Novel Microfluidic Platforms for the Programmable Synthesis of Semiconductor Nanocrystals

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To my parents,
Georgios and Maria,
and in memory of my grandmother,
Katerina
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Abstract

The parametric screening, optimization and quantitative kinetic investigation of reactions involved in nanocrystal synthesis is often a time-consuming and expensive undertaking. Microfluidic reactors with integrated optical detection systems have shown numerous advantages compared to flask reactors for the synthesis of nanocrystals, most notably in their ability to control the physical properties of the product and their ability to rapidly screen parameters for reaction optimization. Despite the recognized advantages of microfluidic technology, there is a lack of high-efficiency microfluidic platforms suitable for the synthesis of a range of semiconductor nanocrystals with a concurrent real-time spectroscopic analysis of their physicochemical and photophysical characteristics. The primary goal of this thesis was to create novel segmented-flow, microfluidic platforms with incorporated in-situ optical detection systems for efficient and fast screening of reaction conditions and a better understanding of the mechanisms of semiconductor nanocrystal (quantum dots) synthesis.

Several novel microfluidic platforms were developed for the precision synthesis of existing and novel semiconductor nanocrystals. A droplet-based microfluidic platform with a novel, in-line near infrared optical detection system was built for the controlled and reproducible synthesis of lead chalcogenide - lead sulfide (PbS) and lead selenide (PbSe) - nanocrystals. Monodisperse nanocrystals were synthesized over a wide range of experimental conditions, with real-time assessment and fine-tuning of material properties being achieved using NIR fluorescence spectroscopy. Importantly, we showed for the first time that real-time monitoring of the synthetic process allowed for rapid optimization of reaction conditions and the synthesis of high quality PbS nanocrystals, emitting in the range of 765 – 1600 nm, without any post-synthetic processing. The segmented-flow capillary reactor exhibited stable droplet generation and reproducible synthesis of PbS nanocrystals with high photoluminescence quantum yields (28%) over extended periods of time (3 – 6 h). Furthermore, the produced NIR-emitting nanoparticles were successfully used in the fabrication of Schottky solar cells, exhibiting a power conversion efficiency of 3.4% under simulated AM 1.5 illumination. Moreover, the microfluidic platform was used to synthesize PbSe nanocrystals having photoluminescence peaks in the range of 860 – 1600 nm, showing the exceptional control and stability of the reactor.

Due to the fast reaction kinetics involved in the synthesis of various quantum dots including PbS NCs, we designed an innovative microfluidic configuration for extracting rapid kinetic information on a millisecond time-scale and at high-temperatures. The early-time kinetics (<1 s) of PbS quantum dot formation were probed, allowing for high-throughput and real-time optical analysis of the reactive process with millisecond time resolution. The reaction platform enabled the concurrent investigation of the emission characteristics of PbS quantum dots and a real-time estimation of their size and concentration during nucleation and growth.
These investigations revealed a two-stage mechanism for PbS nanoparticle formation. The first stage corresponded to the fast conversion of precursor species to PbS crystals, followed by the growth of the formed particles. The growth kinetics of the PbS nanoparticles followed the Lifshitz–Slyozov–Wagner model for Ostwald ripening, allowing direct estimation of the rate constants for the process. In addition, the extraction of absorption spectra of ultrasmall quantum dots was demonstrated for first time in an online manner.

We also investigated the formation of CuInS$_2$/ZnS using a two-stage microfluidic reactor integrated with a fluorescence optical detection system, which was able to monitor the reaction parameters prior and after the addition of the shell material. By injecting a ZnS single source precursor in the droplets containing CuInS$_2$ cores, we were able to obtain core-shell nanocrystal populations emitting between 580 and 760 nm with narrow size distributions (90-95 nm) and without the need of purification steps. In-line monitoring allowed for rapid assessment of optimum reaction parameters (Cu/In, (Cu+In)/S, Zn/(Cu+In) molar ratios, temperatures and reaction time) which led to the formation of CuInS$_2$/ZnS with high QYs reaching 55% within a few seconds (compared to minutes or hours in flask reactors).

Furthermore, understanding of the parameters governing the formation of a novel class of semiconductor nanocrystals (CsPbX$_3$, X = Br, I and Cl and Cl/Br and Br/I mixed halide systems) is still very limited due to extremely fast reaction kinetics and multiple variables involved in ion-metathesis-based synthesis of such multinary halide systems. Using a droplet-based microfluidic platform, we investigated the synthesis of CsPbX$_3$ nanocrystals. The combination of online photoluminescence and absorption measurements and the fast mixing of reagents within such a platform allowed the rigorous and rapid mapping of reaction parameters, including molar ratios of Cs, Pb and halide precursors, reaction temperatures and reaction times. This translates into enormous savings in reagent usage and screening times when compared to analogous batch synthetic approaches. The early-stage insight into the mechanism of nucleation of metal halide nanocrystals suggested similarities with multinary metal chalcogenide systems, albeit with much faster reaction kinetics in the case of halides. Furthermore, we showed that microfluidics-optimized synthesis parameters are also directly transferrable to the conventional flask-based reaction.

Last, an optical system which is able to perform time-correlated single photon counting in flow was also built for in-situ monitoring of nanocrystal photophysics. A suitable algorithm for real-time fluorescence decay curve analysis allowed for rapid and real-time extraction of average fluorescence lifetimes of CsPbX$_3$ nanocrystals in a high-throughput manner. Fluorescence lifetimes for all halide systems in the range of 5–42 nm were estimated by a systematic variation of precursor molar ratios and temperature. This system may be of immense value for nanocrystal chemists as it provides a direct way to optimize particle photophysics.

Verschiedene neuartige mikrofluidische Plattformen wurden zur Präzisionssynthese von neuartigen und existierenden Halbleiternanokristallen entwickelt. Eine mikrofluidische Plattform basierend auf Tröpfchen mit einem neuartigen integrierten optischen Detektionssystem im Infrarotbereich wurde zur kontrollierten und reproduzierbaren Synthese von Bleichalkogeniden - Bleisulfid und Bleiselenid - Nanokristallen gebaut. Monodisperse Nanokristalle wurden über einen weiten Bereich von experimentellen Parametern synthetisiert und Echtzeitbewertung und Feineinstellung der Materialeigenschaften mittels Nahinfrarotspektroskopie erreicht wurden. Wesentlich ist, dass wir zum ersten Mal zeigten, dass Echtzeitüberwachung des synthetischen Prozesses uns erlaubt die Reaktionsbedingungen schnell zu optimieren und PbS Nanokristalle, die im Bereich von 765 - 1600 nm emittieren, ohne Nachbereitung zu synthetisieren. Der mit segmentiertem Fluss arbeitende Kapillarreaktor zeigte stabile Tröpfchenbildung und die reproduzierbare Synthese von PbS Nanokristallen mit hohen Photolumineszenzausbeuten (28%) über einen ausge dehnten Zeitraum (3 - 6 h). Ausserdem wurden die dargestellten NIR-emittierenden Nanopartikel erfolgreich in der Fabrikation von Schottky Solarzellen, die eine Leistungsumwandlungseffizienz von 3.4% unter simulierter Belichtung von AM 1.5 erreichten, eingesetzt. Desweiteren wurde die mikrofluidische Platform verwendet um PbSe Nanokristalle mit Photolumineszenzmaxima im Bereich von 860 - 1600 nm zu synthetisieren, was die aussergewöhnliche Kontrolle und Stabilität des Reaktors bewies.

Aufgrund der schnellen Reaktionskinetik der Synthese verschiedener Quantenpunkte (inklusive PbS Nanokristalle), entwarfen wir eine innovative mikrofluidische Konfiguration um schnelle kinetische Informationen in Millisekunden-Größenordnung bei hohen Temperaturen zu erhalten. Die Anfangskinetik (<1 s) der PbS Quantenpunktbildung wurde untersucht, was die optische Hochdurchsatz- und Echtzeitanalyse mit Millisekunden-Präzision des Reaktionsprozesses erlaubte. Die Reaktions-
platform ermöglichte die gleichzeitige Untersuchung der Emissionscharakteristik von PbS Quantenpunkten und eine Echtzeitabschätzung ihrer Größe und Konzentration während Keimung und Wachstum.

Diese Untersuchungen enthüllten einen zweistufigen Mechanismus der PbS Nanopartikelbildung. Der erste Schritt besteht aus der schnellen Umwandlung der Vorstufenspezies zu PbS Kristallen, mit anschließendem Wachstum der gebildeten Teilchen. Die Wachstumskinetik der PbS Nanopartikel folgte dem Lifshitz-Slyozov-Wagner Modell für Ostwald Reifung, was die direkte Abschätzung der Geschwindigkeitskonstanten für den Prozess erlaubte. Zusätzlich wurden zum ersten Mal Absorptionsspektren von ultrakleinen Qunatenpunkten während des Prozesses aufgenommen. Ausserdem untersuchten wir die Bildung von CuInS$_2$/ZnS mit einem zweistufigen mikrofluidischem Reaktor mit einem integrierten Fluoreszenz-Detektionssystem, das die Beobachtung der Reaktionsparameter vor und nach der Zugabe des Schalenmaterials erlaubte. Durch Injektion einer ZnS Vorstufe in die Tröpfchen mit den CuInS$_2$ Kernen war es uns möglich zwischen 580 und 760 nm emittierende Kern-Schale Nanokristalle mit schmalen Verteilungen (90-95 nm) ohne Aufreinigung zu erhalten. Echtzeitbeobachtung erlaubte die schnelle Bewertung der optimalen Reaktionsparameter (Cu/In, (Cu+In)/S, Zn/(Cu+In) molare Verhältnisse, Temperatur und Reaktionszeit) was zur Bildung von CuInS$_2$/ZnS mit hohen Quanatenausbeuten von 55% während weniger Sekunden führte (im Vergleich zu Minuten bis Stunden in Reaktionskolben).


Zuletzt wurde ein optisches System gebaut, das zeitkorrelierte Einzelphotonenzählung im Durchfluss erlaubt um die in-situ Beobachtung der Nanokristallphotophysik zu ermöglichen. Ein geeigneter Algorithmus zur Analyse von Fluoreszenzabklingkurven erlaubte die Echtzeitextraktion von durchschnittlichen Fluoreszenzlebenszeiten von CsPbX$_3$ Nanokristallen mit hohem Durchsatz. Fluoreszenzlebenszeiten al-
ler Halogenidsysteme zwischen 5-42 ns wurden ermittelt durch eine systematische Veränderung der Molaren Verhältnisse Vorstufen sowie der Temperatur. Dieses System könnte von immensem Wert für Nanokrystalchemiker sein, das es einen Direkte Möglichkeit zur Optimierung der Partikelphotophysik darstellt.
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Chapter 1

Microfluidic Reactors for Nanocrystal Synthesis

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1.1 Introduction

The discovery of novel properties, processes, and phenomena at the nanoscale has in recent years created revolutionary opportunities for the creation of new materials and devices with outstanding chemical, physical and biological properties. In this respect, nanocrystalline materials are of special interest owing to their tuneable physicochemical properties and their potential use as functional elements in biological sensing, optoelectronics, photovoltaics, energy storage, fiber-optic communications, medical imaging and catalysis.

The physical characteristics of nanomaterials (such as particles, rods and tubes) are in large part governed by quantum confinement effects with properties such as the optical band gap often differing considerably from the bulk semiconductor.\textsuperscript{1,2} As these properties are ultimately regulated by the physical dimensions of the crystallite, there is considerable interest in developing processing or synthesis methodologies that are versatile, robust, efficient and high-throughput and yield nanoparticles of well defined size and shape.

The past decade has seen a steady rise in the use of microfluidic reactors for nanocrystal synthesis, with numerous studies reporting improved reaction control relative to conventional batch chemistry.\textsuperscript{3-5} However, flow synthesis procedures continue to lag behind batch methods in terms of chemical sophistication and the range of accessible materials, with most reports having involved simple one or two-step chemical procedures directly adapted from proven batch protocols. This chapter specifically discusses the current status of microscale methods for nanocrystal synthesis, and considers what role microfluidic reactors might ultimately play in laboratory-scale research and industrial production.

1.1.1 Semiconductor Nanocrystals (Quantum Dots)

Colloidal semiconductor nanocrystals (NCs) or quantum dots (QDs) are tiny particles whose size is in the range of 1-10 nm and are composed of a semiconductor core surrounded by a layer of organic ligands.\textsuperscript{1,2} Colloidal NCs have been of great interest due to their tunable optical and electronic properties, which can be controlled by particle dimensions.\textsuperscript{6-8} The strong size dependence of their absorption and photoluminescence spectra can be explained by the quantum confinement phenomenon described in Figure 1.1. When the radii of colloidal semiconductor NCs are smaller than the exciton Bohr radius, the electronic structure of the crystal consists of discrete atomic-like states.\textsuperscript{9} As the size of a semiconductor crystal decreases the difference in energy between the valence and conduction band increases. This results to the release of a certain amount of energy when the crystal returns to its ground state, which corresponds to a color shift from blue to red in the emission.
QDs are characterized by broad absorption bands, narrow emission linewidths, high photostability and high fluorescence quantum efficiencies.\textsuperscript{6–8} Since their luminescence can cover UV, visible and near-IR wavelengths, they have found significant application in multiplexed labeling and tracking of cells or molecules in biological environments,\textsuperscript{11,12} illumination and displays and single photon sources.\textsuperscript{10,13,14} The controlled synthesis of colloidal semiconductor NCs is of central importance in nanoscale science and technology. Their synthesis, however, is a complex undertaking that requires a combination of skill, intuition and extensive experimentation to obtain high quality particles of well-defined size and shape.\textsuperscript{1,2} Indeed the formidable difficulty of preparing pure, defect-free colloidal semiconductor NCs is the main obstacle to the full exploitation of many nanoscale phenomena.

1.2 Nucleation and Growth Theory for Colloidal Nanocrystals

In common with colloidal systems, nanocrystals are created via a three-stage process (Figure 1.2).\textsuperscript{10,15} In the first stage molecular precursors rapidly decompose into a mixture of solvents and organic ligands. The monomer concentration increases until critical supersaturation is reached (stage 1). At this point, seed particles precipitate spontaneously from solution (nucleation, stage 2). This is followed by a period in which the newly formed seeds capture dissolved atoms or molecules from solution, and grow to form the desired nanocrystal until complete depletion.
of monomers (growth, stage 3). However, further growth of the formed nanocrystals may occur due to Ostwald ripening, where large nanoparticles compete with small nuclei during formation. This often leads to the dissolution of smaller particles at the expense of further growth of the larger ones. This process typically results to the formation of polydisperse samples. Nucleation is only possible if the condensed phase is thermodynamically stable, and is understood through Gibbs-Thompson theory.

\[ S_r = S_\infty \exp \left( \frac{2\gamma V_m}{r RT} \right) \]  

(1.1)

The solubility of a nanoparticle of radius \( r \) \( (S_r) \) is given by

where the surface energy is \( \gamma \), the molar volume of a monomer is \( V_m \), the ideal constant is \( R \) and the temperature is \( T \). The solubility of the bulk crystal is \( S_\infty = S_{r\to\infty} \). Thus, the chemical potential \( \mu_r \) of the nanoparticle is

\[ \mu_r = \mu^o + RT \ln S_r = \mu^o + RT \ln S_\infty + \frac{2\gamma V_m}{r} \]  

(1.2)

The chemical potential of a monomer depends on its concentration \([M]\), i.e.

\[ \mu_M = \mu^o + RT \ln[M] \]  

(1.3)

The nucleation process \( M_{\text{solution}} \rightarrow M_{\text{nanoparticle}} \) has a Gibbs free enthalpy, \( \Delta G = n(\mu_r - \mu_M) \) with mole number \( n = V_r/V_m \). The volume of the nanoparticle with radius \( r \) is \( V_r = 4\pi r^3/3 \). Thus

\[ \Delta G = \frac{4\pi r^3}{3V_m} \left( RT \ln S_\infty + \frac{2\gamma V_m}{r} - RT \ln[M] \right) \]  

(1.4)

\[ = \frac{8\pi^2 r^2 \gamma}{3} - \frac{4\pi r^3 RT}{3V_m} \ln \frac{[M]}{S_\infty} \]  

(1.5)

The first term in equation 1.5 is due to the surface energy and the second term defines the free enthalpy release due to crystallization. Both terms compete against each other. Their relative strength is proportional to the surface to volume ratio \((3/r)\). For small nanoparticle radii, the surface term dominates and prevents nucleation. Beyond a critical radius, \( r_c \), the crystallization energy grows and enables nucleation. The quantity \( \omega = [M]/S_\infty \) is called the saturation parameter. Only for
supersaturated solutions where \( \omega > 1 \) (and thus \( \ln \omega > 0 \)) will the crystallization energy overcompensate the surface energy. The critical value is determined from 
\[ \frac{\partial \Delta G}{\partial r} |_{r=r_c} = 0. \]
Hence,
\[ r_c = \frac{4}{3} \frac{\gamma V_m}{RT \ln \omega} \]  
(1.6)
\[ \Delta G_c = \Delta G |_{r=r_c} = \frac{128 \pi \gamma^3 V_m^2}{(9 RT \ln \omega)^2} \]  
(1.7)
This critical point indicates that only sufficiently large nanoparticles (with \( r > r_c \)) are stable against surface tension effects. The free enthalpy \( \Delta G_c \) can be interpreted as an activation energy for the nucleation reaction. In terms of Arrhenius’ law, this gives rise to a nucleation rate, \( k \), i.e.
\[ k := -\frac{d}{dt} \left[ M \right] = A \exp \left( -\frac{\Delta G_c}{RT} \right) = A \exp \left( -\frac{128 \pi \gamma^3 V_m^2}{(9 \ln \omega)^2 (RT)^3} \right) \]  
(1.8)
where the pre-exponential factor \( A \) is only weakly temperature dependent. Consequently, the nucleation speed (\( \ln k \sim \frac{1}{T^3} \)) strongly depends on temperature.\(^{19}\)

After nucleation in an oversaturated solution, nanoparticles grow by the combination of nuclei with free monomers that diffuse to the surface. Depending on which of the two processes – reaction and diffusion – is slowest, growth will be reaction controlled or diffusion controlled. With a diffusion constant, \( D \), and reaction constant, \( k \), the growth rate of a spherical particle is found to be:\(^{20}\)
\[ \frac{dr}{dt} = D \frac{[M] - [M_e]}{r - D/k} \]  
(1.9)
Analysis with the Gibbs-Thompson law (1.1) yields,
\[ \frac{dr}{dt} = D \frac{[M_\infty] \omega^{-1} - \omega^{(\frac{2}{3} - 1)}}{r - D/k} \]  
(1.10)
Accordingly, the growth rate depends upon the particle radius. Only for a radius exceeding the critical value will the rate become positive. Moreover, the growth rate decreases with particle radius, such that an initially broad size distribution will become narrower due to non-uniform growth, \( i.e. \) small particles grow faster than large particles. This effect is called size focussing.\(^{21}\)

Once the monomer concentration has been strongly depleted, a new growth mechanism called Ostwald ripening\(^{17}\) may occur. Monomers are in chemical equilibrium between the solid and solution meaning that monomers continuously dissolve from and recombine with nanoparticles.\(^{22}\) Since the solubility of smaller grains is higher than that of larger grains, monomers diffuse from the surface of small grains to that of large grains. Hence, large grains grow by absorption of monomers dissolved from smaller grains. Consequently, the size distribution broadens again and also becomes asymmetric.\(^{15,16}\)
This effect is undesirable in quantum dot synthesis since it reduces the monodispersity of the sample. A good choice of the monomer concentration is crucial in triggering nucleation and achieving size-focussing of the nanoparticle sample.

Accordingly, to synthesize nanocrystal populations with low polydispersity it is necessary to perform the reaction in a way that allows nucleation to occur over an extremely short period of time, with additional material then being supplied at a rate that enables nuclei growth to occur, but without the solute concentration reaching a level that will promote further nucleation. This scenario can be expressed using a La Mer diagram (Figure 1.3), which illustrates the variation of solute concentration as a function of time.\textsuperscript{23} The solute (dissolved feed-stock) is typically formed by chemical reaction. As the reaction proceeds, the solute concentration increases and eventually exceeds the supersaturation concentration and a critical concentration at which nucleation occurs. Nucleation (and the ensuing growth of these nuclei) lowers the solute concentration below the critical nucleation concentration (preventing further nucleation) but to a level that is still sufficient to allow particle growth. Particles then grow at a rate that consumes further solutes generated by reaction. Thermodynamically, particle growth reduces the free energy of the system so that (in the absence of competing processes) growth will continue until all solute molecules are consumed. It should also be noted that nanoparticles are only obtained if growth stops when particles are still in the nanometer size range, otherwise there is propensity for particle aggregation. A common way to prevent aggregation and growth arrestation is to cover particles with surfactant molecules. This approach is versatile and allows both the size and the shape of nanoparticles to be controlled by varying the type, concentration, and time-of-addition of the surfactants.\textsuperscript{1,2}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_1.3.png}
\caption{Schematic illustration of nanoparticle nucleation and growth. Nucleation starts after supersaturation of monomers followed by a subsequent growth of nuclei. Ostwald ripening becomes the dominant growth mechanism after depition of monomers.\textsuperscript{10}}
\end{figure}
1.2.1 Conventional Synthetic Methods

There are two broad approaches for forming NCs: top-down and bottom-up methods. In the top-down methodology, nanometer-sized structures are directly engineered from bulk materials using micromachining methods such as photolithography and etching\textsuperscript{24}. Although such methods are well established, the creation of structural dimensions below 100 nm requires the use of sophisticated lithographic techniques such as electron beam and X-ray lithography. Such approaches are technically challenging, costly and despite possessing high levels of reproducibility do not readily lend themselves to the large-scale production of NCs. On the other hand, bottom-up approaches involve the chemical growth of crystals in an atom-by-atom fashion until the required NC size and shape is achieved\textsuperscript{2,25}. In particular, wet-chemical methods are adept in synthesizing a wide range of different types NCs with uniform size and shape. Among several synthetic approaches, the hot-injection” and the ”heat-up” methods are the most reliable means of producing high-quality nanocrystals in large quantities.\textsuperscript{20,26}

The heart of the hot-injection” method involves the rapid injection of a precursor solution into a hot solution of precursors and ligands. The use of relatively high temperatures \textit{e.g.} 200-300 °C allows for a fast homogeneous nucleation which is followed by the subsequent growth of crystals at lower operating temperatures.\textsuperscript{20} The first successful formation of high-quality NCs \textit{via} the hot injection approach was reported in 1993.\textsuperscript{7} Herein, Murray and coworkers prepared CdE (E = S, Se, Te) nanocrystals using dimethylcadmium as a precursor and a mixture of organophosphine and organophosphine oxide as the coordinating solvent. Phosphine selenide - telluride and bis(trimethylsilyl) sulfide were used as the chalcogenide source. The synthesized nanocrystal population was highly luminescent with low size distribution and with facile tuning of optical properties over the visible region.

This approach to nanocrystal synthesis catalysed enormous activity in the nanotechnology community and since this publication there have been numerous attempts using this technique for the successful synthesis of various NCs. Subsequently, a variety of metal, metal oxide and semiconductor NCs (binary, ternary, quaternary and core-shell),\textsuperscript{2} with low size distributions and high quantum yields (for the quantum dot syntheses) have been prepared. Additionally, better insight into metal precursors, ligands and coordinating solvents has led to a refined control over the growth rate of reactions leading to the formation of more stable NCs of consistent size and shape. In addition to the formation of spherical NCs, more complicated NC architectures have been reported by careful selection of metals and ligands which sensitively affect the shape dynamics of the synthesized NCs.
Over the past decade "heat-up" synthesis of colloidal NCs has also been very popular in the nanotechnology community.\textsuperscript{26} The formation of NCs using this methodology is performed by continuously heating the reaction mixture (see Figure 1.5). Despite, the similarities with the "hot-injection" approach there are a multitude of challenges that have to be addressed in a "heat-up" synthesis for controlling the factors affecting particle growth. For instance, since it is difficult to decouple nucleation and growth, a better insight into precursor reactivity must be gained to generate a sufficient number of nuclei at early times of reaction, with subsequent growth of these nuclei into bigger crystals. Addressing these challenges could broaden the applicability of the approach, leading to a facile scalable production of high-quality nanocrystals.
1.3 Beyond Batch

Although this approach is the most common means of producing large quantities of nanomaterials, and a variety of sophisticated chemical strategies have been successful in producing near defect-free nanoparticles of consistent size, shape, and chemical composition, implementation remains a complex and costly undertaking, requiring a combination of skill, experience and intuition to obtain well-defined nanoparticles of the desired properties.27,28

Over the years a multitude of synthetic strategies have been reported for producing high quality nanocrystals. Many of these methods, however, suffer from significant batch-to-batch variability arising from inadequate reaction control. In 2002, the use of microfluidic reactors was proposed for nanocrystal synthesis, reasoning that a reduction in reaction volume would ensure better uniformity in the thermal and chemical environment, which in turn would lead to improved product control.29 A simple demonstration of the idea was provided, using the direct reaction of cadmium nitrate and sodium sulphide (with sodium polyphosphate as a capping agent) to form cadmium sulphide nanocrystals of tuneable band gap. While this and related work demonstrated the feasibility of adapting a conventional batch synthesis route to flow - and in particular demonstrated the ease with which reaction conditions could be systematically varied in a flow environment - it did not explicitly show improvements in the quality of nanocrystals when compared to batch.

In the ensuing twelve years, there have been hundreds of reports of nanocrystal syntheses in microfluidic reactors, ranging widely in sophistication and complexity with regards to the microfluidic network employed, the synthetic strategy and the nature of the particles produced. There have been many articles reviewing the application of microfluidic reactors in nanocrystal synthesis, and it is not the intention to add to that list here.30–37 Rather, the aim herein is to identify areas where microfluidic methods offer advantages over batch procedures, and to draw attention to a number of challenges that should be addressed to realize their full potential for nanocrystal synthesis.

In conventional batch processes it is difficult to ensure consistent reaction conditions from one synthesis to the next, especially when reactions are carried out manually. Minor variations in the times, locations and rates of precursor addition or the way in which the reaction is eventually quenched can have a strong influence on the final product, meaning that the quality of the nanocrystals obtained will vary greatly from one batch to the next. Furthermore, inhomogeneities in the temperature or chemical composition of the reaction mixture due to uneven heating or inadequate mixing can be an unwanted source of polydispersity. In moving to a microfluidic format improved sample consistency can be achieved by virtue of the reduced reaction volumes, which ensure a more uniform reaction environment. Nanocrystal properties can be readily tuned by varying the volumetric flow rates of the injected reagents or the temperature distribution along the flow profile. Finally, once the desired conditions have been determined, an arbitrary
amount of optimised, highly consistent material can be obtained by operating the reactor continuously until production requirements have been met. This at least is the goal. To what extent can it be achieved?

1.3.1 Single-phase versus Two-phase Reactors

Reactors for nanocrystal synthesis fall into two broad categories: capillary- and chip-based systems. Capillary reactors are generally simpler in structure and more easily fabricated, using simple fluidic components joined by appropriate lengths of tubing. Chip-based systems are typically fabricated from a plastic, glass or silicon substrate, using soft-lithography, wet etching or micromachining techniques, and can be precisely tailored to the individual requirements of the reaction. For example multiple chemical processes (e.g. heating, mixing, cooling, reagent addition) can be integrated onto a monolithic, small-footprint device. Both types of reactor have been applied to good effect in nanocrystal synthesis.\textsuperscript{38–41} Choice is largely a matter of taste: does one prefer the convenience of capillaries or the highly integrated nature of chip-based systems?

On a different level, microfluidic reactors can be categorised as single-phase or two-phase reactors. Most research to date has focused on single-phase reactors, in which miscible streams of reagents are injected into a channel or capillary where they mix and react (Figure 1.6). Single-phase reactors offer a high degree of synthetic flexibility, tolerating a wide range of flow rates and solvents. In addition, they facilitate the easy injection of additional reagents in a controlled manner through the use of downstream inlets in the reaction channel, making it straightforward to conduct multistep reactions and produce more complex structures.\textsuperscript{42} Two issues, however, limit their performance. First, the flowing liquid drags against the channel walls inducing a parabolic velocity profile across the flow path, with the fluid moving fastest at the channel centre; this in turn generates a distribution of residence times within the reactor, leading to undesirable dispersion in nanoparticle properties.\textsuperscript{43} Second, precursor and/or product deposition on the walls can lead to fouling, which affects the flow and ages the reactor. Left unchecked this can, and frequently does, lead to eventual failure through blockage.
Figure 1.6: Cartoon showing three types of fluid flow in a microfluidic channel: (a) single-phase continuous flow, where contact with the channel walls leads to a parabolic flow profile; (b) segmented or slug flow where the reaction mixture is divided up into discrete units by an immiscible fluid; (c) droplet flow where the reaction mixture is completely isolated from the channel walls by the immiscible fluid.  

Two-phase reactors elegantly overcome both drawbacks of single-phase reactors. Injection of an additional immiscible fluid (which can be a gas or a liquid) into the channel divides the reaction mixture into a succession of discrete slugs or droplets (Figures 1.6(b) and 1.6(c)) that pass through the reactor at a common speed, eliminating velocity dispersion. In the case of slug flow, the reaction mixture still makes contact with the channel wall, but abrasion from the second phase can help to reduce or even eliminate fouling, prolonging reactor lifetimes. Yen et al. were the first to use gas-liquid segmented flow reactors for high temperature nanocrystal synthesis, reporting the synthesis of CdSe from cadmium 2,4-pentanedionate and selenium at 260°C. They achieved good size control by tuning the injection rates of the cadmium and selenium precursor solutions and reported significantly narrower emission spectra than an equivalent single-phase synthesis, consistent with the non-dispersive motion of the reagent slugs.

In the case of droplet flow, the reaction mixture is fully isolated from the wall by the immiscible liquid, thereby preventing reagent deposition from happening in the first place. Furthermore, if the droplets are large enough to fill the cross-section of the channel, they are forced to move in a direction parallel to the channel and cannot take unguided off-axis routes that would induce velocity dispersion. The use of droplet reactors for nanocrystal synthesis was first demonstrated by Shestopalov and coworkers. They used chip-based oil-water droplet reactors operating at room temperature to prepare cadmium sulphide quantum dots from ionic cadmium and sulphur precursor solutions. Chan and co-workers subsequently developed a high temperature chip-based droplet reactor in glass, using octadecene as the droplet phase, a high boiling point perfluorinated polyether as the carrier fluid and a surface coating of perfluoroalkylsilane to ensure preferential wetting of the
channel walls by the carrier phase. They were able to controllably synthesise high quality CdSe by reacting cadmium oxide and elemental selenium in the presence of oleic acid and trioctylphosphine at 300 °C, achieving stable operation for up to five hours of continuous use.

Nightingale et al. later developed a capillary-based droplet reactor, using polytetrafluoroethylene tubing, capable of operating at temperatures of up to 250 °C. Using the same carrier fluid and reagents as Chan et al. they synthesized CdSe quantum dots continuously over a 24 hour period, obtaining consistent product over the full duration of the synthesis run, with no drift in the spectral properties of the resultant particles. They applied the same reactor to the synthesis of nanocrystalline silver, titania and (in later work) superparamagnetic iron oxide, reporting good operational stability in all cases. Indeed, the titania synthesis involved the formation of insoluble titanium oxide hydrate intermediates, clearly visible as blue clouds inside the droplets, yet did not cause reactor fouling. The authors noted anecdotally that during six months of testing with a wide variety of materials systems and synthesis routes they had yet to experience a single instance of reactor fouling, confirming the effectiveness of the droplet regime in preventing reactor fouling. Capillary reactors have most recently been applied by Lignos et al. to the high temperature synthesis of near-infra-red-emitting PbS and PbSe nanocrystals, with excellent operational stability again being reported over prolonged (three hour) operation.

The best flow regime is dependent on the chemistry at hand. When single-phase flow can be used, it is clearly the simplest method to implement. However, there are few (if any) situations where single-phase flow can be expected to offer a clear performance advantage over two-phase flow, and the circumstances in which it can be reliably applied are limited. In our experience single-phase reactors are suited to a narrow range of low temperature chemistries. High temperature reactions in organic solvents inevitably cause single-phase reactors to foul, and should instead be carried out in two-phase reactors. For research purposes, slug-flow and droplet-flow may often be used interchangeably. In the current thesis droplet-based systems are exclusively used due to their increased resilience to reactor fouling.

One issue with two-phase systems is the potential influence of the second (supposedly inert) phase on the nucleation and growth kinetics of the nanocrystals (and hence on their final crystal structure, defect levels and polydispersity). While the second phase is typically chosen to be unreactive, some degree of interaction with the solvent phase is inevitable due to the high interfacial contact areas. If any reagents or reaction products are soluble in the carrier liquid, they will partition between the two phases on the basis of relative solubility. Fluorous carrier liquids for instance can support high levels of dissolved gases, allowing gaseous side products from a reaction to leech from the solvent into the carrier liquid. Conversely, pre-dissolved gases in the carrier liquid (originating for example from imperfect degassing or deliberate loading) may pass into the solvent phase. The effects of solute exchange between the two phases has been largely overlooked in the literature, but can clearly be expected to have a significant influence on the final
particle properties. Indeed, at an extreme level, it forms the basis of multiphase synthesis routes where precursors are dissolved in separate phases and meet and react at the phase boundaries. Multiphase chemistries have been widely exploited in batch nanocrystal synthesis but, with a few notable exceptions,$^{50,51}$ have rarely been applied on the microscale. This is somewhat surprising since the large interfacial contact areas and short diffusion distances in microreactors should enhance reaction rates relative to batch reactions, leading to shorter nucleation times and better controlled product.

1.4 Where next?

1.4.1 Plug-and-play droplet manipulation

From a stability perspective, droplet-based microfluidic reactors represent a near ideal environment in which to perform nanocrystal synthesis, but they are not without their own limitations. To date they have been largely restricted to simple one-step procedures, in which all reagents are loaded into the droplets at the outset. There are very few reports of multistep nanocrystal synthesis in droplet reactors due to the difficulty of performing discrete chemical operations on individual droplets in a moving droplet stream.

In the past decade a wide range of creative solutions have been devised for manipulating droplets, including synchronization, loading, merging, splitting, trapping, dilution and concentration.$^{52}$ Using an appropriate series of these operations, it is possible to envisage sophisticated multistep synthesis procedures being carried out in a single uninterrupted production line. Many of these techniques, however, have been developed for analytical applications where reliable operation is required only over a narrow set of operating conditions. In particular, many droplet procedures have been specifically developed for the manipulation of aqueous droplets, limiting the range of chemistries and materials to which they can be applied. What is required for droplet chemistry to become a standard tool for nanocrystal (and other) synthesis is a series of robust, modular components that can be easily inserted into a droplet-based fluidic network and readily applied to a broad range of solvents and reaction conditions: the flow-based equivalent of Quickfit glassware in batch chemistry. Until such tools are routinely available, droplet reactors will continue to lag behind single-phase reactors in terms of the range of accessible chemistries and materials. The most important operation for multistep chemistry is reagent addition, which requires the ability to deliver precise quantities of reagents to the droplets as they move. One way to do this is via droplet fusion; i.e. introducing new reagents into the flow reactor as a separate droplet stream which is then merged with the original droplet stream on a pairwise basis. This can be achieved using special channel architectures to bring the droplets together, sometimes assisted by the application of an electric field to lower the interfacial tension between droplets. For example, Hung and co-workers used this approach in a polydimethyl-
siloxane (PDMS) device to generate CdS nanocrystals from an alternating train of Cd$_2^+$ and S$_2^-$ containing aqueous droplets in silicone oil, using a tapered chamber to induce pairwise droplet merging. They identified a narrow range of flow conditions over which reliable pairwise merging could be achieved, with conditions outside this range leading to random coalescence of multiple droplets or no merging at all. Frenz et al. later reported an improved chip-based procedure, using an AC electric field to induce pairwise fusion of two water-in-oil droplet streams at flow-rate ratios of up to 1:5. The reactor was successfully applied to the synthesis of superparamagnetic iron oxide nanoparticles by incorporating an iron salt precursor and ammonium hydroxide into the two droplet streams, with co-precipitation of the iron oxide particles occurring after droplet merging due to the increased pH.

The above methods were applied in aqueous systems, although it is possible that the method of Hung et al. could be generalized to organic droplets. (The second method relies on electrofusion and cannot therefore be applied to non-polar organic solvents). The two techniques, moreover, were applied to a single droplet-fusion step and it is not clear whether they could be applied repeatedly to carry out multistep chemical operations. As an alternative to droplet fusion, direct injection can be used to add reagents. In this approach, the new reagent is injected into the flowing droplet stream as a continuous laminar stream that spontaneously adds to the droplets as they pass. In principle direct injection is the easier of the two methods to implement since it does not rely on special channel structures or extraneous equipment. In practice, however, it is typically rather unreliable, with the injected reagent adding inconsistently to the flowing droplets and frequently forming new droplets in preference to adding to the existing ones.

In recent work Nightingale and co-workers reported an improvement to the direct injection method, in which a third inert gaseous phase was injected alongside the solvent and the immiscible fluid. The gas maintained an even separation of solvent droplets, ensuring they received equal amounts of the injected reagent, and also suppressed the unwanted formation of new droplets. Using this approach they carried out a five-step quantum dot synthesis, in which feedstock was repeatedly added to the growing nanocrystals to sustain particle growth. This is the first example of a multistep dosing procedure being applied to the field of nanocrystal synthesis. Techniques like this one, which offer a means of repeatedly dosing droplets, can be expected to play a critical role in extending the reach of microfluidics in nanocrystal synthesis.

Beyond synthesis of the nanocrystal itself, additional steps such as surface modification, purification and phase transfer are typically required to obtain a usable material. In virtually all cases, these procedures are carried out using standard batch techniques and little if any work has been reported on in-line post-synthesis processing. Such processing is particularly important for a production environment where the ability to combine synthesis and purification/treatment in a single continuous process would significantly enhance efficiency, reliability and control. The need for robust post-processing methodologies is set to grow steadily as quantum
dots and other precision engineered nanocrystals gain deeper industrial traction, and the need to purify, functionalise or otherwise modify large (kilogram) quantities arises. Batch purification procedures, which typically rely on repeated cycles of washing and centrifugation, are ill-suited to large volumes. A fully integrated flow-based procedure capable of converting injected reagents to fully processed ready-to-use nanocrystals would consequently have significant industrial benefit.

1.4.2 In-line analysis for product optimisation

Full exploitation of microfluidic synthesis procedures requires real-time information about the progression of the reaction, allowing appropriate changes to be made to the reaction conditions to optimise yield, size-distributions or physico-chemical properties. Optical techniques are especially easy to integrate with microfluidic devices due to their non-invasive nature, and can generate useful and immediate information about the nanocrystal properties. Absorption and fluorescence methods are routinely used to extract information about size distributions and surface uniformity. However there is a much broader range of optical methods that could in principle be employed, with light-scattering and time-resolved fluorescence spectroscopy being particularly interesting in this regard due to their respective abilities to probe particle size and fluorescence quantum efficiency. Beyond optical methods there is a range of other techniques that can provide important information about crystal structure, crystallite shape or reaction yield. Size exclusion chromatography, gel electrophoresis and particle tracking can provide information about size distributions, while nuclear magnetic resonance spectroscopy can characterise nanocrystal surface chemistry. Traditionally these analysis techniques have been considered off-line techniques but, as new miniaturised systems are developed and equipment costs fall, it is becoming possible to integrate dedicated analysis systems into flow reactors, greatly increasing the information yield.

In the simplest case, this information can be used to manually tweak the reaction conditions to obtain a superior product. However, by coupling both the sensor(s) and reactor to real-time control algorithms, the entire process of nanocrystal synthesis can be automated, with the control algorithm repeatedly and systematically updating the reaction conditions until a desired end-point is achieved. This approach was used by Krishnadasan et al. to develop a fully automated system for synthesizing CdSe quantum dots of a desired emission wavelength and optimized fluorescence quantum yield. Toyota et al. later reported a rapid screening system for CdSe quantum dots, using five parallel microreactors and inline fluorescence spectroscopy to rapidly trawl through multiple reaction conditions with a view to obtaining improved particle characteristics and uncovering new mechanistic information (Figure 1.7). Taking the idea of self-optimisation one step further, instead of designing specific reactors for a particular chemical procedure (as is done now), one might consider the development of generic multipurpose reactors whose architectures can autonomously adapt to a new set of reagents so as to achieve a given objective. (The software controlling the reactors might even sug-
gest changes or extensions to the reactor if the objective proves unachievable with the original reactor configuration). This open-ended approach to reactor design could potentially drive chemical exploration in highly productive directions that a human chemist would never consider taking in advance.

Figure 1.7: Schematic of a microfluidic system developed by Toyota et al. for the rapid combinatorial synthesis of CdSe quantum dots. Reprinted with permission from ref. 63. Copyright 2010 American Chemical Society.

The use of autonomous control and rapid screening methodologies could transform nanocrystal science, enabling the discovery of superior-performing or novel particles that form under conditions outside the usual bounds of chemical exploration. However, while much of the technology already exists for applying such techniques, uptake has been slow. Even outside the field of nanocrystal synthesis, there are relatively few examples of self-optimising microreactors being used to improve on manual procedures (refer to McMullen and Jensen for a comprehensive review64). In part this is because the techniques remain hard to apply, requiring a broader range of skills than are typically found in a single person or small group of researchers. Requisite expertise spans the fields of synthetic chemistry, microfluidics, sensor design/integration, computational science, and applied mathematics. To change this situation, easy-to-use software tools are needed that place automation technologies in the hands of the practicing chemist. Until that happens, we are unlikely to realise the full potential of microfluidics for nanocrystal synthesis.
1.4.3 Scale out

To date there has been little interest in microfluidic reactors as a potential production technology for nanocrystals due to a widespread perception that microfluidic reactors cannot satisfy industrial demand. This perception is certainly reinforced by the literature, where virtually all reports of materials synthesis in microreactors nanocrystalline or otherwise have involved small sub-gram levels of production. Throughput may be raised substantially by upping reagent concentrations, increasing flow rates and scaling out, i.e. operating N identical reaction channels in parallel to achieve an N-fold increase in output relative to a single-channel reactor. Scaling out is an especially attractive approach since it requires no changes to the reactor geometry, and so allows material throughput to be increased without any changes to the underlying process chemistry. Hence, in contrast to the scaling up of batch reactions, scaling out can in principle be implemented without any detriment to product quality or yield.

Despite its obvious importance, scale out has been a rather neglected aspect of microfluidic reactor technology, with only a handful of reports describing its application to large-scale materials production. The most notable success in this area was reported by Chambers and co-workers, who developed a thirty-channel device for the direct fluorination of organic molecules using fluorine gas. They noted that twenty such reactors would have a combined throughput of 3 kg per day, comparable to many fine-chemical processes. The extension of this approach to nanocrystals is appealing, but nanocrystal synthesis raises additional challenges due to the substantial risk of reactor fouling and the need to maintain identical conditions in all channels at all times (so as to ensure product consistency). In recent work Nightingale and co-workers reported a five-channel droplet-based microfluidic reactor for CdTe synthesis designed specifically to address these issues. The precursor solution and carrier fluids were drawn from separate reservoirs, and split five ways using passive flow dividers. Individual streams of the precursor solution and carrier fluid were then merged on a pairwise basis in five separate droplet generators, creating parallel droplet streams in five intertwined capillaries. The intertwined capillaries were passed into a heated oil bath to initiate nucleation and growth, and the entire droplet stream from each one was then collected in a single beaker. The carrier fluid sank to the bottom of the beaker, leaving the product as a discrete layer on top. During a nine hour production run, 54.4 g of material was produced corresponding to a production rate of 145 g per day. Absorption and fluorescence spectroscopy showed no change in product properties between channels and over time, confirming the stability of the multichannel droplet reactor.
The 145 g per day level of throughput - whilst in itself a significant production rate for nanomaterials - was obtained using a modest five-way level of parallelisation. With only minimal changes to the reactor architecture, it should thus be feasible to expand the architecture to forty channels or more, providing ready access to production rates in excess of 1 kg per day. A key challenge now is to apply scale out procedures to multistep chemistries, rather than the simple single-step synthesis used by Nightingale et al. to access a broader range of materials systems. This is likely to require the development of robust fault-tolerant architectures that can withstand the failure of individual channels so that localized problems in a single channel do not cause catastrophic failure of the entire system. Little work has previously been carried out to address these issues, and the feasibility of applying scale out methods on a massively parallel multistep basis remains an open question. The answer to this question may ultimately determine whether microfluidics has a role to play in future industrial production.

1.4.4 Thinking in Flow

Until now nanoparticle synthesis in microreactors has largely involved simple albeit well controlled adaptations of conventional macroscale synthesis procedures. However, microfluidics offers the chance to rethink the entire approach to nanoparticle synthesis by using techniques that are not available in macroscale chemistry. There have already been some efforts to exploit these advantages. For instance Erdem et al. reported a silicon-based segmented flow microreactor for the synthesis

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Figure 1.8: Top: schematic of a scaled-out five-channel droplet flow reactor developed by Nightingale et al. for the synthesis of CdTe quantum dots at a rate of 145 g per day. Bottom: normalised solution-phase emission spectra of CdTe collected at hourly intervals from each of the five reaction lines over a period of nine hours. Adapted from ref. with permission from The Royal Society of Chemistry.
of TiO$_2$ nanoparticles, incorporating separate hot and cool temperature zones to define a short period of nucleation followed by a longer period of slow, controlled growth processes that are hard to separate in a batch system due to the difficulty of changing temperatures quickly. However, this kind of thinking-in-flow needs to go much further, with new chemistries being developed that are specifically tailored to exploit the advantages of a flow-based microscale environment. One very interesting option here is to use non-photochemical laser-induced nucleation processes to initiate particle formation. In contrast to a batch environment (where this approach has previously been applied), illuminating a specific point on the flow profile would sequentially activate the entire reaction volume. By defining a sufficiently tight illumination zone, it should be possible to confine the nucleation phase to a millisecond duration or less, far shorter than could be achieved by heating and cooling (Figure 1.9). Improvements in size and shape control could be significant.

Many batch syntheses perform best under reflux conditions that cannot be used in flow. As an effective alternative, however, flow reactions can be readily performed under supercritical conditions through the use of a back pressure regulator that permits fluid flow only after a target pressure has been reached. In this way the boiling point of the solvent can be increased above its standard value, allowing higher reaction temperatures to be accessed. Early work by Marre, Park and co-workers confirmed the importance of supercritical reactions for nanocrystal synthesis. They developed a pressurized high-temperature microreactor to synthesise quantum dots under supercritical conditions (Figure 1.10), showing that synthesis in supercritical hexane led to narrower emission linewidths and population size distributions than the equivalent reaction in liquid (i.e. non-supercritical) squalane. There is a clear need to build on this work, with a view to exploring and exploiting the wider chemical parameter space that supercritical conditions unlock.
1.5 Specific Aims

- Development of novel segmented flow microfluidic platforms for the synthesis of high-quality binary, core/shell and multinary semiconductor NCs, with a concurrent real-time investigation of their nucleation and growth kinetics

The first aim of this thesis is the realization of new droplet-based microfluidic systems able to operate at high temperatures and high droplet-volumetric flow rates (>1 mL/min) for the facile production of NCs with narrow size distribution and high quantum yield. Subsequently, a multi-stage droplet-based platform is developed for synthesis of more complicated architectures. In addition, development and integration of novel optical detection techniques based on fluorescence and absorption spectroscopy allows for the extraction of real time information regarding the size, morphology, chemical composition and size distribution of the synthesized NCs. More importantly real-time information of NCs optical characteristics provides a novel tool for the quantitative understanding of high-temperature kinetics for systems with rapid nucleation and growth stages.

- Improvement of current synthetic techniques and development of novel methodologies for the formation of IV-VI, perovskite and non-heavy metal NCs

The use of documented procedures allows characterization of the efficacy of the developed techniques against standard methodologies. Current methods are often time-consuming and unsuited...
to multiparametric screening of reaction conditions. One of the major goals of this thesis is to use capillary-based reactors with a droplet-based format designing new synthetic procedures for the formation of bespoke PbS, PbSe, PbS/CdS, CuInS₂, CuInS₂/ZnS and CsPbX₃ (where X = Cl, Br, I) NCs. Operational stability of the developed reactors together with the on-line analytics provides an ideal environment to tailor different synthetic processes and to screen reaction conditions in a high-throughput manner.

- **Development of on-the-fly time-correlated single photon counting for the rapid optimisation of NCs photophysics**

  In most situations, the reported quantum yields of NCs synthesized in either flask or microfluidic environments are characterized by wide variations. The effects of NC composition, surface environment and particle-ligand interactions affect the excited state relaxation process and thus the luminescence quantum yield. To date, the majority of fluorescence lifetime measurements are performed after particle purification, where aspects of information regarding photoluminescence efficiency might be lost. The ability to perform fluorescence lifetime measurements in an on-line manner offers new possibilities for evaluating the factors that govern the PL efficiency of synthesized NCs. Particularly, integrated time-correlated single photon counting allows for real-time fluorescence lifetime measurements with 25 ps temporal resolution. Understanding the fundamental processes influencing relaxation processes in NC systems provides fast optimization of NC photophysics and thus allows better engineering of NC properties.

### 1.6 Thesis Overview

This thesis reports the realization of effective droplet-based microfluidic setups that incorporate novel optical detection schemes for the formation and real time characterization of highly luminous and monodisperse semiconductor NCs. Chapter 2 describes the microfluidic systems used together with the on-line optical detection techniques. Chapter 3 reports a detailed study of lead sulfide (PbS) and lead selenide (PbSe) synthesis, together with their use in the fabrication of Schottky solar cells. Chapter 4 describes the investigation of nucleation and growth kinetics of PbS NCs through on-line millisecond absorbance measurements at high operating temperatures. Chapter 5 presents the synthesis of non-heavy metal semiconductor NCs; specifically copper indium sulfide (CuInS₂) and copper indium sulfide / zinc sulfide (CuInS₂/ZnS) in a multi-stage droplet-based microfluidic reactor. Chapter 6 reports the formation and the fast parametric phase space mapping of cesium lead halide (CsPbX₃, where X = Cl, Br, I) perovskite NCs. Chapter 7 describes the realization of on-the-fly luminescence lifetime measurements of CsPbX₃ NCs. Finally, Chapter 8 presents the conclusions and the future challenges.
Chapter 2

Microfluidic Platforms Integrated with Real-time Optical Detection Systems
2.1 Introduction

The use of miniaturized systems for the manipulation and processing of fluid samples has gained significant interest in the synthesis of nanocrystal populations of controlled size and size distribution. At a basic level, microfluidic activities have been motivated by the fact that physical processes can be more easily controlled when instrumental dimensions are reduced to the micron scale. Additional benefits include the ability to process sub $\mu$L volumes of fluid, reduced instrumental footprints, lower unit costs, facilitate integration of functional components within monolithic substrates and the capacity to exploit atypical fluid behaviour in both time and space.\(^4,71\)

To date the vast majority of research in NC synthesis has focused on the use of batch systems for synthesis. However, a major issue for batch reactors relates to batch to batch reproducibility.\(^3,4\) This is limited by variations in physical conditions within the reactor such as temperature, concentration and reaction time. Unfortunately, this often leads to the synthesis of NC populations with broad size distributions and thus the scale up of batch reactors to the industrial scale remains challenging. Besides the difficulty in synthesizing uniform NCs in large reaction volumes, another key challenge is to develop strategies for understanding the reaction mechanism during synthesis.\(^2,4\) When designing high-quality NCs, nucleation and growth phases must be characterized in detail. This is particularly challenging with batch methodologies since observation of particle growth is most normally achieved using offline optical techniques such as fluorescence spectroscopy, absorption spectroscopy, electron microscopy and X-ray scattering. Unfortunately, offline monitoring techniques do not reveal important information regarding the initial stages of reaction, especially on a millisecond (ms) timescale. In some studies, \textit{in-situ} photoluminescence (PL) measurements for assessing the reaction mechanisms of fast reactions have been reported.\(^72–74\) However these are rather ineffective at extracting kinetic information since heat and mass transfer are slow within macroscale reactors, particularly during reagent mixing.

Droplet-based microfluidic systems have become increasingly popular as reaction environments and overcome all of the above limitations through the formation of discrete and isolated droplets with volumes on the pico- to nanoliter scale. The adoption of such platforms improves heat and mass transfer and provides excellent control over reaction parameters ensuring product-to-product reproducibility.\(^3,4\) Droplet-based microfluidics with integrated monitoring systems are particularly suited for synthesis of uniform NCs and the rapid screening of reaction conditions. Moreover, real-time detection systems allow for detailed investigation of reaction kinetics at the nucleation level leading to better design of material properties.\(^75\)

The development of microfluidic platforms with \textit{in-situ} monitoring systems, which are versatile with regard to temperature, solvents, ligand and reagent are of undoubted importance in the colloidal synthesis of NCs. These platforms should allow for the production of a wide range of NCs with programmable chemical
and physical properties in a rapid fashion. In this chapter, we introduce the development of novel droplet-based microfluidic platforms equipped with real-time monitoring systems that are able to precisely control reaction conditions for the synthesis of bespoke semiconductor NCs, whilst also being able to rapidly assess material properties such as size, size distribution, shape and composition. The use of such platform can provide important information about the photophysical properties of NCs, which is of particular importance for emerging applications such as photovoltaics, lighting, displays and biomedical applications.

2.2 Microfluidic Platform with In-line Photoluminescence VIS-NIR Detector

The reproducible synthesis of lead chalcogenide NCs (PbS, PbSe), with programmable physical and chemical characteristics, is performed within a droplet-based microfluidic platform with a novel in-line NIR fluorescence spectroscopic detector. Fluorescence spectroscopy has proved to be exceptionally powerful in providing real time information regarding the size, shape, chemical composition and sizedistributions of compound semiconductor NCs.\textsuperscript{43,47,49,76} The photoluminescence of the PbS and PbSe NCs can be monitored in real-time through use of an in-line fluorescence spectrometer, which facilitates the rapid screening of a wide range of experimental conditions on short time scales.

2.2.1 Construction of the Microfluidic Reactor

Polytetrafluoroethylene (PTFE) tubing (Internal Diameter - ID 250 µm) was attached to glass syringes using polyether ether ketone (PEEK) luer-lock interconnects (Upchurch Scientific, Germany) and on the other end to a PEEK cross (Upchurch Scientific, Germany). PTFE tubing (30 cm, Outer Diameter - OD 1/16\′′, ID 500 µm) was also attached to the PEEK cross and immersed in an oil bath. A PEEK union (Upchurch Scientific, Germany) was used to connect the PTFE tubing with high-purity perfluoroalkoxy alkane (PFA) tubing (OD 1/16\′′, ID 500 µm) for fluorescence measurements.

2.2.2 In-line Photoluminescence Measurements

High-purity PFA tubing (OD 1/16\′′, ID 500 µm) was connected with PTFE tubing, which was immersed in an oil bath, and it attached onto two three-axis translation stages (1/2\′′ Travel Translation Stages, Thorlabs Germany). An additional three-axis stage was used to hold a long multimode fiber with a core diameter of 400 µm (QP100-2-UV-VIS, Ocean Optics, UK) which was coupled to an InGaAs array spectrometer (Sol 1.7, 900-1700 nm, BWTEK, UK). Emission spectra between 700 and 950 nm were recorded using a fiber-optic coupled CCD Spectrometer (QE65
The three-axis stages were used to move the tubing and fiber to a desired position for alignment. A red light-emitting diode (LED) (M625L3-Mounted High-Power LED, Thorlabs, Germany) was used to excite individual droplets containing the synthesized NCs. The collimated beam was focused into the capillary channel using an aspheric lens (A240TM-B-f, AR: 650-1050 nm – A240TM-C-f, AR: 1050-1620 nm, Thorlabs, Germany) and a 20x objective (CFI S Fluor 20x, Nikon, Switzerland). Figure 2.1 illustrates the in-line PL setup. Calibration of the optical configuration was performed by injecting a solution of PbS NCs emitting at 1100 nm while adjusting the position of the tubing for obtaining maximum PL intensity from the standard solution. This procedure was performed prior to each experiment.

**Figure 2.1: Image of the actual in-line detection system**

### 2.3 Microfluidic Platform for On-line Absorbance and Photoluminescence Measurements

The early-time kinetics (<1 s) of lead sulfide (PbS) QD formation are probed using a novel droplet-based microfluidic platform, which allows for high-throughput and real-time optical analysis of the reactive process with millisecond time resolution. Accordingly, this enables the concurrent investigation of the emission characteristics of PbS NCs and a real-time estimation of their size and concentration during nucleation and growth. The droplet-based microfluidic platform integrated with on-line spectroscopic analysis provides a new tool for the quantitative extraction of high temperature kinetics for systems with rapid nucleation and growth stages.
2.3.1 Microfluidic Reactor

Figure 2.2 illustrates the microfluidic platform used for kinetic measurements and synthesis of PbS and CsPbX$_3$ NCs. Precision syringe pumps (neMESYS Low Pressure Syringe Pumps, Cetoni GmbH, Germany) were used to inject the dispersed and carrier fluids (Galden, Blaser Swisslube AG, Germany) into a PEEK cross (P-729, Upchurch Scientific, Germany) to form nanoliter droplets. The cross and syringes carrying the precursor solutions were connected using PTFE tubing (ID - 250 $\mu$m, OD - 1/16″, Upchurch Scientific, Germany) using PEEK fingertight fittings (F-127, Upchurch Scientific, Germany). The carrier fluid was transferred to the PEEK cross through fluorinated ethylene propylene (FEP) tubing (ID 750 $\mu$m, OD 1/16″, Upchurch Scientific, Germany). The formed droplets containing the reaction mixture were subsequently directed through PFA tubing (ID 500 $\mu$m, OD 1/16″, Upchurch Scientific, Germany) coiled around a copper-heating rod (diameter = 1.5 cm) to allow both the initiation of reaction and online detection of the formed NCs (Figure 2.2). The heating block was engraved using standard milling procedures to allow the tubing to sit within a defined groove (of radius 800 $\mu$m). The temperature of the copper rod was controlled using a heating cartridge (6.5x40 mm, 100 W, Farnell, Switzerland), which was embedded inside the heating rod (Figure 2.3). Temperature was monitored using a thermocouple (Sensor, Thermoelement Type K - 0.5 mm, Farnell, Switzerland), which was inserted into the copper block close to the surface. Temperature control was realized using a PID controller (CN7800, Omega, USA) with an observed temperature variation from the set point of less than 0.1 °C. The heating rod was placed on top of a motorized rotation stage (CR1/M-Z7E, Thorlabs, Germany), which was also mounted on a motorized linear translation stage (MTS25/M-28E, Thorlabs, Germany). The axial and rotational movement of the heating rod was controlled using in house Labview software to ensure facile monitoring of the synthesized NCs. By moving the heating rod to different positions, measurements can be performed at different points along the tubing. This provides access to both short reaction times (ms time scale) and to longer reaction times (seconds to several minutes).
Figure 2.2: Schematic of the droplet-based microfluidic platform integrated with on-line absorbance and fluorescence detection for kinetic analysis of PbS QD synthesis.

Figure 2.3: Close-up view of the heating rod illustrating the motivation of formed droplets through PFA tubing.

2.3.2 PbS QD Synthesis

On-line Photoluminescence Optical System

To study the high temperature PL characteristics of synthesized NCs, we altered the PL detection system demonstrated in Section 2.2. A red light-emitting diode (LED) (M625L3-Mounted High-Power LED, Thorlabs, Germany) was used as an
excitation source for all fluorescence measurements. The collimated beam was directed towards a dichroic beam splitter (Multiphoton LP-Strahlenteiler HC 665 LP, AHF, Germany) and then focused into the microfluidic channel using an aspheric lens (A240TM-f = 8.0 mm-Numerical aperture (NA) 0.50, Thorlabs, Germany). Emission originating from the microfluidic channel was collected by the same lens, passed through the dichroic beam splitter, a long-pass filter (635 LP Edge Basic Longpass-Filter, AHF, Germany) and coupled via a 10x objective (RMS10X – NA 0.25, Thorlabs, Germany) to a fiber spectrometer (PRo+, Ocean Optics, UK) through a 2 m long multimode fiber with a core diameter of 400 µm (QP100-2-UV-VIS, Ocean Optics, UK) (Figure 2.4). The spectrometer comprised a 20 µm entrance slit, a 600 lines mm⁻¹ grating and a detector containing 2048 pixels. The spectrometer was operated between 400 and 1100 nm, and data recorded using a 100 ms integration time. The entire system was enclosed in a black box to minimize stray light pollution.

**On-line Absorbance Optical System**

For all absorbance measurements a halogen lamp (HL-2000 HP, Ocean Optics, UK) was used as the illumination source. The output was collimated (F230SMA-C, Thorlabs, Germany) and shaped into a line oriented along the direction of flow via a planoconvex cylindrical lens (LJ4709RM, Thorlabs, Germany) having a focal length of 50 mm. Absorbance detection in droplet microfluidic reactors is challenging due to the limited optical pathlength defined by the inner capillary diameter. To circumvent sensitivity issues associated with reduced pathlengths, we implemented a geometry where a sheet of light propagates in a tangential manner through the curved path of the tubing to approximately match the length of the reaction plugs (2 mm) (Figure 2.4). Such an illumination profile maximizes the incident light intensity, maintains illumination uniformity along the tubing and in turn minimizes contributions from stray light and scattering. A multimode fiber mounted on a three-axis stage was placed along the optical axis of the light sheet to collect the transmitted light. The other end of the fiber was connected to either a visible or NIR spectrometer. Figure 2.5 shows a photograph of the microfluidic platform integrated with the optical systems.

### 2.3.3 CsPbX₃ NC Synthesis

All experiments for the synthesis of CsPbX₃ were performed using the microfluidic platform described above but with the following changes:

1. A UV LED (M405L2-UV Mounted LED, 1000 mA, 410 mW, Thorlabs, Germany) was used as an excitation source for fluorescence measurements.

2. The dichroic beam splitter (ZT405rdc-UF1, Chroma, Germany)

3. The long-pass filter was not used for fluorescence measurements
Both detection systems were calibrated prior to each experiment, with a similar procedure described in Section 2.2 prior to each experiment. A standard solution of PbS NCs emitting at 1100 nm was injected into the PFA tubing coiled around the heating rod. PL and absorption measurements from the standard solution were recorded to obtain the maximum attainable intensities at different positions of the heating rod. The two motorized stages were programmed to travel at different positions using Labview software provided by ThorLabs.
2.4 Multi-Stage Droplet-based Microfluidic Platform with Integrated Fluorescence Systems

The synthesis of core-shell NCs of defined structure using batch reactors, requires multiple steps for the sequential addition of monolayers on the surface of the core. In a single microfluidic reactor, the synthesis of core-shell structures is generally challenging. Therefore, the realization of multi-stage microfluidic reactors is necessary to allow sequential addition of new reagents in a controlled manner. In addition, multi-stage microfluidic platforms allow independent and precise control of each reaction step facilitating the production of complex nanocrystal structures. Herein, a novel multi-stage microfluidic platform was developed for the high-temperature synthesis of core-shell, non-heavy metal NCs (CuInS$_2$/ZnS). A segmented flow regime was preferred for the synthesis of monodisperse CuInS$_2$ cores, with the ZnS shell growth occurring in a second step.

2.4.1 Microfluidic Platform

Figure 2.6 illustrates the microfluidic platform used for the synthesis of CuInS$_2$ NCs. Precision syringe pumps (neMESYS Low Pressure Syringe Pumps, Cetoni GmbH, Germany) were used to inject the dispersed phase into a PEEK cross (P-729, Upchurch Scientific, Germany) for initial mixing of the reagent solutions. Then, the solution and the carrier fluid (Galden, Blaser Swisslube AG, Germany) were directed to a PEEK T-junction (P-727 PEEK Tee, Upchurch Scientific, Germany) to form nanoliter droplets. The cross, the T-junction and the syringes carrying the precursor solutions where connected through PTFE tubing ((ID 250 µm, OD 1/16'', Upchurch Scientific, Germany) using PEEK fingertight fittings (F-127, Upchurch Scientific, Germany). The carrier fluid was transferred to the PEEK cross through FEP tubing (ID 750 µm, OD 1/16'', Upchurch Scientific, Germany). The formed droplets containing the reaction mixture were subsequently directed through PTFE tubing (ID 500 µm, OD 1/16'', Upchurch Scientific, Germany) coiled around a copper-heating rod (diameter = 1.5 cm) (Stage 1) to allow the initiation of reaction of the CuInS$_2$ NCs (core NCs) (Figure 2.6). The droplets containing the CuInS$_2$ NC solution were directed via a high-purity PFA tubing (OD 1/16'', ID 500 µm) (for the fluorescence detection of the synthesized cores) to another T-junction (P-727 PEEK Tee, Upchurch Scientific, Germany) where a solution of Zn precursor was injected into the droplets. Droplet, after the addition of the Zn precursor were transported through PFA tubing (ID 500 µm, OD 1/16'', Upchurch Scientific, Germany) coiled around a second copper-heating rod (diameter = 1.5 cm) (Stage 2) for the ZnS shell growth. Finally, high-purity PFA tubing (OD 1/16'', ID 500 µm) was connected with the PTFE tubing for the second fluorescence measurement. The temperature of both copper rods was controlled in an independent manner using two heating cartridges (6.5x40mm, 100 W, Farnell, Switzerland), which were embedded inside the heating rods. Both temperatures were monitored using thermocouples (Sensor, Thermoelement Type K - 0.5 mm,
Farnell, Switzerland), which were inserted into the copper blocks close to the surface. Temperature control was realized using two PID controllers (CN7800, Omega, USA) with an observed temperature variation from the set point of less than 0.1 °C.

### 2.4.2 Two-stage Photoluminescence Detection

The detector consists of two identical photoluminescence optical systems, which were placed after the synthesis of the core NC solution and after the growth of the shell (Figure 2.6). For simplicity, one of the photoluminescence optical systems is described. A UV LED (M405L2-UV Mounted LED, 1000 mA, 410 mW, Thorlabs, Germany) was used as an excitation source for fluorescence measurements. The collimated beam was directed towards a dichroic beam splitter (ZT405rdc-UF1, Chroma, Germany) and then focused into the microfluidic channel using an aspheric lens (A240TM-f = 8.0 mm – NA 0.50, Thorlabs, Germany). Emission originating from the microfluidic channel was collected by the same lens, passed through the dichroic beam splitter, a long-pass filter (442 LP Edge Basic Longpass-Filter, AHF, Germany) and coupled via a 10x objective (RMS10X – NA 0.25, Thorlabs, Germany) to a fiber spectrometer (PRo+, Ocean Optics, UK) through a 2 m long multimode fiber with a core diameter of 400 µm (QP100-2-UV-VIS, Ocean Optics, UK). The spectrometer comprised a 20 µm entrance slit, a 600 lines mm\(^{-1}\) grating and a detector containing 2048 pixels. The spectrometer was operated between 400 and 1100 nm, and data recorded using a 100 ms integration time. The UV LEDs from both detection systems were controlled using LED drivers (T-Cube LED Driver 1200 mA with Trigger Mode) which were externally controlled by home-made LabView software. The software triggers the excitation sources in an alternate fashion with a time interval of several seconds to observe the fluorescence signal from both core and core-shell NCs. A laboratory-grade fiber splitter was used to transfer the fluorescence from both optical systems to the spectrometer. The entire system was enclosed in a black box to minimize stray light pollution.

Figure 2.6 illustrates the two-stage microfluidic platform together with the in-line monitoring system for the detection of the synthesized core-shell NCs.
2.5 Time-correlated Single Photon Counting in Flow

The ability to perform time-correlated single photon counting (TCSPC) measurements in flow is valuable in understanding the excitation dynamics of synthesized NCs. Since the fluorescence lifetime is independent of fluorophore concentration, evaluation of the fluorescence lifetime components will reveal whether an increase in emission intensity is due to an observed increase in fluorescence quantum efficiency or product yield. At a more basic level, extraction of the decay time components allows investigation of both radiative and non-radiative processes, and provides a direct way of optimising nanoparticle photophysics. Here, TCSPC measurements were performed using a confocal detection system and fluorescence decay curves analysis was achieved using an in-house Labview algorithm, which can perform real-time analysis using multi-exponential and stretched-exponential models.
2.5.1 Time Correlated Single-Photon Counting

TCSPC is recognized to be the gold-standard technique for determining the fluorescence time of a sample.\textsuperscript{77,78} This method records the time dependent intensity profile of the emitted light upon pulsed excitation by a laser pulse over multiple excitation-emission cycles. An important aspect of TCSPC is that less than one photon can be detected per laser pulse. It should be noted that if more than one photon is detected per laser pulse, measurements will be biased towards detection of photons arriving at shorter times. This is because only the first photon can be observed with TCSPC. This phenomenon is known as pulse pile-up and it must be considered when measured lifetimes are in the nanosecond range.\textsuperscript{77,78} As fluorescence is excited repetitively over multiple cycles, the time interval between excitation and detection signals is measured by electronics which mimic the function of a stopwatch. This means that there will be one photon or no photons at all in many cycles. All the readings are stored in a histogram of counts versus time. Photons arriving at $t+\Delta t$ are located into a specific bin. The width of the bin defines the time resolution of the detection system. The typical output of such a time-resolved fluorescence measurement is a histogram mimicking the molecular fluorescence decay. The decay of an excited population to the ground state can be expressed as:

$$\frac{dn(t)}{dt} = (k_r + k_{nr}) n(t)$$

(2.1)

where $n(t)$ is the number of excited molecules at time $t$ following excitation, $k_r$ is the radiative rate constant and $k_{nr}$ is the non-radiative rate constant. This defines an exponential decay of the excited state population, \textit{i.e.}

$$n(t) = n_0 \exp(-t/\tau)$$

(2.2)

Eq. 2.2 can be written in terms of the time-dependent intensity and expressed as a single exponential decay, \textit{i.e.}

$$I(t) = I_0 \exp(-t/\tau)$$

(2.3)

where $I_0$ is the intensity at $t = 0$ and $\tau = (k_r + k_{nr})^{-1}$, (note that the fluorescence quantum yield $\phi = \frac{k_r}{k_r + k_{nr}}$). For a multi-exponential decay Eq. 2.3 can be written as,

$$I(t) = \sum_i \alpha_i \exp(-t/\tau_i)$$

(2.4)

where $\alpha_i$ are the pre-exponential factors (amplitudes) and $\tau_i$ are the component decay times. For a multiexponential decay the average fluorescence lifetime can be given by,
\[ \tau = \frac{\sum_i a_i t_i^2}{\sum_i a_i t_i} \] (2.5)

Since the excitation pulse is not a delta-function and the instrument takes a finite time to respond, the instrument response function (IRF) is quantified and deconvoluted from measured decays prior to fluorescence lifetime components. The IRF is the response profile of the instrument to scattered photons. In all fluorescence lifetime experiments performed in this thesis, a water solution of quenched erythrosine B was used for measuring the IRF.\[^{77,78}\]

Selecting the appropriate model to describe the intensity decay kinetics is not a simple task, especially when the decay is complex. Fitting is performed by a least-squares analysis which incorporates a \textit{a priori} model that may describe the experimental data. Subsequently, a set of adjustable parameters are optimized to achieve the best possible agreement between the model and the actual data.\[^{77,78}\] To accomplish that, the reduced chi-squared parameter (goodness of fit) is minimized and is given by:

\[ \chi^2 = \sum_{k=1}^{n} \left[ \frac{N(t_k) - N_c(t_k)}{\sigma_k} \right]^2 \] (2.6)

where \( n \) is the number of channels or datapoints used for the analysis, \( N(t_k) \) are the measured data, \( N_c(t_k) \) is the calculated decay and \( \sigma_k \) is the standard deviation of each point (where \( \sigma_k = \sqrt{N(t_k)} \)). The Marquardt-Levenberg optimisation algorithm is most commonly used for finding the best fit.\[^{79}\] Initial values of the model parameters (\textit{i.e.} \( a_i \) and \( \tau_i \)) should be provided for the fitting process, so that the true global minimum is found.\[^{79}\]

### 2.5.2 Confocal Fluorescence Spectroscopy

Confocal microscopy is commonly used in biological research (in both \textit{in vivo} and \textit{ex vivo} studies) and in single molecule detection.\[^{80}\] The key advantage of a confocal microscope over a conventional system is that it only detects light from a defined focal plane while rejecting any out-of-focus light.\[^{80,81}\] The excitation beam is focused by a microscope objective in the sample and resulting fluorescence is collected by the same objective. The use of a small pinhole aperture ensures that only light emitted from a desired volume is collected and directed towards a sensitive photomultiplier tube. Since, confocal microscopy is a sensitive detection technique it is ideal for investigating dynamic events in biological species such as cells or nanostructures (quantum dots, carbon nanotubes).\[^{80,81}\] A simplified schematic illustrating the key components of a confocal fluorescence spectrometer is provided in Figure 2.7.
In Focus
Out-of-Focus
Detector
Lens
Pinhole
Lens
Dichroic Mirror
Objective Lens
Laser Lens
Light from focal plane
Light from below focal plane

Figure 2.7: Schematic diagram illustrating the principle of confocal laser microscopy. The resulting fluorescence from a desired volume, which is collected by a photomultiplier tube, passed first through a pinhole, which is essential to block any out-of-focus light resulting in low background noise.

2.5.3 Confocal Time-Resolved Fluorescence Detection

Time-resolved fluorescence measurements require the use of a pulsed light source. A variety of lasers can provide pulses below 10 ps in width at repetition rates between several kilohertz and hundreds of MHz. For all TCSPC experiments, light from a 488 nm pulsed diode laser (P-C-485B, <90 ps pulse width, PicoQuant GmbH, Germany) is directed towards a laser clean-up filter (F1) (F49-488, Chroma, Germany) and then coupled by a fiber delivery system (FC) with single mode fiber (SM)(KineFLEX-P-3-S-488, QIOPTIQ, Germany) (Figure 2.8). Light exiting the fiber is then collimated by an infinity-corrected 10x magnifica-
tion microscope objective (Olympus 10x NA 0.25, Thorlabs, Germany) for laser beam expansion and directed onto the back port of the microscope. Expansion of the laser beam ensures that the beam nearly fills the entire back aperture of an objective lens (∼6.5 mm) to minimize the laser spot diameter at the focal point. Subsequently, a dichroic mirror (DM) (F48-510, Chroma, Germany) reflects the light into a 40x oil immersion objective (40x Plan Fluor Nikon NA 0.75, Nikon, Switzerland). Fluorescence from the sample is collected by the same objective lens and is the filtered by an emission filter (F2) (F76-490: 488 LP Edge Basic Longpass Filter) which is installed in the microscope filter cube together with the dichroic mirror. A mirror (M1), which is installed in the microscope, reflects the fluorescence to the detection path.

Fluorescence is then focused by an achromatic tube lens (L1) - also installed in the microscope - onto a 30 µm pinhole (PH) (P30S Mounted Precision Pinhole, Thorlabs, Germany) to reject out-of-focus photons (Figure 2.9). A collimating lens (L2) (100 mm, Thorlabs, Germany) collimates the light and a holographic notch filter (NF) (F40-487: Single Notch Filter for 488 nm - E grade, Chroma, Germany) removes residual back-reflected excitation light, before the fluorescence is directed onto a continuously variable neutral density filter wheel (FW) (Cage-Compatible, Cont. Variable, Refl. ND Filter Wheel, OD = 0 - 2.0, M4 Tap, Thorlabs, Germany). The neutral density filters provide adjustable attenuation of the fluorescence signal. Attenuation is expressed using optical density, OD, and defined by equation 2.7, i.e.

\[ OD = -\log T \] or \[ T = 10^{-OD} \]  

(2.7)

Finally, the fluorescence is focused by a lens (L3) and directed onto the APD detector (APD Excelitas, SPCM-AQRH 13, Excelitas, Germany).
Figure 2.8: (a) A schematic and (b) image of the excitation module. The inset shows the single mode (SM) fiber, which directs the light towards a 10x objective for laser beam expansion. Subsequently the light enters the back port of the microscope.
2.5.4 Microfluidic Setup

The system employs compact electronics for time-correlated single photon counting, allowing for fluorescence lifetime measurements with 25 ps temporal resolution. The TCSPC electronics are based on a TimeHarp 260 stand-alone module (PicoQuant GmbH, Germany). This system can record digital photon detection signals in time-tagged, time-resolved (TTTR) mode, allowing the delay time of each fluorescence photon with respect to the laser pulse to be recorded.
polydimethylsiloxane (PDMS) microfluidic chip using PFA tubing. The PDMS microfluidic chip was placed on top of the microscope stage and it consists of a straight channel of 150 µm width and 80 µm height.

2.5.5 On-line Decay Data Analysis Software

In house software (written in the LabView programming environment) was used to calculate in real-time the fluorescence lifetime of the synthesized NCs. Multi-exponential up to third order or stretched exponential decay models can be fitted to the experimental data. A Levenberg-Marquard optimisation algorithm was used for the fitting procedure and a Richardcon-Lucy algorithm was used for the deconvolution of IRF from the recorded decay profiles. The software allows variation of the number of fit parameters, with the initial parameters being provided manually to start the fitting procedure. Fitting of the fluorescence decays of the synthesized NCs (enclosed in individual droplets) can be performed in high-throughput and the average fluorescence lifetime calculated in an automatic manner. More detailed information regarding the LabView software and the calculation procedures is provided in Appendix B and Chapter 7 respectively.
Chapter 3

Droplet-based Microfluidic Synthesis of Monodisperse IV–VI Semiconductor Nanocrystals Using In-Line NIR Fluorescence Detection

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3.1 Introduction

The development of effective strategies for the controlled synthesis of near-infrared (NIR) active colloidal quantum dots (QDs, also known as semiconductor nanocrystals, NCs), with size-tunable emission and absorption spectra, remains a significant challenge.\textsuperscript{1,82–84} III–V, II–VI and IV–VI type NIR QDs (including InAs, GaAs, PbS, PbSe, CdTe, HgTe)\textsuperscript{1,84,85} exhibit superior fluorescence quantum yields and photostability when compared to conventional organic fluorophores that are commonly used in optoelectronic devices or \textit{in vivo} imaging.\textsuperscript{84} Of all such materials, lead sulfide (PbS) NCs are presently the most intensely researched due to their utility in ultrasensitive photodetectors\textsuperscript{86} and as the absorber material in solution-processed solar cells.\textsuperscript{87–90}

Despite significant advances in the synthesis of high quality QDs using segmented flow microfluidics, the vast majority of case studies have focused on the formation of II–VI semiconductor NCs of controlled size, shape, and chemical composition.\textsuperscript{91} Lead chalcogenide QDs, such as PbS, PbSe, and PbTe, are recognized to be interesting active candidates in a variety of applications, including solar cells,\textsuperscript{90,92,93} photodetectors,\textsuperscript{94,95} NIR lasers,\textsuperscript{96} and biological imaging.\textsuperscript{97} Lead sulfide NCs are IV–VI semiconductor materials that possess small band gaps (0.8–1.6 eV), along with stable and tunable emission in the NIR region of the electromagnetic spectrum and high luminescence quantum yields (typically between 10 and 40%).\textsuperscript{82} A variety of macroscale top-down\textsuperscript{98} and bottom-up strategies\textsuperscript{99–101} have been shown to be successful in producing high-quality PbS and PbSe QDs. Of these, the hot injection method proposed by Hines and Scholes in 2001 still remains the most widely used method for obtaining near monodisperse and size-tunable PbS NCs (4–10 nm, with typical standard size deviations of 10–15%), with optical bandgaps in the range of 800 to 1800 nm.\textsuperscript{99} Specifically, the reaction between lead(II) oleate and bis(trimethylsilyl) sulfide (TMS$_2$S) in the presence of oleic acid (OA) and octadecene (ODE) is utilized. Alternative synthetic methods, using batch\textsuperscript{102,103} and segmented flow reactors,\textsuperscript{104} have also been established for the formation of PbS NCs. However, both lead to the formation of particles within a limited size range. Accordingly, a platform that combines the intrinsic advantages of droplet-based microfluidics and the rapid in-line characterization of the synthesized particles is needed for the production of IV–VI QDs with programmable chemical and physical characteristics.

To this end, we now report a one-stage approach for the synthesis of size-tunable and monodisperse lead chalcogenide NCs using a droplet-based capillary reactor. The capillary reactor is able to generate highly monodisperse droplets for the fast mixing of precursor solutions. Moreover, we show for the first time that the photoluminescence of the synthesized PbS and PbSe QDs can be monitored in real-time through the use of an in-line fluorescence spectrometer, which facilitates the rapid screening of a wide range of experimental conditions on short time scales. Through adaptation of the reaction system reported by Hines \textit{et al.} and application of direct sample heating,\textsuperscript{99} PbS NCs with narrow size distributions (5–7%) and band
edge emission between 765 and 1580 nm can be produced in an efficient manner. To ensure both size-tunability and low population size-dispersion a wide range of temperatures (80–155 °C), reaction times (3–30 s), and OA/ODE concentration ratios were explored. Importantly, our approach allows the reproducible synthesis of ultrasmall QDs, having PL peaks in the range of 765–850 nm. Finally, the droplet-based capillary reactor was successfully applied to the synthesis of monodisperse PbSe QDs with photoluminescence emission in the range of 860–1600 nm.

3.2 Methods

3.2.1 Materials

Lead(II) acetate trihydrate (Pb(CH₃CO₂)₂·3H₂O, ≥ 99.99%, powder), bis(trimethylsilyl)sulfide (TMS₂S, synthetic grade), selenium (Se, 95%, powder), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), squalene (99+%), trioctylphosphine (TOP, 97%), ethanol over molecular sieve (H₂O ≤ 0.01%), and n-hexane absolute over molecular sieve (H₂O ≤ 0.01%) were purchased from Sigma-Aldrich and used as received. Toluene anhydrous (99.8%) and tetrachloroethylene (99%) were purchased from ABCR-Chemicals. Galden PFPE was purchased from Blaser Swisslube AG.

3.2.2 Preparation of Precursors

PbS Synthesis

In a three-neck flask, Pb(CH₃CO₂)₂·3H₂O (1 mmol, 0.379 g), ODE (5–9 mL), and OA (5–1 mL) were dried at 120 °C under a vacuum for 2 h to dissolve the lead salt and dry the solution. The solution was then allowed to cool before being loaded into a 10 mL gastight glass syringe (Hamilton, Switzerland). In a glovebag (Sigma-Aldrich), the sulfur precursor solution was prepared by mixing TMS₂S (210 µL, 1 mmol) with ODE (20 mL). The solution was then loaded in a 10 mL gastight glass syringe. The Galden continuous phase was loaded in a 25 mL gastight glass syringe (Hamilton, Switzerland).

PbSe Synthesis

In a three-neck flask, Pb(CH₃CO₂)₂·3H₂O (1.2 mmol, 0.456 g), squalene (7.5–8.5 mL), and OA (1.5–2.5 mL) were dried at 120 °C under a vacuum for 2 h to dissolve the lead salt and dry the solution. The solution was then allowed to cool before being loaded into a 10 mL gastight glass syringe (Hamilton). In a glovebox, the selenium precursor solution was prepared by dissolving Se (9 mmol, 0.711 g) in TOP 9 mL. The solution was then loaded in a 10 mL gastight glass syringe. The
Galden continuous phase was degassed prior to each experiment, and loaded in a 25 mL gastight glass syringe (Hamilton, Switzerland).

3.2.3 Construction of the Microfluidic Reactor

Detailed information regarding the microfluidic reactor is demonstrated in Chapter 2. The microfluidic platform for the synthesis of NIR-emitting PbS QDs is demonstrated in Figure 3.1.

![Figure 3.1: Schematic of the droplet-based microfluidic reactor used for synthesis of PbS NCs, including an in-line NIR fluorescence detection system. Bottom inset: Image of generated droplets containing synthesized PbS QDs.](image)

3.2.4 Synthesis and In-line Characterization of PbS QDs

In a typical experiment, Nemesys precision syringe pumps were used to inject dispersed and carrier fluids into a PEEK cross at different (Pb+S)/Galden flow rate ratios. A section (10–60 cm) of PTFE tubing was immersed in an oil bath, where the set point temperatures ranged from 80 to 155 °C. For PbSe QD synthesis, the microfluidic reactor (Figure 3.1) was flushed with N$_2$ since PL spectra of the synthesized particles are sensitive to residual air inside the tubing. The generated droplets were heated inside the oil bath and the reaction time calculated by measuring the time that it takes for individual droplets to traverse the heated segment. Droplets containing synthesized QDs were then cooled to 25 °C and motivated into the in-line NIR optical system. In-line NIR fluorescence spectroscopy
was performed by exciting individual droplets using a 625 nm LED, with emission being captured by a fiber-optic coupled InGaAs array spectrometer. Emission spectra in the range of 700–950 nm were recorded using a fiber-optic coupled CCD Spectrometer. All recorded spectra were analyzed using a homemade Matlab script (see Appendix A). The reaction product was collected from the end of the PFA tubing in a vial on top of an ice bath. Details regarding the in-line monitoring system are demonstrated in Chapter 2.

### 3.2.5 Off-line QD Characterization

PbS particles were washed in air using anhydrous solvents. Conversely, PbSe particles were washed in an inert atmosphere. Hexane (300 µL) and ethanol (300 µL) were added to the crude solution followed by centrifugation to separate the QDs from the organic ligands. Obtained PbS QDs were redispersed in hexane and again precipitated with ethanol in two additional washing steps and then redispersed in 300 µL of toluene. Samples were then dried under vacuum to remove toluene and redispersed in tetrachloroethylene (TCE) for absorption and photoluminescence measurements. Absorption spectra of the synthesized NCs were measured using a Cary 5000 UV–vis–NIR spectrometer. Offline photoluminescence measurements were conducted in a homemade setup using a cuvette holder with four light ports and optical fibers. For fluorescence quantum yield measurements, all samples were excited at 960 nm. Measured intensities were corrected to account for the spectral response of the spectrometer. The infrared dye IR-26 (Exciton Inc.) dissolved in 1,2-dichloroethane was used as a fluorescence standard with recently corrected absolute fluorescence quantum yields by Semonin et al.\textsuperscript{105} To obtain fluorescence quantum yields for PbS NCs in colloidal solution, integrated luminescence intensities were directly compared to that of IR-26, taking into account the optical density at the excitation wavelength. To avoid reabsorption of emitted light, the optical density of the PbS sample at the excitation wavelength was kept below 0.1. Transmission electron microscopy of the samples was carried out using a FEI Tecnai F30 microscope operating at 300 kV.

### 3.2.6 Schottky Solar Cell Fabrication

The washing procedure for the preparation of PbS QDs for solar cell devices was performed as follows: hexane 10 mL and ethanol (10 mL) were added to the crude solution followed by centrifugation to separate QDs from organic ligands. The PbS QDs were then redispersed in hexane (10 mL) and precipitated again with ethanol (10 mL). After another washing cycle with ethanol/hexane, the particles were redispersed in chloroform (5 mL). A part of this solution was further precipitated from chloroform with methanol (15 mL) and then redispersed in chloroform.

PbS QDs were deposited onto a pre-patterned ITO substrate using an iterated two-step method consisting of spin-coating and subsequent replacement of the
OA ligands with 1,4-benzenedithiol. The total active layer (140 nm thick) was thermally annealed at 140 °C. The device was finished by thermal evaporation of LiF (1 nm) and Al (100 nm) layers.

Current–voltage characteristics were recorded using a Keithley 2400 Source Meter with the device being kept in a nitrogen glovebox. Measurements were performed in the dark and under illumination from a Steuernagel Solar Constant 1200 metal halide lamp calibrated to 1 sun intensity and corrected for spectral mismatch with an air mass (AM) 1.5G spectrum using a Si reference cell. Contributions to the photocurrent from regions outside the anode/cathode overlap area were eliminated using a mask with a slightly smaller aperture than the device area.

3.3 Results and Discussion

3.3.1 PbS QD Synthesis and Characterization

Figure 3.2: (a) Absorption spectra of PbS QDs synthesized in a droplet-based capillary reactor. Black line: R.t = 15 s, 125 °C, Pb/S = 1, ODE/OA = 5.67. Red line: R.t = 11 s, T = 130 °C, Pb/S = 1, ODE/OA = 5.67. Blue line: R.t = 14 s, T = 135 °C, Pb/S = 1, ODE/OA = 5.67. (b,c) TEM micrographs of 3.8 ± 0.2 nm (R.t = 6 s, T = 145 °C, Pb/S = 1, ODE/OA = 3, \( Q_{Galden} = 95 \mu L/min, Q_{Pb} = Q_S = 30 \mu L/min \)) and 4.5 ± 0.3 nm (R.t = 11 s, T = 150 °C, Pb/S = 1, ODE/OA = 3, \( Q_{Galden} = 70 \mu L/min, Q_{Pb} = Q_S = 20 \mu L/min \)) PbS NCs synthesized in droplets of ODE in Galden.

Our microfluidic system allows for the generation of monodisperse droplets or slugs (Figure 3.1, bottom inset) over a wide range of flow rates and temperatures. The integrated fluorescence detection system enables the optimization of particle characteristics through variation of temperature, reaction time (R.t.) and precursor/surfactant/solvent ratios (Figure 3.2).
The narrow size distribution and the shape-uniformity of the synthesized PbS QDs were further confirmed by Transmission Electron Microscopy (TEM) imaging (Figure 3.2b, c). These particle populations have diameters of 3.8 ± 0.2 nm and 4.5 ± 0.3 nm, respectively (see Figure 3.3 for corresponding size distribution histograms). Moreover, the synthesis of PbS NCs is confirmed by XRD analysis (Figure 3.4) and by Fourier transform infrared spectroscopy (Figure 3.5) where the wavenumbers separation between $\text{as(COO-) - 1525 cm}^{-1}$ and $\text{s(COO-) - 1393 cm}^{-1}$ is $132 \text{ cm}^{-1}$ and it can be assigned to a bidentate coordination.

**Figure 3.3:** QD size distribution histograms. The histograms are extracted from particles shown in the TEM micrographs of Figure 3.2b and 3.2c respectively. The particle populations have diameters of $3.8 \pm 0.2 \text{ nm}$ and $4.5 \pm 0.3 \text{ nm}$ respectively.

**Figure 3.4:** X-ray diffraction diagram (XRD) of the synthesized PbS quantum dots. The diffraction peaks match well with the standard peaks of PbS nanocrystals.
Figure 3.5: FTIR spectra for PbS quantum dots. The wavenumbers separation between as(COO−)-1525 cm⁻¹ and s(COO−)-1393 cm⁻¹ is 132 cm⁻¹ and it can be assigned to a bidentate coordination.

Figure 3.6: In-line photoluminescence spectra of PbS QDs synthesized by the droplet-based capillary reactor. Tuning of (a) the PL peak position and (b) FWHM in nm and eV with temperature (T = 95–155 °C, increasing in 10 °C increments), holding the reaction time constant at 11 s, the Pb/S ratio equal to 1, and the ODE/OA ratio at 5.67 (the total flow rate (Q) is constant at \( Q_{Galden} = 50 \mu\text{L/min}, Q_{\text{Pb}} = Q_S = 20 \mu\text{L/min} \)) PbS synthesized in droplets of ODE in Galden.

Figure 3.6a demonstrates how particle emission can be tuned by systematic variation of the operating temperature while all other reaction conditions are fixed (R.t = 11 s, ODE/OA = 5.67, Pb/S = 1). Increasing the temperature at a constant residence time results in the shift of the band edge emission to longer wavelengths, due to the production of larger particles, and a broadening (Figure 3.6b) of the band edge emission linewidth. Both observations suggest that the growth of PbS NCs follows the same reaction model demonstrated in CdSe and PbSe synthesis. Analyzing the behavior of the emission linewidth in terms of energy (Figure 3.6b, blue line), it is observed that the full width at half maximum (FWHM) varies between 0.12 and 0.19 eV.
Figure 3.7: In-line photoluminescence emission spectra of PbS nanocrystals synthesized in a droplet-based microfluidic reactor. Variation of the PL peak position with temperature holding the reaction time at 10 s, the Pb/S ratio equal to 1 and the ODE/OA ratio at 3 (the total flow rate is constant at: $Q_{Galden} = 70\,\mu\text{L/min}, Q_{Pb} = Q_{S} = 20\,\mu\text{L/min}$). Operation at temperatures higher than 155 °C led to emission linewidth broadening, without a significant change in PL peak position.

Figure 3.8: TEM micrograph of PbS nanocrystals with an average size of 2.5 nm synthesized in nanoliter droplets of ODE within a Galden continuous phase.

Generally, reactions carried out at temperatures over 155 °C result in broad size distributions (see Figure 3.7) due to the formation of nonspherical PbS particles. Moreover, it is striking to note that syntheses at temperatures below 85 °C provide for the controlled synthesis of ultrasmall PbS QDs with PL peaks in the range of 750–800 nm (see Figure 3.8).
The effect of reaction time on PbS QD size was investigated by varying the flow rates of the individual input streams. In all cases, the reaction temperature was maintained at 135 °C. Inspection of Figure 3.9a demonstrates that the PL peak shifts to longer wavelengths as the reaction time is increased from 7 to 23 s, at a
constant ODE/OA ratio of 11.5. Furthermore, it is observed that the formed PbS NCs are relatively small, with PL emission in the range of 850–930 nm. Nevertheless, it can be seen that the reaction time has a much weaker influence on the PL peak than the operating temperature. Previous studies on PbS synthesis suggest that low ODE/OA ratios favor the formation of large PbS NCs of about 6.5 nm in diameter. Figures 3.9b and c show the variation of the excitonic peak as the ODE/OA ratio is decreased from 5.67 to 2.33 respectively. Such a variation allows control of the band edge emission between 1050 and 1300 nm. Increasing the reaction time (Figure 3.9d) initially causes particle self-focusing, (i.e. the FWHM of the band edge emission decreases), followed by a tendency toward size broadening. Similar behavior is observed for all three ODE/OA ratios (Figure 3.9d, e, f). This trend can be explained using colloidal growth theory developed by Peng et al. Here, size focusing occurs when the nanocrystal diameter is larger than a critical size. Under these conditions, small particles grow faster than larger particles. However, after depletion of molecular precursors the critical diameter shifts to a value larger than the average particle size present. This causes size broadening of the synthesized NCs, since large particles continue to grow while small particles shrink. In addition, an ODE/OA ratio < 1.33 leads to the formation of PbS particles emitting between 1300–1600 nm with broad size distributions.

Figure 3.10: Variation of peak emission wavelength as a function of reaction time at different operating temperatures (95, 110, 135, and 145 °C. In each case, the ODE/OA ratio and the Pb/S ratio equal 5.67 and 1, respectively. The reproducibility of the PL peak position using the droplet-based reactor is confirmed through use of the 11 s residence time experiment (dashed line). The projected wavelengths are in agreement with those acquired in Figure 3.6

The effect of reaction time on particle characteristics was further explored by performing the synthesis at four different temperatures, while keeping all other experimental conditions constant (ODE/OA = 5.67, Pb/S = 1). It is noticeable from Figure 3.10 that the droplet-based reactor functions with precise control over a range of different reaction conditions. The red-shift in the band edge emission as a function of residence time is evident for all tested temperatures. In addition,
the excellent reproducibility in synthesized particle size is apparent for a residence time of 11 s (Figure 3.10, dashed line), where the obtained PL data, from four different series of measurements, are identical to those presented in Figure 3.6a for the same experimental conditions.

Figure 3.11: Long-term stability measurements of the PbS quantum dot formation in a droplet-based reactor. (a,c) Emission spectra and (b,d) PL peak and FWHM variation over 3 h and 6 h of continuous operation. The reaction conditions were fixed at R.t = 11 s, T = 135 °C, ODE/OA = 3, Pb/S = 1, Q_{Galden} = 70 \mu L/min, Q_{Pb} = Q_{S} = 20 \mu L/min.

To assess the stability and reproducibility of the microfluidic reactor, a long-term evaluation of photoluminescence characteristics of the produced particles was conducted, where reaction conditions were kept constant for a period of 3 h (Figure 3.11a - b) and 6 h (Figure 3.11c - d), respectively. The PL spectra (Figure 3.11a) and variation of the emission peak wavelength and FWHM (Figure 3.11b) were recorded as a function of time. It can be seen that the PL peak is essentially invariant around 1308 ± 11 nm with a FWHM of 158 ± 6 nm over this period. The small variations from the mean value are attributed to fluctuations in the
temperature of the heating bath from the set point ($\pm 1 ^\circ C$).

### 3.3.2 PbS Schottky-type Solar Cell Fabrication

Furthermore, the superior quality of the synthesized QDs was confirmed by measurement of fluorescence quantum yields, which were as high as 28% (with respect to IR-26$^{105}$ in 1,2-dichloroethane) for PbS QDs, synthesized in our droplet-based microfluidic system (Table 3.1).$^{103,109}$ The measured fluorescence quantum yields for particles synthesized in our microfluidic reactors are significantly higher than fluorescence quantum yield values obtained from batch-synthesized NCs (which yield values between 7 and 12%).

*Table 3.1: Fluorescence quantum yield measurements for PbS nanocrystals synthesized in a capillary-based microfluidic reactor.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{\text{peak}}$</th>
<th>$A_{\text{peak}}($std)</th>
<th>relQY($\text{std}$)</th>
<th>relQY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.04</td>
<td>1.98</td>
<td>0.02</td>
<td>8.01</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>1.98</td>
<td>0.02</td>
<td>12.22</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>1.98</td>
<td>0.02</td>
<td>16.72</td>
</tr>
<tr>
<td>4</td>
<td>0.02</td>
<td>1.98</td>
<td>0.02</td>
<td>28.01</td>
</tr>
</tbody>
</table>

In addition, the NIR-emitting NCs were successfully used to fabricate Schottky-type solar cell devices (this work was performed by Mark J. Speirs and Maria A. Loi). The photovoltaic devices consist of a PbS nanocrystal layer sandwiched between an indium tin oxide (ITO) and a LiF/Al electrode. The fabricated devices were shown to function with an excellent efficiency of 3.4% a short-circuit current, $J_{\text{sc}}$ of 13.9 mA cm$^{-2}$ and an open-circuit voltage, $V_{\text{oc}}$ of 0.45 V (Figure 3.12).

### 3.3.3 PbSe QD Synthesis and Characterization

To demonstrate the broader applicability of the droplet-based microfluidic reactor for the synthesis of IV–VI colloidal QDs, we finally describe the controlled formation of PbSe NCs. Since PbSe QDs are not air-stable,$^{110,111}$ it was necessary to flush all tubing with $N_2$ for several minutes and de-gas the oil phase prior to each experiment. Adapting the reaction system suggested by Talapin and Murray$^{112}$ and applying the same synthetic procedure used for the synthesis of PbS NCs, we performed the synthesis of PbSe QDs in an efficient manner.
Figure 3.12: Current density–voltage characteristics (J–V) under illumination (solid) and in the dark (dashed) of devices fabricated using the PbS solution, which was washed 4 times. The inset in the top left shows the external quantum efficiency (EQE) of the same device.

Figure 3.13: In-line photoluminescence spectra of the PbSe QDs synthesized by the droplet-based capillary reactor. (a) Tuning of the PL peak position (T = 90–140 °C, increasing by 10 °C), holding the reaction time at 70 s, the Pb/Se ratio equal to 1, and the Squalene/OA ratio at 5.67 (the total flow rate is constant at $Q_{\text{Galden}} = 70 \mu\text{L/min}$, $Q_{\text{Pb}} = Q_{\text{Se}} = 20 \mu\text{L/min}$). (b) Comparison of the peak wavelength shift of the PbS and PbSe QDs as a function of temperature ($R.t_{\text{PbSe}} = 70$ s, $R.t_{\text{PbS}} = 11$ s).

By a systematic variation of the operating temperature and keeping all the other experimental parameters fixed ($R.t = 70$ s, Squalene/OA = 5.67, Pb/Se = 1), monodisperse PbSe NC populations could be formed (Figure 3.13a) with an opti-
cal bandgap that varies between 860 and 1300 nm (PbSe particles emitting in the range of 1300–1600 nm were also synthesized, see Figure 3.14). TEM images (Figure 3.15) confirm the narrow size distribution of the synthesized PbSe particles. Comparing the PL peak shift of the synthesized PbS and PbSe QDs as a function of temperature (Figure 3.13b), it is apparent that temperature has a stronger influence on the emission peak wavelengths of the synthesized PbSe particles than those of PbS QDs. However, PbS particles emitting in the range of 800–1400 nm are formed at a much faster rate (R.t = 11 s) than PbSe NCs (R.t = 70 s) under the same operating temperatures.

![Figure 3.14: In-line photoluminescence emission spectra of PbSe nanocrystals synthesized in a droplet-based microfluidic reactor. Variation of the PL peak position with temperature and reaction time at a fixed Squalene/OA ratio of 3. Blue line: T = 120 °C, R.t = 120 s, Black line: T = 120 °C, R.t = 90 s, Pink line: T = 100 °C, R.t = 60 s, Red line: T = 90 °C, R.t = 60 s.](image)

![Figure 3.15: TEM micrographs of PbSe nanocrystals synthesized in droplets of ODE in Galden, with an average size of 3.8 nm and 5.5 nm respectively.](image)
3.4 Conclusions

We have demonstrated a controlled droplet-based microfluidic platform for the synthesis of monodisperse PbS and PbSe QDs under a wide range of experimental conditions and with rapid in-line photoluminescence characterization. The synthesized particles have narrow size distributions, in the range of 5–7%. The process control and optimization of reactions were achieved via in situ monitoring of photoluminescence from individual droplets. Notably, the synthesized PbS QDs, emitting between 765 and 1580 nm, exhibit significantly higher quantum efficiencies (~28%) than those synthesized using conventional macroscale reactors (~12%). Reactor operation over long periods (3–6 h) of time further confirms the stability of our droplet generation and the precise control over particle formation. Adapting the same methodology for the production of PbS and PbSe quantum dots (5 production lines) as demonstrated recently for CdSe NCs,\textsuperscript{30} and by keeping the same reactor dimensions and a total flow rate of precursors of 50 µL/min, it is feasible to achieve 135 mg/h (27 mg/h per production line - The quantity was calculated from the concentration of particles in the samples which were used for the solar cell fabrication) which correspond to 3.2 gr per day. In addition, PbS-based Schottky solar cells were fabricated using the synthesized particles, which demonstrated excellent power efficiencies in excess of 3%. Moreover, the synthesis and size tuning of monodisperse PbSe particles, with an optical bandgap in the range of 860–1600 nm, ensures the versatility of the droplet-based capillary reactor. Adoption of the proposed methodology allows for high-throughput kinetic measurements with millisecond time resolution for systems with very short nucleation and/or growth times, which are typically performed using the hot-injection method (Cd, Pb, and non-heavy metal chalcogenides, as an example). Finally, process scale-out can efficiently accelerate the production of a wide range of NIR emitting nanomaterials with narrow size distributions at a gram to kilogram per day production level.
Chapter 4

Millisecond Monitoring of PbS Nanoparticle Nucleation and Growth Using Droplet-Based Microfluidics

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4.1 Introduction

The physical characteristics of semiconductor nanocrystals are in large part governed by quantum confinement effects, with properties such as the optical band gap differing considerably from the bulk semiconductor. Since these properties are ultimately regulated by the physical dimensions of the crystallite, there is considerable interest in developing robust synthetic strategies together with optical spectroscopies that allow an assessment of nucleation and growth kinetics. Conventional macroscale reactors are typically used to synthesize nanoparticles using standard synthetic methods. Indeed, flask-based methods have been used to synthesize a wide variety of quantum dots, such as CdSe, CdS, InP, HgTe, PbS, PbSe, and ternary/quaternary metal chalcogenide nanocrystals using hot injection approaches. Unfortunately, the temporal and spatial variation of physical conditions, such as temperature, pressure, and reagent concentration within macroscale reactors, has deleterious effects on both particle nucleation and growth.

On a more general level, macroscale techniques are rather ineffective in providing information regarding nucleation and growth of nanocrystalline materials, since the extraction of kinetic data must typically be performed using offline analytical methods, such as transmission electron microscopy. Many ex situ spectroscopic tools, such as absorption and fluorescence spectroscopy, X-ray scattering, and Fourier transform IR spectroscopy, have been used to characterize the growth mechanisms of semiconductor nanoparticles. However, important information regarding the initial stages of the reaction (on the millisecond to second timescale) and its temporal evolution are normally inaccessible, since the reaction must be quenched prior to the analytical measurement. For this reason, quantitative assessments of reaction mechanisms are normally costly, complex and time-consuming endeavors, due to the need for large quantities of precursors and continuous washing of the formed particles. Accordingly, a more complete understanding of the (synthetic) process would not only allow for the development of design rules for bespoke nanoparticle synthesis but also the avoidance of defects in the formed material.

PbS quantum dots possess a small band gap and exhibit exceptional electronic and optoelectronic properties for near-IR (NIR) applications. Since their luminescence can span a broad spectrum of wavelengths in the NIR, they have found significant application in Schottky-based solar cells, photodiodes and in both in vitro and in vivo biological imaging. It is surprising therefore that the mechanism of PbS nanoparticle formation, particularly at early reaction times, is relatively unexplored. Since the synthesis of PbS nanoparticles with low size distributions can in principle be achieved by a detailed evaluation of the nucleation and growth stages, there is a recognized need for the integration of in situ optical detection techniques to allow the extraction of kinetic data. Importantly, there are literature reports describing real-time kinetic analysis of compound semiconductor nanoparticles in macroscale reactors. Specifically, Qu et al. reported...
the *in situ* monitoring of the nucleation and growth of CdSe quantum dots which was performed by recording absorbance spectra using a fiber optic dip probe. Size and concentration data could be extracted directly from absorption spectra, which were recorded with ms time resolution. Furthermore, the authors were able to probe the temporal evolution of photoluminescence (PL) emission, which in turn revealed that the reaction process involves particle size focusing and subsequent broadening of the particle size distribution. However, issues with injection reproducibility, together with temperature variations within the reactor volume, led to uncertainties in the calculation of particle sizes and concentrations at very early timescales. Such issues highlight that the control of temperature, particle concentration and pressure are crucial in extracting precise kinetic data from such systems.

In recent years, both continuous and segmented-flow microfluidic reactors have shown significant utility in synthetic chemistry. Indeed, they have become popular tools in the production of quantum dots of exceptional quality. The precise and rapid control of reaction temperatures, reaction times and reagent concentrations together with the integration of inline analytics are especially attractive for the quantitative analysis of nucleation and growth of colloidal nanoparticles. The benefits of microfluidic technology have been extensively discussed in refs., and allow the controllable formation of nanoparticle formulations of exceptional homogeneity, including metal, metal oxide and semiconductor nanocrystals. Amongst this growing list of materials and applications are a small number of studies that report the integration of spectroscopic detection techniques for reaction monitoring and optimization, as well as process automation. Such methods include inline fluorescence spectroscopy and X-ray scattering using free space optics or integrated detectors. For example, Yue et al. demonstrated the integration of UV-vis absorption spectroscopy within a gas-liquid or liquid-liquid capillary reactor for real-time measurements of the size and concentration of gold nanoparticles. The authors described two detection systems, either comprising a polyether ether ketone (PEEK) flow cell located downstream of the flow reactor or monolithically integrated waveguides. Using the latter they were able to extract average crystallite size and concentration under variable flow conditions. Unfortunately, the use of such reactors does not allow for real-time absorption measurements at high temperatures (>100 °C) since detection is performed downstream of the heating zone. To this end, we have demonstrated a microfluidic platform for the synthesis of monodisperse PbS and PbSe quantum dots in capillary reactors using inline NIR fluorescence spectroscopy. The approach shows exceptional stability and reproducibility for the generation of nanoparticles emitting between 765 and 1580 nm and with fluorescence quantum efficiencies of up to 30%. However, such microfluidic platforms are best suited to probing reactions timescales larger than 1 s. Accordingly, the investigation of reaction kinetics at early times (<1 s) remains an unmet challenge.
4.2 Methods

4.2.1 Materials

Lead(II) acetate trihydrate \((\text{Pb(CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O} \geq 99.99\%, \text{powder})\), bis(trimethylsilyl)sulfide \((\text{TMS}_2\text{S, synthetic grade})\), oleic acid \((\text{OA, 90\%, 99\%})\), 1-octadecene \((\text{ODE, 90\%})\), ethanol over molecular sieve \((\text{H}_2\text{O} \leq 0.01\%))\), and n-hexane absolute over molecular sieve \((\text{H}_2\text{O} \leq 0.01\%))\) were purchased from Sigma-Aldrich, Switzerland and used as received. Toluene anhydrous \((99.8\%))\) and tetrachloroethylene \((99\%))\) were purchased from ABCR-Chemicals. Galden perfluoropolyether PFPE was purchased from Blaser Swisslube AG, Germany.

4.2.2 Preparation of Precursors

In a three-neck flask, \(\text{Pb(CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O} (1 \text{mmol, 0.379 g})\), \(\text{ODE (7.5-9.5 mL)}\), and \(\text{OA (2.5-0.5 mL)}\) were dried at 120 °C under a vacuum for 2 h to dissolve the lead salt and dry the solution. The solution was then allowed to cool before being loaded into a 10 mL gastight glass syringe (Hamilton). In a glovebag (Sigma-Aldrich), the sulfur precursor solution was prepared by mixing \(\text{TMS}_2\text{S (210 µL, 1 mmol)}\) with \(\text{ODE (20 mL)}\). The solution was then loaded in a 10 mL gastight glass syringe (1000 Series, Hamilton). The Galden continuous phase was loaded in a 25 mL gastight glass syringe (1000 Series, Hamilton).

Figure 4.1 demonstrates the two synthetic approaches that were applied in the droplet-based platform.

![Figure 4.1: Reaction of lead acetate and bis(trimethylsilyl)sulfide to form PbS quantum dots, with oleic acid as a capping ligand.](image)

4.2.3 Offline QD Characterization

\(\text{PbS particles were washed in air using anhydrous solvents. Hexane (300 µL) and ethanol (300 µL) were added to the crude solution followed by centrifugation to separate the quantum dots from the organic ligands. Obtained PbS quantum dots were redispersed in hexane, and again precipitated with ethanol for two additional}

washing steps and then redisperssed in 300 $\mu$L of toluene. Samples were then dried under vacuum to remove toluene and redisperssed in tetrachloroethylene for absorption and photoluminescence measurements. Transmission electron microscopy of the samples was carried out using a FEI Tecnai F30 microscope operating at 300 kV.

![Diagram of droplet-based microfluidic platform and optical system](image)

**Figure 4.2:** (a) Schematic of the droplet-based microfluidic platform integrated with online absorbance and fluorescence detection for kinetic analysis of PbS quantum dot synthesis. (b) Enlarged schematic view of the integrated optical system. This allows simultaneous performance of both absorbance and fluorescence spectroscopy.
4.2.4 Experimental Procedure

Precision syringe pumps were used to inject the solutions of Pb and S precursor solutions and the carrier fluid into a cross-mixer to form a segmented flow of nanoliter droplets. The carrier and regent flow rates were kept fixed at 60 and 30 µL/min, respectively. The microfluidic system allowed independent control of the flow rate ratio between the lead and the sulfur precursors and at the same time the flow rate ratio between the precursors and the carrier fluid (Figure 6.1). The droplets are passed through a heating zone to initiate the reaction. Emission and absorption spectra are collected at different points across the heating zone. It is important to note that the reactor design enables the simultaneous extraction of both optical absorption and fluorescence emission to quantitatively assay nucleation kinetics. The operation of the heating system is described in Chapter 2 in detail.

4.2.5 On-line Photoluminescence Measurements & On-line Absorbance Measurements

Detailed information regarding the on-line photoluminescence and absorption optical system is described in Chapter 2. All collected data were analyzed using an in-house MATLAB algorithm. Each absorption spectrum was generated from a weighted average of 300-600 scans with an integration time of 500-800 ms. To precisely define the absorption peak, the second derivative of the absorption spectrum was calculated. Each photoluminescence spectrum was generated from a weighted average of 300-600 scans with an integration time of 100 ms.

4.3 Data Analysis

4.3.1 Absorption Spectra

The following steps describe the procedure for calculating the nanoparticle radius and concentration from the on-line absorbance spectra. Moreover, Figure 4.3 graphically describes the calculation procedure.

1. First, spectra were analyzed to confirm whether the absorption decreases by more than one standard deviation over the acquired wavelength range. If not, the spectrum was discarded since it would correspond to that of the carrier fluid. Subsequently, spectra were weighted with their overall variance (summed over all wavelengths). The weighted average represents the on-line absorption measurement, i.e.

\[
A(\lambda) = \frac{\sum_i (\Delta A_i)^2 A_i(\lambda)}{\sum_i (\Delta A_i)^2}
\]  

(4.1)
where \( i \) denotes the sample number. Spectra acquired using the Ocean Optics spectrometer have a resolution of \( \delta \approx 0.7 \text{ nm} \), whereas spectra recorded using the BWTEK spectrometer have a resolution of approximately \( 1.7 \text{ nm} \).

2. The spectra were smoothened with a moving average filter of width \( 61\delta \approx 43 \text{ nm} \), where \( \delta \) is the resolution of the spectrometer.

3. The first derivative of the absorption spectrum was calculated using the following equation:

\[
A'(\lambda) \approx \frac{A(\lambda + \delta) - A(\lambda)}{\delta} \quad (4.2)
\]

4. To identify the absorption peak corresponding to the band gap, the second derivative of the absorption peak was calculated according to:

\[
A''(\lambda) \approx \frac{A(\lambda + \delta) + A(\lambda - \delta) - 2A(\lambda)}{\delta^2} \quad (4.3)
\]

The absorption peak wavelength, \( \lambda_{\text{max}} \), was identified as the point where \( A'' \) reaches its minimum value.

5. The particle radius was extracted from the absorption peak \( \lambda_{\text{max}} \) using an empirical equation, defined by Cademartiri et al.\(^{126} \), i.e.

\[
E_g^*/eV = 0.41 + \frac{0.96}{(r/\text{nm})^2} + \frac{0.85}{(r/\text{nm})} \quad (4.4)
\]

where \( r \) is the radius of the particle and \( E_g^* \) is the band gap.

The radius of the particle is a function of the band gap energy \( E_g^* = \hbar c/\lambda_{\text{max}} \), with solutions for the particle radius being

\[
r = \frac{b \pm \sqrt{b^2 + 4(E_g^* - a)c}}{2(E_g^* - a)} \quad (4.5)
\]

Since in both cases \( a \) is the bulk band gap which is smaller than the nanoparticle band gap, \( a = E_g < E_g^* \), and the confinement energy term \( c \) is positive, \( (c > 0) \). The square-root term is the largest in the numerator and only positive solutions are physically reasonable.

6. The concentration \( c \) of the synthesized quantum dots was calculated using the Beer-Lambert law Yu:2004eh i.e.

\[
c = \frac{A(\lambda_{\text{peak}})}{\varepsilon(\lambda_{\text{peak}})L} \quad (4.6)
\]

Here, the absorption pathlength was assumed to be 1 cm. The size-dependent extinction coefficient was obtained from Ref.\(^{126} \) i.e.

\[
\varepsilon(M^{-1}\text{cm}^{-1}) = 19600(r(\text{nm}))^{2.32} \quad (4.7)
\]
The quantum dot peak absorbance was calculated from the raw absorbance data \( A_r \) by subtraction of the broad background which has a negative slope. To ensure the slope of the spectrum is zero in the vicinity of the band gap absorbance peak, the slope at the peak \( A'(\lambda_{\text{max}}) \) was calculated and subtracted from the derivative absorbance. The baseline-corrected absorbance is then obtained using

\[
A_c(\lambda) = A_c(\lambda_0) + \int_{\lambda=\lambda_0}^{\lambda} (A'_r(\lambda') - A'(\lambda_{\text{max}})) d\lambda' \quad (4.8)
\]

\[
= A_r(\lambda) - (A_c(\lambda_0) - A_c(\lambda_0)) - (\lambda - \lambda_0)A'(\lambda_{\text{max}}) \quad (4.9)
\]

Here \( \lambda_0 \) is the minimum wavelength recorded by the spectrometer. The integration constant \( A_c(\lambda_0) \) must be determined appropriately to yield the correct absorbance. One method involves setting the corrected spectrum to zero at the inflection point on the short-wavelength (high energy) side of the peak where a local minimum exists.

**Figure 4.3:** Graphical representation of the data analysis process for the calculation of size and concentration of the generated PbS nanocrystals. (A) Normalized absorption spectra depicting the peak wavelengths and localized maxima extracted from the first derivatives of the absorption spectra. (B) First derivative of absorption spectra. (C) Second derivative of absorption spectra. (D) Baseline-corrected absorbance spectra.
4.3.2 Photoluminescence Emission Spectra

Steps 1-3 (Section 4.3.1) used in the analysis of recorded photoluminescence spectra for averaging between multiple spectra, smoothing and identifying the position of the PL peak. FWHM values were determined by calculating the linewidth of the band at an intensity equal to 0.5$I_{max}$.

4.3.3 Reaction Time

The axial and rotational movement of the heating rod was controlled using in-house Labview software to ensure facile monitoring of the optical characteristics of the synthesized nanoparticles. By moving the heating rod to different positions, we can perform measurements at different points within the tubing. Since the tubing length defines the reaction time then heating rod rotation provides access to very short reaction times (ms timescales) and linear movement provides access to longer reaction times. The total flow rate is calculated using: $Q_{tot} = \frac{dV}{dt}$. Given a segment of length $\Delta x$ and cross-sectional area $A = \pi r^2$, where $r$ is the radius of the tubing, the flow rate can be expressed as

$$Q_{tot} = \frac{dV}{dt} = A \frac{\Delta x}{\Delta t}.$$  \hspace{1cm} (4.10)

The time interval $\Delta t$ indicates the duration of flow through the segment. The reaction time is then given by:

$$\Delta t = \frac{A\Delta x}{Q_{tot}}.$$  \hspace{1cm} (4.11)

The length of the tubing, which is wrapped around the heating rod, is determined from the radius of the heating rod $R$, the helix wave vector $k$, the winding number $N$ and the rotation angle at the final position $\phi$ (see Figure 6.1), i.e.

$$\Delta x = (2\pi N + \phi) R \sqrt{1 + (kR)^2}.$$  \hspace{1cm} (4.12)

4.4 Results & Discussion

4.4.1 Temperature Dependence of the Production Rate of PbS NCs

Figure 4.4a illustrates a series of online absorption spectra of synthesized PbS nanoparticles as a function of temperature with all the other reaction conditions being constant (reaction time = 1 s, 1-octadecene (ODE)/oleic acid (OA) = 19, Pb/S = 1). As illustrated in Figure 4.4b, an increase in the operating temperature for a given reaction time results in a red-shift of the absorption maximum between 680 and 860 nm. Furthermore, Figure 4.4c shows the evolution of the particle size, directly extracted from the peak absorbance using Eq. 4.4.126
Figure 4.4: (a) Online absorption spectra of PbS quantum dots at different operating temperatures (120-150 °C) after 1 s of reaction, variation of (b) absorption maximum, and (c) particle diameter as a function of temperature. All the other experimental parameters were fixed, i.e. $R_t = 1$ s, $ODE/OA = 19$, and $Pb/S = 1$. 
It is observed that increasing the temperature from 120 to 150 °C results in an increase in the mean PbS nanoparticle diameter from 2.35 to 2.9 nm. In addition, it is noticeable that high ODE/OA ratios (>11.5) together with low reaction times (<2 s) favor the synthesis of ultrasmall quantum dots (with diameters between 1.5 and 2.5 nm).

Figure 4.5: (a) In situ NIR absorption spectrum of PbS quantum dots recorded after an 8.5 s reaction time (T = 90 °C, ODE/OA = 9, Pb/S = 1). The diameter of particles extrapolated from the online absorption measurement is calculated to be 3.9 nm. (b) TEM image of a PbS nanoparticle population formed in the microfluidic platform under the same experimental conditions. The mean particle diameter is calculated to be 4.1 nm, with a standard deviation of 0.6 nm. (c) Histogram of the nanoparticle size distribution. The histogram is produced by image analysis of TEM images.
To assess the validity of inferring particle size in an online fashion, absorption measurements and Eq. 4.4 and 4.7 were used to calculate the mean size of particles produced at a temperature of 90°C (Figure 4.5a). This value was then compared to a TEM analysis of at least 1000 particles produced under the same conditions. The mean diameter of particles calculated from online absorption measurements was 3.9 nm, whilst the TEM analysis yielded a mean value of 4.1 ± 0.6 nm. This confirms an excellent correspondence between online absorbance measurements and offline TEM analysis.

4.4.2 Time-Resolved Analysis of Nucleation & Growth

Kinetic analysis of nanoparticle formation on millisecond timescales has previously been shown using stopped-flow methodologies. Indeed, Brazeau et al. described a stopped-flow technique for the kinetic analysis of PbS nanoparticle synthesis. In this study the authors utilized the aqueous reaction between Pb(NO)₂ and Na₂S at temperatures up to 45°C. Successful interpretation of the kinetic mechanism was realized using both Ostwald Ripening and Oriented Attachment kinetic models. Unfortunately synthetic methods, for the formation of monodisperse PbS quantum dots, almost exclusively involve the adoption of high temperatures ranging from 80 to 160°C and the use of toxic starting materials. Stopped-flow systems most usually operate at low temperatures and require large assay volumes, whereas the described droplet-based microfluidic platform is well-suited for performing high-temperature colloidal syntheses consuming minimal volumes of reagent. Additionally, the ability to generate and assay highly uniform droplets containing the same concentration of reagents via absorption and fluorescence spectroscopy, offers a direct route to the rapid extraction of kinetic information.

Figure 4.6 illustrates the evolution of extracted absorption spectra, together with the calculated size of the formed particles as a function of reaction time with all other experimental conditions (ODE/OA = 9, Pb/S = 1) being constant. Inspection of Figure 4.6a – e shows the redshift of the absorption maximum while increasing the reaction time for all tested operating temperatures. The average particle size at a given time and temperature was calculated according to Eq. 4.4. Such an analysis confirmed that PbS quantum dots with a mean diameter between 2.7 and 3.5 nm could be reproducibly synthesized within extremely short reaction times. At low operating temperatures (<90°C), the maxima of the first exciton peaks could be defined only after 3 s.
Figure 4.6: In situ observation of the nucleation and growth of PbS nanoparticles by real-time absorption measurements. (a-e) Temporal evolution of the absorption spectra and (f-k) size of the synthesized PbS quantum dots by controlled tuning of the reaction time at four different temperatures (90, 110, 120, 130, and 140°C) while all the other experimental parameters remained constant (ODE/OA = 9, Pb/S = 1). For operating temperatures of 110, 120, and 130°C, the LSW equation was used only for the experimental points above 1 s, which indicates the growth regime. For 140°C, the transition point was fixed at 0.7 s.
It is noticeable from Figure 4.6i that the formation of particles having a mean diameter of 2.94 nm was observed only after 100 ms, with the particles growing to 3.35 nm over the next 1700 ms. Moreover, Figure 4.6f – k indicates that the growth rates increase rapidly as a function of temperature. Such behavior has been previously noted by Zhang et al. who investigated the dependence of the growth rate as a function of temperature. In simple terms, the growth rate increases since higher temperatures favor the rapid consumption of monomers. However, it is also noticeable that the growth rate of the particles is markedly different at times below and above 0.7-1.2 s, depending on the operating temperature. As illustrated in Figure 4.6i, at times between 0 and 1 s (Stage 1), particle growth is much slower than for times above 1 s (Stage 2). To investigate such behavior, particle concentrations were calculated and are shown in Figure 4.7.

![Figure 4.7: Temporal evolution of the concentration of the PbS quantum dots synthesized by the droplet-based microfluidic platform at (a) 130 °C and (b) 140 °C.](image)

During Stage 1, the concentration of the formed nanoparticles increases dramatically to a maximum value of \( \sim 2.9 \times 10^{-3} \text{mL}^{-1} \). This suggests the continuous formation of new particles whose diameter remains constant at 2.94 nm in the first 1 s (nucleation stage). After a threshold concentration is reached, there is a subsequent decrease in the particle concentration with a concurrent linear increase in crystal size (growth stage). This behavior is clearly confirmed at higher operating temperatures (Figure 4.6k), while the transition point between stages was moved to 0.7 s. In addition, Figure 4.8 provides TEM images of the synthesized PbS nanoparticles after Stage 1 and Stage 2 while the operating temperature is set to 140 °C, which confirm our \textit{in situ} calculations of the mean particle diameters. In Figure 4.6f – h, there were no defined absorption peaks below 0.8 s and accordingly extraction of particle diameter information was not feasible.
Figure 4.8: (a) TEM micrograph of a PbS nanoparticle population formed in the microfluidic platform after 2 s of reaction time at 140 °C (Stage 2). (b) Nanoparticle size distribution histogram revealing a mean diameter of 3.57 nm and a standard deviation of 0.28 nm. (c) TEM micrograph of PbS nanoparticles synthesized after 1 s of reaction time at 140 °C (Stage 1). (d) Nanoparticle size distribution histogram. The mean particle diameter was calculated to be 2.93 nm with a standard deviation of 0.6 nm. Both histograms were produced by image analysis of TEM micrographs with a sample of 100 particles.

The linear behavior exhibited within Stage 2 can be understood using the Lifshitz, Slyozov, and Wagner (LSW) model,\textsuperscript{16,17} \textit{i.e.}

\[ R(t)^3 - R(0)^3 = kt \] \hspace{1cm} (4.13)

Here $R$ is the particle radius and $k$ is the temperature dependent material constant.
Ostwald Ripening is the dominant growth mechanism for PbS quantum dots, with ripening being controlled by volume diffusion in the liquid medium. Best fits for the temporal evolution of the cube of quantum dot radius for temperatures between 80 and 140 °C are shown in Figure 4.9. For each temperature, the rate constants of the synthesized quantum dots can be directly extracted by fitting to the LSW growth model (Table 4.1). It is noted that, growth in Stage 1 cannot be precisely described by existing kinetic models since there is a lack of experimental points at temperatures between 70 and 120 °C and reaction times below 500 ms.

Table 4.1: The values of $k$ at different temperatures, which were extracted from the Ostwald Ripening model for the growth of PbS quantum dots.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>k(nm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.37</td>
</tr>
<tr>
<td>90</td>
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</tr>
<tr>
<td>110</td>
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<tr>
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<td>1.27</td>
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<tr>
<td>140</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Figure 4.9: Temporal evolution of the cube of the quantum dot radius at (a) 90 °C, (b) 110 °C, (c) 120 °C, (d) 130 °C and (e) 140 °C. The continuous lines are best fits of the experimental data using LSW equation.

Significantly, PL measurements were performed at the same time as absorption measurements for a variety of operating temperatures and reaction times. Figure 4.10 shows the temporal evolution of the band edge emission spectrum of the formed nanoparticles together with its full-width-at-half-maximum (FWHM) at a temperature of 120 °C. It can be seen that the position of the PL maximum remains relatively constant until 1200 ms. For longer reaction times, the band edge emission
maximum shifts to longer wavelengths, indicating particle growth. Results from the real-time monitoring of absorption and PL spectra indicate a stepped kinetic mechanism composed of two stages as previously discussed. Additionally, Figure 4.10c demonstrates the evolution of the FWHM of the band edge emission over time. During Stage 1, the FWHM remains constant (128-130 nm), but decreases towards a minimum value of 112 nm during Stage 2, i.e. size focusing\textsuperscript{49} of the formed nanoparticles. Above 2.6 s, the FWHM begins to increase, implying size broadening of the formed PbS quantum dots.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.10.png}
\caption{Temporal evolution of A) the photoluminescence emission spectra of the formed PbS nanoparticles, B) the peak wavelength of the band-edge emission, and C) the FWHM of the band-edge emission at a constant operating temperature of 120 °C, an ODE/OA ratio of 9 and a Pb/S ratio of 1.}
\end{figure}
4.5 Summary

We have established a novel droplet-based microfluidic method for performing online kinetic measurements in high-temperature colloidal crystallization. Specifically, the microfluidic platform is successful in synthesizing PbS quantum dots of exceptional quality in an ultrafast manner, whilst also allowing quantitative kinetic measurements to be performed with ms resolution. Such developments have allowed the extraction of absorption spectra of ultrasmall quantum dots (with absorption maxima in the range of 650-750 nm) in an online fashion for the first time. Kinetic analysis indicates that at high operating temperatures the mechanism of PbS quantum dot formation is divided into two steps during early reaction times. In a first step (<1 s) nucleation occurs, where PbS particles of constant size are continuously formed. This is followed by a second stage involving growth of the formed particles with an overall concentration decrease. This second stage of the reaction is consistent with the Ostwald Ripening kinetic model providing the temperature-dependent material constants. This proposed mechanism was further confirmed by simultaneous PL measurements, which reveal both the focusing and broadening of the particle size distribution. Significantly, the microfluidic approach is applicable to the study of the fast kinetics of a wide range of nanomaterial syntheses and ion exchange reactions. Finally, we expect that combination of the proposed platform with novel chemistries will allow for fast and reliable extraction of the size, shape, and crystal structure of new colloidal nanoparticles.
Chapter 5

Microfluidic Synthesis of CuInS$_2$ and CuInS$_2$/ZnS Nanocrystals
5.1 Introduction

Investigation of effective strategies for the controlled formation of non-heavy metal semiconductor nanocrystals (NCs) is of high interest with regard to replacing (toxic) binary Cd- or Pb- chalcogenides which are toxic and they are commonly used in optoelectronic devices and biological imaging. A major line of research efforts has revolved around multinary I–III–VI$_2$ chalcogenides such as CuInS$_2$, CuInSe$_2$, AgInS$_2$, and Cu$_2$ZnSnS$_4$. An intrinsic advantage of such compounds compared to binary non-heavy metal chalcogenides is that their emission can be tuned across the visible to near IR region of the electromagnetic spectrum through control of particle size. Of all such Cd- and Pb- free NCs, CuInS$_2$ NCs have received much attention since 2008 and are recognized to be interesting candidates for the fabrication of thin film solar cells and light-emitting devices as well as in vivo biological probes.

Unsurprisingly, in conventional macroscale reactors the properties of CuInS$_2$/ZnS (in terms of particle size, size dispersion and optical properties) may vary from batch to batch due to variations of physical conditions within the reactor, and most importantly the addition of supplementary reagents for the formation of core-shell structures remains a complex undertaking. It should be noted that shell growth is typically achieved by successive ion layer adhesion and reaction (SILAR), which requires core particle purification and its transfer to a second reactor for shell growth. This requirement increases the time of experimentation and hinders the scalable production of multinary composites with binary shells.

Microfluidic reactors have shown great promise for the controlled and on-demand production of complex NC structures with uniform physicochemical properties. Rapid mass and heat transfer in microfluidic environments, efficient decoupling of nucleation and growth stages, facile multi-step addition of reagents for precise control of particle composition and fast parametric screening of reaction parameters for rapid reaction optimization are major advantages when compared to conventional macroscale reactors. Continuous microfluidic syntheses of semiconductor NCs with core-shell morphologies have already been reported, including the formation of CdS/ZnS, CdSe/ZnS, CdTe/ZnS, ZnSe/ZnS, InP/ZnS, CdSe/CdS/ZnS, CdSeS/ZnS, Cu-In-(Zn)-S/ZnS, and Ag-In-Zn-S/ZnS NCs. Unfortunately, the effectiveness of continuous flow microfluidic reactors in generating core-shell NCs of defined size and composition is somewhat compromised by the interaction of fluid with the microfluidic channel. Furthermore the
parabolic velocity profile which is established over the cross-section of the channel generates a significant (and unavoidable) residence-time distribution that leads to NCs of varying size. This is particularly problematic, since the formation of well-defined core-shell NCs requires low and precise concentrations of shell composites to avoid any secondary nucleation. These limitations can be suppressed through the use of segmented-flow reactors and multi-step dosing of reagents.\(^3\)\(^4\) Droplet-based microfluidic systems allow isolation of the reaction mixture for formation of core particles and at the same time precise addition of the shell material into individual droplets, either by droplet-merging or direct injection, to ensure the controlled formation of multiple-layer shell deposition on the surface of core particles.\(^4\)\(^6\)\(^9\) Interestingly, multi-step synthesis in droplet-based formats for the synthesis of core-shell semiconductor NCs has rarely been reported.\(^1\)\(^7\)\(^2\) This is most likely because dosing droplets with specific amounts of reagents remains a non-trivial operation. Indeed, to date there has been only one example reporting the multistep dosing of individual droplets for the sequential growth of CdSe NCs.\(^5\)\(^6\) Herein, we build a two-stage droplet-based microfluidic platform for the controlled synthesis of CuInS\(_2\)/ZnS NCs. The use of the proposed platform allows for precise control over reaction parameters such as temperature (between 100 and 240 °C) for CuInS\(_2\) synthesis and ZnS shell growth, reaction times (between 2 and 3 minutes) in both reaction stages and individual adjustment of Cu/In, S/(Cu+In) and Zn/(Cu+In) molar ratios for the synthesis of size-tunable and photostable CuInS\(_2\)/ZnS NCs. The microfluidic platform allows for a continuous formation of core-shell CuInS\(_2\)/ZnS NCs by direct injection of shell material to each individual droplet containing CuInS\(_2\) NCs without the need of purification of the core particles. Moreover, an integrated PL optical detection system allows real-time screening of material characteristics before and after shell growth. The resulting CuInS\(_2\)/ZnS NCs are tunable between 580 and 760 nm and they are characterized by narrow emission linewidths between 95 and 105 nm. Additionally, the resulting QYs of CuInS\(_2\) and CuInS\(_2\)/ZnS NCs reach up to 12% and 55% respectively.

### 5.2 Methods

#### 5.2.1 Materials

Copper (I) iodide (CuI, 99.999%), indium (III) acetate (In(OAc))\(_3\), 99.99%), sulfur (S), 1-dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), zinc acetate (Zn(OAc))\(_2\), 99.99%) oleic acid (OA, 90%), oleylamine (OLA, 90%), ethanol over molecular sieve (H\(_2\)O ≤ 0.01%), and n-hexane absolute over molecular sieve (H\(_2\)O ≤ 0.01%) were purchased from Sigma-Aldrich, Switzerland. Toluene anhydrous (99.8%) was purchased from ABCR-chemicals, Germany. Galden PFPE carrier fluid was purchased from Blaser Swisslube AG.
5.2.2 Preparation of Precursors

**CuInS\textsubscript{2} Synthesis**

For the copper precursor solution, CuI (0.095 g, 0.5 mmol) and OLA (0.5 mL) were mixed with ODE (3.3 mL) in a three-neck flask and stirred at 120 °C for 1.5 h under argon. For the indium precursor solution In(OAc)\textsubscript{3} (0.15 g, 0.5 mmol), OA (0.35 mL) and OLA (0.15 mL) were mixed with ODE (3.3 mL) in a three neck flask and stirred at 120 °C for 1.5 h under Ar. For the sulfur solution, S (0.032 g, 1 mmol), DDT (1 mL) and ODE (4 mL) were stirred at 120 °C for 1.5 h under argon in a three neck flask. After cooling, all three solutions and Galden carrier fluid were loaded into 10 mL gastight glass syringes.

**CuInS\textsubscript{2}/ZnS Synthesis**

The Cu, In and S precursor solutions were prepared in the exact same manner as described in the previous section. For the zinc solution, Zn(OAc)\textsubscript{2} (0.36 g, 4 mmol) and OLA (1 mL) were mixed with ODE (4 mL) in a three-neck flask and stirred at 160 °C for 20 min under Ar. The solution was then allowed to cool and loaded into a 10 mL gastight glass syringe.

5.2.3 Offline Particle Characterization

Toluene (300 µL) and ethanol (300 µL) were added to the crude solution followed by centrifugation to separate the synthesized NCs from the organic ligands (4500 rpm for 5 min). Collected NCs were redispersed in hexane, and again precipitated with ethanol for two additional washing steps and then redispersed in 300 µL of hexane. Absorption spectra and offline photoluminescence measurements for fluorescence quantum yield calculations were collected using Fluoromax-4 and Fluorolog iHR 320 spectrofluorimeters. PL QYs of the synthesized NCs in hexane were calculated by comparing their integrated emission with that of a Rhodamine 6G solution in ethanol (QY = 95% in absolute ethanol, λ\textsubscript{ex} = 530 nm). To avoid reabsorption of emitted light, the optical density of all samples at the excitation wavelength was kept below 0.1. The QY was calculated according to eq. 5.1.

\[
QY = QY_{dye} \cdot \frac{S_{QD}}{S_{dye}} \cdot \frac{Abs_{dye}}{Abs_{QD}} \cdot \frac{n^2_{QD}}{n^2_{dye}}
\]  

(5.1)

Here \(QY_{dye}\) is the absolute QY reported for Rhodamine 6G (95% in ethanol),\textsuperscript{173} S is the integrated area under the fluorescence spectrum, Abs is the absorbance at 488 nm and n is the refractive index of toluene or ethanol for the synthesized QDs and Rhodamine 6G. All optical measurements were performed at room temperature. X-ray diffraction measurements (XRD) (Oxford Excalibur Diffractometer
equipped with a Sapphire CCD) were performed using MoKα radiation. XRD samples were prepared by evaporating a concentrated NC hexane suspension on a small glass slide. For high-resolution transmission electron microscopy (TEM) the sample was dispersed in ethanol and droplets of the suspension were deposited on a lacey carbon foil supported on a Cu grid (Okenshoji, Japan). Images of the synthesized NCs were obtained using an FEI Technai F30 microscope operated at 300 kV. An energy-dispersive X-ray spectrometer attached to this microscope (EDAX Gemini) was used to perform a qualitative elemental analysis at selected areas.

5.3 Results & Discussion

5.3.1 Size Tuning of CuInS₂ Nanocrystal Cores

The initial goal was to synthesize CuInS₂ NC populations with low size distribution and high quantum yields using a droplet-based capillary reactor with an in-line fluorescence detection system (Figure 5.1). This allowed screening of reaction parameters that affect particle growth and the optical properties of the synthesized NCs. Here we focus on the synthesis of CuInS₂ NCs following previously reported macroscale synthetic procedures using CuI and In(OAc)₃ as the metal precursors and DDT as the sulfur source and capping ligand (since it forms thiolates with various metal salts, which decompose during heating leading to the corresponding metal sulfides). Stoichiometric sulfur was additionally used to accelerate reaction kinetics by having an excess of the sulfur source inside the formed droplets. In flask-based syntheses metal precursors mixed together in an ODE solution followed by hot injection of a DDT solution into the reaction mixture form CuInS₂ NCs in the sub-10 nm range. However, this procedure entails the detailed investigation of compositional effects on optical properties of the particles, since metal salts are premixed at certain ratios prior to injection of DDT. An important variation with respect to previously reported synthetic methods is the separation of all precursor solutions (dissolved in ODE together with OA and OLA), allowing for a precise control of precursor reactivities during the synthesis. Accordingly, parameters such as Cu/In and S/(Cu+In) molar ratios were explored in detail.
Independent Composition Control of CuInS$_2$ NCs

The bandgap of CuInS$_2$ NCs is highly-dependent on the Cu/In molar ratio, where Cu-deficient CuInS$_2$ NCs are found to have wider bandgaps. However, further investigation is needed to elucidate the effects of Cu/In ratio on the physicochemical characteristics of the particles. Figure 5.2a shows the evolution of PL spectra of CuInS$_2$ cores, which were prepared with Cu/In molar ratios (R$_1$) between 0.3 and 1.8 at 180°C. The reaction time was approximately 15s demonstrating the much faster formation of CuInS$_2$ NCs when compared to flask-based approaches where the reaction time is normally minutes to hours. Indeed, after performing the reaction for periods of 1-2 minutes, we concluded that reaction time is not a size-tuning parameter for the synthesis of CuInS$_2$ cores (indicating that the reaction completes in a few seconds). As observed in 5.2, a systematic increase of Cu/In molar ratio leads to a red shift in the PL spectra from 695 to 760 nm and an associated increase in FWHM. Monodisperse CuInS$_2$ cores, with FWHM in the range of 115-125 nm, were synthesized when the Cu/In molar ratio varied between 0.3 and 0.4.
Another critical reaction parameter that affects particle size and thus the optical properties of CuInS$_2$ is the molar ratio between S and (Cu+In) ($R_2$). For this reason, we sought to develop a better understanding of the optimum $R_2$ molar ratios in the synthesis of monodisperse CuInS$_2$ NCs. For all the experiments conducted in this study, $R_1$ was set to 0.4, which was defined as the optimum $R_1$ value. Figure 5.3 reports the effect of $R_2$ on the PL spectra, PL peak wavelength and FWHM and absorption characteristics. Variation of $R_2$ from 0.35 to 2.65 leads to a blue-shift of the band-edge emission from 780 to 700 nm (Figures 5.3a – b). The inset of Figure 5.3b shows emission from various CuInS$_2$ NCs with different $R_2$ molar ratios under a 365 nm UV lamp. Moreover, analysis of the effect of $R_2$ on the FWHM and absorption spectra, indicates that high values of $R_2$ ($R_2 \geq 1.2$) lead to PL emission spectra with narrow emission linewidths and well-defined absorption peaks (see for example the absorption spectrum for an $R_2$ value of 2.65). Importantly, CuInS$_2$ NCs synthesized with Cu/In and S/(Cu+In) molar ratios of 0.4 and 2.65 respectively (PL peak wavelength at 700 nm), exhibit fluorescence quantum yields of 12.4%, which is similar to the highest quantum yields reported for flask-based syntheses over many minutes of reaction.
5.3.2 Parametric Investigation of CuInS\textsubscript{2}/ZnS Nanocrystal Synthesis

Surface passivation of CuInS\textsubscript{2} NCs by means of epitaxial growth of a wider bandgap material (commonly ZnS) has proved to be an efficient approach for enhancing both stability and fluorescence quantum yields. Although several methods have been proposed for shell addition, they have proved to be rather time-consuming and complicated, leading to batch-to-batch variabilities and limited scale-up possibilities.\textsuperscript{164,174,175} The majority of these methods are based on the dropwise addition of the shell material in a solution containing purified core CuInS\textsubscript{2} cores. Alternative methods have been suggested, and involve a single source precursor which decomposes at high reaction temperatures.\textsuperscript{176,177} Herein, we use a similar approach, where Zn(OAc)\textsubscript{2} thermally decomposes to ZnS. This allows for the direct injection of Zn precursor solution (Zn(OAc)\textsubscript{2} and OLA in ODE) into droplets containing the CuInS\textsubscript{2} cores, without any intermediate purification steps. Variation of the flow
rate of the Zn precursor solution could allow for the addition of various concentrations of the Zn into droplets - meaning control over the number of ZnS monolayers. The resulting droplets were then directed into the second heating zone for further growth of the ZnS shell. Moreover, a second in-line PL detection system allowed for rapid detection of PL variations after the formation of CuInS$_2$/ZnS NCs and thus further optimization of reaction parameters.

**Zn/(Cu+In) Molar ratio**

After identifying the optimum conditions for synthesizing high-quality CuInS$_2$ cores, we then explored the amount of ZnS precursor needed to achieve monodisperse and highly luminescent CuInS$_2$/ZnS NCs, and the effect of Zn/(Cu+In) molar ratio (R$_3$) on PL and absorption characteristics. Figure 5.4a–b presents the raw PL spectra and FWHM as a function of R$_3$, while keeping reaction time fixed at 32 s. It is noticeable that overcoating with ZnS resulted in a dramatic increase in PL intensity when compared to the bare CuInS$_2$ cores. Moreover, an increase of the Zn/(Cu+In) molar ratio from 0.2 to 2.3 leads to the blue-shift of PL spectra from 700 (core particle emission) to 660 nm. The blue shift can be attributed to the combined effects of surface passivation by ZnS as well as the shrinking of CIS core. Further increase of R$_3$ results in a dramatic improvement of PL emission intensity while the PL peak position remains constant. These PL variations are directly detectable using the in-line PL detection system and thus allow for the rapid assessment of the CuInS$_2$/ZnS NC synthesis. In addition, the FWHM of CuInS$_2$/ZnS NCs are as low as 93 nm for those emitting at 661 nm, suggesting the formation of core-shell structures with as narrow or narrower emission linewidths than those previously synthesized in batch reactors. These narrow emission linewidths demonstrate the excellent control of reaction conditions using our multi-step droplet-based microfluidic platform. Although, R$_3$ variation is critical in defining the PL characteristics of core-shell NCs, ZnS passivation of CuInS$_2$ did not affect absorption spectra (5.4c), thus excluding the possibility of diffusion of Zn ions into CIS core. Importantly, after shell growth, the PL QYs of the CuInS$_2$/ZnS NCs emitting between 635 and 690 nm exceed 40%, whereas the maximum value attained for 659 nm emitting core-shell structures was 55% (see Table 5.1 for QYs of various CuInS$_2$/ZnS NCs). These results suggest that the synthesized core-shell NCs exhibit similar efficiencies to those synthesized in flask-based reactors. We believe that adding additional Zn injection steps for sequential growth of ZnS shells would allow for the formation of core-shell structures with even higher stability and enhanced PL efficiencies.
Figure 5.4: The effect of \( \text{Zn}/(\text{Cu+In}) \) molar ratio \( (R_3) \) on PL and absorption characteristics of \( \text{CuInS}_2/\text{ZnS} \) NCs. Tuning of (a) PL spectra, (b) FWHM by a systematic variation of \( R_3 \) from 0.2 to 2.3. (c) Absorption spectra \( \text{CuInS}_2/\text{ZnS} \) NCs while \( R_3 \) is equal to 1, 5, and 12. Other parameters were: \( R_1 = 0.3, R_2 = 2.65, \) reaction time = 32 s, \( T_{\text{core}} = 180^\circ \text{C} \) and \( T_{\text{shell}} = 230^\circ \text{C} \)

<table>
<thead>
<tr>
<th>( \text{Zn}/(\text{Cu+In}) )</th>
<th>max QY (%)</th>
<th>FWHM (nm)</th>
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</thead>
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<td>10.0</td>
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Characterization of Nanocrystals using TEM, EDX and XRD

The synthesized \( \text{CuInS}_2 \) and \( \text{CuInS}_2/\text{ZnS} \) NCs were further analyzed through TEM. TEM images of \( \text{CuInS}_2 \) and \( \text{CuInS}_2/\text{ZnS} \) NCs are shown in Figure 5.5. \( \text{CuInS}_2 \) cores have diameters of 3.20±0.23 nm, which increases to 3.61±0.12 nm after the addition of the ZnS shell. High-resolution TEM indicated that the synthesized \( \text{CuInS}_2/\text{ZnS} \) NCs have a chalcopyrite structure, which is further confirmed by the XRD pattern. The lattice plane spacings (Figure 5.5c) corresponding to the (111) and (220) planes of the cubic structure are 0.32 nm and 0.20 nm respectively. These results confirm that CIS/ZnS NCs with cubic structure have been successfully synthesized.
In addition, EDX spectra (Figure 5.7) of both the core and core-shell NCs further confirm the addition of ZnS shell around the CuInS$_2$ core. In the top panel of (Figure 5.7) only Cu-, In- and S- related peaks were observed, whereas in the case of CuInS$_2$/ZnS NCs, Zn- related peaks are clearly visible. In addition, ZnS passivation leads to a considerable decrease of the intensities of Cu- and In- related peaks.
The Effect of Temperature on the Spectral Properties

The two-stage microfluidic platform allows for independent control of the temperature of the 1st stage (T\text{core} - Synthesis of the CuInS\textsubscript{2} cores) and that of the second stage (T\text{shell} - Synthesis of the CuInS\textsubscript{2}/ZnS core-shell NCs). This feature allows for convenient tuning of PL and absorption spectra of CuInS\textsubscript{2}/ZnS NCs starting from CuInS\textsubscript{2} cores with different diameters. Temperature-dependent PL and absorption spectra of the core-shell structures starting from different core sizes are shown in Figure 5.8. Notably, PL spectra can be tuned from 580 to 760 nm while increasing T\text{core} from 100 to 240 °C. Figure 5.8b shows that the optimal temperature range in stage 1 that provides for satisfactory FWHM is between 140 and 200 °C. Absorbance spectra 5.8c are in accordance with \textit{in-situ} PL measurements and clearly illustrate the size focusing and broadening that is evident in Figure 5.8b.
Figure 5.8: The effect of temperature of stage 1 (core NC synthesis) on (a) PL spectra, (b) FWHM and (c) absorbance spectra of CuInS₂/ZnS NCs. Other parameters were: \( R_1 = 0.4, R_2 = 2.65, R_3 = 3, \) reaction time = 32 s and \( T_{\text{shell}} = 230 \, ^\circ\text{C}. \) (d) Colloidal solutions of various CuInS₂/ZnS in toluene under UV lamp (\( \lambda = 365 \, \text{nm} \)).

Finally, we decided to investigate the effect of \( T_{\text{shell}} \) on the PL properties of the core-shell structures by varying the temperature of the second stage between 150 and 230 °C. Results of this study demonstrate minimal PL tuning via \( T_{\text{shell}} \) variation, suggesting completion of shell growth even at low temperatures. PL intensities were higher for NCs synthesized at \( T_{\text{shell}} = 230 \, ^\circ\text{C} \), however reactions at temperatures higher than 230 °C led to the formation of large aggregates.

### 5.4 Conclusions

In summary, we have designed a two-stage droplet-based microfluidic platform with integrated PL optical detection system for the synthesis of CuInS₂/ZnS NCs, together with the rapid screening of reaction parameters affecting the core and shell synthesis. The two stage microfluidic platform allowed for ZnS passivation on the CuInS₂ cores without any purification steps and provided high-quality CuInS₂ and CuInS₂/ZnS NCs with PL QYs reaching 12 and 55% respectively, with a reaction time of only a few seconds. Moreover, compositional screening of the core and core-shell structures enabled the identification of optimum reaction conditions for the synthesis of monodisperse CuInS₂/ZnS NCs with FWHMs between 90 and 95 nm. Stable core-shell structures emitting between 580 and 760 nm were synthesized by individual assessment of reaction temperatures at the two positions. Adoption of
the proposed methodology could further improve the PL quantum efficiency of such synthesized NCs through use of a multi-step addition of Zn precursor during the second heating stage. This will allow for sequential growth of the shell material leading to core-shell structures with a controlled number of monolayers. Finally, high-throughput production of high-quality ternary and core-shell ternary-binary NCs with narrow size distributions can be produced using a scaled out version of the proposed two-stage platform.
Chapter 6

Synthesis of Cesium Lead Halide Perovskite Nanocrystals in a Droplet-based Microfluidic Platform: Fast Parametric Space Mapping

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6.1 Introduction

In recent years, multiple reports have demonstrated the outstanding optoelectronic characteristics of lead halide semiconductors with perovskite crystal structures, primarily, hybrid organic-inorganic lead halide perovskites such as CH$_3$NH$_3$PbX$_3$ (X=Cl, Br or I, or mixed Cl/Br and Br/I systems) in the form of thin films, microcrystals and bulk single-crystals. For instance, CH$_3$NH$_3$PbX$_3$ perovskites have been used as inexpensive absorber layers in solar cells with certified power conversion efficiencies of up to 20%, in highly sensitive solution-cast photodetectors operating in the visible, ultraviolet, X-ray spectra regions, in light emitters and as optical gain media for lasing.

Unsurprisingly, the outstanding photophysical characteristics of lead halide perovskites have motivated significant research into nanostructures, such as nanocrystals (NCs). Most efforts in the last two years have focused on supported and colloidal CH$_3$NH$_3$PbX$_3$ NCs. In parallel, fully inorganic cesium-based cuisines CsPbX$_3$ have also received great attention since early 2015. Very recently, facile one-pot colloidal syntheses based on ionic metatheses reactions in organic solvents have yielded colloidal 5-12 nm CsPbX$_3$ NCs, with strong emission, photoluminescence (PL) quantum yields (QYs) of up to 90% and narrow emission full width at half maxima (FWHM, 12-40 nm for PL peaks ranging from 410 nm for CsPbCl$_3$ to 700 nm for CsPbI$_3$). Based on these optical characteristics, CsPbX$_3$ NCs represent highly attractive alternatives to more traditional and toxic Cd-chalcogenide quantum dots (QDs, i.e. semiconductor NCs possessing size-dependent band-gap energies). The facile anionic compositional tuning of PL properties with high precision (± 1 nm) from blue to red by forming Cl/Br and Br/I solid solutions is the major and inherent advantage of CsPbX$_3$ NCs. Cd chalcogenides cannot be efficiently wavelength-tuned by adjusting their anionic composition, but must be quantum-size-engineered via ultra-precise colloidal synthesis that provides accurate control over the size-dispersion. For instance, PL tuning of CdSe NCs in the blue-green-orange region of the visible spectrum requires that particle are extremely small (≤ 5 nm) and such NCs usually exhibit rather low PL QYs (≤ 5%) due to mid-gap trap states. Bright and tunable emission from Cd-chalcogenides is best achieved through complex size- and morphology-engineered nanoheterostructures, such as core-shell morphologies, with independent control of the core and shell compositions and thicknesses (e.g. CdSe$_{core}$/ZnCdS$_{shell}$ or giant-shell CdSe$_{core}$/CdS$_{shell}$) and anisotropic CdSe-CdS dot-in-rod and platelet-like morphologies. In these structures, wide-gap shell materials serve the purpose of efficient electronic surface passivation to ensure high PL QYs from CdSe regions. Herein lies the second key advantage of lead halide perovskites - high tolerance of their band structure to structural defects, such as vacancies of atoms or, as in the case of NCs, surface dangling bonds. Hence the realization of high PL QYs does not require electronic passivation with wider-gap shells, and thus greatly reduces the overall cost and complexity of the synthetic procedure. Furthermore, it should be noted that halides are less susceptible to photo-degradation. The main challenge for lead halide NCs, however, is their...
small but finite solubility in water and polar solvents, which currently precludes many biological applications and restricts the list of solvents and non-solvents that can be used for isolation and dispersion of such NCs.

In this study we sought to develop a better understanding of the kinetics and factors governing the formation of CsPbX$_3$ NCs. Owing to the rather fast underlying ionic metathesis reaction, the nucleation and the growth of CsPbX$_3$ NCs occurs on unusually fast timescales (over a millisecond to several seconds time span),$^{214}$ which contrasts with the slower and thus better controlled molecular-like elemental steps that occur during the nucleation of more covalently bonded metal chalcogenides or pnictides. Fast rates of formation of CsPbX$_3$ NCs are comparable to (or faster than) the speed of homogeneous mixing of reagents and heat transfer in standard batch systems. Accordingly, we have engendered rapid and controlled mass transport through the use of a microfluidic technology,$^{2–4}$ which is capable of performing ultra-fast kinetic measurements and reaction optimization through the use of efficient, on-line PL and absorption measurements. Specifically, we show how the adoption of microfluidic technology yields unique and in-situ insights into the early stages of the formation of CsPbX$_3$ NCs (within the first 0.1-5 seconds). We find that NC growth is complete, i.e. PL characteristics become constant, within this short period of time, for all tested reaction conditions. Furthermore, we demonstrate parametric screening in a manner and on timescales that are inconceivable for batch syntheses. One synthesis run in our microfluidic platform requires a few mls of reagents, and over 1-5 hours of experimental time is equivalent to between 200 and 1000 batch reactions, depending upon which parameters are being screened. Clearly, this translates into time and cost savings of months-to-years and between 10 and 100 kilograms of reagents when compared to standard batch-based screening. We exemplify such efficient screening by testing the effects of Pb:Cs and Br:Cl and I:Br molar ratios at various temperatures. We discuss the key observations and conclusions from this multi-parametric study and compare the results to the conventional batch syntheses.

6.2 Methods

6.2.1 Materials

Cesium carbonate (Cs$_2$CO$_3$, Aldrich, 99.9%), lead bromide (PbBr$_2$, ABCR, 98%), lead chloride (PbCl$_2$, ABCR, 99.999%), lead iodide (PbI$_2$, ABCR, 99.999%), 1-octadecene (ODE, 90%), trioctylphosphine (TOP, ABCR, 97%), oleic acid (OA, Sigma Aldrich, 90%), oleylamine (OLA, Acros, ≥ 96%) and n-Hexane (Sigma Aldrich, ≥ 95%). Galden PFPE fluid was purchased from Blaser Swisslube AG.
6.2.2 Microfluidic Synthesis of CsPbX$_3$ NCs

Cesium Oleate Precursor Solution

In a 100 mL three-neck flask, Cs$_2$CO$_3$ (0.815 g), ODE (50 ml) and OA (7.5 mL) were dried at 120°C under vacuum for 2 h to dissolve the cesium salt and dry the solution. The solution was then allowed to cool and stored under argon for several days without any precipitation at room temperature. For each experiment, 5 mL of precursor solution was loaded into a 10 mL-gas tight glass syringe (Hamilton).

Lead Halide Precursor Solution

PbX$_2$ including PbCl$_2$ (0.045 g), PbBr$_2$ (0.0.089 g) and PbI$_2$ (0.0.089 g) were added in a 20 mL Schlenk flask together with 5 mL-dried ODE. The mixture was then dried under vacuum for 2 h at 120°C. After 2 h, 0.5 - 0.8 mL of dried OA and dried OLA were added under argon until all the PbX$_2$ dissolved completely. The solution was then allowed to cool before being loaded into a 10 mL-gas tight glass syringe (Hamilton). For PbCl$_2$ precursor solution, a higher temperature (150°C) together with the addition of 1 mL of TOP were required to solubilize PbCl$_2$.

Offline Perovskite Characterization

The crude reaction solution was cooled down immediately after droplets exit the heating rod (with an ice bath) and centrifuged. Obtained perovskites were re-dispersed in 200 µL of hexane for additional centrifugation. After centrifugation, the supernatant was kept for off-line absorption and fluorescence measurements. For Transmission electron microscopy (TEM) analysis, 200 µL of hexane was added into the supernatant solution. 100 µL of that solution was mixed with 100 µL of Toluene and 30-60 µL of acetonitrile for particle precipitation. After centrifugation, the particles were redispersed in toluene for long-term storage. Transmission electron microscopy of the samples was carried out using a JEOL JEM-2200FS microscope operating at 300 kV.

6.2.3 Flask-based Synthesis of CsPbBr$_3$ and CsPb(Br/I)$_3$ Nanocrystals

Preparation of Cesium Oleate

Cs$_2$CO$_3$ (0.407 g, Aldrich, 99.9%), OA (1.3 mL, Sigma-Aldrich, 90%) and ODE (20 mL, Sigma-Aldrich, 90%) were added into a 50 mL 3-neck flask, dried for 1 h at 120°C and then stored under N$_2$. Since Cs-oleate precipitates out of ODE at
room-temperature, it must be preheated to 100°C before injection into reaction flask.

**Synthesis of CsPbX₃ NCs**

Dried ODE (5 mL) and different amounts of PbX₂ (PbBr₂; PbI₂) or their mixtures were loaded into a 25 mL 3-neck flask and degassed at 120°C for 10 min. Dried OA (1 mL) and OAm (1 mL) were injected at 120°C under N₂ flow. After complete solubilization of a PbX₂ salt, the temperature was raised to 180°C and Cs-oleate solution (0.8 mL of stock solution prepared as described above) was swiftly injected and immediately after (about 5 seconds) the reaction mixture was cooled down by a water bath. For PL measurements, the sample was diluted in hexane.

### 6.2.4 Experimental Procedure

Precision syringe pumps (neMESYS, Cetoni GmbH, Germany) were used to inject the dispersed phase (PbX₂ and Cs-Oleate precursor solutions) and the carrier fluid (Galden fluorinated fluid, Blaser Swisslube AG, Germany) towards a PEEK cross (P-729, Upchurch Scientific, Germany) to form a segmented flow of droplets. For CsPb(X/Y)₃, the dispersed PbX₂ and PbY₂ precursor solutions were initially injected into a PEEK T-junction before being loaded into the PEEK cross for the droplet formation. The injection cross and the syringes carrying the precursor solutions where connected through polytetrafluoroethylene (PTFE) tubing (ID 250 µm, OD 1/16″, Upchurch Scientific, Germany) using PEEK fingertight fittings (F-127, Upchurch Scientific, Germany). The carrier fluid was transferred to the PEEK cross through FEP tubing (ID 750 µm, OD 1/16″, Upchurch Scientific, Germany). Typical flow rates for the carrier phase were between 10 and 500 µL/min and between 0.1 and 350 µL/min for the dispersed phase. The chemical payload of the formed droplets can be tuned precisely and rapidly by continuous variation of the precursor volumetric flow rates. Particularly, the microfluidic system allowed for individual control of the flow rate ratio between the cesium source and the lead source (R₁) and at the same time the flow rate ratio between the two lead halides (R₂) in mixed halide nanoparticles. Compositional tuning of the absorption and PL spectra of colloidal CsPb(X/Y)₃ nanocrystals could be performed by accurate adjustment of cesium and halide composition. The formed droplets containing the reaction mixture were subsequently directed through PFA tubing (ID 500 µm, OD 1/16″, Upchurch Scientific, Germany) coiled around a copper-heating rod (diameter = 1.5 cm) to allow both the initiation of reaction and on-line detection of the formed perovskite nanoparticles via *in-situ* absorption and fluorescence spectroscopy. The reaction time was controlled either by varying the flow rates of the carrier phase and reagents or through variation of the tubing length. The droplets exiting the heating section were excited by a 365 nm UV lamp demonstrating the generation of perovskite nanoparticles with emission colours in the visible spectral region. *In-situ* fluorescence spectra and absorption spectra of CsPb(X/Y)₃
nanoparticles can be finely tuned over the entire visible spectral region by a systematic variation of the operating temperature, reaction time and compositional tuning of the reagents.

### 6.2.5 Microfluidic Platform and Characterization

The details of the microfluidic platform and the on-line characterization techniques are elaborated in Chapter 2.

![Diagram of microfluidic platform](image)

**Figure 6.1:** (a) Illustration of the droplet-based microfluidic platform integrated with online absorbance and fluorescence detection for the synthesis and real time characterization of CsPbX₃ perovskite NCs. The microfluidic platform allows for precise tuning of the chemical payload of the formed droplets by continuously varying the ratio between the lead and cesium sources (R₁) and the ratio between halides (R₂). Typical flow rates for the carrier phase were 10-500 µL min⁻¹ and 0.1-350 µL min⁻¹ for the dispersed phase. (b) Image of the generated droplets after exiting the heating zone, taken under UV excitation (ex = 405 nm), showing bright PL of CsPbX₃ NCs. (c) Online fluorescence spectra of CsPbX₃ NCs (X: Cl, Br, I and Cl/Br and Br/I mixed halide systems) spanning the whole visible spectral region with narrow emission linewidths.

### 6.3 Results & Discussion

Microfluidic reaction systems are adept in transferring mass and energy rapidly, allowing the creation or homogenization of both temperature and reagent gradients on ultra-short timescales. Facile and fast variation of precursor volumetric flow rates and the ability to sequentially add reagents in a controlled manner enable the production of NCs of varying and complex composition, as well as rapid, accurate, reproducible and economic screening of parameters. Many researchers
have recognized the significance of microfluidics in NC synthesis demonstrating the synthesis of a large variety of colloidal semiconductors, metals and metal oxides. In this setup, the precursors (loaded into precision syringe pumps) are rapidly mixed using a cross-mixing junction and form droplets (within milliseconds) that can be rapidly heated to the desired reaction temperature (ca. 100 ms for the complete temperature ramp). For mixed halide systems (where X and Y are the two halides), PbX$_2$ and PbY$_2$ precursor solutions are pre-mixed at a T-junction mixer before delivering them into the cross-mixer. With T- and cross-junctions, the Pb:Cs molar ratio $R_1$ and halide molar ratios $R_2$ (Br/Cl or I/Br) can be adjusted continuously and independently, generating droplets of various compositions. Control over the reaction time is achieved by controlling the residence time of the droplet in the heated zone. Time-dependent optical measurements are accomplished by spiral rotation of the heating rod with respect to stationary fiber optics for online measurements of the absorption and emission spectra. We recorded early stage kinetics (0.1-10 seconds) for all reaction temperatures (120-200 °C) and over a broad range of $R_1$ and $R_2$ values ($R_1 = 0.9-47$ and $R_2 = 0.07-30$).

### 6.3.1 Fast early-stage reaction kinetics and possible mechanism for the formation of mixed-halide NCs.

Our main initial conclusion is that nucleation and growth are fully complete within 1-5 seconds at all reaction temperatures and precursor concentrations, indicating that time cannot be used as a size-tuning tool in conventional batch syntheses. Here we exemplify the results for CsPbI$_3$ NCs (Figure 6.2). In a previous study, it was shown that measurement of size-dependent absorption and emission spectra from CsPbI$_3$ NCs is nearly impossible for batch reactions due to the phase-transition to the wide-gap (yellow) orthorhombic phase, occurring rapidly for small NC sizes during NC isolation. With our microfluidic platform, we can clearly resolve early size-evolution, as shown for the reaction conducted at 180 °C (Figure 6.2a). Overall, the CsPbI$_3$ absorption maximum can be tuned (by variation of the temperature) between 580 and 670 nm, corresponding to a size-range of 8-12.5 nm (Figure 6.2b, where sizes were estimated from bandgap energies using the effective mass approximation according to Ref. 214).
Online PL spectra closely follow the evolution of absorption spectra, also showing a narrowing of the FWHM to ≤45 nm for CsPbI₃ (Figure 6.3a – c) and ≤25 nm for CsPbBr₃ (Figure 6.3d – f). A very different spectral evolution is observed for mixed-halide systems. Two or more emission peaks are initially found during the period between 500 and 800 ms; for instance, at 510 and 630 nm in I/Br system at 180 °C (Figure 6.3g – h). This can be explained by the formation of small ternary CsPbBr₃ and CsPbI₃ NCs at early times, followed by the production of the homogeneous composition at later times, with a single narrow PL band. CsPbBr₃-related emission eventually disappears, while the growing NCs of the mixed CsPb(Br/I)₃ attain PL maxima at 630 nm, noticeably shorter than the 690 nm representative of pure CsPbI₃ under the same growth conditions. Such evolution may invoke aggregation of ternary halide NCs and/or inter-NC anion exchange, previously observed in post-synthetic mixing of CsPbX₃ NCs.²¹⁵,²¹⁶ Apparently, direct co-precipitation of all four ions does not occur! For comparison, a similar scenario had been reported for the one-pot synthesis of quaternary metal chalcogenide NCs such as Cu₂ZnGeSe₄,²³⁴ Cu₂ZnSnS₄²³⁵ and Cu₂₋ₓZnSeₓS₁₋ₚ,²³⁶ albeit with a much slower progression from the initially formed binary Cu-chalcogenides to ternary and quaternary compositions. Contrary to these chalcogenides, no direct ex-situ characterization (i.e. by electron microscopy) of the transient species is possible for the CsPb(Br/I)₃ system.

Figure 6.2: (a) Temporal evolution of online absorption spectra of CsPbI₃ NCs at 180 °C ($R_1 = 7.8$), (b) Variation of particle diameter as a function of reaction time while temperature remains constant (120-180 °C).
Figure 6.3: Tuning of the emission characteristics of CsPbX₃ perovskite NCs by a systematic variation of the reaction (residence) time from 0.1 to 12 s. CsPbI₃: Temporal evolution of (a) the PL emission spectra, (b) FWHM and (c) PL maximum wavelength at a constant operating temperature of 180 °C and constant molar ratio between the halide and Cs-oleate, $R_1 = 4.7$. The red shift in the CsPbI₃ band edge emission is between 610 and 685 nm. CsPbBr₃: Temporal evolution of (d) the PL emission spectra, (e) FWHM and (f) PL maximum wavelength, at a constant operating temperature of 160 °C and constant molar ratio between the halide and Cs-oleate, $R_1 = 2.2$. After 3 s, CsPbBr₃ NCs reach a critical size where growth stops. CsPb(Br/I)₃: temporal evolution of (g) the PL emission spectra and (h) normalized PL spectra at 180 °C; $R_1 = 4.3$ and $R_2 = 1.6$. 
6.3.2 Tuning of optical properties by growth temperature.

In the following discussion the effects of precursor concentrations (through control of $R_1$ and $R_2$) are presented for reaction times of at least 3 seconds, as this would give optimized reaction conditions that can be realistically attained in a batch reaction in common laboratory glassware. Figure 6.4 reports the maximal attainable effect of temperature on the most relevant characteristics - the wavelengths of the PL maximum and the PL FWHM. Systematic variation of the operating temperature from 90-230 °C leads to a red-shift in the band edge emission of both ternary (CsPbBr$_3$ and CsPbI$_3$) and quaternary halide perovskites (Br-Rich and I-Rich CsPb(Br/I)$_3$ NCs). The key message here is that the optimal temperature range for maintaining a satisfactory FWHM is between 130 and 200 °C for all compositions.

Figure 6.4: Variation of (a) peak emission wavelength and (b) the FWHM as a function of temperature for various halide compositions. (CsPbBr$_3$: $R_1 = 2.2$, reaction time - 3 s; Br-rich CsPb(Br/I)$_3$: $R_1 = 3.6$, $R_2 = 0.17$, reaction time - 5 s; I-rich CsPb(Br/I)$_3$: $R_1 = 3.6$, $R_2 = 6.0$, reaction time - 5 s – CsPbI$_3$: $R_1 = 6.5$, reaction time - 3 s.

6.3.3 Lead-to-cesium molar ratio (parameter $R_1$) and halide ratios ($R_2$)

The mass-balance of the synthesis of CsPbX$_3$ NCs can be expressed as:

$$2\text{Cs-Oleate} + 3\text{PbX}_2 \longrightarrow 2\text{CsPbX}_3 + \text{Pb(Olate)}_2$$

PbX$_2$ is the sole source of X-ions and hence 1/3 of Pb will always be spent for the formation of lead oleate as byproduct. Accordingly, $R_1 \geq 1.5$ is generally required to run the synthesis stoichiometrically or under Pb-rich conditions; meaning that in the latter case there is still PbX$_2$ unreacted or combined into mixed lead halide-oleate such as PbBr(oleate). Such species are presumably also surface-binding. Thus, a different behavior might be expected for Cs-rich conditions ($R_1 > 1.5$), where
the residual, potentially surface active component is Cs-oleate. In fact, reactions conducted at 1.2-1.3 do yield CsPbX$_3$ NCs but with very poor colloidal stability. The further decrease of R$_1$ to 1 corresponds to the formation of a hypothetical two-dimensional perovskite Cs$_2$PbBr$_4$ (or a solution of this compound), thus explaining why we do not observe the formation (of appreciable amounts) of CsPbX$_3$ NCs at R$_1$<1. In previous batch investigations, the R$_1$ ratio was thus arbitrarily set to 3.76 in all experiments for both single- and mixed-halide systems, without any optimization.\textsuperscript{214} We therefore sought to broadly examine whether this R$_1$ value is indeed best suited for all halide compositions - CsPb(Cl/Br)$_3$, CsPbBr$_3$, CsPb(Br/I)$_3$ and CsPbI$_3$. Figure 6.5 highlights that this Pb/Cs molar ratio has a dramatic effect on CsPbX$_3$ PL intensity and FWHM, as well as on PL peak position. As expected, low values of R$_1$ (≤1), usually lead to poorly defined PL features. On the other hand, excessively high R$_1$ values lead to CsPbX$_3$ NCs with broad size distributions and reduced PL intensities. Importantly, the optimal R$_1$ range, in terms of FWHM and PL intensity, is not identical for all halide compositions. Mixed-halide CsPb(Br/I)$_3$ NCs exhibit a strong dependence of optimized R$_1$ on the halide ratio R$_2$. For instance, the synthesis of Br-rich CsPb(Br/I)$_3$ NCs requires an R$_1$ = 2.0-2.6, while for I-rich CsPb(Br/I)$_3$ R$_1$ a value between 3.1 and 4.7 should be used. These results highlight the indispensable role of high-throughput microfluidic screening methods in understanding such complex systems. In general, in an experiment with N synthetic variables (R$_1$, R$_2$, temperature, etc.), each having M levels (defining the selected range of each factor), the overall number of required experimental iterations scales as $M^N$. The time needed for these iterations is then given by $M^N * t$, where t is the time for one iteration.\textsuperscript{237} Hence fast reactions (small t) will gain most from experimentation using microfluidics. Furthermore, CsPbX$_3$ NCs are represented, in fact, by five systems (3 ternary and 2 quaternary).
Figure 6.5: The effect of the Pb-to-Cs molar ratio ($R_1$) on the PL characteristics of CsPbX$_3$ NCs. Colors in the PL spectra correspond to various $R_1$ values indicated in the corresponding legends. For CsPb(Cl/Br)$_3$ at 150 °C, CsPbBr$_3$ at 180 °C 175 °C, Br-rich and I-rich CsPb(Br/I)$_3$ at 170 °C, and CsPbI$_3$ at 155 °C shown are $R_1$-dependent PL spectra with true comparison of intensities (a, c, d, e, g, i) and FWHM (b, d, f, h, j). For all systems the reaction time was 5 s, except for CsPbI$_3$ (3 s).

Figure 6.6 demonstrates how the band edge emission of Br/I perovskites can be tuned from 523 to 667 nm through a continuous variation of $R_2$ from 0.3 (for Br-
rich NCs) to 14.33 (for I-rich NCs), while maintaining a FWHM below 45 nm (Figure 6.6b). At the transition from I-rich to Br-rich CsPb(Br/I)$_3$ NCs we find a dramatic increase in the FWHM beyond that expected from the conversion of energy to wavelengths ($1/\lambda$; e.g. 100 meV corresponds to FWHM = 23 nm at 530 nm and 25 nm at 560 nm but as high as FWHM = 45 nm at 620 nm). This can be corrected by readjustment of the $R_1$ value to 2.0-2.6 for CsPb(Br/I)$_3$ NCs emitting at 530-590 nm and 3.0-3.5 for longer wavelengths (Figure 6.6b, red line depicts the effect of optimizing $R_1$). Tuning in the blue-green region between 470 and 510 nm is accomplished by varying the Br/Cl ratio ($R_2 = 0.8-10$, Figure 6.6d–e). On-line absorption spectra (Figure 6.7a) are in accordance with the in-situ PL measurements. Temperature has only a subtle effect on the outcome of the synthesis for $T = 130-200$ °C (see Figure 6.7b).

Figure 6.6: Tuning of the (a) PL emission spectra, (b) variation of PL peak wavelength and (c) FWHM of CsPb(Br/I)$_3$ perovskite NCs as a function of the I-to-Br molar ratio ($R_2 = 0.03-14.33$). Other parameters were: $R_1 = 3.5$ (blue curve in Fig. 6.6b) and $R_1 = 2.2-3.5$ (red curve in Fig. 6.6b), $T = 160$ °C, reaction time = 5 s. Figures (d) and (e) illustrate similar $R_2$-dependent study for CsPb(Cl/Br)$_3$ at 160 °C, reaction time = 5 s, and $R_1 = 3.2$. 
Figure 6.7: (a) Online absorption spectra of CsPb(Br/I)$_3$ NCs (T = 130 °C, reaction time 2 s, R$_1$ = 3.1) and (b) compilation of PL peak positions at temperatures of 130 °C (R$_1$=3.1), 175 °C (R$_1$ =2.55), 190 °C (R$_1$ =2.55) as a function of R$_2$.

6.3.4 Implications for conventional batch synthesis in three-neck flasks

We were then intrigued by the question whether powerful screening of parameters by the microfluidic platform can directly advance the batch synthesis of the same perovskite NC material. Figure 6.8 illustrates that indeed conclusions from microfluidic-based screening are directly transferrable to reactions in conventional laboratory glassware (i.e. 25-mL flasks; see details in Methods) used in the original development of CsPbX$_3$ NCs. We emphasize that simultaneous optimization of interlinked parameters R$_1$ and R$_2$ at various temperatures in flask-based reactions
is essentially impossible due to prohibitively high number of individual combinations. Thus far, only \( R_1 = 3.76 \) can be found in previous reports on the synthesis of CsPbX\(_3\) NCs.\(^{197,214–221}\) Herein for the comparison of various batches, it was critical to avoid PL-narrowing (size-selective) during isolation and purification procedures and, therefore, PL characteristics of the flask-based reactions were recorded from crude solutions diluted by hexane. FWHM of the flask-synthesized CsPbBr\(_3\) NCs drops from 25.6 nm to 21.8 nm when \( R_1 \) is reduced from 3.76 to 1.5-2.00 and the PL spectrum acquires a more symmetric, nearly Gaussian-like shape (Figure 6.8a). The same effect is seen also in the flask-syntheses of CsPb(Br/I)\(_3\) NCs at various \( R_2 \) values (Figure 6.8b; results from 22 flask-based syntheses (see Table 6.1). Qualitatively, microfluidics-optimized parameters yield similar results in conventional batch glassware. Since PL peak wavelengths at a given \( R_2 \) are often slightly different for different \( R_1 \) values, Figure 6.8c shows two selected samples with exactly the same PL peak wavelengths reporting the clear narrowing of FWHM with reducing \( R_1 \) (Figure 6.8c). Likewise, Figure 6.8d re-plots the data for \( R_1 = 3.76 \) and \( R_1 = 2.00 \) in FWHM vs. wavelengths coordinates, covering the whole green-to-red spectral range (514-650 nm).
Figure 6.8: Batch synthesis of CsPbBr$_3$ and CsPb(Br/I)$_3$ NCs in conventional laboratory glassware (25 mL three-neck flask) using $R_1$ values optimized by microfluidic screening. Figures (a) and (c) compare the PL spectra with $R_1=3.76$ and $R_1=2$ for CsPbBr$_3$ and CsPb(Br/I)$_3$ NCs ($R_2=0.67$ for blue curve and $R_2=0.43$ for red curve), respectively. (b) Evolution of the FWHM as a function of $R_2$ at five different $R_1$ molar ratios. (d) FWHM vs. PL peak wavelengths for $R_1=2.00$ (lower red curve) and $R_1=3.76$ (upper blue curve). All experiments were performed at 180°C. The dashed circle in (d) shows the samples illustrated in (c).
Table 6.1: Reaction parameters for growing CsPbBr$_3$ and CsPb(Br/I)$_3$ NCs in a 25 mL flask. These PL characteristics are plotted in Figure 6.8.

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>%PbBr$_2$ / PbI$_2$</th>
<th>mmol PbBr$_2$ / mmol PbI$_2$</th>
<th>mmol Cs-Oleate</th>
<th>PL (nm)</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>100 / 0</td>
<td>0.2 / 0</td>
<td>0.1</td>
<td>514.29</td>
<td>21.80</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>90 / 10</td>
<td>0.18 / 0.02</td>
<td>0.1</td>
<td>522.21</td>
<td>22.43</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>80 / 20</td>
<td>0.16 / 0.04</td>
<td>0.1</td>
<td>514.29</td>
<td>25.19</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>70 / 30</td>
<td>0.14 / 0.06</td>
<td>0.1</td>
<td>514.29</td>
<td>28.01</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>60 / 40</td>
<td>0.12 / 0.08</td>
<td>0.1</td>
<td>514.29</td>
<td>33.09</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>50 / 50</td>
<td>0.1 / 0.1</td>
<td>0.1</td>
<td>514.29</td>
<td>34.2</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>40 / 60</td>
<td>0.08 / 0.12</td>
<td>0.1</td>
<td>514.29</td>
<td>36.74</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>80 / 20</td>
<td>0.176 / 0.044</td>
<td>0.1</td>
<td>532.77</td>
<td>25.98</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>75 / 25</td>
<td>0.165 / 0.055</td>
<td>0.1</td>
<td>539.93</td>
<td>27.85</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>70 / 30</td>
<td>0.154 / 0.066</td>
<td>0.1</td>
<td>545.79</td>
<td>31.80</td>
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<tr>
<td>2.2</td>
<td>65 / 35</td>
<td>0.143 / 0.077</td>
<td>0.1</td>
<td>557.63</td>
<td>32.77</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>100 / 0</td>
<td>0.376 / 0</td>
<td>0.1</td>
<td>513</td>
<td>25.59</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>80 / 20</td>
<td>0.3 / 0.076</td>
<td>0.1</td>
<td>518.61</td>
<td>30.44</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>70 / 30</td>
<td>0.263 / 0.1128</td>
<td>0.1</td>
<td>530.57</td>
<td>31.61</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>60 / 40</td>
<td>0.2256 / 0.1504</td>
<td>0.1</td>
<td>556.95</td>
<td>33.37</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>50 / 50</td>
<td>0.188 / 0.188</td>
<td>0.1</td>
<td>605</td>
<td>41.79</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>40 / 60</td>
<td>0.150 / 0.2256</td>
<td>0.1</td>
<td>635</td>
<td>46.89</td>
<td></td>
</tr>
<tr>
<td>3.76</td>
<td>30 / 70</td>
<td>0.1128 / 0.263</td>
<td>0.1</td>
<td>657</td>
<td>44.46</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>50 / 50</td>
<td>0.235 / 0.235</td>
<td>0.1</td>
<td>591.64</td>
<td>44.19</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>45 / 55</td>
<td>0.2115 / 0.2585</td>
<td>0.1</td>
<td>606.94</td>
<td>52.91</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50 / 50</td>
<td>0.25 / 0.25</td>
<td>0.1</td>
<td>588.08</td>
<td>45.97</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>45 / 55</td>
<td>0.225 / 0.275</td>
<td>0.1</td>
<td>611.07</td>
<td>50.43</td>
<td></td>
</tr>
</tbody>
</table>

### 6.3.5 Potential Use in Optoelectronic Applications

Halide perovskites are recognized to be attractive candidates for optoelectronic applications, and particularly for the fabrication of LED displays with a wide gamut of pure colors. All halide systems synthesized in the current microfluidic platforms can access full coverage of the blue and green regions of the electromagnetic spectrum, which enhances the performance of LED displays. To indicate the potential of the droplet-based microfluidic platform in the synthesis of a wide gamut of perovskites suitable for LED device engineering, a CIE chromaticity diagram (introduced by the Commision Internationale de l’Eclairage) was mapped for all the pure colors generated by the formed particles. As can be seen in Figure
6.9, multi-parametric tuning (e.g. temperature and reagent concentrations) of the synthesized perovskites allows for mapping of a wide gamut of pure colors (see the black dots in Figure 6.9 – FWHM and PL maximum wavelength were extracted from the online measurements) particularly in the spectral region between 460 and 630 nm.214 These findings are highly significant for the fabrication of highly efficient and color-pure displays.

![Figure 6.9](image)

*Figure 6.9: (a) Online emission from CsPbX₃ perovskite NCs (black data points) plotted on CEI chromaticity coordinates and compared to the most common color standards (LCD TV, dashed white triangle, and NTSC TV, solid white triangle). Radiant Imaging Color Calculator software from Radiant Zemax (http://www.radiantzemax.com) was used to map the colors.*

### 6.4 Conclusions

In summary, we have demonstrated that microfluidic systems are unique tools for studying and optimizing the synthesis parameters associated with the colloidal synthesis of CsPbX₃ NCs, leading to production of materials with superior PL characteristics. Table 6.2 presents the refined parameters that we recommend for the batch syntheses of these NCs. In this regard we note that the temperature in our microfluidic platform is typically between 1 and 10°C higher than the nominal injection/growth temperatures reported for batch syntheses. However, it should be remembered that the actual temperature in the batch synthesis during the first several seconds is lower due to the effect of the injection of cold Cs-oleate precursor.
Table 6.2: Optimized reaction parameters for growing CsPbX$_3$ with narrow FWHM.

<table>
<thead>
<tr>
<th>Type of NC</th>
<th>Temperature (°C)</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>Online FWHM (nm)</th>
<th>PL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPb(Cl/Br)$_3$</td>
<td>130-180</td>
<td>2.2-4.3</td>
<td>1.5-10</td>
<td>20-25</td>
<td>470-500</td>
</tr>
<tr>
<td>CsPbBr$_3$</td>
<td>140-200</td>
<td>1.0-2.4</td>
<td>-</td>
<td>20-25</td>
<td>480-510</td>
</tr>
<tr>
<td>CsPb(Br/I)$_3$</td>
<td>150-220</td>
<td>2.0-2.6</td>
<td>0.1-1.0</td>
<td>25-35</td>
<td>510-580</td>
</tr>
<tr>
<td></td>
<td>150-220</td>
<td>3.2-4.5</td>
<td>1.2-15</td>
<td>35-45</td>
<td>580-660</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>150-200</td>
<td>3.2-7.5</td>
<td>-</td>
<td>38-45</td>
<td>650-690</td>
</tr>
</tbody>
</table>

In addition, microfluidic systems have been shown to successfully unearth unique insights into the early stages of the nucleation and growth (within the initial 0.1-5 seconds) not accessible in batch investigations, where this timescale covers the period during which the mixing of precursors and heat exchange occur. Specifically in regard to CsPbX$_3$ NCs, a fast pathway (precursors) $\rightarrow$ CsPbBr$_3$ NCs + CsPbI$_3$ NCs $\rightarrow$ CsPb(Br/I)$_3$ NCs is observed, presumably accomplished via fast inter-NC anion exchange or fusion of NCs. The overall conclusions from the study of early-stage kinetics and the complete screening of parameter space (here T, R$_1$, R$_2$) are that growth times are fast under all conditions ($\leq$3 s), optimal temperatures are between 140 and 200°C, emission wavelengths can be accurately and reproducibly controlled only via control of halide composition, whereas simultaneous adjustments of R$_1$ and R$_2$ are needed to minimize FWHM.
Chapter 7

In-situ Detection of Composition-Tunable Fluorescence Lifetimes of CsPbX3 (where X = Cl, Br, I) with Droplet-based Microfluidics.
7.1 Introduction

Over the past decade, semiconductor nanocrystals (NCs), also known as quantum dots (QDs), have been greatly studied due to their unique optical properties and potential utility in highly-efficient optoelectronic devices. Particularly, colloidal metal halide perovskite NCs have opened new and exciting opportunities in nanomaterial-based optoelectronic applications including solar cells, lasers and light emitting devices. Since 2014, several synthetic methodologies have been reported for the colloidal synthesis of organometal halide (CH$_3$NH$_3$PbX$_3$) and fully inorganic (CsPbX$_3$) perovskite NCs, where X is Cl, Br, I or a mixture of two halides. CsPbX$_3$ NCs are very attractive materials in this respect due to the precise and facile tuning of their emission and absorption energies over the entire visible region of the electromagnetic spectrum together with their high QYs ($\sim$90%). Moreover, it was recently demonstrated that their fluorescence lifetimes can be tuned in the nanosecond range (1–29 ns) by size and composition variation. Particularly, the ability to tune their fluorescence lifetimes by changing halide composition, offers new opportunities for multiplex barcoding because the lifetime (unlike PL intensity) neither depends on the intensity of the excitation light nor on the sensitivity of the detector.

However, the decay dynamics of CsPbX$_3$ perovskite NCs are not fully understood. For example, there is no global exponential model that is successful in describing decay kinetics of all different halide systems, limiting our understanding of nanocrystal photophysics. Moreover, as was demonstrated in Chapter 6, the most employed synthetic methods for producing all halide systems of CsPbX$_3$ NCs have set Pb:Cs molar ratio ($R_1$) to 3.76 without any further investigation. This indicates that their fluorescence lifetimes have not been fully explored. In this respect, time-resolved fluorescence measurements have proved to be exceptionally powerful for investigating excited state dynamics. Of special note, time-correlated single photon counting (TCSPC), which can provide a detailed analysis of excited states dynamics by evaluating the fluorescence decaytime components. To date, nanocrystal optical characterization, has been typically performed in an off-line manner, using standard methods based on electron microscopy, time-integrated fluorescence and absorption microscopy, light scattering and off-line TCSPC. However the automated synthesis of nanocrystals together with the rapid optimization of their physicochemical and photophysical properties is often challenging due to extensive sample preparation, long measurement times and particle purification which can eventually lead to loss of important information regarding optical properties.

Microfluidic platforms incorporating integrated optical systems allow for controlled synthesis of NCs together with real-time characterization of material properties in a facile and rapid manner. For semiconductor NCs, *in-situ* measurements of the maximum wavelength of the band edge emission, the full width at half maximum of the band edge emission and time-integrated fluorescence intensity allow for direct
determination of average particle size, size distribution and the fluorescence quantum efficiency. Most efforts have focused on the on-line or in-line implementation of analytical techniques, including fluorescence, absorption, x-ray, backscattering and correlation spectroscopies, which mostly focus on unveiling information relating to particle size, shape and size distribution.\textsuperscript{75} In contrast, and in the context of particle photophysics, further investigations are required to develop alternate detection strategies that are efficient in extracting real-time information regarding fluorescence quantum efficiencies and radiative and non-radiative deactivation pathways and can be integrated with the microfluidic reactors.

Herein, we demonstrate for the first time a novel segmented flow microfluidic platform integrated with a microscope-based detection system that is capable of extracting time-resolved fluorescence information from different CsPbX\textsubscript{3} perovskite systems using TCSPC. A rapid fitting algorithm is developed for “on-the-fly” decoding of fluorescence lifetimes of inorganic perovskite systems with single-droplet sensitivity. Fluorescence decay curve analysis can be achieved using single, bi- or tri-exponential models. The ability to perform on-line fluorescence lifetime analysis in flow during the synthesis of perovskite NCs allows for a detailed investigation of NC quantum efficiencies while varying molar ratios of reagents and the temperature of the reaction. The results of this study provide a new way understanding defect emissions and surface traps for samples with ternary and quaternary compositions where surface chemistry of the nanocrystal is complex.

7.2 Methods

7.2.1 Materials

Cesium carbonate (Cs\textsubscript{2}CO\textsubscript{3}, Aldrich, 99.9%), lead bromide (PbBr\textsubscript{2}, ABCR, 98%), lead chloride (PbCl\textsubscript{2}, ABCR, 99.999%), lead iodide (PbI\textsubscript{2}, ABCR, 99.999%), 1-octadecene (ODE, 90%), trioctylphosphine (TOP, ABCR, 97%), oleic Acid (OA, Sigma Aldrich, 90%), oleylamine (OLA, Acros, ≥ 96%), Perfluoroctyltrichlorosilane (PFO, Sigma Aldrich, 97%). Galden PFPE fluid was purchased from Blaser Swisslube AG.

7.2.2 Preparation of Precursors

Cesium Oleate Precursor Solution

In a 100 mL three-neck flask, Cs\textsubscript{2}CO\textsubscript{3} (0.815 g), ODE (40 ml) and OA (2.6 mL) were dried at 120°C under vacuum for 2h to dissolve the cesium salt and dry the solution. The solution was then allowed to cool and stored under argon for several days without any precipitation at room temperature. For each experi-
ment, 5 mL of precursor solution was loaded into a 10 mL-gas tight glass syringe (Hamilton).

**Lead Halide Precursor Solution**

PbX\textsubscript{2} including PbBr\textsubscript{2} (0.0.089 g) and PbI\textsubscript{2} (0.0.089 g) were added in a 20 mL Schlenk flask together with 5 mL-dried ODE. The mixture was then dried under vacuum for 2 h at 120°C. After 2 h, 0.8 mL of dried OA and dried OLA were added under argon until all the PbX\textsubscript{2} dissolved completely. The solution was then allowed to cool before being loaded into a into a 10 mL-gas tight glass syringe (Hamilton).

### 7.2.3 Experimental Procedure

Precision syringe pumps (neMESYS, Cetoni GmbH, Germany) were used to inject the dispersed phase (PbX\textsubscript{2} and Cs-Oleate precursor solutions) and the carrier fluid (Galden fluorinated fluid, Blaser Swisslube AG, Germany) towards a PEEK cross (P-729, Upchurch Scientific, Germany) to form a segmented flow of droplets. For CsPb(X/Y)\textsubscript{3}, the dispersed PbX\textsubscript{2} and PbY\textsubscript{2} precursor solutions were initially injected into a PEEK T-junction before being loaded into the PEEK cross for droplet formation. The injection cross and the syringes carrying the precursor solutions where connected through PTFE tubing (ID 250 \(\mu\)m, OD 1/16\''′, Upchurch Scientific, Germany) using PEEK fingertight fittings (F-127, Upchurch Scientific, Germany). The carrier fluid was transferred to the PEEK cross through fluorinated FEP tubing (ID 750 \(\mu\)m, OD 1/16\''′, Upchurch Scientific, Germany). Typical flow rates for the carrier phase were between 50 and 120 \(\mu\)L/min and between 0.5 and 30 \(\mu\)L/min for the dispersed phase. The chemical payload of the formed droplets can be tuned precisely and rapidly by a continuous variation of the precursor volumetric flow rates. Particularly, the microfluidic platform allowed for independent control of the Pb-to-Cs molar ratio (R\textsubscript{1}) and halide ratios (R\textsubscript{2}, I-to-Br and Br-to-Cl) by adjusting the ratio of the flow rates at the cross and T-junctions, respectively. The formed droplets containing the reaction mixture were subsequently directed through PFA tubing (ID 500 \(\mu\)m, OD 1/16\''′, Upchurch Scientific, Germany) coiled around a copper-heating rod (diameter = 1.5 cm) to allow the initiation of reaction. The reaction time was controlled either by varying the flow rates of the carrier phase or reagents. The droplets exiting the heating section were directed through a PTFE tubing into a straight channel (250\(\mu\)m x 80\(\mu\)m) polydimethysiloxane (PDMS) microfluidic chip for performing PL and time-resolved fluorescence measurements. The microfluidic chip was fabricated using standard soft-lithographic techniques described previously. Silanization of the microfluidic channel was performed prior to each experiment to retain channel hydrophobicity using PFO.
7.2.4 Microfluidic Platform and Characterization

The details of both the microfluidic platform and the online TCSPC detection system are elaborated in Chapter 2. In-situ fluorescence intensity and lifetime measurements of CsPb(X/Y)$_3$ NCs are recorded from individual droplets passing through the microfluidic channel. PL data were recorded with a 100 ms integration time using a fiber spectrometer (PRo+, Ocean Optics, UK) through a 2 m long fiber mounted at one of the ports of the microscope. TCSPC measurements in Time-Tagged-Time-Resolved (TTTR) mode are recorded with a 50-100 ms resolution, 0.025 ns binning time and 10 s acquisition time. On-line fitting of the experimental data was performed using in-house software written in the Labview® graphical programming environment, where multi-exponential models were used to model the TCSPC data for estimating fluorescence decaytimes.

7.2.5 In-situ Estimation of Fluorescence Lifetimes

To ensure the rapid estimation of fluorescence lifetimes in microfluidic droplets (enclosing synthesized NCs) in a high-throughput manner, we developed an in-house Labview® code (see the Appendix B for details of the Labview code) using an optimization algorithm to fit fluorescence decays using a multiexponential fitting function in real-time. As an example, Figure 7.1 shows a screenshot of the real-time fitting of an exponential model to the PL decay of CsPbBr$_3$ NCs. Only a few thousand of photons are detected per droplet, allowing for the extraction of fluorescence lifetime information in a high-throughput manner. The Labview® code generates the average lifetime, exponential parameters, goodness of fit and evolution of residuals.
7.3 Results & Discussion

7.3.1 Calibration of Real-Time TCSPC Measurements

For the calibration of the real-time TCSPC setup and assessment of the accuracy of the developed fitting model, we analyzed the fluorescence decay of 100 μM FITC solution in PBS buffer. The average fluorescence lifetime of FITC in PbS buffer is 4.1 ns with the fluorescence decay curve being modeled by a monoexponential curve. For the measurement, a drop of 200 μL of FITC was placed between two glass coverslips and mounted on the microscope stage. Figure 7.2 displays the fluorescence decay kinetics of FITC in PbS buffer, which confirms the suitability of a monoexponential model and yield an average fluorescence lifetime of 4.18 ns.
7.3.2 Time-resolved Photoluminescence Decays of CsPbX₃ Nanocrystals

By using the droplet-based capillary reactor and a microscope-based detection system, we were able to systematically investigate the effect of different reaction parameters including temperature, R₁ and R₂, on the average fluorescence lifetime of the synthesized CsPbX₃ NCs. Representative time-resolved PL decays from CsPbX₃ NCs are shown in Figure 7.3 with resulting fluorescence lifetimes in the range of 5 to 42 ns.

Figure 7.2: Fluorescence lifetime analysis of 100 µM FITC solution in PBS buffer. Other parameters were: λ_{ex} = 488 nm, pulse width = 80 ps and repetition rate = 20 MHz.
7.3.3 Effect of Pb/Cs Molar Ratio on the Average Fluorescence Lifetime

As mentioned in Chapter 6, the Pb/Cs molar ratio has a significant effect on PL and absorption characteristics of all CsPbX$_3$ halide systems, particularly on the time-integrated PL intensity and FWHM. For this reason, we sought to further investigate whether a change in PL intensity is due to an increase in fluorescence quantum efficiency or product concentration inside the droplets. On-line TCSPC measurements allow for further understanding of the photophysical characteristics of Cs-rich (R$_1$<1.5) and Pb-rich (R$_1$>1.5) CsPbX$_3$ NCs. Concurrent PL and TCSPC measurements were recorded for each individual droplet to allow correlations of PL fluctuations with fluorescence lifetime changes. Figure 7.4 shows the PL spectra and PL decay curves for CsPb(Br/I)$_3$ NCs. The fluorescence decay curves were modeled using a second-order exponential model, described by Eq. 7.1. The average lifetime ($\tau$) was calculated using Eq. 7.2. Parameter estimation was performed in an iterative fashion by minimization of the reduced chi-squared parameter.

$$I(t) = a_1 \exp(t/\tau_1) + a_2 (t/\tau_2)$$  \hspace{1cm} (7.1)

$$\tau = \frac{(a_1 \tau_1^2 + a_2 \tau_2^2)}{a_1 \tau_1 + a_2 \tau_2}$$  \hspace{1cm} (7.2)

where I(t) is the generated decay and a$_1$ and a$_2$ are the amplitudes or pre-exponential factors $\Sigma a_i = 1$.

As highlighted in Figures (7.4a) and (7.4b), changes in PL intensity of CsPb(Br/I)$_3$ NCs were proportional to variations on fluorescence lifetime. An increase of the
Pb:Cs molar ratio from 1.66 to 3.11 leads to an increase of the average fluorescence lifetime from 13.4 to 16.9 ns, whereas a further increase of $R_1$ ratio causes a drop in $\tau$ to 9.6 ns. The shorter decaytime component ($\tau_1$) which values between 2 and 4 ns is related to band recombination while the longer lifetime which values between 13.2 and 18.8 ns (see Table 7.1) is due to the radiative recombination of carriers, and has a strong dependence on the average lifetime.

![Image of decay curves and emission spectra]

**Figure 7.4:** The effect of the Pb-Cs molar ratio ($R_1$) on the (a) PL characteristics and (b) fluorescence decays of CsPb(Br/I)$_3$ NCs at 170 °C. Colors in the PL spectra correspond to various $R_1$ values indicated in the corresponding legends. The PL decays were fitted using a biexponential model. Other parameters were: $\lambda_{ex} = 488$ nm, pulse width = 80 ps and repetition rate = 20 MHz.

**Table 7.1:** Lifetime data of CsPb(Br/I)$_3$ NCs at different $R_1$ ratios.

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$\tau$ (ns)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.66</td>
<td>11.22</td>
<td>2.66</td>
<td>15.44</td>
<td>1.36</td>
</tr>
<tr>
<td>1.91</td>
<td>11.80</td>
<td>2.63</td>
<td>16.13</td>
<td>1.37</td>
</tr>
<tr>
<td>2.22</td>
<td>12.80</td>
<td>2.71</td>
<td>17.54</td>
<td>1.31</td>
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<td>2.61</td>
<td>12.90</td>
<td>3.26</td>
<td>16.52</td>
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<td>3.11</td>
<td>13.50</td>
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<td>18.79</td>
<td>1.27</td>
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<td>6.09</td>
<td>10.05</td>
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<td>8.41</td>
<td>9.60</td>
<td>2.20</td>
<td>13.20</td>
<td>1.23</td>
</tr>
</tbody>
</table>

### 7.3.4 Effect of Reaction Temperature

As previously demonstrated, the exited state lifetime of organic fluorophores is strongly temperature dependent. To extend the optical characterization of CsPbX$_3$...
NCs, we decided to further investigate the time-resolved fluorescence behavior of CsPbX$_3$ NCs as a function of temperature. Figure 7.5 shows the evolution of PL spectra and variation of PL lifetimes of mixed halide CsPbX$_3$ NCs as a function of temperature between 140 and 230 °C. The PL decays of CsPb(Br/I)$_3$ NCs reveal biexponential decay kinetics at all temperatures, with $\chi^2$ values below 1.3. Figure 7.5b shows that the short component of the decay ($\tau_1$) remains essentially constant (2.9-3.9 ns) while increasing the reaction temperature, whereas the long component of the decay ($\tau_2$) increases dramatically from 16.48 to 23.50 ns. The temperature-independent behavior of ($\tau_1$) is likely to be due to confined acoustic phonons in excitonic recombination and results from the superradiant emission, which is possible as long as the radiative rate dominates over dephasing. Conversely, the temperature dependence of the slow component may result from a change in the ground state of the hole. Clearly measured temperature is an important consideration when using TCSPC as a reaction monitoring tool.

![Figure 7.5: (a) Time-integrated PL spectra and (b) average and component PL lifetimes of CsPb(Br/I)$_3$ NCs as a function of temperature ($R_1 = 3.00, R_2 = 0.17$ reaction time 5 s). Other parameters were: $\lambda_{ex} = 488$ nm, pulse width = 80 ps and repetition rate = 20 MHz.](image)

### 7.3.5 Effect of halide ratios

To obtain additional insights into the role of NC composition on PL properties, we also measured the time-resolved photoluminescence of CsPb(Br/I)$_3$ while varying the halide composition. As mentioned in Chapter 6, the band edge emission of Br/I perovskites can be tuned from 523 to 690 nm through a continuous variation of PbI$_2$/PbBr$_2$ halide molar ratio ($R_2$). Adjustment of the anionic composition is a facile manner to tune the PL properties of the synthesized CsPbX$_3$ NCs, while excluding possible size-dependent effects (the size of CsPbX$_3$-based NCs is fixed between 10-12 nm). The time-resolved PL decays of CsPb(Br/I)$_3$ are also fitted using a biexponential decay function. Figure 7.6 presents how the band edge emission and the PL decays of CsPb(Br/I)$_3$ can be tuned as a function of...
By systematic variation of $R_2$ from 0.07 to 11, we managed to tune the PL peak wavelength from 516 to 680 nm leading to a dramatic increase of average PL lifetimes from 9.6 (Br-rich) to 35.2 ns (I-rich), measured from individual droplets with our TCSPC-platform (the values were averaged over hundreds of droplets). This shows the high-sensitivity of our developed platform in identifying lifetime variations in the ns range. A more systematic variation of $R_2$ - with a step of 0.01 for example - would allow us to unveil the PL lifetimes of all mixed halide CsPbX$_3$ NCs.

Figure 7.6: Tuning of (a) the PL peak wavelength and (b) PL lifetimes of CsPb(Br/I)$_3$ NCs as a function of I-to-Br molar ratio ($R_2$) ($R_1 = 2.2$, reaction time 5 s and $T = 190$ °C). (c) $\tau$ vs PL peak wavelength - $\tau$ values were estimated using a biexponential fitting function. Spline curve fitting was used in Figures 7.6a,c. Other parameters were: $\lambda_{ex} = 488$ nm, pulse width = 80 ps and repetition rate = 20 MHz.

7.4 Conclusions

In summary, we have demonstrated that fluorescence lifetimes of CsPbX$_3$ NCs, can be measured precisely and rapidly using a droplet-based microfluidic platform incorporating TCSPC. On-line calculation of radiative lifetimes of the synthesized NCs is achieved by a fitting algorithm with a sensitivity down to the single droplet level. This is the first report of on-the-fly fluorescence lifetime measurements for NCs and suggests great potential for the rapid optimization of NC photophysics using minimal reagent volumes and screening times. The fluorescence lifetimes of different CsPbX$_3$ halide systems in the range of 5-42 ns were extracted using a biexponential model. For CsPb(Br/I)$_3$, composition and temperature variations have a strong influence on PL lifetimes leaving open possibilities for identifying the optimum conditions for achieving even higher QYs. Particularly for Cs-to-Pb and temperature variations, where $\tau_1$ remains practically constant, a global optimization where one of the pre-exponential factors remains constant will allow us to find the globally best solution. In future, a more systematic time-resolved PL study for all CsPbX$_3$ NCs will be performed to understand the physical meaning of the fit parameters. This will allow for further understanding of CsPbX$_3$ photophysics and photochemical stability.
Chapter 8

Conclusions and Future Challenges
8.1 Summary

The primary aim of the proposed studies of this thesis was to create an innovative segmented flow microfluidic platform incorporating novel optical detection systems that allow for the synthesis of a wide range of semiconductor nanocrystals (NCs) with programmable physicochemical properties, together with real-time investigation of their reaction kinetics. Building on the several advantages of microfluidic reactors over conventional macroscale reactors (such as rapid mass and heat transfer, precise control of precursors, lower reagent consumption, real-time monitoring of reaction kinetics and rapid optimization of reaction parameters) we developed tools aimed at understanding the underlying mechanisms of NC synthesis and accelerating the adoption of microfluidic reactors as a standard technology for nanocrystal synthesis. Adopting this kind of “thinking-in-flow” strategy we presented a series of droplet-based capillary platforms together with in-line or on-line analysis systems.

We initially focused on the development of a facile droplet-based platform for the synthesis of quantum dots emitting in the near infrared region (700 - 1600 nm), due to their synthetic difficulty and the lack of in-line NIR detection systems for real-time assessment of their physicochemical properties. The microfluidic reaction platform was shown to be efficient in producing PbS and PbSe QDs with very low size distributions. The in-situ monitoring system allowed for control and optimization of the photoluminescence properties of NCs emitting between 860 and 1600 nm and enabled the production of PbS and PbSe QDs of programmable properties over extended periods of time. Ultimately, this allowed for the fabrications of solar-cell devices exhibiting power efficiencies in excess of 3%.

Driven by the fact that the syntheses of PbS and of other heavy metal QDs are characterized by very short nucleation and growth timescales, we were intrigued to develop an innovative microfluidic platform that could capture reaction kinetics with millisecond time resolution. The limitation of the previously developed platform in assessing very fast reaction kinetics (sub second) was overcome by redesigning both the microfluidic and optical methodology. The developed system provided for the first time on-line PL and absorption measurements at high temperatures, and allowed for accurate and quantitative kinetic analysis of PbS QD formation on a millisecond timescale. Extraction of kinetic parameters and online calculation of particle size and concentration enabled decoupling of nucleation and growth phases. Moreover, the novel optical detection system allowed for the extraction of absorbance information from ultrasmall PbS QDs emitting between 650 and 750 nm.

Furthermore, recognizing the need to replace Cd- or Pb-based QDs by equivalent but non-toxic nanocrystals, we proposed a two-stage droplet-based microfluidic platform for the systematic study of CuInS$_2$/ZnS QDs. The microfluidic system allowed for very fast ZnS shell growth on CuInS$_2$ cores using injection of a single source precursor, without the need for any additional purification steps. Moreover, individual adjustment of various reaction parameters such as $T_{\text{core}}$, $T_{\text{shell}}$, Cu/In,
(Cu+In)/S and Zn/(Cu+In), we were able to elucidate the optimum conditions for synthesizing photostable and monodisperse CuInS$_2$/ZnS QDs with QYs reaching 55% and FWHMs from 90 to 95 nm. In addition, the adoption of a novel optical detection system provided real-time PL information of both the core and core-shell structures. Results suggested that the developed methodology could be adopted for the facile sequential growth of core-shell structures and potentially the high-throughput production of non-heavy metal compounds using a scale-out approach.

By leveraging the advantages of our microfluidic platform we performed the rapid investigation of chemical parameter space of novel NCs with fast reaction kinetics. Particularly, our microfluidic methodology was able to optimize the reaction parameters of the colloidal synthesis of CsPbX$_3$ NCs, which are outstanding alternatives to Cd chalcogenides. It was found that the synthesis of CsPbX$_3$ NCs based on the ionic-metathesis reaction is complete within 5 s for all halide systems. Particularly in regard to mixed-halide perovskites, we demonstrated that their reaction pathway involves fast inter-NC anion exchange or fusion of NCs. By screening parameter space (T, Pb:Cs and PbX$_2$/PbY$_2$ molar ratios), it was found that optimal temperatures were between 140 and 200 °C, emission wavelengths can be accurately and reproducibly controlled only via control of halide composition, whereas simultaneous adjustment of both Pb:Cs and PbX$_2$/PbY$_2$ molar ratios were used to minimize FWHM. Most importantly, these reaction parameters can be directly used in conventional syntheses in common glassware, thus further advancing the synthesis of CsPbX$_3$ NCs. We expect these refined synthesis parameters will be then used by other researchers in their work on CsPbX$_3$ NCs.

Last, we decided to extend our understanding regarding the physicochemical and photophysical properties of NCs by building a time-correlated single photon counting (TCSPC) system that allowed for extensive and real-time characterization of fluorescence lifetimes in flow. Fluorescence decay curve analysis was achieved using a TCSPC detection together with an in-house fitting algorithm able to extract lifetime information at the single droplet level. To obtain additional insights into the photophysics of CsPbX$_3$ NCs, we performed on-the-fly measurements of fluorescence lifetimes between 5 and 42 ns using a biexponential fitting model. Systematic variation of reaction parameters during the synthesis of CsPb(Br/I)$_3$ NCs was shown to have a significant affect on the observed photophysics and extracted fluorescence lifetimes. This study represents the first example of an in-line, time-resolved PL study during the synthesis of fluorescent NCs.

8.2 Future Research Directions

8.2.1 Multistep Growth of Non-Heavy Metal Quantum Dots

The two-stage microfluidic platform which was presented in Chapter 5, allowed the production of CuInS$_2$/ZnS QDs characterized by high-photostability and narrow
size distribution. However, the sequential addition of a shell material on a QD core (estimating accurately the number of monolayers added) and the synthesis of multinary, non-heavy metal QDs with the addition of a shell material would require the use of a multi-stage microfluidic reactor or the addition of multiple injection steps in one of the stages of the existing platform. The latter scheme could be realized by a simple alteration to the existing setup and by adopting the methodology for multistep injection of precursors suggested in a recent study. By integrating fused silica capillaries at different injection points within the second heating stage, controllable amounts of a single or multiple precursors in a flowing stream of droplets could be added. This would be of immense value for the controllable production of ternary and quaternary metal chalcogenides, complex core-shell structures and doped nanostructures.

8.2.2 High-Throughput Formation of Metal Nanocubes/-Nanocages

Gold and silver nanocages are nanostructures that possess an open cage-like morphology whilst maintaining a single conduction surface. The ability to tune surface plasmon resonance (SPR) properties makes their application in sensing, imaging, photonics, plasmonics and information storage potentially significant, and accordingly there has been much interest in their manufacture. However, the development of robust strategies, for the controlled and continuous synthesis of such nanostructures with size tunable properties, remains a significant challenge.

To avoid the limitations of the seeded method such as seed aggregation, poor nanocrystal quality and variability in experimental conditions we propose to use a seedless synthesis of silver (Ag) nanocubes and their subsequent transformation to gold (Au) nanocages by galvanic replacement reactions, using the droplet-based microfluidic platform developed in Chapter 4. On-line absorption measurements are suited to the directed elucidation of particle size and morphology at different reaction times. Moreover, the combination of a second heating stage and multiple injection points across the reaction zone will allow for the multistep addition of HAuCl₄ solution into the liquid segments for the direct transformation of Ag nanocubes to Au nanocages of controlled porosity. This approach has the potential to significantly accelerate the scalable production of hollow NCs with controlled characteristics.

8.2.3 Chip-based Microfluidic Reactors for High Temperature Screening of Reaction Parameter Space

Capillary reactors, such as those proposed in this thesis, are simple in construction and easily applicable to the large-scale production production of various NCs due to the relatively large channel dimensions (250-500 µm). Conversely, chip-based
reactors offer greater flexibility regarding microfluidic design, reagent addition and heating operations and can be directly placed on top of commercial microscopes for the on-line detection of particle characteristics. However, on-line absorbance and fluorescence measurements in chip-based reactors during high-temperature synthesis is challenging.

Although we successfully developed capillary-based microfluidic platforms for the investigation of early time kinetics of various NCs, it was not possible to probe reaction times less than 100 ms due to the resolution of the optical setup. Particularly, for very fast reaction kinetics (as in the case of CsPbX₃) the use of a microfluidic reactor fabricated from glass or silicon and integrated into a microreactor heating stage would allow for rapid kinetic measurements on the microsecond timescales. For examples, a heating stage fabricated by Linkam Scientific Instruments Ltd.249 (which was used in Ref.250) enables precise control of reaction temperature, between -196 and 400 °C, at different regions within the microfluidic reactor and can be directly placed on top of a microscope for high-throughput optical measurements. This system could allow for the investigation of reaction kinetics of existing NCs but also would promote the synthesis of new materials which require temperatures exceeding 300 °C.
Bibliography


[23] LaMer, V. K.; Dinegar, R. H. *Journal of the American Chemical Society* 1950, 72, 4847–4854.


[101] Zhang, Jianbing; Gao, Jianbo; Miller, Elisa M.; Luther, Joseph M.; Beard, Matthew C, ACS Nano 2014, 8, 614–622.


Appendices
Appendix A

Photoluminescence and Absorption Spectra Analysis
PL Spectra Analysis for Chapters 3, 4, 5, 6 and 7

clear all
close all

lam1 = 480;
lam2 = 800;
smooth_length = 20;

font_size = 24;

%%%%%%%%%%%%%%%%% Preparation of Figures %%%%%%%%%%%%%%%%%%%%%
fig1 = figure();
hold on
box on
xlim([400, 800])
xlabel('\lambda (nm)', 'FontSize', font_size)
ylabel('PL (a. u.)', 'FontSize', font_size)
set(gca, 'fontsize', 24)

fig1b = figure();
hold on
box on
xlim([lam1, lam2])
xlabel('Wavelength (nm)', 'FontSize', font_size)
ylabel('Normalized Intensity', 'FontSize', font_size)
set(gca, 'fontsize', 24)

fig4 = figure();
hold on
box on
xlim([00 1.2])
xlabel('Temperature (°C)', 'FontSize', font_size)
ylabel('FWHM (nm)', 'FontSize', font_size)
set(gca, 'fontsize', 24)

fig5 = figure();
hold on
box on
xlim([00 1.2])
xlabel('Temperature (°C)', 'FontSize', font_size)
ylabel('Maximum Wavelength (nm)', 'FontSize', font_size)
set(gca, 'fontsize', 24)

%%%%%%%%%%%%%%%%% Input Parameters %%%%%%%%%%%%%%%%%%%%%
date = '20150507';
deg=380;
rad=deg*pi/180;
tube_length=rad*0.75;
tubing_diameter = 500; % in micrometers
temperature = [110 115 120 125 130 140 150 160 170 190];
flow_rate_PbI2 = 20;
flow_rate_PbBr2 = 9;
flow_rate_Cs = 3;
flow_rate_Oil = 100;
flow_rate = flow_rate_Oil + flow_rate_PbI2 + flow_rate_Cs; % in microliters/ min

time = [];
fwhm = [];
temp = [];
lam_max = [];
legend_text = [];

l = length(temperature);
colors = [linspace(0,1,l).', 1 - 4*(0.5 - linspace(1,0,l).').ˆ2,...
linspace(1,0,l).'];

num_jvals = 1;
num_kvals = 299;

offset = 0;
offset_change = 0;
start = 2;

for i = 1:l
    cd(['/Users/ioannis/Documents/PhD/perovskite/20150507/s'...
        num2str(i+start)]);
    time_i = tube_length*1E-2*pi*(tubing_diameter/2*1E-6)ˆ2*60/...
        (flow_rate*1E-9); % time in minutes
    time = [time, time_i];
    legend_text = [legend_text, [{'T = ' num2str(temperature(i)) '°C'}]];
    j = num_jvals;
    total_weight = 0;
    for k = 0:num_kvals
        % TXT file reading
        textfiles=[char(date) '_'_ num2str(j) '_'_ num2str(k) '.txt'];
        A = dlmread(textfiles);
        x1=A(:,1);
        y1=A(:,2);
        % Allocate imported array to column variable names
        xdist=x1(x1>lam1 & x1<lam2);
ydist=y1(x1>lam1 & x1<lam2);
ydist = smooth(ydist, smooth_length);
ydist = ydist(round(smooth_length/2):(end - ...
round(smooth_length/2)));
xdist = xdist(round(smooth_length/2):(end - ...
round(smooth_length/2)));

scaling_factor = (max(ydist) - min(ydist)) / ...
(max(ydist) + min(ydist));
ydist = ydist * scaling_factor^2;
total_weight = total_weight + scaling_factor^2;

if k == 0
    M=zeros(length(ydist), num_kvals+1);
end
M(:,k+1)=ydist(:,1);
end

Ydist=sum(M,2)/ total_weight;
Ydist = (Ydist - min(Ydist)) / (max(Ydist) - min(Ydist)) + offset;

% calculate first derivative
dYdist = 2*diff(Ydist) ./ diff(xdist);
dYdist=smooth(dYdist, smooth_length);

dYdist = dYdist / (max(dYdist) - min(dYdist));
dxdist = xdist(1:end-1);

% calculate second derivative
d2Ydist = 2*diff(dYdist) ./ diff(dxdist);
d2Ydist = smooth(d2Ydist, smooth_length);

d2Ydist = d2Ydist / (max(d2Ydist) - min(d2Ydist));
d2xdist = dxdist(1:end-1);

% plot
figure(fig1)
plot(xdist,Ydist,'color',colors(i, :],'linewidth',1.1);

figure(fig1b)
plot(xdist,Ydist,'color',colors(i, :],'linewidth',1.1);

% find minimum of second derivative
[d2Y_min,index_0] = min(d2Ydist(round(0.5*smooth_length):(end - ...
round(0.5*smooth_length))));
d2X_min = d2xdist(round(0.5*smooth_length) + index_0);

% find minimum of first derivative to the right of the min. of 2nd der.
dxdist_r = dxdist(dxdist > d2X_min);
[Y_min,index_min] = min(dYdist(dxdist > d2X_min));
X_min = dxdist_r(index_min);

% find maximum of first derivative to the left of the min. of 2nd der.
dxdist_l = dxdist(dxdist < d2X_min);
[Y_max, index_max] = max(dxdist_l(dxdist < d2X_min));
X_max = dxdist_l(index_max);

% lam_max_i = 0.5*(X_min+X_max); lam_max_i = xdist(round(0.5*smooth_length) + index_0);
lam_max = [lam_max, lam_max_i];

half_max_range= xdist(Ydist > 0.5);
fwhm_i = half_max_range(end) - half_max_range(1);

fwhm = [fwhm, fwhm_i];

figure(fig1)
plot(X_min, Ydist(round(0.5*smooth_length) + index_0 + index_min), ...
' o', X_max, Ydist(index_max), ' o','linewidth',1.2);

ind_peak = find(round(xdist) == round(lam_max(i)));

figure(fig1)
plot(lam_max(i), Ydist(ind_peak) , 'd','linewidth',1.3);
hold on
plot(d2X_min, Ydist(round(0.5*smooth_length) + index_0), 'x',...
'linewidth',1.3);

offset = offset + offset_change;

end

%%%%%%%%%%%%%%%%%%%%%%%% Sorting of Investigated Parameter %%%%%%%%%%%%%%%%%
figure(fig4)
[temperature_sort, ind_sort] = sort(temperature);
plot(temperature_sort, fwhm(ind_sort), '--x','linewidth',1.3);

figure(fig5)
plot(temperature_sort, lam_max(ind_sort), '--x','linewidth',1.3);

figure(fig1b)
legend(legend_text, 'Location', 'NorthEastOutside')

%%%%%%%%%%%%%%%%%%%%%%%% Save Figures %%%%%%%%%%%%%%%%%
save_name = '20150507_Temp';
cd('/Users/ioannis/Documents/PhD/Temperature Dependence/CsPbBrI3')

saveas(fig1, [save_name '_PL_fit_check'])
saveas(fig1b, [save_name '_PL_Int'])
saveas(fig4, [save_name '_fwhm'])
saveas(fig5, [save_name '_PL_maximum'])
saveas(fig1,'PL_fit_check.pdf')
saveas(fig1b, 'PL_Int.pdf')
saveas(fig4,'FWHM.pdf')
saveas(fig5,'PL_max.pdf')

PL Stability Measurements for Chapter 3

```matlab
% SECTION TITLE
% Analysis of PL Spectra for Stability Measurements

clear all
clc
textfile = fopen('16092013_stability.txt', 'wt');
s=3;
a=0;
b=1;

% Opening files with 1 digit
for k = 1:9

% CSV file reading
    CSVFilename = ['16092013_stability0000' num2str(k) '.csv'];
delimiter = ',';
startRow = 81;
formatSpec = '%f%f%f%f%f%f%f%*s%*s%*s%*s%*s%*s%*s%*[\n\r]';
fileID=fopen(CSVFilename,'r');
dataArray = textscan(fileID, formatSpec, 'Delimiter', delimiter,...
    'HeaderLines' ,startRow-1, 'ReturnOnError', false);
fclose(fileID);

% Allocate imported array to column variable names
    x1 = dataArray{:, 2};
y1 = dataArray{:, 7};

% Plotting the spectra with similar maximum intensities

    xdist=x1(x1>920);
ydist=y1(x1>920);
Ydist=smooth(ydist,40);
ma=max(ydist);
mi=min(ydist);
Ydist=a+(((Ydist-mi)*(b-a))/(ma-mi));
if (8000<ma)&&(ma<15000)
    figure (1)
    plot(xdist,Ydist,'color',rand(1,3),'LineWidth',2);
    axis([700 1700 0 1.2]);
    set(gca,'FontSize',30,'LineWidth',2)
    xlabel('Wavelength (nm)','FontSize',30,'Fontweight','b')
    ylabel('Normalized Intensity','FontSize',30,'Fontweight','b')
    hold on
```

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%% Calculate Spectra Properties

mi= min(ydist);
d_y=(ma-mi)/2;
Y_fwhm=ma-d_y;
x_above=xdist(ydist>Y_fwhm);
fwhm=x_above(end)-x_above(1);

std=fwhm/2.355;
xm=xdist(ydist==ma);
CV=(std/xm)*100;
Time=k*0.5/60;

fprintf(textfile,'%6s %12s
', 'xm', 'fwhm','std', 'CV');
fprintf(textfile,'%6.2f %12.8f
',xm, fwhm, std, CV);
end
end

%% Opening files with 2 digits
for k = 10:99
%% CSV file reading
CSVFilename = ['16092013_stability000' num2str(k) '.csv'];
delimiter = ',';
startRow = 81;
formatSpec = '%f%f%f%f%f%f%f%f'|\n';
fileID=fopen(CSVFilename,'r');
dataArray = textscan(fileID, formatSpec, 'Delimiter', delimiter,...
'HeaderLines',startRow-1, 'ReturnOnError', false);
fclose(fileID);

%% Allocate imported array to column variable names
x1 = dataArray{:, 2};
y1 = dataArray{:, 7};

%% Plotting
xdist=x1(x1>920);
ydist=y1(x1>920);
Ydist=smooth(ydist,40);
ma=max(ydist);
mi=min(ydist);
Ydist=a+((Ydist-mi)*(b-a))/(ma-mi));

if (8000<ma)&&(ma<15000)
figure (1)
plot(xdist,Ydist,'color',rand(1,3));
hold on

%% Calculate Spectra Properties

mi= min(ydist);
d_y=(ma-mi)/2;
Y_fwhm=ma-d_y;
x_above=xdist(ydist>Y_fwhm);
fwhm=x_above(end)-x_above(1);

%call gaussian distribution fitting function
%pd1 = createFit_normaldist(xdist,ydist);
%std=std(xdist);
%fwhm=std*2.355;
%ma=max(ydist);
try
std=fwhm/2.355;
xm=xdist(ydist==ma);
CV=(std/xm)*100;

Meanpeak(k,:)=xm;
Meanstd(k,:)=std;
Meanfwhm(k,:)=fwhm;
Time=k*0.5/60;

fprintf(textfile,'%6s %12s
', 'xm', 'fwhm','std', 'CV');
fprintf(textfile,'%6.2f %12.8f
',xm, fwhm, std, CV);
if error('error')
end
catch
continue
end
end
end

%% Opening files with 3 digits
for k = 100:999

%% CSV file reading
CSVFilename = ['16092013_stability00' num2str(k) '.csv'];
delimiter = ',';
startRow = 81;
formatSpec = '%f%f%f%f%f%f%f%f
';
fileID=fopen(CSVFilename,'r');
dataArray = textscan(fileID, formatSpec, 'Delimiter', delimiter,...
'HeaderLines' ,startRow-1, 'ReturnOnError', false);
fclose(fileID);

%% Allocate imported array to column variable names
x1 = dataArray{:, 2};
y1 = dataArray{:, 7};

%% Plotting
xdist=x1(x1>920);
ydist=y1(x1>920);
Ydist=smooth(ydist,40);
ma=max(ydist);
mi=min(ydist);
Ydist=a+(((Ydist-mi)*(b-a))/(ma-mi));
if (8000<ma)&&(ma<15000)
figure (1)
plot(xdist,Ydist,'color',rand(1,3));
hold on

%% Calculate Spectra Properties
mi= min(ydist);

\[
d_y = \frac{(m_a - m_i)}{2}; \\
y_{\text{fwhm}} = m_a - d_y; \\
x_{\text{above}} = \text{xdist} \left( \text{ydist} > y_{\text{fwhm}} \right); \\
fwhm = x_{\text{above}}(\text{end}) - x_{\text{above}}(1); \\
\]

% call gaussian distribution fitting function
% pd1 = createFit_normaldist(xdist, ydist);

\[
\text{std} = \text{std}(\text{xdist}); \\
fwhm = \text{std} \times 2.355; \\
\text{ma} = \text{max}(\text{ydist}); \\
\text{try} \\
\text{std} = \text{fwhm} / 2.355; \\
x_m = \text{xdist} \left( \text{ydist} == \text{ma} \right); \\
\text{CV} = (\text{std} / x_m) \times 100; \\
\]

Meanpeak(k, :) = xm;
Meanstd(k, :) = std;
Meanfwhm(k, :) = fwhm;

Time = k \times 0.5/60;

fprintf(textfile, '\%6s \%12s
', 'xm', 'fwhm', 'std', 'CV');
fprintf(textfile, '\%6.2f \%12.8f
', xm, fwhm, std, CV);
if error('error')
  end
catch
  continue
end
end
end

%% Opening files with 4 digits
for k = 1000:9999
  % CSV file reading
  CSVFilename = ['16092013_\_stability0' num2str(k) '.csv'];
  delimiter = ',';
  startRow = 81;
  formatSpec = '%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f%f?f

% Allocation imported array to column variable names
x1 = dataArray{:, 2};
y1 = dataArray{:, 7};
% Plotting
xdist=x1(x1>920);
ydist=y1(x1>920);
Ydist=smooth(ydist,40);
ma=max(ydist);
mi=min(ydist);
Ydist=a+(((Ydist-mi)*(b-a))/(ma-mi));
if (8000<ma)&&(ma<15000)
  figure (1)
end
plot(xdist,Ydist,'color',rand(1,3));
hold on

%% Calculate Spectra Properties

mi= min(ydist);
d_y=(ma-mi)/2;
Y_fwhm=ma-d_y;
x_above=xdist(ydist>Y_fwhm);
fwhm=x_above(end)-x_above(1);

%call gaussian distribution fitting function
%pd1 = createFit_normaldist(xdist,ydist);

%std=std(xdist);
%fwhm=std*2.355;
%ma=max(ydist);
try
std=fwhm/2.355;
xm=xdist(ydist==ma);
CV=(std/xm)*100;
Meanpeak(k,:)=xm;
Meanstd(k,:)=std;
Meanfwhm(k,:)=fwhm;
Time=k*0.5/60;

fprintf(textfile,'%6s %12s
', 'xm', 'fwhm','std', 'CV');
fprintf(textfile,'%6.2f %12.8f
',xm, fwhm, std, CV);
if error('error')
end
catch
continue
end
end
end
fclose(textfile);
hold off
MeanText = fopen('16092013_meanvalues.txt', 'wt');
Meanpeak(Meanpeak==0) = [];
Xmean=mean(Meanpeak);
Meanstd(Meanstd==0) = [];
StdMean=mean(Meanstd);
Meanfwhm(Meanfwhm==0) = [];
FWHMmean=mean(Meanfwhm);
CVMean=(StdMean/Xmean)*100;
[fitresult, gof] = fwhmfit(Meanfwhm);

fprintf(MeanText,'%6s %12s
', 'Xmean', 'FWHMmean','StdMean', 'CVMean');
fprintf(MeanText,'%6.2f %12.8f
',Xmean, FWHMmean, StdMean, CVMean);
fclose(MeanText);
Absorption Spectra Analysis for Chapter 4

%% SECTION TITLE
% Absorption Spectra Analysis of PbS Quantum Dots
clear all
close all

lam1 = 650;
lam2 = 1100;
smooth_length = 61;

font_size = 16;

%%%%%%%%%%%%%%%%% Preparation of Figures %%%%%%%%%%%%%%%%%%%%%
fig1 = figure();
hold on
box on
xlim([lam1, lam2])
xlabel('\lambda (nm)', 'FontSize', font_size)
ylabel('Absorbance (a. u.)', 'FontSize', font_size)
set(gca, 'fontsize', 16)

fig1b = figure();
hold on
box on
xlim([lam1, lam2])
xlabel('\lambda (nm)', 'FontSize', font_size)
ylabel('Absorbance (a. u.)', 'FontSize', font_size)
set(gca, 'fontsize', 16)

fig2 = figure();
hold on
box on
xlim([lam1, lam2])
xlabel('\lambda (nm)', 'FontSize', font_size)
ylabel('Derivative absorbance (a. u.)', 'FontSize', font_size)
set(gca, 'fontsize', 16)

fig3 = figure();
hold on
box on
xlim([lam1, lam2])
xlabel('\lambda (nm)', 'FontSize', font_size)
ylabel('Second derivative absorbance (a. u.)', 'FontSize', font_size)

fig4 = figure();
fig5 = figure();
hold on
box on
xlabel('Reaction time (s)','FontSize',font_size)
ylabel('\lambda_{\text{max}} (nm)', 'FontSize', font_size)
set(gca, 'fontsize', 16)

fig6 = figure();
hold on
box on
xlabel('Reaction time (s)', 'FontSize', font_size)
ylabel('Nanoparticle diameter (nm)', 'FontSize', font_size)
set(gca, 'fontsize', 16)

fig7 = figure();
hold on
box on
xlabel('Reaction time (s)', 'FontSize', font_size)
ylabel('Nanoparticle concentration (mmol L^{-1})', 'FontSize', font_size)
set(gca, 'fontsize', 16)

%%%%%%%%%%%%%%%%% Input Parameters %%%%%%%%%%%%%%%%%%%%%

date = {'20052014', '20052014', '20052014', '20052014', '20052014',
        '20052014', '20052014', '20052014', '20052014'};
tube_length = [12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, 15.5, 16.0];  % in cm
flow_rate = 140;  % in microliters/ min

l = length(tube_length);
time = zeros(1,l);
fwhm = zeros(1,l);
temp = zeros(1,l);
lam_max = zeros(1,l);

colors = [linspace(0,1,l).' , 1 - 4*(0.5 - linspace(1,0,l)').' .^2,...
linspace(1,0,l).' ];
num_jvals = 1;
num_kvals = 299;

offset = 0;
offset_change = 0.25;
start = 0;
for i = 1:l

cd(['/Users/PhD/PbS Kinetics/20140520/S' num2str(i+start)]);

    time(i) = tube_length(i)*1E-2*pi*(tubing_diameter/2*1E-6)^2*60/...
(flow_rate*1E-9); % time in minutes

j = num_jvals;

total_weight = 0;

for k = 0:num_kvals
    % TXT file reading
    textfiles=[char(date(i)) '_' num2str(j) '_' num2str(k) '.txt'];
    A = dlmread(textfiles);
    x1=A(:,1);
    y1=A(:,2);

    % Allocate imported array to column variable names
    xdist=x1(x1>lam1 & x1<lam2);
    ydist=y1(x1>lam1 & x1<lam2);

    ydist=smooth(ydist,smooth_length);
    ydist = ydist(round(smooth_length/2):(end-round(smooth_length/2)));
    xdist = xdist(round(smooth_length/2):(end-round(smooth_length/2)));

    if ydist(1) - ydist(end) < 1*std(ydist)
        ydist = ydist*0;
    end

    scaling_factor = std(ydist);
    ydist = ydist * scaling_factor^2;
    total_weight = total_weight + scaling_factor^2;

    if k == 0
        M=zeros(length(ydist), num_kvals);
    end

    M(:,k+1)=ydist(:,1);

end

Ydist=sum(M,2) / total_weight;

absorbance = Ydist;

Ydist = (Ydist - min(Ydist))/ (max(Ydist) - min(Ydist)) + offset;

% calculate first derivative

dYdist = 2*diff(Ydist) ./ diff(xdist);

dYdist=smooth(dYdist,smooth_length);
dYdist = dYdist/(max(dYdist)-min(dYdist));
dxdist = xdist(1:end-1);

% calculate second derivative

d2Ydist = 2*diff(dYdist) ./ diff(dxdist);
d2Ydist = smooth(d2Ydist,smooth_length);
d2Ydist = d2Ydist/(max(d2Ydist)-min(d2Ydist));
d2xdist = dxdist(1:end-1);

% plot

figure(fig1)
plot(xdist,Ydist,'color',colors(i,:), 'linestyle', '--');
figure(fig1)
plot(xdist,Ydist,'color',colors(i,:), 'linestyle', '--');
figure(fig2)
plot(dxdist,dYdist,'color',colors(i,:), 'linestyle', '--');
figure(fig3)
plot(d2xdist,d2Ydist,'color',colors(i,:), 'linestyle', '--');

% find minimum of second derivative
[d2Ymin,index_0] = min(d2Ydist(round(0.5*smooth_length): end - ...
round(0.5*smooth_length)));
d2Xmin = d2xdist(round(0.5*smooth_length) + index_0);

% find minimum of first derivative to the right of the min. of 2nd der.
dxdist_r = dxdist(dxdist > d2Xmin);
[Ymin,index_min] = min(dYdist(dxdist > d2Xmin));
Xmin = dxdist_r(index_min);

% find maximum of first derivative to the left of the min. of 2nd der.
dxdist_l = dxdist(dxdist < d2Xmin);
[Ymax,index_max] = max(dYdist(dxdist < d2Xmin));
Xmax = dxdist_l(index_max);

fwhm(i) = Xmin-Xmax;
lam_max(i) = 0.5*(Xmin+Xmax);

figure(fig1)
plot(Xmin, Ydist(round(0.5*smooth_length) + index_0 + index_min),... 'o', Xmax, Ydist(index_max), 'o', 'linestyle', ' ');
title(['T = ' num2str(temperature) '°C']);

ind_peak = find(round(xdist) == round(lam_max(i)));
peak_absorbance(i) = mean(absorbance(ind_peak));

figure(fig1)
plot(lam_max(i), Ydist(ind_peak), 'd', 'linewidth', 1.3);
title(['T = ' num2str(temperature) '~{\circ}C']);
hold on
plot(d2X_min, Ydist(round(0.5*smooth_length) + index_0),'x',...
'linewidth',1.3);
title(['T = ' num2str(temperature) '~{\circ}C']);
offset = offset + offset_change;
end

%% Calculation of Particle Diameter and Concentration %

[time_sort, ind_sort] = sort(time);
gap_energy = 1240./lam_max;

% fit (cademartiri 2006)
particle_radius = (0.85 + sqrt(0.85^2 + 4*0.96*(gap_energy - 0.41)))./...
(2*(gap_energy - 0.41));
eps = 19600*particle_radius.^2.32; % M^-1cm^-1 extiction
path_length = 1; % in centimeter
conc = 1000*transpose(peak_absorbance) ./ (eps * path_length) ;% in milli M

figure(fig4)
plot(time_sort, fwhm(ind_sort), '--x','linewidth',1.3);
title(['T = ' num2str(temperature) '~{\circ}C']);
figure(fig5)
plot(time_sort, lam_max(ind_sort), '--x','linewidth',1.3);
title(['T = ' num2str(temperature) '~{\circ}C']);
figure(fig6)
plot(time_sort, 2*particle_radius(ind_sort), '--xb','linewidth',1.3);
title(['T = ' num2str(temperature) '~{\circ}C']);
legend('Cademartiri et al. (2006)', 'Location', 'East')
figure(fig7)
plot(time_sort, conc(ind_sort), '-ob','linewidth',1.3);
% %
legend_text = [];
for i = 1:l
    legend_text = [legend_text, {{'t = ' num2str(time(i),'%.1f') ' s '}}];
end
% figure(fig1b)
legend(legend_text, 'Location', 'NorthEastOutside')
figure(fig2)
legend(legend_text, 'Location', 'NorthEastOutside')
figure(fig3)
legend(legend.text, 'Location', 'NorthEastOutside')

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Save Files %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
save_name = '20052014_S1_to_S9_90';

cd('/Users/PhD/PbS Kinetics/figures/20140520')

saveas(fig1, [save_name '_absorbance_fit_check'])
saveas(fig1b, [save_name '_absorbance'])
saveas(fig2, [save_name '_absorbance_derivative'])
saveas(fig3, [save_name '_absorbance_derivative_2'])
saveas(fig4, [save_name '_fwhm'])
saveas(fig5, [save_name '_abs_maximum'])

%% saves it as .pdf

savefig( [save_name '_absorbance_fit_check'],fig1,'pdf')
savefig( [save_name '_absorbance'],fig1b,'pdf')
savefig( [save_name '_absorbance_derivative'],fig2,'pdf')
savefig( [save_name '_absorbance_derivative_2'],fig3,'pdf')
savefig( [save_name '_fwhm'],fig4,'pdf')
savefig( [save_name '_abs_maximum'],fig5,'pdf')
savefig( [save_name '_particle_radius'],fig6,'pdf')
savefig( [save_name '_particle_concentration'],fig7,'pdf')

%%
Appendix B

TCSPC Labview Software
Figure B.1: Front panel of the in-house Labview software for the fluorescence decay curve analysis.
Figure B.2: Block Diagram of the Labview Software describing the calculation steps.
Figure B.3: Front panel of the SubVI for defining the exponential model.

Figure B.4: Block Diagram of the SubVI for defining the exponential model.