiolates attached to CdSe msQDs have the HOMO and LUMO localized primarily on the ligand, resulting in hole/electron trap states that decrease the luminescence efficiency of the QDs.⁴³ Our calculations on CdSe QDs functionalized with metal–organic complexes, such as Ru(II)–polypyridine dye complexes, via carboxylate linkages also reveal the dye-associated states near the edges of the msQD's band gap, while the energetic position of the dye versus QD states depends on the dye's ligands.³⁵ Thus, isothiocyanate ligands in the black dye lift the dye's occupied orbitals toward the QD's band gap, providing favorable conditions for transfer of the photoexcited hole from the msQD to the dye.³⁵

Recent TDDFT studies of nonstoichiometric CdSe QDs show that carboxylate and dithiocarbamate ligands differently affect the QDs' optical properties.⁴⁴ For carboxylate capping, the ligand states are located deep within the QD's valence and conduction bands, agreeing with our calculations on msQDs.^{34,35} Conversely, dithiocarbamate passivation results in the orbitals of aromatic molecules appearing in the band gap of the QD, while other orbitals near the band gap are delocalized over the QD and ligands. The calculated features explain the red shifts and enhancements of the first excitonic peak in dithiocarbamate-passivated CdSe QDs observed experimentally.⁴⁴

Imperfections in surface passivation such as surface defects introduced by loss of a ligand typically lead to midgap states with the electron density being localized at the defect, which results in weak or completely inactive lowest-energy optical transitions. We found⁴¹ that in CdSe msQDs capped by neutral ligands, such as amines and phosphine oxides (OPM_3), surface reconstructions in polar solvents partially suppress the effect of ligand-associated defects on the absorption spectra as a result of enhanced delocalization of defect-associated states (Figure 4a,b). Conversely, the ligand–QD interface in Si QDs passivated by alkyls is less sensitive to the surface reconstructions independent of the solvent because of stronger Si–C bonding compared with Cd–O or Cd–N coordinate bonds. Therefore, surface defects (lost CH_3 ligands) and/or surface charge lead to trap states within the gap, resulting in red-shifted weakly intense transitions in the absorption of Si QDs⁴⁵ (Figure 4d). For the lowest-energy exciton, the electron density is spread over the Si QD's core while the hole is localized around the defect (Figure 4e), which reduces the intensity of such transitions.

TDDFT was also used to investigate the effects of QD–QD interactions on their photodynamics. Recent experiments on blinking statistics (fluorescence intermittency) of Si QDs revealed that close packing of QDs at distances of ~ 1 nm results in a significant increase in “on” time corresponding to the state with a high quantum efficiency.⁴⁵ Our calculations predict that the energy transfer between the donor/acceptor pair of 1–1.5 nm Si QDs separated by 1 nm occurs in 10–30 ns even in the presence of defect-associated trap states.⁴⁵ Such energy transfer is much faster than electron–hole recombination (100–1000 ns), allowing for fast occupation of long-living trap states in neighboring QDs and forcing their emission to happen from higher-energy optically bright states. This pathway increases the blinking on-time in aggregates of closely packed Si QDs.⁴⁵

All of these reports demonstrate that TDDFT is capable of interpreting and predicting qualitative trends in lower-energy optical transitions in response to modifications of the stoichiometry and ligands at the QD surface. However, because it is a single-reference method, TDDFT is unable to calculate highly correlated electronic states such as double excitations that are important in photovoltaics.

3.2. Beyond and Below TDDFT

There have been many attempts to calculate the optical response of QDs using many-body theories based on the Bethe–Salpeter equation,⁴⁶ quantum Monte Carlo,⁴⁷ coupled cluster,⁴⁸ and configuration interaction (CI) or multiconfiguration self-consistent field^{49,50} methods. High computational cost limits the applications of these methods to clusters that are several atoms in size. Nonetheless, useful insights have been

obtained even by simulating small systems. In particular, the symmetry-adapted cluster CI (SAC-CI) multiconfiguration method applied to Pb_4Se_4 and Cd_6Se_6 allowed us to characterize excited states as single or multiple excitons and explain the difference in carrier multiplication between these systems.⁴⁹ Contrary to CdSe clusters, the sub-band structure and symmetry of electron–hole excitations in PbSe clusters result in dominance of multiple excitons over single excitons. Since similar electronic features are preserved in the density of states (DOS) of 1–2 nm QDs, the findings have been extrapolated to larger nanostructures to clarify why carrier multiplication is more efficient in PbSe QDs than in CdSe QDs. Another example is QDs with magnetic impurities, such as Mn-doped CdSe QDs, where the highly multiconfigurational nature of Mn requires multireference approaches. SAC-CI was used for MnSe_4 fragments cut from a 1–2 nm Mn-doped CdSe QD to explain the mechanism of the second, slow relaxation emission peak observed in experiments.⁵⁰

In photodynamics of nanomaterials, however, not only electron–hole correlations but also electron–phonon couplings have to be considered. This drastically increases the complexity of computational methods, making them numerically unachievable for QDs containing more than 50 atoms. Therefore, simulations of dynamics in QDs have to sacrifice some accuracy of the calculations, typically by neglecting excitonic effects (electron–hole interactions).

Excitonic effects are weak in bulk semiconductors, since the large dielectric permittivity and large exciton Bohr radius lead to significant screening of electron–hole interactions. In QDs, strong wave function confinement increases the excitonic effect.⁵¹ Nonetheless, excitons still can be considered as a small perturbation because the confinement energy is much larger than the electron–hole interaction in QDs. Therefore, a single-particle Kohn–Sham (KS) orbital representation of the excited state, where the excited-state density is approximated as a product of the ground-state electron and hole densities, is a valid zeroth-order approximation for simulations of optical spectra of QDs, being computationally much cheaper than CI or TDDFT simulations.⁷ The validity of this approach is proven by comparison between the KS-based and TDDFT absorption spectra of ligated CdSe msQDs⁴¹ (Figure 4c). Despite a uniform blue shift, KS spectra represent all of the TDDFT-calculated spectral features of $\text{Cd}_{33}\text{Se}_{33}$ QDs capped by OPM_3 ligands.^{28,41} Similar trends were observed in calculations on Si QDs.⁵²

3.3. Phonon-Mediated Photodynamics

After a nanostructure absorbs a photon, the created electron–hole pair undergoes intraband relaxation via interactions with phonons, leading to spatial energy transfer and charge separation phenomena—all of which are important processes in photovoltaics. However, for a correct description of photoexcited dynamics, electronic and nuclear interactions have to be considered beyond the Born–Oppenheimer approximation nonadiabatically. Methods providing direct atomistic simulations of nonadiabatic dynamics (NAD) exist. We name several common approaches: path-integral,⁵³ multiconfiguration time-dependent Hartree,⁵⁴ ab initio multiple spawning (AIMS),⁵⁵ and semiclassical Monte Carlo (SCMC) techniques.⁵⁶ Some of these methods were successfully applied to nanoclusters.

AIMS-NAD applied to hydrogen-passivated Si_9 clusters containing $\text{Si}=\text{O}$ defects reveals ultrafast nonradiative decays

of excitation via conical intersections associated with defects on the oxidized surface of silicon, which explains the decreased quantum yield and the red-shifted, size-insensitive nature of the PL of oxidized Si QDs observed experimentally.⁵⁵ Nonetheless, highly accurate NAD methods are numerically impractical for simulations of hot-exciton dynamics in larger QDs because of the highly dense states and the large number of atoms.

Mixed quantum-classical NAD approaches are more feasible, although they incorporate approximations that are appropriate in limiting cases. Time-domain DFT-based NAD coupled to surface hopping (SH) techniques is the most common approach to QD photodynamics, as presented in recent reviews.^{7,57} These simulations are performed in the adiabatic basis set of single-particle KS orbitals within the classical trajectory approximation using the ground-state density representation to obtain nonadiabatic couplings. The latter ones govern state-to-state transitions according to SH approaches. To improve the accuracy of SH, various decoherence corrections have been implemented, as overviewed in ref 57. Decoherence between excited states and relaxation of an excitation to the thermal equilibrium can be also computed in terms of the reduced density matrix,⁵² an analytically derived method complementary to the SH algorithm. All of these approaches were instrumental in describing energy relaxation process in bare,^{36,26,58} ligated,^{42,59} and doped QDs.⁵²

Using time-domain DFT-SH NAD, we obtained important insights into the effect of surface ligands and decoherence on the loss of photoexcitation to heat (energy relaxation) in QDs. Our calculations established a direct connection between the slow energy relaxation, the phonon bottleneck, and the Zeno effect.³⁶ Quantum confinement can significantly slow electron–phonon relaxation in QDs because of mismatches between the energy splittings of electronic states and phonon energies; known as the phonon bottleneck, this effect remains elusive. Our simulations confirmed that the bottleneck in CdSe QDs occurs under quantum Zeno conditions: to achieve the bottleneck, elastic electron–phonon scattering (decoherence) must be faster than the coherent electronic transitions. These conditions are fulfilled in CdSe QDs only for the lowest electronic states at the very edge of the conduction band³⁶ (Figure 5c).

Both elastic and inelastic electron–phonon interactions play key roles in solar energy harvesting. Coherence of these processes is important for quantum transitions. DFT-SH NAD provides insights into the origin of the pure-dephasing process in the bare and passivated QDs. We found that elastic and inelastic scattering have opposite effects in ligated CdSe msQDs.⁵⁹ Phonon-induced pure-dephasing processes determined by elastic electron–phonon scattering in ligated QDs are much longer than those in bare QDs. The difference is rationalized by the fact that ligands make no direct contributions to the electronic densities of the lower-energy states involved in the superpositions, while they indirectly reduce the mobility and fluctuations of the surface atoms.⁵⁹ In contrast, the higher-energy electronic states involved in the relaxation are delocalized over the QD and the ligands.⁴² Therefore, at excitation energies larger than 2.5 times the QD's band gap, ligand–QD hybridized states facilitate the electron–phonon coupling in the case of inelastic processes, resulting in ultrafast relaxation and rationalizing the absence of a phonon bottleneck at high excitations.⁴² Figure 5a,b details the

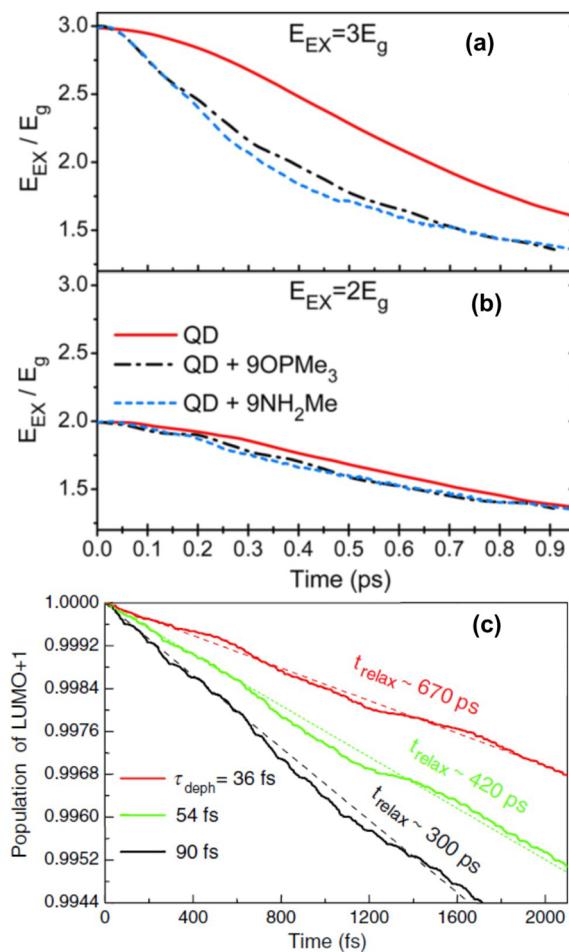


Figure 5. (a, b) Exciton relaxation in bare and ligated $\text{Cd}_{33}\text{Se}_{33}$ excited at energies of (a) 3 and (b) 2 times the band gap. (c) Decay rates of the photoexcited LUMO+1 to LUMO computed for different dephasing times in $\text{Cd}_{33}\text{Se}_{33}$, where dashed-lines are linear fits. (a, b) Reprinted from ref 42. Copyright 2012 American Chemical Society. (c) Reprinted with permission from ref 36. Copyright 2013 American Physical Society.

dependence of the exciton relaxation rate on the ligands passivating the CdSe msQDs.

The established relationship between the phonon bottleneck and the quantum Zeno effect and coherence in elastic and inelastic phonon scattering, together with atomistic details obtained from NAD simulations, provides an understanding of the conditions that must be achieved to control the dissipation process in QDs via synthetic manipulations of surface shells, ligands, dopants, etc., which is critical to our ability to design efficient QD-based materials for solar energy conversion and lighting applications.

4. CONCLUSIONS

We have discussed the significance of the surface passivation of QDs on their photophysical properties. While conventional experiments are incapable of direct measurements of surface effects in QDs, we have presented several examples where first-principles calculations succeed in providing fundamental insights into these issues that allow explanations of experimental trends and observables sensitive to surface defects and ligand passivation. Our discussion of computations used for tackling such effects is focused on method applicability and

accuracy. Calculations confirm that changes in structural and optoelectronic properties are both ligand-type- and QD-type-dependent while also being affected by the confinement. Despite their complexity, insights from calculations generate an understanding of the conditions necessary to control the optical response and phonon-driven dynamics via manipulations of the QD size, surface ligands, and dopants. Thus, simulations directly assist in novel material design strategies as well as inspire new experimental probes focused on nanoscience and nanotechnology.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Biographies

Svetlana Kilina obtained her Ph.D. in Chemistry at the University of Washington in 2007. Starting in 2010, she has been an Assistant Professor at the Chemistry and Biochemistry Department at North Dakota State University. Her research is focused on computational studies of processes happening in nanomaterials upon photoexcitation. She is the recipient of an Early Career Research Award from the Department of Energy and a Sloan Foundations Award.

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ACKNOWLEDGMENTS

The authors are grateful for financial support through DOE Early Career Research Grant DE-SC008446 and Sloan Research Fellowship BR2014-073.

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