Ultrafast Photoinduced Processes in Core and Core–Shell Quantum Dots for Solar Cell Applications “Tiny Crystals for Big Applications”

Qenawy, Mohamed

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Ultrafast Photoinduced Processes in Core and Core–Shell Quantum Dots for Solar Cell Applications
“Tiny Crystals for Big Applications”

Mohamed Ahmed Abdellah

LUND UNIVERSITY

Doctoral Dissertation

Faculty opponent
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Radiation Laboratory and Department of Chemical & Bimolecular Engineering,
University of Notre Dame, Indiana, United States
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Ultrafast Photoinduced Processes in Core and Core–Shell Quantum Dots for Solar Cell Applications

“Tiny Crystals for Big Applications”

Mohamed Ahmed Abdellah

LUND UNIVERSITY

Doctoral Dissertation
Academic thesis, which by due permission of the Faculty of Science, Lund University, will be publicly defended on Friday 13th of March, 2015 at 09:15 a.m. in lecture hall C, at the Center of Chemistry and Chemical Engineering, Getingevägen 60, Lund, for the degree of Doctor of Philosophy in Science.

Cover picture: Quantum dots for solar energy harvesting by Maiy A. El-wakeel.

Mohamed Abdellah
Full name: Mohamed Ahmed Abdellah Qenawy

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Lund 2015
“And your Lord (ALLAH) is going to give you (Prophet Muhammed), and you will be satisfied”
Surat Al-Duhaa 5
Dedicated to,
Soul of my mother
Soul of my father-in-law
Dalia
Eyad, Yahia and Dareen
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Svensk sammanfattning

Arabic summary (الملخص العربي)

References
Abstract

The balance between our demands of energy and the energy we are consuming is not in equilibrium anymore. Therefore, the search for other energy resources is indispensable. Sustainable energy sources offer the alternative to the fossil fuels. Within many types of sustainable energy sources, solar energy offers more than the total global energy consumption. Solar cells are the smart conversion tools to harvest the incident photons and create electricity out of these photons. Solar cells have passed through different generations where two important factors control the solar cells market. The solar cell efficiency and price play the cornerstones in the solar cell marketing. Third generation of solar cells aims to maximize the price–performance equation by using cheap materials without compromising efficiency. Nanomaterials have emerged as the promising building blocks to harvest the solar light in the third generation of the solar cells. Among them, quantum dots (QDs) can be used as viable candidate due to their superb features such as high extinction coefficient, a tunable absorption edge, and the possibility to generate and collect multiple excitons by using single, high energy photon. Both the behaviors of photoexcited electrons and holes determine the overall efficiency of QD based solar cells. This thesis presents a systematic study of the ultrafast photoinduced charge dynamics in QD solar cell materials including the charge transfer, exciton migration, carrier trapping and their influence on real solar cell performance. The materials investigated start with conventional neat core CdSe QDs and extend to gradient Cd\textsubscript{1-x}Se\textsubscript{x},Zn\textsubscript{y}S\textsubscript{y} core–shell (CS) QDs. The latter are used to obtain improved optical and device performance. The electron injection from CdSe into ZnO nanowires were first observed to be very fast (few ps). This fast electron injection encourages us to study the possibility to inject multiple electrons from a QD under high excitation conditions. We revealed that a competition between electron injection and Auger recombination occurs.

Compared with electrons, the photoinduced holes are more likely to be trapped. However, such trap states sometimes can be radiative with long lifetime up to tens of microseconds in oleic acid capped CdSe QDs. In this scenario, the hole injection in p-type QD solar cells are proved to be less efficient (<10%) compared with electron injection in n-type counterparts. It is highly affected by the surface trapping sites induced by the linker exchange process. The hole injection can then be improved by passivating the surface trap sites using core shell structures. Besides electron or hole
injection, exciton migration can also occur via Förster resonant energy transfer (FRET). We found that FRET between QDs would enable to make use of the absorption of light by the indirectly attached QDs in QD-sensitized metal oxide (MO) anodes. In well-organized multi-sized QD mixtures, the energy transfer is even more pronounced. We experimentally observed the FRET process in randomly arranged multi-sized QD assembly and tandem stacked QD layers by using time-resolved and steady-state spectroscopies. Theoretical simulations where dipole distribution model was introduced for coupling calculations complies well with the experimental results. In order to minimize the effect of surface defects and improve the photostability of QD solar cells, we investigated the core–shell QD system where the surface trapping of carriers can be well passivated by shell materials with enhanced optical properties and device performance. Herein, a wider band gap semiconductor is employed as a shield shell around the active core in gradient growth, known as gradient Cd$_{1-x}$Se$_{1-y}$Zn$_x$S$_y$ CSQDs. Such QDs offer higher photostability, higher fluorescence quantum yield, and less interfacial defects than the conventional step-like CSQDs. We first characterized the gradient CSQDs using steady-state optical spectroscopy and HR-TEM images in order to determine their dimensions and to evaluate the shell thickness. Then XRD and EDX were used to characterize the chemical composition and the crystal structures.

The photodynamic of these CSQDs in photovoltaic systems was also studied. We first found that the electron injection from the active core to n-type MO showed relatively larger exponential shell thickness dependence compared with step-like CSQDs. We established that the highest electron injection efficiency (~ 80%) can be found with shell thickness up to 1.3 nm. Such shell also allows high surface passivation providing optimal conditions for charge collection in solar cells. Finally, we integrated our knowledge about the electron and hole behaviors to explain the solar cell performances according to the core–shell structure. We confirmed that the hole trapping is the critical factor for QD-sensitized solar cell efficiency. The trapping can be well repaired by using optimal core–shell structure.
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“A person who is not thankful to his benefactor is not thankful to ALLAH”,

Prophet Muhammed

First of all, praise is to ALLAH, the most Merciful for his gifts.

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Mohamed Abdellah
Lund 2015
List of Papers

This thesis is based on the following papers:

I. Karel Žídek, Kaibo Zheng, Carlito S. Ponseca, Jr., Maria E. Messing, Reine Wallenberg, Pavel Chábera, Mohamed Abdellah, Villy Sundström, and Tõnu Pullerits
   “Electron Transfer in Quantum-Dot-Sensitized ZnO Nanowires: Ultrafast Time-Resolved Absorption and Terahertz Study”

II. Karel Žídek, Kaibo Zheng, Mohamed Abdellah, Nils Lenngren, Pavel Chábera, and Tõnu Pullerits
   “Ultrafast Dynamics of Multiple Exciton Harvesting in the CdSe-ZnO System: Electron Injection versus Auger Recombination”

    *Contributed equally to this work*
    “Ultra Long-Lived Radiative Trap States in CdSe Quantum Dots”

    *Contributed equally to this work*
    “Ultrafast Charge Transfer from CdSe Quantum Dots to p-Type NiO: Hole Injection vs. Hole Trapping”

V. Kaibo Zheng, Karel Žídek, Mohamed Abdellah, Magne Torbjörnsson, Pavel Chábera, Shuyan Shao, Fengling Zhang, and Tõnu Pullerits
   “Fast Monolayer Adsorption and Slow Energy Transfer in CdSe Quantum Dot Sensitized ZnO Nanowires”
VI. Kaibo Zheng, Karel Žídek, Mohamed Abdellah, Nan Zhu, Pavel Chábera, Nils Lenngren, Qijin Chi, and Tõnu Pullerits

“Directed Energy Transfer in Films of CdSe Quantum Dots: Beyond the Point Dipole Approximation”


VII. Mohamed Abdellah, Karel Žídek, Kaibo Zheng, Pavel Chábera, Maria E. Messing, and Tõnu Pullerits

“Balancing Electron Transfer and Surface Passivation in Gradient CdSe/ZnS Core-Shell Quantum Dots Attached to ZnO”


VIII. Mohamed Abdellah, Rebecca Marschan, Karel Žídek, Maria E. Messing, Abdallah Abdelwahab, Pavel Chábera, Kaibo Zheng, and Tõnu Pullerits

“Hole Trapping: The Critical Factor for Quantum Dot Sensitized Solar Cell Performance”


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Contribution report

The project was initiated by Prof. Tõnu Pullerits.

Without the fantastic co-authors none of these papers would be available.

I. Within the team, I prepared and characterized the samples, also I helped in experimental data collection, and I was involved in the paper writing.

II. Within the team, I prepared and characterized the samples, also I helped in experimental data collection, and I was involved in the paper writing.

III. With the co-authors, Khadga and I are equally contributing to this work by designing and preforming the experiments, data analysis and writing the manuscript. I prepared and characterized the studied samples.

IV. With the co-authors, Kaibo, Karel and I are equally contributing to this work by designing and preforming the experiments, data analysis and writing the manuscript. I prepared and characterized the studied samples.

V. With the co-authors, I contributed to this work by preparing and characterizing the studied samples, also I put hand in the experimental data analysis and writing the manuscript.

VI. Within the team, I prepared and characterized the samples, also I helped in experimental data collection, and I was involved in the paper writing.

VII. With the co-authors, I prepared and characterized the samples, I designed and preformed the experiments, I analyzed the data, and I wrote the first draft of the manuscript.

VIII. With the co-authors, I prepared and characterized the samples, I designed and preformed the experiments, I analyzed the data, and I wrote the first draft of the manuscript.
I am a co-author of the following papers which are not included in this thesis:

I. Karel Žídek, Kaibo Zheng, Pavel Chábera, Mohamed Abdellah, and Tõnu Pullerits
   “Quantum Dot Photodegradation due to CdSe-ZnO Charge Transfer: Transient Absorption Study”

II. Kaibo Zheng, Karel Žídek, Mohamed Abdellah, Pavel Chábera, Mahmoud S. Abd El-sadek, and Tõnu Pullerits
    “Effect of Metal Oxide Morphology on Electron Injection from CdSe Quantum Dots to ZnO”

III. Khadga J. Karki, Fei Ma, Kaibo Zheng, Karel Žídek, Abdelrazek Mousa, Mohamed Abdellah, Maria E. Messing, Reine Wallenberg, Arkady Yartsev, and Tõnu Pullerits
     “Multiple Exciton Generation in Nano-Crystals Revisited: Consistent Calculation of the Yield Based on Pump-Probe Spectroscopy”
     *Scientific Reports*, 3, (2013), DOI: 10.1038/srep02287.

IV. Nils Lenngren, Tommy Garting, Kaibo Zheng, Mohamed Abdellah, Noëlle Lascoux, Fei Ma, Arkady Yartsev, Karel Žídek, and Tõnu Pullerits
    “Multiexciton Absorption Cross Sections of CdSe Quantum Dots Determined by Ultrafast Spectroscopy”

V. Thorsten Hansen, Karel Žídek, Kaibo Zheng, Mohamed Abdellah, Pavel Chábera, Petter Persson, and Tõnu Pullerits
    “Orbital Topology Controlling Charge Injection in Quantum-Dot-Sensitized Solar Cells”

VI. Carlito S. Ponseca, Jr., Tom J. Savenije, Mohamed Abdellah, Kaibo Zheng, Arkady Yartsev, Torbjörn Pascher, Tobias Harlang, Pavel Chábera, Tõnu Pullerits, Andrey Stepanov, Jean-Pierre Wolf, and Villy Sundström


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“Thermally Activated Exciton Dissociation and Recombination Control the Carrier Dynamics in Organometal Halide Perovskite”


VIII. Karel Žídek, Kaibo Zheng, Mohamed Abdellah, Pavel Chábera, Tõnu Pullerits, and Masanori Tachyia

“Simultaneous Creation and Recovery of Trap States on Quantum Dots in a Photoirradiated CdSe–ZnO System”


IX. Karel Žídek, Mohamed Abdellah, Kaibo Zheng, and Tõnu Pullerits

“Electron Relaxation in the CdSe Quantum Dots–ZnO Composite: Prospects for Photovoltaic Applications”

*Scientific Reports*, 4, (2014), DOI: 10.1038/srep07244.
# Abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PVs</td>
<td>Photovoltaics</td>
</tr>
<tr>
<td>1st GPVs</td>
<td>First generation photovoltaics</td>
</tr>
<tr>
<td>2nd GPVs</td>
<td>Second generation photovoltaics</td>
</tr>
<tr>
<td>3rd GPVs</td>
<td>Third generation photovoltaics</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>QDSCs</td>
<td>Quantum dots solar cells</td>
</tr>
<tr>
<td>QDSSCs</td>
<td>Quantum dots-sensitized solar cells</td>
</tr>
<tr>
<td>OSCs</td>
<td>Organic solar cells</td>
</tr>
<tr>
<td>NCs</td>
<td>Nanocrystals</td>
</tr>
<tr>
<td>QDs</td>
<td>Quantum dots</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence band maximum</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>EBE</td>
<td>Exciton binding energy</td>
</tr>
<tr>
<td>MEG</td>
<td>Multiple exciton generation</td>
</tr>
<tr>
<td>SCs</td>
<td>Solar cells</td>
</tr>
<tr>
<td>MO</td>
<td>Metal oxide</td>
</tr>
<tr>
<td>CSQDs</td>
<td>Core–shell quantum dots</td>
</tr>
<tr>
<td>CSS</td>
<td>Core–shell–shell</td>
</tr>
<tr>
<td>TOPO</td>
<td>Tri-\textit{n}-octylphosphine oxide</td>
</tr>
<tr>
<td>OA</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting-diodes</td>
</tr>
<tr>
<td>TVs</td>
<td>Televisions</td>
</tr>
<tr>
<td>NWs</td>
<td>Nanowires</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>TR</td>
<td>Time-resolved</td>
</tr>
<tr>
<td>TA</td>
<td>Transient absorption</td>
</tr>
<tr>
<td>PD</td>
<td>Photo diode</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>(N)</td>
<td>mean number of excited electron-hole pairs per QD</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TOP</td>
<td>Tri-(n)-octylphosphine</td>
</tr>
<tr>
<td>MPA</td>
<td>Mercaptopropionic acid</td>
</tr>
<tr>
<td>TMAOH</td>
<td>Tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>ODE</td>
<td>1-octadecane</td>
</tr>
<tr>
<td>HMTA</td>
<td>Hexamethylenetetramine</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped SnO(_2)</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time-correlated single photon counting</td>
</tr>
<tr>
<td>ns</td>
<td>Nanosecond</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>fs</td>
<td>Femtosecond</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>AugR</td>
<td>Auger recombination</td>
</tr>
<tr>
<td>(r)</td>
<td>Particle radius</td>
</tr>
<tr>
<td>(E_{\text{g,eff.}})</td>
<td>Effective band gap</td>
</tr>
<tr>
<td>(E_{\text{g}}(\infty))</td>
<td>Bulk band gap</td>
</tr>
<tr>
<td>(m_e)</td>
<td>Electron effective mass</td>
</tr>
<tr>
<td>(m_h)</td>
<td>Hole effective mass</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Relative permittivity</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>(\alpha_b)</td>
<td>Bohr exciton radius</td>
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<td>(\Delta E_C)</td>
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<td>Charge transfer state</td>
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<td>PLE</td>
<td>Photoluminescence excitation</td>
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</table>
*PEE* Photoinduced emission enhancement

*λ* Reorganizational energy

**IA-QDs** Indirect attached QDs to MO

*R* The fraction of IA-QDs

**DA-QDs** Direct attached QDs to MO

**FRET** Förster resonance energy transfer

**IPCE** Incident photon-to-electron conversion efficiency

**k_{ET}** Energy transfer rate

**R_{DA}** Donor–acceptor distance

**1/R^6** Distance term

**L_D** Diffusion length

**B** Dispersion factor

**β** Distance exponential dependence factor

**η_{inj}** Electron injection efficiency

**η_{EC}** Electron collection efficiency

**η_h** Hole collection efficiency
Chapter 1: Introduction

1.1 Sustainable energy sources:

In the modern society, energy is the engine of economic development. More than 85% of the global energy consumption comes from the fossil fuels such as oil, natural gas, and coal. During 2013, the world consumed about 4200 million tons of oil, 3100 million tons of oil equivalent of natural gas, and 3900 million tons of oil equivalent of coal according to BP statistical review report. Burning these fossil fuels as an energy source has a huge deteriorating impact on the environment. Due to the shortage and pollution from the fossil energy sources, governments and scientists in many countries have been making effort to find an alternative energy sources “sustainable energy sources”. There are several types of sustainable energy sources such as nuclear, hydroelectric, wind, geothermal, and solar (photovoltaics).

Harvesting the energy from Sun has many advantages. Compared to nuclear power plants, solar sources (see figure 1.1A) are technically facile and safe. Moreover, they are free of gas pollution and territory limitation, as long as solar radiation is sufficient in that area. It is reported that 1% of the solar power is more than enough for the total global energy consumption if it could be converted into electricity or fuel. Over the past years, conversion of light into the electrical energy has been explored using different materials. The first generation of photovoltaics (1st G) includes semiconductor solar cells mainly based on Si material with high efficiency. The second generation (2nd G) of solar cells was aimed to reduce the high costs of the first generation solar cells through the utilization of thin film technology with the challenge of increasing the thin film absorption to compensate for the reduced thickness in the photoactive layers. The 2nd G PVs are considered as low cost/low efficiency devices compared to 1st G counterparts. The third generation (3rd G) of PVs should combine the cheap material processing typical for the 2nd G with the high conversion efficiency of the first generation. The 3rd G is based mainly on nanostructured materials with three major types that have dominated research in recent years (see figure 1.1B): (a) dye-sensitized solar cells (DSSCs), (b) bulk heterojunction (BHJ) PV cells or organic PV cells, and (c) quantum dot solar cells (QDSCs). The later considered as “The Next Big Thing” in photovoltaics.
Introduction

Figure 1.1: A) Solar radiation spectrum outside of the atmosphere (yellow area) compared to the sea-level radiation (red area), and B) reported efficiency of quantum dot solar cells (QDSCs, black) compared to dye sensitized solar cells (DSSCs, red) and various types of organic solar cells (OSCs, blue).

1.2 Quantum Dot (QD):

Quantum dot (QD) is a semiconductor nanocrystal (NC) with a size of 2-10 nm. In the bulk semiconductor the charge carriers can be considered as being free particles with a modified mass (the so-called effective mass). When the size of material approaches the exciton Bohr radius (typically several nanometers), the picture changes into the “particle-in-box” problem. The term “dot” in quantum dot refers to confinement of electrons and holes in all three dimensions. This is an extension of quantum “wires” and quantum “wells” that confine excitons in one and two dimensions, respectively (see figure 1.2A).

In semiconductors, exciton (electron-hole pair) is created after the absorption of a photon with energy above the semiconductor band gap energy. Band gap is the minimum energy difference between the highest occupied state in the valence band (VBM) and the lowest occupied state in the conduction band (CBM). Depending on the electron momentum at the CBM and VBM, the band gap can be either direct or indirect. Most of the semiconductors have direct band gap where the CBM and VBM occur at the same value of electron/hole momenta (CdSe, CdTe, and many others). On the other hand some semiconductors, such as Si, have the indirect band gap where the CBM and VBM occur at different values of electron/hole momenta.
Figure 1.2: A) Quantum well (2D), quantum wire (1D) and quantum dot (0D), and B) quantum dot size related to the conduction band and valence band.

Even though the initial theory behind the exciton has existed since the 1930’s, it was not until the 1980’s that researchers began to focus on the effect of quantum confinement on excitons in semiconductor materials. In the 1970’s, advances in microfabrication led to quantum confinement in two-dimensional wells, eight years later was reported the first demonstration of one-dimensional wires. Finally, about 30 years ago in the former Soviet Union, Aleksey Ekinov and Alexander Efros explained the spectral differences of what appeared to be tiny particles of variable sizes. One to two years later, Louis Brus in the United States and Arnim Henglein in Germany discovered striking color change of II-VI semiconductor nanoparticles grown as aqueous colloidal suspensions.
1.3 Quantum Dot (QD) properties:  

Due to the quantum confinement effect, the energy levels are quantized depending on the QD’s size.\textsuperscript{18} As the NC’s size decrease (smaller than exciton radius), the quantum confinement becomes more dominant, and consequently the QD properties will change. As a result of the quantum confinement effect, the band gap becomes wider (see figure 1.2 B) and QDs therefore absorb at higher energies. Also the oscillator strength is concentrated into a few transitions as a result of changes in the density of electronic states from the bulk size to the QD size. The QDs’ photoluminescence (PL) depends on the QD’s size as well, following the band gap changes\textsuperscript{19} (see figure 1.3A).

An interesting feature of semiconductor QDs is the symmetric and relatively narrow emission peak redshifted with respect to the corresponding absorption peak. The red shift of the emission is known as Stokes shift. Stokes shift is the difference between positions of the band maxima of the absorption and emission spectra in wavelength or frequency unit. This difference comes from the fact that, after the excitation, the QDs tend to relax by emitting photons with some energy losing as dissipation of thermal phonons in a crystal lattice. PL wavelength depends on the QD material and size, as stated before (see figure 1.2 B). The PL from QDs usually feature a high quantum yield (QY \approx 0.2–0.9)\textsuperscript{20}. Moreover, QDs excel in high molar extinction coefficients, better photostability compared with common standard fluorophores, as well as the high resistance to photo- and chemical degradation\textsuperscript{21-25}.

In QDs, the excitons (electron-hole pairs) occupy discrete energy states similar to electrons of a single atom and that is why the QDs are sometimes referred to as the “artificial atoms”\textsuperscript{18} (see figure 1.3 A). After excitation with sufficient energy photon, the QDs’ electrons will be excited from the valence band (VB) to the conduction band (CB) leaving the positive quasi-particles holes in the VB. Holes can be considered as a mobile positive charge in the VB. Then both the electrons and holes rapidly lose their energy and jump to levels near the bottom of their conduction band (CBM) and the top of their valence band (VBM), respectively (see figure 1.3 A). As the electrons relax across the band gap to recombine with the holes, the energy released by recombination from the excited state to the ground state can be calculated as the sum of the electron and hole confinement energy, the exciton binding energy (EBE), and the band gap energy.\textsuperscript{24} In QDs, a photon with energy twice higher than the band gap can create multiple excitons, this phenomenon is called “multiple exciton generation” (MEG) (see
The same phenomenon exists also in bulk semiconductors. Efficient formation of more than one electron-hole pair out of one incident high energy photon is potentially very important from solar cell application point of view. Recently, several studies have proven the successful utilization of MEG to enhance the quantum efficiency of QD-sensitized solar cells (SCs) based on QD-metal oxide (MO) system.

**Figure 1.3:** A) Excitation, relaxation (cooling) and electron-hole recombination in QD, and B) multiple exciton generation in QD 1) excitation with high energy photon, 2) the electron relax to the CBM releasing its energy to process 3, and 3) creating another exciton by using the energy of process 2).

### 1.4 Core–shell quantum dots (CSQDs):

As the crystal becomes smaller, the proportion of the atoms on the surface increases, which has an impact on the nanoparticle properties. In general, during the synthesis of QDs, some atoms on the crystal facet are incompletely bonded within the crystal lattice which leads to one or more of “dangling bonds”. Most nanocrystals are highly faceted, what leads to an array of dangling bonds with a band energy level similar to the crystal itself. These states could work as a trap states if their energy is located within the QD band gap resulting in: i) reducing the overlap between the electron and hole, and ii) increasing the nonradiative depopulation pathways of the excited states. One way that minimize the surface states, is by passivating the nanocrystals surface using organic ligands (capping agents) like tri-\textit{n}-octyolphosphine oxide (TOPO) or oleic acid (OA). Capping agents adsorb to the nanocrystal surface through dative ligand–metal bonds between the ligand active group and the metal atoms on the nanocrystal surface.
Nonpolar end group ligands solubilize the nanocrystals in nonpolar solvents and the same holds for polar end group ligands in case of polar solvent.\(^9\)

Another more effective way to passivate the surface defect states is to coat the semiconductor nanocrystal with an inorganic shell with higher band gap thereby insulating the excitons in the core from the surface states. In other words, core–shell quantum dots (CSQDs) can be broadly defined as comprising core (inner semiconductor) and a shell (outer semiconductor). In solid state devices, this process is quite simple, as overgrowth of an inorganic layer with a wider band gap can be readily achieved with complete surface passivation. However, the task is more challenging in preparing colloidal CSQDs such as CdSe–ZnS and CdSe–CdS CSQDs with sufficient and stable PL. CSQDs can be categorized based on the band gaps of both the core and the shell materials into many types, each useful for different applications (see chapter 4 for more details).\(^3\)

1.5 Quantum dots applications:

Both neat core and CSQDs are gradually attracting more and more attention, since these nanocrystals have emerged at the frontier of material science and many other fields, such as biomedicals, pharmaceuticals, optics, and catalysis. In the next subsections, some of the QDs important applications will be listed.

1.5.1 QDs for biomedical applications: QDs are mainly used for controlled drug delivery\(^3\), for bioimaging\(^4\), cell labeling\(^5\), as biosensors\(^5\), and in tissue engineering applications.\(^6\)

1.5.2 QDs for light emitting diodes (LED), electricity in–light out: one strikingly beautiful aspect of colloidal QDs is the way their emission colors change with their size (band gap). This allows QDs to be used as ultra-efficient light-emitting-diodes. Recently, Sony Corporation of Tokyo announced that using QDs for flat-screen televisions (TVs) will transmit more richly colored images than other TVs on the market.\(^7\)

1.5.3 QDs for solar cells (SCs), light in–electricity out: “No signs of abating”.\(^8\) Colloidal QDs films form the core of solar cells devices. Figure 1.5 shows the principle of operation of three types of solar cells that employ semiconductor QDs as light harvesters.\(^9\) In these types, the QDs film absorb the light to produce electron-hole pair, which must then be separated and extracted at the opposite electrodes.\(^8\) Since, the first report on infrared colloidal QD solar cells
on 2005 much progress has been made towards technologically relevant efficiencies. Efforts have been made to improve the efficiency of QD based solar cells leading to enhance the efficiency from 2% in 2008 to around 3% in 2009-2010, 4.6% in 2011 for metal/QDs device, and 6% in 2011 as well by optimizing the device architecture and its constituent materials. Recently, by engineering the QDs band alignment both the performance and the stability of the QD (semiconductor bulk heterojunction) solar cells were improved (certified efficiency ~ 8.6%).

![Figure 1.5: Schematic diagram of QDs based solar cells](image)

**1.6 Quantum dots toxicity:**

QD toxicity has been the major roadblock for using these materials in clinical research and applications. Along with composition, the physical and surface characteristics (size, shape, surface charge, and capping agent) of the QDs play the major role in the toxicity. In 2006, Nawrot et al. have reviewed current understanding of the impact of cadmium (Cd) on human health. Current understanding states that environmental exposure to Cd increases total mortality in a continuous fashion, without any evidence of critical dosage. They have noted that tubular kidney starts at urinary Cd concentrations between 0.5 and 2 μg urinary Cd per g creatinine. In addition, recent investigation focusing on bone effects showed increased risk of osteoporosis even at urinary Cd as low as 1 μg Cd per g creatinine. For the pulmonary toxicity, which refers to the side effect on the lungs developed by interaction with nanoparticles. This is important for work place exposures resulting from preparation of large quantities of nanomaterials as powders that can be dispersed to the air. Fortunately, most colloidal QDs like those used in this thesis do not form dry powders. Even upon solvent evaporation they typically remain waxy due to the large amount of organic molecules encapsulating them.
(capping agent). In general working with QDs is safe provided that one shows care and respect starting from the synthesis until using them for different application and final disposal.
Chapter 2: Experimental methods

In this chapter, the preparation of different samples and the experimental methods used in this thesis are presented.

2.1 Materials:

All chemicals used in the synthesis were purchased from Sigma–Aldrich without further purification. Cadmium oxide (99.5%), selenium (>99.5%), oleic acid (OA, >99%), and trioctylphosphine (TOP, >90%) were used to prepare neat CdSe quantum dots (QDs). In addition, zinc acetate (99%) and sulfur (99%) for gradient Cd$_{1-x}$Zn$_x$Se$_{1-y}$S$_y$ core–shell QDs. Mercaptopropionic acid (MPA, >95%) and tetramethylammonium hydroxide (TMAOH, 25% wt. in methanol) were used to exchange the ligand of QDs for sensitization on metal oxide (MO). Solvents used in the QD synthesis and ligand exchange included 1-octadecene (ODE, 90%), toluene (anhydrous, 99.8%), methanol (anhydrous, 99.8%), acetone (HPLC, >99.8%), ethanol (99.7%). Zinc acetate (>99%), ethylamine (>99.5%) and 2-methoxyethanol (anhydrous, 99.8%) were used to prepare ZnO seed layer for nanowires synthesis, and the precursors for ZnO NWs growth included zinc nitrate hexahydrate (>99%) and hexamethylenetetramine (HMTA, >99%). ZnO and TiO$_2$ nanoparticles (NPs) were purchased from Sigma–Aldrich with average particle size (<35 nm and 15-20 nm, respectively). For p-type NiO mesoporous films, anhydrous NiCl$_2$ and polyethyleneoxide–polypropyleneoxide–polyethyleneoxide triblock co-polymers (F108) were purchased from Sigma–Aldrich without further purification as well.

2.2 Synthesis of neat CdSe QDs:

In a three-neck flask, a 70 ml octadecene ODE solution containing 5.54 g OA and 0.51 g CdO was first heated to 180 °C to form a clear solution under N$_2$ atmosphere. 1.3 mmol Se powder and 0.5 g trioctyolphosphine (TOP) were dissolved in 10 ml ODE by stirring for 1 hour under N$_2$ atmosphere as well. The obtained TOP-Se solution was quickly injected in the three-neck flask. During the injection of TOP-Se solution, the Cd$^{2+}$ precursor solution was heated up to 180, 200, 220, 240, 280 and 320 °C to obtain different sizes of QDs. After 2 minutes reaction, the flask was removed from the heater and cooled down to room temperature. Finally, methanol and acetone were added to
Experimental methods

precipitate the QDs, which were consequently redissolved in toluene. The purification procedures were repeated twice in order to remove unreacted materials before using the QDs for any measurements.

2.3 Synthesis of gradient Cd$_{1-x}$Zn$_x$Se$_{1-y}$S$_y$ CSQDs:

Cd$_{1-x}$Zn$_x$Se$_{1-y}$S$_y$ gradient CSQDs were prepared via single-step hot injection method. Typically, 0.4 mmol (0.05 g) of CdO, 4.0 mmol (0.88 g) of zinc acetate, 17.6 mmol of oleic acid and 20 ml of 1-octadecene (ODE) were placed in a round flask. The mixture then heated to 150 °C, degased for 20 min, filled with N$_2$ gas, and further heated to 310 °C to obtain a clear solution of Cd- and Zn-oleate. At this temperature (injection temperature), 0.4 mmol (0.03 g) of Se powder, and 4.0 mmol (0.13 g) of sulfur powder both dissolved in 3.0 ml TOP under N$_2$ gas were quickly injected into the cationic oleate reaction flask. After the injection the growth temperature was adjusted to 300 °C for different shell growth time 5sec, 1, 3, 5, 10, and 15 min where part of the reaction mixture was cooled down using ice bath to eliminate the QD’s growth. As prepared QDs were purified using 1:3 chloroform-acetone mixture twice and finally the purified QDs were redispersed in hexane.

2.4 QDs surface ligand exchange:

Attachment of the QDs to the MO was carried out by exchanging the capping agent of as-obtained oleic acid-capped QDs with MPA linker. MPA is a bifunctional molecule to link the QD to the MO via its two terminals (-SH and –COOH). Therefore, 1.0 ml oleic acid-capped QDs with the concentration of 0.4 mM was mixed with 0.1 ml MPA and 1.0 ml acetone. The mixture was stirred for 30 min. Afterwards 0.5 ml of ethanol was added to the mixture, which was then stirred another 15 min. The resulting reactants were centrifuged at 3500 rpm for 5 min and the supernatant was discarded. The resulting precipitates were redissolved in ethanol. Finally, TMAOH was added drop wisely, so that a totally clear solution containing MPA-capped QDs was formed. In order to prepare MO NPs film, purchased ZnO NPs, and TiO$_2$ NPs suspension was doctor-bladed on a glass substrate then annealed at 450 °C for 30 min and then dried at room temperature. Then the MO films were immersed into MPA-capped QDs ethanol solution in the dark. Afterwards, the films were washed thoroughly with ethanol and dried using N$_2$ gas. In paper VI, the linker exchange was carried out on the substrate directly. Where, two sizes of QDs were mixed with 1:1.
volume ratio, and then spin-coated onto a glass substrate at a spinning rate of 1000 rpm for 30 s. Afterwards 10% mercaptopropionic acid (MPA) in methanol was spin-coated with the same condition to exchange the oleic acid capping agent of the as-obtained QDs. Then the film was rinsed using methanol and toluene to remove excessive QDs and MPA. This deposition process is repeated for several times to form a thick layer of QDs.

### 2.5 ZnO NWs and NiO mesoporous films preparation:

The synthesis of n-type ZnO NWs followed the widely known hydrothermal method. Briefly, 50 mM solution of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and ethanolamine in 2-methoxyethanol was spin-coated onto a fused silica substrate for 3 times and then sintered at 450 °C for 30 min in ambient to form a thin seed layer. The hydrothermal growth of highly oriented ZnO NWs on the seeded substrate was carried out at 92.5 °C in aqueous solution containing 20 mM HMTA and zinc nitrate. After the growth, the sample was carefully rinsed in deionized water and dried at 100 °C. For p-type NiO MO, by dissolving anhydrous NiCl₂ (1.0 g) and polyethyleneoxide–polypropyleneoxide–polyethyleneoxide triblock copolymers F108 (1.0 g) into a mixture of Milli-Q water (12.0 g) and ethanol (24.0 g). The solution was kept in room temperature for 1 day for stabilization, and then centrifuged. The obtained supernatant solution was doctor-bladed on a glass substrate and dried at room temperature. The dried film was then calcined in air at 400 °C for 0.5 h.

### 2.6 QDs characterization:

Steady-state absorption and emission spectra were measured using an Agilent 845x spectrophotometer and Spex 1681 spectrometer, respectively. The photoluminescence quantum yield (PL QY) of the QDs was measured and estimated by comparing the QDs’ PL intensities with that of standard rhodamine 6G dye at the same optical density (0.07). The morphologies of QDs studied in this thesis were characterized via high resolution analytical transmission electron microscopy (HR-TEM, JEOL 3000F microscope equipped with an Oxford SDD x-ray analyzer) in order to obtain the average size of the QDs. Chemical composition of CSQDs was estimated from the energy-dispersive X-ray spectroscopy (EDX) spectra corresponding to the HR-TEM images. Here TEM is operated in scanning transmission electron microscopy (STEM) mode probing the information of the local chemical composition of the sample. The
Experimental methods

morphology of multi-sized QD (paper VI) assemblies was imaged in the tapping mode by an atomic force microscopy (AFM) (AFM 5500 System, Agilent Technologies).

2.7 Solar cell device fabrication:

In paper VIII to fabricate the photoanode for solar cells, TiO$_2$ paste (Ti-Nanoxide HT) was coated on the surface of fluorine-doped SnO$_2$ (FTO) by doctor-blading technique. After annealing at 450 °C for one hour, the obtained TiO$_2$ mesoporous film is suitable for QD sensitization. The sensitization time was varied for different QDs to keep the same optical density. Finally, freshly prepared photoanode was scratched to area ~ 0.25 cm$^2$. In order to complete the solar cell, 1.0 M Na$_2$S/1.0 M S solution used as an electrolyte and FTO glass coated with 200 Å Platinum was used as a cathode.$^{52}$

2.8 Transient absorption spectroscopy (TA):

Transient absorption measurements were carried out on a femtosecond laser setup based on the MaiTai-pumped Spitfire Pro XP (Spectra Physics) with the central output wavelength of 800 nm and 1 kHz repetition rate delivering ~80 fs pulses. The beam was split into two parts: one for pumping a collinear optical parametric amplifier (TOPAS-C, Light Conversion) to generate the pump beam (470 nm), and the second one was either focused onto a CaF$_2$ crystal or a thin sapphire plate to generate a white light continuum (for transient spectra measurements), or was used for pumping a second TOPAS-C to generate narrow-band probe pulses at certain wavelength depending on the purpose of the measurement (for kinetics measurements). The delay between the pump and probe pulses was introduced by a delay line. The mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam. Generally, we used thin-film samples of QDs on MO (OD ~ 0.05) and colloidal samples in the 1-mm quartz cell (OD between 0.2 ~0.4). During measurements the film samples were kept in N$_2$ atmosphere to avoid possible photodegradation (see figure 2.1).
Experimental methods

2.9 Time-resolved PL spectroscopy (TRPL):

2.9.1 Time-correlated single photon counting (TCSPC): Time-resolved PL measurements were performed using a time-correlated single-photon counting device (PicoQuant). A pulsed diode laser at different repetition rates was used to excite the
sample at 438 nm. The pulse duration of the laser was about 200 ps. The PL from the sample was filtered using long-pass filters from 520 nm to pick up only band edge emission. The emitted photons were focused onto a fast avalanche photodiode (SPAD, Micro Photon Device). The response time of the photodiode was <50 ps. The excitation photon flux was controlled using neutral filters with different optical density.

2.9.2 Streak camera: here the laser source for the time-resolved photoluminescence setup is a titanium:sapphire passively mode-locked femtosecond laser (Spectra-Physics, Tsunami), emitting at 820 nm with 80 MHz repetition rate and 150 fs pulse length. In order to exclude the possible photocharging process in QDs, we also measured decay kinetics of QDs with different pump repetition rates (80 MHz to 1.6 MHz) tuned by a pulse picker keeping the pulse energy unchanged. The laser pulses were frequency-doubled to 410 nm by a second-harmonic generator (Photop technologies, Tripler TP-2000B). Time-resolved photoluminescence spectra were detected in a picosecond streak camera (C6860, Hamamatsu, time resolution < 1 ps) coupled to a Chromex spectrograph, triggered by the Ti:sapphire laser. A long-pass filter from 490 nm was used in front of the spectrograph to cut off the scattering from the excitation pulses.

2.10 Time-resolved terahertz spectroscopy (THz):

The same laser system used in TA measurements was utilized for THz spectroscopy. The laser beam was split into three. The first beam generates THz radiation by optical rectification in a 1 mm thick (110) ZnTe crystal. The second beam was used in another (110) ZnTe crystal for detection of THz pulses via electro-optical sampling. The third beam seeds an OPA (Topas) generating 529 nm pulses used for sample photoexcitation with a fluence of $6.3 \times 10^{14}$ photons/cm$^2$/pulse (mean number of excited electron-hole pairs per QD, $\langle N \rangle = 1.2$). To avoid absorption of THz radiation due to water vapor and possible photodegradation of the sample, the THz apparatus was placed in a pure nitrogen atmosphere.

2.11 X-ray diffraction (XRD):

XRD experiments were carried out at the Beamline I711, in MAX IV Laboratory. The energy of the incident X-ray is 12.5 keV (wavelength 0.99 Å). For the sample preparation, 0.5 mm glass capillaries with the colloidal CSQDs solutions were gently heated to fully evaporate the solvent. The XRD patterns were measured at room temperature, in the atmosphere.
Chapter 3: Exciton dynamics in QDs

3.1 Motivation:

A better understanding of exciton dynamics in nanomaterials is thus important both fundamentally and technologically.

In order to fully understand the dynamics of charge transfer from QD to metal oxide (MO) in solar cell system, which is the main aim of the thesis, steady-state optical properties of QD and the exciton dynamics within QD need to be discussed first. In this chapter, we will start with the steady-state optical properties (absorption and emission) of QDs. The ultrafast exciton dynamics within QD will be covered. We continue with describing electron injection to metal oxide (MO), multiple electron injection vs Auger recombination (AugR) to MO, hole trapping by trap states and hole injection to p-type MO. Finally energy transfer within CdSe QDs/MO system and multi-sized CdSe QDs assembles will be discussed.

3.2 Steady-state absorption and emission:

As we discussed in chapter 1, semiconductor optical properties are determined by the electronic structure of the semiconductor. In QDs, the size (quantum confinement) has a great effect on both optical absorption and photoluminescence (PL). As the size of QDs decreases, blue shift in both optical absorption and PL occurs. This can be accounted for using the particle-in-sphere model for a sphere with radius $r$:

$$E_{g,\text{eff}}(r) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8 e^2}{\varepsilon r}, \quad (1)$$

where, $E_g(\infty)$ is the bulk band gap, $m_e$ and $m_h$ are the electron and hole effective masses respectively, and $\varepsilon$ is the relative permittivity of the semiconductor.

In eq. 1 the second term on the right hand side shows that the effective band gap is inversely proportional to the square of the particle’s radius $r$ and thus increases as the size decreases, while the third term on the right hand side, due to electron-hole Coulombic attraction results in a decrease in the band gap with increasing particle radius. However, for small particles (small $r$) the second term is dominating and thus the effective band gap increases with decreasing $r$. 

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Exciton dynamics in QDs
Quantum confinement becomes pronounced when the QD’s size is comparable or smaller than the Bohr exciton radius ($a_B$):

$$a_B = \frac{\varepsilon \varepsilon_0 h^2}{\pi \mu e^2}, \quad (2)$$

In eq. 2 $\varepsilon$ and $\varepsilon_0$ denote the relative permittivity of the semiconductor and the permittivity of the vacuum, respectively, $\mu$ is the electron and hole reduced mass $m_e m_h / (m_e + m_h)$, and $e$ is the electron charge. For example the Bohr radius of bulk CdSe is $\sim 5.6$ nm. CdSe NCs with sizes comparable to this radius then exhibit a noticeable blue-shifts in both absorption and PL spectra compared to the bulk spectra. Figure 3.1 A shows the absorption spectra of CdSe QDs with different sizes.

The energy band of QDs would be split into discrete states due to the quantum confinement both in CB and VB. In the absorption spectra, such discrete states would induce pronounced exciton peaks. In particular, clear exciton peak would be observed near the absorption band edge due to the electronic transition from the VBM to the excitonic state that is located just below the CBM. The difference between the band gap and the excitonic state energy emerges due to the electron-hole interaction and is referred to as exciton-binding energy ($EBE$). The recorded $EBE$ value of CdSe QDs, for instance, is size dependent and can reach 1.0 eV for the 2.8 nm QDs size.

Apart from absorption spectroscopy, we can also utilize photoluminescence (PL, see Figure 3.1 B) to probe the excitonic states near the band edge or within the band gap (i.e defect/trap states). For a typical NC, PL spectrum contain emission from both band edge and trap states. The trap states which are located within the band gap form a red-shifted PL band compared to the band edge emission (because of the reduced transition energy between these states and the opposite band). The trap emission is usually very broad because of various trap states with different properties exist. In practice it is possible to passivate the surface trap states of QDs using organic capping agent like oleic acid (OA), tri-n-octylphosphine oxide (TOPO), by surface modification techniques or by growing a semiconductor shell around the core (core–shell structure). This will result in enhanced band edge emission (discussed more in chapter 4). Some other QDs were found to be weakly luminescent or even non-luminescent at room temperature like PbI$_2$ and CuS. This property is mainly due to the indirect band gap character of these materials and the high density of internal and/or trap states which act as PL quenchers.
Figure 3.1: A) Absorption spectra of CdSe QDs with different sizes in toluene, B) emission (PL) spectra from different sizes of CdSe QDs in toluene, and C) schematic illustrating the optical band edge absorption and the exciton binding energy (EBE).

3.3: Exciton dynamics:

In QDs, absorption of a photon with energy larger than the QD band gap results in excitation of an electron in the CB and a hole in the VB. The carriers are bound to each other by Coulombic interaction and form an exciton due to large EBE. Initially, within few tens of fs, an electronic dephasing takes place. Electronic dephasing is considered as a dynamics process in which the energy is conserved while the phase memory of the quantum state is lost. This process is considered as the fastest event that excitons experience in semiconductors. For instance in CdSe QDs, the electronic dephasing times at 15 K has been reported to be 85 fs based on three pulse photon echo measurements. After the excitation with high energy photon, both electron and hole have excessive kinetic energy (KE). Dissipation of this energy due to interaction between electrons/holes and phonons on time scale of hundreds of fs is resulting in...
Exciton dynamics in QDs

intraband relaxation of the electron to the CBM and the hole to VBM. This intraband relaxation is followed by radiative (emitting a photon) or nonradiative (producing heat) recombination.

Figure 3.2: Dynamic processes in QD: 1) electron and/or hole relaxation through electron-phonon coupling, 2) electron trapping into trap states and the same may occur for the hole (hole trap states), 3) radiative and nonradiative band edge electron-hole recombination, and 4) radiative and nonradiative trapped electron-hole recombination.

In semiconductor NCs, dynamic processes are generally more complicated compared to the bulk semiconductor due to the presence of many band gap states. These states are often referred to as surface states or trap states. Depending on the application of interest for the semiconductor NCs, these surface states or trap states can be unwanted or useful. For example, in the catalytic application, these states are useful where electron or hole trapping will prevent the recombination and subsequent redox reaction may occur using the trapped carriers. In contrast, for photovoltaics or luminescence application these states are usually undesirable.

In the QDs which are free from trap states, the electron and hole will primarily recombine radiatively which leads to high PL quantum yield (PL QY), and exciton lifetime on the order of a few to a few tens of ns (for direct band gap QD). On the other hand, in the QDs with trap states, trapping process of electrons and/or holes by these states becomes significant and occurs on time scale of a few ps to a few tens of ps (see figure 3.2). As a consequence of high density of trap states, the band edge PL intensity and the PL QY are very low. In QDs solar cells, especially QDs-sensitized solar cells (QDSSCs), the trap states are usually induced by surface dangling bonds which are always far from the interface to the acceptor and thus prevent the charge transfer processes. Therefore, reduction of such trap states is very important for photovoltaics application. Here, the charge separation plays a crucial role while the trapping of the charge carriers is a strong competitive to the charge transfer to MO.
Exciton dynamics in QDs

More details about the charge (electron/hole) injection will be discussed in the following sections.

In some cases, depending on the density and energy of the trap states, the trapped carriers (electron and/or hole) can relax to deeper traps within the band gap. The lifetime of the charge carrier in deep trap states can be as long as tens of ns to μs or even longer. The experimentally observed lifetime of a given state \( \tau_{Ob} \) depends on radiative and nonradiative lifetimes, \( \tau_R \) and \( \tau_{nonR} \) respectively. For an ideal crystal where the PL QY is high (~100%), \( \tau_{nonR} \) is very long leading to \( \tau_{Ob} = \tau_R \). In reality, this is a seldom case where the observed lifetime has contributions from both radiative and nonradiative lifetimes as follows:

\[
\frac{1}{\tau_{Ob}} = \frac{1}{\tau_R} + \frac{1}{\tau_{nonR}}, \quad (3)
\]

\[
PL \ QY = \frac{\tau_{Ob}}{\tau_R}, \quad (4)
\]

In the rest of this chapter, the main objectives of papers I-IV will be presented in the following order: Papers I and II contain work on the electron injection from CdSe QDs to ZnO (MO). Paper III analyses the hole trapping process and its long-lived component, whereas the paper IV studies the hole injection from QDs to p-type MO. In addition, exciton (electron-hole pair) transfer is presented in papers V and VI. As a result of our work on neat CdSe QDs, a surface modification is necessary. Therefore, chapter 4 mainly focus on \( \text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y \) gradient CSQDs and how controlling the shell thickness improves the QD’s properties for solar cell applications.
3.4 Paper I “Electron injection from QDs to MO”:

Studies of electron injection from QDs to MOs by using standard techniques (pump-probe in the visible range, time-resolved PL) bring an ambiguity in interpretation. A depopulation of QDs can be observed, however, without a possibility to distinguish electron trapping from electron injection. Reported time scales of electron transfer therefore varied from picoseconds up to nanoseconds, even for similar QD-MO systems, and various interpretations of the observed kinetics can be found. In this paper, ultrafast electron injection from CdSe QDs to ZnO NWs is observed to take place on the picosecond time scale (3–12 ps) depending on the QD’s size by using ultrafast time-resolved absorption technique (see figure 3.3 A). The electron injection to the MO was further proved by terahertz (THz) spectroscopy technique where the conductivity spectrum and rising signal confirms that the electrons arrive in the MO in similar timescale as they leave the QDs (see figure 3.3 B).

**Marcus theory of electron transfer:** On 1992 Rudolph Marcus got the Nobel Prize in chemistry for his theory of electron transfer. Tvrdy et al. used Marcus theory to describe the electron injection rate from CdSe QDs to MOs as a function of the QD sizes. In many-state Marcus model, where the electron is transferred from a discrete molecule-like state in QD to a continuum of states in MO, the transfer rate can be expressed as:

$$k_{et} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} \rho(E)|\bar{H}(E)|^2 \frac{1}{\sqrt{4\pi \lambda kT}} \exp\left(-\frac{(\lambda + \Delta G + E)^2}{4\lambda kT}\right), \quad (5)$$

where, \(\rho(E)\) is the MO density of states (DOS), \(|\bar{H}(E)|^2\) is the electronic coupling matrix element, \(\lambda\) is the reorganizational energy, \(k\) is Boltzmann constant, \(T\) is the temperature, and \(\Delta G\) is the free energy change. The free energy change \(\Delta G\) can be expressed as:

$$\Delta G = \Delta E_{et} + \Delta E_C, \quad (6)$$

where, \(\Delta E_{et}\) is the difference between the electron initial energy state (QD’s CB) and the electron final state (MO’s CB) and the Coulombic term \(\Delta E_C\) arises from electron and hole interaction. In other words, the electron energy difference acts as a driving force for the electron transfer process where the Coulombic interaction energy acts against the electron transfer process. Figure 3.3 C demonstrates that the electron...
injection rates with different driving forces induced by different QD sizes can be well fitted by Marcus theory.

Figure 3.3: A) Normalized TA kinetics of neat QDs (dotted lines) and QDs-sensitized ZnO NWs (solid lines) for different size of CdSe QDs, B) TA kinetics compared to THz kinetics of (2.9 nm) QDs-ZnO NW, C) electron transfer rate ($k_{et}$) dependence on the free energy change ($\Delta G$) described by Marcus theory, and D) schematic illustrating the CTS model of the electron injection.

In addition to the fast injection (~6 ps) a slower kinetic component of about ~100 ps is clearly present in both TA and THz signal. This indicates the two-step electron transfer via charge transfer state (CTS). Such model has been proposed previously in dye-ZnO systems. In the CTS model, a fast electron injection is followed by a slower process where the CTS dissociates and electrons are released to the NW bulk (see figure 3.3 D). The ultrafast electron injection (~ps) has important implications for exploiting the multiple exciton generation (MEG) in QD-sensitized SCs. In this context, the injection process has to compete with other fast loss channels, like Auger recombination (AugR).
3.5 Paper II “Multiple exciton harvesting”:

Performance–cost balancing is a crucial factor for solar cell expansion as a sustainable source of energy. For example the single-junction SCs efficiency is restricted to be below the Shockley–Queisser limit of about 32%. The **Shockley–Queisser limit** originates from the fact that only photons with energy higher than or equal to the band gap can be used to create excitons. Photons with energy less than the band gap will be not absorbed and photons with energy higher than the band gap will create excitons with excess energy which will be lost as heat. QDs have a unique property which can break the Shockley–Queisser limit *via* the so-called **multiple exciton generation** (MEG). Instead of thermal relaxation, the excess energy can be used to excite one or more electron-hole pairs. The harvesting of multiple electrons out of one excited QD would increase the efficiency of SCs. Efficient MEGs in various materials of QDs and QD–MO systems have been reported. On the other hand, utilization of MEG is limited by AugR where the recombination energy of one electron-hole pair is transferred to electron or hole in the second electron-hole pair, which relaxes rapidly *via* thermal relaxation.

In this paper, we study the electron injection under multiexciton conditions (high excitation intensity). In paper I, we showed that the electron injection is very fast within few to few tens of picoseconds for one electron-hole pair per QD (low excitation intensity). Under multiexciton condition, a solid foundation for distinguishing the competition between AugR and electron injection was revealed. Electron injection rates from QDs to MOs strongly depend on the distance (shell thickness in this case) between QDs and MOs. Three samples representing fast (sample F, no shell), intermediate (sample I, thin shell), and slow (sample S, thick shell) electron injection rate were chosen in this study (see figure 3.4 A).

A typical sign for multiple excitons in QDs is the rapid AugR leading to a kinetic component which is significantly shorter than the single electron-hole pair recombination on the nanosecond time scale. AugR contribution was determined from the difference between TA decay kinetics under low and high excitation conditions in the absence of the MO. Introducing the MO under the same excitation conditions will affect the kinetics by the fast electron injection process. Thus for the studied samples, AugR-electron injection lifetime ratio is 0.01, 1.2, and 4.5 for samples F, I, and S, respectively.
Exciton dynamics in QDs

Figure 3.4 B shows the effect of MO on the dynamics under high excitation intensity. For sample S, AugR is more dominant where TA dynamics under different excitation intensities are the same for attached and unattached QDs. Sample I presents a combination of electron injection and AugR. At low excitation intensity, a fast TA decay is due to electron injection. By increasing the intensity TA decay becomes faster due to AugR. For instance, the mean lifetime changes from 60 ps at low excitation (electron injection only, $k_{\text{inj}}$) to 35 ps at high excitation (electron injection and AugR, $k_{\text{tot}}$) with AugR lifetime $\sim 80$ ps (the same in the absence of ZnO NWs $\sim 73$ ps).

Finally, the competition between electron injection and AugR is presented in sample F. As the excitation intensity increases the TA decay becomes slower till excitation intensity reaches $\sim 700$ $\mu$J/cm², then, TA signal decays faster. The slow decay ($\sim 50$ ps) can be understood as a competition between the second electron injection and trion decay (positive trion is a QD contain two holes and one electron). Comparison of the slow decay lifetime ($\sim 50$ ps) and the reported trion lifetimes ($\sim 140$ ps)\(^81\), indicates

Figure 3.4: A) Normalized TA kinetics of pure QDs (dotted lines) and sensitized ZnO NWs (solid lines) for samples F, I, and S, B) normalized TA kinetics for samples F, I, and S attached to ZnO NWs under different excitation intensity (all excitation intensities are in $\mu$J/cm²), C) schematic illustration of the 2nd electron injection $\text{vs}$ AugR, and D) electron injection rate dependence on QD size (orange squares) fitted by Marcus theory (solid orange line) adopted from paper I; Auger biexciton recombination rates (our results, dark cyan circles) and from ref\(^80\) (dark cyan triangles) fitted by $D^p$ function ($p = 4.9$, dark cyan line).
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presence of an efficient injection of the second electron to MO. At higher intensity, the 
TA dynamics becomes faster (see figure 3.4 B) due to AugR from more than doubly 
excited QDs.

It is also essential to evaluate the size dependence of AugR rate. By the same methods, 
AugR contribution can be extracted for different QD sizes. Like pervious results\textsuperscript{80,82,83}, 
AugR lifetime becomes significantly shorter for smaller QDs. The obtained QD size 
dependence of AugR rates can be well fitted by a $D^p$ function ($p = 4.9$) which is in line 
with previously reported dependences (see figure 3.4 D).\textsuperscript{84} We demonstrate that, the 
multiple exciton harvesting efficiency changes significantly with QDs' size. Already 
within the narrow range of QD sizes (2–4 nm) the efficiency of the first exciton 
harvesting can vary from 30% to 70% for this particular system (QD-linker-ZnO 
NWs).
3.6 Paper III “Ultra-long-lived trapped holes in QDs”:

After the formation of excitons, not all the carriers (electrons and holes) undergo a prompt recombination. Some of them get trapped by defects and/or surface states. This affects the dynamics of excitons\(^{85}\), reduces the PL yield\(^{86}\), and hinders the charge transport.\(^{87}\) Recent studies have shown that the charge trapping is not always detrimental to QDs application, and in some systems the trapped states can be used to broaden the PL spectrum for potential application in white light-emitting-diodes.\(^{88,89}\)

In this paper, we investigate the PL from the trapped states in oleic acid capped CdSe QDs with various sizes (2.3-7.0 nm). The PL from the trapped states (due to localized carriers) can be observed with red-shift to the PL from the band edge recombination (due to delocalized carriers). In our investigation we found that the smaller the size, the larger is the contribution of the red-shifted bands.\(^{90}\) We attribute this to the increase in the surface-to-volume ratio with the decreasing size of the QDs, and therefore we associate such red-shifted PL bands to surface trap states. We also found that this red-shifted emission consists of at least two bands contributing to the surface states related PL (see figure 3.6 A, PL\(_1\) and PL\(_2\)), which indicates that more than one type of surface states are radiative.

Furthermore, our photoluminescence excitation (PLE) measurements show that the excitons above the band edge can get localized (trapped) at the surface and contribute much more to the surface PL than the excitons excited at the band edge (see figure 3.6 B). This means that the trapping process is more efficient when the QDs are excited above the band edge.\(^{91,92}\) Time-resolved PL (TRPL) helps us to understand the dynamics of these trap states. Typically, localized carriers at shallow traps can delocalize again at room temperature and contribute to the band edge PL, while the carriers at deep traps are difficult to delocalize with lifetime longer than 2.5 \(\mu\)s (time window for TRPL) in room temperature (see figure 3.6 C). Using ultrasensitive femtosecond pump–nanosecond probe setup, a very long-lived component (> tens of \(\mu\)s) has been observed. The photobleach signal suggests that the electrons remain delocalized and do not recombine with the holes within few tens of ns (single exciton life time in CdSe QDs), which means that the holes remain trapped on the microsecond time scale (see figure 3.6 D). Our results add more evidence that the majority of the trapped carriers in CdSe QDs are holes.
Figure 3.6: A) Normalized PL from 2.3 nm CdSe QDs with red-shifted emission from the trapped hole states (PL₁ and PL₂); inset: hole multi-trap states model, B) PLE spectrum of 2.3 nm CdSe at different emission wavelengths, C) band edge (blue line), trap-state emission (black line) decay obtained by using a sharp edge filter, and the fit (red lines), and D) TA kinetics of CdSe QDs at different pump intensities; inset: TA decay in early time scale (5-20 μs).
3.7 Paper IV “Hole injection vs hole trapping”:

The aim of this work is to evaluate the hole injection from QDs to p-type MO (namely, NiO). Hole injection and hole trapping have similar spectroscopic signatures and it is a challenge to separate them from each other. Furthermore, the trapping process directly interferes with injection hindering the efficient charge transfer. In addition, we studied the dependence of hole injection on QD sizes and proved that the passivation of hole traps by core–shell structure is beneficial for efficient hole injection.

In this work, we mainly used TRPL to analyze the hole dynamics in QDs because other methods such as TA signals in visible spectral region are mainly sensitive to the electrons in QDs’ CB. One difficulty to identify the hole injection process in QD-NiO system is the competition from hole trapping induced by linker molecule exchange from oleic acid (OA) to short chain thiol-based linker (e.g. mercaptopropionic acid, MPA). By comparing the TA and PL kinetics between OA-capped QDs and MPA-capped QDs, we can prove the hole trapping process within 4 ps (see figure 3.7 A). However, the major fast hole trapping (~4 ps) induced by ligand dangling bond can be significantly reduced by photoirradiation (known as photoinduced emission enhancement “PEE”). This effect is commonly explained by surface passivation induced by the chemical change of QD’s surface during the irradiation process.

In this scenario, we can start to investigate the hole injection in QD-NiO system after such “photoirradiation passivation” which would exclude the fast quenching process by surface traps. The situation is different for QDs attached to NiO where we used a global fitting of TA spectra in QD-NiO resulting in two components. The long-lived component (~6 ns) can be assigned to exciton recombination whereas the fast component (~200 ps) (see figure 3.7 B) can be explained by employing a charged-QD model. Here, the hole injection from QD to MO will leave a charged-QD behind. If negatively charged, the QD’s absorption edge will show a red shift on the scale of a few meV. In our case, the difference between original and 10 meV shifted absorption spectrum gives the TA fast component spectrum (see figure 3.7 B inset). This provides an evidence for the charged QD model and at the same time directs towards the hole injection to NiO, because the hole trapping itself does not lead to such behavior.

This fast component (~200 ps) is analogous to what we found in TRPL measurements. The multi-exponential fitting of PL kinetics of QD-NiO exhibits an additional fast decay component (~380 ps) compared to those of neat QDs samples.
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Therefore, it can be assigned to hole injection from QDs to NiO (see figure 3.7 C). Similar to electron injection to ZnO NWs in paper I, we used Marcus theory (eq. 5) to study the hole injection rates dependence on the QD’s size. We have modified the free energy change term ($\Delta G$) calculation (see eq. 7) to account for the hole properties:

$$\Delta G = \Delta E_h + \Delta E_C, \quad (7)$$

where $\Delta E_h$ stands for the hole energy difference between the initial (QD’s VB) and the final energy (MO’s VB) states. $\Delta E_h$ has the same value since the VBM for CdSe is independent of the QD’s size when attached to MO. The second term $\Delta E_C$ is the Coulombic interaction between the electron and hole.

Figure 3.7: A) TA kinetics at the band edge absorption and PL decay of OA-and MPA-capped CdSe QDs on glass, B) TA spectral components extracted from TA spectra; inset: steady-state absorption (cyan line) and change in absorption after a shift of the spectrum by 10 meV (blue line), C) PL decay for CdSe QDs on glass; inset: PL decay for CdSe QDs with different size attached to NiO, D) hole injection rate vs driving force of different QDs sizes, and E) schematic illustration of hole trapping vs hole injection to MO.

Figure 3.7 D shows the hole injection rate dependence on the QD’s size according to eq. 5. We found that the hole injection rate for CdSe-NiO system is more than an order of magnitude slower than the electron injection rate for CdSe-ZnO system (paper I). This can be explained by the hole effective mass being larger than the electron effective mass and the MO’s permittivity being higher for ZnO than NiO. However,
the most critical factor limiting the hole injection efficiency is the hole trapping which is strongly competing with the hole injection. We found that growing the shell (1.3 nm thickness) around the active core will passivate the hole trap states. Consequently, the hole injection efficiency was enhanced from less than 10% to 50% for core only and core–shell QDs, respectively.
3.8 Paper V “Energy transfer in CdSe-ZnO NWs system”:

One of the important requirements for efficient photoinduced charge separation is the direct contact between the light absorber and the electron acceptor. However, multilayers of QDs absorber can boost the solar cell performance as has been reported for ligand-free QDs.\textsuperscript{98} Although many models are used to explain the charge collection from indirectly attached QDs (IA-QDs). In this work we attribute it to the energy transfer mediated charge collection. Here, the photodynamics in multilayer MPA-capped CdSe QDs sensitized ZnO NWs with different sensitization time were studied. Analogous to previous reports,\textsuperscript{99} \textit{in situ} steady-state absorption spectroscopy was used here to quantify the adsorbed amount of QDs on the MO surface. Adsorption can be described as a combination of a Langmuir-type submonolayer formation and adding further layers of indirectly attached QDs (aggregation) (see figure 3.8 A). The fraction of IA-QDs ($R$) can be calculated as follows:

$$R = \frac{[P_{ag}]}{([P_{ag}]+[P_{Lang}])}, \quad (8)$$

where, $[P_{ag}]$ and $[P_{Lang}]$ are the concentration of IA-QDs and submonolayer adsorbed QDs, respectively.

The TA decay kinetics for sensitized ZnO NWs by CdSe QDs show similar decay components for the electron injection (~10 ps) and CTS dissociation (~100 ps) (paper I). However, the nanosecond component (~3.6 ns) varies with different QDs sensitization time (see figure 3.8 B). Based on the correlation between the component amplitude ($A_3$ from the fitting) and the IA-QDs fraction $R$ (calculated from eq. 8) (see inset of figure 3.8 B) we assign this component to the excitation energy transfer from the indirectly attached QDs. In addition, the continuous enhancement of the incident photon-to-electron conversion efficiency indicates that the absorbed photons by IA-QDs also yield charge carriers. Energy transfer (exciton migration) is the most plausible mechanism for our system, where the exciton migrates from the IA-QDs to the QDs adjacent to the MO. Exciton migration from the higher energy (smaller) QDs within the size distribution of the QDs sample can be confirmed from the steady-state PL where a pronounced red shift (40 meV) and narrowing of the emission spectrum can be found in the film of QDs. In contrast to that, no such narrowing occurred in QD solution (see figure 3.8 C).
Another evidence for the FRET in our sample can be found in TA decay kinetics for neat QDs on glass, which shows a biexponential character with a conventional radiative exciton recombination (~ 10 ns) and a faster (~ 660 ps) component corresponding to the energy transfer from small QDs to larger ones. Finally we can evaluate the energy transfer time constant from the IA-QDs to the DA-QDs as:

\[ 1/\tau_{ET} = 1/\langle \tau \rangle - 1/\tau_{QD}^0, \quad (9) \]

where, \( \langle \tau \rangle \) is the TA lifetime of IA-QDs (3.6 ns), and \( \tau_{QD}^0 \) is the exciton lifetime of QDs without any transfer process. We obtain the energy transfer time constant \( \tau_{ET} \) from IA-QDs around 5 ns (see figure 3.8 D). The energy transfer time is significantly
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longer than electron injection time. In order to improve this, a well-designed QD tandem layers with different sizes to provide an ideal spectral overlap for efficient FRET is indispensable.
3.9 Paper VI “Energy funneling through multi-sized QD films”:

After we have proven the exciton migration from IA-QDs to DA-QDs due to the QDs size distribution in QDs-ZnO NWs system, we turn to study the directed exciton migration from small to large QDs in more organized multi-sized QD mixtures. Exciton migration study is also essential for other QD’s applications as light emitters, lasers and solar cells. In the development of such devices, QDs are considered as densely packed to form a thin film with strong absorption and emission. Indeed, FRET is an important mechanism due to the electronic coupling between the closely packed QDs.

Here, we report the investigation of FRET dynamics in densely packed multi-sized CdSe QDs (we used three different QDs: QDs-A, 2.3 nm, QDs-B, 3.7 nm, and QDs-C, 6.7 nm) based on TA spectroscopy and theoretical modeling. Firstly, steady-state PL spectroscopy for multi-sized CdSe QDs film (A+B) shows a typical indication of FRET: a significant increase of the red emission on the expense of the blue emission due to exciton migration from small QDs to large QDs (see figure 3.9 A). However, steady-state PL spectra do not provide a full proof of FRET, therefore, we used TA measurements to prove the FRET presence and to reveal its time scale. TA spectra at different delays ($t$) for singly-sized QDs ($\Delta \alpha_A(t)$, $\Delta \alpha_B(t)$, $\Delta \alpha_C(t)$) and for different combinations of QDs ($A+B$, $A+C$, $B+C$) ($\Delta \alpha_{A+B}(t)$) at the same delays were recorded, then fitted using the sum of TA spectra for singly-sized QDs at the same delays:

$$\Delta \alpha_{A+B}(t) = k_A(t)\Delta \alpha_A(t) + k_B(t)\Delta \alpha_B(t).$$ (10)

The ratio of single-color spectrum ($k_A(t)/k_A(0)$ for QD-A, and $k_B(t)/k_B(0)$ for QD-B) corresponds to the FRET-related change of the excited state population in A and B relative to their initial population. This ratio gives us valuable information about FRET dynamics, if this ratio stays the same at different delays for A and B (for example, A+B mixture in solution) this means no FRET dynamic within A and B mixture (see figure 3.9 B and C). On contrary, for the same mixture in the film form, a significant decrease of the ratio of QD-A accompanied by increase of the ratio of QD-B with similar kinetics can be observed. The same effect takes place for the other pair combinations (see figure 3.9 D). For all possible QD pair combinations, the FRET times were estimated based on the analysis to be 1-3 ns for different combinations.
Figure 3.9: A) Steady-state PL spectra of QD-A and QD-B individually and a mixture of QDs-(A+B) on glass, B) TA spectra of QD-A, QD-B, and QD-C individually in solution and a mixture of QDs-(A+B+C) in solution as well, C), ratio of single-color spectrum as a function of pump–probe delay times of QDs-(A+B+C) in solution, and D) ratio of single-color spectrum as a function of pump–probe delay times of QDs with different combinations on glass.

The estimated values did not follow the \( \frac{1}{R_{DA}^6} \) dependence according to the standard FRET rate expression (eq. 11).

\[
k_{ET} = \frac{1}{\tau_{ET}} = \frac{R_{DA}^6 n^4}{\hbar} \left( \frac{2\pi}{\mu_0 \mu_a^2 K^2 \theta} \right). \tag{11}
\]

where, \( R_{DA} \) is the donor-acceptor distance, \( \mu_0 \) and \( \mu_a \) are the donor and acceptor dipole moments, respectively, \( K^2 \) refers to the orientation factor of the dipole–dipole interaction, \( n \) is the medium’s refractive index, and \( \theta \) is the spectral overlap between the normalized donor emission and acceptor absorption line shapes. Apparently the simple dipole–dipole description of FRET is not sufficient because of the distance between donor and acceptor is smaller than the QD dimensions.

We took into account the dipole moment distribution over the whole QD using Bessel function to describe the exciton wavefunction density in spherical QDs. The
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function drops quickly with increasing the distance from the QD’s center, but still the dipole distribution influences the interaction of two close QDs (see figure 3.10 A, lower inset). In order to incorporate the dipole distribution into the FRET theory, we have modified the “1/R^6” term (distance term). Namely, we numerically integrate the dipole–dipole interaction over the volume of donor and acceptor. Our calculations show that for distances less than 10 nm between donor and acceptor (here, for our combinations the center-to-center distances range 3-5 nm) the point–dipole underestimates the resulting FRET rate but for larger distances the point–dipole approximation is sufficient (see figure 3.10 A). For closely staked QDs, the correction of the distance term based on Bessel distribution can be more than 50% (see figure 3.10 A, upper inset).

In reality, the QD–QD distances given by the film morphology play also an important role in FRET rate. In the previous reports often the ideally stacked QD layers were used to calculate the FRET rate. We have used atomic force microscopy (AFM) and found a big deviation from the ideal model due to the fabrication procedure. The QDs tend to aggregate into clusters after ligand exchange. We compared our experimental FRET rates to the calculated rates based on our modifications. As the distance between QD and the closest neighbor is not a single value, but a distribution, our calculations result in a distribution of FRET rates around mean value on the nanosecond time scale. For all the combinations, the mean FRET rates agree with the FRET rates obtained experimentally (see figure 3.10 B).

Finally, we study the directed energy funneling between tandem layers of QDs with different sizes. We use steady-state PL for different combinations of QD monolayers where QD-C is used as the exciton final acceptor and QD-A is the donor. In between the A and C monolayers we deposit one or two layer(s) of QD-B. In both cases (A+B+C) and (A+2B+C) (see figure 3.10 C), about 90% of the excitons from QD-A is taken off due to fast FRET compared to the exciton life time in QD-A. The extra QD-B layer did not affect the exciton migration from QD-A but it decreases the number of excitons transferred to the QD-C by 20%. This pronounced effect of the extra QD-B layer on the exciton migration stimulated us to extract the exciton diffusion length L^D for B-C QDs combination with different number of QD-B layers. We estimate the diffusion length to be 9.0 nm. For a single layer of QD-B, 95% of excitons transferred to QD-C (FRET lifetime 3.0 ns, exciton lifetime 28 ns). On the other hand, for many QD-B
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layers ($L_D \sim$ two layers of QD-B), many excitons cannot reach B/C interface and recombine before the final destination (QD-C) (see figure 3.10 D).

Figure 3.10: A) Distance term of FRET for $\delta$-function approximation ($1/R_D^6$, black points) and Bessel function model (red points); lower inset: the corresponding density of dipole moments in the models; upper inset: correction ratio obtained via Bessel function, B) left panels: experimental ratio of the excitons transferred to donor (blue lines) compared to the theoretical prediction (red lines), and right panels: distribution of FRET lifetimes for each pair combination, C) PL spectra of ordered QDs films, and D) PL ratio between QD-B on glass and QD-B with top layer of quencher (QD-C) as a function of the number of QD-B layers in order to extract the exciton diffusion length $L_D$. 

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Chapter 4: Photoinduced dynamics in core–shell QDs

4.1 Motivation:

Understanding the fundamental science and the synthetic methodologies of the nano-heterostructures provides a wealth of new materials, devices, and applications.

Nano-heterostructure crystals (such as, semiconductor-core–semiconductor-shell QDs) feature highly diverse physical and chemical properties, as we will discuss later. Great flexibility in tuning the optical and electronic properties can be achieved by integrating the nanomaterials into the nano-heterostructures (for example, core–shell quantum dots, CSQDs). Such structures often lead to significantly improved device performance. Since 1990, CSQDs have been actively investigated in order to overcome the surface photodegradation of core-only nanocrystals. Coating a semiconductor QDs (CdSe QDs) by another semiconductor (such as ZnS) can enhance the chemical, thermal, and photochemical stability compared to the neat QDs. In the CSQDs, the semiconductor shell is grown on the semiconductor core. The shell improves the surface passivation of the core by separating the surface dangling bonds from the core material with an energy barrier in-between. Optical and electronic properties can be tuned easily by engineering the band alignment between core and shell materials and consequently it opens the door for these materials to be useful to a wide variety of fields.

4.2 Classification of core–shell QDs:

Depending on the VB and CB of the core and shell semiconductors, CSQDs can be classified into three main categories. Type I CSQDs, reverse type I CSQDs, and type II CSQDs.

In the type I CSQDs, a shell with a wider band gap than the core is grown around the core, aiming to improve the properties of the active core (see figure 4.1). For instance, the shell can passivate the surface traps (usually induced by dangling bonds) on the core’s surface with energy barriers. This leads to the enhancement of the PL QY.
by reducing the non-radiative recombination from the traps (e.g., CdSe–ZnS CSQDs). CSQDs usually show red-shifted excitonic peaks compared with the core materials due to the partial leakage of the exciton wavefunctions from the core into the shell.

![Diagram of CSQDs types](image)

**Figure 4.1:** Different types of CSQDs compare to neat core depending on the band gaps energy of both core and shell materials.

In reverse type I CSQDs, a wider band gap core is coated with a narrower band gap shell. Thus, the carriers are partially or completely induced and confined in the shell which improves the charge extraction and injection (e.g., CdS–CdSe and ZnSe–CdSe). The excitonic peak can be red-shifted by increasing the shell thickness. In order to improve the photostability and the PL QY properties, growing a second shell with wider band gap than the first one (core–shell–shell structure, CSS) is needed.

In the type II CSQDs, either the CBM or the VBM of the core is located within the band gap of the shell. Consequently, the resulted effective band gap is always smaller than each one of the constituting core and shell materials (see figure 4.1). This alignment leads to spatial separation of the electrons and holes into the core or the shell depending on their band alignment. Manipulating the shell thickness of this type leads to tuning the emission color which is of the main interest in such system (e.g., CdTe–CdSe and CdSe–ZnTe). The PL lifetime for this type of CSQDs is much longer compared to type I CSQDs due to the lower wavefunctions overlap of the electrons and the holes. Again growing a second shell with wider band gap (CSS) is needed here to improve the photostability and the PL QY. Quasi-type II CSQDs denote a structure,
where one of the carriers is delocalized over the CSQD volume and the other carrier is mainly confined within the core only.\textsuperscript{103}

Among all above-mentioned types of CSQDs, the transition from the core to the shell materials is sharp, resulting in step-like band alignment.\textsuperscript{107} In such case, continuously growth of shell in type I CSQDs would greatly reduce the PL QY.\textsuperscript{107} This is due to the lattice mismatch between the core and the shell layers, the nonuniform growth of the shell, and the formation of grain boundaries between small clusters in the shell layer.\textsuperscript{20, 64} \textit{The lattice mismatch} refers to the situation where two materials featuring different lattice constants are brought together with interface between them. All these effects will induce defects acting as carrier traps and hence reducing the PL QY.

On the contrary to step-like CSQDs, one can also form so-called \textbf{the gradient type I CSQDs} (see figure 4.1), where the composition changes smoothly in the radial direction and resulting in a gradual band change from the core to the shell. In this case, the above-mentioned shell induced defects can be minimized, and the PL QY can be enhanced. In particular, in gradient CSQDs the soft confinement of electrons and holes can reduce the unwanted Auger rate compared with step-like CSQDs which have sharp steps of potential change.\textsuperscript{29, 83, 108} In the following section we will explain the general aspects of designing the gradient type I CSQDs (Cd\textsubscript{1-x}Zn\textsubscript{x}Se\textsubscript{1-y}S\textsubscript{y}) which are used in this thesis in order to improve the core properties for solar cell applications.

\subsection*{4.3 Important aspects for preparing the gradient type I CSQDs:}

In the following section we will discuss the preparation of gradient Cd\textsubscript{1-x}Zn\textsubscript{x}Se\textsubscript{1-y}S\textsubscript{y} CSQDs of type I in details. In general for step-like CSQDs, cores with a known diameter were used as a seed to grow the shell around in a two-steps synthesis procedure (core synthesis followed by purification process and then growing the shell over the core). This two-steps synthesis route might create interfacial defects between core and shell due to the lattice mismatch. However, in order to prepare the gradient type I CSQDs, we employed the single-step synthesis procedure where the core and shell materials are introduced at the same time during the growth. The gradient structure is greatly determined by the following important factors during the synthesis: the composition of the core and shell materials, the shell precursor’s materials, the chemical...
reactivity of the different precursors, the reaction temperature, and the shell thickness control.

We will start by choosing the core and shell materials, where the lattice mismatch between them plays an important role. For CSQDs, the smaller the lattice mismatch the lower the density of core–shell interface defect states would occur. For the type I step–like CSQDs (sharp core–shell interface), the PL QY is increasing with the shell thickness up to ~0.7 nm (~2.4 monolayers) and then is decreasing due to the formed defects due to the lattice mismatch between the core (CdSe) and the shell (ZnS).\textsuperscript{107,109,110} On the other hand, the PL QY of the gradient CSQDs increases gradually with the shell thickness up to ~1.6 nm due to the successive relaxation of the core–shell interface strain via chemical composition gradient.\textsuperscript{20} For the thicker shell (>1.6 nm), the QY does not increase any more due to lattice imperfections within the shell.\textsuperscript{109,110}

The selection of the shell precursor’s materials is another important issue to be taken into account to avoid side reactions and unwanted products. In addition, some precursors require special precautions especially when they are highly toxic and/or pyrophoric chemicals. For instance ZnS, is one of the most used shell materials for numerous II–VI and III–V semiconductor NCs.\textsuperscript{106} The ZnS shell can be grown based on using diethylzinc and hexamethyldisilathiane as Zn and S precursors, respectively. However, these two chemicals are pyrophoric and toxic, respectively. Therefore, alternative precursors were employed in our gradient CSQDs namely zinc carboxylates and elemental sulfur which are more suitable for large scale CSQDs production.\textsuperscript{106}

In the single-step synthesis of the gradient Cd\textsubscript{1-x}Zn\textsubscript{x}Se\textsubscript{1-y}S\textsubscript{y} QDs, both Cd\textsuperscript{2+} and Zn\textsuperscript{2+} add together with oleic acid in presence of non-coordinating solvent (namely, 1-octadecene). Then after the formation of Cd-oleate and Zn-oleate, a mixture of the anionic precursors (Se\textsuperscript{2-} and S\textsuperscript{2-}) in TOP is quickly injected into the cationic mixture. Thus, the chemical reactivity difference between the cationic (Cd\textsuperscript{2+} and Zn\textsuperscript{2+}) and the anionic (Se\textsuperscript{2-} and S\textsuperscript{2-}), indeed, is very important. In our CSQDs, even if the initial concentration of the Zn\textsuperscript{2+} cation was 10 times higher than Cd\textsuperscript{2+} (in precursor solution), after 5 sec of the reaction the amount of reacted Cd\textsuperscript{2+} was 20 times higher than Zn\textsuperscript{2+} (determined using EDX, see the following sections). This shows that the chemical reactivity of Cd\textsuperscript{2+} is much higher than Zn\textsuperscript{2+}. In the same manner, the chemical reactivity of Se\textsuperscript{2-} is much higher than S\textsuperscript{2-}. Due to both the initial concentration difference and the chemical reactivity difference between Cd\textsuperscript{2+}(Se\textsuperscript{2-}) and Zn\textsuperscript{2+}(S\textsuperscript{2-}), the gradient shell is
formed after 5 sec when the concentrations of Cd\(^{2+}\) and Se\(^{2-}\) decreased drastically while the concentrations of Zn\(^{2+}\) and S are still high to form the gradient shell.

Choosing the proper injection and growth temperatures is very important for successful CSQDs synthesis. In order to avoid the shell material nucleation, both injection and growth temperatures were chosen to be below the ZnS nucleation temperature. Finally, controlling the shell thickness is very important and it was the keystone of our study. We controlled the shell thickness by cooling the reaction mixture suddenly after the desired growth time by using an ice bath.

### 4.4 Characterization of type I gradient Cd\(_{1-x}\)Zn\(_x\)Se\(_{1-y}\)S\(_y\) CSQDs:

Most of the basic techniques used to characterize the neat core QDs can be used also for the CSQDs characterization. In the following sections we will present the different techniques used to characterize the gradient CSQDs. Starting with steady-state optical spectroscopy techniques and high resolution transmission electron microscopy (HR-TEM) in order to determine the core size and to estimate the shell thickness for different CSQDs. Then we conducted X-ray based spectroscopies in order to characterize the crystalline and composition such as, X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX).

#### 4.4.1 Core size determination and shell thickness estimation for gradient CSQDs:

The dimensions of our CSQDs (core sizes and shell thickness) were obtained via HR-TEM. The results were verified by the steady-state optical spectroscopies using the known size dependences of the absorption spectra (see figure 4.2 A). The HR-TEM images are show in figure 4.2 B. By careful analysis of the CSQDs HR-TEM images and subtracting the core size (3.0 nm) we determined the shell thickness for different growth time to be 0.6, 1.3, 1.6, 1.9, and 2.3 nm for 1, 3, 5, 10, and 15 min. Figure 4.2 A, presents the steady-state UV-Vis absorption and PL for core (sample (i)) and CSQDs with different thicknesses (ii, iii, and iv for 0.6, 1.3, and 2.3 nm shell thicknesses, respectively). The excitonic peak is well resolved for the core which can be used to estimate the QD size according to the previous reports.\(^{11}\) It revealed the size of 3.0 nm for our core QDs consistent with the TEM observations. Such excitonic peaks
can also be shown in the CSQDs with different shell thicknesses up to \( \sim 1.3 \) nm (see figure 4.2 A, red lines). For QDs with the thickest shell (\( > 1.3 \) nm), there is no pronounced excitonic peak (see figure 4.1 A) due to the carrier confinement reduction by extension of the electron and hole wavefunctions into the shell material.\(^{112}\) For all the samples, the PL spectrum consists of a single band (FWHM < 33 nm) indicating relatively narrow QD size distribution (see figure 4.2 A, black lines).

![Figure 4.2](image)

**Figure 4.2:** A) Steady-state UV-Vis (red lines) and PL (black lines) of the core (i) and CSQDs of different shell thicknesses (ii, iii, and iv for 0.6, 1.3, and 2.3 nm shell thicknesses, respectively), B) HR-TEM for the same samples as A).

### 4.4.2 Structural characterization of gradient CSQDs:

In order to better understand the optical properties of our gradient CSQDs, one needs to get insight into the exact structures of the QDs. Particularly, we have studied the chemical composition and crystalline structures for our QDs with different shell thickness. We employed EDX and synchrotron-based XRD to estimate the composition and the crystal structure. Figure 4.3 A shows the XRD patterns for the neat core and the gradient Cd\(_{1-x}\)Zn\(_x\)Se\(_{1-y}\)S\(_y\) CSQDs of different shell thicknesses. We call the pure CdSe QDs as neat cores, and we use them as references. The neat core is compared to CSQDs with six different shell thicknesses, \( \sim \)“0”, 0.6 1.3, 1.6, 1.9, and 2.3 nm obtained by growth times of 5 s, 1, 3, 5, 10 and 15 min, respectively. For the CSQDs of 5 s growth time, it has intermediate properties between the neat core and the CSQDs with a 0.6 nm shell thickness, therefore we call it “0” nm CSQDs. We also show the XRD spectra of the CdSe and ZnS zinc blende structures. The XRD patterns of our CSQDs were analyzed in terms of these two structures where the core is more
like CdSe phase and the thickest shell is approaching the ZnS phase. The fitting results provide the lattice parameters for both phases, where one lattice constant is close to the core (CdSe) and the other is close to the shell (ZnS) (see figure 4.3 B). A clear decrease in the core unit cell constant as the shell grows up to 1.3 nm is observed. This can be attributed to the compressive strain of the shell on the core. For CSQDs with thicker shell thickness than 1.3 nm, the strain in the core is released. The reason behind this phenomena is not clear, but it may relate to the defect sites which are induced by the growth of the shell.

Figure 4.3: A) XRD patterns of neat core and CSQDs of different shell thicknesses compared to zinc blende CdSe\textsuperscript{113} and ZnS\textsuperscript{114}, B) lattice constants of CdSe core (black) and ZnS shell (red) as a function of the shell thickness, the gray and red areas present the lattice constants of bulk CdSe and ZnS, respectively, and C) EDX average element ratio for different growth time for Cd/(Cd+Zn), dark yellow line and Se/(Se+S), orange line.

EDX spectra were used to evaluate the chemical composition for the different CSQDs (see figure 4.3 C). EDX revealed that due to the difference in chemical reactivity between Cd (Se) precursor and Zn (S) precursor, at the early stage of the reaction (5 sec) Cd-rich (Cd\textsubscript{1.3}Zn\textsubscript{0.7}Se\textsubscript{1.5}S\textsubscript{0.5}) core (small band gap) is formed first, followed
by an alloyed shell over the core. Later the Zn-rich (ZnS) shell (wide band gap) will externally coat the core.²⁰
4.5 Paper VII “Electron injection from gradient Cd$_{1-x}$Zn$_x$Se$_{1-y}$S$_y$ CSQDs to MO”:

The overall device efficiency of a QD-sensitized solar cells is determined by many factors such as light harvesting, charge separation, and charge transport. If one utilizes CSQDs in solar cells, the enhanced photostability and the reduction of charge recombination by surface trapping is expected, but the existence of shell may also hinder the charge transfer process from QDs compared to neat QDs. Thus those effects should be overviewed comprehensively during the evaluation of CSQDs in solar cell applications. In this paper we studied the dependence of both the electron injection and the trap passivation on the shell thickness in gradient Cd$_{1-x}$Zn$_x$Se$_{1-y}$S$_y$ CSQDs/ZnO NPs system. We managed to estimate an optimal condition for the best overall electron collection efficiency.

Figure 4.4: A) TA kinetics of gradient CSQDs of different shell thicknesses (ii, iii, and iv for 0.6, 1.3, and 2.3 nm shell thicknesses, respectively) compared to core QDs (i) (red circles are from experiment and red lines are fitted data for QDs in solution; black circles and black lines represent the experimental and fitted data for QDs attached to ZnO NPs), B) mean decay rate dependence on the shell thickness for QDs in solution (red), QDs attached to ZnO NPs (black), and reported values for step-like CSQDs of the same materials (blue), C) electron injection efficiency and PL QY as a function of shell thickness, and D) energetic scheme for electron tunneling through the shell followed by electron injection to ZnO NPs for step-like CSQDs (upper) and gradient CSQDs (lower).
Photoinduced dynamics in core–shell QDs

TA decay was used to study the electron dynamics in QDs, as we discussed previously. The TA kinetics of unattached CSQDs were fitted using a biexponential function resulting in a minor subnanosecond and a dominant nanosecond components \( A_1 = 20–45\%, \tau_1 = 0.1–0.3 \text{ ns} \); \( A_2 = 55–80\%, \tau_2 = 12–18 \text{ ns} \) (see figure 4.4 A, red lines). The observed multiexponential decay has the same character as previously reported decays of single exciton in CdSe QDs affected by fluctuating rates of nonradiative processes (QDs charging, change in surroundings, etc.).\(^{115–116}\) The decay of neat CSQDs was then compared to the CSQD-MO case. Clearly, the attachment of the QDs to the MO affects the TA decay kinetics due to the electron injection from QDs to MO (see figure 4.4 A, black lines). The experimental data could not be reproduced by a simple multi-exponential function and therefore we employed a stretched-exponential function:

\[
\Delta A(t) = \Delta A(0) \times \exp \left[ -\left( \frac{t}{\tau_{SE}} \right)^B \right], \quad (12)
\]

The function has been previously used to describe the dynamics in disordered nanomaterials and electron injection in QD-MO systems.\(^{117–118}\) Here, \( \tau_{SE} \) is the decay time and \( B \) is the dispersion factor \((0 < B < 1)\) which reflects the disorder degree for the studied system. It should be noted that we use \( B \) instead of commonly used \( \beta \) to avoid confusion with the later used \( \beta \) factor. The thicker the shell, the more the disorder in the system for gradient CSQDs can occur due to different composition and thickness might vary from QD to another. By using the fitting data, we calculated the mean lifetime of the stretched-exponential function:

\[
\langle \tau \rangle_{\text{CSQDs-ZnO}} = \frac{\tau_{SE}}{B} \cdot \Gamma \left( \frac{1}{B} \right), \quad (13)
\]

where \( \Gamma \) stands for the Gamma function.

The calculated \( \langle \tau \rangle_{\text{CSQDs-ZnO}} \) shows a clear dependence on the shell thickness ranging from 6 ps for core to 15 ns for 2.3 shell thickness. Then the electron injection rate was calculated for each shell thickness by comparing \( \langle \tau \rangle_{\text{CSQDs-ZnO}} \) and \( \langle \tau \rangle_{\text{CSQDs}} \) as follows:

\[
k_{ET}(d) = \left( \frac{1}{\langle \tau \rangle_{\text{CSQDs-ZnO}}} \right) - \left( \frac{1}{\langle \tau \rangle_{\text{CSQDs}}} \right), \quad (14)
\]

Due to the uncertainty in stretched-exponential fit, the TA mean decay time of the thickest shell layers becomes slower after the attachment. Therefore, we consider the injection rate for 1.9 and 2.3 nm shell thickness as \( \sim 0 \). In Figure 4.4 B we compare
the mean decay rates as a function of the shell thickness for reported step-like CdSe–ZnS CSQDs\(^\text{110}\) (blue line) and for the gradient Cd\(_{x}Zn_{1-x}Se_{y}S_{1-y}\) CSQDs (black). Both CSQD structures follow the expected exponential dependence eq. 15. This dependence is a result of the distance that electron has to tunnel through the shell in order to be injected to ZnO NPs.

\[
k_{\text{ET}}(d) \propto (e^{-\beta d}), \quad (15)
\]

The typical \(\beta\) values for step-like CSQDs are reported to be 0.33–0.35 Å\(^{-1}\) depending on the shell material.\(^\text{110}\) However, for the gradient CSQDs a larger \(\beta\) value (0.51±0.05 Å\(^{-1}\)) was obtained. In the step-like CSQDs as the shell thickness increases, only the energy barrier width increases (see figure 4.4 D, upper panel). In case of the gradient CSQDs both the barriers’ width and height increase as the shell thickness increase (see figure 4.4 D, lower panel) which explains the stronger shell thickness dependence of the injection rates.

For the solar cell applications, the electron injection efficiency is the important parameter. We can calculate the efficiency based on the experimental data as follows:

\[
\eta_{\text{inj}} = \frac{k_{\text{ET}}}{k_{\text{ET}} + k_{R}}, \quad (16)
\]

Even if the electron injection rate drops quickly with the shell thickness, the electron injection efficiency stays almost unaffected for the shell thickness up to 1.2 nm due to the long recombination lifetimes in QDs (see figure 4.4 C, black line). Moreover we have studied surface passivation of QDs by measuring the PL QY for each shell thickness (unattached QDs). For 1.2 nm shell thickness the PL QY is about two times higher than the core QDs (see figure 4.4 C, blue line). By combining the information about electron injection and surface passivation we obtain the optimal shell thickness \(\sim 1.2\) nm, which acts as a shield around the core against surface degradation and surface trap states, at the same time keeping high electron injection efficiency \(> 80\%\).
4.6 Paper VIII “hole trapping vs. quantum dot sensitized solar cell performance”:

In general, solar cell efficiency depends on the behavior of both photoexcited electrons and holes. In this paper, we confirm the role of the shell thickness in the real CSQDs solar cell device within certain shell thickness range. We prove that this happens by decreasing the surface defect states which acts as hole traps (see paper IV). Moreover, we combined our knowledge about the electron (paper VII) and hole behavior to explain the dependence of solar cell efficiency on QD shell thickness.

Figure 4.5: A) PL decay of MPA-CSQDs with different shell thickness compared to MPA-CdSe QDs up to 1.5 ns, B) PL decay of the early time (up to 75 ps) for the neat core and different CSQDs, C) I-V characteristics for the core CdSe QDs compared to the CSQDs with different shell thickness (all are compared to the dark current, gray area), D) electron collection efficiency (e collection eff., blue line), electron injection efficiency (e Inj. eff., black line, according to ref.120), hole scavenging efficiency (h scavenging eff., red line), and combined efficiency (pink line) as a function of shell thickness, and E) scheme for electron and hole tunneling through the shell followed injection to MO and $S^2-/S_2^2-$ electrolyte, respectively.

Linker exchange is necessary to attach the QDs to the MO. However, the exchange introduces numerous surface defects acting as trapping centers resulting in drastic drop in PL QY for neat core after the linker exchange. We have studied the effect of linker exchange on the CSQDs, where the effect of traps is diminished by the shell
layer. Figures 4.5 A and B represent the PL decay kinetics for CSQDs before attachment to MO. By using the multiexponential function to fit the decay of the studied QDs, we revealed two fast decay components (9–18 ps and ~ 120 ps) for the neat core, “0” nm and 0.6 nm shell thickness samples. These fast components are related to defect states of different origins. Independent of the origin of these traps, the fast components were gradually diminished with increasing the shell thickness and they have been completely vanished by the 1.3 nm thick shell, when the QD’s surface is almost completely passivated.

In order to study the passivation effect on real device performance, we fabricated several sets of solar cell devices. Figure 4.5 C shows the current–voltage (I–V) characteristics of the gradient CSQDs-based devices compared to neat core QDs-based device. The measurements were done under a simulated AM1.0G solar irradiation (light intensity of 100 mW/cm$^2$). The solar cell efficiency increases with QD shell thickness reaching the maximum value at 1.3 nm shell thickness and then starts to decrease. Furthermore, we have evaluated the cells’ performance by calculating the electron collection efficiency (ECE). ECE is the ratio between the extracted electrons out of the device and the number of photons absorbed by the device:

$$\eta_{EC} = \frac{\text{electrons/t}}{\text{absorbed photons/t}},$$

(17)

The electron collection efficiency increases with the shell thickness reaching 6% for 1.3 nm shell thickness. Then for thicker shell the electron collection efficiency decreases again. We can compare the observed values with electron and hole injection efficiencies. For the thin shell thickness the electron injection efficiency (see paper VII) is very high and drops exponentially with increasing the shell thickness as the core/MO distance increase. Consequently, the electron collection efficiency drops with increasing the shell thickness. Thus the low value of $\eta_{EC}$ for the thin shell is related to the hole trapping process.

In order to quantify the hole collection efficiency we have assumed that the radiative dipole of the excited electron–hole pair where the hole is trapped is negligible. We managed to quantify also the hole collection efficiency (untrapped holes). These untrapped holes can be efficiently scavenged by the electrolyte, thereby $\eta_h$ is the hole collection efficiency. We quantify $\eta_h$ by evaluating the proportion of the untrapped holes as a ratio of the PL intensity at the 1.5 ns delay and PL amplitude in the PL dynamics in Figure 4.5 D as follows:
\[ \eta_h = \frac{I_{t=1.5\ ns} - I_{\text{prezero}}}{I_{t=0} - I_{\text{prezero}}}, \]  

where, \( I_{t=1.5\ ns} \) is the PL intensity at 1.5 ns, \( I_{t=0} \) is the PL amplitude, and \( I_{\text{prezero}} \) is the intensity before time zero which is due to long PL lifetime (~ tens of ns) compare to the time window. The time 1.5 ns was chosen as a delay long enough to allow complete hole trapping yet fast enough that exciton recombination does not play a prominent role. Total charge collection efficiency is the product of electron and hole injection efficiencies. It agrees very well with the charge collection efficiency obtained from real solar cell performance measurements (see figure 4.5 D pink line).

Figure 4.5 D summarizes the photodynamics of the gradient CSQDs in real solar cell device. Here, the neat CdSe QDs without any shell protection feature high electron injection efficiency (~100%), while most of the holes (> 80%) cannot be collected due to the hole trapping process. Thus, the trapped holes are not able to be injected to the electrolyte probably due to insufficient driving force. Passivation of the hole traps using core–shell structures provides an efficient way to enhance the hole collection. However, shell is also an energy barrier preventing the electron/hole transfer from the core. Fortunately, Cd\(_{1-x}\)Zn\(_x\)Se\(_{1-y}\)S\(_y\) CSQDs with shell thickness up to 1.3 nm can offer electron injection efficiency up to 80% and at the same time an efficient passivation for the hole traps. Also, based on the charge carrier photodynamics we calculated the charge carrier (electron and hole) injection efficiency and used these efficiencies to predict the charge collection efficiency. The result is in good agreement with the obtained values (see figure 4.5 D pink line). Figure 4.5 E illustrates the 1.3 nm shell thickness device with efficient electron and hole injection.
Chapter 5: Conclusions and future work

5.1 Conclusions:

We believe that an important way to improve the application of QDs in solar cell fields, is to understand the photoinduced dynamics in such systems. The thesis presents the fundamental science of the ultrafast photoinduced dynamics in CdSe QDs and gradient Cd$_{1-x}$Zn$_x$S$_{1-y}$S$_y$ CSQDs. We covered, almost all, the possible carrier’s dynamics (electron injection, hole trapping/injection, and exciton migration) in these QDs between the folds of this thesis.

We observed directly, by using the combination of time-resolved absorption and THz spectroscopy, the ultrafast electron injection from neat CdSe QDs to the n-type MO namely, ZnO NWs. We proved that the electron injection-driving force dependence can be described by the well-known Marcus theory for charge transfer. Such ultrafast electron injection process encouraged us to study the multiple electron injection under high excitation intensity condition. Multiple electron transfer is a prerequisite for successful utilization of multiple exciton generation for photovoltaics. We observed a competition between the electron injection process and AugR (multiexcitons quenching) process under these conditions. Indeed, we found that the second electron injection is possible, however the multiple exciton harvesting can be efficient only within a narrow range of QD sizes for the CdSe-MPA/ZnO NWs system.

Defect and/or surface states play an important role in the charge collection in QDs solar cells. We determined the lifetime of the deep trapped holes for OA capped-CdSe QDs to be around few tens of microsecond at room temperature. Moreover, we revealed that at least two different types of surface states (traps) contribute to the surface PL. Excitons with energy higher than the band gap have higher chance to get trapped by surface states than the band gap excitons. When utilizing QDs in p-type solar cells, we managed to distinguish between the hole trapping and hole injection processes in QDs/NiO mesoporous film system. We found that the hole trapping process is more dominant especially after linker exchange process. Passivating of the hole trap states using core–shell structure is found to enhance the hole injection efficiency from < 10%
Conclusions and future work

to 50%. Similar to electron injection process, hole injection from CdSe QDs to NiO followed the Marcus theory for charge transfer.

Besides the charge transfer, exciton migration may also occur in QD solar cell system. Understanding the Förster resonance energy transfer (FRET) in QDs system is therefore of fundamental and technological significance. In conventional QDs-sensitized solar cell structures, we found the energy transfer between QDs in QD-MPA/ZnO NWs system is ~ 5 ns. We also studied the FRET in densely packed multi-sized CdSe QDs films. We revealed that point–dipole approximation for FRET is insufficient in this case. We suggested to use a model taking into account the distribution of the electronic transition densities in the QDs and using the real film morphology (center-to-center distance) revealed by AFM images. By taking these two aspects into account we were able to fully describe the FRET kinetics in our system.

Conventional neat core QDs usually suffer from surface defects as charge traps in solar cell application. This can be well solved by using core-shell structure to passivate the surface traps and reduce charge recombination. Here we investigate the photodynamic of gradient Cd\textsubscript{1-x}Zn\textsubscript{x}Se\textsubscript{1-y}S\textsubscript{y} core–shell QDs in solar cells. Growing the shell in the gradient way reduces the interfacial defects and also the unwanted AugR compared with step-like counterparts. In this context, we were interested to study the electron photoinduced injection from the gradient Cd\textsubscript{1-x}Zn\textsubscript{x}Se\textsubscript{1-y}S\textsubscript{y} CSQDs to n-type ZnO NPs. We observed the typical exponential injection rate dependence on the shell thickness (\(\beta = 0.51\ang^{-1}\)). Compared to step-like CSQDs (\(\beta = 0.35\ang^{-1}\)), gradient CSQDs have stronger electron injection rate dependence on the shell thickness. We attributed this enhanced dependence to the gradient feature where both the barriers’ width and height change as the shell thickness increase. Although the shell materials always serve as barriers against the charge injection, we found that ~ 1.2 nm shell thickness still offers ~ 80% electron injection efficiency from the CSQDs to ZnO NPs and at the same time keeps high PL QY (~ 70%) which reflects high surface passivation.

Combining our findings regarding the hole trapping process and the performance of CSQDs-based solar cells, both in respect to the shell thickness. We found that the hole traps are almost diminished for ~1.3 nm shell thickness. As a results, solar cell based on the CSQDs exhibits efficiency 2.5 times higher than neat core CdSe QDs-based device. Finally, we managed to predict the solar cell device performance based on both electron and hole injection dynamics. Such way to predict the device performance provides
opportunity to optimize the core–shell QD materials for photovoltaics prior to making real device.

5.2 Future work:

In the last few years, the limiting factors in QDSCs have been more clear thanks to the understanding of charge transfer processes. In the following paragraph we will overview some of these factors in order to draw the possibility of future work for the QDs solar cell applications.

First of all, based on our findings in this thesis, we revealed that establishing core–shell structure is indispensable to diminish the hole trapping sites which are the main restriction to the hole transfer efficiency. Therefore, study the hole dynamics, especially the injection through the gradient shell will add more important information to complete the full picture about charge transfer in the CSQDs system.

Secondly, better understandings for the QDs crystal structure and the way it correlates to the electronic and the optical properties of CSQDs materials are needed. This open the door to modify and optimize these materials not only in solar cell applications but also in other applications such as light-emitting-diodes.

Thirdly, as for board interests in the community, engineering the CSQDs structures to optimize the light harvesting and charge separation is needed.

Last but not least, another important building block in QDSCs: the electrolyte also need to be noticed. Better understanding of the charge transfer and recombination dynamics in both liquid and solid electron/hole transfer materials would be meaningful to boost the device efficiency.
Svensk sammanfattning


Jämfört med elektroner så har fotoinducerade hål större sannolikhet att fängas. Men sådana typer av fälltillstånd kan ibland vara radiativa med långa livstider, upp till några

Fotodynamiken hos dessa CS-kvantprickar i fotovoltaiska system studerades också. Vi trodde först att elektroninjektionen från den aktiva kärnan till MO av n-typ visade relativt stort exponentiellt beroende av tjockleken på skalet jämfört med stegvisa kärn–skalkvantprickar. Vi fastställde att det högsta elektroninjektionutbytet (~80 %) kan uppnås när skalet har en tjocklek upp till 1,3 nm. Ett sådant skal tillåter också hög ytpassivering vilket ger optimala förhållanden för laddningsuppsamling i solceller. Till slut integrerade vi vår kunskap om beteendet av elektroner och hål för att förklara solcellsprestanda enligt kärn–skalstrukturen. Vi bekräftade att hälfällor är den kritiska
faktorn för verkningsgraden hos solceller gjorda av kvantprickar. Fällornas påverkan kan gottgöras väl genom att använda optimala kärn–skalstrukturen.
إن استهلاك العالم للطاقة في زيادة مستمرة وقد أصبح البديل عن بعض مصادر أخرى للطاقة لا غنى عنه ويُمثل الحقيل المطلوب للعديد من الدول والمشروعا. تُمثل مصادر الطاقة المتاحة مصدراً أمراً البديل للوقود الحديدي الذي يُعتبر عامل زائر للعديد من الدول في إعادة استخدام الطاقة. من بين العديد من مصادر الطاقة المتاحة تُمثل الطاقة الشمسية المصدر الأهم وحالة من حيث مما تابعة ومهما. قد تؤدي العلاقة بديلاً مما أن فقط 1% من الطاقة الشمسية القادمة إلى سطح الأرض تُشير لاستهلاك العالم هذا ما يُعنى إلى بنيان أو وقود.

تُعتبر الطاقة الشمسية الأداة الأساسية التي يُمكننا أن نجد الطاقة الشمسية إلى شعاعية من خلال دعم فوتوبراد الطاقة الصناعية وتوسيع نطاقاتها العديدة التي يدورها يمكن تقليدها إلى الإنتاجات المختلفة عمولة الطاقة الصناعية. وعلى ذلك فإن ضعف الطاقة الشمسية بأمر من جمل ملء المحال بين الصحراء والشغاب، يأتي الجيل الأول للطاقة الشمسية على إعادة استخدام السامويون تُستخدم للنمو وتحقيق هذا الجيل على شعاعية كنتي الآن ومنها على مساحة النقل، أما في الجيل الثاني من الطاقة الشمسية فقد تم استخدام مواد رئيسيه الثم مثل السامويون الغير متعدد. حيث الطاقة الجيل الثاني شعاعية متأصلة معاً أحيى إلى اليد عن مواد مستقلة رئيسيه الثم وهي نفس الوقعة لما شعاعية عالية في امتصاص الطاقة الصناعية. وبناءً على هذا يستخدم الجيل الثالث من الطاقة الشمسية.

هناك العديد من المواد التي استخدم في الجيل الثاني من الطاقة الشمسية من أبرزها أجهزة الرياح النانومتري (الموجودة محدود وحجم من 8-10 نانومتر) وتمييز الشواط من خلال مادة متعددة من الكيماويات في مجال الطاقة الشمسية من أهم هذه المركبات، معالج يتم إنتاجها على حجم ما يمكننا طية في منطقة امتصاصاً للنمو على النقل الطيفي - المهدية على توليد أكبر من حامل للشغاب (زوج من إلكترونات -إلكترون) من فوتوبرادي ذو دائماً طاقة عالية. يعد مسار شعلن من إلكترونات ويرفع بعد امتصاص الفوتوبرادي لاعباً ماماً جداً في تحديد شعاعية الجليد الشمسية، وعليه فإن دراسة مسار هذه الشعاعية يعتبر أهم الفرق ليس في مصدر شعاعية الكليا الشمسية القائمة على هذه المواد.

في هذه الدراسة تم دراسة تفاعلية عناً من إلكترونات وفوقية تقنية أتمتص الطاقة ل_objs لقياس درجة الشعاعية الشمسية القائمة على هذه المواد. لقد تم التوقيع إلى أن انتقال البلاشفة من المواد مع الابتعاد إلى مسؤولية إلكترونيات في هذه المادة ينacle في بعض من البلاشفات. هذه العملية مهيئة السرجة فتحت الباب لدراسة إمكانيات استغلال أنظمة الطاقة الشمسية في إطار استهلاك فوتوبراد.
الملخص العربي
حذاء طاقة عالية جداً. أظهرت هذه الدراسة على أن هناك مismatch بين انتقال الإلكترونات الثاني وما يعرف بإتحاد أوبر (Auger Recombination).

وعادة ما يُعتبر أن العوامل المساهمة في هذا الانتقال بين الإلكترون والفجوة من النوعين مع الملوث في مجال فعالة بالبنية المادية. بحيث يتم دراسة هذا الفعل باستخدام أداة ما تعرف بـ "أوهاي" أو "أوهاي" أو "أوهاي".

تقوم على سلسلة الشوائب سلسلة. تشمل ذلك العوامل شملة لل المهنيين وفقاً وديناً ونوداً فاقداً شملة للتقدير في هذا المصدر، الشوائب طويلة جداً (الاعدادات من الميكروشل). ويعد دراسة ديناميكية إتقال الفجوة من الشوائب سلسلة إلى مستقبل الفجوة (NiO). وتساوى إلى أن هناك تتاح فوعاً عملية إتقال الفجوة في سلسلة السطح والنقلية إتقالاً إلى المستقبل. وفقاً أن تقليل عدد هذه الشوائب على سلسلة الشوائب، تجولة نظامية إتقال الفجوة من الشوائب سلسلة إلى المستقبل من 10 إلى 50% من الطرق المعروفة لتقليل عدد الشوائب على سلسلة الشوائب، استعادة غشاء من شبة موصل (Core–shell quantum dots).

هذا هو عبارة عن نوع من الإلكترون – الفجوة قبل الإلكترون وهو exciton وهو عبارة عن نوع من الشوائب – الفجوة في سلسلة الإلكترون وهو نموذجة طويلة ومستقلة من الشوائب.

أظهرت الطرق المفيدة لزيادة إتقال الفحاء هو شكل ذو موصل أو (Core–shell quantum dots). كما يمكن استخدام الطرق المفيدة لزيادة إتقال الفحاء هو شكل ذو موصل أو (Interfacial defects) (Shell thickness).

ويمكن أن يكون من الممكن تحويل الشوائب الشمسي إلى سلسلة الشوائب، من النوعين باستخدام الشوائب، بفعل التحام الفجوة (ZnO Nanoparticles) من النوعين باستخدام الشوائب (Gradient core–shell quantum dots) على إتقال الإلكترون من الشوائب إلى المستقبل (Shell thickness) ودراسة تأثير سلسلة الشوائب. هذه الشوائب إلى المستقبل الشمسي، ومع السلاسل التي لا تتأثر على سلسلة إتقال الإلكترونات، في نفس الوقت توفر إتقال عالية من عوامل السطح (مساعد الشгоائدة).

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فمنا أيضاً بدراسة انتقال الغطاء من الشواطئ حدود (Gradient core–shell quantum dots) ودراسة تأثير سماكة الغطاء على انتقال الغليان. تم التوصل إلى أن انتقال الغليان لا يعتمد بصورة مباشرة على سماكة الغطاء. أجرى فمنا بدراسة تأثير سماكة الغطاء على كفاءة الغليان الخمسية. تم التوصل إلى أنه عند سماكة حوالي 1.3 نانومتر تم تسجيل أعلى كفاءة (2.5 مرة أعلى من الكليه بدون أي غطاء). في نفس السياق تم محاولة الثقاب المتوقعة لقلل سماكة من خلال دراسة حيوية مختلفة من الأنتونوات والغليان.
References

8. QD Image by using Mercury softwear.


References


