Ultrafast photoexcitation dynamics of low dimensional PbSe nanostructures

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NANYANG
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Nanostructures**

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School of Physical & Mathematical Sciences

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Abstract

Multiple exciton generation (MEG) in PbSe quantum dots (QDs) opens up new opportunities to improve solar cell efficiency beyond the Shockley-Queisser limit. Despite the demonstration of efficient MEG efficiency in PbSe QDs, power conversion efficiency of PbSe QDs solar cells remains low. One of the limitations to the concept of MEG solar cells is that after MEG, excitons recombine very fast via Auger recombination and unavailable to extract at the electrodes. So far charge extraction is limiting the advantages of MEG in solar cells. Auger recombination time is proportional to the volume of the nanostructures.

Therefore, Auger recombination rate should be low in elongated nanostructures such as nanowires (NWs, 1D) and nanosheets (NSs, 2D). Efficient MEG can be achieved along the confined directions of 1D and 2D nanostructures and charges can move along the elongated direction. To optimize the quantization, Auger recombination, charge extraction and transport properties of nanodevices, a detailed understanding of photoexcitation dynamics of carriers on the femtosecond scale is needed.

In this work, photoexcitation dynamics of low dimensional PbSe nanostructures are explored by studying the transient absorption (TA) spectra and dynamics. We investigated MEG QY and the origin of the photon energy threshold for MEG in PbSe QDs. The comparison of visible TA spectra and dynamics for different pump wavelengths, below, close and above MEG threshold provides unambiguous evidence of the role of the Σ transition in slowing down the exciton cooling process, which allows MEG taking over the phonon relaxation process. Moreover, we infer that the MEG QY could be measured directly from the visible TA spectra.

Quantum confined PbSe NWs of bandgap 0.72 eV was synthesized. In addition, two more optical transitions are observed in the absorption spectra. These three optical transitions are also predicted by the density function theory (DFT) calculations. TA spectra and dynamics were measured with excitation wavelength of 800 nm. Dispersive TA spectra of PbSe NWs were observed at short pump-probe delays (within 1 ps) due to the extended length of the NWs. After 3 ps, dispersive TA spectra changes to absorptive TA spectra and shows the optical transitions. Anisotropy was also observed in the photoexcitation dynamics of PbSe NWs, which is explained classically by the dielectric mismatch and long aspect ratio of NWs.

To our best knowledge, this is the first report for the synthesis of quantum confined PbSe NSs. Quantum confined PbSe NSs of bandgap 0.64 eV were synthesized using the microwave-assisted technique. In addition one more optical transition is observed in the absorption spectra. These two transitions are also predicted by DFT calculations. TA spectra of PbSe NSs were measured with a pump wavelength of 800 nm and probe wavelength range from 950 nm to 1500 nm. At low pump fluence, TA spectra were dominated by the photo-bleaching of the second transition. However, at high pump fluence, TA spectra were dominated by the nonlinear absorption of the excitons. Anisotropy is also observed in PbSe NSs which is the combined effect of intrinsic and extrinsic anisotropies.

In conclusions, we propose that ordered PbSe NWs and NSs architectures can be employed to design MEG solar cells for effective carrier extraction along preferential axis to improve the solar cell efficiency. PbSe NWs and NSs can also be used as large-scale nanodevices like single NW and NS FET. The nonlinear properties of PbSe NSs can be used in pulse shaping of the laser beam, ultrafast switch, high power IR sensor and IR eye protector etc.

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List of abbreviations

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
ΔA	Change of absorption
ΔR	Change of reflection
ΔT	Change of transmission
AFM	Atomic force microscope
BBO	Beta barium borate
CCD	Charge coupled device
CM	Charge multiplication
DFT	Density function theory
E_g	Bandgap
ESA	Excited state absorption
FET	Field-effect transistor
fs	Femtosecond
HRTEM	Highly resolved transmission microscope
IPA	Isopropyl alcohol/ Isopropanol
IR	Infrared
LED	Light emitting diode
LO	Lead oleate

MEG	Multiple exciton generation
MIR	Mid-infrared
ND	Neutral density
NIR	Near-infrared
NR	Nanorod
ns	Nanosecond
NS	Nanosheet
NW	Nanowire
OL	Optical limiting
OPA	Optical parametric amplifier
PCE	Power conversion efficiency
PDA	Photo-diode array
ps	Picosecond
QD	Quantum dot
QY	Quantum yield
RSA	Reverse saturation absorption
SEM	Scanning electron microscope
SH	Second harmonic
TA	Transient absorption
TDPA	Tetradecyl phosphonic acid
TEM	Transmission electron microscope
TH	Third harmonic
TMDC	Transition metal dichalcogenides

TOP

Trioctylphosphine

TOPSe

Trioctylphosphine selenide

WLC

White light continuum

XRD

X-ray diffraction

YAG

Yttrium aluminum garnet

Chapter 1: Introduction

Fundamental properties such as bandgap and carrier transport of semiconducting materials change when at least one dimension is smaller than the exciton Bohr radius of the bulk material. Therefore, a wide range of research is focused on the fabrication, design and characterization of zero-dimensional (0D, quantum dots), one-dimensional (1D, nanowires) and two-dimensional (2D, nanosheets/quantum well) nanostructures. Due to rigorous efforts in this field, novel materials and phenomena such as multiple exciton generation (MEG),^{1, 6} large absorption cross-section^{7, 8} and reduced electron-phonon relaxation rate at nanometer size are discovered.^{5, 9} Therefore, significant efforts have been dedicated to studying nanomaterials and nanostructures in last few decades, which led to a number of exciting applications such as solar cells,¹⁰⁻¹² nanophotonics,^{3, 13} nanoelectronics,^{14, 15} nanolaser,^{3, 16} thermoelectrics,^{17, 18} cancer therapy,^{19, 20} chemical and biological sensing.²¹

To optimize the properties of nanodevices like the speed of commercial application and power consumption, a detailed understanding of photoexcitation dynamics of carriers on the femtosecond (fs) scale is needed, e.g. charge separation at the nanoscale interface competing with charge recombination, thermal relaxation, energy transfer, play a crucial role in determination of the overall device performance. After photoexcitation, carrier cooling takes place within a picosecond (ps) followed by carrier transport on ps to nanosecond (ns) time scale.²² In addition, carrier transport along and perpendicular to the axis of anisotropic nanodevice is not the same and helps optimizing nanodevice for thermoelectric¹⁷ and optoelectronic applications.^{23, 24} Therefore, photoexcitation dynamics of carriers in the nanostructures is interesting to understand the fundamental properties and their deviation from

the bulk materials. In order to understand the carrier dynamics in semiconducting nanostructures, several questions have to be addressed.

- i. How does carrier confinement in 0D, 1D, and 2D affect the ultrafast carrier dynamics?
- ii. How do carriers lose their spin and electronic energies in the confined energy levels?
- iii. How fast do carriers transfer from one energy level to another energy level?
- iv. What are the relaxation pathways after photoexcitation?²⁵

To answers all these questions an experimental technique, which is capable of measuring the response of carriers in broad energy range on fs time scale should be applied.

All these requirements can be accomplished by femtosecond transient absorption (TA) spectroscopy (pump-probe spectroscopy), which is capable of measuring with time resolution of 100 fs and a broad range of excitation photon (pump) energy and scanning energy (probe). Therefore, TA spectroscopy attracts much attention to study the photoexcitation dynamics of the carrier in nanostructures, for understanding the fundamental properties of nanostructures.

1.1. Motivation

Most of the photoexcitation dynamics are studied in III-IV and II-VI semiconductors with wurtzite or zinc blende structures. However, IV-VI semiconductor nanostructures, especially PbSe nanostructures with cubic rock salt crystal structure have received much attention recently. Bohr radius (46 nm) is rather large in PbSe, which results in strong quantum confinement in relatively large nanostructures.²⁶ PbSe has small and almost equal electron and hole effective mass ($\sim 0.1m_e$).²⁷ Moreover, it has small and narrow bandgap (0.28 eV) at L-point of the Brillion zone.⁴ Due to the strong quantum confinement, the bandgap of PbSe nanostructures can be tuned

from mid-infrared (MIR) to near infrared (NIR).^{4, 28-30} In addition, due to the large dielectric constant ($\epsilon_{\infty} = 23$),^{31, 32} asymmetric nanostructures show anisotropy.³³

PbSe quantum dots (QDs, 0D) are widely explored as materials for solar cells,^{34, 35} infrared (IR) lasers,^{36, 37} and photodiodes^{38, 39} applications. Especially, PbSe QDs solar cells have shown peak external photocurrent quantum efficiency of more than 100% via MEG.⁴⁰ Efficient MEG has been observed in PbSe QDs.⁴¹⁻⁴⁸ However, there is still an on-going debate about the parameters influencing the MEG quantum yield (QY).⁴⁹

Conversely, PbSe NWs, are not explored widely. Quantum confinement in PbSe NWs has been explored both experimentally⁵⁰ and theoretically.^{51, 52} High MEG QY has been detected in PbSe nanorods (NRs) compared to spherical QDs.⁵³⁻⁵⁵ However, the ultrafast carrier dynamics in the PbSe NWs has not yet been studied.

To the best of our knowledge, no one has reported the synthesis of quantum confined PbSe NSs yet. However, limited available theoretical studies have provided the information about optical transitions in PbSe NSs.^{32, 56}

In this work, we are exploring and presenting the synthesis and detailed study of the photoexcitation dynamics of carriers in the PbSe nanocrystals with different dimensionality, namely QDs, NWs and NSs.

1.2. Quantization effects on optoelectronic, anisotropic properties and multiple exciton generation in low dimensional nanostructures

In order to understand the effect of quantum confinement on the nanomaterial properties, it is first necessary to study the optoelectronic properties of bulk semiconductors. Solid state properties of bulk semiconductors were explained by Sommerfeld.⁵⁷ He assumed potential

energy of electrons is constant inside the crystal and the interaction between atomic core and electrons is negligible.^{57, 58} However, in ideal crystals ions are distributed periodically and affect the electronic dispersion relations. Therefore, electrons can be found in potential $V(\mathbf{r})$ with the periodicity $\mathbf{L}$ inside the crystal and thus $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{L})$ can be presented. According to the Bloch theorem, wave function of the periodic potential can be written as the product of the plane wave ($e^{i\mathbf{k}\cdot\mathbf{r}}$) and the periodicity of the Bravais lattice $u_{\mathbf{k}}(\mathbf{r})$.⁵⁷ This problem can be solved easily by considering electrons in a box of side L . The wave function of the free electron in the crystal lattice can be defined as shown in equation 1.1.

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{(i\mathbf{k}\cdot\mathbf{r})} = \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{L}) \quad (1.1)$$

$$\text{Where } u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{L}) \quad (1.2)$$

$$\text{and } k = \pm \frac{2n\pi}{L} \quad (1.3)$$

where n is an integer.

$$\text{Free electron energy, } E = \frac{\hbar^2 k^2}{2m} \quad (1.4)$$

Where m is the mass of the electron, $\hbar = \frac{h}{2\pi}$ and h is the Planck constant.

By applying the periodic potential in the crystal structures, the dispersion relation of electrons is changed. When the wavelength of traveling electron is much higher than the lattice constant then it is not affected by the periodic potential. However, the electron is influenced by the periodic potential when the wavelength of traveling electron is shorter than the lattice constant.

k-Space can be considered as a sphere of radius k . For simplicity, 2-dimensional k-space is shown in figure 1.1. Every k-point in the k-space has two electrons of opposite spins. These states start to fill with the electron of lowest energy or small k value electron. The highest energy of the levels is called the Fermi energy E_F and the corresponding radius of the sphere is k_F , which separates unoccupied and occupied levels. The volume of one state is $(2\pi/L)^3$ in k-space. A number of electrons (N) inside a sphere of radius k are given by equation 1.5.

$$N = 2 \cdot \frac{\text{volume of the sphere of radius } k}{\text{volume of the one state}} \quad (1.5)$$

Figure 1.1: Two dimensional projection of 3D k-space.

$$N = 2 \cdot \left(\frac{\frac{4}{3} \pi k^3}{\left(\frac{2\pi}{L} \right)^3} \right) = \frac{V}{3\pi^2} k^3 \quad (1.6)$$

where V is the volume of the box.

A number of states per energy unit ($D(E)$) can be calculated using equation 1.7.

$$D(E) = \frac{dN}{dE} \quad (1.7)$$

Therefore for bulk material, where electrons are moving free in all three directions, a number of states ($D^{3D}(E)$) can be calculated using equations 1.4, 1.6 and 1.7.

$$D^{3D}(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} \quad (1.8)$$

And the density of states (ρ^{3D}) of bulk material is given by $D^{3D}(E)/V$.

$$\rho^{3D}(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} \quad (1.9)$$

Figure 1.2: Band structure of bulk PbSe.⁴

The electronic band structure of bulk PbSe rock-salt lattice is shown in figure 1.2. Both of the conduction band minimum (CBM) and valence band maximum (VBM) are situated at the L

point in the Brillouin zone, which is fourfold degenerate (eightfold including spin degeneracy).⁴ The energy difference between CBM and VBM (0.28 eV) is the direct band gap of the bulk PbSe.⁴ Second extreme point at the Σ point in the Brillouin zone with energy difference of 1.55 eV is the second band gap and called Σ point or Σ transition.^{4, 32} Another extreme at Δ point in the Brillouin zone with energy difference of around 2 eV is also observed.^{4, 9, 32}

1.2.1. Quantization effects on optoelectronic properties

In 2D nanostructures/NSs, electrons are confined in one direction (x) and free in other two directions (y, z). Therefore, the wave function of the electrons in 2D system can be written as the product of the confined electron wave function($\psi(x)$)and the free electron wave function ($\varphi(y, z)$).

$$\Psi_k(x, y, z) = \psi(x)\varphi(y, z) \quad (1.10)$$

$$\Psi_k(x, y, z) = \sqrt{\frac{2}{L_x}} \cos\left(\frac{n_x \pi x}{L_x}\right) \varphi(y, z) \quad (1.11)$$

Where, n_x is an integer and $k_x = \frac{n_x \pi}{L_x}$ at the boundary. After solving the Schrodinger equation with zero potential energy, the discrete energy of the electron is presented in equation 1.12.

$$E_{n_x} = \frac{\hbar^2 \pi^2}{2m} \frac{n_x^2}{L_x^2} \quad (1.12)$$

$$\text{and } \varphi(y, z) = \sqrt{\frac{4}{L_y L_z}} e^{i(k_y y + k_z z)} \quad (1.13)$$

$$k_y = \frac{2n_y\pi}{L_y} \text{ and } k_z = \frac{2n_z\pi}{L_z} \quad (1.14)$$

where n_y and n_z are integers.

The total energy of the electron (E) is the sum of the energies of the confined electron and the free electron.

$$E = \frac{\hbar^2\pi^2}{2m} \frac{n_x^2}{L_x^2} + \frac{\hbar^2}{2m} [k_y^2 + k_z^2] \quad (1.15)$$

Electrons are free in a circle of radius k in k-space and can be calculated using equation 1.16.

$$N = 2 \cdot \frac{\text{area of the sphere of radius } k}{\text{area of the one state}} \quad (1.16)$$

$$\text{and } \rho^{2D}(E) = \frac{m}{\hbar^2\pi} \quad (1.17)$$

The density of states in 2D nanostructures is energy independent. However, $\rho^{2D}(E)$ depends on the sum of the quantized energy levels.

$$\text{Therefore, } \rho^{2D}(E) = \frac{m}{\hbar^2\pi} H(E - E_c) \quad (1.18)$$

Where, $H(E-E_c)$ is a step function and E_c is the conduction band minima of the quantized energy levels.

In 1D nanostructures/NWs, electrons are confined in two directions (x, y) and free in one direction (z). Therefore, the wave function of the electrons in 1D system can be written as shown in equation 1.19.

$$\Psi_k(x, y, z) = \sqrt{\frac{4}{L_x L_y}} \cos\left(\frac{n_x \pi x}{L_x}\right) \cos\left(\frac{n_y \pi y}{L_y}\right) \phi(z) \quad (1.19)$$

Where, n_x, n_y are integers and $k_x = \frac{n_x \pi}{L_x}$, $k_y = \frac{n_y \pi}{L_y}$ at the boundary. After solving the Schrodinger equation with potential energy 0, discrete energies of electrons are shown in equation 1.20.

$$E_{n_x} = \frac{\hbar^2 \pi^2}{2m} \frac{n_x^2}{L_x^2} \text{ and } E_{n_y} = \frac{\hbar^2 \pi^2}{2m} \frac{n_y^2}{L_y^2} \quad (1.20)$$

$$\text{and } \phi(z) = \sqrt{\frac{2}{L_z}} e^{ik_z z} \quad (1.21)$$

Where $k_z = \frac{2n_z \pi}{L_z}$ and n_z is an integer.

$$\text{Total energy of electrons, } E = \frac{\hbar^2 \pi^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right] + \frac{\hbar^2 k_z^2}{2m} \quad (1.22)$$

$$\text{Density of states in 1D nanostructures, } \rho^{1D}(E) = \frac{1}{\pi \hbar} \left(\frac{m}{2} \right)^{\frac{1}{2}} E^{-\frac{1}{2}} \quad (1.23)$$

In 0D nanostructures/QDs, electrons are confined in all three directions. Total discrete energy (E) of electrons is presented in equation 1.24.

$$E = \frac{\hbar^2 \pi^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \quad (1.24)$$

$$\text{Density of states, } \rho^{0D}(E) = 2 \sum_{n_x n_y n_z} \delta(E - E_c) \quad (1.25)$$

Where δ is the Dirac delta function and E_c is the minimum of the conduction band.

If E_g is the fundamental bandgap of the material then transition energies in quantum confined nanostructures can be defined as shown below.

Transition energies of NSs (2D),

$$E^{NS} = E_g + \frac{\hbar^2 \pi^2}{2m} \frac{n_x^2}{L_x^2} \quad (1.26)$$

Transition energies of NWs (1D),

$$E^{NW} = E_g + \frac{\hbar^2 \pi^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right] \quad (1.27)$$

Transition energies of QDs (0D),

$$E^{QD} = E_g + \frac{\hbar^2 \pi^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \quad (1.28)$$

First transition energy of nanostructures is considered as the bandgap of the nanostructure.

Therefore, it is clear from above equations when the size of nanostructures is reduced, the bandgap is increased. For a given size of nanostructures, bandgap increases with decreasing the dimensionality (3D-0D) of the nanostructures as shown in equation 1.29.

$$E_g < E_g^{NS} < E_g^{NW} < E_g^{QD} \quad (1.29)$$

where E_g^{NS} , E_g^{NW} and E_g^{QD} are the bandgap of the NSs, NWs and QDs respectively.

Due to the absence of density of states below the bandgap, the density of states can be expressed as shown below.

Figure 1.3: Density of states in bulk (3D, blue), nanosheets (2D, red), nanowires (1D, green) and quantum dots (0D, black).²

$$\rho^{3D}(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} (E - E_g)^{\frac{1}{2}} \quad (1.30)$$

$$\rho^{2D}(E) = \frac{m}{\hbar^2 \pi} H(E - E_g^{NS}) \quad (1.31)$$

$$\rho^{1D}(E) = \frac{1}{\pi \hbar} \left(\frac{m}{2} \right)^{\frac{1}{2}} (E - E_g^{NW})^{-\frac{1}{2}} \quad (1.32)$$

$$\rho^{0D}(E) = 2 \sum_{n_x n_y n_z} \delta(E - E_g^{QD}) \quad (1.33)$$

The density of states are continuous in bulk, steps in NS, like saw tooth in NW and sharp lines in QD, as shown in figure 1.3.

Figure 1.4: Absorption spectra of PbSe NSs (red), NWs (green) and QDs (black).

From the above discussion, we can observe the relative quantization effects on nanostructures; however real quantization effect on a particular nanostructure is complex due to the several other effects like Coulomb interaction, atomic interaction and crystal structure etc.

Experimentally measured absorption spectra of PbSe NSs (thickness 4.3 nm), NWs (diameter 4.7 nm) and QDs (4.3 nm) of similar thickness/diameter are shown in figure 1.4. Bandgap of PbSe bulk is 0.28 eV.⁵⁹ Bandgap of PbSe NSs, NWs, and QDs are 0.64 eV, 0.72 eV and 0.95 eV respectively. Therefore, for a given diameter/thickness, the bandgap of nanostructures increases with decreasing the dimensionality of the nanostructures (from 3D-0D), shown by equation 1.29 and figure 1.4.

1.2.2. Auger recombination

In Auger recombination, electron and hole recombine nonradiatively and transferred this energy to the third carrier (electron or hole), which is further excited to the higher energy state as shown in figure 1.5 (a).^{60, 61} Auger recombination rate is higher in QDs in comparison to the bulk semiconductors. This has been recognized to the strong Coulomb interactions in QDs, as well as to the relaxation of the momentum conservation rule. The Auger recombination rate in QDs is much faster than radiative recombination. In PbSe QDs, it is around 100 ps while the radiative recombination is on the microsecond scale. Fast Auger recombination is one of the signatures of the presence of multiple excitons and is used in experiments to determine MEG efficiencies. Chapter 3 deals with the measurements of MEG efficiency in PbSe QDs.

In semiconductors, mainly two types of the Auger process occur, namely interband and intraband Auger process. In interband Auger process, an electron transfer from the conduction band to the valence band and transfer its energy to another electron in the conduction band

(radiation-less interband transition). This electron moves to the higher energy level (figure 1.5 (a)). However, in intraband Auger process, electron transfer from higher conduction band energy level to the lower conduction band energy level (radiationless intraband transition) and transfer its energy to the another electron in the conduction band. As a result, this electron moves to the higher energy level (figure 1.5 (b)).⁶²⁻⁶⁴

Figure 1.5: (a) Interband and (b) intraband Auger process in semiconductors.

1.2.3. Anisotropy of low dimensional nanostructures

When the materials properties such as absorption, fluorescence and conductivity are not same in all the measured direction these types of the materials are called anisotropic materials.^{7,}

⁶⁵ Anisotropy can be intrinsic due to the crystal structure of the material and/or extrinsic due to the dielectric difference among the host medium and the nanostructures material.^{15, 66} It will be discussed in detailed in chapter 4 and 5. Nanostructures with dielectric constant of ϵ_m are considered in a host medium of dielectric constant of ϵ_h . When the polarization of the applied electric field (light) is parallel ($\parallel$) or perpendicular ($\perp$) to the axis/plane of the nanostructures (figure 1.6) then, the relation between the electric field inside the nanostructures and the

absorption cross-sections (σ) for similar thickness/diameter (d) and length (l) of nanostructures are given in table 1.1.^{7,8}

The electric field inside the NSs and NWs is always stronger when applied electric field is parallel to NS plane/NW axis. Similarly, absorption cross-sections of NSs and NWs are higher in the case of parallel polarization. However, QDs do not show any anisotropy due to the symmetric shape.

Table 1.1: Electric field inside the nanostructures and absorption cross-section of the nanostructures, when the polarization of the applied electric field (light) is parallel ($\parallel$) or perpendicular ($\perp$) to the axis/plane of the nanostructures.

Nanostructure	$E_{\parallel}$	$E_{\perp}$	$\sigma_{\parallel}$	$\sigma_{\perp}$
NSs	E_0	$\frac{1}{\epsilon_r} E_0$	$A d l^2$	$A \frac{d l^2}{\epsilon_r^2}$
NWs	E_0	$\frac{2}{1 + \epsilon_r} E_0$	$B 0.25 d^2 l$	$B \frac{d^2 l}{(1 + \epsilon_r)^2}$
QDs	$\frac{3}{2 + \epsilon_r} E_0$	$\frac{3}{2 + \epsilon_r} E_0$	$C \frac{1.5 d^3}{(2 + \epsilon_r)^2}$	$C \frac{1.5 d^3}{(2 + \epsilon_r)^2}$

where $\epsilon_r = \frac{\epsilon_m(\omega)}{\epsilon_h(\omega)}$ and $\epsilon_r > 1$. A, B and C are the proportional constants for NSs, NWs and QDs respectively.

In the case of $d \ll l$, the relation between the absorption cross-sections of NSs, NWs and QDs is presented in equation 1.34.

$$\sigma^{NS} > \sigma^{NW} > \sigma^{QD} \quad (1.34)$$

Overall, it is clear from equation 1.34 that NSs has highest and QDs has lowest absorption cross section among all these structures.

Figure 1.6: Representation of the polarization of incident electric field parallel to the plane of NS and growth axis of the NW and QDs.

1.2.3 Quantization effect on multiple exciton generation

The power conversion efficiency of a single p-n junction solar cell can be theoretically as high as 33% (Shockley-Queisser limit).¹ Most of the absorbed photon energy in conventional solar cells

Figure 1.7: Multiple exciton generation in quantum confined nanostructures.³

is wasted in the form of heat.⁴⁸ Indeed, in a semiconductor, when the energy of the absorbed

photon is higher than the bandgap energy, hot excitons are generated. Hot excitons quickly cool down to the band edge and typically release their excess energy to phonons. In bulk semiconductors, the distribution of energy levels is continuous, which make phonon coupling very efficient and consequently the excess energy of hot excitons is quickly dissipated into heat. The process of hot excitons cooling is a major energy loss channel in photovoltaic devices.^{48, 67} In contrast, energy levels are discrete in quantum confined nanostructures and the energy difference between two consequent energy levels can be much higher than the phonon energy; as a result, phonon coupling strength is reduced. Therefore, when the energy of the absorbed photon is at least twice of the energy bandgap, a significant portion of the excess energy of hot excitons can be transferred to electrons in the valence band⁹ and one or more new excitons can be created. This process is known MEG,^{40, 43, 44, 53, 54, 68-72} shown in figure 1.7. In principle, it allows to large improvement in the solar cell power conversion efficiency (PCE).^{12, 40, 73, 74}

Figure 1.8: Comparison of the power conversion efficiency of solar cell with and without MEG.¹

By this phenomenon, Shockley-Queisser limit can be broken and PCE of the solar cell can reach up to 45% (figure 1.8, curve $M_{\max}$).¹ Curve “N” represents the PCE of the single junction solar cell without MEG (one exciton per absorbed photon). Curve “M = 2” for MEG efficiency 2 (two excitons per absorbed photon) shows that PCE can reach up to 40%. Therefore, by generating only one extra exciton the PCE of the solar cell can reach up to 40%, a significant improvement compared to the Shockley-Queisser limit of 33%.

Minimum excitation photon energy to start the MEG phenomenon in semiconductors is called the MEG threshold energy. For one exciton generation, absorbed photon energy should be $\geq E_g$ and for two exciton generation, photon energy should be $\geq 2E_g$ (energy conservation rule). In bulk semiconductors, both of the conservation rules (energy and momentum) should be satisfied. Therefore, threshold energy in bulk semiconductors is $4 - 6E_g$. This threshold energy in the bulk semiconductor is generally out of the solar spectrum. The use of small bandgap semiconductors is also not useful because the photovoltage would be too low. So, the efficiency of the solar cell would not increase. However, in quantum confined nanostructures, only energy conservation is required and momentum conservation is relaxed.^{6, 75, 76} Ideally, MEG photon threshold energy is $2E_g$ in quantum confined nanostructures.^{9, 77, 78} Experimentally, it can be higher due to several effects such as electronic structure, size and shape of the nanostructure etc. Therefore, the threshold energy in quantum confined nanostructures is $2 - 4E_g$, which is relatively lower than the threshold energy of bulk semiconductors.⁷⁹ This energy generally falls in the solar spectrum. The MEG efficiency is also high in quantum confined nanostructures.⁴⁵ Cooling rate of single hot exciton is reduced and MEG rate is enhanced in quantum confined nanostructures.⁹

MEG efficiency in PbSe NRs is reported higher than the PbSe QDs and MEG threshold energy is also found lower than QDs.⁵³ Moreover, MEG efficiency in PbS NSs is reported higher than the PbS NRs and MEG threshold lower than NRs.⁸⁰ Physics is not clear about these behavior of NRs and NSs.⁷² Many factors could be responsible for these behaviors, large absorption cross-section due to geometric anisotropy, and behavior of 1D/2D exciton in nanostructures and different electronic structures etc.

Therefore, photoexcitation dynamics of carriers is an interesting research direction for understanding the fundamental properties of low dimensional nanostructures.

1.3. Goal of the thesis

In this thesis, low dimensional PbSe nanostructures were synthesized and ultrafast optical properties of carriers were studied by ultrafast optical pump-probe spectroscopy. The aim is to gain insight into the efficiency and mechanism of MEG and to increase the understanding of other important optical properties of PbSe QDs, NWs, and NSs, such as the high energy optical transitions, anisotropy, and broadband nonlinear absorption.

1.4. Structure of the thesis

In chapter 2 of the thesis, synthesis and structural analysis of quantum confined low dimensional PbSe nanostructures, and detailed of pump-probe spectroscopy is presented. In chapter 2, some factors are also addressed that influence the shape and structures of PbSe nanostructures in the synthesis.

In chapter 3, a study of MEG in PbSe QDs using the pump-probe spectroscopy is presented. In this chapter, we determine MEG QY, MEG threshold energy and the origin of the threshold

energy for MEG in PbSe QDs. Experimental evidence of the phonon bottleneck around the Σ point is presented. Moreover, by comparing the TA dynamics at and above the PbSe QDs bandgap, we also infer that the MEG QY could be measured directly from the visible TA spectra (above the bandgap).

Chapters 4 and 5 deal with the optical transitions in PbSe NWs and NSs respectively. These transitions are confirmed by density function theory (DFT) and tight binding calculations.⁵¹ High energy optical transitions are studied using pump-probe spectroscopy. Anisotropy has also been observed in PbSe NWs and NSs. In addition, pump fluence dependent nonlinear NIR broadband TA spectra and dynamics are studied in PbSe NSs. Finally, in the last part of this thesis (chapter 6), conclusions and perspectives for future work are presented.

Chapter 2: PbSe Nanostructures and Experimental Techniques

2.1. Introduction

This chapter presents a detailed study into the synthesis and structural analysis of PbSe QDs, NWs and NSs. In the first section of this chapter, the structure analysis of monodisperse PbSe QDs for three different sizes is presented. The study is also further extended to PbSe NWs, synthesis procedure and structure analyses are presented in the second section. The diameter of these NWs was measured to be ~ 4.7 nm. In the third section of this chapter, the synthesis and structure analysis of quantum confined PbSe NSs is presented. To our best knowledge, this is the first work to report the synthesis of quantum confined PbSe NSs. The thickness of synthesized hexagonal NSs-like morphology PbSe NSs is ~ 4.3 nm.

2.2. Synthesis and structural characteristic of PbSe nanostructures

2.2.1. PbSe quantum dots (QDs)

In 1997, A. Lipovskii *et. al.*, was the first to report the successful synthesis of PbSe QDs in the glass matrix.²⁸ Later in 2001, C.B. Murray *et.al.* developed a wet-chemical method to synthesize high-quality PbSe QDs.²⁹ These QDs were bound by small organic molecules, which make them soluble in organic solvents. Presently, these PbSe QDs are commercially available. Three different types of PbSe QDs having an absorption peak at 1100 nm (QD₁), 1200 nm (QD₂) and 1300 nm (QD₃) were bought from NN Crystal US Corporation to study the photoexcitation dynamics. They were all suspended in hexane with an initial concentration of 10 mg/ml.

Figure 2.1: TEM images of PbSe (a) QD₁, (b) QD₂ and (c) QD₃. Size distribution of (d) QD₁, (e) QD₂ and (f) QD₃.

Particle size and morphology of PbSe QDs were determined using JEOL JEM-2010/UHR transmission electron microscope (TEM) at operating voltage of 200 kV. The hexane suspended PbSe QDs were dropped on a holey carbon-coated copper grid and dried in vacuum for overnight before conducting the measurements. QDs average sizes were determined from TEM images using the Image J software. From these images, individual particle sizes were extrapolated and a histogram distribution was generated. The average QD's size was then calculated by Gaussian fitting of the histograms. TEM images of PbSe QD₁, QD₂ and QD₃ are shown in figure 2.1(a), (b) and (c) respectively. All QDs have a spherical shape and their average diameters estimated from the TEM images are 3.6 ± 0.3 nm, 3.8 ± 0.5 nm and 4.3 ± 0.5 nm for QD₁, QD₂, and QD₃, respectively. QDs sizes distributions for QD₁, QD₂ and QD₃ are shown in figure 2.1 (d), (e) and (f), respectively.

2.2.2. PbSe nanowires (NWs)

Synthesis of PbSe NWs was performed using the method developed by *K.S. Cho et.al.*⁸¹ This method consists of three steps. In the first step, the lead oleate (LO) solution was prepared by dissolving 760 mg lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$), 2 ml oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$) and 10 ml of diphenyl ether in a three neck flask. The solution was heated in nitrogen gas flow at $\sim 110^\circ\text{C}$ for 30 minutes and then at $\sim 150^\circ\text{C}$ for 30 minutes and subsequent natural cooling to $\sim 60^\circ\text{C}$. In the second step, 4 ml of 0.167 M trioctylphosphine selenide (TOPSe) solution was prepared by dissolving 53 mg Se powder in required amount of trioctylphosphine (TOP) in a one-neck flask. It was kept under nitrogen gas flow for 5 minutes and then heated at $\sim 50^\circ\text{C}$ for 2 hours. In the third step, both of the solutions LO and TOPSe were mixed and immediately injected by a syringe in vigorous stirring hot solution of 0.2g tetradecyl phosphonic acid (TDPA) in 15 ml diphenyl ether solution at 250°C . After 50s reaction, the reaction mixture was cooled down to room temperature by an air gun. An equal volume of hexane was mixed in the reaction mixture and centrifuged for 20 minutes at 4000 rpm. Centrifugation process was repeated three times for washing the PbSe nanostructures. Precipitated nanostructures were dispersed in chloroform.

To perform the structural analysis of these structures, scanning probe microscope (SEM) was used. SEM images show that this method not only develops the NWs but also develop the other nanostructures such as spheres (figure 2.2 (a)), stars (figure 2.2 (b)), pyramids with thick NRs (figure 2.2 (c)) and NRs (figure 2.2 (d)).

Since acetic acid (CH_3COOH) and water are byproducts in LO formation reaction (as shown below in reaction 2.1), therefore different nanostructures are possible to develop. Such structure variation was also observed by *A. J. Houtepen et al* during the synthesis of PbSe nanocrystals.⁵⁹

Figure 2.2: SEM image of PbSe (a) sphere, (b) stars, (c) pyramids with nanorods and (d) nanorods.

Therefore to block the formation of other nanostructures, LO preparation method was modified. In the new method, 446 mg PbO was used instead of lead acetate trihydrate to dissolve in 2 ml oleic acid and 10 ml diphenyl ether in three neck flask. The solution was heated in a vacuum for 30 minutes at 110⁰C followed by nitrogen gas flow at 150⁰C for 30 minutes to get LO solution and later the solution was left to cool down to 60⁰C, naturally. In this method, the possibility of acetic acid formation as a byproduct was ruled out. The remaining steps of the synthesis were same.

Figure 2.3: (a) TEM image of PbSe NWs, (b) HRTEM image of PbSe NWs showing the growth direction. Inset of the figure shows the diameter distribution of PbSe NWs.

Figure 2.3 (a) shows the TEM image of synthesized PbSe NWs. As shown from HRTEM image of PbSe NWs (figure 2.3 (b)), d-spacing is 0.30 nm, which corresponds to (200) plane, simplified (100) plane. These observations suggest that growth of the NWs proceeds along the (100) direction.^{81, 82} The diameter of PbSe NWs measured by Gaussian distribution (inset of figure 2.3 (b)) is 4.7 ± 0.6 nm and length is on μm scale.

2.2.3. PbSe nanosheets (NSs)

In literature, only few research groups' report the synthesis of PbSe NSs, however, the thickness of the reported NSs is not enough to show the quantum confinement effect.^{83, 84} Here, we have developed a novel synthesis method for synthesizing the quantum confined PbSe NSs of sufficient thickness. The setup, as shown in Figure 2.4 was enacted by carving out a parallel cavity in a domestic microwave oven that allowed a quartz enclosure with an outer diameter of 19 mm to pass through it. Further, the quartz enclosure was secured from both sides by connecting it to the in-flow of gas on the one end and outflows of gas on the other end. The gas

flow arrangement connected with the quartz enclosure was also connected with a vacuum oil

Figure 2.4: Setup for the synthesis of PbSe NSs.

pump to evacuate any air inside the outer quartz jacket (enclosure). In addition, a further arrangement was made for the real-time pressure measurement inside quartz jacket and knobs (MFC) to control (either decrease or increase) the gas flow. As the system makes use of microwave for synthesis, the whole assembly other than the gas source required being inside a protective cabinet to avoid health hazards emanating from microwave radiation.

The setup was put to use to synthesize the highly sought after materials for scientific research such as WS_2 , MoS_2 and WSe_2 bulk and NSs by loading the charge consist of the stoichiometric amount of the metallic powder and sulfur inside a quartz ampoule having an outer diameter of 13 mm.⁸⁵ The ampoule was evacuated to a low pressure of few mbar and sealed simultaneously. The sealed ampoule containing the stoichiometric charge was then transferred

inside the outer quartz enclosure and pushed exactly inside the area covered by microwave cavity.

Next, the quartz jacket was secured from both side and evacuated to the order of 10^{-2} mbar. After achieving this, slowly the argon gas was released in the quartz jacket and the value of that was monitored through digital pressure gauge. The low pressure was maintained to allow plasma generation. Once all the above is accomplished, microwave power was turned on results plasma generation of argon gas. After few minutes, it was able to ignite the selenide plasma inside the material and synthesis takes place to give the intended compound (in grams). On an average, few hours were required for this process to synthesize the compound depending on the type of constituent material and the desired morphology (thickness and lateral dimensions).

Figure 2.5: XRD of PbSe NSs.

For the synthesis of PbSe NSs, 1.09 g Pb and 0.49 g Se powders were sealed inside the quartz ampoule and inserted in developed setup. Synthesis reaction takes 2 hours for PbSe NSs which produce a gray powder as the end product. This gray powder was transferred in Isopropyl alcohol (IPA) and sonicated for 30 minutes. After the sonication, the sample was left for 5 minutes and

then lixiviated the solution. The upper part of the solution was kept and used for the measurements and rest was disposed of. The crystal structure of the synthesized NSs was characterized by X-ray diffraction (XRD). Figure 2.5 shows its XRD pattern, which confirms the cubic PbSe structure ([01-071-4753] PbSe (clausthalite, syn), $a = 6.14 \text{ \AA}$, Fm-3m).

Figure 2.6: (a) SEM image (b) AFM image (inset shows thickness profile) of PbSe nanosheets (c) HRTEM image of a single PbSe nanosheet. (d) SEM image of a single PbSe NS with the facets indexed.

The size and morphology of the synthesized PbSe NSs were characterized by SEM and TEM. Figure 2.6 (a) shows SEM image of PbSe NSs, where hexagonal NSs-like morphology

with lateral dimensions of 100s nm to μm scale is dominating. Atomic force microscopy (AFM) was used to measure the thickness of PbSe NSs (figure 2.6 (b)). Averaged measured thickness of NSs is 4.3 ± 0.4 nm (inset of figure 2.6 (b)). The HRTEM image of PbSe NSs as shown in figure 2.6 (c) reveals lattice spacing of 0.22 nm and 0.19 nm correspond to the (220) and (311) planes of the cubic PbSe crystal structure, respectively. This shows that the micrometer-sized NSs are bound by (220) and (311) planes facets (figure 2.6 (d)). Growth direction of PbSe NSs is orthogonal to the (220) and (311) planes, which is along the $(\bar{2}24)$ plane with an angle of 48° to the geometric surface.

2.3. Transient absorption spectroscopy

TA spectroscopy is a fundamental and versatile technique to probe and characterize the excitation dynamics in various photo-sensitive chemicals, physical and biological systems. In this technique, two ultra-short pulses are, namely, pump and probe. The pump beam is used to promote a fraction of molecules to excited states. The probe beam that passes through the sample with a delay of Δt with respect to the pump is used to detect the perturbation effect by the pump beam in the sample. The probe beam should be much weaker than the pump beam so as to avoid multi-photon/multistep excitation during probing. By means of measuring the difference of the light transmission (ΔT) in transmission geometry or the reflection (ΔR) in reflection geometry with and without pumping, one can determine the difference in light absorption (ΔA) between the excited sample and that in equilibrium. Through varying the delay time Δt and recording the ΔT or ΔR at each delay time, the temporal profile of the dynamics can be gained. By choosing different wavelengths λ , the spectral profile of the dynamics can also be acquired. The bandwidth of the pump pulse should be narrow in order to enable selective excitation of an optical transition. The probe pulse is generally white light.

The working principle of the transient pump-probe technique is shown in figure 2.7. The TA signal can be measured in term of $\Delta T/T$ (normalized change in the transmission).

$$\frac{\Delta T}{T} = \frac{T^{\text{on}}(\lambda_{\text{pr}}, \tau) - T^{\text{off}}(\lambda_{\text{pr}}, \tau)}{T^{\text{off}}(\lambda_{\text{pr}}, \tau)} \quad (3.1)$$

where $T^{\text{on}}(\lambda_{\text{pr}}, \tau)$ and $T^{\text{off}}(\lambda_{\text{pr}}, \tau)$ are the transmission of the probe at delay τ when the pump is on and off respectively. Absorbance (A) of the sample can be defined as shown in equation 2.2.

$$A = -\log_{10} T \quad (3.2)$$

Therefore, change in the absorbance (ΔA) can be measured using equation 2.3

$$\Delta A = -\log_{10} \left(\frac{T^{\text{on}}(\lambda_{\text{pr}}, \tau)}{T^{\text{off}}(\lambda_{\text{pr}}, \tau)} \right) \quad (3.3)$$

By using equation 2.1, equation 2.3 can be simplified as shown below.

$$\Delta A = -\log_{10} \left(1 + \frac{\Delta T}{T} \right) \quad (3.4)$$

When $\Delta T \ll T$,

$$\Delta A = -\frac{1}{2.3} \left(\frac{\Delta T}{T} \right) \quad (3.5)$$

Therefore, pump-probe signal can be measured as a normalized change in the transmission

$\left(\frac{\Delta T}{T} \right)$ by using equation 2.1 or as a change in the absorbance (ΔA) by using equation 2.5.

Figure 2.7: Schematics of pump probe technique. (a) Principle of pump probe technique (b) Energy levels in materials (c) steady state measurements (d) Broad band probe and (e) Transient absorption spectra.

Due to the absorption of the pump pulse, electronic transitions occur from the ground state (S_0) to upper excited states as shown in figure 2.7 (b) followed by a delayed weak broadband probe scans of the sample (figure 2.7 (d)). At the bandgap of the material, most of the electrons absorb the pump photon energy and excite to the higher energy states. As a result, a large population of the probe photons is not absorbed and show negative signal ($-\Delta A$), photobleaching (PB) as shown in figure 2.7 (e). The lowest excited state may also be optically coupled to the ground state and there is a possibility to observe stimulated emission (SE). Pump excited electron can further absorbing the probe photon energy and reach to the higher excited states. In this case, signal (ΔA) is positive, photoinduced absorption (PA) as shown in figure 2.7

(e). This positive ΔA can be related to the excited state absorption (ESA) and/or coulomb interaction of the excitons.

A femtosecond laser system, consisting of Ti-Light-200 oscillator and Integra-C-2.5FS amplifier from Quantronix, is used in the pump-probe setup. The output power of the amplifier is 2W (800 nm, ~100 fs pulse width) with 1 kHz repetition rate. This pump-probe setup can be divided into two parts. First part is for measuring TA spectra in the visible region as shown in

Figure 2.8: Schematic of pump-probe set up for transient absorption spectra measurements (a) in the visible region and (b) in the NIR region.

figure 2.8 (a) and the second setup for measuring NIR TA spectra as shown in figure 2.8 (b). In both of the configurations, the fundamental (800 nm), second (SH, 400 nm) and third (TH, 267 nm) harmonic were used as pump beams. The SH was generated using a type-1 BBO crystal (phase matching angle 29.2°) while the TH was generated by the sum frequency generation of 400 nm and 800 nm in a type-2 BBO crystal (phase matching angle 55.5°). The pump laser power was adjusted by a neutral density (ND) filters.

The white light continuum (WLC) was used as probe light in both configurations. WLC, which is the third order non-linear phenomenon was generated by tight focusing of the laser beam in a non-linear medium. Laser pulse width, beam shape and power play a crucial role in WLC generation and its stability. Therefore, pulse width, beam shape and power were optimized by adjusting the compressor of the amplifier, iris and ND filter, respectively, to stabilize the WLC. Visible WLC was generated by focusing the 800 nm beam into a 2 mm thick sapphire plate (figure 2.8 (a)). Laser power was adjusted by ND filters and residual of 800 nm laser in WLC was blocked by a notch filter. WLC was focused on the sample and the spectra were measured using CCD camera (Entwicklungsburo Stresing) with a detection range spanning from 200 nm to 950 nm. The NIR WLC probe light for NIR TA measurements was generated by focusing 1620 nm laser beam from the optical parametric amplifier (OPA, Palitra-FS Quantronix) into a 4 mm thick yttrium aluminum garnet (YAG) crystal (figure 2.8 (b)).⁸⁶ The residue of 1620 nm from the NIR WLC was filtered by a short-pass mirror (Thorlabs DMSP1500). WLC was focused on the sample and the signal was detected by a NIR photodiode array (PDA) (Entwicklungsburo Stresing) in the range from 950 nm to 1500 nm. For acquiring TA spectra, the pump beam was modulated by a shutter and the differential spectrum of WLC (with and without pump) was recorded and averaged by the CCD/PDA.

The time delay between pump and probe was adjusted using a delay stage for the pump beam. In the pump probe setup, all the three pump wavelengths follow the same path to exciting the sample. However, both of the probe beams namely, visible WLC and NIR WLC follow the different optical path. OPA is also used to measure kinetics at different probe wavelengths. As we change the wavelength by OPA, the optical path of the probe beams changes. Therefore, it is

wise to delay the pump instead of probe, to avoid the complicated probe alignment through the delay stage.

The temporal resolution of the 800 nm of pump wavelength pulse at the sample was measured by the auto-correlation method and it was around 100 fs. The temporal resolution of 400 and 267 nm of pump wavelengths were measured by the deconvolution of the kinetics and it was around 200 fs.

2.4. Conclusions

The diameter of three PbSe QDs was measured using TEM and their diameters are 3.6 ± 0.3 nm, 3.8 ± 0.5 nm and 4.3 ± 0.5 nm. PbSe NWs of diameter 4.7 ± 0.6 nm were synthesized and the length of the NWs was few μm scale along the (100) crystal axis. PbSe NSs was synthesized using the microwave-assisted technique. To our best knowledge, this is the first report on the synthesis of quantum confined PbSe NSs. The thickness of synthesized hexagonal NSs-like morphology PbSe NSs is 4.3 ± 0.4 nm and lateral dimensions are in the range of 100s nm to few μm . NSs are bound by (220) and (311) planes facets and the growth direction of PbSe NSs is along the $(\bar{2}24)$ plane with an angle of 48° with the geometric surface of NSs. Finally, the details of the pump-probe spectroscopy used for the further ultrafast dynamics were presented at the end of this chapter.

Chapter 3: Photoexcitation Dynamics of PbSe Quantum Dots (QDs)

3.1. Introduction

The power efficiency of a single semiconductor junction solar cell can be, theoretically, as high as 33%.¹ At the moment in a conventional solar cell, most of the absorbed energy is dissipated in heat. Indeed, in a semiconductor, when the energy ($h\nu$) of an absorbed photon is higher than the energy bandgap (E_g), hot excitons are generated. Hot excitons quickly cool down to the band edge and release their excess energy to phonons (thermal dissipation). When the energy of the absorbed photon is at least twice the energy bandgap, a significant portion of the excess energy of hot excitons can be transferred to electrons in the valence band,⁹ and one or more new excitons can be created. This process is known as MEG^{40, 43, 44, 53, 54, 68-72} and, in principle, it allows to highly improve the solar cell PCE.^{12, 40, 73, 74}

Typical MEG QY values in QDs are between 1 and 3 with photon energy excitation from 2 to 5 times the bandgap of the QDs.^{48, 75, 87-89} However, there is still an on-going debate about the parameters influencing the MEG QY,⁴⁹ since other works have shown very low MEG QY even for much higher photon energy.⁹⁰⁻⁹³ One of the reasons for this inconsistency may be the complicated competition of MEG and hot exciton de-excitation process, especially at higher excited states. In particular, one of the open questions is how the threshold energy for MEG is influenced by other physical phenomena. In principle, the threshold should be two times E_g , but it turns out to be higher since phonon relaxation rates are normally larger than MEG rate. Recently it has been pointed out that the electronic transition, corresponding to the Σ point in the Brillouin zone⁴ (Σ transition), could play an important role in determining the threshold for

MEG.⁹ It has been suggested that the hot exciton cooling process could slow down around this level, allowing the MEG process to overcome the cooling rate of phonon.⁹ This would imply that MEG has an energy threshold strictly higher than the Σ transition. The Σ transition is observed in both bulk and QDs and its position shifts towards higher energy with decreasing the size of QDs.⁴

PbSe QDs are widely explored as a material for solar cell, IR lasers, diodes, and IR-detectors applications. Due to the large Bohr radius (46 nm), PbSe QDs show strong quantum confinement effects²⁸ exhibiting narrow emission from NIR to MIR.³⁰ In PbSe QDs, most of the previous spectroscopic studies have been performed near the band edge,^{6, 43, 48, 94-97} which is at the bottom of the cooling cascade process through the higher energy states. In these studies, only the cooling process from the lowest levels, from 1P to 1S, is assessed by probing states in the NIR, close to the QD bandgap. However, the competition between hot exciton cooling and MEG cannot be observed and quantified in the band edge measurements.

In this chapter, we determine MEG threshold energy and MEG QY for PbSe QDs of three different sizes through the NIR TA spectra. We also investigated the origin of the threshold energy for MEG in PbSe QDs through the analysis of TA spectra, in the visible region close to the Σ transition, at different pumping energies. We show evidence of a reduction of the hot exciton cooling down via phonon relaxation around the Σ point, where the MEG starts taking over the phonon relaxation process. Moreover, by comparing the TA dynamics at and above the PbSe QDs bandgap, we also infer that the MEG QY could be measured directly from the visible TA spectra (above the bandgap), which is generally easier to measure comparing to the NIR TA spectra.

3.2. Steady-state optical properties of PbSe QDs

Three different types of PbSe QDs having diameters of 3.6 ± 0.3 nm (QD₁), 3.8 ± 0.5 nm (QD₂) and 4.3 ± 0.5 nm (QD₃) respectively were filled in quartz cuvettes of 1 mm optical path length for all the optical measurements. Absorption and photoluminescence (PL) spectra of PbSe QDs were measured by Perkin Elmer Lambda 750 UV/Vis/NIR spectrophotometer and FluoroLog-3 spectrophotometer respectively, shown in figures 3.1(a) – (c). In figures 3.1 (a), (b) and (c) absorption (left axis) and PL (right axis) spectra of QD₁, QD₂ and QD₃ are shown, with first excitonic absorption peaks at ~ 1100 nm, ~ 1200 nm and ~ 1300 nm and PL peaks at ~ 1170 nm, ~ 1260 nm and ~ 1350 nm, respectively. The well-defined first excitonic peaks in the absorption spectra of all QDs samples correspond to the bandgap energy (E_g) value. As expected, we consistently observe a red shift in the measured first excitonic absorption as well as PL peaks coincide well with increasing size of QDs.

3.3. Optical transitions in PbSe QDs

Here, we will focus our discussion on QD₁ only since we found similar trends for all QDs. To identify the optical transitions of the three QDs, the second derivative of their absorption spectra were calculated and reported in figure 3.2 for QD₁.^{4, 98, 99} The first minima of the second derivative curve in figure 3.2 around 600 nm has been unambiguously assigned to the Σ transition.^{4, 95} The assignment of the second dip (~ 870 nm) is still under debate. Hui *et al* assigned, on the basis of theoretical calculations using $k \cdot p$ model,^{26, 100, 101} to the $1S_{he}1P_{eh}$ transition, that is not optically allowed. Liljeorth *et al* and several others defined this second

Figure 3.1: Steady state absorption (left axis) and photoluminescence spectra (right axis), with 800 nm excitation wavelength for (a) QD₁, (b) QD₂ and (c) QD₃.

transition as $1P_{\text{he}}1P_{\text{eh}}$ based on pump-probe measurements and density of states measured by scanning tunneling spectroscopy.^{46, 102-104} The last minima of the second derivative curve at ~ 1100 nm which corresponds to the first excitonic absorption peak, is assigned to the 1S-1S transition.⁴

Figure 3.2: Absorption spectra (black line) of PbSe QD₁ with its second derivative (blue line).

3.4. Multiple exciton generation in PbSe QDs

Pump-probe spectroscopy (Transient absorption spectroscopy) has been used to measure MEG in PbSe QDs. Details of pump-probe spectroscopy are given in chapter 2.

3.4.1. Multiple exciton generation probed at Bandgap

For all the wavelengths (energies) used as a pump, the laser fluence should be low enough to guarantee that just one photon is absorbed by each QD. In order to avoid multi-photon absorption in TA measurements, we investigated fluence dependent conditions for all the pump wavelengths. Figure 3.3 shows the case for 800 nm pump and 1100 nm probe. The curves with fluences below $10 \mu\text{J}/\text{cm}^2$ show overlapping dynamics, which is indicative that below that value

there are no second order effects and less than one photon has been absorbed on average by each QD. So we used $10\mu\text{J}/\text{cm}^2$ as excitation fluence in all our measurements at 800 nm. Similarly, optimum low fluences for 400 nm and 267 nm pump have been investigated and TA measurements performed.

Figure 3.3: QD₁ peak normalized kinetics probed at 1100 nm, with 800 nm pump at different fluencies. Symbols are data points and solid lines are bi- exponential curve fits.

NIR TA spectra of QD₁ at pump wavelengths of 800 nm (corresponding to 1.38Eg), 400 nm (2.75Eg) and 267 nm (4.14Eg) are shown in figures 3.4 (a) - (c). The NIR TA spectra, figure 3.4 (a), (b) and (c) display the same three main features, which show a different time evolution for the three pumping energies. The positive band around 1000 nm is due to the ESA of the excitons.^{100, 101} The main negative signal dominating the spectra at around 1100 nm corresponds to the ground state photobleaching (GSB). The GSB is due to the removal of the charge carriers from the valence band and it represents the 1S-1S transition as discussed before.^{4, 88, 105} In addition to the GSB valley a broad positive band at longer wavelengths due to the Coulomb

Figure 3.4: TA spectra of PbSe QD₁ at pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm.

interaction between the excitons is observed.⁸⁸

In figure 3.5 the GSB dynamics of QD₁ for different pump wavelengths are reported normalized to their tail at long time scale. After excitation with 800 nm (1.38Eg, black circle), the kinetics presents a fast rise (<0.5 ps), a small and fast decaying differential signal in first few ps due to a small amount of multi-photon absorption followed by a very long decay, much longer than our time scale of 1 ns. The long decay has been attributed to single exciton radiative recombination, which is of the order of microseconds in PbSe QDs.^{92, 94} The kinetics with 400

Figure 3.5: Tail normalized kinetics of PbSe QD₁ with probe wavelength of 1100 nm and pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm.

nm pump (2.75Eg, blue squares) shows the fast rise and then fast decay in first tens of ps and followed by long decay. The fast decay could be due to the Auger recombination of multiple hot excitons in QDs before relaxing into the long-lived single excitonic state.⁹² For 267 nm excitation (4.14Eg, red triangles), we observe a slow rise (around 1 ps) in comparison to 400 nm and 800 nm excitation (< 0.5 ps), and first decay component around 50 ps due to Auger recombination followed by long decay. The slow rise time can be explained as the cool down process of hot excitons towards the band edge and the fast decay is due to a more efficient Auger

recombination of multiple excitons. Moreover, it is reflected also in a blue shift of GSB signal (~10 nm at 1 ps delay) in figure 3.3 (c).⁸⁸ The observation of Auger recombination of hot excitons and their lifetime in PbSe QDs coincide well with results reported in the literature.^{92, 94}

From these decays it is possible to evaluate the MEG process and its QY, The MEG QY is defined as the number of excitons generated per photon absorbed. Experimentally, MEG QY can be calculated as A/B from the dynamics of exciton GSB signal at the bandgap.^{41, 48} Indeed, assuming A being the maximum amplitude value of the dynamics, which is at around 1 ps in our cases, and B being the amplitude of dynamics at long delay time, as shown in figure 3.5, MEG QY can be calculated as A/B for all the dynamics:^{41, 48}

$$\text{MEG QY} = A/B \quad (3.1)$$

Ideally, MEG QY=1 is expected for 800 nm (1.38Eg) excitation as the photon energy is less than two times the bandgap. A slightly higher MEG QY=1.13 is obtained in our measurements, which is most probably due to the small contribution of multiphoton absorption in QDs. A MEG QY=1.28 was obtained at 400 nm (2.75Eg) excitation, which implies the multiple excitons were likely generated by one photon since the excitation photon energy is more than two times of the bandgap energy (2.75Eg). On the other hands MEG QY=2.01, meaning that two excitons were generated per absorbed photon when excitation was 267 nm (4.14Eg). MEG QY of QD₂ and QD₃ were also determined at the same excitation wavelength and summarizes in table 3.1. MEG QY varies for different sizes of QDs as a function of excitation photon energy and the bandgap energy ratio ($h\nu/E_g$). MEG QY trend as a function of $h\nu/E_g$ has been reported in figure 3.6. MEG QY values below the 2Eg are not considered for the analysis. Here, we see the trend that

MEG QY of smaller sized QDs is higher than the larger sized QDs at given $h\nu/E_g$, which is consistent with the literature. From a

Table 3.1: Pump wavelengths, corresponding $h\nu/E_g$ values and MEG QY for QD₁, QD₂ and QD₃.

Pump Wavelength (nm)	QD ₁		QD ₂		QD ₃	
	$h\nu / E_g$	MEG QY	$h\nu / E_g$	MEG QY	$h\nu / E_g$	MEG QY
800	1.38	1.13	1.50	1.15	1.63	1.16
400	2.75	1.28	3.00	1.31	3.25	1.38
267	4.12	2.01	4.49	2.29	4.87	2.51

linear fit, the extracted MEG QY at $4E_g$ for QD₁, QD₂ and QD₃ are 2.00, 1.96 and 1.90 respectively.⁸⁰ Here, we conclude that photons energy at 400 nm is close to the threshold energy for the MEG process to overcome the phonon relaxations. Our results are consistent with the threshold values of $2.5E_g - 3.0E_g$ reported for similar sizes PbSe QDs.⁷⁹

Figure 3.6: MEG QY of PbSe QD₁ (black circles), QD₂ (red squares) and QD₃ (blue triangles) as a function of $h\nu/E_g$. Dash lines are guide to eye.

3.4.2. Coulomb shift and Coulomb interaction in photoexcited PbSe QDs

Coulomb energy shift is the shift in the absorption spectra of excited quantum dots (QDs) with respect to the unexcited QDs. This spectral shift arises due to the adjustment in the mutual electron-electron, hole-hole and electron-hole Coulomb interactions upon addition of an exciton to an existing excited QD.⁵

When a photon is absorbed by a QD, an electron transfers from an initial state (i) to excited state (j) (figure 3.7 (a)) and the photon energy is balanced by the difference $\Delta E_{0,ij}$, as given in equation 3.2.

$$\Delta E_{0,ij} = E_{e,j} + E_{h,i} - J_{eh,ji} \quad (3.2)$$

where, $E_{h,i}$ and $E_{e,j}$ are the hole and electron energy levels, respectively. $J_{eh,ji}$ is the Coulomb interaction energy between a hole in state i and an electron in state j (figure 3.7 (a)).^{5, 106, 107} The subscript 0 in $\Delta E_{0,ij}$ term, denote the unexcited QD. If excited QD has N excitons, the transition among the same electron states will arise at an energy difference of $\Delta E_{N,ij}$. The $\Delta E_{N,ij}$ will be differ from $\Delta E_{0,ij}$ (figure 3.7 (b)) due to the large density of electrons and holes. $\Delta E_{N,ij}$ can be calculated using equation 3.3.

$$\Delta E_{N,ij} = \Delta E_{0,ij} - \sum_k (J_{eh,jk} - J_{hh,ik}) - \sum_l (J_{he,il} - J_{ee,jl}) \quad (3.3)$$

where, k and l indicate the states of existed electrons and holes in the QD. The spectral shift $\Delta_{N,ij}$ (Coulomb shift), due to the addition of the exciton to an excited QD, can be calculated using the equation 3.4.

$$\Delta_{N,ij} = \Delta E_{N,ij} - \Delta E_{0,ij} = - \sum_k (J_{eh,jk} - J_{hh,ik}) - \sum_l (J_{he,il} - J_{ee,jl}) \quad (3.4)$$

The Coulomb shift ($\Delta_{N,ij}$) can cause same electronic transition at different photon energy in the absorption spectra. In transient absorption spectra, $\Delta_{N,ij}$ depends on the pump, probe photon energy and the time delay between pump and probe pulses. Equation 3.4 can further be simplified as the following equation.

$$\Delta_{N,ij} = N\Delta \quad (3.5)$$

Figure 3.7: (a) Scheme for electron-hole Coulomb interaction due to the generation of an electron-hole pair (j, i) in an unexcited QD and (b) Coulomb interaction due to the generation of the same electron-hole pair (j, i) in excited QD, which have already an electron-hole pair (l, k). (c) Demonstration of the Coulomb shift ($\Delta_{N,ij}$) in the absorption spectrum of excited (α^*) with respect to the unexcited (α) QD.⁵

where, Δ is the Coulomb shift due to the addition of one exciton to the excited QD, which already have an exciton. Therefore, Coulomb shift is proportional to the number of excitons present in the QD.

Figure 3.7 (c) shows the absorption spectra of QDs before (α) and after (α^*) excitation.

Coulomb shift or spectral shift due to coulomb interaction can be calculated using equation 3.6.⁵

$$\Delta_{N,ij} = \frac{\alpha(E) - \alpha^*(E)}{d\alpha(E)/dE} \quad (3.6)$$

where, $\alpha(E) - \alpha^*(E)$ is the change in absorption which can be measured by transient absorption spectroscopy and $d\alpha(E)/dE$ represents the first derivative of the study state absorption spectra of QDs.

Visible TA spectra in the range from 480 nm to 720 nm with 800 nm excitation (where no MEG process occurs) at 5 and 100 ps pump-probe delays are shown in figures 3.8 (a), (b) and (c) for QD₁, QD₂ and QD₃ respectively together with their first derivative of absorption spectra. TA spectra show a photo-induced absorption signal (positive) over all the visible range. In a previous work the photo-induced absorption peak in PbSe QDs has been attributed due to the Coulomb interaction between the excitons generated by the pump and the excitons generated by the probe pulse.⁵ The Coulomb interaction energy, J , can be calculated using equations 3.4, 3.5 and 3.6. The authors found that the Coulomb interaction is nearly wavelength independent above 550 nm and that the transient signal close to the band edge photo-bleaching signal has a rise time, followed by a very slow dynamics, corresponding to the band-edge exciton lifetime. Our data, above 550 nm well reproduce the previous observations. In addition, we also present data in the spectral range below 550 nm showing that J decreases fast below 530 nm and vanishes for 480 nm, implying that Coulomb interaction is not effective at highly excited energy levels. Fast decay kinetics for the peak centered ~525 nm is due to a thermalization process within the fine energy levels far from the band edge. The thermalization does not affect the photo-bleaching of 1100 nm probe (black circles in figure 3.5) because the population of the band edge energy level does not change, but it can affect the Coulomb interaction with higher energy states.

Figure 3.8: TA spectra at 5 ps (gray line) and 100 ps (blue line) delays with first derivative of absorption spectra (red line) of (a) QD₁, (b) QD₂ and (c) QD₃ using 800 nm pump wavelength.

3.4.3. The role of Σ energy level in the threshold energy for MEG in PbSe QDs

In order to study the single exciton relaxation below, around and above the MEG threshold energy, we analyze the TA spectra (figure 3.9) and dynamics (figures 3.10 (a), (b) and (c)) with pump wavelengths of 800 nm, 400 nm and 267 nm for QD₁. We focus our discussion here on QD₁ since we found similar trends for all QDs. In figure 3.9, TA spectra of QD₁ at 5 ps delay for the three pump wavelengths are reported, the spectra are qualitatively similar for any other delays. The spectrum with pump wavelength at 400 nm (close to the MEG threshold) exhibits more intense and structured photoinduced signal at 525 nm and 625 nm, while the spectra with 800 nm and 267 nm pump are very similar showing a less structured signal. TA spectra at three pump wavelengths show peaks at 525 nm, 625 nm and 700 nm.

Figure 3.9: TA spectra (at 5 ps delay) of QD₁ using pump wavelengths of 800 nm (below MEG threshold energy, black line), 400 nm (around MEG threshold energy, blue line) and 267 nm (above MEG threshold energy, red line).

Figure 3.10 shows the normalized dynamics of the hot excitons, TA signal generated by 800 nm (a), 400 nm (b) and 267 nm (c) excitations and probed at 525 nm, 625 nm and 700 nm.

The TA dynamics were deconvoluted and fitted by a single exponential rise and decay plus a constant for the long decays. In figure 3.10 (a), where no MEG process occurs, the fast rise/decay times are about 0.2 ps/2 ps for 525 nm, 0.3 ps/3 ps for 625 nm and 0.5 ps/4 ps for 700 nm respectively. After the very fast decay, the curves reach an almost asymptotic value for all wavelengths, as illustrated in the inset of figure 3.10 (a). This very long decay time is associated with the radiative recombination of the excitons at the band edge.⁵ The TA dynamics of QD₁ excited at 400 nm are reported in figure 3.10 (b) showing a remarkable difference from the decays obtained with 800 nm excitation. Indeed, the rise times at 525 nm are similar with both pump excitations (0.2 ps at 800 nm, 0.1 ps at 400 nm), while the rise times at 625 nm (1ps) and 700 nm (2 ps) are longer for 400 nm pump. Moreover, TA dynamics present rather long decay times (5 ps at 525 nm, 10 ps at 625 nm and 13 ps at 700 nm probe) as compared to those observed at 800 nm and 267 nm pump case. This will be discussing later. We remind that the Σ transition wavelength lays around 600 nm, i.e. in between the 525 nm and the 625 nm peaks, as illustrated in figure 3.2. Given that the Σ transition is around 600 nm in PbSe QDs, the hot exciton generated by the 400 nm pump thermally relaxes towards the Σ level, thus, the fast rise of photo-induced absorption signal probing at 525 nm can be related to the quick thermal relaxation of hot excitons towards the Σ level. Around the Σ transition, there is a bottleneck for the phonons, which slows down the thermal relaxation of the hot exciton. The suppression of the exciton relaxation rate in discrete energy levels in semiconductors is known as phonon bottleneck.¹⁰⁸ In quantum confined semiconductors, energy levels are quantized. If the energy level spacing is higher than the phonon energy, the phonon mediated scattering processes will be reduced because energy and momentum conservation prevent transitions mediated by a single phonon emission. As a result, exciton relaxation rate is slowed down in quantum confined

Figure 3.10: Normalized TA dynamics of QD₁ using pump wavelengths of (a) 800 nm, (b) 400 nm and (c) 267 nm. In each figure, probe wavelengths are 525 nm (black), 625 nm (blue) and 700 nm (red). Inset of figures show kinetics for long delays. Symbols are data points and solid lines are bi-exponential curve fit lines.

nanostructures.^{109, 110} Therefore, the hot exciton dynamics probed above 600 nm (625 nm and 700 nm) present a much slower rise and longer decay time. The long decay after 30 ps reflects the exciton radiative lifetime. Since the MEG process starts to be efficient only for pump energies above 400 nm (see figure 3.5 and table 3.1), we can argue that this slowing of the cooling process is essential for MEG to overcome the phonon relaxation channels.

TA dynamics of the QD₁ pump by 267 nm beam shows a similar trend to that of 800 nm pump (figure 3.10 (c)) with a slightly longer rise time (about 1 ps). The fast decay times are 3.5 ps, 4 ps and 4.5 ps for 525 nm, 625 nm and 700 nm probing wavelength, respectively. The analogy of 800 nm and 267 nm pump dynamics implies that the hot exciton relaxes following the same process once generated regardless of whether the MEG occurred in QD₁. On the other hand, around the MEG threshold energy (figure 3.10 (b)), the phonon bottleneck due to the Σ transitions become significant so hot exciton cooling process has to overtake the phonon relaxation channel in order to overcome the MEG threshold. And it is clear that when pump energy is well above threshold, MEG dominates over phonon relaxation: the highly energetic exciton generated by the 267 nm pump photon quickly decays to the band edge, by creating additional excitons; the additional excitons recombine non-radiatively via Auger recombination by giving up their energy to the third charge; finally, the only one exciton remained recombines radiatively.

3.4.4. Multiple exciton generation probed above bandgap

Here, we suggest that it is possible to estimate the MEG QY by comparing the dynamics in the visible region following the same definition of MEG QY at bandgap. In other words, the ratio between the values of A/B for the kinetics in the visible with different excitations can be an

Figure 3.11: Tail normalized kinetics of QD₁ with probe wavelength of 525 nm and pumping wavelengths of 800 nm (black circle), 400 nm (blue square) and 267 nm (red triangle). Symbols are data points and solid lines are bi-exponential curve fit.

estimation of the MEG QY. Indeed, the A/B ratio has been measured at 525 nm probe wavelength ($(A/B)_{525}$) and at excitations wavelengths of 800 nm, 400 nm and 267 nm for all the QD₁, QD₂, and QD₃ as shown in figure 3.11 (for QD₁) and table 3.2. Since there is no MEG with

Table 3.2 Peak to tail ratio $(A/B)_{525}$ and MEG QY₅₂₅ of PbSe QD₁, QD₂ and QD₃ at 525 nm probe wavelength and at 800 nm, 400 nm and 267 nm pump wavelengths.

Pump wavelength (nm)	$(A/B)_{525}$			MEG QY ₅₂₅		
	QD ₁	QD ₂	QD ₃	QD ₁	QD ₂	QD ₂
800	3.9	5	12	1	1	1
400	4	5.8	13.12	1.02	1.16	1.09
267	8.2	11.45	28.5	2.10	2.29	2.38

800 nm excitation and this kinetics represents the Coulombic interaction of that single exciton. Therefore, $(A/B)_{525}$ for all three excitation wavelengths are normalized with respect to the $(A/B)_{525}$ value obtained at 800 nm, results are shown in table 3.2. MEG QY₅₂₅ is comparable to

the MEG QY for all three measured QDs as shown in table 3.1. Therefore, here we demonstrate MEG QY can be measured in the visible region above the bandgap of QDs. This observation deserves further investigation.

3.5. Conclusions

In this work, TA spectra and their dynamics in NIR and visible regions of PbSe QDs of three sizes ranging from 3.6 nm to 4.3 nm are presented. MEG QY at the four times of the QD bandgap is 2.00, 1.96 and 1.90, for QD₁, QD₂ and QD₃ respectively.

Visible TA spectra have been studied around Σ transition for different pump energies: below, close and above MEG threshold. We found that Coulomb interaction is not effective at higher energy levels. Our analysis shows the role of the Σ transition in slowing down the exciton cooling process, which may be associated with the MEG threshold energy. The Σ energy level behaves like a saddle point, confirming that the threshold energy for MEG should be higher than the Σ energy. The universality of this behavior is confirmed by the similar behavior displayed by the different sizes QDs. At the end, we show that TA spectra and dynamics in the visible range can provide essential information to interpret the dynamics of MEG and possibly use to assess MEG QY.

Chapter 4: Photoexcitation Dynamics of PbSe Nanowires (NWs)

4.1. Introduction

Semiconducting NWs are the bridge between the Nano-world and the macroscopic world.¹⁴ Therefore, these nanostructures are very interesting for fundamental research in NW lasers, solar cells, LEDs, photodetectors, FETs etc.^{15, 111-113} If the diameter of the NWs is smaller than the Bohr radius of the material, quantum confinement arises in the account which results in the change in the electronic properties. Hence, electronic properties can be modified by changing the diameter of NWs.^{50, 114, 115} Moreover, NWs have high carrier transport properties in comparison to nanocrystals.^{25, 31} In addition, optoelectronic properties of NWs also depend on the dielectric mismatch between the NWs material and the host medium due to the large aspect ratio (length to diameter ratio).^{116, 117}

Due to the large Bohr radius (46 nm) and large dielectric constant ($\epsilon_{\infty} = 23$), PbSe NWs exhibit strong quantum confinement effect as well as anisotropy and high carrier transport properties.^{31, 32} These features make PbSe NWs interesting for fundamental research.

In this chapter, we observed quantum confined optical transitions of PbSe NWs in the steady state absorption spectra. At the same time, those were confirmed by the DFT calculated absorption spectra and by tight binding calculations.⁵¹ TA spectra of PbSe NWs show dispersive TA spectra at short pump-probe delays due to the extended length of the NWs. Later on, dispersive spectra change to absorptive and show mentioned optical transitions in the spectra; and kinetics of observed transitions we have studied. Anisotropy has also been observed in the

kinetics of PbSe NWs, which is explained classically by the dielectric mismatch and long aspect ratio of the NWs.

4.2. Steady-state optical properties of PbSe NWs

PbSe NWs of diameter ~ 4.7 nm, dispersed in chloroform were taken in a 1mm of the optical path length quartz cuvette and the absorption spectra measured, which is shown in figure 4.1 (a, red curve). Excitonic features are not clear here. Absorption spectra of these NWs were further measured on CaF_2 substrate (black curve in figure 4.1 (a)). From this spectrum it is clear that excitonic features of nanostructures are dominated in the form of a film. Therefore, much clear features of the absorption spectra of PbSe NWs are observed. Due to the quantization bandgap of quantum confined nanostructures is shifted toward higher energy in comparison to the bulk material. Here, first excitonic peak at ~ 0.72 eV (1725 nm) corresponds to the bandgap of the PbSe NWs is observed. Similar excitonic peak in the quantum confined PbSe NWs has been observed by J. E. Boercker *et.al.*⁵⁰

Figure 4.1: (a) Absorption spectra of PbSe NWs measured on CaF_2 substrate (black line) and in chloroform (red line) (b) DFT calculated imaginary dielectric function ϵ_2 of PbSe NWs of diameter 2.51 nm.

4.3. Optical transitions in PbSe NWs

As shown in figure 4.1 (a), three optical transitions P_1 (0.72 eV), P_2 (0.89 eV) and P_3 (1.03 eV) are observed in the absorption spectra of PbSe NWs. These three transitions are predicted by the DFT calculations too. Figure 4.1 (b) shows the plot of the imaginary dielectric constant (ϵ_2), calculated using DFT, as a function of the energy for PbSe NWs of diameter 2.51 nm. Due to the limitation of the DFT, calculations were not performed for the experimental diameter (~ 4.7 nm) of the NWs. However, we can observe three optical transitions in the calculated spectra of PbSe NWs (figure 4.1 (b)), which support these three transitions in our experimental absorption spectra of PbSe NWs. A.C. Bartnik *et.al.* performed tight binding calculations for PbSe NWs of diameter 4 nm.⁵¹ Similar to first transition P_1 (~ 0.72 eV), they found the first transition at ~ 0.73 eV and denoted by $1\Sigma_{1/2}^h \rightarrow 1\Sigma_{1/2}^e$ transition. Similar to transitions P_2 (0.89 eV) and P_3 (1.03 eV), Two close transitions $1\Pi_{3/2}^h \rightarrow 1\Pi_{3/2}^e$ and $1\Pi_{1/2}^h \rightarrow 1\Pi_{1/2}^e$ around 1 eV were also observed by A.C. Bartnik *et al.*⁵¹ Above discussion suggest that three transitions P_1 (0.72 eV), P_2 (0.89 eV) and P_3 (1.03 eV) exist in the absorption spectra of quantum confined PbSe NWs.

4.4. Ultrafast dynamics of higher energy transitions

NIR TA spectra of PbSe NWs were measured using pump-probe setup discussed in chapter 2. Pump photon energy of 1.55 eV (800 nm, fluence $\sim 100 \mu\text{J}/\text{cm}^2$) and NIR WLC as a probe were used in the measurements. For polarization dependent pump probe measurements, the polarization of the probe beam was fixed and the polarization of the pump beam was changed using the half wave plate according to the requirement. In addition to that, the polarization of pump beam was also cleaned using the polarizer.

If the angle between the pump and probe polarization is θ , the anisotropy (r) of molecules (nanostructure) at a particular delay time can be expressed as:¹¹⁸

$$r \propto (3 \cos^2 \theta - 1) \quad (4.1)$$

From equation 4.1, one can observe that the anisotropy of molecule (nanostructure) is zero at angle $\theta = 54.7^\circ$. Therefore, this angle ($\theta = 54.7^\circ$) between pump and probe polarization is called magic angle. When the angle between the pump and the probe polarization is set at the magic angle the transient absorption signal is independent of the orientation of the molecules (nanostructure). Therefore, to avoid any contribution of anisotropy from molecules (nanostructures), pump probe measurements can be performed at magic angle. Since we are interested to see the anisotropic properties of nanostructures, we did not perform measurement at magic angle. Therefore, polarizations dependent measurements were performed when; pump and probe were cross and parallel polarization to each other.

NIR TA spectra of PbSe NWs (pump and probe were cross-polarized to each other) in the probe energy range of 0.85 eV to 1.3 eV (~ 950 nm to ~ 1450 nm) are shown in figure 4.2 (a) and dynamics at 0.89 eV energy is shown in figure 4.2 (b). Negative absorbance change ($-\Delta A$) corresponds to a pump-induced decrease of absorption in the NW, while positive absorbance change ($+\Delta A$) corresponds to an increase of the absorption. When probe scanned NWs before the pump excitation (negative time delay) then ΔA is nearly zero (figure 4.2 (b)). This indicates excited states are relaxed before absorbing the next pump pulse. Note that pulse repetition rate of our laser is 1 kHz.

Figure 4.2: PbSe NWs (a) NIR TA spectra and (b) kinetics of P_2 transition with probe energy of 0.89 eV and the pump energy of 1.55 eV (800 nm). In figure 4.2 (b) black circles are the data points and the decay is mono-exponentially fit with a constant for long live component.

Just after the excitation (<1 ps), high electron-hole density leads to the band gap renormalization of the PbSe NWs and complex refractive index vary as a function of the carrier density.¹¹⁹⁻¹²¹ Therefore, dispersive transient absorption spectra are observed (figure 4.2 (a) and (b)).^{99, 114, 115} Hot carriers thermalized very fast (within 3 ps). Therefore, in the following 3 ps, TA spectra change from dispersive to absorptive spectra. Now, remaining carriers are relaxed to the quantum confined states and dominating by the photobleaching corresponding to the transitions in the NWs. P_2 transition observed clearly in the TA spectra (figure 4.2 (a)). However, P_3 transition is not observed clearly. It can be because P_2 and P_3 are located very close to each other. They might overlap with each other and P_2 dominates over P_3 transition. The intra-band transition time of P_2 and P_3 towards P_1 were calculated using a de-convoluted mono-exponential function with a constant (Amplitude) for long live component, fitting of the decay kinetics. The decay time of transition P_2 and P_3 are ~ 5.5 ps (figure 4.2 (b)) and ~ 6.5 ps (figure 4.3 (b)), respectively.

4.5. Photo-excitonic anisotropy of PbSe NWs

In this section, we discuss photo excitonic anisotropy of PbSe QDs and NWs using pump-probe spectroscopy. PbSe QDs do not show any anisotropic effect in the TA kinetics with excitation at 1.55 eV and probe at the bandgap (1.1 eV, figure 4.3) due to the isotropic shape of the QDs.

Figure 4.3: Dynamics of PbSe QDs with pumping energy of 1.55 eV and probe of 1.1 eV (band gap). Black circles and red squares are corresponding to parallel and cross polarization of pump and probe.

However, the anisotropic effect is observed in the PbSe NWs (figure 4.4). These observations can be explained classically by a dielectric constant difference among the host medium and the nanostructures. Therefore, first, we analyze the dielectric effect on the absorption cross-section of nanostructures.

Absorption cross-section of nanostructures can be calculated using equation 4.2.

$$\sigma = \frac{\omega}{n_h c} V |f(\omega)|^2 (2n_m k_m) \quad (4.1)$$

where ω is the excitation angular frequency, n_h is the refractive index of the host medium, c is the speed of light, V is the volume of the nanostructure, $|f(\omega)|$ is the local field factor defined as the ratio of the electric field inside to the outside of the nanostructure. n_m and k_m are the real and imaginary refractive index of the nanostructure.⁷

Figure 4.4: Dynamics of PbSe NWs with 1.55 eV of pump energy and 1.03 eV probe. (a) Absolute (b) Normalized to peak. black circles (parallel polarization) and red squares (cross polarization) are data points. Solid lines are mono-exponential fit of the data.

QDs can be considered as a sphere of uniform dielectric medium (ϵ_m) in a host medium of dielectric constant ϵ_h . When a uniform electric field (E) is applied on the QDs then the electric field inside the QDs (E_{QD}) can be calculated by solving the Laplace's equation.⁸

$$E_{QD} = \frac{3}{2 + \epsilon_r} E \quad (4.2)$$

$$\text{Where, } \epsilon_r = \frac{\epsilon_m(\omega)}{\epsilon_h(\omega)} \quad (4.3)$$

Therefore,

$$f_{\text{QD}} = \frac{E_{\text{QD}}}{E} = \frac{3}{2 + \epsilon_r(\omega)} \quad (4.4)$$

In NWs, when the applied electric field (E) is parallel to the growth axis of the NWs then electric field ($E_{\text{NW}}^{\parallel}$) inside the NWs does not change.

$$\text{Therefore, } E_{\text{NW}}^{\parallel} = E \quad (4.5)$$

$$\text{and } f_{\text{NW}}^{\parallel} = 1 \quad (4.6)$$

When applied electric field is perpendicular to the growth axis of the NWs then the electric field inside the NW is reduced and given by equation 4.8.

$$E_{\text{NW}}^{\perp} = \frac{2}{1 + \epsilon_r(\omega)} E \quad (4.7)$$

$$\text{and } f_{\text{NW}}^{\perp} = \frac{2}{1 + \epsilon_r(\omega)} \quad (4.8)$$

For a given NW, the ratio of the absorption cross section, when applied electric field is perpendicular and parallel to the growth axis can be calculate using equation 4.2,4.7 and 4.9.

$$\frac{\sigma_{\text{NW}}^{\perp}}{\sigma_{\text{NW}}^{\parallel}} \propto \left| \frac{f_{\text{NW}}^{\perp}(\omega)}{f_{\text{NW}}^{\parallel}(\omega)} \right|^2 \propto \left| \frac{2}{1 + \epsilon_r} \right|^2 \quad (4.9)$$

Hence, Absorption cross-section of the NWs is larger in the case when applied electric field is parallel to the growth axis of the NWs. Therefore; NWs have higher optical absorption when the light is parallel polarized to the axis of the NW in comparison to when the light is perpendicularly polarized to the NW axis (figure 4.5 (a)). For anisotropic photo-excitation

analysis, TA kinetics with 1.55 eV pump energy and probe energy of 1.03 eV energy was performed to avoid the $+\Delta A$ signal in the kinetics. More negative ΔA signal is observed when

Figure 4.5: Schematic diagram of (a) the electric field of light interacting with a NW. (b) A subgroup of the NWs parallel to the applied optical electric field absorb the light most strongly (blue).

the pump and probe have the same polarizations (parallel polarizations) than the polarizations are perpendicular to each other (crossed polarized) as shown in figure 4.4 (a). NWs are randomly oriented in solution; the pump beam selects a subgroup of the NWs those are aligned parallel to the electric field of the pump (figure 4.5 (b)). When NWs are aligned parallel to the polarization of the pump they absorb stronger. However, NWs absorb much less, when they aligned perpendicularly to the electric field of the pump polarization due to the small absorption cross-section (equation 4.9). A probe pulse polarized parallel to the pump (parallel polarization) interacts with the pump selected photoexcited subgroup to have less absorption, it shows strong negative signal. However, perpendicularly polarized probe with respect to the pump (cross polarization) absorbed by the NWs, those absorbed less amount of pump show less negative ΔA (figure 4.4 (a)). In the case of parallel polarization, large numbers of photons are absorbed which generate a large number of excitons. Due to the high exciton density, they recombine very fast in

comparison to the cross polarization case as shown in figure 4.4 (b). This behavior of the TA kinetics shows that carriers recombine very fast when the absorbing light is parallel polarized to the growth axis of the NWs in comparison to when the absorbing light is perpendicularly polarized to the growth axis of the NWs.

4.6. Conclusions

Three transitions P_1 (0.72 eV), P_2 (0.89 eV) and P_3 (1.03 eV) are observed in the absorption spectra of quantum confined PbSe NWs of diameter 4.7 ± 0.6 nm. These three transitions are also predicted by the DFT simulation. Dispersive TA spectra of PbSe NWs were observed at short pump-probe delays (within 1 ps) due to the extended length of the NWs. After 3 ps, dispersive TA spectra changes to absorptive TA spectra and show the optical transitions. Anisotropy was observed in PbSe NWs, which is explained classically by the dielectric mismatch and long aspect ratio of NWs.

Chapter 5: Photoexcitation Dynamics of PbSe Nanosheets (NSs)

5.1. Introduction

Graphene is the most studied 2D material and is applied in various technologies.¹²²⁻¹²⁴ The favorable outcome of graphene applications encouraged the exploration of other 2D materials in the nanoscience.^{123, 125-128} Several 2D materials like transition metal dichalcogenides (TMDC), zeolite, CuSe, CdSe, PbS, and GeSe NSs, etc. are synthesized.^{66, 128-133} These 2D materials are considered as potential candidates for the optoelectronic and photonic devices due to their electroluminescence, photoluminescence, anisotropy and nonlinear absorption etc.

Due to the large Bohr radius (46 nm) and large dielectric constant ($\epsilon_{\infty} = 23$), PbSe NSs can show strong quantum confinement as well as anisotropy and high carrier transport.^{32, 56} These special properties can make PbSe NSs interesting for fundamental research. To the best of our knowledge quantum confined PbSe NSs has not been synthesized and characterized till now.

In this chapter, we observed quantum confined optical transitions of PbSe NSs in the steady state absorption spectra. At the same time, those were confirmed by the DFT calculated band structure, absorption spectra and by tight binding calculations in the literature.⁵⁶ TA spectra of PbSe NSs measured with 800 nm excitation (fluence 2.5 mJ/cm²) are dominated by the photo-bleaching of the P₂ transition. Anisotropy is also observed in PbSe NSs. However, the decay times of P₂ transition are similar in both the polarization cases (parallel and cross-polarized pump and probe with each other). Broadband nonlinear TA is also observed with high excitation fluence (7.5 mJ/cm²). It can generate within few hundreds of fs and live for a long time (more

than our measured time scale, 1 ns). This nonlinear property of PbSe NSs can be used in the ultrafast switch, laser mode-locking, NIR eye protector and high-power NIR sensors etc.^{134, 135}

5.2. Steady-state optical properties of PbSe NSs

PbSe NSs of thickness ~ 4.3 nm, dispersed in Isopropanol (IPA) were taken in a 1mm of the optical path length quartz cuvette and sonicated for 30 minutes. After that, the absorption spectrum was measured, shown in figure 5.1. First excitonic peak at ~ 0.640 eV (1940 nm) due to quantum confinement, corresponds to the bandgap of the PbSe NSs.

Figure 5.1: Absorption spectra of PbSe NSs in Isopropanol.

5.3. Optical transitions in PbSe NSs

As shown in figure 5.1, two optical transitions P_1 (0.640 eV) and P_2 (0.857 eV) are observed in the absorption spectra of PbSe NSs. These two transitions are also predicted by the DFT calculations, as shown in figure 5.2 (a) and (b). Figure 5.2 (a) shows the plot of the DFT

calculated imaginary dielectric constant (ϵ_2) as a function of the energy for PbSe NSs (thickness 1.81 nm). As stated above due to the limitations of the DFT, calculations were not performed for

Figure 5.2: (a) DFT calculated imaginary dielectric function ϵ_2 and (b) band structure of PbSe NSs of thickness 1.81 nm.

the experimental thickness (~ 4.3 nm) of the NSs. However, we can observe two clear optical transitions in the calculated spectra and band structure of PbSe NSs (figure 5.2 (a) and (b)), which strongly support these two transitions in the experimental absorption spectra of PbSe NSs. Jun Yang *et.al.* performed tight binding calculations for PbSe NSs of a series of thicknesses.⁵⁶ Similar to first transition P_1 (~ 0.64 eV) in the experimental case, they found the first transition for the similar thickness of PbSe NSs at ~ 0.5 eV and denoted as h_1 - e_1 transition. Similar to P_2 (~ 0.857 eV), They found the second transition h_2 - e_2 at ~ 0.99 eV.⁵⁶ These are close to experimentally observed optical transitions in the PbSe NSs. Above discussion suggests that two transitions P_1 (~ 0.64 eV) and P_2 (~ 0.857 eV) exist in the absorption spectra of quantum confined PbSe NSs.

5.4. Ultrafast dynamics of higher energy transitions

NIR TA spectra of PbSe NSs were measured using pump-probe setup discussed in chapter 2. Pump photon energy of 1.55 eV (800 nm, fluence $\sim 2.5 \text{ mJ/cm}^2$) and NIR WLC as a probe were used in the measurements. Pump and probe were cross polarized to each other. NIR TA spectra of PbSe NSs in the probe energy range of 950 nm to 1500 nm ($\sim 0.827 \text{ eV}$ to $\sim 1.3 \text{ eV}$) are shown in figure 5.3. Negative absorbance change ($-\Delta A$) correspond to a pump-induced decrease of absorption in the NS, and $+\Delta A$ correspond to an increase of the absorption. NIR TA in figure 5.3 shows broad positive TA spectra at shorter wavelengths. It can correspond to the ESA, exciton- biexciton transition and carrier induced broadening.^{136, 137} Moreover, at $\sim 1450 \text{ nm}$ ($\sim 0.857 \text{ eV}$) TA spectra are dominated by the photo-bleaching of the P_2 .

Figure 5.3: NIR TA spectra of PbSe NSs at excitation wavelength of 800 nm (1.55 eV).

5.5. Photo-excitonic anisotropy of PbSe NSs

Kinetics of P_2 transition at 1450 nm probe and 800 nm of pump wavelength are shown in figure 5.4 (a). Black circles correspond to parallel polarization (pump and probe are parallel polarized

to each other) and red squares correspond to cross polarization (pump and probe are perpendicularly polarized to each other). The intra-band transition times (~ 1 ps) of P_2 towards P_1 were calculated using a de-convoluted mono-exponential function with a constant, fit of the decay dynamics.

The anisotropy of PbSe NWs is explained classically in chapter 4. Similarly, the electric field inside the NSs and absorption cross section of NSs can be calculated by the classical electrodynamics. For simplicity, NS is considered as a thin sheet of dielectric constant ϵ_m in a host medium of dielectric constant ϵ_h .

Figure 5.4: (a) Kinetics of P_2 transition with probe energy of 0.857 eV (~ 1450 nm) and (b) tail normalized kinetics with pumping energy of 1.55 eV (800 nm). Black circles (parallel polarization) and red squares (cross polarization) are the data points and the solid lines are mono-exponential fit of the data points.

when the applied electric field (E) is parallel to the geometric plane of the NS then the electric field ($E_{NS}^{\parallel}$) inside the NS does not change.

$$\text{Therefore, } E_{\text{NS}}^{\parallel} = E \quad (5.1)$$

$$\text{and local field factor } f_{\text{NS}}^{\parallel} = 1 \quad (5.2)$$

When applied electric field is perpendicular to the geometric plane of the NS then the electric field inside the NS is reduced, equation 5.3.

$$E_{\text{NS}}^{\perp} = \frac{1}{\epsilon_r(\omega)} E \quad (5.3)$$

$$\text{Where, } \epsilon_r = \frac{\epsilon_m(\omega)}{\epsilon_h(\omega)} \quad (5.4)$$

$$\text{and, } f_{\text{NS}}^{\perp}(\omega) = \frac{1}{\epsilon_r(\omega)} \quad (5.5)$$

For a given NS, the ratio of the absorption cross section, when applied electric field is perpendicular and parallel to the geometric plane can be calculate using equations 4.1, 5.2 and 5.5.

$$\frac{\sigma_{\text{NS}}^{\perp}}{\sigma_{\text{NS}}^{\parallel}} \propto \left| \frac{f_{\text{NS}}^{\perp}(\omega)}{f_{\text{NS}}^{\parallel}(\omega)} \right|^2 \propto \left| \frac{1}{\epsilon_r(\omega)} \right|^2 \quad (5.6)$$

Hence, absorption cross-section of the NS is larger in the case when applied electric field is parallel to the geometric plane of the NS.

As discussed in the case of NWs in chapter 4, in the pump-probe experiment, pump selects a subgroup of NSs, which are parallel to its electric. When the electric field of the probe (1450 nm) is parallel to the pump (parallel polarization) strong photo-bleaching is observed. However,

perpendicularly polarized probe with respect to the pump (cross polarization) show less photo-bleaching (figure 5.4 (a)). Therefore, due to the geometric anisotropy, PbSe NSs show strong photo-bleaching when pump and probe are polarized parallel (figure 5.4 (a)). However, the decay times (~ 1 ps) are similar in both cases. Figure 5.4 (b), after 1 ps delay both of the kinetics (parallel polarized and cross polarized) behaves similarly.

The assignment of a specific polarization direction of 2D PbSe NSs is rather difficult because of its 2D geometry. However, the 2D PbSe NSs may be treated as a biaxial crystal with (220) and (311) in-plane directions. Individual polarization along these crystallographic directions should show dependence at an angle of 42° (angle between the crystal growth axis and the normal of the geometric plane) apart. Similar polarization dependence has been observed in PbS and ReS₂ NSs.^{138, 139} Therefore, observed anisotropy is the combined anisotropy of extrinsic anisotropy due to dielectric mismatch and intrinsic anisotropy due to the crystal structure of NSs. Extrinsic anisotropy favors the high absorption in the parallel polarization leads to strong bleaching signal (figure 5.4 (a)). However, intrinsic anisotropy favors at 42° of polarization. Therefore, intrinsic anisotropy is almost equally distributed in parallel and cross polarization cases. It can be due to the equal contribution of intrinsic anisotropy to the parallel and cross polarization cases, excitons decay with same rate (~ 1 ps) as shown in figure 5.4 (b).

5.6. Broadband nonlinear transient absorption in the NIR

Pump fluence dependent NIR TA spectra of PbSe NSs with 800 nm excitation are shown in figure 4.5 (a) – (c). As discussed before, NIR TA spectra with a pump fluence of 2.5 mJ/cm^2 are dominated by the photo-bleaching of the P₂ transition at 1450 nm (figure 5.5 (a)). As the pump fluence is increased from 2.5 mJ/cm^2 to 5 mJ/cm^2 , the amplitude of photo-bleaching in contrary

Figure 5.5: TA spectra of PbSe NSs with the excitation of 800 nm and fluences of (a) 2.5 mJ/cm², (b) 5.0 mJ/cm² and (c) 7.5 mJ/cm². Pump and probe are cross polarized to each other.

decreased and become broad (figure 5.5 (b)). Moreover, the TA spectra are reversed from negative to positive within ~ 3 ps. At high electron density in the conduction band, an electron can be excited to the higher excited state and thus the overall absorption will increase. Therefore, TA spectra at ~ 3 ps become positive. Some other nonlinear processes like two-photon absorption/ multi-photon absorption can also take place.^{140, 141} As pump fluence is increased from 5.0 mJ/cm^2 to 7.5 mJ/cm^2 , whole the measured broad NIR TA spectra become featureless positive TA, called reverse saturation absorption (RSA).¹⁴² At this high fluence two-photon absorption/multi-photon absorption and/or ESA are dominant respect to the photo-bleaching.¹⁴³ Fluence-dependent kinetics of PbSe NSs at a pump wavelength of 800 nm and probe wavelength 1450 nm is shown in figure 5.6. It shows, at 7.5 mJ/cm^2 , RSA signal rises very fast and decays more than 50% within 3 ps and followed by long decay, much longer than measured time scale of 1 ns.

Figure 5.6: Fluence dependent kinetics of PbSe NSs with 800 nm of pump wavelength and 1450 nm of probe wavelength.

Mechanism of observed nonlinear absorption is not clear till now. Possible mechanisms of RSA are discussed. RSA might be occurring due to the nonlinear scattering caused by the microbubble generation in the solvent.^{134, 140} PbSe NSs in the IPA solvent might be locally heated by high power laser irradiation. In this condition, NSs dissipate heat in the surrounding solvent and generate micro-bubbles in the solvent. Incident laser is scattered by these micro-bubbles and decrease the transmission. If the input fluence is increased further, NSs become heated; they become the center for micro-bubble growth instead of transferring the heat to the surrounding solvent. After a critical fluence, NSs might get sublimated and generate micro-plasma. The nonlinear scattering from the micro-bubbles and from the micro-plasmas reduces transmission and show a strong optical limiting (OL) response (saturation absorption and RSA, etc).^{134, 144} In another possible mechanism, at high exciton density polaronic states are generated from the initial electron–hole gas and show strong TA in the NIR.¹⁴⁵

5.7. Conclusions

Two transitions P_1 (0.640 eV) and P_2 (0.857 eV) are observed in the absorption spectra of quantum confined PbSe NSs of thickness 4.3 ± 0.4 nm. These two transitions are also predicted by DFT. TA spectra of PbSe NSs, measured with a pump wavelength of 800 nm (fluence 2.5 mJ/cm^2) and probe wavelength range from 950 nm to 1500 nm. TA spectra were dominated by the photo-bleaching of the P_2 transition (0.857 nm, ~ 1450 nm). Anisotropy is also observed in PbSe NSs which is the combined effect of intrinsic and extrinsic anisotropies. The decay times of P_2 transition (1 ps) are similar in both the polarization cases (parallel and cross-polarized pump and probe with each other). Broadband nonlinear TA (950 nm to 1500 nm) is also observed in PbSe NSs with pump wavelength of 800 nm and fluence of 7.5 mJ/cm^2 . This signal generated

within first few hundreds of fs and exists for longer times (more than our measured time window of 1 ns).

Chapter 6: Conclusions and Perspectives

6.1. Conclusions

The conclusions of our major findings are presented in the following points

- I. We study the TA spectra and their photoexcitation dynamics in NIR and visible regions of PbSe QDs of three sizes ranging from 3.6 nm to 4.3 nm. MEG QY was measured at different photo-excitation photon energies: in small size PbSe QDs, $QY = 2$ when the photon energy four times exceeds the bandgap and decreases with the increase of the QDs size. We also investigated the origin of the threshold energy for MEG in PbSe QDs through the analysis of TA spectra, in the visible region close to the Σ transition, at different pump energies. We found that Coulomb interaction is not effective when excited high energy levels of the PbSe QDs. We show evidence of a reduction of the hot exciton cooling down via phonon relaxation around the Σ point, where the MEG starts taking over the phonon relaxation process. Moreover, by comparing the TA dynamics at and above the PbSe QDs bandgap, we also infer that the MEG QY could be measured directly from the visible TA spectra (above the bandgap), which is generally easier to measure comparing to the NIR TA spectra.
- II. PbSe NWs of diameter 4.7 ± 0.6 nm was synthesized and the length of the NWs was found to be on few-microns scale along the (100) crystalline axis. We observed that the presence of the acetic acid in the synthesis reaction change the shape and size of the NWs. We found quantum confined optical transitions of PbSe NWs in the steady state absorption spectra, confirmed by the DFT calculated the absorption spectra.⁵¹ TA spectra of PbSe NWs show dispersive TA at short pump-probe delays due to the long length of

the NWs. Later on, dispersive spectra change to absorptive and show photo-bleaching corresponding to the optical transitions in the spectra. Anisotropy has also been observed in the kinetics of PbSe NWs, which is explained classically by the dielectric mismatch and long aspect ratio of the NWs.

To our best knowledge, this is the first report of the synthesis of quantum confined PbSe NSs. The thickness of synthesized hexagonal NSs-like morphology PbSe NSs is 4.3 nm and lateral dimensions are in the range of several hundred nm to few μm . From the TEM analysis, it was found that PbSe NSs are bound by (220) and (311) planes facets and the growth direction of PbSe NSs is along the $(\bar{2}24)$ plane with an angle of 48° with the surface of NSs. We observed quantum confined optical transitions of PbSe NSs in the steady state absorption spectra. Those were confirmed by the DFT calculated band structure and absorption spectra.⁵⁶ TA spectra of PbSe NSs measured with 800 nm excitation (fluence 2.5 mJ/cm^2) and probe wavelength range of 950 nm to 1500 nm, are dominated by the photo-bleaching of the second transition (P_2) at 1450 nm. Anisotropy is also observed in PbSe NSs and the decay times of P_2 transition are similar in both of the polarization cases (parallel and cross-polarized pump and probe with each other). Broadband nonlinear TA is also observed with high excitation fluence (7.5 mJ/cm^2). NIR TA can generate within few hundreds of fs and live longer than 1 ns.

6.2. Perspectives

PCE of the solar cell can be increased using the MEG. Peak external photocurrent quantum efficiency has been reported more than 100% via MEG in a PbSe QDs solar cell.⁴⁰ Due to the strong quantum confinement, Auger recombination rate is higher in the QDs. Therefore, it is challenging to extract MEG generated charge carriers at the electrodes in short Auger recombination time. Moreover, charge transport is also weak in QDs. However, in elongated nanostructures, these problems can be reduced.

Due to the small radius, NWs are strongly confined in two dimensions, while the third dimension is free along the length of the NW. In PbSe NWs, the electron-hole separation is expected along the radius of the NWs and the absorption cross-section and carrier transport enhancing due to the length of NWs.⁵¹ Auger recombination rate is inversely proportional to the volume of the nanostructures.¹⁴⁶ Therefore, MEG generated carriers can stay for a long time in PbSe NWs and it can be possible to extract them at the electrodes, at the same time carrier transport will be enhanced along the NW length. Therefore, it is possible to enhance the PCE of PbSe NWs solar cells via MEG.

Other possible applications of PbSe NWs are NIR photodiode, polarized photodiode, field effect transistor (FET), IR sensors and laser.

We open the way to synthesize the PbSe NSs and one can optimize the synthesizing method to get desired thickness and lateral dimensions. Optoelectronic properties of NSs are also depending on the lateral dimensions.^{117, 147} So, one can study the lateral dimension-dependent properties of PbSe NSs.

Due to the small thickness, NSs are strongly confined in one dimension, while the other two dimensions are free. Carrier transport should be high along the geometric plane of the NS and Auger recombination should be reduced due to the large volume of the NSs. Therefore, it is possible to reach higher PCE in PbSe NSs solar cells via MEG.

PbSe NSs can also be used as large-scale devices like single NS FET due to its large surface area. Due to the observed nonlinear properties of PbSe NSs, they can be used in pulse shaping of the laser beam, ultrafast switch, high power IR sensor, detector and IR eye protector etc.^{134, 135}

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List of Publications

Journal Articles

1. Hot exciton cooling and multiple exciton generation in PbSe quantum dots, **M. Kumar**, S. Vezzoli, Z. Wang, V. Chaudhary, R. V. Ramanujan, G. G. Gurzadyan, A. Bruno and C. Soci, Phys. Chem. Chem. Phys, 2016, 18, 31107.
2. Small size effects on electron transfer in P3HT/InP quantum dots, J. Yin, **M. Kumar**, Q. Lei, L. Ma, R. S. S. Kumar, G. G. Gurzadyan, and C. Soci, J. Phys. Chem. C, 2015, 119, 26783.

Book Chapter

Photoinduced charge transfer dynamics at hybrid GaAs/P3HT interfaces, J. Yin, **M. Kumar**, M. Panahandeh-Fard, Z. Wang, F. Scotognella, C. Soci: Ultrafast Dynamics in Molecules, Nanostructures and Interfaces, G. G. Gurzadyan, G. Lanzani, C. Soci, T. C. Sum Ed., 2014, World Scientific Publishing Series in Optics and Photonics – Vol. 8 (ISBN 978-981-4556-91-0).

Conferences

1. Multiple exciton generation in low-dimensional PbSe nanostructures, **M. Kumar**, A. Bruno, J. Yin, Z. Wang, P. Lova, G. G. Gurzadyan, C. Soci (Talk). Conference on Materials for Advanced Technologies (ICMAT) 2015, Singapore, 28 June - 3 July 2015.
2. Dimensionality effects on charge transfer at polymer/III-V heterointerfaces, J. Yin, **M. Kumar**, Q. Lei, G. G. Gurzadyan, C. Soci (Talk). Conference on Materials for Advanced Technologies (ICMAT) 2015, Singapore, 28 June - 3 July 2015.

3. Dimensionality effects on multiple exciton generation in PbSe nanostructures, **M. Kumar**, A. Bruno, J. Yin, P. Lova, Z. Wang, G. G. Gurzadyan, C. Soci (Talk). E-MRS Spring Meeting 2014, Lille, May 11-15, 2015.
4. Hybrid nanoplasmonic colloidal systems for the enhancement of the optical response of carbon, M. Glaske, A. Bruno, **M. Kumar**, G. G. Gurzadyan, C. Soci, T. Bisswanger, R. Bandstaetter, S. Vaitiekienas, P. Kusch, S. Reich, A. Setaro (Talk). E-MRS Spring Meeting 2014, Lille, May 11-15, 2015.
5. Ultrafast electron transfer from P3HT to InP quantum dots: ligand and size effects, J. Yin, **M. Kumar**, Q. Lei, L. Ma, R.S.S. Kumar, C. Soci (Talk). MRS Spring Meeting, San Francisco (California), 6-10 April 2015.
6. Effect of ligands exchange on charge dynamics in PbS:P3HT hybrid systems for solar cells applications, A. Bruno, C. Borriello, T. Di Luccio, C. Minarini, **M. Kumar**, R.S.S. Kumar, C. Soci (Talk). MRS Spring Meeting, San Francisco (California), 6-10 April 2015.
7. Multiple exciton generation in low dimensional PbSe nanostructures, **M. Kumar**, A. Bruno, P. Lova, G. G. Gurzadyan, C. Soci (poster). MRS Spring Meeting, San Francisco (California), 6-10 April 2015.
8. Carrier multiplication in low dimensional PbSe nanostructures, **M. Kumar**, A. Bruno, A. Chaturvedi, P. Lova, Z. Wang, G. G. Gurzadyan, C. Soci (Poster). IPS Meeting 2014, Singapore, 26-28 February 2015.
9. Exciton diffusion length of P3HT determined by GaAs quencher, J. Yin, **M. Kumar**, L. Ma, R.S.S. Kumar, G. G. Gurzadyan, C. Soci (poster). European Optical Society Annual Meeting (EOSAM) 2014, Berlin, September 15-19, 2014.

10. Morphological and optical characterization of CuO, D. Cortecchia, D.G. Figueroa del Valle, I. Kriegel, J. Yin, M. Panahandeh-Fard, **M. Kumar**, H. Sun, F. Scotognella, C. Soci (poster). European Optical Society Annual Meeting (EOSAM) 2014, Berlin, September 15-19, 2014.
11. Study on the transient absorption of CuO/ZnO thin film heterojunction, D. Cortecchia, D.G. Figueroa del Valle, I. Kriegel, J. Yin, M. Panahandeh-Fard, **M. Kumar**, H. Sun, F. Scotognella, C. Soci (poster). European Optical Society Annual Meeting (EOSAM) 2014, Berlin, September 15-19, 2014.
12. Polaron photogeneration in P3HT-PCBM bulk heterojunctions revealed by infrared photoinduced absorption spectroscopy, M. Panahandeh Fard, Z. Wang, **M. Kumar**, C. Soci (poster). The International Society for Optical Engineering (SPIE) Optics & Photonics, San Diego, August 17-21, 2014.
13. Ultrafast electron transfer from P3HT to pyridine-capped InP quantum dots, J. Yin, **M. Kumar**, Q. Lei, M. Panahandeh-Fard, D. Cortecchia, Z. Wang, R.S.S. Kumar, C. Soci (talk). E-MRS Spring Meeting 2014, Lille, May 26-30, 2014.
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17. Kinetics of interfacial charge transfer at P3HT:GaAs heterointerfaces, M. Panahandeh-Fard, J. Yin, M. Kurniawan, Z. Wang, **M. Kumar**, T.C. Sum, C. Soci (talk). Conference on Materials for Advanced Technologies (ICMAT) 2013, Singapore, June 30-July 5, 2013.
18. Ultrafast charge transfer dynamics in P3HT-GaAs heterointerfaces, M. Panahandeh-Fard, J. Yin, M. Kurniawan, Z. Wang, **M. Kumar**, T.C. Sum, C. Soci (talk). IPS Meeting 2013, Singapore, 4-6 March 2013.