

Atomistic Model of Fluorescence Intermittency of Colloidal Quantum Dots

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Optoelectronic applications of colloidal quantum dots demand a high emission efficiency, stability in time, and narrow spectral bandwidth. Electronic trap states interfere with the above properties but understanding of their origin remains lacking, inhibiting the development of robust passivation techniques. Here we show that surface vacancies improve the fluorescence yield compared to vacancy-free surfaces, while dynamic vacancy aggregation can temporarily turn fluorescence off. We find that infilling with foreign cations can stabilize the vacancies, inhibiting intermittency and improving quantum yield, providing an explanation of recent experimental observations.

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Colloidal quantum dots (CQDs) are attractive materials for low-cost, solution processed optoelectronic devices, such as light-emitting diodes and lasers, markers for bioimaging, solar cells, and logic circuits, due to their band gap tunability, high photostability, and high carrier mobilities [1–3]. Optoelectronic applications demand high photoluminescence quantum yields and narrow emission linewidth; however, achieving these remains a challenge due to the ubiquity of electronic trap states. Traps lead to high non-radiative recombination rates, fluorescence intermittency [4–7], and diffusion of the emission wavelength [8–10].

Over the past decade robust passivation schemes have been developed that rely on the growth of thick shells to protect the CQD core [11–13]. These address the intermittency problem by suppressing nonradiative Auger recombination [14] and decoupling the core from surface defects. While the transport-inhibiting thick shells that suppress exciton dissociation are desirable in light-emitting diodes and lasers [15], applications requiring ambipolar transport over several hundreds of nanometers, such as photovoltaics and photodetectors [1,2], demand improved passivation without using thick shells. Thin-shell or shell-free QDs offer the added advantage of narrower emission linewidths and the smaller sizes preferable for *in vivo* imaging [3,11].

It is thus of urgent importance to find means of providing effective passivation in shell-free CQDs. Development of novel passivation schemes requires a thorough understanding of the atomistic origin of traps, which is still lacking due to the complexity of the problem. This complexity is highlighted by the observation of power-law scaling of blinking probabilities on time scales as long as minutes, remarkably long for a nanoscale process [16,17].

Theoretical simulations can elucidate the origin of surface traps; however, high computational cost has to date precluded density functional theory (DFT) simulations for realistically sized CQDs. Moreover, explicit simulation of the dynamic changes that occur on extremely slow time scales remains

unattainable using fully *ab initio* methods. The very large number of degrees of freedom in structures that consist of thousands of atoms further complicates the problem. Interpretation of experimental data has thus been so far based on semiempirical simulations [18–23]. These studies have led to diverse conclusions [24–26] likely due to difficulties in parametrizing for a mixed organic-inorganic environment.

In this letter, we show how dynamic activation and rearrangement of surface traps can cause fluorescence intermittency and spectral diffusion in CQDs. Our DFT simulations of CdSe CQDs with realistic ligands show that the formation of surface vacancies is energetically favored and can assist in surface passivation. Discretized diffusion of vacancies about the surface leads to activation and deactivation of electronic traps on macroscopic time scales, while thermal fluctuations can activate traps during femtosecond intervals, decreasing quantum yield.

Simulations were performed using CP2K software [27] employing a mixed atomic orbitals plus plane-waves approach. Simulation details are presented in the Supplemental Material [28]. For zinc blende CQDs, several shapes can be achieved experimentally, with spherical being the most common [29–31]. In a spherical CQD, both Cd-terminated and Se-terminated (111) facets are present. Elimination of one of them leads to a tetrahedral shape, while enhanced growth along both directions leads to cubes terminated by (100) facets.

We start from an ideal spherical model exposing (100) and (111) facets [Fig. 1(a)]. The CQDs of a 3.6 nm size (~1200 atoms) were cut from a bulk CdSe, discarding all surface atoms singly bound to the surface. The (100) facets expose Cd atoms with two dangling bonds that can be perfectly passivated by oleic acid (OA) or Cl, both similar electronically [32] and employed interchangeably experimentally [29,33]. On (111) facets all atoms are triply bound to the surface and thus possess only a single dangling bond. Such surface termination was shown to produce no surface states in smaller DFT models [26,32,34] and we used the unpassivated (111) facets as a

starting point for our larger model. Special care is taken to select a geometry with a balance of anions, cations, and ligands, leading to a closed electronic shell condition [35], which is essential for band gap opening [32,36].

The results for the idealized spherical CQD are shown in Fig. 1. We find that trap states associated with Se-terminated (111) facets are formed on the valence band side, and with Cd-rich (111) facet on the conduction band side. Such trap states will be detrimental to emission and transport properties. We therefore sought strategies to eliminate these electronic traps.

We attempted to passivate the (111) facets using various ligands with little success. Adsorption of carboxylates on Cd (111) facets resulted in trap states arising from the lone electron pairs of the carboxyl groups, similar to observations in smaller models [26]. For Se-terminated (111) facets, a different type of ligand is required since anionic ligands such as oleic acid, halides, trioctylphosphine oxide, are repelled from the anionic Se sites. The CdOA^{1+} species were found to bind strongly without inducing the carboxyl-related traps, however, still incapable of eliminating the original surface state. Some syntheses employ trioctylphosphine (TOP) selenide as a precursor. Our calculated binding energy of TOP to Se (111) facet is 4.2 eV, comparable to that of carboxylate binding to Cd facets. However, TOP termination also failed to provide the sought passivation for Se (111) facets [28].

In order to understand the origin of the traps on (111) facets we performed simulations for bulk (111) slabs. These too exhibited surface states. Using the crystal orbital overlap population analysis [37] we have found that in-gap states are formed from the antibonding Cd-Se orbitals [28]. Populating these orbitals weakens the Cd-Se bond, rendering surface atoms prone to desorption. This can leave behind a vacancy, consistent with the known reconstructions of bulk CdSe surfaces [38,39]. The main driving force for bulk surface reconstructions, however, is the electron counting rule, i.e., the closed electronic shell condition

[40], which requires the presence of both anions and cations on any surface in order to avoid the partial filling of the dangling bonds and eliminate the surface states. In contrast, in CQDs, this charge-orbital balance [35] can be satisfied more easily due to the presence of Cd-rich facets providing electrons to populate the Se-rich ones.

We thus created a CQD model with several vacancies on Se- and Cd-terminated (111) facets. This allowed for a complete elimination of the surface states and led to clearly resolved quantum confined levels with *s*, *p*, *d*, *f* envelopes (Fig. 2). To our knowledge, this is the first DFT model with realistic ligands exhibiting such qualities. Most previous semiempirical [22,23] and *ab initio* models [41] relied on passivation with artificial hydrogenlike atoms to eliminate surface states. Nevertheless, semiempirical models typically provide a reliable description of band gap, spin-orbit, and Coulomb interactions at a lower computational cost. We believe that our current findings will enhance the existing models by enabling proper inclusion of surface effects.

The formation energy of vacancies in bulk CdSe is 2–3 eV, corresponding to a formation probability of $\sim 10^{-18}$ [42]. For this reason it is generally believed that, in a CQD of less than 10000 atoms, there can be no vacancies. In addition, the abundance of surfaces provides plenty of opportunities for vacancy annihilation [43]. Several recent cation exchange studies, however, argue that the mechanism should involve vacancies [44–46]. Similarly, a cation exchange process required for quantum well intermixing in epitaxial structures also relies on cation vacancies, albeit the activation energies can reach 3.5 eV and thus requires the temperatures above 900 °C [47].

To verify the possibility of vacancy formation in CdSe CQDs we calculated the respective formation energies. It should be noted that Cd dangling bonds in the conduction band are empty, leading to the change of Cd orbitals

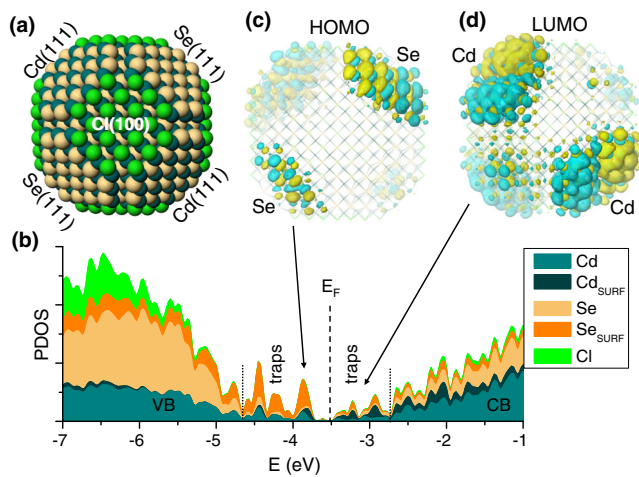


FIG. 1 (color online). Surface states in a spherical CdSe CQD with unpassivated (111) facets. (a) Model, (b) projected DOS, (c) Se-related surface state on the valence band side, (d) Cd-related state on the conduction band side.

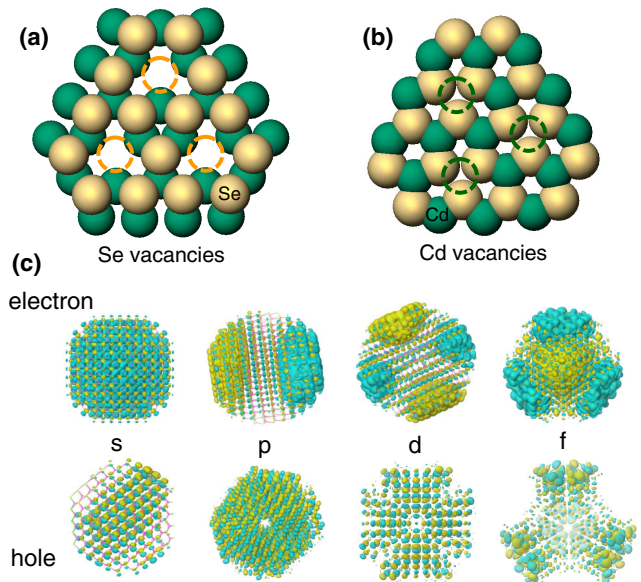


FIG. 2 (color online). Elimination of surface traps with the aid of Cd and Se vacancies. (a) and (b) (111) facets with vacancies, (c) corelike electron and hole states in a passivated CQD.

hybridization from sp^3 to sp^2 . The resulting planarization of the Cd-Se bonds in the surface plane [Fig. 2(b)] leads to a strong compressive strain, effectively pushing Cd atoms out, making ejection of Cd favorable by 0.15 eV, as also noted previously for bulk Cd(111) surface [26,38]. The binding energy of Se atom on (111) facet is found to be 2.8 eV, and reduces to 2.2 eV if desorbed in the form of TOP-Se. While these energies would preclude the desorption at room temperatures, it should be noted that a uv wavelength photoexcitation with a subsequent thermalization of the carrier is equivalent to heating the CQD up to 200 °C, as discussed previously [19], making Se desorption viable. A Cd vacancy in the core is 1.8 eV less stable than on surface, while the difference is only 0.5 eV for a Se vacancy.

Formation of vacancies plays another important role in CQDs, namely, it simplifies the stoichiometry self-regulation. Stoichiometry is critical to achieving the closed electronic shell condition in CQDs [35]. Without vacancies, the stoichiometry is very much geometry dependent and often the perfect charge-orbital balance is not easily attainable. For example, the model presented in Fig. 1 had to be artificially charged or extra ligands had to be added in order to move the Fermi level into the band gap. Otherwise, unbalanced stoichiometry results in degenerate electronic doping. Such doping is undesirable in optical applications of CQDs as it can enhance the Auger recombination processes [1,4–6] and also lead to defect formation as a form of self-compensation [32].

We note that the capacity of vacancies to move around the surface, similar to fluxionality of the CQD surface observed experimentally [19,48], could provide a mechanism for slow and discrete variations in electronic configuration of a CQD. This can potentially explain the fluorescence blinking and the emission wavelength diffusion. Two types of blinking are distinguished, one with long-lived carrier trapping and the resulting OFF states due to Auger recombination of the remaining trion [14], and another with a fast nonradiative recombination through a trap [4,7,49]. While the former can potentially be activated by the absorption of two photons in a thick-shell CQD, the latter requires random activation of the trap state, which is likely surface related [4,50,51]. To explore this possibility we investigated different patterns of vacancy distribution on surfaces, and quantified the corresponding transition energy barriers.

Figure 3 shows that some vacancy patterns, particularly vacancy aggregates, can activate a surface state, leading to an OFF state in a blinking trajectory [17]. Interestingly, vacancy-related traps have been also suggested as a source of rarely observed blinking in epitaxial QDs [52,53]. The Cd vacancy aggregate is less favorable by 0.8 eV, while the Se vacancy aggregates require only 0.1 eV. Less dramatic vacancy rearrangements slightly polarize the core wave function [Figs. 3(b) and 3(c) LUMO], leading to band gap changes on the order of 15 meV, consistent with experimental spectral diffusion observations [8,10].

Transition barriers for Cd and Se vacancy diffusion calculated using the nudged elastic band method [54] range

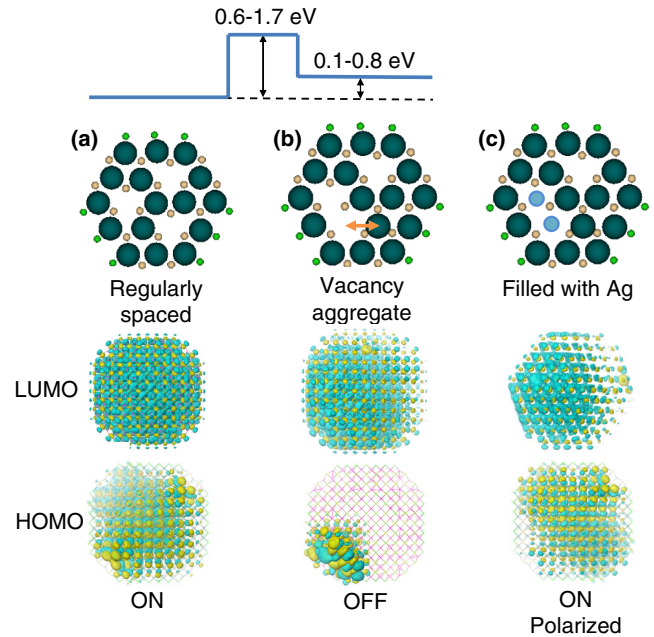


FIG. 3 (color online). Relation of vacancy surface diffusion to blinking and spectral diffusion. (a) regularly spaced Cd vacancies, (b) vacancy aggregate, (c) Ag-infilled vacancy aggregate.

from 0.6 to 1.7 eV, depending on the particular local configuration, such as surface vacancy density or presence of surface ligands [28]. At 300 K, this covers transition rates from 300 s^{-1} to many orders of magnitude slower—calculated using the Arrhenius rate equation assuming a 10^{13} prefactor—consistent with the power-law blinking kinetics on millisecond to minute time scales observed experimentally [5]. The energy difference between the initial and final state leads to inequivalent energy barriers for activation and deactivation of the trap (Fig. 3), providing a mechanism for asymmetry between the ON and OFF times statistics.

In contrast to previously posited diffusion of ligands [26], vacancy positions are discretized, allowing for discrete jumps in emission wavelength observed experimentally [8,10]. Moreover, after any jump, the vacancy has a chance to return to its previous position or move to a new one, explaining the short-time correlations leading to a “two steps forward, one step back” pattern in emitted wavelength observed experimentally [10,55]. Given the high energy cost of some of the above processes, this may require photoexcitation as an additional source of energy [19], consistent with the photoactivation behavior observed experimentally [49].

We further sought ways of achieving surface passivation without reliance upon vacancies, our goal being to eliminate the source of fluctuations responsible for blinking. Recently, a significant improvement of CdSe CQD photoluminescence quantum yield has been reported using Ag doping [56]. Silver atoms were allegedly occupying the interstitial sites, in contrast to substitutional sites expected for an atom of comparable size to Cd. Our calculations on a CQD with surface vacancies show that Ag substitutional and interstitial defects in the core are isoenergetic; however, an Ag atom

filling the surface vacancy is more stable by at least 0.6 eV. (In these simulations, the number of atoms is kept constant by exchanging a Cd atom between the core site and a surface vacancy [28].) The Ag substitutional defect behaves akin to a Cd vacancy, forming a deep hole trap when within the core, whereas passivating when on the surface. Interestingly, Ag interstitials do not form trap states. Figure 3(c) shows that infilling the surface Cd vacancies with Ag prevents trap formation even in the aggregated configuration, suggesting an explanation for improved quantum yields observed experimentally. Measurements of the blinking statistics of Ag-treated CQDs would provide the means to verify this explanation for the role of silver. A thorough screening of other cations could reveal comparable healing effects. Similarly, replacing surface Se with Cl also improves passivation, although a larger number of Cl substitutes are required to achieve the efficacy of a few Se vacancies [28].

Shells were previously developed as a means of decoupling any surface-associated electronic traps from CQD core states. Our simulations on a 3 nm CdSe core with a 0.8 nm CdS shell (~2500 atoms total) show that the CQD electronic structure remains sensitive to the surface configuration. Unpassivated (111) facets can still form surface states penetrating deep into the band gap despite the presence of a shell. This is consistent with the observation that a much thicker shell (> 2.4 nm) is typically needed in order to eliminate blinking [4,11,13]. Similarly, interfacial trap states that arise due to a lattice constant mismatch are often invoked to explain spectroscopic observations in giant-shell CQDs. Calculated formation energies for the Cd vacancy at the core-shell interface in our thin-shell model are comparable to those in shell-free dots, still too high to warrant their existence. Simulations on thicker shells will be a subject of future studies.

To understand the dynamics of carrier capture into a trap, we carried out Born-Oppenheimer molecular dynamics simulations of a CdSe CQD passivated by surface vacancies. Figure 4 shows the resulting trajectories of a few conduction and valence band edge energy levels of a nominally trap-free CQD. Surprisingly, deviations from the ideal structure due to thermal vibrations cause the surface trap states observed in the unpassivated CQD to reappear in the passivated one as well, though only temporarily. Such vibrational coupling of traps with the core state, in contrast to thermal population of a trap band, was recently proposed to explain the deep trap level emission in CdSe CQDs [48,57]. The amount of time a CQD resides in an ON state before it recombines radiatively on a nanosecond time scale is diminished by the femtosecond intervals of activated trap, effectively reducing the probability for radiative recombination. This process explains why not only the time average but also the ON state itself has a quantum yield below 100%. Similarly, nominally dark OFF state may have periods of trap-free configurations, explaining a nonzero quantum yield for OFF states.

Trap states that can disappear and reemerge on short time scales are considered shallow, as expected for states delocalized over an entire facet and discussed here. More

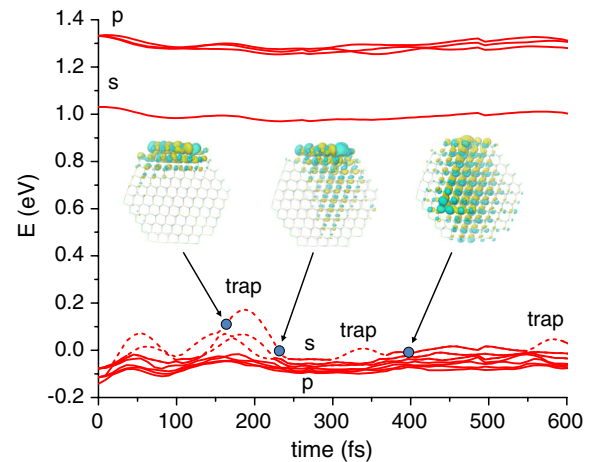


FIG. 4 (color online). Shallow trap dynamics of a CdSe CQD passivated by Cd and Se vacancies. Trap levels are represented by dashed lines.

localized traps, deep enough to avoid crossing the band edges under thermal fluctuations, are also envisioned [32]. Capture into such traps is possible, e.g., via an Auger process, as was recently described experimentally [58] and theoretically [59,60]. In both cases, surface dynamics presented here provides a mechanism for random activation of such traps.

In conclusion, we have found that surface vacancies provide an energetically favorable mechanism for surface passivation and stoichiometry adjustment in colloidal quantum dots. At the same time, the rearrangement of vacancies provides an atomistic mechanism for discrete spectral diffusion and switching between optically active and dark configurations. We propose a first-principles framework in which suboptimal photoluminescence quantum yield and blinking are caused by shallow and deep traps that can be dynamically activated on a range of time scales from femtoseconds to seconds. We find that infilling of surface vacancies with foreign cations or anions can inhibit blinking, opening a path for novel passivation techniques. The universality of intermittency in nanoscale light emitters [16] and nanoscale conductors of electric current [61] makes our findings relevant to the fields of organic electronics, carbon nanotubes, semiconductor nanorods, nanowires, and epitaxial quantum dots.

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