SYNTHESIS OF NANOSCALE SEMICONDUCTOR HETEROSTRUCTURES FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT

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With the demand for renewable sources of energy on the rise, significant effort needs to be invested in the development of inexpensive and efficient light-harvesting materials. Among those, colloidal semiconductor nanocrystals are emerging as a promising class of nanomaterials with the potential to produce a significant technological impact on solar cell and photodetection industries. One branch, multicomponent semiconductor nanocrystals, is of special interest. NCs offer the key advantages of bulk semiconductors, thermal stability, excellent absorbance across the solar spectrum, and a high density of states in the conduction band, while their nanoscale dimensions allow for a tuning of their bandgaps and easy solution processing of as-prepared nanoparticle colloids into thin film devices. The benefit of the multicomponent nanocrystals is the ability to tailor the spatial distribution of the carriers in one of two ways. By varying the coupled semiconductor materials, both carriers can reside on one side of the materials’ junction (type-I heterostructure), or on opposite sides of it (type-II heterostructure). Here we report on a colloidal synthesis of PbSe/TiO₂ heterostructures, comprising small-diameter PbSe nanocrystals epitaxially grown onto the surface of TiO₂ nanorods, colloidal deposition of plasmatic-size gold tips onto semiconductor nanorods under ambient light, and a colloidal synthesis of a PbSₓTe₁₋ₓ semiconductor nanocrystals alloy.
The most exciting phrase to hear in science, the one that heralds new discoveries, is not "Eureka!" ("I found it!") but rather "hmm....that's funny..."

- Isaac Asimov
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CHAPTER 1 - INTRODUCTION

1.1 Background

Quantum dots (QDs) are nanocrystalline semiconductors consisting of a few hundred to thousands of atoms each, whose excitons are confined in all three spatial dimensions. Their size ranges from 2 to about 20 nm, and as a result, they have properties that are between those of bulk semiconductors and those of discrete molecules\(^1\). In this size range, the electronic structure and optical properties of materials can be changed by varying the size of the crystal, leading to new phenomena, such as the size dependent band gap of these nanocrystal (NC) semiconductors\(^2,3\). This opens up many new avenues for research and device application.

To date, inorganic semiconductors have been the most popular material used for electronic and optical devices because they present higher carrier mobilities, photo stability, thermal stability, and light absorption properties than alternative materials. On the other hand, they are expensive to fabricate and require very high temperature treatments, so compromises need to be made between device performance and fabrication costs. Their applications range from photovoltaics to lasers, and development of these areas could be increased with the application of a lower cost alternative to current devices that need single crystal semiconductors to function. This is where quantum dots can be put to use commercially. They can be used as the basis for the manufacture of large area, low cost devices. When coupled with other materials such as organic semiconductors\(^4\) and with processes such as spin coating or inkjet printing, the costs of optical and electrical devices can be dramatically reduced. Quantum dot nanocrystals are thermodynamically stable and are made through facile colloidal synthesis, where they can then self assemble into superlattice structures. When properly made, these nanocrystals can fit the requirements for many optic and electrical devices. Quantum dots are a particularly sought after...
route from photovoltaics and lighting applications due to their tunable bandgap, small exciton binding energy, high luminescence efficiency\textsuperscript{5}, and low thermal conductivity\textsuperscript{6}. Already there has been a great deal of success with lighting applications, fluorescent tags, and lasers using the “tunability” of these crystals\textsuperscript{7,8}. Quantum Dots also have a number of medical applications, such as fluorescent probes to tag tumors and act as dyes\textsuperscript{9,10}.

1.2 Synthesis

Colloidal Synthesis, developed by Murray et al\textsuperscript{11} in 1993, is one of the most efficient and appealing methods for crystal formation for specific reasons. The first of these has already been mentioned, the superior control over the shape and size of the nanocrystals and the ease of which the procedure can be changed to tailor these qualities for different applications. Another important reason is the ease of which the quantum dots can be synthesized with relatively basic and inexpensive equipment and chemicals while still creating quality uniform nanocrystals (within a 5-10\% deviation), which is extremely important when it comes to applications such as biomedical tagging.

Quantum Dots are created from an assortment of different materials and material combinations, and through multiple different methods. Usually colloidal synthesis is performed with the combination of suitable precursors such as inorganic salts or metallic compounds. The two precursors are placed into two separate 3 neck vials and dissolved in a solvent. The purpose of the solvent is twofold, helping to disperse the precursors to optimize growth and also to control the speed of the reaction. Along with the solvent, a ligand or “surfacant” is used. The ligands of choice are generally carboxylic and phosphoric acids such as oleic acid, alkylphosphine oxides such as TOP, or a number of other materials that can be used as surfactants. These molecules play crucial roles in the nucleation and growth of the nanocrystals,
by balancing the speed of their growth to prevent them from growing too large too quickly by binding to the precursors and helping them to dissolve. In order to be sure the solution is pure, the solvent and ligands are often heated to high temperatures under a vacuum to remove impurities. This is important due to the fact that many of the materials used in this synthesis are pyrophoric. Under an inert atmosphere of usually nitrogen or argon, one or both of the solutions is heated to a high temperature, between 150 and 300°C, where the precursors become monomers. These are combined through a method called hot injection or through steady heating so that the nucleation and growth of the nanocrystals can be uniform and the final product will have a narrow size distribution \(^{11}\). This is where the initial stage of nanocrystal formation, nucleation, occurs \(^{11,12}\).

Figure 1.1 - TEM image of Colloidally Synthesized Quantum Dots
For all crystal growth, not just quantum dots, nucleation is the initial stage. When the precursors are combined, the solution becomes supersaturated and, as such, is unable to keep all of the monomers dissolved. Because of this, the solution is able to overcome a barrier when groups of atoms begin to form stable crystal structures that do not decay. This occurs at a high temperature, where it is still possible for these “seeds” to dissolve back into the solution. If the total amount of precursors used in the reaction is constant (which can be achieved through multiple injections), the fast nucleation creates a high concentration of nuclei which forms smaller NCs, slow nucleation provides low concentration of seeds consuming the same amount of precursors, thus resulting in larger particles. 

Figure 1.2 - Growth of a quantum dot.

The next stage is the growth of the crystal to the appropriate size. Here, the solution is cooled from the nucleation temperature, and the monomers begin to bond to the crystals. The monomers continue to bond with the crystals, reducing their surface energies, toward a lower more stable state. At the point where there are no longer enough free monomers, the smaller crystals begin to re-dissolve into the solution, creating more monomers and driving the growth of the larger NC’s. As a result, average particle size increases with time, and the particle concentration decreases. This occurs due to the higher surface energy of these smaller crystals and the fewer atoms at the surface producing weaker bonds. This process is referred to as Ostwald ripening, and is not always a desirable effect since it significantly increases the
variation in crystal size. Usually the process is stopped before this happens, or if the nanocrystals are meant to be larger, more precursors are injected into the system. By varying the temperate, ligands, molar rations of the precursors and other factors it is possible to vary the size of the nanocrystals. For example, lowering the concentration of surfactants in reaction mixture can also lead to smaller nanoparticles.\textsuperscript{15}

In order to retrieve the quantum dots for use from the solution, it is necessary to precipitate them. This is another place where the aforementioned ligands come into play. These organic molecules now surround the structure and, by their own organic properties, make it so that their inorganic cores can now be soluble and stable, thus they can be processed. By dissolving the final solution into a solvent that the nanocrystals are soluble in, and then adding a solvent that they are not, it is possible to gradually reduce the amount of impurities left behind after the reaction (excess precursors). The solutions are agitated and then centrifuged. By centrifuging, the solvent and the “non-solvent” are separated, the quantum dots staying in the solvent, and the impurities distributed through the both the solvent and the non-solvent. The non-solvent is then removed, and the process is repeated. Assuming an equal amount of solvent and non-solvent, the amount of impurities is reduced exponentially with each iteration. This is also an efficient way to reduce the distribution of sizes present in the solution. By adding small amounts of the non-solvent to the cleaned solution, it is possible to remove the smaller quantum dots in a fashion similar to removing the impurities.

Starting with simple spherical nanoparticles, it is now possible to create increasingly complex constructions that can have any range of sizes and shapes. In more detailed procedures, nanocrystals with much different lattice structures can be made. Generally, their creation depends on how quickly the crystals form in the solution, based on temperature and ligands used.
One example would be CdTe, which can form either the zinc blende or the wurtzite structure. At lower temperatures, the formation of the cubic zinc blend dominates but, as the temperature rises, the CdTe tends to form the wurtzite lattice more readily. Through other changes in the process, it is possible to form nanorods, nanowires, and even tetrapods.

1.3 Multicomponent Nanocrystal Heterostructures

Through colloidal synthesis, it is also possible to create multicomponent heterostructures that open up additional avenues for manipulation of their bandgaps and other properties by bringing together fundamentally different components to create materials that have combined properties not found in the original nanostructures.

![Figure 1.3 - Examples of Multicomponent Heterostructures](image)

These heterostructures nanocrystals (HNCs) can be made through a multistep process that begins with pre-synthesized nanocrystal seeds that are used as the nucleation point for other
materials. One such example would be core-shell nanocrystals that combine two different semiconductor materials by epitaxially growing a uniform shell of one around the core of the other $^{16,17}$. These heterostructures can range from uniformly covered core-shells to dumbbells and tetrapods, depending on the interfacial energy, lattice matching, and the reaction conditions. It is even possible to use seeds other than spherical nanoparticles, such as nanorods and tetrapods, which results in highly anisotropic structures where the new material is selectively deposited on the tips of nanorods or tetrapods.

The choice of the materials for these nanostructures can have a significant effect on the electron and hole wave functions in the structures, which also changes their electronic and optical properties. When a narrow bandgap semiconductor is combined with a wide bandgap semiconductor, the excited electron and hole will be strongly confined to the narrow bandgap semiconductor; this is called a type-I heterostructure $^{17,18}$. Different properties are found when the semiconductors have staggered bandgaps, the valence and conduction band of one material being both higher or lower than those of the other material, this being called a type-II heterostructure $^{19}$ Here the electron and hole are spatially separated, which increased the time it takes for them to recombine, making it easier for them to be separated $^{20}$. For this reason they are sought after materials for applications in photovoltaics $^{21}$ and lasing $^{22}$. 
1.4 Nanocrystal Semiconductor Devices

With their easily tailored properties, and relatively low cost of fabrication, quantum dots are being considered and used for a number of different applications such as LEDs, solar cells, and photodetectors.

1.4.1 LEDs

First reported in 1994 by Corvin et al, quantum dots LEDs, also known as QD-LEDs, have been explored as the light emitting materials for thin film LEDs. Among the strong points of NC-based LEDs are their high color purity (narrow gaussian emission spectrum), lower operation power, and tunability of the emission color from UV to near-IR by simply varying the
NC size, and due to the fact they are inorganic, they last longer and do not suffer from a photo-bleaching effect. In a QD-LED, a layer of nanocrystals that correspond to the desired wavelength of light are placed between an electron transporting layer and a hole transporting layer. When a voltage is applied across the device, the electrons and holes recombine in the NC layer and generate a photon. With this method it is even possible to render white light similar to that of incandescent bulbs. Along with this, they are even being researched for use in diode lasers.

1.4.2 Solar Cells

Another viable application of semiconductor nanocrystals is photovoltaics. Quantum dot solar cells, also known as nanocrystal solar cells, are part of the third generation of solar cells and were first researched in 1991 with application to TiO\textsubscript{2} nanorods. Demand for energy is increasing, and so as we turn to renewable sources, much effort is being put into the creation of inexpensive and efficient photovoltaic materials and devices. Semiconductor NCs fit these qualifications and are considered one of the best candidates due to their inexpensive solution based synthesis and their electrical and optical properties.

One example of nanocrystals based solar cells is the dye-sensitized solar cell. Here molecular sensitizers, such as PbS quantum dots are bonded to TiO\textsubscript{2} nanorod electrodes placed in an electrolyte. Here the sensitizers are used to absorb the incident photons and transfer the excited electrons into the TiO\textsubscript{2}’s conduction band. The sensitizers oxidize the electrolyte, which is then later reduced at the counter electrode, effectively converting light energy in to electrical energy and creating a current that can be run through a load. So far efficiencies of up to 11% have been recorded with this type of device.
1.4.3 Photodetectors

The detection capabilities of silicon, the most widely used photodetector material, break down when it enters the IR spectrum, and alternative detectors are extremely expensive and delicate. For these reasons it would be very desirable to find an alternative material that has high detectivity at a relatively low cost, and recent developments make NC based photodetectors a viable substitute\textsuperscript{27}, which are receiving growing attention. Nanocrystal based devices are more flexible, can have more area, are less expensive, have higher sensitivity, less internal noise current, shortest response time and low frequency operation than other photodetectors and can be tuned to detect from the visible spectrum up to 3500 nm\textsuperscript{28}.

Devices made from these materials work by changing their electrical conductivity when under illumination. When the nanocrystals are struck by incident photons, they generate additional carriers, which allow the passage of current through the semiconductor material. These devices are generally constructed with metal contacts on either side of a thin film of semiconductor nanomaterial, and attached to a bias supply and an ammeter. When light strikes
the device, the detector reads an amount of current as the light detected. Examples of the device’s construction can be seen in figure 1.6.

Figure 1.6 - Example construction of a nanocrystal based photodetector \(^{28}\)
CHAPTER 2 – LINKER-FREE MODIFICATION OF TiO₂ NANORODS WITH PbSe NANOCRYSTALS

2.1 Introduction

Titanium dioxide is an important photovoltaic and photocatalytic material\textsuperscript{29}, which utilization in dye-sensitized solar cells\textsuperscript{30}, and hydrogen production\textsuperscript{31} is encouraged by its low fabrication costs and minimal environmental hazards. Efficient harvesting of solar radiation within TiO₂ generally requires extending its absorption range into the visible and near infrared by introducing an appropriate sensitizer that engages in electron-transfer reaction with an oxide material upon receiving a photon of light. To date, the most common strategy for the sensitization of TiO₂ involves modification of its surface with organic-based transition metal complexes, such as porphyrins\textsuperscript{32} or Ru-complexes.\textsuperscript{30} On the other hand, incorporation of semiconductor nanocrystals (NC) as sensitizers is now being actively explored\textsuperscript{33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48} due to a number of advantages offered by inorganic NCs, including wider absorption profile, superior resistance to photobleaching and continuous tunability of NC conduction levels.

As shown by recent reports, successful modification of anatase TiO₂ or amorphous TiO\textsubscript{x} with colloidal CdSe\textsuperscript{40}, InAs\textsuperscript{49}, PbSe\textsuperscript{50}, and PbS\textsuperscript{51} NCs can be achieved in a reproducible manner leading to heterostructures that exhibit photoinduced charge separation. In these works, however, deposition of colloidal nanocrystals onto the oxide material still relies on organic linkers or non-epitaxial contacts with NC ligands\textsuperscript{50}, which makes it difficult to extract photoinduced carriers from NC domains leading to the decrease in electron transfer rates and carrier trapping at hybrid interfaces. For instance, surprisingly slow photoinduced electron transfer has been reported in organically coupled PbS-TiO₂ systems.\textsuperscript{51} To avoid these problems, several groups have
attempted in situ growth of CdS$^{52,53,54}$ NCs onto mesoporous TiO$_2$ films in ionic solutions. While the observation of the 2-3 fold increase in the solar conversion efficiency of such films was encouraging, the quality and size-distribution of NCs fabricated using this approach was inferior to those synthesized through colloidal techniques, making it difficult to control relative positions of electron energy levels in a donor-acceptor system.

Here we demonstrate a colloidal route to the synthesis of PbSe/TiO$_2$ hetero-nanocrystals (HNCs), comprising 2-5 nm PbSe NCs grown directly on the surface of TiO$_2$ nanorods (NRs). As a main benefit of colloidal injection techniques, the present approach allows for a controlled adjustment of the sensitizer electronic levels via tuning the average NC diameter during synthesis, which is critical for the experimental realization of a desired type II (staggered) offset of donor and acceptor conduction band edges. Moreover, formation of a near-epitaxial interface between PbSe and TiO$_2$ domains enables a rapid injection of photoinduced carriers into the oxide material, which was demonstrated via a 50-fold increase in the photoinduced electron transfer rate between PbSe and TiO$_2$ domains, as compared to organically linked lead chalcogenide-TiO$_2$ assemblies.$^{51}$
Figure 2.1 - (a) Size-dependent energies of 1S(e) electronic levels for PbSe NCs and TiO₂ nanorods. Photo-induced electron transfer from PbSe to TiO₂ is energetically allowed if PbSe diameter is less than 5 nm. (b) Schematic representation of the Volmer–Weber regime of hetero-epitaxial growth, where the energy of PbSe/TiO₂ interfaces is reduced through the formation of island-like features.

2.2 Experimental Section

2.2.1 Chemicals

1-octadecene (ODE, 90% Aldrich), oley amine (OLAM, 70% Aldrich), oleic acid (OA, 90% Aldrich), titanium tetrachloride (TiCl₄, 99.9% Aldrich), lead (II) oxide powder (PbO, 99.999% Aldrich), selenium powder (Se, 99.5% Acros), sulfur (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), tri-n-octylphosphine oxide (TOPO, 99%, Aldrich), selenium (99.5+%, Acros), hexane (anhydrous, 95%, Aldrich), methanol (anhydrous, EMD), toluene (anhydrous, 99.8%, Aldrich), chloroform (anhydrous, 99+%, Aldrich). All chemicals were used
as received without any further purification. All reactions were performed under argon atmosphere using the standard Schlenk technique.

2.2.2 Preparation of injection precursors

The lead precursor was prepared by dissolving 0.45 g (2.0 mmol) of lead oxide in a mixture of 1.6 g of OA and 4 g of ODE by heating the flask to 200°C for 30 minutes. Prior to the injection the temperature of the Pb solution was lowered to 140 °C. 1 M TOP-Se solution was prepared by dissolving 0.21 g of Se in 2.7 ml of TOP at room temperature and heated up to 100 °C prior to injection. Two different approaches were used to prepare a selenium stock solution. As a low-reactive precursor, 0.04 g of selenium was combined with 3 ml of ODE and subsequently heated up to 200 °C to form a clear solution. Prior to the injection, the mixture was cooled down to the room temperature. As a more reactive source of selenium, 0.3 ml of hexamethyldisilthiane was combined with 3 ml of degassed ODE at room temperature.

2.2.3 Synthesis of PbSe/TiO₂ heterostructures

A one-pot synthesis of PbSe/TiO₂ proceeded via the initial growth of TiO₂ nanorods onto which PbSe NCs were subsequently grown by injecting lead selenide precursors at lower temperature. Typically, 6.5 mmol of OLAM, and 1 mmol of OLAC were mixed in a three-neck flask and degassed using mechanical vacuum pump at 120° C for 30 min minutes. The mixture was subsequently switched to argon and 1 mmol of TiCl₄ was injected into the flask at 40° C. The reaction flask was then heated up to 300°C and kept at that temperature for 30 minutes. To initiate the growth of PbSe NCs the temperature of the reaction mixture was lowered to 190 °C and warm precursors of Pb (T=100 °C) and Se (T=80 °C) were injected simultaneously. Typically 3-5 ml of lead and 1.3-3 ml of Se stock solutions were used during the first injection.
The subsequent injection(s) were made 4 min after the first (or previous). Grown nanostructures were purified using several toluene/ethanol extractions.

2.2.4 Characterization

UV-vis absorption and photoluminescence spectra were recorded using CARY 50 Scan spectrophotometer and Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy measurements were carried out using JEOL 3011UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal hexane solution onto a formvar-coated copper grid and letting it dry in air. X-ray powder diffraction measurements were carried out on Scintag XDS-2000 X-Ray Powder Diffractometer. Energy Dispersive X-ray (EDX) emission spectra were measured using an EDAX X-ray detector located inside a scanning electron microscope. The electron beam was accelerated at 20kV.

2.2.5 Fluorescence lifetime measurements

FL lifetime measurements were performed using a time correlated single photon counting setup utilizing SPC-630 single photon counting PCI card (Becker& Hickle CmbH), picosecond diode laser operating at 400 nm, as an excitation source (Picoquant), and id50 avalanche photodiode (Quantique). The repetition rate of the laser was chosen to allow for a 1000 ns time window, while the pulse fluence was adjusted to produce about 1 emission photon per 100 excitation pulses (excitation power was 100μW ).

2.3 Results and Discussion

In the case of colloidal heterostructures, the type of inorganic interface that forms at the boundary of the two material domains is determined by the relationship between the total surface energy of the composite nanoparticle and the solid-solid interfacial energy related to the
mismatch-induced strain between the two lattices. If the interfacial strain exceeds the surface tension of either material, such structure may undergo a spatial rearrangement that eliminates some of the interfacial region by increasing the overall surface area\textsuperscript{55}. This scenario is clearly observed for PbSe/TiO\textsubscript{2} heterostructures, where a large lattice mismatch of either 6.7 % or 18 % corresponding to merging of 010 and 110 (Fig. 2.3b) or 001 and 100 faces of anatase TiO\textsubscript{2} and rock-salt PbSe crystal lattices, leads to the Volmer-Weber growth of the PbSe material, characterized by the formation of small PbSe islands throughout the surface of TiO\textsubscript{2} (Fig. 2.1b). One potential benefit associated with such a growth mode is the possibility of increasing the optical extinction coefficient of these nanoparticles by sintering several PbSe sensitizers per single TiO\textsubscript{2} NR. Since the light absorption cross section of 2-nm PbSe NCs, is generally small ($\approx 2 \times 10^{-15}$ cm$^2$, $\lambda=400$)\textsuperscript{56}, the maximum number of electron-hole pairs generated in a single PbSe/TiO\textsubscript{2} structure, under ambient illumination (photon flux $\approx 3 \times 10^{21}$ m$^{-2}$s) is less than one, which is not expected to produce non-linear charging effects\textsuperscript{57}. As a result, increasing the number of PbSe sites in PbSe/TiO\textsubscript{2} heterostructures should result in a linear increase of the power conversion efficiency in NC-sensitized solar cells. Another benefit of the Volmer-Weber growth regime is the thermodynamically-stable formation of small-diameter PbSe NCs, which is critical for the realization of a type II heterojunction between PbSe and TiO\textsubscript{2} materials. Indeed, according to the energy diagram of electronic states in PbSe NCs (Fig. 2.1a), calculated from electron injection studies\textsuperscript{58,59} and empirical scaling of band edge absorption, the transfer of photoinduced electrons from PbSe to TiO\textsubscript{2} is energetically permissible only if the size of PbSe is less than 5 nm.
Schematics of the one-pot approach to the synthesis of PbSe/TiO$_2$ HNCs are illustrated in Fig. 2.2a. Growth of TiO$_2$ NRs was performed according to a method adapted from Ref. 60 by heating TiCl$_4$ to 300 °C in the presence of oleic acid (OA) and oleylamine (OLAM). This approach makes use of high concentration of Ti precursor in the reaction mixture to yield high-aspect ratio anatase nanorods elongated along the <001> crystallographic direction. Upon formation of TiO$_2$ NRs, the temperature of the reaction mixture was lowered to 180 °C for the
growth of PbSe NCs. Typically, a single injection of Pb and Se precursors leads to the formation of 2-3 nm PbSe islands on the surface of nanorods. A small amount of isolated PbSe NCs (<10% of nanoparticles) was also observed in as-prepared reaction mixture and was subsequently reduced to less than 2% after the purification stage (Fig. 2.4a). Additional injections of precursors were needed to fuel the growth of PbSe islands beyond 3 nm in size.

Transmission electron microscopy (TEM) analysis of PbSe/TiO$_2$ HNCs reveals a qualitative difference between the shapes of PbSe NCs forming on the surface of TiO$_2$ NRs as a result of a single and multiple injections of Pb and Se precursors. The initial injection leads to the formation of several small-diameter PbSe sites per single NR (Figs. 2.2b, 2.2c), with an average site diameter of 1.8-3.0 nm and size dispersion of 10-14% (Fig. 2.3). We estimate that the number of PbSe NCs per single TiO$_2$ NR is 21±6, where the dispersion in the number of dots is mainly determined by the dispersion of NR surface areas.

![Figure 2.3 - Distribution of PbSe diameters in PbSe/TiO$_2$ heterostructures fabricated using a single injection of precursors. The effect of precursor concentration on the average NC diameter is illustrated by two exemplary distributions.](image-url)
Doubling the concentration of precursors for the first injection was found to produce a 10-15\% increase in the density of PbSe dots on the surface of TiO$_2$, but did not affect the average dot size. According to a high resolution TEM image of a typical PbSe/TiO$_2$ HNC in Fig. 2.2c, PbSe dots appear to be uniformly scattered over the entire NR surface and exhibit a moderate dispersion of sizes. A near-symmetric placement of PbSe dots on the surface of TiO$_2$ can be explained in terms of fundamental energy requirements on the deposition of secondary material in hetero-epitaxial growth. Namely, spatially isotropic addition of PbSe monomers onto TiO$_2$ NRs initially results in the formation of a thin PbSe shell. Subsequent lateral expansion of the shell is associated with the mismatch-induced increase of the interfacial energy, which promotes the collapse of the PbSe layer into segregated islands.
Secondary injections of precursors were used to induce the growth of larger PbSe NCs on TiO₂ surfaces, (Figs. 2.2d, 2.2e). The amount of PbSe sites per single NR in this case is reduced to one (Fig. 2.2e) or two (Fig. 2.6a), which indicates that some of the smaller islands can coalesce into bigger nanoparticles, as evident in the transitional heterostructure (Fig. 2.6a). Such transformation is thermodynamically favorable since the combined surface area of PbSe NCs is reduced during aggregation, causing the reduction in the total surface energy of the heterostructure. A high resolution TEM image of a PbSe/TiO₂ HNC comprising a single 5-nm PbSe NC (Fig. 2.2e), confirms that the surface of a NR is virtually free of small PbSe sites, which supports the coalescence-induced formation of large PbSe NCs. For these structures the
volume of the PbSe crystal phase is approximately equal to that of TiO₂, as can be deduced from near-equal amplitudes of elemental peaks in energy dispersive x-ray (EDX) spectra (Fig. 2.5d).

Optical properties of PbSe/TiO₂ HNCs incorporating 1.9-nm PbSe NCs are analyzed in Fig. 2.5. The absorption profile of PbSe/TiO₂ is characteristic of type II heterostructures with non-zero photon absorption in the spectral range below the band gap of both PbSe and TiO₂ materials. This is expected due to excitations of intermediate states that exist at the junction of both materials. The highest energy excitonic feature, corresponding to the band edge absorption in PbSe NCs can also be identified near 700 nm. Its spectral position correlates well with an estimated from TEM average PbSe size of 1.9 nm (Fig. 2.3).

Figure 2.6 – (a, b) PbSe/TiO₂ heterostructure fabricated using a secondary injection of precursors. The effect of precursor concentration on the average NC diameter is illustrated by two exemplary distributions. (c, d) TEM images of PbS/TiO₂ heterostructures fabricated using a single injection of precursors.
As-prepared PbSe/TiO$_2$ HNCs, comprising small-diameter PbSe NCs show a weak emission feature (emission quantum yield < 0.5%) in the 650-900 nm range, as shown in Fig. 2.5a. Both the position and the width of the FL peak are consistent with the expected 1S(e)-1S(h) recombination of carriers in 1.9-nm PbSe NCs, implicating the band-edge origin of the emission$^{62}$. Surprisingly, the contribution of trap states into the FL signal, expected due to a large surface area of PbSe NCs and the possible formation of electron-trapping defects along the strained interface of PbSe and TiO$_2$ domains, was not significant, as evident by the lack of emission originating from below the PbSe band gap.

The dynamics of carrier decay was further investigated using FL lifetime measurements (Fig. 2.5b). The observed emission lifetime of 2.1 ns is substantially shorter then expected for 1S(e)1S(h) excitons in PbSe NCs, for which room-temperature values in excess of 500 ns were reported$^{63}$. We also note that for small-diameter PbSe NCs, FL lifetimes are expected to increase due to the inverse correlation of the radiative rate and NC band gap$^{64}$. In general, there are two main factors that can potentially lead to such a dramatic decrease of FL lifetimes in PbSe/TiO$_2$ HNCs: electron trapping at defects and oxidation of PbSe NCs via carrier transfer to TiO$_2$. As mentioned above the signature of trap states emission was not observed in the FL spectra. Likewise, the FL relaxation trend is not typical of carrier traps that generally contribute a long-lived component with decay constants in excess of 1 μs. Therefore, the observed rapid quenching of FL is attributed to the transfer of photoinduced electrons from PbSe NCs to TiO$_2$ NRs. Based on the observed excited-state lifetime, we conclude that the characteristic timescale for photoinduced electron transfer is 2.1 ns, which is significantly faster than the 100-ns electron transfer times observed for organically linked PbS-TiO$_2$ systems.$^{51}$
In summary, we report on a solution-phase synthesis of PbSe/TiO$_2$ heterostructures, comprising small-diameter PbSe nanocrystals grown on the surface of TiO$_2$ nanorods. Fabricated materials exhibit an efficient conversion of visible light energy via a rapid transfer of photoinduced electrons into TiO$_2$ domains. From the general perspective, the present synthesis demonstrates an all-inorganic modification of TiO$_2$ surfaces with semiconductor NCs, and could be extended to other nanocrystalline systems. Moreover, the heteroepitaxial growth of lead chalcogenides is not limited to TiO$_2$ NRs and can be adapted to other nanostructured forms of TiO$_2$ including porous films and nanotubes, whereby introducing a colloidal route to sensitization of TiO$_2$ surfaces without organic-molecular bridging.
CHAPTER 3 – GROWTH OF PLASMONIC-SIZE Au DOMAINS ON SEMICONDUCTOR NANORODS IN OLEYLAMINE

3.1 Introduction

Colloidal deposition of metal domains onto semiconductor nanocrystals provides a simple chemical route to construct hybrid nanoscale composites with functionalities that extend beyond those of isolated materials\textsuperscript{65,66,67,68,69,70,71,72,73}. The presence of strong carrier confinement in these nanoparticles combined with tunable geometry of the semiconductor-metal interface gives rise to novel optoelectronic properties that can potentially contribute to a wide range of applications\textsuperscript{74,75,76}. Recently, Au/CdS and Au/CdSe heterostructures comprising gold domains grown onto cadmium chalcogenide semiconductor nanorods have emerged as a model system for studying such hybrid nanomaterials\textsuperscript{77,78,79,80,81,82}. Besides being a system of choice for advancing synthetic protocols and investigating plasmon-exciton interactions, these nano-composites have also been considered for applications in areas of solution-processed solar cells\textsuperscript{83,84} and nanoscale wiring\textsuperscript{85}. For instance, CdSe NRs capped with gold on both ends lead to a $10^5$-fold increase in carrier conductivity as compared to pristine CdSe nanorods placed over metal contacts\textsuperscript{85}, which demonstrates the potential of these heterostructures as nanoscale electrical interconnects. On the other hand, CdS NRs capped with gold on one end only can be harnessed as charge-separating units in photocatalytic and photovoltaic devices\textsuperscript{74}.

To date, the deposition of gold domains onto CdS NRs has been demonstrated using both thermal\textsuperscript{78} and light-assisted\textsuperscript{80} approaches. The former method was initially reported by Mokari et al.\textsuperscript{69} for the synthesis of Au/CdSe nano-composites and relied on the reduction of AuCl$_3$ salts in a toluene suspension of CdSe nanorods, dodecyldimethylammonium bromide (DDAB), and dodecylamine (DDA). A partial reduction of Au ions in solution followed by their accumulation...
at lattice defects resulted in the formation of small gold islands along lateral surfaces, as well as larger gold domains at both selenium (sulfur) and cadmium-rich facets of CdSe (S) NRs. The use of prolonged reaction times in this case, facilitated a selective growth of gold domains onto one (matchsticks) or both (barbells) tips of semiconductor nanorods, with average sizes of gold domains reaching 10 nm only after 3 days of the reaction time. Such slow, tip-selective deposition was attributed to electrochemical Ostwald ripening\textsuperscript{86}, by which smaller Au domains are dissolved in favor of the larger tip. A significant increase in the rate of Au addition onto one of the nanorod facets was recently demonstrated by Carbone et. al\textsuperscript{80}, through a light-assisted gold deposition. It was shown that ultraviolet (UV) irradiation of Au/CdS nano-composites promotes the transfer of excited electrons from CdS NRs to Au domains, which accelerates the process of AuCl\textsubscript{3} reduction at one of the tips. As a result, the light-assisted approach can enable the growth of Au tips in excess of 10 nm, which leads to efficient plasmon oscillations evidenced in absorption spectra of Au/CdS colloids through a characteristic plasmon peak.

At present, a limited control over the size and spatial arrangement of gold domains is achieved by balancing the interplay of thermal deposition, electrochemical Ostwald ripening, and light-induced reduction of gold. Recent experiments\textsuperscript{81} demonstrate that a judicious combination of light- and thermal-assisted routes can, in principle, be employed to manipulate the structure of Au/CdS nano-composites. On the other hand, a more rigorous approach yielding a wider range of domain sizes and structural types of Au/CdS colloids and relying on a single synthetic variable is needed to expand Au/CdS morphologies and enable better reproducibility of experimental results.

Here we demonstrate a simple synthetic strategy for the deposition of gold tips ranging from 2 to ~20 nm in size, onto either one or both facets of CdS nanorods. The synthesis is
performed under ambient light and without the use of DDA and DDAB surfactants. The size and the spatial arrangement of Au domains is controlled by adjusting the growth temperate of the reaction solution comprising a mixture of AuCl$_3$ and pre-fabricated CdS NRs in oleylamine, and generally yields plasmonic-size (d > 10 nm) Au tips in less than 30 minutes of the reaction time, corresponding to a 100-fold reduction of the growth time in comparison with previously reported protocols$^{78}$. The present approach to growing gold domains is largely independent of the nanorod aspect ratio and can be extended to spherically shaped CdS nanocrystals (NCs) as well, resulting in the formation of Au/CdS hetero-dimers. To the best of our knowledge, the present synthesis is the first experimental report on growing large-size (d > 10 nm) Au domains onto semiconductor nanorods without relying on UV illumination of the reaction mixture.

The choice of oleylamine as a reaction solvent was encouraged by the possibility of increasing the reaction temperature to above 80 °C, which enables a thermal decomposition of AuCl$_3$ salts into AuCl-oleylamine complexes$^{87}$ and the subsequent reduction and self-assembly of Au ions onto CdS. Compared to a conventional synthesis of Au/CdS nano-composites in toluene/DDAB/DDA mixture, the high-temperature deposition route, reported here, provides excessive free energy available for monomer reorganization, which may help in alleviating strain-induced interfacial defects, thereby improving inter-domain charge transfer characteristics. In addition, the use of oleylamine as a stabilizing ligand on gold nanoparticles can also benefit the large scale production of metal/semiconductor nano-composites, as this solvent is commercially available and relatively inexpensive.
3.2 Experimental section.

3.2.1 Chemicals

Gold (III) chloride (99%, Aldrich), oleylamine (tech., 70%, Aldrich), sulfur (99.999%, Acros), 1-octadecene (ODE, tech., 90%, Aldrich), cadmium oxide (99.99%, Aldrich), oleic acid (OA, tech., 90%, Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), tri-n-octylphosphine oxide (TOPO, 99%, Aldrich), n-octadecylphosphonic acid (ODPA, PCI Synthesis), n-hexylphosphonic acid (HPA, PCI Synthesis), octadecylamine (ODA, 90%, tech., Acros), hexane (anhydrous, 95%, Aldrich), methanol (99.8+, EMD), chloroform (anhydrous, 99+, Aldrich), ethanol (anhydrous, 95%, Aldrich) and toluene (anhydrous, 99.8%, Aldrich) were used as purchased. All reactions were performed under argon atmosphere using the standard Schlenk technique.

CdS nanorods were synthesized using a seeded-type approach by introducing small-diameter CdS nanocrystals into the reaction mixture for nucleating the growth of linear CdS extensions, according to the procedure adapted from Ref. 88. Original CdS seeds were not distinguishable in fabricated CdS nanorods.

3.2.2 Synthesis of CdS Nanocrystals.

CdS seeds were fabricated according to the procedure reported in Ref. 89. In a typical synthesis, the mixture of cadmium oxide (0.0384 g), OA (0.9 mL), and ODE (12.0 mL) in a 50 mL 3-neck flask was heated to 300° C until the solution turned optically clear and colorless. At this point, a sulfur precursor solution made by dissolving sulfur powder (0.0048 g) in ODE (4.5 mL) at 200° C was quickly injected, and the temperature was stabilized at 260° C for the nanocrystal growth. The reaction was stopped after 3-5 min, and nanocrystals were isolated from the growth solution by precipitation with acetone, followed by repeated hexane/methanol
extractions. The average diameter of fabricated CdS nanocrystals was in the range of 3.5-4.0 nm, depending on the growth time.

3.2.3 Synthesis of CdS Nanorods.

The amount of CdS seeds for the synthesis of CdS nanorods was calculated using an empirical approach, whereby the product of the particle absorption at 400 nm (excitonic feature) and the volume of the colloidal suspension (in mL) was set to be in the range of 5-10. Overall, it was determined that using lower amounts of CdS seeds generally yields high-aspect ratio nanorods, however, when less than 5 units of CdS is used for seeding, a small amount of tetrapods can also form during the reaction. In a typical synthesis of CdS nanorods, CdS seed powder was dispersed in 1.8 mL of TOP and subsequently introduced (at 60 °C) into the sulfur injection solution, previously prepared by dissolving sulfur (0.120 g) in TOP (1.81 mL) at 200 °C. Separately, the mixture of cadmium oxide (0.060 g), TOPO (3.0 g), ODPA (0.290), and HPA (0.080 g) in a 50 mL 3-neck flask was exposed to vacuum at 150 °C for ca. 30 min. Subsequently, the system was switched to Ar flow and heated to above 350 °C until the solution turned optically clear and colorless. At this point, TOP (1.81 mL) was added to the flask as the Cd precursor coordinating solvent. The rod growth was initiated by a quick injection of the seed/sulfur solution at 380 °C. After the temperature recovered to 350 °C the nanorods were allowed to grow for an additional 7-9 min. Purification of CdS nanorods was similar to those of CdS seeds.

3.2.4 Deposition of gold tips onto CdS NRs.

For the deposition of gold, 3 ml of oleylamine were degassed in vacuum at 120°C for 1 hour and subsequently cooled down to 60°C. After purification, all of the oleylamine then
injected into the three-neck flask containing 0.0113g of gold (III) chloride, and the temperature was raised to 60 °C. When the solution became yellow and clear (approximately after 5 min of heating), 4 mg of CdS nanorods in dissolved in 0.1 ml of toluene were injected via syringe. The exact amount of CdS NRs for the synthesis of Au/CdS nano-composites was calculated using an empirical approach, whereby the nanorod absorption at 450 nm (excitonic feature) times the volume of the colloidal suspension (in mL) was set to be in the range of 18 to 25. For instance, Au/CdS nano-composites shown in Figure 3.1a were synthesized using 20 units of CdS NRs (4 mg). Upon injection of CdS NRs into AuCl3/oleylamine mixture, the heat was brought to the flask and the solution was heated at a rate of 1.5-3 °C/min. When the desired temperature was reached, the reaction was stopped by removing the heating mantle from the flask and adding 5 ml of toluene.

3.2.5 Purification of Au/CdS nano-composites.

The final product was precipitated from toluene by adding ethanol at room temperature. The subsequent cleaning was done using toluene/ethanol extraction.

3.2.6 Characterization.

UV-vis absorption spectra were recorded using CARY 50 Scan spectrophotometer and Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy measurements were carried out using JEOL 311UHR operated at 300 kV. High angular annular dark field scanning transmission electron microscopy was performed using JEOL 2010 transmission electron microscope. Specimens were prepared by depositing a drop of nanoparticle solution in toluene onto a carbon-coated copper grid and letting it dry in air. X-ray powder diffraction measurements were carried out on Scintag XDS-2000 X-Ray Powder
Diffractometer. Energy Dispersive X-ray (EDX) emission spectra were measured using an EDAX X-ray detector located inside a scanning electron microscope. The electron beam was accelerated at 10kV.

3.3 Results and Discussion.

Synthesis of isolated gold and silver nanocrystals via a reduction of metal salts by oleylamine ligands has been previously demonstrated in several reports\(^{90,91,92,93,94}\). In these works, the reaction of AuCl\(_3\) or HAuCl\(_4\) with oleylamine was allowed to proceed in a single phase solvent (e.g. toluene) at 60-80 °C leading to a slow reduction of gold(III) ions to gold(I) and subsequently to neutral gold clusters. Close monitoring of the growth kinetics during the synthesis has revealed\(^{94,95}\) that oleylamine molecules formed complex aggregates with gold salt instantly upon mixing of these two agents. At an elevated temperature (< 80 °C), these complexes decomposed into very small particles, which eventually recombined together into larger and thermally stable nanocrystals with an average size ranging from 5 to 10 nm. Within this approach, the nanoparticle growth rate could be tuned either by adjusting the concentration of oleylamine in the toluene solution or by varying the reaction temperature. Alternatively, in the present synthesis we simplify the control over nanoparticle growth by employing oleylamine both as a reducing agent and the reaction solvent. This results in a fixed ratio of gold to oleylamine in the solution, such that the nanoparticle growth rate can be tuned solely by varying the temperature of the reaction mixture.

In a typical synthesis, CdS nanorods were first prepared by growing CdS linear extensions from (000±1) faces of small-diameter CdS seeds\(^{96}\), according to a procedure modified from Ref. 88 (for details of the synthesis see the Experimental section). Fabricated CdS NRs were washed several times using toluene/ethanol combination and stored for later use. For the
deposition of gold, 3 ml of oleylamine were degassed in vacuum at 120°C for 1 hour and subsequently cooled down to 60°C. After purification, all of the oleylamine was then injected into the three-neck flask containing 0.0113 g of gold (III) chloride, and the temperature was raised to 60 °C. When the solution became yellow and clear (approximately after 5 min of heating), 4 mg of CdS nanorods in 0.1 ml of toluene were injected via syringe. The exact amount of CdS NRs for the synthesis of Au/CdS nano-composites was calculated using an empirical approach, whereby the nanorod absorption at 450 nm (excitonic feature) times the volume of the colloidal suspension (in mL) was set to be in the range of 18 to 25. For instance, Au/CdS nano-composites shown in Figure 3.1a were synthesized using 20 units of CdS NRs (corresponding to 4 mg). Upon injection of CdS NRs into AuCl₃/oleylamine mixture, the heat was brought to the flask and the solution was heated at a rate of ~ 1.5-3 °C/min. When the desired temperature was reached, the reaction was quenched by removing the heating mantle from the flask and injecting 5 ml of room-temperature toluene.

Transmission electron microscopy (TEM) images of Au/CdS nano-composites in Figure 3.1 demonstrate the effect of the reaction temperature on the size of gold tips. Heating the
AuCl$_3$/oleylamine mixture to approximately 105 °C promotes the formation of 4-5 nm Au domains on both sides of CdS nanorods (Figure 3.1c). Some side-wall growth of smaller gold nanocrystals is also observed at this stage and is attributed to the reduction-induced assembly of Au clusters along defects of the CdS lattice. The two examples of Au/CdS nano-composites in Figure 3.2 (b,c) demonstrate that the growth of Au NCs at defects of the CdS lattice can be suppressed in nanorods exhibiting a better lattice quality. Using high-resolution TEM analysis we were able to capture the defect growth kinetics through observing a step-by-step formation of small Au nanoparticles from surface-trapped Au ions. The reduction of Au(III) and Au(I) in this case is accelerated by a continuous supply of electrons from the TEM gun. Deposition of large-diameter gold tips onto one of the nanorod facets (Figure 3.1a,b) is achieved by increasing the temperature of the reaction mixture to above 120 °C. This promotes the dissolution of smaller Au domains and simultaneous assembly of larger Au nanoparticles via electrochemical Ostwald ripening$^{86}$. The resulting matchstick-shaped nano-composites are clearly identified by the color contrast in high angular annular darkfield scanning transmission electron microscopy (HAADF-STEM) images, shown in Figure 3.2. For a fixed molar ratio of AuCl$_3$ to CdS NRs, the size of Au tips in one-sided heterostructures depended primarily on the final temperature of the reaction mixture, such that increasing the final temperature from 110 to 140 °C resulted in a continuous tuning of the tip diameter from 6 to 16 nm (see Table I). We found that it was essential to keep the heating rate below 3.3 °C/min to ensure the development of large-size Au domains, whereas heating of the solution at a faster rate (>4 degrees/minute) leads to the formation of isolated gold NCs that consume a large portion of AuCl$_3$ from the solution thus limiting the growth of Au tips.
Figure 3.2 - (a,b). HAADF-STEM images of Au/CdS heterostructures showing the color contrast between gold (bright) and semiconductor (dark) domains. (c, d). TEM images of the two areas shown in (a) and (b).

High-resolution TEM (HR-TEM) images in Figures 3.1 b,e confirm the crystalline nature of fabricated nano-composites. Both CdS and Au domains show characteristics lattice fringes indexed to respective spacing values of hexagonal wurtzite and face-centered cubic (fcc) crystal phases. The analysis of several specimens has revealed that the lattice of CdS nanorods was generally preserved during the high-temperature synthesis with the exception of some scattered
lattice irregularities represented by small gold domains forming along the defects and the opposite tip of CdS nanorods. Such side-wall nucleation of gold shows a set of small-size (1 nm < d < 2 nm) gold nanocrystals that form on the surface of a CdS NR. The structure of large-diameter gold tips deposited onto one side of CdS NRs is investigated in Figure 3.1e. Judging by the spacing of (111) and (200) atomic planes, the growth of Au tips occurs in the face-centered cubic phase with multiple twinnings of the nanoparticle shape. X-ray powder diffraction (XRD) measurements of Au/CdS samples (Figure 3.1a) further confirm the crystallinity of gold domains, which was evidenced by the set of characteristic fcc (111), (200), and (220) reflections in the XRD spectrum, observed alongside the smaller-amplitude Bragg peaks of the wurtzite CdS lattice. The stronger signal from Au domains is believed to be due to the larger volume fraction of plasmonic-size Au tips in Au/CdS heterostructures, as was confirmed by measurements of nanoparticle elemental composition using the energy dispersive x-ray (EDX) technique (see Figure 3.3b).
Figure 3.3 - (a). XRD spectrum of Au/CdS matchsticks comprising 9-nm gold domains. (b). Elemental composition of Au/CdS samples measured by means of EDX technique. The molar ratio of Au to Cd in this case was 2.05 to 1.

The effect of the reaction temperature and the heating rate on the shape of Au domains is further investigated in Figure 3.4 and Table I. The initial enhancement in the average size of gold tips beyond those of defect-localized domains was observed at $T \approx 95$-$100$ °C. At these temperatures, the heating rate of the solution plays a critical role in determining whether the tip grows on one or both sides of CdS nanorods, such that a faster heating rate ($\approx 3$ degrees/minute) leads to the formation of barbell-shaped nano-composites (Figure 3.4b), whereas slow heating ($\approx 1.5$-$2.3$ degrees/minute) promotes the growth of Au/CdS matchsticks (Figure 3.4a). The average
size of gold domains was measured to be 3.2 nm (matchsticks) and 4.9 nm (barbells) with the associated dispersion of sizes of 12% and 11%, respectively. For the case of nano-barbells, further increase in the temperature of the solution to 120 °C results in the dissolution of one of the tips and simultaneous selective growth of the other, leading to an almost exclusive formation of matchstick-shaped heterostructures (Figure 3.4c), regardless of the heating rate (Table 3.1). As a result, the largest value of the tip diameter for nano-barbells obtained in this work was limited to 6 nm (at ~ 110 °C), due to the transformation of these structures into matchstick-shaped composites at higher temperatures. Upon additional increase of the reaction temperature to 130 °C, the average size of the larger tip grew to 12.6 nm, while the shape of Au domains deviated from the spherical. This trend is clearly observed in the final sample synthesized at 140 °C (Figure 3.4e), where a variety of Au shapes, including triangular, pyramidal, and cylindrical can be identified. The increase of the reaction temperature was accompanied by the growing dispersion of NC sizes, which changed from 7% for 8.0-nm tips to 10% for 15-nm domains.

Further investigation will be needed to optimize the reported synthetic protocols in order to enable lower dispersion of shapes for Au tips with diameters greater than 15 nm. For instance, introduction of additional stabilizing ligands other than oleylamine may be useful in achieving the desired size-focusing of Au nanoparticles.
Table 3.1 - The effect of the reaction temperature and the heating rate on the average size of Au domains. For nano-composites that contain tips on both facets of CdS NRs, sizes of the larger and the smaller tips were determined.
Figure 3.4 - TEM images and statistical size distributions of Au/CdS nano-composites grown at five different temperatures. Average diameters of Au domains for these samples were (a). \( d=3.15 \) nm (b). \( d=4.87 \) nm (c). \( d=8.7 \) nm (d). \( d=12.6 \) nm (e). \( d=15.67 \) nm.
Changes in optical properties of Au/CdS nano-composites during the growth of Au domains are investigated in Figure 3.5. At T=90 °C, the absorption profile of Au/CdS nanoparticles exhibits noticeable changes from that of pure CdS nanorods, with the main difference occurring in the wavelength range above \(\lambda=550\) nm, where the absorption of heterostructures is increased. This red tail is attributed to the contribution from interfacial trap states as well as to optical transitions in small-size gold clusters forming on the surface of CdS nanorods. The disappearance of the excitonic feature in CdS NRs at this stage is attributed to the delocalization of carriers into small gold clusters and oleate complexes that form on the semiconductor surface. Spectral changes occurring during the initial heating of the mixture are accompanied by the visible change of the solution color from yellow to light brown, while further heating of the flask to above 100 °C results in additional darkening of the solution and correlated increase in the amplitude of the absorption tail (for \(\lambda > 500\) nm). At this stage of the reaction, the average size of the Au tip reaches 4 nm, giving rise to a small absorption feature at \(\lambda=550\) nm, corresponding to the surface plasmon resonance in Au nanoparticles\(^{97,98,99}\). With growing size of Au domain this peak becomes narrower and more prominent, which is accompanied by a gradual change in the solution color from dark brown to violet. For tips greater than 9 nm in diameter, the amplitude of the plasmon peak became comparable to that of an excitonic absorption feature in CdS nanorods (Figure 3.5, red curve), while, for Au NCs with sizes of 20 nm and greater this absorption feature becomes inhomogenously broadened due to large dispersions of Au shapes (prisms, rods, spheres, etc.).
Figure 3.5 - Evolution of the Au/CdS absorption spectra during the synthesis. The initial spectrum (blue curve) represents the absorbance of pure CdS nanorods. The average size of gold domains for the subsequent spectra are as follows: green ≈ 2.9 nm, olive ≈ 8.1 nm, red ≈ 15.7 nm.

The described method for the deposition of gold tips onto CdS is independent of the nanorod aspect ratio and can be extended to nanocrystals with other spatial symmetries. For instance, heterostructures comprising spherical CdS domains can be potentially employed as model systems for studying non-linear optical behavior on nanoscale\textsuperscript{100,101}, thereby contributing to the fundamental understanding of exciton-plasmon coupling in metal-semiconductor nano-composites. Figure 3.6 shows several TEM images of Au/CdS hetero-dimers comprising low-aspect-ratio wurtzite CdS NCs used for seeding the growth of gold domains at three different reaction temperatures. Similar to nanorods, the low-temperature (T<95 °C) growth of gold tips onto nearly spherical CdS NCs occurs primarily at surface defects that localize the assembly of small gold clusters, as shown in Figure 3.6c. Increasing the reaction temperature to above 130 °C
causes some of smaller domains to dissolve in favor of a single Au nanoparticle that can grow both on facets and lateral walls of elongated CdS NCs (Figure 3.6 a,b). The size of these Au tips can be tuned in the range of 5 to 15 nm, using the same range of reaction temperatures as in the case of nanorods-shaped semiconductor domains. The apparent similarity between the shape of gold domains of fabricated Au/CdS hetero-dimers and those of CdS nanorods indicates that the rate of Au deposition onto CdS is not strongly correlated with the nanorod aspect ratio.

Figure 3.6 - Au/CdS nano-composites synthesized from low-aspect-ratio nanocrystals. The growth of nanoparticles was terminated at reaction temperatures of: (a) 145 °C, (b) 130 °C, and (c) 95 °C.
As highlighted by previous investigations\textsuperscript{84,102}, gold-modified tips of semiconductor nanorods can serve as anchoring points for self-assembly of Au/semiconductor nano-composites into a series of two-dimensional patterns, including end-to-end “chains” and vertical arrays. This functionality provides an important foundation for the development of nanoscale devices, as it leads to improved charge carrier transport and novel optical properties. Here, we demonstrate the assembly of oleylamine-grown Au/CdS nano-composites into long chains and two-dimensional superlattices, simply by adjusting the concentration of nanoparticles in the solution. Figure 3.7 shows end-to-end assembly of Au/CdS heterostructures obtained by slow evaporation of nano-barbells in toluene onto a TEM grid. The present assembly method was applied to as-prepared nano-composites without modification of Au tips with molecular iodine, which was previously

![Figure 3.7 - Evaporation-induced assembly of Au/CdS nano-composites into (a) end-to-end “chains” and (b) two-dimensional superlattices.](image)
used in rendering such assemblies\textsuperscript{102}. The two-dimensional superlattices of Au/CdS heterostructures comprising 3-nm Au tips were fabricated by slow evaporation of the high-concentration nanoparticle solution\textsuperscript{103,104}, which resulted in the vertical assembly of nanorods over (0.1-0.3)$^2$ $\mu$m$^2$ areas on a TEM grid. Expectedly, the degree of vertical alignment was the highest for nano-composites with small-diameter Au domains (>50% for d<3 nm), and was close to zero for heterostructures comprising large diameter gold tips (<1% for d=10 nm).

In conclusion, we have developed a simple chemical route for growing gold domains onto CdS nanorods in oleylamine. The size of Au NCs can be precisely tuned by adjusting the temperature of the reaction mixture, while the shape of Au/CdS nano-composites (matchstick or barbells) is controllable via the reaction rate. In contrast to conventional techniques for growing gold tips on semiconductor nanorods, the present method does not employ DDA/DDBA reducer/surfactant combination and can yield large-size Au tips without relying on UV-irradiation of the reaction mixture. Fabricated Au/CdS nano-composites show evaporation-induced self-assembly onto TEM grids either through end-to-end or side-by-side coupling of Au domains, which should facilitate their integration into large-area optoelectronic devices.
CHAPTER 4 – PROPERTIES OF PbS\textsubscript{x}Te\textsubscript{1-x} ALLOY NANOCRYSTALS

4.1 Introduction

Semiconductor alloy nanocrystals (AB\textsubscript{x}C\textsubscript{1-x}) \textsuperscript{105,106,107,108,109} are becoming increasingly important in many areas of nanoscale engineering because of the continuous tunability of their physical and optical properties through gradual variation of the composition variable \( x \). This added degree of freedom allows tuning an exciton energy of alloy nanoparticles independently of their size, which can be used to extend the nanocrystal (NC) emission range into parts of the spectrum that are not easily accessible with binary quantum dots (QDs) or to achieve a wide range of fluorescence colors from nanoparticles of the same diameter. Further optimization of nanocrystal properties is also possible by varying the ratio of alloying elements throughout the quantum dot, such that either homogeneous or gradient nanocrystal composition, often with distinctly different properties, can be formed. Owing to their superior luminescent properties that are on par with binary nanocrystals, ternary alloys are now well suited for many practical realizations, including quantum dot-based LEDs,\textsuperscript{110} where emission at a specific wavelength is often required; in vivo imaging\textsuperscript{111,112,113,114}, where small diameter infrared fluorescence labels are preferred; solar cells\textsuperscript{115,116}, where a wide range of absorption and the small size of NC sensitizers are an advantage, and photodetectors where the flexibility and the infrared absorption capabilities are of importance.

To date, several II-IV semiconductor alloy nanocrystals have been synthesized: CdS\textsubscript{x}Se\textsubscript{1-x}\textsuperscript{105}, Cd\textsubscript{x}Zn\textsubscript{1-x}Se\textsuperscript{117}, Cd\textsubscript{x}Zn\textsubscript{1-x}Te\textsuperscript{108,118}, Cd\textsubscript{x}Se\textsubscript{1-x}Te\textsubscript{1-x}\textsuperscript{119}, CdSe\textsubscript{x}Te\textsubscript{1-x}\textsuperscript{106}, and HgSe\textsubscript{x}S\textsubscript{1-x}.\textsuperscript{5} There have also been a number of IV-VI alloys produced PbSe\textsubscript{x}S\textsubscript{1-x}\textsuperscript{120,121}, Pb\textsubscript{1-x}Sm\textsubscript{x}Se\textsuperscript{122}, PbSn\textsubscript{x}Te\textsubscript{1-x}\textsuperscript{123}. It has been shown that when the two chalcogen element’s ratios are stochiometricaly varied, the resulting alloy’s properties have a pronounced non-linear dependence on said ratio \textsuperscript{105,117}. For
example, the emission ranges of CdS$_x$Te$_{1-x}$ were found to be out of the range of the contributing CdS and CdTe binary QDs. These non-linear effects, also known as “optical bowing” have previously been observed in bulk semiconductors and have been explained by Bernard and Zunger$^{124}$ who identified three structural and electronic factors leading to nonlinearity in ternary compounds (i) different ions in the alloy have different atomic sizes, (ii) these ions have different electronegativity values, and (iii) the binary structures have different lattice constants. Thus far the bowing effect has been confirmed for ternary quantum dots that were based on S/Se and Se/Te combinations, few reports of S/Te have been made and none where Pb is the metallic component. S/Te based alloys should exhibit more extensive nonlinearity, resulting from the large differences in their atomic radii and electronegativities. We aim to explore the combination of chalcogens by studying the optoelectric properties of PbS$_x$Te$_{1-x}$ alloy nanocrystals. The use of Pb was inspired by the theoretical work done by Zaoui et al $^{125}$ where the electronic structure of PbS$_x$Te$_{1-x}$ is investigated. The fact that the difference between the electron Bohr radii of S and Te are so different that it is possible for the bowing effect to extend the bandgap of the nanocrystals farther into the infrared than the constituent parts can reach, making them ideal candidates for application to IR photodetectors.

In this work a synthesis of PbS$_x$Te$_{1-x}$ nanocrystal semiconductors is reported via the traditional colloidal method. The nanocrystals that are synthesized are shown to be neither PbS nor PbTe but a homogenous combination of the two. Further research is needed to see whether “optical bowing” is present.
4.2 Experimental Section

4.2.1 Chemicals.

1-octadecene (ODE, 90% Aldrich), oleylamine (OLAM, 70% Aldrich), oleic acid (OA, 90% Aldrich), Tri-n-octylphosphine (TOP, 97+%, Strem Chemicals), lead (IV) acetate (Pb(C₂H₃O₂)₄, 99.99+% Aldrich), Sulfur (99.999%, Acros), Tellurium powder (30 mesh, 99.997%, Aldrich), 1- octadecene (ODE, tech., 90%, Aldrich), methanol (anhydrous, Aldrich), toluene (anhydrous, 99.8%, Aldrich), chloroform (anhydrous, 99+% Aldrich). All chemicals were used as received without any further purification, with the exceptions of ODE and OLAM which were dried at 150°C under argon for one hour immediately before use. All reactions were performed under argon atmosphere using the standard Schlenk technique.

4.2.2 Synthesis of PbS Nanocrystals.

PbS nanocrystals were fabricated according to a modified procedure used by Hines et al. A solution with OLAM as the surfactant and sulfur powder was used in place of the TMS precursor. In an average synthesis, the mixture of lead (IV) acetate (0.4433 g), OA (5 mL), and ODE (5 mL) in a 50 mL 3-neck flask was heated to 150°C until the lead was completely dissolved and the solution turned optically clear and light yellow. At this point, a sulfur precursor solution made by dissolving sulfur powder (0.02 g) in OLAM (2 mL) at 150°C was quickly injected, and the temperature was stabilized at 150°C for the nanocrystal growth. The reaction was stopped after 4-8 min, by rapidly cooling the vessel in a water bath. The nanocrystals were precipitated from the crude solution by repeatedly adding toluene and methanol followed by centrifuging. Once precipitated, the nanocrystals were redispersed into anhydrous toluene.
4.2.3 Synthesis of PbTe Nanocrystals.

PbTe nanocrystals were fabricated according to a procedure based on the one used by Murphy et al. In a regular synthesis, the mixture of lead (IV) acetate (0.4433 g), OA (2 mL), and ODE (5 mL) in a 50 mL 3-neck flask was heated to 150° C until the lead was completely dissolved and the solution turned optically clear and light yellow. At this point, a tellurium precursor solution made by dissolving tellurium powder (0.064 g) in TOP (1 mL) at 150° C was quickly injected, and the temperature was stabilized at 150° C for the nanocrystal growth. The reaction was stopped after 4-8 min, by rapidly cooling the vessel in a bath of ice-water. Due to the air sensitivity of the PbTe nanocrystals, the vessel was then transferred to a gas hood where the rest of the procedures are completed. Once in the gas hood, the nanocrystals were precipitated from the basic solution by repeatedly adding toluene and methanol followed by centrifuging. Once precipitated, the nanocrystals were redispersed into anhydrous toluene.

4.2.4 Synthesis of PbS\textsubscript{x}Te\textsubscript{1-x} Alloy Nanocrystals.

The alloyed PbS\textsubscript{x}Te\textsubscript{1-x} nanocrystals were fabricated using a combination of the two previous methods based on varying the value of x. For a general synthesis, the two procedures are halved and put together. This means that the mixture is now composed of lead (IV) acetate (0.4433 g), OA (3.5 mL), and ODE (5 mL) all combined in a 50 ml 3-neck flask which is heated to 150°C until the lead donor is dissolved per the previous procedures. The injected solution is now made up of dissolving tellurium powder (0.032 g) in TOP (0.5 mL) and dissolving sulfur powder (0.01 g) in OLAM (1 mL) at 150°C in a single flask. One it has been injected, the temperature is stabilized at 150°C for crystal growth. The reaction is stopped at 4-8 minutes by quenching the vessel in a water bath. The crystals were precipitated in a similar method to that of the PbS and the PbTe, using toluene and methanol.
4.2.5 Characterization

UV-vis absorption spectra were recorded using CARY 50 Scan spectrophotometer and Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. High resolution transmission electron microscopy measurements were carried out using JEOL 311UHR operated at 300 kV. High angular annular dark field scanning transmission electron microscopy was performed using JEOL 2010 transmission electron microscope. Specimens were prepared by depositing a drop of nanoparticle solution in toluene onto a carbon-coated copper grid and letting it dry in air. X-ray powder diffraction measurements were carried out on Scintag XDS-2000 X-Ray Powder Diffractometer. Energy Dispersive X-ray (EDX) emission spectra were measured using an EDAX X-ray detector located inside a scanning electron microscope. The electron beam was accelerated at 10 kV.

4.3 Results and Discussion

Homogeneous PbS$_x$Te$_{1-x}$ nanocrystals were synthesized by the rapid injection of S/Te precursors with a carefully controlled molar ratio. The as synthesized nanocrystals were investigated by means of transmission electron microscopy and scanning electron microscopy to collect statistically reliable data for the nanocrystal size, shape, makeup, and crystallinity. Typical TEM images of large-diameter PbS$_x$Te$_{1-x}$ nanocrystals are shown in Figure 4.1.
Figure 4.1 - High-resolution TEM images of PbS$_x$Te$_{1-x}$ nanocrystals with homogeneous composition of S and Te chalcogens. The scale bars for the two images are 5 nm on the top and 20 nm on the bottom.

The shape of most nanoparticles appeared to be cubic (rock salt structure), similar to those of both PbTe and PbS. By examining multiple isolated specimens under high magnification (up to ×600 K), we estimated the average width of nanoparticles to be 9.6 nm. Considering the size of the nanoparticles, the distribution of their diameters was not large (SD 14%). Also by using the TEM, the lattice spacing was measured, and found to be a new homogeneous lattice spacing rather than a gradient or that of either PbS or PbTe. In fact it was
Energy dispersive X-ray emission spectra were measured to study the elemental composition of fabricated alloys. For this purpose, toluene suspension of purified PbS\(_x\)Te\(_{1-x}\) nanocrystals was evaporated onto a carbon substrate and loaded into SEM equipped with an X-ray detector. Figure 4.2 shows a typical X-ray spectrum obtained at 20 kV, along with peak assignments for Pb, S, and Te elements. After integrating the peak area, we converted the X-ray count into the elemental weight percentages using quantification software (EDAX Genesis). The resulting stoichiometric ratio of elements Pb/S/Te was found to be 48:41:11, respectively. The amount of Pb in the sample was approximately balanced by the combined amounts of S and Te, which indicates that most of the unreacted ions were removed during purification. From the ratio of S to Te, we determine the stoichiometry of the homogeneous alloy NCs, fabricated by using equal portions of chalcogens precursors, to be PbS\(_{0.2}\)Te\(_{0.8}\).

Figure 4.2 - Energy dispersive X-ray emission spectrum of homogeneous PbS\(_x\)Te\(_{1-x}\) alloy nanocrystals.
It was also found that the alloy is not as air sensitive as either of its constituent parts. Due to the fact that PbTe is extremely air sensitive, it is necessary to perform the entire synthesis and post processes under argon, and even then there is a great deal of apparent degradation in the nanocrystals. Similar is true for PbS, though it is not nearly as air sensitive as the PbTe and does not need to be post processed under argon, there is still some evidence of degradation. This is even less true with the PbS\textsubscript{x}Te\textsubscript{1-x} alloy which shows an increased resistance to air over time, and is able to survive in a suspension for extended periods of time. It is currently not known why this occurs, but it is speculated that the outer layer of the NC oxidizes, protecting the inner layer.

Due to the large mismatch of the PbTe and PbS lattice spacings, it was not expected for a homogeneous alloy to be synthesized; normally nanocrystals with a gradient are formed. With the success of the synthesis of the PbS\textsubscript{x}Te\textsubscript{1-x} alloy, continued research looks promising.
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