Influence of Polytypism on Electronic Structure of CdSe/CdS and CdSe/CdSe Core/Shell Nanocrystals

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Abstract

CdSe/CdS dot-in-dot nanocrystals (NCs) have proven potential for opto-electronic applications. Depending on the synthetic procedure, it is possible to obtain NCs with pure wurtzite (WZ) phase, pure zinc-blende (ZB) phase, or a polytypic form where the CdSe core has ZB phase and the CdS shell WZ phase. Here we show theoretically that the electronic structure of polytypic CdSe/CdS NCs closely resembles that of their WZ counterparts. Quantum confinement, strain and built-in electric fields are comparable, which results in electron-hole overlap having similar dependence on the core size and shell thickness. This explains recent experiments showing close exciton lifetimes in both structures. We also investigate polytypic NCs where both core and shell are made of CdSe, albeit with ZB and WZ structure, respectively. In this case, spontaneous polarization has a drastic influence, inducing a sharp transition from type-I to type-II regime with increasing shell thickness. This provides interesting opportunities for tuning carrier-carrier interactions.

Introduction

Colloidal NCs with a CdSe core embedded in a thick CdS shell have taken a leading position in the research of semiconductor nanostructures for opto-electronic applications owing to their high luminescence quantum yield, narrow emission linewidth and reduced blinking.[1] In bulk CdSe and CdS crystals, WZ phase is more stable than ZB one. However, the energy difference is small, ≤ 1.4 meV/atom.[2] As a consequence, in NCs –where the surface to volume ratio is high– one can grow either phase through appropriate choice of synthetic temperature or ligands.[3–7] In the last years, this has made possible the synthesis of CdSe/CdS NCs with pure WZ phase,[8–12] pure ZB phase[5,13–15] or a polytypic form where the CdSe core has ZB phase and the CdS shell WZ one.[16–18]

Several spectroscopic studies have analyzed the near-band-edge luminescence of such systems. In all instances, a pronounced dependence of the emission energy on the core and shell size was observed, consistent with a quasi-type-II band alignment where holes are localized inside the core and electrons delocalized over the entire NC. The study of radiative lifetime however reveals significant differences between WZ and ZB crystal structures. For thick shells, pure WZ NCs display lifetimes of up to 600 ns,[11] about one order of magnitude longer than those of pure ZB NCs.[14,15] Even though the multi-exponential photoluminescence decay of WZ CdSe/CdS quantum dots makes the exact determination of their lifetimes problematic,[19] the large variation evidences fundamental differences between the two systems.

Theoretical studies have provided accurate descriptions of the band structure of both ZB[20,21] and WZ[22] CdSe/CdS NCs. With unstrained band-offsets being similar, differences arise from the different impact of strain and built-in electric fields. The question follows of whether polytypic NCs inherit the behavior of ZB or WZ structures. Because exciton recombination takes place in the core, one might guess that ZB behavior prevails. However, long radiative lifetimes of up to 300 ns have been experimentally reported,[17] and a direct comparison with WZ NCs recently showed very similar single exciton lifetimes in both systems. This suggests that the band profiles is actually close to that of pure WZ phase.[23] The aim of the present work is to provide a theoretical

description of the band structure of polytypic CdSe/CdS heterocrystals, explaining the similarities with respect to the better-known case of WZ NCs, and analyzing the differences.

Our calculations, based on k·p theory, confirm that the electronic structure of polytypic NCs resembles that of their WZ counterparts. Hydrostatic strain leads to a substantial decrease of the conduction band offset –thus stimulating electron delocalization– and built-in electric fields arising from the WZ shell are felt inside the ZB core. Consequently, electron-hole wave functions show quantitatively similar dependence on the core and shell sizes. The main distinction arises from spontaneous polarization, which is weaker than in pure WZ phase. This should lead to shorter radiative lifetimes for large core sizes. The presence of alloyed ZB interlayers, which are often found in polytypic NCs,[23] barely changes this picture.

We further investigate polytypic NCs made of CdSe only, but with different crystal structure in the core (ZB) and shell (WZ). These turn out to be strain-free systems with type-II band profile and a strong permanent dipole moment arising from spontaneous polarization. These features render polytypic CdSe NCs appealing for applications requiring flexible control of electron-hole charge separation.

Methods

The excitonic electron and hole states are calculated with Hamiltonians of the form:

$$H_j = H_j^{kin} + V_j + V_j^{e-h}, \tag{1}$$

where $j = e, h$ stands for electron or hole, H_j^{kin} is the kinetic energy term, V_j the single-particle confinement potential and V_j^{e-h} is Coulomb attraction exerted upon carrier j by the other carrier. The single-particle confinement can be split into several terms:

$$V_j = V_j^{conf} + V_j^{str} + V_j^{pz} + V_j^{sp}. \tag{2}$$

where V_j^{conf} the confining potential defined by the band offsets between bulk CdSe and CdS, V_j^{str} the strain induced deformation potential, V_j^{pz} the strain induced piezoelectric potential and V_j^{sp} the spontaneous polarization potential.

Strain maps are calculated in the continuous medium model by minimizing the elastic energy. The boundary conditions are zero normal stress for the free surface.[24] The strain tensor elements, ensuing piezoelectric polarization vector and potential are obtained using the multiphysics mode of Comsol 4.2 software. For electron states, H_j^{kin} is a 3D single-band effective mass Hamiltonian. For hole states, it is a 3D six-band Hamiltonian for either [111]-grown zinc-blende or wurtzite including A-band, B-band and C-band with spin-orbit interaction, as well as position dependent mass (Burt-Foreman-like).[25] The strain-induced deformation potential term, V_j^{str}, is isomorphic to the kinetic energy term,[26] while the piezoelectric and spontaneous polarization potentials, V_j^{pz} and V_j^{sp}, are diagonal. V_j^{e-h} is obtained by iterative resolution of the Schrodinger-Poisson equation, within a self-consistent Hartree procedure, taking into account the dielectric mismatch with the dielectric surroundings of the NC. Material parameters are given in the Supporting Information.

Results and discussion

We will compare three different models of CdSe/CdS dot-in-dots. The first one is a WZ/WZ core/shell NC with abrupt interface, see Figure 1(a). The second one is a ZB/WZ (polytypic) NC also with abrupt interface, Figure 1(b). The third one a ZB/WZ NC but including a 2-nm thick diffusion layer in between the core and the shell, Figure 1(c). The interlayer, which accounts for the usual alloying observed in standard polytype dots,[23] has ZB structure and $CdSe_xS_{1-x}$ composition, with x varying exponentially from the core interface ($x = 1$) to the shell interface ($x = 0$).

Figure 1(d-f) shows the corresponding conduction and valence band-edge profiles along the c-axis of the WZ phase, which we assume aligned with the [111] ZB direction. Dashed lines represent the unstrained band-offset confinement potentials V_j^{conf}, while solid lines are used for full potential of non-interacting carriers, V_j, including strain deformation potential, piezoelectricity

and spontaneous polarization. By comparing panels (d) and (e), one immediately realizes that the band profile is very similar in WZ/WZ and ZB/WZ NCs with abrupt interface. Strain deformation potential pushes up conduction band and heavy hole band (A-band), and built-in electric fields are formed due to strain-induced piezoelectricity together with spontaneous polarization arising in the WZ phase. As a result, the conduction band offset decreases in about 40% with respect to the unstrained band-offset. For WZ/WZ (ZB/WZ) NCs, the effective band-offset decreases from 0.34 eV to ~ 0.20 eV (from 0.435 eV to ~ 0.25 eV). Hence, both systems show strain-enhanced electron delocalization into the shell.

Figure 1: (a-c) Schematic of the CdSe/CdS NCs under study. R is the core radius and H the shell thickness. In (c), we include a 2-nm-thick alloyed interlayer with exponential change of composition between core and shell. (d-f) Corresponding single-particle potential profiles along c axis. Dashed line is used to show unstrained confining potential V_j^{conf}, solid lines for complete potential excluding only electron-hole interaction, V_j. Different colors are used for conduction band (black), A-band (red), B-band (green) and C-band (blue). In (d-f), the core has $R = 1.5$ nm radius and the shell $H = 5$ nm.

Another important observation is that significant built-in electric fields are felt inside the core both in WZ/WZ and ZB/WZ NCs. For pure WZ NCs, the lattice mismatch between CdSe core and CdS shell is 3.9%. This leads to sizable strain-induced piezoelectricity.[22] Similar piezoelectric fields build up in polytypic NCs, because the lattice mismatch between [111]-grown ZB CdSe and WZ CdS is also $\sim 3.9\%$ (see lattice parameters in Supporting Information). On the other hand, the electric field induced by spontaneous polarization is proportional to the polarization mismatch at the core/shell interface. For WZ/WZ heterocrystals, $P_{sp}^{CdSe} = -6$ mC/m^2 and $P_{sp}^{CdS} = -2$ mC/m^2.[27,28] For ZB/WZ heterocrystals, instead, the polarization vanishes inside the core because of the cubic lattice symmetry, $P_{sp}^{CdSe} = 0$ mC/m^2. Therefore, the polarization mismatch is larger for WZ/WZ interfaces than for ZB/WZ ones. Since the resulting field adds up to piezoelectricity, the total electric field inside the core is slightly stronger in WZ/WZ NCs, 32 mV/nm vs. 16 mV/nm in Figure 1(d) and (e), respectively. The fact that polytype NCs exhibit internal fields of tens of mV/nm inside the core is remarkable. It was not trivial that in spite of the cubic symmetry of the core lattice, such magnitude could be achieved. In fact, the fields are strong enough to open venues

for exciton wave function modulation via internal fields, as we recently suggested for pure WZ NCs.[22]

The presence of an alloyed interlayer does not substantially change the above picture. As shown in Figure 1(f), the interlayer introduces a smooth confinement potential between core and shell. However, the strain reduction of the effective offset between core and shell and the built-in field inside the core are similar to those in abrupt interface NC. This is because the compressive strain inside the core remains the same with or without interlayer (see Supporting Information), as it is ultimately set by the lattice mismatch with the thick CdS shell. The moderate influence of alloyed interlayers on the electronic structure is consistent with similar findings in pure ZB NCs.[20]

We next illustrate the exciton wave function dependence of thick-shell polytypic NCs on the core size. Figure 2 shows the squared electron-hole overlap (proportional to radiative lifetimes) of ZB/WZ NCs with abrupt interface, alloyed interlayer, and –for comparison– that of a pure WZ NC. In all cases the pattern is similar. At first, increasing core size leads to larger overlap. This is the typical behavior of quasi-type-II systems.[17] The hole ground state is confined inside the core for any size, because of the large valence band offset. By contrast, the electron sees a shallow potential barrier. Hence, when the core is small, the electron ground state spreads into the shell to minimize kinetic energy, but as the core becomes larger it gradually localizes inside the core well. For larger cores (e.g. $R > 2$ nm for WZ NCs), however, the electron-hole overlap decreases again. This is because the effect of the built-in fields scales with the core size, which enables a gradual transition towards type-II excitons, with well separated electron and hole, potentially leading to long radiative lifetimes.[22]

We note that this behavior is shared by pure WZ and polytypic NCs, but it is absent in pure ZB NCs where no internal fields appear.[20] The resulting electron-hole overlaps are similar for WZ and polytypic NCs, consistent with experiments showing similar lifetimes.[11,17,23] However, the transition towards type-II exciton takes place faster for pure WZ NCs than for ZB/WZ ones owing to the stronger internal field. We then predict radiative lifetimes of polytypic NCs should be systematically shorter than those of WZ NCs when the core is large. The seemingly different

behavior of alloyed NCs in Figure 2 is simply because in our simulation the interlayer increases the effective size of the core.

Maybe we should add ZB/ZB calculation in figure and see if overlap is larger, for H=5 nm

Figure 2: Electron-hole overlap as a function of core size for the three models of CdSe/CdS NCs. In every case, for large enough radius the internal fields make the overlap decreases. Solid black line: ZB/WZ NC, abrupt interface. Dashed black line: ZB/WZ NC with alloyed ZB interlayer. Dotted blue line: WZ/WZ NC, abrupt interface. In all NCs $H = 5$ nm. For the alloyed NC, the interlayer is 2 nm thick.

Figure 3 compares the electron and hole charge densities for a few low lying exciton states in the three prototypical CdSe/CdS NCs we consider. The wave function localization is similar for polytypic and pure WZ structures. For a typical core radius of $R = 1.5$ nm,[17] the electron ground state is largely confined inside the core, but the excited states already occupy the shell. The hole, instead, remains in the core owing to the large band-offset.

Figure 3: Excitonic electron and hole charge density in the three models of CdSe/CdS NCs, WZ/WZ (top panels), ZB/WZ (mid panels) and ZB/WZ with alloying (bottom panels). The charge densities are similar for polytypic and WZ heterocrystals. In all cases $R = 1.5$ nm and $H = 5$ nm.

Having studied polytypic CdSe/CdS NCs, we now turn to the case of pure CdSe polytypes. It is known that CdSe dots with ZB phase become unstable with increasing size.[4,5] In what follows we consider a colloidal CdSe dot with ZB phase, which at a certain volume starts growing in WZ phase, thus forming a fully CdSe yet polytypic core/shell NC. The resulting band profile, shown in Figure 4(a), is quite peculiar. Neglecting built-in fields (dashed line), the band alignment is staggered, with the bottom of the conduction band in the core and the top of the valence band in the shell. Notice however that the band-offsets are small (94 meV for the conduction band, *XXX* for the valence band). The NC is strain free (as mentioned before, the lattice constants of CdSe in [111]-grown ZB and in WZ are nearly identical), so there is no piezoelectricity. Yet, if the crystal growth is ordered, spontaneous polarization should be present. In fact, the polarization mismatch between the WZ shell ($P_{sp} = -6$ mC/m^2) and the ZB core ($P_{sp}^{CdS} = 0$ mC/m^2) is largest than in

CdSe/CdS heterocrystals. Consequently, strong internal fields build up (~ 20 mV/nm in the core, ~ 50 mV/nm in the shell).

The band profile described above makes the electronic structure of CdSe polytype NCs very sensitive to the geometry. To illustrate this point, in Figure 4(b) we show the excitonic electron and hole charge densities in a NC with thin (left column) and thick (right column) shell. When the shell is thin, electron and hole are largely localized inside the core, but when the shell becomes thicker the potential drop along the c-axis becomes very large (tenths of V) and charges move towards opposite sides of the shell. The charge separation leads to dark excitons for much thinner shells than in CdSe/CdS, as one can notice by comparing Figure 4(c) with Figure 2.

Figure 4: Band structure of polytypic CdSe-only NCs with ZB core and WZ shell. (a) Band profile. Solid (dashed) lines are used when including (neglecting) spontaneous polarization. Notice the type-II band alignment, with strong built-in electric fields. (b) Exciton's electron (top row) and hole (bottom row) charge densities, for a NC with $R = 1.5$ nm and thin ($H = 1$ nm, left column) or thick ($H = 3$ nm, right column) shell. If the shell is thick, the strong internal field separates electron and hole completely. (c) Electron-hole overlap as a function of NC shell thickness for several radii. The exciton becomes dark rapidly.

Figure 4 evidences that polytypic CdSe are potentially interesting structures for tuning carrier-carrier interactions, which is an important capability for several opto-electronic applications.[17,29] The combination of low band offsets and strong built-in fields allows for an efficient yet controllable exciton lifetime through the core and shell thickness. The polytypic nature may make polarization effects more robust than in WZ CdSe dots. In the latter structures, permanent dipole moments have been reported and often ascribed to spontaneous polarization.[27,30,31] The polarization strength is however believed to be quenched by several surface effects, including screening by passivating ligands, surface reconstruction and relaxation,[32] non-stochiometric cation termination of the NCs,[33] and migration of mobile surface charges.[34] In polytypical structures, the internal field inside the core is related to the polarization mismatch at the core/shell interface, which is far from the external surface and hence less sensitive to such effects.[35,36] On the other hand, as compared to CdSe/CdS heterostructures, the low band offsets of CdSe-only polytypes should imply weaker Auger recombination,[37,38] which is convenient for several optical applications.

Conclusions

We have studied the influence of polytypism in ZB/WZ core/shell NCs using k·p theory. In CdSe/CdS heterocrystals, we find quantum confinement, strain and internal electric fields are comparable to those of pure WZ NCs. Interfase alloying softens the confinement potential, but leaves strain and built-in fields essentially unaltered. As a result, low-energy excitons of polytypic NCs have quantitatively similar properties to their WZ counterparts, which is consistent with experiments. We predict however that spontaneous polarization is less pronounced than in WZ heterocrystals, which should translate into shorter radiative lifetimes when cores are large.

In CdSe/CdSe NCs, polytypism leads to a core/shell structure with low band offsets and no strain. Spontaneous polarization emerges as a leading factor determining the electronic structure. If the total volume of the NC is small, quantum confinement and Coulomb interaction keep electron and hole close to each other, but with increasing volume the strong internal fields (tens of mV/nm) lead to a fast transition towards a type-II system, with well separated electron and hole charges. The high sensitivity of the exciton wave function to the NC volume suggests these could be advantageous structures for opto-electronic applications where tuning of carrier-carrier interactions is required, such as lasing, non-linear optics, photodetectors and photovoltaic cells.[29]

Acknowledgement

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