Charge Injection, Charge Trapping and Charge Transfer in Quantum-Dot Solids

SIMON CHRISTIAN BÖHME

Charge Injection, Charge Trapping and Charge Transfer in Quantum-Dot Solids

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus Prof.ir. K.C.A.M. LUYBEN, voorzitter van het College voor Promoties,

> in het openbaar te verdedigen op dinsdag 3 maart 2015 om 15:00 uur

> > door

Simon Christian BÖHME Diplom-Physiker (Universität Konstanz, Duitsland) geboren te Friedrichshafen, Duitsland Dit proefschrift is goedgekeurd door de promotoren:

Prof. dr. L.D.A. Siebbeles Prof. dr. D. Vanmaekelbergh

Copromotor:

Dr. A.J. Houtepen

Samenstelling promotiecommissie:

Rector Magnificus
Prof. dr. L.D.A. Siebbeles
Prof. dr. D. Vanmaekelbergh
Dr. A.J. Houtepen
Prof. dr. B. Dam
Prof. dr. F.M. Mulder
Prof. dr. E. Vlieg
Dr. I. Infante

voorzitter Technische Universiteit Delft, promotor Universiteit Utrecht, promotor Technische Universiteit Delft, copromotor Technische Universiteit Delft Technische Universiteit Delft Radboud Universiteit Nijmegen Vrije Universiteit Amsterdam

Research described in this thesis was carried out in the framework of the Joint Solar Programme (JSP) of HyET Solar, Nuon and the Foundation for Fundamental Research on Matter (FOM), which is part of The Netherlands Organisation for Scientific Research (NWO).



ISBN 978-94-6108-921-2

Copyright © 2015 by S.C. Böhme Cover graphic: artist's impression of the title of this thesis Cover graphic designed by: Martin Härtlein, FUZZYFUSION, www.fuzzyfusion.de Printed by: Gildeprint – The Netherlands



An electronic version of this thesis is freely available at http://repository.tudelft.nl

TABLE OF CONTENTS

1	Inti	roduction	1	
	1.1	Quantum Dots	1	
		1.1.1 Electronic Structure	3	
		1.1.2 The Surface	7	
		1.1.3 Synthesis	9	
	1.2	Quantum-Dot Solar Cells	10	
	1.3	Band Offset and Charge Separation	12	
	1.4	Trapping and Recombination	15	
	1.5	Relevance of Research on Photovoltaic Energy Conversion for a		
		Sustainable Energy Future	17	
	1.6	Outline of this Thesis	19	
	REF	ERENCES	20	
2	Ele	ctrochemical Charging of CdSe Quantum-Dot Films:		
	Dep	pendence on Void Size and Counterion Proximity	27	
	2.1	Introduction	27	
	2.2	Experimental Details	29	
	2.3	Determination of $1S_e$ and $1P_e$ Energy Levels	31	
	2.4	Void Size Limited Electron Injection	35	
	2.5	Ligand Length and Cation Size	37	
	2.6	Comparison to Ionic Lattices	39	
	2.7	Conclusions	41	
	REFI	ERENCES	43	
	APP	ENDIX A	47	
3	In S	itu Spectroelectrochemical Determination of		
	Bar	d Offsets in Quantum-Dot Films	53	
	3.1	Introduction	53	
	3.2	Experimental Details	57	
	3.3	Energy Levels in QD Films	61	
		3.3.1 Spectroelectrochemical Assessment of the 1Se Electron Level in Films		
		of PDSe QDs	61	
		3.3.2 Energetics of Electron Injection	65	
		3.3.3 Spectroelectrochemical Assessment of Confined Electron Levels in Films of CdSe ODs	69	
	3.4	Band Offset in a QD Heterostructure	71	
	3.5	Dependence of Band Offset on QD Size	76	
	3.6 Conclusions			
	REFERENCES			
	APP	ENDIX B	83	

4	Electrochemical Control over Photoinduced Electron				
	Transfer and Trapping in CdSe-CdTe Quantum-Dot Solids				
	4.1 Introduction	89			
	4.2 Experimental Details	90			
	4.3 Steady-State and Transient Absorption	92			
	4.4 Fast Electron Trapping in CdTe QD Films	95			
	4.5 Demonstration of Electron Transfer in CdTe-CdSe Multilayer Films	99			
	4.6 Electrochemical Gating Controls Electron Trapping	102			
	4.7 Electrochemical Gating Enables Electron Transfer	105			
	4.8 Conclusions	107			
	REFERENCES APPENDIX C				
5	The Density of Trap States and Auger Mediated Electron				
	Trapping in CdTe Quantum-Dot Solids	125			
	5.1 Introduction	125			
	5.2 Experimental Details	126			
	5.3 Transient Absorption Reveals Electron Dynamics	130			
	5.4 Time-resolved Photoluminescence Reveals Hole Contribution	133			
	5.5 Fitting of Electron and Hole Dynamics	135			
	5.6 DFT calculations relate trapping to structural properties of the QD surface	138			
	5.7 Auger Mediated Electron Trapping and DOTS	142			
	5.8 Conclusions	146			
	REFERENCES	147			
	APPENDIX D	150			
Su	nmary	157			
Sa	nenvatting	161			
Ac	knowledgments	167			
Cu	rriculum Vitae	171			
Lis	t of Publications	173			

1. INTRODUCTION

1.1. QUANTUM DOTS

Semiconductor nanocrystals, also called quantum dots (QDs), have been attracting considerable attention over the past three decades with potential applications as biomarkers, in LEDs, solar cells, photodetectors, or thermoelectrics. A large share of this interest roots in the size-dependence of their optoelectronic properties, resulting from their spatial extent of only a few nanometers. For example, the apparent color of CdSe QDs can be conveniently tuned throughout the entire visible spectrum. Figure 1.1a shows the absorption spectra (solid lines) and photoluminescence spectra (dashed lines) of CdSe QDs ranging from 2.5 nm to 5 nm in diameter. When their size is reduced, the photoluminescence band and the absorption onset shift to the blue and spectral features become more pronounced. Both can be explained by a transition of their properties from being more bulk-like to more molecule-like. Figure 1.1b sketches this situation, depicting the discrete energy levels in QDs. Presenting an intermediate case between two extremes, a QD can either be considered a large molecule (consisting of hundreds to thousands of atoms) or a crystal whose dimensions have been reduced from infinite (bulk) to a small chunk of several nanometers. Choosing the latter, one describes the "squeezing" of the electron and hole wave functions to spatial extents smaller than the Bohr radius, the "natural" size of an electron-hole pair in a macroscopic (bulk) crystal. This confinement increases the kinetic energy of both charge carriers, which is now not only given by crystal material or temperature, but to a large extent by the size of the crystal. The nanocrystal is termed a nanoplatelet, nanosheet or quantum well, if it is confined in one dimension, a nanorod or nanowire, if confined in two dimension, and a quantum dot (QD), if confined in three dimensions.



Figure 1.1 a) Absorption spectra (solid lines) and photoluminescence (PL) spectra (dotted lines) of CdSe QDs of various sizes. The size-dependent red-shift of the 1S maxima is indicated with an arrow. Absorption spectra were normalized at 400 nm, PL spectra at the respective 1S maximum. (b) Particle-in-a-sphere model depicting the increased band gap $E_{g,QD} > E_{g,bulk}$ of a QD and its discrete energy levels nl. For comparison, to the left and right the energy level diagram of a molecule and a bulk crystal is displayed, respectively. (c) High resolution STEM image of a PbSe QD. Crystal orientations are denoted in brackets. The upper left inset shows the proposed shape of a cube with truncated [110] and [111] facets. The lower left inset shows a Fourier transformation of the STEM image, revealing the rock salt crystal structure. Courtesy of W. H. Evers, TU Delft. (d) Kinetic confinement energies of energy levels nl. The quantum number n is represented as a number, while l is given as a letter (S for l = 0, P for l = 1, ...).

Figure 1.1c displays a high resolution STEM image of a PbSe QD, revealing the ordered arrangement of Pb and Se atoms into a crystalline lattice of an extent of a few nanometers. Different crystal facets terminate the lattice, indicated by their Miller indices. Not seen in this STEM image is that organic ligands form a capping layer which terminates the crystal surface. This capping layer is discussed in section 1.1.2. Preceding this section, section 1.1.1 introduces the electronic structure of a (bare) QD.

1.1.1. ELECTRONIC STRUCTURE

A first estimate of the extra kinetic energy due to size-confinement can be obtained with the particle-in-a-box model and Heisenberg's uncertainty relation $\Delta x \Delta p_x \ge \hbar/2$, in which Δx is the size of the box in x direction and Δp_x is the momentum of the particle in x direction. In case of the QD, the box can be considered a cube ($\Delta x = \Delta y = \Delta z$), with $\Delta p \equiv \Delta p_x + \Delta p_y + \Delta p_z = 3\Delta p_x$, and the kinetic energy can be approximated by $3\Delta p^2/(2m_0) = 3\hbar^2/(8m_0\Delta x^2)$, where m_0 is the mass of the electron. This predicts a dependence on the square of the reciprocal size of the QD. A better description of an electron in a QD can be obtained by solving the (time-independent) Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2 + V(\mathbf{r})\right)\Psi(\mathbf{r}) = \mathbf{E}\,\Psi(\mathbf{r})$$
(1.1)

for a particle in a sphere of radius R with an infinite potential well at the QD boundary

$$V(\mathbf{r}) = \begin{cases} V_0 & , \mathbf{r} < R \\ \infty & , r \ge R \end{cases}$$
(1.2)

where V_0 is the bulk potential, in case of the electron the conduction band (CB) energy in Figure 1.1c. The wave functions $\Psi(\mathbf{r})$ in Equation (1.1) then have the form

$$\Psi(\mathbf{r}) = \Psi_{nlm}(\mathbf{r}, \theta, \phi) = C \cdot J_1(\mathbf{k}_{nl}\mathbf{r}) \cdot \mathbf{Y}_l^m(\theta, \phi)$$
(1.3)

where *C* is a constant, $J_l(\mathbf{k}_{nl}, r)$ are spherical Bessel functions of lth order and $\mathbf{Y}_l^m(\theta, \phi)$ are spherical harmonics. Due to the infinite potential well, $J_l(\mathbf{k}_{nl}, r) = 0$ at the QD surface, allowing only momenta k_{nl} which satisfy the condition

$$k_{nl} = \frac{1}{R} \zeta_{nl} \tag{1.4}$$

where ζ_{nl} is the *n*th zero of the Bessel function $J_l(\mathbf{k}_{nl} r)$. This yields discrete eigenvalues for the energy

$$E_{nl} = V_0 + \frac{\hbar^2 \zeta_{nl}^2}{2m_0 R^2}$$
(1.5)

with the quantum confinement term displaying the already deduced $1/R^2$ dependence on the QD radius. Each energy level E_{nl} is (2l + 1)-fold degenerate and the confinement term of the first ten levels is depicted in Figure 1.1d. Similar to molecules, the radial quantum number n is given as a number and the angular momentum l as a letter (S for l=0, P for l=1,...).

In QDs, the spacing between adjacent E_{nl} levels typically decreases towards higher energies, partially due to finite potential barriers. Therefore, a typical QD absorption spectrum as shown in Figure 1.1a is characterized by pronounced peaks due to sizeconfinement close to the band gap but is bulk-like at higher energies, typically starting from ~ 3eV.

Table 1.1 Electron and hole effective masses¹ in CdSe, CdTe, PbSe and PbS, the materials studied in this thesis.

	CdSe	CdTe	PbSe	PbS	
m_e^* / m_0	0.13	0.09	0.05	0.09	
m_{h}^{*} / m_{0}	0.45	0.12	0.05	0.09	

So far, the particle-in-a-sphere model considered a sphere filled with vacuum. To account for the periodic potential created by all atoms in the nanocrystal, one can refine this model with an "effective mass approximation"² in which the electron mass m_0 in Equation 1.5 is replaced by an effective mass m_e^* or m_h^* for electrons or holes, respectively. These effective masses are defined as the reciprocal curvature of the energy bands in k-space and express how easily an electron or hole moves in an (externally applied) electric field. Table 1.1 gives the (band edge) effective masses of the materials studied in this thesis. From the larger effective mass of holes as compared to electrons in CdSe and CdTe, one can predict that hole levels are more closely spaced than electron levels. In PbS and PbSe, both electron and hole levels should show similar quantum confinement.

Next to the kinetic energy, also Coulomb interactions of charge carriers in a confined volume are increased, due to enhanced wave function overlap. In case of an electron-hole pair, the quasi-particle produced after optical excitation, the total energy is lowered and given by the Brus equation²⁻⁴

$$E_{nl}^{opt}(R) = E_{gap,bulk} + \frac{\hbar^2}{2R^2} \left(\frac{\zeta_{n_e l_e}^2}{m_e^*} + \frac{\zeta_{n_k l_h}^2}{m_h^*} \right) + E_{eh}^{dir} + \sum E^{pol}$$
(1.6)

where $E_{g,bulk} = E_{nl}^{opt} (R \to \infty)$ is the bulk band gap, m_e^* and m_h^* are the electron and hole effective masses, E_{eh}^{dir} is the direct Coulomb attraction of the electron-hole pair and the remaining term contains polarization energies, arising from the Coulomb interaction of a charge with its image charge across the QD boundary. These electrostatic terms are given by⁴

$$E_{eh}^{dir} \approx -\frac{1.79e^2}{4\pi\varepsilon_0\varepsilon_{in}R}$$
(1.7)

and

$$\sum E^{pol} = E_e^{pol,self} + E_h^{pol,self} + E_{eh}^{pol,cross}$$
(1.8)

with

$$E_{e}^{pol,self} = E_{h}^{pol,self} \approx \frac{e^{2}}{8\pi\varepsilon_{0}R} \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in}\varepsilon_{out}}$$
(1.9)

$$E_{eh}^{pol,cross} \approx -\frac{e^2}{4\pi\varepsilon_0 R} \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in}\varepsilon_{out}}$$
(1.10)

in which ε_{in} and ε_{out} are the dielectric constant inside and outside of the QD, $E_e^{pol,self}$ and $E_h^{pol,self}$ are the electron and hole polarization energy and $E_{eh}^{pol,cross}$ is the cross-polarization energy. The latter describes the interaction of a charge with the image charge of the opposite type of charge carrier. The former two describe the interaction of a charge with its image charge and is the energy to pay (win) due to loss (gain) of

solvation, in case the dielectric screening \mathcal{E}_{out} outside is smaller (larger) than the screening \mathcal{E}_{in} inside. Sometimes, these solvation terms are referred to as "self-energies". Equations (1.9) and (1.10) confirm the intuitive picture that for an exciton, in first approximation, all polarization terms cancel, leaving the Coulomb and kinetic confinement terms as the only contribution to the size-dependent band gap. In case of weak confinement, *i.e.* for large particles, the kinetic confinement energy (increasing as $1/R^2$) is still smaller than the Coulomb energy (increasing in magnitude as 1/R). However, it exceeds the Coulomb term in case of strong confinement, *i.e.* for small particles. In the latter case, the Coulomb contribution is usually treated using perturbation theory.

Equations (1.6) to (1.10) were given for the case of an exciton inside a QD, as studied in optical experiments. In case of (spectro-)electrochemical experiments as presented in this thesis, one needs to consider the case of an unequal number of electrons and holes inside the QD as well as interaction with charges outside a QD. Chapter 3 briefly discusses how the above equations may be extended to include these cases.

The effective mass approximation presented in Equation (1.6) is the minimum level of accuracy to understand the main trends and concepts of energy levels in QDs. A satisfactory description of optoelectronic properties, however, requires further refinements by including exchange interaction, shape anisotropy, internal crystal field anisotropy, nonparabolicity of bands, and mixing of bands (intervalley and interband scattering).⁵⁻⁷ The most accurate calculations up to date include many-body interactions *via* atomistic models such as the (semi-)empirical pseudopotential method (EPM),^{6, 7} tight-binding calculations,^{4, 8, 9} or DFT calculations.¹⁰⁻¹²

In general, it has been found that the quantum numbers n and l originating from the effective mass approximation are not sufficient to describe a quantum confined state. The angular momentum of the atomic orbitals in the lattice (*i.e.* the symmetry of the Bloch function) and the spin S must be included to yield the total angular momentum F = l + S + L as a good quantum number. Therefore, the notation $n_c l_{c,F_c}$ has been established to describe quantum confined states. ¹³The index c = e, h describes which type of charge carrier, *i.e.* if electron or hole, is considered, and F_c denotes their total angular momentum. Accordingly, optical transitions from hole to electron states are denoted as $n_h l_{h,F_h} n_e l_{e,F_e}$. Sometimes, the index c or F_c is omitted if designation remains sufficiently clear: for example, " $1S_{3/2} 1S_e$ " is commonly used to describe the lowest-energy transition in Cd chalcogenide QDs.

The absorption spectrum in Figure 1.1a is not a sum of delta-functions ("spike-like", as would be the case for discrete energy levels), but shows considerable broadening of transitions. This is due to homogeneous (Lorentzian) and inhomogeneous (Gaussian) broadening. Homogeneous broadening is typically on the order of a few μeV^{14} only and arises from the finite lifetime of the excited states (on the order of *ns*), dictated by Heisenberg's uncertainty relation. In contrast, inhomogeneous broadening accounts for most of the observed line width: due to the $1/R^2$ dependence of quantum-confined energy levels, even the currently achieved small size dispersions of ~ 5% lead to a broadening of absorption transitions of tens to hundreds of *meV* line width.

1.1.2. THE SURFACE

In the preceding section, the QD was assumed to be bare, surrounded by vacuum or a dielectric medium. While such a description might yield qualitative descriptions such as the size-dependent change of the band gap, a satisfactory description of optoelectronic properties needs to account for the surface of a QD. At the surface, the crystal symmetry is broken, giving rise to facet formation, under-coordinated bonds, surface reconstructions with accompanying anomalies in bond length and angle, as well as room for physisorbed or chemisorbed species. In many cases, this manifold of surface configurations gives rise to electron and hole trap states within the band gap, which effectively quench excitations in a QD. A common strategy to (electronically) passivate these detrimental surface states is to attach organic ligands to the terminating atoms of the crystal lattice, as depicted schematically in Figure 1.2a. If the formed bond is sufficiently strong, the bonding and antibonding orbital can be pushed outside the band gap, eliminating mid-gap states. In most applications, such mid-gap states would otherwise limit device performance, as they *e.g.* reduce photo-voltage and photo-current (in solar cells) or the luminescence efficiency (in LEDs).

However, the functionality of the capping layer exceeds the mere role of eliminating trap states within the band gap. Ligands have been shown to represent a tool to shift energy levels by as much as 1.5 eV,¹⁵ influence the photoluminescence quantum yield,^{16, 17} relax size-confinement,¹⁸ or enable charge transfer and charge transport.¹⁹⁻⁴⁰ Hence, the option to tune optoelectronic properties of QDs *via* their ligands poses both challenges and opportunities for a careful design of their properties. An illustrative example for the latter

can be found in surface states of very small QDs: while they may quench the band edge luminescence, they simultaneously give rise to a broad and tunable (trap-related) emission over the whole visible range, enabling white light LEDs comprised of a single type of QD.⁴¹

Next to organic ligands, inorganic ligands are currently explored as a promising alternative passivating species with prospects of additional control over photoluminescence efficiency, electron mobility, doping, magnetic susceptibility, and catalytic performance.⁴² A third, and widely used, option to passivate a QD is to grow an inorganic shell around the core. Such core-shell QDs offer improved stability and, in case of careful engineering of the core-shell interface, enable near-unity photoluminescence quantum yields.⁴³



Figure 1.2 Schematic of a QD (blue filled circle) surrounded by organic capping ligands (zigzag lines), in dispersion (a) and in a film (b). Note that the QDs and ligands are not drawn to scale. To stabilize a QD in dispersion, typically longer alkylchains (long grey zigzag line, e.g. oleic acid) are used. To fabricate conductive films, ligands are usually exchanged to shorter ligands of a length of only a few C atoms (short green zigzag lines, e.g. 1,2-ethanedithiol).

A major advantage of organic ligands, however, is their ease of replacement by other types of ligands. This roots in their dynamic equilibrium with the crystalline core, indicated by an arrow in Figure 1.2a: while the time-averaged concentration of ligands may be constant, individual ligands fluctuate between being bound to the surface and being desorbed (free), at a rate which may exceed 50 Hz.⁴⁴ Moreover, a recent STEM

study of CdSe QDs proposed significant motion of surface atoms upon excitation by a photon or electron.⁴⁵ This highly dynamic configuration of the surface can be exploited to quantitatively exchange ligands by exposing the QDs to a non-solvent and simultaneously offering an excess of the new ligand to be attached. Films with almost an arbitrary choice of new ligands (see Figure 1.2) can be grown using such a replacement scheme, either in a Layer-by-Layer (LbL) fashion *via e.g.* sequential spin coating or dip coating, or as a post-processing treatment to the entire film by dipping the film into a solution containing the new ligand. A more detailed explanation of the Layer-by-Layer dip coating technique can be found in the experimental sections of the following chapters.

In general, a division of properties related to the surface and the bulk becomes blurry in the case of QDs, considering that about 10-50 % of all atoms of a QD are at the surface, for diameters in the range 10 to 2 nm.^{46, 47} Interaction with ligands are therefore crucial in the description of a QD's optoelectronic properties, as discussed in Chapters 2, 4 and 5 of this thesis.

1.1.3. SYNTHESIS

Semiconductor QDs of high quality (*i.e.* of small size dispersion and with low defect densities) can be grown *via* colloidal synthesis. At elevated temperatures (typically between ~ 80 °C and ~ 350 °C), an oversaturated solution containing inorganic precursor compounds and organic ligands reacts by forming nuclei of inorganic monomers, followed by growth of the monomers. Both nucleation and growth exhibit kinetic and thermodynamic barriers which can be tuned conveniently by *e.g.* the precursor concentration, temperature, or ligand interaction. Details to materials and reaction conditions of QD syntheses employed in this work can be found in the experimental sections of the following chapters. To achieve a small size-dispersion (and therefore uniform optoelectronic properties), a "hot-injection" method is commonly used, in which a cold precursor is rapidly injected into a hot solution containing the complementary precursor, under vigorous stirring. Such procedure assures that nucleation occurs as a concerted action, *i.e.* for all formed monomers at the same time. The concomitant reduction in precursor concentration and temperature then oppresses further nucleation events while still allowing growth of the formed nuclei.

1.2. QUANTUM-DOT SOLAR CELLS

The size-tunable band gap of QDs and prospects of cheap, low temperature solution processing, on flexible substrates,⁴⁸ are of interest for application in devices such as LEDs and solar cells. In LEDs, quantum confinement is an advantage as the discrete energy levels result in "single color" emission of narrow band width. This allows a high color rendering index, *i.e.* the color of objects appears very similar as it would under "natural" (black-body) illumination. Displays using QDs have recently been introduced to the market.^{49, 50} In solar cells, on the other hand, absorption rather than emission is the quantity of interest. The size-tunability of the entire absorption spectrum allows optimization with respect to the solar spectrum and, thus, increases the choice of materials to be used as absorber. For example, the band gap of silicon can be realized while avoiding the drawback of an indirect band gap as in silicon. In general, materials with a direct band gap allow the absorber layer to be thinner, as their absorption is stronger. This lowers material costs and enables flexible devices. The important added bonus is that lower diffusion lengths are required and, hence, lower purity. This means low cost synthesis techniques may be used.

Furthermore, QDs hold promises for high-efficiency solar cells which (1) make use of multi-junctions,^{51, 52} or (2) extract the photo-generated charge carriers in a "hot" state, before carrier cooling,⁵³⁻⁵⁶ or (3) exploit the concept of carrier multiplication.^{52, 57-62} Solar cells based on concept (1) make use of multi-junctions to harvest light in a stack of different band gaps to better exploit the solar spectrum. This increases the maximum theoretically achievable efficiency to 40-60 %, depending on the number of junctions employed. Unlike conventional multi-junctions based on combinations of III-V semiconductors, e.g. Ge/GaInAs/GaInP, the ability to tune the band gap by QD size allow QD multi-junctions made of a single material and therefore elegantly circumvents problems arising from material discontinuities such as lattice mismatches. Concept (2) states that higher photo-voltages can be achieved by extracting photo-generated charge carriers in a "hot" state, after electronic thermalization but before carrier cooling to the band edges, via selective energy contacts.^{54, 55} The reported slow (nanosecond) carrier cooling in core-shell QDs⁶³ improve the likelihood of this process. However, while theoretically efficiencies up to 66 % could be achieved,⁵⁴ no convincing demonstration of a working device has been presented up to date. Concept (3) relies on a process termed "carrier multiplication", which produces two or more electron-hole pairs at the cost of one photon. In this process, a photon with an energy exceeding twice the band gap produces a high-energy electron-hole pair which relaxes to the band edges by promoting valence band electrons across the band gap *via* impact ionization, thereby creating additional electron-hole pairs. Full utilization of this process increases the maximum theoretically achievable efficiency of a single band gap solar cell from 33.7% (Shockley-Queisser limit) to 44.4%.^{58, 64} The optimum band gap shifts from 1.34 eV to ~ 0.7 eV.⁵⁸ The occurrence of carrier multiplication has been proven, both in solution^{57, 65-67} and in films.⁶⁸⁻⁷¹ The most compelling evidence has been offered in working solar cells, where external quantum efficiencies exceeded 100 %.⁶¹



Figure 1.3 Schematic of selected charge carrier dynamics in a QD solar cell following photo-excitation. Once free charges are formed (1), carriers may be collected at external electrodes to generate a photovoltage and photocurrent (2a). Charge trapping (2b) competes with carrier collection, leading to lower photovoltaic efficiency (3a), decreasing to a minimum if further recombination pathways are available (3b).

QD solar cells have shown a fast learning curve in their first decade of existence,⁷² from < 1 % in 2005 to a record efficiency of 8.6 % in 2014.⁷³⁻⁷⁵ QD architectures building on Schottky junctions, depleted heterojunctions, tandem cells and quantum funnels have been explored.⁷⁶ Already today, many niche markets can be assessed with QD solar cells, thanks to the manifold of available (and partially demonstrated) solution processing techniques, *e.g.* spin-coating, Layer-by-layer (LbL) dipcoating, spray-painting, ink-jet

printing, or reel-to-reel printing.⁷⁶ High-efficiency devices have been demonstrated on curved and flexible substrates,⁴⁸ enabling the use of more unusual substrates, such as textiles. QD solar cells might even compete in the race for bigger shares in global electricity generation. Depending on the further development of the market dominating Si based solar cells, an efficiency improvement of QD solar cells up to 10-15 % would be needed to offer a competitive cost-efficiency ratio, the figure of merit for large scale implementation of any type of solar cell.⁵¹ To do so, one might expect that a higher mobility of charges due to increased inter-particle coupling in a QD film might fuel this development. However, it has recently been proposed that a main obstacle in reaching higher efficiencies are not low mobilities, but high defect densities,⁷³ see Figure 1.3. Next to realizing low trap densities, a second major task for photovoltaic applications is to separate charges in order to produce a photocurrent which can be extracted via external electrodes. Generally, this is achieved by incorporating a band offset in the material stack, see section 1.3. In this thesis, both challenges are being addressed: chapter 3 presents a method to determine band offsets in situ and chapter 4 reports charge separation rates, while chapters 4 and 5 move the spotlight to trapping at defect sites.

While careful engineering of the charge carrier dynamics, *i.e.* the rate of charge carrier multiplication, cooling, transfer, trapping, transport and collection may enable higher efficiencies and therefore an attractive market position of QD solar cells, several other questions are still to be addressed in future fundamental and applied research, such as: (1) material scarcity and (2) toxicity of currently employed elements (PbS, PbSe, CdSe, CdTe, *etc.*), and (3) air-stability without expensive and tedious encapsulation strategies.

1.3. BAND OFFSET AND CHARGE SEPARATION

A common strategy in the design of solar cells is to incorporate a rectifying junction which separates electrons and holes. This can be a heterojunction of two different materials such as the donor-acceptor junction in organic photovoltaics which relies on a band offset of the two comprising materials, see Figure 1.4a. Alternatively, it can be a homojunction such as the p-n junction in Si solar cells, which forms a built-in field due to a difference in doping level and thereby creates a driving force for charges separation, see Figure 1.4b. Here, we will briefly discuss the motivation for charge separation and give examples of how a band offset (or built-in field) can be realized and determined.



Figure 1.4 (a) Donor-acceptor interface in a molecular heterojunction, depicting the respective LUMO and HOMO. If an optical excitation (red pulse) creates an electron (filled circle) – hole (open circle) in the donor phase, the pair can dissociate by transferring the electron to the acceptor. This is energetically allowed, due to a difference in the respective electron affinities χ_{donor} and $\chi_{acceptor}$, termed the band offset. (b) P-n junction of an inorganic semiconductor device at short circuit, characterized by a uniform Fermi level throughout the device. A space-charge region (shaded area) develops as electrons from the n-doped region accumulate at the p-doped side of the interface and holes from the p-doped region accumulate at the n-doped side of the interface. This gives rise to a built-in electric field and band bending, facilitating the separation of charges after optical excitation.

In organic solar cells, the exciton binding energy is strong (> $k_B T$) and an electron-hole pair likely annihilates *via* geminate recombination before it dissociates. While advantageous in lighting applications (such as OLEDs), a solar cells requires charge separation, as electron and hole need to be extracted in separate contacts to produce a photo-current and photo-voltage. Therefore, organic solar cells typically employ an interface between an (electron) "donor" (molecule) and an (electron) "acceptor" (molecule), as depicted in Figure 1.4a. The free energy difference between donor and acceptor increases the likelihood of charge separation, as only for one type of charge carrier transfer to the neighboring material is energetically a down-hill reaction. The depicted case is also referred to as "type-II" band offset. Due to charge separation, the lifetime of both charge carriers can be increased. Moreover, the staggered band alignment leads to rectifying behaviour with preferential carrier collection at opposite electrodes, generating a photo-voltage and photo-current. In inorganic (bulk) solar cells, such as Si solar cells, the exciton binding energy is typically low, due to higher dielectric constants as well as smaller effective masses. Consequently, photo-generated electron-hole pairs dissociate spontaneously into free charge carriers, without the aid of an interface. Nevertheless, electrons and holes still need to be collected at opposite electrodes in order to produce a photocurrent. To do so, Si solar cells rely on a built-in electric field produced by a p-n-junction, developing when a pdoped (electron deficient) and n-doped (electron rich) material is brought into contact, see Figure 1.4b. Equilibrium, *i.e.* a shared Fermi level throughout the device, is reached by electrons accumulating in the p-doped side of the interface and holes accumulating in the n-doped side of the interface, creating a "space-charge region". As a result, electrons in conduction and valence band experience "band bending", which separates the charges spatially: after optical excitation, electrons and holes in the space-charge region move towards opposite ends, towards the n-doped and p-doped region, respectively. The spatial separation into separate domains ensures that electrons and holes are predominantly collected at opposite electrodes, enabling exploitation of a photo-current and a photo-voltage. An additional advantage is that outside the space charge region the lifetime τ of the majority charge carrier (electrons in the n-doped layer and holes in the p-doped layer) is increased as recombination with the now scarcely available minority charge carrier is less likely. This increases the diffusion length $L = \sqrt{D\tau}$, D being the diffusion coefficient.

Quantum-Dot junctions form an intermediate case, resembling either organic devices (forming a band offset of the donor-acceptor junction) or inorganic solar cells (featuring band bending in a p-n junction). The closer analogy depends on *e.g.* the dielectric constant and effective mass of the employed materials. In 2005, Gur et al.⁷⁷ imitated the organic donor-acceptor junction by fabricating a type-II heterojunction of CdTe and CdSe QDs, thereby significantly improving QD solar cell efficiencies (up to 3 %).

Their material choice was motivated by the large range of size combinations, over which these two materials form a type-II band offset, due to their ~ 0.5 eV difference in both bulk ionization energy and bulk electron affinity.⁷⁸ While cells made from the respective single materials only showed modest photovoltages and no rectifying behavior, a bilayer of both materials exhibited significantly higher photovoltages and rectifying behavior. This showed that the single material cells lack contact selectivity, while the donor-acceptor interface is necessary for producing a photovoltaic effect. A similar result using different means is achieved in the current record QD solar cells based on ZnO

nanoparticles and PbS QDs. Charges in these devices are very mobile, in some cases even showing band-like transport,^{35, 79} due to the large dielectric constant (\mathcal{E}_{opt} (PbS)=17)⁸⁰ and small exciton binding energy ($\langle k_B T \rangle$). While photogenerated excitons dissociate easily, charges still need to be guided to opposite electrodes. To do so, these cells rely on band bending *via* doping, similar to the p-n junction described above. Variations on this theme include the depleted heterojunction and Schottky solar cells, or solar cells with a gradient in band alignment.⁸¹⁻⁸³

In both cases, careful engineering of the band alignment at an interface is key to optimizing device performances: while lacking or inappropriate band offsets prevent charge transfer, too large band offsets will reduce the open circuit voltage. In this respect, it is unfortunate that in the majority of cases, band offsets are unknown. References to literature values for the electron affinity or ionization potential are dangerous, as reported energies vary by as much as 1 eV. As discussed in more detail in Chapter 3, this can partially be attributed to differences in the dielectric environment and the measurement technique used. To enable a better estimation of the band offset for the material combination studied, both the description of fundamental processes in QDs and the optimization of device performances requires an *in situ* measurement of the band offset. In chapter 3, we suggest that spectroelectrochemistry enables such measurements.

1.4. TRAPPING AND RECOMBINATION

The primary challenge for photovoltaics is to scavenge photo-excited charge carriers into an external electrical circuit before they dissipate their energy in one of the many available decay processes. Figure 1.5 illustrates this problem by sketching the manifold of available charge carrier decay processes following photo-excitation of an electron-hole pair. To reach high photovoltaic conversion efficiencies, charge extraction as described in the previous section must be faster than the charge carrier decay. The first loss of free energy typically occurs *via* cooling: on a (sub-)picosecond timescale, charge carriers thermalize to their respective band edges by heating the crystal lattice (phonon emission) and/or coupling to ligand vibrations.^{63, 84-87} A variant of this process is Auger-assisted cooling, in which the excess energy of one type of carrier is transferred to the other type of carrier, which then thermalizes to the band edge.⁸⁸



Figure 1.5 Schematic of charge carrier decay mechanisms following photo-excitation (1) into a higher-energetic state (dashed lines). Electron and hole lose excess energy *via* cooling to the respective band edges (2), either *via* multi-phonon emission (zigzag lines) or *via* an Auger-type energy transfer (solid lines) and subsequent phonon emission. In the presence of defect states in the band gap, further energy loss occurs *via* trapping (3a), either by electron transfer according to Marcus theory, emitting phonons, or by an Auger-mediated trapping process. the ground state is recovered (3b) *via* Auger recombination, transferring energy to a third charge carrier, or *via* radiative recombination, emitting a photon.

Next to cooling, charge carriers may get trapped in defect states. This process has often been formulated using a Marcus-type transfer formalism. The energy lost in this process is accommodated by rearrangements of the nuclei and coupling to phonons. In case of trapping to a deep defect state, the associated large free energy loss would require emission of a multitude of phonons, rendering this process slow and therefore improbable. In this case, Auger-mediated trapping is more likely to occur: similar to Auger-assisted cooling, the excess energy is transferred to another charge carrier which dissipates its gained energy in a subsequent process. This possibility is discussed in Chapter 4 of this thesis. Note that both trapping processes might not only occur from the band edges, as suggested in Figure 1.5, but also from a "hot" (higher energy) state. Finally, charge carriers can decay to the ground state *via* radiative recombination (emission of a photon) or *via* Auger recombination (transfer of energy to another charge carrier). In principle, all described processes need to be studied, understood and steered to yield the best performance of the device of interest. In this thesis, we mainly focus on trapping and recombination, as these are major decay pathways impacting QD based devices such as solar cells and LEDs. Radiative recombination in QDs typically occurs on the nanosecond to microsecond time scale and can be observed using laser spectroscopy. Auger recombination and trapping can be considerably faster, occurring often on a picosecond time scale. To monitor these processes, sufficient time resolution is needed and in this thesis is achieved using ultrafast laser spectroscopy, namely transient absorption and time-resolved photoluminescence spectroscopy. Analysis of the decay of transient absorption and luminescence features can offer answers to questions such as: at which carrier density does Auger recombination become a major loss mechanism?⁸⁹ Or how fast much carrier collection at external electrodes occur to outcompete trapping?⁷³ In chapter 5, the magnifying glass is placed upon the trapping process in CdTe QD films. It aims to reveal the role of the surface in this process by studying the implications of ligand density and dangling bonds on the density of trap states.

1.5. RELEVANCE OF RESEARCH ON PHOTOVOLTAIC ENERGY CONVERSION FOR A SUSTAINABLE ENERGY FUTURE

Research described in this thesis was carried out in the framework of the Joint Solar Programme (JSP) of HyET Solar and the Foundation for Fundamental Research on Matter (FOM), which is part of The Netherlands Organisation for Scientific Research (NWO). In the following, we will give a motivation for research on photovoltaic energy conversion and discuss the possible role of solar cells in assuring a sustainable energy future.

The earth's fortunate position in relation to the sun enabled evolution to bring forth astonishing forms of life. Unfortunately, our today's ecological footprint is larger than the earth, *i.e.* we spend resources faster than they recover.^{90, 91} In addition, the emission of greenhouse gases due to combustion of oil, gas and coal alters the protective atmosphere surrounding the earth. As a result, the climate is currently changing to a larger extent than can be explained by natural fluctuations alone.⁹² In order to prevent undesirable consequences for the quality of life on earth,⁹³ especially for future generations, sustainability must be regained. 30 TW of carbon-emission-free power needs to be provided by 2050 to slow down and eventually stabilize the rise in global

temperature and sea level.⁹⁴⁻⁹⁶ This requires tremendous efforts by politics, industry and last, but not least, us consumers. Regarding more sustainable electricity generation, increasing the market share of solar cells is a promising solution: sunlight is available everywhere, arriving with predictable fluctuations, from a source that is effectively inexhaustible. As a result, the risk of geopolitical conflicts are lower than for the more traditional resources such as gas and oil. Competition of land use with agriculture is minimized since the needed area for photovoltaic installations is small. Given the tremendous energy flux from the sun reaching the earth (~ 1000 W/m²) and assuming 10 % efficiency of photovoltaic modules, 0.2 % of the earth's surface must be covered to provide 100 % of the world's electricity demand. In comparison, the Sahara covers 1.8 % of the earth's surface, roads 0.2 % and golf courses 0.02 %. First efforts are underway to exploit the photovoltaic potential of this otherwise "lost" areas.⁹⁷

During their guaranteed lifetime of 20-30 years, solar cells in photovoltaic modules operate emission-free. Only during their production, energy is required. However, this energy is harvested again within < 1 to 3 years after installation, depending on the used technology and location.98 That means, photovoltaic modules convert 10-30 times more energy than was used in their production. Consequently, about 95 % less greenhouse gases are emitted during the entire life-cycle of a photovoltaic module compared to the traditional burning of fossil fuels such as coal or gas.99 In 2011, the United Nations Environmental Programme Finance Initiative (UNEP FI) estimated the costs of climate change to US \$6.6 trillion in 2008, 11% of the value of the global economy at the time (GDP).¹⁰⁰ In a fair comparison, these costs must be accounted for when calculating the "true cost" of electricity generated via different technologies. According to a study by Epstein et al.,¹⁰¹ the negative impact on the climate translate into additional costs for coal of 12 US¢/kWh in 2011. Combined with other external costs such as arising from air pollution, toxicity and transport, the authors estimated the true cost of electricity converted by coal in the US to be 30-39 US¢/kWh in 2011, much higher than the residential market price of 12 US¢/kWh. In contrast, the true cost of electricity from photovoltaics (11-27 US¢/kWh) was barely higher than its market price of 10-25 US¢/kWh. Estimates for both technologies were already corrected for received subsidies. Hence, electricity from photovoltaics is cheaper than electricity from coal. Similar comparisons can also be made when estimating the true cost of nuclear energy.¹⁰² The above comparisons are expected even more favorable in future, as the price of solar energy decreases while the price of fossil energy is increasing.¹⁰³

While the economic advantages of photovoltaics funneled in average annual growth rates of world-wide PV installations as high as 44 % (in the period from 2000 to 2013).¹⁰³ a major challenge remains: installation costs are high ($1 \in per 1$ W peak capacity installed), posing an obstacle to a more wide-spread use, especially in developing countries. Unfortunately, the "packaging" of solar cells (i.e. their protection from weather influence) and the balance of system costs (*i.e.* all costs additional to the cost of a PV module, such as wiring, mounting, inverters, operation, etc.) are major cost factors which are difficult to reduce. Nevertheless, some cost reduction can still be achieved by using less and cheaper material in the active part of a solar cell while maintaining or increasing the efficiency of the cell. Solution to this challenge are increasingly searched in nanotechnology, employing organic molecules, perovskites, or quantum dots.⁷² The case of quantum-dot solar cells is discussed in section 1.2. A significant advantage over conventional silicon solar cells are potentially reduced production costs due to solutionprocessing at low temperatures. Less clear are the questions how (nano-)toxicity¹⁰⁴ and limited abundance of elements in the earth's crust¹⁰⁵ can be coped with and which efficiencies⁷² can be reached.

1.6. OUTLINE OF THIS THESIS

In chapter 2, absolute energetic positions of confined electron levels in CdSe QD films are determined *in situ* using spectro-electrochemistry. Attention is payed to the effect of void size and ligand length on electrochemical charge injection. Chapter 3 extends this methodology to QD films containing two types of materials and determines their band offsets. Chapter 4 reports on ultrafast electron trapping in CdTe QD films and dispersion using ultrafast transient absorption spectroscopy. It demonstrates that in a film containing CdTe to CdSe QDs (featuring a favorable type-II band offset) electron transfer can occur only if the competing trapping channel is switched off, *via* ligand chemistry and/or control of the Fermi level. At last, chapter 5 elaborates on the Fermi level dependence of electron and hole trapping rates. The density of trap states throughout the band gap is assessed by combining ultrafast transient absorption and time-resolved photoluminescence spectroscopy with electrochemical control of the Fermi level.

REFERENCES

- 1. Landolt-Börnstein Group III Condensed Matter: Non-Tetrahedrally Bonded Elements and Binary Compounds I. Springer Berlin Heidelberg: 1998; Vol. 41C.
- 2. Brus, L., A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites. J. Chem. Phys. 1983, 79, 5566.
- 3. Brus, L., Electronic wave functions in semiconductor clusters: experiment and theory. The Journal of Physical Chemistry 1986, 90, 2555-2560.
- 4. Delerue, C., Lannoo, M., Nanostructures: Theory and Modeling. Springer Berlin Heidelberg: 2004.
- 5. Efros, A. L.; Rodina, A. V., Band-edge absorption and luminescence of nonspherical nanometersize crystals. Physical Review B 1993, 47, 10005-10007.
- 6. Franceschetti, A.; Zunger, A., Direct Pseudopotential Calculation of Exciton Coulomb and Exchange Energies in Semiconductor Quantum Dots. Physical Review Letters 1997, 78, 915-918.
- 7. An, J. M.; Franceschetti, A.; Dudiy, S. V.; Zunger, A., The Peculiar Electronic Structure of PbSe Quantum Dots. Nano Letters 2006, 6, 2728-2735.
- 8. Lippens, P. E.; Lannoo, M., Calculation of the band gap for small CdS and ZnS crystallites. Physical Review B 1989, 39, 10935-10942.
- 9. Lannoo, M.; Delerue, C.; Allan, G., Screening in Semiconductor Nanocrystallites and Its Consequences for Porous Silicon. Physical Review Letters 1995, 74, 3415-3418.
- Azpiroz, J. M.; Ugalde, J. M.; Infante, I., Benchmark Assessment of Density Functional Methods on Group II–VI MX (M = Zn, Cd; X = S, Se, Te) Quantum Dots. Journal of Chemical Theory and Computation 2013, 10, 76-89.
- Azpiroz, J. M.; Infante, I.; Lopez, X.; Ugalde, J. M.; De Angelis, F., A first-principles study of II-VI (II = Zn; VI = O, S, Se, Te) semiconductor nanostructures. Journal of Materials Chemistry 2012, 22, 21453-21465.
- 12. Malet, F.; Mirtschink, A.; Cremon, J. C.; Reimann, S. M.; Gori-Giorgi, P., Kohn-Sham density functional theory for quantum wires in arbitrary correlation regimes. Physical Review B 2013, 87, 115146.
- 13. Norris, D. J.; Bawendi, M. G., Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots. Physical Review B 1996, 53, 16338.
- 14. Palinginis, P.; Tavenner, S.; Lonergan, M.; Wang, H., Spectral hole burning and zero phonon linewidth in semiconductor nanocrystals. Physical Review B 2003, 67, 201307.
- 15. Wang, C.; Shim, M.; Guyot-Sionnest, P., Electrochromic Nanocrystal Quantum Dots. Science 2001, 291, 2390-2392.
- 16. Knowles, K. E.; Tice, D. B.; McArthur, E. A.; Solomon, G. C.; Weiss, E. A., Chemical Control of the Photoluminescence of CdSe Quantum Dot–Organic Complexes with a Series of Para-Substituted Aniline Ligands. Journal of the American Chemical Society 2009, 132, 1041-1050.
- 17. Morris-Cohen, A. J.; Donakowski, M. D.; Knowles, K. E.; Weiss, E. A., The Effect of a Common Purification Procedure on the Chemical Composition of the Surfaces of CdSe Quantum Dots Synthesized with Trioctylphosphine Oxide. The Journal of Physical Chemistry C 2009, 114, 897-906.
- Frederick, M. T.; Amin, V. A.; Swenson, N. K.; Ho, A. Y.; Weiss, E. A., Control of Exciton Confinement in Quantum Dot–Organic Complexes through Energetic Alignment of Interfacial Orbitals. Nano Letters 2012, 13, 287-292.

- Koole, R.; Luigjes, B.; Tachiya, M.; Pool, R.; Vlugt, T. J. H.; de Mello Donegá, C.; Meijerink, A.; Vanmaekelbergh, D., Differences in Cross-Link Chemistry between Rigid and Flexible Dithiol Molecules Revealed by Optical Studies of CdTe Quantum Dots. The Journal of Physical Chemistry C 2007, 111, 11208-11215.
- 20. Wang, S.; Wang, L.-W., Exciton Dissociation in CdSe/CdTe Heterostructure Nanorods. The Journal of Physical Chemistry Letters 2011, 2, 1-6.
- 21. Wang, H.; McNellis, E. R.; Kinge, S.; Bonn, M.; Cánovas, E., Tuning Electron Transfer Rates through Molecular Bridges in Quantum Dot Sensitized Oxides. Nano Letters 2013, 13, 5311-5315.
- 22. Tvrdy, K.; Frantsuzov, P. A.; Kamat, P. V., Photoinduced electron transfer from semiconductor quantum dots to metal oxide nanoparticles. Proceedings of the National Academy of Sciences 2010, 108, 29-34.
- Hyun, B.-R.; Zhong, Y.-W.; Bartnik, A. C.; Sun, L.; Abruña , H. D.; Wise, F. W.; Goodreau, J. D.; Matthews, J. R.; Leslie, T. M.; Borrelli, N. F., Electron Injection from Colloidal PbS Quantum Dots into Titanium Dioxide Nanoparticles. ACS Nano 2008, 2, 2206-2212.
- Pijpers, J. J. H.; Koole, R.; Evers, W. H.; Houtepen, A. J.; Boehme, S.; de Mello Donegá, C.; Vanmaekelbergh, D.; Bonn, M., Spectroscopic Studies of Electron Injection in Quantum Dot Sensitized Mesoporous Oxide Films. The Journal of Physical Chemistry C 2010, 114, 18866-18873.
- 25. Robel, I.; Kuno, M.; Kamat, P. V., Size-Dependent Electron Injection from Excited CdSe Quantum Dots into TiO2 Nanoparticles. Journal of the American Chemical Society 2007, 129, 4136-4137.
- 26. Talgorn, E.; de Vries, M. A.; Siebbeles, L. D. A.; Houtepen, A. J., Photoconductivity Enhancement in Multilayers of CdSe and CdTe Quantum Dots. ACS Nano 2011, 5, 3552-3558.
- 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 Letters 2012, 12, 303-309.
- Zhu, H.; Song, N.; Lian, T., Controlling Charge Separation and Recombination Rates in CdSe/ZnS Type I Core–Shell Quantum Dots by Shell Thicknesses. Journal of the American Chemical Society 2010, 132, 15038-15045.
- Choi, J.-H.; Fafarman, A. T.; Oh, S. J.; Ko, D.-K.; Kim, D. K.; Diroll, B. T.; Muramoto, S.; Gillen, J. G.; Murray, C. B.; Kagan, C. R., Bandlike Transport in Strongly Coupled and Doped Quantum Dot Solids: A Route to High-Performance Thin-Film Electronics. Nano Letters 2012, 12, 2631-2638.
- 30. Choi, J. J.; Luria, J.; Hyun, B.-R.; Bartnik, A. C.; Sun, L.; Lim, Y.-F.; Marohn, J. A.; Wise, F. W.; Hanrath, T., Photogenerated Exciton Dissociation in Highly Coupled Lead Salt Nanocrystal Assemblies. Nano Letters 2010, 10, 1805-1811.
- Gao, Y.; Aerts, M.; Sandeep, C. S. S.; Talgorn, E.; Savenije, T. J.; Kinge, S.; Siebbeles, L. D. A.; Houtepen, A. J., Photoconductivity of PbSe Quantum-Dot Solids: Dependence on Ligand Anchor Group and Length. ACS Nano 2012, 6, 9606-9614.
- 32. Guyot-Sionnest, P., Electrical Transport in Colloidal Quantum Dot Films. The Journal of Physical Chemistry Letters 2012, 3, 1169-1175.
- 33. Koole, R.; Liljeroth, P.; de Mello Donegá, C.; Vanmaekelbergh, D.; Meijerink, A., Electronic Coupling and Exciton Energy Transfer in CdTe Quantum-Dot Molecules. Journal of the American Chemical Society 2006, 128, 10436-10441.
- 34. Law, M.; Luther, J. M.; Song, Q.; Hughes, B. K.; Perkins, C. L.; Nozik, A. J., Structural, Optical, and Electrical Properties of PbSe Nanocrystal Solids Treated Thermally or with Simple Amines. Journal of the American Chemical Society 2008, 130, 5974-5985.
- Lee, J.-S.; Kovalenko, M. V.; Huang, J.; Chung, D. S.; Talapin, D. V., Band-like transport, high electron mobility and high photoconductivity in all-inorganic nanocrystal arrays. Nat Nano 2011, 6, 348-352.

- 36. Lefrancois, A.; Couderc, E.; Faure-Vincent, J.; Sadki, S.; Pron, A.; Reiss, P., Effect of the treatment with (di-)amines and dithiols on the spectroscopic, electrochemical and electrical properties of CdSe nanocrystals' thin films. Journal of Materials Chemistry 2011, 21, 11524-11531.
- 37. Liu, Y.; Gibbs, M.; Puthussery, J.; Gaik, S.; Ihly, R.; Hillhouse, H. W.; Law, M., Dependence of Carrier Mobility on Nanocrystal Size and Ligand Length in PbSe Nanocrystal Solids. Nano Letters 2010, 10, 1960-1969.
- Sandeep, C. S. S.; Azpiroz, J. M.; Evers, W. H.; Boehme, S. C.; Moreels, I.; Kinge, S.; Siebbeles, L. D. A.; Infante, I.; Houtepen, A. J., Epitaxially Connected PbSe Quantum-Dot Films: Controlled Neck Formation and Optoelectronic Properties. ACS Nano 2014.
- Talgorn, E.; Moysidou, E.; Abellon, R. D.; Savenije, T. J.; Goossens, A.; Houtepen, A. J.; Siebbeles, L. D. A., Highly Photoconductive CdSe Quantum-Dot Films: Influence of Capping Molecules and Film Preparation Procedure. The Journal of Physical Chemistry C 2010, 114, 3441-3447.
- 40. Vanmaekelbergh, D.; Liljeroth, P., Electron-conducting quantum dot solids: novel materials based on colloidal semiconductor nanocrystals. Chemical Society Reviews 2005, 34, 299-312.
- Krause, M. M.; Mooney, J.; Kambhampati, P., Chemical and Thermodynamic Control of the Surface of Semiconductor Nanocrystals for Designer White Light Emitters. ACS Nano 2013, 7, 5922-5929.
- Nag, A.; Chung, D. S.; Dolzhnikov, D. S.; Dimitrijevic, N. M.; Chattopadhyay, S.; Shibata, T.; Talapin, D. V., Effect of Metal Ions on Photoluminescence, Charge Transport, Magnetic and Catalytic Properties of All-Inorganic Colloidal Nanocrystals and Nanocrystal Solids. Journal of the American Chemical Society 2012, 134, 13604-13615.
- 43. Chen, O.; Zhao, J.; Chauhan, V. P.; Cui, J.; Wong, C.; Harris, D. K.; Wei, H.; Han, H.-S.; Fukumura, D.; Jain, R. K.; Bawendi, M. G., Compact high-quality CdSe–CdS core–shell nanocrystals with narrow emission linewidths and suppressed blinking. Nat Mater 2013, 12, 445-451.
- 44. Morris-Cohen, A. J.; Malicki, M.; Peterson, M. D.; Slavin, J. W. J.; Weiss, E. A., Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots. Chemistry of Materials 2012, 25, 1155-1165.
- 45. McBride, J. R.; Pennycook, T. J.; Pennycook, S. J.; Rosenthal, S. J., The Possibility and Implications of Dynamic Nanoparticle Surfaces. ACS Nano 2013, 7, 8358-8365.
- 46. Roduner, E., Size matters: why nanomaterials are different. Chemical Society Reviews 2006, 35, 583-592.
- 47. de Mello Donegá, C., Synthesis and properties of colloidal heteronanocrystals. Chemical Society Reviews 2011, 40, 1512-1546.
- Kramer, I. J.; Moreno-Bautista, G.; Minor, J. C.; Kopilovic, D.; Sargent, E. H., Colloidal quantum dot solar cells on curved and flexible substrates. Appl. Phys. Lett. 2014, 105, -.
- 49. Patel, P., The First Full-Color Display with Quantum Dots. 22nd of February 2011 ed.; MIT Technology Review: <u>http://www.technologyreview.com/news/422857/the-first-full-color-displaywith-quantum-dots/</u>, 2011.
- 50. Bourzac, K., Quantum dots go on display. Nature 2013, 493.
- Graetzel, M.; Janssen, R. A. J.; Mitzi, D. B.; Sargent, E. H., Materials interface engineering for solution-processed photovoltaics. Nature 2012, 488, 304-312.
- 52. Semonin, O. E.; Luther, J. M.; Beard, M. C., Quantum dots for next-generation photovoltaics. Materials Today 2012, 15, 508-515.
- 53. Saeed, S.; de Jong, E. M. L. D.; Dohnalova, K.; Gregorkiewicz, T., Efficient optical extraction of hot-carrier energy. Nat Commun 2014, 5.
- 54. Ross, R. T.; Nozik, A. J., Efficiency of hot-carrier solar energy converters. Journal of Applied Physics 1982, 53, 3813-3818.

- 55. Würfel, P.; Brown, A. S.; Humphrey, T. E.; Green, M. A., Particle conservation in the hot-carrier solar cell. Progress in Photovoltaics: Research and Applications 2005, 13, 277-285.
- 56. König, D.; Casalenuovo, K.; Takeda, Y.; Conibeer, G.; Guillemoles, J. F.; Patterson, R.; Huang, L. M.; Green, M. A., Hot carrier solar cells: Principles, materials and design. Physica E: Low-dimensional Systems and Nanostructures 2010, 42, 2862-2866.
- 57. Schaller, R. D.; Klimov, V. I., High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion. Physical Review Letters 2004, 92, 186601.
- 58. Hanna, M. C.; Nozik, A. J., Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. Journal of Applied Physics 2006, 100, -.
- 59. Klimov, V. I., Detailed-balance power conversion limits of nanocrystal-quantum-dot solar cells in the presence of carrier multiplication. Appl. Phys. Lett. 2006, 89, -.
- 60. Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C., Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple Exciton Generation to Third-Generation Photovoltaic Solar Cells. Chemical Reviews 2010, 110, 6873-6890.
- 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.
- 62. Beard, M. C.; Luther, J. M.; Semonin, O. E.; Nozik, A. J., Third Generation Photovoltaics based on Multiple Exciton Generation in Quantum Confined Semiconductors. Accounts of Chemical Research 2012, 46, 1252-1260.
- 63. Pandey, A.; Guyot-Sionnest, P., Slow Electron Cooling in Colloidal Quantum Dots. Science 2008, 322, 929-932.
- 64. Beard, M. C.; Midgett, A. G.; Hanna, M. C.; Luther, J. M.; Hughes, B. K.; Nozik, A. J., Comparing Multiple Exciton Generation in Quantum Dots To Impact Ionization in Bulk Semiconductors: Implications for Enhancement of Solar Energy Conversion. Nano Letters 2010, 10, 3019-3027.
- 65. Trinh, M. T.; Houtepen, A. J.; Schins, J. M.; Hanrath, T.; Piris, J.; Knulst, W.; Goossens, A. P. L. M.; Siebbeles, L. D. A., In Spite of Recent Doubts Carrier Multiplication Does Occur in PbSe Nanocrystals. Nano Letters 2008, 8, 1713-1718.
- 66. Pijpers, J. J. H.; Ulbricht, R.; Tielrooij, K. J.; Osherov, A.; Golan, Y.; Delerue, C.; Allan, G.; Bonn, M., Assessment of carrier-multiplication efficiency in bulk PbSe and PbS. Nat Phys 2009, 5, 811-814.
- McGuire, J. A.; Joo, J.; Pietryga, J. M.; Schaller, R. D.; Klimov, V. I., New Aspects of Carrier Multiplication in Semiconductor Nanocrystals. Accounts of Chemical Research 2008, 41, 1810-1819.
- 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 Letters 2012, 12, 1588-1591.
- 69. Aerts, M.; Suchand Sandeep, C. S.; Gao, Y.; Savenije, T. J.; Schins, J. M.; Houtepen, A. J.; Kinge, S.; Siebbeles, L. D. A., Free Charges Produced by Carrier Multiplication in Strongly Coupled PbSe Quantum Dot Films. Nano Letters 2011, 11, 4485-4489.
- 70. Sandeep, C. S. S.; Cate, S. t.; Schins, J. M.; Savenije, T. J.; Liu, Y.; Law, M.; Kinge, S.; Houtepen, A. J.; Siebbeles, L. D. A., High charge-carrier mobility enables exploitation of carrier multiplication in quantum-dot films. Nat Commun 2013, 4.
- Trinh, M. T.; Limpens, R.; de Boer, W. D. A. M.; Schins, J. M.; Siebbeles, L. D. A.; Gregorkiewicz, T., Direct generation of multiple excitons in adjacent silicon nanocrystals revealed by induced absorption. Nat Photon 2012, 6, 316-321.
- 72. Best Research-Cell Efficiencies. National Renewable Energy Laboratory, Golden, CO, USA: <u>http://www.nrel.gov/ncpv/images/efficiency_chart.jpg</u>, 2014.

- Zhitomirsky, D.; Voznyy, O.; Levina, L.; Hoogland, S.; Kemp, K. W.; Ip, A. H.; Thon, S. M.; Sargent, E. H., Engineering colloidal quantum dot solids within and beyond the mobility-invariant regime. Nat Commun 2014, 5.
- 74. Maraghechi, P.; Labelle, A. J.; Kirmani, A. R.; Lan, X.; Adachi, M. M.; Thon, S. M.; Hoogland, S.; Lee, A.; Ning, Z.; Fischer, A.; Amassian, A.; Sargent, E. H., The Donor–Supply Electrode Enhances Performance in Colloidal Quantum Dot Solar Cells. ACS Nano 2013, 7, 6111-6116.
- 75. Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G., Improved performance and stability in quantum dot solar cells through band alignment engineering. Nat Mater 2014, 13, 796-801.
- 76. Sargent, E. H., Colloidal quantum dot solar cells. Nat Photon 2012, 6, 133-135.
- 77. Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P., Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution. Science 2005, 310, 462-465.
- Wei, S.-H.; Zhang, S. B.; Zunger, A., First-principles calculation of band offsets, optical bowings, and defects in CdS, CdSe, CdTe, and their alloys. Journal of Applied Physics 2000, 87, 1304-1311.
- 79. Talgorn, E.; Gao, Y.; Aerts, M.; Kunneman, L. T.; Schins, J. M.; Savenije, T. J.; van HuisMarijn, A.; van der ZantHerre, S. J.; Houtepen, A. J.; SiebbelesLaurens, D. A., Unity quantum yield of photogenerated charges and band-like transport in quantum-dot solids. Nat Nano 2011, 6, 733-739.
- Jasieniak, J.; Califano, M.; Watkins, S. E., Size-Dependent Valence and Conduction Band-Edge Energies of Semiconductor Nanocrystals. ACS Nano 2011, 5, 5888-5902.
- Tang, J.; Wang, X.; Brzozowski, L.; Barkhouse, D. A. R.; Debnath, R.; Levina, L.; Sargent, E. H., Schottky Quantum Dot Solar Cells Stable in Air under Solar Illumination. Advanced Materials 22, 1398-1402.
- Pattantyus-Abraham, A. G.; Kramer, I. J.; Barkhouse, A. R.; Wang, X.; Konstantatos, G.; Debnath, R.; Levina, L.; Raabe, I.; Nazeeruddin, M. K.; Gral[^]tzel, M.; Sargent, E. H., Depleted-Heterojunction Colloidal Quantum Dot Solar Cells. ACS Nano 2010, 4, 3374-3380.
- Luther, J. M.; Gao, J.; Lloyd, M. T.; Semonin, O. E.; Beard, M. C.; Nozik, A. J., Stability Assessment on a 3% Bilayer PbS/ZnO Quantum Dot Heterojunction Solar Cell. Advanced Materials 2010, 22, 3704-3707.
- Hannah, D. C.; Brown, K. E.; Young, R. M.; Wasielewski, M. R.; Schatz, G. C.; Co, D. T.; Schaller, R. D., Direct Measurement of Lattice Dynamics and Optical Phonon Excitation in Semiconductor Nanocrystals Using Femtosecond Stimulated Raman Spectroscopy. Physical Review Letters 2013, 111, 107401.
- 85. Sippel, P.; Albrecht, W.; Mitoraj, D.; Eichberger, R.; Hannappel, T.; Vanmaekelbergh, D., Two-Photon Photoemission Study of Competing Auger and Surface-Mediated Relaxation of Hot Electrons in CdSe Quantum Dot Solids. Nano Letters 2013, 13, 1655-1661.
- 86. Guyot-Sionnest, P.; Shim, M.; Matranga, C.; Hines, M., Intraband relaxation in CdSe quantum dots. Physical Review B 1999, 60, R2181-R2184.
- 87. Klimov, V. I.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G., Electron and hole relaxation pathways in semiconductor quantum dots. Physical Review B 1999, 60, 13740-13749.
- Hendry, E.; Koeberg, M.; Wang, F.; Zhang, H.; de Mello Donegá, C.; Vanmaekelbergh, D.; Bonn, M., Direct Observation of Electron-to-Hole Energy Transfer in CdSe Quantum Dots. Physical Review Letters 2006, 96, 057408.
- 89. Gao, Y.; Sandeep, C. S. S.; Schins, J. M.; Houtepen, A. J.; Siebbeles, L. D. A., Disorder strongly enhances Auger recombination in conductive quantum-dot solids. Nat Commun 2013, 4.
- 90. Wackernagel, M.; Rees, W., Our Ecological Footprint: Reducing Human Impact on the Earth. New Society Publishers: 1996.
- 91. Fiala, N., Measuring sustainability: Why the ecological footprint is bad economics and bad environmental science. Ecological Economics 2008, 67, 519-525.

- 92. IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA: http://www.ipcc.ch/report/ar5/wg1/, 2013.
- 93. Pereira, H. M.; Leadley, P. W.; Proença, V.; Alkemade, R.; Scharlemann, J. P. W.; Fernandez-Manjarrés, J. F.; Araújo, M. B.; Balvanera, P.; Biggs, R.; Cheung, W. W. L.; Chini, L.; Cooper, H. D.; Gilman, E. L.; Guénette, S.; Hurtt, G. C.; Huntington, H. P.; Mace, G. M.; Oberdorff, T.; Revenga, C.; Rodrigues, P.; Scholes, R. J.; Sumaila, U. R.; Walpole, M., Scenarios for Global Biodiversity in the 21st Century. Science 2010, 330, 1496-1501.
- Hoffert, M. I.; Caldeira, K.; Jain, A. K.; Haites, E. F.; Harvey, L. D. D.; Potter, S. D.; Schlesinger, M. E.; Schneider, S. H.; Watts, R. G.; Wigley, T. M. L.; Wuebbles, D. J., Energy implications of future stabilization of atmospheric CO₂ content. Nature 1998, 395, 881-884.
- Hoffert, M. I.; Caldeira, K.; Benford, G.; Criswell, D. R.; Green, C.; Herzog, H.; Jain, A. K.; Kheshgi, H. S.; Lackner, K. S.; Lewis, J. S.; Lightfoot, H. D.; Manheimer, W.; Mankins, J. C.; Mauel, M. E.; Perkins, L. J.; Schlesinger, M. E.; Volk, T.; Wigley, T. M. L., Advanced Technology Paths to Global Climate Stability: Energy for a Greenhouse Planet. Science 2002, 298, 981-987.
- Davis, S. J.; Caldeira, K.; Matthews, H. D., Future CO2 Emissions and Climate Change from Existing Energy Infrastructure. Science 2010, 329, 1330-1333.
- 97. Hendriks, R., SolaRoad in gebruik genomen. 24th of October 2014 ed.; Verkeersnet.nl: 2014.
- 98. de Wild-Scholten, M. J., Energy payback time and carbon footprint of commercial photovoltaic systems. Solar Energy Materials and Solar Cells 2013, 119, 296-305.
- 99. Olson, C.; Veltkamp, A.; Sinke, W. In The external costs of electricity generation: A comparison of environmental damage of silicon photovoltaic electricity, produced with different electricity mixes, vs natural gas and coal, 27th European Photovoltaic Solar Energy Conference and Exhibition, Frankfurt, Germany, Frankfurt, Germany, 2012.
- 100."Universal Ownership: Why environmental externalities matter to institutional investors". United Nations Environment Programme Finance Initiative & Principles for Responsible Investment: <u>http://www.unpri.org/files/6728_ES_report_environmental_externalities.pdf</u>, 2011.
- 101. Epstein, P. R.; Buonocore, J. J.; Eckerle, K.; Hendryx, M.; Stout Iii, B. M.; Heinberg, R.; Clapp, R. W.; May, B.; Reinhart, N. L.; Ahern, M. M.; Doshi, S. K.; Glustrom, L., Full cost accounting for the life cycle of coal. Annals of the New York Academy of Sciences 2011, 1219, 73-98.
- 102. Levelized Cost and Levelized Avoided Cost of New Generation Resources in the Annual Energy Outlook 2014. 17th of April 2014 ed.; U.S. Energy Information Administration: http://www.eia.gov/forecasts/aeo/electricity_generation.cfm, 2014.
- 103. Burger, B., Photovoltaics Report. Fraunhofer-Institut für Solare Energiesysteme ISE: <u>http://www.ise.fraunhofer.de/en/news/news-2012/fraunhofer-ise-publishes-photovoltaics-report,</u> 2014.
- 104.Warheit, D. B., Debunking Some Misconceptions about Nanotoxicology. Nano Letters 2010, 10, 4777-4782.
- 105. Wadia, C.; Alivisatos, A. P.; Kammen, D. M., Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment. Environmental Science & Technology 2009, 43, 2072-2077.

2 ELECTROCHEMICAL CHARGING OF CDSE QUANTUM DOT FILMS: DEPENDENCE ON VOID SIZE AND COUNTERION PROXIMITY

2.1. INTRODUCTION

Colloidal Quantum Dot (QD) solids are promising for cost- and energy-efficient light harvesting, detection and generation due to their tunable bandgap, solution processability¹ stability,^{2, 3} and anticipated cost-efficiency.^{4, 5} Encouraging device efficiencies have been achieved in the fields of photovoltaics,^{4, 6-8} LEDs⁹⁻¹¹ and (IR) photodetectors.¹² A compelling strategy to improve their luminescence (for LEDs) and charge extraction properties (for photovoltaics and photodetectors) is the implementation of a heterostructure consisting of two different semiconductor materials: by tuning the energy levels at either side, both the direction and rate of charge transfer can be controlled. However, the measurement of absolute energy levels (vs.

vacuum) remains a challenge. While a variety of experimental techniques is available, each one has its own pitfalls: Ultraviolet Photoelectron Spectroscopy (UPS) can only determine energy levels of samples in vacuum¹³ and Photoelectron Spectrocopy in Air (PESA) only of samples in air.¹⁴ Whereas the former measurement may be irrelevant for an actual device configuration, the latter has to cope with the poor stability of QDs in air. In addition, both are intrinsically limited to the surface of the film. This drawback is shared by Kelvin probe measurements.¹⁵ Finally, electrochemistry can determine energy levels of the entire volume of a sample and under a variety of dielectric environments.¹⁶ However, the commonly employed cyclic voltammetry measurement mode (CV) per definition cannot distinguish between QD levels and defect states resulting from impurities or the surface of a QD. Since surface defects are abundant and very sensitive to a sample's preparation conditions and history, CV measurements often feature a large sample-tosample variation and their interpretation is difficult. Hence, it is not surprising that the spread in literature values for energy levels determined by CV measurements surpasses 1.5 V. This discourages any effort to improve the performance of a working device via careful fine-tuning of its energy level alignment based on the existing literature of energy levels.

On the other hand, *spectro*-electrochemistry adds to the reliability of electrochemical energy level studies since it simultaneously probes changes in transmission and/or luminescence as a function of the applied potential to the sample. This way, it is possible to unambiguously distinguish charges in (optically active) QD orbitals from charges in defect states.¹⁶⁻²¹ Such "electrolyte gating" (also called "electrochemical gating")¹⁶ has been successfully exploited by several groups to study absolute energy levels,¹⁹ investigate charge associated absorption changes and fluorescence quenching,^{20, 22} blinking characteristics^{23, 24} or induce order-of-magnitude increases in steady-state conductivities.^{21, 25}

One reason for the success of the above spectroelectrochemical studies roots in the nanoporous morphology of a QD film: simultaneous with the injection of electrons or holes into the QD film, electrolyte counterions (present in the voids of the films) allow for a nanoscale charge compensation. Hence, while only the surface of a macroscopic semiconductor crystal can be charged, it is possible to charge the complete "bulk" volume of a QD film. Furthermore, one would expect that the type of counterion has little influence on the efficiency and energy of charging the QD film as long as the counterions are electrochemically inactive.

In this report, we determine the absolute energies of the 1S_e and 1P_e electron levels in CdSe QD films by spectroelectrochemistry. In particular, the spotlight is moved to charge injection in QD films whose conductivities are increased *via* reduced interparticle spacing by short cross-linking molecules, i.e. the ligands. We find that in those films the maximum number of injectable electrons is limited by the size of the film's voids. The latter can be tuned *via* the diameter of the QDs and the length of the ligands that separate them. Furthermore, we report two peculiar observations concerning the absolute electron energy levels: (1) they depend on the cation size; this is not expected given the assumption that the cation is electrochemically inactive (see above). (2) They depend on the length of the binding group of a linker, but not its length.¹⁴ Both observations suggest that the cation tends to approach the QDs as close as possible and that the proximity of the cations and the negatively charged QDs is an important factor in the overall energy of the system.

2.2. EXPERIMENTAL DETAILS

QD synthesis

QDs were synthesized following Mekis et al.:²⁶ two precursors were prepared in a N_2 purged glovebox by dissolving 0.474 g Se (325 mesh) in 6 ml TOP (trioctylphosphine) and 0.36 g Cd(Ac)₂ in 9 ml TOP, respectively. 24g of TOPO (Trioctylphosphine oxide) was heated to 180 °C in vacuum under periodic flushing with N₂. After cooling down to 100 °C, 15g HDA (1-hexadecylamine) and 0.45 g TDPA (1-tetradecylphosphonic acid) were added and dried at 120 °C in vacuum during 30 min under periodic flushing with N₂. The TOP-Se precursor was injected and the solution was heated to 300 °C under N₂ flow. Under vigorous stirring, the TOP-Cd(Ac)₂ precursor was injected to induce nucleation of CdSe nanoparticles. During the growth at 280 °C aliquots were taken to monitor the growth rate. After the desired QD size was reached, the reaction was stopped by cooling down to room temperature. Toluene was injected to avoid solidification of the TOPO. The obtained dispersion was purified by repeated washing with MeOH and precipitation of particles in a centrifuge at 3000 rpm for 5 min. The final stock of particles was dispersed in Chloroform.

QD film processing by LbL dipcoating procedure

QD films were grown in a layer-by-layer (LbL) dipcoating procedure in a N_2 purged glovebox. ITO substrates were first immersed for 30 s in a concentrated QD dispersion, subsequently immersed for 30 s in a stirred MeOH solution containing 10 vol-% of the desired ligand and finally rinsed by residing 60 s in stirred MeOH. Using this procedure, the original insulating ligands are replaced by the new desired ligand. Typically, the above procedure was repeated 20 times to yield films roughly 20 QD monolayers thick. After dipcoating, the film was kept on a hotplate at 70 °C to evaporate residual solvent. For all the films, a small region on the edge of the substrate remained uncoated for contacting in electrochemical measurements.

Spectroelectrochemical measurements

Our electrochemical setup consists of a CHI832B bipotentiostat (CH Instruments, Inc.) with an Ag wire pseudo-reference electrode and a Pt sheet counter electrode in an air-tight Teflon container (see Figure 2.1a). The Ag wire pseudo-reference electrode (-5.01 V vs. vacuum) was calibrated with a ferrocene/ferrocinium couple.^{27, 28} In a N₂ purged glovebox, the cell is loaded with a QD film and filled with an electrolytes consisting of anhydrous acetonitrile (\geq 99.8 %, Sigma-Aldrich) and either 0.1 M LiClO₄ (lithium perchlorate, battery grade, 99.99 %, Aldrich), 0.1 M TBAPF₆ (tetrabutylammonium hexafluorophosphate, \geq 99.0 %, Fluka) or 0.1 M TOABF₄ (tetraoctylammonium tetrafluoroborate, \geq 97.0 %, Aldrich). All chemicals were used as received.

We perform electrochemical measurements in the so-called "differential capacitance" mode.^{16, 29} The charging current is integrated during a fixed time interval following a potential step yielding the differential capacitance, *i.e.* the injected charge per potential step $\Delta Q / \Delta V$. This removes the contribution of faradaic background currents in the electrolyte. Secondly, the electric double layer capacitance can be corrected for by a separate differential capacitance measurement of a bare ITO substrate. The so obtained differential capacitance of the QD film then reveals the sample characteristic charging and discharging features much more clearly than common CV measurements (see Appendix A).

In the same experimental setup, UV-VIS absorption measurements are performed using a HL-2000 halogen lamp (Ocean Optics) and a USB2000+ spectrometer (Ocean Optics). After passing through the electrochemical cell *via* two windows in the Teflon container,
the light is collected in an optical fiber and its intensity is adjusted by a diaphragm and collimating lenses. The absorption bleach spectrum of each potential step is taken after the electrochemical current has decayed to a stable level.



Figure 2.1 (a) Schematic of the spectroelectrochemical setup: via the potentiostat a voltage is applied between the Ag wire pseudo-reference electrode and the QD film on an ITO substrate, both of which are immersed in the supporting electrolyte. Simultaneously, the electrochemical charging current is measured by a counter electrode and the change in the QD film absorption is monitored by a UV-VIS spectrometer. (b) Schematic of the electron injection process: raising the Fermi level of the ITO from within the QD bandgap (black dashed line) to above the bandgap (blue continuous line) allows electron injection into an electronic level of the QD film. This blocks transitions to this level and thereby bleaches the absorption.

2.3. DETERMINATION OF 1S_E AND 1P_E ENERGY LEVELS

QDs with diameters ranging from 2.4 nm to 8 nm were synthesized following the procedure by Mekis et al.²⁶ QD films were grown on ITO substrates with a layer-by-layer (LbL) dipcoating method in a N_2 purged glovebox. Charge injection into CdSe QD films was investigated using a spectroelectrochemical setup in which the sample's substrate served as the working electrode in a three-electrode electrochemical cell (see Figure 2.1a). The Fermi level of the QD film is raised by a negative voltage between the sample's

substrate and the Ag wire pseudo-reference electrode (see Figure 2.1b). The resulting injection of electrons in the QD film and simultaneous charge compensation by cations in the electrolyte is monitored by a change in the absorption of the QD film. See methods section for details.

Known size confinement effects such as an increase of the bandgap and discretization of electronic states are observed in an absorbance measurement of our QD dispersions of five different diameters (see Figure 2.2a). Compared to the spectrum of the original dispersion, the QD films with diaminoethane (2DA), diaminobutane (4DA), diaminohexane (6DA) and diaminooctane (8DA) show a minor redshift and some broadening of the lowest energy transition (see Appendix A). In Figure 2.2b, the spectrum of a 8DA-linked film of 8 nm QDs is fitted by multiple Gaussians in the energy region between 1.65 and 3.45 eV to unveil the underlying optical transitions. Following Norris and Bawendi³⁰, the first Gaussian can be assigned to the nearly overlapping $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$ transitions at 1.9 eV, the second Gaussian can be ascribed to the $1P_{3/2}1P_e$ transition at 2.05 eV and the third Gaussian may originate from the $3S_{3/2}1S_e$, $1S_{1/2}2S_e$ and $4S_{3/2}2S_e$ transitions at 2.3 eV. The relatively large size of the QDs precludes a more detailed assignment of transitions.



Figure 2.2 (a) Absorption spectra of QD dispersions with diameters ranging from 2.4 nm to 8 nm. For clarity, the spectra are offset vertically. (b) The absorption spectrum of a 8DA-linked film of 8 nm QDs (black continuous line) can be fitted by multiple Gaussians (black dashed lines). Starting from about -1 V vs. the Ag pseudo-reference electrode, the QD film gets reduced inducing an absorption bleach of these transitions. The involved electron levels are indicated by vertical dashed lines. The supporting electrolyte is 0.1 M LiClO4 in anhydrous acetonitrile.

We now endeavor to determine the absolute energy of the confined electron levels for some of the observed transitions. Upon applying a negative potential on the sample's substrate (in case of a conductive film equivalent to shifting the Fermi level of both substrate and sample towards vacuum), we witness a negative change in the film's absorption (see Figure 2.2b) compared to the absorption at open circuit. This absorption bleach is seen at the lowest energy transitions. At about -1 V vs. the Ag wire pseudo-reference potential, first the transitions involving the $1S_e$ electron level start to bleach and disappear completely at about -1.5 V, whereas from about -1.2 V also the transitions involving the $1P_e$ level start to bleach.

The number of charges injected into a QD energy level i ($i = 1S_e, 1P_e$) can be determined^{25, 31} from

$$\left\langle n_{opt,i}(V) \right\rangle = g_i \cdot \int_0^\infty \frac{A_i(V) - A_i(V_{oc})}{A_i(V_{oc})} dE$$
(2.1)

with $\langle n_{opt,i}(V) \rangle$ the average number of electrons per QD in level *i* at an applied potential V, g_i the degeneracy of this level and $A_i(V)$ the absorption resulting from all transitions to level *i* at this potential, with V_{oc} the open circuit potential. In the following, $(A_i(V) - A_i(V_{oc}))/A_i(V_{oc})$ is called the "relative bleach". Consequently, the average total number of electrons per QD in quantum confined levels is $\langle n_{opt,ior}(V) \rangle = \sum_i \langle n_{opt,i}(V) \rangle$.

This incremental filling of electronic states in a QD film is illustrated in Figure 2.3 as the differential bleach $\Delta A_{1Se}/\Delta V$ and the differential capacitance $\Delta Q/\Delta V$. The former yields the density of optically active states $\Delta < n_{opt,i} > /\Delta V$ according to Equation 2.1, while the latter relates to the "electrochemical" DOS $\Delta < n_{ec} > /\Delta V = (\Delta Q/\Delta V)/(e \cdot N)$ with $< n_{ec} >$ the average number of electrons injected into the film per QD, *e* the elementary charge and *N* the number of QDs in the film. This "electrochemical" DOS³² includes optically dark electrons which may reside, for instance, in surface states. Hence, if the only charging that occurs is charging of the QD energy levels, the differential optical bleach and the differential capacitance should rise simultaneously with decreasing voltage. Indeed, the first wave in the differential capacitance clearly coincides with filling of 1S_e electron levels (blue open circles in Figure 2.3), whereas the second wave in the differential capacitance is related to charging of 1P_e states (green open triangles). We can

thus conclude that within the observed time window (see Appendix A) there is negligible charging of states other than the quantum confined ones.



Figure 2.3 Differential Capacitance $\Delta Q/\Delta V$ (filled diamonds) and differential absorption bleach $\Delta A/\Delta V$ at transitions involving the 1Se level (open circles) and 1Pe level (open triangles), respectively.

The reversible charging and discharging of QD films hence enables the observation of quantum size confinement both optically and electrochemically. First, in the case of 8 nm QDs, we find the $1S_e$ and $1P_e$ levels to reside at -3.85 and -3.7 eV vs. vacuum (or at -1.15 and -1.3 V vs. the Ag pseudo-reference electrode, respectively), as inferred from the extrema in the differential bleach. This experimentally determined 1Se-1Pe intraband separation of 0.15 eV is close to the expected intraband separation based on photoluminescence excitation data of Norris and Bawendi:30 their reported difference of 0.15 eV between the $1S_{3/2}1S_e$ and $1P_{3/2}1P_e$ transition translates into a $1S_e-1P_e$ intraband separation of 0.11 eV, using effective masses of 0.13 m_0 and 0.44 m_0 for electron and hole, respectively. It also agrees with the infrared absorption data of smaller QDs in solution: the reported 1Se-1Pe intraband separation of QDs with diameters between 2.7 and 5.4 nm ranges from 0.27 to 0.5 eV.¹⁹ Second, we find that in films of 3.7 nm QDs the injection into 1Se electron orbitals occurs at a 0.16 eV higher potential than in films of 8 nm QDs (see Appendix A). This agrees reasonably with the 0.21 eV offset expected from the 0.27 eV larger confinement energy (see Figure 2.2a) and the above electron and hole effective masses.

2.4. VOID SIZE LIMITED ELECTRON INJECTION

Using Equation 2.1 we have determined the average number of electrons per QD $< n_{tot} >$ for various QD diameters and diamine ligand lengths. Figure 2.4a shows $< n_{tot} >$ vs. applied potential for three films in a 0.1 M LiClO₄ electrolyte: 3.7 nm QDs and 8DA ligands (triangles), 8 nm QDs with 6DA (circles) and 8DA ligands (squares). For all films the number of injected charges is found to saturate at a certain potential: applying a more negative potential does not result in additional injection of electrons into the QD energy levels. The value of $< n_{tot} >$ at which this saturation occurs varies for the different films. For the 8 nm QD diameter film with 8DA ligands the maximum occupation of quantum confined electron levels is 5.5 electrons per QD. However, reducing either QD diameter (from 8 nm to 2.4 nm) or ligand length (from 8DA = octanediamine to 2DA = ethanediamine) results in fewer electrons injected (see Figure 2.4b).

We hypothesize that the maximum number of injected electrons per QD is limited by the size of the film's voids. Consequently, in case of very small voids, *i.e.* for densely packed films cross-linked *via* 2DA, insufficient cation compensation permits charging only at the surface of the entire film. This situation is equivalent to charging of a *planar* semiconductor: the potential drops in the depletion region where charging is possible.¹⁶ The bulk of the film remains uncharged. In this picture, efficient charge injection requires voids to be large enough for hosting electrolyte cations, as it is the case in the films of large QDs with long ligands.

To test this hypothesis, in the following we estimate the sizes of both the cations and the voids. The sizes of the former can be found in literature and range from 0.5 nm (*i.e.* Li⁺, solvated by acetonitrile molecules)³³ to 0.93 nm (*i.e.* TOA⁺, "solvated" by its alkyl chains)³⁴, the sizes of the latter are calculated in a hard sphere model. Herein, the QDs are modeled by hard spheres forming a closed-packed fcc lattice, as Murray et al.³⁵ have found evidence of fcc stacking in self-assembled CdSe QD lattices. We assume that the available void volume for uptake of electrolyte cations is given by the largest possible spheres that fit in the octahedral and tetrahedral voids of this stack. For N ligand-free QDs of radius R, there are N octahedral and 2N tetrahedral voids of radii 0.414 R and 0.225 R, respectively.³⁶



Figure 2.4 (a) Saturation of the number of electrons injected for films of 8 nm QDs with 6DA (circles) and 8DA ligands (squares), respectively, and a film of 3.7 nm QDs with 8DA ligands (triangles). (b) Experimentally determined maximum number of electrons per QD $< n >_{tot}$ (bars) and calculated void volume assuming stiff ligands (line with diagonal markers) and flexible ligands (line with vertical markers), respectively, as explained in the text. The films are categorized by their QD diameter and their ligand length, the latter ranging from two (2DA) to eight (8DA) C atoms. The supporting electrolyte is 0.1 M LiCLO4 in acetonitrile. (c) Schematic of a tetrahedral void in the hard sphere model. The fourth and out-of-plane QD is half-transparent, the calculated void volume for stiff and flexible ligands by a filled and dashed circle, respectively.

Due to the ligands on the QDs, the volume of both voids is enlarged, as sketched in the two scenarios in Figure 2.4c: either the ligands are assumed "stiff", in which case they merely increase the apparent radius R of the QD, or they are "flexible" in the sense that they permit full penetration of electrolyte ions and could thus be seen as a solvent that increases the distance between QDs. In Figure 2.4c, a tetrahedral void in the stiff case is sketched as a filled orange circle, a void in the flexible case is sketched as a dashed orange circle. The combined volume of the one octahedral void and the two tetrahedral ligands of length *l* can then be voids per QD for calculated ลร $V_{\text{stiff,tot}} = 4/3 \cdot \pi \cdot \left[(0.414 \cdot (R+l))^3 + 2 \cdot (0.225 \cdot (R+l))^3 \right] \text{ in case of stiff ligands and}$ $V_{\text{flex tot}} = 4/3 \cdot \pi \cdot [(0.414 \cdot (R+l) + l)^3 + 2 \cdot (0.225 \cdot (R+l) + l)^3]$ in case of flexible ligands, respectively. Both calculated volumes are shown in Figure 2.4b for different QD diameters and various ligands. The increase in the calculated void volume qualitatively agrees with the trend observed in the experimentally determined average electron

occupation $< n_{tot} >$ per QD. This shows that if there is more volume available for cation uptake (in case of large QDs and long ligands), more electrons can be injected into the QDs.

The qualitative agreement of the hard sphere model with the measured average electron occupation $\langle n_{tot} \rangle$ is remarkable given the crude assumptions of the model. Specifically, our films will not be as ordered as assumed in the above hard sphere model. It is known that dipcoating results in glassy, rather than ordered films^{37, 38}. Furthermore, we so far neglected any interaction between injected electrons and electrolyte cations. For high degrees of charging with multiple cations per void as observed in the films with 8 nm QDs and long 8DA ligands, this should lead to deviations from our hard sphere model.

Summarizing, we show here that the small interparticle spacing of highly conductive QD films necessarily limits their electrochemical charging ability. This is in line with a puzzle presented in an earlier report:³⁹ CdSe QD films treated with NaOH were found to be chargeable up a concentration that amounts to charging of the first monolayer at the surface of the film. Exposure to NaOH effectively removes all ligands leaving OH⁻ at the surface.⁴⁰ We suggest that in this case the voids in the film have been too small for cation uptake. The importance of nanoporosity for efficient charging has also been demonstrated in a recent study on graphene based electrochemical capacitors:⁴¹ increasing the porosity in graphene layers was the recipe to achieve capacitors of both high power density and high energy density.

2.5. LIGAND LENGTH AND CATION SIZE

In the following we want to address the *energetics* of electron injection in CdSe QD films. As outlined above, we draw our motivation from the large spread in reported values for QD electron energy levels. Figure 2.5a shows the potential dependent charging of films of 8 nm QDs with ligands of varying length. For the 6DA and 8DA ligands, the bleach of the $1S_{3/2}1S_e$ transition saturates at ~ 1, indicating full (two-fold) charging of the $1S_e$ level. This is in line with the conclusion above that in these films in total more than four or five electrons can be injected, respectively. However, for the shorter 6DA ligands we observe



Figure 2.5 (a) Potential dependence of the relative bleach at the $1S_{3/2}1S_e$ transition (open symbols) and its derivative (closed symbols) for films of 8 nm QDs cross-linked with 2DA (triangles), 6DA (circles) or 8DA (squares), respectively. Gaussian fits to the bleach derivatives are shown as continuous lines. (b) Schematic illustrating increased proximity of cation and QD for decreasing ligand length. Note that the QDs, ligands and Li⁺ ions are not sketched with their true relative size. (c) Bleaching of a 8DA-linked film of 8 nm QDs in acetonitrile electrolytes using cations of increasing size: from Li⁺ (squares) to TBA⁺ (upward triangles) to TOA⁺ (downward triangles). (d) Schematic illustrating the different sizes of used electrolyte cations. Note that the QDs and ions are not sketched with their true relative size.

a ~ 200 meV lower injection potential (defined as the minimum of the derivative of the relative bleach). While for the 2DA ligands the incomplete relative bleach at saturation due to reduced void size precludes a quantification of the shift, the high relative bleach at low potentials for 2DA ligands confirms the trend that electron injection occurs at lower

potential when the ligand length is decreased. The same qualitative trend of a lowering of the injection potential also holds for films of 3,7 nm diameter QDs (see Appendix A).

While it is conceivable that the ligand itself causes a shift of the energetic position of the QD electron levels, a recent study using photoelectron spectroscopy in air (PESA) showed only negligible variations in the energy levels for films of QDs with varying length of the amine capping.¹⁴ We therefore hypothesize that the distance between cation and injected electron in the QD determines the injection potential instead: an increased proximity of the charges on cation and QD imposes an attractive Coulomb interaction, thereby lowering the electrochemical potential of injection.

To corroborate this hypothesis, we also varied the cation size, with Li⁺ < TBA⁺ < TOA⁺ .^{33, 42} Figure 2.5c displays the charging of a film with 8 nm QDs and 8DA ligands. The large void size in this film allows facile counterion penetration, even in case of the largest ion TOA⁺. This is evident from the complete bleach of the $1S_{3/2}1S_e$ transition for all cations used. We observe a lowering of the injection potential by 500 meV when the size of the cation reduces from TOA⁺ to TBA⁺ to Li⁺. This is consistent with the above proposed scenario in which the proximity of the charges on cation and QD lowers the electrochemical potential of injection.

2.6. Comparison to Ionic Lattices

One might compare the charged QD film to an ionic lattice comprised of negative charges (being the electrons in the QD film) and positive charges (being the electrolyte cations in the voids of the QD film). One could assume that, as is the case for atomic ionic lattices, the cations sit symmetrically between the QDs in the center of the voids. As a result, the total potential of the lattice and, thus, the electrochemical potential of electron injection, should only slightly depend on the ligand length (due to lattice contraction, see Appendix A) and should not depend on the size of the cation.

In strong contrast to this picture, Figures 5a and 5c show that the injection potential is lowered by 200 meV due to a decrease in the ligand length and by 500 meV due to a decrease in cation size. Therefore, we suggest that, unlike cations in atomic ionic lattices, the cations in a film of QDs try to approach the charged QDs as close as possible. Their proximity to the QDs, and hence the film's potential, is controlled by the ligand length and the cation size: the ligand acts as a "spacer", increasing the film's potential with increasing ligand length; the cation size leads to the same effect by controlling the proximity of the charge on the ion and the electron on the QD *via* the thickness of the ion's solvation shell (in case of Li⁺) or the length of its alkyl side chain (in case of TBA⁺ and TOA⁺), respectively.

Apparently cations in QD films do not behave like cations in ionic lattices. This can be understood when we consider that in atomic ionic lattices steric hindrance is responsible for locating the cations in the center of a void. The size ratio between cations and anions is much larger (~1:1) than the QD:cation size ratio. The similarity of the ionic radii of anions and cations immobilizes the cations in the (center of the) small voids of the anionic sublattice. In QD lattices, however, the large ratio in size of QD and cation creates voids that are larger than the cation and permit the cation to "move".

Voids in real films are even larger, since dipcoating results in glassy, rather than ordered films.^{37, 38} Disorder gives rise to inclusions of large voids where the electrochemical potential of electron injection will be controlled by the ligand length and cation size, as they determine the distance between electron and cation (see Figure 2.5). This situation is similar to the charging of a planar semiconductor. Hence, the charged QD film can be modeled by specific optimized electron/cation pairs and absence of ion-lattice periodicity.

Similarly, mesoporous oxide films in dye or QD sensitized solar cells feature larger voids (a few to a few tens of nanometers) and their conduction band minima were found to shift substantially with surface functionalization.^{43:46} Apparently, both the mesoporous oxide films and our CdSe QD film compare better to a planar bulk semiconductor than to atomic ionic lattices. Studies on dye sensitized solar cells already paid substantial attention to the choice of the electrolyte: charge transfer rates could be influenced^{47:49} and the overall device performance optimized^{43, 50} solely by the choice of the electrolyte salt and its concentration. It was found that the conduction band position of metal oxide particles and thus the open circuit voltage mainly depends on the charge-to-size ratio of the electrolyte cation. Specifically, an increasing concentration of Li⁺ led to significant shifts of the metal oxide conduction band edge away from vacuum, lowering the V_{oc}.^{44:46} In general, this trend is known to pronounce with increasing cationic charge-to-radius ratio and decreasing pH.^{43:45} The underlying origin of the positive shifts for small cations continues to stimulate debate with explanations put forward ranging from a reduced

distance between charges of opposite sign⁴⁴ to facilitated cation intercalation into the sample's lattice.^{45, 51-57}

We find a similar trend in our spectroelectrochemical study on CdSe QD films: in case of sufficiently large QDs, a decrease of the ligand length or a decrease of the cation size lowers the electrochemical potential for electron injection into the discrete levels. This is consistent with enhanced Coulomb attraction between electron and cation. Thus, the proximity between injected electron in the QD and cation in the void determines the electronic energy level. This finding sheds light on the origin of the present spread in literature values for one and the same QD electron energy level. The sensitivity of the electrochemical potentials to QD ligands and electrolyte composition should be borne in mind when using electrochemistry to determine absolute energy levels in conductive QD films. In such measurements, the motivation for using small cations and long ligands is two-fold: (1) the necessary porosity for introducing cations is given and (2) the ligands act as "spacers" keeping the cations at a distance, thereby allowing less perturbation of the film's energy levels by cations themselves. However, the choice of both the ligand and the electrolyte also allows control of absolute energy levels in QD films. In QD sensitized solar cells in particular, this can be exploited when engineering the free energy difference between injecting QD electron level and the metal oxide conduction band to optimize the short-circuit current J_{sc} and open circuit voltage V_{oc} of the device.

2.7. CONCLUSIONS

In conclusion, we report electrochemical charge injection of up to 5.5 electrons per QD, yielding the absolute energetic position of both $1S_e$ and $1P_e$ electron levels in CdSe QD films. The maximum electron occupation in quantum-confined states is limited by the uptake of charge compensating electrolyte cations. We identify the physical size of film voids as the main bottleneck, resulting in efficient charging for large QDs with long ligands and small electrolyte cations. Furthermore, the potential of the $1S_e$ energy level shifts away from vacuum, if (1) quantum confinement decreases, or if the distance between cation and QD decreases due to (2) small cations or (3) decreased length of the QD ligand. Such influence of the film morphology, surface functionalization as well as the electrolyte composition on the QD energy levels must not be neglected in

electrochemical measurements of QD films. On the other hand, spectroelectrochemistry serves as a tool to sense and control electrostatic interactions with the electrolyte, illuminating the route towards an optimized design of future optoelectronic devices such as QD sensitized solar cells.

REFERENCES

- 1. Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P., Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution. *Science* 2005, 310, 462-465.
- Luther, J. M.; Gao, J.; Lloyd, M. T.; Semonin, O. E.; Beard, M. C.; Nozik, A. J., Stability Assessment on a 3% Bilayer PbS/ZnO Quantum Dot Heterojunction Solar Cell. Adv. Mater. 2010, 22, 3704-3707.
- 3. Tang, J.; Wang, X.; Brzozowski, L.; Barkhouse, D. A. R.; Debnath, R.; Levina, L.; Sargent, E. H., Schottky Quantum Dot Solar Cells Stable in Air under Solar Illumination. *Advanced Materials* 2010, 22, 1398-1402.
- Sargent, E. H., Infrared photovoltaics made by solution processing. Nat. Photonics 2009, 3, 325-331.
- 5. Sargent, E. H., Colloidal quantum dot solar cells. Nat. Photonics 2012, 6, 133-135.
- 6. Gur, I., Air-stable all-inorganic nanocrystal solar cells processed from solution (21 Oct, pg 462, 2005). Science 2005, 310, 1618-1618.
- Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D.; Chou, K. W.; Fischer, A.; Amassian, A.; Asbury, J. B.; Sargent, E. H., Colloidalquantum-dot photovoltaics using atomic-ligand passivation. *Nat. Mater.* 2011, 10, 765-771.
- Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; Kemp, K. W.; Kramer, I. J.; Ning, Z.; Labelle, A. J.; Chou, K. W.; Amassian, A.; Sargent, E. H., Hybrid passivated colloidal quantum dot solids. Nat Nano 2012, 7, 577-582.
- 9. Anikeeva, P. O.; Halpert, J. E.; Bawendi, M. G.; Bulović, V., Quantum Dot Light-Emitting Devices with Electroluminescence Tunable over the Entire Visible Spectrum. *Nano Letters* 2009, 9, 2532-2536.
- Zhang, Y.; Xie, C.; Su, H.; Liu, J.; Pickering, S.; Wang, Y.; Yu, W. W.; Wang, J.; Wang, Y.; Hahm, J.-i.; Dellas, N.; Mohney, S. E.; Xu, J., Employing Heavy Metal-Free Colloidal Quantum Dots in Solution-Processed White Light-Emitting Diodes. *Nano Lett.* 2011, 11, 329-332.
- Sun, L.; Choi, J. J.; Stachnik, D.; Bartnik, A. C.; Hyun, B.-R.; Malliaras, G. G.; Hanrath, T.; Wise, F. W., Bright infrared quantum-dot light-emitting diodes through inter-dot spacing control. *Nature Nanotech.* 2012, 7, 369-373.
- 12. Konstantatos, G.; Sargent, E. H., Nanostructured materials for photon detection. *Nature Nanotech.* 2010, 5, 391-400.
- Munro, A. M.; Zacher, B.; Graham, A.; Armstrong, N. R., Photoemission Spectroscopy of Tethered CdSe Nanocrystals: Shifts in Ionization Potential and Local Vacuum Level As a Function of Nanocrystal Capping Ligand. ACS Applied Materials & Interfaces 2010, 2, 863-869.
- 14. Jasieniak, J.; Califano, M.; Watkins, S. E., Size-Dependent Valence and Conduction Band-Edge Energies of Semiconductor Nanocrystals. ACS Nano 2011, 5, 5888-5902.
- Gao, J.; Luther, J. M.; Semonin, O. E.; Ellingson, R. J.; Nozik, A. J.; Beard, M. C., Quantum Dot Size Dependent J–V Characteristics in Heterojunction ZnO/PbS Quantum Dot Solar Cells. *Nano Letters* 2011, 11, 1002-1008.
- Vanmaekelbergh, D.; Houtepen, A. J.; Kelly, J. J., Electrochemical gating: A method to tune and monitor the (opto)electronic properties of functional materials. *Electrochim. Acta* 2007, 53, 1140-1149.
- 17. Guyot-Sionnest, P., Charging colloidal quantum dots by electrochemistry. *Microchimica Acta* 2008, 160, 309-314.

- 18. Guyot-Sionnest, P.; Wang, C., Fast Voltammetric and Electrochromic Response of Semiconductor Nanocrystal Thin Films *The Journal of Physical Chemistry B* 2003, 107, 7355-7359.
- 19. Shim, M.; Guyot-Sionnest, P., N-type colloidal semiconductor nanocrystals. *Nature* 2000, 407, 981-983.
- 20. Wang, C. J.; Shim, M.; Guyot-Sionnest, P., Electrochromic nanocrystal quantum dots. *Science* 2001, 291, 2390-2392.
- 21. Yu, D.; Wang, C. J.; Guyot-Sionnest, P., n-type conducting CdSe nanocrystal solids. *Science* 2003, 300, 1277-1280.
- 22. Jha, P. P.; Guyot-Sionnest, P., Trion Decay in Colloidal Quantum Dots. ACS Nano 2009, 3, 1011-1015.
- 23. Galland, C.; Ghosh, Y.; Steinbruck, A.; Sykora, M.; Hollingsworth, J. A.; Klimov, V. I.; Htoon, H., Two types of luminescence blinking revealed by spectroelectrochemistry of single quantum dots. *Nature* 2011, 479, 203-207.
- 24. Jha, P. P.; Guyot-Sionnest, P., Electrochemical Switching of the Photoluminescence of Single Quantum Dots. J. Phys. Chem. C 2010, 114, 21138-21141.
- 25. Houtepen, A. J.; Kockmann, D.; Vanmaekelbergh, D., Reappraisal of Variable-Range Hopping in Quantum-Dot Solids. *Nano Lett.* 2008, 8, 3516-3520.
- Mekis, I.; Talapin, D. V.; Kornowski, A.; Haase, M.; Weller, H., One-pot synthesis of highly luminescent CdSe/CdS core-shell nanocrystals via organometallic and "greener" chemical approaches. J. Phys. Chem. B 2003, 107, 7454-7462.
- 27. Ruch, P. W.; Cericola, D.; Hahn, M.; Kötz, R.; Wokaun, A., On the use of activated carbon as a quasi-reference electrode in non-aqueous electrolyte solutions. *Journal of Electroanalytical Chemistry* 2009, 636, 128-131.
- Wang, Y.; Rogers, E. I.; Compton, R. G., The measurement of the diffusion coefficients of ferrocene and ferrocenium and their temperature dependence in acetonitrile using double potential step microdisk electrode chronoamperometry. J. Electroanal. Chem. 2010, 648, 15-19.
- 29. Hulea, I. N.; Brom, H. B.; Houtepen, A. J.; Vanmaekelbergh, D.; Kelly, J. J.; Meulenkamp, E. A., Wide Energy-Window View on the Density of States and Hole Mobility in Poly(p-Phenylene Vinylene). *Physical Review Letters* 2004, 93, 166601.
- Norris, D. J.; Bawendi, M. G., Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots. Phys. Rev. B 1996, 53, 16338-16346.
- 31. Houtepen, A. J.; Vanmaekelbergh, D., Orbital occupation in electron-charged CdSe quantum-dot solids. J. Phys. Chem. B 2005, 109, 19634-19642.
- 32. Memming, R., Experimental Techniques. Wiley-VCH Verlag GmbH: 2007; p 61-80.
- 33. Spångberg, D.; Hermansson, K., The solvation of Li+ and Na+ in acetonitrile from ab initio-derived many-body ion-solvent potentials. *Chem. Phys.* 2004, 300, 165-176.
- 34. Due to the high charge-to-radius ratio, Li⁺ will have a solvation shell in acetonitrile. The radius of the solvated Li⁺ was calculated by Spangberg et al. [ref. 28] to be 0.5 nm. For TBA⁺ and TOA⁺ we neglect solvation shells, since their alkyl side chains may already provide sufficient solvation. The ion radii are then estimated from the length of the constituent bonds: 0.52 nm and 0.93 nm for of TBA⁺ and TOA⁺, respectively.
- 35. Murray, C. B.; Kagan, C. R.; Bawendi, M. G., Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. *Ann. Rev. Mater. Sci.* 2000, 30, 545-610.
- 36. Shriver, D.; Atkins, P., Inorganic Chemistry. 4th edition ed.; W. H. Freeman: 2006.
- 37. Law, M.; Luther, J. M.; Song, Q.; Hughes, B. K.; Perkins, C. L.; Nozik, A. J., Structural, Optical, and Electrical Properties of PbSe Nanocrystal Solids Treated Thermally or with Simple Amines. *Journal of the American Chemical Society* 2008, 130, 5974-5985.

- Luther, J. M.; Law, M.; Song, Q.; Perkins, C. L.; Beard, M. C.; Nozik, A. J., Structural, optical and electrical properties of self-assembled films of PbSe nanocrystals treated with 1,2-ethanedithiol. ACS Nano 2008, 2, 271-280.
- 39. Yu, D.; Wehrenberg, B. L.; Jha, P.; Ma, J.; Guyot-Sionnest, P., Electronic transport of n-type CdSe quantum dot films: Effect of film treatment. J. Appl. Phys. 2006, 99.
- 40. Nag, A.; Kovalenko, M. V.; Lee, J. S.; Liu, W. Y.; Spokoyny, B.; Talapin, D. V., Metal-free Inorganic Ligands for Colloidal Nanocrystals: S(2-), HS(-), Se(2-), HSe(-), Te(2-), HTe(-), TeS(3)(2-), OH(-), and NH(2)(-) as Surface Ligands. J. Am. Chem. Soc. 2011, 133, 10612-10620.
- El-Kady, M. F.; Strong, V.; Dubin, S.; Kaner, R. B., Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors. *Science* 2012, 335, 1326-1330.
- 42. Memming, R., Principles of Semiconductor Physics. Wiley-VCH Verlag GmbH: 2007; p 1-21.
- 43. Haque, S. A.; Palomares, E.; Cho, B. M.; Green, A. N. M.; Hirata, N.; Klug, D. R.; Durrant, J. R., Charge Separation versus Recombination in Dye-Sensitized Nanocrystalline Solar Cells: the Minimization of Kinetic Redundancy. *Journal of the American Chemical Society* 2005, 127, 3456-3462.
- 44. Morris, A. J.; Meyer, G. J., TiO2 Surface Functionalization to Control the Density of States. The Journal of Physical Chemistry C 2008, 112, 18224-18231.
- 45. Ardo, S.; Meyer, G. J., Photodriven heterogeneous charge transfer with transition-metal compounds anchored to TiO₂ semiconductor surfaces. *Chem. Soc. Rev.* 2009, 38, 115-164.
- 46. Bisquert, J.; Fabregat-Santiago, F.; Mora-Seró, I.; Garcia-Belmonte, G.; Barea, E. M.; Palomares, E., A review of recent results on electrochemical determination of the density of electronic states of nanostructured metal-oxide semiconductors and organic hole conductors. *Inorganica Chimica Acta* 2008, 361, 684-698.
- 47. Pijpers, J. J. H.; Ulbricht, R.; Derossi, S.; Reek, J. N. H.; Bonn, M., Picosecond Electron Injection Dynamics in Dye-Sensitized Oxides in the Presence of Electrolyte. *The Journal of Physical Chemistry* C 2011, 115, 2578-2584.
- Koops, S. E.; O'Regan, B. C.; Barnes, P. R. F.; Durrant, J. R., Parameters Influencing the Efficiency of Electron Injection in Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* 2009, 131, 4808-4818.
- 49. O'Regan, B. C.; Durrant, J. R., Kinetic and Energetic Paradigms for Dye-Sensitized Solar Cells: Moving from the Ideal to the Real. Accounts of Chemical Research 2009, 42, 1799-1808.
- 50. Fabregat-Santiago, F.; Bisquert, J.; Garcia-Belmonte, G.; Boschloo, G.; Hagfeldt, A., Influence of electrolyte in transport and recombination in dye-sensitized solar cells studied by impedance spectroscopy. Solar Energy Materials and Solar Cells 2005, 87, 117-131.
- Lemon, B. I.; Hupp, J. T., Electrochemical Quartz Crystal Microbalance Studies of Electron Addition at Nanocrystalline Tin Oxide/Water and Zinc Oxide/Water Interfaces: Evidence for Band-Edge-Determining Proton Uptake. The Journal of Physical Chemistry B 1997, 101, 2426-2429.
- 52. Lyon, L. A.; Hupp, J. T., Energetics of Semiconductor Electrode/Solution Interfaces: EQCM Evidence for Charge-Compensating Cation Adsorption and Intercalation during Accumulation Layer Formation in the Titanium Dioxide/Acetonitrile System. J. Phys. Chem. 1995, 99, 15718-15720.
- 53. Van de Walle, C. G.; Neugebauer, J., Universal alignment of hydrogen levels in semiconductors, insulators and solutions. *Nature* 2003, 423, 626-628.
- 54. Boschloo, G.; Fitzmaurice, D., Electron Accumulation in Nanostructured TiO2 (Anatase) Electrodes. The Journal of Physical Chemistry B 1999, 103, 7860-7868.
- 55. Kopidakis, N.; Benkstein, K. D.; van de Lagemaat, J.; Frank, A. J., Transport-Limited Recombination of Photocarriers in Dye-Sensitized Nanocrystalline TiO2 Solar Cells. The Journal of Physical Chemistry B 2003, 107, 11307-11315.

- 56. Halverson, A. F.; Zhu, K.; Erslev, P. T.; Kim, J. Y.; Neale, N. R.; Frank, A. J., Perturbation of the Electron Transport Mechanism by Proton Intercalation in Nanoporous TiO2 Films. *Nano Letters* 2012, 12, 2112-2116.
- 57. Wei, D.; Scherer, M. R. J.; Bower, C.; Andrew, P.; Ryhänen, T.; Steiner, U., A Nanostructured Electrochromic Supercapacitor. *Nano Letters* 2012, 12, 1857-1862.

APPENDIX A

A.1 Absorption Spectra

The usual size confinement effects are observed in our CdSe QD dispersions of different diameter (see Figure 2.6). Film formation *via* Layer by Layer (LbL) dipcoating from these dispersions does not substantially relax the confinement. This is illustrated in the inset of the same figure, where the absorption spectrum of a dispersion of 8 nm QDs is compared with that of films of the same QDs, cross-linked by either 4DA (diaminobutane), 6DA (diaminohexane) or 8DA (diaminooctane). Despite some broadening and red-shift of the absorption for the films, the confinement features are preserved.



Figure 2.6 Absorption spectra of QD dispersions with diameters ranging from 2.4 nm to 8 nm. Inset: A dispersion of 8 nm QDs (continuous line) and obtained LbL dipcoated films cross-linked by 4DA (dotted line), 6DA (dashed line) and 8DA (dashed-dotted line) ligands, respectively.

A.2 Cyclic Voltammetry (CV) and Differential Capacitance Measurement

In our differential capacitance measurements, the electrochemical current between working and counter electrode is monitored as a function of time. Commonly, we integrate this current over 3 s following a potential step of 25 meV. Division by the potential step yields the differential capacitance. Prior to integration, the current is corrected for a faradaic background contribution, *i.e.* the remaining current after an exponential decay due to film charging. The hereby obtained differential capacitance for a film of 8 nm QDs with 8DA ligands on a ITO substrate is shown in Figure 2.7 together with a cyclic voltammetry (CV) scan of the same film. Note that both the CV and the differential capacitance scans contain both the signal of the QD film and the ITO substrate. The contribution of the ITO substrate to the total differential capacitance is constant over the studied potential range and responsible for the non-zero signal in the bandgap of the sample (around -o.6 V).



Figure 2.7 Differential Capacitance (left axis) and CV (right axis) of a film of 8 nm QDs with 8DA ligands. The scan directions are indicated by arrows.

A.3 Influence of Film Thickness

Next to the effect of the charge-to-radius ratio of the cation, part of the shift of the injection potential is also due the morphology of the film. Specifically, higher injection potentials are required for thicker films as seen in Figure 2.8 on the example of films of 8 nm QDs with 8DA ligands. We hypothesize that due to the inhomogeneity of the films and a concomitant pore size dispersion, surface-near regions of the film can be penetrated more easily by electrolyte ions. In case an overpotential is needed to drive cations into deeper layers, this establishes a gradient of the required injection potential. Such situation is conceivable, if cations encounter an increasing probability of "blocked" pores on their transit from the bulk electrolyte phase to the bottom layers. If an overpotential is sufficient to overcome such obstacles, charge injection is possible, however at increased potentials. For thicker films, this effect enhances.

To allow for comparison of the various ligands, we processed and studied films with comparable thicknesses in the main article. For the measurements employing various cation types, we even used the same film.



Figure 2.8 Potential dependent relative absorption bleach for QD films of 8 nm QDs with 8DA ligands, grown for three (triangles), ten (squares) and twenty LbL cycles (circles), respectively.

A.4 Ligand Dependence

The same qualitative trend of a lowering of the electrochemical potential of charge injection and a widening of the differential bleach with decreasing ligand length is seen both for 3.7 nm and 8 nm QDs. However, this only holds for the regime where the pore size is still not limiting the incorporation of cations. Notably, in the case of decreased pore size, for example in films of 3.7 nm QDs with short ligands, the injection potential rises again with decreasing ligand length (see Figure 2.9b). Consulting the results of Figure 4 of the main article, we infer that such a transition from a decrease to an increase of the potential with the ligand length occurs in a regime where less than one electron per QD can be injected. From this, we conclude that both Coulomb attraction and steric repulsion determine the electrochemically determined $1S_e$ energy level and density of states. For films of large (8 nm) QDs with long (8DA) ligands, the Coulomb attraction between cations and injected electrons dominates the injection potential.

In films of 8 nm QDs, however, we argued in Chapter 2 that the 200 meV shift of the injection potential for shorter ligands can be assigned to an enhanced attractive Coulomb interaction between electron and electrolyte cation. In this scenario, both charges would try to minimize their distance, until ultimately controlled by the ligand length of one

single electron-cation pair. This can explain the observed shift. We exclude here an additional collective contribution to the shift due to a contraction of the ionic lattice in case of a decrease in ligand length. This is justified, as such a lattice contraction for the studied ligand length and QD diameters would only account for less than 10% of the experimentally observed shift of 200 meV.



Figure 2.9 (a) Dependence of the relative bleach (open symbols) and the differential relative bleach (closed symbols) at the $1S_{3/2}1S_e$ transition on the distance of the Li⁺ ion to the QD surface for films of 3.7 nm QDs with 2DA (upward triangles), 4DA (downward triangles) and 8DA ligands (squares). Gaussian fits proportional to $e^{(-(V-V_0)^2/2\sigma)}$ are depicted by solid lines. (b) Fit parameters injection potential V_0 and width σ as a function of number of C atoms in the ligand for films with 3.7 nm QDs (diamonds) and 8 nm QDs (triangles), respectively.

ligand	Injection potential	Injection potential	Width
		[v vs. Ag wire]	[v]
2DA	-4.02	-0.98	0.25
6DA	-3.99	-1.02	0.15
8DA	-3.85	-1.15	0.13
2DA	-3.41	-1.59	0.22
4DA	-3.77	-1.23	0.15
8DA	-3.70	-1.31	0.10
	ligand 2DA 6DA 8DA 2DA 4DA 8DA	ligand Injection potential [V vs. vacuum] 2DA -4.02 6DA -3.99 8DA -3.85 2DA -3.41 4DA -3.77 8DA -3.70	ligand Injection potential [V vs. vacuum] Injection potential [V vs. Ag wire] 2DA -4.02 -0.98 6DA -3.99 -1.02 8DA -3.85 -1.15 2DA -3.41 -1.59 4DA -3.77 -1.23 8DA -3.70 -1.31

Table 2.1 Fit parameters to the differential bleaches in Figure 2.9

A.5 Cation Dependence

The derivatives to the $1S_{3/2}1S_e$ absorption bleach of a CdSe QD film - measured using different electrolyte cations as presented in Figure 2.5c - can be fitted by a Gaussian density of states proportional to $e^{(-(V-V_0)^2/2\sigma)}$. The free parameters of the fits – injection potential V_0 and width σ – are displayed in Figure 2.10 and summarized in Table 2.2.



Figure 2.10 The fit parameters injection potential (open circles) and width (closed circles) of the Gaussian fits in Figure 2.5c.

Table 2.2 Fit parameters to the differential bleaches in Figure 5c of the main article

Electrolyte cation	Injection potential [V vs. Ag wire]	Injection potential [V vs. vacuum]	Width [V]
Li	-1.15	-3.85	0.13
TBA	-1.30	-3.70	0.14
TOA	-1.62	-3.39	0.24

B IN SITU SPECTROELECTROCHEMICAL DETERMINATION OF BAND OFFSETS IN QUANTUM-DOT FILMS

3.1 INTRODUCTION

Charge transfer at an interface is a fundamental process in many electronic devices, as it allows one to separate charge carriers and guide them into different spatial domains. In photoelectrochemical cells, for instance, this allows water splitting. In solar cells, this concept is used to generate a photocurrent and a photovoltage. To this end, many device designs employ a semiconductor heterojunction comprised of two distinct materials, such as a donor-acceptor (D-A) junction. Upon photoexcitation, disparate energy levels in the conduction and valence band of donor and acceptor (LUMO and HOMO in molecules) lead to charge transfer in one preferential direction. In case of a "type-II" band alignment (see Figure 1.4a), this allows charge separation with electrons and holes accumulating at opposite sides of the interface. To control the direction of charge transfer, knowledge of absolute and relative energy levels in the heterojunction is of paramount importance. A large experimental toolbox is available to study the rate of a charge transfer process, including ultrafast pump-probe spectroscopy. The observed charge transfer rate is then described employing a theoretical model that often involves the free energy difference between donor and acceptor, such as in Marcus theory. It would therefore be insightful to experimentally determine this free energy difference, *i.e.* the band offset in films. This would enable the experimental verification of the employed charge transfer model and the prediction of charge transfer rates in unknown material combinations. The latter allows for a more deliberate design of devices, accelerating their development and reducing their cost by limiting the choice of candidate materials to be investigated.

Unfortunately, realization of this concept is severely hindered by the fact that literature values for (supposedly identical) absolute energy levels vary by more than 1 eV, often exceeding typical free energy differences between materials in heterojunctions. Partially, this can be explained by differences in the experimental techniques used to derive these values. As remarked in section 2.1, each of the commonly used techniques has their own pitfalls: for example, Ultraviolet Photoelectron Spectroscopy (UPS),¹ Photoelectron Spectrocopy in Air (PESA)² and Kelvin probe measurements³ only access the surface of a sample. The assessment of energetics at distances exceeding a few nanometers away from the surface is generally not possible. In addition, measurements are often performed under vacuum, probing energy levels in a different environment than present in the final device.

Electrochemical measurements such as the commonly employed Cyclic Voltammetry (CV) technique offer an alternative approach:⁴⁻⁶ films exceeding one micrometer thickness can easily be measured if the film is sufficiently porous to allow penetration of electrolyte ions.^{5, 7} In the commonly employed Cyclic Voltammetry (CV) mode of operation, the potential applied to the sample is scanned in a cyclic fashion and energy levels are assigned on basis of oxidation and reduction peaks in the charging current. However, reduction and oxidation peaks can be due to either quantum confined states or defect states, complicating their assignment. Moreover, Faradaic background currents in the electrolyte may conceal CV oxidation and reduction peaks. To rule out the ambiguity of the origin of charging currents, simultaneous detection of changes of optical and/or electrolyte gating") experiments combine electrochemical charging of QD films with simultaneous detection of associated changes in the conductance, photoluminescence or absorption of the QD film.⁴⁻⁶

In this chapter, we choose the latter and perform spectroelectrochemical measurements on films of CdSe and PbSe QDs. If charges are injected into a quantum confined energy level, they will induce absorption bleaches at all inter-band transitions to this level and induce absorption due to intra-band transitions from this level.⁸ The voltage at which such absorption changes occur can then be directly converted to an absolute energy scale by calibration of the (fixed) potential of the reference electrode. This electrochemical potential for charge injection is close (within k_BT) to the energy (the enthalpy) of the level of interest. The described spectroelectrochemical approach does not only allow a more accurate determination of energy levels than simple CV measurements, it also allows the *in situ* determination of band offsets in semiconductor heterojunctions, provided that the different materials have different optical characteristics, *i.e.* band gaps. This is the subject of this chapter, which reports on the band offset between CdSe and PbSe in films containing QDs of both materials.



Figure 3.1 Schematic of the in-situ assessment of absolute energy levels via spectroelectrochemistry. The sample is a QD film on a conductive substrate (ITO), immersed in an electrochemical cell containing a solution of Li⁺ClO4⁻ in acetonitrile as the electrolyte. Top: at open circuit, the Fermi level (E_F) in the QD is within the band gap and QDs are uncharged. Bottom: if the Fermi level in the ITO is raised sufficiently by applying a voltage between ITO and reference electrode (Ref), electrons are injected into the QD. As a response, Li+ cations will penetrate the voids in the QD film to compensate the injected charge. Since the QD is small compared to typical depletion widths, negligible band bending occurs and the Fermi level in the QD is constant throughout the film. Here, the situation of one electron per QD is depicted.

Figure 3.1 depicts a schematic of such a spectroelectrochemical experiment for a QD film on a conductive substrate. The film is immersed in an electrolyte, here $Li^+ClO_4^-$ in acetonitrile. The top panel illustrates the equilibrium situation, *i.e.* no voltage is applied between ITO and the (pseudo-)reference electrode. In this case, the Fermi level (E_F, dashed line) lies within the band gap and the QDs are uncharged. The bottom panel shows the situation when a voltage is applied between ITO and reference electrode. If the voltage is sufficiently large, the Fermi level is moved into the conduction band of the QD film and electrons are injected into the QDs. In response, Li⁺ cations of the electrolyte are attracted by the negative charge in the QD film and will penetrate the voids of the QD film. This leads to macroscopic charge compensation. Effectively, the system (consisting of both QDs and electrolyte) remains "uncharged", while inside the QDs, high charge densities can be reached. In the depicted case, every QD contains one electron on average, corresponding to a charge density on the order of 10^{18} to 10^{21} cm⁻³ for QDs with diameters ranging from 1 to 10 nm. This is considered the "degenerate" (or "heavy") doping regime for conventional semiconductor devices. Doping levels of up to ten charges per QD have been demonstrated by electrochemical charging, yielding information of both hole and electron quantum confined levels.^{5, 8-10} Due to electrolyte penetration throughout the pores of the QD film, the Fermi level is constant throughout the film. Band bending is negligible as the QDs (few nanometers in diameter) are smaller than typical depletion width in semiconductors (tens to hundreds of nanometers).⁵

This presents a major difference to Field Effect Transistors (FETs), where only planar charge compensation is provided and depletion regions form. As a consequence, the gate coupling in FETs (*i.e.* the ratio between effective shift of the Fermi level and applied voltage) is much lower than in an electrolyte-gated device where it is close to unity.

In this chapter, we will focus on (inter-band) absorption bleaches of the lowest-energy (band gap) transitions in films of PbSe and CdSe QDs to determine the absolute energy of their respective $1S_e$ levels. Next, we will fabricate composite films containing both type of QDs to determine their band offset *in situ* and demonstrate the importance of the dielectric environment on the *in situ* band offset. Finally, we will show how the size of one of the QDs (PbSe) affects the band offset between PbSe and CdSe.

3.2 EXPERIMENTAL DETAILS

QD synthesis

CdSe QDs were synthesized as described in section 2.1, following Mekis et al.:¹¹ QDs with a diameter of 9.7 nm were obtained, as determined from the 1S peak of their absorption spectra and the sizing curve given by de Mello Donegá and Koole.¹² PbSe QDs of three different size ("S", "M", and "L", with diameters of 4.1 nm, 5.3 nm, and 6.0 nm, respectively) were synthesized following the recipe by Steckel at al.¹³ A first synthesis yielded QDs of size S and M. A second synthesis yielded QDs of size L.

Film Processing and Ligand Exchange

All QD films studied in this chapter were grown on ITO substrates in a layer-by-layer (LbL) dip coating procedure in a N₂ purged glove box: the substrates were first immersed for 30 s in a QD dispersion with a QD concentration on the order of 10⁻⁵ M, subsequently immersed for 30 s in a stirred 0.1 M solution of 1,6-hexanedithiol (6DT) ligands in MeOH, and finally dipped twice for 10s in stirred MeOH to rinse excess ligands. Using this procedure, the original insulating ligands are replaced by the shorter bidentate ligands to allow for charge transport between QDs. The above procedure was repeated 10-20 times to yield films roughly 10-20 QD monolayers thick. A small region on the edge of the ITO substrate remained uncoated to provide electrical contact in electrochemical measurements.

Electrochemical Control of the Fermi Level

Electrochemical control of the Fermi level in QD films as well as measurement of potential dependent changes in the absorption followed the procedure described in section 2.1. However, in this chapter, an additional spectrometer (NIRQuest 256, Ocean Optics) was used to extend the probe range to the near-infrared, to about 2400 nm (0.52 eV). This way, the band edge transition of both PbSe and CdSe QDs can be acquired simultaneously. For all films, the potential was scanned in a cyclic fashion (CV mode), starting from open circuit potential (inside band gap, usually close to o V), scanning at a rate of 10 mV/s, first in negative direction (towards the 1S_e level), and repeating a cycle two to three times. Absorption difference spectra (with respect to the absorption at open circuit potential) were taken every 10-20 mV and the acquired spectra during the

first leg of the first cycle are shown in the figures of the results section. Unless stated otherwise, all potentials are given with respect to a Ag wire pseudoreference electrode immersed in the electrolyte. Its potential (- 4.75 eV vs. vacuum) was calibrated with a ferrocene/ferrocinium couple and was stable within 20 meV. The convention was used that a negative potential corresponds to a shift of the sample's Fermi level towards vacuum.



Figure 3.2 Absorption spectra of pure and composite QD films with 6DT ligands, comprising PbSe QDs of three different sizes and CdSe QDs of 9.7 nm. (a) *Top:* Film of PbSe QDs only (5.3 nm, size "M", with 1S peak at 0.78 eV), depicted as dark blue solid line. A linear fit to the almost featureless absorption above 1.5 eV is shown as a light blue dotted line. *Middle:* Film of CdSe QDs only (9.7 nm, with 1S peak at 1.91 eV). *Bottom:* Bilayer (dark green solid line) consisting of a film of CdSe QDs on top of a film of PbSe QDs of size M. A (light blue dotted) line was fit to the spectrum to emulate the (almost featureless) PbSe contribution above 1.5 eV. Subtraction of the extrapolated PbSe contribution yields the CdSe contribution to the spectrum (light green solid line). (b) Absorption spectra of all bilayer QD films studied in this chapter. *Top:* Bilayer with PbSe QDs of size M (5.3 nm, with 1S peak at 0.78 eV). *Bottom:* Bilayer with PbSe QDs of size "L" (6.0 nm, with 1S peak at 0.71 eV).

Linear absorption spectra

Figure 3.2 displays the absorption spectra of all QD films studied in this chapter. In the top panel of Figure 3.2a, the absorbance of a pure film of PbSe QD (of size M) is shown (blue solid line), below that the absorbance of a pure film of CdSe QDs (yellow solid line), and below that the absorbance of a bilayer comprising a film of CdSe QDs grown on top of a film of PbSe QDs of size M (green solid line). To separate the absorbance contribution of both types of QDs, a line is fitted to the bilayer spectrum from ~ 1.55 eV to ~ 1.75 eV and extrapolated to 2.5 eV to emulate the (almost featureless) PbSe contribution in the region from 1.9 to 2.5 eV (blue dotted line). Subtraction of this simulated PbSe contribution yielded the CdSe contribution to the bilayer spectrum (light green solid line). In Figure 3.2b, the PbSe and CdSe contribution of composite films comprised of both type of QDs are shown, both around their respective 1S peak. Bilayers featuring CdSe QDs and PbSe QDs of size S, M, and L are shown as blue, yellow, and red solid lines, respectively. All composite films show very similar CdSe 1S maxima, at 1.905±0.050 eV.

Spectroelectrochemical Measurements

When a negative potential is applied to a QD films in an electrolyte containing 0.1 M LiClO₄ in anhydrous acetonitrile, next to absorption bleaches due to state filling, we often observe a strong and broad induced absorption background (ΔA >0), increasing towards higher probe energies and increasing with potential. In principle, red shifts of the absorption spectrum, increased scattering, increased reflection, or a combination thereof can lead to such a background. To identify the cause, further experiments are necessary. However, we note that the background appears and disappears slower than the bleach of the 1S transitions and shows a hysteresis with regard to the applied potential. This suggests that it is caused by a slow process, possibly (1) the injection of charges into defect states within the band gap, or (2) the slow rearrangements of electrolyte ions in the voids of the QD film and a slight "breathing" of the film itself. The first hypothesis suggest that the background is caused by an increased absorption due to charged traps. The second hypothesis suggests that scattering is the likely explanation.



Figure 3.3 Processing approach of difference absorption data in spectro-electrochemical measurements of this chapter, on the example of a composite film of PbSe and CdSe QDs with diameters of 5.3 and 9.7 nm, respectively. (a) Typical difference absorption spectrum of the film, at various negative potentials, *i.e.* for raised Fermi levels. A broad induced absorption background (ΔA >o) is visible over the entire spectrum, increasing with decreasing potential. To correct for this background in the energy region of the absorption bleaches (for PbSe between ~ 0.7 and ~ 0.9 eV in the near-infrared and for CdSe between ~ 1.7 and ~ 2.15 eV, shown as grey shaded areas), we fit a straight line through two points defining the respective energy regions. For -1.29 V, these fits are shown as black dashed lines. (b) Same spectra as in (a), but after subtraction of the fitted background. Subtraction was performed individually for the NIR and VIS range.

To correct for this background, we perform a subtraction as shown in Figure 3.3. In our regions of interest around the respective 1S bleaches of PbSe and CdSe (shown as grey shaded areas, from ~ 0.7 to ~ 0.9 eV for PbSe and from ~ 1.7 to ~ 2.15 eV for CdSe), we simulate the induced background by fitting a straight line through two points defining the respective energy regions. For -1.29 V, these fits are shown as black dashed lines. Subsequently, these fits are subtracted from the difference absorption spectra to yield the spectra shown in Figure 3.3b. For the visible and near-infrared region, this subtraction was performed individually. Such a correction is not *per se* justified for a broad wavelength range, but, due to the slowly varying induced absorption background, is a

good estimate around the fitted 1S peaks. Therefore, if not stated otherwise, we apply this correction to all spectroelectrochemical measurements, but only show the region in the vicinity of the respective 1S bleaches.

Differential Capacitance Measurements

To correct for Faradaic background currents in the electrolyte and to determine the steady-state capacitance, we perform differential capacitance measurements. To this end, we scan the potential in a step-like fashion. After each potential step (of 50 mV), we record the electrochemical charging current, *i.e.* the current between sample and a Pt sheet counter electrode. The initial peak current quickly decays to an almost constant level within the first 0.5 s following the step. Since the constant current after decay of the initial dynamics can be attributed to Faradaic background currents in the electrolyte, we subtract this constant level and obtain the current contribution due to electrochemical charging of the film. This background corrected current is integrated and divided by the potential step to yield the differential capacitance, in units of C/V. The differential capacitance is due to the conduction and valence band states in the QD, and due to the double layer capacitance of the QD film as well as the parts of the ITO substrate which are in direct contact with the electrolyte. To correct for the double layer capacitance, we subtract a (potential independent) value of about $3 \cdot 10^{-5}$ C/V for each film.

3.3 ENERGY LEVELS IN QD FILMS

We begin with the spectroelectrochemical determination of energy levels for a pure film with PbSe QDs of 5.3 nm diameter (size "M"). Its absorption spectrum is shown in the top panel of Figure 3.4a. A pronounced peak at 0.795 eV due to the $1S_h1S_e$ transition as well as a small feature at 1.02 eV is observed which has been assigned to the $1P_h1P_e$ transition.¹⁴ After the sample has been placed inside an electrochemical cell, the Fermi level in the sample is raised by applying a negative voltage between sample and Ag pseudoreference



Figure 3.4 Spectroelectrochemical determination of the absolute energetic position of the $1S_e$ level in a film of 5.3 nm Pbse QDs (size "M", 1S peak at 0.795 eV). (a) Upper half: linear absorption spectrum. Lower half: difference absorption spectra for potentials ranging from mid-gap (-0.42 V) to -1.39 V, as given in the legend. No correction for a photoinduced absorption background was performed. The numbers in brackets indicate the acquisition order. (b) Difference absorption image obtained during the CV scan between o and -1.4 V, as given in Panel I of (c). ΔA is displayed by false colors. Time runs from bottom to top. (c) Panel I: CV scan, starting from mid-gap (-0.42 V). An arrow indicates the scan direction. Panel II: differential capacitance on the forward scan (grey filled circles) and the backward scan (grey open circles). An arrow indicates the scan direction bleach $\Delta A/A$ at 0.795 eV. Panel IV: the energetic position of the 1Se level at occupation by one electron is indicated by a horizontal bar. All potentials are given with respect to the Ag pseudo-reference electrode (left axis) and vacuum (right axis).

electrode. Starting from about -0.8 V, a bleach of the absorption ($\Delta A < 0$) at the $1S_h1S_e$ transition appears, see bottom panel in Figure 3.4a. Note that these spectra were not corrected for an induced absorption background, since for this sample that effect was negligible. The $1S_h1S_e$ bleach increases with voltage up to -1.1 V, reducing the absorption at the 1S peak by roughly 40 %, and then slightly decreases again for more negative voltages.

Next to a bleach at the band edge, one observes a slight bleach at 0.9 eV and a red shift at 1.0 eV. The latter coincides with a peak in the linear absorption spectrum at the same energy, which we assigned to $1P_h1P_e$ transition. The former might be due to the formally (dipole-)forbidden $1S_h1P_e$ and $1P_h1S_e$ transitions.^{14, 15} Both the slight bleach at 0.9 eV and the red shift at 1.0 eV appear at the same voltage (about -0.8 V) as the band edge bleach, suggesting that the filling of the $1S_e$ level is their cause.

After -1.4 V, the scan direction is reversed and the potential cycled twice between 0 and -1.4 V at a constant rate of 10 mV/s. Figure 3.4b shows the recorded difference absorption as a false color image. The second CV cycle almost completely reproduces the absorption features of the first cycle, demonstrating that electrons can be reversibly injected and emptied from the $1S_e$ level. However, a pronounced hysteresis is observed: on the backward scan, the bleach magnitude is lower and the potential of the bleach onset illdefined. Moreover, the $1S_h1S_e$ bleach decreases again already before the potential scan direction is reversed, from about – 1.1 V on the forward scan. Tentatively, we attribute the early bleach decrease and the hysteresis to slow trap filling at negative potentials. This trap filling is continuous and eventually leads to a reduction of the number of $1S_e$ electrons due to Coulomb repulsion among (an increasing number of) electrons in traps.

Figure 3.4c-I shows the simultaneously monitored electrochemical current in the CV scan, with an arrow indicating the scan direction and the potential at the start of the scan. Only one weakly pronounced reduction feature between -1.05 and -1.10 V is observed on the forward scan, while no oxidation feature could be resolved, in stark contrast to the strong optical absorption bleaches revealing filling and emptying of the $1S_e$ level. This highlights the added value of simultaneous collection of optical data for the determination of absolute energy levels, its increased sensitivity and reduced ambiguity concerning the type of energy level probed. Therefore, in this chapter we infer energy levels solely from difference absorption data.

As a control experiment, we further perform a differential capacitance measurement, *i.e.* we determine the amount of charge injected into the system after a small potential step

of 50 mV (see section 3.1 for details of this method). This quantity, in units of C/V and corrected for Faradaic background currents in the electrolyte, is depicted in Figure 3.4c-II. Filled and open grey circles show the differential capacitance for the forward and backward scan, respectively. A grey arrow indicates the scan direction and potential at start. At negative potentials exceeding – 0.7 V, charge is injected into the QD film. At about -1.0 V, a peak of the differential capacitance is observed. The backward scan reproduces the forward scan, apart from a small difference in magnitude.

The investigate whether the differential capacitance reflects injection of electrons into the $1S_e$ level or injection into defect states in the band gap, we determine the number of $1S_e$ electrons $n_{1S}(V)$ from the difference absorption data in Figure 3.4a, depicted as red circles in Figure 3.4c-III. This number is inferred from the relative absorption bleach according to

$$n_{1S_{e}}(V) = g_{1S_{e}} \cdot \frac{\Delta A_{1S_{h}1S_{e}}(V)}{A_{1S_{h}1S_{e}}(V_{oc})}$$
(3.1)

where g_{1S_e} is the degeneracy of the 1Se level ($g_{1S_e}=8$ in the case of PbSe) and $\Delta\!A_{\!\scriptscriptstyle IS,IS}\left(V
ight)$ is the absorbance difference at potential V with respect to the absorbance $A_{
m 1S, 1S,}(V_{oc})$ at open circuit potential V_{oc} . The number of 1Se electrons are inferred from the absorbance (difference) at 0.795 eV, indicated by a red arrow in Figure 3.4a. From about – 0.8 V, electrons are injected into the $1S_e$ level. At – 0.87 V, an average population of one electron per QD is reached, indicated by a dashed vertical line. The population reaches a maximum of 3.1 electrons/QD at - 1.09 V. Its derivative with respect to potential, $dn_{1Se}(V)/dV$, equals the contribution of $1S_e$ injection to the differential capacitance shown in Figure 3.4c-II, given in units of charge per potential step. Since the steepest slope in $n_{1S}(V)$ is observed at the same potential as the maximum in the differential capacitance, *i.e.* at about – 1.0 V, the differential capacitance predominantly reflects injection of 1Se electrons. A second contribution to the differential capacitance might be due to the filling of trap states, the proposed cause for the decrease of the $1S_{3/2}1S_e$ bleach (see above). Traps in the band gap would explain the early onset of charge injection (at about -0.5 V), preceding the onset of the absorption bleach at about – 0.75 V. Traps above the 1Se level would explain that the maximum of the differential capacitance (at – 1.0 V) is reached only after a maximum of $dn_{1se}(V) / dV$ is observed (at – 0.9 V). Note that a quantification of the trap density would require a slower scan rate than used here (~ 50 mV/min), as the injection into trap states is expected to be slow.

3.3.2 ENERGETICS OF ELECTRON INJECTION

A relevant quantity for the study of charge transfer and charge transport as well as the utilization of these processes in devices is the energy at which one electron occupies the $1S_e$ level, as this is the energy that needs to be paid for injecting or transferring an electron to the $1S_e$ level. For an electron in the $1S_e$ level of a single QD, this "quasiparticle" energy is given by

$$E_{1Se}^{qp} = E_{EA,bulk} + E_e^{kin} + E_e^{pol,self}$$
(3.2)

where $E_{EA,bulk}$ is the electron affinity in bulk, E_e^{kin} is the kinetic confinement energy, and $E_{\perp}^{pol,self}$ is the polarization energy to pay (win) in case the dielectric screening outside the QD is smaller (larger) than the screening inside the QD. The term $E_{a}^{pol,self}$ is also called the "self-energy" or charging energy of an electron. The kinetic confinement and polarization term were already introduced in Section 1.1.1 and are given by $E_e^{kin} = h^2 / (8m_e * R_{OD}^2)^{16}$ where $m_{_{\! P}}^{} *$ is the electron effective mass and $R_{_{OD}}^{}$ the QD radius, and by $E_e^{pol,self} \approx e^2 / (8\pi \varepsilon_0 R_{OD}) \cdot \left[(\varepsilon_{OD} - \varepsilon_{out}) / (\varepsilon_{OD} \varepsilon_{out}) \right]$,¹⁷ where ε_{OD} and ε_{out} are the dielectric constants inside and outside the QD, respectively. We use here the high-frequency dielectric constants, $\varepsilon_{OD} = 23$ for PbSe and $\varepsilon_{OD} = 6$ for CdSe,¹⁸ as under confinement the kinetic energy of the electron exceeds typical phonon frequencies.¹⁹ The dielectric constant outside is an effective dielectric constant with contribution from ligands and electrolyte in the voids ($\varepsilon_{void} \approx \varepsilon_{electrolyte} \approx 2$) as well as surrounding QDs, see Figure 3.5. Assuming a filling fraction between 0.3,²⁰ and using Bruggeman effective medium theory,²¹ this yields $\varepsilon_{out} \approx 5$ for PbSe and $\varepsilon_{out} \approx 3$ for CdSe. For the QDs studied in this chapter, this leads to self-energies between 30 meV (for CdSe QDs) and 60 meV (for the small PbSe QDs).

This differs from the case of optical excitation where the electron interacts with the simultaneously excited hole (given by the direct Coulomb interaction and cross-polarization terms in Equation (1.6)). Generally, this means that the quasi-particle energy level for a single electron is higher (closer to vacuum) than the level for an electron in the presence of a hole. In principle, spectroelectrochemistry can determine this quasi-particle energy level: Figure 3.4c-IV shows the energy corresponding to one electron per QD as a horizontal red bar, at -3.88 eV vs. vacuum.



Figure 3.5 Schematic of the dielectric environment inside a QD film where one electron (e⁻) resides inside a QD and is charge compensated by a neighboring Li⁺ counterion. The dielectric constant inside a QD is given by \mathcal{E}_{QD} and outside by an effective dielectric constant \mathcal{E}_{out} with contributions from neighboring QDs, ligands, and electrolyte.

However, so far we have neglected the influence of the electrolyte. As shown in Figure 3.1, injection of one electron per QD into the $1S_e$ level occurs if and only if a combination of conditions are met: the Fermi level in the ITO must be lifted to the quasi-particle energy E_{1Se}^{qp} in the QDs, and the energetics must be favorable to allow Li⁺ ion penetration into the voids of the QD film while ClO_4^- remain in the bulk of the electrolyte or move away from the QD film. Thus, the electrochemical potential μ_{1Se} at which $1S_e$ injection occurs, can formulated by

$$\mu_{1Se} = E_{1Se}^{qp} + E^{EL} \tag{3.3}$$

where E^{EL} denotes the sum of the terms ascribed to the presence electrolyte, given by

$$E^{EL} = E_{Li}^{pol,self} + \Delta E_{Li}^{solv} + E_{Li,ClO_4}^{diss} + E_{e,Li}^{dir} + J_{e,Li}^{dir} + J_{e,e}^{dir} + J_{Li,Li}^{dir}$$
(3.4)

It contains the self-energy $E_{Li}^{\textit{pol,self}}$ of the Li* cation in the voids of the QD film, a possible energy penalty $\Delta E_{Li}^{\textit{solv}}$ for reduced solvation of Li* ions by acetonitrile moelcules, a possible energy penalty $E_{Li,ClO_4}^{\textit{diss}}$ for dissociation of Li*ClO₄- ion-pairs, the direct Coulomb attraction $E_{e,Li}^{\textit{dir}}$ between an electron and a Li* cation, and finally many body terms describing the interaction of all charges in the sample, attractive between electrons and Li* ions ($J_{e,Li}^{\textit{dir}} < 0$), but repulsive between electrons ($J_{e,e}^{\textit{dir}} > 0$) and between Li* ions ($J_{Li,Li}^{\textit{dir}} > 0$).
At occupation of one electron per QD, the film may be approximated by a ionic lattice, comprised of an (ordered) array of negative charges (the electrons) and positive charges (the Li⁺ counterions). In this case, the last four terms containing the direct Coulomb interactions can be combined into a single term $M \cdot E_{e,Li}^{dir}$, where M is the Madelung constant of the lattice. Madelung constants depend on the type of ionic lattice formed, but are typically on the order of 1.5 – 2 for lattices of monovalent ions.

The term E_{Li,ClO_4}^{diss} may be neglected as the concentration of ion-pairs in our 0.1 M LiClO₄ electrolyte solution is low.²² Moreover, the number of electrolyte cations in the entire electrochemical cell greatly exceeds the typical number of injected charges into the film, such that free, *i.e.* un-paired, cations are always available for charge compensation, rendering $E_{Li,ClO_4}^{diss} \approx 0$.

Finally, we discuss the energy penalty ΔE_{Li}^{solv} due to a possibly necessary shedding of the solvating acetonitrile shell surrounding Li⁺ ions upon penetration of small voids in the QD film. We argue that the solvation energy of Li⁺ in acetonitrile is large (5.3 eV)²³ which makes the shedding of the solvation shell unlikely: if only one of the four solvating acetonitrile molecules in the first solvation²³ shell would be shed, an energy penalty exceeding 1 eV would need to be paid. This would be inconsistent with the low electrochemical band gap observed in films with large PbSe QDs (see discussion below). Furthermore, since for our QD films with 6DT ligands the voids are large enough to host one Li⁺ ion including its solvation shell,^{7, 24} $\Delta E_{Li}^{solv} \approx 0$. In conclusion, Equation (3.4) may be approximated by

$$E^{EL} \approx E_{Li}^{pol,self} + M \cdot E_{e,Li}^{dir}$$
(3.5)

The self-energy $E_{Li}^{pol,self}$ can be calculated analogue to the case of the electron¹⁷ by assuming that the Li⁺ sits in the center of a void with radius R_{void} and dielectric constant ε_{void} , surrounded by the film with an (effective) dielectric constant ε_{out} . This yields $E_{Li}^{pol,self} \approx e^2 / (8\pi\varepsilon_0 R_{void}) \cdot [(\varepsilon_{void} - \varepsilon_{out})/(\varepsilon_{void} \varepsilon_{out})]$. Due to the slow dielectric relaxation of the solvated Li⁺ ions in the void, static dielectric constants need to be used: $\varepsilon_{void} = 37.5$ for voids filled with acetonitrile, and $\varepsilon_{out} = 68$ for PbSe and $\varepsilon_{out} = 27$ for CdSe. This yields small self-energies for Li⁺ in the voids, as shown in Table 3.1: between + 3 meV (in case of CdSe QDs) and – 8 meV (in case of PbSe QDs of 4.1 nm diameter).

Table 3.1 Electrolyte contribution to the 1S_e energy level at occupation of one electron per QD: Self-energy of the Li⁺ cation, $E_{Li}^{pol,self}$, and ionic lattice energy $M \cdot E_{e,Li}^{dir}$, given by the Madelung constant (M = 1.75) and the direct Coulomb interaction between electron and Li⁺. Their sum is given in the last column.

	QD diameter [nm]	$E_{{\scriptscriptstyle L}i}^{{\scriptscriptstyle pol},{\scriptscriptstyle self}}$ [eV]	$M \cdot E_{e,Li}^{dir}$ [eV]	Sum [eV]
PbSe S	4.1	-0.008	-0.012	-0.020
PbSe M	5.3	-0.006	-0.009	-0.016
PbSe L	6.0	-0.006	-0.008	-0.014
CdSe	9.7	0.003	-0.013	-0.010

The direct Coulomb interaction $M \cdot E_{e,Li}^{dir} = -M \cdot e^2 / \left[4\pi \varepsilon_0 \varepsilon_{eff} \left(R_{void} + R_{void} \right) \right]$ of all electrons and all Li+ ions in the film is comparable, as shown in Table 3.1 for the Madelung constant M = 1.75 , *i.e.* for the case of the rock-salt lattice. While the rock-salt configuration was used as an example, different ionic lattice structures are conceivable. However, the Coulomb interaction will be comparable for all lattice types, as Madelung constants of typical ionic lattices of monovalent ions do not vary much. Finally, a disordered film of electrons and ions, as likely the case for our sample, may show a reduced stabilizing effect of the Coulomb interaction. In conclusion, the presented values for the direct Coulomb interaction in Table 3.1 are seen to be as a coarse estimate only. However, it is clear that both the self-energy for Li⁺ and the direct Coulomb interaction are small and that their sum is on the order of - 10 meV (for CdSe) and - 20 meV (for PbSe QDs). This means that the presence of the electrolyte in the voids of the QD film has a negligible effect on the quasi-particle energy levels and that electrochemical charging, at least for the case of one electron per QD, does not alter the probed energy level. Expressing this in the language common for the study of Field Effect Transistors (FETs), the "gate coupling", i.e. the ratio between effective shift of the Fermi level and applied voltage, is unity. Therefore, (spectro-)electrochemistry lends itself to the determination of (quasi-particle) energy levels in QD films, provided that voids are sufficiently large, see chapter 2.

3.3.3 SPECTROELECTROCHEMICAL ASSESSMENT OF CONFINED ELECTRON LEVELS IN FILMS OF CDSE QDS

After having assessed the $1S_e$ energy in a film of PbSe QDs and estimated the energetics of electron injection in QD films, we proceed to spectroelectrochemically determining electron energy levels in a film of CdSe QDs with a diameter of 9.7 nm. Figure 3.6a shows the absorption and difference absorption spectra of this film. Selected transitions are indicated by numbers 1-4, and assigned according to Norris and Bawendi:²⁵ feature 1 is due to the (close spaced) $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$ transitions around 1.91 eV, feature 2 due to the $1P_{3/2}1P_e$ transition at 2.06 eV, feature 3 due to the $3S_{1/2}1S_e$ transition at 2.35 eV and feature 4 at 2.5 eV due to the $1P_{1/2}^{so}1P_e$, $1S_{1/2}2S_e$, or $4S_{3/2}2S_e$ transition. At negative potentials exceeding – 0.9 V, the absorption at transitions 1 and 3 start to bleach simultaneously. At about – 1.2 V, the first absorption peak is completely bleached, *i.e.* $\Delta A_{1S3/2 \rightarrow 1Se} (-1.2V) / A_{1S3/2 \rightarrow 1Se} (0V) = -1$, and transitions 2 and 4 start to bleach, up to – 1.5 V, where the potential is reversed.

Figure 3.6b displays difference absorbance data of the entire CV scan as a false color image. Transition 1 and 3 as well as 2 and 4 bleach and recover in a concerted action. This points towards filling and emptying of identical energy levels, based on the assignment of Norris and Bawendi the $1S_e$ and $1P_e$ level, respectively. The symmetry of the image with respect to the potential turning points (y axis) show that bleaching proceeds reversible and reproducible. Figure 3.6c depicts the electrochemical charging current during the CV scan (Panel I), a differential capacitance scan (Panel II), and the number of electrons in the 1Se and 1Pe level as inferred from the difference absorbances (Panel III). As in the case of the PbSe QD film, the CV scan lacks well-resolved reduction and oxidation features, while the differential capacitance reveals three pronounced injection regimes, marked by asterisks. The first regime (*) is not accompanied with optical changes (see Panel III), suggesting charging of trap states within the band gap. The second regime (**) coincides with injection of 1Se electrons as inferred from the bleaching of the 1S_{3/2}1Se and 2S_{3/2}1Se transition at 1.91 eV (dark blue line), and the third regime (***) coincides with injection of $1P_e$ electrons as inferred from the bleaching of the $1P_{3/2}1P_e$ transition at 2.06 eV (light blue line). This allows us to establish the energy diagram depicted in Panel IV: the energy corresponding to occupation of one electron per QD in the 1Se level, i.e. $\Delta A_{1S3/2 \rightarrow 1Se}(\breve{V})/A_{1S3/2 \rightarrow 1Se}(0V) = -1/2$ resides at -3.68 eV vs. vacuum. For the 1Pe level, the energy corresponding to occupation electron. i.e. bv one $\Delta A_{1P3/2 \to 1Pe}(V)/A_{1P3/2 \to 1Pe}(0\breve{V}) = -1/6$, lies 0.15 eV higher. After another 0.08 eV,



Figure 3.6 Spectroelectrochemical determination of the absolute energetic position of the 1S_e and 1S_e level in a film of 9.7 nm Cdse QDs (1S peak at 1.91 eV). (a) *Upper half:* linear absorption spectrum. *Lower half:* difference absorption spectra for potentials ranging from open circuit potential (-0.03 V) to -1.49 V, as given in the legend. The numbers in brackets indicate the acquisition order. (b) Difference absorption image obtained during the CV scan between 0 and -1.5 V, as given in Panel I of (c). ΔA is displayed by false colors. Time runs from bottom to top. (c) *Panel I:* CV, starting from open circuit potential (-0.03 V). An arrow indicates the scan direction. *Panel II:* differential capacitance. Filled grey circles depict the forward scan, empty grey circles the backward scan. A grey arrow indicates the scan direction. The three features (*), (**) and (***) are discussed in the main text. *Panel III:* number of electrons in the CdSe 1S_e and 1P_e level. For the 1S_e level, this number is deduced from the relative absorption bleach at transition 3 (light blue solid line). *Panel IV:* absolute energies of the 1S_e and 1P_e levels.

half of the $1P_e$ level is occupied. This energy spacing is in coarse agreement with the expectation (0.11 eV) based on the energy difference between the $1S_{3/2}1S_e$ and $1P_{3/2}1P_e$ transition (0.15 eV) and effective masses of 0.13 and 0.44 for electron and hole, respectively.

3.4 BAND OFFSET IN A QD HETEROSTRUCTURE

Based on the spectroelectrochemical measurements for a pure film of PbSe QDs with a diameter of 5.3 nm (shown in Figure 3.4) and a pure film of CdSe QDs with a diameter of 9.7 nm (shown in Figure 3.6), one would expect a band offset of 0.2 eV between the respective $1S_e$ states in both films. To test this hypothesis, we fabricated an alternating multilayer of both type of QDs by alternatingly depositing a layer of PbSe QDs, then a layer of CdSe QDs, and repeating this cyle twelve times. The absorption spectrum of the resulting film is shown as a black solid line in the top panel of Figure 3.7a. The estimated CdSe contribution (see section 3.1 for details) is displayed as grey solid line. A fit consisting of a sum of Gaussians is given as a blue dashed line. Fitted transitions involving the $1S_e$ and $1P_e$ level are depicted by green and red dashed lines, respectively, and higher energy transitions by grey dashed lines. These fits were performed to quantify the bleaches upon electrochemical charging and to correlate them with distinct optical transitions, enabling the assignment of the level to which charges are injected into.

Difference absorption spectra at potentials ranging from open circuit (- 0.3 V) to – 1.3 V are given in the bottom panel and color-coded as given in the legend. The $1S_{h}1S_{e}$ transition in PbSe at a probe energy of 0.795 eV (indicated by a red arrow) is bleached from about – 0.55 V, whereas the CdSe $1S_{3/2}1S_{e}$ transition at a probe energy of 1.905 eV (indicated by a dark blue arrow) bleaches only at potentials exceeding about – 0.75 V. The CdSe $1P_{3/2}1P_{e}$ transition at a probe energy of 2.05 eV (indicated by a light blue arrow) is not bleached within the range of applied potentials. The shown difference absorption spectra were collected during the forward scan of the first of two cycles in the CV scan that is shown in Figure 3.7b-1. A change in slope at – 0.55 and -0.80 V on the forward scan corresponds to appearance of PbSe and CdSe absorption bleaches, respectively, at similar potentials. This suggests that injection into the PbSe and CdSe $1S_{e}$ states is the dominant current and that the density of defect states is low or that their charging is slow compared to the scan rate of 10 mV/s of the CV. This picture is confirmed in the differential capacitance depicted in

Figure 3.7b-II. No charge is injected into the QD film up to - 0.50 V, after which two charging waves around - 0.65 and - 1.00 V are observed.



Figure 3.7 Spectroelectrochemical determination of the band offset in an alternating multilayer of 5.3 nm Pbse QDs (size "M", 1S peak at 0.785 eV) and 9.7 nm CdSe QDs (1S peak at 1.905 eV). (a) Absorption (*top*) and difference absorption spectra at various potentials (*bottom*). The contribution of CdSe (grey solid line) to the absorption spectrum is obtained as described in the experimental section and fitted with a sum of 6 Gaussians (blue dashed line). Transitions involving the 1S_e and 1P_e level are depicted by green and red dashed lines, respectively, and higher energy transitions by grey dashed lines. (b) *Panel I:* CV, starting from -0.3 V. An arrow indicates the scan direction. *Panel II:* differential capacitance, starting from o V. Filled grey circles depict the forward scan, empty grey circles the backward scan. *Panel III:* number of electrons in the PbSe 1S_e level (red circles) CdSe 1S_e level (blue triangles), respectively, as deduced from the relative absorption bleach at the respective band gap transitions. *Panel IV:* energetic position of both 1S_e levels, featuring a separation of 0.52 eV.

It is also consistent with the optical assessment, summarized in Figure 3.7b-III. Here, as for the pure films, the number of electrons in the $1S_e$ level of PbSe (red circles) and CdSe (blue triangles) is inferred from the relative absorption bleaches at the respective lowestenergy transition, at 0.785 eV for PbSe and 1.905 eV for CdSe). The onset of the absorption bleaching coincides with the onset for electrochemical charge injection (see Figure 3.7b-I and Figure 3.7b-II), while an average occupation of one electron per QD is reached at the potentials indicated by horizontal bars in Figure 3.7b-IV, equivalent to the PbSe $1S_e$ state at -4.15 eV vs. vacuum and the CdSe $1S_e$ state at -3.63 eV vs. vacuum. The determined band offset of 0.52 eV between CdSe and PbSe in the alternating multilayer film is much higher than the band offset of 0.20 eV that we estimated based on the respective levels in the pure films (see section 3.3).

One can imagine that this difference is due to a different dielectric environment. To investigate this hypothesis, we also fabricated a bilayer, consisting of a thick layer of CdSe QDs on top of a thick layer of PbSe QDs, grown *via* LbL dipocating with 15 LbL cycles for each type of QD. This allows for phase separation of both types of QDs within the composite film and minimizes their mutual interaction. In fact, such a layer stack mimics the situation of two pure films stacked on top of each other. If the dielectric environment plays a dominant role in determining the band offset, bilayer and pure films should show a similar offset. Figure 3.8a illustrates the number of electrons in the PbSe $1S_e$ level (filled circles) and CdSe $1S_e$ level (open triangles) in pure films of 5.3 nm PbSe QDs (black) and 9.7 nm CdSe QDs (grey) as well as a bilayer (yellow) and an alternating multilayer (blue) of both types of QDs. The energy corresponding to one electron per QD is indicated by dotted and dashed lines for PbSe and CdSe, respectively.

Compared to the pure film, the CdSe $1S_e$ level has a higher potential in both the bilayer and alternating multilayer film. On the other hand, the PbSe $1S_e$ levels in the composite films reside at lower potential than in the pure film. The combined effect of a higher CdSe and a lower PbSe potential leads to a larger band offset in the bilayer (0.61 eV) and alternating multilayer (0.52 eV) compared to the hypothetical band offset in pure films (0.20 eV). The large difference in band offset between bilayer film and extrapolation from $1S_e$ levels in pure films is incompatible with a large influence of the layer stack on the band offset as a result of altered dielectric environment. If this were the case, the bilayer and pure films should exhibit comparable band offsets, while the alternating multilayer would deviate. Moreover, Table 3.1 showed that the effect of the electrolyte on the $1S_e$ levels is small, on the order of 10 to 20 meV for our PbSe and CdSe QD films. This suggests that the



difference in the dielectric environment of pure film, bilayer and alternating multilayer cannot explain the observed variations in their respective $1S_e$ levels.

Figure 3.8 Energy levels and band offset depending on layer stack. (a) Number of electrons in the PbSe $1S_e$ level (filled circles) and CdSe $1S_e$ level (open triangles), respectively, for a film of PbSe QDs only (black), CdSe QD only (grey), a bilayer (yellow), and an alternating multilayer (dark blue). The potential at which the respective $1S_e$ level is occupied by one electron is indicated by dotted (PbSe) and dashed (CdSe) lines, respectively. The spread in potential is illustrated as red and blue shaded area, respectively. The band offset based on the single layers (0.21 eV) is much smaller than the band offset in the bilayer (0.61 eV) or multilayer (0.52 eV). (b) Differential capacitance scans for all films, consistent with the band estimates in (a).

Alternatively, the surface of the QD film may explain differences in the measured energy level structure: the stoichiometry,²⁶ ligand density,^{26, 27} type²⁸⁻³⁰ and anchor group³¹ as well as charged surface traps⁴ have all been shown to shift energy levels. In all our QD films, thiol ligands were used as the organic capping. Thiols are known to affect energy levels of QDs due to surface dipoles.^{1, 31} Hence, their density on the QD surface will

determine the $1S_e$ energy for an electron in the QD. While the same dithiol ligands were used in pure films, bilayer and alternating multilayer, it is conceivable that slight variations in ligand coverage of the QDs are present in the different stacks and therefore lead to a difference in the energetic position of the $1S_e$ level.

An additional shift can result from charged surface traps.⁴ Chapter 5 demonstrates the importance of traps in QD films and show they are filled, *i.e.* charged, when the potential is varied. Charged surface defects were so far not considered in our description of the energetics of electrochemical charge injection (see section 3.2.2), but may strongly influence these energetics by additional Coulomb interactions with electrons in the QD and Li⁺ cations in the electrolyte. While both the quantification of the density of defect states (see chapter 5) and its effect on the energy level diagram are difficult, a first estimate can be obtained from differential capacitance measurements, as these record injection into both optically active (quantum confined) and passive (defect) states. Figure 3.8b shows the differential capacitance of all films. For clarity, only the forward scan is depicted. Comparison with the spectroelectrochemical data of Figure 3.8a shows that only few charges are injected into states within the band gap. This can either be result of a low defect density or a slow injection of charges into defect states which cannot keep up the pace of our scan speed (50 – 100 mV/min).

Finally, a high density of electrochemically injected charges may influence the determination of energy levels in QD films. In the case of the PbSe-CdSe alternating multilayer, almost seven electrons have been injected into PbSe QDs before the CdSe $1S_e$ level starts to be occupied. One might argue that for these high charge densities, the assumption that electrochemical charge injection has a minor effect on the determined energy levels (see Table 3.1) might not hold any more. However, in section 3.5 we show that the assumption does hold, at least for large PbSe and CdSe QDs.

In conclusion, the observed variations in the studied film stacks and the experimental difficulty to quantify the effect of surface charges on the energy level structure show that the extrapolation of energy levels obtained for pure films to respective energies in a heterostructure should be avoided. This highlights the importance of assessing the band offset *in situ* for the sample of interest.

3.5 DEPENDENCE OF BAND OFFSET ON QD SIZE

To further test the capabilities of spectroelectrochemical *in situ* determination of band offsets, we assess the dependence of band offset on the size of one of the QDs. To this end, we fabricated bilayers containing a film of CdSe QDs on top of a film of PbSe QDs of three distinct sizes: size "L" with a diameter of 6 nm, size "M" with a diameter of 5.3 nm, and size "S" with a diameter of 4.1 nm. The band offset of the bilayer with PbSe QDs of size M (0.61 eV) has already been determined in Figure 3.8. The expectation for the remaining two films is that the band offset is larger for PbSe QDs of 6.0 nm diameter and smaller for PbSe QDs of 4.1 nm.

Figure 3.9a shows the absorption (top panel) and difference absorption spectra (bottom panel) of the film with the larger PbSe QDs. A black solid line shows the absorbance around the $1S_h1S_e$ transition of the PbSe QDs (at 0.69 eV, indicated by a red arrow) and a grey solid line shows the CdSe contribution (obtained as discussed in section 3.2) around the CdSe $1S_{3/2}1S_e$ transition (at 1.91 eV, indicated by a dark blue arrow). To assign features in the absorption spectrum to either $1S_e$ or $1P_e$ level, the CdSe contribution has been fitted as described above.

We now perform a CV scan (see Figure 3.9b-l), starting from o V, beginning in negative scan direction, reversing the potential at – 1.6 and + 0.25 V, and cycling the potential for two consecutive times. Up till the first potential turning point at – 1.6 V, difference absorption spectra with respect to the absorbance at o V are recorded and displayed in Figure 3.9a. Initially, slight bleaching of the PbSe $1S_h1S_e$ transition is observed, becoming significant from about – 0.2 V and almost reaching transparency, *i.e.* $\Delta A_{1Sh \rightarrow 1Se} / A_{1Sh \rightarrow 1Se} \approx -1$, at about – 1.0 V. Bleaching of the $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$ transitions in CdSe occurs at more negative potentials, starting at about – 1.0 V and reaching a plateau at about – 1.5 V. This saturation suggests that at -1.5 V, the $1S_e$ level is completely filled (with two electrons). The $1P_e$ level continues to be charged, as deduced from the increasing absorption bleach at 2.05 V (light blue arrow). Upon reversal of the scan direction, both CdSe and PbSe recover their ground state absorbance, until at positive potentials, the PbSe $1S_h1S_e$ transition gets bleached again. At a potential of + 0.27 V, on average one hole per PbSe QD is injected.



Figure 3.9 Spectroelectrochemical determination of energy levels in a bilayer of 6.0 nm Pbse QDs ("L" size, 1S peak at 0.69 eV) and 9.7 nm CdSe QDs (1S peak at 1.91 eV). (a) *Upper half*: linear absorption spectrum of the bilayer film. In the region from 1.7 to 2.2 eV, only the CdSe contribution to the spectrum is shown and fitted (see main text for details). *Lower half*: difference absorption spectra for various potentials as indicated in the legend. (b) *Panel I*: CV, starting from open circuit potential (-0.02 V). An arrow indicates the scan direction. *Panel II*: number of electrons in the PbSe 1S_e or 1S_h level (red solid line), in the CdSe 1S_e level (dark blue solid line), and the CdSe 1P_e level (light blue solid line), respectively, as deduced from the relative absorption bleach $\Delta A/A$ at 0.69, 1.91, and 2.05 eV, respectively. *Panel III*: absolute energies of the PbSe 1S_h and 1S_e level as well as the CdSe 1S_e and 1P_e level. The level spacing is depicted by arrows.

Figure 3.9b-II summarizes this observation by showing the potential dependent number of electrons in the $1S_e$ or $1S_h$ level of PbSe (red line), as well as the $1S_e$ level (dark blue line) and $1P_e$ level (light blue line) of CdSe. The energies corresponding to occupation of one electron per QD are shown in Figure 3.9b-III as horizontal bars *versus* an absolute energy

scale. The PbSe 1S_h-1S_e inter-band separation of 0.67 eV (the "electrochemical band gap") is in coarse agreement with the optical band gap of 0.69 eV. As explained in the Appendix B.1, one would expect the electrochemical band gap to be slightly larger than the optical band gap. A possible explanation for the small discrepancy can be found in the assumed ordered structure of the QD film and the assumption of a ionic lattice of charges and counterions. In fact, our films are glassy in nature and counterions apparently do not reside in the center of a void (as in a ionic lattic), but at the QD surface, as was found for CdSe QDs (see chapter 2).⁷ This may increase the attractive Coulomb interaction between injected charges and counterions and explain the smaller electrochemical band gap.

The coarse agreement between electrochemical and optical band gap demonstrates that the gate coupling, *i.e.* the ratio of Fermi level shift and applied voltage, is close to unity. This verifies our experimental approach of deducing absolute energy levels directly from the applied potential.

This approach seems even valid for injection of a large number of electrons: as illustrated in Figure 3.9b-III, the $1S_{e}$ - $1P_{e}$ separation in the CdSe QDs is 0.17 eV, similar to the same measurement on the pure film. Apparently, also after injection of a large number of electrons into the $1S_{e}$ levels of PbSe (about 7) and CdSe (about 2), injection of electrons into the CdSe $1P_{e}$ level still occurs with a gate coupling of close to unity.

Finally, the band offset between CdSe and PbSe amounts to 0.87 eV. This is significantly larger than the offset for smaller PbSe QDs of 5.3 nm (0.61 eV, see Figure 3.8a), in agreement with the expectation.

To verify the trend, we also determine the band offset for a bilayer with PbSe QDs of a 4.1 nm diameter. Figure 3.10a presents an overview of the $1S_e$ levels in the CdSe and PbSe QDs of all assessed bilayers, depicted by a blue line with triangles and a red line with circles, respectively. Both values are plotted with respect to vacuum and as a function of the PbSe band gap. For comparison, also the energies of the pure films are appended, as open triangle and open circle, respectively.

A large variation between $1S_e$ levels of about 0.5 eV is apparent, both for CdSe and for PbSe. While size-dependent shifts may be expected for PbSe, the CdSe variations must be of other origin. As discussed above, we suggest that these may arise from differences in ligand densities and defect densities, while differences in dielectric environments play a minor role.



Figure 3.10 (a) Absolute energies of the $1S_e$ level in PbSe and CdSe QDs in bilayer films (filled symbols) as function of the PbSe band gap, for the three studied PbSe sizes "L", "M", and "S". The respective $1S_e$ energies of a pure film of CdSe QDs and a pure film of PbSe QDs of size M are shown as open symbols. (b) Band offset between CdSe and PbSe QDs in bilayer films (filled green circles) as function of the PbSe band gap. A linear fit of slope – 2.9 (grey dashed line) serves as a guide to the eye.

While the variations of the $1S_e$ levels are strong, the band offset exhibits a clear sizedependent trend. Figure 3.10b shows the band offset as a function of PbSe band gap. A linear fit with a slope of (-) 2.9 is included to guide the eye. The slope of (-)2.9 is rather steep, steeper than expected based upon the optical band gap alone (~ - 0.5 due to identical effective masses and the small exciton binding energy in PbSe). Hence, other contributions must be present, possibly the energy penalty that needs to be paid for incomplete charge compensation.

Incomplete charge compensation might occur if (1) the film offers too small voids (as is the case for small PbSe QDs) and/or (2) if the voids are already fully occupied by counterions due to *e.g.* a high number of charged sub-gap states that were charge compensated before the Fermi level reaches the electrochemical potential for $1S_e$ injection. If only a tiny fraction of the injected electrons in the film lacks a counterion, the total energy of the system increases strongly due to long-range Coulomb repulsions with other electrons. As this situation could already explain the lack of charging in films of CdSe QDs with small voids (see Chapter 2), we propose that such reasoning might also be hold for the strong dependence of the band offset on the band gap of the PbSe QDs.

3.6 CONCLUSIONS

In this chapter, we have demonstrated that spectroelectrochemistry can be used to determine band offsets in QD films *in situ*. Extrapolation of band offsets from pure films are inaccurate, since: (1) the dielectric environment is altered, and (2) variations in ligand and defect densities lead to large differences in the determined energy levels, precluding a valid estimate for the exact band offset in a heterojunction. We fabricate PbSe and CdSe heterojunction, both as a bilayer and as an alternating multilayer film, showing a similar (type-I) band offset, with the CdSe $1S_e$ level having a 0.5 – 0.6 eV higher potential. Finally, a decrease of the band offset is observed for decreasing size of the PbSe QDs, *i.e.* for increasing PbSe band gap, in agreement with the expectation.

REFERENCES

- 1. Munro, A. M.; Zacher, B.; Graham, A.; Armstrong, N. R. Photoemission Spectroscopy of Tethered CdSe Nanocrystals: Shifts in Ionization Potential and Local Vacuum Level As a Function of Nanocrystal Capping Ligand. ACS Applied Materials & Interfaces 2010, 2, 863-869.
- 2. Jasieniak, J.; Califano, M.; Watkins, S. E. Size-Dependent Valence and Conduction Band-Edge Energies of Semiconductor Nanocrystals. ACS Nano 2011, 5, 5888-5902.
- Gao, J.; Luther, J. M.; Semonin, O. E.; Ellingson, R. J.; Nozik, A. J.; Beard, M. C. Quantum Dot Size Dependent J-V Characteristics in Heterojunction ZnO/PbS Quantum Dot Solar Cells. Nano Letters 2011, 11, 1002-1008.
- 4. Houtepen, A. J.; Vanmaekelbergh, D. Orbital Occupation in Electron-Charged CdSe Quantum-Dot Solids. *The Journal of Physical Chemistry B* 2005, 109, 19634-19642.
- 5. Vanmaekelbergh, D.; Houtepen, A. J.; Kelly, J. J. Electrochemical gating: A method to tune and monitor the (opto)electronic properties of functional materials. *Electrochimica Acta* 2007, 53, 1140-1149.
- 6. Guyot-Sionnest, P. Charging colloidal quantum dots by electrochemistry. *Microchimica Acta* 2008, 160, 309-314.
- Boehme, S. C.; Wang, H.; Siebbeles, L. D. A.; Vanmaekelbergh, D.; Houtepen, A. J. Electrochemical Charging of CdSe Quantum Dot Films: Dependence on Void Size and Counterion Proximity. ACS Nano 2013, 7, 2500-2508.
- 8. Wehrenberg, B. L.; Guyot-Sionnest, P. Electron and Hole Injection in PbSe Quantum Dot Films. Journal of the American Chemical Society 2003, 125, 7806-7807.
- 9. Roest, A. L.; Kelly, J. J.; Vanmaekelbergh, D. Coulomb blockade of electron transport in a ZnO quantum-dot solid. *Appl. Phys. Lett.* 2003, 83, 5530-5532.
- 10. Wehrenberg, B. L.; Yu, D.; Ma, J.; Guyot-Sionnest, P. Conduction in Charged PbSe Nanocrystal Films. *The Journal of Physical Chemistry B* 2005, 109, 20192-20199.
- 11. Mekis, I.; Talapin, D. V.; Kornowski, A.; Haase, M.; Weller, H. One-pot synthesis of highly luminescent CdSe/CdS core-shell nanocrystals via organometallic and "greener" chemical approaches. J. Phys. Chem. B 2003, 107, 7454-7462.
- 12. de Mello Donegá[®], C.; Koole, R. Size Dependence of the Spontaneous Emission Rate and Absorption Cross Section of CdSe and CdTe Quantum Dots. *The Journal of Physical Chemistry C* 2009, 113, 6511-6520.
- Steckel, J. S.; Yen, B. K. H.; Oertel, D. C.; Bawendi, M. G. On the Mechanism of Lead Chalcogenide Nanocrystal Formation. *Journal of the American Chemical Society* 2006, 128, 13032-13033.
- 14. Schins, J. M.; Trinh, M. T.; Houtepen, A. J.; Siebbeles, L. D. A. Probing formally forbidden optical transitions in PbSe nanocrystals by time- and energy-resolved transient absorption spectroscopy. *Physical Review B* 2009, 80, 035323.
- 15. Trinh, M. T.; Houtepen, A. J.; Schins, J. M.; Piris, J.; Siebbeles, L. D. A. Nature of the Second Optical Transition in PbSe Nanocrystals. *Nano Letters* 2008, 8, 2112-2117.
- 16. Brus, L. A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites. *J. Chem. Phys.* 1983, 79, 5566.
- 17. Delerue, C., Lannoo, M. Nanostructures: Theory and Modeling. Springer Berlin Heidelberg: 2004.
- 18. Landolt-Börnstein Group III Condensed Matter: Non-Tetrahedrally Bonded Elements and Binary Compounds I. Springer Berlin Heidelberg: 1998; Vol. 41C.

- Sandeep, C. S. S.; Cate, S. t.; Schins, J. M.; Savenije, T. J.; Liu, Y.; Law, M.; Kinge, S.; Houtepen, A. J.; Siebbeles, L. D. A. High charge-carrier mobility enables exploitation of carrier multiplication in quantum-dot films. *Nat Commun* 2013, 4.
- Sandeep, C. S. S.; Azpiroz, J. M.; Evers, W. H.; Boehme, S. C.; Moreels, I.; Kinge, S.; Siebbeles, L. D. A.; Infante, I.; Houtepen, A. J. Epitaxially Connected PbSe Quantum-Dot Films: Controlled Neck Formation and Optoelectronic Properties. ACS Nano 2014.
- 21. Bruggeman, D. A. G. Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen. Annalen der Physik 1935, 416, 636-664.
- 22. Seo, J.-S.; Cheong, B.-S.; Cho, H.-G. Solvation of LiClO4 and NaClO4 in deuterated acetonitrile studied by means of infrared and Raman spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2002, 58, 1747-1756.
- 23. Bryantsev, V. Calculation of solvation free energies of Li+ and O2 ions and neutral lithium– oxygen compounds in acetonitrile using mixed cluster/continuum models. *Theor Chem Acc* 2012, 131, 1-11.
- 24. Spångberg, D.; Hermansson, K. The solvation of Li+ and Na+ in acetonitrile from ab initioderived many-body ion-solvent potentials. *Chemical Physics* 2004, 300, 165-176.
- 25. Norris, D. J.; Bawendi, M. G. Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots. *Physical Review B* 1996, 53, 16338.
- 26. Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *Journal of the American Chemical Society* 2013, 135, 18536-18548.
- 27. Kim, D.; Kim, D.-H.; Lee, J.-H.; Grossman, J. C. Impact of Stoichiometry on the Electronic Structure of PbS Quantum Dots. *Physical Review Letters* 2013, 110, 196802.
- Nag, A.; Chung, D. S.; Dolzhnikov, D. S.; Dimitrijevic, N. M.; Chattopadhyay, S.; Shibata, T.; Talapin, D. V. Effect of Metal Ions on Photoluminescence, Charge Transport, Magnetic and Catalytic Properties of All-Inorganic Colloidal Nanocrystals and Nanocrystal Solids. *Journal of the American Chemical Society* 2012, 134, 13604-13615.
- 29. Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. Improved performance and stability in quantum dot solar cells through band alignment engineering. *Nat Mater* 2014, 13, 796-801.
- 30. Ning, Z.; Voznyy, O.; Pan, J.; Hoogland, S.; Adinolfi, V.; Xu, J.; Li, M.; Kirmani, A. R.; Sun, J.-P.; Minor, J.; Kemp, K. W.; Dong, H.; Rollny, L.; Labelle, A.; Carey, G.; Sutherland, B.; Hill, I.; Amassian, A.; Liu, H.; Tang, J.; Bakr, O. M.; Sargent, E. H. Air-stable n-type colloidal quantum dot solids. Nat Mater 2014, 13, 822-828.
- 31. Yaacobi-Gross, N.; Soreni-Harari, M.; Zimin, M.; Kababya, S.; Schmidt, A.; Tessler, N. Molecular control of quantum-dot internal electric field and its application to CdSe-based solar cells. *Nat Mater* 2011, 10, 974-979.

APPENDIX B

B.1 Optical Versus Electrochemical Band Gap

The optical band gap is given by

$$E_{g}^{opt}(R) = E_{EA} - E_{IP} + \frac{h^{2}}{8R_{QD}^{2}} \left(\frac{1}{m_{e}^{*}} + \frac{1}{m_{h}^{*}}\right) - \frac{1.79e^{2}}{4\pi\varepsilon_{0}\varepsilon_{QD}} + \sum E^{pol,opt}$$
(3.6)

Where $E_{_{EA}}$ is the electron affinity, $E_{_{IP}}$ is the ionization potential, $R_{_{QD}}$ and $\varepsilon_{_{QD}}$ are the radius and dielectric constant of the QD, respectively, and m_e^* and m_h^* are the electron and hole effective masses, respectively. In the case of an exciton, the sum of the polarization terms $\sum E^{pol,opt}$ is approximately zero and can be neglected. The electrochemical band gap can be defined as the difference between the electrochemical potentials for injection of a 1S_e electron and a 1S_e hole, *i.e.*

$$E_{gap}^{EL} = \mu_{1Se} - \mu_{1Sh} = E_{1Se}^{qp} + E_{1Se}^{EL} - E_{1Sh}^{qp} - E_{1Sh}^{EL}$$
(3.7)

The electrochemical potential for $1S_e$ injection has been given in Equations (3.3) and (3.5). The electrochemical potential for $1S_h$ injection can be calculated accordingly, by replacing the electron with the hole and the Li⁺ cation with the ClO_4^- anion. This yields

$$E_{gap}^{EL} \approx E_{EA} - E_{IP} + \frac{h^2}{8R_{QD}^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{2Me^2}{4\pi\varepsilon_0\varepsilon_{out}\left(R_{QD} + R_{void}\right)} + \sum E^{pol,EL}$$
(3.8)

where the polarization terms

$$\sum E^{pol,EL} = E_e^{pol,self} + E_h^{pol,self} + E_{Li}^{pol,self} + E_{ClO_4}^{pol,self}$$
(3.9)

do not cancel as in the case of an exciton. These terms are given by

$$E_{e}^{pol,self} = E_{h}^{pol,self} \approx \frac{e^{2}}{8\pi\varepsilon_{0}R_{QD}} \frac{\varepsilon_{QD} - \varepsilon_{out}}{\varepsilon_{QD}\varepsilon_{out}}$$
(3.10)

and

$$E_{Li}^{pol,self} = E_{Clo_4}^{pol,self} \approx \frac{e^2}{8\pi\varepsilon_0 R_{void}} \frac{\varepsilon_{void} - \varepsilon_{out}}{\varepsilon_{void} \varepsilon_{out}}$$
(3.11)

As given in Table 3.1, the self-energy of Li⁺ was estimated with - 6 meV, the electron selfenergy can be estimated with + 40 meV. The sum of all polarization terms is therefore + 68 meV. Combined with the attractive Coulomb interaction (- 16 meV), all electrostatic terms add up to + 52 meV. As the Coulomb terms for an exciton amount to - 37 meV, the electrochemical band gap is expected to be be about 90 meV *larger* than the optical band gap. However, the measured electrochemical gap is about 20 meV *smaller* than the optical band gap. The discrepancy may be partially due to the glassy nature of the film, changing the assumed effective dielectric constant and Coulomb interactions between injected charges and counterions in the electrolyte.

<u>B.2</u> Spectroelectrochemical Assessment of Energy Levels in <u>Bilayers of PbSe and CdSe QDs</u>



Figure 3.11 Spectroelectrochemical determination of energy levels in a bilayer of 5.3 nm Pbse QDs (size "M", 1S peak at 0.82 eV) and 9.7 nm CdSe QDs (1S peak at 1.905 eV).



Figure 3.12 Spectroelectrochemical determination of energy levels in a bilayer of 4.1 nm Pbse QDs (size "S", 1S peak at 0.87 eV) and 9.7 nm CdSe QDs (1S peak at 1.905 eV).

ELECTROCHEMICAL CONTROL OVER PHOTOINDUCED ELECTRON TRANSFER AND TRAPPING IN CDSE-CDTE QUANTUM-DOT SOLIDS

4.1. INTRODUCTION

Charge transfer lies at the heart of operation of many devices such as LEDs, solar cells, thermoelectrics and photoelectrochemical solar fuel cells. In all such devices colloidal semiconductor Quantum Dots (QDs) are investigated as electron donors and/or acceptors.^{1, 2} Understanding the fundamental laws governing the charge transfer process between QDs is therefore a key to further advances in these devices. Various studies have been conducted to reveal the efficiency and rate of charge transfer processes in QDs in solution or attached to a semiconductor surface.³⁻¹⁰ Parameters that commonly determine the rate of charge transfer are the driving force between donor and acceptor,¹⁰ the width and height of an energy barrier, given by the distance and energy landscape between donor and acceptor, respectively,⁶ and by the dielectric environment.¹⁰ However, the efficiency of charge transfer is not just influenced by the charge transfer rate, but also by the rate of competing processes. The initial aim of this study was to study electron transfer from CdTe to CdSe QDs since these materials are

known to form a type II band offset.¹¹⁻¹⁴ However, we found that sub-picosecond electron trapping in CdTe QDs obstructs electron transfer to CdSe QDs. Therefore, we first performed a systematic investigation of the trapping processes in CdTe QDs and then set out to reduce the trapping rates and to allow charge transfer to CdSe QDs to occur. We demonstrate that thiol ligands reduce the electron-trapping rate sufficiently, albeit only just, for electron transfer to take place. However, full control over charge trapping and charge transfer is enabled by applying an electrochemical potential to the QD films. This allows filling of trap states, thereby switching off electron trapping and enabling electron transfer from CdTe to CdSe QDs.

4.2. EXPERIMENTAL DETAILS

Materials

1,2-ethanediamine (99.5 %, Fluka); 1,2-ethanedithiol (98 %, Fluka); oxalic acid (anhydrous, 99 %, Sigma-Aldrich); 1,8-octanediamine (98 %, Aldrich); methanol (anhydrous, 99.8 %, Sigma-Aldrich); butanol (anhydrous, 99.8 %, Sigma-Aldrich); acetonitrile (anhydrous, 99.8%, Sigma-Aldrich); LiClO₄ (battery grade, dry, 99.99%, Aldrich); Se (325 mesh, 99.99 %, ChemPur); Te (-18+60 mesh, 99.999 %, Alfa Aesar); Cd(Ac)₂ (anhydrous, 99.999 %, Strem Chemicals); trioctylphosphine (97 %, Aldrich); trioctylphosphine oxide (99 %, Aldrich); 1-hexadecylamine (technical grade, 90 %, Alfa Aesar); 1-tetradecylphosphonic acid (98 %, Alfa Aesar); 1-octadecene (technical grade, 90 %, Aldrich); oleic acid (technical grade, 90 %, Aldrich). All materials were used as received.

QD Synthesis

CdSe QDs with 4.9 nm diameter were synthesized following the recipe by Mekis *et al.*¹⁶ two precursors were prepared in a N₂ purged glove box by dissolving 0.474 g Se (325 mesh) in 6 ml TOP (trioctylphosphine) and 0.36 g Cd(Ac)₂ in 9 ml TOP, respectively. Subsequently, the synthesis was done in a Schlenk line providing oxygen- and water-free conditions. 24 g of TOPO (trioctylphosphine oxide) was heated to 180 °C in vacuum under periodic flushing with N₂. After cooling down to 100 °C, 15 g HDA (1-hexadecylamine) and

0.45 g TDPA (1-tetradecylphosphonic acid) were added and dried at 120 °C in vacuum during 30 min under periodic flushing with N₂. The TOP-Se precursor was injected and the solution was heated to 300 °C under N₂ flow. Under vigorous stirring, the TOP-Cd(Ac)₂ precursor was injected to induce nucleation of CdSe nanoparticles. After growth at 280 °C, the reaction was stopped by injection of cold toluene and external cooling. The obtained dispersion was purified by repeated washing with anhydrous MeOH and precipitation of particles in a centrifuge at 3000 rpm for 5 min. The final stock of particles was dispersed in Chloroform.

We synthesized CdTe QD dispersions with diameters of 3.7 nm and 6.3 nm, respectively, following the procedure described by Kloper *et al.*³⁹ At 310 °C in N₂ atmosphere, a TOP-Te precursor in ODE (octadecene) is injected rapidly to a Cd-(oleate)₂ precursor in ODE under vigorous stirring. Growth took place at 270 °C and was stopped after several minutes by injection of cold toluene. The dispersions were purified as follows: anhydrous MeOH and anhydrous BuOH were added as nonsolvents to precipitate the QDs in a centrifuge at 3500 rpm during 7 min. Typically, the volume ratio was 1:1:2 (reaction solution:MeOH:BuOH). Subsequently, the precipitate was redispersed in chloroform and the whole purification procedure was repeated once.

Film Processing and Ligand Exchange

Films for electrochemical studies are deposited on an ITO substrate; all other films are deposited on a quartz substrate. Films with either 2DT, 2DAc, 2DA or 8DA ligands are grown in a layer-by-layer (LbL) dip coating procedure in a N_2 purged glove box: the substrates were first immersed for 30 s in a concentrated QD dispersion, subsequently immersed for 30 s in a stirred 1 M solution of the desired ligand in MeOH, and finally dipped twice for 10s in stirred MeOH to rinse excess ligands. Using this procedure, the original insulating ligands are replaced by the shorter bidentate ligands. The above procedure was repeated 10-20 times to yield films roughly 10-20 QD monolayers thick. In CdTe-CdSe multilayer films, the substrates were alternatively dipped in CdTe and CdSe QD dispersions. For electrochemical measurements, a small region on the edge of the ITO substrate remained uncoated to provide electrical contact.

Broadband Transient Absorption Measurements

Broadband transient absorption (TA) measurements were performed on either QD dispersions in chloroform in a 2 mm cuvette or on films on a quartz substrate in an air-

tight cell containing N₂. Optical densities were typically between 0.05 and 0.2 to provide uniform excitation densities. Samples were excited with ~ 200 fs pump pulses from an OPA (Light Conversion ORPHEUS) after a regenerative amplifier (Light Conversion PHAROS), at a repetition rate of 2500 Hz. Absorption spectra in the visible (450 - 900 nm) were recorded with an Ultrafast Systems HELIOS spectrometer at a repetition rate of 5000 Hz using broadband probe pulses from a sapphire crystal pumped by 1030 nm. A variable delay of – 10 to 3000 ps between probe and pump pulses was introduced to yield difference absorption spectra, as a function of pump – probe delay and probe energy. Due to dispersion in optical components between the white light generating crystal and the photodetector, the "time zero", *i.e.* the point of time where pump and probe show maximum temporal overlap, depends on the probe wavelength. Dispersion corrected 2D TA data with identical time zero for all wavelengths were obtained by subtracting a thirdorder polynomial fit to the "coherent artifact"^{40, 41} from the raw data. About 10 000 difference absorption spectra were obtained per pump – probe delay.

Electrochemical Control of the Fermi Level

The Fermi level of our QD films on ITO was controlled by a CHI832B bipotentiostat (CH Instruments, Inc.), while immersed in an airtight glass container with an Ag wire pseudoreference electrode and a Pt sheet counter electrode (see inset in Figure 4.4). The Ag wire pseudoreference electrode (- 5.01 V versus vacuum) was calibrated with a ferrocene/ferrocinium couple. In a N₂ purged glove box, the cell is loaded with a QD film and filled with an electrolytes consisting of anhydrous acetonitrile and 0.1 M LiClO₄ (lithium perchlorate). All chemicals were used as received. The electrochemical cell is placed such that TA measurements are possible, with both pump and probe beams passing through the front window, the QD films and the back window of the cell. For all applied potentials reported in the main text, care was taken that the absorption of the unexcited sample did not change with respect to open circuit potential. Hence, no charges were injected into quantum confined levels.

4.3. STEADY-STATE AND TRANSIENT ABSORPTION

CdTe and CdSe QDs between 3 and 6 nm were synthesized according to reported recipes.^{15, 16} The organic ligands on the QD surface are oleic acid (OA) and

trioctylphosphine (TOP) for CdTe QDs and hexadecylamine (HDA), trioctylphosphine (TOP), trioctylphosphine oxide (TOPO) and tetradecylphosphonic acid (TDPA) for CdSe QDs. Figure 4.1a shows absorption and emission spectra of dispersions of the synthesized QDs.

Photoconductive films of these QDs on quartz or indium doped tin oxide (ITO) substrates were prepared with a layer-by-layer (LbL) dip coating process in a N₂ purged glove box; see methods section for details. The long insulating ligands that result from the QD synthesis are replaced by shorter bidentate ligands, either 1,2-ethanediamine (2DA), 1,2-ethanedithiol (2DT) or oxalic acid (2DAc). Whereas they differ in their functional group, all of these new ligands contain only two carbon atoms as a "spacer". These shorter ligands are intended to increase the electronic coupling between QDs.¹²



Figure 4.1 a) Absorption spectra (solid lines, *versus* left axis) and photoluminescence (PL) spectra (dotted lines, *versus* right axis) of CdSe and CdTe QDs in dispersion with diameters ranging from 3 to 6 nm. Absorption spectra are normalized at 400 nm and PL spectra at their respective $1S_{3/2}1S_e$ peak. Spectra are offset for clarity. The $1S_{3/2}1S_e$ absorption peak wavelengths are denoted in the legend. b) Schematic of electron transfer from CdTe to CdSe QDs due to the type II band alignment¹¹⁻¹⁴ that is expected for all combinations of CdSe and CdTe QDs displayed in (a). Blue and red arrows schematically indicate size dependent variations in QD band gap and, hence, energy level alignment.

As stated above, the aim of this work is to study charge transfer between CdTe and CdSe QDs. Figure 4.1b shows a schematic of the band alignment between CdTe and CdSe QDs. For common QD sizes, these materials are expected to form a type II band alignment with both HOMO and LUMO levels of CdSe at a lower energy than the levels in CdTe.¹¹⁻¹⁴ This is the case for all combinations of sizes in Figure 4.1a, in spite of large differences in their band gap. Hence, upon photoexcitation of CdTe QDs, electron transfer to CdSe QDs could take place. To reveal the time dependent population of electrons in CdTe and CdSe QDs, we measure the time and energy dependent change in absorption $\Delta A(E,t) = A^*(E,t) - A(E)$ between the excited (A^{*}) and unexcited (A) sample in broadband transient absorption (TA) measurements. As shown in the Appendix C, this change in absorption allows to deduce the density of excitations per unit area $N^{*}(t)$ via

$$\Delta A(E,t) = \sigma^*(E) \cdot N^*(t) / \ln 10 \tag{4.1}$$

where the cross section of a single excitation $\sigma^*(E)$ is derived from the signal at time zero according to

$$\sigma^*(E) = \frac{\Delta A(E,t=0) \cdot \ln 10}{I_0 \cdot F_4}$$
(4.2)

with I_0 the excitation fluence and F_A the fraction of absorbed pump light, obtained by measuring the transmission through the QD film in an integrating sphere, thereby correcting for reflection and scattering.

In this work we display excitation density normalized transient absorption data as $(\Delta A(E,t)/(I_0F_A))$. At time zero, this "absorption bleach per excitation" is directly related to the cross section per excitation $\sigma^*(E)$ via Equation 4.2. For all later times, it shows the decay of excitations according to Equation 4.1. Electron transfer in films containing CdTe donor and CdSe acceptor QDs can be inferred from an increasing absorption bleach at the CdSe $1S_{3/2}1S_e$ transition and can be quantified by first determining $\sigma^*(E)$ for individual CdSe and CdTe QD films.

Initial TA measurements on films that contained CdTe donor QDs (either 3.7 or 6.3 nm in diameter) and CdSe acceptor QDs (4.1 nm in diameter), both capped with 2DA ligands, did not show any signals belonging to the acceptors, indicating that negligible electron transfer took place. Instead, only a very short-lived bleach of the $1S_{3/2}1S_e$ transition in the CdTe QDs was observed, which decayed on a timescale of a picosecond. We hypothesized

that this is due to fast electron trapping in CdTe QDs. If this trapping is much faster than the electron transfer time to CdSe QDs, no donor-acceptor signal will be observed.

TA measurements on various CdTe QD dispersions are presented in the Appendix C. They show two important characteristics: (1) the bleach of the $1S_{3/2}1S_e$ transition is due to $1S_e$ electrons only. The presence of a $1S_{3/2}$ hole results in a much smaller bleach, if any, than the presence of a $1S_e$ electron. This is in line with previous work from the Klimov¹⁸ and Kambhampati groups¹⁹, and has been attributed to the higher degeneracy of the $1S_{3/2}$ hole level compared to the $1S_e$ electron level in cadmium chalcogenides.²⁰ Therefore we will assume here that the kinetics of the $1S_{3/2}1S_e$ bleach represent the kinetics of $1S_e$ electrons and that any fast decay of this signal is due to electron trapping. At the end of this report, we present experimental evidence for this assignment using electrochemical control of the Fermi level. (2) We observe large sample-to-sample variations in the rate of electron trapping. We find for instance that the rate of electron trapping increases with increased number of washing steps in the purification of the QD dispersions. This is consistent with a report by Morris-Cohen *et al.*²¹ who observed a loss of ligands and a drop in PL quantum yield during purification. Such a loss of ligands may result in a higher number of traps on the QD surface.

4.4. FAST ELECTRON TRAPPING IN CDTE QD FILMS

We prepared films of 6.3 nm CdTe QDs *via* layer-by-layer dipcoating, during which the original oleic acid ligands are exchanged for 1,2-ethanediamine (2DA), 1,2-ethanedithiol (2DT) or oxalic acid (2DAc). The decreased distance between QDs results in enhanced electronic coupling as evidenced by a much increased photoconductivity.^{14, 22}

The films with 2DA, 2DT and 2DAc ligands are excited at 670 nm, at the blue edge of their $1S_{3/2}1S_e$ transition, with ~180 fs pulses at a fluence of $2.5 \cdot 10^{13}$ photons per cm², a FWHM of 8 nm and at a repetition rate of 2500 Hz. Transient absorption spectra of the samples are recorded with a broadband probe pulse of ~180 fs at a repetition rate of 5000 Hz, as a function of time delay with respect to the pump pulse. This yields the 2D TA images shown in Figures 2a-c for films with 2DA, 2DT and 2DAc ligands, respectively. The bleach per excitation $\Delta A/(I_0 \cdot F_A)$ is shown in false colors. The linear absorption spectra are displayed as black solid lines *versus* the right axis. The image has been corrected for

dispersion of the probe light as outlined in the Appendix C. For all TA data in the remainder of this document similar excitation conditions are ensured with fluences on the order of 10¹³ photons per cm², leading to an average of 0.1 excitations per QD. The exact fluence for each data set is given in Table 4.2 in the Appendix C. To better resolve both fast and slow dynamics, the time axis is displayed on a linear scale from -1 to 10 ps and on a logarithmic scale from 10 to 3000 ps.



Figure 4.2 Effect of ligand anchor group on electron trapping behavior: 2D TA image displaying the bleach per excitation $\Delta A/(I_0.F_A)$ for films of 6.3 nm CdTe QDs capped with 2DA (a), 2DT (b) and 2DAc (c) after excitation at 670 nm. The linear absorption spectra are plotted *versus* the right axis. The pump wavelength is indicated with grey arrows. (d) Transient absorption spectra at 5 ps pump-probe delay (e) kinetics of the $1S_{3/2}1S_e$ bleach, together with tri-exponential fits (see main text). (f) sketch of the proposed electron trapping process.

The dominant feature is an absorption bleach of the $1S_{3/2}1S_e$ transition around 700 nm, indicative of charges populating the $1S_{3/2}$ hole and/or $1S_e$ electron state. However, the population persists only for a short time: for 2DA and 2DAc ligands, its picosecond decay is three orders of magnitude faster than for the same QDs with the original ligands in dispersion (see Figure 4.7d, 2a and 2c). Only 2DT ligands lead to a slightly longer lifetime (see Figure 4.2b). A comparison of the $1S_{3/2}1S_e$ bleach kinetics of the three films as well as the dispersion with the original ligands is shown in Figure 4.2e.

For all samples, the decay must be non-radiative in nature, as the observed kinetics are much faster than the reported radiative lifetime of 38.8 ns for CdTe QDs of this size.²³ The decay could hence be due to electron trapping, or non-radiative electron-hole recombination. We discard Auger recombination as the major decay mechanism, as typical Auger lifetimes are on the order of tens to hundreds of picoseconds²⁴ and thus longer than our observed decay. Consequently, we identify electron trapping as the origin of the fast decay of the $1S_{3/2}1S_e$ bleach.

The $1S_{3/2}1S_e$ decay kinetics of the CdTe QD dispersions and films are well described by a triexponential function of the form $\Delta A(t) = \sum_i c_i \cdot \exp(-t/\tau_i)$, where i = 1, 2, 3 and c_i and τ_i are the amplitudes and lifetimes of the exponential components. The fits are displayed as blue dashed lines in Figure 4.2e. We chose $\tau_3 = 38.8$ ns to match the radiative lifetime,²³ and left all other parameters free. The fit parameters are shown in Table 4.1. In addition to the radiative decay, at least two components are required for a good fit. This suggests that two types of traps must be present. The assignment of the lifetimes τ_1 and τ_2 to specific surface sites is of great interest, but is beyond the scope of this work. We will discuss the nature of these traps in a forthcoming publication.

Material	Diameter	Ligands	Material	Lifetimes [ps]		
	[nm]		Probed	$ au_1$	$ au_2$	$\mathcal{T}_{3}^{}$ (fixed) ²³
CdTeª	3.7	TOP, oleic acid	CdTe	2.8 ± 0.1	46 ± 2	22200
CdTeª	6.3	TOP, oleic acid	CdTe	192 ± 34	942 ± 301	38800
CdTe⁵	6.3	2DA	CdTe	< 0.2	1.6 ± 0.1	38800
CdTe⁵	6.3	2DAc	CdTe	< 0.2	3.1 ± 2.1	38800
CdTe⁵	6.3	2DT	CdTe	5.3 ± 0.2	76 ± 3	38800
CdSe/CdTe ^b	4.1/6.3	2DT	CdSe	2.9 ± 0.1	327 ± 20	26000
CdSe/CdTe ^b	4.1/6.3	2DT	CdTe	0.22 ± 0.01	2.4 ± 0.1	-
CdSe/CdTe ^b	4.1/6.3	2DA	CdSe	0.23 ± 0.01	2.3 ± 0.3	26000
CdSe/CdTe [♭]	4.1/6.3	2DA	CdTe	0.23 ± 0.01	2.3 ± 0.3	38800

Table 4.1 Overview of lifetimes obtained from a tri-exponential fit to the TA decays atthe ${}_{3/2}IS_e$ transition. ^a In dispersion (CHCl₃), ^b As film

For the 2DT capped film $\tau_1 = 5.3 \pm 0.2$ ps and $\tau_2 = 76 \pm 3$ ps best describe the data. The diamine and diacid capped films feature significantly shorter lifetimes: the slower component is $\tau_2 = 1.6 \pm 0.1$ ps for 2DA and 3.1 ± 2.1 ps for 2DAc, respectively, while the fast component (τ_1) even falls short of our instrument response time, for both ligands. This sets an upper limit $\tau_1 \leq 0.2$ ps for 2DA and 2DAc. Significant decay during the pump pulse is also the reason why the bleach magnitude for films with these ligands is lower than for films with 2DT ligands.

Even for the QD film with dithiol ligands, the observed kinetics are three orders of magnitude faster than the radiative decay (see Table 4.1). Apparently, the preparation of conductive QD films has resulted in the introduction of very efficient electron traps. We further point out that for the 2DA and 2DAc capped films, the lifetimes are even shorter than typical cooling times. Since trapping competes with electron cooling, high energy excitation results in a small $1S_e$ population per incident photon (see Figure 4.8). As discussed for the QD dispersions in the Appendix C, insufficient ligand coverage can lead to accelerated trapping in solution. We speculate here that ligand density (partly) also explains the observed trend in the films: the diamine (2DA) and diacid (2DAc) ligands lead to a shorter lifetime than the dithiol ligands (2DT), in line with their smaller binding strengths.^{9, 25, 26}

The TA spectra at 5 ps in Figure 4.2d reveal a broad photoinduced absorption (PA) feature below the band gap and extending to the infrared. This positive PA "shelf" feature is only seen for 2DA and 2DAc ligands and not for 2DT ligands. It is furthermore also observed for a dispersion with QDs of 3.7 nm diameter that featured a low PL quantum yield and fast trapping (see Figure 4.7b). Its 1/e lifetime is typically hundreds of ps (see Figure 4.9 in Appendix C) and its magnitude seems to be related to a short lifetime of the $1S_{3/2}1S_e$ bleach, as it is hardly pronounced for 2DT ligands. This photoinduced absorption has been observed previously,²⁷⁻²⁹ and was tentatively assigned to intraband transitions which receive oscillator strength from the presence of a trapped electron. The fact that this PA "shelf" feature is particularly pronounced for the films with 2DA and 2DAc ligands further suggests that trapping is significant in these films. Summarizing the results of Figure 4.7 and Figure 4.2, we find that electron trapping is efficient in CdTe QDs. Particularly the processing of QDs into photoconductive films leads to very efficient electron trapping.

4.5. DEMONSTRATION OF ELECTRON TRANSFER IN CDTE-CDSE MULTILAYER FILMS

Next we investigate electron transfer between CdTe and CdSe QDs in QD films. We start by determining the bleach per excitation $\Delta A/(I_0 \cdot F_A)$ for 2DT capped single component films of 4.9 nm CdSe QDs (see Figure 4.3a) and 6.3 nm CdTe QDs (see Figure 4.3b). The CdSe QD film has been excited at 620 nm and the CdTe QD film at 670 nm. Both films exhibit a bleach maximum at their $1S_{3/2}1S_e$ transition, at 610 nm for CdSe and at 700 nm for CdTe, respectively. While also for the CdTe QD film the TA spectrum is non-zero at around 610 nm, the absorption changes are both positive and negative and most likely result from spectral shifts rather than bleaches due to state-filling.³⁰ After integration over the region of the CdSe $1S_{3/2}1S_e$ transition (563 to 660 nm), the CdTe TA signal is negligible compared to the signal integrated over the region of the CdTe $1S_{3/2}1S_e$ transition (630 to 755 nm). This will facilitate the spectral assignment to either CdSe or CdTe in the films comprising both materials.

Before continuing with the composite films, we first quantify how much absorption bleach is produced by a single excitation. Figure 4.3c shows this quantity $\int_{1S_{32}1S_e} \Delta A(E,t) / (I_0 \cdot F_A \cdot \ln 10) dE$ for single component films of CdTe QDs (red filled circles) and CdSe QDs (blue open circles), respectively, where the integration over the $1S_{3/2}1S_e$ transition has been introduced to average over all QDs in the ensemble and to account for spectral shifts. At time zero, this quantity equals $\sigma_{ss}^* \equiv \int_{1S_{sy2}1S_e} \sigma^*(E) dE$, the

cross section per excitation as given in Equation 4.2, integrated over the $1S_{3/2}1S_e$ transition. Note that the integration changes the unit of the resulting quantity to $eV \cdot cm^2$. In Figure 4.3c, the $1S_{3/2}1S_e$ integrated cross section is indicated by dashed lines, being larger for CdTe (σ_{SS} * = - 2.8·10⁻¹⁶ cm²) than for CdSe (σ_{SS} * = - 0.9·10⁻¹⁶ cm²). It may be compared to the $1S_{3/2}1S_e$ integrated linear absorption cross section per QD given in ref. 19. We find that the cross section per excitation determined here is 53% of the linear absorption cross section for the CdSe QDs and 66% of the linear absorption cross section for the CdTe QDs. These values represent the degeneracy of the electron and hole states. A bleach of 75% would be expected in the standard effective mass model.²⁰



Figure 4.3 Demonstration of Electron Transfer from CdTe to CdSe QDs. TA spectra at selected pump-probe delays for films of 2DT capped 4.9 nm CdSe QDs (a) and 2DT capped 6.3 nm CdTe QDs (b). The spectral region around the pump wavelength shows significant pump scatter and is not shown. The linear absorption spectra are plotted as black solid lines versus the right axis. (c) cross section per excitation $\sigma_{\rm SS}$ *, integrated over the 1S3/21Se transition, for films of 2DT capped CdTe (red filled circles) and CdSe (blue open circles) QDs, respectively, as obtained from the measurements in (a) and (b), see main text. (d) 2D TA image displaying the bleach per excitation $\Delta A/(I_o \cdot F_A)$ for a QD solid comprising both 2DT capped CdSe QDs (4.9 nm) and 2DT capped CdTe QDs (6.3 nm) after selective excitation of the CdTe QDs at 670 nm. The linear absorption spectrum of the film is plotted as black solid line versus the right axis. The pump wavelength is indicated with a grey arrow. (e) spectra of this film at selected pump-probe delays, along with its linear absorption spectrum and that of single layers of either CdSe or CdTe. The inset is a magnification of the spectral region marked by the black box. (f) kinetics of the CdSe $1S_{3/2}1S_e$ (610 nm) and CdTe $1S_{3/2}1S_e$ (700 nm) transition for the measurement in (d). The black line displays the kinetics obtained by subtracting the kinetics at 700 nm (scaled by 0.055) from the kinetics at 610 nm. A fit consisting of a single-exponential ingrowth and a bi-exponential decay is shown as a grey dashed line.

Next, films of both donor (CdTe) and acceptor (CdSe) QDs were prepared in an alternating multilayer architecture: first approximately a monolayer of 4.9 nm CdSe QDs is deposited, followed by a monolayer of 6.3 nm CdTe QDs and this sequence is repeated 5 times. In between the QD depositions, the original ligands are exchanged to 2DT ligands, as these are (1) short enough to provide the necessary wave function overlap between donor and acceptor QDs and (2) are the ligands with the longest lifetimes in our single

component films (see Figure 4.2e). Finally, the alternating multilayer ensures contact of each CdTe QD with CdSe QDs.¹⁴

CdTe QDs were excited selectively with pump pulses (670 nm) having sufficient energy to induce optical transitions across the band gap of CdTe (710 nm), but not CdSe (610 nm). After excitation, only the electron is expected to transfer from CdTe to CdSe QDs, while the hole should stay in CdTe QDs. Both the 2D TA image in Figure 4.3d and the spectra at selected pump-probe delays in Figure 4.3e show an instantaneous bleach at the CdTe $1S_{3/2}1S_e$ transition (around 700 nm) and a delayed bleach at the CdSe $1S_{3/2}1S_e$ transition (around 610 nm). Figure 4.3f displays the kinetics of both features, where the 700 nm feature has been scaled by a factor 0.055 for clarity. The decay at 700 nm can be attributed to depopulation of 1Se electrons in CdTe. The bleach at 610 nm features an instantaneous rise at time zero, followed by an ultrafast decay within the first 0.5 ps. Subsequently, it increases again over 20 ps until it decays on a nanosecond time scale. These rich kinetics at 610 nm arise both from CdSe and CdTe QDs, as the smallest CdTe QDs have a minor spectral overlap with CdSe QDs (see Figures 3a and 3b). We attribute the initial rise and fast decay to small CdTe QDs as suggested by the similarity of the kinetics at 610 nm and the kinetics at 700 nm (scaled by a factor 0.055) during the first 0.5 ps. In contrast, the subsequent increase of the 610 nm bleach originates from a bleach of the $1S_{3/2}1S_e$ transition in CdSe, as inferred from the spectra in Figure 4.3e. This indicates an electron transfer process.

To extract the kinetics of electron transfer to CdSe from the signal at 610 nm, we subtract the scaled kinetics at 700 nm from the kinetics at 610 nm, depicted as a black line in Figure 4.3f. A fit consisting of a single-exponential ingrowth and a bi-exponential decay is shown as a grey dashed line. The time constants are $\tau_{cdSe,1} = 2.9 \pm 0.1$ ps for the ingrowth, and $\tau_{cdSe,2} = 327 \pm 20$ ps and $\tau_{cdSe,3} = 26$ ns for the decay, respectively, where $\tau_{cdSe,3}$ has been fixed at the radiative decay time of the CdSe QDs.²³ On the other hand, the CdTe bleach kinetics at 700 nm can be fitted with a bi-exponential decay with time constants $\tau_{cdTe,1} = 0.22 \pm 0.01$ ps and $\tau_{cdTe,2} = 2.4 \pm 0.1$ ps. The latter is very close to the ingrowth time constant $\tau_{cdSe,1}$. Hence, we assign $\tau_{cdSe,1}$ to electron transfer from the CdTe 1S_e to the CdSe 1S_e level. The $\tau_{cdTe,1}$ component is assigned to very efficient electron trapping in the CdTe QDs. Its value of 0.22 ps is likely limited by the instrumental time resolution and is hence an upper limit.

The electron transfer time found here is in line with the reported transfer time between CdSe QDs and SnO₂ of 3 ± 1 ps and 25 ± 2 ps, when separated by a molecular bridge

slighter shorter (HS-CH₂-COOH) or longer (HS-[CH₂]₃-COOH) than ours.⁴ It is also similar to reported electron transfer times in solution, 2 ps from CdSe QDs to methylene blue,³¹ 2.3 ps from PbS QDs to methylene blue³¹ or 3.8 ps from PbS QDs to 1,4-benzoquinone.³² The component $\tau_{CdSe, 2}$ (327 ps) is attributed to electron trapping, as it is shorter than the radiative lifetime and there are no holes for Auger recombination in CdSe. Such relatively slow decay is also observed in the control experiment with CdSe QDs only (see Figure 4.3c). This further corroborates that electrons have arrived in CdSe QDs.

The efficiency of electron transfer η_{ET} from CdTe to CdSe QDs can be determined by comparing the observed absorption bleach of the CdSe $1S_{3/2}1S_e$ transition after electron transfer to the cross section per excitation σ_{SS} * in the single component CdSe QD film as determined above:

$$\eta_{\rm ET} = \frac{\max\left\{-\int\limits_{1S_{3/2}1S_{\rm e}} \Delta A(E,t)dE\right\}}{-\sigma_{\rm SS}*I_0F_A\ln 10}$$
(4.3)

The max function indicates that we take the highest value of the integrated transient absorption signal in the CdSe QD $1S_{3/2}1S_e$ spectral region (*i.e.* the maximum of the bleach transient). As discussed above we assume that the bleach of the $1S_{3/2}1S_e$ is due to electrons only. In this case the hole (present in the determination of σ_{ss} *) may be neglected and Equation 4.3 is valid. For the CdSe-CdTe QD film discussed here, a transfer efficiency of 5% is obtained. This low value is the result of the competition between electron transfer with a rate of ~ (2.9 ps)⁻¹ and very fast electron trapping in CdTe QDs with a rate of \geq (0.22 ps)⁻¹. A straightforward estimate of the transfer efficiency based on these rates gives $\eta_{\rm ET} \leq (2.9)^{-1} / \left[(2.9)^{-1} + (0.22)^{-1} \right] = 7.1\%$, in close agreement with the value of 5% obtained via Equation 4.3.

4.6. ELECTROCHEMICAL GATING CONTROLS ELECTRON TRAPPING

While we have shown above that with 2DT ligands electron transfer from CdTe QDs to CdSe QDs may be observed, the transfer yield is low (5 %) as electron trapping is faster
than electron transfer. In the following, we attempt to eliminate electron trapping via electrochemical gating: we immerse a CdTe QD film on an ITO substrate in an electrochemical cell containing 0.1 M LiClO₄ in acetonitrile, a Ag pseudo-reference electrode and a Pt counter electrode. The ITO substrate serves as a working electrode whose Fermi level can be changed in a controlled and reversible fashion by setting a voltage versus the calibrated Ag pseudo-reference electrode (- 5.01 V versus vacuum). Unless stated otherwise, all potentials mentioned hereafter are given with respect to this Ag pseudo-reference electrode. Upon changing the potential, no charges are injected into the 1S_e electron level, as no steady state $1S_{3/2}1S_e$ bleach is observed.³³ However, electron traps may be filled. In fact, for CdTe QDs, injection of electrons into the $1S_e$ level is difficult, possibly as a result of a large number of traps within the band gap that need to be filled first.

Figure 4.4b shows a 2D TA image of a film of 6.3 nm CdTe QDs with 1,8-octanediamine (8DA) ligands on ITO, after photo-excitation at 460 nm. Longer ligands were chosen here as these facilitate cation uptake and result in more efficient charging.³³ The film was immersed in the electrochemical cell described above and held at open circuit potential. This situation is comparable to the conventional TA measurements on CdTe films in Figure 4.2. In agreement with Figure 4.2, the 1/e lifetime of the $1S_{3/2}1S_e$ bleach is 35 ps; the majority has decayed even within the first 5 ps, indicating fast electron trapping (see kinetic trace in Figure 4.4d). The decay is even faster when the Fermi level is moved to + 0.23 V, *i.e.* closer towards to $1S_{3/2}$ hole level (see Figure 4.4a and 4.4d): now, the 1/e lifetime has decreased to 1.4 ps. This accelerated decay is most likely also the reason why the maximum bleach is less than half that of the open circuit case: electrons get trapped within the time duration of the pump pulse. We attribute such fast decay to a higher electron trapping rate as more electron traps are unoccupied at + 0.23 V. We now move the Fermi level towards the $1S_e$ level, to – 0.7 V. In this case, a much slower decay of the $1S_{3/2}1S_e$ bleach is observed (see Figure 4.4c and 4.4d): the 1/e lifetime has increased to 1 ns. Hence, by raising the Fermi level by 1 V, we could slow down electron trapping by three orders of magnitude. Similar effects are also seen for other QD sizes as well as for dithiol ligands (1,6-hexanedithiol) and shorter diamine ligands (1,2-ethanediamine and 1,7heptanediamine). Summarizing, the decay of the $1S_{3/2}1S_e$ bleach becomes slower when the Fermi level gets closer to the 1Se level, a situation in which more electron traps are occupied and more hole traps are unoccupied. This corroborates our above assignment that the 1S_{3/2}1S_e bleach decay reflects electron (and not hole) trapping, as hole trapping would show the opposite effect, *i.e.* it would be faster at - 0.7 V than at + 0.23 V.



Figure 4.4 Switching Off Electron Trapping. 2D TA image of a film of 6.3 nm CdTe QDs with 8DA ligands on an ITO substrate after 460 nm excitation (a) at + 0.23 V versus Ag pseudo-reference electrode, (b) at open circuit, corresponding to – 0.22 V, and (c) at – 0.7 V, respectively. (d) kinetics of the $1S_{3/2}1S_e$ transition at 700 nm for all applied potentials. The schematic in the second row sketches the filling of traps states going from (a) to (c), using an electrochemical cell (lower right) to control the Fermi level.

One could argue that electron trapping may be induced by ultrafast hole trapping followed by rapid electron-hole recombination, rather than taking place on electron traps directly. The above results however show that this is not the case. In this scenario the $1S_{3/2}1S_e$ bleach decay would be governed by the availability of hole traps. This would lead to increased electron trapping when the Fermi level is raised closer to the $1S_e$ level as this leads to a higher number of available hole traps, opposite to the observation. Hence, we conclude that there is a large number of electron traps throughout the band gap that lead to fast electron trapping if they are empty, but that this trapping channel can be switched off by raising the Fermi level.

To the best of our knowledge, this is the first time that electrochemical control of the Fermi level has been combined with TA spectroscopy to identify, monitor and reduce trapping in QD films. Especially for samples in which trapping is a major decay channel, such as for our CdTe QDs, this technique offers a powerful method to study and control trapping. First, as the trapping rate depends on the density of trap states, it opens up the possibility to map the density of trap states (DOTS). Second, it improves the passivation of the QD surface and circumvents the problem of achieving sufficient ligand coverage, a common challenge^{34, 35} due to *e.g.* the inherent dynamic character of the surface.³⁶

4.7. ELECTROCHEMICAL GATING ENABLES ELECTRON TRANSFER

In the following, we exploit the electrochemical control of the Fermi level to improve the yield of electron transfer from CdTe to CdSe QDs. Alternating multilayers of both CdSe QDs (4.9 nm) and CdTe QDs (6.3 nm) are deposited on ITO and the QD ligands are exchanged to 2DA. In an electrochemical cell containing a 0.1 M LiClO₄ in acetonitrile, CdTe QDs are selectively excited at 680 nm. Figure 4.5a shows the obtained 2D TA image at open circuit potential with the bleach per excitation $\Delta A/(I_0 \cdot F_A)$ shown in false colors. At time zero, several spectrally narrow extrema appear which can be attributed to stimulated Raman excitations of acetonitrile.³⁷³⁸

In addition, a short-lived bleach at the CdTe $1S_{3/2}1S_e$ transition (700 nm) and negligible signal at the CdSe $1S_{3/2}1S_e$ transition (610 nm) are seen. This is consistent with the previously observed fast electron trapping in CdTe QDs with 2DA ligands (see Figure 4.2a), which obstructs electron transfer to CdSe QDs. This is further illustrated by the kinetic traces in Figure 4.5c and the spectra at selected pump-probe delays in Figure 4.5d. Whereas the CdTe $1S_{3/2}1S_e$ bleach decays rapidly, it does not lead to a bleach at the CdSe $1S_{3/2}1S_e$ transition, at any pump-probe delay. In contrast, raising the Fermi level to - 1.35 V leads to a bleach both at the CdTe and CdSe $1S_{3/2}1S_e$ transition (see Figure 4.5b). The $1S_{3/2}1S_e$ integrated bleach kinetics in Figure 4.5f show that the CdSe bleach is significant and appears simultaneously with the decay of the CdTe bleach.



Figure 4.5 Electrochemistry enables charge transfer in a CdTe-CdSe QD film. Bleach per excitation $\Delta A/(I_0 \cdot F_A)$ for a 2DA capped QD multilayer of both CdSe QDs (4.9 nm) and CdTe QDs (6.3 nm) on ITO after excitation at 680 nm, in an electrochemical cell containing 0.1 M LiClO₄ electrolyte. (a) 2D TA image at open circuit with the film's linear absorption spectrum plotted as black solid line *versus* the right axis. The pump wavelength is indicated with an arrow and Raman excitations of acetonitrile at time zero with labels (1), (2), (2*) and (1*). (b) 2D TA image after the film's Fermi level has been raised to -1.35 V *versus* Ag pseudo-reference electrode. (d) and (e) display spectra at selected pump-probe delays, while (c) and (f) show the ingrowth and decay of the bleach per excitation for CdSe (circles) and CdTe (continuous lines), respectively, integrated over the $1S_{3/2}1S_e$ transition. The integration boundaries for CdSe and CdTe are indicated with dark grey and light grey boxes, respectively. Fits to the traces in (f) are displayed as dashed lines.

A tri-exponential fit to the CdTe decay (grey dashed line) yields the time constants $\tau_{CdTe, 1} = 0.23 \pm 0.01$ ps, $\tau_{CdTe, 2} = 2.3 \pm 0.3$ ps and $\tau_{CdTe, 3} = \tau_{rad} = 38.8$ ns. The CdSe kinetics are well-described with a bi-exponential ingrowth where the time constants $\tau_{CdSe, 1} = \tau_{CdTe, 1}$ and $\tau_{CdSe, 2} = \tau_{CdTe, 2}$ have been set to the respective CdTe decay constants, and a single-exponential decay with the radiative lifetime of CdSe QDs $\tau_{CdSe, 3} = 26$ ns. The fit is displayed as the light green dashed line. The good agreement between the data and fits containing only the radiative lifetime and two time constants describing both the ingrowth of the CdSe bleach and the decay of the CdTe bleach suggests that electron trapping is negligible and $\tau_{CdSe, 1} = \tau_{CdTe, 1}$ and $\tau_{CdSe, 2} = \tau_{CdTe, 2}$ are electron transfer

times. While the latter is comparable with the transfer time of 2.9 ± 0.1 ps in the CdTe-CdSe QD multilayer with 2DT ligands in conventional TA (see Figure 4.3 and Table 4.1), the former is very close to the ~ 200 fs time resolution of the experiment, indicating an accelerated transfer channel. This fast transfer is in line with the magnitude of the CdTe bleach at early times, which is a factor 2 lower than expected from Equation 4.2, using the excitation cross section of the single component CdTe QD film (see Figure 4.3f).

The transfer yield at -1.35 V is 95 %, as determined *via* Equation 4.3. Estimating a combined error of 20 % in the determination of the pump fluence and the CdSe QD excitation cross section, we conclude that the transfer yield is close to unity. This is corroborated by the fits of the kinetics (Fig. 6e) that suggest that electron trapping is absent.

Thus, electrochemical control of the Fermi level clearly enables much higher electron transfer efficiencies than does exchanging the 2DA ligands for 2DT ligands (see Figure 4.3). As the rate of electron transfer is similar in both cases, one can attribute this to a reduction of the trapping rate in CdTe QDs. This is in line with the same finding for the single component films (see Figure 4.2 and 4.4) and consistent with the lack of trapping in the model to fit the CdTe bleach kinetics in Figure 4.5f. The absence of trapping in the fit to the CdSe bleach kinetics completes the picture: apparently, the rise of the Fermi level has also filled electron traps in CdSe and, hence, reduced the trapping rate in this material as well.

4.8. CONCLUSIONS

In conclusion, electron trapping is a common process in CdTe QDs. Broadband TA measurements in dispersion reveal that the lifetime of the $1S_{3/2}1S_e$ bleach depends on the QD surface quality which is affected by *e.g.* the purification protocol after synthesis. In films with short bidentate ligands, electron trapping is further accelerated with amines and acids leading to considerable trapping even within the duration of the exciting laser pulse (< 0.2 ps). Using thiol ligands, trapping can be slowed down. This allows electron transfer to CdSe QDs, which form a type II band offset with CdTe QDs. However, the yield of electron transfer is low (5 %) as electron trapping is still faster than electron transfer. Using a novel combination of electrochemical gating and TA, we show that electrochemical control of the Fermi level in CdTe QD films decreases the trapping rate by

three orders of magnitude. This leads to an efficiency of electron transfer from CdTe to CdSe QDs of close to unity. We propose that this method can also be applied to other materials, offering facile, controllable and reversible control of the Fermi level. It opens up the possibility of studying the density of trap states (DOTS) as well as the systematic investigation of electron transfer without the complication of trapping.

REFERENCES

- 1. Nozik, A. J., Quantum Dot Solar Cells. *Physica E* 2002, 14, 115-120.
- 2. Wright, M.; Uddin, A., Organic—Inorganic Hybrid Solar Cells: A Comparative Review. Sol. Energy Mater. Sol. Cells 2012, 107, 87-111.
- 3. Tvrdy, K.; Frantsuzov, P. A.; Kamat, P. V., Photoinduced Electron Transfer from Semiconductor Quantum Dots to Metal Oxide Nanoparticles. *Proc. Natl. Acad. Sci. USA* 2010, 108, 29-34.
- 4. Wang, H.; McNellis, E. R.; Kinge, S.; Bonn, M.; Cánovas, E., Tuning Electron Transfer Rates through Molecular Bridges in Quantum Dot Sensitized Oxides. *Nano Lett.* 2013, 13, 5311-5315.
- 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.
- 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.
- Hyun, B.-R.; Zhong, Y.-W.; Bartnik, A. C.; Sun, L.; Abruña , H. D.; Wise, F. W.; Goodreau, J. D.; Matthews, J. R.; Leslie, T. M.; Borrelli, N. F., Electron Injection from Colloidal PbS Quantum Dots into Titanium Dioxide Nanoparticles. ACS Nano 2008, 2, 2206-2212.
- Morris-Cohen, A. J.; Frederick, M. T.; Cass, L. C.; Weiss, E. A., Simultaneous Determination of the Adsorption Constant and the Photoinduced Electron Transfer Rate for a CdS Quantum Dot–Viologen Complex. J. Am. Chem. Soc. 2011, 133, 10146-10154.
- Pijpers, J. J. H.; Koole, R.; Evers, W. H.; Houtepen, A. J.; Boehme, S.; de Mello Donega, C.; Vanmaekelbergh, D.; Bonn, M., Spectroscopic Studies of Electron Injection in Quantum Dot Sensitized Mesoporous Oxide Films. J. Phys. Chem. C 2010, 114, 18866-18873.
- 10. Tisdale, W. A.; Zhu, X.-Y., Artificial Atoms on Semiconductor Surfaces. Proc. Natl. Acad. Sci. USA 2011, 108, 965-970.
- 11. Wei, S.-H.; Zhang, S. B.; Zunger, A., First-Principles Calculation of Band Offsets, Optical Bowings, and Defects in CdS, CdSe, CdTe, and Their Alloys. J. Appl. Phys. 2000, 87, 1304-1311.
- Gross, D.; Mora-Seró, I.; Dittrich, T.; Belaidi, A.; Mauser, C.; Houtepen, A. J.; Como, E. D.; Rogach, A. L.; Feldmann, J., Charge Separation in Type II Tunneling Multilayered Structures of CdTe and CdSe Nanocrystals Directly Proven by Surface Photovoltage Spectroscopy. J. Am. Chem. Soc. 2010, 132, 5981-5983.
- Wang, Y.; Wang, L.; Waldeck, D. H., Electrochemically Guided Photovoltaic Devices: A Photocurrent Study of the Charge Transfer Directionality between CdTe and CdSe Nanoparticles. J. Phys. Chem. C 2011, 115, 18136-18141.
- 14. Talgorn, E.; de Vries, M. A.; Siebbeles, L. D. A.; Houtepen, A. J., Photoconductivity Enhancement in Multilayers of CdSe and CdTe Quantum Dots. ACS Nano 2011, 5, 3552-3558.
- Kloper, V.; Osovsky, R.; Kolny-Olesiak, J.; Sashchiuk, A.; Lifshitz, E., The Growth of Colloidal Cadmium Telluride Nanocrystal Quantum Dots in the Presence of Cd^o Nanoparticles. J. Phys. Chem. C 2007, 111, 10336-10341.
- Mekis, I.; Talapin, D. V.; Kornowski, A.; Haase, M.; Weller, H., One-Pot Synthesis of Highly Luminescent CdSe/CdS Core–Shell Nanocrystals *via* Organometallic and "Greener" Chemical Approaches. J. Phys. Chem. B 2003, 107, 7454-7462.
- 17. Gao, Y.; Aerts, M.; Sandeep, C. S. S.; Talgorn, E.; Savenije, T. J.; Kinge, S.; Siebbeles, L. D. A.; Houtepen, A. J., Photoconductivity of PbSe Quantum-Dot Solids: Dependence on Ligand Anchor Group and Length. ACS *Nano* 2012, 6, 9606-9614.

- 18. Klimov, V. I., Optical Nonlinearities and Ultrafast Carrier Dynamics in Semiconductor Nanocrystals. J. Phys. Chem. B 2000, 104, 6112-6123.
- 19. Kambhampati, P., Hot Exciton Relaxation Dynamics in Semiconductor Quantum Dots: Radiationless Transitions on the Nanoscale. J. Phys. Chem. C 2011, 115, 22089-22109.
- 20. Efros, A. L.; Rodina, A. V., Band-Edge Absorption and Luminescence of Nonspherical Nanometer-Size Crystals. *Phys. Rev. B* 1993, 47, 10005-10007.
- 21. Morris-Cohen, A. J.; Donakowski, M. D.; Knowles, K. E.; Weiss, E. A., The Effect of a Common Purification Procedure on the Chemical Composition of the Surfaces of CdSe Quantum Dots Synthesized with Trioctylphosphine Oxide. J. Phys. Chem. C 2009, 114, 897-906.
- 22. Talgorn, E.; Moysidou, E.; Abellon, R. D.; Savenije, T. J.; Goossens, A.; Houtepen, A. J.; Siebbeles, L. D. A., Highly Photoconductive CdSe Quantum-Dot Films: Influence of Capping Molecules and Film Preparation Procedure. J. Phys. Chem. C 2010, 114, 3441-3447.
- 23. de Mello Donegá[®], C.; Koole, R., Size Dependence of the Spontaneous Emission Rate and Absorption Cross Section of CdSe and CdTe Quantum Dots. J. Phys. Chem. C 2009, 113, 6511-6520.
- 24. 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.
- Fritzinger, B.; Moreels, I.; Lommens, P.; Koole, R.; Hens, Z.; Martins, J. C., In Situ Observation of Rapid Ligand Exchange in Colloidal Nanocrystal Suspensions Using Transfer NOE Nuclear Magnetic Resonance Spectroscopy. J. Am. Chem. Soc. 2009, 131, 3024-3032.
- 26. Koole, R.; Schapotschnikow, P.; de Mello Donegá, C.; Vlugt, T. J. H.; Meijerink, A., Time-Dependent Photoluminescence Spectroscopy as a Tool to Measure the Ligand Exchange Kinetics on a Quantum Dot Surface. ACS Nano 2008, 2, 1703-1714.
- 27. Malko, A. V.; Mikhailovsky, A. A.; Petruska, M. A.; Hollingsworth, J. A.; Klimov, V. I., Interplay between Optical Gain and Photoinduced Absorption in CdSe Nanocrystals. *J. Phys. Chem. B* 2004, 108, 5250-5255.
- 28. McArthur, E. A.; Morris-Cohen, A. J.; Knowles, K. E.; Weiss, E. A., Charge Carrier Resolved Relaxation of the First Excitonic State in CdSe Quantum Dots Probed with Near-Infrared Transient Absorption Spectroscopy. J. Phys. Chem. B 2010, 114, 14514-14520.
- Saari, J. I.; Dias, E. A.; Reifsnyder, D.; Krause, M. M.; Walsh, B. R.; Murray, C. B.; Kambhampati, P., Ultrafast Electron Trapping at the Surface of Semiconductor Nanocrystals: Excitonic and Biexcitonic Processes. J. Phys. Chem. B 2012, 117, 4412-4421.
- 30. Trinh, M. T.; Houtepen, A. J.; Schins, J. M.; Hanrath, T.; Piris, J.; Knulst, W.; Goossens, A. P. L. M.; Siebbeles, L. D. A., In Spite of Recent Doubts Carrier Multiplication Does Occur in PbSe Nanocrystals. *Nano Lett.* 2008, 8, 1713-1718.
- 31. Zhu, H.; Yang, Y.; Lian, T., Multiexciton Annihilation and Dissociation in Quantum Confined Semiconductor Nanocrystals. Acc. Chem. Res. 2012, 46, 1270-1279.
- 32. Knowles, K. E.; Malicki, M.; Weiss, E. A., Dual-Time Scale Photoinduced Electron Transfer from PbS Quantum Dots to a Molecular Acceptor. J. Am. Chem. Soc. 2012, 134, 12470-12473.
- 33. Boehme, S. C.; Wang, H.; Siebbeles, L. D. A.; Vanmaekelbergh, D.; Houtepen, A. J., Electrochemical Charging of CdSe Quantum Dot Films: Dependence on Void Size and Counterion Proximity. ACS Nano 2013, 7, 2500-2508.
- Morris-Cohen, A. J.; Malicki, M.; Peterson, M. D.; Slavin, J. W. J.; Weiss, E. A., Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots. Chem. Mater. 2012, 25, 1155-1165.
- 35. Anderson, N. C.; Owen, J. S., Soluble, Chloride-Terminated CdSe Nanocrystals: Ligand Exchange Monitored by ¹H and ³¹P NMR Spectroscopy. *Chem. Mater.* 2012, 25, 69-76.

- 36. McBride, J. R.; Pennycook, T. J.; Pennycook, S. J.; Rosenthal, S. J., The Possibility and Implications of Dynamic Nanoparticle Surfaces. ACS Nano 2013, 7, 8358-8365.
- Kovalenko, S. A.; Dobryakov, A. L.; Ruthmann, J.; Ernsting, N. P., Femtosecond Spectroscopy of Condensed Phases With Chirped Supercontinuum Probing. Phys. Rev. A 1999, 59, 2369-2384.
- 38. The extrema labelled (1) and (1*) can be attributed to CH stretch vibrations (2950 cm-1) and the extrema (2) and (2*) to CN stretch vibrations (2250 cm-1).]
- 39. Kloper, V.; Osovsky, R.; Kolny-Olesiak, J.; Sashchiuk, A.; Lifshitz, E., The Growth of Colloidal Cadmium Telluride Nanocrystal Quantum Dots in the Presence of Cd^o nanoparticles. *J. Phys. Chem.* C 2007, 111, 10336-10341.
- 40. Lebedev, M. V.; Misochko, O. V.; Dekorsy, T.; Georgiev, N., On the Nature of "Coherent Artifact". J. Exp. Theor. Phys. 2005, 100, 272-282.
- 41. Dietzek, B.; Pascher, T.; Sundström, V.; Yartsev, A., Appearance of Coherent Artifact Signals in Femtosecond Transient Absorption Spectroscopy in Dependence on Detector Design. *Laser* Phys. Lett. 2007, 4, 38-43.

APPENDIX C

C.1 Chirp Correction of Transient Absorption Data

The probe pulse in our broadband transient absorption (TA) measurements is subject to a "chirp", where the blue part of the probe spectrum is at the leading edge (in time) and the red part of the spectrum at the tailing edge. This wavelength dependent temporal shape of the pulse is due to a dispersion in optical components traversed by the probe pulse between the white light generating crystal and the photodetector. It causes "time zero", *i.e.* the point of time at which pump and probe show maximum temporal overlap, to depend on the probe wavelength. To illustrate the case, Figure 4.6a displays a 2D TA image for a quartz substrate, without a QD film and before chirp correction. Subpicosecond oscillations coined the "coherent artifact"^{1, 2} are observed when pump and probe arrive simultaneously at the sample. We use the maxima of these oscillations to define our wavelength dependent "time zero". To obtain chirp corrected 2D TA images as shown with identical time zero for all wavelengths (as shown in Figure 4.6b and throughout the main text), we subtract a third-order polynomial fit to this "coherent artifact" from the raw data (shown as a white dashed line in Figure 4.6a).



Figure 4.6 2D TA images of a quartz substrate after excitation at 480 nm before (a) and after (b) correction for a chirp of the probe pulse. The chirp correction is performed by subtracting a polynomial fit to the "coherent artifact"^{1, 2}, shown by a white dashed line in (a).

C.2 Fluence of the Photo-Excitation

Table 4.2 gives an overview of the fluences employed in the measurements reported in the main text. Typically, this resulted in excitation densities on the order of 0.1 per QD, as derived according to³ $I_0 \cdot \sigma_{\lambda,pump} \cdot (1 - e^{-A_{\lambda,pump} \cdot \ln 10}) / (A_{\lambda,pump} \cdot \ln 10)$, where I_0 is the incident light intensity and $\sigma_{\lambda,pump}$ and $A_{\lambda,pump}$ the absorption cross section and absorption at the pump wavelength, respectively.

Figure	Sample	Pump wavelength	Fluence [photons per cm ²
		[nm]	per pulse]
4 . 2a-c	3.7 nm CdTe, dispersion in	460	3.5·10 ¹³
	chloroform		
4.2d-f	6.3 nm CdTe, dispersion in	670	3.4·10 ¹³
	chloroform		
4.3	6.3 nm CdTe, films	670	2.5·10 ¹³
4.4a+c	4.9 nm CdSe, film	620	3.2·10 ¹³
4.4b+c	6.3 nm CdTe, film	670	2.5·10 ¹³
4.4d-f	4.9 nm CdSe and 6.3 nm CdTe,	670	3.4·10 ¹³
	multilayer film		
4.5	6.3 nm CdTe	460	8.3·10 ¹³
4.6	4.9 nm CdSe and 6.3 nm CdTe,	680	7.6·10 ¹²
	multilayer film		

Table 4.2 Overview of fluences for the measurements presented in the main text

<u>C.3</u> Determination of the Density of Excitations from Transient Absorption Data

Linear absorption is given by the Lambert-Beer law:

$$I(E) = I_0(E) \cdot 10^{-A(E)}$$

= $I_0(E) \cdot 10^{-\sigma(E) \cdot n \cdot l/\ln 10}$
= $I_0(E) \cdot e^{-\sigma(E) \cdot N}$ (4.4)

where I and I_0 are the transmitted and incident light intensity, respectively, $\sigma(E)$ is the absorption cross section per QD, n is the QD density per unit volume, I the thickness of the sample and N is the QD density per unit area. Analogously, the absorption change in TA measurements can be expressed as

$$\Delta \mathbf{A}(E,t) = \sigma^*(E) \cdot N^*(T) / \ln 10 \tag{4.5}$$

where $\sigma^*(E)$ is the cross section of a single excitation and $N^*(t)$ is the density of excitations per unit area. At time zero (t = o), the latter equals $N^*(0) = I_0 \cdot F_A$, where I_0 is the excitation fluence and F_A is the fraction of absorbed pump light, obtained by measuring the transmission through the QD film in an integrating sphere, thereby correcting for reflection and scattering. This yields the cross section for a single excitation

$$\sigma^{*}(E) = \frac{\Delta A(E, t = 0) \cdot \ln 10}{N^{*}(t = 0)}$$

$$= \frac{\Delta A(E, t = 0) \cdot \ln 10}{I_0 \cdot F_A}$$
(4.6)

In this work we display excitation density normalized transient absorption data as $\frac{\Delta A(E,t)}{I_0 \cdot F_A}$. This "absorption bleach per excitation" is directly related to the cross

section per excitation $\sigma^*(E)$ via eq. (3). Electron transfer in films containing CdTe donor and CdSe acceptor QDs can be inferred from an increasing absorption bleach at the CdSe $1S_{3/2}1S_e$ transition and can be quantified by first determining $\sigma^*(E)$ for individual CdSe and CdTe QD films.



C.4 Electron Dynamics in CdTe QD Dispersions

Figure 4.7 a) 2D TA image of 3.7 nm CdTe QDs in chloroform, as a function of probe wavelength and time delay after excitation at 460 nm. The change in absorption, ΔA , is shown in false colors, while the linear absorption is plotted as a black solid line *versus* the right axis. The peaks of the lowest energy optical transitions are indicated with arrows. b) Probe spectra at various time delays as indicated in the legend. c) Kinetics of the probe spectra averaged over the $2S_{3/2}IS_e$ (yellow continuous line) and $1S_{3/2}IS_e$ transition (red continuous line), respectively. A tri-exponential fit to the data is shown as blue dotted line. d) 2D TA image (false colors) and linear absorption spectrum (black solid line) of 6.3 nm CdTe QDs in chloroform after excitation at 670 nm. e) Probe spectra at various time delays. The pump wavelength is indicated with a grey arrow. f) Kinetics of the probe spectrum averaged at the $1S_{3/2}IS_e$ transition (black solid line), as well as a tri-exponential fit (blue dotted line).

Figure 4.7a-c shows a broadband transient absorption measurement on CdTe QDs of 3.7 nm diameter in chloroform with TOP and oleic acid/oleate forming the ligands on the surface of the QDs (see experimental section). The sample is excited with ~180 fs pump pulses at a fluence of 3.5·10¹³ photons per cm², centered at 460 nm, with a FWHM of 8 nm and at a repetition rate of 2500 Hz. Transient absorption spectra of the sample are recorded with a broadband probe pulse of ~180 fs at a repetition rate of 5000 Hz, as a function of time delay with respect to the pump pulse. This yields a 2D TA image as shown

in Figure 4.7a. The image has been corrected for dispersion of the probe light as outlined above. For all TA data in the remainder of this document similar excitation conditions are ensured with fluences on the order of 10¹³ photons per cm². The exact fluence for each data set is given in Table 4.2. To better resolve both fast and slow dynamics, the time axis is displayed on a linear scale from -1 to 10 ps and on a logarithmic scale from 10 to 3000 ps. Several positive and negative features are seen which can be assigned with the aid of the linear absorption spectrum of the dispersion, depicted by a black line *versus* the right axis. The wavelengths corresponding to the three lowest energy optical transitions are indicated with arrows and assigned according to the sizing curve of Groeneveld et al.⁴

Figure 4.7b shows selected TA spectra at various pump-probe delays. The dominant feature in the TA spectra is a negative signal (absorption bleach) around 605 nm, which decays on a nanosecond time scale. It results from a bleach of the $1S_{3/2}1S_e$ band edge transition, as a result of population of $1S_{3/2}$ holes and/or $1S_e$ electrons. Likewise, the second bleach feature around 560 nm can be assigned to the $2S_{3/2}1S_e$ transition. The kinetics of both the $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$ bleach are shown in Figure 4.7c, obtained by averaging the 2D TA image in Figure 4.7a from 555 to 567 nm and 576 to 635 nm, respectively. Both features exhibit the same decay kinetics, which indicates that they likely result from the same species: a hole, an electron or their pair (exciton). We note that the decay of these signals is much faster than the expected radiative lifetime of 22.2 ns.⁵ This implies that the decay is due to non-radiative processes such as electron and/or hole trapping.

Hole trapping cannot explain the data: the hole is expected to quickly relax to the $1S_{3/2}$ state. Such a $1S_{3/2}$ hole does not bleach the $2S_{3/2}1S_e$ transition. Hence, hole trapping would result in different kinetics for the bleach of the $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$ transitions. The decay could hence be due to electron trapping, or non-radiative electron-hole recombination. We attribute it to the former. In line with previous work from the Klimov⁶ and Kambhampati groups⁷, we assume that the $1S_{3/2}1S_e$ bleach is predominantly due to electrons. These authors state that the hole contribution is negligible, as a result of the higher degeneracy of the $1S_{3/2}$ hole level compared to the $1S_e$ electron level in cadmium chalcogenides.⁸ Therefore we will assume here that the kinetics of the $1S_{3/2}1S_e$ bleach represent the kinetics of $1S_e$ electrons and that any fast decay of this signal is due to electron (and not hole) trapping. At the end of this report, we present experimental evidence for this assignment using electrochemical control of the Fermi level.

The decay of both the $1S_{3/2}1S_e$ and $2S_{3/2}1S_e$ bleach is well described by a tri-exponential function of the form $\Delta A(t) = \sum_{i=1}^{i=1} c_i \cdot \exp(-t/\tau_i)$, where i = 1, 2, 3 and c_i and τ_i are the amplitudes and lifetimes of the exponential components. We choose $\tau_3 = 22.2$ ns, the radiative lifetime in CdTe QDs of this size,⁵ and leave all other parameters free. In addition to the radiative decay, at least two components ($\tau_1 = 2.8 \pm 0.1$ ps and $\tau_2 = 46 \pm 2$ ps) are required for a good fit (see Table 1). This suggests that two additional decay pathways must be present for the electron.

In addition to absorption bleach features, red shifts are observed of the $1P_{3/2}1P_e$ transition (at 515 nm) and of the $1S_{3/2}1S_e$ transition (at 605 nm, overlapping with the bleach of the same transition). Both are assigned to the Stark effect, in which a charge carrier in one energy level induces a shift of transitions between other energy levels, sometimes referred to as biexciton shifts.⁹⁻¹¹ We note that due to these red shifts the bleach maxima in Figure 4.7b are somewhat blue shifted from the maxima in the linear absorption spectrum.

Figure 4.7d displays a 2D TA image of 6.3 nm CdTe QDs in chloroform with ligands comprised of TOP and oleic acid/oleate after photo-excitation with a pump pulse of 3.4.1013 photons per cm², centered at 670 nm. TA spectra at selected time delays in Figure 4.7e show that, while bleaches and spectral shifts of higher-energy transitions overlap due to reduced size-confinement, the $1S_{3/2}1S_e$ transition is clearly bleached and dominates the spectrum. However, this bleach persists significantly longer than for the 3.7 nm QDs (see Figure 4.7f): a tri-exponential fit to the data yields lifetimes of τ_1 = 192 ± 34 ps, τ_2 = 942 ± 301 ps and au_3 = 38.8 ns. Again, au_3 was fixed at the radiative lifetime reported by de Mello Donegá and Koole.⁵ The first two components au_1 and au_2 exceed the ones of the smaller QDs by one to two orders of magnitude, in line with the increased PL quantum yield of this sample. A recent study revealed that aging of CdTe QDs reduces their $1S_{3/2}1S_e$ bleach lifetime significantly.¹² We remark here that the same effect is induced also by the purification procedure after QD synthesis, increasing with the number of washing steps (see Figure 4.8), consistent with a report by Morris-Cohen et al.¹³ who observed a loss of ligands and a drop in PL quantum yield during purification. It has been suggested that the result of such a loss of ligands and the origin of a reduced PL quantum yield are traps on the surface. Following work of the Weiss13-15 and Owen16, 17 groups, the observed spread in both lifetimes for the studied QD dispersions likely depends on ligand coverage. The QD dispersions investigated here appear to feature two types of electron traps, as suggested by the two additional components τ_1 and τ_2 needed to fit the

decay of the $1S_{3/2}1S_e$ bleach. The assignment of these lifetimes to specific surface sites is of great interest, but is beyond the scope of this work. We will discuss the nature of these traps in a forthcoming publication.

C.5 Effect of Washing After QD Synthesis

Repeated washing with a mixture of BuOH and MeOH in the purification procedure after QD synthesis leads to lower PL yields and an accelerated decay of the $1S_{3/2}1S_e$ bleach in CdTe QDs (see Figure 4.8).



Figure 4.8 Effect of Loss of Ligands: Normalized bleach $\Delta A/\langle N_{Abs} \rangle$ for a dispersion of 3.9 nm CdTe QDs washed once (a) and three times (b), respectively, following excitation at 450 nm with 2.9·10¹³ photons per cm². $\langle N_{Abs} \rangle$ is the average number of initial excitations per QD. The linear absorption spectra are plotted versus the right axis. (c) kinetics of the $1S_{3/2}IS_e$ bleach. The inset shows the first 5 ps of the decay.

C.6 Electron Cooling Versus Electron Trapping

Figure 4.9a compares the kinetics of the bleach per excitation $\Delta A/(I_0 \cdot F_A)$ at the $1S_{3/2}1S_e$ transition for a film of 2DT capped 6.1 nm CdTe QDs after "hot" excitation (480 nm pump with 2.5·10¹³ photons per cm²) and "cold" excitation (670 nm pump with 3.4 ·10¹³ photons per cm²). As seen by the smaller magnitude of the bleach for hot excitation, we can infer that the yield of $1S_e$ electrons amounts to only 37 % of that of cold excitation. This can be rationalized in a simple model (see Fig. S2c) containing the excitation rate and decay rates from the $1P_e$ and $1S_e$ level: at time zero, the $1P_e$ level is populated within the laser pulse duration by absorption of pump photons (k_{IRF}). From the $1P_e$ level, electrons can either get trapped with a rate $k_{trap,1Pe}$ or cool down to the $1S_e$ level with a rate k_{cool} . In the $1S_e$ level, electrons are assumed to undergo a bi-exponential trapping process with rates $k_{trap,1Se,1}$ and $k_{trap,1Se,2}$ as inferred from the fit to Figure 3d. To keep the model simple, we

exclude the subsequent radiative decay as its slow decay showed to have negligible influence on the other rates. The yield of $1S_e$ electrons is then given by

$$\eta_{cool} = \frac{k_{cool}}{k_{cool} + k_{1Se,trap,1} + k_{1Se,trap,2} + k_{1Pe,trap}}$$
(4.7)

To obtain $k_{1Pe,trap}$, we monitored the decay of the $1P_{3/2}1P_e$ bleach after hot excitation (see Figure 4.9b). A single-exponential fit convolved with a Gaussian instrument response function (IRF) yields a decay rate $k_{1Pe,decay} = 1.51$ ps. According to the rate model in Figure 4.9c, we then can express the trapping rate from the $1P_e$ level as $k_{1Pe,trap} = k_{1Pe,decay} - k_{cool}$, yielding

$$k_{cool} = \frac{k_{1Se,trap,1} + k_{1Se,trap,2} + k_{1Pe,decay} + k_{cool}}{(1/\eta_{cool} - 1)}$$
(4.8)

Solving this equation with respect to k_{cool} gives us

$$k_{cool} = \eta_{cool} \cdot (k_{1Se,trap,1} + k_{1Se,trap,2} + k_{1Pe,decay})$$
(4.9)

Inserting η_{cool} =0.37, $k_{1Se,trap,1}$ = (5.3 ps)⁻¹, $k_{1Se,trap,2}$ = (76 ps)⁻¹ and $k_{1Pe,decay}$ = (1.5 ps)⁻¹ results in a 1S_e \rightarrow 1P_e cooling rate k_{cool} = (3.2 ps)⁻¹ and a 1P_e trapping rate $k_{1Pe,trap}$ = (2.9 ps)⁻¹. We point out that the obtained cooling time is considerably larger than typical cooling times in high-quality CdSe QDs (~ 200 fs), where electron cooling occurs via an Auger-like energy transfer to the hole.¹⁸ However, in films of hexanedithiol capped QDs a relaxation time of 1.7 ps has been found¹⁹ and in pyridine capped QDs a cooling process as long as 200 ps²⁰. This has been explained by the presence of an ultrafast hole trapping/transfer process which competes with electron cooling via Auger-like energy transfer to the hole. Ultrafast hole trapping might also be the reason for prolonged electron cooling in our CdTe QD film. In this respect it is interesting to compare the obtained cooling time to the 1.5 ps delay between the maxima of the $1P_{3/2}1P_e$ and $1S_{3/2}1S_e$ bleach (see Figure 4.9b). The latter is equal to the $1S_e \rightarrow 1P_e$ cooling time in case no decay from the 1Se level is present, but is only a lower limit in case of decay from the 1Se level, consistent with our obtained $1S_e \rightarrow 1P_e$ cooling time. However, direct measurement using e.g. two-photon photoemission (2PPE)¹⁹ or stimulated Raman spectroscopy²¹ would be necessary to further quantify the cooling time. In this work, we only want to use the rough agreement between the proposed model with the observed rates in TA measurements to verify that we witness fast trapping from the $1S_e$ level in CdTe QD films and possibly also trapping from the $1P_e$ level in case of hot excitation.



Figure 4.9 Cooling and Trapping. TA kinetics displaying the bleach per excitation $\Delta A/(I_0 \cdot F_A)$ for a film of 6.3 nm CdTe QDs capped with 2DT ligands. (a) kinetics of the $1S_{3/2}IS_e$ bleach after 480 nm excitation with 2.5·10¹³ photons per cm² ("hot", red line) and 670 nm excitation with 3.4 ·10¹³ photons per cm² ("cold", blue line), respectively. (b) kinetics of the $1P_{3/2}IP_e$ bleach (green line) and $1S_{3/2}IS_e$ bleach (red line), respectively, after excitation at 480 nm with 2.5·10¹³ photons per cm². (c) schematic of the proposed model describing the fate of an electron after "hot" excitation into the $1P_e$ level (see main text).

C.7 Photoinduced Absorption "Shelf" Signal

For dispersions and films with short life-time of the $1S_{3/2}1S_e$ bleach, a broad photoinduced absorption (PA) "shelf" feature below the bandgap can be observed (see Figures 2b and 3d). For the film of 6.3 nm CdTe QDs capped with 2DA ligands measured in the main text (see Figure 3a), Figure 4.10 displays the kinetics of both the PA "shelf" feature (red line) and the $1S_{3/2}1S_e$ bleach (blue line).



Figure 4.10 Kinetics of the photoinduced absorption "shelf" signal at 850 nm (red line) and the ${}_{3/21}S_e$ bleach (blue line) for the TA measurement shown in Figure 3a in the main text. The sample is a film of 6.3 nm CdTe QDs capped with 2DA ligands.

C.8 Estimation of Band Alignment of CdTe and CdSe QDs

For the CdTe-CdSe films studied, we estimate the alignment of the quantum confined levels based on the reported electron affinities, *i.e.* -3.58 eV and -4.0 eV vs vacuum for CdTe and CdSe, respectively,²² with an added term containing only the quantum confinement. The latter is inferred from the reported size dependence of the $1S_{3/2}1S_e$ and $1P_{3/2}1P_e$ transition^{4, 5, 23} which is assumed to be distributed to electron and hole levels according to their effective masses (0.1 and 0.8, respectively, for CdTe, and 0.11 and 1.14, respectively, for CdSe). Figure 4.11 shows the calculated alignment of the $1P_e$, $1S_e$, $1S_{3/2}$ and $1P_h$ level in the studied CdTe-CdSe films. In this simple model, the offset of the CdTe and CdSe $1S_e$ levels (~ 0.42 eV) is larger than the difference between $1P_e$ and $1S_e$ level in CdSe (0.17 eV). Hence, it is conceivable that electron transfer from CdTe to CdSe QDs can occur both *via* the $1P_e$ and $1S_e$ level in CdSe. However, we note that the above simple model does not catch the complexity of the energetic landscape in real QD films which may experience significant contributions from the ligand and the dielectric environment. Thus, further studies are needed to accurately determine the energy level alignment and test the above hypothesis that the CdSe $1P_e$ level is involved in electron transfer.



Figure 4.11 Estimated energies of the $_{1}P_{e}$, $_{1}S_{e}$, $_{1}S_{_{3/2}}$ and $_{1}P_{h}$ level in the CdTe and CdSe QDs employed in the CdTe-CdSe QD films studied. The offsets of these levels are denoted by arrows.

REFERENCES of APPENDIX C

- 1. Lebedev, M. V.; Misochko, O. V.; Dekorsy, T.; Georgiev, N., On the Nature of "Coherent Artifact". J. Exp. Theor. Phys. 2005, 100, 272-282.
- Dietzek, B.; Pascher, T.; Sundström, V.; Yartsev, A., Appearance of Coherent Artifact Signals in Femtosecond Transient Absorption Spectroscopy in Dependence on Detector Design. *Laser* Phys. Lett. 2007, 4, 38-43.
- Trinh, M. T.; Houtepen, A. J.; Schins, J. M.; Hanrath, T.; Piris, J.; Knulst, W.; Goossens, A. P. L. M.; Siebbeles, L. D. A., In Spite of Recent Doubts Carrier Multiplication Does Occur in PbSe Nanocrystals. *Nano Lett.* 2008, 8, 1713-1718.
- Groeneveld, E.; Delerue, C.; Allan, G.; Niquet, Y.-M.; de Mello Donegá, C., Size Dependence of the Exciton Transitions in Colloidal CdTe Quantum Dots. J. Phys. Chem. C 2012, 116, 23160-23167.
- 5. de Mello Donegá[®], C.; Koole, R., Size Dependence of the Spontaneous Emission Rate and Absorption Cross Section of CdSe and CdTe Quantum Dots. J. Phys. Chem. C 2009, 113, 6511-6520.
- 6. Klimov, V. I., Optical Nonlinearities and Ultrafast Carrier Dynamics in Semiconductor Nanocrystals. J. Phys. Chem. B 2000, 104, 6112-6123.
- 7. Kambhampati, P., Hot Exciton Relaxation Dynamics in Semiconductor Quantum Dots: Radiationless Transitions on the Nanoscale. J. Phys. Chem. C 2011, 115, 22089-22109.
- 8. Efros, A. L.; Rodina, A. V., Band-Edge Absorption and Luminescence of Nonspherical Nanometer-Size Crystals. *Phys. Rev. B* 1993, 47, 10005-10007.
- 9. Franceschetti, A.; Zunger, A., Optical Transitions in Charged CdSe Quantum Dots. Phys. Rev. B 2000, 62, R16287-R16290.
- 10. Houtepen, A. J.; Vanmaekelbergh, D., Orbital Occupation in Electron-Charged CdSe Quantum-Dot Solids. J. Phys. Chem. B 2005, 109, 19634-19642.
- 11. Klimov, V. I., Spectral and Dynamical Properties of Multilexcitons in Semiconductor Nanocrystals. *Annu. Rev. Phys. Chem.* 2007, 58, 635-673.
- Saari, J. I.; Dias, E. A.; Reifsnyder, D.; Krause, M. M.; Walsh, B. R.; Murray, C. B.; Kambhampati, P., Ultrafast Electron Trapping at the Surface of Semiconductor Nanocrystals: Excitonic and Biexcitonic Processes. J. Phys. Chem. B 2012, 117, 4412-4421.
- 13. Morris-Cohen, A. J.; Donakowski, M. D.; Knowles, K. E.; Weiss, E. A., The Effect of a Common Purification Procedure on the Chemical Composition of the Surfaces of CdSe Quantum Dots Synthesized with Trioctylphosphine Oxide. J. Phys. Chem. C 2009, 114, 897-906.
- 14. Morris-Cohen, A. J.; Malicki, M.; Peterson, M. D.; Slavin, J. W. J.; Weiss, E. A., Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots. *Chem. Mater.* 2012, 25, 1155-1165.
- 15. Morris-Cohen, A. J.; Frederick, M. T.; Cass, L. C.; Weiss, E. A., Simultaneous Determination of the Adsorption Constant and the Photoinduced Electron Transfer Rate for a CdS Quantum Dot–Viologen Complex. J. Am. Chem. Soc. 2011, 133, 10146-10154.
- 16. Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S., Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *J. Am. Chem.* Soc. 2013, 135, 18536-18548.

- Anderson, N. C.; Owen, J. S., Soluble, Chloride-Terminated CdSe Nanocrystals: Ligand Exchange Monitored by 'H and ³'P NMR Spectroscopy. *Chem. Mater.* 2012, 25, 69-76.
- Hendry, E.; Koeberg, M.; Wang, F.; Zhang, H.; de Mello Donegá, C.; Vanmaekelbergh, D.; Bonn, M., Direct Observation of Electron-to-Hole Energy Transfer in CdSe Quantum Dots. *Phys. Rev. Lett.* 2006, 96, 057408.
- 19. Sippel, P.; Albrecht, W.; Mitoraj, D.; Eichberger, R.; Hannappel, T.; Vanmaekelbergh, D., Two-Photon Photoemission Study of Competing Auger and Surface-Mediated Relaxation of Hot Electrons in CdSe Quantum Dot Solids. *Nano Lett.* 2013, 13, 1655-1661.
- 20. Guyot-Sionnest, P.; Shim, M.; Matranga, C.; Hines, M., Intraband relaxation in CdSe quantum dots. *Phys. Rev. B* 1999, 60, R2181-R2184.
- Hannah, D. C.; Brown, K. E.; Young, R. M.; Wasielewski, M. R.; Schatz, G. C.; Co, D. T.; Schaller, R. D., Direct Measurement of Lattice Dynamics and Optical Phonon Excitation in Semiconductor Nanocrystals Using Femtosecond Stimulated Raman Spectroscopy. Phys. Rev. Lett. 2013, 111, 107401.
- 22. Wei, S.-H.; Zhang, S. B.; Zunger, A., First-Principles Calculation of Band Offsets, Optical Bowings, and Defects in CdS, CdSe, CdTe, and Their Alloys. J. Appl. Phys. 2000, 87, 1304-1311.
- 23. Norris, D. J.; Bawendi, M. G., Measurement and Assignment of the Size-Dependent Optical Spectrum in CdSe Quantum Dots. *Phys. Rev. B* 1996, 53, 16338.

5 THE DENSITY OF TRAP STATES AND AUGER MEDIATED ELECTRON TRAPPING IN CDTE QUANTUM-DOT SOLIDS

5.1. INTRODUCTION

Charge trapping at defect sites is common in colloidal Quantum-Dot (QD) films and a major loss mechanism in optoelectronic devices in general as trapping often leads to recombination and the loss of charge carriers. In devices made of crystalline bulk materials the most common defects are impurities or defects of the crystal structure such as vacancies or interstitial atoms. However, in multi- and nano-crystalline materials, surface defects play a dominant role. In CdTe solar cells, for example, grain boundaries were identified as the major defect site. Strategies to decrease the associated losses includ grain growth¹ (*i.e.* diminish the number of grain boundaries) and electronic passivation with CdCl₂ or MgCl₂.² In devices employing QDs, surface defects are even more important as the surface area is very high. Therefore, a large body of empirical work reported recipes for electronic passivation, using inorganic shells or ligand exchange.³ Until now, only a few (largely theoretical) studies propose an explanation of the physical and chemical processes responsible for trapping.⁴⁷ The exact nature of the involved

surface traps remains poorly understood. On the experimental side, measurements of the density of states (DOS) within the band gap are rare and limited to PbS QDs,⁸⁻¹⁰ and on the theoretical side, the calculation of the surface for realistic QD sizes with realistic ligands remains a challenge.^{5, 11} A deeper understanding of charge trapping is necessary to advance the science and application of QDs.

In this study, we assess the density of trap states (DOTS) throughout the band gap in films of CdTe QDs using a novel combination of electrochemical control of the Fermi level and ultrafast transient absorption (TA) and time-resolved PL spectroscopy. Recently, we have shown that electron trapping in QD films can be slowed down down by three orders of magnitude by electrochemically filling trap states.¹² Here, we present a detailed energy-dependence of the trapping rate and derive from it the number of available traps. This allows us to map the DOTS throughout the band gap. We find a DOTS that is well described by a Gaussian centered ~0.42 eV above the valence band edge. Density Functional Theory (DFT) calculations relate the experimentally determined DOTS to the configuration of Te atoms at the surface, allowing for a complete picture of surface trapping. Surprisingly the subgap states near the valence band act as very efficient electrons traps, while hole trapping is an order of magnitude slower. This discrepancy can be explained by Auger mediated electron and hole trapping.

5.2. EXPERIMENTAL DETAILS

Materials

1,7-heptanediamine (98 %, Aldrich); methanol (anhydrous, 99.8 %, Sigma-Aldrich); butanol (anhydrous, 99.8 %, Sigma-Aldrich); acetonitrile (anhydrous, 99.8%, Sigma-Aldrich); LiClO₄ (battery grade, dry, 99.99%, Aldrich); Te (-18+60 mesh, 99.999 %, Alfa Aesar); trioctylphosphine (97 %, Aldrich); 1-octadecene (technical grade, 90 %, Aldrich) and oleic acid (technical grade, 90 %, Aldrich) were all used as received.

QD Synthesis

CdTe QDs with a diameter of 3.7 nm were synthesized following the procedure described by Kloper *et al.*¹³ At 310 °C in N_2 atmosphere, a TOP (trioctylphosphine) - Te precursor in ODE (octadecene) is injected rapidly to a Cd-(oleate)₂ precursor in ODE under vigorous stirring. Growth took place at 270 °C and was stopped after several minutes by injection of cold toluene. The dispersion was purified by adding anhydrous MeOH and anhydrous BuOH as nonsolvents at a volume ratio of 1:1:2 (reaction solution:MeOH:BuOH) to precipitate the QDs in a centrifuge at 3500 rpm during 7 min. Subsequently, the precipitate was redispersed in chloroform and the whole purification procedure was repeated once.

Film Processing and Ligand Exchange

Films with 7DA ligands are grown on ITO substrates in a layer-by-layer (LbL) dip coating procedure using a mechanical dipcoater (DC Multi-8, Nima Technology) in a N_2 purged glove box: the substrates were first immersed for 30 s in a concentrated (~ 10⁻⁵ M) QD dispersion, subsequently immersed for 30 s in a magnetically stirred 0.1 M solution of the 7DA ligand in MeOH, and finally dipped twice for 10s in stirred MeOH to rinse excess ligands. Using this procedure, the original insulating ligands are replaced by the shorter bidentate ligands. The above procedure was repeated 10-20 times to yield films roughly 10-20 QD monolayers thick. A small region on the edge of the ITO substrate remained uncoated to provide electrical contact in electrochemical measurements.

Linear Absorption Spectra

Linear absorption spectra were recorded in a Perkin Elmer λ 900 absorption spectrometer equipped with an integrating sphere to correct for scattering and reflection. Figure 5.1a shows linear absorption spectra of CdTe QDs of 3.7 nm diameter, either as a dispersion in hexane with oleic acid (OA) ligands (black line) or deposited as a film, with ligands exchanged to 1,7-heptanediamine (7DA, red line). Both spectra were normalized to one at the $1S_{3/2}1S_e$ peak and offset for clarity. In the film, quantum confinement is preserved, as the $1S_{3/2}1S_e$ peak remains a pronounced feature of the absorption spectrum.

Broadband Transient Absorption Measurements

Broadband transient absorption (TA) measurements were performed in the low fluence limit (< 0.1 excitations per QD, where the TA kinetics were independent on pump fluence) on a film with an optical density of about 0.25 at the pump wavelength to provide uniform excitation densities. The sample was excited in the electrochemical cell with ~ 180 fs pump pulses from an OPA (Light Conversion ORPHEUS) pumped by an amplified fs laser (Light Conversion PHAROS SP), at a repetition rate of 2500 Hz. Absorption spectra in the visible (450 - 900 nm) were recorded with an Ultrafast Systems HELIOS spectrometer at a repetition rate of 5000 Hz using broadband probe pulses from a sapphire crystal pumped by the 1030 nm fundamental of the laser. A variable delay of – 10 to 3000 ps between probe and pump pulses was introduced to yield difference absorption spectra, as a function of pump – probe delay and probe energy. Due to dispersion in optical components between the white light generating crystal and the photodetector, the "time zero", *i.e.* the point of time where pump and probe show maximum temporal overlap, depends on the probe wavelength. Dispersion corrected 2D TA data with identical time zero for all wavelengths were obtained by subtracting a third-order polynomial fit to the "coherent artifact"^{14, 15} (see Appendix C.1 for details of the method), obtained on a blank ITO electrode in the same electrochemical cell, from the raw data. About 10 000 difference absorption spectra were obtained per pump – probe delay.

Streak Camera Measurements

Time- and wavelength-resolved photoluminescence (PL) measurements were performed using a streak camera (Hamamatsu C568o). The sample was excited with ~ 150 fs laser pulses from a Ti:sapphire laser (Chameleon Ultra by Coherent, Inc.), centered at 400 nm, at a repetition rate of 4 MHz. The pump beam was focused and had a diameter of about 40 µm at the position of the sample, leading to an excitation fluence of about $4\cdot10^{13}$ photons per cm² per pulse. PL of the sample was collected in reflection geometry with a parabolic mirror, dumping the direct (specular) reflection *via* a hole in the center of the mirror. The collected PL was focused by a lens with 200 mm focal length and fed into a spectrograph (Princeton Instruments Acton SP2300) through an entrance slit with a width of 100 µm. The PL was then measured by the streak camera in the slow sweep mode, over a time window of about 2 ns.

Electrochemical Control of the Fermi Level

The Fermi level of our QD films on ITO was controlled by a CHI832B bipotentiostat (CH Instruments, Inc.), while immersed in an airtight quartz electrochemical cell with an Ag wire pseudoreference electrode and a Pt sheet counter electrode (see inset in Figure 5.1). The Ag wire pseudoreference electrode (- 4.75 V vs. vacuum) was calibrated against the ferrocene/ferrocinium couple.¹⁶ In a N₂ purged glove box, the cell is loaded with a QD film, filled with 0.1 M LiClO₄ in anhydrous acetonitrile and sealed with an O-ring to assure airfree conditions. All chemicals were used as received. The electrochemical cell is placed such that TA measurements are possible, with both pump and probe beams passing

through the front window, the QD films and the back window of the cell. Figure 5.1b sketches the experimental procedure. The Fermi level of the QD films is controlled by the applied voltage between the film and the pseudo-reference electrode.

The porous nature of the QD films causes electrolyte ions to permeate the whole film.^{17, 18} In contrast to electrochemical experiments on 2D samples, 3D porous QD films are fully depleted allowing for homogeneous charging throughout the film. The potential drops between QD film and the reference electrode, in the electrolyte solution, resulting in a Fermi level in the QD film that is constant and equal to the Fermi level in the ITO electrode.

We use the convention that a decreasing voltage corresponds to a shift of the Fermi level towards vacuum. For all applied potentials reported in the main text, care was taken that the absorption of the unexcited sample did not change with respect to open circuit potential. This ensures that no charges were injected into quantum-confined levels, as they would lead to a bleach of the $1S_{3/2}1S_e$ absorption.^{17, 19 18}



Figure 5.1 (a) Linear absorption spectrum, normalized at the ${}_{3_{1}2}IS_{e}$ peak, for CdTe QDs with original ligands in hexane (black line) and as a film with 7DA ligands (red line). For clarity, spectra are offset vertically. (b) Schematic of the experiment: the Fermi level of the sample is controlled by the applied voltage in an electrochemical cell, while spectroscopic information is collected either by a streak camera or a transient absorption setup.

5.3. TRANSIENT ABSORPTION REVEALS ELECTRON DYNAMICS

Figure 5.1a shows linear absorption spectra of CdTe QDs of 3.7 nm diameter, either as a dispersion in hexane with oleic acid (OA) ligands (black line) or deposited as a film, with ligands exchanged to 1,7-heptanediamine (7DA, red line). A film on an indium doped tin oxide (ITO) substrate has been obtained using a Layer-by-Layer (LbL) dip-coating procedure as explained in the methods section. Both spectra were normalized to one at the $1S_{3/2}1S_e$ peak and offset for clarity. In the film, quantum confinement is preserved as the $1S_{3/2}1S_e$ peak remains a pronounced feature of the absorption spectrum.

Figure 5.1b sketches the experimental procedure. The QD film on ITO substrate is immersed in an electrochemical cell (see Methods). The Fermi level of the QD films is controlled by the applied voltage between the film and the pseudo-reference electrode (-4.75 eV vs. vacuum). The porous nature of the QD films causes electrolyte ions to permeate the whole film.^{17, 18} This allows for homogeneous charging and, hence, a constant shift of the Fermi level with respect to conduction and valence band, throughout the film. The electrochemical cell is placed in a fs TA or a streak camera setup to perform ultrafast optical measurements. TA measurements are performed to determine the electron trapping rates and PL measurements to determine the hole trapping rates. This is motivated by the fact that for our CdTe QD films, TA is mainly sensitive to the 1S_e electron,^{12, 20-22} whereas PL is equally sensitive to both 1S_e electron and 1S_{3/2} hole.

Figures 2a-c show 2D TA images for a film of 7DA capped CdTe QDs, which display the change in absorption ΔA as a function of probe wavelength and time delay between the probe pulse and a pump pulse at 400 nm with a fluence of 2.0 x 10¹³ photons per cm² per pulse. Figure 5.2a shows the response at open circuit potential (-0.02 V vs. the Ag quasi-reference electrode), where the dominant feature is an absorption bleach (ΔA <0) of the 1S_{3/2}1S_e transition at 610 nm. This corresponds to an electron occupying the 1S_e state and/or a hole occupying the 1S_{3/2} state. For cadmium chalcogenide QDs, it has been shown that the 1S_{3/2}1S_e bleach is dominated by electrons.^{12, 20-22} It has been proposed that this is due to the fact that the DOS near the valence band edge is much higher than the DOS near the conduction band edge. As a result a single electron results in a much larger bleach than a single hole. Therefore we assume that the hole contribution can be neglected and the observed TA signal only originates from 1S_e electrons.

Apart from the $1S_{3/2}1S_e$ bleach, a broad photoinduced absorption (PA) "shelf" feature²³⁻²⁵ within the band gap is observed as well as red shifts of all optical transitions in the spectrum.²¹⁻²³ These features have all been observed and explained before. We focus on the $1S_{3/2}1S_e$ bleach feature, as its time evolution represents the decay of electrons from the $1S_e$ level. As shown in Figures 2a and 2e, this decay is on the order of tens of picoseconds and therefore much shorter than the radiative lifetime of 22.2 ns in solution.²⁶ Hence, the decay must be non-radiative in nature. Following the argumentation in our previous work,¹² we assign it to electron trapping.

When the potential is decreased to -0.3 V, *i.e.* the Fermi level is raised towards vacuum by 0.3 eV, the bleach becomes more pronounced and its lifetime longer, see Figure 5.2b. The trend continues when the potential is further decreased to -1.0 V (Figure 5.2c). A full dependence on the potential is given in Figures 2d and 2e, which display the TA spectra (averaged between 10 ps and 3 ns) and the kinetics (averaged between 590 and 700 nm), respectively.



Figure 5.2 TA images after 400 nm excitation for a film of 7DA treated CdTe QDs with a diameter of 3.7 nm at (a) open circuit = -0.02 V, (b) -0.3 V and (c) -1.0 V vs. Ag wire, after excitation at 400 nm with a fluence of 2.0 x 10^{13} photons per cm² per pulse. (d) Spectra averaged from 10 ps to 3 ns (e) kinetics at the $1S_{3/2}IS_e$ transition, averaged from 590 to 700 nm (f) $1S_{3/2}IS_e$ bleach at 100 ps, for all applied potentials.

Figure 5.2e shows that, upon filling the electron traps (i.e. when the potential is decreased), both the electron lifetime and the maximum bleach increase. The former indicates slower trapping on a pico- to nanosecond time scale, the latter points towards less sub-picosecond trapping, as such fast trapping is in competition with electron cooling to the $1S_e$ state and reduces the maximum transient occupation of the $1S_e$ level.

Figure 5.2f summarizes the effect by displaying the bleach 100 ps after excitation for all applied voltages: the bleach increases monotonously when the potential is decreased, down to -1.3 V. This is due to electrochemical filling of traps. When the traps are filled with electrons, electron trapping is reduced, resulting in longer electron lifetimes. The largest increase occurs between 0 and -0.5 V. Hence, in this potential range a large density of trap states must exist. Below -1.3 V, the signal reduces. Auger recombination between charges electrochemically injected in the 1S_e level and the photogenerated exciton could in principle explain the reduced bleach at negative potentials. For certain materials (e.g. for PbS QD films) we do indeed observe this. However, the electrochemical injection of electrons in the 1S_e level should result in a steady state bleach of the $1S_{e1}S_{3/2}$ transition and such a bleach does not occur here. Therefore Auger recombination is discarded. In stead we suggest that the decrease in the observed transient absorption bleach is due to the at low reduction potential of Cd²⁺ in CdTe and a concomitant irreversible reduction of the CdTe QD film.²⁷

As we have argued previously,¹² the physical origin of the observed electron traps most likely lies in insufficient surface passivation. We believe that the dip-coating procedure used to grow these films leads to partial removal of ligands and incomplete recapping of the freed surface states with new ligands (7DA in this case). Below we will show strong evidence for this scenario.

To investigate the position of the large DOTS with respect to valence and conduction band, we determined the energy of the $1S_{3/2}$ level spectro-electrochemically *via* a steadystate absorption bleach of the $1S_{3/2}1S_e$ transition upon shifting the Fermi level downward (see Figure 5.8). The $1S_{3/2}$ level lies at +0.25 V, *i.e.* at -5.0 eV vs. vacuum. The energy of the $1S_e$ level (-1.75 V or -3.0 eV vs. vacuum) is estimated by adding the optical band gap (-2.0 eV). A direct spectro-electrochemical determination of this level was not possible due to the low reduction potential of Cd^{2+} in CdTe, leading to irreversible dissolution of the film prior to electron injection into the $1S_e$ level.²⁷ Our own determination of the $1S_e$ and $1S_{3/2}$ levels is in line with previous assessments.²⁸ We therefore conclude that the large DOTS is located in the lower part of the band gap, close to the $1S_{3/2}$ level. It is worth a note that the Fermi level in dry CdTe QD films is close to the $1S_{3/2}$ level. This was determined by comparing the electron dynamics in TA experiments on dry films with those of electrochemically controlled films to thos in identical dry films. At ~0 V the electrons dynamics are identical implying that the Fermi level in the dry film is 0 V vs. the Ag pseudoreference electrode, i.e. 0.25 V above the $1S_{3/2}$ level. Thus, the dry film appears to be unintentionally p-doped, its Fermi level is below the DOTS and empty traps are available for electron trapping.

5.4. TIME-RESOLVED PHOTOLUMINESCENCE REVEALS HOLE CONTRIBUTION

As the TA measurements do not reveal hole dynamics, we also performed time-resolved PL measurements with a streak camera setup. PL is equally sensitive to the presence of $1S_{3/2}$ holes as it is to $1S_e$ electrons, since both are required for emitting a photon. Hence, both the hole and the electron decay are represented in the PL kinetics. Figures 3a-c display time- and wavelength-resolved PL images at open circuit potential (-0.05 V), -0.3 V and -1.0 V, respectively, after excitation at 400 nm with a fluence of 4.8 x 10¹³ photons per cm² per pulse.

The main feature in the PL images is emission at the $1S_{3/2}1S_e$ transition, whose intensity and lifetime increase when the Fermi level is moved towards vacuum. Figure 5.3d shows spectra at several potentials, averaged over all time delays. For all potentials emission from the band gap, around 620 nm, is dominant, with an intensity that increases with decreasing potential. Below -1.3 V, as in the TA measurements, the signal decreases again which might be explained by sample degradation.²⁷ Figure 5.3e reproduces the trend of the TA measurements: in the $1S_{3/2}1S_e$ kinetics, averaged from 550 to 700 nm, both the PL peak and lifetime increases with decreasing potential, down to -1.3 V. Figure 5.3f displays the PL counts at 100 ps: while at this time delay almost no PL is detected at open circuit potential (-0.05 V), the PL signal is increased by a factor 85 at -1.3 V. Overall, the PL quantum yield increases by a factor 20, as inferred from integrating the PL image with respect to time and wavelength.



Figure 5.3 Streak camera PL images for a film of 7DA treated CdTe QDs with 3.7 nm diameter at (a) open circuit = -0.02 V, (b) -0.3 V, and (c) -1.0 V vs. Ag wire pseudo reference electrode, after excitation at 400 nm with a fluence of 4.8×10^{13} photons per cm² per pulse (d) spectra averaged over all time delays (e) kinetics at the $1S_{3/21}S_e$ transition, averaged from 550 to 700 nm (f) PL counts in (e), at 100 ps.

According to Shockley-Read-Hall recombination theory²⁹ charge capture at a trap at energy E_t occurs with a rate $k_e(E_t, E_F) = c_e \cdot [1 - f(E_t - E_F)] \cdot \rho_t$ for the electron and with a rate $k_h(E_t, E_F) = c_h \cdot f(E_t - E_F) \cdot \rho_t$ for the hole, with c_e and c_h the electron and hole capture cross section, respectively, $f(E_t - E_F)$ the trap occupation according to Fermi-Dirac statistics and ρ_t the density of trap states. Within this picture, electron ($\tau_e = 1/k_e$) and hole ($\tau_h = 1/k_h$) lifetimes both change with Fermi level, but inversely. The PL intensity is proportional to the product of electron and hole concentrations, $I_{PL} \propto n_e \cdot n_h \propto \exp(-(k_e + k_h) \cdot t) = \exp\{-[c_e + (c_h - c_e) \cdot f(E_t - E_F)] \cdot \rho_t \cdot t\}$. If, for the moment, we assume that c_e and c_h are independent on energy, it is found that for equal capture cross sections ($c_e = c_h$), the PL lifetime $\tau_{PL} = 1/(k_e + k_h + k_{rad})$ is independent of potential, for $c_e > c_h$ it increases with increasing Fermi level lets us conclude that the capture cross section for electrons is much higher than for holes and that the PL quenching is dominated by electron trapping.

We now quantify the electron and hole trapping rates by fitting the TA and PL kinetics. Both data sets are simulated with the model sketched in Figure 5.4d. Herein, a 1S_e electron can decay either *via* radiative recombination with a 1S_{3/2} hole with rate constant k_{rad} or *via* trapping to one of N_e available electron traps with rate constant k_e . The ground state is recovered by recombination with a 1S_{3/2} hole with rate constant k_{rec} . Similarly, a 1S_{3/2} hole can decay *via* radiative recombination with a 1S_e electron with rate constant k_{rad} or *via* trapping to one of N_h available hole traps with rate constant k_{rec} . The ground state is recovered by recombination with a 1S_{3/2} hole with rate constant k_{rec} . Similarly, a 1S_{3/2} hole can decay *via* radiative recombination with a 1S_e electron with rate constant k_{rad} or *via* trapping to one of N_h available hole traps with rate constant k_h , from where it may recombine with a 1S_e electron with rate constant k_{rec} . The rate constants and number of available traps are a function of the Fermi level.

The observed kinetics are clearly not single exponential. We attribute this to sample inhomogeneity. Individual QDs will contain a variable number of unpassivated surface sites that leads to trapping and, consequently, will have varying trapping rates. We model this inhomogeneity by simulating the observed ensemble population by a sum of three sub-populations, indicated with indices i = 1, 2, 3: one with fast trapping, one with intermediate trapping and one with slow trapping. We do not imply that there are three separate trapping rates. These three rates are simply used to model the distribution of trapping rates in a mathematically simple way.

We fit TA and PL data after 2 ps, when charges have relaxed to the respective band edges. Then, the charge occupation in the QD films can be described by the densities of three species: QDs with a $1S_e$ electron and a $1S_{3/2}$ hole ($n_{eh,i}$), QDs with a $1S_e$ electron and a trapped hole ($n_{e0,i}$), and QDs with a trapped electron and a $1S_{3/2}$ hole ($n_{0h,i}$), where the index i denotes the sub-populations of QDs with fast, intermediate and slow traps, respectively. The time evolution of the densities is obtained from the model sketched in Figure 5.4d, yielding the following rate equations

$$\frac{dn_{eh,i}}{dt} = -(k_{rad} + k_{e,i} + k_{h,i}) \cdot n_{eh,i}$$
(5.1)

$$\frac{dn_{e0,i}}{dt} = +k_{h,i} \cdot n_{eh,i} - (k_{e,i} + k_{rec}) \cdot n_{e0,i}$$
(5.2)

$$\frac{dn_{0h,i}}{dt} = +k_{e,i} \cdot n_{eh,i} - (k_{h,i} + k_{rec}) \cdot n_{0h,i}$$
(5.3)

As discussed above, the TA kinetics of the $1S_{3/2}1S_e$ bleach represent the $1S_e$ electron decay, while the PL kinetics represent both $1S_e$ electron decay and $1S_{3/2}$ hole decay. Hence, the TA signal is given by

$$\Delta A(t) \propto \sum_{i=1}^{3} \left(n_{eh,i}(t) + n_{e0,i}(t) \right)$$
(5.4)

and the PL signal by

$$I_{PL}(t) = \sum_{i=1}^{3} n_{eh,i}(t)$$
(5.5)

The TA decay contains fewer parameters as it does not distinguish between $n_{eh,l}$ and $n_{eo,i}$ and is effectively independent of hole trapping. Hence, we start by modelling the TA data. Figure 5.4a shows TA data (closed circles), normalized to the peak signal, and fits (solid lines) from +0.3 V to -1.3 V. The fit results for the high $(k_{e,1}(E_F))$, intermediate ($k_{e,2}(E_F)$) and small $(k_{e,3}(E_F))$ electron-trapping rate constants are shown in Figure 5.4c. As expected, electron trapping monotonously decreases when the Fermi level is moved towards vacuum, to more negative potentials.

PL is determined by the same electron trapping processes as in TA, while additionally hole trapping accelerates the decay. We therefore fix the electron trapping rate constants $k_{e,1}(E_F)$, $k_{e,2}(E_F)$ and $k_{e,3}(E_F)$, the recombination rate k_{rec} and the population fractions $n_{eh,i} / \sum_{i=1}^{3} n_{eh,i}$, $n_{e0,i} / \sum_{i=1}^{3} n_{e0,i}$ and $n_{0h,i} / \sum_{i=1}^{3} n_{0h,i}$ to the respective values obtained from the TA fit, leaving the hole trapping rates $k_{h,1}(E_F)$, $k_{h,2}(E_F)$ and $k_{h,3}(E_F)$ as the only free parameters. The fits to the normalized PL decays from -0.05 V to -1.3 V are shown in Figure 5.4b. Hole trapping rate constants are on the order of 10¹⁰ s⁻¹, 10⁹ s⁻¹ and 10⁸ s⁻¹ for the three subpopulations of QDs (Figure S3)) and are, in each case, an order of magnitude lower than the electron trapping rate constants.

Most hole trapping occurs beyond the 1 ns timescale of the experiment. Further, both the TA and the PL decay are dominated by electron trapping. This makes the fits less sensitive to hole trapping than to electron trapping and precludes a quantitative assessment of the Fermi level dependence of the hole trapping rate constant.



Figure 5.4 Normalized TA (a) and PL kinetics (b) at selected potentials. The time axis is linear up to 50 ps and logarithmic afterwards. Data points are depicted by markers, while solid lines depict fits using the rate model sketched in (d) and expained in the main text. All rate constants are allowed to depend on the Fermi level in the film which is given by the applied voltage. Both TA and PL data were simulated assuming three populations within the films with independent electron trapping rate constants $k_{e,1}$, $k_{e,2}$ and $k_{e,3}$, respectively. The fit results for both data sets are shown in (c), with red, blue and green circles depicting the electron trapping rates of the populations 1, 2 and 3, respectively. The potential dependence of all three populations is fitted globally with an error function and depicted by a red, blue, and green solid line, respectively. (e) Derivative of the fitted error function (red solid line) and the estimated position of the 1S_e level (blue shaded region) and $1S_{3/2}$ levels (yellow shaded region), respectively.

While the rate constants $k_{e,i}$ vary by an order of magnitude, their potential dependence is identical within the noise of the measurement (see Figure S4). This suggest that the nature of the trapping process is the same in all cases, or at least that the trap energy is very similar. This support our initial interpretation made above, that the three trapping rates represent QDs with a different number of the same traps.

An error function was fitted globally to the electron rate constants (using the reciprocal standard deviation of the fitted rate constant as weight factor) and the resulting error function is shown as the solid lines in Figure 5.4c. The rationale behind using an error function is that its derivative, a Gaussian function, would likely describe the DOTS accurately. This Gaussian is shown in Figure 5.4e. Its center is located at -0.18 V (-4.57 eV vs. vacuum or 0.43 eV above the $1S_{3/2}$ level) and its FWHM is 0.42 V. The position of the $1S_e$ electron and $1S_{3/2}$ hole level is marked with a blue and yellow shaded region, respectively. The width of the shaded regions indicates the estimated uncertainty in the exact position of those levels.

5.6. DFT CALCULATIONS RELATE TRAPPING TO STRUCTURAL PROPERTIES OF THE QD SURFACE

We now relate the observed DOTS to structural properties of the nanocrystal surface *via* DFT calculations. The prevailing picture in the literature is that sufficient ligand coverage is key for electronically passivating the otherwise defect-rich QD surface.^{23, 30-34} This is in line with PL quantum yield measurements for CdSe QDs from the group of Weiss³³ and with time-resolved PL and TA data of CdTe QDs from our own group.¹² These studies show that an increasing number of purification steps in the post-synthesis treatment decreases the PL quantum yield and accelerates charge trapping, attributed to a loss of ligands. Owen's group has shown that the dependence of PL quantum yield on ligand coverage is super-linear, suggesting that a few missing ligands can be compensated by surface reconstruction, while ligand removal above a certain threshold leads to surface states within the band gap.³⁰ We consider that the same applies to the CdTe QD films studied here. Film formation includes extensive exposure to methanol and replacing ligands (1,7-heptanediamine). Both could induce the removal of ligands from the CdTe surface, probably in the form of Z-type Cd-(oleate)₂. ^{30, 31}

The reference QD model for our DFT calculations has been constructed by cleaving a zincblende CdTe lattice from which we have extracted a non-stoichiometric QD cluster, $Cd_{40}Te_{31}$, of about 1.5 nm in size. This model displays a Cd:Te ratio of 1.29, a ligand coverage of about 2.9 nm⁻² and a pseudo-pyramidal shape (see Figure 5.5a). Charge neutrality in the model system is maintained by adding 18 formate anions, HCOO⁻, to
emulate the native oleate ligands and to compensate for the excess Cd²⁺ ions. This model shows a significant geometrical reconstruction on the surface after addition of the formate anions, however preserving the underlying zinc-blende shape. The DOS of this system is also shown in Figure 5.5: the HOMO and LUMO are delocalized orbitals and no states appear in the band gap. We note that Cd and Te are 4-coordinated in the center of the cluster and 3-coordinated at the surface. This lower coordination apparently does not lead to dangling bonds inside the band gap; the corresponding orbitals have energies inside the conduction and valence bands.



Figure 5.5 (a) Fully passivated $Cd_{40}Te_{31}$ (HCOO)₁₅ QD and its DOS (pink = Cd, blue = Te, red = O, brown = C, and white = H atoms); (b) CdTe QD and its DOS after removal of one Cd(HCOO)₂ and *before* surface reconstruction, and (c) CdTe QD and its DOS after removal of one Cd(HCOO)₂ and *after* surface reconstruction. All calculations have been performed with DFT at the PBE/def2-SV(P) level of theory. The colors in the DOS panels indicate contribution from the ligands (black), the Te atoms (red) and the Cd atoms (blue). In panel (b) the contribution of the dangling 2-coordinated Te (green) and Cd (orange) atoms has also been included.

From the fully relaxed structure of $Cd_{40}Te_{31}(HCOO)_{18}$ we subsequently remove one Cd atom and two formate anions to simulate Z-type ligand removal. Afterwards, the system is allowed to reconstruct and find its most stable structure. The DOS before and after surface reconstruction is shown in Figure 5.5. The eye-catching feature is that, before surface reconstruction (Figure 5.5b), the QD features two 2-coordinated dangling Te and Cd atoms, which are described by two molecular orbitals (one occupied and the other empty) close to the valence band edge and mostly localized on the 4p and 5s orbitals of the Te and Cd atoms, respectively. This shows that 2-coordinated surface atoms do form states in the band gap. Because the two 2-coordinated surface atoms are spatially close to each other, after reconstruction, the occupied 4p orbital on Te donates its electrons to the empty 5s orbital on Cd and forms a bond (see Figure 5.5c). In this case, both Te and Cd increase their coordination number and their orbitals delocalize inside the conduction and valence band, removing the mid-gap states. The QD has self-healed.

As shown in Appendix D.4, self-healing *via* surface reconstruction is no longer possible once several ligands have been removed. After removal of three Cd(HCOO)₂, the number of trap states increases linearly with the number of removed Cd(HCOO)₂. The computed structure reveals under-coordinated Te atoms as the origin of the traps, while Cd atoms always remain sufficiently coordinated. As a result, no traps are found in the vicinity of the conduction band, while a large DOTS is formed near the valence band. The position of this DOTS is in agreement with the experimentally observed DOTS, suggesting that insufficient ligand coverage and 2-coordinated Te atoms are responsible for charge trapping.

In our calculations, the computed DOTS lies below the Fermi level and can therefore only act as a source of hole traps. In the experiments however, we find that many of the surface states are empty and act as electron traps (*i.e.* the QD films are unintentionally p-type). To simulate this, we computed the electronic structure of an oxidized $Cd_{37}Te_{31}(HCOO)_{12}$ ⁺ model, featuring one di-coordinated Te atom. To avoid spurious effects from the excess of cationic charge, we add a perchlorate anion as a spectator ligand, which keeps the overall system neutral. The geometry and the computed DOS for this system are shown in Figure 5.6.



Figure 5.6 (a)-(b) Fully relaxed structures for the neutral and oxidized CdTe QD models, respectively, and (c)-(d) their DOS. (e)-(f) Schematic molecular orbital diagrams that show the interaction between a 3-coordinated Te atom, Te (A), and the adjacent undercoordinated Te atom, Te(B), for the neutral and oxidized species. In the latter case a weakly bonded dimer is formed. The antibonding orbital is only partially occupied and can also act as an electron trap.

A first observation is that the oxidized QD (Figure 5.6b) presents a geometry similar to the neutral QD, with only one significant difference: the 2-coordinated Te atom, denoted as Te(B), is spatially closer to the 3-coordinated Te atom, Te(A). Oxidation shrinks the Te(A)-Te(B) bond length from 4.00 Å to 3.45 Å. To understand this, we plot a scheme of the molecular orbitals patterns for the neutral (Figure 5.6e) and oxidized (Figure 5.6f) species. When the QD cluster is neutral (i.e. the Fermi level is near midgap), the 5p orbital on Te is doubly occupied and remains mostly unbound. The loss of one electron implies the oxidation of the 5p orbital on Te(B), which becomes a weak electron acceptor. This orbital interacts with the closest electron donor in the neighborhood, i.e. the 5p on Te(A), in a bonding/anti-bonding fashion. Note that the anti-bonding orbital is singly occupied, which means that (1) the Te-Te bond is weak, (2) this orbital can act as both electron and hole trap, and (3) the Fermi level is shifted towards the valence band.

One can generalize this view for larger QD, for which the number of under-coordinated Te atoms is high. A half-filled DOTS (as roughly the case in dry QD films in the experiments) means that many of these Te atoms are oxidized and form weakly bound Te-Te dimers on the QD surface each displaying a half-populated antibonding orbital that act both as electron and hole trap. Electrochemical filling of these traps breaks the Te-Te bonds, resulting in under-coordinated Te atoms at the QD surface, with 5p lone-pairs acting mostly as hole traps.

5.7. AUGER MEDIATED ELECTRON TRAPPING AND DOTS

We now discuss in more detail how the electron and hole trapping rate constants depend on the DOTS and the energy loss involved in the trapping process. We start by expressing the electron trapping rate constants as:

$$k_{e,i}(E_F) = N_i \cdot \int_{-\infty}^{+\infty} \rho(E) \cdot (1 - f(E - E_F)) \cdot c_e(E) dE$$
(5.6)

Herein, the index *i* denotes the population (i = 1, 2, 3), N_i the respective number of traps per QD, $\rho(E)$ is the (normalized) DOTS, $f(E - E_F)$ the Fermi-Dirac distribution and $c_e(E)$ the capture rate constant of an electron by a trap at energy E. If we neglect thermal broadening of the Fermi-Dirac distribution at room temperature, since $k_{\rm B}T$ is smaller than our experimental potential step size (100 meV), Equation 5.6 simplifies to

$$k_{e,i}(E_F) = N_i \cdot \int_{E_F}^{E_{1Se}} \rho(E) \cdot \mathbf{c}_e(E) dE$$
(5.7)

We restrict the upper integration bound to the 1S_e electron level, assuming that trapping only takes place at states within the band gap. For the hole, an equivalent reasoning holds, leading to $k_{h,i}(E_F) = N_i \cdot \int_{E_{IS32}}^{E_F} \rho(E) \cdot c_h(E) dE$, where $c_h(E)$ is a hole specific capture rate constant. Therefore, the DOTS $\rho(E)$ can be retrieved from either electron or hole trapping rates, *via*

$$\rho(E_F) = -\frac{1}{N_i c_e(E_F)} \cdot \frac{dk_{e,i}(E_F)}{dE_F}$$
(5.8)

or equivalently via $\rho(E_F) = (N_i c_h(E_F))^{-1} \cdot dk_{h,i}(E_F) / dE_F$, as shown in Appendix D.3. As our electron trapping rates could be determined with greater accuracy, we choose the derivation from electron trapping rates. In Equation 5.8, the index indicating the Fermi level may be omitted, since we neglect thermal broadening.

A challenge lies in estimating the capture rate constant $c_e(E)$, for which the nature of the trapping process must be known. This is the topic of a lively discussion currently held in the literature. In the debate, several mechanisms have been proposed, ranging from resonant trapping^{4, 35} to shallow trapping³⁶ to deep trapping,^{8, 12, 35, 37} to either a single³⁶ or multiple defect states,³⁸ either described by Marcus theory, Marcus-Jortner theory,^{36, 39, 40} or by Auger induced trapping.^{4, 35} To reveal which mechanisms is applicable to trapping in our QD films, we choose to compare three scenarios: (1) the electron capture rate constant is constant in energy, (2) electron capture can be explained as an electron transfer process according to Marcus theory, and (3) electron capture is Auger-mediated, as sketched in Figure 5.7a.

Scenario (1) implies that our measurement presents a direct determination of the DOTS, as it would equal the (scaled) $dk_e(E_F)/dE_F$ shown in Figure 5.4e. Scenario (2) has previously been invoked by Mooney et al. to explain surface trapping in CdS, CdSe and CdSe/ZnS QDs.^{36, 40} In these studies, the authors proposed a semi-classical Marcus-Jortner formalism with strong coupling of the surface state to the LO phonon (Huang-Rhys parameter ~ 10), a reorganization energy of 15 meV and a trap depth of 50 meV. While the experimental approach could not distinguish between electron and hole trapping, their model successfully described the strong temperature dependence of the observed surface PL. In our case, however, this model fails, as the depth of the electron trap is much larger than the reorganization energy, on the order of 1.6 eV. As a result, both the Marcus and the Marcus-Jortner model predict unphysically low electron trapping rates, unable to reproduce the pico-second electron lifetimes observed in TA and PL. For hole trapping the situation is different: the trap depth is much smaller (~0.4 eV) and the hole-trapping rate is lower. In this case trapping may possibly be explained by the Marcus or Marcus-Jortner model.

Auger mediated trapping is shown schematically in Figure 5.7a. This process involves the trapping of the electron (hole) by scattering with the geminate hole (electron). The energy difference in the trapping process is not dissipated to phonons, but is given to the second charge carrier, which subsequently cools down to the band edge. Unlike the Marcus model, the Auger process permits large energy losses for the electron in the

trapping process. From the schematic in Figure 5.7a it is clear that one of the factors that determines the rate of this Auger trapping process is the DOS at the energy of the final hot charge carrier. Since hole trapping involves energy dissipation of ~0.4 eV this corresponds to the electron being promoted to a state ~0.4 eV above the $1S_e$ level, where the DOS will be low. For electron trapping the hole is excited to a state ~1.6 eV below the $1S_{3/2}$ level, where the DOS will be much higher. In addition the DOS in the valence band is much higher than the DOS in the conduction band. Both effects will lead to an Auger trapping rate that is much higher for electrons than for holes. Thus, we propose that Auger mediated trapping can explain the observed order of magnitude difference in electron and hole trapping rates.

We quantify the rate of Auger mediated electron trapping using Fermi's golden rule. For a process where the electron goes from its initial state at energy E_{1Se} to final state at energy $E' = E_{1Se} - \Delta E$, by promoting a $1S_{3/2}$ hole to states deeper into the valence band we obtain the following capture rate constant (see Appendix D.3):

$$c_{e,Auger}(E') = \frac{2\pi}{\hbar} \cdot \left| M \right|^2 \cdot \rho(\mathbf{E}_{1S3/2} - \Delta E)$$
(5.9)

where $\rho(\mathbf{E}_{1S3/2} - \Delta E)$ is the density of valence band states at energy ΔE below the $1S_{3/2}$ level and *M* is the matrix element for this process.

The two factors determining the capture cross section are, thus, the matrix element and the density of valence band states at energy ΔE below the $1S_{3/2}$ level. Inserting Equation 5.9 into Equation 5.7 yields the electron-trapping rate constant, which of course also depends on the density of trap states.

Califano at al. have shown that matrix elements for Auger mediated trapping do not vary much with energy.⁴ These authors considered hole trapping at relatively shallow trapping sites and the corresponding Auger excitation of electrons to 1P_e states. We propose that a similar process occurs for very deep traps. In that case the higher DOS at the final energy of the scattered charge carrier would make this process even faster.

If we assume, following Califano et al., that the matrix element in Equation 5.9 is constant then the energy dependence of the capture rate constant only comes from $\rho(\mathrm{E_{1S3/2}}-\Delta E)$. Auger-mediated electron trapping implies that about ~ 1.6 eV of energy is transferred to the hole. At these energies, the DOS in the valence band approached the bulk DOS and will be independent on nanocrystal size. This allows us to

use the DOS from the DFT calculation described above (for the cluster model $Cd_{37}Te_{31}(HCOO)_{12}$) to assess the energy dependence of Auger recombination. This DOS is shown in Figure 5.7a together with a schematic of the Auger process. It is clear that at the relevant energies in the valence band the DOS is high and relatively constant. Finally this allows us, by combining Equation 5.9 with Equation 5.8 to derive the DOTS from the measured electron trapping rate constants depicted in Figure 5.4e.



Figure 5.7 (a) Schematic of Auger mediated electron and hole trapping to a trap state at the QD surface, at an energy close to the valence band edge. Electron trapping proceeds faster due to a larger density of acceptor states for the scattered hole (deep in the valence band) compared to a sparser density of acceptor states for the scattered electron (close to the conduction band edge). The occupied and unoccupied molecular orbitals (grey and red horizontal bars, respectively) and the density of states (light blue shaded area) were obtained from DFT calculations for a Cd₃₇Te₃₁(HCOO)₁₂ QD with insufficient ligand coverage (see main text). The dark blue shaded area depicts the hole acceptor states for the range of Fermi levels within our experimental probe window (double-headed arrow). (b) Derivative of the electron trapping rate (red dashed line) and DOTS (green solid line) according to Equation 5.8 and Equation 5.9.

Figure 5.7b shows the normalized DOTS (green solid line) so obtained from the derivative of the fitted electron trapping rate (red dashed line, dk_e/dV). The former closely resembles the shape of the latter. This is due to the rather flat DOS in the valence band (dark blue shaded region in Figure 5.7a) corresponding to the probed Fermi levels within

the band gap (double-headed arrow). A Gaussian fit to the DOTS is centered at -4.58 eV vs. vacuum (0.42 eV above the $1S_{3/2}$ level) and has a FWHM of 0.44 eV.

We conclude that a Marcus(-Jortner)-type trapping mechanism fails and an Auger mediated trapping mechanism succeeds in explaining the observed fast electron trapping to deep traps, close to the $1S_{3/2}$ level. On first sight, this is in contrast to the Marcus-Jortner model with shallow traps proposed by Mooney et al.^{36, 40} However, we propose that both results can be reconciled by assuming a similar trap density close to the valence band, but different Fermi levels in the experiments: we suggest that the latter was near mid-gap for Mooney et al. and that, consequently, the authors observed *hole* trapping to shallow defects; in our case, the Fermi level was near the valence band, leading to *electron* trapping, involving the same defect state.

5.8. CONCLUSIONS

We report the first experimental determination of the density of trap states (DOTS) of a film of CdTe QDs, using a novel combination of electrochemistry and ultrafast spectroscopy. The occupation of traps within the band gap is controlled *via* reversible electrochemical doping and monitored via transient absorption and time-resolved photoluminescence spectroscopy. When traps are empty, electron trapping proceeds on a (sub)-picosecond time scale; when traps are filled electrochemically, this process takes nanoseconds. We obtain the DOTS by fitting the decay of transient absorption and timeresolved photoluminescence signals at various Fermi levels within the band gap. A DOTS close to the valence band is found, 0.42 eV above the $1S_{3/2}$ level and with a FWHM of 0.44 eV. DFT calculations confirm a large DOTS close to the valence band and assign it to dicoordinated Te atoms at the QD surface, as a result of a loss of ligands during film processing. Time-resolved photoluminescence experiments reveal that hole trapping also occurs, albeit at least one order of magnitude slower than electron trapping. The slower hole trapping and the fast capture of electrons by traps close to the valence band can be explained by an Auger mediated trapping mechanism. The combination of our unique experimental determination of the DOTS with the theoretical modeling of the QD surface reveals the nature of the charge trapping mechanism in QD films. The assignment of the DOTS to the exact composition and geometry of the surface pinpoints the bottlenecks for improving QD based devices.

REFERENCES

- Panthani, M. G.; Kurley, J. M.; Crisp, R. W.; Dietz, T. C.; Ezzyat, T.; Luther, J. M.; Talapin, D. V. High Efficiency Solution Processed Sintered CdTe Nanocrystal Solar Cells: The Role of Interfaces. Nano Letters 2013, 14, 670-675.
- 2. Major, J. D.; Treharne, R. E.; Phillips, L. J.; Durose, K. A low-cost non-toxic post-growth activation step for CdTe solar cells. *Nature* 2014, 511, 334-337.
- 3. Donega, C. d. M. Synthesis and properties of colloidal heteronanocrystals. *Chemical Society Reviews* 2011, 40, 1512-1546.
- 4. Califano, M.; Gómez-Campos, F. M. Universal Trapping Mechanism in Semiconductor Nanocrystals. *Nano Letters* 2013, 13, 2047-2052.
- 5. Voznyy, O.; Thon, S. M.; Ip, A. H.; Sargent, E. H. Dynamic Trap Formation and Elimination in Colloidal Quantum Dots. *The Journal of Physical Chemistry Letters* 2013, 4, 987-992.
- 6. Voznyy, O. Mobile Surface Traps in CdSe Nanocrystals with Carboxylic Acid Ligands. The Journal of Physical Chemistry C 2011, 115, 15927-15932.
- Voznyy, O.; Sargent, E. H. Atomistic Model of Fluorescence Intermittency of Colloidal Quantum Dots. Phys. Rev. Lett. 2014, 112, 157401.
- Bozyigit, D.; Volk, S.; Yarema, O.; Wood, V. Quantification of Deep Traps in Nanocrystal Solids, Their Electronic Properties, and Their Influence on Device Behavior. Nano Letters 2013, 13, 5284-5288.
- 9. Bozyigit, D.; Wood, V. Electrical characterization of nanocrystal solids. Journal of Materials Chemistry C 2014, 2, 3172-3184.
- Katsiev, K.; Ip, A. H.; Fischer, A.; Tanabe, I.; Zhang, X.; Kirmani, A. R.; Voznyy, O.; Rollny, L. R.; Chou, K. W.; Thon, S. M.; Carey, G. H.; Cui, X.; Amassian, A.; Dowben, P.; Sargent, E. H.; Bakr, O. M. The Complete In-Gap Electronic Structure of Colloidal Quantum Dot Solids and Its Correlation with Electronic Transport and Photovoltaic Performance. *Adv. Mater.* 2014, 26, 937-942.
- 11. Voznyy, O.; Zhitomirsky, D.; Stadler, P.; Ning, Z.; Hoogland, S.; Sargent, E. H. A Charge-Orbital Balance Picture of Doping in Colloidal Quantum Dot Solids. ACS Nano 2012, 6, 8448-8455.
- Boehme, S. C.; Walvis, T. A.; Infante, I.; Grozema, F. C.; Vanmaekelbergh, D.; Siebbeles, L. D. A.; Houtepen, A. J. Electrochemical Control over Photoinduced Electron Transfer and Trapping in CdSe-CdTe Quantum-Dot Solids. ACS Nano 2014, 8, 7067-7077.
- Kloper, V.; Osovsky, R.; Kolny-Olesiak, J.; Sashchiuk, A.; Lifshitz, E. The growth of colloidal cadmium telluride nanocrystal quantum dots in the presence of Cd^o nanoparticles. J. Phys. Chem. C 2007, 111, 10336-10341.
- 14. Lebedev, M. V.; Misochko, O. V.; Dekorsy, T.; Georgiev, N. On the Nature of "Coherent Artifact". Journal of Experimental and Theoretical Physics 2005, 100, 272-282.
- Dietzek, B.; Pascher, T.; Sundström, V.; Yartsev, A. Appearance of coherent artifact signals in femtosecond transient absorption spectroscopy in dependence on detector design. *Laser Physics Letters* 2007, 4, 38-43.
- Ruch, P. W.; Cericola, D.; Hahn, M.; Kötz, R.; Wokaun, A. On the use of activated carbon as a quasi-reference electrode in non-aqueous electrolyte solutions. *J. Electroanal. Chem.* 2009, 636, 128-131.
- Vanmaekelbergh, D.; Houtepen, A. J.; Kelly, J. J. Electrochemical gating: A method to tune and monitor the (opto)electronic properties of functional materials. *Electrochimica Acta* 2007, 53, 1140-1149.

- Boehme, S. C.; Wang, H.; Siebbeles, L. D. A.; Vanmaekelbergh, D.; Houtepen, A. J. Electrochemical Charging of CdSe Quantum Dot Films: Dependence on Void Size and Counterion Proximity. ACS Nano 2013, 7, 2500-2508.
- 19. Houtepen, A. J.; Vanmaekelbergh, D. Orbital occupation in electron-charged CdSe quantumdot solids. J. Phys. Chem. B 2005, 109, 19634-19642.
- 20. Efros, A. L.; Rodina, A. V. Band-edge absorption and luminescence of nonspherical nanometersize crystals. *Physical Review B* 1993, 47, 10005-10007.
- 21. Klimov, V. I. Optical Nonlinearities and Ultrafast Carrier Dynamics in Semiconductor Nanocrystals. *The Journal of Physical Chemistry B* 2000, 104, 6112-6123.
- 22. Kambhampati, P. Hot Exciton Relaxation Dynamics in Semiconductor Quantum Dots: Radiationless Transitions on the Nanoscale. *The Journal of Physical Chemistry* C 2011, 115, 22089-22109.
- Saari, J. I.; Dias, E. A.; Reifsnyder, D.; Krause, M. M.; Walsh, B. R.; Murray, C. B.; Kambhampati,
 P. Ultrafast Electron Trapping at the Surface of Semiconductor Nanocrystals: Excitonic and Biexcitonic Processes. *The Journal of Physical Chemistry B* 2012, 117, 4412-4421.
- 24. Malko, A. V.; Mikhailovsky, A. A.; Petruska, M. A.; Hollingsworth, J. A.; Klimov, V. I. Interplay between Optical Gain and Photoinduced Absorption in CdSe Nanocrystals. *The Journal of Physical Chemistry B* 2004, 108, 5250-5255.
- 25. McArthur, E. A.; Morris-Cohen, A. J.; Knowles, K. E.; Weiss, E. A. Charge Carrier Resolved Relaxation of the First Excitonic State in CdSe Quantum Dots Probed with Near-Infrared Transient Absorption Spectroscopy. *The Journal of Physical Chemistry B* 2010, 114, 14514-14520.
- 26. de Mello Donegá⁽²⁾, C.; Koole, R. Size Dependence of the Spontaneous Emission Rate and Absorption Cross Section of CdSe and CdTe Quantum Dots. *The Journal of Physical Chemistry C* 2009, 113, 6511-6520.
- 27. Chen, S.; Wang, L.-W. Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution. *Chemistry of Materials* 2012, 24, 3659-3666.
- 28. Jasieniak, J.; Califano, M.; Watkins, S. E. Size-Dependent Valence and Conduction Band-Edge Energies of Semiconductor Nanocrystals. ACS Nano 2011, 5, 5888-5902.
- 29. Neamen, D. A. Semiconductor physics and devices: basic principles. McGraw-Hill: 2003.
- Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *Journal of the American Chemical Society* 2013, 135, 18536-18548.
- 31. Anderson, N. C.; Owen, J. S. Soluble, Chloride-Terminated CdSe Nanocrystals: Ligand Exchange Monitored by 1H and 31P NMR Spectroscopy. *Chemistry of Materials* 2012, 25, 69-76.
- 32. Morris-Cohen, A. J.; Malicki, M.; Peterson, M. D.; Slavin, J. W. J.; Weiss, E. A. Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots. *Chemistry* of Materials 2012, 25, 1155-1165.
- 33. Morris-Cohen, A. J.; Donakowski, M. D.; Knowles, K. E.; Weiss, E. A. The Effect of a Common Purification Procedure on the Chemical Composition of the Surfaces of CdSe Quantum Dots Synthesized with Trioctylphosphine Oxide. *The Journal of Physical Chemistry* C 2009, 114, 897-906.
- 34. Knowles, K. E.; Tice, D. B.; McArthur, E. A.; Solomon, G. C.; Weiss, E. A. Chemical Control of the Photoluminescence of CdSe Quantum Dot–Organic Complexes with a Series of Para-Substituted Aniline Ligands. *Journal of the American Chemical Society* 2009, 132, 1041-1050.
- 35. Cohn, A. W.; Schimpf, A. M.; Gunthardt, C. E.; Gamelin, D. R. Size-Dependent Trap-Assisted Auger Recombination in Semiconductor Nanocrystals. *Nano Letters* 2013, 13, 1810-1815.

- 36. Mooney, J.; Krause, M. M.; Saari, J. I.; Kambhampati, P. Challenge to the deep-trap model of the surface in semiconductor nanocrystals. *Physical Review B* 2013, 87, 081201.
- 37. Bozyigit, D.; Jakob, M.; Yarema, O.; Wood, V. Deep Level Transient Spectroscopy (DLTS) on Colloidal-Synthesized Nanocrystal Solids. ACS Applied Materials & Interfaces 2013, 5, 2915-2919.
- Knowles, K. E.; McArthur, E. A.; Weiss, E. A. A Multi-Timescale Map of Radiative and Nonradiative Decay Pathways for Excitons in CdSe Quantum Dots. ACS Nano 2011, 5, 2026-2035.
- 39. Krause, M. M.; Mooney, J.; Kambhampati, P. Chemical and Thermodynamic Control of the Surface of Semiconductor Nanocrystals for Designer White Light Emitters. ACS Nano 2013, 7, 5922-5929.
- 40. Mooney, J.; Krause, M. M.; Saari, J. I.; Kambhampati, P. A microscopic picture of surface charge trapping in semiconductor nanocrystals. *The Journal of Chemical Physics* 2013, 138, 204705-9.

APPENDIX D

D.1 Spectro-electrochemical determination of the absolute energetic position of the 1S_{3/2} level



Figure 5.8 Spectro-electrochemical determination of the absolute energetic position of the $1S_{3/2}$ level: (a) Difference absorption spectra for several potentials, with respect to open circuit potential (~-0.05 V) (b) Difference absorption at the $1S_{3/2}1S_e$ transition (averaged from 585 nm to 640 nm), shown as red circles, in comparison with an error function fit, shown as red continuous line. The dashed vertical line indicates the position of the $1S_{3/2}$ level.

D.2 Fit of hole trapping rate constants

The hole trapping rate constants are obtained by fitting the normalized PL decay at the $1S_{3/2}1S_e$ transition with the rate model sketched in Figure 4c of the main text. The results are shown in Figure 5.9, together with the electron trapping rates that were already displayed in Figure 4d of the main text and obtained from fitting the normalized TA bleach of the $1S_{3/2}1S_e$ transition. Figure 5.10 shows a global fit to the (scaled) rate constants.



Figure 5.9 Electron trapping rate constants (closed circles) obtained from a fit of the TA bleach and hole trapping rate constants (open circles) obtained from a fit of the PL signal. Red, blue and green colors denote the first, second and third sub-population of QDs, respectively, featuring fast, intermediate and slow trapping, respectively. The lowest hole trapping rate constant k_{h_3} is not displayed as the corresponding lifetime exceeds the observation window of our experimental setup (3 ns)



Figure 5.10 Normalized electron trapping rate constants obtained from a fit of the TA bleach (closed circles). The solid line is a global fit to the data. While the rate constants $k_{e,1}$ vary by an order of magnitude, their potential dependence is identical within the noise of the measurement.

D.3 Derivation of capture and trapping rate constants

In an Auger-mediated trapping process, initially the first electron is at energy E_{1Se} in the conduction band, while the second electron is in the valence band, at energy E'', with $E'' < E_{1S3/2}$. The Auger scattering immobilizes the first electron at a trap within the band gap at energy E', losing the energy $\Delta E' = E_{1Se} - E'$, while the second electron is promoted to the $E_{1S3/2}$ level, gaining the energy $\Delta E'' = E_{1S3/2} - E'''$. Energy conservation demands $\Delta E' = \Delta E''$.

The Auger trapping rate can be calculated according to Fermi's Golden Rule

$$k_{e,Auger}(\mathbf{E}',\mathbf{E}'') = \frac{2\pi}{\hbar} \cdot \left| \left\langle \mathbf{i}_{1}, \mathbf{i}_{2} \right| \Delta H \left| f_{1}, \mathbf{f}_{2} \right\rangle \right|^{2} \cdot \delta \left(\mathbf{E}' + \mathbf{E}_{1S_{3/2}} - \mathbf{E}_{1Se} - \mathbf{E}'' \right)$$
(5.10)

where $|i_1, i_2\rangle$ and $|f_1, f_2\rangle$ are the combined initial and final state of the two scattered electrons and ΔH is their Coulomb interaction. The delta function $\delta \left(\mathbf{E'} + \mathbf{E}_{1S_{3/2}} - \mathbf{E}_{1Se} - \mathbf{E'''} \right)$ ensures energy conservation.

To reproduce the experiment, we sum over all available trap states, resulting in

$$k_{e,Auger}(\mathbf{E}',\mathbf{E}'') = \frac{2\pi}{\hbar} \cdot \int_{n'=0}^{\infty} \int_{n''=0}^{\infty} |M|^2 \cdot \delta\left(\mathbf{E}' + \mathbf{E}_{1S_{3/2}} - \mathbf{E}_{1Se} - \mathbf{E}''\right) dn'' dn'$$
(5.11)

where M is the matrix element as defined above and n' and n'' are the states of first and second electron. It is useful to switch to the energy representation ($dn = \rho(E)dE$), in which $\rho(E)$ is the density of states and the Fermi-Dirac distribution $f(E-E_F)$ describes which states $|f_1\rangle$ are available for electron trapping. This yields

$$\rho(\mathbf{E}') \cdot \left(1 - f(E' - \mathbf{E}_{r})\right)$$

$$k_{r, Auger}(\mathbf{E}', \mathbf{E}'') = \frac{2\pi}{\hbar} \cdot \int_{E' - \infty}^{z_{rec}} \times \int_{E' - \infty}^{z_{rec}} |M|^{2} \cdot \rho(E'') \cdot \delta\left(\mathbf{E}' + \mathbf{E}_{rec} - \mathbf{E}_{rec} - \mathbf{E}''\right) dE'' dE'$$
(5.12)

We limited the integration to $E' = E_{1Se}$ and $E'' = E_{1S^{3/2}}$, since we imposed the boundary condition that the initial state of the first electron is the $1S_e$ state and the final state of the second electron is the $1S_{3/2}$ level.

The first two factors in the left integral sum over all available trap states. The remaining terms are:

$$c_{e,Auger}(E') = \frac{2\pi}{\hbar} \cdot \int_{E_{-\infty}}^{E_{1S22}} |M|^2 \cdot \rho(E'') \cdot \delta(E' + E_{1S_{32}} - E_{1Se} - E'') dE''$$
$$= \frac{2\pi}{\hbar} \cdot |M|^2 \cdot \rho(E' + E_{1S_{32}} - E_{1Se})$$
(5.13)

This is the rate with which a trap at energy E' captures an electron. This leads to

$$k_{e,Auger}(\mathbf{E}') = \int_{E'=-\infty}^{E_{1Se}} \rho(\mathbf{E}') \cdot (1 - f(E' - \mathbf{E}_F)) \cdot c_{e,Auger}(E') dE'$$
(5.14)

being solely determined by integration over the density of trap states $\rho(E')$, the Fermi-Dirac distribution and a capture rate per trap state at energy E'.

One can simplify this equation by assuming that thermal broadening is negligible, as it is small (\sim 50 meV) compared to our experimental step size in potential (\sim 100 meV). This yields

$$k_{e,Auger}(E') = \int_{E'=E_F}^{E_{1Se}} \rho(E') \cdot c_{e,Auger}(E') dE'$$
(5.15)

So far we have assumed discrete states with infinite lifetimes. In reality homogeneous (Lorentzian) broadening due to finite lifetimes will smear out the transitions. Homogeneous broadening can be accounted for by replacing $\delta(E' + E_{1S_{3/2}} - E_{1Se} - E'')$

with a broadening term $\chi(\mathbf{E}',\mathbf{E}'')$, equal to $\pi\Gamma[((E_{1S3/2} - E_{1Se} + E' - E'')/\Gamma)^2 + 1]^{-1}$ where \hbar/Γ is the lifetime. This yields the trapping rate

$$k_{e,Auger}(\mathbf{E}',\mathbf{E}'') = \frac{2\pi}{\hbar} \cdot \int_{E'=E_F}^{E_{1Se}} \rho(\mathbf{E}') \int_{E''=-\infty}^{E_{1S3/2}} |M|^2 \cdot \rho(E'') \cdot \chi(\mathbf{E}',\mathbf{E}'') dE'' dE'$$
(5.16)

and the Auger capture rate

$$c_{e,Auger}(E',E'') = \frac{2\pi}{\hbar} \cdot \int_{E''=-\infty}^{E_{153/2}} |M|^2 \cdot \rho(E'') \chi(E',E'') dE''$$
(5.17)

As both thermal (~50 meV) and homogeneous broadening are small compared to the employed potential step size (100 meV), their effect on the determined DOTS will be small.

D.4 DFT calculations of effect of ligand density

To investigate the effect of ligand coverage on the DOTS, we calculate the full DOS of a $Cd_{40}Te_{31}(HCOO)_{18}$ QD, sequentially remove $Cd(HCOO)_2$ ligands and perform a full surface reconstruction after each removal. The result is shown in Figure 5.11.

We observe that after displacing two $Cd(HCOO)_2$ ligands, the surface completely reconstructs and leaves no mid-gap states. However, removal of the third ligand does not lead to a complete reconstruction and one of the Te atoms remains di-coordinated (green color in Figure 5.11 for $Cd_{37}Te_{31}(HCOO)_{12}$). This leads to the formation, right above the valence band, of a doubly-occupied molecular orbital mostly localized on the 5p orbital of the di-coordinated Te atom, which can be considered as a deep (hole) trap state. After each subsequent displacement of a $Cd(HCOO)_2$ ligand, one additional Te atom remains under-coordinated and forms mid-gap states. The DOTS therefore increases with the number of Z-type ligands removed. In the most extreme case where almost all the ligands have been ripped off, i.e. in $Cd_{32}Te_{31}(HCOO)_2$, there are six under-coordinated Te atoms that form a broad DOTS above the VB. The broadening can be ascribed to a significant surface reconstruction that occurs on the QD interface. This occurs because the QDs employed in our models are small in size and are expected to undergo significant structural rearrangements. For larger QDs, on the other hand, we can predict much smaller geometrical reconstructions and consequently much sharper DOTS above the VB.

Note that in all cases studied, Cd atoms are always saturated, either with three or four Te atoms, and the corresponding molecular orbitals are always delocalized inside the conduction band, instead of forming electron trap states. This suggests that during surface reconstruction, under-coordinated Cd atoms, which would act as electron

acceptors, are usually able to find electron donors in the surrounding that saturate them, either directly from the QD surface in the form of 5p lone-pairs of adjacent Te atoms, or from the environment, *e.g.* from ligands or solvent molecules.



Figure 5.11 Plots of CdTe DOS after each removal of Cd(HCOO)₂. The colors in the DOSs indicate contribution from the ligands (black), the Te atoms (red) and the Cd atoms (blue). The contribution from the di-coordinated Te is shown in green. On the top-right of each panel is shown the number of di-coordinated Te atoms that appear after surface reconstruction.

SUMMARY

Colloidal quantum dots (QDs) are semiconductor crystals with spatial extensions of a few nanometers only, containing about 100 – 100 000 atoms. The small size gives rise to fascinating opto-electronic properties such as a size-tunable bandgap. For example, the apparent color of CdSe QDs, determined by absorption and emission of light, can be changed conveniently throughout the entire visible spectrum (from red to blue) merely by decreasing the size of the crystal. Combined with their high luminescence yields and ease of surface functionalization, this opens up the possibility for a variety of applications such as light-emitting diodes (LEDs), photodetectors, biomarkers, lasers, and solar cells.

This thesis assesses the potential of QDs for use in photovoltaics, as the light absorbing material in a solar cell. Photovoltaics, the conversion of sunlight into electricity, is considered a candidate technology for satisfying the ever-growing energy demand of the world economy in a sustainable way. This expectation is based on the continuous energy flux from the sun in form of sunlight, its availability in all parts of the world, and its essentially green-house gas emission free conversion into electricity. However, to increase the market share of solar cells, their cost-efficiency ratio needs to be decreased. To make them affordable for a larger part of the world population, also their total cost should be reduced, minimizing the loans necessary for purchasing a solar panel. Next to organic and perovskite solar cells, is reduced due to their solution-processability at low temperatures and the small amount of material needed to fully absorb all sunlight impinging on the device. In addition, high power conversion efficiencies may be reached by making use of carrier multiplication, band-gap optimization *via* the QD size, stacking of QDs of different size in a multijunction, and hot-carrier extraction.

In this thesis, fundamental processes in QDs after light absorption are studied such as charge transfer between QDs and charge trapping. We monitor these processes using ultrafast transient-absorption and time-resolved photoluminescence spectroscopy, employing laser pulses of a duration of ~ 100 femtoseconds. Special attention is paid to energy losses due to charge trapping. Both charge transfer and charge trapping depend on the alignment of quantum confined states in the QD and localized trap states at the QD surface. We determine the absolute energy of trap states and quantum confined states *via* spectroelectrochemistry.

Chapters 2 and 3 determine absolute energy levels in films of CdSe and PbSe QDs via electrochemical charge injection. The concomitant change in optical absorption of the film allows quantification of the number of charges in quantum confined levels and thereby their energy. First, Chapter 2 defines the conditions that need to be met for electrochemical charge injection into films of QDs. It is found that the maximum number of injected charges depends on the size of voids in the QD films (i.e., the space between the quantum dots). This effect is attributed to size exclusion of countercharges from the electrolyte solution. Further, the energy of the QD levels depends on subtle changes in the QD film and the supporting electrolyte: the size of the cation and the length of the ligands at the QD surface. These nontrivial effects can be explained by the proximity of the cation to the QD surface and a concomitant lowering of the electrochemical potential. Our findings help explain the wide range of reported values for QD energy levels and redefine the limit of applicability of electrochemical measurements on QD films. Finally, this chapter suggests that the dependence of the energy of QD levels on ligand length and counterion size may be exploited in optimized designs of QD sensitized solar cells.

Using the knowledge obtained in chapter 2, chapter 3 employs spectroelectrochemistry to determine the band offset between CdSe and PbSe QDs. In general, the band offset between two materials is defined as the free energy difference between their lowest unoccupied energy levels and is of importance for charge transfer processes. In the case of QDs, the band offset is the difference between their respective $1S_e$ electron levels. This offset is measured *in situ*, in a composite film containing both types of QDs. The $1S_e$ level in the PbSe QDs is found to reside 0.9 to 0.3 eV below the $1S_e$ level of the CdSe QDs, depending on the size of the PbSe QDs. The effect of the dielectric environment on the band offset is minor, as inferred from the small (< 0.1 eV) difference between a bilayer film (with separate PbSe and CdSe phases) and a film with alternating layers of PbSe and CdSe (where each QD has a neighbour of opposite material). However, the respective $1S_e$ levels vary markedly, by 0.5 eV. We attribute these variations to differences in the surface

chemistry between the QD films. These shifts highlight the importance of assessing the band offset *in situ* for the sample of interest. Extrapolation of energy levels obtained for pure films to respective energies in a heterostructure is inaccurate.

Chapter 4 discusses photoinduced charge transfer between CdTe and CdSe QDs in a QD film. This is a fundamental process that needs to take place in solar cells, after absorption of a photon and before charge transport to the electrodes where a photovoltage and photocurrent may be extracted. For the composite QD films studied here, this process is expected to be efficient, since CdTe and CdSe form a type-II heterojunction, with both the $1S_e$ electron and $1S_{3/2}$ hole level lying higher in CdTe than in CdSe. However, we find that very efficient electron trapping in CdTe QDs obstructs electron transfer to CdSe QDs under most conditions. Only the use of thiol ligands results in somewhat slower electron trapping; in this case the competition between trapping and electron transfer results in a small fraction of electrons being transferred to CdSe. However, we demonstrate that electron trapping can be controlled and even avoided altogether by using the unique combination of electrochemistry and transient absorption spectroscopy. When the Fermi level is raised electrochemically, traps are filled with electrons and electron transfer from CdTe to CdSe QDs occurs with unity efficiency. These results show the great importance of knowing and controlling the Fermi level in QD films and open up the possibility of the systematic investigation of the intrinsic electron transfer rates in donor acceptor films.

Chapter 5 takes a closer look at the detrimental trapping process in QD films. Extending the experimental approach of chapter 4, a combination of electrochemical control of the Fermi level with ultrafast transient absorption and time-resolved photoluminescence spectroscopy is employed to determine the density of trap states in CdTe Quantum-Dot solids. We find a high density of very efficient electron traps ~ 0.35 eV above the valence band, distributed over ~ 0.3 eV. Electrochemical filling of these traps increases the electron lifetime and the photoluminescence quantum yield by more than one order of magnitude, while hole trapping to these states is one order of magnitude slower. Both observations can be explained by Auger mediated trapping. Density Functional Theory calculations identify the traps as under-coordinated Te atoms at the Quantum Dot surface. The combination of our unique experimental determination of the density of trap states with the theoretical modelling of the Quantum Dot surface allows us to identify the mechanism and exact chemical reaction at play during charge trapping in the QDs.

SAMENVATTING

Colloïdale kwantum punten (Engels: *quantum dots*, afkorting: *QDs*) zijn halfgeleider nanokristallen met ruimtelijke dimensies van maar een paar nanometer. Ze bevatten ongeveer 100 tot 100 000 atomen per nanokristal. De kleine grootte zorgt voor fascinerende opto-elektronische eigenschappen zoals een bandkloof (Engels: *band gap*) die afhangt van de grootte. Bijvoorbeeld de kleur van CdSe QDs, die wordt bepaald door absorptie en emissie van licht, kan eenvoudig worden aangepast door het hele zichtbare spectrum heen (van rood naar blauw), simpelweg door de grootte van het kristal te verkleinen. Gecombineerd met hun hoge luminescentie lichtopbrengst en de gemakkelijke functionalisatie van het oppervlak geeft dit mogelijkheden voor allerlei toepassingen zoals licht-emitterende diodes (LEDs), fotodetectoren, biomarkers, lasers en zonnecellen.

In dit proefschrift wordt de waarde van QDs als licht-absorberend fotovoltaïsch materiaal in een zonnecel geëvalueerd. Fotovoltaïsche materialen, waarin zonlicht wordt omgezet in elektriciteit, worden gezien als een kandidaat om aan de immer groeiende vraag naar energie van de wereldeconomie te voldoen, op een duurzame manier. Deze verwachting is gebaseerd op de continue energiestroom van de zon in de vorm van zonlicht, de beschikbaarheid ervan in alle delen van de wereld en dat de conversie van zonlicht naar elektriciteit in essentie vrij is van de emissie van broeikasgassen. Niettemin, om het marktaandeel van zonnecellen te vergroten moet de verhouding tussen kosten en efficiëntie omlaag.

Om zonnecellen voor een groter deel van de wereldbevolking betaalbaar te maken moeten ook de totale kosten omlaag, wat de leningen zal minimaliseren die nodig zijn om een paneel aan te schaffen. Behalve de organische en perovskiet zonnecellen hebben ook QD zonnecellen de belofte om te voldoen aan beide eisen. De kosten van QD zonnecellen zijn lager vanwege hun verwerkbaarheid als oplossing en bij lage temperatuur en de kleine hoeveelheid materiaal die nodig is om alle zonlicht te absorberen die op de zonnecel valt. Ook kan een hoge conversie-efficiëntie worden behaald door gebruik te maken van ladingsvermenigvuldiging, optimalisatie van de bandkloof, stapelen van QDs van verschillende grootte in een multi-junctie, en extractie van hete ladingen.

In dit proefschrift worden de fundamentele processen in QDs bestudeerd die plaatsvinden na lichtabsorptie, zoals ladingsoverdracht en het 'gevangen' worden van ladingen (Engels: *trapping*). We volgen deze processen met ultrasnelle tijds-opgeloste absorptie en fotoluminescentie spectroscopie, gebruikmakend van laser pulsen met een tijdsduur van ~100 femtoseconde. Speciale aandacht is er voor energieverliezen door trapping. Zowel ladingsoverdracht als trapping hangen af van de precieze verhouding van de kwantum-opgesloten toestanden in de QD en de gelokaliseerde traptoestanden op het oppervlak van de QD. We meten de absolute energie van traptoestanden en kwantum-opgesloten toestanden via spectroelektrochemie.

In hoofdstuk 2 en 3 worden de absolute energieniveaus in dunne lagen van CdSe en PbSe QDs bepaald via elektrochemische injectie van ladingen. De bijbehorende verandering van optische absorptie maakt het mogelijk om het aantal ladingen in kwantum-opgesloten niveaus te kwantificeren, en daarmee ook hun energie. Hoofdstuk 2 bepaalt ten eerste de condities waaraan elektrochemische ladingsinjectie in dunne lagen van QDs moet voldoen. We vinden dat het maximale aantal van geïnjecteerde ladingen afhangt van de leegtes tussen de QDs in de laag, dus de hoeveelheid ruimte tussen de dots. Dit effect wordt toegeschreven aan uitsluiting op basis van grootte van tegenladingen uit de elektrolyt oplossing. Er wordt verder gevonden dat de energie van de QD niveaus afhangen van subtiele veranderingen in de QD laag en de elektrolyt: de grootte van het kation en de lengte van de liganden op het QD oppervlak. Deze niet-triviale effecten kunnen worden uitgelegd door de nabijheid van het kation bij het QD oppervlak en de bijbehorende verlaging van de elektrochemische potentiaal. Onze bevindingen helpen om de grote variatie van gerapporteerde waarden voor de QD energieniveaus te verklaren en herdefiniëren de grenzen aan het toepassen van elektrochemische metingen aan QD lagen. Tot slot suggereert het hoofdstuk dat de afhankelijkheid van de QD energieniveaus van de ligandlengte en de grootte van het tegen-ion kan worden gebruikt om het ontwerp te optimaliseren van QD gesensibiliseerde zonnecellen.

In hoofdstuk 3 wordt, gebruikmakend van de kennis opgedaan in hoofdstuk 2, spectroelektrochemie gebruikt om het energiebandverschil (Engels: band offset) te bepalen tussen CdSe en PbSe QDs. Het energiebandverschil wordt in het algemeen gedefinieerd als het verschil in vrije energie tussen hun laagste niet-bezette energie niveaus en is belangrijk voor ladingsoverdrachtprocessen. In het geval van QDs is het energiebandverschil het verschil tussen hun 1Se elektron niveaus. Dit verschil wordt in situ gemeten in een composiet laag van beide typen QDs. Het 1Se niveau in de PbSe QDs bevindt zich 0.9 tot 0.3 eV onder het 1Se niveau van de CdSe QDs, afhankelijk van de grootte van de PbSe QDs. Het effect van de diëlektrische omgeving is klein, wat volgt uit het kleine (< 0.1 eV) verschil tussen een bilaag (met gescheiden PbSe en CdSe fasen) en een laag met alternerende lagen van PbSe en CdSe (waarin iedere QD een buur heeft van het tegengestelde materiaal). Echter, hun 1Se niveaus verschillen behoorlijk, met 0.5 eV. We schrijven deze variaties toe aan het verschillen in oppervlaktechemie tussen de QD lagen. Deze verschuivingen benadrukken de noodzaak om het energiebandverschil in situ te bepalen voor het betreffende sample. Extrapolatie van energieniveaus bepaald voor pure lagen naar energieniveaus in heterostructuren in onnauwkeurig.

In hoofdstuk 4 wordt ladingsoverdracht bestudeerd dat plaatsvindt tussen CdTe en CdSe QDs in een dunne laag, nadat licht in geabsorbeerd. De ladingsoverdracht is een fundamenteel proces dat nodig is in een zonnecel, na fotonabsorptie en voor ladingstransport naar de elektroden waar een fotovoltage en fotostroom kan worden onttrokken. Voor de samengestelde QD lagen die hier worden bestudeerd wordt er verwacht dat dit proces efficiënt is, omdat CdTe en CdSe een type-II heterojunctie vormen waarbij zowel het $1S_e$ elektron als het $1S_{3/2}$ gat niveau hoger liggen in CdTe dan in CdSe. We vinden echter dat zeer efficiënt trappen van ladingen in CdTe ervoor zorgt dat er geen ladingstransport plaatsvindt naar CdSe in bijna alle gevallen. Alleen het gebruik van thiol-liganden resulteert in iets langzamere elektron trapping; in dit geval resulteert de competitie tussen trapping en elektronoverdracht in een kleine fractie elektronen die wel overspringt naar CdSe. We demonstreren hier echter dat elektron trapping beïnvloed en zelfs compleet voorkomen kan worden door gebruik te maken van de unieke combinatie van elektrochemie en tijds-opgeloste absorptie spectroscopie. Als het Ferminiveau elektrochemisch wordt verhoogd, zullen traps gevuld worden met elektronen en kan ladingsoverdracht tussen CdTe en CdSe met 100% efficiëntie plaatsvinden. Deze resultaten laten zien dat het zeer belangrijk is het Fermi-niveau in QD lagen te kennen en te controleren en het opent de mogelijkheid om de intrinsieke snelheid van elektronoverdracht in donor-acceptor lagen systematisch te onderzoeken.

In hoofdstuk 5 wordt het nadelige trapping proces in QD lagen nader onderzocht. Voortbouwend op de experimentele aanpak van hoofdstuk 4 wordt een combinatie van elektrochemische controle van het Fermi-niveau samen met ultrasnelle tijds-opgeloste absorptie en luminescentie spectroscopie gebruikt om de dichtheid van trap toestanden in CdTe QD lagen te bepalen. We vinden een hoge dichtheid van zeer efficiënte elektron traps ~ 0.35 eV boven de valentieband, verdeeld over ~ 0.3 eV. Elektrochemisch opvullen van deze traps verhoogt de elektron levensduur en de fotoluminescentie kwantumopbrengst met meer dan een ordegrootte, terwijl gat trapping naar deze toestanden een ordegrootte langzamer is. Beide observaties kunnen verklaard worden door trapping met behulp van een Auger process (Engels: *Auger mediated trapping*). Density Functional Theory (DFT) berekeningen laten zien dat de traps ondergecoördineerde Te atomen op het QD oppervlak zijn. De combinatie van onze unieke experimentele bepaling van de dichtheid van trap toestanden, samen met het theoretisch modelleren van het QD oppervlak, maakt het mogelijk om het mechanisme en de precieze chemische reactie van het trappen van ladingen in de QD te identificeren.

Vertaald door Michiel Aerts

ACKNOWLEDGMENTS

I experienced the past four years of research as a gift. I am very grateful for it and want to thank everybody who has contributed to it and accompanied me along the way.

I want to begin by thanking Dr. Arjan Houtepen for arranging the funding that enabled my doctoral studies. Arjan, together we embarked on the vessel of science and by your always knowledgeable, encouraging and stimulating supervision we reached our destination. Most rewarding in my opinion, however, was the spotting of the numerous unknown creatures along the way. Was it a mermaid? Or just a fish? From your ever enthusiastic advice, I learnt how to discern most of the spotted creatures. And also, how to spread the word in case it was a mermaid. I wish you to find lots of them in the future!

Of course a vessel would be nothing without an experienced captain. I was lucky to have two of them, Prof.dr. Laurens Siebbeles and Prof.dr. Daniël Vanmaekelbergh, and receive their esteemed advice. Thanks for accepting me on the crew and arranging further funding. Discussions on the bridge and at captain's lunches were valuable and helped us in the spotting process.

Coming by boat from Spain, Sinterklaas and ... correction: Dr. Ivan Infante and Dr. Jon Mikel Azpiroz from the Euskal Herriko Unibertsitatea (UPV/EHU) in San Sebastian, brought us valuable gifts. (Theoretical) language problems were soon overcome and we greatly enjoyed your (DFT) gifts.

My gratitude extends to FOM, TU Delft and all Dutch tax payers who were appreciated benefactors financing our endeavours. Most crucial, however, were the technicians of our crew who designed and maintained all gear fantastically. We would not have spotted nor caught anything without you. Thanks Martien Vermeulen, Jos Thieme, John Suijkerbuijk, and Ruben Abellón for your professional work at all times. Thanks to the onboard workshop led by Nico Alberts for the frequent repair and improvement of our sails. Paul Rijkers and Edwin Uytenbroek, thanks for the digital navigation tools. Thanks, Cecilia Quick-Verdier, Karin Wilhelm and Heleen van Rooijen, for the good administration and your helpfulness. At last, I do not want to forget all the sailors who kept the ship in good shape, up to the bathroom. Without all your effort, sailing would not have been so efficient and pleasant.

Speaking of which: a big cheers to all you fellow mates on board who made this trip so much fun. I remember quite some coffee table discussions and the eventual trips ashore at night in the cities at which we anchored (mainly in Delft, but also in the famous ports of Veldhoven, Fuengirola or Boston). What is there more gezellig than a beer in a good ol' pub? To continue with all the other essential grain products: thanks for all the daily bread we shared, the Friday beers we enjoyed, and the occasional cake treats. The latter were good fuel for our Amsterdam Half Marathons. And thanks of course for all the home-made delicacies from our international crew. Far too seldom on the table, because far too delicious. But well, I guess they placed your home on my list of countries to visit. Mates, thanks for the good spirit at any occasion, for chatting about life outside science and for every smile in the hallway.

A special Ahoi to Dr. Sybren ten Cate, Lucas Kunneman, Dr. Wiel Evers, and finally Prashant Bhaskar: Thanks for being great cabin mates, for sharing the personal life (from weekend plans to great life events) and nerdy life (the numerous discussions about comrade Igor, Physics in general, derivations and lab plans on the blackboard ... with the lab plans often even implemented in practice, thanks to your great help). Thanks Lucas and Wiel for being my paranymphs.

Fishing in the unknown needs a good portion of experience. Thanks to all fellows and friends) who shared their experiences with me, especially Dr. Suchand Sandeep. In turn, I was happy to pass on my own experiences to the MSc and BSc mates. You were quick learners, finally independent and gave me a hand in many tasks. I am pleased to see that Hai Wang really loved the job and became a great fisherman himself. Hai, good luck for fi(ni)shing your own thesis soon.

Michiel Aerts, thanks for the Dutch translation of my summary. And Fuzzy, thanks for the great cover design. In the end, a good physicist and a good graphic designer are not so dissimilar: both master the art of abstraction.

Having started these acknowledgments, I already knew that I could never finish them. How to name everybody who should appear here? I tried. But I most probably failed. Nevertheless: be assured - even when your name is not explicitly mentioned - that I appreciated your support. When reading these lines, you will all know that you contributed your part in making this thesis possible. Allow me to thank you all by sharing the following quote with you:

"People will forget what you said. People will forget what you did. But people will never forget how you made them feel."

- Maya Angelou

Thank you all. For letting me feel how exciting, fun and rewarding research can be. And for distracting me from it. I will forget part of our conversations, our joint experiments and our joint activities. However, just as Maya Angelou expressed it above, I will never forget how you all made these four years a pleasant time in my life, a time rich in lessons in both my professional and personal life.

At last, it is strictly impossible to adequately thank, with a few printed words, for the biggest contributions. Nevertheless: Mutti und Vati, Euch will ich nicht nur für die letzten vier Jahre danken. Euch danke ich auch dafür, dass ich überhaupt diese Doktorarbeit habe beginnen können. Danke für das Studium und alle vorangegangene Erziehung. Ich denke ich muss hier Maya Angelou's Zitat selbst noch etwas weiterführen: "I will never forget how you made me feel, even before I could remember." Danke für alle Liebe und Unterstützung, die ihr mir gegeben habt und gebt, jetzt und seit Anfang an, noch bevor ich überhaupt ein Gedächtnis hatte und Eure Liebe und Unterstützung bewusst habe wahrnehmen dürfen. Einschließen möchte ich auch Großvati, Opa, und Heinrich, die mir wohl die Lust aufs Forschen vererbt und vermittelt haben. Y gracias a mi Claudita, por acompañarme, aguantarme, soportarme, amarme, y ser la mejor razón de dejar el trabajo y volver a la casa. Ya terminé …

CURRICULUM VITAE



Simon Böhme was born on the 11th of March 1984 in Friedrichshafen, Germany. After completing secondary education in 2003 at the Hariolf-Gymnasium in Ellwangen, Germany, he spent a Voluntary Social Year at the Montessori Kinderhaus in Wiesbaden, Germany. In 2004, he began his studies in Physics at the University of Konstanz, Germany, graduating in

2010 with the degree "Diplom-Physiker" from the same university. During his studies, he worked as a guest researcher on topics related to semiconductor physics and solar electricity generation: in 2007, he investigated polymer solar cells in the group of Dr. Sjoerd Veenstra at the Energy Research Centre of The Netherlands (ECN) in Petten; in 2009 and 2010, he studied charge carrier dynamics in nanoporous semiconductor films using THz-Spectroscopy in the group of Prof.dr. Mischa Bonn at the FOM-Institute AMOLF in Amsterdam.

From 2010 to 2014 he undertook doctoral studies at the TU Delft in the Opto-electronic Materials Group under the supervision of Prof. dr. Laurens Siebbeles and Dr. Arjan Houtepen, being externally advised also by Prof. dr. Daniël Vanmaekelbergh. In this time, he shed light on charge transfer and charge trapping processes in inorganic semiconductor nanocrystals (Quantum Dots) pinpointing bottlenecks for more efficient light generating and harvesting. The main results of his research are described in this thesis as well as a number of publications.

LIST OF PUBLICATIONS

Publications covering the topics of this thesis

<u>S.C. Boehme</u>, D. Vanmaekelbergh, L.D.A. Siebbeles, A.J. Houtepen; In Situ Spectroelectrochemical Determination of Band Offsets in Quantum-Dot Films. *In Preparation*.

<u>S.C. Boehme</u>, J.M. Azpiroz, Y. Aulin, F.C. Grozema, D. Vanmaekelbergh, L.D.A. Siebbeles, I. Infante, A.J. Houtepen; The Density of Trap States and Auger Mediated Electron Trapping in CdTe Quantum-Dot Solids. *Submitted*.

<u>S.C. Boehme</u>, T.A. Walvis, I. Infante, F.C. Grozema, D. Vanmaekelbergh, L.D.A. Siebbeles, A.J. Houtepen; Electrochemical Control over Photoinduced Electron Transfer and Trapping in CdSe-CdTe Quantum-Dot Solids. ACS *Nano.* **2014**, *8* (7), 7067-7077.

<u>S.C. Boehme</u>, H. Wang, L.D.A. Siebbeles, D. Vanmaekelbergh, A.J. Houtepen; Electrochemical Charging of CdSe Quantum Dot Films: Dependence on Void Size and Counterion Proximity. ACS Nano **2013**, *7* (3), 2500-2508.

Other publications by the author

C.S.S. Sandeep, J.M. Azpiroz, W.H. Evers, <u>S.C. Boehme</u>, I. Moreels, S. Kinge, L.D.A. Siebbeles, I. Infante, A.J. Houtepen; Epitaxially Connected PbSe Quantum-Dot Films: Controlled Neck Formation and Optoelectronic Properties. ACS *Nano* **2014**, 8 (11), 11499-11511.

J.J.H. Pijpers, R. Koole, W.H. Evers, A.J. Houtepen, <u>S. Boehme</u>, C. de Mello Donega, D. Vanmaekelbergh, M. Bonn; Spectroscopic Studies of Electron Injection in Quantum Dot Sensitized Mesoporous Oxide Films. *The Journal of Physical Chemistry* C **2010**, *114* (44), 18866-18873.

L.H. Slooff, <u>S. Böhme</u>, W. Eerenstein, S.C. Veenstra, W. Verhees, J.M. Kroon, T. Söderström; Fabrication and Characterisation of Polymer Based Solar Cells. *Proc. SPIE 7052, Organic Photovoltaics IX*, 705217 (San Diego, CA, USA. August 26, **2008**). Doi:10.1117/12.794504

W. Eerenstein, L.H. Slooff, <u>S. Böhme</u>, E. Voroshazi, S.C. Veenstra, J.M. Kroon; Multi-Junction Polymer Solar Cells. Proc. 23rd European Photovoltaic Solar Energy Conference (Valencia, Spain. September 1-5, **2008)**. Doi:10.4229/23rdEUPVSEC2008-1CO.5.2