Carrier dynamics in photovoltaic nanostructures

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Chapter 1: Introduction

1.1 A global Energy Perspective

The supply of secure, clean, and sustainable energy is one of the major scientific and technical challenges of the 21st century. In 2001, the world energy consumption amounted to $4.25 \times 10^{20}$ J, corresponding to an average energy consumption rate of 13.5 terawatt (TW)\(^1\). The majority of this energy (86%) was obtained from fossil fuels\(^2\). In principle, the total fossil fuel reserves are still abundant: based on the 1998 energy consumption, 50-150 years of oil, 60-160 years of gas, and 1000-2000 years of coal and tar sands are available\(^3\).

However, one of the major drawbacks of a fossil fuel based energy supply is the emission of CO\(_2\). During the past 650,000 years, the atmospheric CO\(_2\) concentration has been between 200 and 300 ppm\(^4\). Anthropogenic CO\(_2\) emission from 50 years of fossil fuel combustion has raised the concentration to above 380 ppm. It has been estimated that CO\(_2\) concentrations will reach more than double the pre-anthropogenic values within the 21st century\(^2\). Such high CO\(_2\) concentrations have been predicted\(^4\) to lead to an increase of the average temperature of the earth surface with 3-5°C. This forecast is based on natural climate changes in the past, by looking at ancient glacial cycles (going back millions of years in time)\(^4\). The effect of this temperature rise on the weather is not exactly known due to uncertainties in climate models, but climate scientists predict extreme rainfall and droughts, and increasing intensity of hurricanes due to rising sea temperatures. A substantial rise of sea-levels can be predicted with higher accuracy, since historical climate data documents show a clear correlation between CO\(_2\) concentrations and the sea level\(^4\).

A possible approach to reduce CO\(_2\) emissions is to reduce the energy consumption, i.e. burn less fossil fuel. However, there is a direct correlation between the energy use of a country and its GDP (Gross Domestic Product). Since there exists no country developing policy against economic growth, future energy demand is expected to increase considerably as a result of economic growth and the growing world population. In light of reduction of CO\(_2\) emissions, the main route for producing large amounts of carbon-free power is to use renewable energy. Of all the available renewable energy resources, sunlight is by far the largest resource available. The energy from sunlight that reaches the earth in 1 hour ($4.3 \times 10^{20}$ J) is enough to fulfill the global annual energy consumption ($4.25 \times 10^{20}$ J in 2001)\(^3\). To utilize this vast energy resource, capture and storage of solar energy is required on a large scale against low costs. Possible technologies for utilization of solar energy include:
Chapter 1: Introduction

- Solar thermal technologies: integrated capture, conversion and storage of solar energy as heat
- Biomass: storing solar energy in fast-growing crops (e.g. switch grass)
- Artificial photosynthetic systems: conversion of solar energy in chemical bonds using synthetic or biomimetic catalysts
- Photovoltaics: direct conversion of solar energy in electricity by a solar cell

This thesis focuses on investigating new concepts for the last-mentioned technology in the above list, i.e. photovoltaics. Currently, the most employed solar cell technology is based on silicon. For fundamental reasons (see section 1.3), however, the maximum theoretical conversion efficiency for silicon solar cells is limited to 30% (without sun concentration). In the last decade, several promising alternatives have been proposed to overcome this upper limit in efficiency. These approaches have been called “third generation concepts”, and deal with the development of highly efficient solar cells at low cost. Among these concepts, different approaches to convert the sunlight more efficiently into electricity utilize nanostructured semiconducting materials like Quantum Dots (QDs). Several special properties make QDs promising for achieving better solar cell performances and these particular properties are discussed in the next sections. Besides gains in conversion efficiency, colloidal QDs are also promising from an economical viewpoint since they can be synthesized via chemical procedures at relatively low temperatures. Chemical processes are easily scalable and synthesis at low temperatures requires relatively little energy input, allowing for the production of large quantities of QDs at low cost, in contrast to the production of crystalline bulk semiconductors.

1.2 Bulk semiconductors versus Quantum Dots

Nearly all solar cell concepts make use of inorganic semiconducting materials, either in their bulk or nanostructured form. Fig. 1.1 depicts the differences in energy structure between a bulk semiconductor and a nanostructured semiconductor (in this case a QD). In bulk material, a large number of atoms (of order $10^{20}$ or more) is brought together to form a solid. Unlike the presence of discrete energy states in atoms, the energy diagram of a bulk material is described by the existence of energy bands and bandgaps: the formation of energy bands can be described by the Nearly Free Electron Model, in which the electrons are treated as waves that interact with the lattice potential. The electron waves reflect and refract from mirror planes that arise from the periodic crystal lattice, resulting in forbidden states (located in the bandgap) that originate from destructive interference of forward and backward travelling electron waves. Constructive interference, in contrast, results in
allowed energy levels. Since the Pauli exclusion principle prevents two identical electrons from occupying the same energy level, a buildup of occupied states with increasing energy occurs, resulting in energy bands: the distance between energy levels within these bands is negligible, as a result of which an energy band can be considered as a continuum of states (Fig 1.1). An alternative approach to describe energy bands is the Tight Binding model. This approach is analogous to the formation of bonding and anti-bonding orbitals in molecules. The electronic structure of a solid is described by a superposition of wave functions for isolated atoms located at each atomic site.

Figure 1.1 In bulk semiconductors, a continuum of energy levels is grouped in valence and conduction bands that are separated by the bandgap $E_g$. Because of strong spatial confinement of electron and hole wavefunctions in a QD, the energy levels are discrete and the energy gap is a function of the QD diameter.

Both the Nearly Free Electron model and the Tight Binding model result in the same energetic diagram for a bulk semiconductor (left picture in Fig. 1.1): the highest occupied energy band is named the valence band and lowest unoccupied band is the conduction band. In between these bands is the bandgap, $E_g$, determines whether a material can be considered a semiconductor or an insulator. Materials with $E_g > 4$ eV are called insulators, whereas materials with $E_g < 4$ eV are denominated as semiconductors. As a result of this specific electronic band structure, a semiconductor has an electrical conductivity between that of a conductor and an insulator. At temperatures around 0 K, a semiconductor is insulating since all electrons
reside in the completely filled valence band where their mobility is low. By applying an electrical potential or by optical excitation, electrons are transferred from the valence band into the conduction band, leaving behind unoccupied levels in the valence band that are usually referred to as ‘holes’. Both the valence band holes and conduction band electrons can contribute to the electrical conductivity. Hence, applying an electrical potential or optical excitation changes the state of a semiconductor from insulating into conducting.

In contrast to the large number of atoms in bulk material, semiconductor nanocrystals consist typically of only 100 – 10000 atoms (right panel Fig. 1.1). Spherical nano-particles (quantum dots, QDs) have the most basic nanocrystal morphology. They can be synthesized using colloidal chemistry with nearly atomic precision8-10. More complex geometries include nanorods (elongated nanocrystals)10, tetrapods11, and hyperbranched nanoparticles12. The energetic structure of QDs changes dramatically with respect to bulk because of quantum confinement effects13. Whereas in bulk, photo-generated carriers can move freely throughout the material, the quasi-particles in QDs (electrons, holes, excitons) that are generated by photo-excitation are confined in the three spatial directions of the QD volume. Since the length-scale of the quasi-particle wavefunctions is typically larger than the QD size, the QD should be considered as a quantum box with respect to the quasi-particles. In contrast, the QD size (1 – 10 nm) is larger than the lattice constant for the most common semiconductors and the QD can be treated as a macroscopic crystal with respect to the lattice properties. Hence, in spite of the absence of energy bands and an energy dispersion relationship, the bulk values for effective masses can be used for QDs. This approximation is generally referred to as the Effective Mass Approximation (EMA)13.

Solving the ‘particle in a box’ problem for a one-dimensional potential well, results in a discrete set of energy levels (see right panel of Fig 1.1), analogous to the hydrogen atom. The energy values are given by13:

\[ E_n = \frac{\pi^2 \cdot \hbar^2}{2m^* \cdot d^2} n \]  

(1.1)

where \( \hbar \) is Planck’s constant, \( m^* \) is the carrier effective mass, \( d \) is the QD diameter, and \( n \) is the principal quantum number. In case the potential walls of the box are infinitely high, the wave functions vanish at the surface and the probability of finding a particle inside the QD is exactly unity (see left panel of Fig. 1.2). In reality, the potential walls often have a finite height resulting in leakage of wave functions outside the QD volume (when \( |x| > d/2 \), see right panel of Fig. 1.2). For visual clarity, Fig. 1.2 shows the wavefunction distribution in a one-dimensional potential well. In reality, a QD is of course a three-dimensional object, in which the energy levels are calculated using a spherical potential well.
Chapter 1: Introduction

The degree of quantum-confinement can be quantified by two quantities: the size of the quantum dots characterized by the diameter $d$ and the exciton Bohr radius, $a_b$. The concept of excitons is known from bulk materials, where a positive hole and negative electron interact via Coulombic attraction to form a bound electron-hole pair. In analogy to the hydrogen atom (where there is similar Coulomb interaction between the proton and electron), the length scale of the exciton is characterized by $a_b$, which is a bulk material property:

$$a_b = \frac{\varepsilon \cdot h^2}{\mu \cdot e^2} \tag{1.2}$$

In equation 1.2, $\varepsilon$ is the dielectric constant of the semiconductor host material, $\mu$ is the electron-hole reduced mass ($\mu = m_e^{-1} + m_h^{-1}$), and $e$ is the elementary electron charge. The degree of carrier confinement in a specific QD can be evaluated by considering the total energy of an exciton in the ground state. This quantity can be expressed as a sum of the bulk bandgap energy, the Coulombic attraction energy, and the confinement energy:

$$E_{1s} = E_{g,\text{bulk}} - 1.786 \frac{e^2}{\varepsilon \cdot d} + \frac{\pi^2 \cdot h^2}{2\mu \cdot d^2} \tag{1.3}$$
Strong confinement corresponds to the limit where $d < a_0$; in this situation, the Coulomb-term contribution in equation 1.3 becomes negligible, since the Coulombic contribution to the overall exciton energy scales with $1/d$, whereas the confinement energy scales with $1/d^2$. In the situation where the contribution of Coulombic interaction to $E_{1S}$ is negligible, electrons and holes are often treated as 'uncorrelated' particles. The position of the discrete $1S$ energy states (determining the emission wavelength) of these uncorrelated electrons and holes is determined by the ‘confinement term’ in equation 1.3. Reducing the QD size leads to enhanced confinement, resulting in larger values for the $1S$ transition. This effect is visualized in Fig. 1.3, where the photo-emission of QDs of increasing size experiences a red-shift.

**Figure 1.3** A set of flasks containing CdSe QDs of different sizes, illuminated by UV light emitting diodes. Going from left to right, the QD diameter increases; clearly, the emission wavelength shifts from blue wavelengths (large $1S$ transition) to red wavelengths (smaller $1S$ transition) for increasing the QD diameter.

### 1.3 Solar cells

The operating principle of solar cells relies on the conversion of energy of light into electrical energy. Semiconducting materials facilitate this conversion process in all currently-known solar cell concepts. An intrinsic semiconductor in a dark environment at room temperature is highly resistive, since most electrons reside in the completely filled valence band. Only solids with partially filled energy bands are good electronic conductors, because transport of carriers through a material occurs via unoccupied energy states. When a semiconductor is illuminated, absorption of light leads to photo-generation of electrons in the conduction band and holes in the valence bands. After this absorption process, electrons and holes need to be separated in order to prevent electron-hole recombination. In silicon
solar cells, separation of photo-generated free electrons and holes is usually achieved by a built-in electric field provided by a p/n-junction. By selectively doping two sides of a silicon wafer p type and n type, a potential barrier between the two regions is achieved that acts as a membrane. The p/n-junctions results in a low resistance path for electrons to the n contact and a low resistance path for holes to the p contact. Hence, selective extraction of electrons and holes at metal contacts can be achieved and the resulting current can do electrical work in an external circuit.

Unfortunately, the maximum theoretical light-to-current conversion efficiency of a single-junction solar cell is limited to 30% (the so-called Shockley-Queisser limit\(^2\)), and efficiencies of commercial solar cells are typically only 10 – 20%. Two fundamental loss mechanisms (governing the low conversion efficiencies) for a silicon-based solar cell are depicted in Fig. 1.4. Firstly, the infrared part of the solar spectrum is not absorbed by silicon, since the infrared photons do not have enough energy to excite electrons over the bandgap (1.1 eV for silicon, corresponding to a photon wavelength of \(\lambda \sim 1100 \text{ nm}\)). Secondly, the absorption of photons with energy in excess of the bandgap results in generation of ‘hot’ electrons and holes. These ‘hot charge carriers’ relax to the band edges via sequential emission of phonons on ultrafast timescales\(^{14}\). Via this so-called ‘thermalization’ process, the excess energy of visible photons is converted into phonons (or lattice vibrations). Consequently, a large part of the visible part of the solar spectrum is not converted into electricity but lost as heat.

Figure 1.4 Left: solar spectrum and conversion efficiency by a silicon solar cell. Right: schematic of mismatch between solar spectrum and silicon solar cell. The excess energy of visible photons is lost via thermalization of hot carriers to the band edges. The IR part of the solar spectrum is not absorbed since the bandgap of silicon is too high.
The above-mentioned loss mechanisms are typical for solar cells consisting of a single semiconducting absorber material. To overcome the fundamental drawbacks of ‘single-junction’ silicon cells, various research strategies exist that aim at minimizing thermalization losses. One approach is a tandem cell configuration, in which multiple p-n junctions are stacked on top of each other, each one tuned to absorb a particular frequency of the solar spectrum. Following this strategy, highly efficient tandem cells have been reported, with an efficiency of up to 41.1% (Fraunhofer Institute, January 2009)\textsuperscript{15}. These tandem cells consist of multiple layers of different III-V semiconductors, which are semiconducting alloys of elements from group III and V of the periodic system (e.g. GaAs). III-V materials are often chosen because of the high absorption coefficients and the possibility of tuning the bandgap by stoichiometric variation of ternary (e.g. GaInAs) and quaternary alloys\textsuperscript{16}. As an example, Figure 1.5 schematically depicts a GaInP/GaAs cell in which the two layers are connected in series\textsuperscript{16}. In such a configuration, the voltages of the two cells are added up. It is required that the currents from each cell are matched for an optimal cell performance. Further challenges of multi-layer tandem cells include mismatches in lattice constants and different thermal expansivity of various cell components (potentially leading to defective interfaces)\textsuperscript{16}. The major drawback of this concept is the high production costs, explaining why this technology is currently not employed on a large scale for terrestrial applications. Nonetheless, III-V tandem cells are widely used in aerospace applications (e.g. satellites), for which the efficiency is more important than the cost of the solar cell.

As mentioned in section 1.1, QDs are promising materials for more efficient light conversion. The reasons why QDs are considered attractive, besides low-cost synthesis, include their size-tunable bandgap, the expected reduced cooling rates of hot charge carriers, and the potential occurrence of efficient Carrier Multiplication (CM). CM is the process in which absorption of a single high-energy photon results in the generation of multiple electron-hole pairs. QD solar cell concepts based on reduced cooling rates and CM

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure15.png}
\caption{Schematic representation of a III-V tandem cell. In most multi-layer tandem cells, the cells are connected in series in a ‘two terminal’ configuration.}
\end{figure}
rly on special mechanisms of carrier relaxation in QDs due to quantum-confinement. Therefore, different carrier relaxation (or recombination) mechanisms in bulk and QDs are discussed in the next section.

1.4 Carrier recombination and relaxation in bulk and QDs

The transition in which a charge carrier is transferred from a high energy to a low energy state is called carrier recombination or relaxation\(^1\). In a bulk semiconductor, excited state electrons can relax via various relaxation pathways (see Fig. 1.6), the most important of which are listed below\(^1\):

1. Radiative recombination: electron in conduction band recombines with hole in the valence band by emitting a photon.
2. Auger recombination: three-particle process in which an electron for instance recombines with a hole by simultaneously transferring the recombination energy to a third particle. Auger rates typically depend on carrier density.
3. Relaxation of hot carriers via sequential emission of phonons (thermalization). In most bulk semiconductors, this process occurs with rates of \(\sim 1-2\) eV/ps.
4. Trapping into defects: electrons in the conduction band relax to defect levels in the bandgap. Recombination is possible into physical defects (vacancies, grain boundaries, surface states, etc.) and chemical defects in the form of impurities.

![Figure 1.6](image.png)

Radiative and Auger relaxation (recombination processes 1 and 2) are inevitable relaxation processes, since the transition probabilities originate from the existence of energy bands. The associated relaxation rate strength depends on the coupling between the initial and the final state and on the number of pathways via which the transition can occur (i.e. the density
of final states). The transition rate in these relaxation processes is described by Fermi’s Golden rule:

$$k_{if} = \frac{2\pi}{\hbar} \left| \langle \Psi_f | V_{\text{Coul}} | \Psi_i \rangle \right|^2 \rho_f$$

(1.4)

where $k_{if}$ is the transition rate, $\Psi_f$ and $\Psi_i$ are the wavefunctions of the final and initial states, respectively, $V_{\text{Coul}}$ is an operator for the Coulombic interaction that couples in the final and initial states, and $\rho_f$ is the density of final states. The inverse of the transition rate, $1/k_{if}$, is related to the lifetime of the excited state $\tau$.

Thermalization of hot carriers (relaxation process 3) in bulk material occurs via interactions of hot carriers with the crystal lattice, i.e. the hot carrier relaxes by sequential emission of longitudinal optical (LO) phonons (having an energy of $\sim 40$ meV). This relaxation process, in which the excess energy of hot carriers is converted into lattice vibrations or heat, typically occurs on a $< 1$ ps timescale. Relaxation process 4 in Figure 1.6 involves trapping of carriers in physical defects such as vacancies or dislocations or in chemical defects such as impurities. This relaxation process can in principle be avoided by using a perfect crystalline sample with passivated surfaces.

Relaxation of carriers in QDs proceeds via the same pathways as in bulk. However, the relaxation rates of the various relaxation processes change considerably in QDs as a result of the discretization of energy levels and the spatial confinement of electronic wave functions. First, by confining the wave functions in the small QD volume, carrier-carrier Coulomb interactions are strongly enhanced in QDs, leading to higher relaxation rates of radiative and Auger processes (see Eq. 1.4). Second, leakage of wave functions outside the QD (see Fig. 1.2) enhances recombination rates, since the dielectric constant outside the QDs is typically smaller than within the QD material. As a result, the leaking parts of the wave function experience strongly reduced dielectric screening and the Coulomb interaction is further enhanced. Third, the spacing between discrete energy levels is rather large, typically 250 - 550 meV for the electron 1S $\rightarrow$ 1P transition. Thermalization of hot carriers in bulk occurs by sequential emission of LO phonons ($\sim 40$ meV energy). To accommodate relaxation of a hot carrier in the 1P state of a QD, however, the simultaneous emission of about 10 LO phonons is required, which is a phenomenon with a very low probability. The absence of a phonon-mediated relaxation channel for hot charge carriers is usually called the ‘phonon-bottleneck’. Finally, the surface-to-volume ratio is much higher in QDs leading to large amount of surface defects, via which relaxation and recombination processes can proceed.
1.5 Quantum Dots as solar cell materials

As a result of the special carrier recombination and relaxation mechanisms, QDs can potentially convert parts of the solar spectrum into electricity that are not converted in conventional solar cells. Below, two different concepts are discussed of how QDs can potentially absorb sunlight with fewer losses. Also, the extraction of carriers from QDs into an external circuit is discussed.

1.5.1 Hot Carrier QD solar cell

As described in section 1.3, two inherent limitations in conversion efficiency in single-gap solar cells are the rapid thermalization of hot carriers and the absence of absorption of light with below-gap photon energy. About 20 years ago, it was proposed to overcome these fundamental limitations in a so-called ‘hot carrier’ solar cell, in which extraction of hot carriers through selective contacts should occur before thermalization can take place. This should be achieved in a low bandgap bulk semiconducting material (absorbing IR photons) in which intraband carrier relaxation is significantly slowed down. After photogeneration of hot carriers, the distribution of the kinetic energies of the hot carrier population is brought into equilibrium within ~ 100 fs through elastic carrier-carrier scattering. This equilibrium of ‘hot’ carriers can be described by a chemical potential that is naturally higher than the potential of ‘cold’ charge carriers. In normal semiconducting materials like silicon, this equilibrated hot electron-hole plasma subsequently thermalizes via interactions with the lattice within ~ 1 ps. If this electron-phonon thermalization can be slowed down significantly and if the hot carriers can be extracted through a selective contact, the resulting photo-voltage of the extracted carriers is higher than in a solar cell in which the excess energy of hot carriers is lost via thermalization.

Until now, the hot carrier solar cell is still conceptual and no proof-of-principle has been realized, as it has been challenging to find a suitable material in which interactions of hot carriers with the lattice are sufficiently suppressed. The emphasis of hot carrier solar cell research has been on finding suitable bulk semiconducting materials. Recently, however, it was proposed that semiconducting QDs are promising candidates for use as absorbing materials in hot carrier solar cells. The discrete and tunable energy levels make QDs potentially suitable for this purpose since (1) carrier cooling rates are potentially reduced because of the phonon-bottleneck, (2) charge and energy transfer can be controlled to a large extent, and (3) high-energy excitonic states can be occupied by a combination of inter-band (near IR – visible) and intra-band (near IR) transitions in parallel with high-energy transitions in the visible-near UV. These three characteristics are schematically represented in Figure 1.7. The concepts of Fig. 1.7 rely on the use of QD “molecules”, i.e. coupled QDs with different energy gaps. Hot electrons can be generated by populating hot carriers.
energy levels directly with UV or blue photons. Subsequently, separation of the hot electron from the hole occurs by charge transfer to the adjacent QD. Charge transfer is only allowed when the alignment of energy levels between the different QDs is appropriate: without extra energy input, electrons can only go downwards in energy during a charge transfer process. Because of this requirement, it is dictated that the two QDs within the molecule should have different radii (larger radius → smaller gap) in case QDs of the same materials are used. When the molecule consists of QDs of different material, the sizes of the dots are dictated by the energy alignment between the different QDs. An alternative method of generating a hot charge carrier is that a visible photon creates an electron in the 1S (cold) energy level after which the subsequent absorption of an IR photon promotes the electron to a hot energy level. In both scenarios, the hot electron needs to be extracted into a wide-gap bulk semiconductor sufficiently fast to prevent recombination of hot carriers to cold energy levels. The utilization of hot carriers in solar cells is advantageous because it results in higher photo-voltages. The simultaneous use of a larger part of the solar spectrum (i.e. sub-gap photons) and the more efficient use of above-gap photons leads in theory to solar cell efficiencies of ~ 65% for unconcentrated sunlight\textsuperscript{16}. Before these theoretical predictions can be fulfilled, the fundamental properties of intraband relaxation pathways for carriers within QDs and charge extraction from QDs need to be understood and controlled.

![Figure 1.7 Schematic representation of a hot carrier QD solar cell. Using QD molecules, hot energy levels can be populated directly by absorption of high-energy photons, or by subsequent absorption of visible and IR light. Fast extraction of hot electrons is required to prevent recombination to cold levels.](image)

1.5.2 QD solar cell based on Carrier Multiplication

Absorption of above-gap photons results in hot carriers with excess kinetic energy. An alternative approach to the hot carrier concept is to utilize the excess energy of the hot carriers by means of Carrier Multiplication (CM). CM is the process in which the excess energy of hot carriers is used to excite additional electrons over the bandgap. In case of
efficient CM, absorption of a single high-energy photon results in multiple electron-hole pairs, leading to higher photo-currents for a given solar flux.

CM occurs only when the photon energy $E_{ph}$ is larger than twice the value of $E_g$, due to energy conservation restrictions. At visible photon energies, CM has been shown to be relatively inefficient for bulk materials like silicon and germanium. In bulk materials, CM occurs through impact ionization, which is a non-radiative Auger recombination mechanism occurring with a rate defined by Fermi’s golden rule (equation 1.4). As such, impact ionization is the inverse process of the Auger recombination pathway depicted as process no. 2 in Fig. 1.6. The efficiency of CM in bulk material is determined by two competitive processes for relaxation of hot carriers (see Figure 1.8): relaxation by (phonon-mediated) thermalization and relaxation via impact ionization. CM has been expected to be more efficient in QDs due to: 1) expected slow phonon-mediated relaxation because of the discretization of energy levels (phonon-bottleneck effect) and 2) stronger Coulombic interaction between carriers resulting in higher impact ionization rates. The latter argument follows from equation 1.4: the rate of the Auger process is increased when Coulombic coupling between the initial and final states is stronger.

Figure 1.8 Illustration of CM in bulk and QDs. The efficiency of CM is determined by two competitive processes that are involved in the relaxation of hot carriers: 1) relaxation via sequential emission of phonons, and 2) relaxation via impact ionization. In bulk materials, the phonon-mediated relaxation pathway dominates and the CM efficiency is relatively low. CM was predicted to be enhanced in QDs because of slower phonon-mediated relaxation (due to the phonon-bottleneck effect) and the higher rates of relaxation via impact ionization resulting from stronger Coulombic interactions in QDs.

CM in QDs has received considerable attention following the initial report of efficient CM in PbSe QDs. In this report, on average 2.18 excitons were observed per absorbed 3.1 eV photon in PbSe QDs with $E_g = 0.81$ eV. Over the past years, many groups have reported efficient CM in a range of QD materials including PbSe, PbTe, CdSe, and InAs. More recently, however, these high efficiencies and even the occurrence of CM in QDs has
been questioned in PbSe\textsuperscript{31}, CdSe\textsuperscript{32}, and InAs\textsuperscript{33,34} QDs. To evaluate the potential of CM for QD solar cells, several issues need to be addressed. First of all, the mechanism for efficient CM in QDs compared to bulk needs to be understood. A thorough understanding of the mechanism of CM in QDs would allow one to engineer the QD (material, size, surface passivation, etc.) for optimal CM efficiency. Secondly, CM generates multiple excitons per QD that need to be extracted before recombination. This is not a trivial question, since multi-excitons recombine on a timescale of typically ~ 10-100 ps\textsuperscript{35}, in contrast to the long radiative lifetimes (~ 100 ns) of single excitons. Hence, carrier extraction needs to take place on a picosecond timescale to utilize the full potential of CM.

Before CM can be applied successfully in a QD solar cell, fundamental knowledge on carrier dynamics in QDs needs to be acquired. The work presented in this thesis comprises research on the CM efficiency in QDs compared to bulk, the timescale of multi-exciton recombination, and carrier extraction dynamics.

1.5.3 Extraction of carriers from QDs

QD solar cells based on hot carriers or CM will only work if extraction of carriers into an external circuit can be achieved with minimum losses. A configuration to extract the photo-generated carriers from QDs is the ‘Grätzel-cell’ concept\textsuperscript{36,37}. The conventional Grätzel cell is based on a nanocrystalline TiO\textsubscript{2} film that is sensitized with a ruthenium-based dye. The TiO\textsubscript{2} film is interpenetrated by a hole-transporting material, usually a liquid electrolyte containing an iodine/iodide redox couple. After absorption of sunlight by the dyes, charge separation is achieved by ultrafast injection of electrons from the excited dye into the TiO\textsubscript{2} anode. Subsequently, the electrons move through the semiconductor film towards the current collector and the external circuit. The remaining cationic dye is oxidized by the iodide ions in the electrolyte: \(2h^+ + 2I^- \rightarrow I_2\). The formed iodine molecules migrate towards the cathode of the electrochemical cell, where the iodine is reduced to iodide by the electrons that re-enter the system via the external circuit. The idea of a QD-sensitized solar cell (QDSSC) is to replace the dyes with QDs and exploit the potential advantages of QDs like the possibility of hot carrier extraction and CM. The schematic layout of such QDSSC is given in Figure 1.9. QDs can be linked chemically to the oxide surface using bifunctional molecules such as Mercapto Propionic Acid (MPA)\textsuperscript{38}. In an efficient QD solar cell, charge transfer of electrons into the TiO\textsubscript{2} should proceed faster than recombination pathways like intraband relaxation (hot carrier concept) or multi-exciton recombination (CM concept). For electron injection to be fast and efficient, the QD energy levels have to be positioned above the oxide conduction band edge. This can be achieved by careful selection of the oxide material and the QD size. In dye-sensitized Grätzel cells, electron injection has been shown to be an important limitation for device performance\textsuperscript{39,40}, even when injection from dyes is known to occur on picosecond timescales\textsuperscript{39,41}. It is not obvious
that electron injection from QDs occurs on similarly fast timescales, since the carriers in QDs are confined in a potential well and hence have to overcome a significant potential barrier. Therefore, elucidation of carrier dynamics in oxide-QD systems and the parameters that determine electron injection from QDs is a crucial step in understanding and optimizing QD-sensitized solar cells.

![Diagram of a QD-sensitized solar cell and energetic band diagram](image)

**Figure 1.9** a) Schematic layout of a QD-sensitized solar cell (QDSSC), analogous to the Grätzel cell, in which QDs are chemically linked to a mesoporous TiO$_2$ film. After excitation, electrons are injected from the excited QD into the TiO$_2$ conduction band and the remaining holes in the oxidized QD migrate towards the cathode via an electrolyte. b) Energetic band diagram of a QD sensitized solar cell.

### 1.6 Outline of this thesis

This thesis aims at evaluating the potential of Quantum Dots (QDs) as light-absorbing materials in solar cells. The steps immediately following photo-excitation of QDs will determine the overall light conversion efficiency. Carrier cooling, carrier recombination, and carrier extraction into a bulk wide-bandgap semiconductor are pivotal processes that need to be understood before a QD-based solar cell can be properly designed and optimized. All these processes occur on (sub)pico-second timescales, explaining why the use of spectroscopic techniques with high time-resolution is essential. Chapter 2 deals with the experimental techniques that are used for studying ultrafast carrier dynamics in QDs. The focus in Chapter 2 lies on TeraHertz time-domain spectroscopy (THz-TDS) and on the analysis of (transient) THz spectra. Chapter 3 presents a fundamental study of carrier dynamics in InAs QDs, including exciton polarizability and intraband relaxation of hot electrons. In Chapter 4, the timescale of multi-exciton recombination is investigated and the efficiency of Carrier Multiplication in InAs QDs is determined. Subsequently, CM is investigated in bulk PbSe and PbS in Chapter 5 and a comparison is made between the
occurrence of CM in QDs and bulk material. In Chapter 6, the dynamics of charge extraction of electrons from PbSe QDs into mesoporous oxide films is investigated. Also, the effect of ‘solar cell conditions’ (i.e. the presence of an electrolyte) on the dynamics of charge extraction is studied in Chapter 7. Finally, an outlook on the potential of QDs as light absorbing materials in future solar cells is given in Chapter 8.

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Chapter 1: Introduction

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