

# Temperature Dependence of Excitonic Radiative Decay in CdSe Quantum Dots: The Role of Surface Hole Traps

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## ABSTRACT

Using atomistic, semiempirical pseudopotential calculations, we show that if one assumes the simplest form of a surface state in a CdSe nanocrystal—an unpassivated surface anion site—one can explain theoretically several puzzling aspects regarding the observed temperature dependence of the radiative decay of excitons. In particular, our calculations show that the presence of surface states leads to a mixing of the dark and bright exciton states, resulting in a decrease of 3 orders of magnitude of the dark-exciton radiative lifetime. This result explains the persistence of the zero-phonon emission line at low temperature, for which thermal population of higher-energy bright-exciton states is negligible. Thus, we suggest that surface states are the controlling factor of dark-exciton radiative recombination in currently synthesized colloidal CdSe nanocrystals.

Colloidally synthesized CdSe quantum dots have a high photoluminescence (PL) quantum yield reaching up to 85% even at room temperature,<sup>1</sup> indicating that nonradiative decay channels are weak and spurring interest in various optoelectronic applications such as diodes<sup>2</sup> and lasers.<sup>3</sup> This motivated numerous recent experimental studies on the PL decay mechanisms in these systems,<sup>4–13</sup> where a multiexponential PL decay was evidenced in ensembles of CdSe nanocrystals of different sizes.<sup>5,8,12,13</sup> The temperature dependence of the long-time PL decay is usually interpreted in terms of a three-level system: the electronic ground state, a lower-energy “dark” (i.e., optically forbidden) exciton state  $X_D$ , and a higher-energy “bright” (i.e., optically allowed) exciton state  $X_B$ . The dark and bright excitons are separated by the exchange splitting  $\Delta$ , which is of the order of a few meV in CdSe quantum dots in the nanometer size range. The high-temperature ( $T > 10$  K) PL decay time can then be explained by thermal population of the bright exciton state, which is expected to have an intrinsic radiative lifetime of  $\sim 10$  ns. The low-temperature ( $T < 10$  K) PL decay, however, reveals a number of puzzling features (Figure 1, circles): (i) Measurements show a decay time  $\tau$  of  $\sim 1$   $\mu$ s at  $T \sim 1$  K.<sup>8</sup> This is surprising, because the dark exciton is expected<sup>14</sup> to have a much longer radiative recombination lifetime. (ii) The saturation temperature  $T_0$  (corresponding to the “kink” in the experimental  $\tau(T)$  curve, shown in Figure 1) is nearly size-independent. Since  $T_0$  depends on the exchange splitting

$\Delta$ , which increases with decreasing size, one would expect  $T_0$  to increase as the size of the quantum dot is reduced.

Fluorescence line narrowing experiments<sup>15</sup> have shown that, as the temperature decreases, the intensity of the one-phonon and two-phonon replicas in the emission spectrum increases at the expenses of the zero-phonon line. This observation has led to the suggestion that the dominant decay channel for dark excitons consists of phonon-assisted radiative recombination.<sup>14,15</sup> This mechanism may explain the microsecond low-temperature radiative lifetime. However, the persistence of the zero-phonon line at temperatures below 2 K<sup>15</sup>—at which thermal population of the bright-exciton states becomes negligible—suggests the presence of a *direct* radiative recombination channel for the dark exciton that has

scheme. We use a position-dependent dielectric screening function for the direct and exchange Coulomb integrals. We expand the exciton states using  $N_v = 30$  valence states and  $N_c = 7$  conduction states, corresponding to CI basis sets of 840 configurations for neutral excitons and 24 780 configurations for positively charged excitons. More details on this procedure can be found in ref 18.

Previous quantitative pseudopotential calculations<sup>18</sup> showed that  $X_B$  and  $X_D$  derive primarily from the lowest conduction state  $e_1$  and the highest valence state  $h_1$  (Figure 2a, upper panel), which, including spin, yield a  $2 \times 2$  exciton manifold. This 4-fold exciton multiplet is split by exchange interactions into two 2-fold degenerate states (Figure 2a, lower panel): a lower energy, optically forbidden “dark” state  $X_D$  and a higher energy, optically allowed “bright” state  $X_B$ . Their radiative decay channel is indicated in the lower panel of Figure 2a (transitions labeled 1 and 2).  $X_D$  and  $X_B$  are separated by the electron–hole exchange splitting energy  $\Delta$ , ranging from 5 to 16 meV for dots with sizes  $R = 19.2$ –

assisted radiative recombination of the dark exciton, enabled by the presence of *surface* states, is responsible for the low-temperature lifetime of the zero-phonon PL peak.

The calculations were performed using a fully atomistic theory that accounts for many-body effects. We consider here nearly spherical wurtzite CdSe quantum dots of radius  $R = 10.3, 14.6,$  and  $19.2 \text{ \AA}$ . The surface atoms were passivated by ligands.<sup>16</sup> The hole and electron single-particle energies  $\{\epsilon_{h,e}\}$  and wave functions  $\{\psi_{h,e}\}$  were computed using the semiempirical nonlocal pseudopotential method (including spin–orbit effects) described in refs 17 and 18. The single-particle Schroedinger equation was solved in a plane-wave basis set. The many-body excitonic energies  $\{E^{(i)}\}$  and wave functions  $\{\Psi^{(i)}\}$  were expanded in terms of single-substitution Slater determinants  $\{\Phi_{h,e}\}$ , constructed from the single-particle wave functions of electrons and holes

The corresponding many-body Hamiltonian is solved within the framework of the configuration interaction (CI)

of the neutral exciton  $\langle\tau(X)\rangle$  for two dot sizes as a function of temperature. We see that for  $T > 10$  K, the lifetime  $\langle\tau(X)\rangle$  is in good agreement with the experimental results.<sup>8</sup> Figure 3 shows the high-temperature radiative lifetime  $\langle\tau(X)\rangle$  as a

of neutral and charged excitons with similar lifetimes. Moreover, electrostatic force microscopy measurements performed on CdSe nanocrystals on insulator–metal substrates<sup>20</sup> found a positive charge on half of the investigated nanocrystals. These observations suggest that dark excitons in charged nanocrystals may have a different radiative recombination rate compared to neutral nanocrystals.

To test these ideas we calculated the excitonic manifold and the temperature-dependent radiative lifetimes of positively charged  $X^+$  ( $2h + 1e$ ) and negatively charged  $X^-$  ( $1h + 2e$ ) excitons in CdSe nanocrystals. Figure 2b (lower panel) shows that the lowest energy state of  $X^+$  is a 2-fold degenerate *bright* exciton<sup>21</sup> derived from the  $(e_1^1 h_1^2)$  single-particle configuration, followed by three 2-fold degenerate dark exciton states derived mainly from the  $(e_1^1 h_1^1 h_1^3)$  configuration. Similarly, for  $X^-$  (not shown in Figure 2) the lowest energy exciton state is bright. The lowest energy transition in both  $X^+$  and  $X^-$  is therefore optically allowed and has a short lifetime ( $\sim 10$  ns). As a result, our calculated  $\langle\tau(X^+)\rangle$  and  $\langle\tau(X^-)\rangle$  exhibit an almost  $T$ -independent value of  $\sim 10$  ns, as shown in Figure 1. We conclude that charged excitons, where the charge resides in the dot interior, do not explain the behavior of the measured lifetimes at low temperature.

*The presence of surface states reduces the radiative lifetime of dark excitons:* The removal of a passivant from a surface Se atom creates a surface state that can be either in the gap or resonant with the valence band.<sup>22</sup> The removal of a passivant from a surface Cd atom leads instead to surface states that are resonant with the conduction band or at its edge.<sup>22</sup> In this work we investigate the effects of hole traps on exciton recombination, so we consider only surface states obtained by removing Se-passivating atoms. We have previously studied the consequences of unpassivated surface anions on the optical spectrum of CdSe<sup>23</sup> and InP<sup>24</sup> nanocrystals. In particular, we found that an unpassivated Se atom located on the  $(000\bar{1})$  Se-terminated facet of a 19.2 Å radius CdSe nanocrystal leads to a surface-localized hole-trap state in the band gap,<sup>23</sup>

$\langle\tau(X_s^0)\rangle \approx \langle\tau(X_s^+)\rangle \approx \langle\tau(X)\rangle$ , and is consistent with the measured PL decay time. In the case of  $X_s^+$ , this occurs because the main contribution to the thermally averaged lifetime  $\langle\tau(X_s^+)\rangle$  at high temperature comes from all four band edge exciton states (dark and bright), as their energies are within 8–12 meV. Furthermore, since the decay times of the three bright states are close to  $\tau(X_B)$  and their separation from the dark state is close to  $\Delta$ , it follows that  $\langle\tau(X_s^+)\rangle \approx \langle\tau(X)\rangle$  at high  $T$ . Similarly, we find that for  $X_s^0$   $\langle\tau(X_s^0)\rangle \approx \langle\tau(X)\rangle$ .