Charge separation and photoconductivity in hybrid nanostructures

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"...there is no greater folly than to be very inquisitive and laborious to found out the causes of such a phenomenon as never had an existence, and therefore men ought to be cautious and to be fully assured of the truth of the effect before they venture to explicate the cause."

The Displaying of Supposed Witchcraft (1677), by John Webster
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1 Introduction

The research on high performing solution-processable semiconductors addresses the need for cheap mass production of electronic and optoelectronic devices. In this context, colloidal semiconductor nanocrystals (NCs) have gained wide interest during recent years due to their easy solution synthesis, processability and wide scope of applications, ranging from biology to electronics, including photosensing and photovoltaic devices. An important parameter of semiconductor NCs is the width of the energy gap between the bottom of the conduction and the top of the valence energy band. In bulk semiconductors, i.e., in samples of macroscopic sizes, the gap only depends on the type of material. When sample size can be controlled and reduced down to the nanoscale, electronic excitations react to spatial constraint by modifying their energy due to quantum effects. Semiconductor NCs that exhibit size-controlled optical and electronic properties are often referred to as quantum dots (QDs).

Semiconductor QDs can be prepared either by physical or chemical methods. Molecular beam epitaxy and metalorganic chemical vapour deposition are techniques that belong to the first approach and require high-energy input. On the other hand, soft chemical synthesis needs much lower energy input and allows for the fabrication of colloidal semiconductor QDs. These latter are made by an inorganic core overcoated by a shell of ligand molecules and, consequently, can be manipulated like large molecules. Organic ligands passivate QD surface, permit to manage QD growth and aggregation, and determine the solubility and reactivity of the QD with respect to the environment. However, due to the presence of ligands on the QD surface, electronic states in the inorganic core weakly interact with the surrounding medium. This leads to inefficient charge photogeneration and unsatisfactory transport properties. The low effectiveness of these processes represents a serious obstacle for the use of QDs and NCs in electronic and optoelectronic devices. Overcoming these bottlenecks represents one of the major challenges in the research field of nanoscience and nanotechnology. So far, several ingenious strategies have been reported in literature addressing these issues. Here, we mention briefly the basic, inspiring concepts.

One driving idea aims at lowering the potential barrier for charge hopping by striping off the capping ligands after QD film deposition or by replacing them with very short capping molecules. Charge separation following photon absorption can be driven by the Schottky barrier formed at the interface between the NC film and a metal surface. Carrier dissociation can be also assisted by traps, e.g., created at the QD surface after ligand removal followed by oxidation process. In this way, ultra-high sensitive photodetectors have been very recently demonstrated. A different
approach for charge splitting takes advantage of the possibility to grow heterostructures; allowing spatial separation of electron and hole wavefunctions, like in CdSe/CdTe NCs, where a spherical core, CdSe, is surrounded by a CdTe shell. Alignment of electronic levels at the inorganic/inorganic interface is such that charge split is energetically favoured\textsuperscript{10,11}. The control over electron and hole wavefunctions, besides being useful for photodetector and photovoltaic devices, can be also exploited for nonlinear optics, quantum optics and low-threshold lasers.

A different approach makes use of semiconductor NCs blended with organic semiconductors to form a bulk heterojunction. The organic/inorganic interface acts as the building block for charge splitting, while the interpenetrating NC and polymer networks could provide the pathways for charge transport. A promising hybrid composite, which will be investigated in this thesis, is made by lead sulphide QDs and fullerene derivatives. This blend benefits from the sensitivity of PbS to the infra-red spectrum, the potential for carrier multiplication\textsuperscript{12,13} (the phenomenon that allows to create more than one electron-hole pair for each absorbed photon), and the good electron transport properties of fullerenes\textsuperscript{14}. The dependence of the band-gap on the nanocrystal size offers the opportunity of controlling the energy level alignment at the interface with fullerene, which ultimately determines the possibility of free charge generation at the heterojunction following optical excitation, a basic optical process in optoelectronic devices. Semiconductor heterojunctions are classified according to the relative alignment of the electron affinity (EA) and ionisation potential (IP) of the two materials. In a type I heterojunction, the band edges of one semiconductor fall within the energy gap of the second (straddling gaps). A type II heterojunction is formed when a staggered level alignment sets in. Only in this latter case, charge separation at the junction interface is energetically favourable and thus the junction may serve to the conversion of photogenerated excitons into free charged carriers.

In this thesis, we report an investigation of the excited-state dynamics, charge separation and charge transport properties in thin film made by two novel types of NC heterojunctions:

- The hybrid heterojunction formed between the soluble derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) of fullerene and PbS QDs. When considering this structure, a threshold size for PbS nanocrystals is expected for which a transition occurs from type I to type II heterojunction. The occurring of electron transfer from PbS QDs to fullerene, the critical QD size and emission wavelength below which charge separation takes place are extremely relevant to optoelectronic applications in the near infrared spectral region and deserve a direct experimental assessment. The knowledge of the electron transfer dynamics
at the fullerene/nanocrystal interface and its competition with multi-excitation annihilation processes are also significant for the exploitation of carrier multiplication\textsuperscript{15,16}.

- The heterojunction formed by CdSe/CdS dot/rod nanocrystals. This system represents a recently developed class of heterostructures, formed by a spherical CdSe core, subsequently covered by a rod-shaped CdS shell.\textsuperscript{17,18,19,20} While bulk CdSe and CdS have in principle a type-I band alignment, with CdSe band energies both enclosed within CdS ones, the two conduction bands are so close to each other that conduction electron wavefunctions can significantly spread into the rod, realizing what is sometimes referred to as a quasi-type II heterojunction.

Films of PbS QDs/PCBM and CdSe/CdS dot/rod nanocrystal were used to fabricate photodetectors. A consistent part of the work of this thesis was devoted to the development of these devices and to assess their optoelectronic response.

The thesis is structured as follows:

In Chapter 2, we present a short introduction to the experimental methods used to characterize samples optically and electrically.

In Chapter 3, we present and discuss experimental results obtained in PbS QDs/PCBM (subsections 3.1) and CdSe/CdS dot/rod NCs (subsections 3.2). In subsection 3.1, we shortly introduce the PbS QDs/PCBM blend. In paragraph 3.1.1, we discuss the hybrid heterojunction and the performance of the photoconductive detector made using this blend. In paragraph 3.1.2, we focus on the photophysics of the electron transfer from PbS QDs to PCBM, and its quantum-size dependence. In subsection 3.2, we shortly introduce the photophysics of CdSe/CdS dot/rod heterostructures. In paragraph 3.2.1, we report on experimental results concerning the spectroscopic investigation of CdSe/CdS dot/rod heterostructures. This study mainly addresses nonlinear optical properties, which are also related to the degree of charge separation at the heterojunction. In paragraph 3.2.2, we report on the fabrication and characterization of photoconductive detectors made using these dot/rod NCs, after a suitable treatment of the NC surface. Main conclusions and perspectives are drawn in paragraphs 3.1.3 and 3.2.3.

In Appendix A, we provide a short review of the basic working principles of photodetectors. In Appendix B, we report further details on the methods and supplies used to fabricate photodetectors. In Appendix C, we report a short overview of electronic states in quantum dots. In Appendix D, we provide a short summary of the basic properties of fullerene and PCBM.
2 Methods

2.1 Time resolved ultrafast spectroscopy

2.1.1 Pump&probe technique

Detection systems commonly used in optoelectronics, like photodiodes, stroboscopic oscilloscopes and similar devices, can reach only time resolution around $10^{-10}$ s. As many non-stationary processes in solid state physics are much faster, this operation range is insufficient. One of the main optical methods used in ultrafast spectroscopy to achieve subpicosecond time resolution is the so called pump&probe technique. The temporal resolution of this optical spectroscopy is actually limited by the laser pulse duration. The pump&probe method bases on the following principle: a short laser beam is split into two parts, one of which is temporally delayed with respect to the other. The beams travel along different optical paths before they join up again (Figure 2.1—1).

![Figure 2.1—1 General idea of pump-probe spectroscopy](image)

The first beam, the pump, strikes the investigated sample, delivering the energy to transfer electrons to the excited state. The changes in the system are investigated by the second part of the beam, the probe, much lower in intensity, and coming into the sample with certain delay introduced by the variable length of the optical path. The intensity of the transmitted probe beam is recorded as a function of the delay between it and the pump. Thus, the resolution of this method does not depend on the response time of the electronic receiver used to record the dynamics of the investigated pico- or femtosecond process.
The delay of the probe beam with respect to the pump is $\Delta t = \frac{\Delta x}{c}$, where $\Delta x$ is the optical path difference and $c$ is the velocity of light. Recording the signal for different delays, the dynamics of the excited state can be monitored. The time resolution of this method depends solely on the pulse duration.

Pump and probe beams may have different or equal wavelengths. When using tuneable light sources, like parametric amplifiers, parametric oscillators, parametric generators and higher harmonic generators or white supercontinuum sources, the wavelengths of the pump and/or probe can be modified. In the most optimal set-up, the tunability of the pump and probe should be independent of each other.

The physical understanding of the method can be given in a simple model of two level system of energies $E_1$ and $E_2$. The initial population has a Boltzmann-type distribution. If the system is excited with the pump pulse of high intensity and frequency $\omega = \frac{(E_2 - E_1)}{h}$, a considerable part of the molecules will be transferred to the upper state. As a consequence, there are fewer molecules at the lower level $E_1$ than there were before pump excitation. Therefore, the probe, delayed with respect to the pump by the time $\Delta t$, monitors the transient absorption $A(E_1 \rightarrow E_2)$ that is smaller than the absorption $A_0$ recorded for the same probing pulse in absence of the pump. When $\Delta t$ increases and exceeds the lifetime of the excited level $\tau_1$ ($\Delta t > \tau_1$), the return of excited molecules to the
ground state can be observed, leading to the recovery of the initial absorption value. Changes in the absorption spectrum may involve spectral shifts and optical density changes in the sample for a given wavelength. Analyzing those spectral changes and temporal bleaching gives information about the dynamics of the investigated system and can provide information about new species or transitions created by the incident light.

The probe transmission through the sample is given by the correlation function

$$T^*(\omega, \tau) = \frac{\int dt \cdot I_{pr}(t - \Delta t) \cdot \exp\left(-\sum_{kj} \sigma_{kj}(\omega) \cdot N_k(t) \cdot D \right)}{\int dt \cdot I_{pr}(t)}$$

where $I_{pr}(t)$ is probe intensity, $\sigma$ absorption cross-section of the sample and $D$ is sample thickness. $N_k(t)$ is the population of $k$-level during and after the pump. Other characters stay for already mentioned or standard meaning.\(^{23}\)

To observe large changes inside the system, the pump beam intensity should reach almost the saturation level $I_s$, while the probing beam power should be kept as low as possible, just to probe the changes. $I_s$ is given by

$$I_s = \frac{h\nu}{2\sigma p}$$

where $\nu$ is the frequency of the laser beam, $\sigma$ is absorption cross section, and $t_p$ is the exciting pulse duration. The higher the absorption cross-section is and the longer the lifetime of excited states are, the easier it is to obtain high dynamic range in the detection of the differential transmission.\(^{24}\)

What is measured in experiment is basically the change of optical density of the sample with respect to the presence or lack of the pump, so the variation of the absorption of the probe. For small signals (usually in working conditions the variation of the optical density does not exceed 10%), the following simplification is applied:

$$\Delta OD = -\ln\left(\frac{T^*}{T}\right) = -\ln\left(1 + \frac{\Delta T}{T}\right) \approx -\frac{\Delta T}{T}$$

where $T^*$ is the transmission through the sample in presence of the pump, while $T$ in the not excited material, and $\Delta T \equiv T^* - T$.

Thanks to this approximation, derivation of a directly interpretable equation is possible. When assumed that

$$\Delta OD = -\ln \left(\frac{\exp\left[-\sum_{kj} \sigma_{kj}(\omega) \cdot N_k(t) \cdot D \right]}{\exp\left[-\sum_{kj} \sigma_{kj}(\omega) \cdot N_k \cdot D \right]}\right) = -\ln \left(\exp\left[-\sum_{kj} \sigma_{kj}(\omega) \cdot \Delta N_k(t) \cdot D \right]\right) = \sum \sigma_{kj}(\omega) \cdot \Delta N_k(t) \cdot D$$
where $\Delta N_k(t)$ is the difference in population of the $k$-level, induced by the pump, calculation the quantity of actual observable goes as
\[
-\frac{\Delta T}{T} = \sum \sigma_{\omega}(\omega) \cdot \Delta N_k(t) \cdot D
\]
and the population of the excited level is considered 0 when pump is not present.

Photobleaching, stimulated emission and photoinduced absorption (also called excited state absorption) contribute to the transmission difference spectrum. Photobleaching means that optical density of the sample was locally reduced due to the ground state depletion. This spectrum corresponds to the conventional absorption spectrum. Stimulated emission is a process happening on similar way to lasing, when radiative relaxation from excited state is amplified by the presence of resonant photon. Stimulated emission spectrum resembles the photoluminescence one, and must be corrected by Einstein factor $\omega^3$. The last component, the excited state absorption, leads to negative change in transition, as it originated from transitions of newly promoted electron to even higher laying levels. The probability of this process is highly intensity dependent.

2.1.2 Time- and spectral-resolved photoluminescence

The detection of a high-speed optical signal is indispensible in many optoelectronic systems. The operational principle of standard photodetectors is based on the generation of photocarriers by the injection of an optical signal into a semiconductor/metal, where detected photons are translated into photocurrent. Photodetectors commonly used for measuring dynamics of ultra-fast optical signals are streak-cameras or fast photo receivers, of various constructions, depending on the wavelength of application and duration of investigated processes.

Schematic representation of the streak-camera working principle and construction are represented on Figure 2.1—3.

![Figure 2.1—3 Construction of the streak-camera](image)

The heart of the device is the streak tube which converts the information in the time domain to a spatial domain. A light pulse of short duration hits a photocathode which causes
the emission of photo-electrons inside the tube. This so-created electron bunch contains the same time structure as the incident light pulse. The electrons are electrically focused and accelerated towards the other end of the tube where they hit a phosphor screen. The electrons are, however, deflected vertically by an electric field during their transit through a pair of deflection plates. This deflection field has an ultra-fast time slope. This causes the electrons in the bunch to be deflected differently, the initially emitted electrons hit the phosphor screen at the bottom and the latter electrons higher positions. The intensity profile along the stripe-like image (a ‘streak’) left on the phosphor screen gives the time profile of the input light impulse.\textsuperscript{26}

![Streak camera operation timing](image)

Figure 2.1—4 Streak camera operation timing\textsuperscript{27}

With respect of the measurement demands (expected decay time, signal strength, background offset) the streak camera may operate in two modes: single sweep or synchroscan. Single sweep mode is so called due to the fact, that only one sweep is involved (a single shot). The time range covered with this mode spans from 60 ps to 10 ms. A ramp voltage is applied to deflection electrodes during the sweep (Figure 2.1—5).

![Sweep voltages for single sweep and synchroscan configurations](image)

Figure 2.1—5 Sweep voltages for single sweep and synchroscan configurations\textsuperscript{28}
When the sweep is repeated with high speed, the configuration is called synchrosan. A high frequency sine wave is applied to the deflection electrodes (Figure 2.1—5). Synchronizing the repeated sweep frequencies with the high-repetition laser frequency allows accumulating streak images at fixed position on phosphor screen. This assures very high signal to noise ratio, thus allows detection of weak signals. The operation time window covers decays from several hundred picoseconds to 2 or 3 nanoseconds with a best resolution of a few picoseconds.
2.2 Imaging techniques

2.2.1 Atomic Force Microscope (AFM)

Among many types of scanning probe microscopes, the atomic force microscope (AFM) seems to be the most frequently used, due to high accuracy and easiness of usage. Images are created by successively scanning the material line by line with the physical probe – in case of the AFM when the probe is in close proximity to the sample a deflection of the silicon cantilever occurs according to Hooke's law. The deflection can be measured by spectroscopic means as presented on the sketch below (Figure 2.2—1). Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals, capillary or electrostatic forces, chemical bonding or even magnetic or Casimir forces and others.

![Deflection detection in AFM](image)

Resolution of measurement can go down to fraction of nanometre, which is much beyond the diffraction limit of optical microscopy. What puts limits on the resolution is the quality of the tip; the sharper it is the higher resolution can be obtained. A few instruments operate in UHV but the majority operates in ambient atmosphere, or in liquids.

In the contact mode operation, the static tip deflection is used as a feedback signal. The force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. By moving the tip across the sample in parallel lines the picture is created, imaging the morphology. In the semicontact mode, the cantilever is externally oscillated at its fundamental resonance frequency or close to it. The oscillation amplitude and phase are modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation...
provide information about the sample's characteristics. Both methods can be applied to create the
height image but the tapping mode gives additional information with respect to the contact mode –
even if the morphology of the sample seems to be homogenous, materials of different origin can give
various responses in the phase of the tip oscillations. Although any mode applied will give the
topographical picture of scanned surface, only the semicontact mode is revealing potential phase
segregation even in case of smooth surface.

The contact mode is the most common mode used in the atomic force microscope. The
force on the tip is repulsive with a mean value of $10^{-9}$ N. This force is set by pushing the cantilever
against the sample surface with a piezoelectric positioning element. In contact mode AFM the
deflection of the cantilever is sensed and compared in a DC feedback amplifier to some desired
value of deflection. If the measured deflection is different from the desired value the feedback
amplifier applies a voltage to the piezo to raise or lower the sample relative to the cantilever to
restore the desired value of deflection. The voltage that the feedback amplifier applies to the piezo is
a measure of the height of features on the sample surface. It is displayed as a function of the lateral
position of the sample.

Tapping mode is a key advance in AFM. This potent technique allows high resolution
topographic imaging of sample surfaces that are easily damaged, loosely hold to their substrate, or
difficult to image by other AFM techniques. Tapping mode overcomes problems associated with
friction, adhesion, electrostatic forces, and other difficulties that an plague conventional AFM
scanning methods by alternately placing the tip in contact with the surface to provide high resolution
and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode
imaging is implemented in ambient air by oscillating the cantilever assembly at or near the
cantilever's resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever
to oscillate with a high amplitude (typically greater than 20 nm) when the tip is not in contact with
the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or
tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and
lifts off, generally at a frequency of 50,000 to 500,000 cycles per second. As the oscillating
cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily
reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation
amplitude is used to identify and measure surface features.

During tapping mode operation, the cantilever oscillation amplitude is maintained
constant by a feedback loop. Selection of the optimal oscillation frequency is software-assisted and
the force on the sample is automatically set and maintained at the lowest possible level. When the tip
passes over a bump in the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. Conversely, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases (approaching the maximum free air amplitude). The oscillation amplitude of the tip is measured by the detector and input to the controller electronics. The digital feedback loop then adjusts the tip-sample separation to maintain constant amplitude and force on the sample.

When the tip contacts the surface, the high frequency (50 kHz – 500 kHz) makes the surfaces stiff, and the tip-sample adhesion force is greatly reduced. Semicontact mode prevents the tip from sticking to the surface and causing damage during scanning. Unlike contact mode, when the tip contacts the surface, it has sufficient oscillation amplitude to overcome the tip-sample adhesion forces. Also, the surface material is not pulled sideways by shear forces since the applied force is always vertical. Another advantage of the tapping mode technique is its large, linear operating range. This makes the vertical feedback system highly stable, allowing routine and reproducible sample measurements.\(^29\)

![Building-blocks of atomic force microscope (a), with explanation of the signal gathered in height and phase domain in case of contact (b) and tapping (c) modes](image)

Problems with contact mode are caused by excessive tracking forces applied by the probe to the sample. The effects can be reduced by minimizing tracking force of the probe on the sample, but there are practical limits to the magnitude of the force that can be controlled by the user during operation in ambient environments. Under ambient conditions, sample surfaces are covered by a layer of adsorbed gases consisting primarily of water vapour and nitrogen which is 10-30 monolayers thick. When the probe touches this contaminant layer, a meniscus forms and the cantilever is pulled by surface tension toward the sample surface. The magnitude of the force
depends on the details of the probe geometry, but is typically on the order of $10^{-7}$ N. This meniscus force and other attractive forces may be neutralized by operating with the probe and part or the entire sample totally immersed in liquid. There are many advantages to operate AFM with the sample and cantilever immersed in a fluid like elimination of capillary forces, the reduction of Van der Waals' forces and the ability to study technologically or biologically important processes at liquid solid interfaces. In addition, a large class of samples, including semiconductors and insulators, can trap electrostatic charge (partially dissipated and screened in liquid). This charge can contribute to additional substantial attractive forces between the probe and sample. However there are also some difficulties involved in working in liquids, such as, \textit{i.e.}, sample damage on hydrated and vulnerable biological samples. Also semiconductor wafers cannot practically be immersed in liquid.

The apparatus used in this study was NT-MDT Smena Scanning Probe Microscope, consisting of a stand-alone measuring head and an electronic module which is computer controlled. One of the advantages of here used instrument is no limitation at the sample size and shape, so the scanning could be performed at exactly same films as used for spectroscopic or electric studies. For this study the AFM was used in contact mode for robust samples (like empty gold electrodes) and semicontact (tapping) mode in case of cast films. Measurements were performed in ambient conditions.

\subsection{2.2.2 Confocal microscopy}

For optical visualization, inverted microscope Eclipse TE2000 by Nikon was used with several objectives of various magnifications and numeric apertures. Possibility to attach the photo camera to the instrument enables taking pictures and provides general morphological information, but what is more important, this microscope can be incorporated with computer and several lasers into confocal system. Confocal microscopy is used mostly to increase the resolution of obtained picture, as well as facilitating scanning across the sample in Z direction. Images can be acquired point-by-point and reconstructed with a computer, allowing three-dimensional visualization of topologically-complex objects. Simplified construction is presented below at Figure 2.2—3
For samples excitation three types of CW lasers were connected by optical wire to the microscope head: 405 nm InGaN diode laser (Coherent), 543.5 nm He-Ne laser (Melles-Griot) and argon laser (SpectraPhysics) operating at 488 nm as presented on the cartoon below (Figure 2.2—4).
2.3 Electrical characterization

Complementary information about electro-optically active system may be provided by standard measurements of current flow under a given voltage as a function of the power of the incident light. Charge transport properties also critically depend on the sample morphology as it was shown in many cases.\textsuperscript{31}

Current-voltage characteristics of investigated materials were taken using gold electrodes shaped into interdigitated structures. Photolithography procedure is briefed in Appendix B and design and details of the bought microchips are presented there as well.

For the determination of the type of carriers, the field-effect transistor configuration was applied. This is one of the techniques used to measure charge carriers’ mobilities over microscopic distances. Thanks to that configuration, the mobilities may be calculated from data collected during standard I-V characterisation of transistor. The drain-to-source current flows via a conducting channel that connects the source and the drain. The conductivity is varied by the electric field that is produced when a voltage is applied between the gate and source terminals; hence the current flowing between the drain and source is controlled by the voltage applied between the gate and source.

In the linear regime of the current-voltage characteristic, the figures of merit can be calculated from following equation:

\[ I_{SD} = \frac{W}{L} \mu C (V_G - V_T) \cdot V_{SD} \]

and in saturated regime from:

\[ I_{SD} = \frac{W}{2L} \mu \cdot C (V_G - V_T)^2 \]

where \( I_{SD} \) and \( V_{SD} \) are current and voltage between source and drain, \( V_G \) is gate voltage, \( V_T \) is the threshold voltage at which the current start to rise, \( C \) stays for capacitance for gate dielectric and \( W \) and \( L \) are the width and length of conductive channel, respectively. In field effect transistors the charges travel in a very narrow channel (~nm wide) at the interface between the semiconductor and dielectric. Transport may be interfered by defects, nonuniformity of the film, polarity of the dielectric and presence of traps at the interface. What affects the measurement results is also contact resistance at the source and drain metal/semiconductor interface. Important factor is also gate voltage, as the mobility seems to depend strongly on that value. If the voltage is low, the structural defects, impurities and other traps may lead to underestimation of the mobilities, while at higher \( V_G \) this effect is less influential. The charge carrier density is gate-voltage dependent as well.\textsuperscript{32}
2.4 Experimental set-ups

2.4.1 Optical and electrical characterisation of PbS/PCBM heterojunction and photodetector fabrication (relevant to Par. 3.1.1)

Oleic-acid-capped PbS crystals were synthesized similarly to the preparation method reported in ref. 33. The fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was obtained by Solenne BV. The samples for electrical measurements were spin-coated (thickness ~100 nm) from a chlorobenzene solution onto Si/SiOx substrates with interdigitated finger-like electrodes. For field-effect transistor measurements, the active layer was spin-coated on substrates composed by a heavily doped p-type Si substrate that served as the gate electrode with 200 nm of thermally grown SiO₂, used as the dielectric layer with a capacitance per unit area of 17nFcm⁻². The source and drain electrodes consisted of 10 nm of Ti and 30 nm of Au.

Samples for optical characterization were drop-cast (thickness ~1600 nm) onto quartz substrates from the same solution. The sample cross sections were inspected by a ZEISS 1540 XB cross beam electron microscope. For this purpose first a Pt layer was deposited with the focused ion beam. Than a trench was sputtered with 20 keV Ga ions and the secondary electron images were taken with 5 kV acceleration voltage and an in-lens detector.

Time-resolved photoluminescence measurements were performed exciting the samples at 800 nm by a Ti:Sapphire laser providing 150 femtosecond pulses. The photoluminescence emission was detected by a spectrometer coupled with a Hamamatsu streak camera with a cathode sensitive in the near infrared spectral range.

Differential transmission decays are obtained with a two colour pump-probe set up. The samples were excited with pulses from a regenerative amplifier (784 nm wavelength, 150 fs duration, 1 kHz repetition) and were probed with infrared (~1280 nm wavelength) pulses from a tuneable parametric amplifier. The pump beam, 5 µW in average intensity, was focused to a ~150 µm spot on the sample, corresponding to much less than one excitation per dot, in order to avoid nonlinear processes shortening the exciton lifetime; the probe sampled the inner half of the spot, to ensure homogeneous excitation.

Electrical measurements were carried out in a home-built probe station under high vacuum (10⁻⁶ mbar) with Keithley 4200 semiconductor analyzer at room temperature. To prevent parasitic currents and to electronically isolate the silicon substrate a sheet of mica was used between the silicon substrate of the devices and the copper chuck. The illumination of the samples was
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provided by a 532 nm fibre-coupled laser allowing a homogeneous illumination of the sample with a power of 6.0 mW/cm². The photocurrent was measured with a lock-in amplifier illuminating the sample with a halogen lamp through an Acton monochromator (Spectra Pro 2150i).

2.4.2 Optical and electrical characterisation of PbS/PCBM heterojunction with respect to nanocrystal size (relevant to Par. 3.1.2).

PbS nanocrystals were synthesized by hot synthesis method. Nanocrystals of different diameters were obtained varying PbO/oleic acid ratio in the stock solution; no size selective precipitation was performed afterwards. PCBM (C₇₂H₁₄O₂; [6,6]-phenyl-61-butyric acid methyl ester) was purchased from Solenne BV. PCBM and nanocrystals were separately solved in toluene; hybrid blends were made by mixing solutions of components. Optical characterization of individual materials and blends was performed on films obtained through drop-cast of solutions on microscope glass slides.

Time-resolved differential transmission decays were measured with a pump-probe setup. The output of Quantronix Integra C regenerative amplifier (784 nm in wavelength) was split to generate a pump beam to excite samples and a white supercontinuum probe on a sapphire plate (with a broad spectrum extending in the infrared up to 1600 nm). Repetition rate of the regenerative amplifier was 1 kHz and pulse duration 150 fs. The pump intensity was kept low enough (below 50 µW over ~140 µm spot, which corresponds to energy density of 30 µJ cm⁻² per pulse) to create on average less than 1 exciton per nanocrystal per pulse. Delay between pump and probe beams was computer-controlled by varying the length of the delay line. The probe beam transmitted through the sample was dispersed in a 25 cm focal length Acton 2300i spectrometer equipped with a 150 g/mm grating and detected with an InGaAs line CCD camera (Andor IDUS, 16 bit, 512 pixels). The pump beam was chopped mechanically at 12.5 Hz frequency, so that differential transmission was calculated as the difference between transmission spectra with and without the presence of pump pulses. Probe spectra were measured at 25 Hz frequency rate, therefore accumulating 40 ‘pump-on’ and 40 ‘pump-off’ probe spectra for each acquisition. For each value of pump-to-probe delay, 200 of such cycles were averaged, obtaining in about 10 s acquisition time a sensitivity as low as 2x10⁻⁴. A full spectrogram obtained with the transient absorption method described in the experimental section is shown in Figure 2.4—1.
Figure 2.4—1  CCD image of differential transmission signal of \( \varphi = 3.3 \) nm PbS/PCBM drop-cast blend, with transmission spectrum and decay times shown as cross-sections on the sides.

For time-resolved photoluminescence decays of PbS/PCBM thin films, samples were excited by 150-fs pulses, 800 nm in wavelength, from an 80 MHz mode-locked Ti:Sapphire oscillator (Coherent Mira) coped with pulse speaker when necessary to lower the repetition rate. Photoluminescence was detected with a Hamamatsu streak camera equipped with an infrared-sensitive photocathode; used both in synchroscan (higher temporal resolution) and single sweep mode.

For photoluminescence decays in the nanosecond time scale (pure PbS thin films and non-transferring blend) we instead employed the same kHz amplifier as for transient absorption. For detection we used infrared fast InGaAs photodiode (New Focus model 1811 IR DC-125MHz Low Noise Photoreceiver) connected to digital sampling oscilloscope (Tektronix model TDS 5104 Digital Phosphor Oscilloscope) recording 2500 points and averaging over \( 10^4 \) acquisitions per scan.
Electrical characterization was performed on interdigitated finger-like electrodes spaced by 20 µm, prepared by optical lithography and evaporation of Ti/Au on glass substrates. The material was drop-cast from the toluene solution in equal amounts for all used samples. The devices were tested in ambient conditions. The current–voltage characteristics were acquired using a Keithley 236 source measure unit. The photocurrent spectra were recorded at 100 V bias, by lock-in technique using the lock-in amplifier from Stanford Research SR510, the light beam was chopped at 33 Hz by mechanical chopper. As illumination source we used a white-light halogen lamp. For IV characteristics we used the full spectrum of lamp (7.5 mW/cm²), while for responsivity spectra the monochromatic illumination was obtained by using a 0.15 m SpectraPro monochromator from Acton. The photoresponsivity was determined by calibrating the setup with a highly sensitive calibrated power meter.

2.4.3 Optical characterization of CdSe/CdS dot/rods (relevant to Par. 3.2.1)

Nanocrystal preparation: CdSe/CdS dot-rod sample were grown and purified according to previously published protocol. Special care was taken to remove traces of tetrapods be means of size-selective precipitation. The smoothness of the rods was varied by using different amounts of propylphosphonic acid and by the growth time. For example, Sample 4, which had the smoothest surface and smallest width of all, was grown using 25 mg of propylphosphonic acid (PPA) and growth time of 20 min. More bumpy morphologies such as Samples 1 and 2 were obtained by using lower concentration of PPA and extending growth time to 40 min. An estimate of nanocrystal sizes from TEM images gives: Sample 1: diameter 5 nm, length 50-60 nm, original CdSe seed diameter 4.1 nm; Sample 2: diameter 5.5 nm, length 50-60 nm, original CdSe seed diameter 3.1 nm; Sample 3: diameter 5 nm, length 20-30 nm, original CdSe seed diameter 5.1 nm; Sample 4: diameter 4.5 nm, length 40-50 nm, original CdSe seed diameter 3.5 nm.

Time-resolved photoluminescence: Optical excitation was provided by 150 fs pulses from a frequency-doubled Ti:Sapphire regenerative amplifier (Quantronix Integra C) with 3.1 eV photon energy and 1 kHz repetition rate. Laser pulses were focused down to a 130 µm spot on the nanocrystal solution. Photoluminescence was measured with a C5680 Hamamatsu streak camera. The temporal resolution in the configuration we employed was ~100 ps. Decay traces were extracted from streak-camera spectrograms by integrating over a ~50 nm-wide spectral window that included both exciton and biexciton emission.

Transient absorption: The absorption spectrum was probed with white-light continuum 150 fs-long laser pulses, 450 nm to 700 nm in spectrum, generated by focusing the output of
the regenerative amplifier (Quantronics Integra), attenuated to approximately 1µJ energy per pulse, on a 1 mm-thick sapphire plate. Probe pulses had a variable delay with respect to pump pulses (394 nm wavelength, 150 fs-long, same as photoluminescence excitation). Pump and probe beams (1 mm in waist) crossed with a ~5° relative angle on a 1 mm-thick quartz cuvette filled with nanocrystals dispersed in toluene. The cumulative effect of spectral chirp and wavefront distortion of laser pulses resulted in a 200-fs time-delay resolution for experiments. The concentration of nanocrystals was chosen to keep the optical density of the whole cuvette around 0.3 at 400 nm in wavelength, guaranteeing the best compromise between uniformity of excitation and magnitude of the absorption signal. Optical spectra were recorded with a CCD camera (Princeton Instruments VersArray) coupled to a grating spectrometer (Acton SP2500i). Sample transmission was measured by dividing the spectrum of white light pulses sent through the sample by the spectrum of similar pulses split before reaching the sample. Differential transmission $\Delta T = (T_{on} - T_{off})/T_{off}$ was obtained by recording sequential transmission spectra with ($T_{on}$) and without ($T_{off}$) pump pulses illuminating the sample. Typical sensitivity to differential absorption changes in our set-up was about $2 \times 10^{-4}$.

Absorption and differential absorption spectra could be traced back through the relation linking absorption $\alpha$ and transmission $T$, when reflection and scattering are neglected: $\alpha = 1 - T$. The linear absorption $\alpha_0$ was instead measured with a spectrophotometer. We estimated an uncertainty of about 10% on the absolute value of $\alpha_0$ at 610 nm, as a result of noise and offset fluctuations affecting the linear absorption measurement at very low absorbance values. Such uncertainty is propagated to differential absorption values $\Delta \alpha/\alpha$.

### 2.4.2 Electrical characterisation of CdSe/CdS dot/rods (relevant to Par. 3.2.2)

CdSe/CdS nanocrystals were chosen from previously investigated batches of materials by selecting the sample with highest exciton-exciton repulsive interaction.

Electrical characterization was performed on interdigitated finger-like electrodes, initially on home-made by photolithography methods and then on chips bought from Fraunhofer Institute spaced by 2.5 µm, (see Appendix B for detailed datasheet). The material was drop-cast from the toluene solution, characterised and then immersed in hydrazine monohydrate solution to remove capping from the nanocrystals (see Appendix B for detailed procedure) and characterised again. The devices were tested in glow-box purified with oxygen and water free gas. The current–voltage characteristics were acquired using a Keithley 6487 picoammeter. The noise determination was done by lock-in technique using the lock-in amplifier from Stanford Research Systems (model SR 830 DSP), the light beam was chopped at regulated frequency by mechanical chopper. As illumination
source we used a broad spectrum illuminator giving power of 1 mW/cm$^2$. Incident beam was filtered by high-pass filter, cutting at 450 nm (SPF-450-2x2). For the degradation measurement sample was placed in sealed chamber inside glow-box, then chamber was removed outside and opened to expose to ambient conditions, and current characteristic at 10 V bias under illumination was taken in real time, sampling every 1 ms. For signal restoration, the chamber was evacuated by rotary pump to obtain vacuum and then device was again biased at 10V and illuminated, the signal was recorded in intervals (at time 0, after 10 min, 60 min, 2.5 h, 12 h and 48 h).
3 Results and discussion

3.1 Organic/inorganic hybrid structures

Organic semiconductors hold great promise owing to the inexpensive techniques used for their processing, though their low performances in terms of charge carrier mobility, stability in ambient conditions and the difficulty to obtain materials absorbing in the near infrared spectral range are pitfalls far to be solved. Colloidal inorganic nanocrystals are emerging as valid substitute materials due to their elevate stability in ambient conditions and the possibility of an extremely broad and tuneable spectral response\(^{37,38,39,40}\). In particular, for applications requiring absorption and/or emission of light in the near infrared, inorganic nanocrystals, especially those made of PbS and PbSe, show great advantages with respect to other solution-processable materials, as thanks to quantum confinement their fundamental absorption edge can be tuned in the wavelength range between 850-3500 nm\(^{41,42,43}\). These nanocrystals are synthesized in colloidal form by capping them with a molecular ligand shell, determining their solubility and limiting their charge transport properties\(^{44,45}\). Nevertheless, their near infrared activity has been exploited in devices such as light emitting diodes\(^{46,47}\) solar cells\(^{48,49}\) and photodetectors\(^{50,51}\). The latter show detectivities even outperforming epitaxially grown devices when the nanocrystal ligand shell is manipulated after the film preparation\(^{52}\). However, a strong power non-linearity of the photodetectors\(^{53}\) and a fast degradation of the device performances\(^{54}\) results from the ligand manipulation.

An alternative approach for the fabrication of photodetectors based on colloidal nanocrystals relies on blending inorganic nanocrystals in organic semiconducting matrices such as polyphenylenevinylene derivatives\(^{55}\), polythiophenes\(^{56}\), or pentacene\(^{57}\). In devices such as hybrid solar cells\(^{58,59}\) and photodetectors\(^{60,61}\) the nanocrystals act as electron acceptors and the transport mostly depends on the hole transport properties of the polymers resulting in strongly limited device performances.

Improvements in the overall device performances have been recently demonstrated by using needle-like fullerene crystals photosensitized by nanocrystals\(^{62}\). The devices benefit from the higher carrier mobility in C60 crystals as compared to conjugated polymers. However, the performances of these devices are far to reach the one of the ligand manipulated ones and the needle-like crystals do not allow a controllable device fabrication.

In this thesis, we replace C60 with its soluble derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) to overcome the drawbacks inherent to the low solubility of C60. We use
blends of colloidal PbS nanocrystals and PCBM to obtain hybrid thin films. These films are used to fabricate photodetectors with spectral sensitivity covering the visible and near infrared range till 1300 nm.\textsuperscript{63}

In paragraph 3.1.1, we report on device fabrication and characterization. We show device performances close to the ones of commercial near infrared detectors working in room temperature. The active layer composed of PbS nanocrystals and PCBM exploits ultrafast charge transfer from the nanocrystals fully covered by bulky oleic acid ligands to the fullerene, as is highlighted by time-resolved photoluminescence and by pump and probe measurements. Field-effect transistor measurements evidenced that the electrons are the mobile carriers in our photodetectors, while the holes are trapped in the nanocrystals. Such a configuration allows obtaining photoconductive gain as well as a linear power dependence of the photocurrent. In paragraph 3.1.2, we focus on the photophysics of the electron transfer at the PCBM /nanocrystal interface. We investigated bulk heterojunctions between PbS nanocrystals of various sizes and PCBM. Sub-picosecond spectroscopy techniques on blends were employed to reveal the ultrafast dynamics of photoexcited carriers at the heterojunction, in particular transfer of photoexcited electrons from nanocrystals to PCBM.

### 3.1.1 Solution-processable near infrared photodetectors based on electron transfer from PbS nanocrystals to fullerene derivatives

Photodetectors were fabricated by spin coating a thin film of PbS/PCBM blend (1:1 by weight) onto interdigitated gold electrodes with 5 µm spacing. A cross sectional scanning electron micrograph (SEM) was shown in Figure 3.1—1a) along with the morphology of the thin film measured by atomic force microscopy (AFM) (Figure 3.1—1b). The film appeared as a homogeneous matrix embedding round domains with diameters inferior to 1 µm and heights of ~100 nm, which could not be ascribed to phase segregates by EDX (electron dispersive X-ray spectroscopy) and thus represented rather morphological features.
The current vs. voltage (IV) measurements of the PbS/PCBM blend and of pure PCBM devices performed in dark and under illumination were reported in Figure 3.1—1c and d. The IV characteristics of both the hybrid blend and the PCBM thin film devices were symmetric with respect to zero bias. The photocurrent of the blend had a linear dependence on the bias for values lower than 6 V while for higher bias the dependence was quadratic. The hybrid device biased at 15 V under illumination of 514 nm with 6.0 mW/cm$^2$ showed a current of $\sim$5x10$^{-6}$ A, while the dark current was 4 orders of magnitude lower. This on/off ratio of 10$^{-4}$ exceeded the reported on/off ratio for the C60 needle-like crystals detectors by more than one order of magnitude$^{62}$. The monochromatic quantum efficiency of the blended device at a bias of 15 V was up to 400%, indicating an amplification of the photocurrent$^{64,65}$. The best responsivity value we recorded for the hybrid devices exceeded $\sim$1.6 AW$^{-1}$ for illumination at 514 nm.

The reference device made of a pure PCBM films (Figure 3.1—1d) showed much weaker increase of the current under illumination than the blend. At 15 V under a homogenous illumination of 6.0 mW/cm$^2$ the device delivered $\sim$8x10$^{-9}$ A, while the dark current was $\sim$5x10$^{-11}$ A (limited by our instrument sensitivity). The responsivity of the PCBM device was then 2.5x10$^{-3}$ AW$^{-1}$. Devices fabricated with pure PbS nanocrystals showed currents bordering our detection sensitivity without increment upon illumination; this was due to the insulating nature of the bulky ligand layer surrounding the nanocrystals.
To evaluate the responsivity in the near infrared range we measured the photocurrent spectrum presented in Figure 3.1—2a. The spectrum clearly showed a maximum at 1200 nm and a general shape following that of the optical density as measured from a reference layer on a glass substrate prepared by drop-casting and reported in the same figure. The similar shape confirmed the active role of the PbS nanocrystals in the photocurrent generation. The imperfect matching of the two spectra could be ascribed to the thickness difference (drop-cast vs. spin coated films). The photocurrent at 514 nm was 5 times higher than at the first excitonic absorption peak of PbS, giving rise to a responsivity of 320 mAW⁻¹ at 1200 nm which was still about 100 times higher than reported for the best hybrid infrared detectors.

![Figure 3.1—2](image)

**Figure 3.1—2**  
(a) Optical density (black line) and photocurrent spectrum (red line) of PbS/PCBM thin film. The photocurrent spectrum is measured at a bias of 25V. (b) Power dependence of the photocurrent at 1140 nm illumination. Inset: Power dependence of the photocurrent at 15V bias under 514 nm illumination. (c) Time behaviour of the photocurrent of PCBM and PbS/PCBM thin films before and after switching off the illumination.
An important feature of photoconductive detectors is the power dependence of the photocurrent. A strong decrease in the responsivity upon power increase has been observed in pure nanocrystal photodetectors\textsuperscript{68,69}. In contrast, our PbS/fullerene photodetectors were characterized by an almost linear response of the photocurrent in respect to the illumination power, from the nW to the µW range and both, in the visible and in the near infrared (Figure 3.1—2b and inset). The linear response over several orders of magnitude is an important characteristic that makes these photodetectors appealing for several practical applications. The dynamic response of the blend photodetector was reported in Figure 3.1—2c, only 75% of the current disappeared almost instantaneously when the light had been switched off, while the rest of the current needed over 2 seconds to disappear. This could be indication for carrier trapping, taking place probably at surface states of the colloidal nanocrystals or creation of nanocrystal aggregates. Long living carrier trapping in the PCBM was ruled out because of the faster response observed in the pure PCBM reference sample (Figure 3.1—2c). Furthermore, transport measurements on pure PCBM films revealed a trap-free electron transport.\textsuperscript{70}

The figure of merit for photodetectors is the normalized detectivity defined as

$$D^* = \frac{(A \Delta f)^{1/2} R}{i_n}$$

where \(A\) is the effective area of the device, \(\Delta f\) is the electrical bandwidth, \(R\) is the responsivity and \(i_n\) is the noise current. In our photodetector we have measured a noise current of \(~0.28\) pAHz\(^{-1/2}\) at 6 Hz, while with increasing frequency we found a continuous decrease till the limit of our setup reached at 120 Hz. With the noise current measured at 6 Hz and the responsivity as given above a detectivity \(D^*\sim2.5\times10^{10}\) Jones was obtained at 1200 nm. The noise-equivalent power (NEP) amounted to \(~0.9\) pW Hz\(^{-1/2}\). These achieved values were close to the ones of the best commercial infrared detectors operating at room temperature.

The physical mechanism enabling such elevate performances of oleic acid capped nanocrystals based photodetectors was clarified by time-resolved optical spectroscopy, performed on drop cast films prepared on glass slides. Figure 3.1—3a compared the photoluminescence (PL) decay of the PbS nanocrystals and the PbS/PCBM blend thin films excited at 800 nm where only the inorganic components absorbed. The PL of the nanocrystals decayed exponentially with a time constant of \(~10\) ns, while the PL of the blended thin film was quenched, showing a biexponential behaviour with a fast component of \(~70\) ps and a slower component of \(~580\) ps, shown in detail in Figure 3.1—3b.
Results and discussion

Figure 3.1—3  (a) PL decay of the PbS nanocrystals and the PbS/PCBM blend thin film. The PL is excited at 800 nm. The decays are measured in the maximum of the PL spectrum at ~1350 nm. (b) Pump-probe measurements on the PbS/PCBM blend versus PL decay of PbS/PCBM blend. The pump is at 784 nm and the probe at 1280 nm.

The much faster decay time of the PbS emission could be attributed to an efficient charge transfer from the nanocrystals to the PCBM molecules. The exciton formed by photoexcitation of the nanocrystals could be separated due to the high dielectric constant of the medium (3 nm large PbS nanocrystals show an ε~16$^{71}$) and the higher electron affinity of the fullerene derivative.

An important experimental tool to separately identify the dynamics of electrons and holes is the comparison between time-resolved PL and transient absorption in pump-probe measurements. Figure 3.1—3b showed that the decay of the PL was faster than the one of the transient absorption. While PL is a physical quantity depending on the product of hole and electron populations, bleaching of the probe absorption induced by an ultrafast pump pulse depends on the sum of the hole and electron populations weighted by their relative contributions. One can therefore describe the pump-probe signal as the sum of a decaying component (due to the carriers that are being transferred outside the nanocrystals) and a constant component (due to the oppositely charged carriers remaining inside the crystals) that are approximately equal in magnitude. The photophysical experiments provide therefore evidence for charge transfer (as opposed to energy transfer) at the hybrid nanocrystal/fullerene interface.

The comparison of the relative energy levels of the conduction and valence band of the nanocrystals and the HOMO-LUMO levels (Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital) of PCBM did not immediately show the possibility of any charge transfer between the two materials. An estimation of the energy levels for PbS nanocrystals emitting at 1280 nm from the one of the bulk material gave the lowest unoccupied nanocrystal state at ~4.23 eV$^{72}$ below the vacuum level and the highest occupied nanocrystal state at ~5.18 eV.
Comparing that with the LUMO and HOMO level of PCBM, estimated to be \( \sim 4.2 \) eV and \( \sim 6.0 \) eV below the vacuum level\(^7^3\), resulted in a close matching of the unoccupied states of the PbS crystals and of PCBM. However, as reported previously, in colloidal nanocrystals the electronic states were found generally to be closer at the vacuum level than estimated from the bulk values\(^7^4\), making the transfer of electrons from the PbS to the PCBM energetically favourable. To prove this assumption we have investigated the hybrid blend films in field-effect transistor configuration, allowing the unambiguous assignment of the charge carrier type dominating the transport in the photodetector devices.

The output characteristics of the field-effect transistors having as active layer a thin film blend of PbS nanocrystals and PCBM were reported in Figure 3.1—4. The drain current showed a positive sign for positive drain source voltages \( V_{DS} \) and a saturation behaviour, whereas for negative \( V_{DS} \) the current reversed its sign and diverges. This is the characteristic behaviour for thin film transistors with unipolar electron transport\(^7^5\). Furthermore, the devices showed strong gate dependence and electron mobility values up to \( 3.0 \times 10^{-4} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) as extracted from the linear regime of the transfer characteristics. This mobility value was ascribed to the PCBM, because transistors using oleic acid capped PbS nanocrystals as active layer do not operate.

### 3.1.2 Size-dependent electron transfer from colloidal PbS nanocrystals to fullerene

Charge separation is the crucial process determining whether or not the heterojunction can be the building block for devices converting photoexcited excitons into free charges flowing in a circuit.

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**Figure 3.1—4.** Output characteristics of a field-effect transistor having as active layer PbS/PCBM blend under illumination of 6 mW/cm\(^2\) of 514 nm.
Results and discussion

Figure 3.1—5 a) Sketch of energy level alignment at the PbS nanocrystal/PCBM interface. IP and EA levels of PbS nanocrystals were calculated from the optical bandgap as described in the text (λ_{abs} represented the wavelength of the first excitonic absorption maximum of PbS nanocrystals). b) Sketch of hybrid heterojunction with graphical representation of photoinduced electron transfer from PbS nanocrystal to PCBM molecule. c) TEM image of a PCBM/nanocrystal blend drop cast on an electron microscope carbon grid. PbS nanocrystals were seen immersed into uniform PCBM layer.

Semiconductor heterojunctions are classified according to the relative alignment of the electron affinity (EA) and ionisation potential (IP) of the two materials. In a type I heterojunction, the band edges of one semiconductor fall within the energy gap of the second, while a type II heterojunction is formed when a staggered level alignment sets-in (Figure 3.1—5a). Only in this latter case, charge separation at the junction interface is energetically favourable and thus the junction may serve to the conversion of photogenerated excitons into free charged carriers. PbS nanocrystals and fullerenes can in principle form both kinds of heterojunction. Fullerene derivative bandgaps depend on the exact chemical composition and can be tuned with the addition of organic tate, whose primary role is to increase the solubility. In particular PCBM ([6,6]-phenyl-61-butyric acid methyl ester) LUMO (lowest unoccupied molecular orbital) is usually reported between -4.2 eV\(^76,77\) and -4.3\(^78,79\) eV, although values as high as -3.7 eV have been sometimes assumed\(^80,81\). The bandgap of bulk PbS is 0.41 eV with electron affinity (EA) around -4.6 eV and ionization potential (IP) -5.0 eV.\(^82\) Quantum confinement energy in nanocrystals can increase the optical bandgap up to ~1.5 eV, shifting the EA above the LUMO level of PCBM.\(^83\) When considering hybrid heterojunctions between PbS nanocrystals and PCBM, there exists therefore a critical size for PbS nanocrystals for which a transition occurs from type I to type II heterojunction. The absolute
positions of conduction and valence bands for nanocrystals depend not only on materials, but also on size\textsuperscript{84}, shape\textsuperscript{85} and capping agents\textsuperscript{86}. Nevertheless, some of these effects are difficult to model theoretically with the necessary accuracy to reliably estimate the level crossing; recent reports have even questioned the very existence of band crossing.\textsuperscript{87} The critical nanocrystal size and emission wavelength below which charge separation takes place is extremely relevant to optoelectronic applications in the near infrared spectral region and deserve a direct experimental assessment. The knowledge of the electron transfer dynamics at the PCBM/nanocrystal interface and its competition with multi-exciton annihilation processes are also significant for the exploitation of carrier multiplication\textsuperscript{88} in nanocrystal composites.

In this work we investigated bulk heterojunctions between PbS nanocrystals of various sizes and PCBM (Figure 3.1—5b and c). Time resolved spectroscopy techniques on blends were employed to reveal the ultrafast dynamics of photoexcited carriers at the heterojunction, in particular transfer of photoexcited electrons from nanocrystals to PCBM.

Colloidal PbS nanocrystals of various sizes capped with oleic acid were synthesized by known methods\textsuperscript{89} and characterized by optical spectroscopy, showing the first exciton peak in the absorption spectrum at 1010 nm, 1110 nm, 1150 nm, 1250 nm and 1350 nm (Figure 3.1—6). In order to estimate the nanocrystal diameter, we used the calibration relationship between first excitonic peak position and nanocrystal size from TEM measurements reported in Ref. 90. Accordingly, absorption maxima of our nanocrystals corresponded to nanocrystal diameters of 3.3 nm, 3.7 nm, 3.9 nm, 4.4 nm and 4.9 nm, respectively, covering the interesting size range where a transition between type I and type II alignment with PCBM energy levels was expected. Solution blends were prepared with an excess of PCBM in volume and then drop-cast on a glass slide to form bulk heterojunctions. TEM images (Figure 3.1—5c) confirmed that a considerable fraction of nanocrystals were embedded in a PCBM matrix and did not cluster. Morphology was a crucial feature to be able to probe the heterojunction on the molecular scale. Having isolated nanocrystals in PCBM matrix allowed us to decouple the charge splitting process taking place at the PbS/PCBM molecular interface from more complex phenomena involving exciton hopping within nanocrystal clusters. Films of unblended nanocrystals served as reference.
Results and discussion

Figure 3.1—6  Normalized absorbance (solid line) and photoluminescence (dash line) spectra of PbS nanocrystals of 5 different diameters. Vertical offsets are for clarity.

Time-resolved optical spectroscopy experiments were performed to determine the dependence of the electron transfer time on nanocrystal diameter. PbS nanocrystals were excited with 150 fs-long laser pulses, 800 nm in wavelength, with sub-nJ pulse energies and repetition rates adjustable from 80 MHz to several kHz. Photoluminescence was spectrally and then temporally resolved with an infrared-sensitive streak camera. The photoluminescence decays presented in Figure 3.1—8a and b were measured for films of pure nanocrystals and nanocrystals/PCBM blends prepared with nanocrystals having the largest and smallest sizes, $\phi=4.9$ nm and 3.3 nm, respectively. While for the largest diameter the photoluminescence decay was very similar for pure and blend films (a single exponential fit to the data gave $\tau=40$ ns as characteristic time), the photoluminescence for the smallest nanocrystals from the blend decayed much faster than the reference pure nanocrystal film ($\tau=170$ ps versus 75 ns).

Estimation of photoluminescence decay times of pure nanocrystals in solution and in drop-cast films, and of non-transferring blend (PbS $\phi=4.9$ nm/PCBM) were provided by long time-
scale measurements, either detecting luminescence with a fast photodiode (Figure 3.1—7b and c) or with a streak camera (Figure 3.1—7a).

Figure 3.1—7 Long time range photoluminescence decays of PbS nanocrystals, a) decays of drop-cast thin films of PbS \( \phi = 3.3 \) nm (red line) and PbS \( \phi = 3.3 \) nm/PCBM (black markers) (streak camera, 2ns range); b) decays of drop-cast films of PbS \( \phi = 4.9 \) nm (blue line) and PbS \( \phi = 4.9 \) nm /PCBM (black line), red dash line shows the decay of in solution (ultrafast diode detection); c) decays of solutions of PbS \( \phi = 3.3 \) nm (red line) and PbS \( \phi = 3.3 \) nm/PCBM (black line) (ultrafast diode detection).

At long delays after excitation, the decay time became slower. While the early decay of the photoluminescence was independent of thin film preparation conditions, the intensity of the long-lasting tail was quite sensitive on the procedure used to deposit the film.

Figure 3.1—8 a), b) Normalized time-resolved photoluminescence decays for pure nanocrystals (red lines) and blends with PCBM (black lines) of PbS nanocrystals with diameters \( \phi = 4.9 \) and 3.3 nm. c), d) Decay of differential transmission signal as a function of the pump-probe delay for pure nanocrystals (red lines) and blends with PCBM (black lines) of PbS nanocrystals with diameters \( \phi = 4.9 \) and 3.3 nm.
To detect possible faster decay transients, photoluminescence measurements were complemented by femtosecond transmission experiments, which allowed for a much shorter, sub-picosecond time resolution. Laser pulses, 150 fs-long, 1 kHz repetition rate, were provided by a regenerative amplifier; the pump wavelength (784 nm) was chosen to excite predominantly nanocrystals and not fullerenes. Pump intensity was kept low enough that each pulse created on average less than 1 exciton per nanocrystal (a typical excitation level was 0.2 excitons per pulse in each nanocrystal; incidentally the pump photon energy was too low for carrier multiplication to occur, therefore no multiexcitons were created in the linear regime). Differential transmission of probe pulses resonant with the exciton transition was recorded as a function of the pump-probe delay. The dynamics of differential transmission (Figure 3.1—8c and d) proved to be similar to what was observed in luminescence, with a faster decay in blend films than in pure nanocrystal films for small nanocrystals (ϕ=3.3 nm), while the decay was not affected by the presence of PCBM for larger nanocrystals (ϕ=4.9 nm).

A systematic investigation over various nanocrystal sizes was carried out by repeating the photoluminescence and pump-probe experiments for nanocrystals of intermediate sizes, ϕ=3.7 nm, 3.9 nm and 4.4 nm. As summarized in Figure 3.1—9, a single exponential fit to the decay to the photoluminescence from pure PbS thin films gave characteristic times of 40 ns, 10 ns, 65 ns, 70 ns and 75 ns (±10 ns) for samples with ϕ=4.9 nm, 4.4 nm, 3.9 nm, 3.7 nm and 3.3 nm, respectively (nanocrystals in solution showed much longer decay times, as shown Figure 3.1—7). The decay of nanocrystal emission in blends was shortened to less than 1 ns for nanocrystal sizes equal or smaller than 4.4 nm (single exponential fits in the temporal window 0-100 ps to the data gave τ=140 ps ±20 ps for sizes ϕ=4.4 nm, 3.9 nm, 3.7 nm, 3.3 nm), while the decay of the blend with nanocrystals of ϕ=4.9 nm was hardly distinguishable from the one of pure PbS thin film. Analogously, we observed significantly faster decays of the differential transmission signal with respect to the probe delay in drop cast films of PbS/PCBM containing nanocrystals with diameter ϕ=4.4 nm, 3.9 nm, ϕ=3.7 nm and ϕ=3.3 nm (t=150 ps ±15 ps) than in the sample with nanocrystals ϕ=4.9 nm. Differential transmission spectra of pure nanocrystals of all diameters and PCBM/PbS nanocrystals ϕ=4.9 nm were similar and did not show considerable decay in our scanning range. Overall, all blends except for the one with largest nanocrystals (ϕ=4.9 nm) showed decay times for both photoluminescence and differential transmission much faster than the corresponding reference pure nanocrystal films.
Figure 3.1—9 Photoluminescence (square markers) and transient absorption (circles) decay times as a function of nanocrystal diameter for blends (black markers) and pure nanocrystal films (red markers). Differential transmission decay times of pure PbS nanocrystals and non-transferring blend are not reported as they could not be reliably estimated, due to the limited time range of pump-probe measurements. The dashed lines mark the multiexciton lifetimes for excitation levels creating an average number of $\langle n \rangle$ excitons per nanocrystal as estimated through transient absorption measurements.

The shorter lifetime of both photoluminescence and differential transmission signal at the exciton resonance could be attributed to electron transfer from a PbS nanocrystal to a nearby PCBM molecule. We could speculate that the slowing down of the photoluminescence decay observed at longer delays was due to the decay of the excitations created in nanocrystal clusters. The larger the aggregate, the longer the time excitons took to find a PCBM molecule where they may split. This interpretation was corroborated by the fact that the intensity of the long-lasting tail depended on the preparation, which could influence nanocrystal aggregation.

Time-resolved spectroscopy data indicated that electron transfer to the acceptor molecule was occurring for blends with nanocrystal diameters equal or smaller than $\phi=4.4$ nm, while it did not occur for nanocrystals with diameter $\phi=4.9$ nm. Uncertainties in the determination of nanocrystal size threshold were expected from homogenous and inhomogeneous linewidths in both nanocrystal and PCBM energy levels. We estimated that, for all samples investigated, the dominant contribution to energy linewidths was the $\sim70$ meV (FWHM) of inhomogenous broadening related to the nanocrystal size dispersion, exceeding homogenous broadening ($k_BT \sim 26$ meV).
This experimental finding appeared consistent with the sketch shown in Figure 3.1—5a, where level crossing occurred for nanocrystals of diameter \( \phi = 3.5-5.0 \) nm (with first excitonic peak maximum around \( \sim 1300 \) nm). The dependence of EA on nanocrystal size was calculated within a rather crude approximation\(^9\), in which several phenomena influencing electronic level positions with respect to the vacuum level were neglected, \textit{e.g.}, electron-hole interaction (which should however account for \( \sim 10 \) meV)\(^6\), band dispersion and mixing, electrostatic effects and interface dipole. The present experimental estimation of the critical nanocrystal diameter for electron transfer to occur could thus serve to validate accurate microscopic models addressing the issue of electronic level alignment in the PCBM/nanocrystal heterojunction at the molecular scale.

One could also expect that the time required for electrons to be transferred from nanocrystals to PCBM would depend on the energy jump between levels in the two materials. Results in Figure 3.1—9 indicated that for blends with nanocrystal sizes ranging from 3.3 nm to 4.4 nm there was no significant variation of photoluminescence or differential transmission signal decays as a function of nanocrystal size.

The differential transmission decays for blends of PCBM and nanocrystals smaller than 4.4 nm in diameter were all very similar to each other, \textit{i.e.} the decay time did not depend on the diameter of nanocrystal, as shown in Figure 3.1—10.

![Figure 3.1—10](image-url)

\textbf{Figure 3.1—10} Resemblance of differential transmission decays of nanocrystals with different diameters, pump-probe decays of PbS/PCBM blends with nanocrystals diameter just above the transfer threshold (\( \phi = 4.4 \) nm, blue dash line) in comparison to decays of PbS/PCBM blends with nanocrystals of diameter \( \phi = 3.9 \) nm (green solid line), \( \phi = 3.7 \) nm (red open circles) and \( \phi = 3.3 \) nm (black square markers).
This implied that, in the limited range we could explore, the electron transfer time was not clearly influenced by the nanocrystal diameter, provided that nanocrystals were small enough for charge transfer to occur. Similar results were reported for the electron transfer time from colloidal PbS nanocrystals into TiO$_2$ nanoparticles$^{97}$. On the other hand, in CdSe nanocrystals linked to mesoporous TiO$_2$ electron transfer time was size-dependent, ranging from ~100 ps to several tens of ns$^{98}$ for varying energy difference between the acceptor and donor levels. In PbS/PCBM composite, the change of the EA level for similar variation of the nanocrystal size can be easily calculated assuming equal electron and hole PbS masses$^{99}$ and equates half the energy gap variation, i.e., ~110 meV, but no increase of the transfer time was observed. A microscopic theory should model in a realistic way the donor/acceptor interface to understand which interactions precluded a faster electron extraction from smaller nanocrystal sizes.

Exciting pure nanocrystal samples with higher pump pulse energy, we were able to create multiple excitons in each nanocrystal and observe the shortening of photoluminescence decay time associated with non-radiative multiexciton Auger recombination. When the excitation level was increased to the level of $<n>$=1, a fast components appeared in the transient absorption decay, with a time constant of 450 ps. Higher excitation produced even faster decays: $t$=180 ps, 90 ps and 65 ps for $<n>$=2, 4, 7. (Figure 3.1—11).

It is useful to compare the characteristic time of Auger processes (Figure 3.1—9) with the electron transfer time, as a starting point for establishing the possibility of extracting multiple carriers from each nanocrystal. Shown in Figure 3.1—9 the measured electron transfer time was shorter than Auger recombination time for pump power even exceeding 2 excitons per nanocrystal on average$^{100}$. This effect may enhance the efficiency of short wavelength photon-to-electron
conversion in photodetector\textsuperscript{101} and photovoltaic devices\textsuperscript{102} by exploiting the process of carrier multiplication\textsuperscript{103,104}.

![Figure 3.1—12 Responsivity spectra of PbS/PCBM thin films under CW excitation measured at 100 V bias for PbS/PCBM blends with nanocrystals smaller than transfer threshold (\(\phi = 3.0\) nm, solid blue line) and larger than the threshold (\(\phi = 4.9\) nm - red dash line and \(\phi = 8.0\) nm - black dotted line).](image)

Photocurrent measurements on nanocrystal/PCBM films drop cast on 20 \(\mu\)m-spacing interdigitated electrodes demonstrated that photoelectrons transferred from nanocrystals to PCBM were indeed available for electrical conduction. Responsivity spectra, measured under monochromatic tuneable illumination, are shown in Figure 3.1—12 for blends with nanocrystals in three different sizes. Responsivity extended as far in the infrared range as nanocrystal absorption spectra, proving that the blends were activated by photoexcitations of nanocrystals and not of PCBM. The photocurrent response was at least two orders of magnitude higher for blends containing \(\phi = 3.0\) nm nanocrystals than for the ones with \(\phi = 4.9\) and 8.0 nm nanocrystals. The photocurrent for blends with \(\phi = 4.9\) nm nanocrystals did not peak in correspondence with the first exciton transition of nanocrystals, but at shorter wavelength, an effect that could be due to a remnant subset of smaller nanocrystals in the blend for which charge transfer occurred. Photocurrent was measured under continuous wave white light illumination of 7.5 mW/cm\textsuperscript{2} on interdigitated electrodes separated by 20 \(\mu\)m. Blends of nanocrystals with diameter \(\phi = 3.0\) nm have shown photocurrent formation 2 orders of magnitude higher than those with nanocrystals \(\phi = 4.9\) nm and 3 orders of magnitude higher than PbS/nanocrystals \(\phi = 8.0\) nm (Figure 3.1—13).
Figure 3.1—13 Current-voltage characteristics of PbS nanocrystals (thin lines) and blends (thick lines) under white light illumination 7.5 mW/cm² (red lines) and in dark (black lines).

3.1.3 Conclusions

We demonstrated a solution-processable hybrid organic-inorganic blend of fullerene derivative and PbS nanocrystals as the active medium for photodetectors. We highlighted that the active layer composed by PbS nanocrystals and PCBM exploited photoinduced ultrafast charge transfer from the nanocrystals fully covered by bulky oleic acid ligands to the fullerene, demonstrating a new approach towards efficient photodetectors with respect to the ligand manipulation. Field-effect transistor measurements evidenced that the electrons are the mobile carriers in our photodetectors, while the holes were trapped in the nanocrystals. In this configuration photoconductive gain as well as a linear power dependence of the photocurrent was obtained. The measured detectivity compares to that of commercial photodetectors sensitive in the near infrared, making our hybrid devices appealing for applications in biology and in night vision systems as cost effective alternative to the actual technology.

Also we were able to demonstrate that electron transfer from PbS nanocrystals to PCBM fullerene is tuneable with nanocrystal size. Electron transfer occurs for nanocrystals with diameter 4.4 nm and smaller, not for larger nanocrystals. The crossing between transferring and non-transferring junctions occurred for nanocrystals with optical transitions in the very useful near-infrared range, around 1300 nm in wavelength. For nanocrystals with shorter emission wavelength, electron transfer time was around 130-150 ps, fast enough to compete with recombination processes detrimental for the exploitation of carrier multiplication processes in PbS. Information we gathered may prove crucial to the development of hybrid photodetectors and solar cells based on the PbS nanocrystal/fullerene bulk heterojunction as building block to harvest infrared and near-UV solar emission.
3.2 Core-shell hybrid structures

CdSe/CdS dot/rod nanocrystals represent a novel class of heterostructures, formed by a spherical CdSe core, covered by a rod-shaped CdS shell (scheme in Figure 3.2—1a). While bulk CdSe and CdS have in principle a type-I band alignment, with CdSe band energies both enclosed within CdS ones, the two conduction bands are so close to each other that conduction electron wavefunctions can significantly spread into the rod (Figure 3.2—1c), realizing a quasi-type II heterostructure. In this heterostructure, the highest valence band level is localized in the CdSe core, which thus can act as a trap state for holes. The control of the hole localization through wavefunction engineering may serve as a tool to tune the sensitivity and temporal response of a photoconductive detector. This concept can be shortly illustrated as follows. The sensitivity of a photoconductive detector is related to the gain $G$, i.e., the circuit electrons generated per photoexcited carrier pair. $G$ depends on the charge recombination lifetime $\tau_e$ and the carrier transient time $\tau_{tr}$: $G = \frac{\tau_{tr}}{\tau_e}$, and can be greater than unity (see also Appendix A). Thus, to obtain a high gain, a long recombination time of carriers is necessary. The price to pay for it is the slow response of the device. The optimal trade-off between gain and speed can be achieved only through a full control over charge dissociation, transport and recombination.

In paragraph 3.2.1, we address the nonlinear optical properties of CdSe/CdS dot/rod NCs and investigate the correlation between the strength of nonlinear processes and the degree of electron and hole separation at the dot/rod heterojunction.

In paragraph 3.2.2, we report on the fabrication and characterization of a photoconductive device made with CdSe/CdS dot/rod NC. We choose the dot/rod sample with the highest exciton-exciton repulsion, which, as will be shown in paragraph 3.2.1, are expected to have the highest degree of charge separation at the dot/rod heterojunction. In these devices, chemical techniques were introduced to remove capping ligands from the NC surface, thus enhancing charge transport properties.

3.2.1 Exciton-exciton interaction in colloidal CdSe/CdS dot/rod nanocrystals

Exciton nonlinearities depend on the degree of separation of electron and hole wavefunction. In type II heterostructures, it has been demonstrated that charge separation can lead to large repulsive exciton-exciton interaction. The resulting blueshift of the exciton-to-biexciton transition suppresses to a large extent resonant re-absorption of stimulated emission from single-
exciton states, allowing net optical gain and lasing at excitations corresponding to less than one electron-hole pair per nanocrystal. In this regime, losses inherent to multiexciton recombinations are avoided, resulting in optical gain with a much longer lifetime, an essential step towards the demonstration of lasing under continuous wave operation.

Figure 3.2—1  (a) Sketch of the dot/rod nanocrystal structure. (b) TEM pictures of the four different nanocrystal types we studied. Samples #1 and #2 appeared to have a bump corresponding to the CdSe dot location, while samples #3 and #4 showed a more regular shape across all rod length. (c) Sketch of band alignment at the CdS/CdSe heterostructure interface. (d) Nanocrystal absorption (red lines, left axis) and CW photoluminescence spectra (blue line, right axis); different line styles correspond to different samples, as in the legend; the same line style is used for absorbance and luminescence for each sample; the inset reports a magnification of absorbance in the low-energy tail.

In this paragraph, we set to determine exciton-exciton interaction and optical gain in CdSe/CdS dot/rod nanocrystals.\textsuperscript{109,110} We examined 4 different batches of nanocrystals, with length along the rod axis ranging from around 30 nm to over 50 nm, as visible in the TEM images in Figure 3.2—1b). The main morphology difference between batches could be found on the girth in the vicinity of the CdSe dots, as samples #1 and #2 showed a pronounced CdS bump, while in samples #3 and #4 the rod shape was regular, without bumps. Linear optical properties were found to be similar for all 4 samples batches, as expected from similar nanocrystal shapes and compositions. The optical absorption spectra were all characterized by huge molar extinction factors (in excess of $10^7$ $\text{mol}^{-1} \text{cm}^{-1}$ around 400 nm in wavelength) and were dominated by CdS features, with only shoulders around 600 nm signalling the presence of CdSe, consistent with the fact that CdSe occupied only a few percent of the nanocrystal volume (Figure 3.2—1d). On the contrary, CW
luminescence was emitted almost exclusively around the CdSe bandgap energy and the quantum yield was higher than 70% at all optical excitation energies, meaning that most photogenerated excitations relaxed to the lowest energy allowed by the CdSe/CdS heterostructure. A very narrow-size dispersion of the nanocrystal samples reflected into 30-40 nm FWHM for photoluminescence. Only in sample #3 we found an asymmetric photoluminescence lineshape, probably due to contribution from spurious species.

![Figure 3.2—2](image)

(a) Time-resolved photoluminescence spectrogram (spectrum as a function of time) at low excitations (linear regime), corresponding to 0.07 excitons/dot on average. The upper inset shows two spectral cut, the black one around 0 delay (50 ps window), and the green one at 7 ns (1 ns window). The right panel shows in log scale the temporal evolution of the dot (red line, signal at 620 nm, integrated over a 20 nm window) and rod (blue line, signal at 470 nm, integrated over a 20 nm window). (b) spectrogram at high excitations, corresponding to 26 excitons/dot on average. Upper and side panels were obtained like in (a).
To access photoluminescence dynamics, the emission was time-resolved with a streak camera, after exciting solutions of nanocrystals dispersed in toluene with sub-picosecond laser pulses. The excitation level, or average number of excitons $\langle N \rangle$ created in each nanocrystal, was calculated multiplying the laser photon density $\Phi$ times the absorption cross section $\sigma$ for the nanocrystals at the laser wavelength ($\sigma = 5.4 \times 10^{-14}$ cm$^2$ at 394 nm). The spectrogram in Figure 3.2—2a refers to sample #1, was taken at very low excitation levels and showed that the emission from the CdSe dot decayed with a ~20 ns single exponential time, while a very weak trace of emission from the CdS rod was visible only at early times after excitation and decayed within the time resolution. The long decay of dot emission in such CdSe/CdS heterostructures, compared to bare CdSe or CdSe/ZnS nanocrystals of similar size, has been linked to the reduced electron/hole overlap and consequent reduction in oscillator strength for the excitonic transition. The fast decay of the rod emission could be attributed to hot exciton emission. Similarly long exciton decay times were found in all 4 samples.

Exciton and biexciton decay times ($\tau_X$, $\tau_{BiX}$) were obtained by fitting the normalized photoluminescence signal $S(t)$ with a double exponential of the form: $S(t) = A_X e^{-t/\tau_X} + A_{BiX} e^{-t/\tau_{BiX}}$. While the exciton lifetime $\tau_X$ decreased with increasing excitation, the biexciton one $\tau_{BiX}$ was always found to be (330±30) ps. The exciton lifetime shortening was not permanent and decreasing the excitation power we could revert to the long decay of the linear regime; we could therefore exclude photodamage. We could speculate that such a shortening of the lifetime was due to charges left over in the nanocrystals after exciton-exciton annihilation events.

We justify the use of a double exponential fit function by solving rate equations for exciton ($n_X$) and biexciton ($n_{BiX}$) population dynamics: $n_X = \frac{-n_X}{\tau_X} + \eta \frac{n_{BiX}}{\tau_{BiX}}$, $n_{BiX} = -\frac{n_{BiX}}{\tau_{BiX}}$.

The decay of one biexciton can leave a single exciton in the dot and therefore acts as a source term for $n_X$. The efficiency for such a process is $\eta$, meaning that $1-\eta$ is the probability that after Auger recombination no exciton is left in the dot. Solution of the differential equation yields population decays: $n_X = n_{X,0} e^{-t/\tau_X} + \eta n_{BiX,0} \frac{\tau_X}{\tau_X + \tau_{BiX}} \left( e^{-t/\tau_X} - e^{-t/\tau_{BiX}} \right)$ and $n_{BiX} = n_{BiX,0} e^{-t/\tau_{BiX}}$, where $n_{X,0} = \langle N \rangle e^{-\langle N \rangle}$, $n_{BiX,0} = 1 - e^{-\langle N \rangle} \left( 1 - \langle N \rangle \right)$ are the initial exciton and biexciton densities injected by laser pulses according to Poisson statistics. They correspond to the probability that a laser pulse left a single exciton, $P(1, \langle N \rangle) = \langle N \rangle e^{-\langle N \rangle}$, or two or more excitons, $P(\geq 2, \langle N \rangle) = 1 - e^{-\langle N \rangle} \left( 1 - \langle N \rangle \right)$. We
assumed that in case more than two excitons were created in the nanocrystal, the biexciton level was filled, and the extra exciton occupied higher-energy states, as the lowest conduction band in CdSe is only doubly degenerate. In the experiment, the average number of excitations per dot $\bar{N}$ was determined as $\langle N \rangle = \Phi \sigma$ ($\Phi$ being the photon density per pulse, $\sigma$ the absorption cross section).

The prediction for the normalized photoluminescence signal (exciton and biexciton emission confounded) was obtained as the sum of exciton and biexciton populations, with biexciton population counted twice (given that each biexciton is made of two excitons), and can be expressed in the same form as the biexponential fit function:

$$S(t) = \frac{n_X(t) + 2n_{BX}(t)}{n_{X,0} + 2n_{BX,0}} = A_X e^{-t/\tau_X} + A_{BX} e^{-t/\tau_{BX}}$$

where the two amplitudes $A_X$, $A_{BX}$ for exciton and biexciton decays are:

$$A_X = \frac{\langle N \rangle \left(e^{-\langle N \rangle} + \eta \left[1 - e^{-\langle N \rangle} \langle 1+ \rangle N \rangle \right]\right) \tau_X}{\tau_X - \tau_{BX}}$$

$$A_{BX} = \frac{\left[1 - e^{-\langle N \rangle} \langle 1+ \rangle N \rangle \right] \left[2 - \eta \tau_X / (\tau_X - \tau_{BX}) \right]}{2 - e^{-\langle N \rangle} \langle 2 + \rangle N \rangle}.$$

In Figure 3.2—3 (left panel), we compared such predicted values for relative exciton and biexciton amplitudes with values resulting from fitting the experimental decay curves. The model reproduced the experimental exciton and biexciton contributions assuming a biexciton-to-exciton conversion efficiency $\eta=0.6$.

**Figure 3.2—3** Left panel: Temporal decays of the normalized photoluminescence signal for various excitation levels (from top to bottom the average number of excitons injected per dot per pulse is: 0.07, 0.3, 0.8, 4.4, 26). The red lines represent least square fits to the data with a biexponential decay, as explained in the text. Right panel: amplitude of the exciton (open circles) and biexciton (filled circles) components as obtained from the fits in left panel plotted as a function of the average number of excitons per dot per pulse. The dotted lines are the predictions based on rate equations for exciton and biexciton populations.
The analyses on biexciton decay were presented only for sample #1. In spite of variations in the biexciton binding energy, temporal dynamics were virtually indistinguishable in the four samples we examined. The comparison of photoluminescence decay is reported in Figure 3.2—3 for all four samples in linear regime and high-excitation regime (average number of excitons respectively much smaller than one and larger than 20).

![Photoluminescence decay in all four samples.](image)

The spectrogram evolved significantly for high excitation levels (Figure 3.2—2b), when each nanocrystal was injected with more than one exciton on average. At early times after excitation and for all nanocrystals we considered, the emission from the rod became comparable in intensity to the emission from the dot. At high excitation densities and time 0, additional optical emission appeared at energies higher than exciton transitions, but still much lower than the CdS rod gap, which we attributed to higher excited, multiexciton states in the CdSe core.\textsuperscript{114,115,116} The large broadening of the peak might be an indication of further delocalization of conduction electrons across the rod for such excited states. Emission at the exciton energy in CdSe dots became much faster at higher excitation fluences, a clear indication of multiexciton recombination. The lifetime of biexciton states was estimated to be \(~330\) ps by fitting photoluminescence time decays for various excitation intensities with a double exponential (very similar dynamics were measured in all samples, see supplemental information).\textsuperscript{117} However the decay time for the long excitonic component depended on the excitation power, becoming faster for higher excitation levels (see supplemental information).
Results and discussion

Figure 3.2—5  PL spectra in the high-excitation (blue lines) and linear regimes (red lines) for the samples we considered. Spectra are integrated over a 50 ps window starting with the excitation pulse arrival (the gate duration was chosen shorter than biexciton lifetime). Intensity is in arbitrary units; vertical offsets have been added for clarity. The shift of the biexciton transition with respect to the exciton one is 20 meV for sample #1, 30 meV for sample #2, -3.6 meV for sample #3, -4.5 meV for sample #4.

Differences among various nanocrystals were apparent in the spectral evolution of the exciton peak with increasing excitation fluence. Figure 3.2—5 summarizes the comparison of spectra measured immediately after the arrival of the excitation pulse in the linear and multiexciton regimes (a gate window of 50 ps was selected). A shift appeared in the peak wavelength for the dot emission, which measured the exciton-exciton interaction energy. The observed shift varied from 31 meV to the blue (in sample #2), to 20 meV to the blue (sample #1), to 4.5 meV to the red (samples #3), to 3.6 meV to the red (sample #4), indicating that exciton-exciton interaction could be tuned from attractive (corresponding to a redshift of biexciton transitions with respect to exciton ones, as in conventional core/shell nanocrystal) to repulsive (biexciton is blueshifted with respect to exciton) with minor nanocrystal shape modifications. Nanocrystals with increased girth around the CdSe dot showed exciton-exciton repulsion, which could be attributed to larger spatial separation between electrons and holes, as electrons had a thicker CdS shell to spread into. On the other hand, in nanocrystals without the bump around the CdSe core electrons found a very thin CdS shell in all directions except the rod long axis, so that spreading outside the dot of electron wavefunctions was reduced, resulting in a weak exciton-exciton attraction.118

A complementary tracking of exciton dynamics was provided by a transient absorption experiment, a technique sensitive to bleaching from single carriers (a single electron or hole affects
absorption), while photoluminescence gave information only on the joint population of electrons and holes. Figure 3.2—6a shows the differential transmission spectrum at 1 ps delay between pump and probe pulses in sample #1: it appeared that even at excitation intensities creating less than one exciton per nanocrystal a differential transmission signal was present both at the wavelength of the dot emission and that of the rod emission, a feature common to all measured nanocrystals. The spectrogram (Figure 3.2—5b) and the differential transmission decay curves (Figure 3.2—5d) showed that both rod and dot signals had similar decay rates, with typical times longer than our 0.5 ns observation window.\textsuperscript{119} Given that, under the same conditions, very little luminescence was emitted at the rod transition energy, the observation of bleaching below 500 nm was consistent with the electrons being significantly delocalized over the rod and therefore affecting also CdS transitions. A blow-up of the differential signal dynamics just after the arrival of the excitation pulse (inset in Figure 3.2—5c) hinted at a picosecond rise time for the dot signal, which could be related to the time needed to capture carriers form the rod into the dot.\textsuperscript{120}

The ratio of the differential transmission signal at the rod and dot transition wavelengths has been shown to provide a measure of charge separation in dot/rod nanocrystals,\textsuperscript{121} as the rod signal grows with growing penetration of electron wavefunctions inside the rod shell. In the four samples we measured, the ratio of dot-to-rod differential transmission signals varied and turned out to be correlated to the exciton binding energy: the samples with repulsive exciton-exciton interaction showed a larger rod signal (13 and 7 times larger than the dot signal, respectively for samples #1 and #2) with respect to the samples with attractive interaction (for both samples #3 and #4 the ratio was around 4). Such observation was consistent with the interpretation we gave of exciton-exciton interaction and demonstrated once more that electron confinement in such asymmetric nanocrystals critically depends on shape details around the CdSe dot. Our finding may help reconciling conflicting conclusions reported on electron localization from different experiments on CdSe/CdS dot/rod nanocrystals.\textsuperscript{122,123}

At higher excitation levels, the signal at the rod energy increased much more than the one at the dot energy, similarly to what happened for the photoluminescence signal. In the nonlinear regime, the decays of the dot and rod signals departed significantly from each other: the rod signal decay became much faster and nonexponential, an apparent consequence of multiparticle Auger effects.
Results and discussion

Figure 3.2—6 Pump-probe experiments on sample #2. (a) Differential transmission spectra at 1 ps pump-probe delay, low (black line) and high (green line) excitation levels. (b) Differential transmission spectrogram (spectrum as a function of the pump-probe delay). The tilt of the zero line as a function of wavelength is due to the chirp of the white light pulses; the effect is corrected in the profile plots. (c) Evolution of the differential transmission signal at the dot (red dots, 610 nm) and rod (blue dots, 470 nm) wavelengths as a function of the pump-probe delay; the excitation level corresponds to less than 1 exciton per dot ($<N> = 0.2$). The inset shows the same data on a more limited scale to highlight the rise time for the dot signal. (d) Same as (c), but for a high excitation level (7 excitons per dot on average). (e) Photoluminescence peak intensity as a function of the excitation intensity at dot transition (solid red dots), rod transition (blue dots) and for the exciton transition in commercial core/shell CdSe dots (empty red dots). The red line is the Poisson saturation as explained in the text. (f) Differential transmission peak signal at rod and dot energies as a function of the excitation intensity. The left axis is calibrated in unit of relative differential absorption for the dot transition. The red line is a prediction for differential absorption based on the assumption that exciton repulsion is much larger than transition linewidth (see text).

A detailed comparison of excitation power dependence of both luminescence and differential absorption allowed quantitative estimates of the number of excitons contained in nanocrystals. The peak value of the luminescence signal from streak images (both for dot and rod signals and for a reference sample of commercial core/shell CdSe/ZnS nanocrystals emitting at
620 nm) has been plotted as a function of the average number $\langle N \rangle$ of excitons injected in the nanocrystal (Figure 3.2—6e). When $\langle N \rangle << 1$, the peak luminescence signal was proportional to $\langle N \rangle$ (linear regime); assuming that luminescence from the dot was the only relaxation channel for injected excitons in the linear regime, the slope for the dot luminescence signal in the linear regime was normalized to 1, so that the photoluminescence intensity value around 2 obtained at saturation measured the maximum occupation in the lowest exciton state (the peak value is obtained integrating over exciton and biexciton emission), consistent with the double degeneracy of the conduction band. A very similar photoluminescence saturation was observed for commercial core/shell CdSe/ZnS round nanocrystals.

The rod photoluminescence signal on the contrary kept growing with the excitation power (even superlinearly in a small regime), meaning that many excitons could be stored inside each rod. The red line in Figure 3.2—6e is not a fit to the data, but a theoretical prediction for the number of excitons $n$ inside a dot $n = 2 - e^{-\langle N \rangle} (\langle N \rangle + 2)$, obtained assuming only that excitons are injected with average number $\langle N \rangle$ according to Poisson distribution (the probability of finding $n$ excitons in a nanocrystal is $P(n) = \frac{\langle N \rangle^n e^{-\langle N \rangle}}{n!}$) and that each nanocrystal could contain maximum 2 excitons in its lowest doubly degenerate state.

The evolution of the peak value of the differential absorption signal as a function of $\langle N \rangle$ (Figure 3.2—6) also showed that the signal from the dot saturated for growing excitation intensities, while the signal from the rod kept increasing. To calibrate the magnitude of the differential signal from the dot, we divided the differential absorption $-\Delta \alpha$ by the linear absorption $\alpha_0$ at the corresponding wavelength, so that $0 < -\frac{\Delta \alpha}{\alpha_0} < 1$ meant that bleaching of the transition occurred, while $\frac{\Delta \alpha}{\alpha_0} > 1$ was the condition for optical gain. The differential absorption for the dot signal saturated at a value above 1 and optical gain occurred for $\langle N \rangle$ close to 1. The statistical error on $-\frac{\Delta \alpha}{\alpha_0}$ was however of the order of 10%, owing to the uncertainty on the small values of both $\Delta \alpha$ and $\alpha$ at the dot transition. Thanks to the very high absorption cross section of dot/rod nanocrystals, the gain threshold was reached for extremely low pump fluence, $\sim 10 \mu J/cm^2$, more than 100 times lower than the gain threshold reported for type-II nanocrystals. With such a low threshold comes also a low absolute value for optical gain itself, so that in a working laser device based on dot/rod nanocrystals special care will have to be taken to limit optical losses.

A simple theoretical prediction for differential absorption in the limit that the biexciton repulsion energy $\Delta$ is larger than the exciton emission linewidth $\Gamma$ is that (red line in Figure 3.2—6...
\[ -\frac{\Delta \alpha}{\alpha_0} = \frac{3}{2} \left( 1 - e^{-<N>\Gamma} \right) \]

b) In our case however the benefit of exciton repulsion was limited by the fact that \( \Gamma \) was about three times larger than \( \Delta \), so that the optical gain could be therefore predicted to occur for \( \langle N \rangle_{th} = \frac{2}{3 - e^{-\Delta/\Gamma}} \cong 0.95 \). An even lower gain threshold could be achieved by further optimization of nanocrystal design: smaller CdSe cores, e.g., or thicker rod shells surrounding them, may lead to greater charge separation and larger biexciton repulsion. As an added benefit, the exciton lifetime \( \tau_X \) at gain threshold would increase from 1 ns (the value we measured for \( \langle N \rangle \equiv 1 \)) towards 20 ns (the value we measured in the linear regime for \( \langle N \rangle << 1 \)). The corresponding optical pumping density \( P_{th} \) needed to maintain inversion in CW conditions is given by
\[ P_{th} = \langle N \rangle_{th} \frac{\hbar \omega}{\sigma \tau_X} \]
so that both a long exciton lifetime \( \tau_X \) and the large absorption cross section \( \sigma \) due to the antenna effect of the rod contribute to keep \( P_{th} \) low; its value would therefore jump from approximately 10 kW/cm\(^2\) (for \( \tau_X = 1 \) ns and \( \sigma = 10^{15} \) cm\(^2\)) down to 500 W/cm\(^2\) (for \( \tau_X = 20 \) ns), a value compatible with indirect optical pumping with a blue diode, as demonstrated for polymer lasers.\(^{127}\)

### 3.2.2 Photoconductive detector based on nanocrystalline CdSe/CdS dot-rods

In this paragraph, we report the results of the electrical characterization of photodetectors made by CdSe/CdS dot-rod nanocrystals. As-deposited films were insulating, but the procedure of ligand removing enabled the current flow through the thin film. Detectivity, responsivity, response time and photoconductive gain were estimated (photodetector figures of merit are introduced in Appendix A, with detailed definitions). Device required a controlled atmosphere of working conditions to be operational.
Basing on our recent study\textsuperscript{128}, we choose nanocrystals from batch #1 to investigate charge separation and electron transfer, as this batch showed the highest repulsive exciton-exciton interaction, and thus the highest degree of electron and hole separation. CdSe/CdS core/shell dot-rods were synthesized as reported in Ref. 106 and their principal characteristics are presented in Figure 3.2—7. The asymmetric dot-rods were composed of a CdS core with a ~4 nm diameter, covered by a shell with a ~5 nm diameter and a length of ~50 nm.

For investigating the photodetective response of the material, we deposited nanocrystals from the solution on the substrate containing interdigitated gold electrodes. As the devices were made by simple drop-cast of NCs solved in slow-evaporating solvent, non-homogenous films were obtained (Figure 3.2—8a and d). Our procedure of eliminating the bulky organic ligand from the nanocrystal surface by hydrazine monohydrate also influenced strongly the morphology of the film (see Appendix B for detailed procedure). Removal of the capping molecule was expected to shrink the distance between the individual nanocrystals, but as it could be seen from AFM measurements, this led also to removal of a significant part of the layer volume (Figure 3.2—8b, c and e, f). Thus, the treatment led to creation of long-distance separated clusters of short-cross-linked dot-rods.
Figure 3.2—8 Images of thin film of CdSe/CdS dot-rods, top row – film as-deposited, bottom row – after hydrazine treatment. Figures a) and d) show macroscopic image of the films, while b), c), e) and f) are AFM images.

The current vs. voltage (IV) measurements of the hydrazine treated CdSe/CdS dot-rods thin films devices were performed in dark and under illumination. The light source was a broad spectrum illuminator; the incident beam was filtered with a high-pass filter letting only wavelengths shorter than 450 nm go through – to deliver the excitation directly to the shell. While the core also absorbs in this spectral area, the absorption process is dominated by the shell, due to high volume difference between CdSe and CdS parts. A comparison between the two absorption spectra shows that 95% of absorption of blue-violet light was due to the rod. The films made of as-deposited nanocrystals served as reference. Results reported in this thesis were obtained for the minimal available electrodes spacing (d=2.5 µm).

Devices made without any hydrazine post-deposition treatment did not show any dark or photocurrent in our detection range. Hydrazine treatment changed dramatically the electric response of the device. As shown on Figure 3.2—9a, the hydrazine-treated device of active area $3.75 \times 10^{-3}$ cm$^2$ biased at 10 V showed a photocurrent up to ~1 µA (under illumination of 1 mW/cm$^2$ measured at 380 nm) and the dark current close to 1 nA. The photocurrent curves were symmetrical with respect to zero bias, with initial linear and then quadratic dependence on the applied voltage (from 0 V to 3 V and for 3 V to 10 V, respectively).
Charge separation and photoconductivity in hybrid nanostructures

Agnieszka Gocalinska

Figure 3.2—9  (a) IV characteristic of CdSe/CdS thin film photodetector under illumination (red lines) and in dark (black lines). Dash lines stay for as-deposited material, solid lines for hydrazine-treated; (b) IV characteristic of thin film PCBM device, red line – under illumination, black line – in dark;

For reference, we made thin film device of pure PCBM on identical interdigitated structure. The photocurrent of PCBM measured in the same conditions was up to ~10 nA, so over two orders of magnitude lower than in the nanocrystal device. The dark current of pure PCBM device was in the range of the measurement noise (~1 nA). Then, the on-off ratio for dot-rods (on/off$_{NCs}=10^3$) device was significantly higher than the one measured in the PCBM device (on/off$_{PCBM}=10^1$).

As the excitation was provided in a wide range, 350-450 nm, the monochromatic responsivity and gain might have been only roughly estimated. For light intensity averaged over the spectrum, the responsivity of the nanocrystal device was calculated to be over 0.25 A/W, thus the gain was around ~0.8. Detectivity was higher than 0.5·10$^{10}$ Jones while the measured noise was around ~$\sigma_n=3$ pA/$\sqrt{\text{Hz}}$. The expected device noise figure was estimated to be the effect of the contribution of both dark current noise ($\sigma_{id}$) and thermal noise ($\sigma_{th}$): $\sigma_{\text{exp}} = \sqrt{(\sigma_{id})^2 + (\sigma_{th})^2}$.

Dark current noise was calculated as $\sigma_{id} = \sqrt{2e_i d}$, where $i_d$ is the value of the dark current, and $e$ stays for electron charge. The thermal noise depended on device resistance ($\rho$) as follows: $\sigma_{th} = \frac{4k_B T}{\rho}$. As the measured dark current under voltage of 10 V was in range of ~10$^{-9}$ A and the device resistance ~1 GΩ we could calculate approximately the contributions to be $\sigma_{id} = 20 \text{ fA}/\sqrt{\text{Hz}}$ and $\sigma_{th} = 4 \text{ fA}/\sqrt{\text{Hz}}$, thus the expected noise figure of the device was $\sigma_n = 20 \text{ fA}/\sqrt{\text{Hz}}$. However, the measured noise was much higher, thus we can suspect that it was introduced by the home-built probe station, not by the device itself. That leaves an open window for establishing the real value of the noise in this photodetector, and - if the actual noise was much
closer to the expected value – the detectivity could be several orders of magnitude higher than already evaluated.

Temporal analysis showed that the photocurrent disappeared instantly after illumination had been switched off and signal went back to initial value just when the incident beam had been restored (Figure 3.2—10a inset). We used the lock-in set-up to assess the photodetector frequency response. We measured the photocurrent intensity as a function of the frequency of a chopper installed on the illuminating beam. The roll-off frequency (at which the signal drops to half of the maximum value) was equal to $f=60$ Hz, regardless of the voltage applied to the device (Figure 3.2—10a). That corresponds to a response time of $\tau=6$ ms.

The dependence of the photocurrent intensity with respect to the illumination power of hydrazine-treated dot-rod device was presented on Figure 3.2—10b. The device was characterized by a linear dependence of the photocurrent with respect to the illumination power ranging from 1 to over 100 nW without showing any saturation trend.

When charge separation is due to trapping one of the charges on surface defects, then photocurrent saturation as a function of illumination power is often observed. This phenomenon is due to the limited number of available traps, which become saturated at high illumination rates. The lack of any saturation behaviour in our study suggests that charge dissociation was not assisted by defect states at the nanocrystal surface, but more likely, to hole localization in the CdSe core of the dot/rod structure.
The response time of the CdSe/CdS thin film photodetector was 6 ms, much faster than the one observed in nanocrystal/PCBM films and in detectors made by oxidized QDs with surface states acting as traps. The decay time of the photocurrent mainly depends on the time required by the carrier to diffuse in proximity to the opposite charge. The efficiency of current flow through the nanocrystal layer is a rather complex process, depending on size and shape of individual nanocrystals, on coupling between nanocrystals, and the continuity of carrier paths to electrodes. Drop-casting from slowly evaporating solvent led to creation of inhomogeneous layer and subsequent removal of the bulky ligand with the hydrazine solution caused considerable spatial separation of nanocrystal clusters.

Ambient condition reduced significantly the photodetector performance; the exposure to environment reduced the photocurrent to almost zero in the first minute, with no detectable on-off ratio (Figure 3.2—11).

Similar behaviour was observed in system made of spherical CdSe nanocrystals. In this material, when the organic ligand had been removed by methanol, the formation of photocurrent was quenched below detection range. It was ascribed by authors to the formation of a large number of surface traps. Indeed, we observed quenching of the photocurrent when the devices made of CdSe/CdS dot-rods treated with hydrazine solution were operating in ambient conditions, but when our photodetector was kept in vacuum or controlled glow-box atmosphere the influence of surface traps was not that significant and high responsivity could be obtained. Also the degenerated device performance could be restored to the initial value after keeping it in vacuum for about 2h (Figure 3.2—11, inset).
3.2.3 Conclusions

Ultrafast spectroscopy was used to investigate the nonlinear response of CdSe/CdS dot/rod nanocrystals. Experimental data revealed that exciton-exciton interaction can be sensitively tuned, from attractive to repulsive, with minor modifications in the nanocrystal shape. Experimental results suggested that the strength of the exciton-exciton repulsive interaction depends on the degree of electron and hole separation at the heterojunction. Exciton-exciton repulsion is a very beneficial feature to achieve lasing under CW or quasi-CW pumping, especially when coupled with the antenna effect provided by the CdS rod and the large photoluminescence quantum yield. Present experimental results validate the use of CdSe/CdS dot/rod nanocrystals as materials of choice to combine ultra-low gain threshold with long lifetime gain.

In paragraph 3.2.2, we showed that the conductivity of nanocrystal layer may be highly improved by modification of the nanocrystal surface. Electrical characterization of CdSe/CdS dot-rods with high exciton-exciton repulsion suggests that charge dissociation following optical excitation takes place at the heterojunction interface. According to EA and IP level alignment, the hole may be trapped inside the CdSe core, and the electron, being spread along CdS rod, should mainly contribute to the current when an external voltage is applied. Photoconductive devices show a good detectivity with a temporal response much faster than the one measured in nanocrystal/PCBM devices. As ligands at the nanocrystal surface were removed, water-free and oxygen-free environment was critical for the photodetector performance. An improvement of the procedure used to strip out organic ligands from the nanocrystal surface in thin films could further shorten the temporal response of the detector. Experimental results of this thesis represent the first test assessing the potential of quasi-type II heterostructure as photoconductive materials. Further developments should take advantage of the possibility to control the photoconductive gain and response time by acting on the degree of hole localization inside the nanostructure, which could be obtained, e.g., by growing a thicker CdS shell.
Appendix A
Photodetectors

Photodetection

Photosensors are devices used to detect electromagnetic signal by measuring photon flux or optical power of incident beam. There are two main types of structures, which can be used for light sensing – thermal detectors and photoelectric detectors. Thermal detectors convert absorbed photon energy into heat, and due to the nature of this they are slow and inefficient. Photodetectors are made of p-n junctions, which can be used in two basic architectures: photoconductive and photovoltaic. In the photovoltaic mode, the electron and hole pairs are generated due to light absorption at the interface and then charges are collected at one of the ends of the junctions, leading to the potential difference. A current flows if the device is loaded. So in this mode the light detection is simply done on the bases of an unbiased diode. Conversely, the photoconductive mode requires reverse bias of the diode and the electron-hole pairs are separated by the high electric field in the depletion layer. The drift of carriers creates the current in external circuit. This mode of operation gives faster response of the detector, than the photovoltaic, as the carriers are being swept away quickly by electric field.132

Silicon and germanium, in spite of being indirect bandgap materials, are widely used as detector materials for popular applications. Silicon detectors are commonly used to detect light of wavelengths from 0.4 to 1.0 μm, while germanium detectors are used at longer wavelengths up to 1.8 μm. In$_{0.53}$Ga$_{0.47}$As lattice matched to InP has a cut wavelength of 1.65 μm and is especially useful for telecommunication photodetectors as it includes both the 1.3 and 1.55 μm windows, where the optical dispersion and attenuation in standard silica fibres are at their respective minima.

To be able to characterize photodetectors, some figures of merit have been introduced. One of them is the responsivity, defined as input-output gain of the sensor, where the output will be the electrical signal obtained under optical input. It is usually expressed in amperes per watt and is a function of the operation wavelength. The following expression of the responsivity is used:

\[ R_\lambda = \frac{i}{I \cdot A}, \]

where \( i \) [A] is the current under illumination of power \( I \) [W/cm$^2$] of wavelength \( \lambda \) on device of effective area \( A \) [cm$^2$].
To be able to compare detectors of different types, independently of their sizes and shapes, specific detectivity $D^*$ is also given as a figure of merit of the device.

$$D^* = \frac{\sqrt{A \cdot \Delta f \cdot R}}{i_n}$$

is measured in the units of Jones [cm$^2$/Hz/W]; $A$ is the effective area of the detector in [cm$^2$], $\Delta f$ the electrical bandwidth in [Hz], and $R$ the responsivity in [$A/W$] measured under the same conditions as the noise current $i_n$ in [A]. Detectivity is used to characterize performance, as it is equal to the reciprocal of noise equivalent power (NEP), normalized to unit area and unit bandwidth.

In case of n-type semiconductors, photoconductive gain ($G$) is usually defined as the average number of circuit electrons $Q$ generated per photoexcited carrier pair, i.e.,

$$G = \frac{Q}{e} = \frac{\mu_e V_0 \tau_e}{L^2},$$

where $V_0$ stays for applied voltage, $L$ is the length of semiconductor, $\tau_e$ is lifetime of free electron and $\mu_e$ is its mobility. Electron lifetime is the time during which the charge stays in the conduction band, causing the current to flow with drift velocity ($v_d$) dependent on carrier mobility and electric field ($E$): $v_d = \mu_e E$. For p-type semiconductors in above mentioned definition, holes and their mobility and lifetime should be considered. The equation for photodetector gain shows clearly that for voltage large enough the value of the gain may be bigger than unity – thus more than one electron can be created under absorption of a single photon. This happens when the lifetime of an electron $\tau_e$ is longer than the transit time $\tau_{tr}$ necessary for the carrier to overcome the whole length of semiconductor.$^{133}$

As high gain and responsivity originate from efficient transport of one carrier combined with long-lived trapping of the carrier of the opposite type (because, as already explained, gain depends on the electron lifetime and the transient time: $G = \frac{\tau_e}{\tau_{tr}}$ and responsivity can be defined by gain: $R \lambda = \frac{i}{I \cdot A} = \frac{\eta \lambda G}{h \nu}$, where $\eta$ is absorbance quantum efficiency), the effective trapping of one of the carriers is necessary. The higher the responsivity of the sensor, the better the performance of the device. Thus to obtain high gain in a photodetecting system long recombination time of carriers is necessary. The price to pay for it is the slow response of the device. Final performance is always a trade-off between gain and speed, so as, depending on application, optimization should be done to balance those parameters in a way that responsivity is sufficiently high and response time short enough.
**Infrared photodetectors**

As all photodetectors can be divided into two broad classes, namely majority and minority carrier devices\textsuperscript{134}, there are six infrared material systems:

- **Direct bandgap semiconductors (minority carriers):**
  - binary alloys: InSb, InAs;
  - ternary alloys: HgCdTe, InGaAs;
  - type-II, -III superlattices: InAs/GaInSb, HgTe/CdTe;

- **Extrinsic semiconductors (majority carriers):**
  - Si:As, Si:Ga, Si:Sb;
  - Ge:Hg, Ge:Ga;

- **Type-I superlattices (majority carriers)**
  - GaAs/AlGaAs quantum well photodetectors

- **Silicon Schottky barriers (majority carriers)**
  - PtSi, IrSi

- **Quantum dots (majority carriers):**
  - Epitaxially grown quantum dot photodetectors (InAs/GaAs);
  - Colloidal quantum dots photodetectors (PbSe, CdSe, CdS, PbS);

- **High-temperature superconductors (HTSC) (minority carriers).**\textsuperscript{135}

  The time schedule of introducing different types of infrared sensing devices is presented at Figure I.
Photodetection in visible range is currently well established and efficiently introduced into devices. The most widely used variable-gap semiconductor for IR photodetectors, HgCdTe ternary alloy seems to be nearly ideal material. It has tailorable energy bandgap over the 1–30 µm range and large optical coefficients that enable high quantum efficiency. These properties are due to the energy band structure of this zinc-blende semiconductor. Moreover, in HgCdTe it is possible to obtain both low and high carrier concentrations, high mobility of electrons, and low dielectric constant. The extremely small change of lattice constant with composition makes it possible to grow high quality layered and graded gap structures. Therefore, HgCdTe can be used for detectors operated at various modes (photoconductor, photodiode or metal–insulator–semiconductor detector). But there are existing drawbacks: weak Hg–Te bond, which results in bulk, surface and interface instabilities, relatively high dark current, problems with uniformity and yield and, most significant disadvantage, high thermal carrier generation. That makes them usable only with expensive cooling systems as to assure high detectivity the device must be coped with cryostat to keep it at low (77 K) temperature, especially when applied to detection of far infrared. This drawback can be ruled out by choosing another type material, like quantum wells or quantum dots, as thermal generation of electrons in nanocrystals is significantly reduced due to the energy quantization in all three dimensions. The electron relaxation time from excited states increases due to phonon bottleneck and allows room temperature operation.

Figure I  History of the development of infrared detectors and systems. Three generation systems can be considered for principal military and civilian applications: first generation (scanning systems), second generation (staring systems—electronically scanned) and third generation (multicolour functionality and other on-chip functions)\textsuperscript{136}.

Photodetection in visible range is currently well established and efficiently introduced into devices. The most widely used variable-gap semiconductor for IR photodetectors, HgCdTe ternary alloy seems to be nearly ideal material. It has tailorable energy bandgap over the 1–30 µm range and large optical coefficients that enable high quantum efficiency. These properties are due to the energy band structure of this zinc-blende semiconductor. Moreover, in HgCdTe it is possible to obtain both low and high carrier concentrations, high mobility of electrons, and low dielectric constant. The extremely small change of lattice constant with composition makes it possible to grow high quality layered and graded gap structures. Therefore, HgCdTe can be used for detectors operated at various modes (photoconductor, photodiode or metal–insulator–semiconductor detector). But there are existing drawbacks: weak Hg–Te bond, which results in bulk, surface and interface instabilities, relatively high dark current, problems with uniformity and yield and, most significant disadvantage, high thermal carrier generation. That makes them usable only with expensive cooling systems as to assure high detectivity the device must be coped with cryostat to keep it at low (77 K) temperature, especially when applied to detection of far infrared. This drawback can be ruled out by choosing another type material, like quantum wells or quantum dots, as thermal generation of electrons in nanocrystals is significantly reduced due to the energy quantization in all three dimensions. The electron relaxation time from excited states increases due to phonon bottleneck and allows room temperature operation.
Appendix B
Devices: details and fabrication methods

Photolithography

1) Substrate preparation:

a) glass substrates: microscopic slides of 1 mm thickness have been cut to fit desired structure size and washed with warm water with soap, and flushed with clean water. Glass pieces were then immersed in so called Piranha etch (containing sulphic acid H₂SO₄ and hydrogen peroxide H₂O₂ in ratio 7:3) for 1 minute, transferred to demineralised water to remove the etchant, then slides were immersed in clean acetone for 1 minute. Finally each glass piece was flushed with demineralised water, followed by rinsing with clean acetone and finished with demineralised water flush. The procedure was ended by drying the substrate with compressed air.

b) PET substrates: plastic pieces were cut from the roll and carefully inspected for scratches. Then they were washed with warm water with soap, and subsequently flushed with demineralised water and acetone. Procedure was finished as above, by rinsing the substrates with demineralised water and blow-drying with compressed air.

2) Gold deposition: K450 Emiltech sputter and gold target was used for covering the substrates with metal layer. Operation conditions were 1·10⁻¹ bar vacuum, stabilized by needle intake of pure argon flow and 20 mA deposition current. To obtain total substrate covering with nontransparent conductive layer, the deposition was carried on for 12 minutes, resulting in even coating of 100 nm layer.

3) Photoresist coating: Shipley Microposit S1813 positive photoresist kit was used. Resin was drop-cast on clean substrates and left for one minute to improve adhesion and spin-coated subsequently for 1 minute at minimum 1000 RPM. Coated glass or PET pieces were then left for drying at room temperature for 1.5h or at hotplate 60°C for 10 minutes.

4) Exposition: dry coated substrates were transferred to the UV lamp (Kinsten KVB-30D), covered with mask (ink-printed on PET, shaped to form interdigitated structure with down to 25 µm spacing between electrodes) and weighted with glass piece to improve contact. Photoresist was illuminated for 90 sec. throughout the mask.
5) Development: structure was then covered with developer for 10 sec., flushed with demineralised water and blow-dried with compressed air.

6) Etching: for gold etching the solution containing pure iodine, potassium iodine and demineralised water was used in I:KI:H₂O ratio as 1:4:40. Solution was sprayed on substrate and left on the surface for 10 to 30 sec., for glass and PET respectively. Residues were removed by flushing with demineralised water. Structure was dried with compressed air.

7) Photoresist lift-off: pure acetone was used to remove remaining photoresist. Again, demineralised water flushing and blow-drying finished the last step of procedure.

For evaluating the results each prepared pair of electrodes was checked for shortcuts with electric tester and inspected under optical microscope to localize any remaining photoresist traces and exclude overdeveloped structures. AFM measurements have shown that obtained devices have short edges and confirmed thickness of the gold layer.
**Interdigitated electrodes for electrical characterization**

Organic semiconductors and other low-temperature processable materials are a new materials class which opens up many new applications which can be summarized as ‘Organic and Large-Area Electronics’ (OLAE). In future, devices based on organic semiconductors and other low-temperature processable materials will be ubiquitous in everyday life. One important core element for the success for the new industry is the organic material itself.

To achieve best performance the organic material has to be optimized and the fabrication quality has to be stabilized. For monitoring the quality during research, development and fabrication new quality test procedures have to be developed. In relation to the traditional semiconductor business the organic semiconductor community has not defined the quality procedures so far.

Reference organic transistor parameters, for instance charge mobility and material conductivity, are a key aspect to evaluate new organic semiconductors or to monitor the organic material quality. To evaluate these parameters the Fraunhofer IPMS offers test structures, with are designed to investigate and control the quality of organic semiconductors.

![High quality interdigital structures for transistor reference, charge mobility, and conductivity measurements](image)

Based on a stable fabrication process in a high-quality semiconductor line on 150 mm silicon wafer these test structures allow to investigate organic material performance on stabilized backgrounds.
### Appendix B

#### Devices: details and fabrication methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate (Gate)</td>
<td>n-doped silicon (doping at wafer surface: $n\approx 3\times 10^{17} \text{ cm}^{-2}$) 150 mm wafer according Semistandard (675 ± 40 \text{ µm} thickness)</td>
</tr>
<tr>
<td>Gate Oxide</td>
<td>230 ± 10 nm SiO$_2$ (thermal oxidation) Other oxide thicknesses (90 ... 300 nm) can be realized on request</td>
</tr>
<tr>
<td>Contacts (Drain/Source)</td>
<td>30 nm Au with 10 nm high work function adhesion layer (ITO) (structured by lift-off technique)</td>
</tr>
<tr>
<td>Test chip size</td>
<td>15 x 15 mm$^2$</td>
</tr>
<tr>
<td>Test chip transistor</td>
<td>4 transistors L = 2.5 µm, W = 10 mm 4 transistors L = 5 µm, W = 10 mm 4 transistors L = 10 µm, W = 10 mm 4 transistors L = 20 µm, W = 10 mm</td>
</tr>
<tr>
<td>configurations</td>
<td>Contact pads 0.5 x 0.5 mm$^2$</td>
</tr>
</tbody>
</table>

![Figure III](image.png)

**Figure III** Scheme of the microchip used for electrical measurements
**Surface treatment of CdSe/CdS dot-rods**

CdSe/CdS colloidal nanocrystals were capped with oleic acid molecules during synthesis to control growth process of particles. Post-synthesis, the ligand served as a spacer, preventing aggregations effects, and as a passivation layer, isolating the nanoparticles from environmental influence.

Hence those organic molecules are insulating, the charge conduction in thin film created by deposition of dot-rods was highly limited. To enable electron flow through the nanocrystals layer, the oleic acid has been removed and substituted by much shorter inorganic molecules of hydrazine.

Oleic acid is mono-unsaturated fatty acid and it has the chemical formula \( \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH} \). The structure of the molecule is presented below.

[Image of oleic acid molecule]

**Figure IV** Graphical representation of oleic acid molecule, red balls are representing oxygen, grey – hydrogen, black modules – carbon atoms.

Hydrazine monohydrate is an inorganic chemical compound with the formula \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \). It is a colourless liquid with an ammonia-like odour. It is highly toxic and dangerously unstable, and is usually handled in solution for safety reasons. The figure below shows simplified sketch of the molecule.
Figure V  Cartoon of hydrazine monohydrate, the molecule on top is a water molecule, bottom is an anhydrous hydrazine molecule (red ball represents oxygen, grey – hydrogen, blue - nitrogen atoms)

For electrical characterization samples were prepared as follows: thin film of CdSe/CdS dot-rods was deposited by drop-cast from toluene solution on a substrate with interdigitated electrodes. When the solvent evaporated, sample was immersed in 1 Mol solution of hydrazine monohydrate in acetonitrile for 2 h. The process was finished by washing the sample with pure acetonitrile and leaving it to dry out. The procedure was carried out in controlled, oxygen- and water-free atmosphere, to prevent influence of ambient condition on striped nanocrystal surface. As a result, oleic acid molecules were removed, enabling better conductivity of created nanocrystal film.
Appendix C
Electronic states in quantum dots

A basic description of the size dependent electronic properties of nanoscale semiconductors can be given in the frame of a particle-in-a-box model.

Model of a particle of mass $m_0$ inside symmetric spherical well of potential with radius $a$

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases}$$

and values:

$$\Phi_{n,l,m}(r, \theta, \phi) = C \frac{j_l(k_{n,l}r)Y_l^m(\theta, \phi)}{r} \text{, where } C \text{ is normalization constant, } Y_l^m(\theta, \phi) \text{ is a spherical harmonic, } j_l(k_{n,l}r) \text{ is the } l\text{-th order spherical Bessel function and } k_{n,l} = \frac{\alpha_{n,l}}{a}, \text{ where } \alpha_{n,l} \text{ stays for the } n\text{-th zero of } j_l. \text{ The wavefunctions are simple atomic-like orbitals due to the symmetry of the considered example. Those orbitals can be labelled using quantum numbers } n (1, 2, 3\ldots), l (s, p, d) \text{ and } m.$$

The energy then can be expressed by:

$$E_{n,l} = \frac{\hbar^2 k_{n,l}^2}{2m_0} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_0 a^2} \text{ and is identical to the kinetic energy of free particle, with correction to the influence of spherical boundary conditions resulting in quantized wave vector } \mathbf{k}_{n,l}. \text{ What is most important in the above quoted equation is that energy is quadratically dependent on the particle radius } a.$$

Going deeper with the considerations, conduction and valence band can be described by simple isotropic bands within effective mass approximation. The Bloch function of an electron inside the crystal is represented by:

$$\Psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \text{ where } u_{nk}(\mathbf{r}) \text{ is a periodic function characteristic for the crystal and wavefunctions are labelled by the band index } n \text{ and wave vector } \mathbf{k}.$$

Graphical representation of the energy levels of the wavefunctions very often is simplified to band diagram (Figure VI, main cartoon and a and b insets); initially in basic form of effective mass approximation in direct gap semiconductors, the curves representing $E(\mathbf{k})$ have parabolic shapes near extrema. In this simplification effective mass $m_{eff}$ is the mass of free particle and is represented on graphs as the curvature of the band at $k=0$. 

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To describe the eigenfunctions of the electrons in a crystal structure, it is enough to plot the diagram of each band reduced to the first Brillouin zone (the smallest repeating cell within periodic structure in reciprocal space) (Figure VIc). In effective mass approximation expressions representing energies of bands are:

\[ E^c_k = \frac{\hbar^2 k^2}{2m^c_{\text{eff}}} + E_g \]

for conduction and

\[ E^v_k = -\frac{\hbar^2 k^2}{2m^v_{\text{eff}}} + E_g \]

for valence band. The \( E_g \) stays here for semiconductor band gap and the energies are relative to the top of the valence band. The effective mass approximation is introduced to simplify influence of complicated periodic potential of crystal lattice which affects the carrier movement. Replacing the original mass of an electron and the hole by their effective masses enables using all standard calculation methods and ignoring the lattice influence.

In case of nanocrystals one difficulty stands out in using the effective mass approximation and leads to so called envelope function approximation. To be able to keep using effective mass concept it is necessary to assume that periodic Bloch functions are still good representations of electron and hole wavefunction – that is – that nanocrystal is still a bulk material with dimensions much bigger than lattice constant of semiconductor. Accepting this idea, the parabolic band scheme may be still used to calculate electron levels in quantum dots. Single particle
(Ψ_{sp}) wave function can be written as linear combination of Bloch functions:

\[ \Psi_{sp}(\vec{r}) = \sum_k C_{nk} u_{nk}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \]

where \( C_{nk} \) are expansion coefficients which ensure that the sum satisfies the spherical boundary conditions of the nanocrystal. Assuming that periodic Bloch functions \( u_{nk} \) depends weakly on the vector \( k \), the previous equation may be simplified to:

\[ \Psi_{sp}(\vec{r}) = u_{n0}(\vec{r}) \sum_k C_{nk} e^{i\vec{k} \cdot \vec{r}} = u_{n0}(\vec{r}) f_{sp}(\vec{r}) \]

where \( f_{sp}(r) \) is single particle envelope function. From now on, due to tight binding approximation or linear combination of atomic orbitals approximation, still keeping in mind particle in a spherical box model and effective mass approximation, it is possible to establish electron and holes levels. They can be described as atomic-like orbitals confined within the boundaries of the nanocrystal (1S, 1P, 1D, 2S etc.). In another words, within the effective mass approximation wave functions of electrons and holes inside nanocrystal can be described as a product of periodic Bloch functions and envelope wave functions. The part relating to the carrier motion in crystal lattice potential is the Bloch function, when the envelope function contains the motion in quantum dot confinement potential. But because of the complexity of the band structure, the assumptions made previously are insufficient for accurate nanocrystal calculations.

Starting back from the bulk bands, to better describe them, the so called \( k \cdot p \) method is used. This method is a more sophisticated version of the effective mass approximation. Bulk bands are expanded analytically around selected point in reciprocal space (typically \( k=0 \)) and wave functions are described by using Bloch functions \( u_{nk} \) of energies \( E_{nk} \).

\[ H_0 = \frac{p^2}{2m_0} + V(x) \]

If the single particle Hamiltonian has the form of periodic potential in crystal lattice and periodic function is \( \Psi_{nk}(\vec{r}) = u_{nk}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \), the equation

\[ \left[ H_0 + \frac{1}{m_0} (k \cdot p) \right] u_{nk} = \lambda_{nk} u_{nk} \]

\[ \lambda_{nk} = E_{nk} - \frac{k^2}{2m_0} \]

can be introduced, where \( E_{n0} \) and \( u_{n0} \) are assumed known, the perturbation Hamiltonian around \( k=0 \) may be introduced:

\[ H' = \frac{k \cdot p}{m_0} \]

Calculation of the energies and functions in frames of the nondegenerate perturbation theory to second order is possible with use of following expressions:

\[ E_{nk} = E_{n0} + \frac{k^2}{2m_0} + \frac{1}{m_0} \sum_{m \neq n} \left| \frac{k\cdot\vec{P}_{nm}}{E_{n0} - E_{m0}} \right|^2 \]

and
\[ u_{nk} = u_{n0} + \frac{1}{m_0} \sum_{m} u_{m0} \frac{\vec{k} \cdot \vec{p}_{nm}}{E_{n0} - E_{m0}}, \] where \( \vec{p}_{nm} = \langle \mu_{n0} | \vec{p} | \mu_{m0} \rangle \). The sums are over all bands but those where \( n \neq m \). The dispersion of band \( n \) is due to the coupling with nearby bands.\(^{140}\)

Theoretical modelling of energy levels in PbS and PbSe nanocrystals can be done in the frame of a 4-band model based on a \( k \cdot p \) Hamiltonian, including quantum confinement of charge carriers and dielectric effects.\(^{141}\) But as this method leads to energy levels which are not given with respect to the vacuum, some modification has been introduced. To take into account the electrostatic effects of a charged dielectric sphere and penetration of the carrier wave function into the host, the following extension of effective mass method has been suggested:

\[ E_{QD, vac} = E_{k \cdot p} + \left( 1 - \frac{1}{\varepsilon_{QD}} \right) \frac{e^2}{2a} + \chi_{\text{bulk}} \]

\( E_{QD, vac} \) - the quantum dot energy level in respect to vacuum, is equal to the energy calculated from \( k \cdot p \) method \( (E_{k \cdot p}) \) calculated for bulk crystal in a way, that zero of energy is at the conduction band edge, with correction for dielectric constant of nanocrystal \( (\varepsilon_{QD}) \) of radius \( a \). \( \chi_{\text{bulk}} \) represents electron affinity of bulk semiconductor.\(^1^{42}\).
Appendix D
Fullerene and PCBM

Fullerenes

Since its discovery in ‘80s, carbon allotropes family has been growing in number, adding to the picture new types of fullerenes, nanotubes, nanocones and other forms of molecules constructed of sole carbon atoms. The first discovered, naturally occurring in soot, was buckminnisterfullerene, called C60, as it is build of 60 carbon atoms forming a spheroid shape (truncated icosahedron). Geometrically the molecule is build of twenty hexagons and twelve pentagons (Figure VII). It is the smallest type of fullerene with no two pentagons sharing an edge, and it’s the easiest and cheapest kind to synthesize. Basic properties of the fullerene are summarized in Table 1.

![Schematic representation of single molecule of buckminnisterfullerene](image)

**Figure VII** Schematic representation of single molecule of buckminnisterfullerene

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Fcc</td>
</tr>
<tr>
<td>Crystal formation</td>
<td>hexagonal, cubic</td>
</tr>
<tr>
<td>Density [g/cm(^3)]</td>
<td>1.65</td>
</tr>
<tr>
<td>Index of refraction (at 600nm)</td>
<td>2.2</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>Resistivity (at room temp.) [S/m]</td>
<td>(1 \times 10^{14})</td>
</tr>
<tr>
<td>Lattice constant (fcc) [Å]</td>
<td>14.15</td>
</tr>
</tbody>
</table>
Appendix D
Fullerene and PCBM

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C length [Å]</td>
<td>1.46</td>
</tr>
<tr>
<td>C=C length [Å]</td>
<td>1.41</td>
</tr>
<tr>
<td>Cage mean diameter [Å]</td>
<td>7.11</td>
</tr>
</tbody>
</table>

Table 1 Short summary of properties of buckminnisterfullerene\(^{144}\)

As the bonds between atoms forming the fullerene cage are strong and the C60 particles themselves are highly stress-resistant, they do not appear to interact chemically with each other. This make the structure stable, but as the fullerenes stick together only by van der Waals forces, it makes bulk application of them uneasy, due to too low strength of this bonding for creating durable solids and too small molecule size for lubricants. But the possible advantages of fullerenes demonstrates itself when the molecules are incorporated into blend with other types of materials, like polymers for instance, contributing some of their properties to the final composition.\(^{145}\)

But not only are the mechanical features of the buckminnisterfullerene under scope of ongoing research. Each carbon atom in the structure has sp\(^2\)-like hybridization. Of the 360 electrons (6 per atom), 120 are core electrons, leaving 240 electrons for the valence molecular orbitals. Due to the fact, that the fullerene structure is aromatic, the electrons are free to move on the surface of the molecule. Delocalized electrons help to stabilize the compound, limiting even more its reactivity, and also facilitate the conductivity. 3 of 4 valence electrons of each atom can be ascribed to those forming \(\sigma\) bounds and thus constituting the cage of fullerene and the 4\(^{th}\) one to the most outer molecular orbital, having mainly \(\pi\) character. Charge distribution inside orbitals causes alternating single and double bounds between carbon atoms, 1.45 Å and 1.38 Å long, respectively.\(^{146}\)

Depending on structure, carbon molecules can build materials which are insulating, conductive or semiconductive (even superconductive in case of doped materials). The buckminnisterfullerene is a semiconductor and the quantization effect in nanoparticles due to the spatial confinement makes it attractive for electrical and optical applications. However, different kinds of fullerenes have various energy band gaps. Furthermore, while many fullerenes molecules are highly symmetrical and have degenerate energy levels (in C60 3-fold degenerate LUMO and 5-fold degenerate HOMO)\(^{147}\), organic tale added to increase the solubility makes the levels to split and shifts the initial fullerene bandgap by as much as 0.2eV.\(^{148}\) The shift depends also at the type of derivative, as the same fullerene with various functionalization have different band gaps.
**PCBM**

Pure C60 material has unfortunately the drawback of low solubility (i.e., 2.15 mg/ml in toluene in 300 K). For that reason several derivatives have been introduced, to increase the solubility in organic solvents. The most common one, also used for here presented study, is [6,6]-phenyl-C61-butyric acid methyl ester, known under abbreviation of PCBM. The compound is consistent with C60 chemistry but has increased solubility (10 mg/ml in toluene in 300 K) thanks to the functional group enables solution processing of the material. Individual molecule of PCBM is built up of hollow sphere of fullerene with aromatic derivative of butyric acid methyl ester as presented in Figure VIII.

![Graphical representation of PCBM molecule](image)

As mentioned above, the fullerenes (and PCBM properties are consistent here) present semiconductor energy band gap, which enables them to be used for optical purposes. When considering the absorption, three strong bands at around 3.6 eV, 4.7 eV and 5.6 eV appear, which can be assigned to \(\pi-\pi^*\) transitions, and one broad band at around 2.7 eV, which is considered as a charge transfer exciton-related transition. Band edge absorption is at around 1.7 eV.

It has been demonstrated that during one single nanosecond pulse each C60 molecule can absorb 200-300 eV of energy, or up to 100 photons per molecule. This suggests that the transfer of the initial excitation must be done from singlet to the triplet state within a few picoseconds. The ability to absorb light can be evolved into photogeneration of charges, as the energy delivered to the molecule doesn’t necessary have to be dissipated in radiative or thermal way. Having in mind high conductivity of fullerenes, the photogenerated current can be observed under illumination with energy matching or exceeding the bandgap value. It has been reported that the electron transport in PCBM is space-charge-limited and electron mobility of \(2 \cdot 10^{-7} \text{ m}^2/\text{Vs}\) can be obtained.

Although the conduction properties of fullerenes make them reasonably good candidates for transport materials, there are compounds with higher absorption cross-sections. To exhaust benefits offered by PCBM, the molecules are often incorporated into blends with other electro-
optically active materials, conducting polymers for instance. In most cases PCBM plays the role of electron acceptor, after the photon being absorbed by the polymer is turned into exciton and charges are separated. Heterojunctions made of such compositions (for example using P3HT as light absorbing, electron donor material) are widely used as plastic solar cell devices. Spectroscopic data provides information that after ultra-fast electron transfer takes place from the excited state of polymer to acceptor molecules and in case of PCBM quantum efficiency may reach 100\%.\textsuperscript{151}
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7. Ref. 1, *op. cit.*
8. Ref. 5, *op. cit.*
9. *Ibidem.*
15. Ref. 12, *op. cit.*
22. *Ibidem.*
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Ref. 6, op. cit.

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Ibidem.

Ibidem.

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Ref. 2, op. cit.


Ref. 5, op. cit.

Ref. 50, op. cit.

Ref. 2, op. cit.

Ref. 14, op. cit.


Ref. 73, op. cit.

Bibliography


84 Ref. 59 a, op. cit.


90 Ref. 59 a, op. cit.


92 Ref. 33, op. cit.


94 Differential absorption $\Delta A$ can be calculated from measured differential transmission $\Delta T$ neglecting reflection, through the relation $A=1-T$, implying $\Delta A=-\Delta T$.

95 Ref. 63, op. cit.


98 EA and IP of nanocrystals ($E_{A_{NC}}$, $I_{P_{NC}}$) were calculated using the formula:

$$E_{A_{NC}} = E_{A_{bulk}} + \frac{m_{electron}^*(E_{NC}^g - E_{bulk}^g)}{m_{electron}^* + m_{hole}^*}$$

$$I_{P_{NC}} = I_{P_{bulk}} - \frac{m_{hole}^*(E_{NC}^g - E_{bulk}^g)}{m_{electron}^* + m_{hole}^*},$$

where $E_{NC,bulk}$ are the band gap energies for nanocrystal and bulk semiconductor and $m_{electron,hole}^*$ are effective masses of charges. We used equal effective masses for electron and hole in PbS.


Ref. 13, *op. cit.*

Ref. 3, *op. cit.*


Ref. 17, *op. cit.*

Ref. 18, *op. cit.*

Ref. 19, *op. cit.*

Ref. 20, *op. cit.*

Ref. 17, *op. cit.*

Ref. 18, *op. cit.*

*Ibidem.*

Ref. 19, *op. cit.*

Ref. 19, *op. cit.*

Such decay appeared shorter than the one observed in the low-excitation photoluminescence in Figure 3.2—2a because we could not lower the excitation level as much and still have a detectable signal (0.2 excitons/dot produced ~10^{-3} differential transmission signal, with our sensitivity at ~2x10^{-4}).

Ref. 19, *op. cit.*


A one-dimensional particle-in-a-box calculation of electron and hole wavefunctions for our dot/rod nanocrystals gave an overlap factor for electron and hole wavefunctions in excess of 0.9. Electron and hole masses in CdSe are respectively 0.12 m_e and 0.45 m_e; conduction and valence band offsets are respectively 0.27 eV and 0.51 eV.

Ref. 113, *op. cit.*


*Ibidem.*

*Ibidem.*


Purchased from Evident Technologies, Inc. Nominal radius was 5.8 nm, luminescence emission peak at 620 nm.
125 Ref. 11, op. cit.
126 Ibidem.
129 Ref. 2, op. cit.
130 Ibidem.
136 Adapted from Ref. 135.
138 Datasheet provided by producer, Fraunhofer-Institut Photonische Mikrosysteme, Dresden, Germany.
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140 Ref. 96, op. cit.
141 Ref. 96, op. cit.
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143 http://www.godunov.com/Bucky/
144 Data compiled by the CSC and the Sussex Fullerene Group, University of Sussex
146 Roberto Macoves, Surface electronic structure of fullerides, PhD Thesis
149 Adapted from Solenne webapge http://www.solennebv.com/content/view/30/13/
151 Ref. 14, op. cit.
Publications list


Results presentation by thesis author:

1. Oral communications
   - *Excited states spectroscopy of perovskites doped with lanthanide ions* at Nanomatch Meeting, Varenna, Italy, March 2007.
   - *Investigating the energy and charge transfer in organic-inorganic hybrid systems* at Nanomatch Meeting, Jugowice, Poland, September 2007.
   - *Towards efficient electron extraction from colloidal quantum dots* at Nanomatch Meeting, Zurich, Switzerland, February 2008.
   - *Photoconductive detectors based on colloidal core/shell dot-rod nanocrystals* at Nanomatch Meeting, Peniscola, Spain, April 2009.
   - *Size dependent electron transfer time in PbS/PCBM hybrid structure* at Nanomatch Workshop, Mons, Belgium, October 2009.

2. Poster presentation
   - *Solution processable photodetectors based on colloidal quantum dots and fullerene derivatives* at III Scuola Nazionale sui Materiali Molecolari per Fotonica ed Elettronica, Arbatax, Italy, June 2009, rewarded with honourable mention.
Acknowledgments and credits

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Agnieszka